Polymers for Electronics and Photonics

"Conducting, ferromagnetic, and nonlinear optical properties of polymers"

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ABSTRACT

Recently, polymers show promising prospects as active constituents of optical and electronic devices, especially polymers for nonlinear optics and conducting polymers. In a remote future even organic ferromagnets and molecular electronics may become more than wishful thinking. For this reason several fundamental aspects of these materials are the subject of intensive research. In this paper we will review the present state of the art in these new fields of polymers for electronics and photonics. Special emphasis will be laid on recent results from our laboratories.

1 INTRODUCTION

It is well-known that polymers are important materials in various electronic and photonic applications[1]. For example, packaging and interconnection of electronic components, coatings for optical fibers, optical recording media, polymeric waveguides and lenses, and microlithography[2]. Recently, polymers show also prospects as active constituents of optical and electronic devices[3]. With these applications in mind, the important properties of the polymers studied are physical phenomena like electrical conductivity, ferromagnetism, and nonlinear optical properties as optical switching or frequency doubling. In order to be really useful, the polymers should retain their typical polymer properties like mechanical strength and ease of processing. A combination of properties will afford a new class of active materials in devices. For this reason several fundamental aspects of these materials are the subject of intensive research. High conductivity is measured in a variety of doped polymers and the nonlinear optical properties of polymers exceed those of the best inorganic materials, whilst

very recently an organic polymer is claimed to show ferromagnetism. Although these interesting properties are found in polymers, they show quite a number of disagreeable properties too, such as insolubility and nonprocessability or instability in time. No wonder that a large part of the research going on in this field is aimed at restoring, by means of chemical modifications, some of the properties that make polymers in general such valuable materials. In this paper we will review the present state of the art in these new fields of polymers for electronics and photonics. Successively, we will discuss the conducting, ferromagnetic, and nonlinear optical properties of polymers. Special emphasis will be laid on recent results from our laboratories.

2 CONDUCTING POLYMERS

Since the seminal experiments in 1977 on polyacetylene[4] showing that this polymer could be made electrically conductive upon doping, an intensive research activity has been unfold world-wide[5]. In the years following these first disclosures, polyacetylene has been studied in great detail, eventually leading to improved syntheses and a conductivity of 1.5×10^5 S/cm, which equals that of copper at room temperature[6].
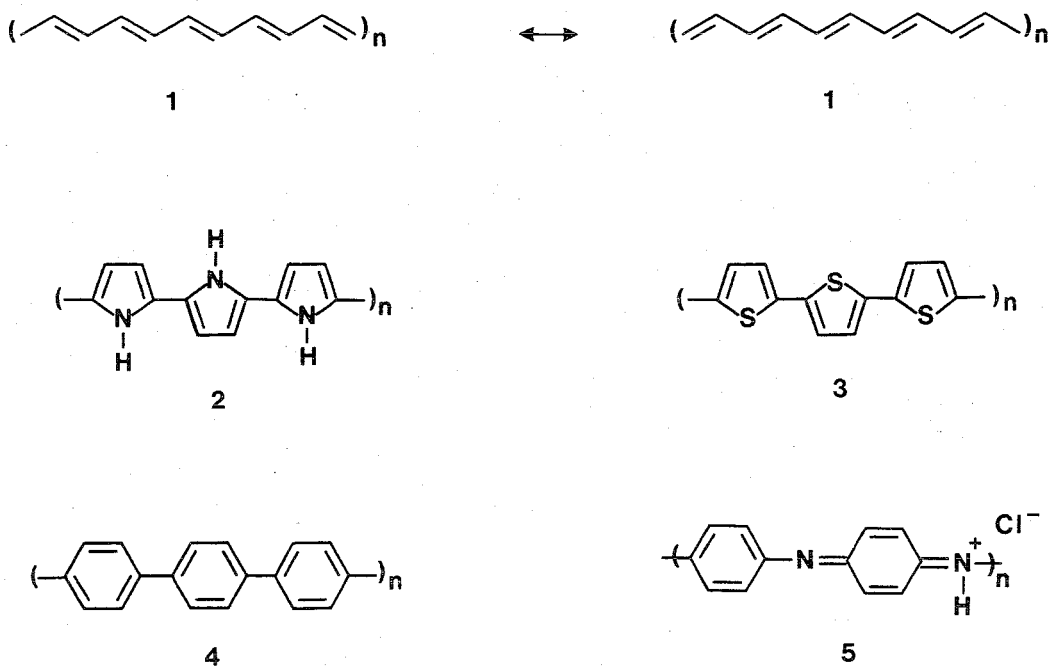

Figure 1 Structures of some principal polymers that can be doped to conductors.

The all-trans structure of polyacetylene (1) is shown in figure 1, together with some other well-studied polymers like: polypyrrole (2), polythiophene (3), poly-p-phenylene (4), and polyaniline (5). They represent the key structures of conducting polymers. The polymers as given in figure 1 are insulators with bandgaps in the order of 1.5 eV or more. In order to become electrically conductive the polymers have to be doped, that is to be oxidized (to p-type conductors) or reduced (to n-type conductors), yielding positively charged backbones or negatively charged backbones, respectively. Not in all cases both types of doping can be realized. For instance, the reduction potential of neutral polypyrrole is so high, that only oxidative doping can occur. With respect to environmental stability this oxidative doping is preferred for all polymers. The doping occurs either simultaneously with the preparation of the polymers (e.g. the electrochemical polymerization of pyrrole and thiophene) or by separate doping with strongly oxidizing agents (e.g. gaseous I_2, AsF_5, etc.).

Several experiments have been performed on conducting polymers to establish the mechanism of conduction in these polymers[7]. Conducting polymers are often divided into two classes, namely those having a degenerated ground state and those where the ground state degeneracy is lifted. Polyacetylene (1) is an example of the first class, where the interchange of double and single bonds involves no loss of energy. Here solitons are considered to be the important excitations [5]. In the other class, comprising compounds like polypyrrole (2), polythiophene (3), and poly-p-phenylene (4), polarons and bipolarons are the dominant charge-storage configurations. Most of these polymers have a nondegenerated ground state that is aromatic , while the quinoid form is of higher energy[8].

Despite numerous reports on the mechanism and theory of conduction in these polymers, exact descriptions are still hard to give, let alone to prove. Only for the very high conductivities recently measured in pure, well-characterized and ordered polymers, the assumptions made in theoretical models may be realistic. For a good review on these aspects we like to refer to several papers in the Handbook of Conducting Polymers[9].

The topics of special interest for polymer chemists are the search for new and better polymers or new procedures to the well-known polymers. In order to improve the properties of conducting polymers emphasis is given to higher conductivity, better environmental stability, and processability. A fundamental approach to increase the conductivity is based on decreasing the bandgap of the undoped polymer[10]. A "pure" intrinsically metallic polymer would be reached at a bandgap of 0 eV. However, such a low bandgap in a simple conjugated polymer is hardly to be expected, as theory gives many reasons for lifting the degeneracy of the extended π-electron groundstate (correlation energy, Peierls effect because of onedimensionality). Up to now the polymer with the lowest bandgap shows a value around 1 eV [10]. However, the search for polymers that really show intrinsic metallic properties remains challenging.

