Universidade de Aveiro Departamento de Química
2012

CARLA ANDREIA
CUNHA VILELA

SÍNTESE DE NOVOS MATERIAIS POLIMÉRICOS DERIVADOS DE ÓLEOS VEGETAIS

SYNTHESIS OF NEW VEGETABLE OIL-BASED POLYMERIC MATERIALS

Universidade de Aveiro Departamento de Química
2012

CARLA ANDREIA CUNHA VILELA

SÍNTESE DE NOVOS MATERIAIS POLIMÉRICOS DERIVADOS DE ÓLEOS VEGETAIS

SYNTHESIS OF NEW VEGETABLE OIL-BASED POLYMERIC MATERIALS

Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Química, realizada sob a orientação científica do Doutor Alessandro Gandini, Professor Convidado do Instituto de Química da Universidade de São Paulo e do Doutor Armando Jorge Domingues Silvestre, Professor Associado com Agregação do Departamento de Química da Universidade de Aveiro

Apoio financeiro da FCT e do POPH/FSE (SFRH/BD/44884/2008) no âmbito do III Quadro Comunitário de Apoio.

FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA

POPH
PROGRAMA OPERACIONAL POTENCIAL HUMANO
QREN
QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL
PORTUGAL 2007.2013
UNIÃO EUROPEIA
Fundo Social Europeu

“Learning is the only thing the mind never exhausts,
never fears and never regrets”.

Leonardo da Vinci

o júri

presidente

Doutor Carlos Fernandes da Silva
professor catedrático da Universidade de Aveiro

Doutor Armando Jorge Domingues Silvestre
professor associado com agregação da Universidade de Aveiro

Doutora Verónica Cortés de Zea Bermudez
professora associada com agregação da Escola de Ciência da Vida e do Ambiente da Universidade de Trás-os-Montes e Alto Douro

Doutor Jorge Fernando Jordão Coelho
professor auxiliar da Faculdade de Ciências e Tecnologia da Universidade de Coimbra

Doutora Ana Margarida Madeira Veigas de Barros Timmons
professora auxiliar da Universidade de Aveiro

Doutor Alessandro Gandini
professor convidado do Instituto de Química da Universidade de São Paulo, Brasil

agradecimentos

Em primeiro lugar gostaria de agradecer aos meus orientadores, Professor Doutor Alessandro Gandini e Professor Doutor Armando Silvestre, por me terem proporcionado a oportunidade de desenvolver este trabalho, pela valiosa orientação científica, pelo incentivo e disponibilidade constantes, e pela amizade ao longo destes anos.

Aos meus colegas dos laboratórios LignoMacro: Andrea Figueiredo, Andreia Sousa, Carina Carvalho, Dora Coelho, Fabiane Oliveira, Gisela Cunha, Joana Mendes, Juan Villaverde, Liliana Tomé, Márcia Neves, Mónica Gomes, Patrícia Ramos, Ricardo Pinto, Rui Domingues, Sónia Santos e Sónia Prozil gostaria de agradecer pelo apoio pessoal e pelo bom ambiente constante.

À Doutora Sónia e ao Doutor Ricardo quero agradecer não só pela vossa amizade, paciência e apoio, mas também pela vossa boa disposição e pelos inúmeros cafés, natas, hambúrgueres e picanhas.

Grazie mille Letizia Cruciani per l'aiuto con le maleodoranti monomeri e polimeri di Diels-Alder.

Ich möchte Professor Meier für die Möglichkeit der Zusammenarbeit mit ihm in der Herstellung von Polymeren aus nachwachsenden Rohstoffen zu danken.

Agradeço a todos os membros do Departamento de Química e do CICECO que de alguma forma contribuíram para este trabalho.

À Fundação para a Ciência e Tecnologia e do POPH/FSE agradeço pelo apoio financeiro na forma de uma Bolsa de Doutoramento (SFRH/BD/44884/2008).

Os últimos são também os primeiros a quem agradeço o apoio incondicional, o amor e a alegria de partilhar o dia-a-dia: à minha mãe, ao meu irmão e ao meu marido!

palavras-chave

Recursos renováveis, óleos vegetais, ácidos gordos, auto-metátese, acoplamento tiol-eno, reação “click” de Diels-Alder, transvinilação, polimerização por etapas, polimerização em cadeia

resumo

A crescente procura de recursos fósseis a que se tem assistido nos últimos anos, tem resultado num crescimento sem precedentes dos preços, com consequências imprevisíveis e que levará, no espaço de décadas, ao seu inevitável esgotamento. A procura de um modelo de desenvolvimento sustentável, baseado em recursos renováveis é o grande desafio que se coloca à civilização no século XXI. A biomassa vegetal, através das designadas “Bio-refinarias”, é uma alternativa lógica para a produção de produtos químicos e de materiais mas também de combustíveis e energia. Os óleos vegetais constituem uma das frações da biomassa vegetal, cuja exploração tem merecido redobrada atenção nos últimos anos, como fonte de materiais e de combustíveis. Assim, a presente dissertação tem por objetivo o desenvolvimento de novos materiais poliméricos derivados de óleos vegetais, seguindo duas abordagens distintas, nomeadamente a preparação de polímeros através de polimerização por etapas e polimerização em cadeia (Parte B e C, respetivamente).

Em primeiro lugar, foram sintetizados poliésteres alifáticos de cadeia longa a partir de monómeros provenientes do óleo de colza (Capítulo III). A auto-metátese do ácido erúcico com catalisadores de ruténio, seguida de hidrogenação da ligação dupla, originou o ácido 1,26-hexacosanodióico, que por sua vez foi convertido em hexacosano-1,26-diol. Subsequentemente, a policondensação do ácido α,ω-dicarboxílico de cadeia longa com o hexacosano-1,26-diol originou o poliéster 26,26. O diácido C26 foi também polimerizado com outros alcano-dióis de cadeia curta, nomeadamente o dodecano-1,12-diol e o butano-1,2-diol, produzindo, respetivamente, os poliésteres 12,26 e 4,26. Estes poliésteres de fontes 100% renováveis possuem valores de M_n na ordem dos 8-14 kDa e valores de PDI entre 2.1 e 2.7. As propriedades destes poliésteres alifáticos foram avaliadas através de várias técnicas, revelando elevada cristalinidade (com uma estrutura cristalina como a do polietileno) e elevadas temperaturas de fusão (74-104 °C), cristalização (68-92°C) e degradação (323-386 °C).

Em segundo lugar, foram sintetizados polímeros lineares termo-reversíveis a partir de derivados do óleo de ricínio (Capítulo IV). Para tal foram preparados monómeros que incorporam anéis furânicos inseridos através do acoplamento tiol-eno, e que posteriormente foram polimerizados pela reação de Diels-Alder (DA) entre os grupos furano (dieno A) e estruturas complementares do tipo maleimida (dienófilo B). Para as polimerizações DA foram consideradas duas abordagens diferentes, nomeadamente (i) o uso de monómeros com dois anéis furânicos terminais em conjunto com uma bismaleimida (sistemas AA+BB) e (ii) a utilização de um monómero que incorpora ambos os grupos reativos, furano e maleimida, na sua estrutura (sistema AB).

resumo
(cont.)

Este estudo demonstrou claramente que ambas as estratégias foram bem sucedidas embora com diferentes resultados em termos da natureza dos produtos obtidos. Estes polímeros lineares apresentam valores relativamente baixos de T_g (-40 to -2 °C) devido à natureza flexível dos grupos separadores das funções reativas, e de M_n (4.5-9.0 kDa) dada a observada tendência de ciclização associada a concentrações baixas de monómero. A aplicação da reação de retro-DA aos polímeros em causa confirmou o seu caráter reversível, ou seja, a possibilidade de promover, em condições controladas, a despolimerização com recuperação dos monómeros de partida. Esta particularidade abre caminhos para materiais macromoleculares originais com aplicações promissoras tais como auto-reparação e reciclabilidade.

Em terceiro lugar, sintetizaram-se polímeros não-lineares termo-reversíveis a partir de derivados do óleo de ricínio (Capítulo V). Para tal foram preparados monómeros trifuncionais e posteriormente polimerizados através da reação de DA entre os grupos reativos complementares furano/maleimida. Foram consideradas três abordagens distintas para preparar estes polímeros não-lineares, nomeadamente através da utilização de (i) um monómero bisfurânico em combinação com uma trismaleimida (sistema A_2+B_3) e (ii) um monómero trisfurânico em conjunto com uma bismaleimida (sistema A_3+B_2) que originaram materiais ramificados ou reticulados, e ainda (iii) a utilização de monómeros assimetricamente substituídos do tipo A_2B ou AB_2 capazes de originar estruturas macromoleculares hiper-ramificadas. Todos os sistemas apresentaram valores de T_g perto de 0 °C, o que era de esperar para estes materiais não-lineares. A aplicação da reação de retro-DA comprovou mais uma vez o caráter termo-reversível das polimerizações em causa.

Em quarto lugar e último lugar, foram preparados copolímeros de acetato de vinilo (VAc) com monómeros derivados de óleo de girassol (Capítulo VI). Ésteres vinílicos de ácidos gordos (FAVE) foram sintetizados por transvinilação dos ácidos oleico e linoleico com VAc catalisada por um complexo de irídio. Os monómeros vinílicos preparados foram caracterizados e posteriormente homopolimerizados e copolimerizados com VAc através do uso dos grupos vinílicos terminais como função inicial de polimerização. A variação do tipo e quantidade de monómero FAVE e da quantidade de iniciador radicalar originou copolímeros de VAc com valores de M_n na gama de 1.2-3.0 kDa e valores de T_g de -5 a 16 °C. Os copolímeros foram avaliados em testes de cura oxidativa através das insaturações nas suas cadeias alifáticas para formar materiais reticulados, e os resultados sugerem que eles podem ser sistemas efetivos de cura para aplicações como tintas, vernizes e outros tipos de revestimento.

Todos os materiais poliméricos preparados ao longo deste trabalho constituem contribuições atrativas para a área dos polímeros oriundos de recursos renováveis e representam uma prova indiscutível de que os óleos vegetais são percursores promissores de materiais macromoleculares com potenciais aplicações.

keywords

Renewable resources, vegetable oils, fatty acids, self-metathesis, thiol-ene coupling, Diels-Alder click reaction, transvinylation, step-growth polymerization, chain-growth polymerization

abstract

The growing demand for fossil resources in the last several years is leading to an unprecedented augment of their price with unpredictable consequences and, in medium/long term, to their inevitable depletion. The search for a model of sustainable development based on renewable resources is the keen challenge of the civilization of the XXI century. The vegetable biomass through the “Biorefinery” concept is the logical detour for the production of chemicals and materials, as well as fuels and energy. Vegetable oils are one of the fractions of vegetable biomass whose exploitation has gained much attention in the last several years as a source of materials and fuels. Therefore, the present dissertation aims at developing novel vegetable oil based polymeric materials. Two main pathways were tackled in this study, namely the preparation of step-growth and chain-growth polymers (Part B and C, respectively).

Firstly, aliphatic polyesters from rapeseed oil based monomers were prepared (Chapter III). The self-metathesis of erucic acid with ruthenium-based catalysts, followed by hydrogenation of the double bond, yielded 1,26-hexacosanedioic acid, which was also converted into the corresponding hexacosane-1,26-diol. Subsequently, the polymerization of the biobased long-chain α,ω-dicarboxylic acid with hexacosane-1,26-diol yielded polyester 26,26. The C26 diacid was also polymerized with short-chain alkanediols, namely dodecane-1,12-diol and butane-1,4-diol, generating polyesters 12,26 and 4,26, respectively. These 100% renewable polyesters have M_n values in the range of 8-14 kDa and PDI values between 2.1 and 2.7. The properties of these aliphatic polyesters were investigated by means of various techniques, revealing high crystallinity (with a polyethylene like crystal structure), melting (74-104 ºC), crystallization (68-92 ºC) and degradation (323-386 ºC for 5 wt% weight loss) temperatures.

Secondly, linear thermoreversible polymers from castor oil derivatives were investigated (Chapter IV). Monomers bearing furan heterocycles appended through thiol-ene click coupling were prepared and, subsequently, polymerized via a second type of click reaction, i.e. the Diels-Alder (DA) reaction between furan (diene A) and maleimide (dienophile B) complementary moieties. Two basic approaches were considered for these DA polymerizations, namely (i) the use of monomers with two terminal furan rings in conjunction with a bismaleimide (AA+BB systems) and (ii) the use of a protected AB monomer incorporating both furan and maleimide end-groups (AB system).

abstract (cont.)

This study clearly showed that both strategies were successful, albeit with different outcomes, in terms of the nature of the ensuing products. These linear polymers possess relatively low T_g values (-40 to -2 ºC) due to the flexible nature of the spacing moieties separating the reactive functions, together with somewhat small M_n values (4.5-9.0 kDa) given the observed tendency to cyclization associated with the relatively low monomer concentrations. The application of the retro-DA reaction to these polymers confirmed their thermoreversible character, i.e. the clean-cut return to their respective starting monomers. This original feature opens the way to original macromolecular materials with interesting applications, like mendability and recyclability.

Thirdly, non-linear thermally labile polymers from castor oil derivatives were studied (Chapter V). Trifunctional monomers were prepared and subsequently polymerized via the DA reaction between furan and maleimide complementary moieties. Three basic approaches were considered for the non-linear DA polymerizations, i.e., the use of (i) a bisfuran monomer in combination with a trismaleimide (A_2+B_3 system) and (ii) a trisfuran monomer in conjunction with a bismaleimide (A_3+B_2 system) leading to branched or cross-linked materials, and (iii) the use of asymmetric monomers incorporating both furan and maleimide end groups (A_2B or AB_2 systems), which lead to hyperbranched structures. All systems displayed T_g values close to 0 ºC, as one would expect for these non-linear materials. The application of the retro-DA to the ensuing polymers confirmed the thermally-reversible character of these polymerizations.

Fourthly, copolymers of vinyl acetate (VAc) and sunflower oil based monomers (Chapter VI) were prepared. Fatty acid vinyl esters (FAVE) were synthesized via a transition-metal catalyzed transvinylation reaction between oleic or linoleic acids and VAc in good yields. The ensuing vinyl monomers were fully characterized and submitted to both free radical homopolymerization and copolymerization with VAc by making use of the terminal vinyl moiety as the initial polymerization function. The variation of the type/amount of FAVE monomers and the quantity of radical initiator yielded VAc copolymers with M_n in the range of 1.2-3.0 kDa and T_g values of −5 to 16ºC. The copolymers were tested in oxidative drying through the unsaturations borne by their fatty acid chains for the formation of a cross-linked final material and the results suggested that they can constitute effective curing systems for such applications as paints, varnishes and other coating processes.

All of these polymeric materials are attractive contributions to the growing realm of polymers from renewable resources and represent an indisputable evidence that vegetable oils are promising precursors of innovative macromolecular materials with potential applications.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS AND SYMBOLS

A	Furan moiety
AIBN	2,2'-Azoisobutyronitrile
B	Maleimide moiety
BP	Benzoyl Peroxide
C1	Grubbs 1st generation catalyst
C2	Grubbs 2nd generation catalyst
C3	Hoveyda-Grubbs 2nd generation catalyst
CTH	Catalytic Transfer Hydrogenation
d	Doublet
dd	Doublet of doublets
DA	Diels-Alder reaction
DCC	*N,N′*-Dicyclohexylcarbodiimide
DCU	1,3-Dicyclohexylurea
DMAP	4-Dimethylaminopyridine
DMF	*N,N′*-Dimethylformamide
DP	Degree of polymerization
DSC	Differential Scanning Calorimetry
EA	Erucic acid
ESO	Epoxidized Soybean Oil
FA	Furfuryl Alcohol
FAVE	Fatty acid vinyl ester
FMS	Furfuryl methyl sulfide
FT	2-Furylmethanethiol
FTIR-ATR	Fourier Transform Infrared Spectroscopy–Attenuated Total Reflectance
GC-MS	Gas Chromatography-Mass Spectrometry
HFIP	1,1,1,3,3,3-Hexafluoro-2-propanol
HPLC	High Performance Liquid Chromatography
I651	IRGACURE® 651 (2,2-dimethoxy-2-phenylacetophenone)
IR	Infrared Spectroscopy
LA	Linoleic Acid
m	multiplet
M	Molecular Ion
MBA	4-Maleimidobutyric Acid
MM	*N*-Methylmaleimide
M_n	Number-average molecular weight

MO	Methyl Oleate
M_w	Weight-average molecular weight
^{1}H NMR	Proton Nuclear Magnetic Resonance
^{13}C NMR	Carbon-13 Nuclear Magnetic Resonance
OA	Oleic Acid
P_c	Cross-linking critical point
PDI	Polydispersity index (M_w/M_n)
r	Functional stoichiometric ratio
retro-DA	Retro-Diels-Alder reaction
s	Singlet
SEC	Size Exclusion Chromatography
SM	Self-metathesis reaction
t	Triplet
TCE	1,1,2,2-Tetrachloroethane
TCE-d_2	Deuterated 1,1,2,2-Tetrachloroethane
T_g	Glass transition temperature
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TFA	Trifluoroacetic acid
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
T_m	Melting temperature
TMS	Trimethylsilyl
UDA	10-Uncedecoic Acid
UDOL	10-Undecenol
UV/Vis	Ultraviolet-visible spectroscopy
VAc	Vinyl Acetate
VIBE	Vinyl isobutyl ether
VS	Vinyl Stearate
XRD	X-ray Diffraction

AA / AA' / A_2	Bisfuran monomers
A_3	Trisfuran monomer
AB	Furan-maleimide monomer
A_2B / AB_2	Bisfuran-maleimide / furan-bismaleimide monomers
BB / B_2	Bismaleimide monomer
B_3	Trismaleimide monomer
1,26-diacid	1,26-Hexacosanedioic acid
1,26-diol	Hexacosane-1,26-diol
VL	Vinyl linoleate

VO	Vinyl oleate
P(AA+BB)	Linear **AA**+**BB** polymer (AA+BB system)
P(AA'+BB)	Linear **AA'**+**BB** polymer (AA+BB system)
P(AB)	Linear **AB** polymer (AB system)
P(A_2+B_3)_0.5	Non-linear **A_2**+**B_3** polymer with *r*=0.5 (A_2+B_3 system)
P(A_2+B_3)_0.75	Non-linear **A_2**+**B_3** polymer with *r*=0.75 (A_2+B_3 system)
P(A_2+B_3)_1.0	Non-linear **A_2**+**B_3** polymer with *r*=1.0 (A_2+B_3 system)
P(A_3+B_2)_0.5	Non-linear **A_3**+**B_2** polymer with *r*=0.5 (A_3+B_2 system)
P(A_3+B_2)_0.75	Non-linear **A_3**+**B_2** polymer with *r*=0.75 (A_3+B_2 system)
P(A_3+B_2)_1.0	Non-linear **A_3**+**B_2** polymer with *r*=1.0 (A_3+B_2 system)
P(A_2B)	Non-linear **A_2B** polymer (A_2B system)
P(AB_2)	Non-linear **AB_2** polymer (AB_2 system)
PE 26,26	Linear polyester from **1,26-diol**+**1,26-diacid**
PE 12,26	Linear polyester from **1,12-diol**+**1,26-diacid**
PE 4,26	Linear polyester from **1,4-diol**+**1,26-diacid**
PE 12,12	Linear polyester from **1,12-diol**+**1,12-diacid**
P(VAc-*co*-VO)_1	Copolymer **VAc+VO** (90:10) with 6% BP
P(VAc-*co*-VO)_2	Copolymer **VAc+VO** (90:10) with 10% BP
P(VAc-*co*-VL)_1	Copolymer **VAc+VL** (85:15)
P(VAc-*co*-VL)_2	Copolymer **VAc+VL** (90:10) with 6% BP
P(VAc-*co*-VL)_3	Copolymer **VAc+VL** (90:10) with 10% BP
P(VAc-*co*-VO-co-VL)	Copolymer **VAc+VO+VL** (90:5:5)
P(VO-*co*-VL)	Copolymer **VO+VL** (50:50)
P(VO)	Homopolymer of **VO**
P(VL)	Homopolymer of **VL**

PART A

Chapter I

General Introduction

"There is little doubt that the use of vegetable oils as a source of original polymers will increase progressively in the near future both in quantity and in the variety of novel macromonomers, and this will not constitute a problem with respect to changes in the global agricultural strategy because, contrary to what is being perceived with the much more massive biofuel domain, the needs of raw materials will always be very modest relative to the essential food and feed requirements."

Alessandro Gandini

Macromolecules 41 (24), 9491-9504, 2008

1. THE CONTEXT

Humankind has named the eras of its history by the materials that it has used to progress namely, the Stone Age, the Bronze Age, and the Iron Age. So, an appropriate name for our own era would be the "Polymer Age".[1] The presence of polymeric materials is found in almost all areas of life, both for high-value applications in electronics, automotive components, precision instruments, aircraft and aerospace industries, as well as for mass-produced products used in the fields of construction, packaging, agriculture, household appliances and leisure goods.[2]

The ever-increasing environmental concerns, as well as the dwindling in crude oil reserves and the rising cost of petroleum-derived commodity chemicals has led to the growing interest in polymeric materials from renewable origin.[3,4] The use of renewable resources, generally understood as "*any animal or vegetable species which is exploited without endangering its survival and which is renewed by biological (short term) instead of geochemical (very long term) activities*",[3] can contribute considerably to a sustainable development of humankind. Thus, the search for a sustainable development based on non-petrochemical feedstock had become one of the social paradigm of the 21st century, since renewable raw materials are potentially capable of providing a wide variety of monomers and polymers as comprehensive as those presently produced by the petrochemical industry.[3,5] Renewable materials can additionally provide polymers with novel properties not readily attained in fossil-based counterparts, e.g. hierarchical structures, environmental compatibility, biodegradability and the capability of chemical modification to suit custom-made applications.[6]

Renewable feedstock, such as the biomass from plant-derived resources, represents a promising opportunity to produce fuels, power, chemicals and materials by using the concept of the biorefinery.[7,8] The biorefinery follows a similar approach to that of the petroleum refinery, but with the main dissimilarity at the input level: biomass and fossil fuels, respectively, as illustrated in Figure 1.[9]

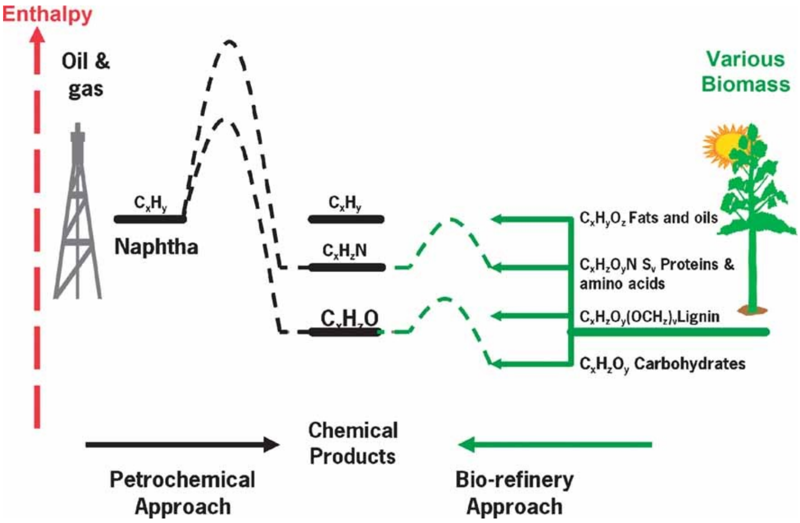


Figure 1. Petrochemical approach versus biorefinery approach (reprinted from [10]).

The purpose of a biorefinery is to generate high-value low-volume (HVLV) and low-value high-volume (LVHV) products, energy and fuels, using several processing technologies that maximize the valuable components and minimize the waste streams.[9,11] Biorefineries can be classified according to:[9,12]

(i) their processing technology: sugar platform, thermo-chemical conversion platform, carbon-rich chains platform, biogas platform and plant products platform;

(ii) their feedstock: lignocellulose biorefineries, whole-crop biorefineries and green biorefineries;

(iii) their technological development: phase I (limited number of feedstock and final products), phase II (fixed number of feedstock, processing flexibility, various final products) and phase III (wide variety of feedstock, multiple processing technologies, broad spectrum of final products). Phase III bio-refineries are also known as *integrated* bio-refineries due to the combination in the same plant of different feedstock and processing technologies to attain a maximum level of flexibility in terms of feedstock, products, energy and fuels production.[9]

The vegetable biomass, with its components, namely carbohydrates, lignin, proteins, oils, and, to a lesser extent, various other chemicals, such as vitamins, dyes, and flavours,[9] has economical and environmental advantages over petroleum-based materials, making it the most attractive alternative to replace fossil resources.[13] It is worth mentioning that of the vast amount of biomass annually renewed in nature, i.e. ~10^{11} tons, only 3.5% are presently used by mankind.[14] Table 1 gives an overview of the different kinds of renewable raw materials, their fields of application and the industries involved.[15] Although carbohydrates (particularly cellulose) are the most important fraction of vegetable biomass,[16] recent studies have demonstrated the need to fully explore this realm.[3,7,17]

Vegetable oils make up one of the biomass fractions whose research, aimed at their valorisation as a source of materials, is gaining momentum.[3,7,18,19] Presently, the attention given to these materials is increasing at a fast pace, since vegetable oils are promising monomers for polymer chemistry as a result of their competitive cost, natural abundance and reactive functionalities.[7,20] Figure 2 shows the life cycle of polymers based on vegetable oils, according to which the biomass from plant-derived resources is extracted in order to yield the vegetable oil. Subsequently, the oil is submitted to chemical modification with the aim of enhancing its reactivity towards a given type of polymerization approach.[21] The polymers are then made available to the consumers and, once used, they become waste, which after degradation and assimilation is reused as biomass and the cycle starts again.

Vegetable oils, which consist mainly of triglycerides, have been used for millennia as sources of polymeric materials in crafting activities related to protective coatings and lackers, mainly for wood artefacts. Since the 19th century, these applications, including printing inks, have gained an industrial status and in the last few decades, research on oil-based polymers has also been focussed on the production of materials for numerous other applications.[18]

Table 1. Industries and material uses of renewable raw materials.[15]

Raw material	Resources	Types of Industry	Applications
Sugar	In Europe: sugar beet Imported: sugar cane	Chemical industry (fermentation), pharmaceutical industry, plastics industry	Bulk chemicals, fine chemicals, polymers, cosmetics, pharmaceuticals, bioethanol.
Starch	Wheat, potato, maize, other cereals	Pulp and paper industry, chemical industry (fermentation), pharmaceutical industry, plastic industry	Paper starch, glues, binders, chemicals, cosmetics, textile starch, bioethanol, polymers.
Natural fibres	Europe: Hemp, flax, nettle, cotton Imported: cotton, kenaf, jute, sisal, ramie	Textile industry, pulp and paper industry, plastic industry	Textiles, technical textile, nonwovens (e.g. insulating materials), fiber reinforced plastics, paper.
Wood	Europe: Softwood, hardwood. Imported: tropical hardwood.	Pulp and paper industry, timber industry, plastic industry	Construction wood, packaging furniture, paper, cellulose.
Cork	Cork oak	Cork industry, construction industry, furniture industry	Corks (for wine), cork products, cork composites.
Vegetable oils	In Europe: rape, sunflower, olive. Imported: soybean, palm oil	Chemical industry, pharmaceutical industry, technical industry, plastics industry	Lubricants, surfactants, binders, paint additives, polymers, polymer additives, linoleum, glycerol (via biodiesel).
Proteins	(Animal tissue, milk protein, yeast extracts)	Pharmaceutical industry, chemical industry, technical industry	Pharmaceutical products, photo films, paper coating, glues, paints, polymers.
Medicinal plants	Different medicinal plants	Pharmaceutical industry	Drugs for pharmaceuticals, health food, cosmetics.

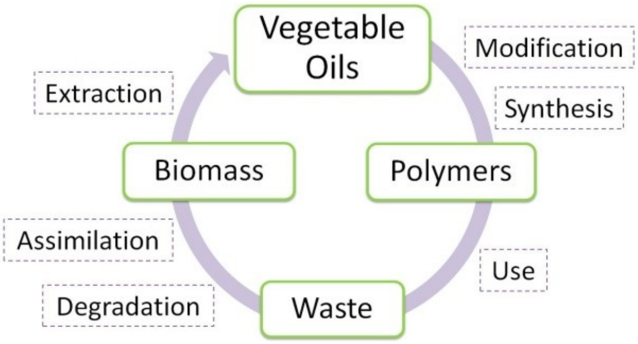


Figure 2. Life cycle of polymers based on vegetable oils.[22]

Currently, the use of vegetable oils is still mainly centred on the carboxyl functionalities, although the transformations involving the alkyl chain of fatty acids are gaining impetus as they are responsible for increasing the number of compounds obtained from vegetable oils.[5] A wide variety of vegetable oil-based polymeric materials are described in the literature. Important recent contributions in this field include the critical appraisal by Xia and Larock[18] on "*vegetable oil-based polymeric materials: synthesis, properties and applications*" and the review by Meier et al.[19] on "*oils and fats as renewable raw materials in chemistry*". The former deals with the use of vegetable oils as renewable raw materials for the synthesis of manifold monomers and polymers, whereas the latter highlights the progress in organic synthesis, catalysis and biotechnology using vegetable oils and their derivatives.

The future development of polymers from vegetable oils will surely be focussed on the increase in the use of vegetable oils as renewable materials in the chemical industry.[5,20] The design of vegetable-oil based polymers should consider sustainability, resource availability, land use, biodiversity, environmental impact, energy efficiency, soil conservation, and consumer demands.[23] This area will continue to face many challenges in handling and converting these renewable feedstock into industrial materials, as well as in controlling the properties of the ensuing polymers on the basis of performance, economical and environmental aspects.[20]

2. OBJECTIVES AND OUTLINE OF THE THESIS

The need to rely less heavily on petroleum is a crucial step towards sustainability and is leading to a greater use of renewable materials, such as vegetable oils, for the development of polymers. Thus, the main objective of this dissertation, organized in four parts and seven chapters, was to develop new monomeric and polymeric materials based on vegetable oils. More specifically, to prepare fatty acid-based monomers with polymerizable moieties capable of generating step-growth and chain-growth polymers with different properties depending on the structure of the initial monomers. The diversity of monomers and polymers successfully synthesized and characterized in this dissertation, confirmed beyond any doubt the usefulness of vegetable oils as a source of original polymer materials.

In **PART A**, a general introduction to the subject is presented in **Chapter I** and the fundamental aspects of vegetable oils and vegetable oil-based monomers and polymers are briefly reviewed in **Chapter II**.

PART B is devoted to the preparation of vegetable oil-based step-growth polymers, namely linear long-chain polyesters, and linear and non-linear thermoreversible polymers.

Chapter III describes the use of rapeseed oil derivatives as building blocks for the synthesis of 100% renewable aliphatic long-chain polyesters. For this purpose, erucic acid, a monounsaturated ω-9 fatty acid, was efficiently self-metathesized (and hydrogenated) to yield a linear saturated long-chain α,ω-dicarboxylic acid. The subsequent direct polycondensation of stoichiometric amounts of this C26 diacid with its corresponding C26 diol (obtained from the diacid via reduction), proved to be a straightforward method to prepare aliphatic long-chain polyesters that are 100% renewable. Their properties were investigated by means of various techniques, revealing high crystallinity, melting and degradation temperatures.

Chapter IV deals with the synthesis of linear thermoreversible polymers based on two renewable resources, i.e. castor oil and furan derivatives. Two click chemistry approaches were applied to these macromolecular syntheses, namely a thiol-ene coupling to convert unsaturated vegetable oil derivatives into bifunctional monomers, and their Diels-Alder (DA) polymerization to obtain linear thermoreversible materials. The depolymerisation of these linear polymers at 110 °C confirmed the clean-cut return to their respective starting monomers. This distinctive feature opens the way to original macromolecular materials with interesting applications, like mendability and recyclability.

Chapter V tackles non-linear thermoreversible polymers as a follow-up to the positive outcome of the linear systems described in the previous chapter. Trifunctional monomers derived from castor oil derivatives and bearing furan and maleimide complementary moieties were prepared and subsequently polymerized through the click-unclick Diels-Alder reaction to yield either hyperbranched or cross-linked materials based on two different renewable resources. The resulting non-linear polymers with thermoreversible features may find applications as amendable, recyclable and controlled phase-changing systems.

PART C is devoted to the preparation of vegetable oil-based chain-growth polymers, i.e. prepolymers for oxidative drying.

Chapter VI looks into the possible valorisation of vegetable oil derivatives, namely oleic and linoleic acids, through the synthesis of oligomeric prepolymers for further polymerization to give a cross-linked final material. Fatty acid vinyl esters monomers were prepared by transvinylation of oleic or linoleic acids with vinyl acetate and subsequently homo- and co-polymerized with vinyl acetate by conventional free radical processes. The ensuing materials were fully characterized and tested in oxidative drying. The results highlighted the adequate response to atmospheric drying and the possible application for the elaboration of original coating compositions based on renewable resources.

Finally, **PART D** highlights the most relevant results and conclusions obtained in this investigation, as well as some hints at future work (**Chapter VII**).

3. REFERENCES

[1] R.G. Griskey, *Polymer Process Engineering*. New York: Chapman & Hall, **1995**.

[2] W. Michaeli, *Plastics processing: an introduction*. Munich: Hanser Press, **1995**.

[3] M.N. Belgacem, A. Gandini (Eds.), *Monomers, polymers and composites from renewable resources*. Amsterdam: Elsevier, **2008**.

[4] A. Gandini, The irruption of polymers from renewable resources on the scene of macromolecular science and technology, *Green Chemistry* **2011**, 13, 1061-1083.

[5] U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J.O. Metzger, M.R. Klaas, H.J. Schäfer, M.P. Schneider, New Syntheses with Oils and Fats as Renewable Raw Materials for the Chemical Industry, *Angewandte Chemie International Edition* **2000**, 39, 2206-2224.

[6] S.J. Eichhorn, A. Gandini, Materials from renewable resources, *MRS Bulletin* **2010**, 35, 187-190.

[7] A. Corma, S. Iborra, A. Velty, Chemical Routes for the Transformation of Biomass into Chemicals*, Chemical Reviews* **2007**, 107, 2411-2502.

[8] H. R. Ghatak, Biorefineries from the perspective of sustainability: Feedstocks, products, and processes, *Renewable and Sustainable Energy Reviews* **2011**, 15, 4042-4052.

[9] S. Fernando, S. Adhikari, C. Chandrapal, N. Murali, Biorefineries: current status, challenges and future direction*, Energy & Fuels* **2006**, 20, 1727-1737.

[10] J. Sanders, E. Scott, R. Weusthuis, H. Mooibroek, Bio-refinery as the bio-inspired process to bulk chemicals, *Macromolecular Bioscience* **2007**, 7, 105-117.

[11] National Renewable Energy Laboratory. Conceptual biorefinery: http://www.nrel.gov/biomass/biorefinery.html (September 2012).

[12] B. Kamm, M. Kamm, Biorefinery systems, *Chemical and Biochemical Engineering Quarterly* **2004**, 18, 1-6.

[13] R. T. Mathers, How Well Can Renewable Resources Mimic Commodity Monomers and Polymers?, *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, 50, 1-15.

[14] L. Shen, J. Haufe, M. K. Patel, Product overview and market projection of emerging bio-based plastics, *PRO-BIP* **2009**: http://www.epnoe.eu/research/Life-Cycle-Analysis (September 2012).

[15] A. Jering, J. Günther, A. Raschka, M. Carus, S. Piotrowski, L. Scholz, Use of renewable raw materials with special emphasis on chemical industry, *ETC/SCP report 1/* **2010**: http://scp.eionet.europa.eu/publications/Use%20of%20RRM/wp/WP2010_1 (September 2012).

[16] T. Werpy, G. Peterson (Eds.), Top Value Added Chemicals from Biomass. Results of Screening for Potential Candidates from Sugars and Synthesis Gas, *Pacific Northwest National Laboratory*, **2004**.

[17] B. Kamm, P. R. Gruber, M. Kamm (Eds.), *Biorefineries-Industrial Processes and Products*, Weinheim: Wiley-VCH, **2006**.

[18] Y. Xia, R. C. Larock, Vegetable oil-based polymeric materials: synthesis, properties and applications, *Green Chemistry* **2010**, 12, 1893-1909.

[19] U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger, H. J. Schäfer, Oils and Fats as Renewable Raw Materials in Chemistry, *Angewandte Chemie International Edition* **2011**, 50, 3854-3871.

[20] C. K. Williams, M. A. Hillmyer, Polymers from renewable resources: a perspective for a special issue of polymer reviews, *Polymer Reviews* **2008**, 48, 1-10.

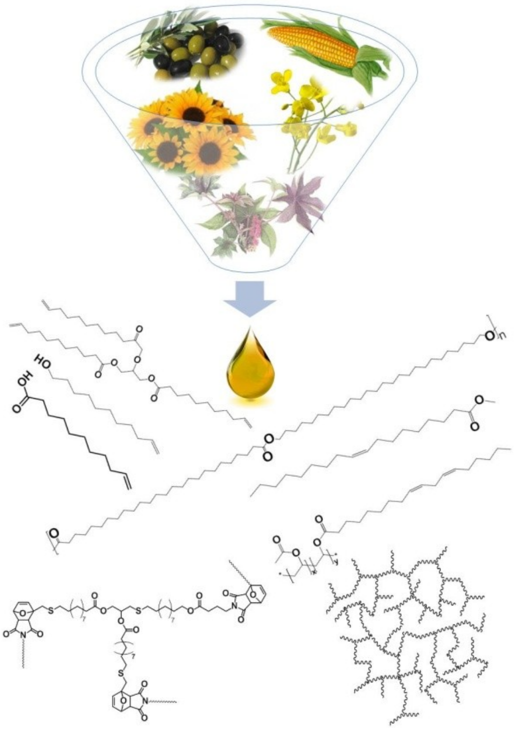
[21] A. Gandini, Polymers from renewable resources: A challenge for the future of macromolecular materials*, Macromolecules* **2008**, 41, 9491-9504.

[22] F. S. Güner, Y. Yağci, A. T. Erciyes, Polymers from triglycerides oils, *Progress in Polymer Science* **2006**, 31, 633-670.

[23] R. P. Wool, X. S. Sun, *Bio-based polymers and Composites*, USA: Elsevier, **2005**.

Chapter II

THE STATE OF THE ART



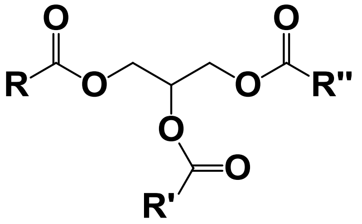
The almost simultaneous publication of books, reviews and monographs on materials from vegetable oils, together with the increasing flow of more specific studies covering the wide range of oils and related chemical modifications, represent an indisputable proof of the growing relevance of this realm.

1. VEGETABLE OILS

Vegetable oils are perceived as one of the most important classes of renewable resources for the chemical industry in the synthesis of fine chemicals, monomers and polymers.[1,2] The following paragraphs outline their structure, sources, properties and applications.

1.1 Structure

Vegetable oils are a mixture of triglycerides, i.e., tri-esters of glycerol with long-chain fatty acids, as shown in Scheme 1. Fatty acids represent 94-96% of the total weight of a triglyceride molecule.[2] Generally, the chain length of fatty acids varies from 14 to 22 carbons (C16 and C18 being the most common), with 0 to 3 double bonds per chain.[2,3,4]



R, R', R'' = alkyl/alkenyl residues

Scheme 1. General structure of a triglyceride, the main component of vegetable oils.

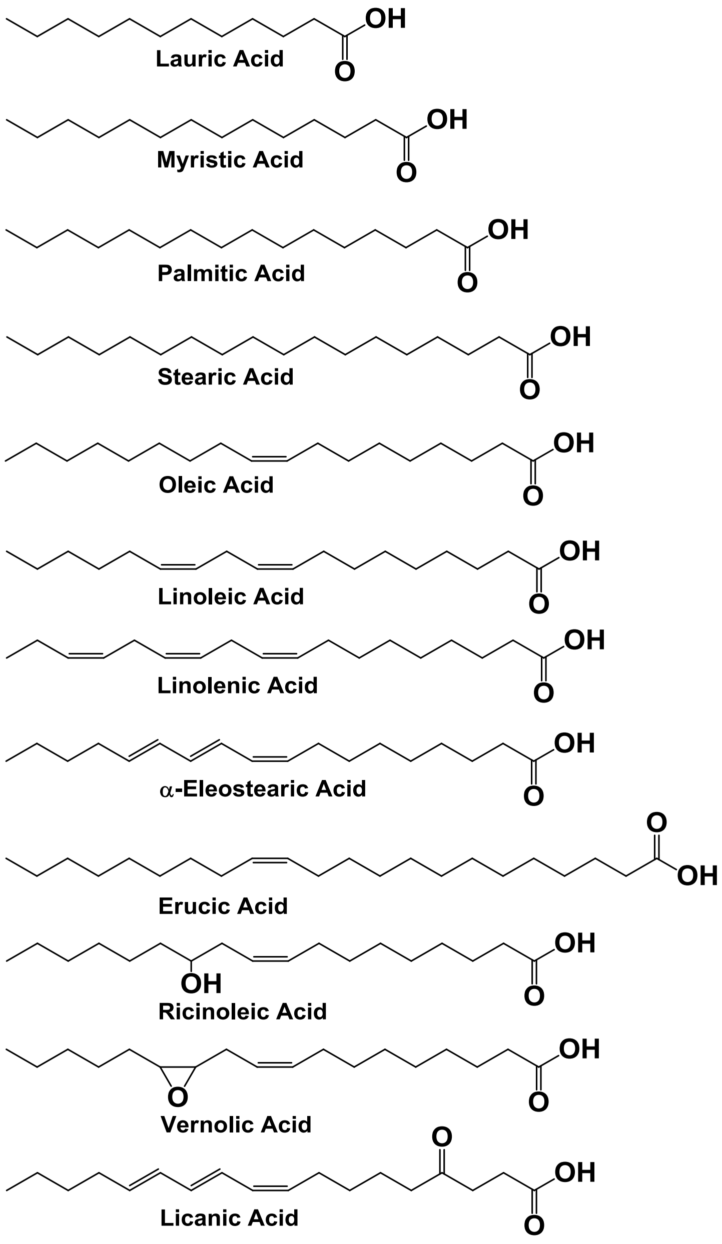
More than 1000 fatty acids have been identified, but only around 20 are present in appreciable quantities in vegetable oils.[5,6] Fatty acid compositions vary according to the plant species, the crop, the season and the growing conditions.[7] Table 2 lists the most common fatty acids in natural oil compositions and Scheme 2 shows their molecular structure.

Table 2. List of the most common fatty acids.[3,8]

Trivial name	**Systematic name**	**Structure (C:DB)***	**Formula**
Lauric acid	Dodecanoic acid	12:0	$C_{12}H_{24}O_2$
Myristic acid	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$
Palmitic acid	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$
Stearic acid	Octadecanoic acid	18:0	$C_{18}H_{36}O_2$
Arachidic acid	Eicosanoic acid	20:0	$C_{20}H_{40}O_2$
Behenic acid	Docosanoic acid	22:0	$C_{22}H_{44}O_2$
Lignoceric acid	Tetracosanoic acid	24:0	$C_{24}H_{48}O_2$
Palmitoleic acid	*cis*-9-Hexadecenoic acid	16:1	$C_{16}H_{30}O_2$
Oleic acid	*cis*-9-Octadecenoic acid	18:1	$C_{18}H_{34}O_2$
Linoleic acid	*cis*,*cis*-9,12-Octadecadienoic acid	18:2	$C_{18}H_{32}O_2$
Linolenic acid	*cis*,*cis*,*cis*-9,12,15-Octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$
α-Eleostearic acid	*cis*,*trans*,*trans* -9,11,13-Octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$
Erucic acid	*cis*-13-Docosenoic acid	22:1	$C_{22}H_{42}O_2$
Ricinoleic acid	12-Hydroxy-*cis*-9-octadecenoic acid	18:1	$C_{18}H_{34}O_3$
Vernolic acid	12,13-Epoxy-*cis*-9-octadecenoic acid	18:1	$C_{18}H_{32}O_3$
Licanic acid	4-Oxo-*cis*,*trans*,*trans*-,11,13-octadecatrienoic acid	18:3	$C_{18}H_{28}O_3$

* *C* indicates the number of carbons and *DB* the number of double bonds in the fatty acid chain

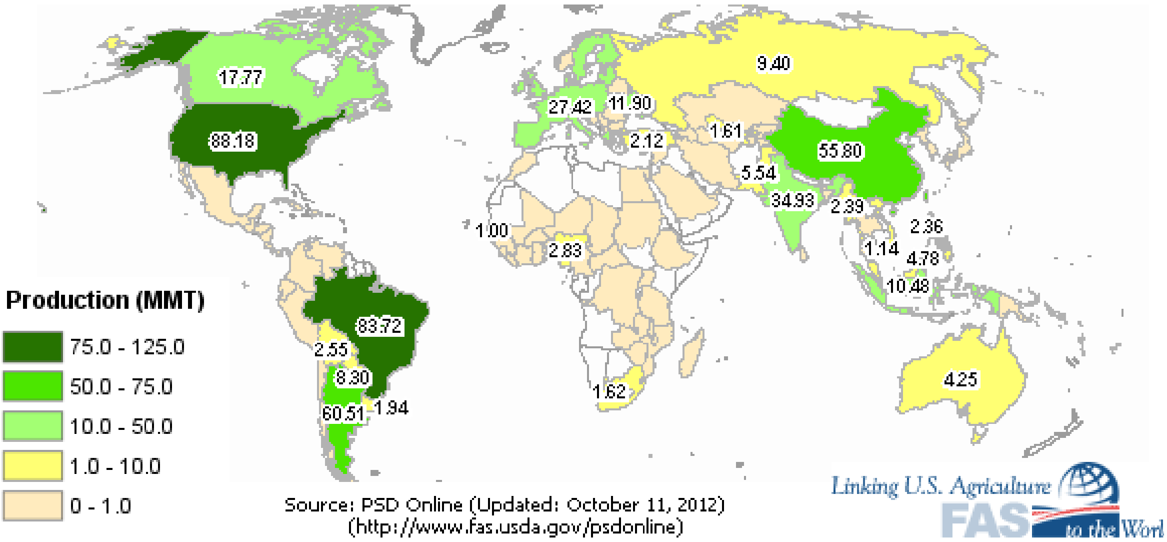
Some fatty acids, like lauric, myristic, palmitic, stearic, arachidic, behenic and lignoceric acid, are saturated, while others are monounsaturated, e.g. oleic and erucic acids, and polyunsaturated, like linoleic and linolenic acid. In most vegetable oils, the double bonds of fatty acids are in the *cis* configuration (e.g. in oleic and linoleic acid) although some small amounts of *trans* isomers may occur (e.g. in α-eleostearic and licanic acid).[9] Additionally, the double bonds are mainly non-conjugated as in linoleic and linolenic acids, whereas a few are conjugated, e.g. in eleostearic and licanic acid.[9] Finally, there are also oils containing fatty acids with other moieties along their chains, like ricinoleic, vernolic and licanic acid with hydroxyl, epoxy and carbonyl groups, respectively.[4,5]



Scheme 2. Molecular structure of some fatty acids.

1.2 Major sources

The world production of major oilseeds has increased in the last ten years from 331 to 457 million tonnes, whereas the area harvested increased from 186 to 234 million acres in the same period of time.[10] According to the United States Department of Agriculture, soybean oilseeds represent over half of the total production of oilseeds and are mainly grown in Brazil, USA and Argentina; followed by rapeseed (grown in EU-27, Canada and China), cottonseed (China and India) and sunflower oilseeds (Ukraine, EU-27 and Russia).[10] Figure 3 shows the total production of major oilseeds around the world for 2012/2013.



Source: PSD Online (Updated: October 11, 2012)
(http://www.fas.usda.gov/psdonline)

Figure 3. Total production of oilseeds 2012/2013 (source: USDA report for October 2012).[10]

Accordingly, the world production of major vegetable oils has risen from 95 million tonnes in 2002/2003 to 154 million tonnes in 2012/2013 at an average rate just over 5 million tonnes a year,[10] as depicted in Table 3. This increasing demand is related, firstly, with the demand to feed a population that is increasing in number and, secondly, with the demand for biodiesel as a partial replacement for fossil fuels.[11] Although the majority of vegetable oils are primarily produced for food and feed purposes, minor vegetable oils like castor and linseed oil are almost solely used for industrial applications.[12]

The palm and soybean oil are the most widespread oils, with an annual production of some 52 and 24 million tonnes, respectively, followed by rapeseed and sunflowerseed oil, with about 23 and 13 million tonnes, respectively.[10] Exports at 64 million tonnes are even more dominated by palm and soybean oil with 40 and 8.5 million tonnes,[10] respectively (Table 3).

Table 3. Major vegetable oils: world production, trade and consumption (million tonnes).[10]

Oils	**2002/2003**	**2012/2013**		
	Production	**Production**	**Exports**	**Consumption**
Coconut	3.16	3.52	1.70	3.75
Cottonseed	3.51	5.16	0.12	5.19
Olive	2.51	2.94	0.77	3.05
Palm	27.71	52.33	40.36	51.69
Palm kernel	3.36	6.09	3.05	5.78
Peanut	4.62	5.18	0.21	5.19
Rapeseed	12.21	23.21	3.62	23.62
Soybean	30.57	42.69	8.50	43.57
Sunflowerseed	8.12	13.13	5.80	13.24
Total	95.76	154.24	64.12	155.06

The majority of oilseeds are transformed into oil and protein meal. The isolation of vegetable oils can be performed by both mechanical or solvent extraction.[3,5,9] The mechanical extraction technology consists in the application of shear forces to the beans, cells and oil bodies with the aim of releasing the oil. This process presents advantages related with its low cost, low investment costs and absence of environmental issues, as well as disadvantages associated with low oil recovery yields.[3,5] On the other hand, the solvent extraction technology consists in the diffusion of an organic solvent (usually hexane) through the seeds, followed by the solubilisation and extraction of the oil. The main advantage of this process is the higher oil recovery, whereas its drawbacks are the higher investment and environmental issues related with the use of volatile organic solvents.[3,5]

After isolation, vegetable oils are refined in order to obtain high-quality products, free from impurities such as phosphatides, free fatty acids, gummy substances, coloured bodies, tocopherols, sterols, hydrocarbons, ketones, aldehydes, etc.[5]

Given that the composition of vegetable oils is variable, so are their applications as renewable feedstock for the production of chemicals.[13] Table 4 shows the composition of some vegetable oils in terms of fatty acid content. For instance, linseed oil consists mainly of linolenic acid triglyceride; corn, cottonseed and soybean oil have linoleic acid as the most abundant constituent; and oleic acid triglyceride is the main component of olive oil. In turn, castor oil is essentially composed of the OH-bearing ricinoleic acid triglycerides (87.5%), whereas oiticica oil consists mainly of the polyunsaturated licanic acid (74.0%).[3]

Nevertheless, the content of the different fatty acids in vegetable oils can be modified by breeding or genetic modification of crops, as reported in the appropriate literature.[14,15] For instance, erucic acid (43.0%) is the main fatty acid in traditionally rapeseed oil, but nowadays a major part of the rapeseed varieties in cultivation are based on zero erucic acid content,[16] given its toxicity for humans when taken in high doses.

Table 4. Fatty acids distribution in several vegetable oils.[2,3,16,17]

Oils	**Fatty acid / %**					
	Palmitic	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**	**Other**
Castor	1.5	0.5	5.0	4.0	0.5	87.5
Corn	10.9	2.0	25.4	59.6	1.2	–
Cottonseed	21.6	2.6	18.6	54.4	0.7	–
Linseed	5.5	3.5	19.1	15.3	56.6	–
Olive	13.7	2.5	71.1	10.0	0.6	–
Oiticica	6.0	4.0	8.0	8.0	–	74.0
Palm	39.0	5.0	45.0	9.0	–	–
Rapeseed	5.0	14.0	15.0	14.0	9.0	43.0
Soybean	11.0	4.0	23.4	53.3	7.8	–
Sunflower	6.0	4.0	42.0	47.0	1.0	–

1.3 Properties

As mentioned above, vegetable oils are a mixture of triglycerides that differ in fatty acids chain composition. Since triglycerides incorporate mostly aliphatic hydrocarbon chains, they are insoluble in water and soluble in solvents like hexane and acetone.[9]

The chemical and physical properties of vegetable oils depend to a great extent on their fatty acid distribution, as well as on the number and position of double bonds within the aliphatic chains.[2,3] Table 5 shows some physical properties, *viz*. the viscosity, specific gravity, refractive index and melting point of common vegetable oils which are important in various chemical engineering unit operations in the natural oil industry.

Vegetable oils with no functional groups other than the ester moieties are Newtonian fluids with low viscosities, but when other functionalities are present in the aliphatic chains, such as unsaturations, epoxy, hydroxyl or carbonyl groups, the viscosity of the oils can increase significantly.[5] For instance, castor oil, a source of ricinoleic acid, displays a high kinematic viscosity (Table 5) mainly due to the presence of both a double bond and a free hydroxyl group.[18] This oil is widely used as lubricant because of its low viscosity variation with temperature.[18]

The specific gravity of vegetable oils are lower than unity, which means that (as expected) the densities of vegetable oils are lower than the density of water.

The refractive index of a medium indicates how much the speed of light is slowed down inside it. This index is a function of the radiation wavelength and the temperature, and is usually measured at 20 °C at the wavelength of the sodium D line (λ=589.3 nm).[19] As an example, sunflower oil has a refractive index between 1.473 and 1.477 (Table 5), which means that the speed of light in this vegetable oil is 1/1.473 = 0.68 times the speed of light in vacuum.

The melting behaviour of vegetable oils depends on the nature of the component triglycerides. Thus, triglycerides that consist mainly of long-chain saturated acids have high melting points, whereas those rich in polyunsaturated acids have lower melting points.[6,20] As illustrated in Table 5, most oils are liquid at ambient conditions, however palm oil, whose melting point ranges from 33 to 40 °C, is semi-solid since it has a high content of saturated fatty acids (see Table 4).

Table 5. Some physical and chemical properties of vegetable oils.[2,3]

Name	Kinematic viscosity (cSt at 37.8 °C)	Specific gravity (20 °C/4 °C)	Refractive index (n_D^{20})	Melting point / °C
Castor oil	293.4	0.951-0.966	1.473-1.480	-20 to -10
Linseed oil	29.60	0.925-0.932	1.480-1.483	-20
Palm oil	30.92	0.890-0.893	1.453-1.456	33 to 40
Soybean oil	28.49	0.917-0.924	1.473-1.477	-23 to -20
Sunflower oil	33.31	0.916-0.923	1.473-1.477	-18 to -16

One of the classical but still useful parameter used in the characterization of vegetable oils is the iodine value defined as the amount of iodine in grams that react with the double bonds present in 100 g of a given oil sample under specified conditions.[7,9,21] So, this index is a measurement of the number of unsaturations in the aliphatic chain and is hence related to several chemical and physical properties of vegetable oils. Additionally, it is used as a quality control method for hydrogenation, standard for biodiesel, and as a measure of oxidative stability of vegetable oils, triglycerides and fatty acids.[21] Table 6 shows typical iodine values of some common vegetable oils. Based on this data, vegetable oils can be divided into three major classes, according to the average degree of unsaturation measured by their iodine value (often referred to as "siccativity"): (i) "drying oils", when the iodine value is higher than 130, e.g. linseed oil; (ii) "semi-drying oils", if the iodine value lies between 90 and 130, e.g. sunflower or soybean oil; and (iii) "non-drying oils", when the iodine value is lower than 90, e.g. palm and olive oil.[2,3]

Hence, the presence of unsaturated acids in vegetable oils provides them with the important commercial property of "drying",[20] i.e. the double bonds of the unsaturated acids react with atmospheric oxygen and then with one another to form a three-dimensional polymeric network with application in paints, varnishes and other coating processes (see Chapter II, section 3.3.1).[22]

Table 6. Iodine values of several vegetable oils.[9]

Oil	**Iodine value (g of I_2 / 100 g of oil)**
Linseed	168-204
Sunflower	125-140
Soybean	123-139
Corn	118-128
Rapeseed	100-115
Cottonseed	98-118
Olive	76-88
Palm	50-55

1.4 Applications

Vegetable oils are primarily used as food and feed. In the food market, the used oils are mainly composed of palmitic, stearic, oleic, linoleic and linolenic acid, and, depending on their specific end-use, different oils bearing different compositions of the mentioned acids are utilized. For instance, common margarines have a higher proportion of triglycerides composed of saturated fatty acids, while cooking and salad oils are richer in triglycerides composed of monounsaturated and polyunsaturated fatty acids, respectively.[23]

Vegetable oils are also used in other areas, like the production of biofuels, lubricants, paints, coatings, inks, plasticizers, agrochemicals, pharmaceuticals and construction materials.[2-4,7,24] In the chemical industry, vegetable oils represent the utmost part of the use of renewable raw materials, since they offer a broad spectrum of possibilities for applications that the petrochemical industry cannot always provide.[1]

The broad spectrum of possible applications that vegetable oil-based products offer is determined by the composition of the fatty acids contained in the oil. For instance, coconut and palm kernel oils are suitable for further processing to surfactants for washing and cleansing, as well as cosmetics, since they consist mainly of short or medium-chain fatty acids (12 to 14 carbon atoms). In turn, palm, soybean, rapeseed and sunflower oils are specially used as raw materials for polymer applications and lubricants, since they are mainly composed of long-chain saturated and unsaturated fatty acids.[25]

The application of vegetable oils in the polymer field makes use of oil derivatives such as epoxides, polyols and dimerization products based on unsaturated fatty acids, to generate plastic additives or components for composites or polymers like polyamides and polyurethanes.[25] Vegetable-oil based polymers have applications in paints, inks and coatings,[26] photoresist processes,[27] toughening agents in PVC and epoxy resins,[28] foams,[29,30] composites,[31] adhesives[32], among others. All of these applications can be derived from bio-based oils using synthetic techniques similar to those used with petroleum-derived monomers.[5]

One of the best known examples of vegetable oil applications that has been used for decades is Linoleum, a natural flooring composite made from linseed oil, wood flour, rosin, limestone and jute.[7,33] Linoleum flooring is an environmentally friendly alternative to other type of floorings with a long history of interior design and architecture due to its practical, economic and hygienic advantages.[34]

Another well-known application of vegetable oils is in the field of fuels. The use of vegetable oils as a fuel dates back to 1900 when Rudolf Diesel developed the first diesel engine which was run with groundnut oil as fuel.[35] Biodiesel contains alkyl fatty esters and is synthesized mainly by the transesterification of vegetable oils with an alcohol, usually methanol, to originate monoalkyl (ethyl or methyl) esters.[36] Nowadays, biodiesel continues to be an attractive alternative fuel to fossil diesel fuel with a worldwide production of 15 000 million litres in 2009 (sixteen times more than in 2001).[43] Biodiesel is about 90% as effective as conventional diesel, but it is not used as a fuel for vehicles in its pure form. In general, it is used as a petroleum diesel additive to reduce levels of pollutants from standard diesel-powered vehicles.[36]

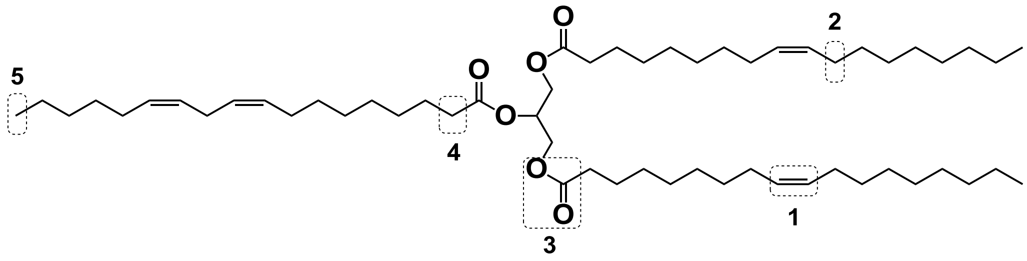
Finally, vegetable oils are also used in the candle industry to replace petroleum-based paraffin waxes, a by-product of the fractionation and refining of the fossil fuel crude oil.[37] Although candles made from paraffin are low-priced for consumers, the rising petroleum prices and environmental concerns have increased people’s interest in using products that are from renewable sources.

