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## Insertion of ester bonds in three terpolymerization systems

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### ABSTRACT

Nonbiodegradable (co)polymers with all-carbon backbone produced via radical polymerization are used in various applications. For some applications, like for example in skincare and haircare, these polymers are nonrecoverable and therefore would be preferably made biodegradable. Therefore, inserting ester bonds in the backbone via radical ring opening terpolymerization of acrylates and 2-methylene-1,3-dioxepane (MDO) could be a suitable approach to obtain biodegradable terpolymers. This report investigates the influence of batch versus semibatch process on the polymerization of three terpolymerization systems *viz.* (i) methacrylamide (MAAM)/*n*-butyl acrylate (nBA)/BMDO (5,6-Benzo-2-Methylene-1,3-Dioxepane), (ii) MAAM/nBA/MDO, and (iii) methyl methacrylate (MMA)/VAc (vinyl acetate) /MDO. We demonstrate the improvement in number of ester groups inserted and the homogeneity of insertion via semibatch polymerization processes. The process is guided via optimal monomer addition feeding profiles generated using the reactivity ratios of comonomers. Such improved insertion was demonstrated by the molecular weight distribution of fragments after alkali degradation in the investigated systems.

### 1. Introduction

Free radical polymers are ubiquitous in modern society due to their applications in packaging materials, plastics, encapsulation materials, pharmaceutical excipients, care chemicals and film formers in coating etc. In spite of superior properties, low cost and high durability, alternatives to these polymers are sought over due to major concern of pollution resulting from accumulation of biodegradation resistant polymeric materials such as plastic microbeads in the environment [1]. A good and well-known way to improve the degradability of a polymer is the insertion of a weak chemical linkage such as ester bonds [2,3] or thioester bonds [4–6] where polymer chains can be hydrolysed into oligomers. If these polymers can be collected, this eases the recycling process, which becomes very similar to recycling PET bottles. After controlled hydrolysis, the oligomers can be reconstituted into new polymer chains, and be used for different applications (e.g. packaging to yarn or packaging to clothes) [3]. This is called open loop recycling. Alternatively, if these polymers are not collected, they undergo environmental hydrolysis and biodegradation by microorganisms [7]. A good path to prepare vinyl polymers that produces oligomers upon

hydrolytic degradation is radical ring opening copolymerization (rROP) of cyclic ketene acetals (CKA) with vinyl monomers [8–10]. In this approach, vinylic free radical monomers are copolymerized with CKA monomers, leading to insertion of a hydrolysable ester linkage in the backbone of the radical polymer where originally only C—C bonds were present. The radical polymerization of CKA can undergo two mechanisms: ring opening, leading ester linkages in the chain (polyesters) and ring retention leading to C—C linkages (poly vinyl acetals) [8,11,12]. The use of commonly available CKA monomer are seven-membered ring CKAs such as 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) or 2-methylene-1,3-dioxepane (MDO). These are good choices for insertion of ester linkages in the radical polymer backbone since their chemical structure dictates (i) a higher steric hindrance for the ring retained radical and (ii) a higher stability for the ring open radical. Both parameters favour ring opening during polymerization vs ring retention [12]. Even though, the incorporation of ester functionality in the backbone of vinyl-based radical polymers improve the biodegradability, retaining the physical properties such as the glass transition temperature ( $T_g$ ), mechanical strength and degradation temperature could be a challenge due to the change in backbone structure of the copolymer

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compared to the original polymer.

To improve and adjust the properties of a material, functional vinyl monomers are often copolymerized or terpolymerized. Copolymerization (two monomers) and terpolymerization (three monomers) are commonly employed in fine tuning and adjusting material's properties of polymer products for a given application. Adjusting the nature and quantity of comonomers enables the synthesis of tailored materials with desired properties. Due to such possibility of obtaining tailored materials, free radically derived terpolymers have been extensively used in personal care products as film formers, fixatives, binders, emulsion stabilizers etc. as evidenced by the large body of patent literature reports in terpolymers related to their use in the personal care domain. Early reviews by Lochhead [13] and Patil [14] highlights several such polymers used in care chemicals. However, because of heightened awareness of their ecological impact and environmental persistence due to non-degradable nature of such polymers there is tremendous regulatory pressure to restrict use of such polymers even though they provide a number of other benefits in formulation stability and sensory aspects [15]. Controlled introduction of degradability in polymer systems leading to environmental biodegradability could be a potential solution to overcome negative ecological impact of such formulation terpolymers. We have earlier reported [16] such uniform introduction in acrylate copolymers using rROP with MDO by applying semi-batch approaches and optimal addition profiles. Such uniform introduction of monomers in terpolymer systems is not trivial and often closed-loop strategy with online monitoring is applied [17].

In a batch process, copolymerization and terpolymerization normally will result in a mixture of polymers with different monomer compositions in the chain. Such mixtures are formed due to the composition drift during polymerization originating from the different reactivity ratios of the monomers in the batch reactor. In copolymerization systems, monomer with higher reactivity ("fast" monomer) is consumed quicker than the monomer with lower reactivity ("slow" monomer). At the starting stage of polymerization reaction (low conversion), polymer chains formed will contain high amount of fast monomer while toward the end stage of the polymerization (high conversion), the polymer chains are rich in slow monomer derived units. In a copolymerization system of vinyl monomer with CKA, the vinyl monomer in the system depletes more rapidly than the CKA monomer [18]. In our previous study on acrylates/MDO copolymerization [16], we managed to partially overcome this issue by using a semibatch process with optimal addition feeding profiles, which are calculated from reactivity ratio values with the MAP software package [19]. The MAP software is based on algorithms developed in the Eindhoven University of Technology under supervision of Prof. Alex van Herk by H. Schoonbrood and R. van Eijnatten. The software is able to work with up to 3 monomers and works in solution and emulsion copolymerization. Based on reactivity ratios (and in the case of emulsion polymerization also monomer partitioning) the software predict addition profiles of monomers as a function of instantaneous conversion. Furthermore, it can generate chemical composition distributions, both based on the theoretical or the experimental addition profiles.

Beside the higher level of incorporation of MDO, aliphatic ester units were more regularly inserted in the polymer chain, less ring retention events occurred, and less residual monomer was produced. Semibatch processes are also successfully applied in academic work previously on butyl acrylate/butyl methacrylate [20], butyl methacrylate/2-hydroxyethyl methacrylate [21] and recently in our team on anethol/vinyl monomers [22]. In industrial copolymer production semi-batch is the standard operating procedure.

Understanding reactivity ratios are essential to control the kinetics of multicomponent polymerization systems. Even though the terpolymerization process is quite common, the literature considerably lacks information on reactivity ratios for those systems. The main reason for the lack of reactivity ratio originate from the complexity of terpolymer composition models. Many researchers have previously reported binary

reactivity ratios derived from copolymerization experiments in models to control the monomer insertions in terpolymerization [17,23–29]. Even though this simplification occasionally leads to successful studies, Scott *et al.* recently demonstrated that terpolymerization kinetic is complex and this binary analogy is not always applicable, in their case solvent effects played a role also [30].

It is known that for these systems, branching can occur (MDO ring open units can undergo 1,4 and 1,7-backbiting [11,16,31–33] and the *n*BA radical can exhibit 1,5-backbiting as well as intermolecular transfer to polymer [34–36] and modify the property of the polymer chain [37]. In the current terpolymerization study, this aspect is not included since the MDO incorporation and uniform degradability in the system is the main focus and the property modulation by branching and ring retention is considered to be negligible. Even though many copolymerization vinyl/CKA systems were studied [8,10,32,33,38–49], only one terpolymerization system containing CKA is reported in the literature. In 2020, Jackson *et al.* terpolymerized 2-(Diethylamino) ethyl methacrylate (DEAEMA), *N*-Hydroxysuccinimide ester methacrylic acid (NSHMA) and MDO by RAFT process [50]. They managed to form pH-responsive and covalently cross-linked degradable nanoparticles. In 1996, Schoonbrood *et al.* managed to carry out a homogeneous emulsion terpolymerization of St, methyl methacrylate (MMA), and methyl acrylate (MA) using an optimal addition rate profile [51]. This feeding profile was determined using binary reactivity ratios also. They demonstrated that the optimal addition profile and addition rate profile as well as the possibility to obtain homogeneous terpolymer composition did not depend only on the reactivity ratios but also on the partitioning of the monomers in the aqueous phase.

A few studies were carried out on copolymerization of methacrylamide and its derivatives with other vinyl monomers. In 2003, Kao *et al.* copolymerized styrene and methacrylamide in 1,4-dioxane [52]. They obtained short block copolymers with a single  $T_g$ . They demonstrated that there is no specific interaction between MAAM and St units. The same year, they studied the thermal behaviour of PMAAM-*co*-MMA [53]. This study demonstrated that for a system MAAM/MMA in 1,4-dioxane, MAAM is the slow monomer. In 2004, Azab *et al.* copolymerized 2-Thiozil Methacrylamide (TMA) with different alkyl acrylates in DMF [54]. They observed alternating copolymers TMA-MA and TMA-ethyl acrylate. In 1986, Staunder *et al.* studied the terpolymerization of the system  $\alpha$ -methylstyrene/acrylonitrile/methacrylamide. They measured the ternary reactivity ratios and observed that they differed from the ones corresponding to the binary system [55]. The third system studied (methyl methacrylate MMA/VAc/MDO) explored represents introduction of degradability in the backbone of film forming and optically clear system MMA/VAc. The aim of this work is to address the issue of obtaining degradable terpolymers based on our previous studies on acrylate/MDO copolymerization [16]. We target to investigate three terpolymerization systems vinyl monomer/vinyl monomer/CKA systems: (i) methacrylamide MAAM/*n*BA/BMDO (ii) MAAM/*n*BA/MDO, and (iii) MMA/VAc/MDO. The system (i) is particularly interesting as terpolymers, MAAM/*n*BA/Styrene (St) are used as film formers and has applications in cosmetic industry [56]. The use of a semibatch process on terpolymerization was investigated. Feeding addition profiles were estimated from binary reactivity ratios. Molecular and thermal characterizations were carried out. Furthermore, the accelerated alkali degradation was studied. Structures of the terpolymers are given in [Supplementary material](#) (Scheme S1).

This is the first report of introduction of degradability by MDO derived ester units in the backbone of a terpolymer and uniform distribution of the weak bonds without using controlled radical polymerization techniques. We try to gather proof for the better uniformity of the terpolymers produced in semi-batch operation by looking at the oligomer lengths after hydrolysis, the glass transition temperatures and the monomer consumption curves.