To the contrary, in the area of processability much progress has been made. Specially designed polymer synthesis has been carried out leading to either soluble precursors or even soluble conductors [11] .
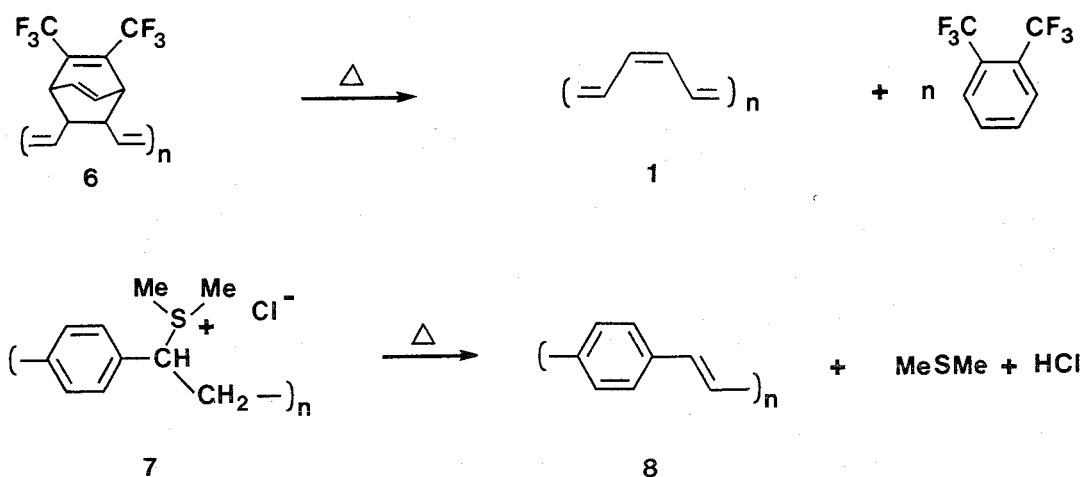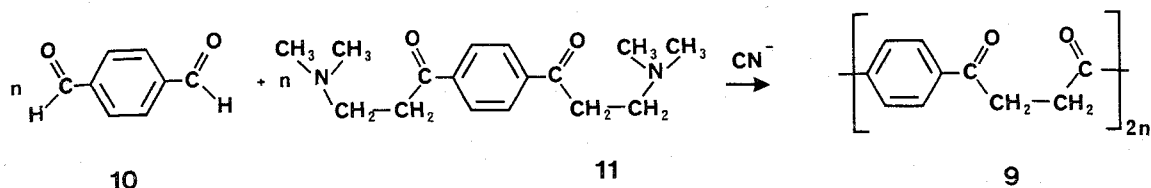
Scheme 1

Feast and Edwards introduced this concept of soluble precursors with their polyacetylene synthesis as outlined in scheme 1 [12]. The soluble precursor **6**, obtained by metathesis polymerization, yielded the socalled Durham polyacetylene in a thermal retro Diels Alder reaction. Another illustrative example is the synthesis of poly-*p*-phenylene-vinylidene **8** from the poly-sulfonium salt **7** by thermal elimination (scheme 1)[13]. When the polymer is stretched during this elimination a highly oriented film is obtained with a high anisotropy in its conductivity after doping (for instance with I_2). The conductivities can become as high as 10^4 S/cm. In these and many other cases the precursor polymers are made processable[11]. Another breakthrough in this area of research was achieved by synthesizing soluble conjugated polymers. This aspect will be discussed in paragraph 2.2 as introduction to self-doped conducting polymers.

2.1 POLYMERS OBTAINED BY THE STETTER REACTION

Since new strategies for polymer synthesis are at the basis of the progress made in the area of processable conducting polymers, we have conducted an investigation to a new synthetic scheme for polyheterocyclic polymers[14]. For heterocyclic polymers, all syntheses known today are based on the coupling of pyrrole or thiophene monomers, either electrochemically[15], by $FeCl_3$ oxidation of pyrrole[16] or by Grignard-type reactions of 2,5-dibromo-thiophene[17]. To date no schemes have been proposed in which the heterocycle is formed during a reaction performed on a preformed polymer. This is surprising, since the synthesis of pyrroles and thiophenes by ring closure of the appropriate precursor is a well-known reaction[18]. The reason that this procedure has never been used in polymer chemistry is probably due to the lack of suitable precursor polymers.

Scheme 2 The Stetter polymerization

We have synthesized such a precursor polymer by using the Stetter reaction (scheme 2). Poly-1,4-phenylene-1′,4′-butanedione **9** was formed in the reaction of terephthalic-dicarboxaldehyde **10** and the bis-Mannich base of 1,4-diacetylbenzene **11** in a yield of 81%. The conversion of **9** into the alternating copolymers of p-phenylene-2,5-pyrrole **12** and p-phenylene-2,5-thiophene **13** is performed with liquid NH_3 and Lawesson's reagent, respectively (scheme 3). Upon doping with either I_2 or AsF_5 both polymers **12** and **13** become electrically conducting with specific conductivities up to 0.1 S/cm.
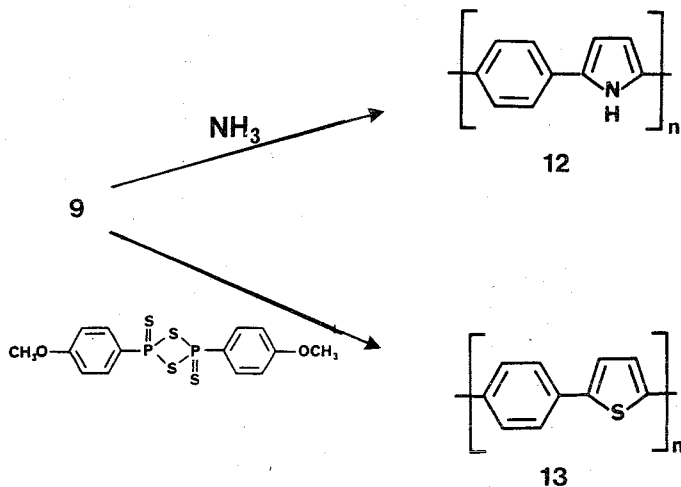
Scheme 3

In order to increase the conductivity to still higher values we will optimize the reactions used in this new strategy. Since it is expected that polymer **9** can be substituted and that also other aromatics than benzene can undergo the Stetter polymerization, we foresee a broad scope for this reaction scheme in the area of conducting polymers.

2.2 SELF-DOPED WATER-SOLUBLE CONDUCTING POLYMERS

Polyheterocyclic polymers that are soluble in the highly doped state were made for the first time by Frommer et al.[19]. However the solvents used were the toxic and environmentally unstable AsF_3-AsF_5 or liquid I_2, being both solvent and dopant simultaneously[19]. More recently, several groups, with seeding work from Elsenbaumer et al., prepared soluble and highly conducting polymers based on polythiophenes substituted with alkyl chains (like **14**, figure 2)[20]. The solubility is achieved through the addition of appropriate side-chains. Elsenbaumer prepared polymers like **14** by coupling of substituted 2,5-diiodo-thiophenes, but later on similar polymers have also been made by electrochemical polymerization of the corresponding monomers[21]. Conductivities in the range of 10-100 S/cm were obtained. Recognized drawbacks of the electrochemical polymerization of thiophene is the relatively high oxidation potential (1.65 eV versus 0.7 eV for pyrrole) and the susceptibility to the reaction for oxygen, leading to sulfon formation. It is a prerequisite to perform the polymerizations in inert media, whilst substituted α-terthienyls can be used to lower the oxidation potential to values of 0.7 eV [22]. In the latter case polymers (like **15**) are obtained with only one substituent per three thiophene units (figure 2).