2. MONOMERS FROM VEGETABLE OILS

The natural abundance and reactive functionalities of vegetable oils make them useful oleochemicals for polymer chemistry.[24] This section deals systematically with triglycerides from vegetable oils as building blocks of new polymeric materials.

2.1 Overview

The triglyceride molecules have several active sites such as the double bonds, the allylic carbons, the ester groups, the α-carbonylic carbons and the ω-carbons (Scheme 3), that can be used to introduce polymerizable groups.[5,31]



(1) double bond
- oxidation
- epoxidation
- hydroformylation
- dimerization
- ozonolysis
- metathesis
- thiol-ene coupling
- hydrogenation
- pericyclic reaction
- sulfonation
- carbonylation

(2) allylic carbon
- halogenation
- hydroperoxidation
- hydroxylation
- electrochemical acetylation

(4) α-carbon
- α-sulfonation
- α-halogenation
- alkylation
- acylation
- Claisen condensation

(3) ester group
- hydrolysis
- alcoholysis
- transesterification
- saponification
- halogenation
- reduction
- amidation

(5) ω-carbon
- ω-oxidation

Scheme 3. Active sites of a triglyceride molecule and some possible reactions of each chemically active site.[12,13,38]

The chemical functionalization of vegetable oils can therefore be performed either at (i) the ester groups of triglycerides or (ii) at any reactive functionality along the aliphatic chain of the fatty acids,[39] as exemplified in Figure 4. In the former case (i), hydrolysis and transesterification are the prime reactions leading to the formation of glycerol and fatty acids or fatty acid esters, respectively. In the latter case (ii), the reactions used to modify triglycerides include epoxidation, metathesis, dimerization, oxidative cleavage, hydroformylation, etc. The majority of the derivatization reactions for product development based on triglycerides are performed at the ester group (around 90%), whereas oleochemical reactions carried out at the double bonds or alkyl chains account for less than 10%.[25]

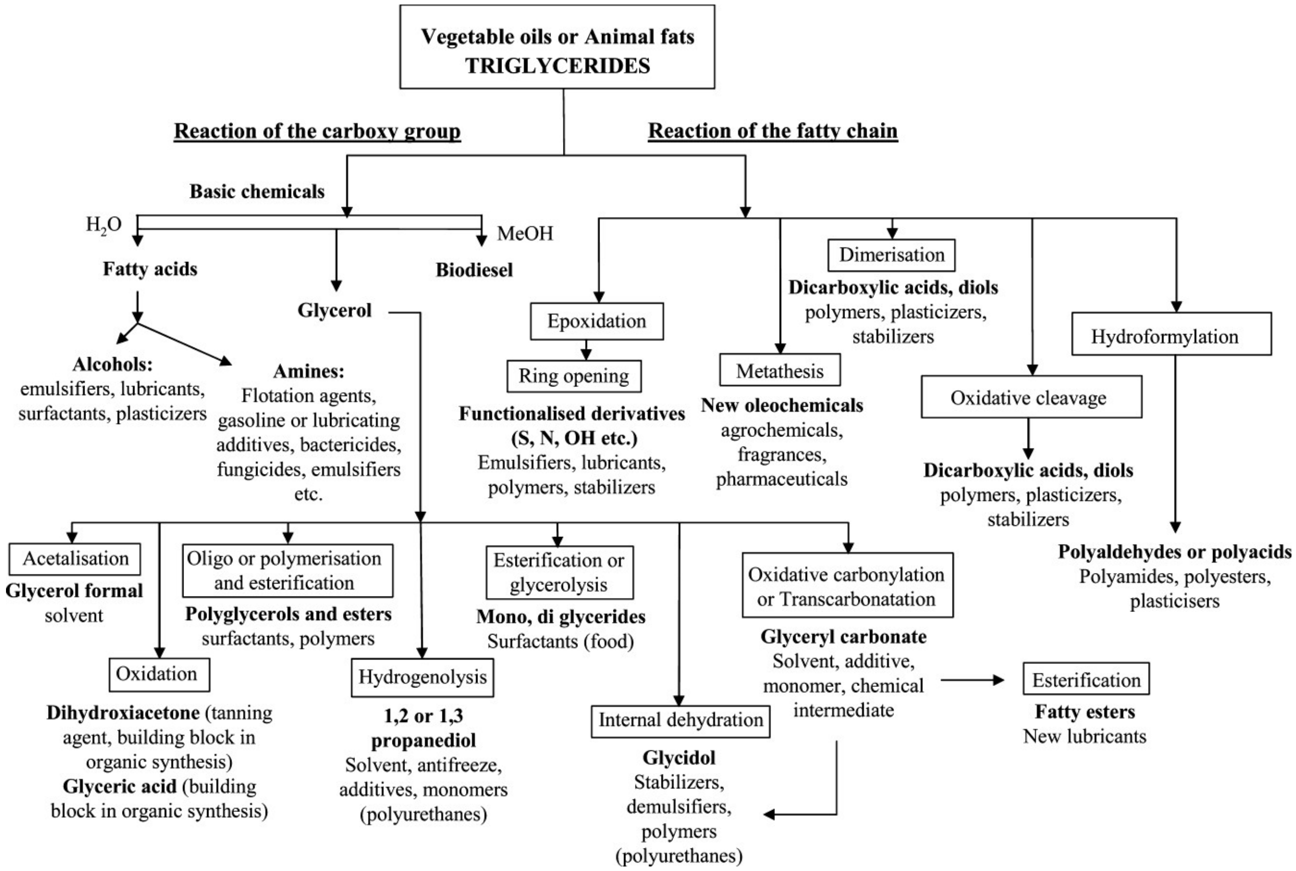


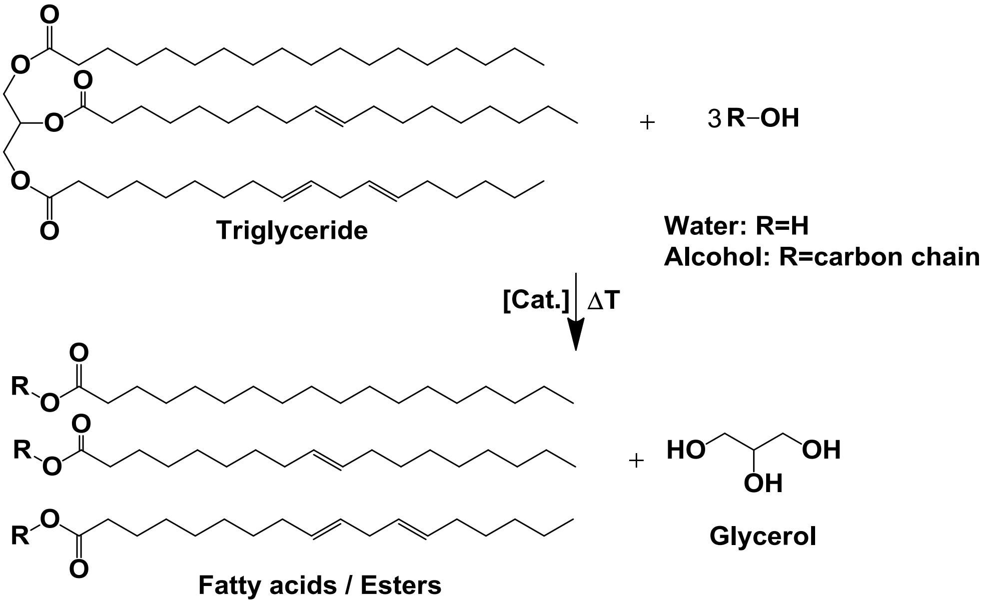
Figure 4. Routes for the preparation of valuable products from fats and oils (reproduced from [13]).

The most important functionalization possibilities of the ester groups and double bonds are extensively reviewed in the literature.[1,13,40-12] Noteworthy contributions include the appraisal by Biermann and co-workers[1] who reviewed each of the above chemical reactions that occur at the fatty acid chain, as well as other reactions like the preparation of aziridines and episulfides, the synthesis of aromatics, pericyclic reactions, radical, thermal, and cationic additions, enzymatic reactions, and microbial transformations. The review by Corma, Iborra and Velty[13] that focuses on the use of fats and oils for the production of chemicals where the authors extensively reviewed the reactions of the carboxy group and of the fatty acid chain of triglycerides. The appraisal of Behr et al.[41] reviews the catalytic processes for the technical use of natural fats and oils with an emphasis on catalytic functionalization reactions at the double bonds of fatty compounds. These processes generated a number of interesting new products in high yield and with diverse possible applications. Ultimately, the review by Meier et al.[12] that highlights the progress in organic synthesis, catalysis and biotechnology using vegetable oils and their derivatives.

2.2 Reactions of the ester group

As already pointed out, hydrolysis of triglycerides to glycerol and fatty acids or the transesterification of triglycerides with an alcohol to glycerol and fatty acid esters are the main reactions occurring at the ester group, as illustrated in Scheme 4.

The transesterification of vegetable oils mostly with methanol is the pathway for biodiesel production,[42] the greener alternative fuel to petro-diesel. Biodiesel production has increased from 900 to 15 000 million litres from 2001 to 2009 and is expected to reach 45 000 million litres by 2020.[43] Besides its dominant use as fuel, other detours are being tackled for alternative applications, e.g. as a green polymerization solvent.[44,45] The surplus glycerol resulting from the process is an intermediate in the synthesis of a large number of industrial commodities[13] and a considerable amount of research has focused on its use as a platform chemical to replace some mainstream petroleum-derived chemicals.[46] Its utilization was broadly reviewed recently[47,48] and includes, for example, the application as a green solvent,[49] hydrogels[50,51] and in the production of synthesis gas.[52]



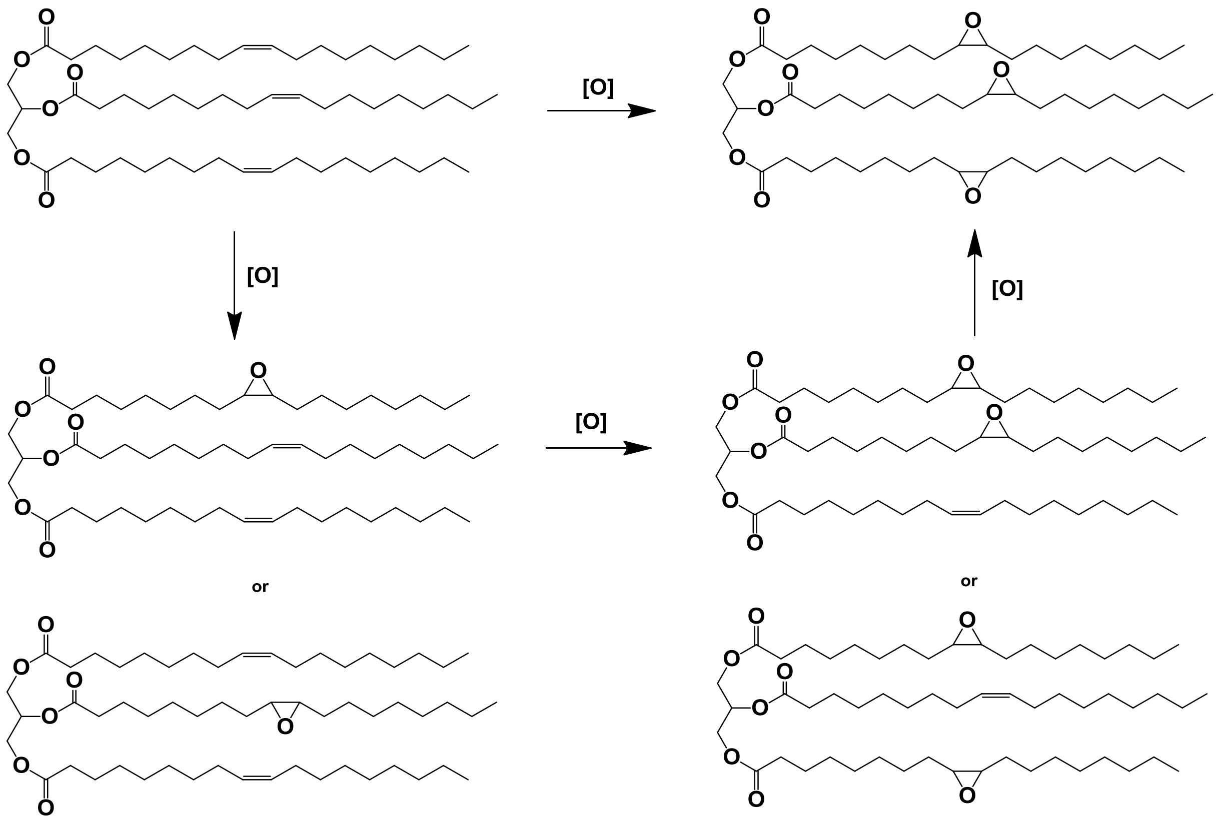
Scheme 4. Chemical conversion of triglycerides by hydrolysis and transesterification.

2.3 Reactions of the aliphatic chain

Vegetable oils/triglycerides have other active sites besides their ester functionality, as epitomized in Scheme 3. Reactions such as epoxidation, hydroformylation, dimerization, thiol-ene coupling, oxidative cleavage, olefin metathesis, etc, that occur at the double bonds of unsaturated oils, fatty acids, or fatty acid esters, are essential for the development of oleochemical monomers for polymers syntheses.[13] Each of these reactions is discussed below and further details related to them are developed in the relevant literature.[1,3,13,25,41]

2.3.1 Epoxidation

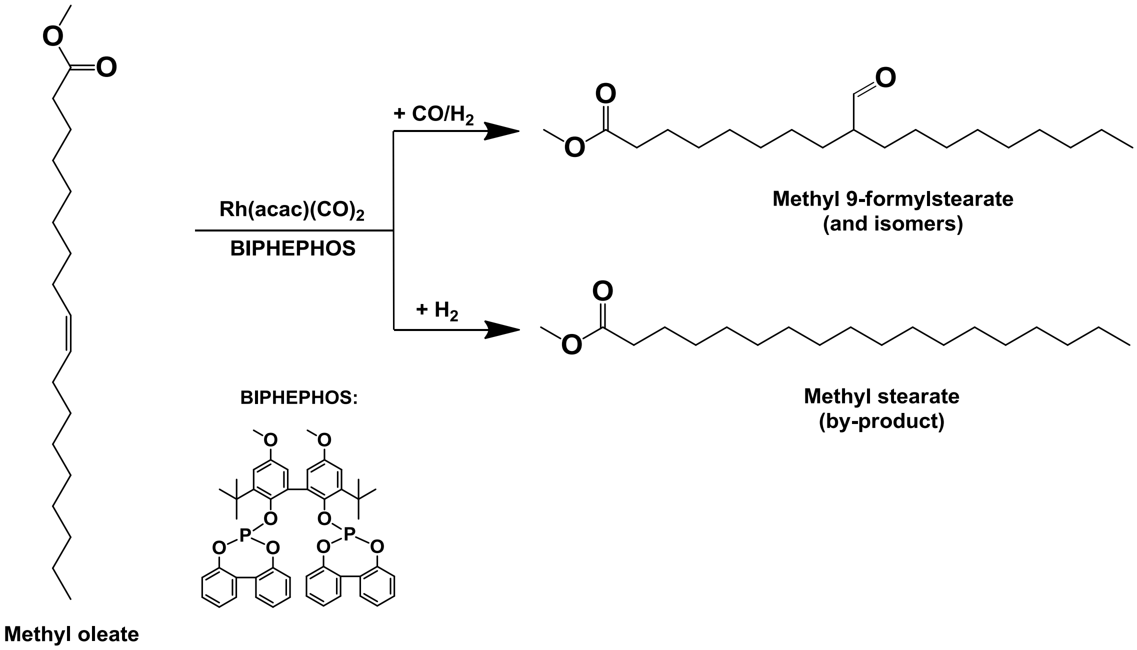
The diversity of epoxidized products obtained by epoxidation of fatty acids and their derivatives is quite broad due to the formation of mono-, di-, or tri-epoxides according to the origin of the oilseed,[13] as depicted in Scheme 5. Fatty acid epoxide derivatives are mainly used as additives in plastics and polyurethane foams.



Scheme 5. Example of the products obtained by epoxidation of trioleate.[13]

2.3.2 Hydroformylation

The hydroformylation reaction is the most important method used to replace a double bond by a carbonyl group.[13,53] This reaction is a functionalization in which the formyl group –CHO is added to the C=C double bond by a homogeneous catalytic reaction with synthesis gas (a mixture of CO and H_2). Thus, hydroformylation, or “Oxo Process”, can be used to obtain aldehydes from triglycerides or fatty acid esters in the presence of homogeneous catalysts based on rhodium or cobalt.[13] As an illustrative example, Scheme 6 shows the hydroformylation reaction of methyl oleate that yields an isomeric mixture of methyl 9-formylstearate and methyl stearate as a by-product.[41] Aldehydes obtained from triglycerides or fatty acid esters are useful for the synthesis of polyols, polyacids, polyesters, and polyamides, which in turn can be applied in the synthesis of diverse polymers.[13]

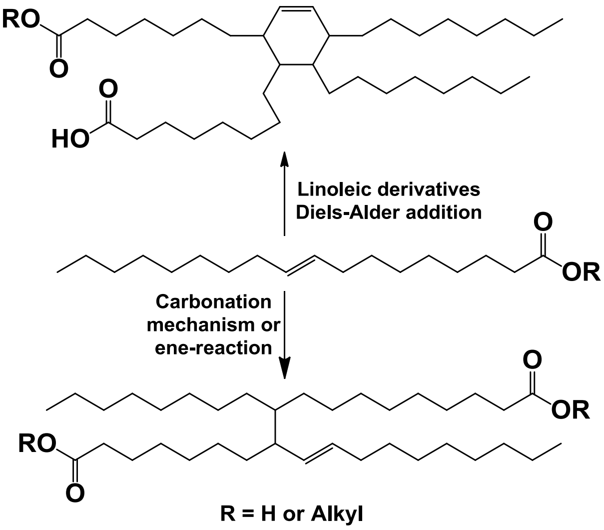


Scheme 6. Hydroformylation of methyl oleate via rhodium catalysis.[41]

2.3.3 Dimerization

The dimerization reaction in this context refers to the combination of two molecules bearing olefinic moieties. Scheme 7 shows some possible routes for the dimerization of a fatty acid derivative. This reaction is vital for the preparation of dicarboxylic acids which are used in the synthesis of polyesters or polyamides.

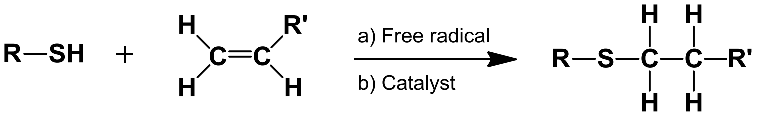
The dimerization of monounsaturated fatty acid derivatives occurs either by ene-reactions or by carbonation mechanisms: both routes originate dimers, and then trimers, and oligomers. Additionally, the dimers can be further hydrogenated into diols that yield intermediates for the preparation of polyethers and polyurethanes.[13] On the other hand, the dimerization of polyunsaturated fatty acid derivatives can adopt other mechanisms, like the Diels-Alder addition that gives cyclohexene rings.[13]



Scheme 7. Possible routes for the dimerization of fatty derivatives.[13]

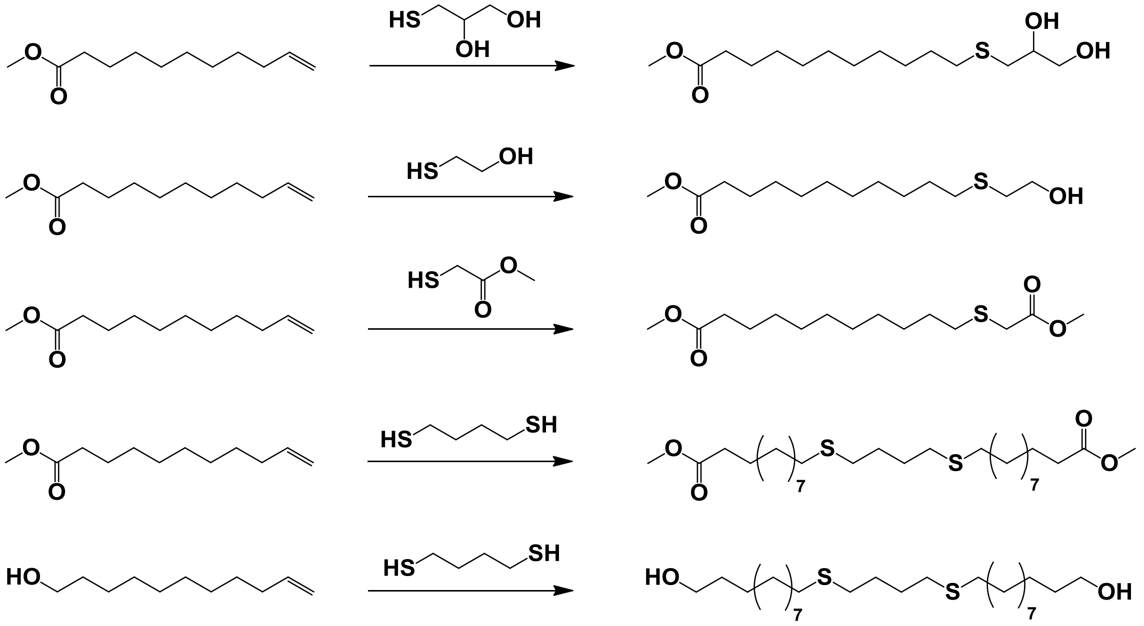
2.3.4 Thiol-ene coupling

The thiol-ene coupling[54-57] is another powerful tool to functionalize double bonds and has attracted the interest of researchers due to its click chemistry character.[55,56] Two thiol reactions of particular interest emerged, namely the thiol-ene free radical addition to electron-rich/electron-poor carbon-carbon double bonds and the catalyzed thiol Michael addition to electron-deficient carbon-carbon double bonds,[57] as shown in Scheme 8.



Scheme 8. General thiol-ene coupling by a) free radical and b) Michael addition reactions.[57]

The thiol-ene coupling has been applied to vegetable oils or their fatty acids to prepare several monomers and polymers.[58-62] For instance, Samuelsson et al.[59] and Claudino et al.[60] investigated the kinetics of the photo-initiated thiol-ene coupling of trifunctional thiols with methyl oleate and methyl linoleate. Bantchev et al.[61] prepared sulphide-modified vegetable oils through the thiol-ene addition of butanethiol to canola and corn oil for such end-use applications as lubricants. Moreover, Türünç and Meier[62] prepared a set of novel monomers derived from 10-undecenoic acid via thiol-ene additions in the absence of solvent and initiator, as illustrated in Scheme 9.

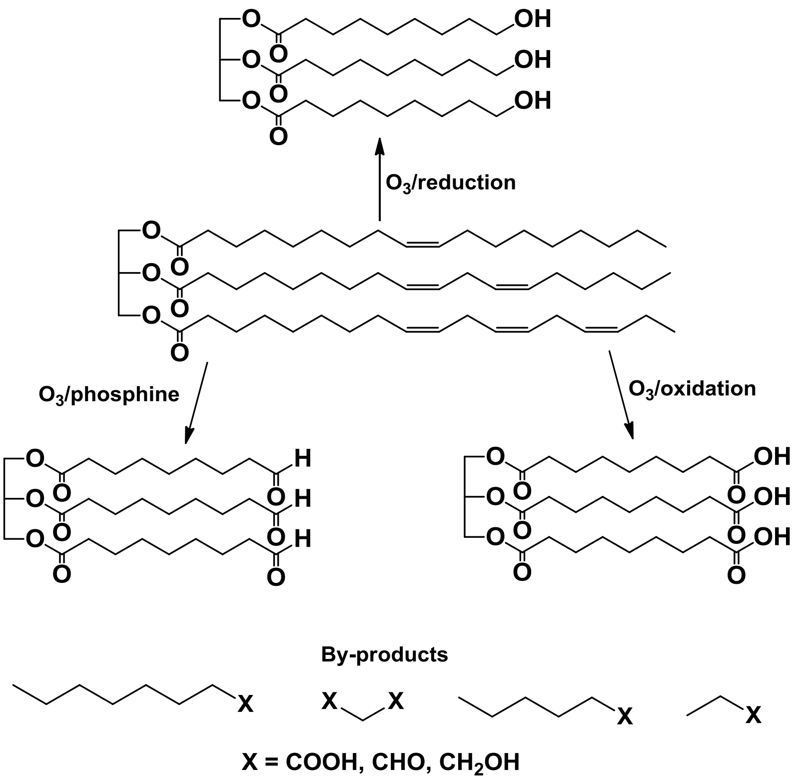


Scheme 9. Examples of monomers derived from 10-undecenoic acid via thiol-ene additions.[62]

2.3.5 Oxidative cleavage

Oxidative cleavage of unsaturated triglycerides is a chemical reaction in which the cleavage of the carbon-carbon double bond generates short chain mono or dicarboxylic acids, aldehydes or alcohols.[41] At an industrial level, this process occurs by ozonolysis, i.e. the ozone-induced cleavage of double bonds.[53] The ozonolysis of vegetable oils and fatty acid derivatives yields attractive difunctional monomers for polymer synthesis.

Scheme 10 shows the reaction products of the ozonolysis of a triglyceride which gives a new triglyceride with shorter chains and three new terminal functional groups (hydroxyl, carbonyl or carboxyl groups). Additionally, mono or dicarboxylic acids, aldehydes or alcohols are formed as by-products.



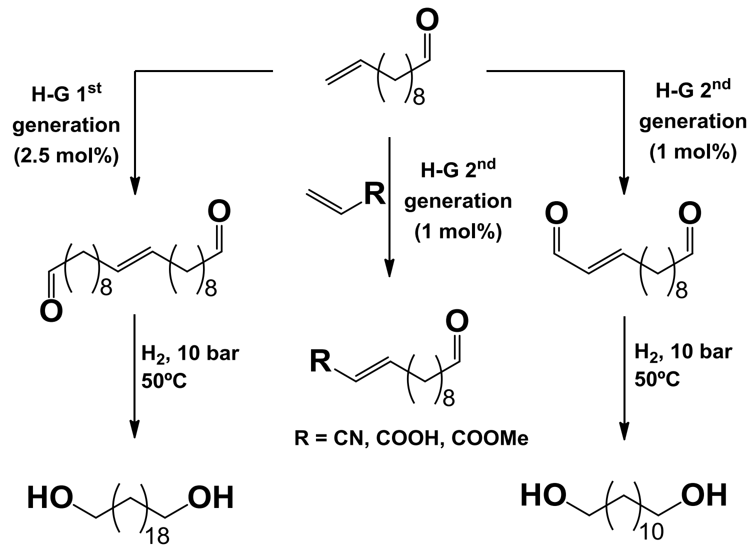
Scheme 10. Reaction products of the ozonolysis of triglycerides.[63]

2.3.6 Olefin Metathesis

Olefin metathesis is a reaction catalyzed by transition metal-carbene complexes of Mo, Pt, Pd, Rh, Ru, Ir, or Os, in which new compounds are formed trough the cleavage of the carbon-carbon double bonds of two olefins and regeneration of two double bonds of the new olefins.[13] This green reaction was recognized in 2005 with the Nobel Prize in Chemistry.[64] The available routes of olefin metathesis comprise self-metathesis (SM), cross-metathesis (CM), ring-closing metathesis (RCM), ring-opening metathesis (ROM), ROM polymerization (ROMP), and acyclic diene metathesis polymerization (ADMET) or acyclic triene metathesis polymerization (ATMET).[65,66]

The metathesis reaction has been extensively used as a versatile tool for vegetable oil-based monomer and polymer synthesis, since it allows the preparation of manifold unsaturated molecules, whose synthesis was quite a challenge by any other means.[66,67] As an illustrative example, Scheme 11 shows the work of Dixneuf et al.[68] on the synthesis of saturated C20 and C12 diols from castor oil derived 10-undecenal, through either self-metathesis or cross-metathesis with acrolein, acrylonitrile, acrylic acid and methyl methacrylate followed by hydrogenation in tandem catalytic reactions.

Other recent examples include for instance the work of Meier's group,[65,67,69-74] who studied e.g. the cross-metathesis of (i) fatty acid methyl esters with methyl acrylate[70,71] and allyl chloride[72] to efficiently yield α,ω-diesters and ω-chloroesters, (ii) fatty alcohols with methyl acrylate,[73] and (iii) unsaturated triglycerides with methyl acrylate.[74]



Scheme 11. Synthesis of saturated α,ω-diols and ω-functional aldehydes from 10-undecenal.[68]

3. VEGETABLE OIL-BASED POLYMERS

Vegetable oils and their derivatives are among the most promising candidates for the preparation of polymeric materials from renewable origin.[17,75] However, the direct use of vegetable oils as monomers is quite a challenge as a result of their heterogeneous nature,[24] often leading to cross-linked structures (e.g. thermosets, coatings, resins).

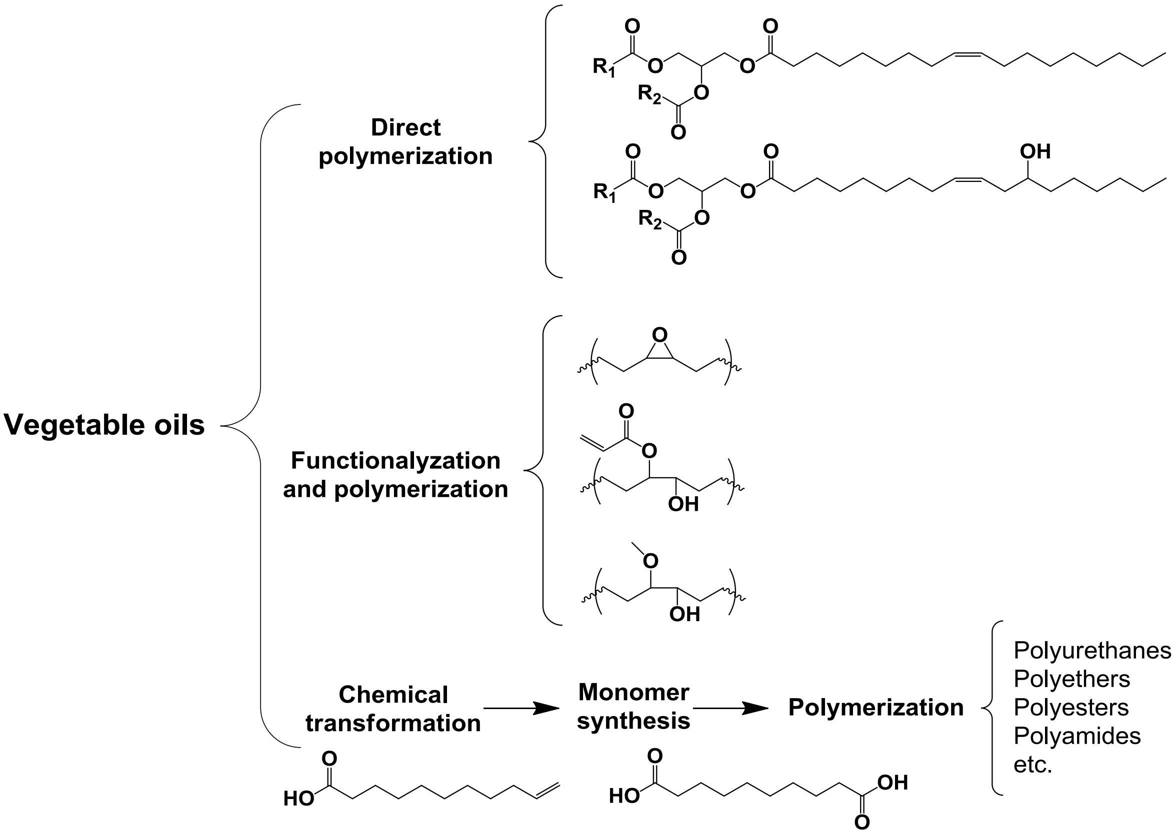
The wide range of polymerization methods that have been applied in the synthesis of vegetable oil-based polymers can be mainly divided into step-growth and chain-growth polymerizations. In the former, the polymer chains are built step by step, from monomers to oligomers to polymers, whereas in latter the monomers are added sequentially one by one to an active site at the end of the growing chain.[76,77]

A brief overview of the current state of the art of the use of vegetable oil renewable resources in polymer science will be presented. Then, step- and chain-growth polymers derived from vegetable oils will be discussed in more detail and illustrated by selected examples.

3.1 Overview

Polymers like gum arabic, rubber latex, and cellulose were used long before the word "polymer" was even coined. This word was introduced by Berzelius more than 170 years ago "*to recognize the fact that two compounds may have the same composition but different molecular weights, and he classified polymerism as a special type of isomerism*".[78,79] The realm of polymer chemistry was born at the interface between many disciplines (chemistry, biology and physics) and today it is more interdisciplinary than ever (chemistry, physics, biochemistry, molecular biology, nanotechnology, electronics, medicine, life sciences, materials, etc.).[78]

Polymers from vegetable oils can generally be prepared by three strategies: (i) the direct polymerization through the double bonds or other reactive functional groups present in the fatty acid chain, (ii) the chemical modification of the double bonds to introduce easily polymerizable functional groups, and (iii) the chemical transformation of vegetable oils to produce platform chemicals that can be utilized to prepare monomers for polymer synthesis,[80] as epitomized in Scheme 12. Polyesters, polyurethanes, vinyl polymer, acrylic resins, epoxy resins, polyesteremides, are examples of polymer types obtained from vegetable oils.[2]



Scheme 12. General strategies for the synthesis of vegetable oil-based polymers.[80]

Polymers from vegetable oils are blooming, as emphasized by the number of reviews, scientific publications, monographs, books and patents on the topic. The research in the field of vegetable oils is being driven on the basis of preliminary chemical modifications to improve the oils specific reactivity en route to polymerization processes.[2-4,7,39,81] For example, Biermann and co-workers[1] published an interesting review on new syntheses with oils as renewable raw materials for the chemical industry. Güner, Yağci and Erciyes[2] presented an extensive appraisal on polymers from triglyceride oils, which cover their structure, property and modification and the synthesis of polymers therefrom, with focus on cross-linked systems to be used in coating and resin applications. Sharma and Kundu[4] published a review on addition polymers from natural oils that discusses the synthesis and characterization of novel addition polymers from several natural oils like soybean, corn, tung, linseed, castor, and fish oil. In another appraisal, Sharma and Kundu[81] reviewed the synthesis of condensation polymers from natural oils. Petrović[63] provided a comprehensive review on polyurethanes from vegetable oils with emphasis on the preparation and structure-property relationships of polyurethanes from different polyols, isocyanates and with different cross-linking degrees. More recently, Xia and Larock[82] reviewed the use of vegetable oils as renewable raw materials for the synthesis of manifold monomers and polymers, whereas Meier et al.[12] highlighted the progress in organic synthesis, catalysis and biotechnology using vegetable oils and their derivatives.

Linseed, sunflower, castor, soybean, oiticica, palm and rapeseed oils are among the most used vegetable oils for the preparation of oil-modified polymers.[2] For instance, linseed oil, with its reactive unsaturated fatty acids that readily cure with oxygen, is usually applied in the production of paint binders. In contrast, castor oil, with its hydroxyl groups, is capable of reacting with isocyanates and carboxyl groups to yield interpenetrating polyurethane-polyester networks.[2] The most prominent examples of polymers from soybean, castor, linseed, tung and canola oil were recently highlighted by Türünç and Meier.[83]

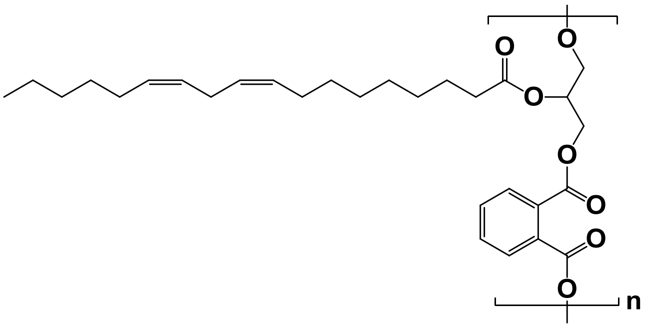
3.2 Vegetable oil-based step-growth polymers

In the subsequent sections some important examples of step-growth polymers, such as polyesters, polyurethanes and polyamides derived from vegetable oils, will be presented.

3.2.1 Polyesters

A commercially important class of polyesters are alkyd resins that represent one of the most relevant and attractive binder systems produced for the coating industry. The word *alkyd* was introduced by Kienle in the 19th century and results from the junction of syllables from alcohol (al) and acid (kyd).[7,22]

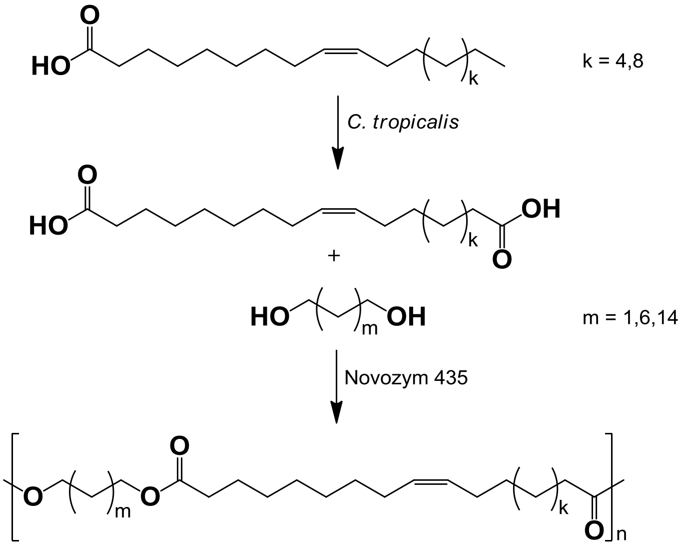
Generally, alkyd resins are prepared from acid anhydrides (e.g. phthalic or maleic anhydride) and polyols (e.g. glycerol or pentaerythritol) and are modified with unsaturated fatty acids to obtain good air drying properties, which make alkyd resins suitable for paint formulations.[7] As an example, Scheme 13 shows the structure of an alkyd resin prepared by heating linseed oil, phthalic anhydride and glycerol.[22] The fatty acid chain corresponds to linoleic acid (C18:2). Recently, Hofland[84] reviewed the topic with emphasis on the new developments in alkyd emulsions and high solids alkyd paints and compares these paint systems with paints based on acrylic dispersions as other environmentally friendly alternatives to conventional paints.



Scheme 13. Symplified molecular structure of an alkyd resin.

Polyesters incorporating long aliphatic chains are another remarkable example of polyesters from vegetable oils and its derivatives. For instance, Petrović et al.[85] synthesized high molecular weight linear polyesters from the methyl ester of 9-hydroxynonanoic acid, with higher melting point and glass transition temperature, better thermal stability and lower solubility in chlorinated solvents than the analogous polycaprolactone. Moreover, Mecking and his team[86-88] have extensively studied the preparation of linear saturated semicrystalline polyesters with long-chain hydrocarbon segments. They synthesized aliphatic long-chain C_{19}, C_{20} and C_{23} monomers[87,88] generated from methyl oleate, undecenoic acid and ethyl erucate, respectively, which were then polymerized with α,ω-diols of different chain lengths to yield saturated polyesters with high melting points.[86-88]

In another vein, Yang et al.[89] obtained unsaturated and epoxidized fatty acid-based polyesters from α,ω-dicarboxylic acids, prepared by the biochemical oxidation of terminal methyl groups of unsaturated fatty acids into carboxylic groups, followed by enzymatically catalyzed polycondensation (Scheme 14). As an example, the unsaturated 1,22-*cis*-9-docosenedioic acid was prepared from erucic acid and submitted to the enzyme-catalyzed polycondensation with 1,8-octanediol to obtain an unsaturated polyester that can be further modified, derivatized, or cross-linked, using the mid-chain unsaturation in order to adjust the material properties.

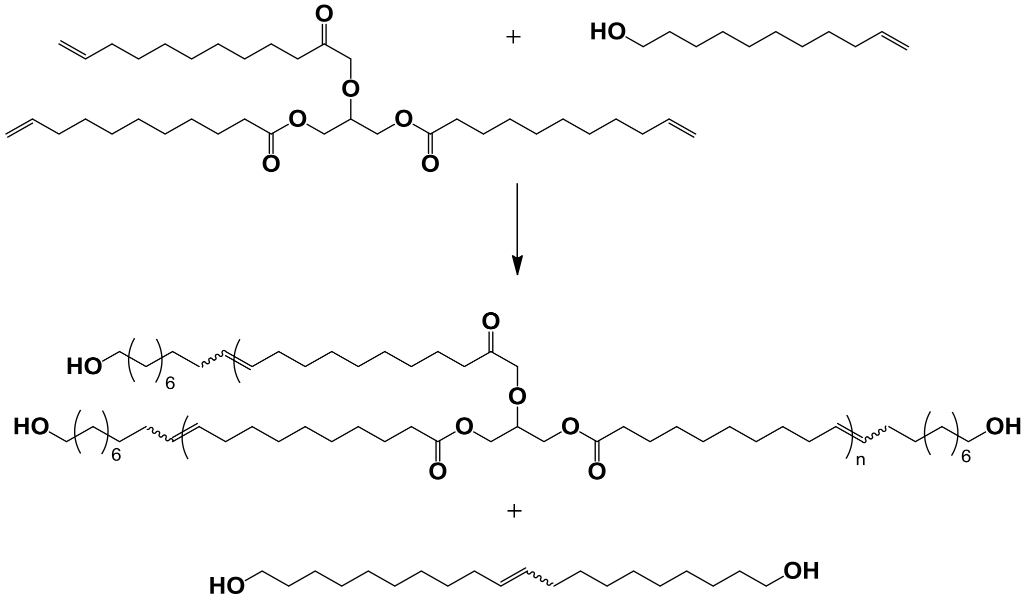


Scheme 14. Biochemical conversion of unsaturated fatty acids into α,ω-diacids and subsequent polycondensation with α,ω-diols.[89]

3.2.2 Polyurethanes

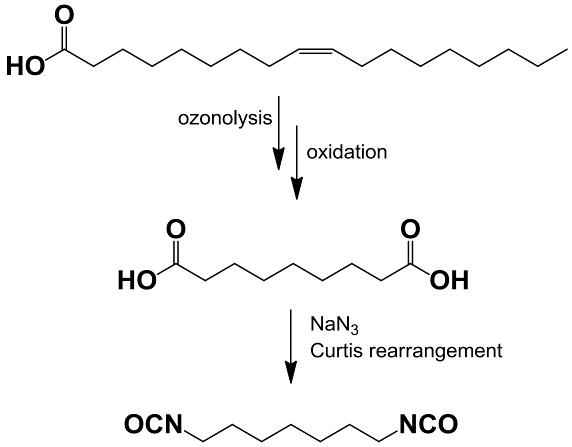
Vegetable oils and its derivatives are also commonly converted into polyols and then copolymerized with isocyanates to obtain polyurethanes (PUs), and depending on the functionality of the initial monomers, linear or cross-linked polymers are formed. Several review articles on PUs from vegetable oils were published recently.[63,81,90,91] Sharma and Kundu[81] provided a broad appraisal on condensation polymers from vegetable oils with focus on PUs based on vegetable oil polyols. Petrović[63] devoted a review to polyols for polyurethanes from vegetable oils, in which the specific nature of vegetable oils and the effect of their structures on the features of polyols and polyurethanes are discussed in detail. Recently, Desroches et al.[91] updated the topic “from vegetable oils to polyurethanes" with emphasis on the synthetic routes for biobased polyol production in the polyurethane industry.

Polyhydroxyl macromonomers, i.e., polyester or polyether diols or polyols, can be synthesized from vegetable oils like soybean, palm, castor, sunflower, rapeseed and linseed. Petrović's group made various contributions to the production of rigid foams from soybean oil-based polyols,[92,93] which showed mechanical and insulating properties similar to those of commercially available petroleum-derived polypropylene-oxide based counterparts.[93] Lligadas and co-workers[94] prepared a polyether polyol with fatty acids which produced hard polyurethanes. Tu et al.[95] also developed vegetable oil-based polyols as alternatives to petroleum-based polyols that gave rise to rigid PU. More recently, Cádiz's group synthesized a series of new polyurethanes from vegetable oil-based polyols, namely (i) PUs from polyether polyols obtained by ionic-coordinative polymerization of epoxidized methyl oleate,[96] (ii) PUs from polyols obtained by ADMET polymerization of a castor oil-based diene,[97] (iii) shape-memory PUs from branched polyols obtained by ATMET polymerization of glyceryl triundec-10-enoate and 10-undecenol (Scheme 15),[98] and (iv) poly-2-oxazoline derived PU thermosets.[99]



Scheme 15. Synthesis of branched polyols via acyclic triene metathesis (ATMET) of glyceryl triundec-10-enoate with 10-undecenol as chain stopper.[98]

Hitherto, almost all bio-based PUs were prepared using polyols derived from vegetable oils in combination with petrochemical-based diisocyanates. Çaylı and Küsefoğlu[100] prepared the first example of a plant-based isocyanate (isocyanate-containing soybean oil) which was then reacted with castor oil and glycerol to give polyurethanes entirely based on renewable resources. Narine and co-workers[101] produced polyurethanes mostly from lipid feedstock by preparing a linear saturated terminal diisocyanate derived from oleic acid (Scheme 16) and reacted it with canola-oil derived polyols to obtain oil-based PUs. The physical properties of these bio-based polyurethanes were comparable to those of their petroleum-derivatives counterparts.

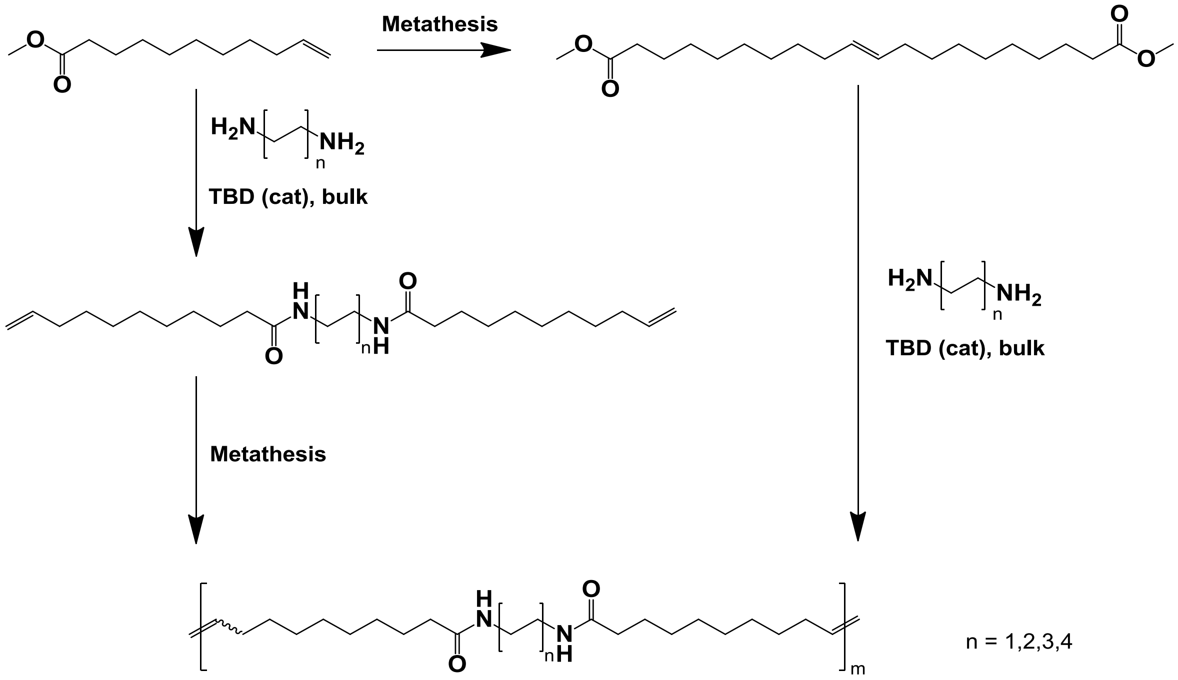


Scheme 16. Synthesis of a diisocyanate from oleic acid.[101]

3.2.3 Polyamides

Polyamides are polymers whose building blocks are joined through amide bonds[53] and are obtained, e.g., by the polymerization reaction of diamines and dicarboxylic acids or aminoacids.[76] Nylon-11 is the best known example of a vegetable oil-based polyamide synthesized from castor oil.[102] This polyamide is produced by the pyrolysis of castor oil to obtain 11-aminoundecanoic acid, followed by its polycondensation to yield nylon-11, a material with excellent dimensional stability and dielectrical properties. The major applications of this polymer are as engineering plastic in the automotive and transport industry, as well as in powder coatings to coat metals that require enhanced abrasion, impact and corrosion resistance.[102]

Other interesting examples include the polyamides produced by Meier's group.[103-105] For instance, the polycondensation of the self-metathesis product of 10-undecenoic acid and 1,6- hexamethylene diamine yielded partially renewable unsaturated polyamides "PA X,20" (Scheme 17) with high melting and degradation temperatures, depending on the structure of the applied monomers.[103]



Scheme 17. Synthesis of unsaturated "PA X,20" from renewable resources.[103]

In another study, substituted polyamides with amide moieties in the polymer backbone, as well as in its side chain, were synthesized and were shown to be photoresponsive, and exhibited a dramatic change of their properties upon irradiation with sunlight.[104] Moreover, a number of linear aliphatic polyamides with good properties as well as copolyamides with adjustable thermal and solubility properties were synthesized from fatty acids with amine moieties introduced via thiol-ene coupling.[105]

3.2.4 Other polymers

In addition to polyesters, polyurethanes and polyamides, there are other step-growth polymers that might be obtained from vegetable oils, e.g., epoxy resins. Epoxy resins are thermosetting epoxide polymers containing aliphatic, cycloaliphatic, or aromatic backbones. These resins are extremely versatile due to the reactivity of the epoxy ring with a wide range of curing agents under diverse conditions and temperatures, and are widely used as adhesives and as matrices in composite materials, due to their remarkable physical and chemical properties.[106] Vegetable oils may be used as renewable and environmentally friendly alternatives to petrochemical raw materials for the synthesis of epoxy resins. For instance, Czub[107] reported that both epoxidized and hydroxylated modified vegetable oils can be used for the synthesis of high-molecular-weight epoxy resins by their melt reactions with Bisphenol A or low-molecular-weight Bisphenol-A based resins.

Another interesting example of step-growth polymers are the poly-α,β-unsaturated aldehydes derived from castor oil via ADMET polymerization prepared by Meier and co-workers.[108] Polymers with molecular weights up to 14 kDa were formed and subsequently reduced to poly-(allyl alcohol), with possible applications in the generation of polymer networks like polyesters, polyurethanes and polycarbonates.

3.3 Vegetable oil-based chain-growth polymers

In the following sections some important examples of chain-growth polymers derived from vegetable oils will be highlighted.

3.3.1 Polymers by free radical polymerization

The multiple C=C bonds of vegetable oils are prone to polymerize by a free radical mechanism. Little attention has been given to free radical polymerization of triglyceride double bonds because of the presence of chain-transfer processes (i.e. the activity of a growing polymer chain is transferred to another molecule).[17]

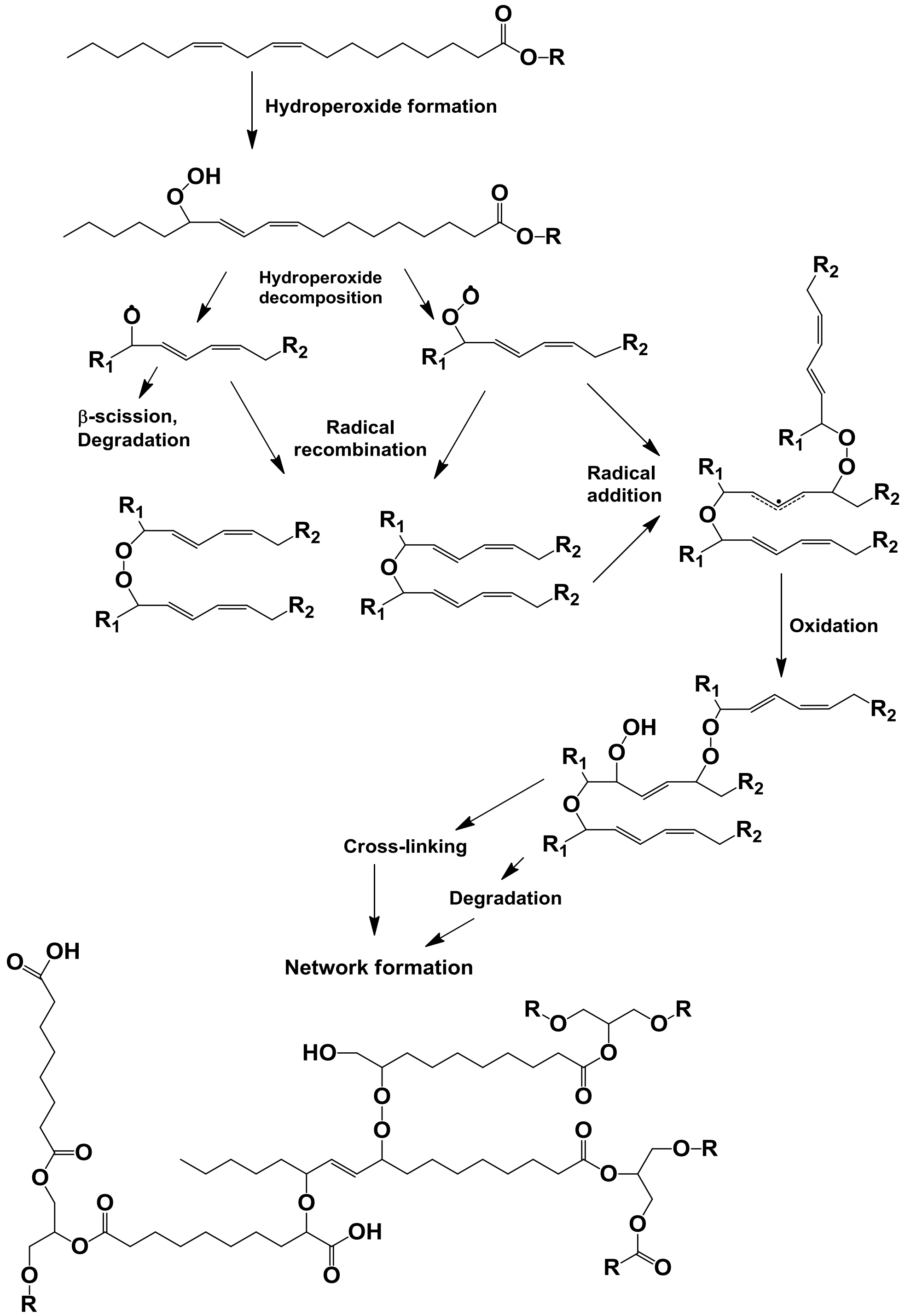
Oxypolymerized oils

Oxypolymerized oils are vegetable oils that are directly polymerized by atmospheric oxygen yielding cross-linked systems. The oxidative cross-linking mechanism of vegetable oils has been extensively studied[22] through the application of several techniques, including: IR[109,110] and NMR[111] spectroscopy, differential scanning calorimetry (DSC),[112] size-exclusion chromatography (SEC)[112] and mass spectrometry (MS)[113].

Drying oils, i.e. oils with high unsaturation level, are widely used as binders and film formers in paint and coating formulations, since they possess a remarkable aptitude to form resins due to autoxidation, peroxide formation and subsequent macroradical couplings.[7,22] Linseed oil is one of the most widely used drying oils in paint formulation.[22,110,112]

Scheme 18 gives an overview of the different steps of the formation of a cross-linked network characteristic of a “dried oil” or a “dried” alkyd paint. The first step is the hydroperoxide formation with simultaneous formation of conjugated double bonds if the fatty acids contain the pentadienyl moiety.[22] The second step, the hydroperoxide decomposition, results in the formation of peroxy and alkoxy radicals whose recombination originates ether and peroxide dimmers. Concomitantly, alkoxy radicals give rise to β-scission reactions which leads to the degradation of the macromolecule and the formation of various oxidation products.[22] Subsequently, the species with conjugated double bonds are prone to radical addition and further oxidation reactions which lead to a network formation linked via ester bonds and ether cross-links.[22]

Hazer’s group took advantage of this procedure by using the polymeric oil peroxy initiators from the autoxidation of linseed and soybean oils, and linoleic acid to induce the free radical polymerization of methyl methacrylate or n-butyl methacrylate in order to obtain grafted copolymers.[114-117]



Scheme 18. Formation of a cross-linked network through oxidative drying.[22]

Other polymers

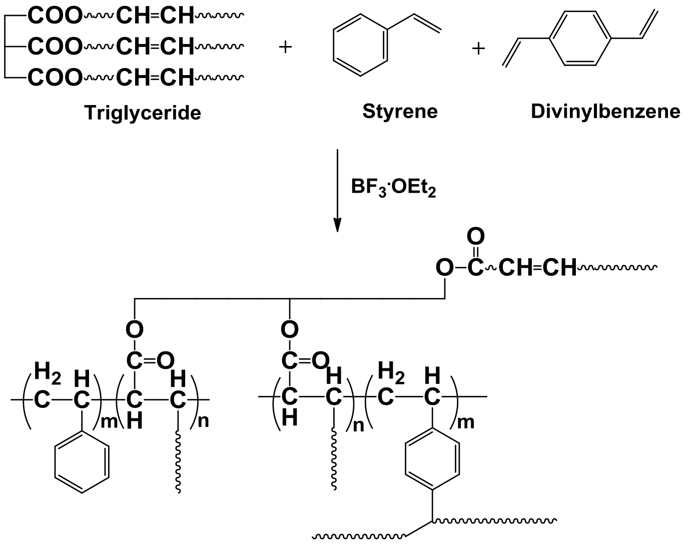
Besides oxypolymerized oils, there are other polymers that might be prepared from vegetable oils by radical polymerization. For instance, conjugated linseed oil (CLIN) and conjugated low-saturation soybean oil (CLS) undergo free radical polymerization initiated by either benzoyl peroxide or *tert*-butyl hydroperoxide or combinations of them.[17] Additionally, CLIN and CLS have been co-polymerized with divinylbenzene and acrylonitrile by free radical polymerization initiated by 2,2'-azoisobutyronitrile (AIBN).[118,119] The ensuing thermosets present a wide range of properties which allow them to be used in applications where petroleum-based polymers are otherwise the main constituents.