## 2. Experimental section/methods

### 2.1. Materials

Methyl methacrylate (MMA, 99 %), Styrene (St,  $\geq 99$  %), *n*-butyl acrylate (nBA,  $\geq 99$  %), vinyl acetate (VAc,  $\geq 99$  %) and 1,4-dioxane (99.8 %) were obtained from Sigma-Aldrich, Methacrylamide (MAAM, greater than 98 %) was provided by Tokyo Chemical Industry Ltd (TCI). Dimethyl sulfoxide (DMSO) and hydrochloric acid (37 %) were obtained from Merck. 2,2'-Azobisisobutyronitrile (AIBN) was obtained from Halo-Chem Pharm. Co. Ltd. Tetrahydrofuran and triethylamine were provided by Fisher chemical. Dichloromethane (DCM), methanol, diethylether (Et<sub>2</sub>O) and tetrahydrofuran (THF) were obtained from VWR Chemicals. DMSO-*d*<sub>6</sub> (D, 99.9 %) and Acetone-*d*<sub>6</sub> (D, 99.9 %) were purchased from Cambridge Inc. Laboratory. Potassium hydroxide (KOH), Sodium bicarbonate (NaHCO<sub>3</sub>) and activated basic alumina were obtained from Alfa Aesar. Pyridine (anhydrous, 99.8 %) was obtained from Sigma Aldrich, acetic anhydride (ACS reagent) was obtained from JT Baker and 4-dimethylaminopyridine (99 %) was provided by Alfa Aesar. MDO and BMDO were synthesized as in ref [12]. Both are petroleum feedstock based monomers. Styrene and *n*-butyl acrylate were passed through activated basic alumina. All other chemicals were used as received.

### 2.2. Polymerization

#### 2.2.1. Batch polymerization

Co- and ter-polymers were prepared in 1,4-dioxane at 10 wt% for MAAM/nBA/CKA and in bulk for MMA/VAc/MDO, this due to solubilities of the terpolymers. The systems MAAM/nBA, MAAM/MDO, and MAAM/BMDO were copolymerized. The systems MAAM/nBA/BMDO, MAAM/nBA/MDO, MAAM/nBA/Styrene and VAc/MMA/MDO were terpolymerized. For each co- and ter-polymerization systems, monomers were added in equal proportion to the batch reactor. Polymerization reactions were carried out under inert atmosphere by removing oxygen from the reaction mixture by bubbling argon for an hour, and at 70 °C. For the systems containing a CKA, the Schlenk flask was previously washed with triethylamine to avoid hydrolysis of the CKA. An example of terpolymerization is described as the following: into a Schlenk flask, 1 g of MAAM, 1.51 g of nBA, 1.22 g of St, AIBN (1 mol% to monomer) and 36 mL of 1,4-dioxane were added. To monitor the reaction by <sup>1</sup>H NMR spectroscopy, DMSO (20 mol% to monomer) was added. The Schlenk flask was degassed by bubbling argon through the solution for 1 h. Then, the mixture was left under stirring at 70 °C for about 24 h. The conversions were monitored by taking aliquots every hour during the first 4 h. A last aliquot was taken before quenching the polymerization to determine the final conversion. Then, the reaction was quenched into ice water. The polymer was then precipitated in Et<sub>2</sub>O, isolated by centrifugation. The polymer was redissolved in DCM, dried with a rotary evaporator and in vacuum oven at 100 °C. Only purified polymers were further analysed.

#### 2.2.2. Semibatch polymerization

Performed on the terpolymerization system. The initial amount of monomers in the flask and to be fed was determined via the MAP (Monomer Addition Profile) software which is a modified version of TRImonomeric Seeded Emulsion Polymerization Simulation (TRISEPS) [51].

In MAP/TRISEPS, the main input parameters are the binary reactivity ratio of the monomers and the monomer composition. In case of ter-polymerization, the least reactive monomer and parts of the more reactive monomers are added to the Schlenk flask before the start of the polymerization and the remaining of the more reactive monomers are then added at a rate such that the ratio of the 3 monomers is kept constant in the polymerization. In this work, the more reactive monomers are fed slowly by linear feeding rate in 8–20 h. The feeding profiles

in MAP are calculated on conversion basis and not on time basis, which means that only the reactivity ratios are needed, and the complex kinetics are not involved. To obtain the monomer addition on time basis, a few experiments are performed to establish iteratively the addition profile on time basis [19,51]. An example of such polymerization is as following: All initiator, all of CKA, part of MAAM and nBA, part of the 1,4-dioxane and DMSO were added into a Schlenk flask (Fig. S24). The ratio of initiator to (total) amount of monomers was the same as in a batch polymerisation. The Schlenk flask was deoxygenated by bubbling argon through the contents for 1 h and maintained under argon atmosphere throughout the polymerisation. Separately, MAAM, nBA, and 1,4-dioxane were degassed in another flask and transferred to air-tight syringe (Hamilton). The flask containing the CKA was placed in an oil bath and the feeding of the remaining MAAM and nBA was started at  $t = 0$  h. Binary reactivity ratios were used to obtain the feeding profile. Feeding profiles are on conversion basis and not on time basis. When semibatch process was used, both cumulative as well as instantaneous conversions were calculated. In the calculation for the cumulative conversion the full amount of monomer that is going to be added was considered, whereas calculation of instantaneous conversion accounted only what has been introduced in the reactor up to a specific time. Reactions conditions and monomer conversions are summarized in Table 1 and Table 2. An example of a semibatch procedure is given below.

Into a Schlenk flask, 58 mg of AIBN, 1.9 g of BMDO (100 % of the total amount), 0.15 g of MAAM (15 % of the total amount), 0.23 g of BMDO (15 % of the total amount), DMSO (20 mol% of total amount of monomer) and 23 mL of 1,4-dioxane were added. The flask was by bubbling argon through the solution during 1 h. Separately, 0.85 g of MAAM (85 % of the total amount), 1.28 g of nBA (85 % of the total amount) were dissolved in 20 mL of 1,4-dioxane. The mixture was also degassed and transferred into a Hamilton syringe, which was connected to a feeding pump. The flask containing AIBN, BMDO, MAAM (15 %) and nBA (15 %) was placed into an oil bath at 70 °C. Then, the monomer feeding was started and last for 24 h (constant rate of 0.833 mL.h<sup>-1</sup>). Aliquot were taken at  $t = 0$ ,  $t = 1$  h,  $t = 2$  h,  $t = 3$  h,  $t = 4$  h,  $t = 24$  h and  $t = 24$  h30 to carry out <sup>1</sup>H NMR analyses. After 24 h30, the polymer was quenched and recovered as explained in section 2.2.1.

### 2.3. NMR spectroscopy

NMR spectra were recorded on a 400 MHz Bruker Ultrashield Avance 400SB Spectrometer equipped with a PBO probe and variable temperatures capabilities, operating at a Larmor frequency of 400.23 MHz for <sup>1</sup>H and 100.65 for <sup>13</sup>C. Data were acquired in acetone-*d*<sub>6</sub> for conversion monitoring and DMSO-*d*<sub>6</sub> for polymer analyses. As polymers precipitated in acetone-*d*<sub>6</sub>, only the monomers signals appeared on spectra, and this limited the overlapping of signals. Analyses of final products was carried out at 50 mg/mL and 300 mg/mL for <sup>1</sup>H and <sup>13</sup>C NMR measurements, respectively. Analyses of some degraded polymers were carried out at 10–20 mg/mL by <sup>1</sup>H NMR. One dimensional <sup>1</sup>H NMR spectra were acquired with 64,746 data points, 16 scans, 29.9585 ppm spectral width (11,990.407 Hz), 1 s delay, 2.70 s acquisition time, and 25° flip angle. One-dimensional <sup>13</sup>C NMR spectra were recorded with 65,536 data points, 4000 scans, 238,2643 ppm spectral width (23,980.814 Hz), 10 s relaxation delay, 1.37 s acquisition time, and a 90° flip angle with inverse gated decoupling. We demonstrated previously that in these conditions, <sup>13</sup>C NMR analyses are quantitative [16]. The chemical shift was referenced to tetramethyl silane (TMS) at 0 ppm for <sup>1</sup>H and <sup>13</sup>C NMR spectra. Full set of NMR spectra (except the four that constitute Figs. 1 and 2) are in Supplementary material (Figs. S6 to S21 and S25 to S28). Even though radical polymerization of MDO is expected to lead to quantitative ring opening [11,12], ring retention, which affects the degradability of polymer chains has previously been observed in both homopolymerization and copolymerization of MDO [31,389,10]. This leads to the formation of units whose acetal quaternary carbon and aliphatic CH<sub>2</sub> groups adjacent to an oxygen atom can be

**Table 1**

Reaction's conditions and monomer conversions for co- and ter-polymerizations with MAAM, nBA, MDO and BMDO.

Polymers	Monomers	Add. Profile	Feed. rate	Time	MAAM Conv.	nBA Conv.	CKA Conv.	Overall Conv.
Polymer 1	MAAM:nBA	Batch	–	21h35m	1	0.98	–	0.99
Polymer 2	MAAM:BMDO	Batch	–	23h45m	0.79	–	0.18	0.50
Polymer 3	MAAM:MDO	Batch	–	22h35m	1	–	0.67	0.82
Polymer 4	MAAM:nBA:BMDO	Batch	–	19h30m	0.93	0.77	0.39	0.69
Polymer 5	MAAM:nBA:BMDO	Semibatch (24 h feed.)	0.83 mL.h <sup>-1</sup>	24h30m	0.90	0.70	0.67	0.47
Polymer 6	MAAM:nBA:MDO	Batch	–	22h30m	1	1	0.68	0.89
Polymer 7	MAAM:nBA:MDO	Semibatch (24 h feed.)	0.75 mL.h <sup>-1</sup>	24h30m	0.86	0.70	0.47	0.67
Polymer 8	MAAM:nBA:St	Batch	–	22h20m	0.46	0.48	0.68*	0.54

All polymerization at equimolar ratio of monomers and run at 70 °C. Initiator was 1 % to total monomer.

\*This correspond to St conversion and not a CKA conversion.

**Table 2**

Reaction's conditions and monomer conversions for co- and ter-polymerizations with MMA, VAc and MDO.

Polymers	Monomers	Add. Profile	Feed. Rate	Time	MMA Conv.	VAc Conv.	MDO Conv.	Overall Conv.
Polymer 9	MMA:VAc	Batch	–	2h15m	0.87	0.50	–	0.69
Polymer 10	MMA:MDO	Batch	–	1h30m	0.94	–	0.24	0.60
Polymer 11	VAc:MDO	Batch	–	1h30m	–	0.89	0.47	0.68
Polymer 12	MMA:VAc. MDO	Batch	–	2h30m	0.96	0.30	0.23	0.49
Polymer 13	MMA:VAc:MDO	Semibatch (8 h feed.)	2.25 mL.h <sup>-1</sup>	8 h	0.93	0.89	0.92	0.91

All polymerization at equimolar ratio of monomers and run at 70 °C. Initiator to total monomer ratio is 1 mol %.