14   **15**
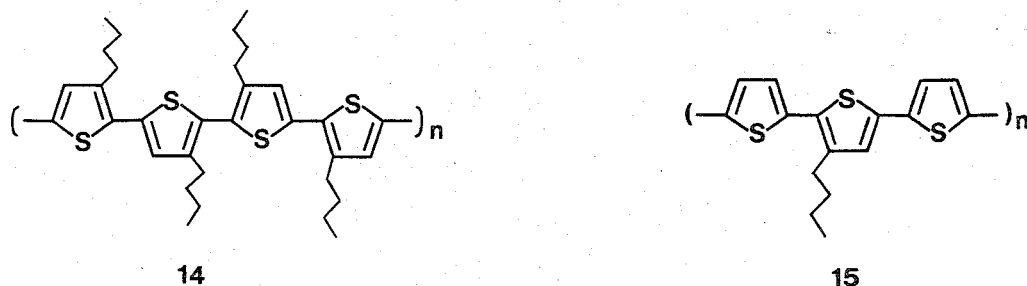
Figure 2

These alkyl substituted polythiophenes initiated our idea to synthesize polythiophenes that are so-called self-doped by the covalent attachment of the counter anion to the polymer chain[23]. The first successful example is given in figure 3, based on a sulfonate anion substituted poly(alkyl)thiophene (**16**). This polymer is made by electrochemical polymerization of the corresponding α-terthienyl **17** in acetonitrile *without the addition of a conducting salt*. The use of a conduction salt is generally considered as obligatory in order to have a sufficient conducting solution. Part of the anions is incorporated in the polymer during its electropolymerization, providing the dopant. In the case of **16** the monomer itself is a salt and addition of another conduction salt can be

omitted. This experimental procedure gives a solid proof that the conduction in the polymer is due to doping with the counterions of the sidechains. The conducting polymer, with conductivities up to 0.01 S/cm, proved to be soluble in water. However, the stability of this doped polymer in aqueous solutions is very limited while in methanol the polymer is already undoped upon solvation. Similar results were found by Wudl et al. by preparing and studying self-doped polythiophene **18** as made via an indirect route[24]. In order to increase the stability of the self-doped polymers we directed our attention to polypyrroles[23,25].
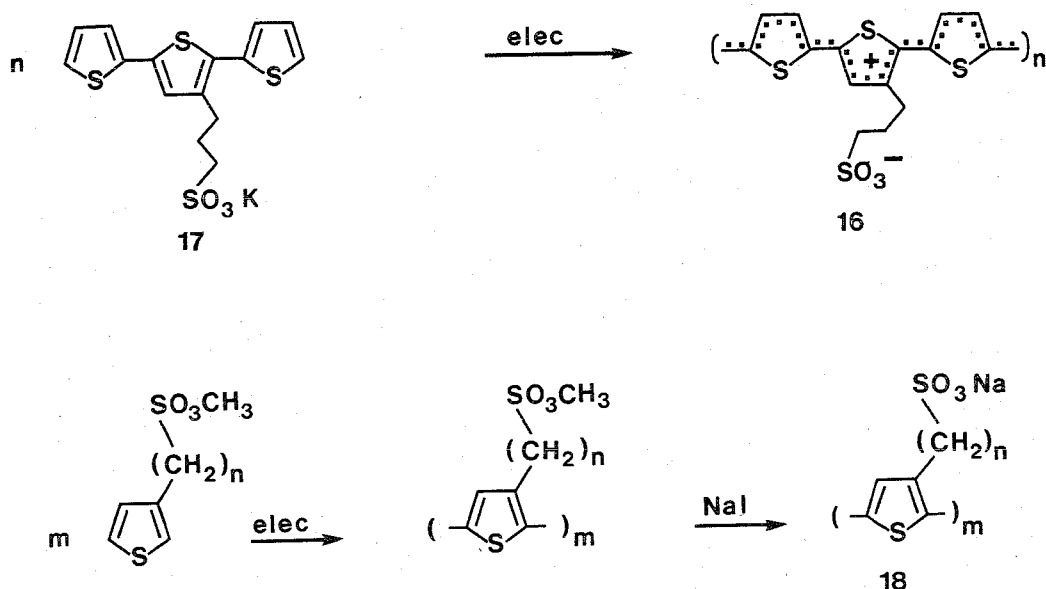
Figure 3

Upon electrochemical polymerization of 3-substituted pyrroles **19a-c** (again without additional conduction salts) an acetonitrile-insoluble polymer is formed as a blue, changing into black, precipitate at the (Pt or ITO) anode. In these polypyrroles part of the sulfonate groups act as a dopant and form "Zwitter-ions" having delocalized positive charges. The remaining sulfonate ions not participating in the self-doping are neutralized with either sodium ions or H_3O^+ (figure 4).

The electronic spectra of solid films of the polypyrroles, prepared on an ITO-glass electrode are compared with those of freshly prepared aqueous solutions of the same polymer (figure 5). Both spectra exhibit low-energy humps that are characteristic for doped conjugated polymers[26]. Contrary to the

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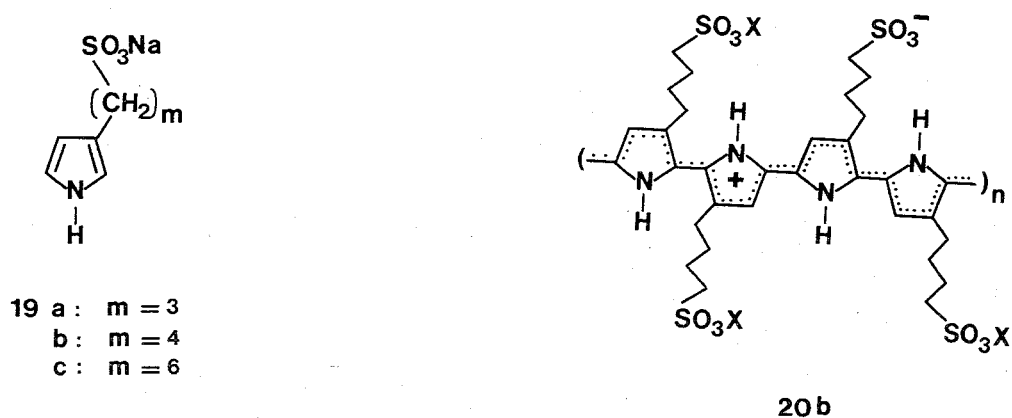
Figure 4 Monomers 19a-c and a sketch of self-doped polypyrrole 20b (X is either H_3O or Na).

self-doped polythiophenes **16**, the aqueous solutions of the polypyrroles **20a-c** are stable (hardly any change in the UV-vis spectrum could be observed after several months). Pressed pellets of the self-doped material showed conductivities of the order of 0.1 to 0.5 S/cm. Films obtained from these solutions by evaporating the water at about 70 °C exhibited a low conductivity of about 10^{-8} S/cm. However, slow evaporation of the solvent at ambient temperature afforded films with a conductivity of 0.01 S/cm.

Figure 5 Electronic spectra of the self-doped polypyrrole 20b. a) Solid film grown on ITO-glass electrodes in acetonitril, b) Aqueous solutions obtained from these films c) Film after the evaporation of water at 70 °C.