In another vein, epoxidized soybean oil (ESO) was converted to its acrylate ester by reaction with acrylic acid, and then free radically polymerized or copolymerized with styrene to yield thermoset resins with mechanical properties similar to commercially available polyester and vinyl ester resins.[120,121] Esen and Küsefoğlu[122] reported the free radical polymerization and co-polymerization of a cinnamate ester of ESO with styrene, vinyl acetate, and methyl methacrylate. In another study, Esen and co-workers[123] homo- and co-polymerized monomethyl maleate esters of epoxidized soybean oil (MESO) and maleinized MESO by free radical mechanism. The ensuing polymers were good candidates for novel liquid moulding resins. Another example was reported by Pelletier et al.[124,125] in which acrylate and urethane moieties were appended on ESO and then irradiated in the near UV in the presence of free radical photoinitiators to yield photocrosslinkable materials with possible use as vehicles in UV inks and other film coatings.

3.3.2 Polymers by cationic polymerization

The carbon-carbon double bonds of vegetable oils are also susceptible to cationic polymerization. Since vegetable oils are multifunctional monomers due to the multiple C=C double bonds, cationic polymerization of vegetable oils results eventually in cross-linked polymers.[17] Mostly Lewis acids, such as $AlCl_3$, $TiCl_4$, $ZnCl_2$, $SnCl_4$ and $BF_3{\cdot}OEt_2$ are used as initiator systems for cationic polymerization under mild conditions[126] and $BF_3{\cdot}OEt_2$ has proved to be the most efficient among them[17].

Larock's group devoted considerable attention to the cationic polymerization of the C=C double bonds of vegetable oils and its derivatives.[127-130] They reported the preparation of thermosetting polymers ranging from rubbers to hard plastics by the cationic polymerization of a variety of vegetable oils, namely fish, tung and soybean oil with petroleum-based comonomers such as styrene, divinylbenzene and dicyclopentadiene in the presence of $BF_3·OEt_2$. The resulting thermosetting materials possess thermal and mechanical properties comparable to those of industrial plastics, as well as some other useful properties, including high damping and shape memory.[128,129] As an illustrative example, Scheme 19 shows the cationic co-polymerization of soybean oil with styrene and divinylbenzene initiated by $BF_3·OEt_2$.



Scheme 19. Cationic co-polymerization of soybean oil with styrene and divinylbenzene.[130]

In another context, Liu and co-workers[131] synthesized drying oil-based polymers with molecular weights in the range of 1-23 kDa by cationic polymerization in supercritical CO_2, to be applied as lubricants or hydraulic fluids. Cádiz and co-workers prepared halogen-free soybean oil thermosets with enhanced flame retardant properties by cationic polymerization of soybean oil, styrene and divinylbenzene with different silicon, boron and phosphorus-containing comonomers.[132-136]

3.3.3 Polymers by anionic polymerization

In anionic polymerizations, the initiator system might be of different classes such as radical anions (e.g., sodium naphthalenide), alkali metals, and alkyllithium compounds (e.g., *sec*-butyllithium).[76] So far only a few examples of anionic polymerization of vegetable oil-derived monomers have been described in the literature.[7,137,138] For instance, Raghunadh et al.[138] studied the anionic polymerization of lauryl methacrylate at -40 °C in THF in the presence of additives (e.g. dilithium salt of triethylene glycol, LiCl, or $LiClO_4$) and obtained polymers with a narrow molecular weight distribution (PDI<1.10). Furthermore, diblock copolymers of methyl methacrylate with lauryl methacrylate resulted in materials with improved properties for application as a new class of thermoplastic elastomers.[138]

4. REFERENCES

[1] U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. O. Metzger, M. R. Klaas, H. J. Schäfer, M. P. Schneider, New Syntheses with Oils and Fats as Renewable Raw Materials for the Chemical Industry, *Angewandte Chemie International Edition* **2000**, 39, 2206-2224.

[2] F. S. Güner, Y. Yağci, A. T. Erciyes, Polymers from triglycerides oils, *Progress in Polymer Science* **2006**, 31, 633-670.

[3] M.N. Belgacem, A. Gandini (Eds.), *Monomers, polymers and composites from renewable resources*. Amsterdam: Elsevier, **2008**.

[4] V. Sharma, P. P. Kundu, Addition polymers from natural oils – A review, *Progress in Polymer Science* **2006**, 31, 983-1008.

[5] R. P. Wool, X. S. Sun, *Bio-based polymers and Composites*, USA: Elsevier, **2005**.

[6] C. Scrimgeour, *Chemistry of Fatty Acids*, in Bailey's Industrial Oil and Fat Products, John Wiley & Sons, **2005**.

[7] M. A. R. Meier, J.O. Metzger, U. S. Schubert, Plant oil renewable resources as green alternatives in polymer science, *Chemical Society Reviews* **2007**, 36, 1788-1802.

[8] B. K. Barnwal, M. P. Sharma, Prospects of biodiesel production from vegetable oils in India*, Renewable and Sustainable Energy Reviews* **2005**, 9, 363-378.

[9] C. E. Stauffer, *Fats & Oils: Practical guides for the food industry,* Minnesota, USA: Eagan Press Handbook Series, **1996**.

[10] United States Department of Agriculture, *Oilseeds: World Market and Trade Archives*, http://www.fas.usda.gov/oilseeds/Current/default.asp (October 2012).

[11] F. D. Gunstone, Supplies of vegetable oils for non-food purposes, *European Journal of Lipid Science and Technology* **2011**, 113, 3-7.

[12] U. Biermann, U. Bornscheuer, M.A. R. Meier, J.O. Metzger, H.J. Schäfer, Oils and Fats as Renewable Raw Materials in Chemistry, *Angewandte Chemie International Edition* **2011**, 50, 3854-3871.

[13] A. Corma, S. Iborra, A. Velty, Chemical Routes for the Transformation of Biomass into Chemicals*, Chemical Reviews* **2007**, 107, 2411-2502.

[14] E. B Cahoon, J. M. Shockey, C. R. Dietrich, S. K. Gidda, R. T. Mullen, J. M. Dyer, Engineering oilseeds for sustainable production of industrial and nutritional feedstocks: solving bottlenecks in fatty acid flux, *Current Opinion in Plant Biology* **2007**, 10, 236-244.

[15] J. M. Dyer, R. T. Mullen, Engineering plant oils as high-value industrial feedstocks for biorefining: the need for underpinning cell biology research, *Physiologia Plantarum* **2008**, 132, 11-22.

[16] A. S. Carlsson, Plant oils as feedstock alternatives to petroleum – A short survey of potential oil crop platforms, *Biochimie* **2009**, 91, 665-670.

[17] Y. Lu, R. C. Larock, Novel polymeric materials from vegetable oils and vinyl monomers: preparation, properties, and applications, *ChemSusChem* **2009**, 2, 136-147.

[18] V. Scholz, J. N. Silva, Prospects and risks of the use of castor oil as a fuel, *Biomass and Bioenergy* **2008**, 32, 95-100.

[19] D. C. Harris, *Quantitative Chemical Analysis*, New York: W.H. Freeman and Company, 5th Ed., **2000**.

[20] W. R. Bloor, Biochemistry of the Fats, *Chemical Reviews* **1925**, 2, 243-300.

[21] G. Knothe, Structure Indices in FA chemistry. How relevant is the iodine value?, *Journal of the American Oil Chemists' Society* **2002**, 79, 847-854.

[22] R. Gorkum, E. Bouwman, The oxidative drying of alkyd paint catalyzed by metal complexes*, Coordination Chemistry Reviews* **2005**, 249, 1709-1728.

[23] J. M. Dyer, S. Stymme, A. G. Green, A. S. Carlsson, High-value oils from plants, *The Plant Journal* **2008**, 54, 640-655.

[24] C. K. Williams, M. A. Hillmyer, Polymers from renewable resources: a perspective for a special issue of polymer reviews, *Polymer Reviews* **2008**, 48, 1-10.

[25] K. Hill, Fats and oils as oleochemical raw materials, *Pure and Applied Chemistry* **2000**, 72, 1255-1264.

[26] G. W. Borden, O. W. Smith, D. J. Trecker, *Radiation curable compositions of acrylated epoxidized soybean oil amine compounds useful as inks and coatings and methods of curing same*, US Patent 3878077, **1975**.

[27] I. V. Steinberg, *Epoxy adhesive containing acrylic acid-epoxy reaction products and photosensitizers*, US Patent 3450613, **1969**.

[28] J. Wypych, *Polyvinyl Chloride Stabilization*, Amsterdam: Elsevier, **1986**.

[29] C. M. Thierfelder, H. M. Teeter, J. C. Cowan, Preparation of foams from vegetable oil derivatives, *Journal of the American Oil Chemists' Society* **1962**, 39, 215-217.

[30] U. Stirna, U. Cabulis, I. Beverte, Water-Blown Polyisocyanurate Foams from Vegetable Oil Polyols, *Journal of Cellular Plastics* **2008**, 44, 139-160.

[31] S. N. Khot, J. J. Lascala, E. Can, S. S. Morye, G. I. Williams, G. R. Palmese, S. H. Küsefoğlu, R. P. Wool, Development and application of triglyceride-based polymer and composites*, Journal of Applied Polymer Science* **2001**, 82, 703-723.

[32] S. P. Bunker, R. P. Wool, Synthesis and characterization of monomers and polymers for adhesives from methyl oleate, *Journal of Polymer Science Part A: Polymer Chemistry* **2002**, 40, 451-458.

[33] G. Heisterberg-Moutsis, R. Heinz, T. F. Wolf, D. J. Harper, D. James, R. P. Mazzur, V. Kettler, H. Soiné, *Floor coverings*, Ulmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2002** (DOI: 10.1002/14356007.a11_263).

[34] S. A. Patrick, Linoleum (Book Review), *Library Journal* **2001**, 126, 72.

[35] A. Murugesan, C. Umarani, R. Subramanian, N. Nedunchezhian, Bio-diesel as an alternative fuel for diesel engines – A review*, Renewable and Sustainable Energy Reviews* **2009**, 13, 653-662.

[36] A. L. Demain, Biosolutions to the energy problem, *Journal of Industrial Microbiology & Biotechnology* **2009**, 36, 319-332.

[37] L. Wang, T. Wang, Chemical modification of partially hydrogenated vegetable oil to improve its functional properties for candles, *Journal of the American Oil Chemical Society* **2007**, 84, 1149-1159.

[38] H. Mutlu, *Sustainable, efficient approaches to renewable platform chemicals and polymers*, PhD Thesis, Karlsruhe Institute of Technology (KIT), Germany, **2012** (http://digbib.ubka.uni-karlsruhe.de/volltexte/documents/2287487).

[39] A. Gandini, Polymers from renewable resources: A challenge for the future of macromolecular materials*, Macromolecules* **2008**, 41, 9491-9504.

[40] J.O. Metzger, U. Bornscheuer, Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification, *Applied Microbiology Biotechnology* **2006**, 71, 13-22.

[41] A. Behr, A. Westfechtel, J. P. Gomes, Catalytic processes for the technical use of natural fats and oils, *Chemical Engineering & Technology* **2008**, 31, 700-714.

[42] S. K. Hoekman, A. Broch, C. Robbins, E. Ceniceros, M. Natarajan, Review of biodiesel composition, properties, and specifications, *Renewable and Sustainable Energy Reviews* **2012**, 16, 143-169.

[43] “*Global biodiesel market almost doubles every year between 2001 and 2009*”, Renewable Energy Magazine **2010**. *Global Biodiesel Market Analysis and Forecasts to 2020*, Global Data Report **2010**.

[44] a) S. Salehpour, M. A. Dubé, Biodiesel: a green polymerization solvent, *Green Chemistry* **2008**, 10, 321-326.

b) S. Salehpour, M. A. Dubé, The use of biodiesel as a green polymerization solvent at elevated temperatures, *Polymer International* **2008**, 57, 854-862.

[45] S. Salehpour, M. A. Dubé, M. Murphy, Solution polymerization of styrene using biodiesel as a solvent: effect of biodiesel feedstock, *Canadian Journal Of Chemical Engineering* **2009**, 87, 129-135.

[46] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, Improved utilisation of renewable resources: New important derivatives of glycerol, *Green Chemistry* **2008**, 10, 13-30.

[47] F. Yang, M. A. Hanna, R. Sun, Value-added uses for crude glycerol–a byproduct of biodiesel production, *Biotechnology for Biofuels* **2012**, 5:13, doi:10.1186/1754-6834-5-13.

[48] R. Dobson, V. Gray, K. Rumbold, Microbial utilization of crude glycerol for the production of value-added products, *Journal of Industrial Microbiology & Biotechnology* **2012**, 39, 217-226.

[49] Y. Gu, F. Jérôme, Glycerol as a sustainable solvent for green chemistry, *Green Chemistry* **2010**, 12, 1127.1138.

[50] S. Salehpour, C. J. Zuliani, M. A. Dubé, Synthesis of novel stimuli-responsive polyglycerol-based hydrogels, *European Journal of Lipid Science and Technology* **2012**, 114, 92-99.

[51] S. Salehpour, M. A. Dubé, Application Properties of Stimuli-Responsive Polyglycerol Hydrogels, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* **2012**, 49, 103-110.

[52] S. J. Yoon, Y.-C. Choi, Y.-I. Son, S.-H. Lee, J.-G. Lee, Gasification of biodiesel by-product with air or oxygen to make syngas, *Bioresource Technology* **2010**, 101, 1227-1232.

[53] F. A. Carey, *Organic Chemistry*, New York: McGraw-Hill International Edition, **2008**.

[54] M. J. Kade, D. J. Burke, C. J. Hawker, The power of thiol-ene chemistry, *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, 48, 743-750.

[55] A. Dondoni, The Emergence of Thiol-Ene Coupling as a Click Process for Materials and Bioorganic Chemistry, *Angewandte Chemie International Edition* **2008**, 47, 8995-8997.

[56] A. B. Lowe, Thiol-ene “click” reactions and recent applications in polymer and materials synthesis, *Polymer Chemistry* **2010**, 1, 17-36

[57] C. E. Hoyle, C. N. Bowman, Thiol-Ene Click Chemistry, *Angewandte Chemie International Edition* **2010**, 49, 1540-1573.

[58] a) C. Lluch, J. C. Ronda, M. Galià, G. Lligadas, V. Cádiz, Rapid Approach to Biobased Telechelics through Two One-Pot Thiol−Ene Click Reactions, *Biomacromolecules* **2010**, 11, 1646-1653.

b) O. Türünç, M. A. R. Meier, Thiol-ene vs. ADMET: a complementary approach to fatty acid-based biodegradable polymers, *Green Chemistry* **2011**, 13, 314-320.

c) C. Lluch, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, “Click” Synthesis of Fatty Acid Derivatives as Fast-Degrading Polyanhydride Precursors, *Macromolecular Rapid Communications* **2011**, 32, 1343-1351.

[59] J. Samuelsson, M. Jonsson, T. Brinck, M. Johansson, Thiol–ene coupling reaction of fatty acid monomers, *Journal of Polymer Science Part A: Polymer Chemistry* **2004**, 42, 6346-6352.

[60] M. Claudino, M. Johansson, M. Jonsson, Thiol–ene coupling of 1,2-disubstituted alkene monomers: The kinetic effect of cis/trans-isomer structures, *European Polymer Journal* **2010**, 46, 2321-2332.

[61] G. B. Bantchev, J. A. Kenar, G. Biresaw, M. G. Han, Free Radical Addition of Butanethiol to Vegetable Oil Double Bonds, *Journal of Agriculture and Food Chemistry* **2009**, 57, 1282-1290.

[62] O. Türünç, M. A. R. Meier, Fatty Acid Derived Monomers and Related Polymers Via Thiol-ene (Click) Additions, *Macromolecular Rapid Communications* **2010**, 31, 1822-1826.

[63] Z. S. Petrović, Polyurethanes from vegetable oils, *Polymer Reviews* **2008**, 48, 109-155.

[64] http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/ (June 2012).

[65] a) A. Rybak, P. A. Fokou, M. A. R. Meier, Metathesis as a versatile tool in oleochemistry, *European Journal of Lipid Science and Technology* **2008**, 110, 797-804.

b) H. Mutlu, L. Montero de Espinosa, M. A. R. Meier, Acyclic diene metathesis: a versatile tool for the construction of defined polymer architectures, *Chemical Society Reviews* **2011**, 40, 1404-1445.

[66] a) J. C. Mol, Application of olefin metathesis in oleochemistry: an example of green chemistry, *Green Chemistry* **2002**, 4, 5-13.

b) J. C. Mol, Catalytic Metathesis of Unsaturated Fatty Acid Esters and Oils, *Topics in Catalysis* **2004**, 27, 97-104.

[67] M. A. Meier, Metathesis with Oleochemicals: New Approaches for the Utilization of Plant Oils as Renewable Resources in Polymer Science, *Macromolecular Chemistry and Physics* **2009**, 210, 1073-1079.

[68] X. Miao, C. Fischmeister, C. Bruneau, P. H. Dixneuf, A Direct Route to Bifunctional Aldehyde Derivatives via Self- and Cross-Metathesis of Unsaturated Aldehydes, *ChemSusChem* **2009**, 2, 542-545.

[69] a) T. T. T. Ho, T. Jacobs, M. A. R. Meier, A design-of-experiments approach for the optimization and understanding of the cross-metathesis reaction of methyl ricinoleate with methyl acrylate, *ChemSusChem* **2009**, 2, 749-754.

b) U. Biermann, J. O. Metzger, M. A. R. Meier, Acyclic triene metathesis oligo- and polymerization of high oleic sun flower oil, *Macromolecular Chemistry and Physics* **2010**, 211, 854-862.

[70] A. Rybak, M. A. R. Meier, Cross-metathesis of fatty acid derivatives with methyl acrylate: renewable raw materials for the chemical industry, *Green Chemistry* **2007**, 9, 1356-1361.

[71] G.B. Djigoué, M.A.R. Meier, Improving the selectivity for the synthesis of two renewable platform chemicals via olefin metathesis, *Applied Catalysis A* **2009**, 368, 158-162.

[72] T. Jacobs, A. Rybak, M. A. R. Meier, Cross-metathesis reactions of allyl chloride with fatty acid methyl esters: Efficient synthesis of α,ω-difunctional chemical intermediates from renewable raw materials, *Applied Catalysis A* **2009**, 353, 32-35.

[73] A. Rybak, M. A. R. Meier, Cross-metathesis of oleyl alcohol with methyl acrylate: optimization of reaction conditions and comparison of their environmental impact, *Green Chemistry* **2008**, 10, 1099-1104.

[74] U. Biermann, M. A. R. Meier, W. Butte, J. O. Metzger, Cross-metathesis of unsaturated triglycerides with methyl acrylate: synthesis of a dimeric metathesis product, *European Journal of Lipid Science and Technology* **2011**, 113, 39-45.

[75] J. P. Jain, M. Sokolsky, N. Kumar, A. J. Domb, Fatty Acid Based Biodegradable Polymer, *Polymer Reviews* **2008**, 48, 156-191.

[76] P. C. Hiemenz, T. P. Lodge, *Polymer Chemistry*, Boca Raton: CRC Press, **2007**.

[77] P.C. Painter, M.M. Coleman, *Fundamentals of Polymer Science: An introductory text*, Pennsylvania: Technomic, 2^{nd}, **1997**.

[78] V. Parcec, Introduction: Frontiers in Polymer Chemistry, *Chemical Reviews* **2001**, 101, 3579-3580.

[79] W. H. Carothers, Polymerization, *Chemical Reviews* **1931**, 8, 354-426.

[80] J. C. Ronda, G. Lligadas, M. Galià, V. Cádiz, Vegetable oils as platform chemicals for polymer synthesis, *European Journal of Lipid Science and Technology* **2011**, 113, 46-58.

[81] V. Sharma, P. P. Kundu, Condensation polymers from natural oils, *Progress in Polymer Science* **2008**, 33, 1199-1215.

[82] Y. Xia, R.C. Larock, Vegetable oil-based polymeric materials: synthesis, properties and applications, *Green Chemistry* **2010**, 12, 1893-1909.

[83] O. Türünç, M. A. R. Meier, In *Biopolymers*, N. T. Dunford (Eds.); *Food and Industrial Bioproducts and Bioprocessing*, Oxford: Wiley-Blackwell, **2012**, 267-292.

[84] A. Hofland, Alkyd resins: From down and out to alive and kicking, *Progress in Organic Coatings* **2012**, 73, 274-282.

[85] Z. S. Petrović, J. Milić, Y. Xu, I. Cvetković, A Chemical Route to High Molecular Weight Vegetable Oil-Based Polyhydroxyalkanoate, *Macromolecules* **2010**, 43, 4120-4125.

[86] F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, Long-chain linear C19 and C23 monomers and polycondensates from unsaturated fatty acid esters, *Macromolecules* **2011**, 44, 4159-4166.

[87] D. Quinzler, S. Mecking, Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization, *Angewandte Chemie International Edition* **2010**, 49, 4306-4308.

[88] J. Trzaskowski, D. Quinzler, C. Bährle, S. Mecking, Aliphatic Long-Chain C20 Polyesters from Olefin Metathesis, *Macromolecular Rapid Communications* **2011**, 32, 1352-1356.

[89] Y. Yang, W. Lu, X. Zhang, W. Xie, M. Cai, R. A. Gross, Two-step biocatalytic route to biobased functional polyesters from ω-carboxy fatty acids and diols, *Biomacromolecules* **2010**, 11, 259-268.

[90] G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, Plant oils as platform chemicals for polyurethane synthesis: current state-of-the-art, *Biomacromolecules* **2010**, 11, 2825-2835.

[91] M. Desroches, M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin, From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products, *Polymer Reviews* **2012**, 52, 38-79.

[92] a) Z.S. Petrović, A. Guo, W. Zang, Structure and properties of polyurethanes based on halogenated and nonhalogenated soy-polyols, *Journal of Polymer Science A: Polymer Chemistry* **2000**, 38, 4062-4069.

b) I. Javni, Z.S. Petrović, A. Guo, R. Fuller, Thermal stability of polyurethanes based on vegetable oils, *Journal of Applied Polymer Science* **2000**, 77, 1723-1734.

c) I. Javni, W. Zang, Z.S. Petrović, Effect of different isocyanates on the properties of soy-based polyurethanes, *Journal of Applied Polymer Science* **2003**, 88, 2912-2916.

d) A. Guo, W. Zang, Z.S. Petrović, Structure-property relationships in polyurethanes derived from soybean oil, *Journal of Material Science* **2006**, 41, 4914-4920.

[93] A. Guo, I. Javni, Z. Petrović, Rigid polyurethane foams based on soybean oil, *Journal of Applied Polymer Science* **2000**, 77, 467-473.

[94] G. Lligadas, J.C. Ronda, M. Galià, U. Biermann, J.O. Metzger, Synthesis and characterization of polyurethanes from epoxidized methyl oleate based polyether polyols as renewable resources, *Journal of Polymer Science A: Polymer Chemistry* **2006**, 44, 634-645.

[95] Y.-C. Tu, P. Kiatsimkul, G. Suppes, F.-H. Hsieh, Physical properties of water-blown rigid polyurethane foams from vegetable oil-based polyols, *Journal of Applied Polymer Science* **2007**, 105, 453-459.

[96] E. del Río, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, Biobased Polyurethanes from Polyether Polyols Obtained by Ionic-Coordinative Polymerization of Epoxidized Methyl Oleate, *Journal of Polymer Science A: Polymer Chemistry* **2010**, 48, 5009-5017.

[97] E. del Río, G. Lligadas, J. C. Ronda, M. Galià, M. A. R. Meier, V. Cádiz, Polyurethanes from Polyols Obtained by ADMET Polymerization of a Castor Oil-Based Diene:

Characterization and Shape Memory Properties, *Journal of Polymer Science A: Polymer Chemistry* **2011**, 49, 518-525.

[98] E. del Rio, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, M. A. R. Meier, Shape Memory Polyurethanes from Renewable Polyols Obtained by ATMET Polymerization of Glyceryl Triundec-10-enoate and 10-Undecenol, *Macromolecular Chemistry and Physics* **2011**, 212, 1392-1399.

[99] E. del Rio, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, Poly-2-oxazoline-derived polyurethanes: A versatile synthetic approach to renewable polyurethane thermosets, *Journal of Polymer Science A: Polymer Chemistry* **2011**, 49, 3069-3079.

[100] G. Çaylı, S. Küsefoğlu, Biobased polyisocyanates from plant oil triglycerides: synthesis, polymerization, and characterization, *Journal of Applied Polymer Science* **2008**, 109, 2948-2955.

[101] L. Hojabri, X. Kong, S.S. Narine, Fatty acid-derived diisocyanate and biobased polyurethane produced from vegetable oil: synthesis, polymerization, and characterization, *Biomacromolecules* **2009**, 10, 884-891.

[102] P. L. Nayak, Natural oil-based polymers: opportunities and challenges, *Polymer Reviews* **2000**, 40, 1-21.

[103] H. Mutlu, M. A. R. Meier, Unsaturated PA X,20 from Renewable Resources via Metathesis and Catalytic Amidation, *Macromolecular Chemistry and Physics* **2009**, 210, 1019-1025.

[104] O. Kreye, O. Türüç, A. Sehlinger, J. Rackwitz, M. A. R. Meier, Structurally Diverse Polyamides Obtained from Monomers Derived via the Ugi Multicomponent Reaction, *Chemistry - A European Journal* **2012**, 18, 5767-5776.

[105] O. Türünç, M. Firdaus, G. Klein, M. A. R. Meier, Fatty acid derived renewable polyamides via thiol-ene additions, *Green Chemistry* **2012**,14, 2577-2583.

[106] A. Gandini, Epoxy Polymers Based on Renewable Resources, in *Epoxy Polymers: New Materials and Innovation*, J. P. Pascault, R. J. J. Williams (Ed.), pp. 55-78, Weiheim: Wiley-VCH, **2010**.

[107] P. Czub, Synthesis of high-molecular-weight epoxy resins from modified natural oils and Bisphenol A or Bisphenol A-based epoxy resins, *Polymers for Advanced Technologies* **2009**, 20, 194-208.

[108] O. Kreye, T. Tóth, M. A. R. Meier, Poly-α,β-unsaturated aldehydes derived from castor oil via ADMET polymerization, *European Journal of Lipid Science and Technology* **2011**, 113, 31-38.

[109] J. Mallégol, J.-L. Gardette, J. Lemaire, Long-term behaviour of oil-based varnishes and paints I. Spectroscopic analysis of curing drying oils, *Journal of the American Oil Chemist's Society* **1999**, 76, 967-976.

[110] J. Mallégol, J. Lemaire, J.-L. Gardette, Drier influence on the curing of linseed oil, *Progress in Organic Coatings* **2000**, 39, 107-113.

[111] S. J. F. Erich, J. Laven, L. Pel, H.P. Huinink, K. Kopinga, Comparison of NMR and confocal Raman microscopy as coating research tools*, Progress in Organic Coatings* **2005**, 52, 210-216.

[112] M. Lazzari, O. Chiantore, Drying and oxidative degradation of linseed oil, *Polymer Degradation and Stability* **1999**, 65, 303-313.

[113] W.J. Muizebelt, M.W.F. Nielen, Oxidative crosslinking of unsaturated fatty acids studied with mass spectrometry, *Journal of Mass Spectrometry* **1996**, 31, 545-554.

[114] B. Çakmakli, B. Hazer, I.O. Tekin, S. Kizgut, M. Koksal, Y. Menceloglu, Synthesis and Characterization of Polymeric Linseed Oil Grafted Methyl Methacrylate or Styrene, *Macromolecular Bioscience* **2004**, 4, 649-655.

[115] B. Çakmakli, B. Hazer, I.O. Tekin, F.B. Cömert, Synthesis and Characterization of Polymeric Soybean Oil-g-Methyl Methacrylate (and n-Butyl Methacrylate) Graft Copolymers: Biocompatibility and Bacterial Adhesion, *Biomacromolecules* **2005**, 6, 1750-1758.

[116] B. Çakmakli, B. Hazer, I.O. Tekin, S. Açikgöz, M. Can, Polymeric Linoleic Acid–Polyolefin Conjugates: Cell Adhesion and Biocompatibility, *Journal of the American Oil Chemist's Society* **2007**, 84, 73-81.

[117] E. Keles, B. Hazer, Autooxidized Polyunsaturated Oils/Oily Acids: Post-it Applications and Reactions with Fe(III) and Adhesion Properties, *Macromolecular Symposium* **2008**, 269, 154-160.

[118] P.H. Henna, D.D. Andjelkovic, P.P. Kundu, R.C. Larock, Biobased Thermosets from the Free-Radical Copolymerization of Conjugated Linseed Oil, *Journal of Applied Polymer Science* **2007**, 104, 979-985.

[119] M. Valverde, D. Andjelkovic, P.P. Kundu, R.C. Larock, Conjugated Low-Saturation Soybean Oil Thermosets: Free-Radical Copolymerization with Dicyclopentadiene and Divinylbenzene*, Journal of Applied Polymer Science* **2008**, 107, 423-430.

[120] L.E. Hodakowski, C.L. Osborn, E.B. Harris, *Polymerizable epoxide-modified compositions*, US Patent 4119640, **1978**.

[121] R. Wool, S. Küsefoğlu, G. Palmese, S. Knot, R. Zhao, *High modulus polymers and composites from plant oils*, US Patent 6121398, **2000**.

[122] H. Esen, S.H. Küsefoğlu, Photolytic and free-radical polymerization of cinnamate esters of epoxidized plant oil triglycerides, *Journal of Applied Polymer Science* **2003**, 89, 3882-3888.

[123] H. Esen, S.H. Küsefoğlu, R. Wool, Photolytic and free-radical polymerization of monomethyl maleate esters of epoxidized plant oil triglycerides, *Journal of Applied Polymer Science* **2007**, 103, 626-633.

[124] H. Pelletier, N. Belgacem, A. Gandini, Acrylate vegetable oils as photocrosslinkable materials, *Journal of Applied Polymer Science* **2006**, 99, 3218-3221.

[125] H. Pelletier, A. Gandini, Preparation of acrylated and urethanated triglycerols, *European Journal of Lipid Science and Technology* **2006**, 108, 411-420.

[126] D. Marks, F. Li, C.M. Pacha, R.C. Larock, Synthesis of Thermoset Plastics by Lewis Acid Initiated Copolymerization of Fish Oil Ethyl Esters and Alkenes, *Journal of Applied Polymer Science* **2001**, 81, 2001-2012.

[127] a) F. Li, R. C. Larock, J. U. Otaigbe, Fish oil thermosetting polymers: creep and recovery behavior, *Polymer* **2000**, 41, 4849-4862.

b) F. Li, D. W. Marks, R. C. Larock, J. U. Otaigbe, Fish oil thermosetting polymers: synthesis, structure, properties and their relationships, *Polymer* **2000**, 41, 7925-7939.

c) F. Li, M. V. Hanson, R. C. Larock, Soybean oil–divinylbenzene thermosetting polymers: synthesis, structure, properties and their relationships, *Polymer* **2001**, 42, 1567-1579.

d) F. Li, R. C. Larock, New soybean oil–styrene–divinylbenzene thermosetting copolymers. v. shape memory effect, *Journal of Applied Polymer Science* **2002**, 84, 1533-1543.

e) D. D. Andjelkovic, R. C. Larock, Novel Rubbers from Cationic Copolymerization of Soybean Oils and Dicyclopentadiene. 1. Synthesis and Characterization, *Biomacromolecules* **2006**, 7, 927-936.

[128] F. Li, R.C. Larock, New soybean oil-styrene-divinylbenzene thermosetting copolymers. I. Synthesis and characterization, *Journal of Applied Polymer Science* **2001**, 80, 658-670.

[129] F. Li, R.C. Larock, New soybean oil-Styrene-Divinylbenzene thermosetting copolymers - IV. Good damping properties, *Polymers for Advanced Technology* **2002**, 13, 436-449.

[130] Y. Lu, R.C. Larock, Fabrication, Morphology and properties of soybean oil-based composites reinforced with continuous glass fibers, *Macromolecular Materials and Engineering* **2007**, 292, 1085-1094.

[131] Z. Liu, B.K. Sharma, S.Z. Erhan, From oligomers to molecular giants of soybean oil in supercritical carbon dioxide medium: 1. Preparation of polymers with lower molecular weight from soybean oil, *Biomacromolecules* **2007**, 8, 233-239.

[132] M. Sacristán, J.C. Ronda, M. Galià, V. Cádiz, Silicon-containing soybean-oil-copolymers. synthesis and properties, *Biomacromolecules* **2009**, 10, 2678-2685.

[133] M. Sacristán, J.C. Ronda, M. Galià, V. Cádiz, Rapid soybean oil copolymers synthesis by microwave-assisted cationic polymerization, *Macromolecular Chemistry and Physics* **2010**, 211, 801-808.

[134] M. Sacristán, J. C. Ronda, M. Galià, V. Cádiz, Synthesis and properties of boron-containing soybean oil based thermosetting copolymers, *Polymer* **2010**, 51, 6099-6106.

[135] M. Sacristán, T. R. Hull, A. A. Stec, J. C. Ronda, M. Galià, V. Cádiz, Cone calorimetry studies of fire retardant soybean-oil-based copolymers containing silicon or boron: comparison of additive and reactive approaches, *Polymer Degradation and Stability* **2010**, 95, 1269-1274.

[136] M. Sacristán, J.C. Ronda, M. Galià, V. Cádiz, Phosphorus-containing soybean oil copolymers: Cross-metathesis of fatty acid derivatives as an alternative to phosphorus-containing reactive flame retardants, *Journal of Applied Polymer Science* **2011**, 122, 1649-1658.

[137] M. K. Mishra, J. Bradley, R. G. Saxton, and A. Duggal, Anionic Polymerization of Long-Chain Alkyl Methacrylates. *Journal of Polymer Science A: Polymer Chemistry* **2001**, 39, 947-950.

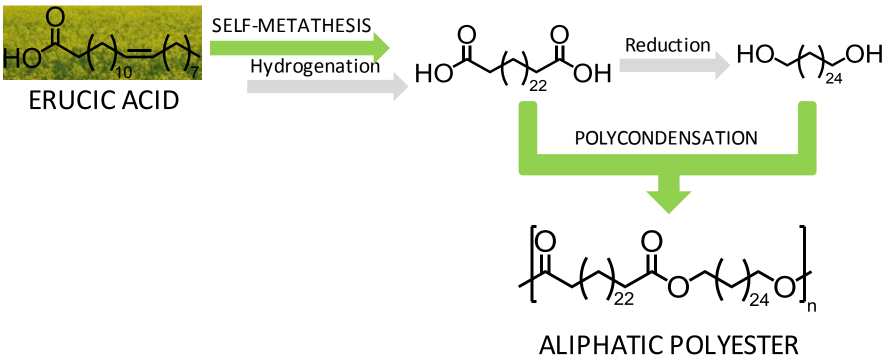
[138] V. Raghunadh, D. Baskaran, S. Sivaram, Living anionic polymerization of lauryl methacrylate and synthesis of block copolymers with methyl methacrylate, *Journal of Polymer Science: Part A: Polymer Chemistry* **2004**, 42, 875-882.

PART B

VEGETABLE OIL-BASED STEP-GROWTH POLYMERS

Chapter III

VEGETABLE OIL-BASED LONG-CHAIN C26 MONOMERS AND THEIR POLYMERS



Renewable long-chain aliphatic polyesters were generated from erucic acid using olefin self-metathesis for monomer synthesis. Polyesterification of the thus obtained 1,26-hexacosanedioic acid with α,ω-diols yielded long-chain aliphatic polyesters with high crystallinity, melting and degradation temperatures.

Parts of this chapter have been published:

C. Vilela, A. J. D. Silvestre, M. A. R. Meier, Plant oil-based long-chain C26 monomers and their polymers, *Macromolecular Chemistry and Physics* **2012**, 213, 2220-2227 (front cover of Macromolecular Chemistry and Physics 21/2012; featured in MaterialsView.com).

1. INTRODUCTION

In polymer chemistry, polyesters include numerous materials with different monomer structures and properties, and find a wide range of applications including bottles, fibres, photographic films, recording tapes, among many others, thus reflecting the high versatility of such an important class of materials.[1] Our interest in vegetable oils and the fatty acids derived thereof stems from the idea that they are attractive substrates for the preparation of aliphatic polyesters. Recent contributions in this field include, for instance, the study of Petrović et al.[2] on high molecular weight linear polyesters from the methyl ester of 9-hydroxynonanoic acid prepared by ozonolysis of castor oil and methanolysis of triglycerides. Moreover, Mecking and his team have investigated aliphatic long-chain C_{19} and C_{23} monomers generated via carbonylation of methyl oleate and ethyl erucate, respectively, and C_{20} monomers prepared via self-metathesis of undecenoic acid and its derivatives.[3,4]

Long-chain aliphatic polyesters can be generated from vegetable oils by three main routes: (i) the polycondensation of hydroxycarboxylic acids, (ii) the polycondensation of a dicarboxylic acid and a diol, or (iii) the ring opening polymerization of lactones.[5] Emphasis in the present chapter is placed on aliphatic polyesters derived from the simple procedure based on the direct polycondensation of aliphatic α,ω-alkanedioic acids and α,ω-alkanediols. The former can be generated by olefin metathesis of unsaturated fatty acids, followed by hydrogenation to the saturated product, while the latter can be obtained from the reduction of the former.

Olefin metathesis, a powerful tool for both organic and polymer chemistry,[6] has gained much attention in the oleochemical field in the last decades,[7-10] since it enables the transformation of vegetable oils and its derivatives into functionalized monomers, polymers, lubricants, fine and specialty chemicals such as cosmetics. The available routes of olefin metathesis comprise self-metathesis (SM), cross-metathesis (CM), ring-closing metathesis (RCM), ring-opening metathesis (ROM), ROM polymerization (ROMP), and acyclic diene metathesis polymerization (ADMET) or acyclic triene metathesis polymerization (ATMET).[7] Among these routes for the preparation of manifold unsaturated molecules, self-metathesis is useful for the synthesis of symmetrical α,ω-dicarboxylic acids from renewable resources, which are important monomers for polymer synthesis.

An unusually long carbon chain fatty acid of interest as a building block in polyester synthesis is erucic acid [*cis*-13-docosenoic acid], a monounsaturated ω-9 fatty acid readily available from rapeseed or crambe oils.[11] The major contributions involving this precursor comprise the work of Mecking and co-workers[3,12] on the preparation of linear saturated semicrystalline polyesters with long-chain hydrocarbon segments based on the complete incorporation of unsaturated fatty acids. The isomerizing carbonylation of ethyl erucate yielded the saturated diethyl-1,23-tricosanedioate, which was then polymerized with tricosane-1,23-diol (formed by the reduction of the 1,23-diacid), dodecane-1,12-diol and hexane-1,6-diol to obtain polyester 23,23, polyester 12,23 and polyester 6,23, respectively, with high melting points.[3,12]

Moreover, Warwel and co-workers[13-15] polymerized symmetrically unsaturated α,ω-dicarboxylic acid methyl esters (C_{10}, C_{12}, C_{18}, C_{20}, C_{26}) with several diols to obtain polyesters with unsaturated moieties. The symmetrical C26 diacid was synthesized by the cross-metathesis of methyl erucate with ethylene to form methyl tetradec-13-enoate and dec-1-ene, followed by metathetical dimerization.[13-15]

In a similar study, Yang et al.[16] obtained unsaturated and epoxidized fatty acid-based polyesters from α,ω-dicarboxylic acids prepared by the biochemical oxidation of terminal methyl groups of unsaturated fatty acids into carboxylic groups, followed by enzymatically catalyzed polycondensation. As an example, the unsaturated 1,22-*cis*-9-

docosenedioic acid was prepared from erucic acid and submitted to the enzyme catalyzed polycondensation with 1,8-octanediol to obtain an unsaturated polyester that could be further modified, derivatized, or cross-linked, using the mid-chain unsaturation in order to adjust the material properties.

To the best of our knowledge, no information was available before this study regarding the application of the saturated α,ω-dicarboxylic acid metathesis product of erucic acid as a building block in polyester synthesis, although the self-metathesis of this C22:1 fatty acid had already been reported.[17,18]

In this vein, the present chapter describes the synthesis of the unsaturated α,ω-dicarboxylic acid obtained from erucic acid by self-metathesis, followed by hydrogenation to yield the saturated 1,26-diacid. Aliphatic polyesters were then prepared by the direct polycondensation of 1,26-hexacosanedioic acid with hexacosane-1,26-diol, obtained from the 1,26-diacid via reduction. For comparison purposes, the saturated 1,26-diacid was also polymerized with short chain diols, namely dodecane-1,12-diol and butane-1,4-diol. The ensuing saturated polyesters were thoroughly characterized by conventional spectroscopic techniques, SEC, TGA, DSC and XRD.

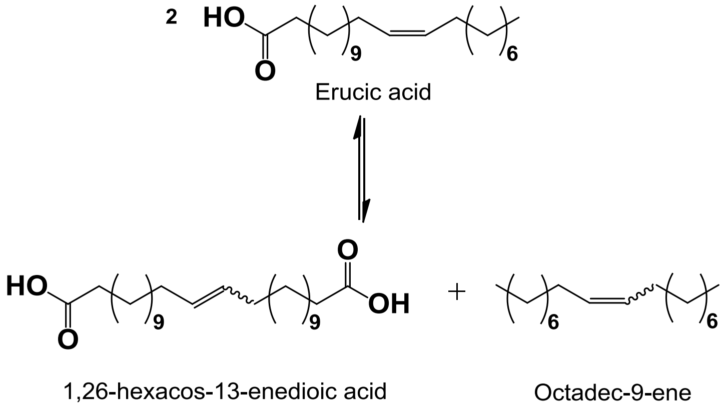
2. RESULTS AND DISCUSSION

2.1 Synthesis and characterization of C26 monomers

In this chapter, symmetrical monomers with C26 aliphatic chains were prepared, namely the unsaturated C26:1 α,ω-diacid (1,26-hexacos-13-enedioic acid), the saturated C26:0 α,ω-diacid (1,26-hexacosanedioic acid) and α,ω-diol (1,26-hexacosanediol).

2.1.1 Monomer 1,26-hexacos-13-enedioic acid

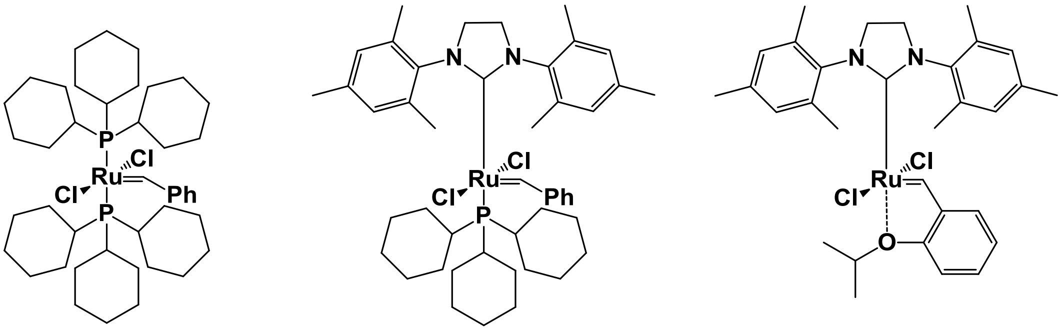
Erucic acid (EA) was used as substrate for the single-step synthesis of the symmetrical long-chain 1,26-hexacos-13-enedioic acid via olefin self-metathesis (SM), as shown in Scheme 20.



Scheme 20. Self-metathesis of erucic acid.

Although the self-metathesis of EA has already been reported using tungsten hexachloride-tetramethyl tin[17] or (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(phenylmethylene)(tricyclohexylphosphine) ruthenium[18] as catalytic systems, a rapid screening with different catalysts, reaction times and temperatures was performed. Thus, the SM of EA to yield the C26 unsaturated diacid was investigated using three ruthenium based olefin metathesis catalysts, namely Grubbs 1st (C1) and 2nd (C2) generation and Hoveyda-Grubbs 2nd generation catalyst (C3) (Scheme 21). With second generation catalysts, the self-metathesis reactions were carried out in the presence of 1,4-benzoquinone as additive to suppress double bond isomerisation, as discussed elsewhere.[19,20]

As expected, the three catalysts were able to promote this reaction, although with different outcomes in terms of conversion. As already discussed in the literature for other substrates,[20] C2 and C3 (2nd generation) were more active than C1 (1st generation) since very low conversions (<<10%) were attained with the latter. From this initial investigation we also learned that the 2nd generation Hoveyda-Grubbs catalyst (C3) was the one that gave better results, most likely due to its high functional group tolerance and catalytic activity,[21] and that 24 hours reaction time were sufficient to complete the reactions. These conditions were thus used for further experiments.



C1
Grubbs Catalyst
1st generation

C2
Grubbs Catalyst
2nd generation

C3
Hoveyda-Grubbs Catalyst
2nd generation

Scheme 21. Investigated ruthenium based metathesis catalysts.

The temperature had a remarkable effect on the conversion of the starting material, leading to 31, 65 and 56% conversion with 0.5% C3 under bulk conditions at 30, 50 and 70°C, respectively. These results might be explained by a crystallization of the unsaturated diacid metathesis product (Scheme 1) at 50 °C, which shifts the metathesis equilibrium towards product formation. At 30 °C, C3 was probably too inactive and at 70°C the diacid was not crystallizing that well. Inspired by this result, we tried to further shift the equilibrium by adjusting the reaction temperature and by adding a cosolvent to delay the crystallization (start of solidification in the solvent free system was observed quickly after ~5 minutes of reaction time). Indeed, adding a small amount of hexane and performing the reaction at 45 °C kept the mixture homogeneous for a longer time (~15-20 minutes), which allowed shifting the equilibrium further to >70% conversion.

Under optimized conditions, conversions of erucic acid up to 73% were obtained by using a 0.3 M solution of EA in n-hexane, 0.5 mol % of C3 and 2 eq (relative to catalyst) of 1,4-benzoquinone at 45 °C during 24 hours. A significant advantage of this procedure is the easy recovery of the desired diacid by simple filtration of the resulting reaction mixture, which results in diacid of > 90% purity, which could then be recrystallized.

The structure of 1,26-hexacos-13-enedioic acid was confirmed by FTIR, ^{1}H and ^{13}C NMR, and GC-MS. The FTIR spectrum of this unsaturated α,ω-diacid showed the typical absorption bands of carboxyl groups and hydrocarbon structures, together with the double bond vibrations (Figure 5). The absorption bands assigned to the aliphatic chain occurred at 2914 and 2847 cm^{-1} (CH_2 stretching modes), while the ones characteristic of carboxyl groups arised at 2674 cm^{-1} (OH stretching), 1699 cm^{-1} (C=O stretching), 1430 cm^{-1} (C-O stretching) and 939 cm^{-1} (OH out-of-plane deformation). The absorption band arising from the double bond appeared at 3003 cm^{-1} (CH stretching).[22]

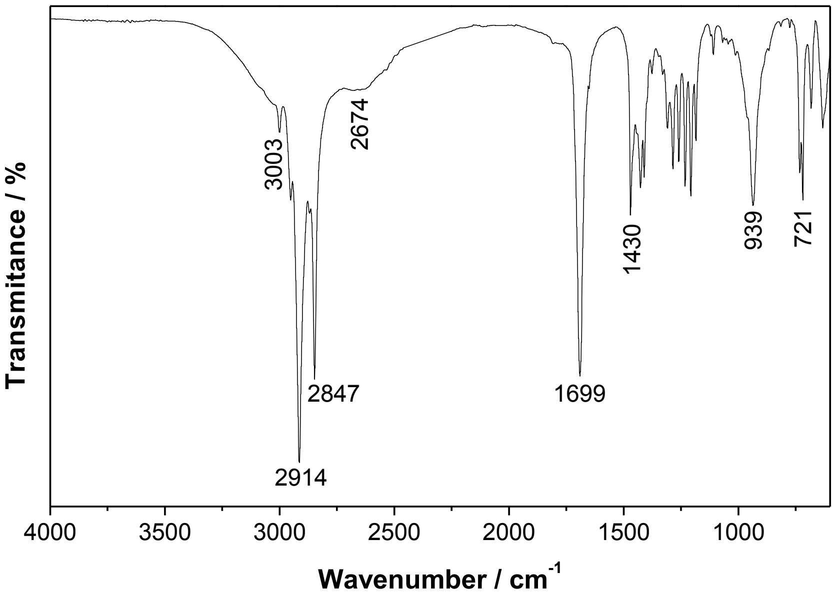


Figure 5. FTIR spectrum of 1,26-hexacos-13-enedioic acid.

The ^{1}H NMR spectrum of 1,26-hexacos-13-enedioic acid (Figure 6) exhibited the general features of a long-chain unsaturated diacid with resonances at δ 5.4 (multiplet from the two olefinic protons), 2.3 (triplet from methylenic group in α position with respect to carbonylic group), 2.0 (multiplet from methylenic group in both sides of olefinic hydrogen), 1.6 (multiplet from methylenic group in β position with respect to carbonylic group) and 1.3 ppm (signal from methylenic groups in the aliphatic chain).

The ^{13}C NMR spectrum (Figure 6) displayed resonances at δ 177.8 (carbonyl carbon of the carboxyl group), 131.5 (unsaturated carbons), 35.0 (methylenic carbons in α position with respect to carbonylic group), 30.7-30.1 (aliphatic CH_2), 26.1 (allylic carbons), 24.7 (methylenic carbons in β position with respect to carbonylic group).

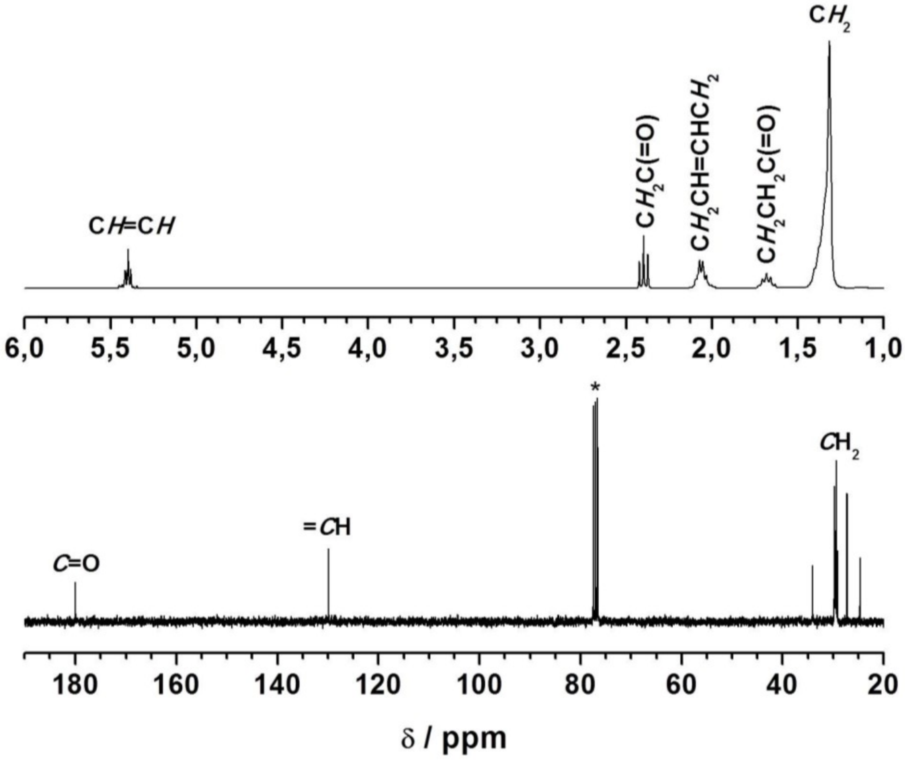
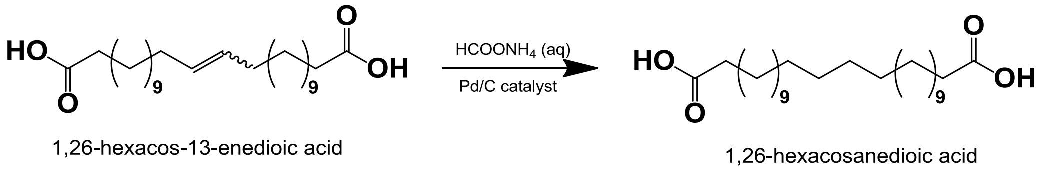


Figure 6. ^{1}H and ^{13}C NMR spectra of 1,26-hexacos-13-enedioic acid in *$CDCl_3$ with peak assignments.

The mass spectrum of the TMS derivative of the intermediate 1,26-hexacos-13-enedioic acid obtained from GC-MS analysis was characterized by a fragmentation pattern with a molecular ion at m/z 568, base peak at m/z 73 and an intense peak at m/z 553 ($[M-15]^+$) attributed to the loss of a methyl group from the TMS ester group. Fragment ions at m/z 73, 75, 117, 129, 204 and 217 were easily recognized as typical of TMS derivatives.[23]

2.1.2 Monomer 1,26-hexacosanedioic acid (1,26-diacid)

The previous unsaturated α,ω-diacid was hydrogenated to its saturated analog (1,26-diacid, Scheme 22) by using a simple catalytic transfer hydrogenation (CTH) system, where palladium on carbon was the catalyst and aqueous ammonium formate was the solvent and hydrogen donor. The structure of this saturated bifuntional monomer was confirmed by FTIR, ^{1}H and ^{13}C NMR spectroscopy, GC-MS and elemental analysis.



Scheme 22. Catalytic hydrogenation of 1,26-hexacos-13-enedioic acid.

The FTIR spectrum of the 1,26-diacid clearly showed the disappearance of the absortion band arising from the double bond at 3003 cm^{-1}, and the presence of the characteristic absorption bands of the aliphatic chain at 2913 and 2845 cm^{-1} (CH_2 stretching) and 720 cm^{-1} (skeletal vibration of $–(CH_2)_n–$) and of the carboxyl groups at 2667 cm^{-1} (OH stretching), 1694 cm^{-1} (C=O stretching) and 1427 cm^{-1} (C-O stretching).[22]

The ^{1}H NMR spectrum (Figure 8) confirmed the expected structure through the presence of the resonances at δ 1.3 ppm (signal from methylene groups in fatty acid chain), δ 1.7 ppm (multiplet from methylene group in β position with respect to carbonyl group) and δ 2.5 ppm (triplet from methylene group in α position with respect to carbonyl group), and the disappearance of the resonances assigned to the olefinic protons at about δ 2.0 and 5.4 ppm.

The ^{13}C NMR profile (Figure 8) of 1,26-diacid was in agreement with the structure proposed by ^{1}H NMR with peaks at δ 24.7 ppm (methylene groups in β position with respect to carbonyl groups), δ 29.1-29.9 ppm (methylene groups in the diacid central chain), δ 34.1 ppm (methylene groups in α position with respect to carbonyl groups) and δ 182.8 ppm (carbonyl carbons of the carboxyl groups), together with the absence of resonances of the unsaturated and allylic carbons at δ 131.5 and 26.1 ppm, respectively.

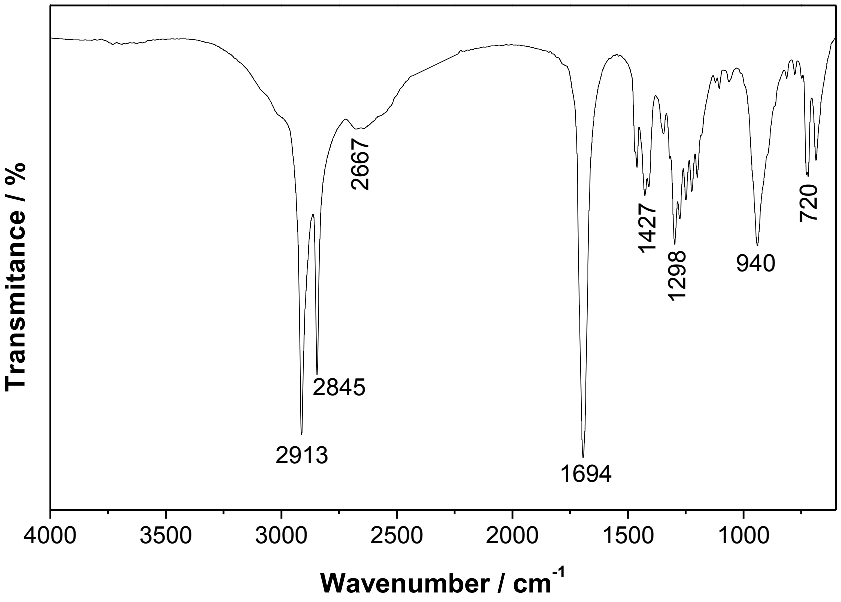


Figure 7. FTIR spectrum of 1,26-diacid.

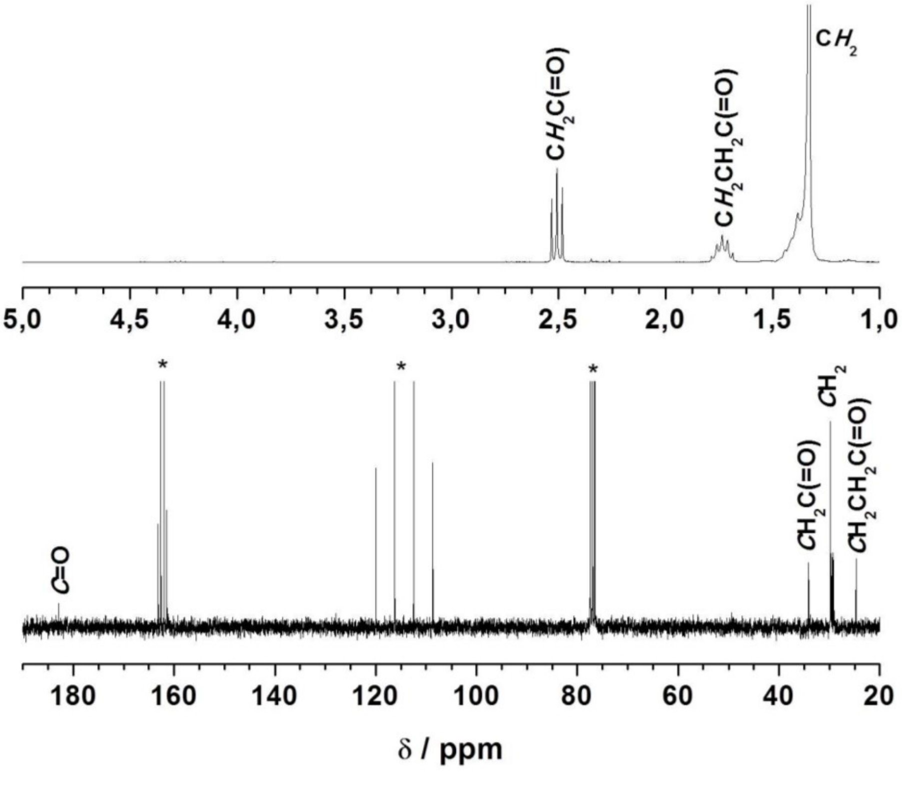


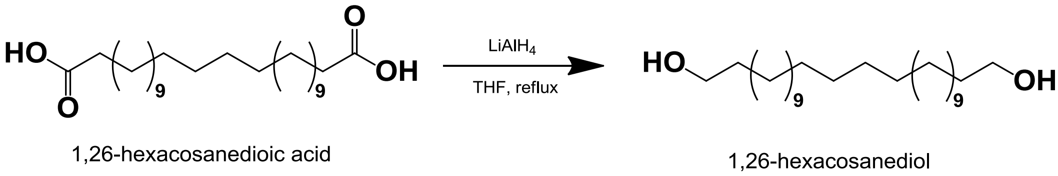
Figure 8. ^{1}H and ^{13}C NMR spectra of 1,26-diacid in *$CDCl_3$/CF_3COOD with peak assignments.