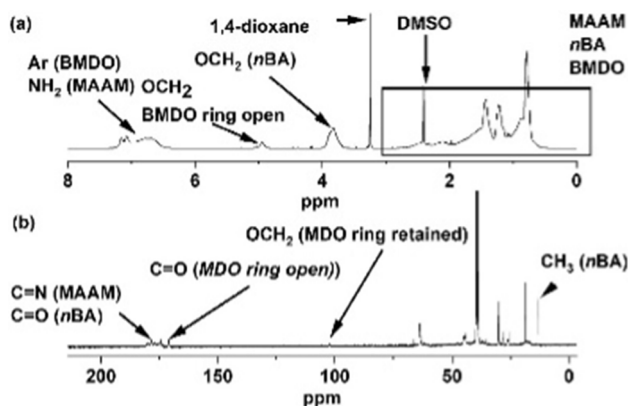


Fig. 1. (a) <sup>1</sup>H NMR spectrum of P(MAAM-co-nBA-co-BMDO) (Polymer 4) recorded at 21 °C in DMSO at 50 mg/mL (b) <sup>13</sup>C NMR spectrum of P(MAAM-co-nBA-co-MDO) (Polymer 7) recorded at 21 °C in DMSO at 300 mg/mL.

detected by <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy ( $\delta = 100\text{--}110$  ppm for quaternary carbon (<sup>13</sup>C NMR),  $\delta = 62$  ppm (<sup>13</sup>C NMR)  $\delta = 3.5$  ppm (<sup>1</sup>H NMR) for CH<sub>2</sub> adjacent to an oxygen atom) [31,39]. The fraction of ring retained unit was determined in this study.

#### 2.4. Gel permeation chromatography (GPC)

GPC was conducted on a Viscotek TDAmx consisting of a GPCmax integrated solvent and sample delivery module, a TDA 302 Triple Detector Array, and OmniSEC software. 2 × PLgel 5 μm Mixed-C (200–2,000,000) columns were applied in sequence for separation. The instrument was calibrated with polystyrene standards (PL2010 – 0100 Polystyrene calibration kit, S-M-10) purchased from Agilent. This set included standards whose Mp is between 580 and 3000000 Da. THF was used as the eluent at 1.0 mL/min with column and detector temperature at 30 °C. For MAAM/nBA/CKA systems: samples were analysed at a concentration of 10 mg/mL and prepared as follows: 15 mg of polymer was dissolved in 1.5 mL of THF. A drop of dioxane was added to dissolve the samples. Then, 1 mL of solution was filtered through PTFE.

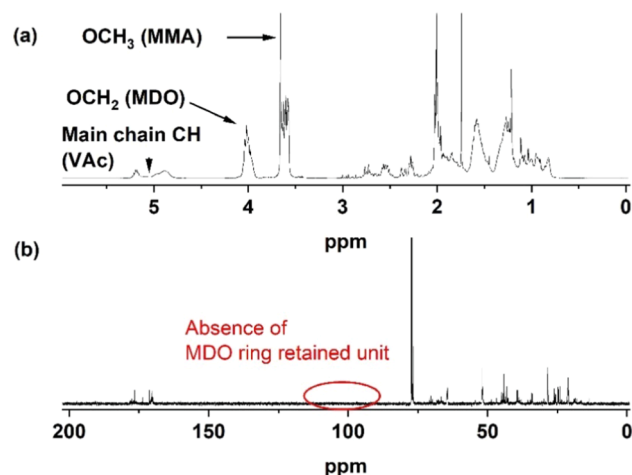


Fig. 2. (a) <sup>1</sup>H NMR spectrum of P(MMA-co-VAc-co-MDO) (Polymer 13) recorded at 21 °C in CDCl<sub>3</sub> at 50 mg/mL (b) <sup>13</sup>C NMR spectrum of P(MMA-co-VAc-co-MDO) (Polymer 13) recorded at 21 °C in CDCl<sub>3</sub> at 300 mg/mL.

GPC chromatograms are presented of Figs. S29 to S32 in Supplementary material.

#### 2.5. Thermal analyses

##### 2.5.1. Thermogravimetric analysis (TGA)

The decomposition temperature of polymers was investigated using the TGA Q500 (TA Instruments). TGA measurements were conducted by ramping the temperature from room temperature to 700 °C at a constant rate of 10 °C/min under a continuous nitrogen flow. The decomposition temperature was defined as the temperature at the onset of the significant weight loss. Results are presented in Supplementary material. DSC thermograms are in Supplementary material (Fig. S22). Degradation temperature values are in Table 3.

Table 3

Thermal properties of polymer and molar mass of polymers/oligomers before and after degradation process.

Polymer	Composition	Deg. T (°C)	T <sub>g</sub> (°C)	Before degradation			After degradation		
				M <sub>n</sub>	M <sub>w</sub>	D	M <sub>n</sub>	M <sub>w</sub>	D
Polymer 1	MAAM. nBA 0.60. 0.40	204.65	18.19; 198.38	3,400	5,600	1.65	–	–	–
Polymer 2	MAAM. BMDO 0.90. 0.10	250.95	NO	–	–	–	–	–	–
Polymer 3	MAAM. MDO (RO). MDO (RR) 0.92. 0.07. 0.01	231.09	165.87	–	–	–	–	–	–
Polymer 4	MAAM. nBA. BMDO (RO). BMDO (RR) 0.50. 0.45. 0.05. 0	229.06	NO	2,400	5,200	2.17	650	1,750	2.65
Polymer 5 (Semibatch)	MAAM. nBA. BMDO (RO). BMDO (RR) 0.46. 0.45. 0.09. 0	201.68	32.30	2,300	4,500	1.96	590	970	1.84
Polymer 6	MAAM. nBA. MDO (RO). MDO (RR) 0.45. 0.39. 0.11:0.04	202.55	NO	7,000	14,400	2.06	470	650	1.38
Polymer 7 (Semibatch)	MAAM. nBA. MDO (RO). MDO (RR) 0.41. 0.37. 0.19. 0.03	194.20	–10.87	2,859	9,000	3.16	480	610	1.27
Polymer 8	MAAM. nBA. St 0.28. 0.23. 0.49	213.46	25.72	10,400	18,500	1.78	11,700	23,400	2.08
Polymer 9	MMA. VAc 0.94. 0.06	320	110.59	30,800	50,300	1.63	–	–	–
Polymer 10	MMA. MDO (RO). MDO (RR) 0.88. 0.12. 0	362	45.64	55,800	109,500	1.96	–	–	–
Polymer 11	VAc. MDO (RO). MDO (RR) 0.67. 0.33. 0	392	–13.12	26,700	54,600	2.04	–	–	–
Polymer 12	MMA. VAc. MDO (RO). MDO (RR) 0.71. 0.18. 0.11. 0	344	25.05	31,300	68,400	2.19	–	–	–
Polymer 13 (Semibatch)	MMA. VAc. MDO (RO). MDO (RR) 0.40. 0.30. 0.30. 0	320	1.74	18,800	48,300	2.57	500	900	1.80

NO: not observed, RO: ring open, RR: ring retained.

### 2.5.2. Differential scanning calorimetry (DSC)

The T<sub>g</sub> of polymers was measured using a DSC 3 Star system Mettler Toledo. DSC measurements were also carried out under nitrogen environment. The sample was heated from –70 °C to 180 °C, held isothermally for 2 min, and subsequently cooled down to –70 °C, then held isothermally for 5 min. The scanning rate for both heating and cooling processes was 10 °C/min. The upper temperature limit was 20 °C below the decomposition temperature. The heat – cool cycle was repeated three times. The first heating and cooling steps are used to erase the thermal history of the samples and detect evaporation of small molecules trapped in the samples. Data analyses for determining T<sub>g</sub> values were carried out using the last heating cycle thermogram. Thermograms are presented in [Supplementary material \(Fig. S23\)](#) and T<sub>g</sub> values are in [Table 3](#).

### 2.6. Accelerated alkali degradation

About 100 mg of the terpolymer was dissolved in 8 mL of THF (added with a few drops of 1,4-dioxane to improve dissolution if necessary). Then a KOH solution (240 mg in 2.5 mL methanol) was added. The solution was stirred for 72 h and acidified with 6 M HCl. For P(MAAM-co-nBA-co-CKA), the solution was dried with a rotary evaporator and then in vacuum oven at 50 °C. It was then dissolved in chloroform and filtered through cotton to remove the salt (KCl) and dried again at 50 °C.

After acidification with HCl, the solvent in P(MMA-co-VAc-co-MDO) solution was evaporated. The resultant crude was added with dichloromethane (DCM), pyridine (4 mL, 2:1) and acetic anhydride (0.04 mL) and catalytic amounts of 4-dimethylaminopyridine. The contents were stirred at room temperature for 16 h. The reaction mixture was diluted with DCM and washed with NaHCO<sub>3</sub>, water, and brine. The DCM layer was separated and evaporated to dryness to get crude acetylated hydrolysed product. Both terpolymers were then analyzed with GPC-THF.

## 3. Results and discussions

The composition of all the co- and ter-polymers was determined by

<sup>1</sup>H NMR spectroscopy. For Polymers 6–8, it was necessary to perform <sup>13</sup>C quantitative NMR spectroscopy as overlap in <sup>1</sup>H NMR spectra prevented the determination of the polymer compositions (see [Figs. S10–S12](#)). [Fig. 1](#) shows the <sup>1</sup>H and <sup>13</sup>C NMR spectra of P(MAAM-co-nBA-co-BMDO) and [Fig. 2](#) shows the <sup>1</sup>H and <sup>13</sup>C NMR spectra of P(MMA-co-VAc-co-MDO), respectively. GPC analyses in THF was carried out for Polymer 1 and Polymer 4 to 13. The number average molecular weight (M<sub>n</sub>), the weight average molecular weight (M<sub>w</sub>) and the dispersities were determined using conventional calibration. Polymer 2 and 3 were not soluble in THF. Degradation in basic conditions was tested for all P(MAAM-co-nBA-co-CKA) terpolymers and for Polymer 13, P(MMA-co-VAc-co-MDO). Resulting oligomers were analysed by GPC. All polymers were analysed by TGA and DSC. The degradation temperature was determined from a significant mass loss step in the mass versus temperature curve. In some cases, a smaller mass loss step was observed around 100 °C due to loss of hydration water (previously absorbed by the sample). T<sub>g</sub>s were taken from the second heating of DSC thermogram (except for polymer 8, whose T<sub>g</sub> is less clear than on first heating). Results are summarized in [Table 3](#).