These first examples of self-doped conducting polymers that are stable as aqueous solutions will no doubt lead to new applications as well as to new insights in the behaviour of charge carriers in conducting polymers.
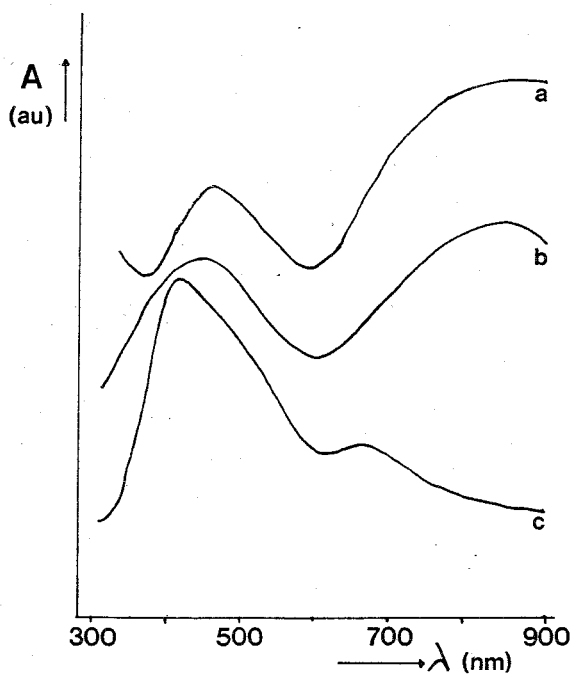

2.3 POLY-1,2-AZEPINES BY THE PHOTOPOLYMERIZATION OF PHENYL AZIDES

Up to now most of the effort to achieve processability of conducting polymers is directed to arrive at soluble (precursor) polymers. This allows films to be cast from solutions of these polymers. In order to produce microscopic structures as may be used in the electronic industry, these films have to be processed using conventional techniques like photolithography, etching etc. In another approach, Wrigthon et al. used patterns of gold electrodes on a substrate to form electrochemically polypyrrole or polyaniline on the gold-patterns only, leading to the production of polymer-based diodes and transistors[27]. We were interested in methods by which conducting polymers could be formed pattern-wise on a substrate via a direct one-step method.
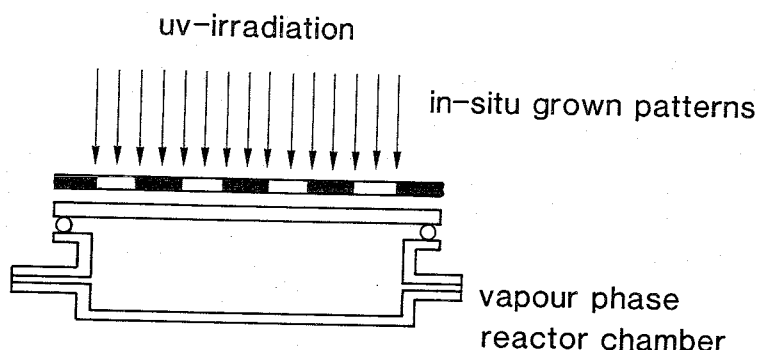
Figure 6 Reaction vessel for poly-1,2-azepine 24 film formation.

In our studies of the photochemistry of phenylazides we first thought that it could possibly provide a new route towards polyaniline. The results showed that a different polymer was formed instead; poly-1,2-azepines. We found that upon irradiation of phenylazides in the gasphase the poly-1,2-azepines are grown on the surface of the reaction vessel[26]. When the irradiation is performed through a photomask, as illustrated in figure 6, high resolution patterns are formed (figures 7 and 8). Upon doping with I_2 or AsF_5 these films (or patterns) become electrically conductive with conductivities up to 0.01 S/cm.
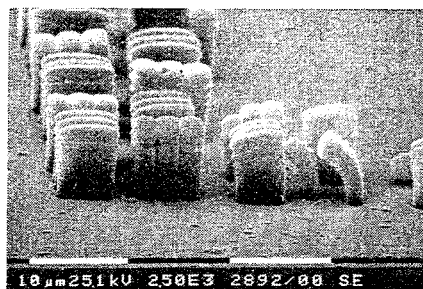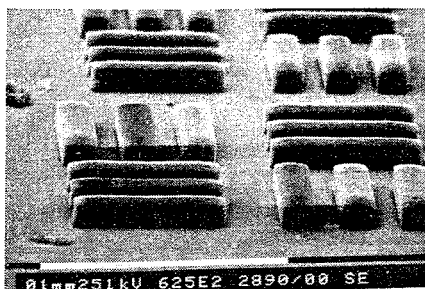
Figures 7 and 8 SEM photographs of poly-1,2-azepine as grown pattern-wise on fused silica using contact illumination. The bars represent 100 μm (fig.7) and 10 μm (fig.8).

Although the photochemistry of phenylazide **21** has been the subject of intensive research since its discovery by Wolff in 1912 [29], only a few contradictory notes have been made concerning the composition of the "tar" and its possible mechanism of formation[30]. In a variety of other reactions both singlet (**22**) and triplet (**23**) phenylnitrenes act as intermediate. Several reactions can be distinguished (scheme 5)[31].
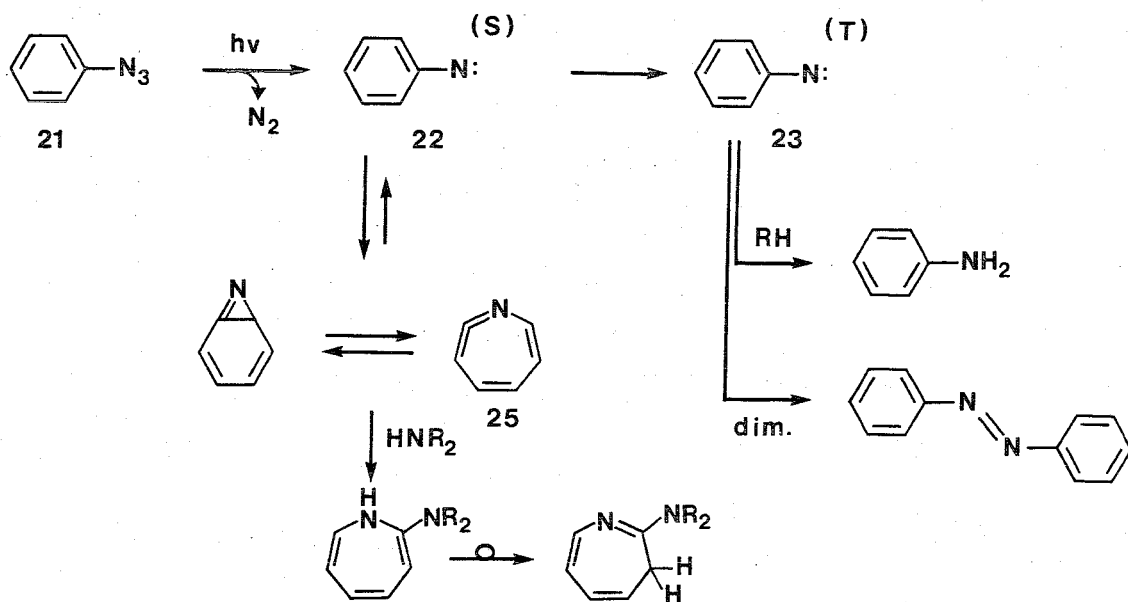
Scheme 5 Phenylazide photochemistry

We have found that the primary product of the photochemistry of phenylazides is the formation of poly-1,2-azepines **24** (Scheme 6)[28]. This polymer is formed via the ring-enlarged aza-cycloheptatetraene (**25**). The structure elucidation of the polymer is based on a variety of spectroscopic data and chemical analysis. The polymerization succeeded with a series of substituted phenylazides (figure 9).
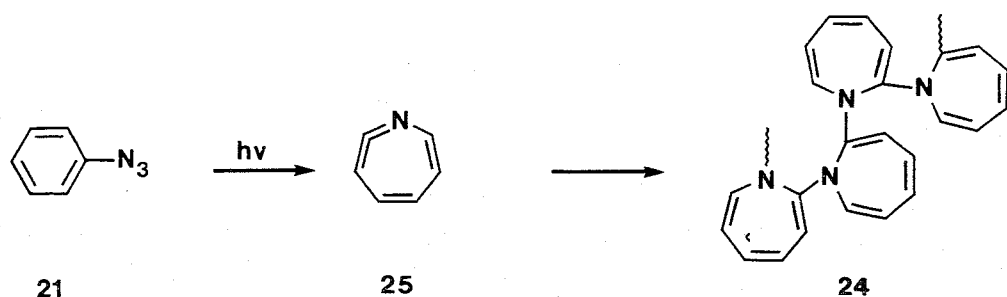
Scheme 6   Photopolymerization of phenylazide 21