The mass spectrum of the TMS derivative of 1,26-diacid obtained from GC-MS analysis was characterized by a fragmentation pattern with a molecular ion at m/z 570, base peak at m/z 204, an intense peak at m/z 555 ($[M-15]^+$) attributed to the loss of a methyl group from the TMS ester group and an ion at m/z 439 ($[M-131]^+$) allocated to the loss of ($(CH_3)_3SiOCOCH_2$) resulting from the McLafferty rearrangement. Fragment ions at m/z 73, 75, 117, 129, 204 and 217 were easily recognized as typical of TMS derivatives.[23]

The calculated (measured) elemental microanalyses results were in a good agreement $C_{26}H_{50}O_4$: % C 73.19 (73.44), % H 11.81 (11.71), % O 15.00 (14.85).

2.1.3 Monomer 1,26-hexacosanediol (1,26-diol)

The 1,26-diacid monomer was reduced to its corresponding α,ω-diol (1,26-diol) using lithium aluminium hydride as reducing agent (Scheme 23). Its structure was confirmed by FTIR, ^1H and ^{13}C NMR spectroscopy, GC-MS and elemental analysis.



Scheme 23. Reduction of 1,26-hexacosanedioic acid.

The FTIR spectrum of 1,26-diol was consistent with the expected structure through the presence of all the relevant peaks, *viz.* (i) the broad absorption band at 3260 cm^{-1} characteristic of hydroxyl end groups and (ii) the symmetric and asymmetric CH_2 stretching vibrations of the aliphatic chain at 2846 and 2914 cm^{-1}, respectively,[22] together with the absence of the characteristic absorption bands of the carboxyl group at 2667, 1694 and 1427 cm^{-1}.

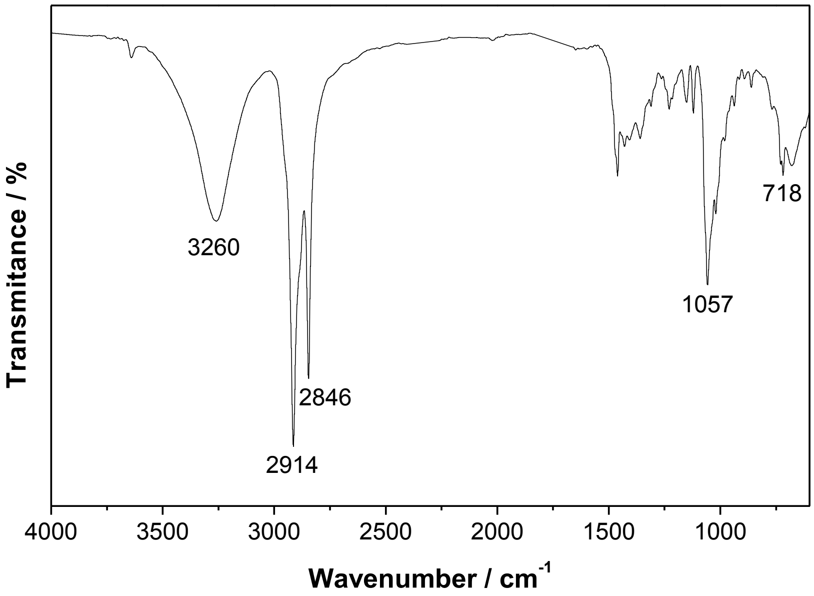


Figure 9. FTIR spectrum of 1,26-diol.

The ^{1}H NMR spectrum in Figure 10 clearly confirmed the structure of 1,26-diol by the presence of the methylene protons attached to the hydroxyl groups at about δ 4.4 ppm, apart from the typical resonances of the methylene protons of the aliphatic chain at δ 1.4 and 1.8 ppm. The nonexistence of the resonances allocated to the protons in the α and β position with respect to the carbonyl group of carboxylic acids, further confirmed the structure of this α,ω-diol.

The ^{13}C NMR spectrum (Figure 10), in addition to the unchanged resonances related to the aliphatic chain carbons (δ 25.5, 29.1-29.7 and 34.3 ppm), showed a signal resonating at δ 69.1 ppm readily identified as the methylene carbons of the hydroxyl groups ($HOCH_2$).

The mass spectrum of the TMS derivative of 1,26-diol was characterized by the molecular ion at m/z 542, the base peak at m/z 149 and a peak at m/z 527 attributed to the loss of a methyl group from the TMS ether moiety. Fragment ions at m/z 73, 75, 89 and 103 were readily identified as typical of TMS derivatives of primary alcohols, while the pair of peaks at m/z 147 and 149 was characteristic of TMS derivatives of diols.[23]

The calculated (measured) elemental microanalyses results were in a good agreement $C_{26}H_{54}O_2$: % C 78.32 (78.67), % H 13.65 (13.33), % O 8.03 (8.00).

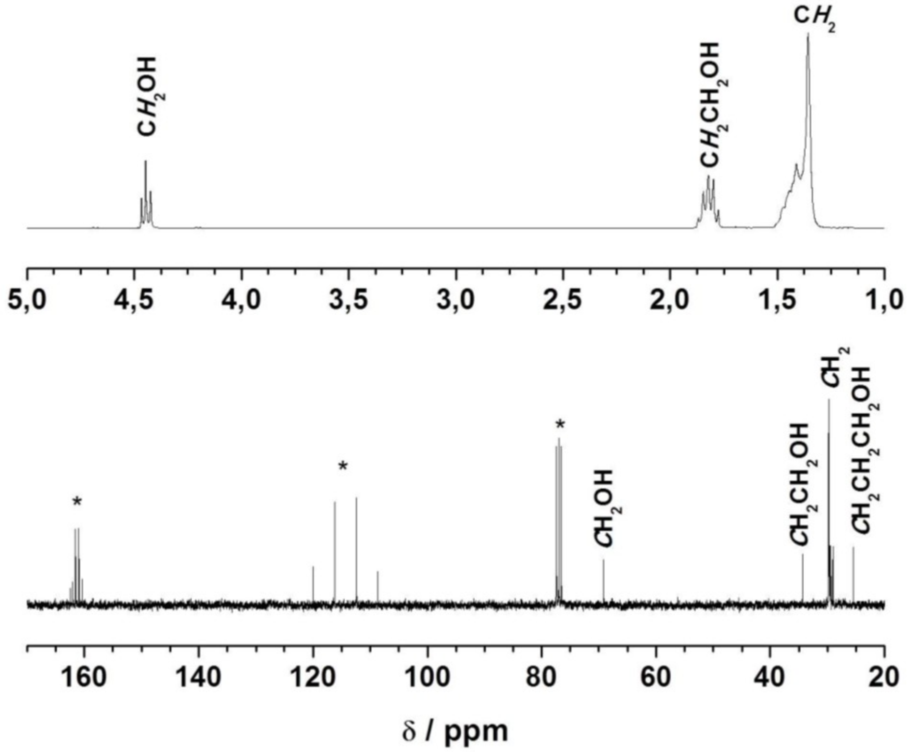
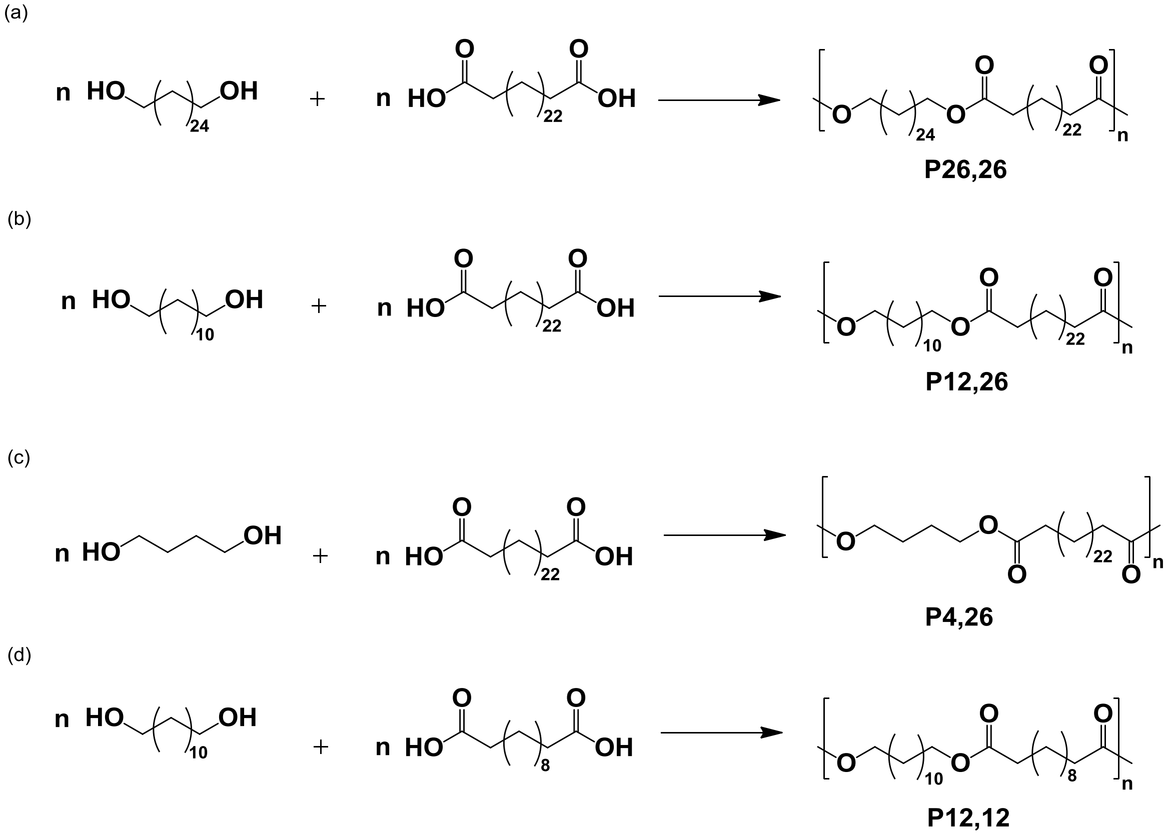


Figure 10. ^1H and ^{13}C NMR spectra of 1,26-diol in *$CDCl_3/CF_3COOD$ with peak assignments.

2.2 Synthesis and characterization of linear aliphatic polyesters

Inspired by the possibility of preparing 100% renewable polyesters from vegetable oils through their fatty acids, stoichiometric amounts of linear α,ω-diacid and α,ω-diol were directly polymerized in bulk at low temperature using bismuth (III) trifluoromethanesulfonate ($Bi(OTf)_3$) as catalyst. The usefulness of this catalyst with one of the least toxic heavy metal ions, Bi^{3+}, has already been shown for the synthesis of other aliphatic polyesters.[24,25] The specific conditions used here were selected on the basis of a previous study.[26]

Four aliphatic polyesters were prepared, namely PE 26,26 from 1,26-diol and 1,26-diacid, PE 12,26 from dodecane-1,12-diol and 1,26-diacid, PE 4,26 from butane-1,4-diol and 1,26-diacid, and PE 12,12 from dodecane-1,12-diol and 1,12-dodecanedioic acid, as illustrated in Scheme 24. This simple green procedure yielded aliphatic polyesters with isolated yields in the range 69-79%. The white powdery polymers were characterized by conventional spectroscopic techniques, SEC, TGA, DSC and XRD. Moreover, the solubility of the polyesters was also assessed using potential solvents. Common organic solvents like dichloromethane, chloroform, tetrahydrofuran, tetrachloroethane and dimethylsulfoxide did not dissolve polyesters PE 26,26 and PE 12,26 at room temperature. Indeed, the only solvents that induced total dissolution at room temperature were trifluoroacetic acid (TFA) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Polyesters PE 4,26 and PE 12,12 were soluble in more manageable solvents like dichloromethane and chloroform. Mixtures of some common solvents containing 10% of TFA or HFIP were effectively used as solvents for NMR and SEC analysis, respectively.



Scheme 24. Polymerization of (a) 1,26-diol with 1,26-diacid, (b) dodecane-1,12-diol with 1,26-diacid, (c) butane-1,4-diol with 1,26-diacid and (d) dodecane-1,12-diol with 1,12-dodecanedioic acid.

2.2.1 Infrared Spectroscopy

The FTIR analysis of the four polyesters was a straightforward way to confirm the formation of the polymers and their expected structures. The corresponding spectra of all polyesters were similar to their precursors, except for the absence of the band allocated to the stretching mode of the OH groups of alcohols (suggesting a high conversion and a high DP) and the presence of the bands at about 1730 and 1170 cm^{-1} attributed to the C=O and C–O stretching vibrations of the ester moiety, respectively. As an example of these features, Figure 11 shows the corresponding spectrum of the saturated polyester PE 26,26.

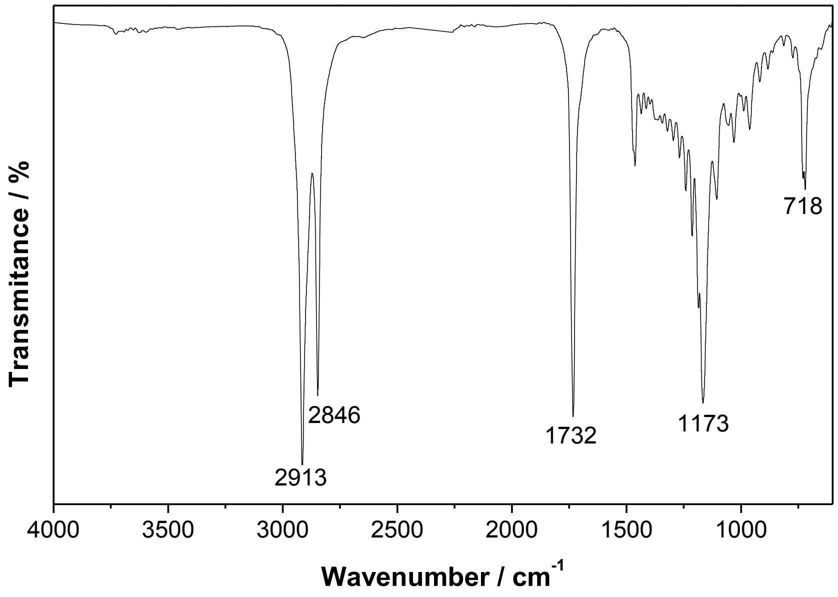


Figure 11. FTIR spectrum of polyester PE 26,26.

2.2.2 Nuclear Magnetic Spectroscopy

The linear aliphatic polyesters were also unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of all the polymers were found to be consistent with the corresponding macromolecular structures regarding both chemical shifts and relative integrations. The comparison of the spectra of the polyesters with those of their corresponding precursors (as exemplified for PE 12,26 in Figure 12), revealed that the

OCH_2 resonance was shifted from δ 4.4 ppm for the diol to δ 4.2 ppm for the polymer, owing to the presence of the neighbouring carbonyl group, which corroborates the formation of the polyesters.

The ^{13}C NMR analysis gave additional evidence of the success of the polyesterification reactions with the emergence of a new resonance at around δ 179.3 ppm arising from the carbon of the C=O of the ester groups, instead of the carbon resonance of the free carboxylic group at δ 182.8 ppm. The above spectroscopic analyses reflect the spectra of all polymers in terms of their basic features.

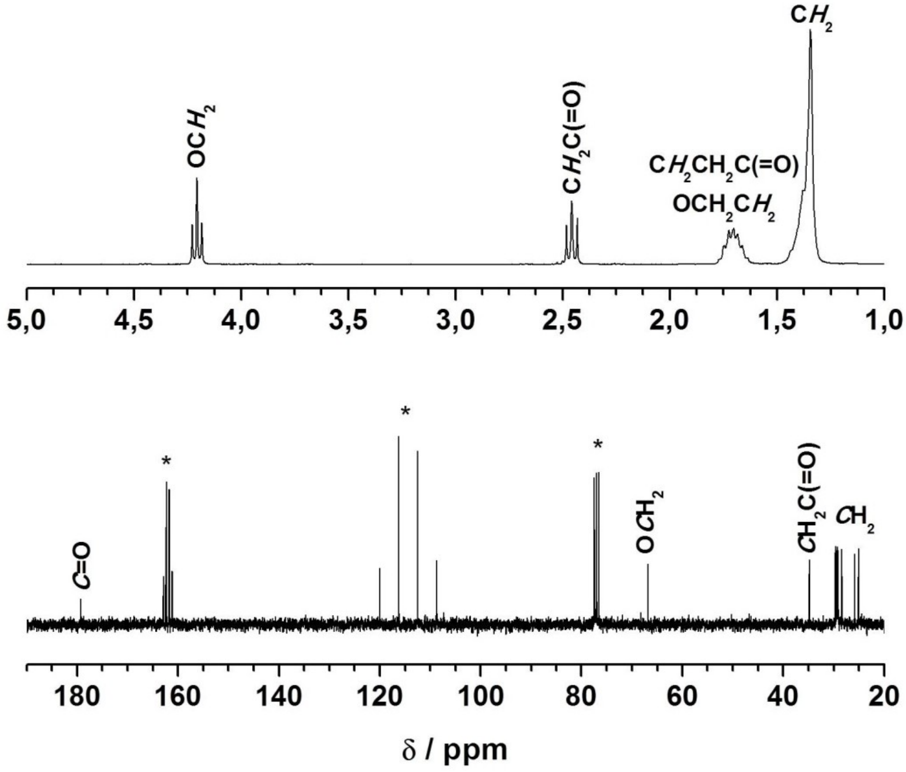


Figure 12. ^{1}H and ^{13}C NMR spectra of polyester PE 12,26 in *$CDCl_3$/CF_3COOD with peak assignments.

2.2.3 Size Exclusion Chromatography

The SEC analysis of the four aliphatic polyesters showed number-average molecular weights (M_n) in the range 8-14 kDa and the polydispersity index (PDI) between 2.1 and 2.7

as expected for linear polycondensation polymers (Table 7). These values are in agreement with the ones obtained by Mecking's group[3,4,12] for similar aliphatic polyesters.

Table 7. Molecular weight results for the synthesized linear aliphatic polyesters.

Polymer	M_w / kDa	M_n / kDa	PDI
PE 26,26	33.8	14.1	2.4
PE 12,26	25.0	11.9	2.1
PE 4,26	19.2	8.0	2.4
PE 12,12	35.6	13.2	2.7

All the SEC chromatograms exhibited monomodal distributions, as exemplified in Figure 13 for PE 12,26. Moreover, the M_n values increased with increasing diol chain length (PE 4,26 < PE 12,26 < PE 26,26), which was similarly observed in previous work by Linko and co-workers.[27]

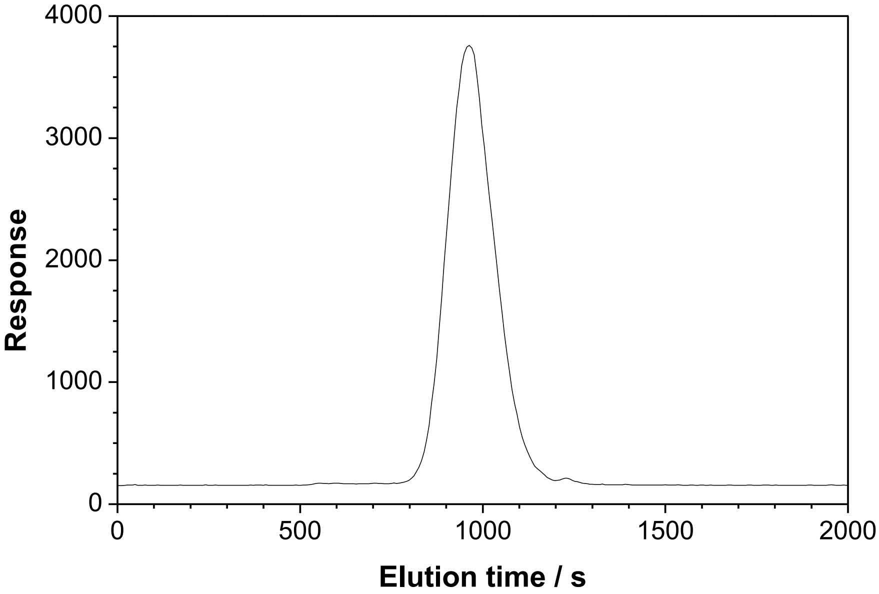


Figure 13. SEC tracing of polyester PE 12,26.

2.2.4 Thermogravimetric Analysis and Differential Scanning Calorimetry

The thermal properties of all the aliphatic polyesters were assessed by TGA and DSC analysis, as summarize in Table 8. According to the TGA data, the polymers presented similar degradation behaviour in a nitrogen atmosphere (see Figure 14 for PE 26,26) with good thermal stability up to 323-386 °C ($T_{d5\%}$) and maximum weight losses (T_{dmax}) between 429-444 °C. A weight loss of 96-98% was obtained at temperatures up to 800 °C.

Table 8. TGA and DSC data for the synthesized linear aliphatic polyesters.

Polymer	**TGA**		**DSC**			
	$T_{d\,5\%}$ / °C	**$T_{d\,max}$ / °C**	**T_m / °C**	**T_c / °C**	**ΔH_m / J g^{-1}**	**χ_c / %** *
PE 26,26	386	431	104	92	224	80
PE 12,26	333	444	95	87	198	71
PE 4,26	323	431	74	68	177	63
PE 12,12	357	429	88	73	153	55

* degree of crystallinity based upon 279 J g^{-1} for 100% crystalline polyethylene[28]

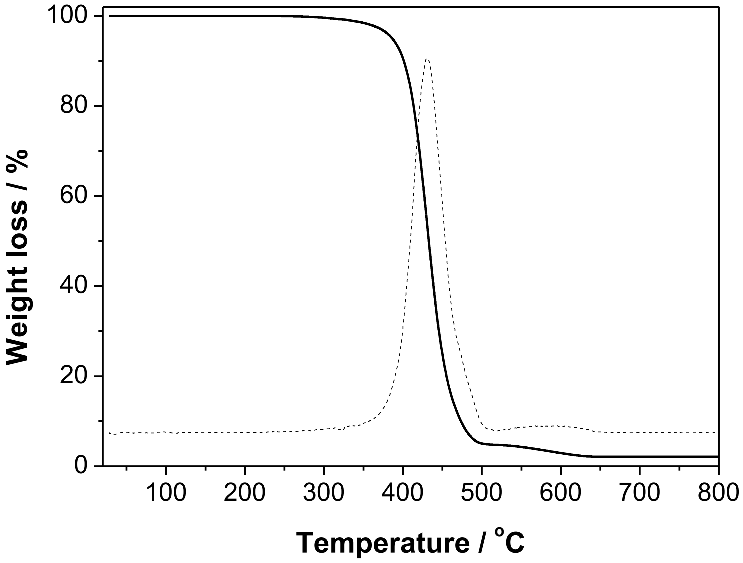


Figure 14. Thermogravimetric curves of polyester PE 26,26: weight loss (solid curve) and its derivative (dotted curve).

The DSC traces of the four polyesters showed a sharp well-defined melting endotherm and crystallization peak (as illustrated in Figure 15 for PE 26,26), implying a high degree of crystallinity of the polyesters. As expected, the polymer resulting from the polycondensation of monomers 1,26-diacid and 1,26-diol (PE 26,26) featured the higher melting (T_m = 104 °C) and crystallization (T_c = 92 °C) temperatures. Decreasing the diol chain length decreased the T_m and T_c values of the corresponding polyesters (PE 12,26 and PE 4,26). The melting temperature of PE 12,12 was consistent with the values obtained by Barbiroli et al.[29] and was lower than the T_m values of polyesters PE 26,26 and PE 12,26. In all instances, the melting temperatures are compatible with those observed for other long-chain aliphatic polyesters[3,4,12,30] and comparable to the T_m values of low density polyethylene. The melting temperature of PE 26,26 is lower than the T_m value of the polyester PE 30,30 prepared by Cho and Lee[30] and higher than the T_m of polyesters PE 19,19 and PE 23,23 obtained by Mecking and his team.[3]

The melting enthalpies, ΔH_m, and degrees of crystallinity, χ_c, (Table 8) of these polymers were calculated and the results showed ΔH_m between 153 and 224 J g^{-1} and χ_c values between 55 and 80%, which are higher than the ones reported in the literature for linear low density polyethylene (LLDPE).[31]

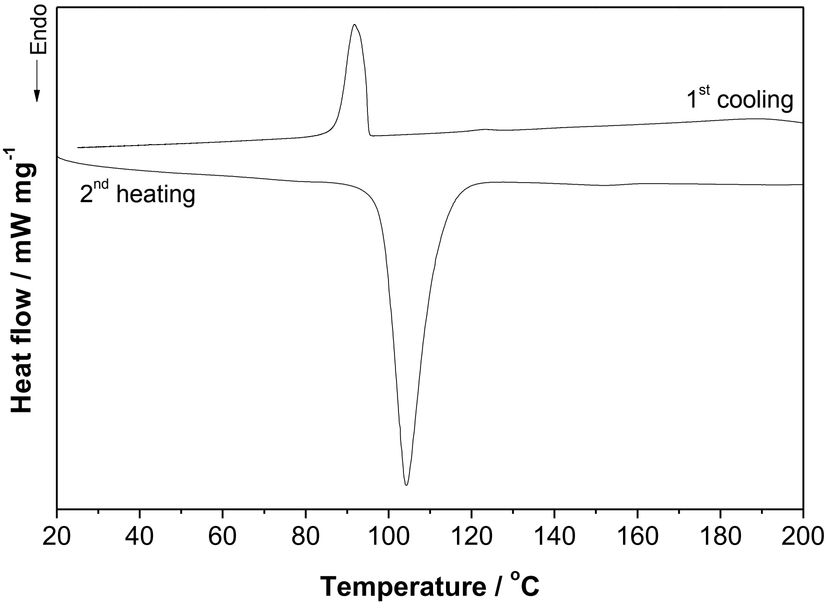


Figure 15. DSC thermogram of polyester PE 26,26.

2.2.5 X-ray diffraction

Aliphatic polyesters are usually semicrystalline materials and the ones we discuss here are no exception. They display very regular structures as indicated by their ^{1}H NMR spectra and DSC thermograms and corroborated by the corresponding XRD patterns. As a typical example, Figure 16 shows the diffractogram of polyester PE 12,26 with two main reflections at 2θ ≈ 21.6° (110) and 24.1° (200) characteristic of a polyethylene like crystal structure.[32,33]

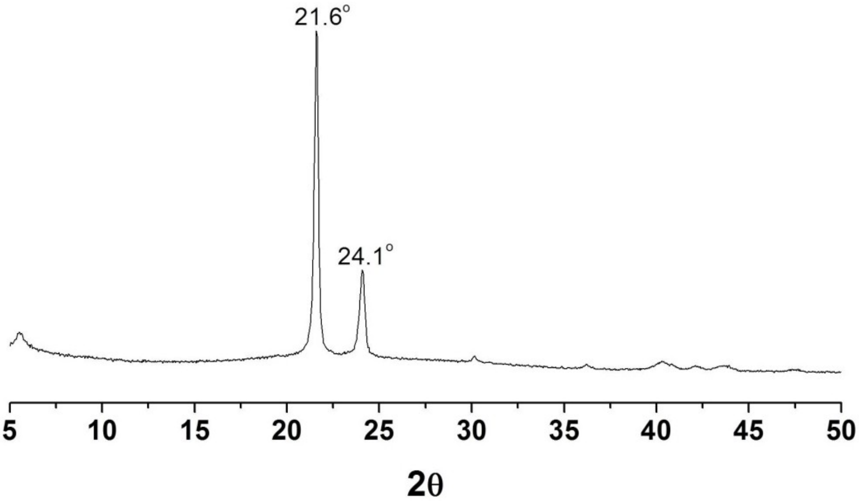


Figure 16. XRD pattern of polyester PE 12,26.

3. CONCLUSIONS

The self-metathesis of erucic acid, followed by hydrogenation, was found to be an successful way to synthesize the saturated 1,26-hexacosadioic acid in an efficient manner. The subsequent reduction of this 1,26-diacid yielded the corresponding 1,26-diol. The most important feature of these two bifunctional monomers (1,26-diacid and 1,26-diol), aside from the long-chain linear segments, is their green character owing to the renewable origin and the synthetic pathways.

The direct polycondensation of the previous monomers is a straightforward method for the preparation of 100% renewable aliphatic long-chain polyesters with M_n in the range 8-14 kDa and PDI values between 2.1 and 2.7. On the whole, these polyesters displayed good thermal stability with temperatures at 5% weight loss in the range 323-386 °C. These semi-crystalline materials exhibited high melting and crystallization temperatures (74-104 °C and 68-92 °C, respectively) with increasing diol chain length.

The possible biodegradability of these polymers together with their renewable origin make them attractive candidates to be used as surrogate of polyethylene or other polyolefins in some specific applications.

4. EXPERIMENTAL

4.1 Materials

Ammonium formate (Sigma-Aldrich, ≥ 98%), bismuth(III) trifluoromethanesulfonate (Aldrich, ≥ 99%), butane-1,4-diol (Sigma-Aldrich, ≥ 99%), 1,12-dodecanedioic acid (Aldrich, 99%), dodecane-1,12-diol (Aldrich, 99%), erucic acid (EA, Sigma, ≥ 99%), bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride (C1, Aldrich, Grubbs 1st generation catalyst), [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (phenylmethylene)(tricyclohexylphosphine) ruthenium (C2, Aldrich, Grubbs 2nd generation catalyst), [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxy-phenylmethylene) ruthenium (C3, Aldrich, Hoveyda-Grubbs 2nd generation catalyst), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Fluka, ≥ 99.8%), lithium aluminium hydride (Aldrich, 95%), palladium on activated carbon (Acros Organics, 10%), tetrahydrofuran (THF, Sigma-Aldrich, anhydrous ≥ 99.9%) and trifluoroacetic acid (TFA, Sigma-Aldrich, ≥ 99.0%) were used as received without any further purification. Polystyrene standards were supplied by Polymer Laboratories. Other chemicals and solvents were of laboratory grades.

4.2 Synthesis of 1,26-hexacos-13-enedioic acid

A) The self-metathesis reaction of erucic acid was carried out using a ruthenium-based catalytic system. The effect of catalyst type and loading, reaction time and temperature, and the presence or absence of solvent on the rate and extent of the self-metathesis reaction of erucic acid was rapidly screened. A typical reaction started with the melting and degassing at 45 °C of the white waxy solid (500 mg, 1.48 mmol) in small conical flasks, followed by the addition of n-tetracosane (60.0 mg, 0.18 mmol) as internal standard. After stirring for 5 min, the t=0 sample was taken and the selected ruthenium-based catalyst was added to the mixture under inert atmosphere. The reaction was performed at a given temperature and time, and was stopped by quenching with an excess of ethyl vinyl ether. All reactions were followed by GC-MS analysis after derivatization.

B) After the screening of the reaction conditions, EA (20.0 g, 59.1 mmol) was melted and degassed at 45 °C, followed by the addition of 1,4-benzoquinone (64.8 mg, 0.60 mmol). After stirring for 5 min, catalyst C3 (184.8 mg, 0.30 mmol) was added to the mixture and the reaction was carried out at 45 °C under inert atmosphere during 24 hours. Since n-hexane was used as co-solvent (0.3 M of EA in n-hexane), the desired dicarboxylic acid was recovered by filtration, recrystallized twice from acetone and obtained in 51.0% yield (6.4 g, 15.1 mmol).

ν_{max}/cm^{-1}: 3003 (unsaturation C–H stretching), 2914 and 2847 (CH_2 stretching modes), 2674 (OH stretching), 1699 (C=O stretching), 1430 (C–O stretching), 939 (OH out-of-plane deformation), 721 (skeletal vibration of $–(CH_2)_n–$).

δ_H (300 MHz, CD_3OD, Me_4Si): 5.4 (2H, m, C*H*=C*H*), 2.3 (4H, t, *J* = 7.39 Hz, $CH_2C(=O)$), 2.0 (4H, m, $CH_2CH=CHCH_2$), 1.6 (4H, m, $CH_2CH_2C(=O)$), 1.3 (32H, m, aliphatic CH_2).

δ_C (75 MHz, CD_3OD, Me_4Si): 177.8 (C=O), 131.5 (=*C*H), 35.0 ($CH_2C(=O)$), 30.7-30.1 (aliphatic CH_2), 26.1 ($=CHCH_2$), 24.7 ($CH_2CH_2C(=O)$).

EI-MS (di-TMS derivative) *m/z* (%): 73 (100.0, $[(CH_3)_3Si]^+$), 75 (74.1, $[(CH_3)_2SiOH]^+$), 117 (32.5), 129 (72.3), 204 (47.9), 217 (25.6), 388 (43.1, $[M-180]^+$), 478 (44.4, $[M-90]^+$), 553 (97.9, $[M-15]^+$), 568 (2.6, $[M]^+$).

4.3 Synthesis of 1,26-hexacosanedioic acid (1,26-diacid)

The hydrogenation of 1,26-hexacos-13-enedioic acid with Pd/C catalyst was adapted from the method reported by Anwer and co-workers,[34] in which the catalytic transfer hydrogenation is conducted under mild conditions. To a 500 mL round-bottom flask were added 10 wt% Pd/C (10%), MeOH (60 mL) and a stir bar. Stirring was begun, and the mixture was brought to reflux. Next was added half of a solution of ammonium formate (3.48 g, 55.2 mmol) in water (60 mL), followed by a solution of 1,26-hexacos-13-enedioic acid (6.0 g, 14.2 mmol) in methanol (60 mL). The remaining ammonium formate (3.48 g) was added after 30 minutes. The catalyst was removed by filtration over celite and solvent removal yielded a white solid in 80.0% yield (4.8 g, 11.4 mmol), mp 126.1 °C (from DSC). Purity of the white saturated diacid (99%) was determined by GC-MS.

ν_{max}/cm^{-1}: 2913 and 2845 (CH_2 stretching modes), 2667 (OH stretching), 1694 (C=O stretching), 1427 (C–O stretching), 940 (OH out-of-plane deformation), 720 (skeletal vibration of $–(CH_2)_n–$).

δ_H (300 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 2.5 (4H, t, *J* = 7.5 Hz, $CH_2C(=O)$), 1.7 (4H, m, $CH_2CH_2C(=O)$), 1.3 (40H, m, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 182.8 (C=O), 34.1 ($CH_2C(=O)$), 29.9-29.1 (aliphatic CH_2), 24.7 ($CH_2CH_2C(=O)$).

EI-MS (di-TMS derivative) *m/z* (%): 73 (85.1, $[(CH_3)_3Si]^+$), 75 (63.7, $[(CH_3)_2SiOH]^+$), 117 (43.2), 129 (51.7), 204 (100.0), 217 (43.4), 439 (11.3), 555 (56.9, $[M-15]^+$), 570 (1.6, $[M]^+$).

Anal. calcd for $C_{26}H_{50}O_4$: C 73.19, H 11.81, O 15.00; **found**: C 73.44, H 11.71, O 14.85.

4.4 Synthesis of hexacosane-1,26-diol (1,26-diol)

1,26-hexacosanedioic acid (2.0 g, 4.7 mmol) was dissolved in anhydrous tetrahydrofuran (20 mL) and slowly added to a stirred and cooled suspension of $LiAlH_4$ (713.5 mg, 18.8 mmol) in anhydrous THF (60 mL). After adding more anhydrous THF (10 mL), the stirred mixture was refluxed for 10 hours. After cooling to room temperature, the reaction was quenched by slowly adding water until gas evolution ceased. A 15% NaOH solution was added to obtain a white precipitate of the inorganic salts, which was removed by filtration and washed with hot THF. After vacuum removal of THF, the thus-obtained solid was thoroughly washed with water and dried at 60 °C in vacuum. Hexacosane-1,26-diol was obtained in 91% yield as a white solid, mp 96.9 °C (from DSC). Purity of the diol (99%) was confirmed by GC-MS.

ν_{max}/cm^{-1}: 3260 (OH stretching), 2914 and 2846 (CH_2 stretching modes), 1057 (OH deformation), 718 (skeletal vibration of $–(CH_2)_n–$).

δ_H (300 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 4.4 (4H, t, *J* = 6.7 Hz, CH_2OH), 1.8 (4H, m, CH_2CH_2OH), 1.4 (44H, m, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 69.1 (CH_2OH), 34.3 (CH_2CH_2OH), 29.7-29.1 (aliphatic CH_2), 25.5 ($CH_2CH_2CH_2OH$).

EI-MS (di-TMS derivative) *m/z* (%): 73 (41.9, $[(CH_3)_3Si]^+$), 75 (44.6, $[(CH_3)_2SiOH]^+$), 89 (3.7), 103 (21.5), 147 (100.0), 149 (75.4), 527 (0.6, $[M-15]^+$), 542 (0.9, $[M]^+$).

Anal. calcd for $C_{26}H_{54}O_2$: C 78.32, H 13.65, O 8.03; **found**: C 78.67, H 13.33, O 8.00.

4.5 Polyesterification reactions

In a 10 mL Schlenk tube, the diacid (2.5 mmol), diol (2.5 mmol) and bismuth (III) trifluoromethanesulfonate (3.3 mg, 0.005 mmol) were heated to 90 °C at 0.01 mbar over the course of 48 hours. After cooling, the solid mixture was dissolved in chloroform/trifluoroacetic acid (1:0.1, ~25 mL) and the polymer precipitated, by pouring the solution into an excess of cold methanol (~2 L) to remove the $Bi(OTf)_3$ and the soluble oligomers. The solids were filtered, dried under vacuum, and weighed. Polymers were obtained as white solids in good yields (79% for PE 26,26, 76% for PE 12,26, 72% for PE 4,26 and 69% for PE 12,12).

Poly[1,26-hexacosadiyl-1,26-hexacosanedioate] (**PE 26,26**)

ν_{max}/cm^{-1}: 2913 and 2846 (CH_2 stretching modes), 1732 (C=O stretching), 1173 (C–O stretching), 718 (skeletal vibration of –$(CH_2)_n$–).

δ_H (300 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 4.3 (t, *J* = 6.7 Hz, OCH_2), 2.5 (t, *J* = 7.6 Hz, $CH_2C(=O)$), 1.7 (m, $CH_2CH_2C(=O)$ and OCH_2CH_2), 1.4 (s, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 179.2 (C=O), 66.8 (OCH_2), 34.8 ($CH_2C(=O)$), 29.7-29.1 (CH_2), 28.4 (OCH_2CH_2), 25.9 ($OCH_2CH_2CH_2$), 25.0 ($CH_2CH_2C(=O)$).

Poly[1,12-dodecadiyl-1,26-hexacosanedioate] (**PE 12,26**)

ν_{max}/cm^{-1}: 2914 and 2847 (CH_2 stretching modes), 1732 (C=O stretching), 1166 (C–O stretching), 720 (skeletal vibration of –$(CH_2)_n$–).

δ_H (300 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 4.2 (t, *J* = 6.7 Hz, OCH_2), 2.4 (t, *J* = 7.5 Hz, $CH_2C(=O)$), 1.7 (m, $CH_2CH_2C(=O)$ and OCH_2CH_2), 1.4 (s, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 179.3 (C=O), 66.8 (OCH_2), 34.6 ($CH_2C(=O)$), 29.8-29.1 (CH_2), 28.3 (OCH_2CH_2), 25.9 ($OCH_2CH_2CH_2$), 25.0 ($CH_2CH_2C(=O)$).

Poly[1,4-butadiyl-1,26-hexacosanedioate] (**PE 4,26**)

ν_{max}/cm^{-1}: 2914 and 2846 (CH_2 stretching modes), 1736 (C=O stretching), 1169 (C–O stretching), 720 (skeletal vibration of –$(CH_2)_n$–).

δ_H (300 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 4.2 (t, *J* = 6.6 Hz, OCH_2), 2.5 (t, *J* = 7.6 Hz, $CH_2C(=O)$), 1.7 (m, $CH_2CH_2C(=O)$ and OCH_2CH_2), 1.3 (s, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 179.6 (C=O), 66.5 (OCH_2), 34.6 ($CH_2C(=O)$), 29.8-29.1 (CH_2), 25.0 (OCH_2CH_2 and $CH_2CH_2C(=O)$).

Poly[1,12-dodecadiyl-1,12-dodecanedioate] (**PE 12,12**)

ν_{max}/cm^{-1}: 2914 and 2848 (CH_2 stretching modes), 1730 (C=O stretching), 1173 (C–O stretching), 720 (skeletal vibration of –$(CH_2)_n$–).

δ_H (300 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 4.2 (t, J = 6.7 Hz, OCH_2), 2.4 (t, J = 7.5 Hz, $CH_2C(=O)$), 1.7 (m, $CH_2CH_2C(=O)$ and OCH_2CH_2), 1.3 (s, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3/CF_3COOD$, Me_4Si): 179.2 (C=O), 66.8 (OCH_2), 34.7 ($CH_2C(=O)$), 29.6-29.1 (CH_2), 28.3 (OCH_2CH_2), 25.8 ($OCH_2CH_2CH_2$), 25.1 ($CH_2CH_2C(=O)$).

4.6 Characterization methods

The FTIR-ATR spectra were taken with a Perkin Elmer FT-IR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. Each spectrum was an average of 32 scans taken with 4 cm^{-1} resolution in the 600-4000 cm^{-1} range.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts (δ) were reported in parts per million (ppm), relative to the internal standard tetramethylsilane (TMS, δ=0.00 ppm).

Gas chromatography-mass spectrometry (GC-MS) analyses were carried out with a Trace GC Ultra 2000 instrument equipped with a Thermo Scientific DSQ II single-quadrupole mass spectrometer and a DB-1 J&W capillary column (30 m x 0.32 mm i.d., 0.25 µm film thickness). Helium at a flow rate of 35 cm/s was used as carrier gas. The conditions adopted for these analyses were: initial temperature, 100°C; ramp at 10 °C/min to 250 °C, hold for 5 minutes; ramp at 10 °C/min to 300 °C, hold for 10 minutes; injector temperature, 250 °C; transfer-line temperature, 280 °C; and split ratio of 1:33. The MS was operated in the electron impact mode with impact energy of 70 eV and data collected at a rate of 1 scan s^{-1} over a range of m/z 33-700. The ion source was kept at 200 °C. Prior to GC-MS analysis, nearly 20 mg of each sample were converted into trimethylsilyl (TMS) derivatives, according to literature.[35] The EI-MS spectra (in the form of TMS derivatives) of the monomers reported here were obtained from the GC-MS runs.

The elemental composition of the synthesized monomers was determined by elemental analysis using a LECO TruSpec CHNS elemental analyzer. All samples were analyzed in triplicate.

The molecular weights and molecular weight distributions of the polymers were determined using a size exclusion chromatographer (SEC) equipped with a PL-EMD 960 evaporative light scattering detector. The column set consisted of a PL HFIPgel guard followed by two PL HFIPgel columns (300 x 7.5 mm), kept at 40 °C. The mobile phase flow rate was 1.0 mL min^{-1} and a v/v/v mixture of dichloromethane/chloroform/HFIP 70/20/10 was used as the eluent. Polystyrene standards were used for narrow standard calibration.

Thermal decomposition temperatures were determined by thermogravimetric analyses (TGA) on a Shimadzu TGA-50 analyzer equipped with a platinum cell. The thermograms were run under nitrogen atmosphere at constant heating rate of 10 °C/min from the 20 to 800 °C. The decomposition onset temperature, T_d, was taken as the temperature at which a 5% loss in weight occurred.

The differential scanning calorimetry (DSC) analyses were carried out on a Shimadzu DSC-50 calorimeter. Samples of 5-6 mg were heated in aluminium DSC capsules from 20 to 200 °C at 10 °C/min in a nitrogen stream. The melting (T_m) and crystallization (T_c) temperatures were recorded as the endothermic peak on the second heating scan and the exothermic peak on the cooling scan, respectively. The enthalpy of melting (ΔH_m) was calculated via the integration of the area below the melting endotherm, while the degree of crystallinity was calculated as the percentage relative to the melting enthalphy value of 100% crystalline sample given for LDPE as 279 J g^{-1} in the literature.[28]

The X-Ray diffraction (XRD) measurements were performed on a Philips X'Pert MPD diffractometer operating with CuK$_\alpha$ radiation (λ = 1.5405980 Å) at 40 kV and 50 mA. Samples were scanned in the 2θ ranges from 5 to 50°, with a step of 0.04° and time per step equal to 50 s.

5. REFERENCES

[1] J. Scheirs, T. E. Long (Eds.), *Modern polyesters: chemistry and technology of polyesters and copolyesters*, West Sussex, England, John Wiley & Sons, **2003**.

[2] Z. S. Petrović, J. Milić, Y. Xu, I. Cvetković, A Chemical Route to High Molecular Weight Vegetable Oil-Based Polyhydroxyalkanoate, *Macromolecules* **2010**, 43, 4120-4125.

[3] D. Quinzler, S. Mecking, Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization, *Angewandte Chemie International Edition* **2010**, 49, 4306-4308.

[4] J. Trzaskowski, D. Quinzler, C. Bährle, S. Mecking, Aliphatic Long-Chain C20 Polyesters from Olefin Metathesis, *Macromolecular Rapid Communications* **2011**, 32, 1352-1356.

[5] F. S. Güner, Y. Yağci, A. T. Erciyes, Polymers from triglycerides oils, *Progress in Polymer Science* **2006**, 31, 633-670.

[6] A. Fürstner, Olefin Metathesis and Beyond, *Angewandte Chemie International Edition* **2000**, 39, 3012-3043.

[7] a) J. C. Mol, Application of olefin metathesis in oleochemistry: an example of green chemistry, *Green Chemistry* **2002**, 4, 5-13.
b) J. C. Mol, Catalytic Metathesis of Unsaturated Fatty Acid Esters and Oils, *Topics in Catalysis* **2004**, 27, 97-104.

[8] A. Rybak, P. A. Fokou, M. A. R. Meier, Metathesis as a versatile tool in oleochemistry, *European Journal of Lipid Science and Technology* **2008**, 110, 797-804.

[9] M. A. Meier, *Metathesis with Oleochemicals:* New Approaches for the Utilization of Plant Oils as Renewable Resources in Polymer Science, *Macromolecular Chemistry and Physics* **2009**, 210, 1073-1079.

[10] H. Mutlu, L. Montero de Espinosa, M. A. R. Meier, Acyclic diene metathesis: a versatile tool for the construction of defined polymer architectures, *Chemical Society Reviews* **2011**, 40, 1404-1445.

[11] A. S. Carlsson, Plant oils as feedstock alternatives to petroleum – A short survey of potential oil crop platforms, *Biochimie* **2009**, 91, 665-670.

[12] F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, Long-chain linear C19 and C23 monomers and polycondensates from unsaturated fatty acid esters, *Macromolecules* **2011**, 44, 4159-4166.

[13] a) S. Warwel, F. Büse, C. Demes, M. Kunz, M. Rüsch gen. Klaas, Polymers and surfactants on the basis of renewable resources, *Chemosphere* **2001**, 43, 39-48.

[14] S. Warwel, C. Demes, G. Steinke, Polyesters by lipase-catalyzed polycondensation of unsaturated and epoxidized long-chain α,ω-dicarboxylic acid methyl esters with diols, *Journal of Polymer Science A* **2001**, 39, 1601-1609.

[15] S. Warwel, J. Tillack, C. Demes, M. Kunz, Polyesters of ω-unsaturated fatty acid derivatives, *Macromolecular Chemistry and Physics* **2001**, 202, 1114-1121.

[16] Y. Yang, W. Lu, X. Zhang, W. Xie, M. Cai, R. A. Gross, Two-step biocatalytic route to biobased functional polyesters from ω-carboxy fatty acids and diols, *Biomacromolecules* **2010**, 11, 259-268.

[17] P. B. Van Dam, M. C. Mittelmeijer, C. Boelhouwer, Homogeneous catalytic metathesis of unsaturated fatty esters: new synthetic method for preparation of unsaturated mono- and dicarboxylic acids, *Journal of the American Oil Chemical Society* **1974**, 51, 389-392.

[18] H. L. Ngo, K. Jones, T. A. Foglia, Metathesis of unsaturated fatty acids: synthesis of long-chain unsaturated-α,ω-dicarboxylic acids, *Journal of the American Oil Chemical Society* **2006**, 83, 629-634.

[19] S. H. Hong, D. P. Sanders, C. W. Lee, R. H. Grubbs, Prevention of Undesirable Isomerization during Olefin Metathesis, *Journal of the American Chemical Society* **2005**, 127, 17160-17161.

[20] G.B. Djigoué, M.A.R. Meier, Improving the selectivity for the synthesis of two renewable platform chemicals via olefin metathesis, *Applied Catalysis A* **2009**, 368, 158-162.

[21] S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, Efficient and Recyclable Monomeric and Dendritic Ru-Based Metathesis Catalysts, *Journal of the American Chemical Society* **2000**, 122, 8168-8179.

[22] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Vol. 1, 3rd Edition, London: Chapman and Hall, **1975**.

[23] The Lipid Library, **2012**. *The Lipid Library: Lipid Chemistry, Biology, Technology and Analysis*, Available from http://lipidlibrary.aocs.org/ (May 2012).

[24] P. Buzin, M. Lahcini, G. Schwarz, and H. R. Kricheldorf, Aliphatic Polesters by Bismuth Triflate-Catalyzed Polycondensations of Dicarboxylic Acids and Aliphatic Diols, *Macromolecules* **2008**, 41, 8491-9495.

[25] A. F. Sousa, A. Gandini, A. J. D. Silvestre, C. Pascoal Neto, J. J. C. Cruz Pinto, C. Eckerman, B. Holmbom, Novel suberin-based biopolyesters: from synthesis to properties, *Journal of Polymer Science A: Polymer Chemistry* **2011**, 49, 2281-2291.

[26] A. F. Sousa, A. J. D. Silvestre, A. Gandini, C. Pascoal Neto, Synthesis of aliphatic suberin-like polyesters by ecofriendly catalytic systems, *High Performance Polymers* **2012**, 24, 4-8.

[27] Y.-Y Linko, M. Lamsa, X. Wu, E. Uosukainen, J. Seppälä, P. Linko, Biodegradable products by lipase biocatalysis, *Journal of Biotechnology* **1998**, 66, 41-50.

[28] M. Run, J. Gao, Z. Li, Nonisothermal crystallization and melting behavior of mPE/LLDPE/LDPE ternary blends, *Thermochimica Acta* **2005**, 429, 171-178.

[29] G. Barbiroli, C. Lorenzetti, C. Berti, M. Fiorini, P. Manaresi, *Polyethylene like polymers. Aliphatic polyesters of dodecanedioic acid 1. Synthesis and properties*, *European Polymer Journal* **2003**, 39, 655-661.

[30] I. Cho, K. Lee, Poly(triacontamethylene triacontanedioate) as polyethylene analogue: properties and enzymatic degradation, *Macromolecular Chemistry and Physics* **1997**, 198, 861-869.

[31] L.-P. Huang, X.-P. Zhou, W. Cui, X.-L. Xie, S.-Y. Tong, Toughening effect of maleic anhydride grafted linear low density polyethylene on linear low density polyethylene, *Journal of Materials Science* **2008**, 43, 4290-4296.

[32] Y.-L. Hsieh, X.-P. Hu, Structural transformation of ultra-high modulus and molecular weight polyethylene fibers by high-temperature wide-angle X-ray diffraction, *Journal of Polymer Science Part B: Polymer Physics* **1997**, 35, 623-630.

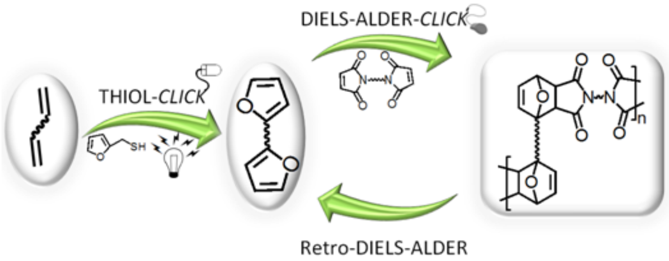
[33] R. Caminiti, L. Pandolfi, P. Ballirano, Structure of polyethylene from X-ray powder diffraction: influence of the amorphous fraction on data analysis. *Journal of Macromolecular Science, Part B Physics* **2000**, B39, 481-492.

[34] M. K. Anwer, D. B. Sherman, J. G. Roney, A. F. Spatola, Applications of ammonium formate catalytic transfer hydrogenation. 6. Analysis of catalyst, donor quantity, and solvent effects upon the efficacy of dechlorination, *Journal of Organic Chemistry* **1989**, 54, 1284-1289.

[35] C. S. R. Freire, A. J. D. Silvestre, C. P. Pascoal Neto, J. A. S. Cavaleiro, Lipophilic Extractives of the Inner and Outer Barks of Eucalyptus globulus, *Holzforschung* **2002**, 56, 372-379.

Chapter IV

LINEAR POLYMERS FROM FURAN/VEGETABLE OIL MONOMERS



Two click chemistry approaches were applied to macromolecular syntheses, namely a thiol-ene coupling to convert unsaturated vegetable oil derivatives into bifunctional monomers, and their Diels–Alder polymerization to obtain linear thermoreversible materials.

Parts of this chapter have been published:

C. Vilela, L. Cruciani, A. J. D. Silvestre, A. Gandini, A Double Click Strategy Applied to the Reversible Polymerization of Furan/Vegetable Oil Monomers, *Macromolecular Rapid Communications* **2011**, 32, 1319-1323.

C. Vilela, L. Cruciani, A. J. D. Silvestre, A. Gandini, Reversible polymerization of novel monomers bearing furan and plant oil moieties. A double click exploitation of renewable resources, *RSC Advances* **2012**, 2, 2966-2974.

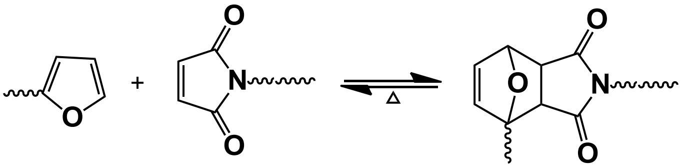
1. INTRODUCTION

Albeit vegetable oils naturally contain functional groups, e.g. double bonds, their reactivity towards polymerization is often scant. Therefore, the introduction of easily polymerizable moieties in their structure opens the way to a panoply of vegetable oil-based polymeric materials. Among the myriad efficient approaches that use the reactivity of double bonds, the thiol-ene coupling and the Diels-Alder (DA) reaction are two well-known click-chemistry mechanisms.

The thiol-ene addition, known for over 100 years, is a well documented reaction,[1-4] which has attracted the interest of researchers due to its click chemistry character.[5] It has been successfully used for the synthesis of star polymers,[6] dendrimers,[7] and disaccharides,[8] among others. In the field of oleochemistry, the thiol-ene coupling with vegetable oils or their fatty acids has been applied to prepare several monomers and polymers.[9-15] For instance, Samuelsson et al.[9] and Claudino et al.[10] investigated the kinetics of the photo-initiated thiol-ene coupling of trifunctional thiols with methyl oleate and methyl linoleate. Bantchev et al.[11] prepared sulphide-modified vegetable oils through the thiol-ene addition of butanethiol to canola and corn oils for such end-use applications as lubricants. Moreover, Türünç and Meier[13] prepared a set of novel monomers derived from 10-undecenoic acid via thiol-ene additions in the absence of solvent and initiator, and their subsequent polymerization yielded a family of linear and hyperbranched polyesters with good thermal properties.

The Diels-Alder reaction, known since 1928, is another prominent example of click chemistry[16] that has been studied very extensively in a variety of contexts,[17-19] including notably the realm of furan polymers[20] because of its potential for the preparation of various macromolecular architectures. These materials, based on renewable resources, possess, in addition to this important feature, promising properties in terms of thermoreversibility, mendability and recyclability.[20-23]

The important peculiarity of the DA reaction, a [4+2] cycloaddition between a conjugated diene and a dienophile typically bearing an alkenyl moiety, apart from its click connotation, is its reversible character, illustrated here (Scheme 25) in the case of the coupling of a furan ring (diene) with a maleimide complementary moiety (dienophile). The temperature is a key factor in determining the position of the equilibrium, which can be shifted heavily from predominant adduct formation (DA reaction), up to ca. 65 °C, to the predominant reversion to its precursors (retro-DA reaction), above ca. 100 °C.[20-26] The kinetic characteristics associated with the course of the forward and backward reactions depend on the specific structure of the substituents attached to both heterocycles, and, of course, the reactant concentration, the medium and the temperature.



Scheme 25. The DA equilibrium between growing species bearing, respectively, furan and maleimide end-groups.

The application of the DA reaction to polymer syntheses based on furan/maleimide reversible couplings has garnered much attention in the last few decades given the fact that furan derivatives descend from renewable resources and are therefore likely to play a growing role in sustainable approaches to (green) chemistry and materials science.[27] Two different approaches dominate this realm, i.e. (i) polymerization reactions calling upon A–A + B–B and A–B monomers and (ii) reversible cross-linking of linear polymers bearing pendant furan or maleimide moieties, based on the temperature sensitivity of the DA equilibrium.[20,21] The fact that the forward DA reaction gives rise to both *endo* and *exo* stereoisomer adducts[28] does not play a significant role in these macromolecular syntheses, since both participate in the chain growth.

The present chapter describes the use of undecenyl compounds as suitable substrates for appending terminal DA functions, *viz.* either two furan (A) heterocycles or a combination of a furan (A) and a protected maleimide (B) end-groups. This was achieved by calling upon the thiol-ene reaction in conjunction with more classical chemical condensations. The ensuing AA and protected AB monomers were then polymerized through the DA reaction, the former with a bismaleimide (BB), the latter on its own, after liberating the maleimide moiety through the retro-DA reaction of the inert adduct.

2. RESULTS AND DISCUSSION

2.1 Synthesis and characterization of bifunctional monomers

As far as we know, the thiol-ene coupling of 2-furylmethanethiol (FT) with alkenyl functions has never been reported and it was therefore vital to investigate it first with simple model compounds.

The reactivity of FT towards both terminal and internal C=C unsaturations was assessed under various conditions using compounds bearing a single alkene moiety. The occurrence of the thiol-ene click reaction was confirmed using vinyl isobutyl ether (VIBE) and vinyl stearate (VS), (i.e. terminal unsaturations), with which coupling did take place, although at more modest rates than with conventional aliphatic thiols (e.g. 1,3-propanedithiol).