### 3.1. Kinetics of batch co- and ter-polymerizations

The kinetics of co- and ter-polymerization reactions was monitored by <sup>1</sup>H NMR spectroscopy. The disappearance of methylene proton of MAAM, nBA, St, MMA, VAc and MDO as well as the disappearance of the O-CH<sub>2</sub> protons of BMDO were compared to the hydrogen signals of DMSO. Details are in [Figs. S1 to S3](#) and Eq. (S1–S3)) in [Supplementary material](#). The evolution of monomer fraction versus time was also monitored. Results are presented in [Figs. S4 and S5](#) and raw data in [Tables S1 to S13](#) in [Supplementary material](#). In the batch copolymerization reactions, from the evolution of the monomer fractions with the overall monomer conversion, reactivity ratios were estimated with the help of the CONTOUR software [57]. Kinetic results are presented in [Figs. 3 and 4](#). Reactivity ratio values are presented in [Table 4](#). For our experiments, the joint Confidence Intervals are shown in S33–35. The JCI's are narrow ridges and the two reactivity ratios are strongly correlated. This is likely due to the fact that only one monomer

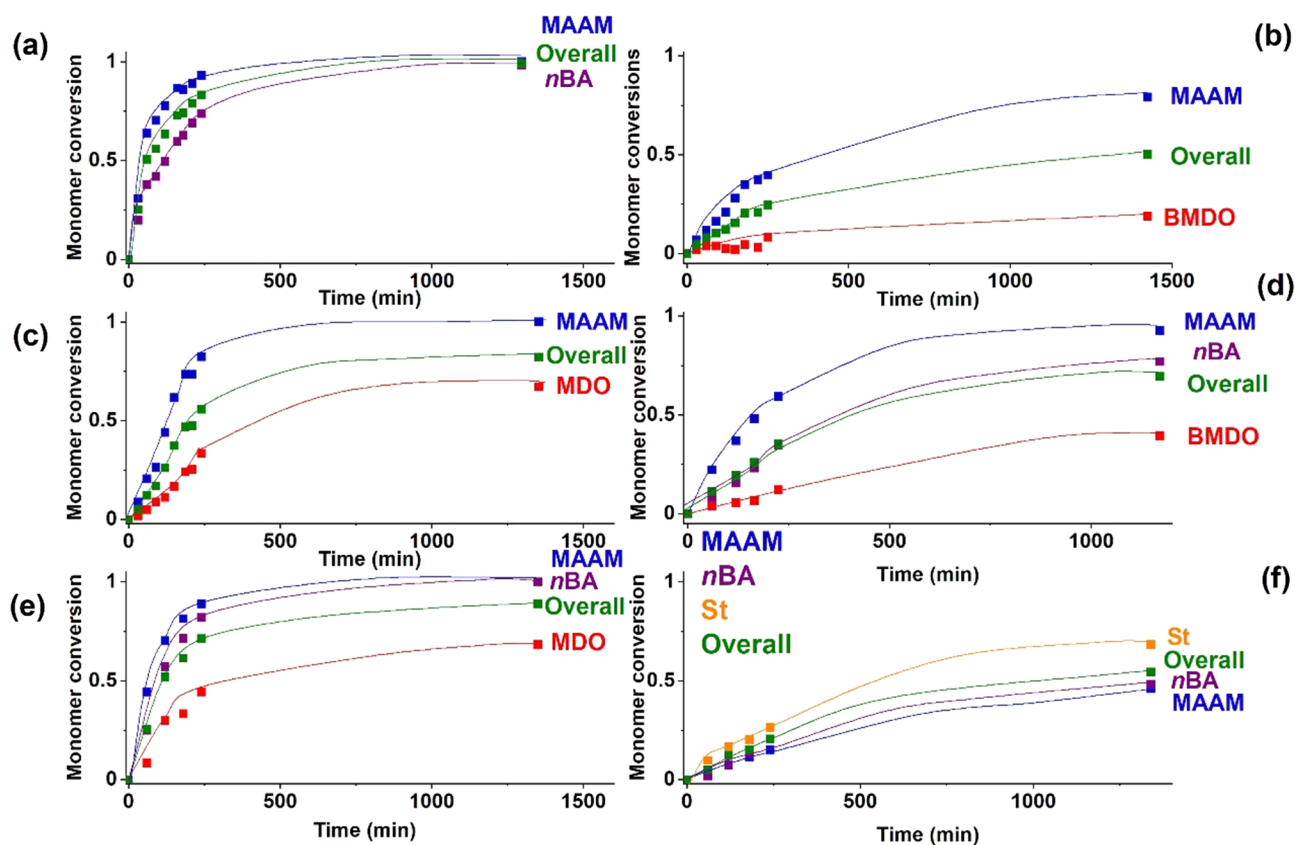


Fig. 3. Evolution of monomer conversion versus time for (a) copolymerization of MAAM and nBA, (b) copolymerization of MAAM and BMDO, (c) copolymerization of MAAM and MDO, (d) terpolymerization of MAAM, nBA and BMDO, (e) terpolymerization of MAAM, nBA and MDO, (f) terpolymerization of MAAM, nBA and St. All polymerizations were carried out in batch, with [monomer] = 10 wt% in 1,4-dioxane and at 70 °C. Lines are only added to guide the eye.

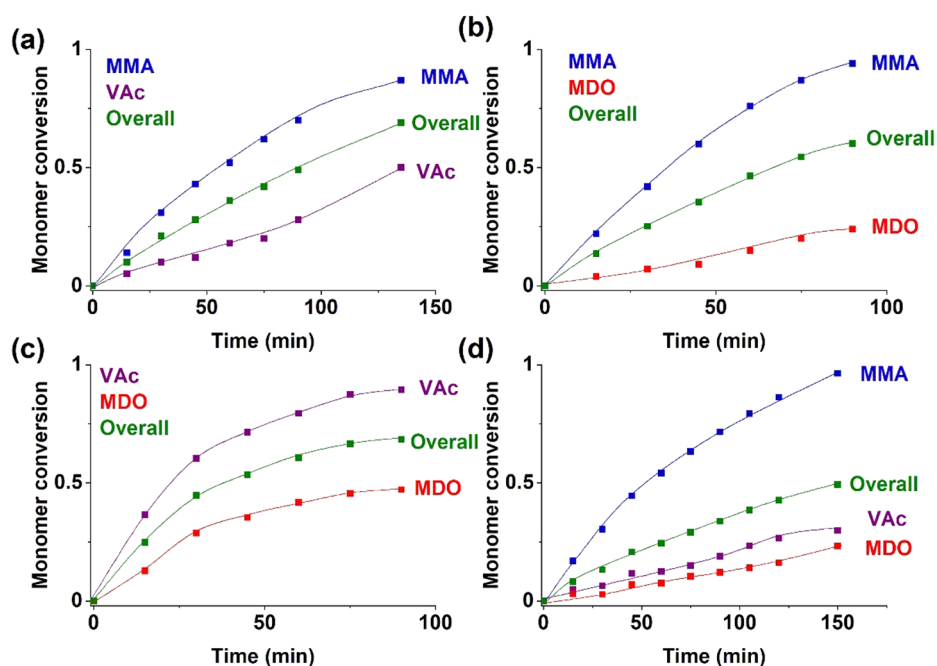


Fig. 4. Evolution of monomer conversion versus time for (a) copolymerization of MMA and VAc, (b) copolymerization of MMA and MDO, (c) terpolymerization of MMA, VAc and MDO. All polymerizations were carried out in batch, bulk and at 70 °C. The lines are only added to guide the eyes.

composition was experimentally studied.

We have to make the remark that the estimates for the reactivity ratios are very crude and are only used to roughly estimate the monomer addition profiles in the semi-batch reactions. As another unknown in the

semi-batch reactions is the conversion-time relationship, we are not so concerned about the accuracy of the reactivity ratios.

From Fig. 3 and Table 4, we can observe that MAAM reacts quicker with itself than with nBA. This does not confirm the results obtained by

**Table 4**  
Binary reactivity ratios of 5 copolymerization systems.

System	Reactivity ratio <sup>1</sup>	Literature
MAAM/nBA	$r_{MAAM} = 3.8(-0.8, +2.8)$ ; $r_{nBA} = 0.9(-0.25, +0.77)$	This work
MAAM/BMDO	$r_{MAAM} = 1.7 \cdot 10^1(-4, +20)$ ; $r_{BMDO} = 0.6(-0.3, +1.3)$	This work
MAAM/MDO	$r_{MAAM} = 6.3(-1.7, +6.5)$ ; $r_{MDO} = 0.37(-0.2, +0.6)$	This work
nBA/BMDO	$r_{nBA} = 3.7$ ; $r_{BMDO} = 0.08$	[49]
nBA/MDO	$r_{nBA} = 1.76$ ; $r_{MDO} = 0.044$	[16]
MMA/VAc	$r_{MMA} = 2.7 \cdot 10^1$ ; $r_{VAc} = 0.010$	[58]
MMA/MDO	$r_{MMA} = 3.5$ ; $r_{MDO} = 0.04$	[33]
VAc/MDO	$r_{VAc} = 1.71$ ; $r_{MDO} = 0.95$	[18]

1. Errors are estimated standard deviations.

Kuo *et al.* who copolymerized MAAM and MMA in 1,4-dioxane and obtained the reactivity ratios  $r_{MAAM} = 0.24$  and  $r_{MMA} = 1.38$  [57]. However, Kuo *et al.* results showed that MMA is preferentially consumed in copolymerization systems with MAAM. Similarly, acrylates are also more incorporated when they copolymerize with acrylamide. Moreover, it is known that methacrylate are preferentially consumed in a copolymerization with acrylate. Thus, it is not a surprise to observe high incorporation of MAAM (tertiary propagating radical) when it copolymerize with BA (secondary propagating radical).

Adding CKA in the batch lowers the rate of MAAM and nBA consumption in the terpolymerization. In our previous study on alkyl acrylates/MDO copolymerization, the opposite effect was observed. Adding MDO in batch boosted the nBA consumption rate. It is known than BMDO and MDO ring open radicals are more reactive toward vinyl monomers than toward themselves [18]. Reactivity ratio values suggests that this effect is more pronounced for the binary system nBA/CKA than for MAAM/CKA. Greater values for the cross-propagation rate coefficients  $k_{CKA-nBA}$  than  $k_{CKA-MAAM}$  are assumed. Binary reactivity ratios imply that nBA radicals have a higher chance to attack CKA than MAAM radicals to attack CKA. Consequently, nBA-CKA-nBA should be the dominant triad containing CKA. This might explain why MDO and BMDO conversions are higher in terpolymerization systems MAAM/nBA/CKA than in copolymerization systems MAAM/CKA (especially for the reactions with BMDO, as observed in Fig. 3) but it does not explain why the overall consumption of monomers is slower. By comparing copolymerizations between MAAM/CKA and terpolymerization of MAAM/nBA/CKA systems, we observe a quicker MAAM consumption but similar rate of CKA consumption. From binary reactivity ratio values, we would expect the presence of nBA to boost the CKA consumption as (i) nBA radicals would cross propagate more with CKA monomers than MAAM radicals with CKA monomers and (ii) nBA radicals would cross propagate more with CKA monomers than with MAAM monomers. However, it is known that binary reactivity ratios are not always suitable to describe a terpolymerization system [30]. As mentioned previously, Staudner *et al.* observed that for the terpolymerization system 2-ethylhexyl acrylate/MAAM/St, ternary reactivity ratios did not corresponds to the ones of the corresponding binary systems [55]. We observe that BMDO reactivity is slower than MDO reactivity. This was observed previously, and it is due to the bulkiness of BMDO. Polyester units from BMDO are not inserted as much as from MDO units in MAAM/nBA/CKA polymerization systems but curiously, BMDO leads to more polyesters units than MDO when polymerized only with MAAM, even if the presence of ring retained units is taken into account. This is not consistent with the observation in Fig. 3.