The virgin poly-1,2-azepines (**24**) are very susceptible to oxidation by air, leading to charged species. When the polymers are subjected to strong oxidants like I_2 or AsF_5, conducting polymers are formed.
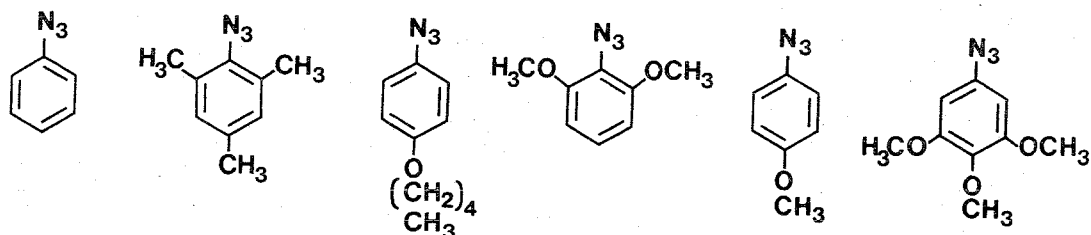
Figure 9   Monomers that are used in the photopolymerization

The formation of conducting poly-1,2-azepines suggests that the charged species formed are stabilized by conjugation or even aromaticity. The species to be expected are radical cations and dications of azepines. Delocalization of these species and 6-π electron aromaticity of the dications is evident both from theoretical studies and from experiments[32]. However, extended conjugation is excluded owing to steric hindrance between individual azepines (similar to ortho-substituted phenyls). Hence a moderate conductivity is expected and found. In order to increase the conductivity from poly-azepines, it seems necessary to synthesize 1,4-azepines. However, no design for such a synthesis is available at this time.

2.4 CONCLUSIONS AND PROSPECTS

The field of conducting polymers is still full of activity, mainly due to progress made in the synthesis of new polymers and the design of new synthetic schemes for the well-known polymers. In the first section of this paper we have given an anthology of our own recent results together with some of the landmarks in the

field worldwide. Higher conductivities are reached and processability is improved. What can we expect in the near future? A further improvement in all areas of conducting polymers can be foreseen, especially since at the present time scientists from several disciplines are cooperating.

One of the reasons for an increasing interest in conducting polymers is the expectation of their use in electronic devices[33]. Several applications are announced and prototype devices have been demonstrated[34]. By far the most studied application is the polymer battery, in which polyaniline (5) and polypyrrole (2) are the important candidates for the electrodes. Other applications are based on the semi-conducting properties of the polymers; e.g. transistors for Liquid Crystal Displays based on processable polythiophenes. Another announced application is found in conducting adhesives. In the future we will probably see more of these types of applications.

3 FERROMAGNETIC POLYMERS

In 1987 the first claims on ferromagnetic properties found in organic polymers were published[35,36]. Together with the comprehensive study of ferromagnetic charge transfer complexes from ferrocene compounds [37] it represents the first experimental counterpart of the theoretical studies published since 1963. In that year, McConnell presented his proposals[38] for high spin charge-transfer complexes from the combination of a triplet and singlet ground state donor and acceptor. In those systems a parallel alignment of all spins is expected. Polymer structures with such a high spin multiplicity were proposed in 1968 by Mataga[39]. Several investigations along the lines of these proposals have been performed.

The experiments following the McConnell model were concentrated on model studies and organometallic stacks **26** (figure 10).

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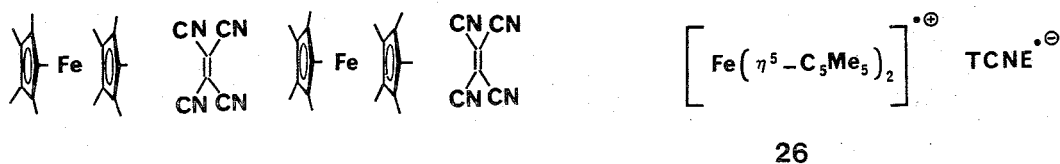
Figure 10

These low-molecular weight charge-transfer complexes exhibit bulk ferromagnetism below the Curie temperature of 4.8 K, as observed by Miller and Epstein[37]. A model of configuration mixing of the lowest charge-transfer excited state with the ground state was developed to understand the magnetic coupling as a function of electron configuration and direction of charge transfer. In a series of studies by Breslow et al. pure organic charge transfer complexes were made[40]. However no bulk ferromagnetism has been observed.

From hard-to-reproduce experiments on the polymer network from 1,3,5-triaminobenzene and iodine, Torrance et al. concluded that it represents the first polymer with bulk ferromagnetism[36]. Despite the possible presence of impurities the work is stimulating for further research. In an elegant study on oligomers of poly-carbenes Iwamura et al. were able to synthesize polycarbenes as given in figure 11 [41].

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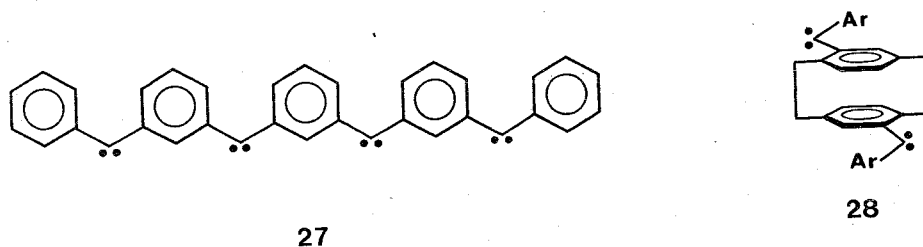
Figure 11

Although intramolecular alignment of the spins is observed in **27** and as a model for intermolecular coupling also in **28**, the bulk properties are those of an antiferromagnet.

Most successful up to now seems to be Ovchinnikov with the preparation of a polydiacetylene with dangling stable nitroxyl radicals **29** [35,42]. The structure of the polymer and its way of preparation are given in scheme 7. The solid state polymerization of **30** is claimed to be feasible by both thermal treatment and by irradiation. Selected samples of the polymer exhibit magnetization values above 1 Gauss and respond noticeably to the field of a permanent magnet. The observed Curie temperatures ranged from 150-190 K up to 310 K for the high magnetization samples. Despite the experimental evidence presented, some scepticism against the results seems justified. Several other laboratories have tried to reproduce Ovchinnikovs results, however, sofar unsuccessfully[43].