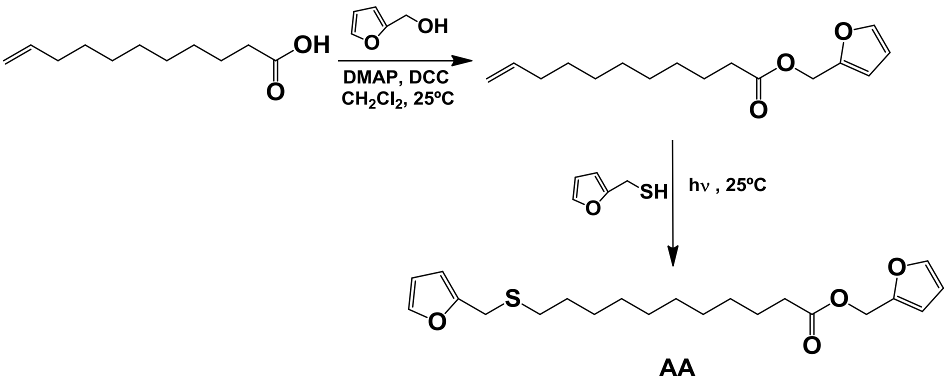
The use of reagents incorporating internal CH=CH groups, like methyl oleate (MO), resulted in a very sluggish process and it was therefore decided to concentrate our study on reagents bearing end-unsaturations. The possibility of a retarding effect associated with the steric hindrance induced by the furan ring was excluded, since the aromatic sulphide counterpart, Ph–CH_2–SH did not display any appreciable rate decrease compared with the aliphatic homologues.

As mentioned above, the basic structure chosen as a typical and viable vegetable oil derivative was ω-undecenoic acid (UDA), i.e. the prominent fragment arising from the pyrolysis of castor oil,[29] and also its reduced derivative undec-10-en-1-ol (UDOL).

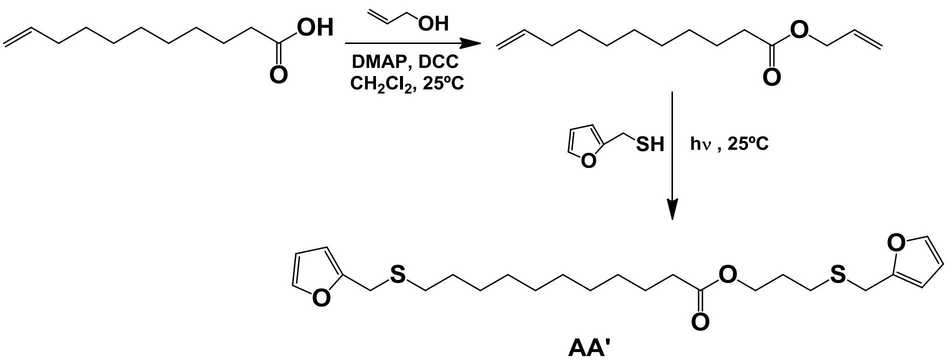
2.1.1 Monomers AA and AA’

Two approaches were adopted to append furan end-groups onto UDA, *viz*. (i) esterification with furfuryl alcohol (FA) at the carboxylic terminal and ene reaction with FT at the unsaturated counterpart (Scheme 26), or (ii) esterification with allyl alcohol (Scheme 27), followed by a double ene reaction with FT at both alkenyl end-groups. In both cases, α,ω-difuran monomers (AA and AA’) were obtained and characterized by FTIR, Raman, ^{1}H and ^{13}C NMR spectroscopy.

The FTIR spectrum of the AA monomer (Figure 17) clearly showed the presence of furan heterocycle bands at 3111, 1600, 1503, 1375, 1215, 1070, 1009, 933, 885, 748, 597 cm^{-1},[30] and the ester C=O and C–O bands at 1735 and 1150 cm^{-1}, respectively.[31] The Raman spectrum clearly indicated the presence of the C–S stretching vibration at 607 cm^{-1} and the absence of the SH band of the thiol moiety in the range 2590-2550 cm^{-1}.[31]



Scheme 26. Synthesis of the AA monomer.



Scheme 27. Synthesis of the AA′ monomer.

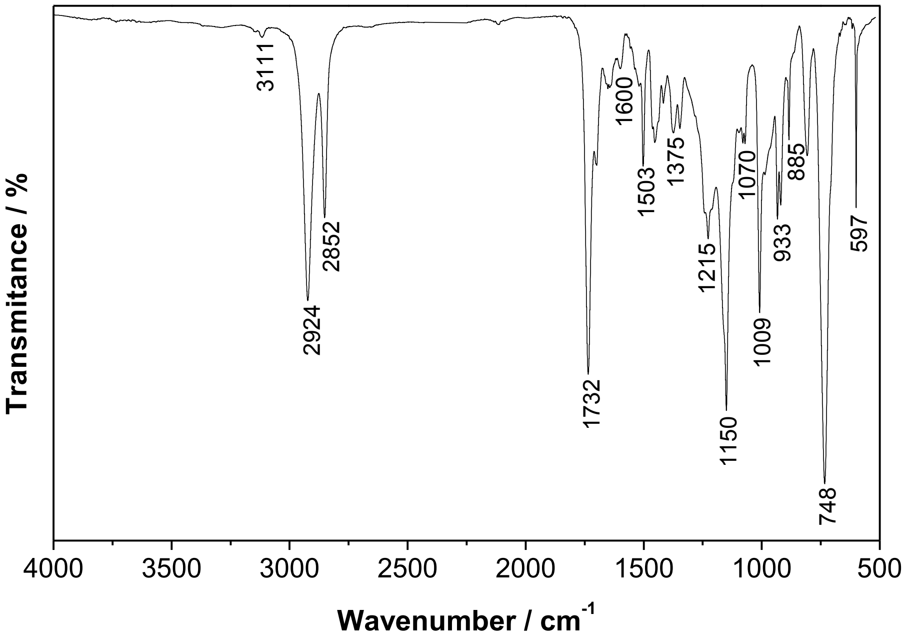


Figure 17. FTIR spectrum of monomer AA.

The ^{1}H NMR spectrum of AA (Figure 18) confirmed the expected structure through the appearance of the typical resonances of the methylene protons of the ester moiety at δ 5.1 ppm (OCH_2–2-furan), the methylene protons attached to the S atom at δ 2.5 ($SCH_2(CH_2)_n$) and 3.7 ppm (SCH_2–2-furan), and the furan heterocycle protons at about δ 6.2 (3-H), 6.3 (4-H), 7.3 (5-H) ppm for 2-furan–CH_2S and δ 6.4 (4-H), 6.5 (3-H), 7.4 (5-H) ppm for 2-furan–CH_2O, apart from the typical resonances of the methylene protons of UDA's aliphatic chain at δ 1.3 (–$(CH_2)_n$–), 1.6 ($CH_2CH_2C(=O)$) and 2.3 ($CH_2C(=O)$) ppm.

The ^{13}C NMR profile of AA (Figure 18) was in agreement with the structure proposed by ^{1}H NMR. The corresponding spectrum, aside from the unchanged resonances related to the aliphatic chain carbons (δ 24.8, 28.3-29.3 and 34.1 ppm), showed signals resonating at δ 31.7 ($\mathit{C}H_2SCH_2$–2-furan), 57.8 ($O\mathit{C}H_2$–2-furan), 107.2 and 110.4 (furan C-4 and C-3), 142.0 (C-5 of 2-furan–CH_2S), 143.2 (C-5 of 2-furan–CH_2O), 149.6 (C-2 of 2-furan–CH_2S), 151.9 (C-2 of 2-furan–CH_2O) and the $C=O_{ester}$ peak at 173.5 ppm.

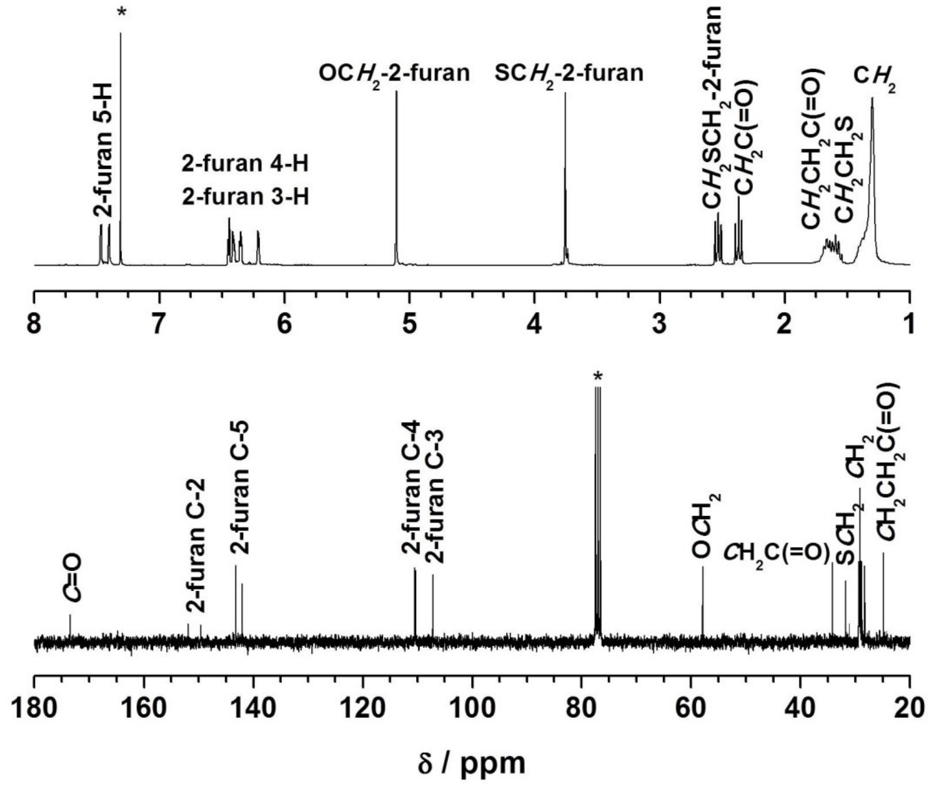
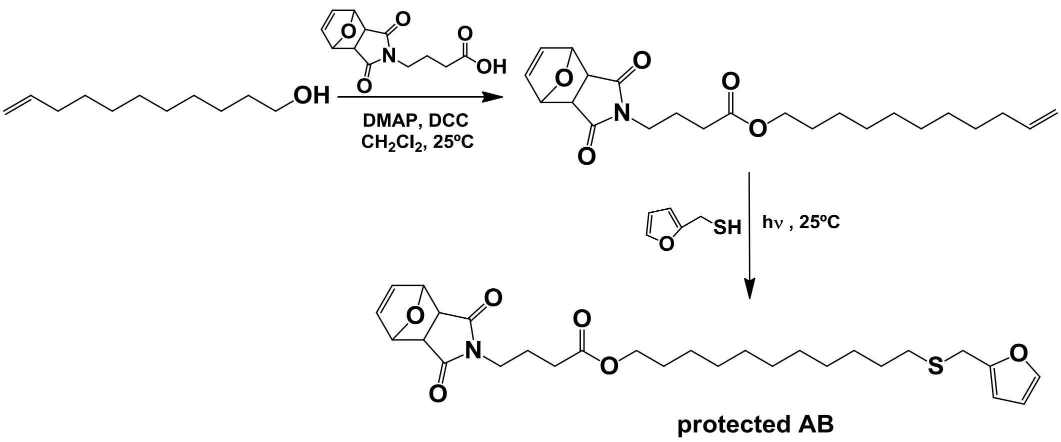


Figure 18. ^{1}H and ^{13}C NMR spectra of monomer AA in $^{*}CDCl_3$.

Similarly, the changes in the FTIR, Raman, ^{1}H and ^{13}C NMR spectra associated with the functionalization of UDA to give monomer AA' (Scheme 27) displayed the same features, confirming that the esterification and the thiol-ene reactions took place equally well, as given in detail in the Experimental section (Chapter IV, Section 4.4).

2.1.2 Protected AB Monomer

The alcohol UDOL was used to prepare the protected AB monomer through esterification of its primary OH end-group with the protected 4-maleimidobutyric acid (MBA) followed by the ene reaction of its terminal unsaturation with FT, as depicted in Scheme 28.



Scheme 28. Synthesis of the protected AB monomer.

The FTIR spectrum (Figure 19) of the protected AB monomer was consistent with the structure shown in Scheme 28, by the presence of all the relevant peaks, *viz*. (i) the asymmetric and symmetric C=O stretching vibrations of imide group at 1772 and 1696 cm^{-1}, respectively[32] (ii) the furan heterocycle bands at 3110, 1602, 1503, 1399, 1245, 1160, 1069, 1009, 917, 878, 735 and 598 cm^{-1},[30] and (iii) the C=O ester band at 1731 cm^{-1} and, at the same time, the absence of the OH band of primary alcohols and the OH and C=O bands of the carboxylic group.[31]

Although this technique did not succeed in identifying the weak ν(C–S) signal, its' identification was possible by Raman spectroscopy with a band at 606 cm^{-1}.[31]

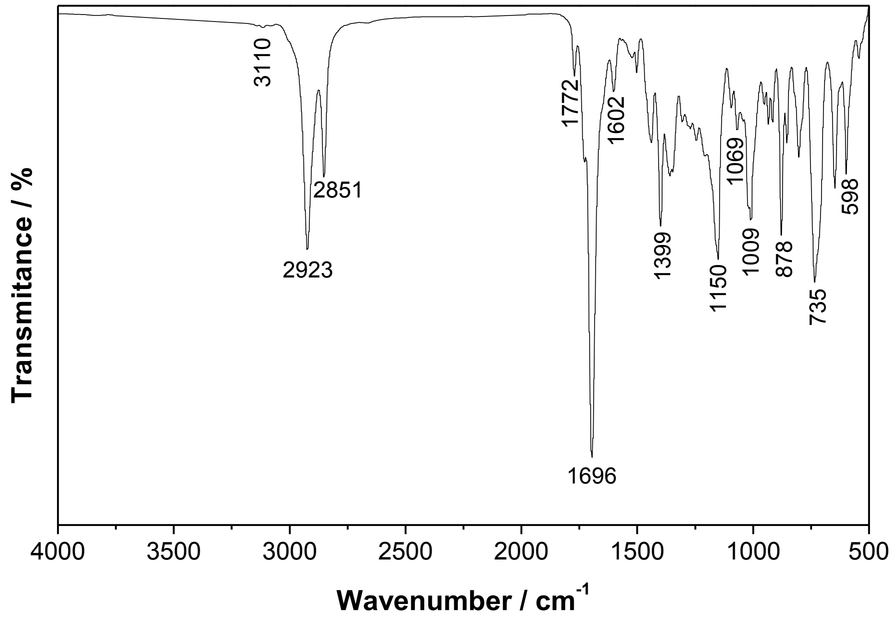


Figure 19. FTIR spectrum of the protected AB monomer.

The ^{1}H NMR spectrum (Figure 20) of the protected AB monomer clearly confirmed its structure through the presence of the protons of the protected maleimide moiety at about 2.9 (=CHCHC*H*CO), 5.3 (=CHC*H*CHCO) and 6.5 (=C*H*CHCHCO) ppm and the methylene protons of the ester group at δ 4.1 ppm (OCH_2), as well as of the 2-furan ring protons at δ 6.2 (3-H), 6.3 (4-H) and 7.4 (5-H) ppm and the methylene protons attached to the S atom at δ 2.5 (SCH_2(CH$_2$)$_n$) and 3.7 ppm (SCH_2–2-furan).

The analysis of ^{13}C NMR spectrum (Figure 20) of the protected AB monomer was also in tune with the proposed structure with, in addition to the carbon resonances related to the aliphatic chain (δ 25.8, 28.5 and 28.8-29.4 ppm), the furan ring carbons (δ 107.2, 110.3, 142.0 and 151.9 ppm) and the protected maleimide carbon resonances (δ 47.3, 81.0, 136.5 and 176.2 ppm), it was also possible to observe signals resonating at δ 31.7 and 64.7 ppm, which were readily identified as the methylenic carbons of the thioether moiety (S*C*H$_2$) and of the ester group (O*C*H$_2$), respectively. It is worth mentioning that the protection of the maleimide group of the AB monomer in the form of its furan-DA adduct, prevented the premature DA polymerization of the intrinsically reactive furan/maleimide moieties.

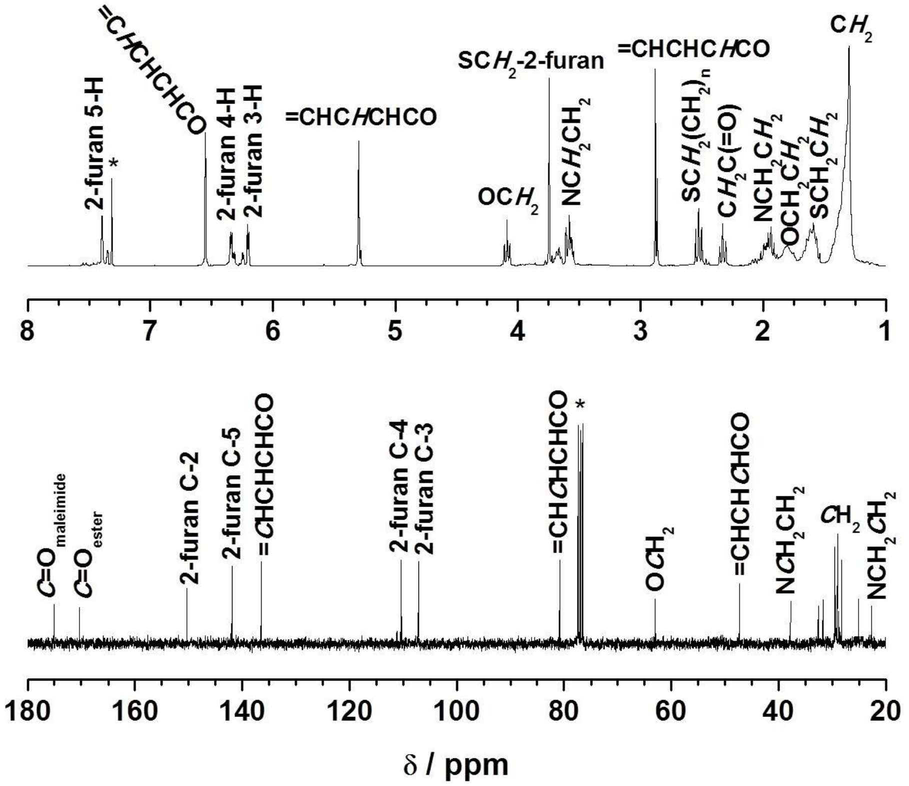


Figure 20. ^{1}H and ^{13}C NMR spectra of the protected AB monomer in *$CDCl_3$.

The common structural feature of these three monomers (AA, AA' and protected AB), besides their terminal DA-reactive furan or maleimide functions, was the long methylene sequence, i.e. the flexible bridge joining them. This suggests that all the ensuing DA polymers, namely those derived from AA and AA' with the equally flexible bridge joining the aliphatic bismaleimide (BB), and that formed by the AB monomer, were expected to have relatively low glass transition temperatures.

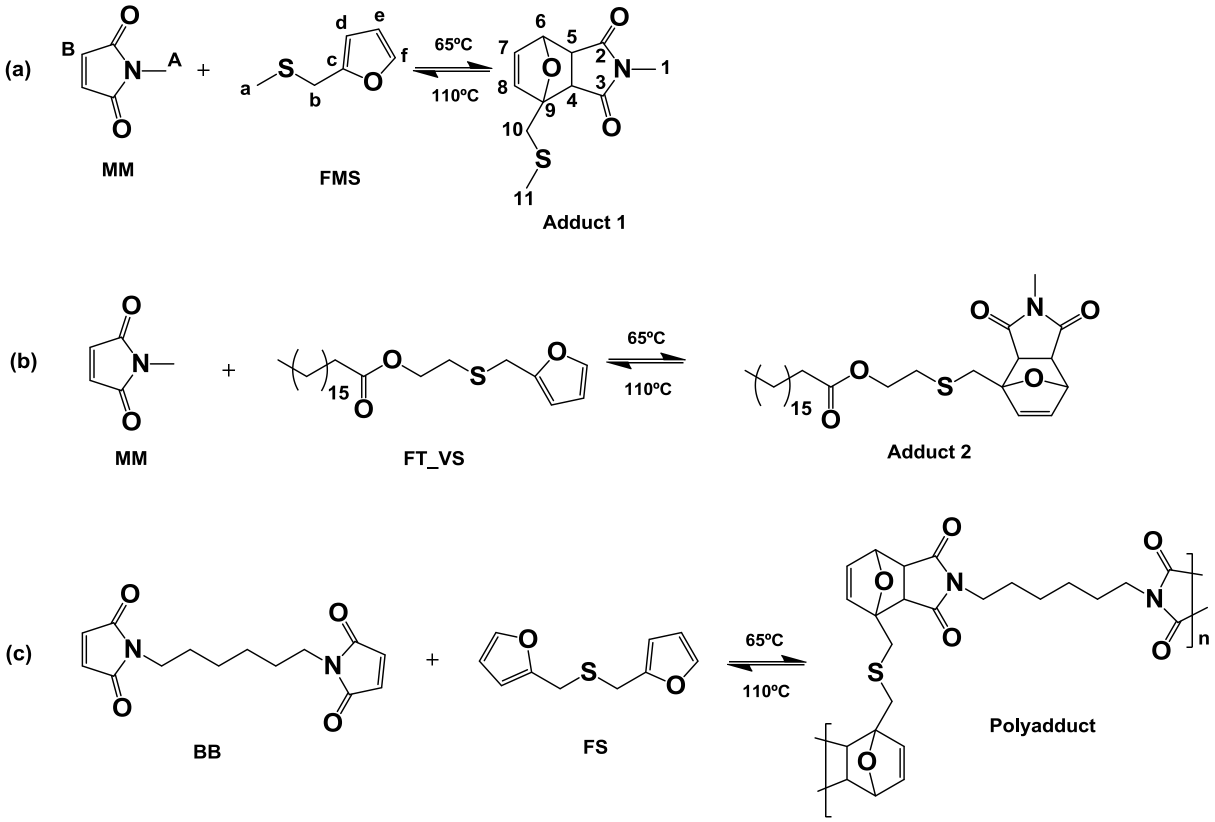
2.2 Synthesis and characterization of linear Diels-Alder polymers

2.2.1 Model systems

To our knowledge practically no information was available on the reactivity of FT as a diene in its DA interaction with maleimide dienophiles. Therefore, preliminary experiments were carried out on increasingly complex model systems, as depicted in Scheme 29.

Furfuryl methyl sulphide (FMS) was found to react with *N*-methylmaleimide (MM) to form the expected adduct (Scheme 29 (a)), and the same occurred with the larger sulphide arising from the ene reaction of FT with vinyl stearate (Scheme 29 (b)).

Additionally, the DA polymerization of furfuryl sulphide (FS) with 1,6-bismaleimidohexane (BB) took place, as expected, to give the corresponding linear polyadduct (Scheme 29 (c)) with a T_g value of -11 °C and a M_w value of 5.5 kDa.



Scheme 29. Diels-Alder reactions of model compounds: (a) *N*-methylmaleimide (MM) with furfuryl methyl sulphide (FMS), (b) MM with 2-(furan-2-ylthio)ethyl stearate (FT_VS), and (c) 1,6-bismaleimidohexane (BB) with furfuryl sulphide (FS).

All these experiments were carried out in both UV cells and NMR tubes and the course of the corresponding DA reactions followed, respectively, by the progressive decrease in (ii) the maleimide band at about 300 nm (loss of the O=C–C=C–C=O conjugation, as shown in the example of Figure 21) and (ii) the resonance intensity of the furan (δ 6.2, 6.3 and 7.4 ppm) and maleimide (δ 6.7 ppm) protons (Figure 22), associated with the formation of the DA adducts.

On the contrary, the retro-DA reaction of these model systems followed the reverse pattern with the gradual increase in (ii) the maleimide band and (ii) the signals attributed to the furan and maleimide moieties (and the corresponding decrease of those associated with the adduct protons).

Compared with other systems previously studied in our laboratory,[24] all these reactions, conducted in the same conditions of concentration, medium and temperature, were found to proceed more slowly, suggesting that the 2-Fu–CH_2–S– group played a (modest) retarding role. Despite this minor quantitative difference, the qualitatively positive outcome of these tests opened the way to the study of the programmed polymerization systems.

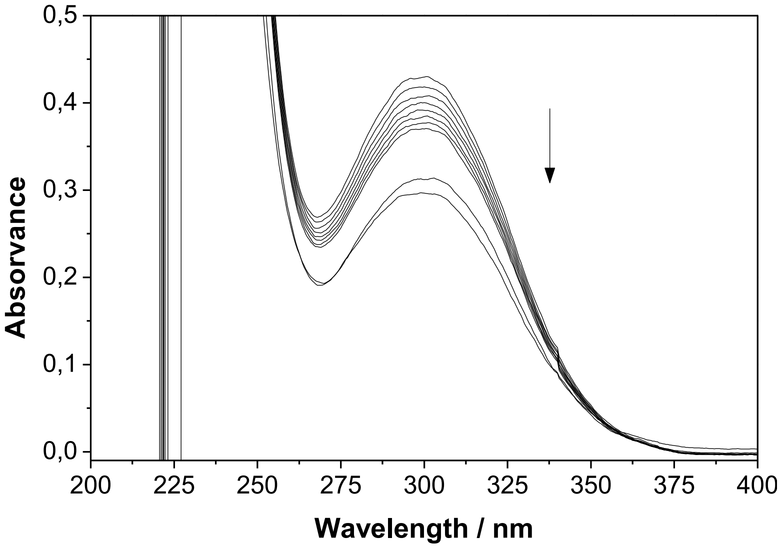


Figure 21. Evolution of the UV spectrum of the reaction mixture during the DA reaction between FMS (0.1 M) and MM (0.1 M) (Scheme 29 (a)) in TCE at 65 °C during 7 hours (spectra taken hourly) and then at 25 °C after 3 and 7 days.

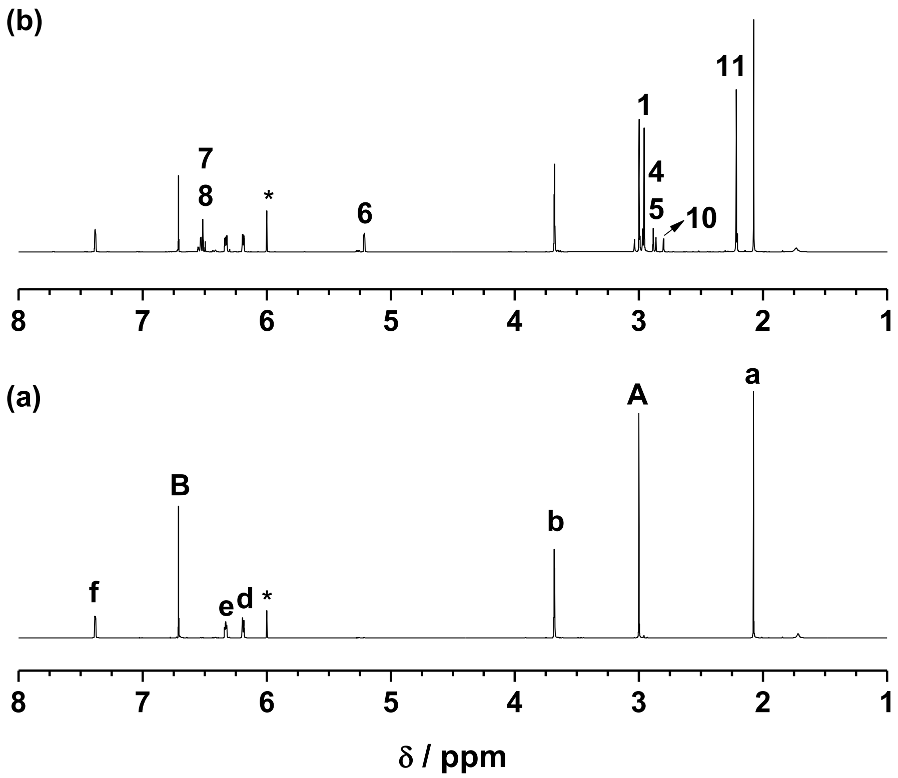
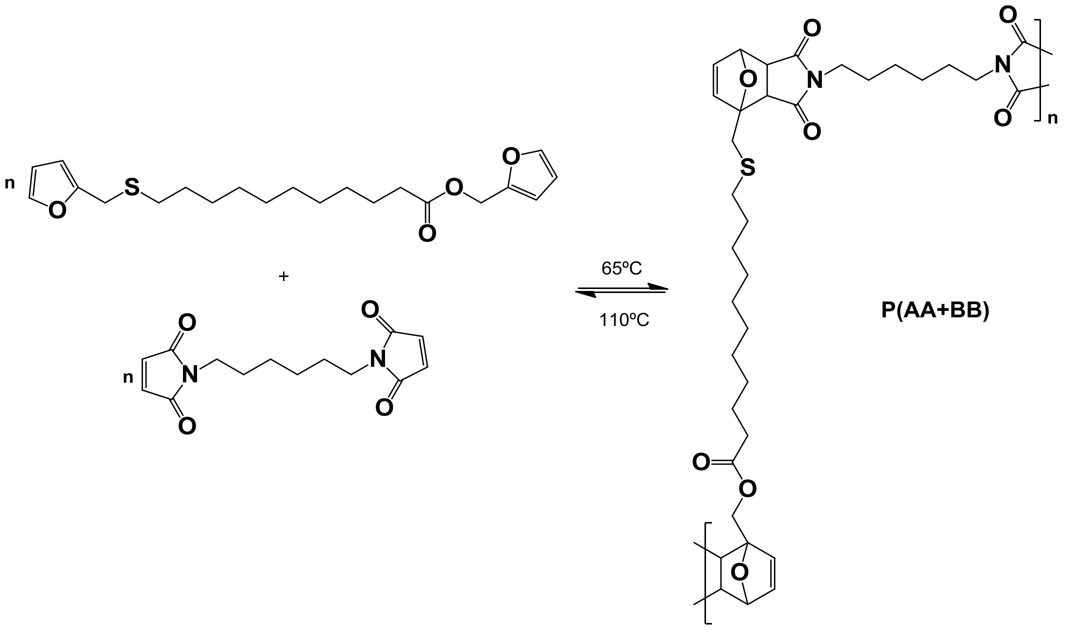


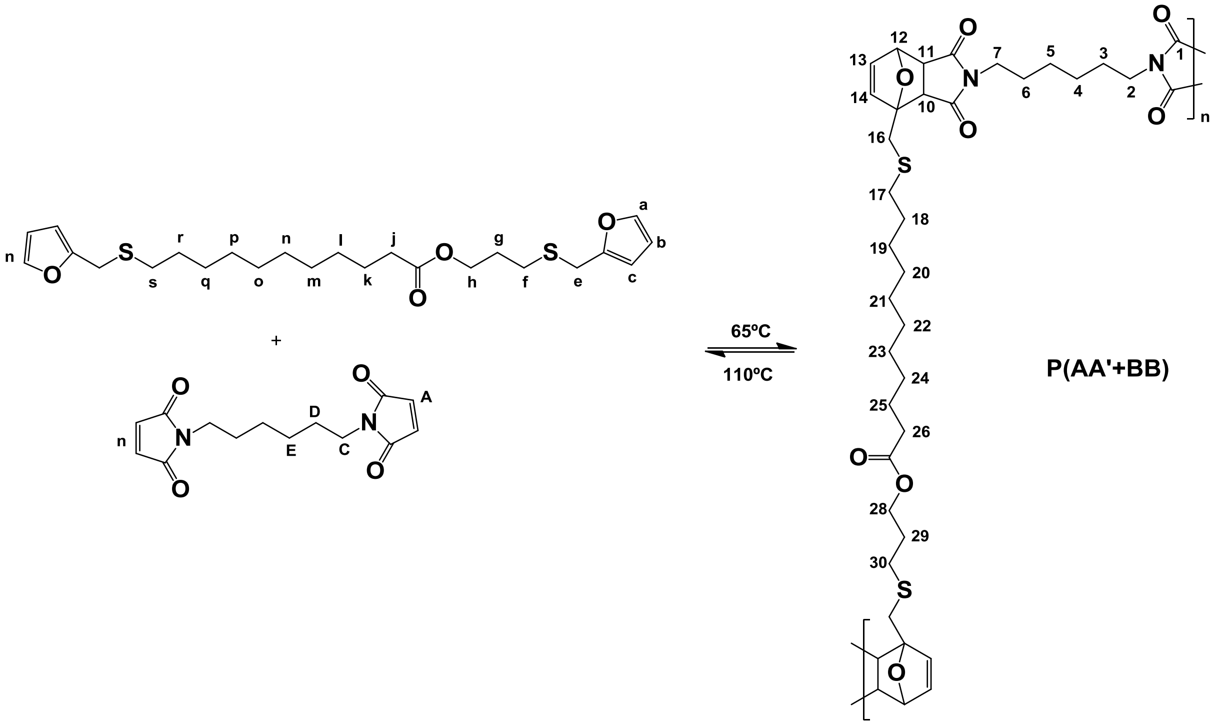
Figure 22. Evolution of the model DA reaction between FMS (0.1 M) and MM (0.1 M) in *TCE-d_2 at 65 °C (a) before (t = 0 hours) and (b) after 24 hours (see Scheme 29 (a) for peak assignment).

2.2.2 Polymerization of AA+BB and AA'+BB systems

The complementary bis-dienophile selected as DA-polymerization comonomer for both the bis-dienes AA and AA' was the 1,6-bismaleimidohexane (BB), i.e. a monomer bearing, as mentioned above, an equally flexible aliphatic bridging structure, leading to the formation of polymers P(AA+BB) (Scheme 30) and P(AA'+BB) (Scheme 31), respectively. All polymerizations were followed by both UV and ^{1}H NMR spectroscopy, as discussed before.



Scheme 30. DA polymerization reaction of the difunctional monomers AA and BB.



Scheme 31. DA polymerization reaction of the difunctional monomers AA’ and BB.

The DA polymerization of AA and AA’ at 65 °C, followed by UV spectroscopy during 8 hours, revealed a progressive decrease in the optical density of the maleimide band at about 300 nm, as shown in Figure 23 for P(AA+BB), accompanied by a corresponding increase in the viscosity of the medium. As reported in previous studies,[24,25] the spectral pattern gave rise to an isosbestic point (progressive replacement of the maleimide peak at ~300 nm by the absorption of the unconjugated carbonyl groups of the adduct at ~260 nm), which suggested the occurrence of a single reaction pathway, *viz*. the DA reaction.

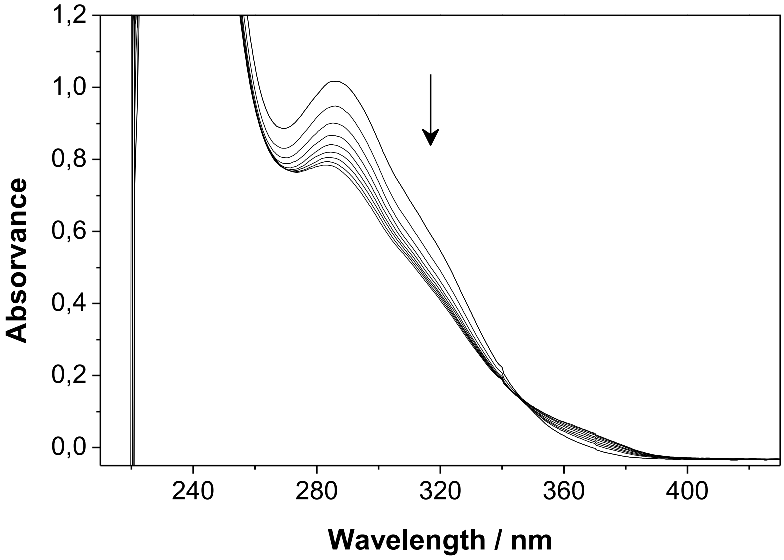


Figure 23. Evolution of the UV spectrum of the maleimide band during the DA reaction between AA (0.1 M) and BB (0.1 M) at 65 °C in TCE for 8 hours.

The concomitant changes in the ^{1}H NMR spectra (as illustrated for P(AA’+BB) in Figure 24) displayed a gradual decrease in the intensity of the maleimide (δ 6.7 ppm, C*H*=C*H*) and furan (c-H at δ 6.2 ppm, b-H at δ 6.3 ppm and a-H at δ 7.4 ppm) proton resonances at a rate similar to that of the UV spectra evolution and the simultaneous surge of the peaks associated with the three sets of protons assigned to the polyadducts, at about δ 2.9 (10-H and 11-H), 5.3 (12-H) and 6.5 ppm (13-H and 14-H).

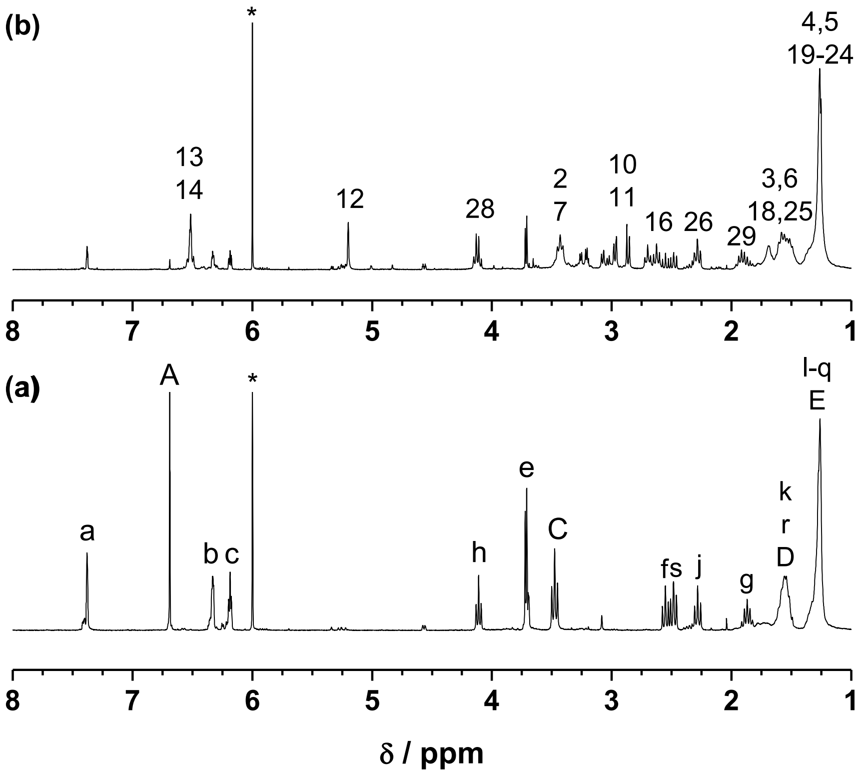


Figure 24. Evolution of ^{1}H NMR spectrum of the DA polymerization between AA′ and BB in *TCE-d_2 at 65 °C (a) before (t = 0 hours) and (b) after 6 days (see Scheme 31 for peak assignment).

Once these polymerizing systems had reached high conversion, both polymers were then submitted to the corresponding retro-DA depolymerisation at 110 °C, followed by ^{1}H NMR spectroscopy. These processes were characterized by the reverse pattern with respect to the polymerizations, consisting in the gradual decrease in the adduct resonance intensities (δ 2.9, 5.3 and 6.5 ppm) and the corresponding growth of the furan (δ 6.2, 6.3 and 7.4 ppm) and maleimide (δ 6.7 ppm) counterparts, together with the decrease in viscosity of the solutions. Within a few days, the spectra revealed the presence of the starting monomers (Figure 25 (b)), thus confirming the thermo-reversible nature of these systems. These regenerated monomers were allowed to cool to 65° C to favour a second polymerization (Figure 25 (c)), emphasizing the reproducibility of these cyclic events, as previously reported.[24,25]

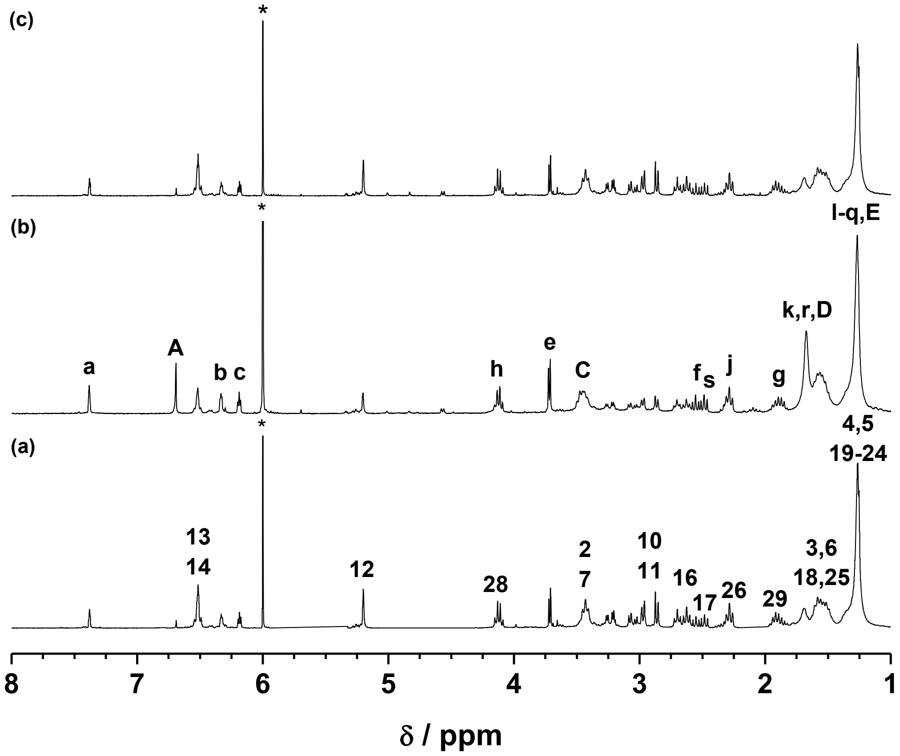
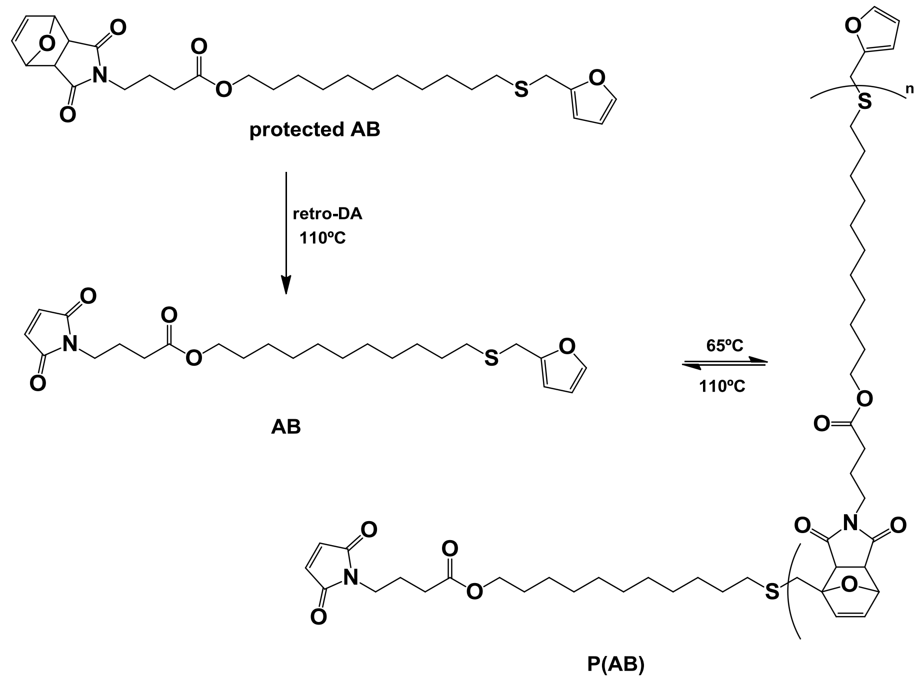


Figure 25. ^{1}H NMR spectrum of (a) polymer P(AA'+BB), (b) retro-DA of P(AA'+BB) after 3 days, and (c) second DA polymerization after 6 days (see Scheme 31 for peak assignment).

2.2.3 Polymerization of AB system

The use of an AB monomer bearing both the furan and the maleimide moieties in its structure represents an interesting alternative for linear DA polymerization, as already shown in other studies,[25,26] since it provides the ideal initial stoichiometry. The synthesis of the AB monomer generated a molecule with a protected maleimide moiety in order to avoid premature polymerization. This stable furan-DA adduct became ready for polymerization after the *in situ* deprotection of the masked end-group by retro-DA reaction at 110 °C, which released furan and regenerated the maleimide moiety. The polymerization could then be initiated by decreasing the temperature to 65 °C (Scheme 32).



Scheme 32. DA polymerization reaction of the difunctional monomer AB.

The ^{1}H NMR spectrum of monomer AB after deprotection (Figure 26) clearly confirmed the deprotection through the presence of the free maleimide protons at δ 6.7 ppm (C*H*=C*H*), plus the absence of the adduct peaks at 2.9 (=CHCHC*H*CO), 5.3 (=CHC*H*CHCO) and 6.5 (=C*H*CHCHCO) ppm.

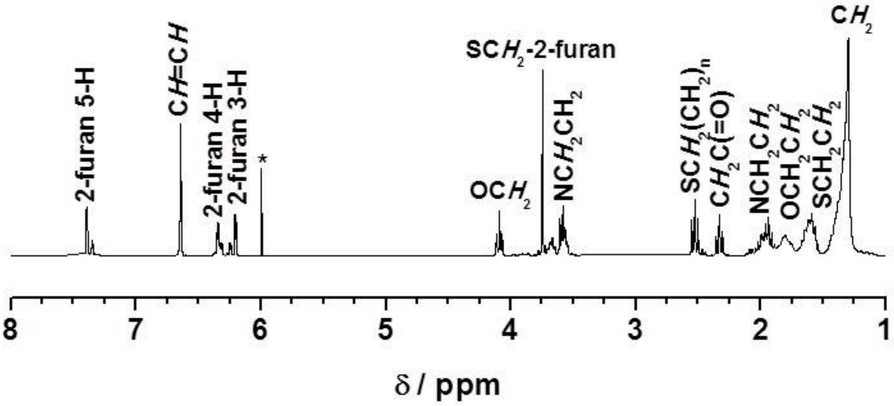


Figure 26. ^{1}H NMR spectrum of monomer AB after *in situ* deprotection at 110 °C for 3 days (*TCE-d$_2$).

The evolution of the DA polymerization of the AB monomer, leading to the formation of P(AB), was also followed by UV and ^{1}H NMR spectroscopy and more qualitatively by the regular increase in the viscosity of the reaction medium. The progress of the UV spectrum with reaction time mimicked the features exemplified in Figure 23, exhibiting again a characteristic isosbestic point.

The ^{1}H NMR analysis of the polymerizing system revealed all the details of the progressive decrease in the signals ascribed to the unreacted furan (δ 6.2, 6.3 and 7.4 ppm) and maleimide moieties (δ 6.7 ppm) and the corresponding increase of those associated with the polyadduct protons at δ 6.5 (=C*H*CHCHCO), 5.3 (=CHC*H*CHCO) and 2.9 (=CHCHC*H*CO) ppm. After this system attained high conversion, the retro-DA depolymerisation was followed at 110 °C for three days by ^{1}H NMR spectroscopy. The expected behaviour was once more observed, *viz*. the increase in the peaks of the furan and maleimide protons to the detriment of the adduct signals, as previously discussed. Thereafter, the system was brought back to 65 °C and left for a number of days in order to promote a second polymerization. The ^{1}H NMR spectrum of the ensuing polymer was analogous to that taken at the end of the first polymerization, thus confirming the reversible nature of this polymerizing system.

It is important to emphasize that the fact that these polymerizations proceeded at a rather slow pace also stems from the modest monomer concentrations adopted here in order to allow UV and NMR spectra to be conveniently monitored. In practical terms, the same systems could obviously be made to polymerize more rapidly at higher concentrations, including in bulk.

2.2.4 Polymer characterization

After isolation, polymers P(AA+BB), P(AA’+BB) and P(AB), mostly brown and sticky materials obtained in average yields of 87%, were characterized by SEC and DSC analysis. Table 9 shows their molecular weight distribution, polydispersity index (PDI) and glass transition temperature (T_g).

Table 9. SEC and DSC results for the synthesized linear polymers.

Polymer	M_w / kDa	M_n / kDa	PDI	T_g / °C
P(AA+BB)	6.5	4.5	1.4	-40
P(AA’+BB)	9.0	5.8	1.5	-28
P(AB)	16.6	9.0	1.8	-2

The number-average molecular weight (M_n) of these three linear polymer systems is in the range of 4.5-9.0 kDa with PDI values all close to 2, in tune with a linear polymerization. The molecular weight distribution curves of all three polymers were characterized by the presence of individual peaks corresponding to a specific compound instead of a distribution of homologues, as exemplified in Figure 27 for polymers P(AA+BB) and P(AA’+BB). These peaks are the evidence of the presence of cyclic oligomers, including the corresponding dimmers, formed during the DA polymerization since a growth associated solely with linear molecules of different size would not originated those peaks in the corresponding SEC tracings. Given the relatively low monomer concentrations used in these DA polymerizations, the occurrence of cyclization seems reasonable, as indeed already observed in a recent study on the DA polymerization of other AB monomers.[26]

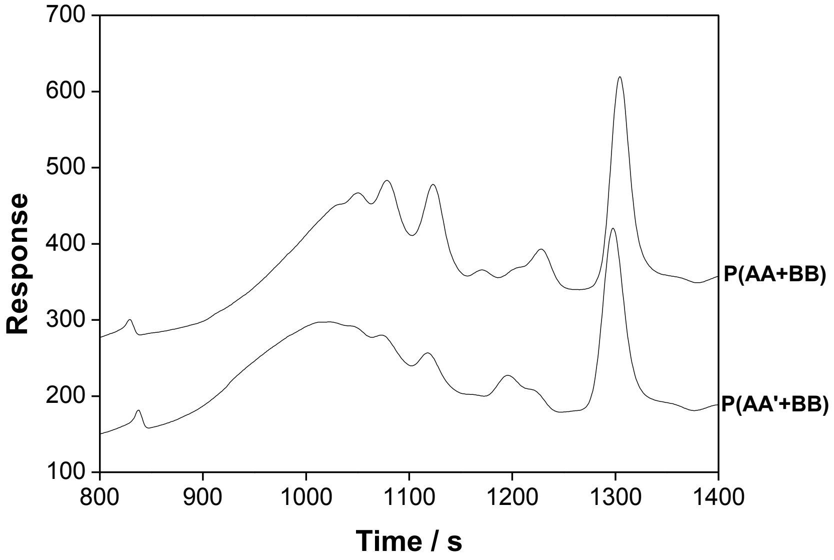


Figure 27. SEC tracing of polymers P(AA+BB) and P(AA’+BB).

The occurrence of cyclization during the polymerization is a limiting factor towards the molecular weight of the polymers, *viz*. the chain growth stops, and hence the somewhat low values of the measured molecular weights. Moreover, the formation of these cycles lowers the T_g of the polymers by acting as internal "plasticizers", i.e., they originate gaps among polymer chains, which increases their mobility, reduces the interchain interactions and increases polymer flexibility.

The DSC analyses of the three thermally labile polymers were performed in the temperature range -80 to 80 °C, due to the occurrence of the retro-DA reaction above the latter temperature. As anticipated for these linear polymers, their T_g values were relatively low as a result of the flexible nature of the spacing moieties separating the reactive functions. Polymer P(AA+BB) has a T_g value lower than the one of P(AA'+BB) counterpart, as indeed perceived given its lower M_n. Polymer P(AB) exhibited the highest T_g value as a result of its highest molecular weight and regular spacing bridge between adducts. Figure 28 displays the typical DSC thermogram of polymer P(AA+BB).

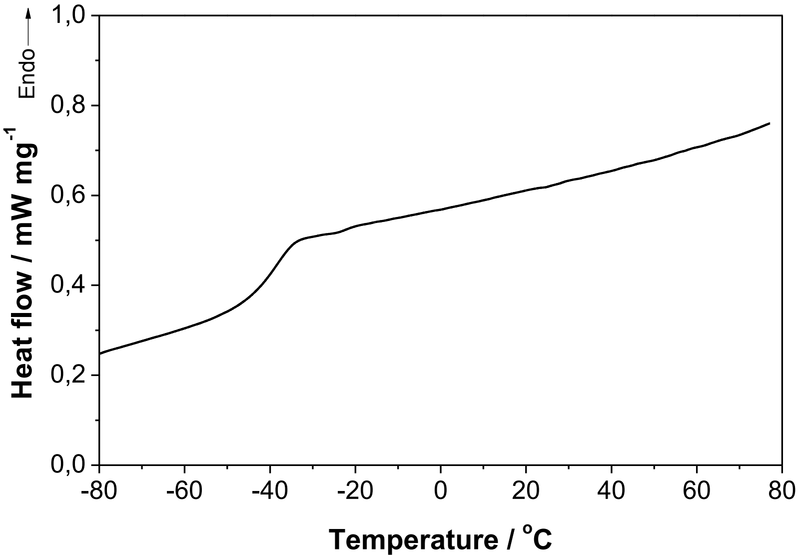


Figure 28. DSC thermogram of P(AA+BB).

3. CONCLUSIONS

The advent of click chemistry has attracted considerable attention in a wide range of synthetic domains, mainly due to its green chemistry connotation and versatility. Therefore, two click approaches were applied to macromolecular synthesis, namely thiol-ene coupling to convert unsaturated vegetable oil derivatives into bifunctional monomers, and their Diels-Alder (DA) polymerization to obtain linear thermoreversible materials. Two basic approaches were considered for these DA polymerizations, namely (i) the use of monomers with two terminal furan rings in conjunction with bismaleimides (AA+BB and AA'+BB systems), and (ii) the use of a protected AB monomer incorporating both furan and maleimide end-groups.

The successful application of the thiol-ene coupling to append furan moieties to molecules issued from vegetable oils was the first positive outcome of this investigation. Thus, novel difuran (AA, AA') and furan/maleimide (AB) monomers with similar bridging groups separating the reactive moieties were efficiently prepared.

The second relevant contribution has to do with the exploitation of the DA polymerization of the ensuing monomers for the preparation of functional macromolecular materials. The DA reaction carried out at 65 °C provided a reasonably high rate of adduct formation while avoiding any detectable incidence of the retro-DA reaction. Furthermore, the DA polymerization/depolymerisation cycles were applied reproducibly. The thermally labile linear polymers exhibited relatively low T_g values (-40 to -2 °C) as a result of the flexible nature of the spacing moieties separating the reactive functions, together with somewhat small M_n values (4.5-9.0 kDa) given the observed tendency to cyclization associated with the relatively low monomer concentrations.

The positive outcome of this study on polymers based on two diferrent renewable resources with novel properties and promising applications like mendability and recyclability, constitute a stimulating encouragement to widen its scope in terms of both the depth of the associated studies and the extension to other substrates.

4. EXPERIMENTAL

4.1 Materials

Allyl alcohol (Aldrich, ≥ 99%), benzyl mercaptan (Aldrich, 99%), chloroform-d ($CDCl_3$, Acros Organics, 99.8 atom % D), *N,N′*-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-dimethylaminopyridine (DMAP, Sigma), furan (Acros Organics, 99%), furfuryl alcohol (FA, Aldrich, 98%), furfuryl methyl sulfide (FMS, SAFC, ≥ 97%), furfuryl sulfide (FS, Aldrich, ≥98%), 2-furylmethanethiol (FT, Aldrich, 98%), *N*-methylmaleimide (MM, Aldrich, 97%), 4-maleimidobutyric acid (MBA, Fluka, ≥98%), methyl oleate (MO, Aldrich, 99%), phenylethyl mercaptan (PEM, SAFC, ≥98%), 1,3-propanedithiol (PDT, Aldrich, 99%), 1,1,2,2-tetrachloroethane (TCE, Sigma-Aldrich, ≥98.0%), 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2, Acros Organics, 99.5 atom % D), 10-undecenoic acid (UDA, Aldrich, 98%), 10-undecen-1-ol (UDOL, Aldrich, 98%), vinyl isobutyl ether (VIBE, Aldrich, 99%) and vinyl stearate (VS, Aldrich, 95%) were used as received without any further purification. Irgacure® 651 (2,2-dimethoxy-2-phenylacetophenone, I651) was generously supplied by BASF-The Chemical Company, Ludvigshafen. Polystyrene standards with molecular weights between 1 700 and 66 000 were supplied by Polymer Laboratories. Other chemicals and solvents were of laboratory grades.

4.2 Synthesis of 4-(3,6-epoxy-1,2,3,6-tetrahydrophthalimido)butanoic acid (protected MBA)

4-maleidobutyric acid (MBA) was used in the synthesis of the AB-type monomer below, thus its maleimide group was previously protected in order to avoid premature DA condensation of the maleimide and furan moieties. A solution of MBA (915.8 mg, 5 mmol) and furan (510.5 mg, 7.5 mmol) in TCE (5 mL) was prepared and left for 72 hours at 65 °C. The remaining furan and the solvent were removed under vacuum. The ensuing pallid yellow solid was then dissolved in dichloromethane, reprecipitated in an excess of diethyl ether, filtered and dried under vacuum. The final product was obtained in 95% yield.

ν_{max}/cm^{-1}: 3040 (C–H stretching of CH=CH), 1777 and 1682 (C=O stretching), 1023 (C–O adduct band).

δ_H (300 MHz, TCE-d_2, Me_4Si): 6.5 (2H, s, =C*H*CHCHCO), 5.3 (2H, s, =CHC*H*CHCO), 3.6 (2H, t, *J* = 6.8 Hz, NC*H*$_2$CH$_2$), 2.9 (2H, s, =CHCHC*H*CO), 2.3 (2H, t, *J* = 7.4 Hz, C*H*$_2$C(=O)), 1.9 (2H, m, NCH$_2$C*H*$_2$).

δ_C (75 MHz, TCE-d_2, Me_4Si): 177.6 ($C{=}O_{acid}$), 176.3 ($C{=}O_{maleimide}$), 136.4 (=*C*HCHCHCO), 80.9 (=CH*C*HCHCO), 47.3 (=CHCH*C*HCO), 37.9 (N*C*H$_2$CH$_2$), 30.8 (*C*H$_2$C(=O)), 22.5 (NCH$_2$*C*H$_2$).

4.3 Synthesis of 1,6-bismaleimidohexane (BB)

The bismaleimide monomer BB was prepared by the classical two-step process involving 1,6-hexanediamine and maleic anhydride, as reported elsewhere.[24] The first step involved the dropwise addition of one equivalent of 1,6-hexanediamine (530 mg, 4.5 mmol) in diethyl ether (20 mL) to two equivalents of maleic anhydride (880 mg, 9.0 mmol) in diethyl ether (30 mL). The reaction was carried out at room temperature for 3 hours and under reflux for another 3 hours. The resultant white precipitate was filtered, washed with diethyl ether and dried under vacuum. The final product was obtained as a white solid in 85% yield.