When CKA is replaced by styrene, the kinetics are completely different. The presence of styrene strongly reduces the kinetics of monomer consumption. This is due to a combination of two effects. First, styrene radicals are stabilized by the presence of the aromatic ring. Finally, nBA radicals are more reactive toward styrene than toward nBA monomers [59] and MAAM radicals are more reactive toward styrene monomers than toward CKA monomers [54].

For the system MMA/VAc/MDO, polymerization reactions were

carried out in bulk, leading to a quicker monomer consumption. Our results confirm previous studies. MMA is reacted quicker than VAc [58], which is quicker than MDO [38,48,60]. This is due to the presence of an oxygen in  $\alpha$  of the radical carbon of VAc. Oxygen is electronegative and exerts an attracting effect and stabilizes the radical. It is known that for copolymerization of VAc and MDO, both reactivity ratio values are close to unity [10,30,41], which should lead to a perfectly random copolymer. As a result, less composition drift is observed than for the system MMA/MDO (Fig. S5). However, even though the observed composition drift for MDO/VAc system is less important than for MDO/MAAM, MDO/MMA, and MDO/nBA systems, it is still clearly visible and our data does not show perfectly random copolymers. A recent study with much more data point from Wenzel *et al.* showed higher difference in reactivity ratio for MDO/VAc system ( $r_{MDO} = 0.43 \pm 0.06$ ;  $r_{VAc} = 3.25 \pm 0.12$ ) [61]. If we compare the bulk terpolymerization of these three monomers to the three different bulk copolymerizations present in this study, we notice that the addition of MDO inhibits the polymerization of VAc but not the polymerization of MMA. It is also interesting to note that no Trommsdorff effect is observed in the co- and terpolymerization with MMA in bulk. This could be due to the rapid conversion of MMA compared to the comonomer(s). In our previous study, we demonstrated that the intrinsic barriers for both ring-retained and ring-open MDO radical to add an acrylate monomer is lower in energy than the intrinsic barrier to add acrylate monomer to an acrylate radical [16]. This may apply for MMA but not for VAc. Another observation is the slower rate of VAc and MDO consumption in presence of MMA. This can be explained by the reactivity ratio values for the system MMA/VAc.  $r_{MMA}$  (27.465) is much higher than  $r_{VAc}$ , which is close to zero (0.012). Consequently, in the terpolymerization system, MMA is almost fully consumed when only less than 30 % of the other monomers have reacted. Binary reactivity ratios seem to correctly describe the kinetics of the terpolymerization of MMA, VAc and MDO.

For the system P(MMA-co-VAc-co-MDO), no ring retention is observed (see Fig. 2b and Fig. S20). Only a small signal at 102 ppm on the <sup>13</sup>C NMR spectrum of P(MMA-co-MDO) is observed (Fig. S19), but with a signal-to-noise ratio below 3, which is the limit of detection. Consequently, it is not possible to confirm the presence of ring retained units. This confirms previous literature results on VAc and MDO copolymerization, where no ring retained unit is observed [60,62].

### 3.2. Thermal analyses

To establish whether the terpolymers are more homogeneous when produced in semi-batch operation, the appearance of the glass transition temperatures in the DSC thermograms can give some indication.

Detailed results are in Table 1, Figs. S22 and S23. DSC thermograms of copolymers P(MAAM-co-BMDO), and terpolymers P(MAAM-co-nBA-co-BMDO) and P(MAAM-co-nBA-co-MDO) produced in batch do not exhibit a glass transition onset, while when these terpolymers are synthesized in semibatch, a single  $T_g$  clearly appears. The presence of a clear glass transition onset shows homogeneous insertion of different monomer units while no well-defined  $T_g$  suggests a long glass transition trajectory, sign of a large heterogeneity of polymer chains. This demonstrates the importance of using a semibatch process in these terpolymerization systems. Units are inserted more regularly. This was observed in our study on acrylate/MDO copolymerization but a  $T_g$  was observed in all cases, regardless the use of batch or semibatch process [16]. Free radical polymerization of three monomers can result in the formation of more heterogeneous polymer chains than polymerization of two monomers. P(MAAM-co-nBA-co-MDO) has a lower  $T_g$  than P(MAAM-co-nBA-co-BMDO). This is due to the high flexibility of MDO derived six carbon units, leading to increased segmental dynamics causing overall lowering of the  $T_g$ . P(MAAM-co-nBA-co-BMDO) and P(MAAM-co-nBA-co-St) have  $T_g$  of 32.30 °C and 25.72 °C respectively. This shows that replacing St units by BMDO ring open units does not significantly reduce the glass transition temperature as anticipated. This



could possibly due to the aromatic ring being part of the polymer backbone reducing segmental mobility in P(MAAM-co-nBA-co-BMDO) compared to the aromatic ring as a side group in P(MAAM-co-nBA-co-St) system. The presence of a single  $T_g$  for P(MAAM-co-nBA-co-St), which is produced in batch, can be explained by the much less pronounced composition drift for the polymerization of this system (see Fig. 3d).

TGA analyses shows that all polymers degrade between 190 and 250 °C, which is very close to the degradation temperature of P(MAAM) [53]. They have high thermal stability. Replacing styrene units by BMDO ring open units does not significantly affect the degradation temperature.

### 3.3. Oligomer analysis after degradation by alkaline hydrolysis

Alkali degradation was tested on one P(MMA-co-VAc-co-MDO), all P(MAAM-co-nBA-co-MDO), all P(MAAM-co-nBA-co-BMDO) and the P(MAAM-co-nBA-co-St) terpolymers.  $^1\text{H}$  NMR analyses of degraded polymers suggest that degradation of P(MAAM-co-nBA-co-CKA) is incomplete and that the ester side chains of nBA are partially hydrolysed. Regarding the degradation of P(MMA-co-VAc-co-MDO),  $^1\text{H}$  NMR analyses show that degradation mostly occurs on side chains. Consequently, only the degradation of P(MAAM-co-nBA-co-MDO) will be discussed. More information is given in section 6 of [Supplementary material](#).

After treatment with base in methanol, all terpolymers were alkali degraded except P(MAAM-co-nBA-co-St) whose only side chains were hydrolysed. Its  $M_n$  remained unchanged as expected. Fig. S26 does not clearly show the hydrolysis of the ester side group of n-BA units. GPC analyses of other terpolymers show a  $M_n$  between 2400 and 7000 g/mol before degradation and 470 and 650 g/mol after degradation. This confirms the incorporation of ester groups in the main chains. An example of GPC chromatogram is given below (Fig. 5).

Fig. 6 shows a rough decrease of the  $M_n$  of oligomers with increasing incorporation of CKA ring open units. Dispersity ( $\mathcal{D}$ ) of the oligomers decreases with CKA ring open units. This is also clear from Fig. S29, GPC chromatograms of oligomers resulting from the degradation of polymers produced in semibatch are not as broad as the ones resulting from the degradation of polymers synthesized in batch. Oligomers resulting from the degradation of terpolymers produced in semibatch exhibit a lower molecular weight and a lower  $\mathcal{D}$ . This confirms that with a semibatch process, (i) more polyester units are inserted and (ii) their insertion is more uniform. More details will be given in the next section.

It is important to note that at this stage, we only obtained a rough estimate of the size of oligomers and we do not know yet the degree of hydrolysis and the composition of hydrolyzed products.

### 3.4. Batch versus semibatch process

A batch process in free radical copolymerization will result in composition drift, except for some special cases. Consequently, a broader copolymer composition distribution (CCD) will be observed. For batch terpolymerization of MAAM, nBA and CKA, composition drift is

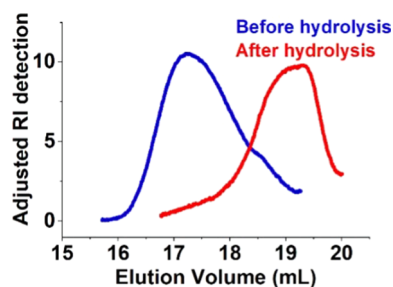


Fig. 5. GPC traces before and after hydrolysis for P(MAAM-co-nBA-co-BMDO) produced in semibatch (polymer 6).