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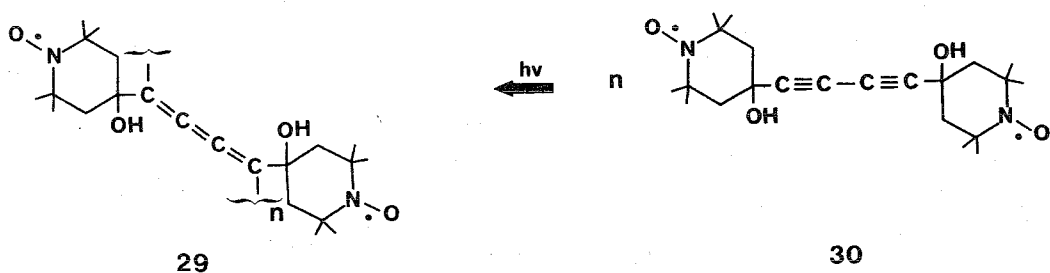
Scheme 7

A variety of other examples for possible high spin polymers possessing free nitroxyl radicals have been investigated. In most cases the spin density is low and hence polymers like **31** (figure 12) are antiferromagnetic[44].
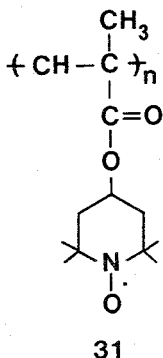
Figure 12   31

3.1 APPROACH TO HIGH SPIN POLYNITROXIDE

One of the major drawbacks of the polynitroxides synthesized sofar is the limited concentration of stable radicals. In an approach to reduce the number of "useless" additional atoms, we have tried to synthesize polynitroxide **32**, one of the polymers with the highest concentration of radicals experimentally possible[45]. The synthetic plan is outlined in scheme 8.
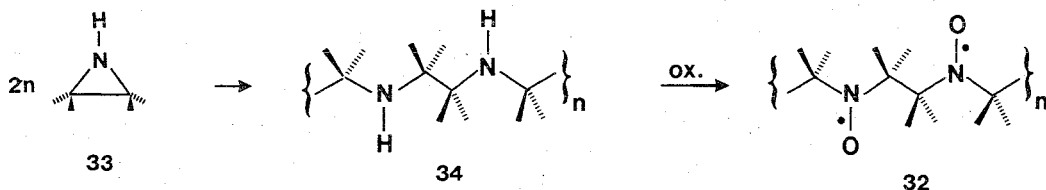
Scheme 8

The oxidation of a secondary amine to a nitroxyl radical is well-documented and known to proceed in high yield[46]. Furthermore, numerous papers concerning aziridine polymerization have appeared[47]. However, no reports are given on the polymerization of the most hindered derivative in the aziridine series, i.e. tetramethylaziridine (**33**). Monomer **33** is made using a slightly modified procedure published earlier[48]. Neat **33** is polymerized at a temperature of 110 °C using BF₃ as the catalyst. After prolonged heating in an inert atmosphere, the polymer complex **34** / BF₃ precipitated from the solution. Although grafting is a well-known side-reaction in aziridine polymerization, structure elucidation of **34** (¹H- and ¹³C- NMR spectroscopy) showed that no grafting had occurred in the polymerization of **33**.
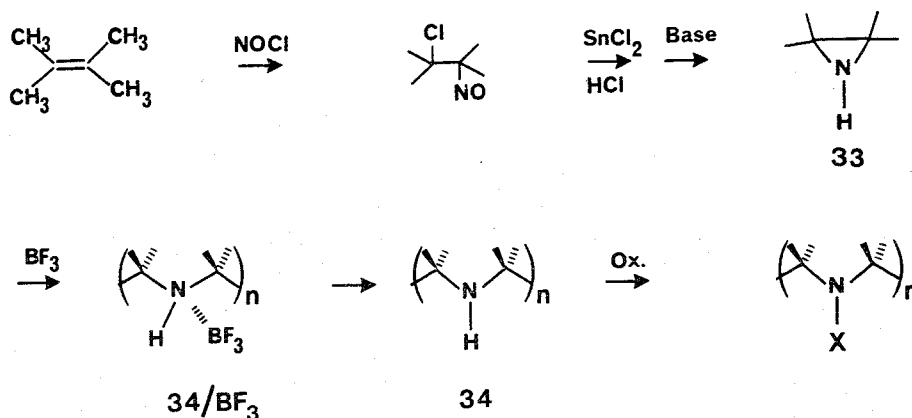
Scheme 9

The yield of the polymer proved to be strongly dependent on the ratio catalyst/monomer, as illustrated in figure 13. Furthermore, the estimated molecular weight on the basis of solubility decreased by increasing yield. The following picture emerges from the experiments: As in common aziridine polymerizations, the aziridine **33** is activated by BF_3 and polymerizes. The polyimine produced is a strongly hindered amine and has to be regarded as a very strong base, that upon formation complexes the acid catalyst BF_3, leading to an inhibition of the polymerization. At high catalyst concentrations many macromolecules can be formed, however, the complexing ratio BF_3 / (monomeric unit) will be high, and hence precipitation occurs at a low molecular weight. At a low catalyst concentration a limited number of higher molecular weight macromolecules is formed.
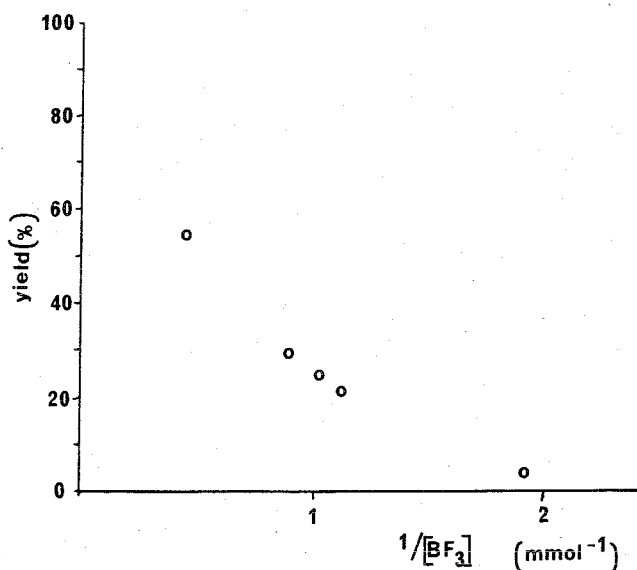
Figure 13 The yield of polymer 34/BF_3 as a function of catalyst concentration. The concentration of monomer 33 is in all cases 5 mmol.

Due to the strong complex formation , it proved to be difficult to obtain the free polyamine **34**. Ultimately **34** was isolated after decomplexation in hot DMSO. The oxidation of **34** to the polynitroxide **32** was performed under a variety of reaction conditions. The maximum conversion obtained up to now is low, being about 10 %. A possible explanation for this low conversion is based on the low solubility of **32** and **34** under the reaction conditions used. The characterization of the ultimate polymer is strongly limited by the presence of (para)magnetism and some inorganic impurities.

Some other approaches to synthesize polynitroxide **32**, to wit the direct polymerization of the monomeric unit tetramethylaziridin-yloxy or the polymerization of the α-nitroso radical were all unsuccessful (scheme 10)[45].
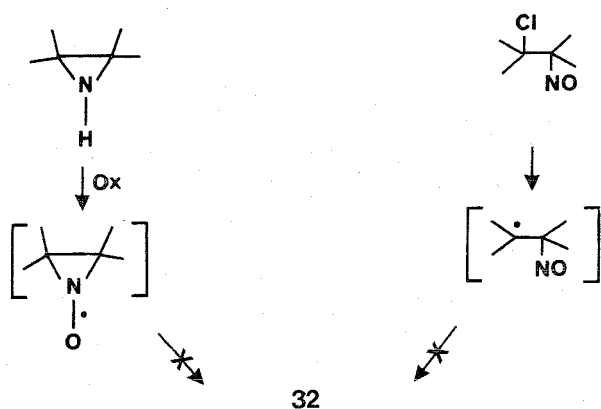
Scheme 10

Many problems are still underlying the research to polymeric ferromagnets. The work is strongly hampered by possible impurities. However, much progress has been made lately. For the time being it is still a scientific challenge to observe ferromagnetism in polymers and organics, and it is yet not worthwhile to speculate on possible applications.

4 POLYMERS WITH NONLINEAR OPTICAL PROPERTIES

Although nonlinear optical properties of materials are known for more than a century, the relevance of organics and polymers in this fascinating area of research originates from a more recent development[49,50,51]. To introduce the subject of this paragraph, the fundamental concepts of nonlinear optics and their relation to chemical structure are briefly summarized.