The second step induced the cyclization of the bismaleamic acid end-groups (1.0 g, 3.2 mmol) through the joint intervention of anhydrous sodium acetate (1.3 g, 16.0 mmol) and acetic anhydride (15 mL). The reaction mixture was stirred at 100 °C for 4-5 hours under a gentle stream of nitrogen. The ensuing mixture was poured onto cold water and the precipitate filtered, washed with water and dissolved in methylene chloride. This solution was again washed with water and the organic fraction dried over sodium sulphate. The solvent was removed under reduced pressure and the ensuing residue washed with toluene (3x10mL). The thus isolated brown solid was purified by silica-gel column chromatography with a 1:2 v/ mixture of petroleum ether/ethyl acetate, which originated BB as a white solid in 49% yield.

ν_{max}/cm^{-1}: 3086 (C–H stretching of CH=CH), 2945 (asCH_2), 2857 (sCH_2), 1765 and 1692 (C=O stretching), 1386, 1326, 1128 and 736 (C–N stretching).

δ_H (300 MHz, TCE-d$_2$, Me$_4$Si): 6.7 (4H, s, C*H*=C*H*), 3.5 (4H, t, *J* = 7.2 Hz, NCH_2CH$_2$CH$_2$), 1.6 (4H, m, NCH$_2$CH_2CH$_2$), 1.3 (4H, m, NCH$_2$CH$_2$CH_2).

δ_C (75 MHz, TCE-d$_2$, Me$_4$Si): 170.8 (C=O$_{\text{maleimide}}$), 133.9 (*C*H=*C*H), 37.5 (N*C*H$_2$CH$_2$CH$_2$), 28.2 (NCH$_2$*C*H$_2$CH$_2$), 26.0 (NHCH$_2$CH$_2$*C*H$_2$).

4.4 Synthesis of furan-2-ylmethyl 11-(furan-2-ylmethylthio)undecanoate (AA)

Monomer AA was synthesized in two steps by making use of a classical chemical condensation in conjunction with the thiol-ene coupling.

Step 1: The esterification of UDA with FA, in the presence of DCC and DMAP, was adapted from the method reported by Rauf and Parveen,[33] in which the direct use of DCC as a carboxylic group activating agent promotes esterification under very mild conditions. So, UDA (737.1 mg, 4.0 mmol), DCC (825.3 mg, 4.0 mmol) and DMAP (50.9 mg, 0.40 mmol) were added to a solution of FA (392.4 mg, 4.0 mmol) in dichloromethane (20 ml). The reaction mixture was left overnight at room temperature under nitrogen. After that period, the precipitated *N,N'*-dicyclohexylurea (DCU) formed during the reaction was filtered off and the filtrate washed with water (2x20 mL), 5% acetic acid solution (2x20 mL) and again water (2x20 mL). The additional DCU was removed by filtration. The organic phase was dried over anhydrous sodium sulphate before vacuum removal of the solvent. The desired intermediate was obtained as a viscous liquid in 95% yield.

Step 2: The previous ene (3 mmol), 2-furylmethanethiol (685.0 mg, 6 mmol) and I651 (15.4 mg, 0.06 mmol) were placed in a glass flask and thoroughly degassed with a stream of nitrogen to remove the air since the thiol is air sensitive. The reaction mixture was irradiated by a UV-light source (Vilber Lourmat UV lamp VL-6-LC, 230V~50/60 Hz) working at 365 nm for 4 hours at room temperature. After this period, the excess thiol was vacuum removed and the ensuing brownish liquid monomer obtained in 97% yield.

ν_{max}/cm^{-1}: 3111 (furan C–H stretching), 2924 (asCH$_2$), 2852 (sCH$_2$), 1735 (C=O), 1600, 1503 and 1375 (furan ring stretching), 1215 and 1070 (furan in-plane CH deformation), 1150 (C–O stretching), 1009 (ring breathing), 933, 885 and 748 (furan C–H out-of-plane deformation), 607 (C–S), 597 (ring deformation).

δ_H (300 MHz, $CDCl_3$, Me_4Si): 7.4 (1H, dd, *J* = 2.0, 0.7 Hz, 5-H of 2-furan–CH_2O), 7.3 (1H, dd, *J* = 1.6, 0.7 Hz, 5-H of 2-furan–CH_2S), 6.5 (1H, d, *J* = 3.0 Hz, 3-H of 2-furan–CH_2O), 6.4 (1H, dd, *J* = 3.2, 1.8 Hz, 4-H of 2-furan–CH_2O), 6.3 (1H, dd, *J* = 3.1, 1.9 Hz, 4-H of 2-furan–CH_2S), 6.2 (1H, d, *J* = 3.5 Hz, 3-H of 2-furan–CH_2S), 5.1 (2H, s, OCH_2–2-furan), 3.7 (2H, s, SCH_2–2-furan), 2.5 (2H, t, *J* = 7.4 Hz, CH_2SCH_2–2-furan), 2.3 (2H, t, *J* = 7.5 Hz, $CH_2C(=O)$), 1.6 (2H, m, $CH_2CH_2C(=O)$), 1.5 (2H, m, CH_2CH_2S), 1.3 (12H, m, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3$, Me_4Si): 173.5 (C=O), 151.9 (C-2 of 2-furan–CH_2O), 149.6 (C-2 of 2-furan–CH_2S), 143.2 (C-5 of 2-furan–CH_2O), 142.0 (C-5 of 2-furan–CH_2S), 110.4 (2-furan C-3), 107.2 (2-furan C-4), 57.8 (OCH_2-2-furan), 34.1 ($CH_2C(=O)$), 31.7 (CH_2S), 28.3-29.3 (aliphatic CH_2), 24.8 ($CH_2CH_2C(=O)$).

4.5 Synthesis of 3-(furan-2-ylmethylthio)propyl 11-(furan-2-ylmethylthio) undecanoate (AA’)

Monomer AA’ was synthesized from UDA, allyl alcohol and FT, following a procedure similar to that reported for monomer AA. It was obtained as a yellow viscous liquid in 90% yield.

ν_{max}/cm^{-1}: 3110 (furan C–H stretching), 2922 (asCH_2), 2851 (sCH_2), 1731 (C=O stretching), 1593, 1502 and 1383 (furan ring stretching), 1244, 1167 and 1070 (furan in-plane CH deformation), 1149 (C–O stretching), 1008 (ring breathing), 933, 885 and 732 (furan C–H out-of-plane deformation), 608 (C–S), 598 (ring deformation).

δ_H (300 MHz, $CDCl_3$, Me_4Si): 7.4 (2H, dd, *J* = 1.7, 0.8 Hz, 2-furan 5-H), 6.3 (2H, dd, *J* = 3.1, 1.8 Hz, 2-furan 4-H), 6.2 (2H, d, *J* = 3.3 Hz, 2-furan 3-H), 4.2 (2H, t, *J* = 6.3 Hz, OCH_2), 3.7 (4H, s, SCH_2–2-furan), 2.6 (2H, t, *J* = 7.5 Hz, $OCH_2CH_2CH_2S$), 2.5 (2H, t, *J* = 7.5 Hz, $SCH_2CH_2(CH_2)_n$), 2.3 (2H, t, *J* = 7.5 Hz, $CH_2C(=O)$), 1.9 (2H, m, $OCH_2CH_2CH_2S$), 1.6 (2H, m, $CH_2CH_2C(=O)$), 1.5 (2H, m, $SCH_2CH_2(CH_2)_n$), 1.3 (12H, m, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3$, Me_4Si): 173.8 (C=O), 151.8 (2-furan C-2), 142.0 (2-furan C-5), 110.3 (2-furan C-4), 107.3 (2-furan C-3), 62.8 (OCH_2), 34.3 ($CH_2C(=O)$), 31.7 (SCH_2), 28.1-29.3 (aliphatic CH_2), 24.9 ($CH_2CH_2C(=O)$).

4.6 Synthesis of 11-(furan-2-ylmethylthio)undecyl 4-(3,6-epoxy-1,2,3,6-tetrahydro-phthalimido)butanoate (protected AB)

The protected AB monomer was prepared from UDA, protected MBA and FT, following a procedure cognate to that described for monomer AA. This monomer was obtained as a dark viscous liquid in 97% yield.

ν_{max}/cm^{-1}: 3110 (furan CH stretching), 2923 (asCH_2), 2851 (sCH_2), 1772, 1728 and 1696 (C=O stretching), 1602, 1503 and 1399 (furan ring stretching), 1245, 1160 and 1069 (furan in-plane CH deformation), 1150 (C–O stretching), 1009 (ring breathing), 917, 878 and 735 (furan C–H out-of-plane deformation), 606 (C–S), 598 (ring deformation).

δ_H (300 MHz, $CDCl_3$, Me_4Si): 7.4 (1H, dd, *J* = 1.7, 0.7 Hz, 2-furan 5-H), 6.5 (2H, s, =C*H*CHCHCO), 6.3 (1H, dd, *J* = 3.1, 1.9 Hz, 2-furan 4-H), 6.2 (1H, d, *J* = 3.4 Hz, 2-furan 3-H), 5.3 (2H, s, =CHC*H*CHCO), 4.1 (2H, t, *J* = 6.7 Hz, OCH_2), 3.7 (2H, s, SCH_2–2-furan), 3.6 (2H, t, *J* = 6.6 Hz, NCH_2CH_2), 2.9 (2H, s, =CHCHC*H*CO), 2.5 (2H, t, *J* = 7.5 Hz, SC$H_2CH_2(CH_2)_n$), 2.3 (2H, t, *J* = 7.5 Hz, CH_2C(=O)), 1.9 (2H, m, NCH_2CH_2), 1.6 (2H, m, OCH_2CH_2), 1.5 (2H, m, $SCH_2CH_2(CH_2)_n$), 1.3 (14H, m, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3$, Me_4Si): 176.2 (C=$O_{maleimide}$), 172.7 (C=O_{ester}), 151.9 (2-furan C-2), 142.0 (2-furan C-5), 136.5 (=*C*HCHCHCO), 110.3 (2-furan C-4), 107.2 (2-furan C-3), 81.0 (=CH*C*HCHCO), 64.7 (O*C*H_2), 47.3 (=CHCH*C*HCO), 38.1 (N*C*H_2CH_2), 31.7 (*C*H_2S), 31.2 (*C*H_2C(=O)), 29.4-28.8 (aliphatic *C*H_2), 28.5 (OCH_2*C*H_2), 25.8 (OCH_2CH_2*C*H_2), 22.8 (NCH_2*C*H_2).

4.7 Diels-Alder polymerizations

AA+BB and AA'+BB systems – A typical procedure applied to follow the polymerizations by using UV spectroscopy is: 0.1 M solutions of monomer AA (18.9 mg, 0.05 mmol) or AA' (22.6 mg, 0.05 mmol) and BB (13.8 mg, 0.05 mmol) in TCE (0.5 mL) were prepared separately and placed in a 0.1 mm Suprasil cell, which was then left in the temperature-controlled spectrophotometer at 65 °C and UV spectra were taken at regular times.

A typical procedure applied to follow the polymerizations by using ^{1}H NMR spectroscopy is: stoichiometric quantities (0.1 mmol) of the two monomers (AA or AA' and BB) were dissolved in 1.0 mL of TCE-d_2, placed in an NMR tube and the initial ^1H NMR spectrum taken instantly at room temperature. The tube was then kept in an oil bath at 65°C and spectra taken at regular intervals. The ensuing polymers were isolated by precipitation into a large excess of petroleum ether, followed by filtration, dissolution in dichloromethane and solvent removal under reduced pressure.

A fraction of the ensuing polymers was dissolved in TCE (1.0 mL) and the retro-DA depolymerisation reactions were followed at 110 °C by UV and ^1H NMR spectroscopy.

AB system – The protected monomer (0.1 mmol) was dissolved in 1 mL of TCE and the solution (0.1 M) brought to 110 °C while a gentle stream of nitrogen was bubbled through it for several hours to remove the furan generated by the retro-DA of the maleimide adduct. The ensuing unprotected AB monomer was then allowed to polymerize at 65 °C and the reaction followed by UV and ^1H NMR spectroscopy. The ensuing polymer was precipitated in an excess of petroleum ether, filtered, dissolved in dichloromethane and vacuum dried. Again, the depolymerisation of the DA polymer was carried out at 110 °C.

4.8 Characterization methods

The FT-IR spectra were taken with a Perkin Elmer FT-IR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. Each spectrum was an average of 32 scans taken with 4 cm^{-1} resolution in the 500-4000 cm^{-1} range.

Raman spectra were measured after 3500 scans with 4 cm^{-1} resolution using a Bruker RFS 100/S FTRaman spectrometer (Nd: YAG laser, 1064 nm excitation) at a power of 150 mW.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts (δ) were reported in parts per million (ppm), relative to the internal standard tetramethylsilane (TMS, $\delta = 0.00$ ppm).

Electronic spectra were taken with a temperature-controlled Jasco V-560 spectrophotometer using 1 cm Hellma Suprasil cells equipped with 9.9 mm quartz spacer and a quartz-to-pyrex graded seal.

The molecular weights and molecular weight distributions of the polymers were determined by size-exclusion chromatography (SEC) with a Varian PL-GPC 110 instrument, using *N,N*-dimethylformamide (DMF) as the mobile phase. Polystyrene standards were used for narrow standard calibration.

DSC thermograms were obtained with a Perkin Elmer Diamond DSC unit using aluminium pans under nitrogen with a heating rate of 10 °C/min in the temperature range of -80 to 80 °C.

5. REFERENCES

[1] C. E. Hoyle, T. Y. Lee, T. Roper, Thiol-enes: Chemistry of the past with promise for the future, *Journal of Polymer Science Part A: Polymer Chemistry* **2004**, 42, 5301-5338.

[2] A. B. Lowe, Thiol-ene “click” reactions and recent applications in polymer and materials synthesis, *Polymer Chemistry* **2010**, 1, 17-36.

[3] M. J. Kade, D. J. Burke, C. J. Hawker, The power of thiol-ene chemistry, *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, 48, 743-750.

[4] C. E. Hoyle, C. N. Bowman, Thiol–Ene Click Chemistry, *Angewandte Chemie International Edition* **2010**, 49, 1540-1573.

[5] A. Dondoni, The Emergence of Thiol–Ene Coupling as a Click Process for Materials and Bioorganic Chemistry, *Angewandte Chemie International Edition* **2008**, 47, 8995-8997.

[6] J. W. Chan, B. Yu, C. E. Hoyle, A. B. Lowe, Convergent synthesis of 3-arm star polymers from RAFT-prepared poly(N,N-diethylacrylamide) via a thiol–ene click reaction, *Chemical Communications* **2008**, 4959-4961.

[7] K. L. Killops, L. M. Campos, C. J. Hawker, Robust, Efficient, and Orthogonal Synthesis of Dendrimers via Thiol-ene “Click” Chemistry, *Journal of the American Chemical Society* **2008**, 130, 5062-5064.

[8] M. Fiore, A. Marra, A Dondoni, Photoinduced Thiol−Ene Coupling as a Click Ligation Tool for Thiodisaccharide Synthesis, *Journal of Organic Chemistry* **2009**, 74, 4422-4425.

[9] J. Samuelsson, M. Jonsson, T. Brinck, M. Johansson, Thiol–ene coupling reaction of fatty acid monomers, *Journal of Polymer Science Part A: Polymer Chemistry* **2004**, 42, 6346-6352.

[10] M. Claudino, M. Johansson, M. Jonsson, Thiol–ene coupling of 1,2-disubstituted alkene monomers: The kinetic effect of cis/trans-isomer structures, *European Polymer Journal* **2010**, 46, 2321-2332.

[11] G. B. Bantchev, J. A. Kenar, G. Biresaw, M. G. Han, Free Radical Addition of Butanethiol to Vegetable Oil Double Bonds, *Journal of Agriculture and Food Chemistry* **2009**, 57, 1282-1290.

[12] C. Lluch, J. C. Ronda, M. Galià, G. Lligadas, V. Cádiz, Rapid Approach to Biobased Telechelics through Two One-Pot Thiol−Ene Click Reactions, *Biomacromolecules* **2010**, 11, 1646-1653.

[13] O. Türünç, M. A. R. Meier, Fatty Acid Derived Monomers and Related Polymers Via Thiol-ene (Click) Additions, *Macromolecular Rapid Communications* **2010**, 31, 1822-1826.

[14] O. Türünç, M. A. R. Meier, Thiol-ene vs. ADMET: a complementary approach to fatty acid-based biodegradable polymers, *Green Chemistry* **2011**, 13, 314-320.

[15] C. Lluch, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, “Click” Synthesis of Fatty Acid Derivatives as Fast-Degrading Polyanhydride Precursors, *Macromolecular Rapid Communications* **2011**, 32, 1343-1351.

[16] H. C. Kolb, M. G. Finn, K. B. Sharpless, Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angewandte Chemie International Edition* **2001**, 40, 2004-2021.

[17] T. J. Brocksom, J. Nakamura, M. L. Ferreira, U. Brocksom, The Diels-Alder Reaction: an Update, *Journal of the Brazilian Chemical Society* **2001**, 12, 597-622.

[18] F. Fringuelli, A. Taticchi, *The Diels-Alder Reaction: Selected Practical Methods*, John Wiley & Sons, West Sussex, **2002**.

[19] K. C. Nicolaou, S. A. Snyder, T. Montagnon, G. Vassilikogiannakis, The Diels–Alder Reaction in Total Synthesis, *Angewandte Chemie International Edition* **2002**, 41, 1668-1698.

[20] M. N. Belgacem, A. Gandini, Furan Chemistry at the Service of Functional Macromolecular Materials: The Reversible Diels-Alder Reaction, *ACS Symposium Series* **2007**, 954, 280-295.

[21] A. Gandini, Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: a review of recent progress, *Polymer Chemistry* **2010**, 1, 245-251.

[22] A. Gandini, in *Green Polymerisation Methods: Renewable Starting Materials, Catalysis and Waste Reduction*, ed. R. T. Mathers and M. A. R. Meier, Wiley-VCH, Weinheim, ch. 3, pp. 29-53, **2011**.

[23] A. Gandini, in *Biopolymers: New Materials for Sustainable Films and Coatings*, ed. D. Plackett, John Wiley & Sons, Weinheim, ch. 9, pp. 179-209, **2011**.

[24] A. Gandini, D. Coelho, A. J. D. Silvestre, Reversible click chemistry at the service of macromolecular materials. Part 1: Kinetics of the Diels–Alder reaction applied to furan-maleimide model compounds and linear polymerizations, *European Polymer Journal* **2008**, 44, 4029-4036.

[25] A. Gandini, D. Coelho, A. J. D. Silvestre, Reversible click chemistry at the service of macromolecular materials. 2. Thermoreversible polymers based on the Diels-Alder reaction of an A-B furan/maleimide monomer, *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, 48, 2053-2056.

[26] A. Gandini, D. Coelho, A. J. D. Silvestre, Reversible click chemistry at the service of macromolecular materials, *Polymer Chemistry* **2011**, 2, 1713-1719.

[27] A. Gandini, The furan/maleimide Diels-Alder reaction: A versatile click–unclick tool in macromolecular synthesis, *Progress in Polymer Science* **2012**, http://dx.doi.org/10.1016/ j.progpolymsci.2012.04.002

[28] H. Kwart, I. Burchuk, Isomerism and Adduct Stability in the Diels-Alder Reaction. I. The Adducts of Furan and Maleimide, *Journal of the American Chemical Society* **1952**, 74, 3094-3097.

[29] M. Van der Steen, C. V. Stevens, Undecylenic Acid: A Valuable and Physiologically Active Renewable Building Block from Castor Oil, *ChemSusChem* **2009**, 2, 692-713.

[30] A. R. Katritzky, J. M. Lagowski, Infrared absorption of heteroaromatic, five-membered, monocyclic nuclei. Part I. 2-Monosubstituted furans, *Journal of the Chemical Society* **1959**, 657-660.

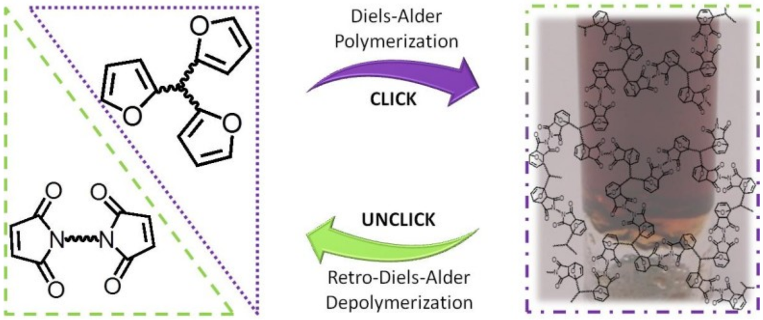
[31] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, London, Chapman and Hall, 3rd edn., **1975**, vol. 1.

[32] H. K. Hall, R. Zbinden, Infrared Spectra and Strain in Cyclic Carbonyl Compounds, *Journal of the American Chemical Society* **1958**, 80, 6428-6432.

[33] A. Rauf, H. Parveen, Direct esterification of fatty acids with phenylalkanols by using dicyclohexylcarbodiimide, *European Journal of Lipid Science and Technology* **2004**, 106, 97-100.

Chapter V

NON-LINEAR POLYMERS FROM FURAN / VEGETABLE OIL MONOMERS



Trifunctional vegetable oil derived monomers with furan and maleimide complementary moieties were prepared and polymerized through the click-unclick Diels-Alder reaction to yield either hyperbranched or cross-linked thermoreversible materials based on two different renewable resources.

Parts of this chapter have been published:

C. Vilela, A. J. D. Silvestre, A. Gandini, Thermoreversible non-linear DA polymerization of furan/plant oil monomers, *Journal of Polymer Science A: Polymer Chemistry* **2013**, accepted.

1. INTRODUCTION

Over the last couple of years, researchers have devoted considerable attention to the synthesis of highly branched[1,2] and cross-linked[3] macromolecular architectures, given their potential as tailor made materials with high performance and/or novel functionality. Several appraisals have been written on the topics reporting remarkable details on the history and current trends in hyperbranched[1,2,4] and cross-linked[3] polymers.

The three-dimensional architecture of hyperbranched polymers together with their unique physical and chemical properties (e.g. low viscosity, good solubility, and large number of functional groups[4]), make them suitable for applications in various fields including coatings, additives, processing aids, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science.[1] In turn, cross-linked polymers with superior mechanical and chemical properties, higher thermal stability, and lower temperature dependence on viscosity than their non-cross-linked analogous,[5] have potential applications in coatings, films, self-healing polymers, textile finishings,[3] among others.

Within the scope of click chemistry, the Diels-Alder (DA) reaction[6,7] does not require an extensive introduction, given its well-established status in macromolecular synthesis.[8] The most attractive feature of this reaction, illustrated here in the case of furan/maleimide couple , is definitely its reversible character, in which the temperature is a key factor, *viz.* the equilibrium can be shifted from predominant adduct formation (DA reaction), up to ca. 65 °C, to the predominant reversion to its precursors (retro-DA reaction), above ca. 100 °C).[8] It is precisely the experimental convenience related with this range of temperatures, together with negligible side reactions and possible thermal degradation mechanisms, that the furan/maleimide couple represents a highly suitable choice to synthesise temperature-sensitive polymers with interesting applications such as recyclable networks, and self-healing materials.[8]

Vegetable oils and their fatty acids are appealing substrates for appending furan and maleimide functions, as indeed demonstrated in the previous chapter (Chapter IV) where unsaturated vegetable oil derivatives were converted into bifunctional monomers through thiol-ene coupling, another click reaction, followed by Diels-Alder polymerization to obtain linear thermoreversible polymers.[9,10]

To the best of our knowledge, there is no published information regarding the use of similar trifunctional vegetable oil derived monomers to prepare non-linear thermoreversible polymers. Nevertheless, polymer networks prepared from the DA coupling of other multifunctional furan and maleimide monomers or macromonomers have already been reported.[8,11,12-16] The first example of thermally mendable cross-linked materials was the pioneering work of Wudl et al.[13,14] almost a decade ago, in which combinations of tetrafuran and bis- or tris-maleimides were made to polymerize in solution or in bulk, and the thermal reversibility and mendability of the ensuing networks studied in detail. This concept has been applied to a whole host of further investigations, both with combinations of monomers and macromonomers and with DA reactions applied to polymers.[15,16]

In this vein, the present chapter reports the synthesis of trifunctional monomers with terminal DA reactive functions, *viz.* (i) three furan moieties (A_3), (ii) a combination of two furan and a protected maleimide moieties (A_2B), or (iii) a combination of a furan and two protected maleimide moieties (AB_2). They were subsequently polymerized through the DA polymerization, the former with a bismaleimide (B_2) and the others on their own, after liberating the maleimide moiety(s) through the retro-DA reaction of its protected adduct.

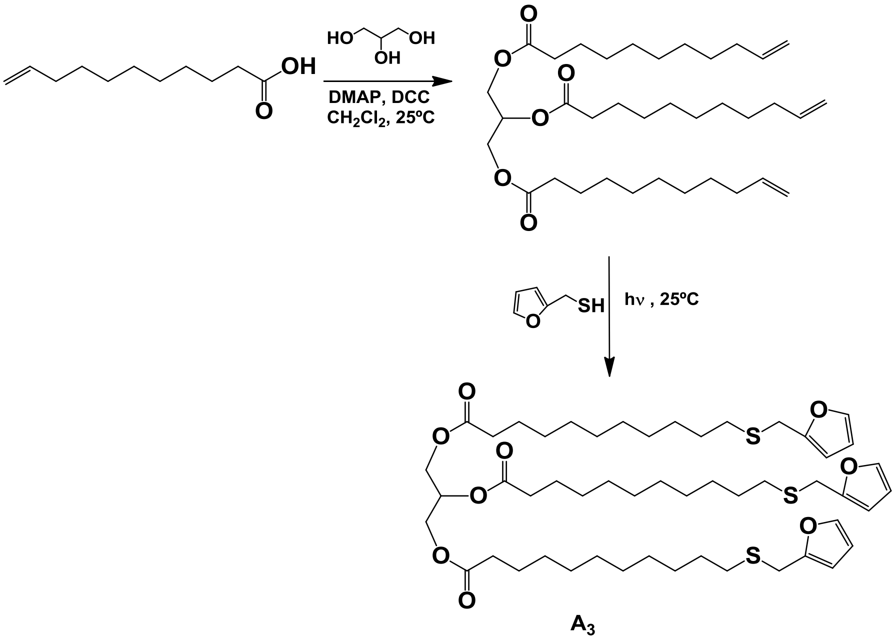
2. RESULTS AND DISCUSSION

2.1 Synthesis and characterization of trifunctional monomers

In this chapter, monomers with three functionalities were prepared in order to obtain non-linear polymers through DA polymerization. The trifunctional monomers A_3, A_2B and AB_2 were prepared using the thiol-ene coupling in conjunction with more classical chemical condensations and were characterized by conventional spectroscopic techniques. The previously synthesized difunctional monomers A_2 and B_2 completed the set of starting reagents.

2.1.1 Monomer A_3

The trifunctional monomer A_3 was synthesized in two steps, as depicted in Scheme 33. First, 10-undecenoic acid was esterified with glycerol under mild conditions and then, the ensuing intermediate was reacted with 2-furylmethanethiol by thiol-ene coupling to yield monomer A_3.



Scheme 33. Synthetic pathway for the preparation of monomer A_3.

The FTIR spectrum of the trisfuran monomer A_3 (Figure 29) was consistent with the expected structure due to the presence of the furan heterocycle bands at 3114, 1596, 1502, 1380, 1204, 1070, 1009, 933, 885, 732, 597 cm^{-1},[17] and the ester C=O and C–O bands at 1736 and 1149 cm^{-1}, respectively.[18]

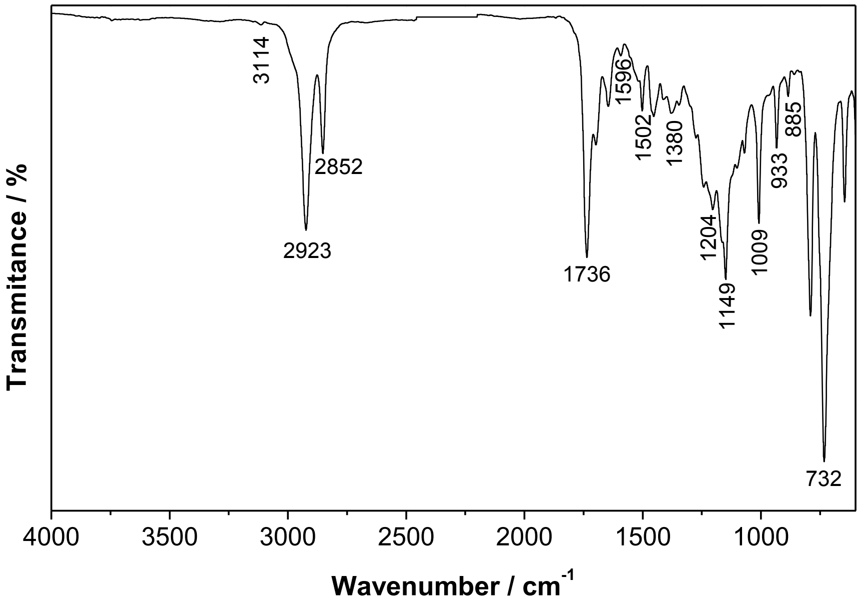


Figure 29. FTIR spectrum of monomer A_3.

The ^{1}H NMR spectrum of monomer A_3 (Figure 30) confirmed the tructure through the appearance of the typical signals of the furan ring protons at about δ 6.2 (3-H), 6.3 (4-H), 7.4 (5-H) ppm, the methylene and methine protons of the ester moieties at δ 4.1-4.3 ($OCH_2CH(–O)CH_2O$) and 5.3 ppm ($OCH_2CH(–O)CH_2O$), respectively, and the methylene protons attached to the S atom at δ 2.5 ($SCH_2(CH_2)_n$) and 3.7 ppm (SCH_2–2-furan), apart from the typical resonances of the methylene protons of UDA's aliphatic chain at δ 1.3 (–$(CH_2)_n$–), 1.6 ($CH_2CH_2C(=O)$) and 2.3 ($CH_2C(=O)$) ppm.

The ^{13}C NMR pattern (Figure 30) corroborate these findings: aside from the unchanged resonances related to the aliphatic chain carbons (δ 24.6, 28.2-29.3 and 34.0 ppm), resonances appeared at δ 31.6 (SCH_2), 62.0 ($OCH_2CH(–O)CH_2O$), 68.7 (OCH_2CH(–

O)CH_2O), 107.1 and 110.2 (furan C-3 and C-4), 141.9 (furan C-5), 151.8 (furan C-2) and the $C=O_{ester}$ peak at 173.2 ppm.

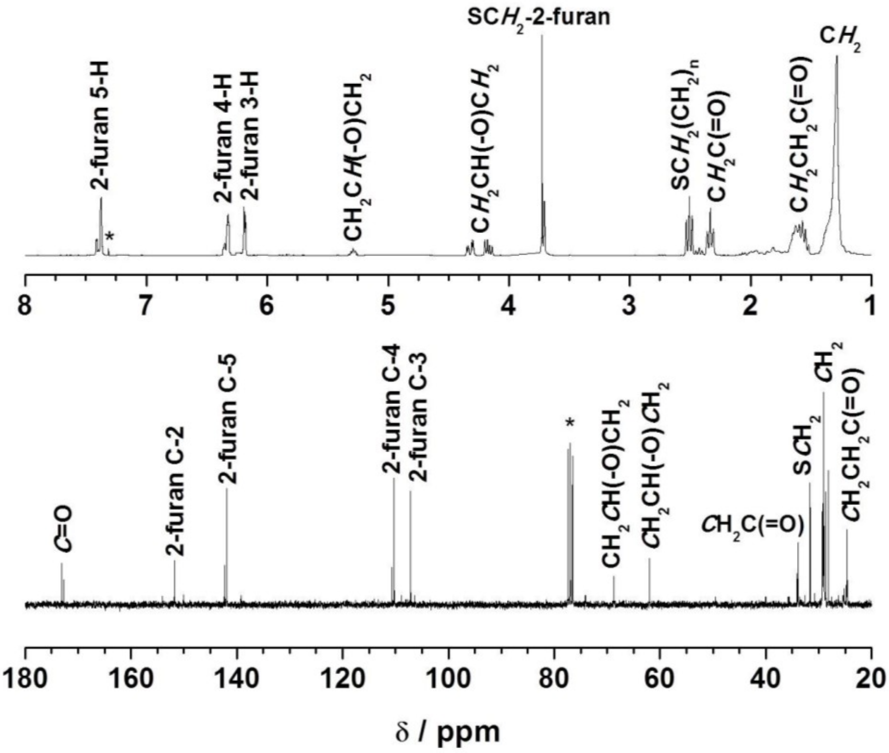


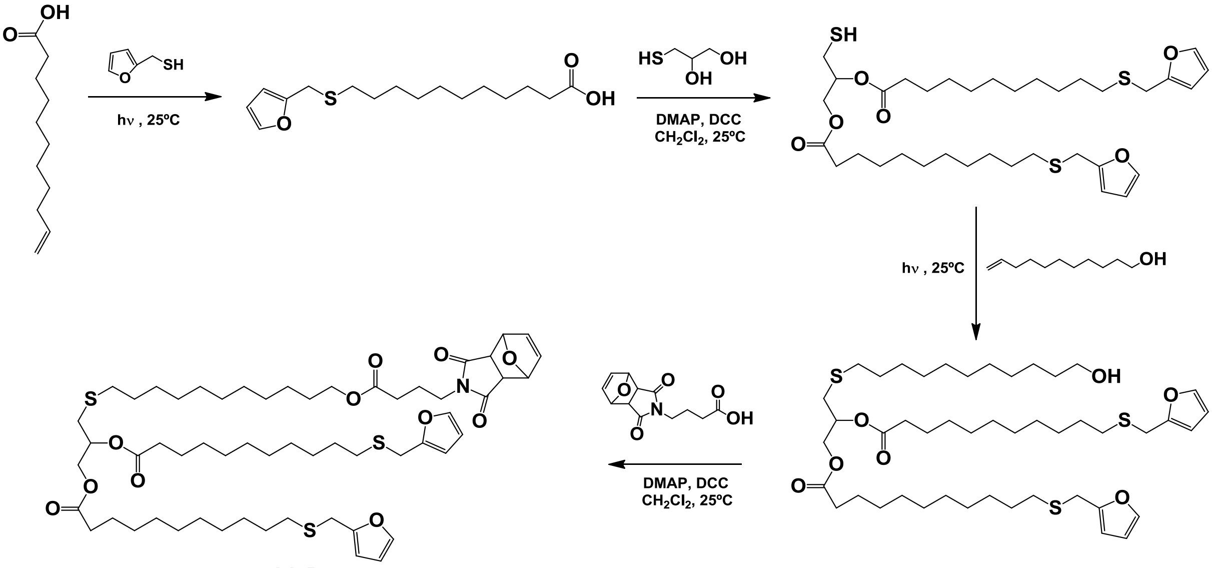
Figure 30. ^1H and ^{13}C NMR spectra of monomer A_3 in *$CDCl_3$.

2.1.2 Protected A_2B and AB_2 monomers

A challenging application of the DA reaction to furan/maleimide polymers is the synthesis and polymerization of monomers bearing both reactive moieties in their structures, i.e. AB, ABn and AnB molecules.

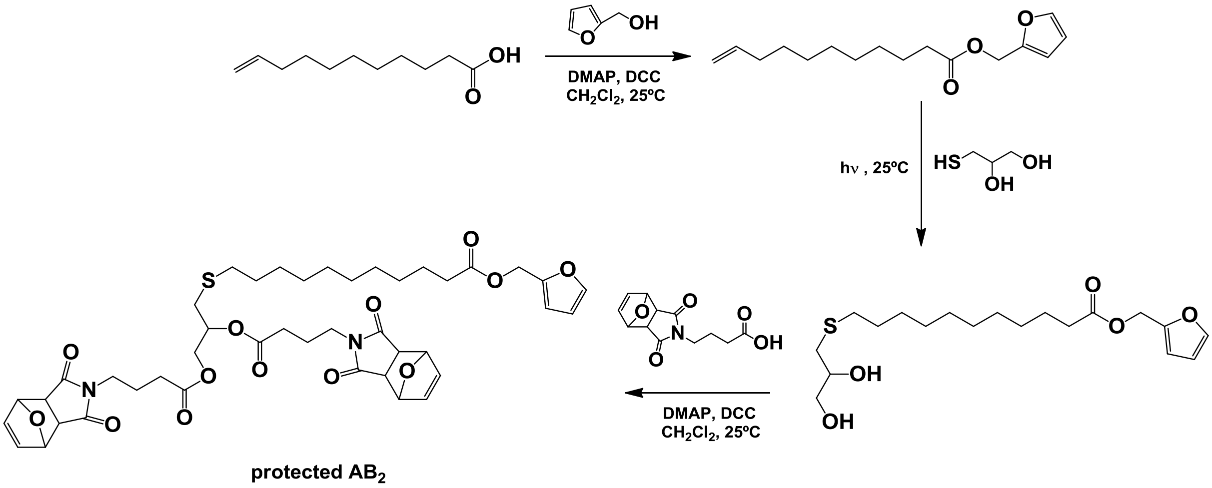
In Chapter IV, an AB monomer from vegetable oil derivatives was synthesized and polymerized through the joint exploitation of two click-chemistry mechanisms, *viz*. the thiol-ene and the DA reactions.[9,10] Here, the synthesis of protected A_2B and AB_2 monomers is reported making use of the same precursors and strategies exploited in the previous chapter. The protected A_2B monomer was synthesized in four steps, whereas the protected AB_2 monomer was prepared in three steps, as depicted in Scheme 34 and Scheme 35, respectively.

The FTIR spectrum of the protected A_2B monomer showed all the relevant peaks, *viz.* (i) the asymmetric and symmetric C=O stretching vibrations of imide group at 1769 and 1699 cm^{-1}, respectively,[19] (ii) the furan heterocycle bands at 3118, 1599, 1503, 1399, 1245, 1160, 1069, 1009, 914, 879, 734 and 598 cm^{-1},[17] and (iii) the C=O ester band at 1733 cm^{-1}.[18]



protected A_2B

Scheme 34. Synthetic pathway for the preparation of protected A_2B monomer.



protected AB_2

Scheme 35. Synthetic pathway for the preparation of protected AB_2 monomer.

The ^{1}H NMR spectrum of protected A_2B monomer (Figure 31) clearly confirmed its structure through the presence protons of the protected maleimide moiety at about δ 2.8 (=CHCHC*H*CO), 5.3 (=CHC*H*CHCO) and 6.5 ppm (=C*H*CHCHCO) and the 2-furan ring protons at δ 6.2 (3-H), 6.3 (4-H) and 7.4 (5-H) ppm, plus the methylene protons attached to the S atom at δ 2.5 ($SCH_2(CH_2)_n$) and 3.7 ppm (SCH_2–2-furan).

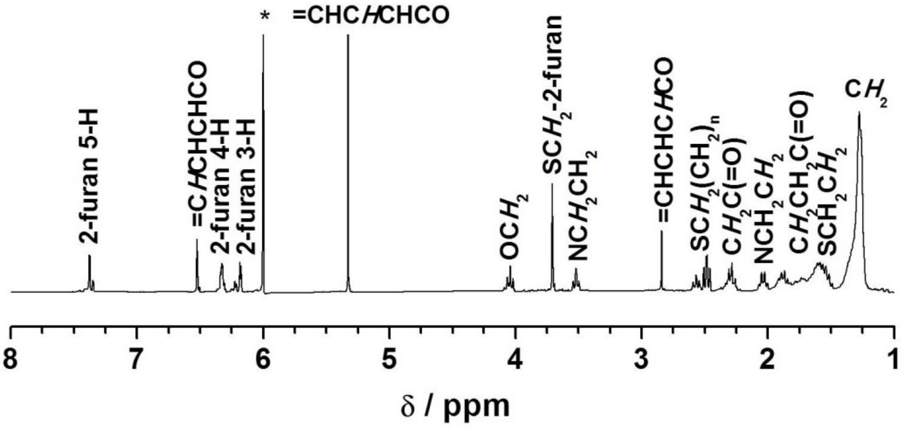


Figure 31. ^{1}H NMR spectrum of protected A_2B monomer in *TCE-d_2.

The ^{13}C NMR spectrum of the protected A_2B monomer was also in tune with the proposed structure with, in addition to the carbon resonances related to the aliphatic chain (δ 25.8, 28.1 and 28.8-29.3 ppm), the furan ring carbons (δ 107.3, 110.4, 141.9 and 151.7 ppm) and the protected maleimide carbon resonances (δ 47.2, 80.8, 136.4 and 176.1 ppm), it was also possible to observe signals resonating at δ 31.7 and 64.7 ppm, which were readily identified as the methylenic carbons of the thioether moiety (S*C*H_2) and of the ester group (O*C*H_2), respectively.

The changes in relation to the FTIR, ^{1}H and ^{13}C NMR spectra associated with the synthesis of the protected AB_2 monomer were similar to the previous monomer, and displayed also the same general characteristics, as given in detail in the Section 4.7 of the present chapter. It is worth mentioning that the protection of the maleimide group of A_2B and AB_2 monomers in the form of its furan-DA adduct prevented the premature DA polymerization of the intrinsically reactive furan/maleimide moieties.

Although these trifunctional monomers possess the same common structural features of the previous bifunctional ones of Chapter IV, namely the terminal DA-reactive furan and/or maleimide functions and the long methylene flexible bridge joining them, they were expected to yield DA polymers with higher glass transition temperatures.

2.2 Synthesis and characterization of non-linear Diels-Alder polymers

As a follow-up to Chapter IV, where the behaviour of linear polymerization systems based on the DA growth of A_2+B_2 and AB molecules was studied,[9,10] the non-linear systems A_2+B_3, A_3+B_2, A_2B and AB_2 were now investigated.

The non-linear DA polymerizations were carried out in the same experimental conditions as the linear ones and using the same spectroscopic tools, i.e. the reactions were followed by both UV and ^{1}H NMR spectroscopy at the appropriate temperature of 65 °C that provides a reasonably high rate of adduct formation while avoiding any detectable incidence of the retro-DA reaction.

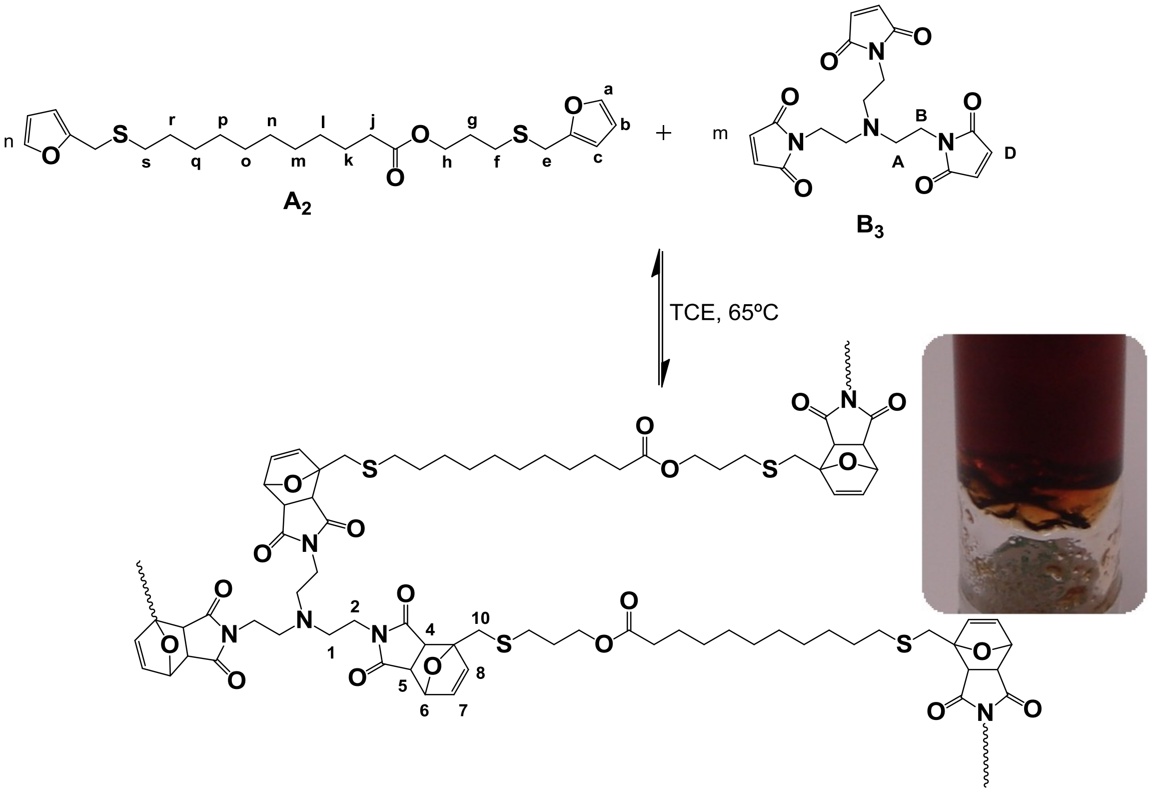
2.2.1 Polymerization of A_2+B_3 system

The first non-linear system involves the DA reaction of the bisfuran A_2 with the trismaleimide B_3 (A_2+B_3 system), as shown in Scheme 36.

Three different [maleimide]/[furan] molar ratios *r*, *viz*. 1.0, 0.75 and 0.50, were studied, which, according to the *Flory-Stockmayer* equation (1) are associated with critical conversions, P_c, for network formation of 71, 81 and 100%, respectively, neglecting intramolecular cyclizations.

$$P_c = \frac{1}{[r + r\rho(m-2)]^{1/2}} \qquad \textbf{(1)}$$

The cross-linking critical point, P_c, is the yield at which cross-linking occurs (i.e. the degree of consumption of the moiety which is in default), *r* is the stoichiometric ratio between B and A groups [$r=N_B/N_A<1$], ρ is the cross-linking parameter [$\rho=N_{B(m)}/N_{B(total)}$], and m is the functionality of the B_m monomer.[5] For this A_2+B_3 system, m was equal to three while ρ was unity.



Scheme 36. Non-linear DA polymerization between bisfuran A_2 and trismaleimide B_3.

The evolution of these DA reactions was followed by monitoring the progressive decrease in the optical density of the maleimide band at about 300 nm, associated with the corresponding loss of conjugation between the two carbonyl groups and the C=C unsaturation bridge that accompanied the DA adduct formation. As a typical example of this behaviour, Figure 32 illustrates the progress of the non-linear polymerization under stoichiometric conditions (r = 1.0). As previously reported for other non-linear DA polymers,[12] the spectral pattern gave rise to an isosbestic point (progressive replacement of the maleimide band at ~300 nm by the absorption of the unconjugated carbonyl groups of the adduct at ~ 260 nm), which suggested the occurrence of a single reaction pathway, *viz.* the DA polymerization.

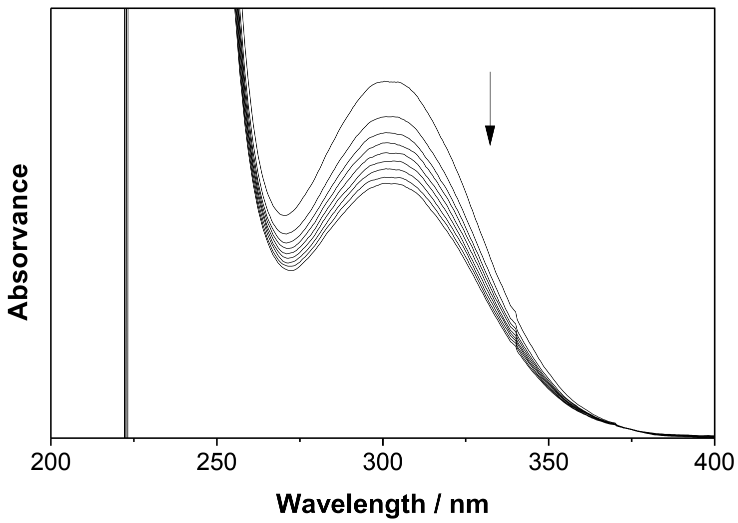


Figure 32. Evolution of the UV spectrum of the maleimide band during de DA polymerization of A_2+B_3 system with r = 1 at 65 °C in TCE for 8 hours (spectra taken hourly).

The concomitant changes in the ^{1}H NMR spectra corroborated the polymer formation through the gradual decrease in the intensity of the maleimide (δ 6.7 ppm, C*H*=C*H*) and furan (δ 6.2, 6.3 and 7.4 ppm) proton resonances at a rate similar to that of the UV spectra evolution and the simultaneous surge of the peaks associated with the three sets of protons assigned to the polyadducts, at δ 2.9, 5.2 and 6.5 ppm. The other two systems (r = 0.75 and 0.50) displayed the exact same behaviour pattern. As an example of these features, Figure 33 displays the ^{1}H NMR spectra of the A_2+B_3 system with r = 1.0. Since a network was formed, i.e. a mixture of cross-linked (gel) and branched (sol) macromolecules, only the latter species were detected and displayed in this situation.

The evolution of the DA reactions was also followed by the progressive increase in the viscosity of the reaction medium. The reactions conducted with r = 1.0, i.e. a stoichiometric balance between furan and maleimide moieties, produced the most rapid thickening and gelled within a few days. Their counterparts with r =0.75 displayed similar features but in a slower manner and the reduction to r = 0.50 only showed a slow progressive increase in viscosity without reaching a gel point, which is compatible with the fact that cross-linking would only be attained at 100% conversion in the absence of ring formation. It is important to emphasize that the increase in viscosity during these reactions was much more dramatic than in the corresponding linear DA polymerizations reported in Chapter IV, as indeed expected for non-linear polymerization.

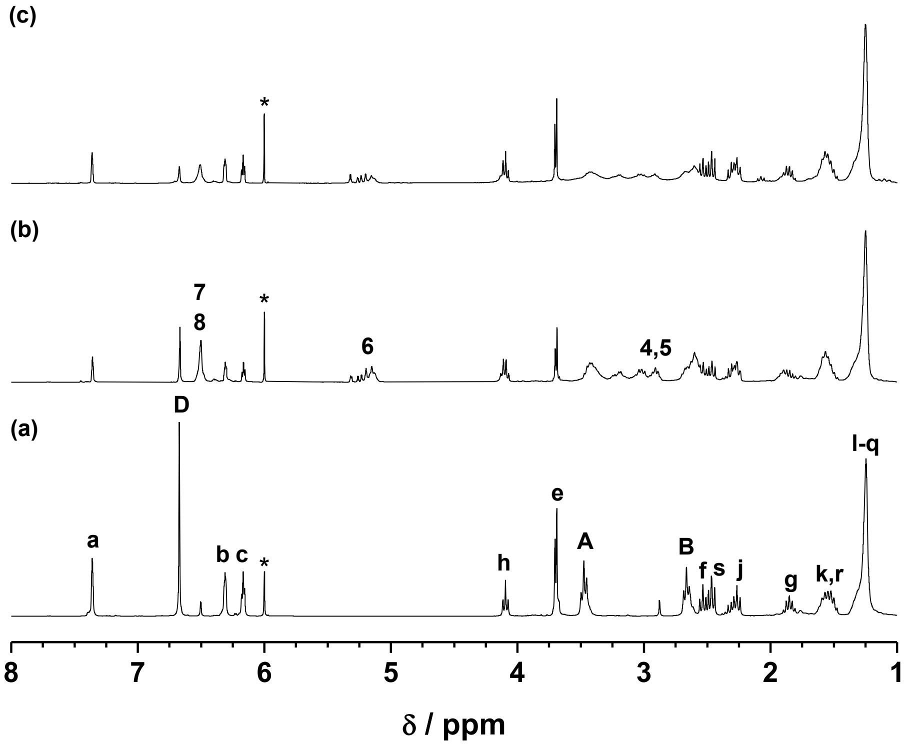


Figure 33. ^{1}H NMR spectra of the evolution of the DA polymerization of the soluble fraction of the A_2+B_3 system with *r* = 1 in *TCE-d_2 at (a) t = 0 days, (b) t = 3 days and (c) t = 6 days (see Scheme 36 for peak assignment).

Once these polymerizing systems had reached high conversion, the gelled products were then submitted to the corresponding retro-DA depolymerisation followed by ^{1}H NMR spectroscopy at the adequate temperature of 110 °C to ensure a major shift of the equilibrium towards monomers formation, while avoiding unwanted side reactions.

These processes were characterized by the reverse pattern with respect to the polymerizations, consisting in the gradual decline in the adduct resonance (δ 2.9, 5.2 and 6.5 ppm) intensities and the corresponding increase of the furan (δ 6.2, 6.3 and 7.4 ppm) and maleimide (δ 6.7 ppm) counterparts (Figure 34), together with the progressive decrease of the viscosity of the medium due to first, the de-crosslinking of the network and then, the depolymerisation of the solubilised macromolecules.

Within a few days, the spectra revealed the presence of resonances of the starting monomers (Figure 34 (b)), thus confirming the thermo-reversible nature of these systems. These regenerated monomers were allowed to cool to 65 °C to favour a second polymerization (Figure 34 (c)), emphasizing the reproducibility of these cyclic events. The other two non-linear systems (*r* = 0.75 and 0.50) displayed the same general features.

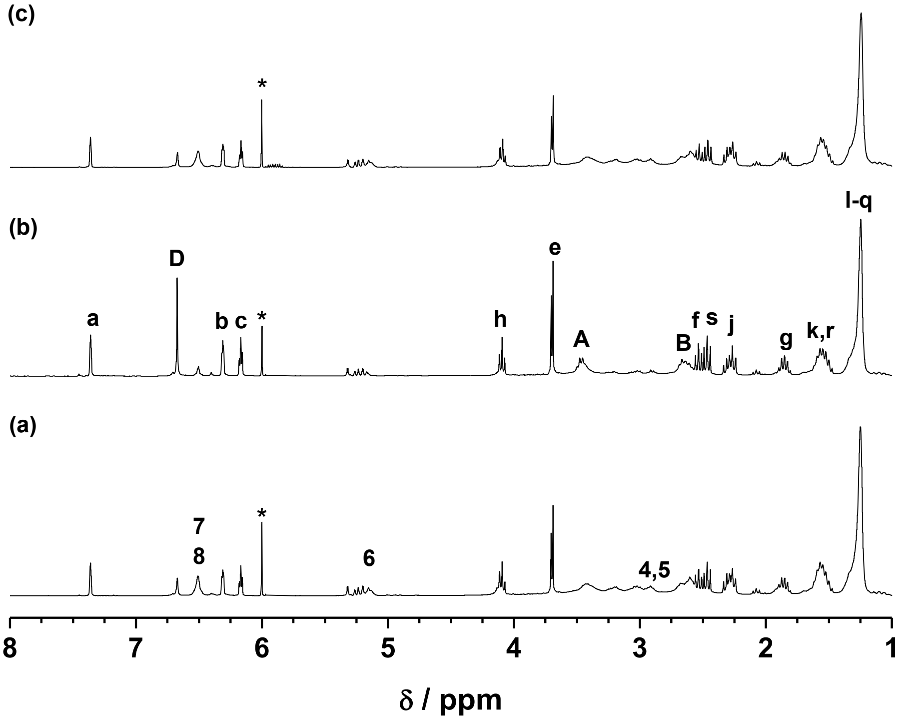
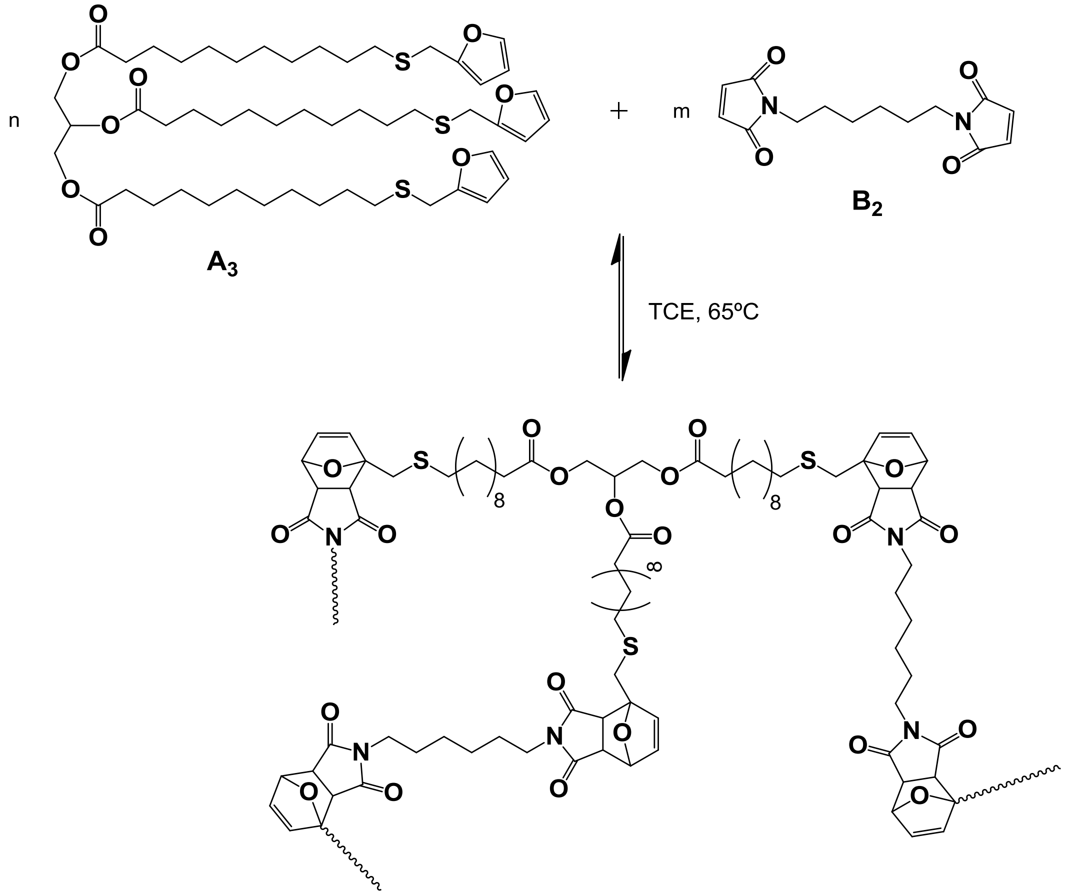


Figure 34. ^{1}H NMR spectra of the evolution of the click-unclick DA polymerization of A_2+B_3 system with *r* = 1 in *TCE-d_2: (a) DA after t = 6 days, (b) retro-DA after t = 6 days and (c) 2nd DA after 6 days (see Scheme 36 for peak assignment).

2.2.2 Polymerization of A_3+B_2 system

The second non-linear DA polymerization system involved the reaction of a trisfuran with a bismaleimide monomer (Scheme 37). Three different [maleimide]/[furan] molar ratios *r*, *viz*. 1.0, 0.75 and 0.50, were again studied and the evolution of each DA polymerization followed by the two spectroscopic techniques and by monitoring the increase in viscosity. The evolution of the DA reations followed by UV spectroscopy showed the expected progressive decrease in the intensity of the maleimide band and again the presence of the characteristic isosbestic point at ~260 nm clearly indicated the absence of side reactions.



Scheme 37. Non-linear DA polymerization between bisfuran A_3 and trismaleimide B_2.