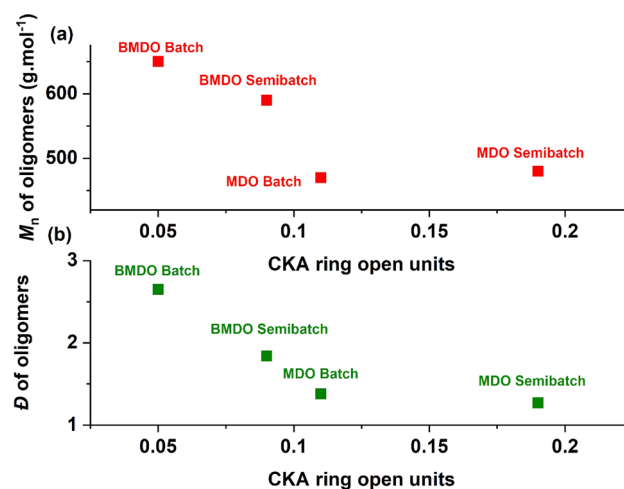
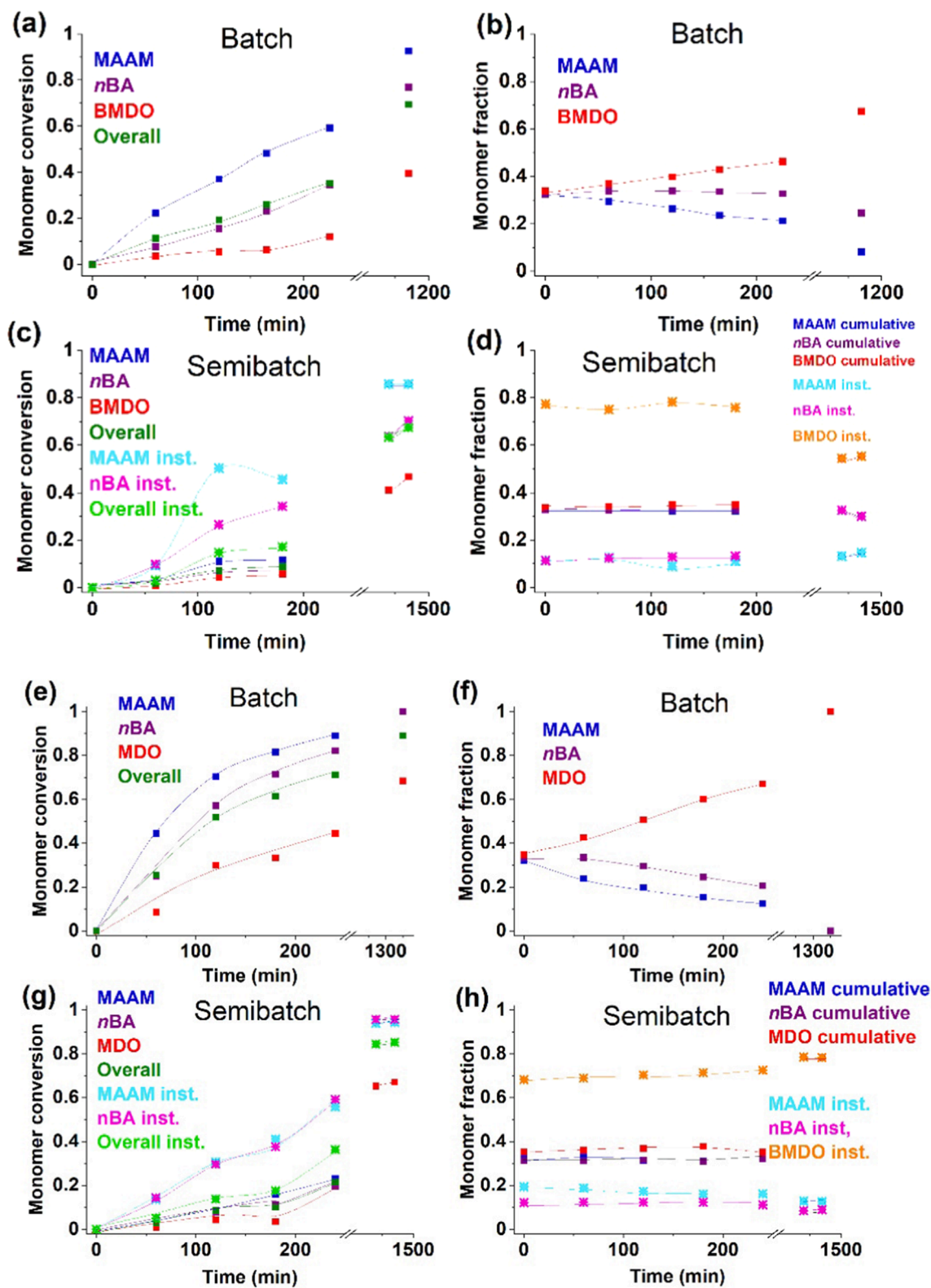


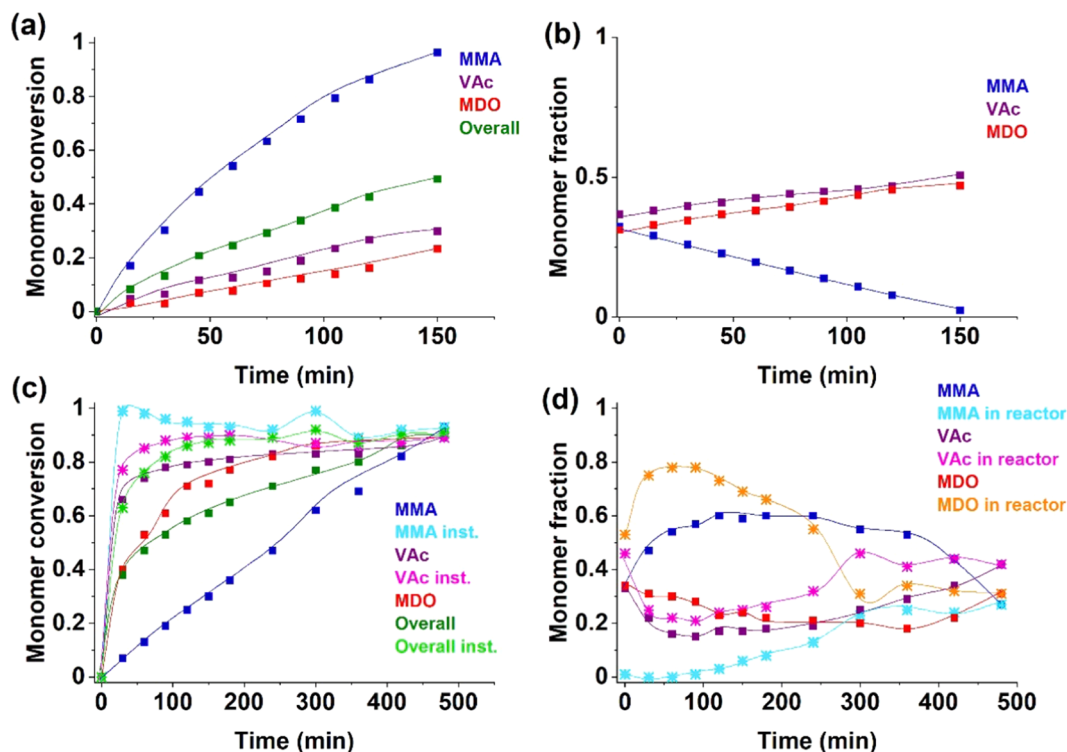
Fig. 6. (a) Number average molecular weight and (b) dispersity ( $\mathcal{D}$ ) of oligomers resulting from degradation of terpolymers P(MAAM-nBA-CKA). The line is added to guide the eye.

observed (see Fig. 7 (a) [reproduced from Fig. 3(d) for comparison] and 7 (b)). Likely, at the early stage of the terpolymerization, chains rich in MAAM and nBA are formed while toward high conversion, more polyesters units are incorporated. For the terpolymerization of MMA, VAc and MDO, Fig. 8 shows that the consumption of MMA is much quicker than the consumption of VAc and MDO. At low conversions, chains rich in MMA are formed and then, more VAc and MDO units are incorporated. To avoid composition drift and enhance the incorporation of ester units in the main chain, we tested semibatch process on MAAM/nBA/BMDO, MAAM/nBA/MDO and MMA/VAc/MDO terpolymerization systems as it was successful for alkyl acrylates/MDO copolymerization systems [16]. In this work, binary reactivity ratios were used to predict the addition feeding profiles (on conversion basis) using MAP software and an initial guess of monomer feed rate is used. A complete work to obtain an optimal monomer addition profile through iterative method in MAP software can be found elsewhere [19]. As the presence of a CKA inhibits the consumption of MAAM and nBA, the feeding time had to be 24 h to obtain acceptable monomer conversions. For the terpolymerization of MMA, VAc and MDO, as the polymerizations are carried out in bulk, 8 h were sufficient to reach high conversion. Addition profiles are presented in Fig. S24 in [Supplementary material](#). Figs. 7 and 8 show a comparison of the evolution of monomer conversions and of monomers fractions versus time for batch and semibatch processes.

From Fig. 7, we note that with a semibatch process (i) the appearance of composition drift is much less prominent, (ii) overall conversions of each monomer are closer to each other, especially at the early stage of the polymerization, and (iii) instantaneous monomer fractions vary only very slightly over time. Even though binary reactivity ratios may not be completely suitable to describe the kinetics of these terpolymerization systems, addition feeding profiles for a semibatch process obtained based on these reactivity ratio allow better incorporation of the slow monomer. However, we note that in the terpolymerization MAAM/nBA/MDO system, the use of a semibatch process does not significantly increase the amount of MDO consumed. In the terpolymerization with BMDO, the amount of BMDO consumed is higher if the polymerization is in semibatch but to a lower extent than in the case of alkyl acrylate/MDO copolymerization [53]. As observed in Fig. 7, the amount of MDO consumed is already high in a batch polymerization. The main difference between these terpolymerization systems and the alkyl acrylate/BMDO copolymerization is the effect of addition of CKA in the batch on the overall kinetics. In this case, the kinetics is slightly inhibited while addition of MDO in a batch with only alkyl acrylates boosted the kinetics. We recently demonstrated that even though single values of the cross propagation rate coefficient of the slower monomer with other



**Fig. 7.** Evolution of monomer conversions and of monomer fractions versus time for (a) and (b) MAAM/nBA/BMDO terpolymerization system in batch (polymer 4), (c) and (d) MAAM/nBA/BMDO terpolymerization system in semibatch (polymer 5), (e) and (f) MAAM/nBA/MDO terpolymerization system in batch (polymer 6), (g) and (h) MAAM/nBA/MDO terpolymerization system in semibatch (polymer 7). The lines are only added to guide the eyes. For the graphs (d) and (f), cumulative fractions take into account the total amount of monomers and instantaneous fractions take into account the amount of monomers in batch.



**Fig. 8.** Evolution of monomer conversions and of monomer fractions versus time for (a) and (b) MMA/VAc/MDO terpolymerization system in batch (polymer 12), (c) and (d) MMA/VAc/MDO terpolymerization system in semibatch (polymer 13). The lines are only added to guide the eyes. For the graph (d), cumulative fractions take into account the total amount of monomers and instantaneous fractions take into account the amount of monomers in batch.

monomers in the system does not determine the addition feeding profile, it plays a major role in the kinetics of the system and thus on the time needed to feed the monomers [22].

Results are slightly different for the semibatch terpolymerization of MMA, VAc, and MDO. From Fig. 8, we note a significant increase of MMA and MDO consumption, but even though initial and final monomer fraction values are close to each other, a fluctuation of monomer fractions is observed over the polymerization process. It is likely due to the optimal addition profile. As 85 % of the VAc is initially introduced in the batch while more than 99 % of the MMA is fed, more VAc and MDO are consumed at early stage of the polymerization.

As expected, the amount of MDO and BMDO incorporated in the terpolymers are higher with a semibatch process, as well as the ratio ring opening (esters) units versus ring retention units (acetals). During a reaction in semibatch, the ratio of CKA to other monomers is higher throughout the feeding process, which favours the insertion of CKA units but the overall monomer concentration is lower, which favours ring opening vs ring retention. Ring retention is a bimolecular reaction whose rate directly depends on monomer concentration [16,63]. On the other hand, ring opening is a unimolecular step, and it is not related to monomer concentration. The disadvantages of semibatch experiment are the reduction of molecular weight and longer reaction times.