The dipole moment, p, of a molecule will change if the molecule is subjected to an electric field, E. Since the response is mainly linear, a power expansion can be used to describe the resulting dipole moment[52]:

$$p = p_0 + \alpha.E + \beta.EE + \gamma.EEE + \ldots$$

Here p, p_0, and E are vectors and α, β and γ tensors, normally referred to as polarizability, hyperpolarizability and second order hyperpolarizability, respectively. Similarly, the polarization in bulk or macroscopic media is given by:

$$P = P_0 + \chi^{(1)}.E + \chi^{(2)}.EE + \chi^{(3)}.EEE + \ldots,$$

where $\chi^{(1)}$, the linear susceptibility, $\chi^{(2)}$ and $\chi^{(3)}$, the second and third order susceptibilities, are the macroscopic counterparts of α, β and γ. The exact relation between molecular polarizabilities and macroscopic susceptibilities is rather complicated and depends on the positions and orientations of the molecules. As a consequence of symmetry, the second order susceptibility is zero in centrosymmetric media. For $\chi^{(3)}$- materials such a rule does not exist. The magnitudes of $\chi^{(3)}$ and $\chi^{(2)}$ depend critically on the directions of field(s) and polarization(s), and both susceptibilities can be greatly enhanced by anisotropy.

For most materials and reasonable fields, the effect of nonlinear response is only small. Therefore, only molecules with an exceptionally high hyperpolarizability β are of interest when applications of nonlinear optics are concerned. The recent increase in interest in second order nonlinearities is motivated by two major applications, to wit light modulators by electro-optical effects (Pockels-effect) and the frequency doubling of laser light. The electro-optical effect is based on the property of materials with a high value of $\chi^{(2)}$ whereby the refractive index is markedly dependent on the applied electric field. The frequency doubling of light by means of nonlinear optical materials (Second Harmonic Generation, SHG) is another manifestation of second-order nonlinearities. For example, light with low energy (e.g. 1.064 μm of a Nd:YAG laser) can be doubled in frequency to the second harmonic (532 nm).

Proposed applications of third order nonlinearities are very intriguing and include

all-optical computing and communication[53]. However, the proposed materials and technologies are still far from adequate. Third order nonlinearities are only large in extended π-electron conjugated systems, and therefore the high $\chi^{(3)}$-polymers are of the same class as those in figure 1. The polymers of choice are polydiacetylenes, as these can be prepared well-oriented in a topochemical polymerization. The solid-state monomer can either be in the form of a crystal or of a Langmuir-Blodgett thin film[54]. Recently a variety of other polymers are the subject of investigation and oriented polyacetylene seems to be comparable to polydiacetylenes[55]. A major drawback of possible applications of $\chi^{(3)}$-polymers is stressed by Stegeman[56], viz. the low absorption demanded for application is hard to combine with the high nonlinearities found today. In this review we will concentrate on the $\chi^{(2)}$- materials.

As stated above, non-zero β- and $\chi^{(2)}$- values can only be found in non-centrosymmetric molecules and media. Even a molecule with an asymmetric charge distribution in a centrosymmetric crystal or in an isotropic liquid or amorphous polymer matrix will exhibit a vanishing small value of $\chi^{(2)}$. Only surface effects, due to the intrinsic anisotropy of surfaces will lead to a minor nonlinear response. The value of β is strongly dependent on the molecular structure. Typically, high values for β are found in molecules in which low-lying charge-transfer transitions are present[46]. In general such molecules possess an electron donor at one side of the molecule and an electron acceptor at the other side, separated by a π-conjugated system. Enormous enhancement of β is found by extending the π-conjugation. Examples are given in figure 14, whilst many others are subject of research.
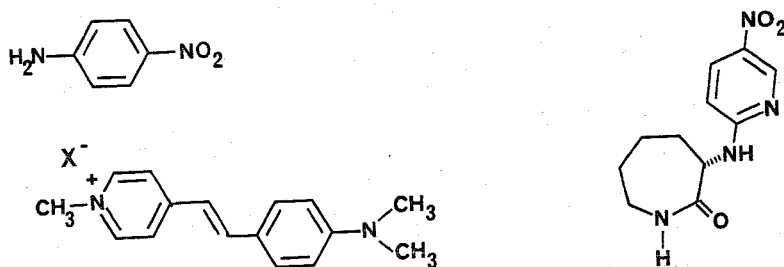
Figure 14

β -Values can be measured by several techniques, including electric field induced second harmonic generation and solvatochromic measurements of absorption and fluorescence[57]. Moreover, quantum mechanical calculations can be used to estimate these nonlinearities[58]. For a more detailed description of the physical backgrounds of nonlinear optics we like to refer to excellent reviews and books[49,50,51].

In order to transform a molecule with a high β value into a material without a centrosymmetric structure three main techniques of material engineering are available:

* Crystal engineering [59] .

The structures that exhibit high β-values possess in many cases a large ground-state dipole moment. As a result of the latter the electrostatic interaction between the molecules is large too, leading to a preference for antiparallel order and, hence, to $\chi^{(2)} = 0$. One way to achieve non-centrosymmetric crystals is obtained by introducing asymmetry in the molecule. Optically active molecules are of special interest since nature does not permit centrosymmetry in crystals of these molecules.

* Langmuir-Blodgett thin film technology [60] .

Amphiphilic molecules with a polar head and an apolar chain form highly ordered monomolecular films at the solvent-air interface. These so-called Langmuir-Blodgett films can be deposited on a substrate, retaining their high ordering. Stable polymer Langmuir-Blodgett films are formed upon topochemical polymerization of amphiphiles provided with polymerizable functionalities like double bonds or diacetylenes. High surface nonlinearities are observed for these thin films when they are built up in such a manner that the amphiphiles with the charge-transfer groups are deposited in a polar alignment.

* The poling of dipoles in a polymer

This subject will be discussed in the next paragraph.

4.1 POLING OF DIPOLES IN A POLYMER

Useful optical polymers with high second order susceptibilities should be both completely transparent. Hence semicrystalline and polycrystalline samples as well as incompatible blends have to be avoided, while anisotropy by a large number of oriented β -molecules or fragments is demanded. The latter can be achieved by applying an external electric field to the polymer. The sequence as used by many investigators and introduced some 10 years ago at our laboratories is outlined in figure 15 for a dipole dissolved in PMMA, the pre-eminent optical polymer[61,62].

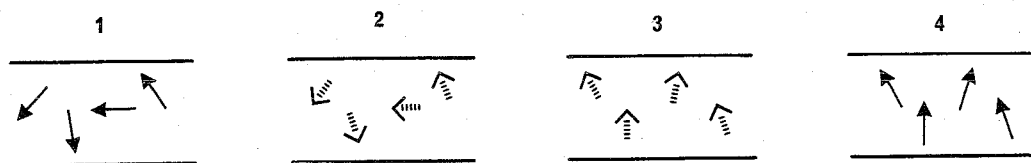**Figure 15** The poling sequence. 1) Glassy PMMA at room temperature with a frozen-in random orientation of the dipoles. 2) Heating above Tg yields a rubbery state with a random orientation and dipoles that are free to rotate. 3) An E-field applied on the PMMA at high T yields a rubbery state with aligned dipoles. 4) Cooling to room tempearture followed by removing the E-field yields glassy PMMA with aligned (frozen-in) dipoles.

A PMMA sheet with a thickness between 1-100 μm is heated just above its Tg to introduce molecular mobility. At that temperature, an external dc-field is applied to the polymer film and as a consequence the dipoles are oriented. The degree of orientation is dependent on the dipole moment of the dipole, the field-strength and the temperature of the experiment[63]. This non-equilibrium state is frozen-in by lowering the temperature, while the field remains. After reaching room temperature the field is removed. The electric field can be applied by using two electrodes sandwiching the polymer film. One of the electrodes can be replaced by a Corona discharge that is applied to the polymer film. With the latter higher fields can be obtained and hence a better alignment.