The use of ^{1}H NMR spectroscopy to follow these polymerizations also revealed all the niceties of the progressive increase in the signals associated with the adduct protons and the corresponding decrease of those allocated to the unreacted furan and maleimide cycles. When complementary moiety stoichiometry was used, a gel or network was produced, whereas as the relative amount of trifunctional monomer declined, the polymerizations originated soluble highly branched polymers. The retro-DA depolymerisation of these materials was monitored at 110 °C by the same techniques and the results also pointed out the thermoreversible character of this system.

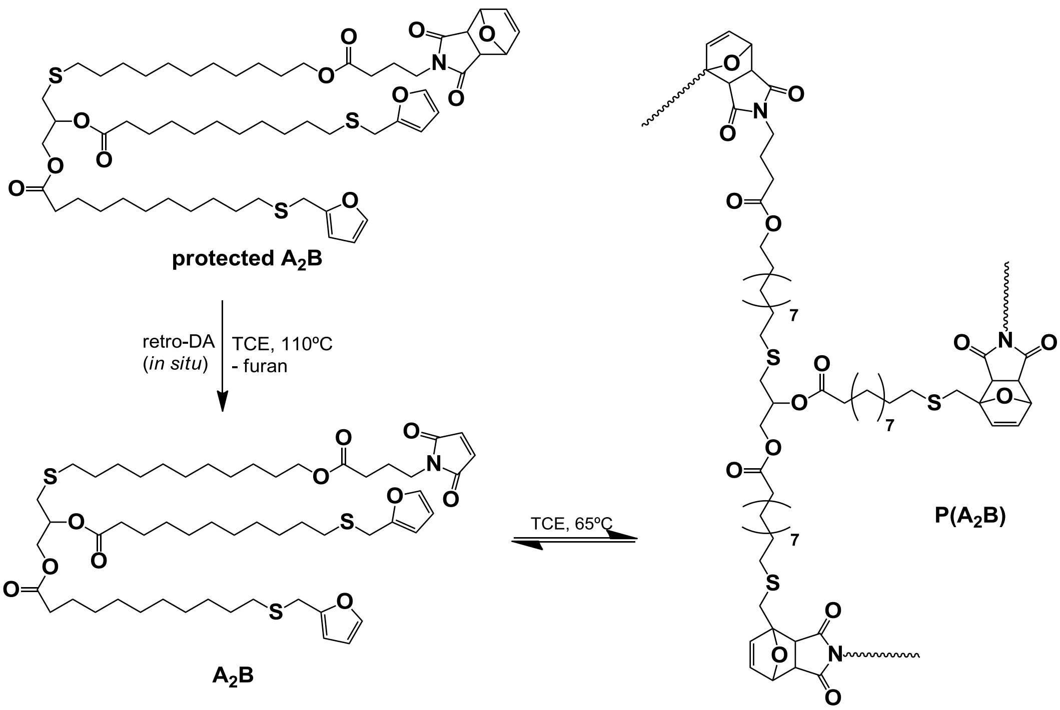
2.2.3 Polymerization of A_2B and AB_2 systems

When asymmetrically substituted AB_n or A_nB (n>1) monomers are polymerized, hyperbranched macromolecules are generated that do not cross-link. The synthesis of the present A_2B and AB_2 monomers gave molecules with one or two protected maleimide moieties, respectively, to avoid premature polymerization. These compounds with stable furan-DA adduct(s) became ready for polymerization after the *in situ* deprotection of the masked end-group by their retro-DA reaction at 110 °C, which released furan and regenerated the maleimide moiety. The polymerization could then be initiated, as depicted in Scheme 38 and Scheme 39, by decreasing the temperature to 65 °C. The ^{1}H NMR spectrum of monomers A_2B and AB_2, despite the evidence of incipient polymerization, clearly confirmed the total deprotection through the presence of the free maleimide protons at δ 6.7 ppm (C*H*=C*H*), together with the absence of the adduct peaks at 2.9 (=CHCHC*H*CO), 5.3 (=CHC*H*CHCO) and 6.5 (=C*H*CHCHCO) ppm.

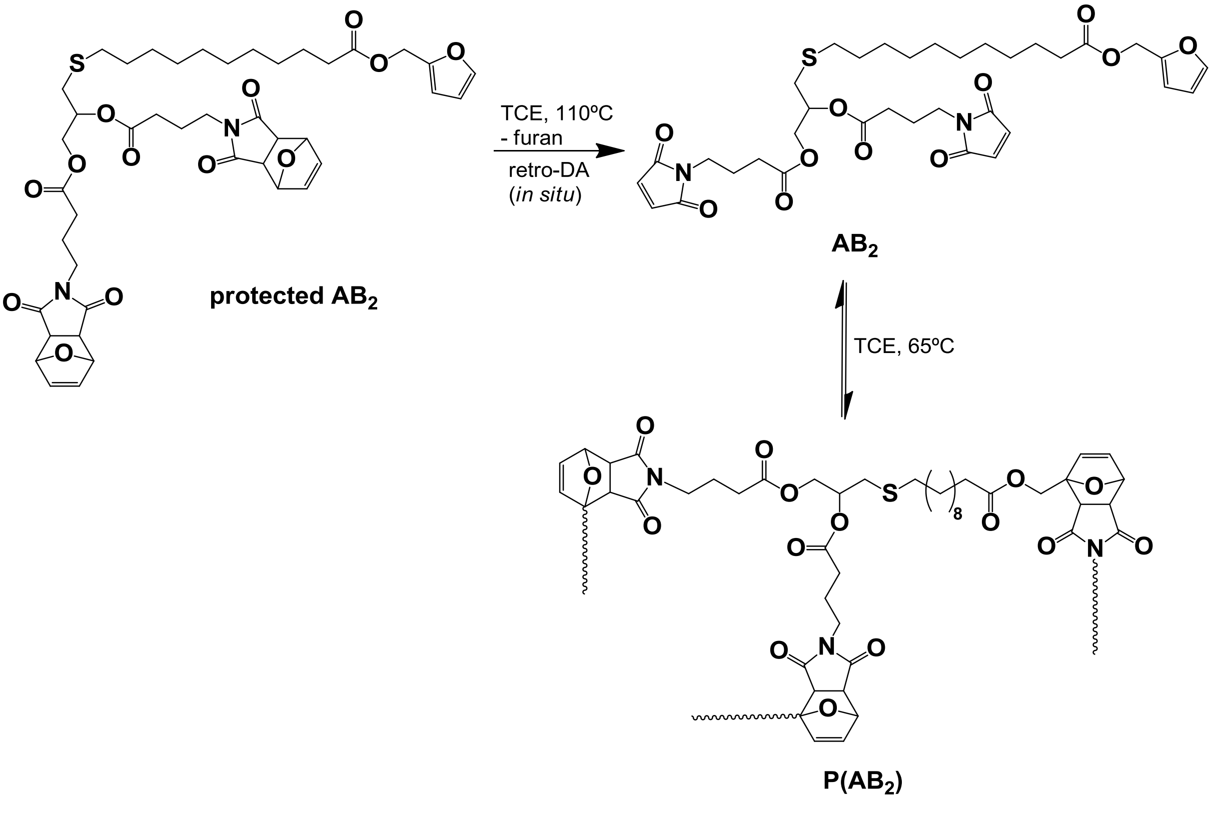
The evolution of the DA polymerization of both monomers, leading to the formation of $P(A_2B)$ and $P(AB_2)$, was also followed by UV and ^{1}H NMR spectroscopy and more qualitatively by the regular increase in the viscosity of the reaction medium.

The progress of the UV spectrum with reaction time mimicked the features epitomized in Figure 32, exhibiting once more a characteristic isosbestic point.

The ^{1}H NMR analysis of the polymerizing system revealed all the details of the progressive decrease in the signals ascribed to the unreacted furan (δ 6.2, 6.3 and 7.4 ppm) and maleimide moieties (δ 6.7 ppm) and the corresponding augment of those associated with the polyadduct protons at δ 6.5 (=C*H*CHCHCO), 5.3 (=CHC*H*CHCO) and 2.9 (=CHCHC*H*CO) ppm.



Scheme 38. Deprotection of monomer A_2B and its non-linear DA polymerization.



Scheme 39. Deprotection of monomer AB_2 and its non-linear DA polymerization.

After these systems attained high conversion, the retro-DA depolymerisation was followed at 110 °C for three days by ^{1}H NMR spectroscopy. The anticipated behaviour was once more observed, *viz*. the increase in the intensity of the peaks pertaining to the furan and maleimide protons to the detriment of the adduct signals.

The systems were then brought back to 65 °C and left for several days to promote a second polymerization. The ^{1}H NMR spectrum of the ensuing polymer was comparable to that taken at the end of the first polymerization, thus confirming the reversible nature of both systems.

2.2.4 Polymer characterization

Once the DA and retro-DA behaviour of all the non-linear polymers was investigated, they were isolated as described below (Section 4.8) in average yields of 80%. Given that polymers P(A_2+B_3)_0.75, P(A_2+B_3)_1.0, P(A_3+B_2)_0.75 and P(A_3+B_2)_1.0 gave mostly a gel fraction and little or no sol, the swollen brown gels became stiff solids after drying. For P(A_2+B_3)_0.5 and P(A_3+B_2)_0.5 the final products were glassy thermoplastic polymers, since critical cross-linking point was not attained. In the case of P(A_2B) and P(AB_2), the isolated polymers were soft materials.

All the synthesized non-linear DA polymers were characterized by SEC and DSC, and Table 10 shows their weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index (PDI). It was not possible to determine the molecular weight of polymers P(A_2+B_3)_0.75, P(A_2+B_3)_1.0, P(A_3+B_2)_0.75 and P(A_3+B_2)_1.0 due to their insolubility in the eluent medium (DMF) as indeed expected given their cross-linked nature. The M_n of P(A_2+B_3)_0.5, P(A_3+B_2)_0.5, P(A_2B) and P(AB_2) are in the range 16-21 kDa with PDI values between 2.0 and 3.2.

All the SEC chromatograms displayed a single broad peak, as epitomized in Figure 35 for polymer P(A_2B). Moreover, the absence of cyclic structures led to higher molecular weights and higher T_g values, as discussed below.

Table 10. SEC results for the synthesized non-linear DA polymers.

Polymer	M_w / kDa	M_n / kDa	PDI
$P(A_2+B_3)$_0.5	35.2	17.6	2.0
$P(A_2+B_3)$_0.75	–	–	–
$P(A_2+B_3)$_1.0	–	–	–
$P(A_3+B_2)$_0.5	49.2	20.5	2.4
$P(A_3+B_2)$_0.75	–	–	–
$P(A_3+B_2)$_1.0	–	–	–
$P(A_2B)$	67.2	21.0	3.2
$P(AB_2)$	53.1	16.6	3.2

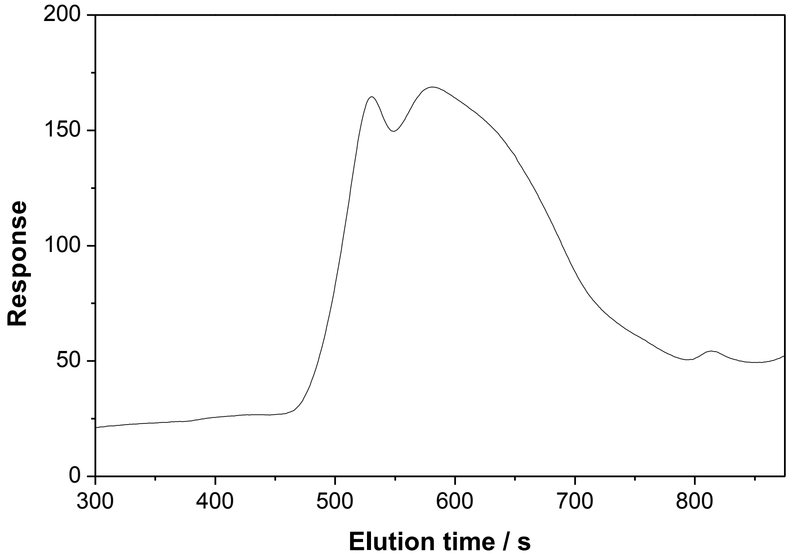


Figure 35. SEC tracing of polymer $P(A_2B)$.

The DSC analyses, performed in the temperature range -80 to 80 °C to avoid the occurrence of the retro-DA reaction, showed T_g's values close to 0 °C, with the exception of polymers $P(A_3+B_2)$_1.0 and $P(AB_2)$ which showed values around 15 and 5 °C, respectively. The higher T_g of $P(A_3+B_2)$_1.0 is probably related with a higher degree of cross-linking.

The similar T_g values among polymers was expected as a result of their analogous structures. As anticipated for these non-linear polymers, their T_g values are higher than the linear counterparts (Chapter IV, section 2.2.4) given their lower polymer flexibility associated with the presence of branching or cross-linking.

3. CONCLUSIONS

The non-linear DA systems studied in this chapter are good examples of click-unclick chemistry applied to macromolecular synthesis involving original monomers derived from two different renewable resources.

A novel trifuran (A_3) and two complex furan-maleimide (A_2B, AB_2) monomers were synthesized via thiol-ene coupling in conjunction with more classical chemical condensations. Three basic approaches were considered for the non-linear DA polymerizations, *viz*. the use of (i) a bisfuran monomer in combination with a trismaleimide (A_2+B_3 system), (ii) a trisfuran monomer in conjunction with a bismaleimide (A_3+B_2 system), and (iii) the use monomers incorporating both furan and maleimide end groups (A_2B or AB_2 systems).

The DA polymerization of A_2+B_3 or A_3+B_2 systems yielded highly branched or cross-linked materials depending on the [maleimide]/[furan] molar ratios, whereas the polymerization of A_2B or AB_2-type monomers originated hyperbranched polymers that do not cross-link.

As expected, the use of complementary moiety stoichiometry produced a gel (network), whereas as the relative amount of trifunctional monomer was decreased, the reactions stopped short of cross-linking, i.e. gave soluble highly branched polymers with M_n in the range 16-21 kDa. These thermally labile non-linear polymers exhibited T_g values close to 0 °C as a result of the lower polymer flexibility associated with the presence of branching or cross-linking. Once again, the results from both UV and ^{1}H NMR studies proved the feasibility of manifold DA/retro-DA cycles.

The thermoreversibility of these non-linear systems opens the way to temperature-sensitive materials with promising applications in numerous domains associated with self-mendability and network recyclability through reversible cross-linking.

4. EXPERIMENTAL

4.1 Materials

Allyl alcohol (Aldrich, ≥99%), acetic anhydride (Fluka, ≥ 99%), chloroform-*d* ($CDCl_3$, Acros Organics, 99.8 atom % D), *N,N'*-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-dimethylaminopyridine (DMAP, Sigma), *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (Acros, 90%), furan (Acros Organics, 99%), furfuryl alcohol (FA, Aldrich, 98%), 2-furylmethanethiol (FT, Aldrich, 98%), glycerol (Sigma, ≥ 99%), 1,6-hexamethylenediamine (HMDA, Aldrich, 98%), 4-maleimidobutyric acid (MBA, Fluka, ≥98%), maleic anhydride (Fluka, ≥99%), anhydrous sodium acetate (Sigma-Aldrich, ≥99%), 1,1,2,2-tetrachloroethane (TCE, Sigma-Aldrich, ≥98.0%), 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2, Acros Organics, 99.5 atom % D), 1-thioglycerol (Sigma, ≥99.0%), tris-(2-aminoethyl)amine (TAEA, Aldrich, 96%), 10-undecenoic acid (UDA, Aldrich, 98%), 10-undecen-1-ol (UDOL, Aldrich, 98%) were used as received. Irgacure® 651 (2,2-dimethoxy-2-phenylacetophenone, I651) was generously supplied by BASF-The Chemical Company, Ludvigshafen. Polystyrene standards were supplied by Polymer Laboratories. Other chemicals and solvents were of laboratory grades.

4.2 Synthesis of 3-(furan-2-ylmethylthio)propyl 11-(furan-2-ylmethylthio)-undecanoate (A_2)

Monomer A_2 was synthesized from UDA, allyl alcohol and FT, according to the two step procedure reported in Chapter IV, section 4.5.

4.3 Synthesis of propane-1,2,3-triyl tris(11-(furan-2-ylmethylthio)undecanoate) (A_3)

A procedure similar to that reported for monomer A_2 was followed. Step 1: UDA (5.5 g, 30.0 mmol), DCC (6.2 g, 30.0 mmol) and DMAP (381.5 mg, 3.0 mmol) were added to a solution of a glycerol (920.9 mg, 10.0 mmol) in dichloromethane (150 ml). The reaction mixture was left overnight at room temperature under nitrogen. After that period, the precipitated *N,N'*-dicyclohexylurea (DCU) formed during the reaction was filtered off and the filtrate washed with water (2x100 mL), 5% acetic acid solution (2x100 mL) and again water (2x100 mL) and the additional DCU removed by filtration. The organic phase was dried over anhydrous sodium sulphate before vacuum removal of the solvent.

Step 2: the ensuing ene (6.0 mmol), FT (4.1 g, 36.0 mmol) and I651 (92.2 mg, 0.36 mmol) were placed in a glass flask and thoroughly degassed with a stream of nitrogen to remove the air since the thiol is air sensitive. The reaction mixture was irradiated with a UV lamp working at 365 nm (Vilber Lourmat UV lamp VL-6-LC, 230V~50/60 Hz) for 4 hours at room temperature. After this period, the excess thiol was vacuum removed and the resulting yellowish solid monomer was obtained in 94% yield.

ν_{max}/cm^{-1}: 3114 (furan C–H stretching), 2923 (asCH_2), 2852 (sCH_2), 1736 (C=O stretching), 1596, 1502 and 1380 (furan ring stretching), 1204 and 1070 (furan in-plane CH deformation), 1149 (C–O stretching), 1009 (ring breathing), 933, 885 and 732 (furan C–H out-of-plane deformation), 597 (ring deformation).

δ_H (300 MHz, $CDCl_3$, Me_4Si): 7.4 (3H, dd, *J* = 2.0, 0.7 Hz, 2-furan 5-H), 6.3 (3H, dd, *J* = 3.1, 1.9 Hz, 2-furan 4-H), 6.2 (3H, d, *J* = 3.4 Hz, 2-furan 3-H), 5.3 (1H, m, $CH_2CH(–O)CH_2$), 4.1-4.3 (2H, ddd, *J* = 17.9, 11.9, 5.1 Hz, $CH_2CH(–O)CH_2$), 3.7 (6H, s, SCH_2–2-furan), 2.5 (6H, t, *J* = 7.2 Hz, $SCH_2CH_2(CH_2)_n$), 2.3 (6H, t, *J* = 7.5 Hz, $CH_2C(=O)$), 1.6 (6H, m, $CH_2CH_2C(=O)$), 1.3 (42H, s, aliphatic CH_2).

δ_C (75 MHz, $CDCl_3$, Me_4Si): 173.2 (C=O), 151.8 (2-furan C-2), 141.9 (2-furan C-5), 110.2 (2-furan C-4), 107.1 (2-furan C-3), 68.7 ($CH_2CH(–O)CH_2$), 62.0 ($CH_2CH(–O)CH_2$), 34.0 ($CH_2C(=O)$), 31.6 (SCH_2), 28.2-29.3 (aliphatic CH_2), 24.6 ($CH_2CH_2C(=O)$).

4.4 Synthesis of 1,6-bismaleimidohexane (B_2)

The bismaleimide monomer B_2 was prepared by the classical two-step process involving 1,6-hexanediamine and maleic anhydride, as reported in Chapter IV, section 4.3.

4.5 Synthesis of tris(2-maleimidoethyl)amine (B_3)

The synthesis of the trifunctional maleimide monomer B_3 called upon the reaction of tris(2-aminoethyl)amine with the furan-maleic anhydride DA adduct (*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride), in stoichiometric conditions, as previously reported.[12]

Step 1: Tris-(2-aminoethyl)amine (2.0 g, 13.7 mmol) was added dropwise to a solution of *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (6.8 g, 41.1 mmol) in methanol (150 mL). The solution was stirred at 56 °C for 3 days and a precipitate formed progressively. The suspension was filtered and the pale yellow solid residue washed with methanol. The final product was dried under vacuum and obtained in 49% yield.

Step 2: A retro-DA reaction was carried out in order to remove the protection of the maleimide groups. A solution of the protected B_3 monomer (2.0 g, 3.4 mmol) in toluene (150 mL) was heated to reflux during 24 hours. The solvent was then removed under reduced pressure and the ensuing yellow solid washed with n-hexane. The final product was dried under vacuum and obtained in 94% yield.

ν_{max}/cm^{-1}: 3096 (C–H stretching of CH=CH), 2950 (asCH_2), 2858 (sCH_2), 1762 and 1687 (C=O stretching), 1382, 1328, 1120 and 734 (C–N stretching).

δ_H (300 MHz, $CDCl_3$, Me_4Si): 6.7 (6H, s, C*H*=C*H*), 3.6 (2H, s, $N_{maleimide}CH_2CH_2N$), 2.8 (6H, s, $N_{maleimide}CH_2CH_2N$).

δ_C (75 MHz, $CDCl_3$, Me_4Si): 170.8 (C=$O_{maleimide}$), 134.0 (*C*H=*C*H), 51.6 ($N_{maleimide}CH_2CH_2N$), 35.7 ($N_{maleimide}CH_2CH_2N$).

4.6 Synthesis of protected A_2B monomer

The protected A_2B monomer was synthesized in four steps making use of the thiol-ene coupling in conjunction with other classical condensation reactions.

Step 1: UDA (1.8 g, 10.0 mmol), FT (2.3 g, 20.0 mmol) and I651 (51.2 mg, 0.20 mmol) were reacted photochemically following the procedure given above for monomer A_3.

Step 2: this intermediate (8.0 mmol) was reacted with 1-thioglycerol (432.6 mg, 4.0 mmol) in the presence of DCC (1.6 g, 8.0 mmol) and DMAP (101.7 mg, 0.8 mmol) again as described for monomer A_3.

Step 3: the ensuing thiol (1.3 mmol) was reacted with UDOL (221.4 mg, 1.3 mmol) using I651 (3.3 mg, 0.013 mmol) using the same conditions given above for monomer A_3.

Step 4: a solution of the latter compound (0.5 mmol) was esterified with 4-(3,6-epoxy-1,2,3,6-tetrahydrophthalimido)butanoic acid (125.6 mg, 0.5 mmol, protected 4-maleidobutyric acid[10]), following the experimental conditions outlined for monomer A_3. The ensuing A_2B monomer was obtained as a dark brown liquid in 85% yield.

ν_{max}/cm^{-1}: 3118 (furan CH stretching), 2923 (asCH_2), 2852 (sCH_2), 1769, 1733 and 1699 (C=O stretching), 1599, 1503 and 1399 (furan ring stretching), 1245, 1160 and 1069 (furan in-plane CH deformation), 1151 (C–O stretching), 1009 (ring breathing), 914, 879 and 734 (furan C–H out-of-plane deformation), 598 (ring deformation).

δ_H (300 MHz, TCE-d_2, Me_4Si): 7.4 (2H, dd, J = 1.7, 0.7 Hz, 2-furan 5-H), 6.5 (2H, s, =C*H*CHCHCO), 6.3 (2H, dd, J = 3.1, 1.9 Hz, 2-furan 4-H), 6.2 (2H, d, J = 3.2 Hz, 2-furan 3-H), 5.3 (2H, s, =CHC*H*CHCO), 4.1 (2H, t, J = 6.8 Hz, OCH_2), 3.7 (4H, s, SCH_2–2-furan), 3.5 (2H, t, J = 6.9 Hz, NCH_2CH_2), 2.9 (2H, s, =CHCHC*H*CO), 2.5 (6H, t, J = 7.5 Hz, SCH_2CH_2(CH_2)$_n$), 2.3 (6H, t, J = 7.5 Hz, CH_2C(=O)), 1.9 (2H, m, NCH_2CH_2), 1.7 (4H, m, CH_2CH_2C(=O)), 1.6 (2H, m, OCH_2CH_2), 1.5 (6H, m, SCH_2CH_2(CH_2)$_n$), 1.3 (38H, m, aliphatic CH_2).

δ_C (75 MHz, TCE-d_2, Me_4Si): 176.1 (C=$O_{maleimide}$), 172.7 (C=O_{ester}), 151.7 (2-furan C-2), 141.9 (2-furan C-5), 136.4 (=*C*HCHCHCO), 110.4 (2-furan C-4), 107.3 (2-furan C-3), 80.8 (=CH*C*HCHCO), 76.9 (CH_2CH(–O)CH_2S), 66.6 (*C*H_2CH(–O)CH_2S), 64.7 (O*C*H_2), 47.2 (=CHCH*C*HCO), 39.9 (N*C*H_2CH_2), 37.9 (CH_2CH(–O)*C*H_2S), 33.8 (S*C*H_2CH_2(CH_2)$_n$), 33.1

($CH_2C(=O)$), 31.7 (SCH_2), 31.2 ($NCH_2CH_2CH_2$), 30.9 ($SCH_2CH_2(CH_2)_n$), 29.3-28.8 (aliphatic CH_2), 28.1 (OCH_2CH_2), 25.8 ($OCH_2CH_2CH_2$), 24.9 ($CH_2CH_2C(=O)$), 22.7 (NCH_2CH_2).

4.7 Synthesis of protected AB_2 monomer

The protected AB_2 monomer was synthesized in three steps also making use of classical chemical condensations in conjunction with the thiol-ene coupling.

Step 1: a solution of UDA (1.8 g, 10.0 mmol), furfuryl alcohol (981.0 mg, 10.0 mmol), DCC (2.0 g, 10.0mmol) and DMPA (127.2 mg, 1.0 mmol) in dry dichloromethane (50 mL) was prepared and left overnight at room temperature under nitrogen. The subsequent workup was the same as that detailed above for monomer A_3.

Step 2: this ene (8.0 mmol) was reacted with 1-thioglycerol (865.3 mg, 8.0 mmol) using I651 (20.5 mg, 0.08 mmol) as photoinitiator and the irradiation protocol described for A_3.

Step 3: the ensuing intermediate (5.0 mmol) was esterified with 4-(3,6-epoxy-1,2,3,6-tetrahydrophthalimido)butanoic acid (2.5 g, 10.0 mmol, protected 4-maleidobutyric acid[10]) in the presence of DCC (2.0 g, 10.0 mmol) and DMAP (127.2 mg, 1.0 mmol), adopting again the procedure given above for monomer A_3. The ensuing AB_2 monomer was obtained as a brownish liquid in 89% yield.

ν_{max}/cm^{-1}: 3117 (furan CH stretching), 2926 (asCH_2), 2853 (sCH_2), 1769, 1733 and 1693 (C=O stretching), 1601, 1503 and 1398 (furan ring stretching), 1245, 1161 and 1095 (furan in-plane CH deformation), 1152 (C–O stretching), 1018 (ring breathing), 918, 876 and 730 (furan C–H out-of-plane deformation), 599 (ring deformation).

δ_H (300 MHz, TCE-d_2, Me_4Si): 7.4 (1H, dd, J = 1.6, 0.8 Hz, 2-furan 5-H), 6.5 (4H, s, =C*H*CHCHCO), 6.4 (1H, d, J = 3.4 Hz, 2-furan 3-H), 6.3 (1H, dd, J = 3.2, 1.8 Hz, 2-furan 4-H), 5.3 (4H, s, =CHC*H*CHCO), 5.0 (2H, s, OCH_2–2-furan), 3.5 (4H, m, NCH_2CH_2), 2.9 (4H, s, =CHCHC*H*CO), 2.5 (2H, t, J = 7.3 Hz, $SCH_2CH_2(CH_2)_n$), 2.3 (6H, t, J = 7.5 Hz, $CH_2C(=O)$), 1.9 (4H, m, NCH_2CH_2), 1.6 (2H, m, $CH_2CH_2C(=O)$), 1.5 (2H, m, $SCH_2CH_2(CH_2)_n$), 1.3 (12H, m, aliphatic CH_2).

δ_C (75 MHz, TCE-d_2, Me_4Si): 176.1 ($C{=}O_{maleimide}$), 173.4 ($C{=}O_{ester}$), 149.5 (2-furan C-2), 143.1 (2-furan C-5), 136.4 (=*C*HCHCHCO), 110.5 (2-furan C-4), 106.3 (2-furan C-3), 80.8 (=CH*C*HCHCO), 77.8 ($CH_2CH(–O)CH_2S$), 66.8 ($\mathit{C}H_2CH(–O)CH_2S$), 57.7 ($O\mathit{C}H_2$-2-furan), 47.2 (=CHCH*C*HCO), 39.9 ($N\mathit{C}H_2CH_2$), 37.8 ($CH_2CH(–O)\mathit{C}H_2S$), 33.7 ($S\mathit{C}H_2CH_2$), 32.6 ($\mathit{C}H_2C(=O)$), 30.9 ($SCH_2\mathit{C}H_2$), 29.4-28.7 (aliphatic $\mathit{C}H_2$), 24.8 ($\mathit{C}H_2CH_2C(=O)$), 22.6 ($NCH_2\mathit{C}H_2$).

4.8 Diels-Alder polymerizations

***A_2+B_3* and *A_3+B_2* systems** – The molar ratios used in this study together with the initial concentrations of the corresponding monomers are presented in Table 11. In the first system (A_2+B_3), the concentration of the difuran monomer was kept constant in all experiments, while in the second (A_3+B_2), it was the concentration of the bismaleimide monomer that was the same in the three experiments.

Table 11. Molar ratio between B (maleimide) and A (furan) groups and the corresponding monomer concentration in a series of non-linear DA polymerizations.

Polymer	*r* (N_B/N_A)	[A_2] / mol dm^{-3}	[A_3] / mol dm^{-3}	[B_2] / mol dm^{-3}	[B_3] / mol dm^{-3}
P(A_2+B_3)_0.5	0.5	0.15	–	–	0.05
P(A_2+B_3)_0.75	0.75	0.15	–	–	0.075
P(A_2+B_3)_1.0	1.0	0.15	–	–	0.10
P(A_3+B_2)_0.5	0.5	–	0.20	0.15	–
P(A_3+B_2)_0.75	0.75	–	0.13	0.15	–
P(A_3+B_2)_1.0	1.0	–	0.10	0.15	–

A typical procedure applied to the use of UV spectroscopy follows: a fivefold dilution of the concentrations reported in Table 11 were prepared in TCE. Then, 0.5 mL of each complementary pair were placed in a 0.1 mm Suprasil cell, which was then left in the temperature-controlled spectrophotometer at 65 °C and UV spectra were taken at regular intervals.

A typical procedure applied to the use of ^{1}H NMR spectroscopy follows: the two complementary monomers were dissolved in 1.0 mL of TCE-d_2, placed in an NMR tube and the initial ^{1}H NMR spectrum taken instantly at room temperature. The tube was then kept in an oil bath at 65 °C and spectra taken at regular intervals. The ensuing polymers were isolated by precipitation into a large excess of petroleum ether, followed by filtration, dissolution in dichloromethane and solvent removal under reduced pressure. When an insoluble fraction was observed, the suspension was filtered and the residue washed with dichloromethane. The residue was dried under vacuum, while the filtrate was precipitated in petroleum ether, filtered and dried under vacuum.

A fraction of the ensuing polymers was dissolved in TCE (1.0 mL) and the retro-DA depolymerisation reactions were followed at 110 °C by UV and ^{1}H NMR spectroscopy.

A_2B and AB_2 systems – The protected monomers (0.1 mmol) were dissolved in 1 mL of TCE and the solution (0.1 M) brought to 110 °C while a gentle stream of nitrogen was bubbled through it for several hours to remove the furan generated by the retro-DA of the maleimide adduct. The ensuing unprotected A_2B or AB_2 monomers were then allowed to polymerize at 65 °C and the reaction followed by UV and ^{1}H NMR spectroscopy. Again, the depolymerisation of the DA polymers was carried out at 110 °C, followed by a 2nd DA polymerization at 65 °C. The polymers were precipitated in an excess of petroleum ether, filtered, dissolved in dichloromethane and vacuum dried.

4.9 Characterization methods

The FT-IR spectra were taken with a Perkin Elmer FT-IR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. Each spectrum was an average of 32 scans taken with 4 cm^{-1} resolution in the 500-4000 cm^{-1} range.

Electronic spectra were taken with a temperature-controlled Jasco V-560 spectrophotometer using 1 cm Hellma Suprasil cells equipped with 9.9 mm quartz spacer and a quartz-to-pyrex graded seal.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts (δ) were reported in parts per million (ppm), relative to the internal standard tetramethylsilane (TMS, δ=0.00 ppm).

The molecular weights and molecular weight distributions of the polymers were determined by size-exclusion chromatography (SEC) with a Varian PL-GPC 110 instrument, using *N,N*-dimethylformamide (DMF) as the mobile phase. Polystyrene standards were used for narrow standard calibration.

DSC thermograms were obtained with a Perkin Elmer Diamond DSC unit using aluminium pans under nitrogen with a heating rate of 10 °C/min in the temperature range of -80 to 80 °C.

5. REFERENCES

[1] C. Gao, D. Yan, Hyperbranched polymers: from synthesis to applications, *Progress in Polymer Science* **2004**, 29, 183-275.

[2] M. Seiler, Hyperbranched polymers: Phase behavior and new applications in the field of chemical engineering, *Fluid Phase Equilibria* **2006**, 241, 155-174.

[3] G. Tillet, B. Boutevin, B. Ameduri, Chemical reactions of polymer crosslinking and post-crosslinking at room and medium temperature, *Progress in Polymer Science* **2011**, 36, 191-217.

[4] D. Yan, C. Gao, H. Frey (Eds.), *Hyperbranched polymers: synthesis, properties and applications*, New Jersey, John Wiley & Sons, **2010**.

[5] G. Odian*, Principles of Polymerization*, 4th ed., New York, John Wiley & Sons, **2004**.

[6] F. Fringuelli, A. Taticchi, *The Diels-Alder Reaction: Selected Practical Methods*, West Sussex, John Wiley & Sons, **2002**.

[7] K. C. Nicolaou, S. A. Snyder, T. Montagnon, G. Vassilikogiannakis, The Diels–Alder Reaction in Total Synthesis, *Angewandte Chemie International Edition* **2002**, 41, 1668-1698.

[8] A. Gandini, The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis, *Progress in Polymer Science* **2012**, http://dx.doi.org/10.1016/ j.progpolymsci.2012.04.002

[9] C. Vilela, L. Cruciani, A. J. D. Silvestre, A. Gandini, A Double Click Strategy Applied to the Reversible Polymerization of Furan/Vegetable Oil Monomers, *Macromolecular Rapid Communications* **2011**, 32, 1319-1323.

[10] C. Vilela, L. Cruciani, A. J. D. Silvestre, A. Gandini, Reversible polymerization of novel monomers bearing furan and plant oil moieties: a double click exploitation of renewable resources, *RSC Advances* **2012**, 2, 2966-2974.

[11] J. R. McElhanon, D. R. Wheeler, Thermally responsive dendrons and dendrimers based on reversible furan-maleimide Diels-Alder adducts, *Organic Letters* **2001**, 3, 2681-2683.

[12] A. Gandini, D. Coelho, M. Gomes, B. Reis, A. J. D. Silvestre, Materials from renewable resources based on furan monomers and furan chemistry: work in progress, *Journal of Materials Chemistry* **2009**, 19, 8656-8664.

[13] X. Chen, M.A. Dam, K. Ono, A. Mal, H. Shen, S.R. Nutt, K. Sheran, F. Wudl, A thermally re-mendable cross-linked polymeric material, *Science* **2002**, 295, 1698-1702.

[14] X. Chen, F. Wudl, A.K. Mal, H. Shen, S. R. Nutt, New thermally remendable highly cross-linked polymeric materials, *Macromolecules* **2003**, 36, 1802-1807.

[15] Y. L. Liu, C. Y. Hsieh, Crosslinked epoxy materials exhibiting thermal remendability and removability from multifunctional maleimide and furan compounds, *Journal of Polymer Science Part A, Polymer Chemistry* **2006**, 44, 905-913.

[16] J. P. Swanson, S. Rozvadovsky, J. E. Seppala, N. E. Mackay, R. E. Jensen, P. J. Costanzo, Development of polymeric phase change materials on the basis of Diels–Alder chemistry, *Macromolecules* **2010**, 43, 6135-6141.

[17] A. R. Katritzky, J. M. Lagowski, Infrared absorption of heteroaromatic, five-membered, monocyclic nuclei. Part I. 2-Monosubstituted furans, *Journal of the Chemical Society* **1959**, 657-660.

[18] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Chapman and Hall, London, 3rd edn., **1975**, vol. 1.

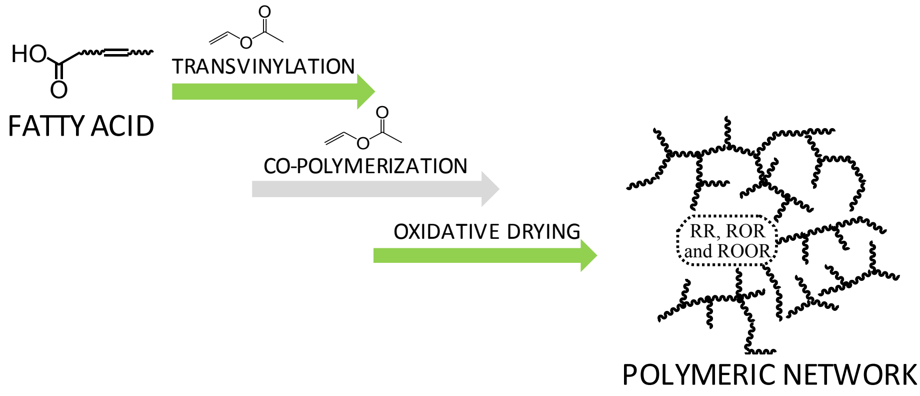
[19] H. K. Hall, R. Zbinden, Infrared Spectra and Strain in Cyclic Carbonyl Compounds, *Journal of the American Chemical Society* **1958**, 80, 6428-6432.

PART C

VEGETABLE OIL-BASED CHAIN-GROWTH POLYMERS

Chapter VI

POLYMERS AND COPOLYMERS FROM FATTY ACID VINYL ESTERS



Fatty acid vinyl ester (FAVE) monomers were prepared via transition-metal catalyzed transvinylation of fatty acids with vinyl acetate, followed by their free radical (co)polymerization, which yielded viscous oligomeric materials that responded adequately to atmospheric drying.

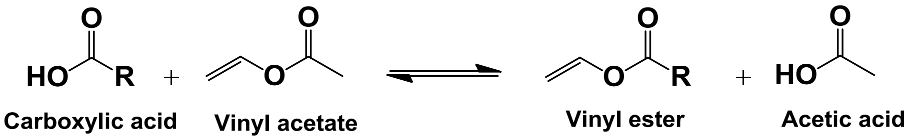
Parts of this chapter have been published:

C. Vilela, R. Rua, A. J. D. Silvestre, A. Gandini, Polymers and Copolymers from Fatty Acid-based Monomers, *Industrial Crops and Products* **2010**, 32, 97-104.

1. INTRODUCTION

Fatty acids derived from vegetable oils are among the most promising candidates for the preparation of polymeric materials based on renewable resources, but the rather low reactivity of their unsaturated aliphatic chains make them ineffective monomers when used as such. This drawback can be overcome by functionalizing them with polymerizable moieties, e.g., vinyl groups introduced by transvinylation.[1,2]

The transvinylation or vinyl interchange (Scheme 40) is a stereospecific reaction[3] in which the vinyl group is transferred between two acidic moieties (e.g. between vinyl acetate and a carboxylic acid).[4]



Scheme 40. Transvinylation reaction of a carboxylic acid with vinyl acetate.

Originally, this equilibrium reaction was carried out in the presence of mercury salts,[5,6] in combination with strong acid promoters such as sulphuric acid. However, the use of mercury salts as transvinylation catalysts is banned today due to their toxicity and volatility. Other catalytic systems that are used to promote transvinylation include palladium catalysts,[7,8] ruthenium[9] and iridium complexes,[2] among others. The transvinylation of fatty acids with the low cost and commercially available vinyl acetate (VAc) is a known reaction[5,10,11] that yields fatty acid vinyl ester (FAVE) monomers that subsequently can be transformed into a variety of end use polymeric products, e.g. coating materials,[12] softening and plasticizing agents,[13] and viscosity improvers for lubricant oils.[14]

Whereas the saturated FAVEs, namely vinyl palmitate and vinyl stearate, behave in a conventional fashion in the polymerization process, unsaturated homologues, like vinyl oleate and vinyl linoleate, display a reactivity that decreases with an increasing number of double bonds,[10,15] due to the fact that these unsaturations promote chain transfer reactions.[13] FAVE monomers, such as vinyl palmitate, vinyl stearate, and vinyl oleate, have already been copolymerized with a variety of monomers of low molecular weight, like for instance vinyl chloride,[16] vinyl acetate,[14,17] butadiene,[18] maleic anhydride,[19] among others. Copolymers containing FAVEs are valuable components with potential application as adhesives,[20] chewing gum bases,[21] synthetic rubbers,[18] oil additives[22] and organic surface coatings.[13]

The suitability of FAVE monomers to be applied as softening and plasticizing agents,[13] and their ability to copolymerize with low molecular weight monomers, e.g. VAc,[17] make them interesting candidates for paint formulations based on vinylic resins. Polyvinyl acetate, P(VAc), is by far the most important vinylic resin, but this homopolymer has the disadvantage of being slightly too hard and brittle to form a continuous film.[23] One approach to circumvent this would be to copolymerize VAc with softer monomers, like highly branched vinyl esters, in a process known as "internal" plasticization.[23] The amount of vinyl esters should not exceed 30% by weight of the monomers used in the polymerization unless greater softness is desired.[18]

In this context, the present chapter deals with the valorisation of vegetable oils by appropriate chemical modifications aimed at improving their applications as coating materials. It first called upon the synthesis of FAVE monomers by the transvinylation of two fatty acids with VAc using a safe and effective catalyst. These monomers were then homo- and co-polymerized with VAc by conventional free radical processes and the ensuing materials fully characterized and tested in oxidative drying. The fact that this investigation was undertaken with model fatty acids, allowed the gathering of experimental data needed for the future evolution to complex combinations of commercially available fatty acid mixtures, like for example Nouracid® SE305 (soya fatty acids) and Nouracid® HE305 (conjugated sunflower oil fatty acids) both supplied by Oleon.[24]

2. RESULTS AND DISCUSSION

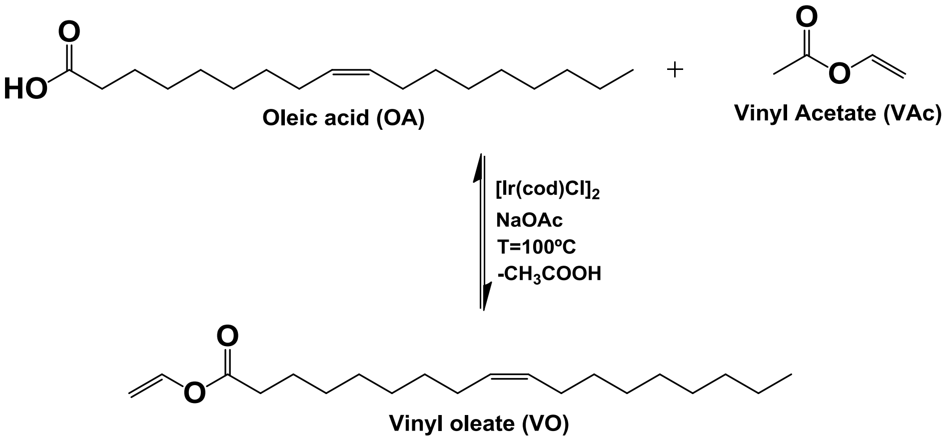
2.1 Synthesis and characterization of FAVE monomers

Oleic and linoleic acids were used as precursors in the synthesis of two fatty acid vinyl ester monomers through the one-pot transvinylation reaction with vinyl acetate (VAc). Even though the transvinylation of fatty acids has already been reported[5,10,11], a rapid screening with different catalytic systems, namely ruthenium on carbon, ruthenium on alumina, ruthenium (III) acetylacetonate, palladium (II) acetate, palladium (II) acetate/1,10-phenanthroline, and bis(1,5-cyclooctadiene)-diiridium(I) dichloride, was performed. The higher conversions reported were attained with the iridium complex ($[Ir(cod)Cl]_2$), a safe and effective catalyst, whose efficiency was previously proved for conventional carboxylic acids.[2]

2.1.1 Monomer vinyl oleate (VO)

Oleic acid (OA) was functionalized by transvinylation with vinyl acetate as shown in Scheme 41. The structure of the ensuing vinyl oleate (VO) was confirmed by FTIR, ^{1}H and ^{13}C NMR spectroscopy and by gas chromatography-mass spectrometry (GC-MS).

The functionalization of OA was first confirmed by FTIR (Figure 36) through the disappearance of the absorption bands of carboxyl groups at about 2674 cm^{-1} (OH stretching), 1706 cm^{-1} (C=O vibration), 1412 cm^{-1} (C–O stretching), 1286 cm^{-1} (in plane OH deformation) and 934 cm^{-1} (OH out-of-plane deformation), together with the corresponding emergence of the characteristic absorption bands of vinyl ester group around 1755 cm^{-1} (C=O stretching), 1645 cm^{-1} (C=C stretching), 1140 cm^{-1} (C–O stretching) and 948 cm^{-1} (CH out-of-plane deformation).[25]



Scheme 41. Transition-metal catalyzed transvinylation of oleic acid with vinyl acetate.

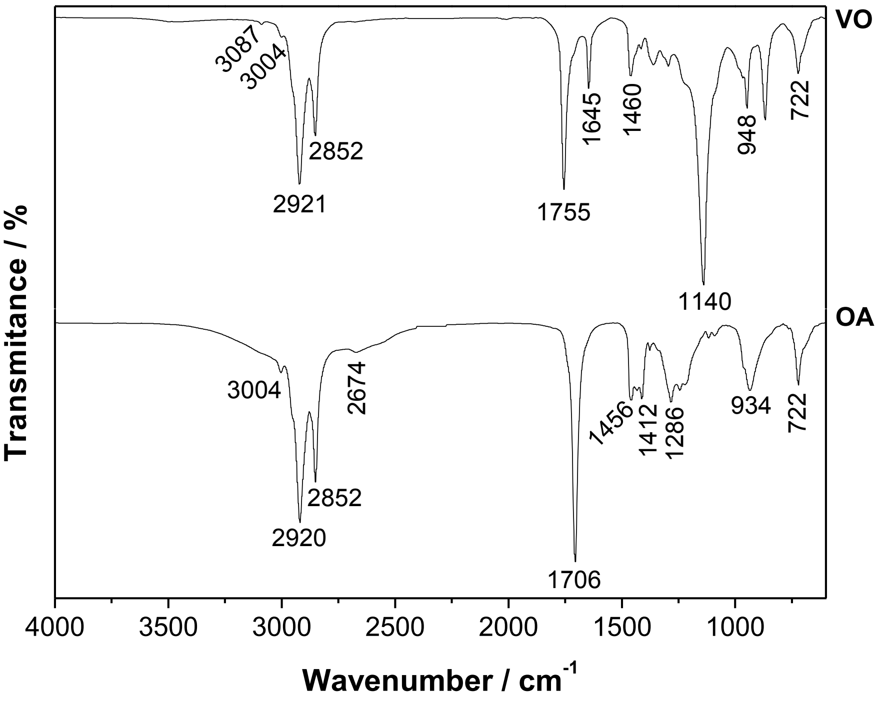


Figure 36. FTIR spectra of OA and VO.

The ^1H NMR spectrum of VO, when compared with that of its corresponding fatty acid precursor, showed the emergence of new resonances typical of the vinyl ester protons at δ 4.5, 4.9 and 7.3 ppm, which gave additional evidence of the occurrence of the transvinylation reaction, apart from the unchanged features related to the unsaturated aliphatic chain. Figure 37 shows the ^1H-NMR spectrum from vinyl oleate with peaks at δ 0.9 ppm (multiplet from terminal methyl group), δ 1.3-1.4 ppm (resonance from methylenic groups in fatty acid chain), δ 1.6 ppm (multiplet from methylenic group in δ position with respect to carbonylic group), δ 2.0 ppm (multiplet from methylenic group in both sides of olefinic hydrogen), δ 2.4 ppm (triplet from methylenic group in δ position with respect to carbonylic group), δ 4.5 and 4.9 ppm (double doublet from methylenic proton of vinyl ester group), and δ 7.3 ppm (double doublet from methynic proton of vinyl ester group). It is important to emphasize that the peaks assigned to the double bonds of the fatty acid chain (δ 5.3 ppm) were preserved, which indicates that they were not involved in side reactions during the transvinylation reaction.

The ^{13}C NMR analysis of VO was in agreement with the structure proposed by ^1H NMR. The corresponding spectrum (Figure 37), in addition to the unchanged resonances related to the unsaturated aliphatic chain (δ 14.1, 22.7, 24.5, 27.2, 29.0-29.7, 31.8, 33.9 and 130.0 ppm), showed a new group of signals resonating at δ 97.4 ppm and δ 141.2 ppm, which were readily identified as methylenic and methinic carbons of the vinyl ester group, respectively.

The functionalization of oleic acid was further confirmed by GC-MS. The mass spectrum of vinyl oleate was characterized by the molecular ion (M) at m/z=308, the base peak at m/z=55, and by an intense fragment at m/z=265 attributed to $[M\text{-}OC_2H_3]^+$. The latter fragment represents the loss of the vinyl-oxy group, which confirms the presence of a vinyl ester moiety. The long series of related ions at m/z=41, 55, 69, 83, 97, 111, 125, etc. are characteristic of the fragmentation of the aliphatic chain of the fatty acid of general formula $[C_nH_{2n-1}]^+$.[26]

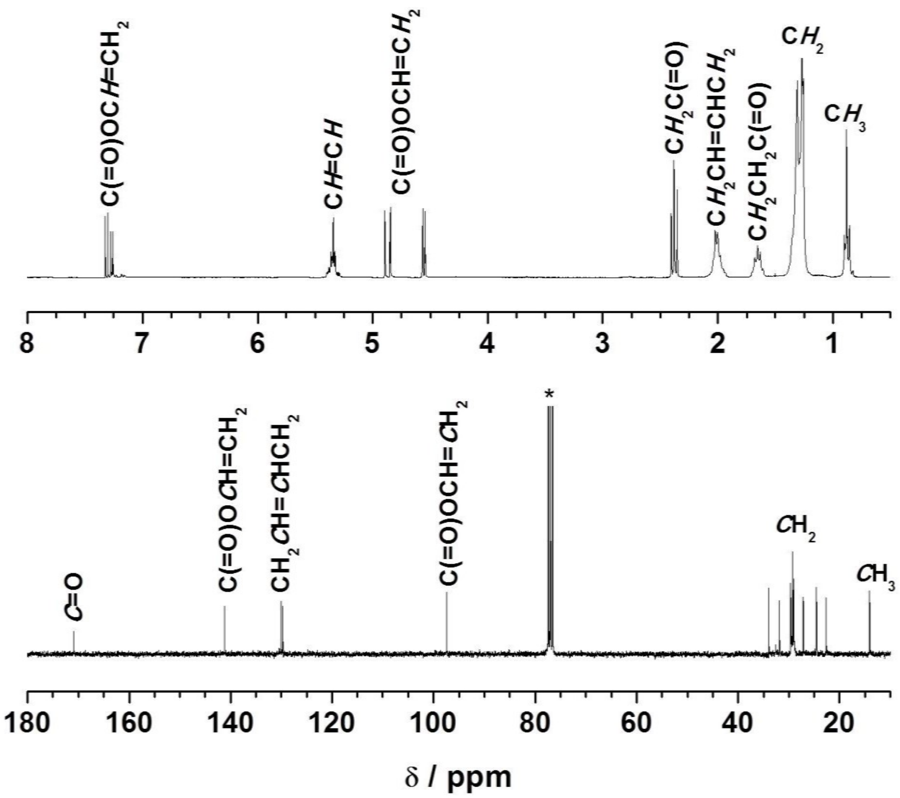


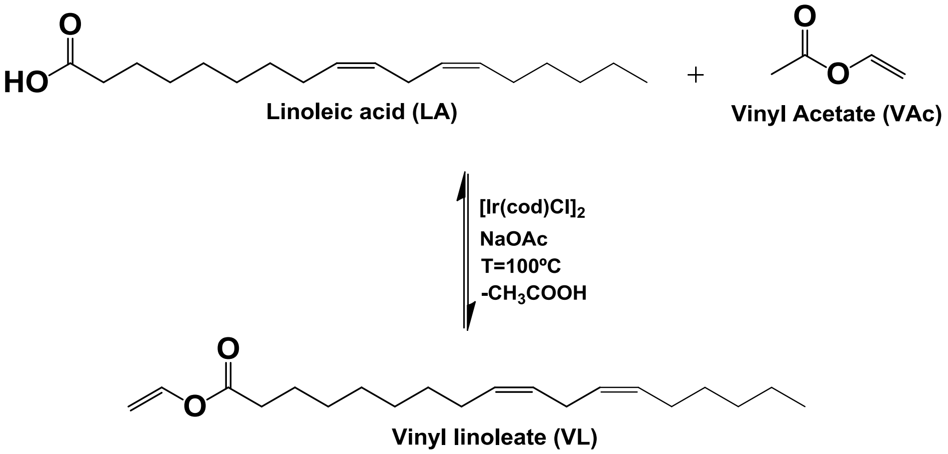
Figure 37. ^{1}H and ^{13}C NMR spectra of VO in *$CDCl_3$ with peak assignments.

2.1.2 Monomer vinyl linoleate (VL)

Scheme 42 depicts the transition-metal catalyzed transvinylation reaction of LA with VAc leading to vinyl linoleate (VL). The changes in the FTIR, ^{1}H and ^{13}C NMR, and EI-MS spectra associated with the transformation of LA into VL showed that the transvinylation took place equally well.

The FTIR spectrum of VL (Figure 38) was consistent with the expected structure, through the presence of all the relevant peaks (1754, 1645, 1138 and 948 cm^{-1}) and the absence of the C=O and OH bands of the carboxylic moiety. This was further corroborated by both its ^{1}H and ^{13}C NMR spectra (Figure 39). The most relevant features in the ^{1}H and ^{13}C NMR spectra included, among others, the resonances of the vinyl ester protons and carbons at, respectively, δ 4.5, 4.9, 7.3 ppm and δ 141.2, 97.4 ppm.

The EI-MS spectrum of VL was characterized by the molecular ion (M) at m/z=306, the base peak at m/z=67, and the fragment at m/z=263 attributed to the loss of the vinyl-oxy group ($[M\text{-}OC_2H_3]^+$).



Scheme 42. Transition-metal catalyzed transvinylation of linoleic acid with vinyl acetate.

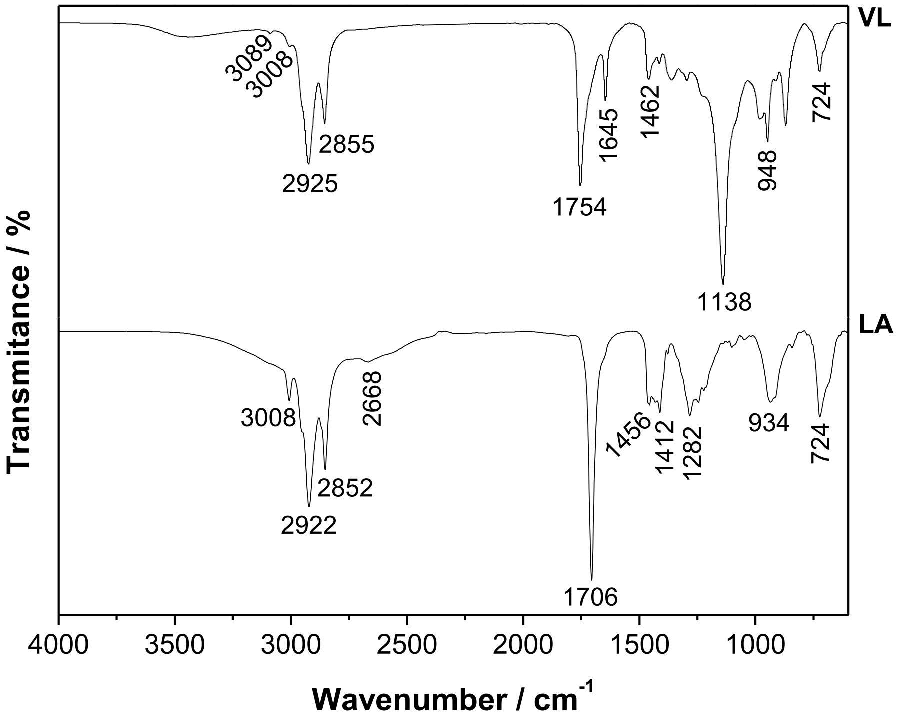


Figure 38. FTIR spectra of LA and VL.

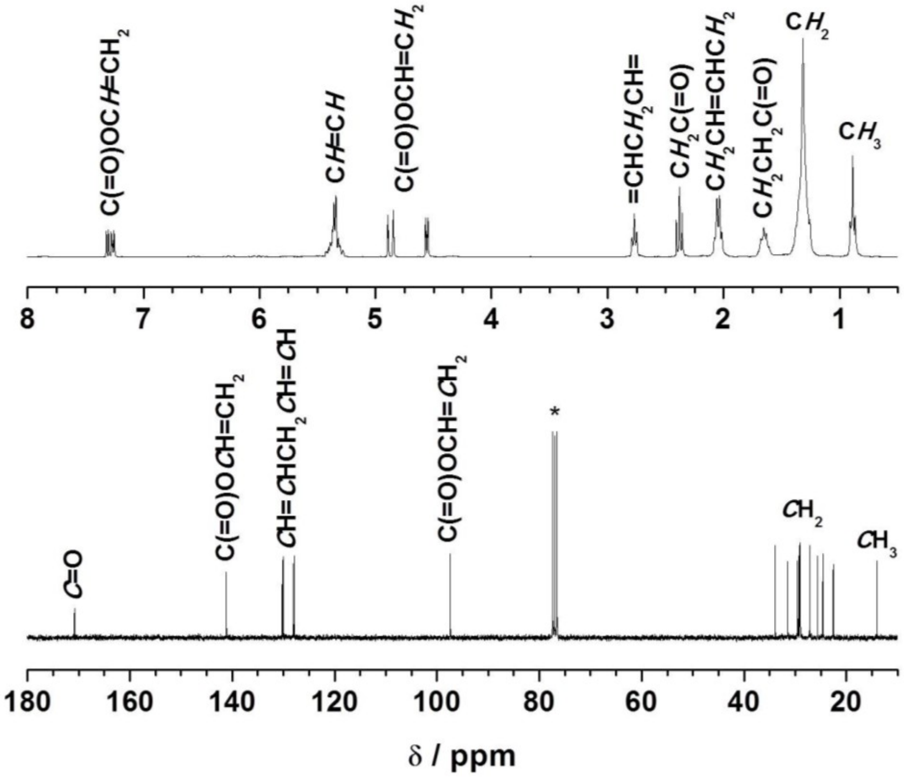


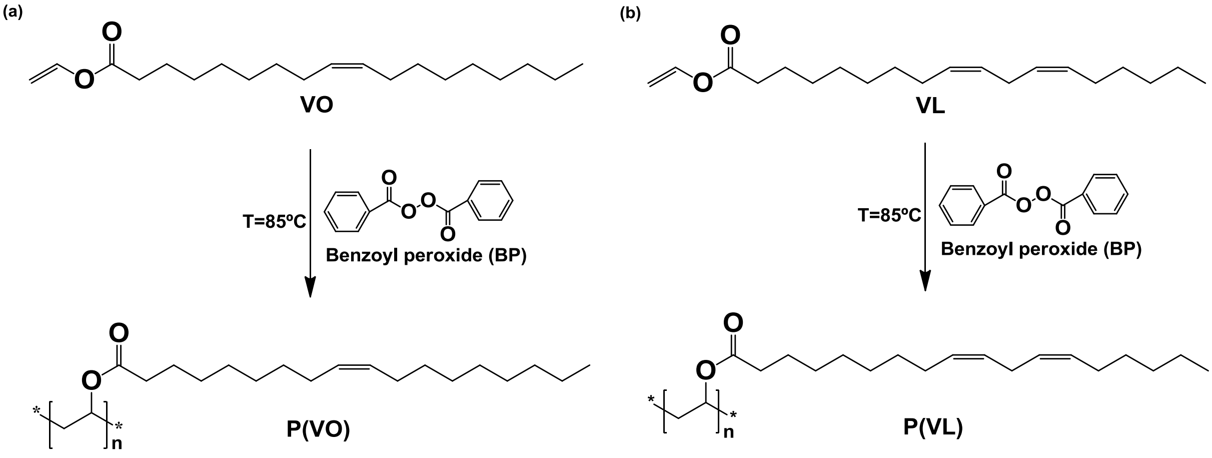
Figure 39. ^{1}H and ^{13}C NMR spectra of VL in *$CDCl_3$ with peak assignments.