### 3.5. Chemical composition distribution (CCD) of terpolymer

As previously described, composition drift is expected for batch terpolymerization because of the different reactivity ratio of the monomers. For such system, a semibatch process affects the kinetic of the polymerization and thus producing co- or ter-polymer with a more homogenous CCD than a batch process. As a further indication here, we briefly look at one of the systems in terms of this CCD. MAP software can estimate the CCD based on the experimental monomer consumption profiles. The CCD estimation by MAP provides a good indication of the distribution of the monomers in the polymer chain which is also

reflected in the  $T_g$ . Fig. 9 shows the CCD of MAAM/nBA/BMDO terpolymer as estimated by MAP from batch, semibatch and the CCD predicted under an optimal addition profile (OAP) process. The CCD of OAP serves as a benchmark and is a theoretical prediction from MAP under an ideal feeding profile. The CCD of Polymer 4 (Fig. 9A) clearly shows composition drift in which initially the terpolymer is rich in MAAM/nBA and as these two monomers are depleted at high conversion, more and more BMDO is incorporated in the terpolymer (forming BMDO rich polymer) and then finally only poly(BMDO) is formed as can be seen in the sharp peak at BMDO. On contrary, the CCD of Polymer 5 obtained through a semibatch process, the CCD (Fig. 8B) is clearly more homogenous and closer to the CCD of OAP (Fig. 9C). It is more near to the centre of the distribution and no poly(BMDO) is formed. The CCD of the other monomer system (MAAM/nBA/MDO and MMA/VAc/MDO) (not shown here) is also calculated and show a significant improvement as compared to its batch process.

The CCD plot of Polymer 4 and 5 is in good agreement with the polymerization kinetics (Fig. 7a-d). In the semibatch process, the conversion of each monomers is closer to each other as compared to the batch process. In terms of the  $T_g$ , Polymer 4 doesn't show a clear transition whereas Polymer 5 shows one clear transition at 32.3 °C indicating a more homogeneous polymer. All these data are consistent with each other.

It is important to note that the CCD predicted by MAP software is not a measured CCD. It is actually very challenging to measure the CCD of a terpolymer. With MAP, the estimated CCD (based on the monomer consumption curves) gives an indication of the distribution of the monomer composition in the polymer chains for any polymerization process.

## 4. Conclusion

Degradable poly(MAAM-co-nBA) can be obtained by terpolymerizing MAAM, nBA and a CKA. The terpolymerization approach is

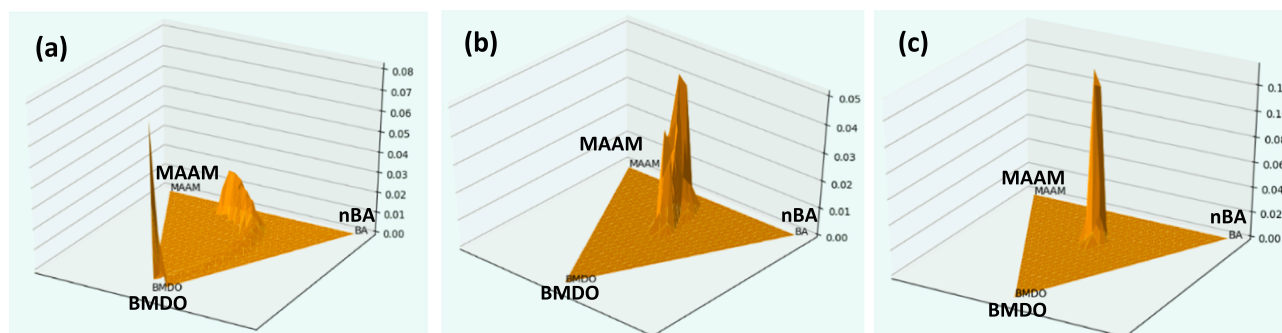


Fig. 9. CCD estimated by MAP for MAAM/nBA/MDO polymerization under (a) batch, (b) semi-batch, and (c) optimal addition profile.

demonstrated to work across different CKA monomers (MDO and BMDO) and different vinylic monomers (vinyl acetate, acrylate, and methacrylate monomers). The incorporation of ester units can be improved by using a semibatch process with optimal addition feeding profiles. These profiles are obtained from reactivity ratios. Even though binary reactivity ratios might not perfectly describe these terpolymerization systems, they are still acceptable to predict the addition feeding profile. Using a semibatch process is very important as it allows obtaining polymers with a well-defined  $T_g$ . Terpolymers were successfully degraded into short oligomers. GPC analyses of these oligomers shows a more random insertion of ester units in the main chain when a semibatch process is used. If in a terpolymer containing MAAM, alkyl acrylate and styrene units the styrene is replaced by BMDO ring open units, neither  $T_g$  nor thermal stability are significantly affected. In general, molecular weights go down with the use of CKAs under the same conditions. One could compensate for this effect, by changing conditions or with the use of a crosslinking agent. These results are important in relation to the feasibility of making existing products more biodegradable, for example, film forming terpolymers used in the personal care products.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2022.111627>.

#### References

- [1] P. Eyerer, *Polymers - opportunities and risks i: general and environmental aspects*, *The Handbook of Environmental Chemistry* 11 (2010).
- [2] Y. Hiraguri, K. Katase, Y. Tokiwa, Biodegradability of poly(ester-ether) and poly(ester) obtained from a radical ring-opening polymerization of cyclic ketene acetals, *J. Macromol. Sci.-Pure and Appl. Chem.* A42 (7) (2005) 901–907.
- [3] D. Bhatia, D. Braun, V. Choudhary, Studies on the copolymerization of cyclic ketene acetals with styrene, *Indian J. Chem. Technol.* 10 (5) (2003) 548–557.
- [4] N.M. Bingham, P.J. Roth, Degradable vinyl copolymers through thiocarbonyl addition-ring-opening (TARO) polymerization, *Chem. Commun.* 55 (1) (2019) 55–58.
- [5] R.A. Smith, G.Y. Fu, O. McAteer, M.Z. Xu, W.R. Gutekunst, Radical Approach to Thioester-Containing Polymers, *J. Am. Chem. Soc.* 141 (4) (2019) 1446–1451.
- [6] N.M. Bingham, Q.U. Nisa, S.H.L. Chua, L. Fontugne, M.P. Spick, P.J. Roth, Thioester-Functional Polyacrylamides: Rapid Selective Backbone Degradation Triggers Solubility Switch Based on Aqueous Lower Critical Solution Temperature/Upper Critical Solution Temperature, *ACS Appl. Polym. Mater.* 2 (8) (2020) 3440–3449.
- [7] F. Kawai, Bacterial-Degradation of Acrylic Oligomers and Polymers, *Appl. Microbiol. Biotechnol.* 39 (3) (1993) 382–385.
- [8] A. Tardy, J. Nicolas, D. Gignes, C. Lafay, Y. Guillauneuf, Radical Ring-Opening Polymerization: Scope, Limitations, and Application to (Bio)Degradable Materials, *Chem. Rev.* 117 (3) (2017) 1319–1406.
- [9] A.W. Jackson, Reversible-deactivation radical polymerization of cyclic ketene acetals, *Polym. Chem.* 11 (21) (2020) 3525–3545.
- [10] S. Agarwal, L.Q. Ren, T. Kissel, N. Bege, Synthetic Route and Characterization of Main Chain Ester-Containing Hydrolytically Degradable Poly(N, N-dimethylaminoethyl methacrylate)-Based Polycations, *Macromol. Chem. Phys.* 211 (8) (2010) 905–915.
- [11] S. Jin, K.E. Gonsalves, A study of the mechanism of the free-radical ring-opening polymerization of 2-methylene-1,3-dioxepane, *Macromolecules* 30 (10) (1997) 3104–3106.
- [12] W.J. Bailey, Z. Ni, S.R. Wu, Synthesis of Poly-Epsilon-Carpolactone via a Free-Radical Mechanism - Free-Radical Ring-Opening Polymerization of 2-Methylene-1,3-Dioxepane, *J. Polym. Sci. Part A-Polym. Chem.* 20 (11) (1982) 3021–3030.
- [13] S.E. Morgan, K.O. Hawelka, R.Y. Lochhead, *Cosmetic Nanotechnology: Polymers and Colloids in Personal Care*, ACS Symposium Series, American Chemical Society: Washington, DC (2007) 4–56.
- [14] A. Patil, M.S. Ferritto, *Polymers for Personal Care and Cosmetics: Overview*, International Symposium on Polymers for Cosmetics and Personal Care / 244th National American-Chemical-Society Meeting, PA, Philadelphia, 2012, pp. 3–11.
- [15] K. Duis, T. Junker, A. Coors, Environmental fate and effects of water-soluble synthetic organic polymers used in cosmetic products, *Environ. Sci. Eur.* 33 (1) (2021).
- [16] J.B. Lena, A.W. Jackson, L.R. Chennamaneni, C.T. Wong, F. Lim, Y. Andriani, P. Thoniyot, A.M. Van Herk, Degradable Poly(alkyl acrylates) with Uniform Insertion of Ester Bonds, Comparing Batch and Semibatch Copolymerizations, *Macromolecules* 53 (10) (2020) 3994–4011.
- [17] A. Urretabizkaia, G. Arzamendi, M.J. Unzué, J.M. Asua, High solids content emulsion terpolymerization of vinyl-acetate, methyl-methacrylate and butyl acrylate.2. Open-loop composition control, *J. Polym. Sci. Part A-Polym. Chem.* 32 (9) (1994) 1779–1788.
- [18] J.B. Lena, A.M. Van Herk, Toward Biodegradable Chain-Growth Polymers and Polymer Particles: Re-Evaluation of Reactivity Ratios in Copolymerization of Vinyl Monomers with Cyclic Ketene Acetal Using Nonlinear Regression with Proper Error Analysis, *Ind. Eng. Chem. Res.* 58 (46) (2019) 20923–20931.
- [19] W. Rusli, S.W. Benjamin Tan, A. Parthiban, A.M. van Herk, Free radical solution copolymerization of monomers of dissimilar reactivity - influencing chemical composition distribution and properties of copolymers of methyl methacrylate and N-vinyl imidazole by varying monomer feeding profiles, *Polymer* 247 (2022), 124774.
- [20] D.H. Li, M.C. Grady, R.A. Hutchinson, High-temperature semibatch free radical copolymerization of butyl methacrylate and butyl acrylate, *Ind. Eng. Chem. Res.* 44 (8) (2005) 2506–2517.