The degree of orientation obtained can be measured in several ways. Obviously, second harmonic generation is one of them, however interpretation of the data in a quantitative manner is subject to a variety of assumptions and measurement inaccuracies. In many cases, SHG is only given in arbitrary units or related to reference samples, and is strongly dependent on the wavelengths used due to resonance effects. Another method uses the changes in the absorption spectrum of the polymer sheet upon poling due to the alignment of the molecular dipoles and, hence, of the transition moments (electrochromism)[61].
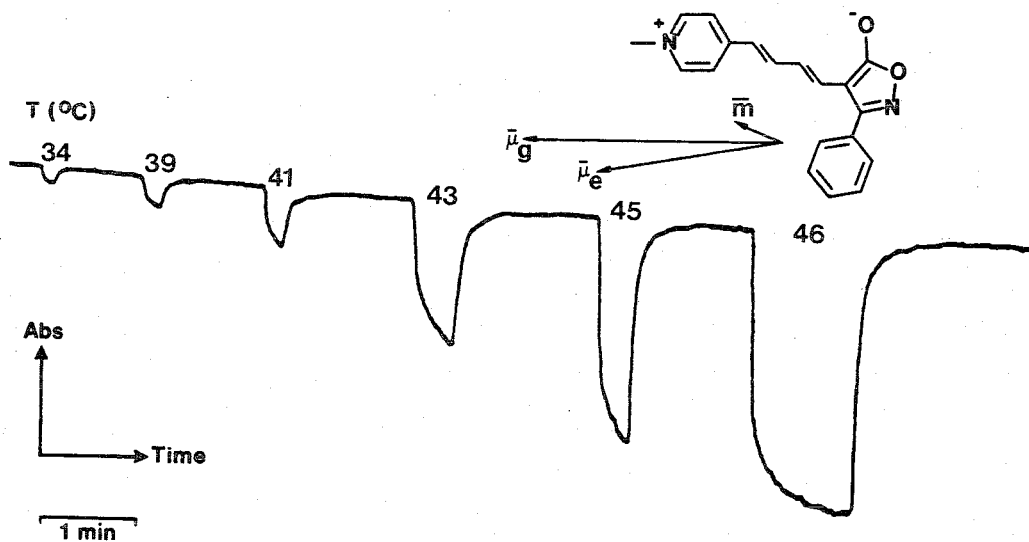
Figure 16 Electrochromic measurements at different temperatures of a dye in a Epikote polyepoxide.

In figure 16, the decrease in absorption of a dye with a high dipole moment dissolved in an epoxide polymer network is given. The alignment is strongly dependent on the temperature used. Only at temperatures reaching Tg a large decrease in absorption is found. The quadratic dependence of applied field and decrease in absorption is illustrated in figure 17 for another dye poled in PMMA at T = 125 °C.

Figure 17 Electrochromic measurements of DANS (4-dimethylamino-4'-nitrostilbene) in PMMA at 125 °C. The change in absorption is measured at a wavelength of 435 nm.

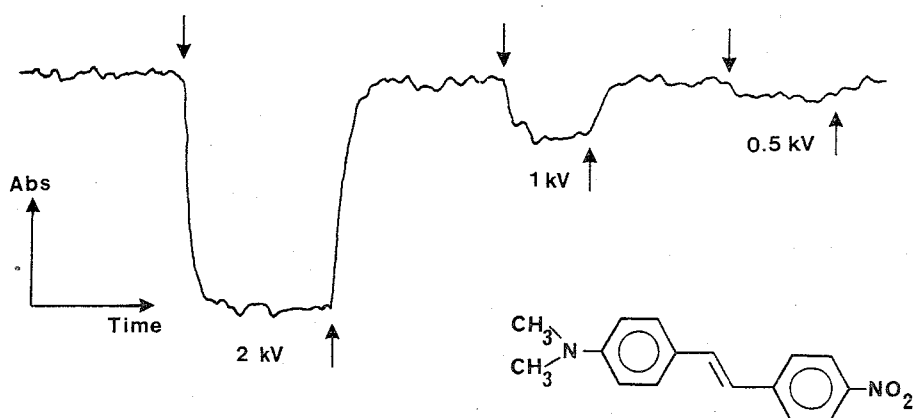Several issues are under investigation with this alignment strategy in mind. First, how can we increase the number of dipoles in the polymer matrix? In most polymers the maximum amount of dipoles that can be dissolved is in the range of 1-5 ww%, only. Polymers with pendent dipoles attached covalently to the polymer backbone allow much larger concentrations. In figure 18, a few examples of monomers from our laboratories are given[64]. Another approach currently under investigation is based on liquid-crystalline materials and their use in nonlinear optics[64].
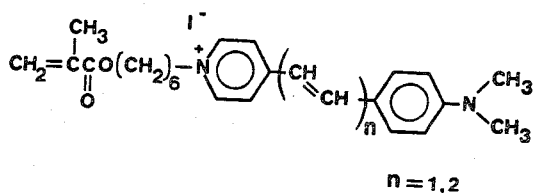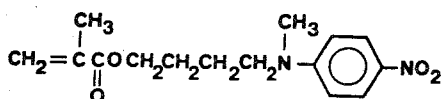
Figure 18

Second, what is the stability of the aligned, non-equilibrium state. As is known from a variety of studies of the molecular mobility of polymers and polymer networks, it is reasonable to assume, that even far below Tg most polymers have some motional freedom. This will lead to a relaxation of the dipoles. The general feeling is, however, that sufficiently stable, highly nonlinear ($\chi^2 > 50$ pm/V, compared to 6 pm/V for $LiNbO_3$) polymers can be made.

4.2 APPLICATIONS OF POLED POLYMERS AND INTEGRATED OPTICS

Being able to produce poled polymers with stable second order nonlinearities, it is possible to construct prototype devices in which the polymer is the active component[65]. As mentioned above major applications are foreseen in light modulation and frequency-doubled diode lasers. Despite the high nonlinearities obtained, fruitful use of these nonlinearities is only possible when an appropriate interactionlength is used, hence waveguide structures are necessary. An example is given in figure 19.
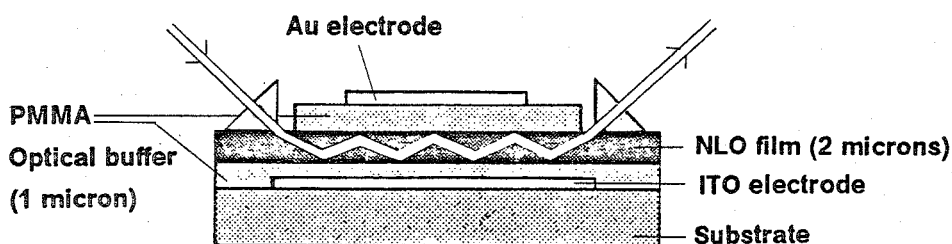

Figure 19 A substrate is covered with a thin (ITO) electrode and an optical buffer is spin-coated on top. PMMA, polyepoxides and silicon rubbers are useful buffers with low refractive index. The nonlinear optical polymer is followed by another optical buffer and a topelectrode. The light is coupled into the waveguide using prisms. The electrodes can be used for both the poling experiment as well as to modulate the refractive index of the polymer.

For frequency doubling, some additional demands should be fulfilled, viz. phase matching and a very low absorption at both the fundamental and second harmonic wavelength. Several proposals have been made to obtain phase matching in polymer waveguides and work along these lines is in progress.

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