In conclusion, this transvinylation procedure, calling upon the use of an iridium-based catalyst and previously applied to conventional carboxylic acids,[2] was shown here to work equally well with long-chain fatty acids.

2.2 Homopolymerization of the FAVE monomers

The free radical homopolymerization of fatty acid-vinyl ester monomers were carried out using vinyl oleate (VO) or vinyl linoleate (VL) as monomers and benzoyl peroxide (BP) as the initiator (Scheme 43). The ensuing homopolymers were characterized by ^{1}H and ^{13}C NMR, SEC and DSC.

The P(VO) homopolymer was obtained as a clear viscous material in 50% yield, whereas P(VL) gave considerably lower yields (< 10%), confirming the reluctance of this dienoic fatty acid ester to undergo homopolymerization.[10,13]



Scheme 43. Free radical homopolymerization of (a) VO and (b) VL.

The ^{1}H NMR analysis (Figure 40) clearly confirmed the homopolymerization of VO by the disappearance/reduction of intensity of the signals assigned to the vinyl proton resonances (δ ~ 4.5, 4.8 and 7.3 ppm) and by the appearance of new resonances characteristic of CH and CH_2 groups (around δ 4.1 and 2.2 ppm, respectively) of the polymer backbone. The ^{13}C NMR analysis of P(VO) was also in tune with its expected regular vinylic structure with the appearance of novel peaks at around δ 67-68 and 39-40 ppm, assigned to CH and CH_2 groups of the polymer backbone.

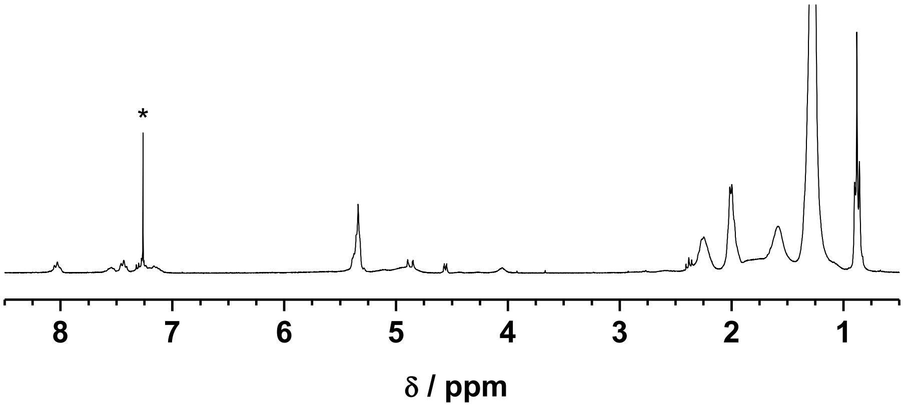


Figure 40. ^{1}H and ^{13}C-NMR spectra of P(VO) in *$CDCl_3$.

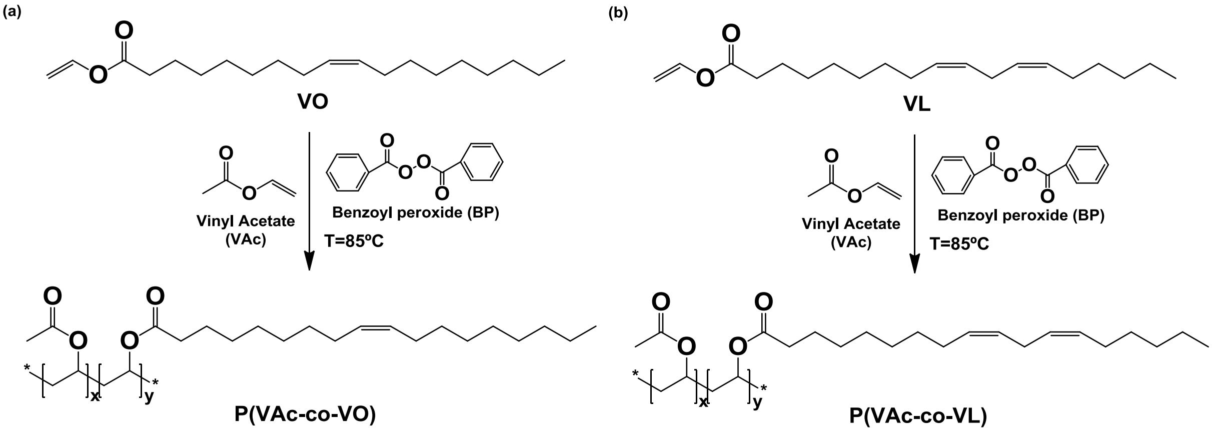
The ^{1}H and ^{13}C NMR spectra of P(VL), a moderately viscous product, confirmed the reluctance of vinyl linoleate to undergo radical homopolymerization, since it did not bear clear-cut resonances characteristic of polymer backbone CH and CH_2 groups, while still displaying those assigned to the vinyl group. This evidence, together with the low polymer yields and the actual consistency of these products, suggest that the VO and VL monomers were transformed into materials of low degree of polymerization (M_n values lower than 1.0 kDa; DP ≈ 3), probably through both vinyl and chain unsaturation radical couplings.

In the ^{1}H NMR spectra of both homopolymers, resonances were also clearly visible around δ 7.1-7.5 and 8.0 ppm (as illustrated in Figure 40 for P(VO)), arising from the initiator fragments (primary radicals), *viz*. Ph–(fragmentation and loss of CO_2) and Ph–(C=O)–O (initiator fragment as such), respectively, present in similar amounts. The detection of these signals as end-groups is associated with the low DP of both homopolymers, which suggests that chain transfer predominated in both processes.

The glass transition temperature (T_g) of the two FAVE homopolymers differed considerably, in tune with the extent of unsaturation of the lateral aliphatic chains, *viz*. an increase in segmental mobility as this parameter increases. The decrease from -15 to -50 °C for PVO and PVL, respectively, reflects this feature in a dramatic way.

2.3 Copolymerization of VAc with FAVE monomers

Vinyl acetate (VAc) was copolymerized with VO or with VL (Scheme 44) at various comonomer ratios and with different radical initiator concentrations (Table 12). Additionally, VO was copolymerized with VL in order to confirm its reluctance to polymerize. The ensuing VAc copolymers were mostly colourless and sticky materials obtained in average isolated yields of 40%, while in the case of P(VO-*co*-VL) a white solid was obtained in 20% yield. All these copolymers were thoroughly characterized, as detailed below.



Scheme 44. Free radical copolymerization of VAc with: (a) VO and (b) VL.

Table 12. Experimental conditions used for the preparation of the different copolymers.

Sample ID	VAc / mol %	VO / mol %	VL / mol %	BP / mol %
P(VAc-*co*-VO)_1	90	10	–	6
P(VAc-*co*-VO)_2	90	10	–	10
P(VAc-*co*-VL)_1	85	–	15	10
P(VAc-*co*-VL)_2	90	–	10	6
P(VAc-*co*-VL)_3	90	–	10	10
P(VO-*co*-VL)	–	50	50	10
P(VAc-*co*-VO-*co*-VL)	90	5	5	10

2.3.1 Infrared Spectroscopy

The analysis of the FTIR spectra of the copolymers was a straightforward way to verify the occurrence of the copolymerization reaction as illustrated in the example of P(VAc-*co*-VL)_1 shown in Figure 41, where the characteristic peaks of the vinylic group, at around 3090 cm^{-1} (CH stretching), 1645 cm^{-1} (C=C stretching), 948 cm^{-1} (CH out-of-plane deformation) and 869 cm^{-1} (CH_2 out-of-plane deformation), disappeared. Additionally, the absorption bands of the vinyl ester groups at 1754 cm^{-1} (C=O stretching) and 1138 cm^{-1} (C–O stretching)[25] also disappeared to be replaced by new peaks characteristic of aliphatic ester groups that emerged at 1732 (C=O stretching vibrations) and 1230 cm^{-1} (C–O stretching vibrations). The fact that the absorption bands of the linoleic aliphatic chain at 3008 cm^{-1} (unsaturated C–H stretching), 2924 and 2855 cm^{-1} (saturated CH_2 stretching), 1435 (H bending of CH_2 and CH_3 groups), and 713 cm^{-1} (skeletal vibration of $-(CH_2)_n-$) remained unaltered after the copolymerization, was a clear indication of their lack of reactivity in the present context, i.e. the propagation reaction involving VL only took place through the vinyl moiety.

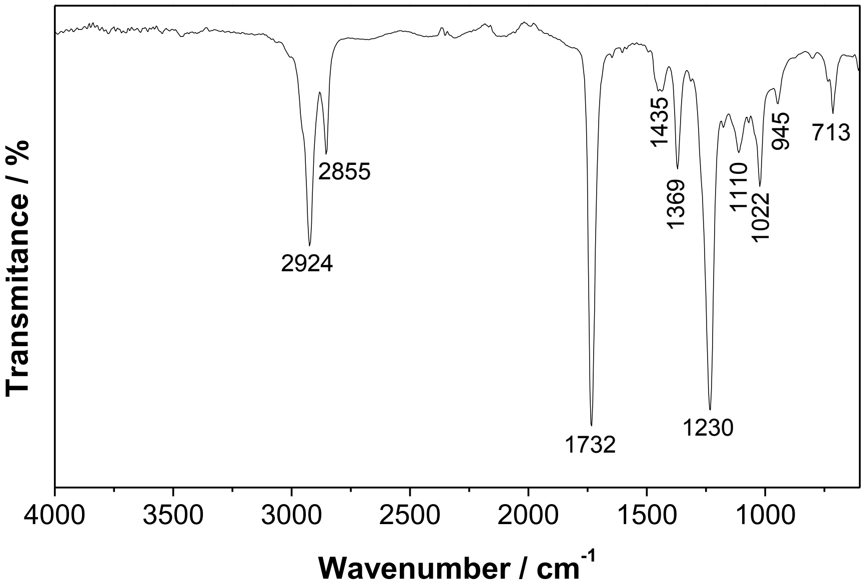


Figure 41. FTIR spectrum of P(VAc-*co*-VL)_1 (See Table 12 for copolymer identification).

2.3.2 Nuclear Magnetic Resonance Spectroscopy

In the ^1H NMR spectra of the copolymers, the disappearance of the resonances assigned to the vinyl protons (δ 4.5, 4.8 and 7.3 ppm) and the emergence of new resonances characteristic of CH (δ ~4.8 ppm) and CH_2 (δ ~1.8 ppm) groups of the polymer backbone, gave a clear-cut confirmation of the involvement of both monomers in chain propagation.

As an example, Figure 42 shows the ^1H NMR spectrum of P(VAc-*co*-VO)_2 and the corresponding peak assignments. The main features here were (i) the resonances assigned to the VO chain at δ 0.9 ppm (CH_3), 1.3 ppm (aliphatic CH_2), 1.6 ppm ($CH_2CH_2C(=O)$), 2.2 ppm ($CH_2CH=CHCH_2$), 2.4 ppm ($CH_2C(=O)$) and 5.3 ppm ($CH=CH$); (ii) the resonance of the acetate group at δ 2.0 ppm ($CH_3C(=O)$); (iii) the absence of the resonances of the vinyl group at δ 4.5, 4.8 and 7.3 ppm, and (iv) the new resonances assigned to the methine (δ ~4.8 ppm) and methylene (δ ~1.8 ppm) protons of the polymer backbone. It is worth mentioning that the presence of the resonances assigned to the fatty acid chain double bonds at δ 5.3 ppm with their expected intensity, indicates that these double bonds were preserved during the radical copolymerization, i.e. that they did not intervene in the propagation reactions. The above analysis reflects the spectra of all other copolymers in terms of their basic features.

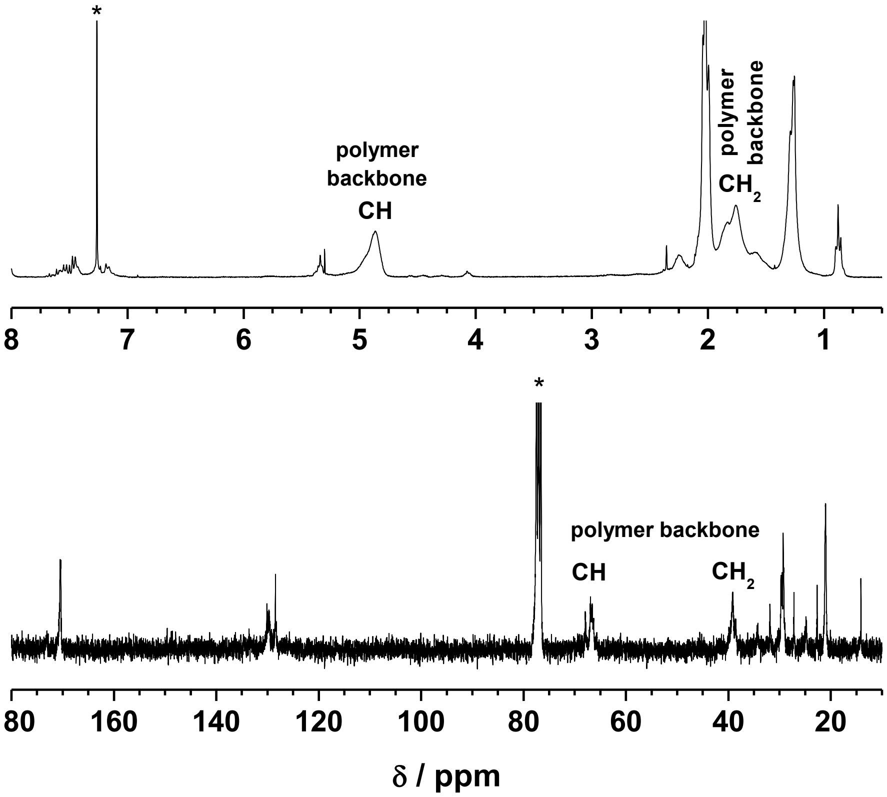


Figure 42. ^{1}H and ^{13}C NMR spectra of P(VAc-*co*-VO)_2 in *$CDCl_3$ (See Table 12 for copolymer identification).

The ^{13}C NMR spectra of all the copolymers also confirmed the occurrence of the copolymerization by the appearance of the resonances of the methine and methylene carbons of the polymer backbone at δ 67-68 and 39-40 ppm, respectively, and the concurrent disappearance of the vinylic carbons of the vinyl ester group (δ 97 and 141 ppm) of the starting monomers. As an example, Figure 42 shows the ^{13}C NMR spectrum of P(VAc-*co*-VO)_2, with peaks at δ 14.1 ppm ($\mathit{C}H_3$), 21.0 ppm ($\mathit{C}H_3C(=O)$), 22.7 ppm ($\mathit{C}H_2CH_3$), 24.8 ppm ($\mathit{C}H_2CH_2C(=O)$), 27.2 ppm ($\mathit{C}H_2CH{=}CH\mathit{C}H_2$), 29.2-29.7 ppm (aliphatic $\mathit{C}H_2$), 31.9 ppm ($\mathit{C}H_2CH_2CH_3$), 34.2 ppm ($\mathit{C}H_2C(=O)$, 39.1 ppm ($\mathit{C}H_2$ of the polymer backbone), 67.9 ppm (*C*H of the polymer backbone), 128.4-130.1 ppm ($CH_2\mathit{C}H{=}\mathit{C}HCH_2$) and 170.5 ppm (*C*=O). This pattern was also observed for all the other copolymers.

The copolymer compositions were assessed based on the comparison of the intensities of the ^{1}H NMR resonances relative to the CH_3 protons of the VAc monomer units (δ ~2.0 ppm) and those belonging to the CH_3 terminal protons of VO or VL monomer units (δ =0.8-0.9 ppm).

In the case of the P(VO-*co*-VL) copolymer, the relative proportion of the monomers was determined by the relative peak integration of the two allylic protons of VL units (δ ~2.7 ppm) and the six olefinic protons of the aliphatic chain of both VO and VL units (δ ~5.3 ppm).

The ensuing compositions, shown in Table 13, were on the whole not very different from the corresponding monomer feed ratios (Table 12). This observation is in tune with two different considerations, one related to the electronic structure of the polymerizing moiety and the other to steric factors. Hence, on the one hand, the three monomers belong to the same vinyl ester family and are therefore expected to display the same reactivity. On the other hand, the proportion of VAc in the monomer feed was chosen purposely to be systematically much higher than that of the fatty acid counterpart in order to minimize any steric problem associated with the incorporation of two or more successive units of the latter. These problems were indeed encountered in the homopolymerization reactions of both VO and VL.

Table 13. Monomer mole fraction of the synthesized copolymers determined by ^{1}H NMR.

Copolymer*	**Mole fraction / mol %**		
	VAc	**VO**	**VL**
P(VAc-*co*-VO)_1	97	3	–
P(VAc-*co*-VO)_2	90	10	–
P(VAc-*co*-VL)_1	83	–	17
P(VAc-*co*-VL)_2	87	–	13
P(VAc-*co*-VL)_3	87	–	13
P(VO-*co*-VL)	–	55	45
P(VAc-*co*-VO-*co*-VL)	95	3	2

*See Table 12 for copolymer identification

2.3.3 Size exclusion Chromatography

The weight-average molecular weight (M_w), number-average molecular weights (M_n) and polydispersity index (PDI) values of the copolymers are given in Table 14. All SEC traces had a similar shape and exhibited a single broad peak, as shown in Figure 43 for P(VAc-*co*-VO)_1 and P(VAc-*co*-VO)_2, with M_n ranging from 1.2 to 3.0 kDa and PDI between 1.7 and 2.7, (i.e. the typical values for a linear free radical copolymerization).

Table 14. Weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index (PDI) of the synthesized copolymers.

Copolymer*	**M_w / kDa**	**M_n / kDa**	**PDI**
P(VAc-*co*-VO)_1	5.2	2.6	2,0
P(VAc-*co*-VO)_2	8.2	3.0	2,7
P(VAc-*co*-VL)_1	4.3	2.3	1,9
P(VAc-*co*-VL)_2	2.3	1.4	1,7
P(VAc-*co*-VL)_3	2.5	1.2	2,1
P(VO-*co*-VL)	1.5	0.9	1,6
P(VAc-*co*-VO-*co*-VL)	7.6	2.2	3,5

*See Table 12 for copolymer identification

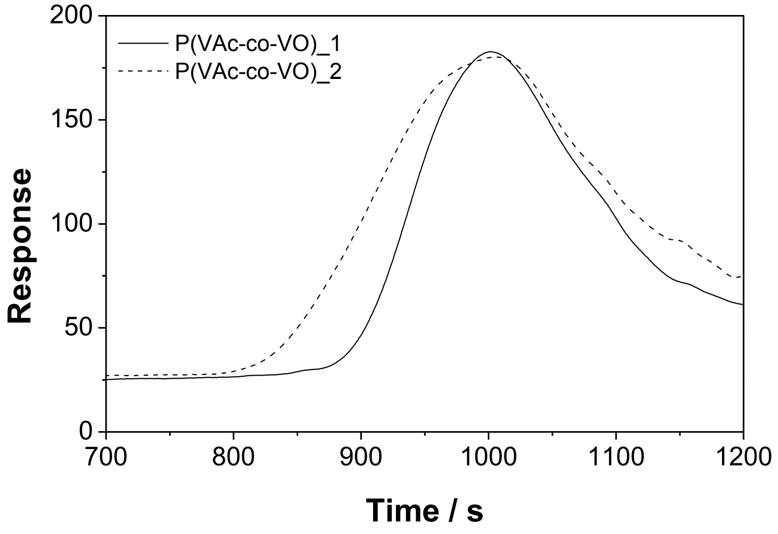


Figure 43. SEC curves of polymers P(VAc-*co*-VO)_1 and P(VAc-*co*-VO)_2 (See Table 12 for copolymer identification).

Interestingly, when the degree of unsaturation of the aliphatic chain of the FAVE increased, the molecular weight decreased from 3.0 kDa in P(VAc-*co*-VO)_2 to 1.2 kDa in P(VAc-*co*-VL)_3, respectively. This result clearly indicates that for a given monomer feed composition, the doubly unsaturated FAVE induced a slower polymerization rate and a higher incidence of transfer reactions, probably by trapping propagating macroradicals to give more stabilized species.

In another vein, the copolymerization of VO with VL confirmed the reluctance of these FAVE to propagate for steric reasons, since the reaction only reached a modest molecular weight of less than 1.0 kDa.

2.3.4 Thermogravimetric Analysis and Differential Scanning Calorimetry

The thermal properties of all the copolymers were assessed by TGA and DCS analysis. The thermal degradation profile of all VAc copolymers followed a two-step pathway with a maximum decomposition temperatures around 340-350 (T_{d1}) and 440-450 °C (T_{d2}), respectively, as typified in Figure 44 for P(VAc-*co*-VL)_2. These degradation processes are characteristic of poly(vinyl acetate), the main component of the copolymers, and correspond to the deacetylation of the polymer pendant ester groups (liberation of acetic acid) and depropagation of the polyolefin backbone, respectively.[27,28,29]

The quantitative figures in Table 15 suggest that the thermal degradation of VAc copolymers was only marginally influenced by the type/amount of FAVE monomers and the quantity of radical initiator. This is not surprising given the predominance of VAc units in all these materials.

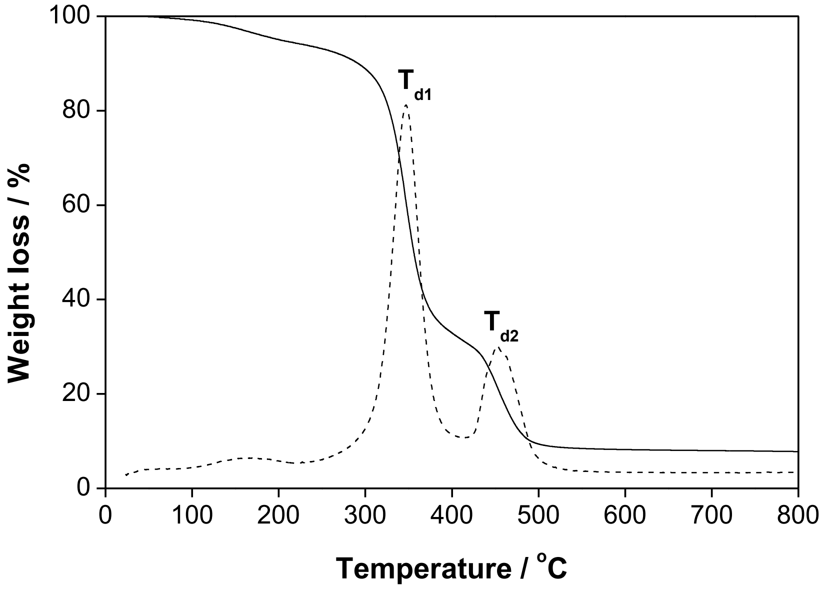


Figure 44. TGA curve of P(VAc-*co*-VL)_2: weight loss (solid curve) and its derivative (dotted curve).

Table 15. TGA and DSC data of the synthesized copolymers.

Copolymer*	T_{d1} / °C	T_{d2} / °C	Weight loss / %		T_g / °C
			T_{d1}	T_{d2}	
P(VAc-*co*-VO)_1	342	449	44	78	5
P(VAc-*co*-VO)_2	345	457	41	81	2
P(VAc-*co*-VL)_1	341	440	34	71	12
P(VAc-*co*-VL)_2	347	452	40	78	16
P(VAc-*co*-VL)_3	347	450	42	78	-5
P(VO-*co*-VL)	353	464	44	87	-35
P(VAc-*co*-VO-*co*-VL)	350	450	41	80	12

*See Table 12 for copolymer identification

In general, the DSC curves of all copolymers exhibited a single, broad glass transition (T_g), which is a characteristic of random copolymers, since they are homogeneous on a molecular scale.[30] A representative DSC curve of P(VAc-*co*-VO)_2 is given in Figure 45.

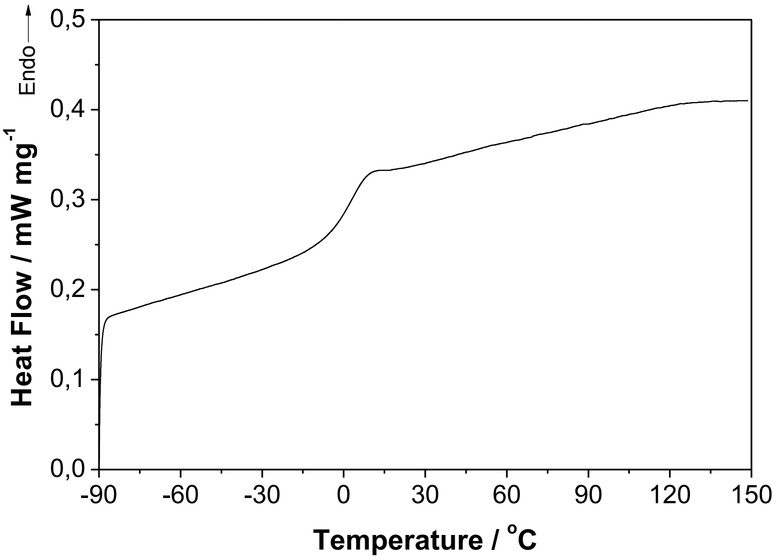


Figure 45. DSC curve of copolymer P(VAc-*co*-VO)_2 (See Table 12 for copolymer identification).

The T_g values listed in Table 15 show that the copolymers had T_gs intermediate between those of the corresponding homopolymers. For instance, P(VAc-*co*-VO)_2 had a T_g around 2°C, which lies between the T_g of poly(vinyl acetate) around 30 °C[31] and that of poly(vinyl oleate) at about -15 °C.

The comparison between the degree of unsaturation in the FAVE comonomers and T_g values of the respective copolymers, showed that a decrease in the former produced an increase in the latter (see Table 15), thus confirming the role of unsaturations already observed in the homopolymers. Hence, the FAVE monomers with lower T_g acted as internal plasticizers for poly(vinyl acetate) by decreasing its T_g. Accordingly, VAc copolymers with T_g from -5 to 16 °C can be prepared by changing the type/amount of the FAVE comonomer.

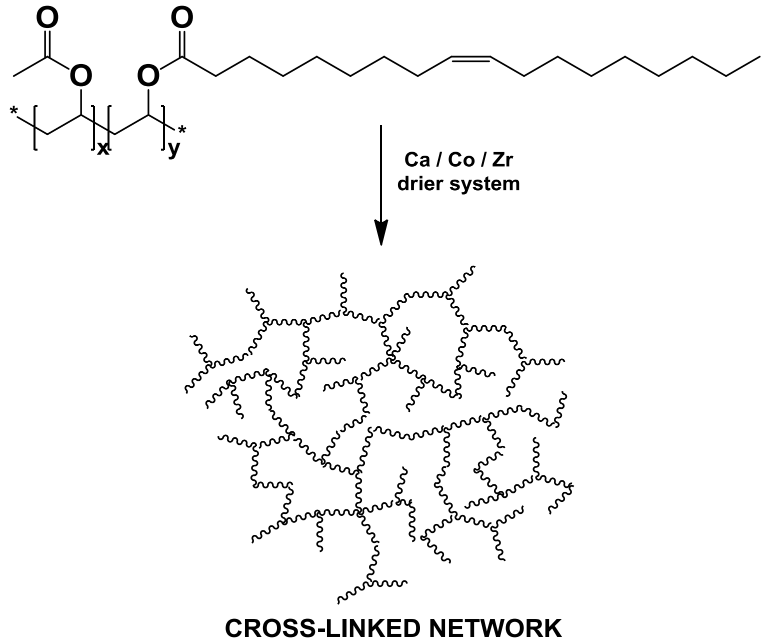
As anticipated for these low-DP materials, their glass transition temperature was also influenced by changes in molecular weight, with lower values of T_g for copolymers with lower M_n. Finally, the P(VO-*co*-VL) copolymer exhibited a T_g of -35 °C, in excellent agreement with the expected halfway value between the T_gs of the corresponding homopolymers.

2.4 Oxidative drying of VAc/FAVE copolymers

Fatty acids and its esters have been used as model compounds to study the cross-linking reactions that occur during the drying process of an alkyd paint.[32] In the drying process of coating formulations, two different stages are identified, namely (i) physical drying, during which the solvent evaporates and a film is formed, and (ii) chemical drying (also called oxidative drying) which takes place through an oxidative polymerization (see Chapter II, section 3.3.1) involving the double bonds of the unsaturated fatty acid chains and giving rise to a three-dimensional polymeric network. The latter stage is dramatically accelerated by the presence of driers, namely soluble metal carboxylates of cobalt, lead, copper and zirconium.[32] Frequently, these driers are used in combinations, e.g. Co/Zr/Ca, Co/Pb/Ca or Mn/Zr/Ca, in order to increase the drying efficiency.[32]

The copolymerization of FAVE monomers with VAc yielded copolymers that merit attention as materials to be applied in coating processes due to their air drying qualities. The drying of films made from various copolymers (Table 12) was studied for several hours at ambient conditions (Scheme 45) and the progressive disappearance of the olefinic bonds was followed by IR spectroscopy. There were no sensible differences among copolymers, but it was noticed that the films which contained more unsaturations dried slightly faster, as one would indeed expect.

An example of FTIR spectra obtained over 140 hours for P(VAc-*co*-VL)_3 cured at ambient conditions, is illustrated in Figure 46. Typically, the cured copolymers exhibited a band at around 3430 cm^{-1}, assigned to hydroperoxide moieties, and a weak band at 1633 cm^{-1}, related to the formation of conjugated double bonds. Additionally, the peaks assigned to the double bonds of the fatty acid chains, namely at 3010 cm^{-1} and 723 cm^{-1}, disappeared, or their intensity decreased considerably, which confirmed the occurrence of oxygen induced polymerization.[33]



Scheme 45. General pathway of the oxidative drying of P(VAc-*co*-VO) copolymer.

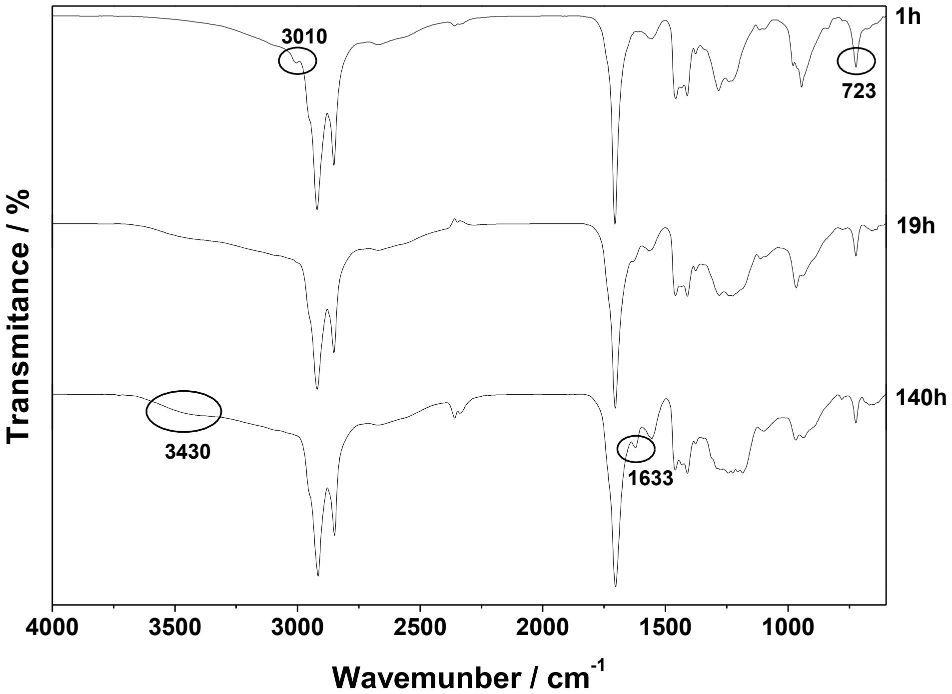


Figure 46. FTIR spectra of ambient cured P(VAc-*co*-VL)_3 copolymer (See Table 12 for copolymer identification).

These preliminary results constitute a clear indication that the copolymers of FAVE and vinyl acetate synthesized in this investigation can be effective curing systems in such applications as paints, varnishes and other coating processes.

3. CONCLUSIONS

The application of an environmentally friendly catalytic system to the transvinylation of fatty acids constitutes the first relevant contribution of this investigation, since it opens the way to possible safe industrial applications of these syntheses.

Despite the reluctance with which FAVE homopolymerize, copolymers were formed with VAc, as confirmed by FTIR, ^{1}H and ^{13}C NMR analysis. The results demonstrated that the comonomer placement in the copolymers was essentially random. The variation of the type/amount of FAVE monomers (VO or VL) and the quantity of radical initiator yielded VAc copolymers with M_n in the range of 1.2-3.0 kDa and T_g from -5 to 16 °C. Furthermore, increasing the degree of unsaturation in the FAVE caused a decrease in the M_n and T_g values and increasing the concentration of radical initiator broadened the molecular weight distribution and decreased the glass transition temperature.

The second novel feature of the study has to do with the exploitation of the ensuing FAVE as monomers and comonomers for the preparation of viscous oligomeric materials which responded adequately to atmospheric drying and hence could be used, after optimization, for the elaboration of original coating compositions based on renewable resources.

Clearly much remains to be done to further the insight into these prepolymers and to widen their scope to more complex substrates. Furthermore, these positive results may lead, in a near future, to move to other polymerizable structures, e.g. acrylic moieties, since P(VAc) paints possess properties slightly inferior to the acrylic paints in terms of toughness, binding power, and resistance to weathering.[23]

4. EXPERIMENTAL

4.1 Materials

The fatty acids used in this study were oleic acid (≥93%, Sigma-Aldrich) and linoleic acid (99%, SAFC). Vinyl acetate and commercial solutions of Ca, Co and Zr salts (5, 2 and 6% w/v, respectively) as drying catalysts were kindly supplied by Resiquímica – Resinas Químicas, SA. Bis(1,5-cyclooctadiene)-diiridium(I) dichloride ($[Ir(cod)Cl]_2$, 97%), benzoyl peroxide, anhydrous sodium acetate (99%), deuterated chloroform ($CDCl_3$, 99.8 atom % D), palladium (II) acetate (98%), 1,10-phenanthroline (≥99%,), ruthenium on carbon (5 wt. % loading), ruthenium on alumina (5 wt.% loading), ruthenium (III) acetylacetonate (97%), and tetrahydrofuran (HPLC grade) were purchased from Sigma-Aldrich. Polystyrene standards were supplied by Polymer Laboratories. Other chemicals and solvents were of laboratory grades. All the above compounds were used as received without any further purification.

4.2. Synthesis of fatty acid vinyl esters

In a typical transvinylation experiment, a mixture of the selected fatty acid (3.5 mmol) and a 10 eq excess of vinyl acetate (VAc) was placed in a two-neck round bottom glass flask equipped with a reflux condenser and thereafter degassed with nitrogen. The catalyst ($[Ir(cod)Cl]_2$, 0.01 eq), along with sodium acetate (0.03 eq), were then added and the reaction mixture was kept under magnetic stirring in a dry nitrogen atmosphere at 100°C for 16 h and 20 h for oleic acid (OA) and linoleic acid (LA), respectively. The reaction mixtures were then poured into water, extracted with dichloromethane, and the organic fraction dried over anhydrous sodium sulphate before removing the solvent in a rotary evaporator. The residues were purified by silica-gel column chromatography with a 4:1 v/v mixture of petroleum ether/dichloromethane, which provided vinyl oleate (VO) and vinyl linoleate (VL) as clear viscous liquids in 90% and 50% yield, respectively.

Vinyl oleate (**VO**)

ν_{max}/cm^{-1}: 3087 (vinyl CH stretching), 3004 (chain unsaturation C–H stretching), 2921 and 2852 (saturated CH_2 stretching modes), 1755 (C=O stretching of vinyl ester), 1645 (non-conjugated C=C stretching), 1460 (H bending of CH_2 and CH_3 groups), 1140 (ester C–O stretching), 948 (CH out-of-plane deformation of $–CH=CH_2$), 868 (CH_2 out-of-plane deformation of $–CH=CH_2$) and 722 (skeletal vibration of $–(CH_2)_n–$).

δ_H (300 MHz, $CDCl_3$, Me_4Si): 7.3 (1H, dd, *J* = 13.9, 6.3 Hz, $C(=O)OCH=CH_2$), 5.3 (2H, m,$CH=CH$), 4.5 and 4.9 (2H, dd, *J* = 6.3, 1.6 Hz, $C(=O)OCH=CH_2$), 2.4 (2H, t, *J* = 7.5 Hz, $CH_2C(=O)$), 2.0 (4H, m, $CH_2CH=CHCH_2$), 1.6 (2H, m, $CH_2CH_2C(=O)$), 1.3 (20H, m, aliphatic CH_2), 0.9 (3H, m, CH_3).

δ_C (75 MHz, $CDCl_3$, Me_4Si): 170.9 (C=O), 141.2 ($C(=O)OCH=CH_2$), 130.0 ($CH_2CH=CHCH_2$), 97.4 ($C(=O)OCH=CH_2$), 33.9 ($CH_2C(=O)$), 31.8 ($CH_2CH_2CH_3$), 29.0-29.7 (aliphatic CH_2), 27.2 ($CH_2CH=CHCH_2$), 24.5 ($CH_2CH_2C(=O)$), 22.7 (CH_2CH_3), 14.1 (CH_3).

EI-MS *m/z* (%): 41 (86, $[M–C_{17}H_{31}O_2]^+$), 55 (100, $[M–C_{16}H_{29}O2]^+$), 69 (96, $[M–C_{15}H_{27}O_2]^+$), 83 (88, $[M–C_{14}H_{25}O_2]^+$), 95 (82, $[M–C_{13}H_{25}O_2]^+$), 97 (78, $[M–C_{13}H_{23}O_2]^+$), 109 (56, $[M–C_{12}H_{23}O_2]^+$), 121 (46, $[M–C_{11}H_{23}O_2]^+$), 135 (46, $[M–C_{10}H_{21}O_2]^+$), 265 (80, $[M–OC_2H_3]^+$), 308 (1, $[M]^+$).

Vinyl linoleate (**VL**)

ν_{max}/cm^{-1}: 3089 (vinyl CH stretching), 3008 (chain unsaturation C–H stretching), 2925 (saturated CH_2 stretching), 2855 (saturated CH_2 stretching modes), 1754 (C=O stretching of vinyl ester), 1645 (non-conjugated C=C stretching), 1462 (H bending of CH_2 and CH_3 groups), 1138 (ester C–O stretching), 948 (CH out-of-plane deformation of $–CH=CH_2$), 869 (CH_2 out-of-plane deformation of $–CH=CH_2$) and 724 (skeletal vibration of $–(CH_2)_n–$).

δ_H (300 MHz, $CDCl_3$, Me_4Si): 7.3 (1H, dd, *J* = 13.9, 6.3 Hz, $C(=O)OCH=CH_2$), 5.3 (4H, m, $CH=CH$), 4.5 and 4.9 (2H, dd, *J* = 6.3, 1.5 Hz, $C(=O)OCH=CH_2$), 2.8 (2H, t, *J* = 5.8 Hz, $CH=CHCH_2CH=CH$), 2.4 (2H, t, *J* = 7.5 Hz, $CH_2C(=O)$), 2.0 (4H, m, $CH_2CH=CHCH_2CH=CHCH_2$), 1.6 (2H, m, $CH_2CH_2C(=O)$), 1.3–1.4 (14H, m, aliphatic CH_2), 0.9 (3H, m, CH_3).

δ_C (75 MHz, $CDCl_3$, Me_4Si): 170.8 (C=O), 141.2 (C(=O)OCH=CH_2), 128 and 130 (CH=CHCH$_2$$C$H=$C$H), 97.4 (C(=O)OCH=$CH_2$), 33.9 ($CH_2$C(=O)), 31.5 ($CH_2CH_2CH_3$), 29.5-29.0 (aliphatic CH_2), 27.1 (CH_2CH=CHCH$_2$CH=CHCH_2), 25.6 (CH=CHCH_2CH=CH), 24.6 (CH_2CH_2C(=O)), 22.6 (CH_2CH_3), 14.2 (CH_3).

EI-MS *m/z* (%): 41 (86, $[M-C_{17}H_{29}O_2]^+$), 55 (91, $[M-C_{16}H_{27}O_2]^+$), 67 (100, $[M-C_{15}H_{27}O_2]^+$), 81 (90, $[M-C_{14}H_{25}O_2]^+$), 95 (84, $[M-C_{13}H_{23}O_2]^+$), 109 (70, $[M-C_{12}H_{21}O_2]^+$), 123 (52, $[M-C_{11}H_{19}O_2]^+$), 135 (45, $[M-C_{10}H_{19}O_2]^+$), 262 (54, $[M-OC_2H_4]^+$), 263 (44, $[M-OC_2H_3]^+$), 306 (4, $[M]^+$).

4.3. Homopolymerization reactions of VO and VL

Homopolymers were prepared by placing the given monomer (VO or VL, 1.5 mmol), 1 ml of toluene and 0.06 eq of benzoyl peroxide (BP) as the free radical initiator in a 25 ml glass flask equipped with a water-cooled condenser and a magnetic stirrer. The relatively high BP concentration with respect to conventional free radical polymerizations, is associated with the intrinsic sluggishness of vinyl monomers bearing a very bulky substituent. Before heating the reaction mixture, it was thoroughly degassed with a stream of nitrogen to remove all traces of atmospheric oxygen. Polymerizations were then carried out at 85 °C for 6 hours under vigorous stirring and a gentle stream of nitrogen. At the end of the reaction, the polymer was precipitated by pouring the reaction mixture into a large excess of methanol and the viscous solid filtered, redissolved in dichloromethane before isolating it by rotary evaporation.

4.4. Copolymerization reactions of VAc with VO or VL

Different proportions of vinyl acetate (VAc), fatty acid vinyl ester (FAVE) monomer(s) and BP (Table 12) were placed, together with 2 ml of toluene, in a 25 ml glass flask equipped with a water-cooled condenser and a magnetic stirrer. The copolymerization reactions also required elevated BP concentrations, as explained above. After nitrogen degassing of residual atmospheric oxygen, the radical copolymerizations were carried out at 85 °C under nitrogen with magnetic stirring for 6 hours. The copolymers were isolated from the reaction mixture by precipitation into a large excess of petroleum ether, followed by filtration of the solid, dissolution in dichloromethane and solvent removal in the rotary evaporator.

4.5. Oxidative drying tests

The fatty acid vinyl esters/vinyl acetate copolymers were mixed with a combined Co/Zr/Ca (4/14/3 g, respectively, per 100 g of copolymer) drier system and the ensuing solution placed as a very thin layer in a Petri dish (to maximize the gas/liquid interface area) and allowed to react with atmospheric oxygen. Periodically, a copolymer sample was collected, isolated and analysed by FTIR.

4.6. Characterization methods

The FTIR spectra were taken with a Perkin Elmer FT-IR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. Each spectrum was an average of 32 scans taken with 4 cm^{-1} resolution in the 600-4000 cm^{-1} range.

The chemical structures were characterized by ^1H and ^{13}C NMR on a Bruker Avance 300 NMR spectrometer operating at 300 and 75 MHz, respectively, using $CDCl_3$ as solvent. Chemical shifts (δ) were reported in parts per million, relative to the tetramethylsilane internal standard (TMS, δ=0.00 ppm).

Gas chromatography-mass spectrometry (GC-MS) analyses were carried out with a Trace GC Ultra 2000 instrument equipped with a mass selective detector DSQ II and a DB-1 J&W capillary column (30 m x 0.32 mm i.d., 0.25 µm film thickness). Helium at a flow rate of 35 cm/s was used as carrier gas. The conditions adopted for these analyses were: initial temperature, 80 °C for 5 minutes; heating rate, 4°C/min; final temperature, 285 °C for 20 minutes; injector temperature, 250 °C; transfer-line temperature, 285 °C; and split ratio of 1:33. The MS was operated in the electron impact mode with impact energy of 70 eV and data collected at a rate of 1 scan s^{-1} over a range of *m/z* 33-700. The ion source was kept at 200°C. The EI-MS spectra of the monomers reported below were obtained from the GC-MS runs.

The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) on a PL-110 SEC instrument using tetrahydrofuran (THF) as the mobile phase, a run time of 30 minutes, a sampling rate of 1 Hz and a column temperature of 50 °C. Polystyrene standards were used for narrow standard calibration.

Thermogravimetric analyses (TGA) were performed using a Shimadzu TGA-50 instrument equipped with a platinum cell. The thermograms were run under a nitrogen atmosphere at a constant heating rate of 10 °C/min from 20 to 800 °C.

The differential scanning calorimetry (DSC) analyses were carried out on a Perkin Elmer Diamond DSC unit. Samples of 5-10 mg were first heated in aluminium DSC capsules from -90 to 150 °C at 10 °C/min in a nitrogen stream to destroy the thermal history and then cooled back to -90 °C and heated to 150 °C for a second test.

5. REFERENCES

[1] R. E. Murray, D. M. Lincoln, New catalytic route to vinyl esters, *Catalysis Today* **1992**, 13, 93-102.

[2] H. Nakagawa, Y. Okimoto, S. Sakaguchi, Y. Ishii, Synthesis of enol and vinyl esters catalyzed by an iridium complex, *Tetrahedron Letters* **2003**, 44, 103-106.

[3] M. B. Smith, J. March, *March's Advanced Organic Chemistry: Reactions, mechanisms and structure*, New Jersey: John Wiley & Sons, 6th ed., **2007**.

[4] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*. 4th ed., Wiley-VCH, **2003**.

[5] R. L. Adelman, The interchange reaction of vinyl acetate with organic acids, *Journal of Organic Chemistry* **1949**, 14, 1057-1077.

[6] a) H. Hopff, M. A. Osman, The vinyl interchange reaction – I: vinyl acetate with carboxylic acids stronger than acetic acid, *Tetrahedron* **1968**, 24, 2205-2214.
b) H. Hopff, M. A. Osman, The vinyl interchange reaction – II: vinyl acetate with carboxylic acids stronger than acetic acid, *Tetrahedron* **1968**, 24, 3887-3890.

[7] J. C. Vallejos, Y. Christidis, *Transvinylation of carboxylic acids*. US Patent 5223621, **1993**.

[8] F. J. Waller, *Catalytic transvinylation of vinyl esters*. US Patent 5214172, **1993**.

[9] R. E. Murray, W.V. Charleston, *Transvinylation reaction*. US Patent 4981973, **1991**.

[10] S. A. Harrison, D.H. Wheeler, The polymerization of vinyl and allyl esters of fatty acids, *Journal of the American Oil Chemists'Society* **1951**, 73, 839-842.

[11] J. M. MacDonald, *Transvinylation using mercuric acetate/perchloric acid catalyst*. US Patent 3560534, **1971**.

[12] P. L. Williams, *Anti-stick coating*. US Patent 2829073, **1958**.

[13] H. M. Teeter, Vinyl monomers derived from fats and oils, *Journal of the American Oil Chemists' Society* **1963**, 40, 143-156.

[14] W. S. Port, J.W. O'Brien, J.E. Hansen, D. Swern, Viscosity index improvers for lubricant oils, *Industrial & Engineering Chemistry* **1951**, 43, 2105-2107.

[15] E. W. Eckey, R. O. Alderson, R. J. Woestman, Production of polyvinyl esters by ester interchange, *Journal of the American Oil Chemists' Society* **1955**, 32, 185-191.

[16] W. S. Port, E. F. Jordan Jr., W. E. Palm, L. P. Witnauer, J. E. Hansen, D. Swern, Polymerizable derivatives of long-chain fatty acids: vinyl stearate and copolymerization of vinyl chloride with other vinyl esters, *Industrial & Engineering Chemistry* **1955**, 47, 472-480.

[17] W. S. Port, E. F. Jordan Jr., J. E. Hansen, D. Swern, Polymerizable derivatives of long-chain fatty acids. VII. Copolymerization of vinyl acetate with some long-chain vinyl esters, *Journal of Polymer Science* **1952**, 9, 493-502.

[18] P. O. Powers, Copolymers of dimethylstyrene vinyl fatty esters with butadiene, *Industrial & Engineering Chemistry* **1946**, 38, 837-839.

[19] C. E. Blades, S. J. Dumovich, *Vinyl stearate-maleic anhydride copolymers*. US Patent 3249592, **1966**.

[20] B. S. Gorton, *Adhesive composition of vinyl ester polymer, polyvinyl alcohol, glyoxal, and a water miscible alcohol*. US Patent 3932335, **1976**.

[21] A. J. Buselli, S. Ariemma, *Vinyl acetate copolymers*. US Patent 3018274, **1962**.

[22] V. N. Bauer, W. L. Horne, H. T. Neher, *Vinyl ester copolymers*. US Patent 2600385, **1952**.

[23] T. J. S. Learner, *Analysis of modern paints*, Getty Publications, Los Angeles, **2004**.

[24] http://www.oleon.com/home/ (November 2012).

[25] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, London: Chapman and Hall, 3rd ed., **1975**, vol. 1.

[26] The Lipid Library, **2010**. *The Lipid Library: Lipid Chemistry, Biology, Technology and Analysis*. Available from: http://lipidlibrary.aocs.org/ (February 2010).

[27] B. J. Holland, J. N. Hay, The thermal degradation of poly(vinyl acetate) measured by thermal analysis-Fourier transform infrared spectroscopy, *Polymer* **2002**, 43, 2207-2211.

[28] T. Uyar, E. Aslan, A. E. Tonelli, J. Hacaloglu, Pyrolysis mass spectrometry analysis of poly(vinyl acetate), poly(methyl methacrylate) and their blend coalesced from inclusion compounds formed with γ-cyclodextrin, *Polymer Degradation and Stability* **2006**, 91, 1-11.

[29] B. Rimez, H. Rahier, G. Van Assche, T. Artoos, B. Van Mele, The thermal degradation of poly(vinyl acetate) and poly(ethylene-co-vinyl acetate), Part II: Modeling the degradation kinetics, *Polymer Degradation and Stability* **2008**, 93, 1222-1230.

[30] A. K. Vegt, *From polymers to plastics*, Netherlands: Delft University Press, **2002**.

[31] J. E. Mark, *Polymer data handbook*, New York: Oxford University Press Inc., **1999**.

[32] R. Gorkum, E. Bouwman, The oxidative drying of alkyd paint catalysed by metal complexes, *Coordination Chemistry Reviews* **2005**, 249, 1709-1728.

[33] M. Lazzari, O. Chiantore, Drying and oxidative degradation of linseed oil, *Polymer Degradation and Stability* **1999**, 65, 303-313.

PART D

Chapter VII

CONCLUDING REMARKS AND PERSPECTIVES

"...the main goal for the researchers in coming years is to produce viable polymers from the natural resources."

V. Sharma and P. P. Kundu

Progress in Polymer Science **2006**, 31 (11), 983-1008.

1. CONCLUDING REMARKS

The interest in monomers and polymers from renewable resources is growing vigorously, as part of the general concern for sustainability and vegetable oils are highlighted as one of the valuable renewable resource for polymers. Thus, the vegetable oil-based monomers and polymers studied in this thesis represent an important contribution to the realm of novel materials derived from renewable resources, as an alternative to fossil based counterparts. Among the panoply of possible working hypotheses, two main pathways were tackled in this thesis, namely the preparation of step-growth and chain-growth polymers (**Part B** and **C,** respectively).

The first step-growth polymer system (**Chapter III**) studied the linear polyesterification of long-chain C26 monomers. For this purpose, erucic acid, a monounsaturated ω-9 fatty acid readily available from rapeseed oil, was efficiently self-metathesized (and hydrogenated) to the linear saturated long-chain α,ω-dicarboxylic acid. The subsequent direct polycondensation of stoichiometric amounts of the previous C26 diacid with its corresponding C26 diol (obtained from the diacid via reduction), proved to be a straightforward method to prepare aliphatic long-chain polyesters that are 100% renewable with M_n in the range 8-14 kDa and PDI values between 2.1 and 2.7. Their properties were investigated by means of various techniques, revealing high crystallinity (with a polyethylene like crystal structure), melting and degradation temperatures that increase with increasing diol chain length. The thermal degradation profile of these polymers revealed a good thermal stability up to 323-386 °C (temperature corresponding to 5% weight loss). The melting and crystallization temperatures ranged from 74 to 104 °C and 68 to 92 °C, respectively. The possible biodegradability of these polyesters together with their renewable origin make them attractive candidates to be used as substitute of polyethylene or other polyolefins in some specific applications.

After these first interesting results, and given the general interest in click chemistry, mainly due to its green chemistry connotation and versatility, the second step-growth polymer system (**Chapter IV**) studied the conversion of an unsaturated acid derived directly from the pyrolysis of castor oil into bifunctional monomers through thiol-ene click reaction, followed by the polymerization via the Diels-Alder reaction, i.e. a second type of click chemistry, to obtain linear thermoreversible polymers. Two basic approaches were considered for these DA polymerizations, namely (i) the use of monomers with two terminal furan rings in conjunction with bismaleimides (AA+BB systems), and (ii) the use of a protected AB monomer incorporating both furan and maleimide end-groups. Both strategies were successful, albeit with different outcomes, in terms of the nature of the ensuing products. The application of the retro-DA reaction to these polymers confirmed their thermoreversible character, i.e. the clean-cut return to their respective starting monomers. These thermally labile linear polymers exhibited relatively low T_g values (-40 to -2 °C), as a result of the flexible nature of the spacing moieties separating the reactive functions, together with somewhat small M_n values (4.5-9.0 kDa) given the observed tendency to cyclization associated with the relatively low monomer concentrations.

The implementation of this novel double-click approach using two sources of renewable resources, and the positive outcome of the first systems to which it was applied, constituted a stimulating encouragement to widen its scope in terms the depth of the associated studies and the extension to other substrates. Thus, the second step-growth polymer system (**Chapter V**) was devoted to the non-linear polymerization of trifunctional monomers, prepared from the same acid, with terminal DA functions. Three basic approaches were considered for the non-linear DA polymerizations, i.e., the use of (i) a bisfuran monomer in combination with a trismaleimide (A_2+B_3 system) and (ii) a trisfuran monomer in conjunction with a bismaleimide (A_3+B_2 system), leading to branched or cross-linked materials, and (iii) the use of asymmetrically AnB or ABn monomers incorporating both furan and maleimide end groups (A_2B or AB_2 systems), which lead to hyperbranched structures. All systems displayed T_g values close to 0 °C, as one would expect for these non-linear materials. Once again the application of the retro-DA to the ensuing polymers confirmed their thermally-reversible character. This chapter, together with the previous one, enabled the joint exploitation of two click reactions to valorise at the same time furans and vegetable oils and, thus, prepare thermally labile materials from renewable resources with great potential to exhibit intelligent features with interesting applications.

In the field of chain-growth polymers, the selected polymer system (**Chapter VI**) investigated the free radical polymerization of vinyl acetate (VAc) with fatty acid vinyl ester monomers (FAVE) to prepare prepolymers for oxidative drying. These monomers were synthesized via the transvinylation of fatty acids with VAc. Although this reaction has been the subject of several studies in the past, it was essential in our context to attempt its implementation within a more “green” connotation, since most studies privileged mercury salts as the catalyst for the reaction. This work showed that iridium-based compounds displayed an excellent catalytic activity, which allowed the preparation of monomers like vinyl oleate and linoleate in good yields through a simple procedure. The idea here was to make use of the terminal vinyl moiety as the initial polymerizing function, mostly through free radical initiation, to obtain VAc copolymers with M_n in the range of 1.2-3.0 kDa and T_g of -5 to 16 °C. Then, a subsequent slower evolution of the ensuing prepolymers was considered through their oxido-polymerization, and hence the formation of a cross-linked final material. This was successfully achieved with both vinyl oleate and vinyl linoleate, albeit with different setting kinetics, favouring the latter because of its higher degree of unsaturation. These results suggested that they can constitute effective curing systems for such applications as paints, varnishes and other coating processes based on renewable resources.

In conclusion, this thesis ventured into the synthesis of structures with different chemical characteristics directly obtained from vegetable oil-derived renewable platform chemicals. Moreover, the investigated polymer systems represent further important evidence that vegetable oils are indeed promising purveyors of groundbreaking macromolecular materials that can be obtained from diverse synthetic pathways.

2. PERSPECTIVES

The aim of this work was to develop new polymeric materials from renewable resources namely vegetable oils derivatives. Clearly, many challenges still exist and the development of superior vegetable oil-based materials emerges as certain. Among the possible lines of pursuit of this work, it would be interesting to tackle the following topics:

(i) the characterization of the long-chain aliphatic polyesters (Chapter III) in terms of mechanical and other properties, e.g. moisture uptake and biodegradability, and the improvement of their features that resemble those of petroleum-based counterparts;

(ii) the optimization of the reaction conditions of the linear and non-linear DA polymerizations (Chapters IV and V) regarding the role of catalysts to accelerate the DA and retro-DA reactions and the use of greener systems, e.g. aqueous system to prepare reversible hydrogels;

(iii) the extension of the double click exploitation (Chapters IV and V) to other substrates like, for instance, linseed and tall oil (high double bond content), together with the tailoring of the properties of the ensuing thermally labile polymers in view of their application as intelligent materials;

(iv) the extension of the transvinylation and copolymerization reactions to more complex mixtures of fatty acids (Chapter VI) and the incorporation of these materials in real waterborne vinyl resin formulations;

(v) the preparation of copolymers from fatty acids with acrylic moieties and the evaluation of their response to atmospheric drying in order to assess their potential in the elaboration of coating compositions based on renewable resources.