- [21] S. Komatsu, T.A. Asoh, R. Ishihara, A. Kikuchi, Facile preparation of degradable thermoresponsive polymers as biomaterials: Thermoresponsive polymers prepared by radical polymerization degrade to water-soluble oligomers, *Polymer* 130 (2017) 68–73.
- [22] J.B. Lena, A.M. van Herk, S. Jana, Effect of anethole on the copolymerization of vinyl monomers, *Polym. Chem.* 11 (35) (2020) 5630–5641.
- [23] L.Q. Ren, C. Speyerer, S. Agarwal, Free-radical copolymerization behavior of 5,6-benzo-2-methylene-1,3-dioxepane and methacrylic acid via the in situ generation of 3-methyl-1,5-dihydrobenzo e 1,3 dioxepin-3-yl methacrylate and 2-(acetoxymethyl)benzyl methacrylate, *Macromolecules* 40 (22) (2007) 7834–7841.
- [24] M. Zelzer, A. Heise, Terpolymerization Kinetics of Amino Acid N- Carboxy Anhydrides, *J. Polym. Sci. Part A-Polym. Chem.* 52 (9) (2014) 1228–1236.
- [25] I. Soljic, A. Jukic, Z. Janovic, Terpolymerization Kinetics of N, N-Dimethylaminoethyl Methacrylate/Alkyl Methacrylate/Styrene Systems, *Polym. Eng. Sci.* 50 (3) (2010) 577–584.
- [26] H.F. Naguib, S.M. Mokhtar, N.Z. Khalil, M.Z. Elsabee, Polymerization kinetics of indene, methyl methacrylate and acrylonitrile and characterization of their terpolymer, *J. Polym. Res.* 16 (6) (2009) 693–702.
- [27] A. Jukic, M. Rogosic, E. Vidovic, Z. Janovic, Terpolymerization kinetics of methyl methacrylate or styrene/dodecyl methacrylate/octadecyl methacrylate systems, *Polym. Int.* 56 (1) (2007) 112–120.
- [28] R.C. Beauchemin, M.A. Dube, Bulk terpolymer composition prediction from copolymer reactivity ratios, *Polym. React. Eng.* 7 (4) (1999) 485–499.
- [29] H.A.S. Schoonbrood, R. vanEijnatten, B. vandenReijen, A.M. vanHerk, A.L. German, Emulsion co- and terpolymerization of styrene, methyl methacrylate, and methyl acrylate .1. Experimental determination and model prediction of composition drift and microstructure in batch reactions, *J. Polym. Sci. Part A-Polym. Chem.* 34(6) (1996) 935-947.
- [30] A.J. Scott, A. Penlidis, Binary vs. ternary reactivity ratios: Appropriate estimation procedures with terpolymerization data, *Eur. Polym. J.* 105 (2018) 442–450.
- [31] S. Maji, M.Y. Zheng, S. Agarwal, Functional Degradable Polymers via Radical Ring-Opening Polymerization and Click Chemistry, *Macromol. Chem. Phys.* 212 (23) (2011) 2573–2582.
- [32] G.E. Roberts, M.L. Coote, J.P.A. Heuts, L.M. Morris, T.P. Davis, Radical ring-opening copolymerization of 2-methylene 1,3-dioxepane and methyl methacrylate: Experiments originally designed to probe the origin of the penultimate unit effect, *Macromolecules* 32 (5) (1999) 1332–1340.
- [33] S. Agarwal, Microstructural characterisation and properties evaluation of poly (methyl methacrylate-co-ester)s, *Polym. J.* 39 (2) (2007) 163–174.
- [34] P. Castignolles, R. Graf, M. Parkinson, M. Wilhelm, M. Gaborieau, Detection and quantification of branching in polyacrylates by size-exclusion chromatography (SEC) and melt-state C-13 NMR spectroscopy, *Polymer* 50 (11) (2009) 2373–2383.
- [35] M. Gaborieau, S.P.S. Koo, P. Castignolles, T. Junkers, C. Barner-Kowollik, Reducing the Degree of Branching in Polyacrylates via Midchain Radical Patching: A Quantitative Melt-State NMR Study, *Macromolecules* 43 (13) (2010) 5492–5495.
- [36] A.M. van Herk, Pulsed initiation polymerization applied to acrylate monomers: Sources of experimental failure, *Macromol. Rapid Commun.* 22 (9) (2001) 687–689.
- [37] P.M. Wood-Adams, J.M. Dealy, A.W. deGroot, O.D. Redwine, Effect of molecular structure on the linear viscoelastic behavior of polyethylene, *Macromolecules* 33 (20) (2000) 7489–7499.
- [38] D.D. Ding, X.Q. Pan, Z.B. Zhang, N. Li, J. Zhu, X.L. Zhu, A degradable copolymer of 2-methylene-1,3-dioxepane and vinyl acetate by photo-induced cobalt-mediated radical polymerization, *Polym. Chem.* 7 (33) (2016) 5258–5264.
- [39] L.F. Sun, R.X. Zhou, Z.L. Liu, Synthesis and enzymatic degradation of 2-methylene-1,3-dioxepane and methyl acrylate copolymers, *J. Polym. Sci. Part A-Polym. Chem.* 41 (18) (2003) 2898–2904.
- [40] J. Tran, E. Guegain, N. Ibrahim, S. Harrisson, J. Nicolas, Efficient synthesis of 2-methylene-4-phenyl-1,3-dioxolane, a cyclic ketene acetal for controlling the NMP of methyl methacrylate and conferring tunable degradability, *Polym. Chem.* 7 (26) (2016) 4427–4435.
- [41] V. Delplace, E. Guegain, S. Harrisson, D. Gigmes, Y. Guillaneuf, J. Nicolas, A ring to rule them all: a cyclic ketene acetal comonomer controls the nitroxide-mediated polymerization of methacrylates and confers tunable degradability (vol 51, 12847, 2015), *Chem. Commun.* 51(66) (2015) 13146-13146.
- [42] M.R. Hill, E. Guegain, J. Tran, C.A. Figg, A.C. Turner, J. Nicolas, B.S. Sumerlin, Radical Ring-Opening Copolymerization of Cyclic Ketene Acetals and Maleimides Affords Homogeneous Incorporation of Degradable Units, *ACS Macro Lett.* 6 (10) (2017) 1071–1077.
- [43] J. Undin, A. Finne-Wistrand, A.C. Albertsson, Copolymerization of 2-Methylene-1,3-dioxepane and Glycidyl Methacrylate, a Well-Defined and Efficient Process for Achieving Functionalized Polyesters for Covalent Binding of Bioactive Molecules, *Biomacromolecules* 14 (6) (2013) 2095–2102.
- [44] S. Choi, K. Lee, S. Kwon, H. Kim, Preparation of fine particles of poly(N-vinyl-2-pyrrolidone-co-2-methylene-1,3-dioxepane) using supercritical antisolvent, *J. Supercrit. Fluids* 37 (3) (2006) 287–291.
- [45] H. Wickel, S. Agarwal, Synthesis and characterization of copolymers of 5,6-benzo-2-methylene-1,3-dioxepane and styrene, *Macromolecules* 36 (16) (2003) 6152–6159.
- [46] Y. Zhang, D.F. Chu, M.Y. Zheng, T. Kissel, S. Agarwal, Biocompatible and degradable poly(2-hydroxyethyl methacrylate) based polymers for biomedical applications, *Polym. Chem.* 3 (10) (2012) 2752–2759.
- [47] L.Q. Ren, S. Agarwal, Synthesis, characterization, and properties evaluation of poly (N-isopropylacrylamide)-co-ester s, *Macromol. Chem. Phys.* 208 (3) (2007) 245–253.
- [48] J. Undin, T. Illanes, A. Finne-Wistrand, A.C. Albertsson, Random introduction of degradable linkages into functional vinyl polymers by radical ring-opening polymerization, tailored for soft tissue engineering, *Polym. Chem.* 3 (5) (2012) 1260–1266.
- [49] J.Y. Huang, R. Gil, K. Matyjaszewski, Synthesis and characterization of copolymers of 5,6-benzo-2-methylene-1, 3-dioxepane and n-butyl acrylate, *Polymer* 46 (25) (2005) 11698–11706.
- [50] A.W. Jackson, L.R. Chennamaneni, P. Thoniyot, Main-chain degradable, pH-responsive and covalently cross-linked nanoparticles via a one-step RAFT-based radical ring-opening terpolymerization, *Eur. Polym. J.* 122 (2020).
- [51] H.A.S. Schoonbrood, R. vanEijnatten, A.L. German, Emulsion co- and terpolymerization of styrene, methyl methacrylate and methyl acrylate.2. Control of emulsion terpolymer microstructure with optimal addition profiles, *J. Polym. Sci. Part A-Polym. Chem.* 34 (6) (1996) 949–955.
- [52] H.C. Kao, S.W. Kuo, F.C. Chang, Effects of inert diluent segment and hydrogen bonding in poly(styrene-co-methacrylamide) copolymers, *J. Polym. Res.-Taiwan* 10 (2) (2003) 111–117.
- [53] S.W. Kuo, H.C. Kao, F.C. Chang, Thermal behavior and specific interaction in high glass transition temperature PMMA copolymer, *Polymer* 44 (22) (2003) 6873–6882.
- [54] M.M. Azab, Study of the copolymerization parameters of 2-thiozyl methacrylamide with different alkyl acrylates, *J. Polym. Res.* 12 (1) (2005) 9–15.
- [55] E. Staudner, G. Kysela, A. Zemlicka, I. Goljer, S. Nosalova, Y. Smandrova, Functional Terpolymers, *Chem. Pap.* 41 (1) (1987) 119–124.
- [56] H. Khakpour, M. Abdollahi, Rheological properties of acrylamide/butyl acrylate/2-acrylamido-2-methyl-1-propane sulfonic acid co- and terpolymers synthesized by heterogeneous and micellar methods, *Polym. Bull.* 74 (12) (2017) 5145–5161.
- [57] A.M. Vanherk, Least-squares fitting by visualization of the sum of squares space, *J. Chem. Educ.* 72 (2) (1995) 138–140.
- [58] M.J. Scora, H. Hua, M.A. Dube, Bulk and solution copolymerization of methyl methacrylate and vinyl acetate, *J. Appl. Polym. Sci.* 82 (5) (2001) 1238–1255.
- [59] F. Ziaee, M. Nekoomanesh, Monomer reactivity ratios of styrene-butyl acrylate copolymers at low and high conversions, *Polymer* 39 (1) (1998) 203–207.
- [60] S. Agarwal, R. Kumar, T. Kissel, R. Reul, Synthesis of Degradable Materials Based on Caprolactone and Vinyl Acetate Units Using Radical Chemistry, *Polym. J.* 41 (8) (2009) 650–660.
- [61] F. Wenzel, S. Hamzehlou, L. Pardo, M. Aguirre, J.R. Leiza, Kinetics of Radical Ring Opening Polymerization of the Cyclic Ketene Acetal 2-Methylene-1,3-dioxepane with Vinyl Monomers, *Ind. Eng. Chem. Res.* 60 (29) (2021) 10479–10488.
- [62] C.A. Bell, G.G. Hedir, R.K. O'Reilly, A.P. Dove, Controlling the synthesis of degradable vinyl polymers by xanthate-mediated polymerization, *Polym. Chem.* 6 (42) (2015) 7447–7454.
- [63] J.Y. Yuan, C.Y. Pan, "Living" free radical ring-opening copolymerization of 4,7-dimethyl-2-methylene-1,3-dioxepane and conventional vinyl monomers, *Eur. Polym. J.* 38 (10) (2002) 2069–2076.