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Maleimide copolymers containing azobenzene moieties – Synthesis and study of liquid crystalline and optical properties.

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ABSTRACT

New reactive copolymers have been synthesized by copolymerization of two functional Nsubstituted-maleimides with styrene. These copolymers, having aldehyde and carboxyl functional groups, were further chemically modified with *p*-aminoazobenzene. After verification of the chemical structures by IR and ¹H-NMR spectroscopy, the copolymers were characterized by solubility, X-ray diffraction measurements and their thermal stability was controlled by thermogravimetrical analysis (TGA). The thermal and thermotropic properties were investigated using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). A comparative study of the photoisomerization in solution and thermal recovery characteristics of azo copolymers vs. the corresponding maleimide model compound has been performed.

Keywords: styrene-maleimide copolymer; azobenzene; liquid crystal, photochromism

Introduction

Azobenzene is a well-known photochromic molecule, being isomerizable from the *trans* (E) to the *cis* (Z) form by UV irradiation and reverses upon thermal heating or visible light irradiation.¹ The reversible *trans-cis* photoisomerization of azobenzene chromophore acts

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as a molecular switch, being responsible for photoinduced optical dichroism and birefringence.²⁻⁴ Also, the azobenzene systems allow the optical control of photoinduced birefringence – fact which has not been observed in other materials.⁵ Important development of the scientific research was ascertained in the area of azobenzene containing polymers, starting from early efforts to covalently bind azobenzene units into the polymeric chains.⁶ until nowadays when new applications have emerged: light-induced surface patterning, colloidal spheres, tunable diffraction gratings,⁷ supramolecular selfassembly and chirality transfer.^{8,9} liquid crystalline elastomers.¹⁰ side-chain azo-polymers useful for encoding information.^{11,12} N-substituted maleimides, which belong to the 1,2disubstituted ethylenic compounds, are attractive monomers for design of special vinyl copolymers. The maleimide ring affords, besides predefined structure distribution by radical polymerization, useful carrier features for many functional groups.¹³ Maleimide copolymers, having good engineering properties like: tractability, high thermal stability and durability, good water, fire and radiation resistance, have many applications in electronics for aircraft and aerospace industry.¹⁴ It was noted that most of the works on photoresponsive azobenzene-containing materials are based on polymeric matrices. In this respect, the interactions between chromophore units are better suppressed in nonpolar polystyrene matrices than in poly(methyl methacrylate) ones.¹¹ For this reason, a series of styrene/maleimide copolymers containing side-chain azobenzene chromophore units have been reported and the tests of their properties showed the accomplishment of demands related to electro-optic coefficient, thermal stability and optical loss.¹⁵⁻¹⁸ The aim of our paper is the synthesis of new maleimide/styrene copolymers containing side-chain azobenzene chromophore units and the investigation of their thermal and optical properties.

Results and Discussion

Synthesis and characterization

N-substituted maleimides are considered as polymerizable electron-poor ethylenic monomers and readily produce alternating copolymers with electron-rich monomers such styrene and vinyl ether derivatives [24]. In view to prepare new maleimide/styrene copolymers containing side-chain azobenzene chromophore units, three functional maleimide monomers: 4-maleimido-benzoic acid (M1), 4-maleimido-benzoyl chloride (M2) and N-(4-formyl-phenoxy-4'-carbonylphenyl)maleimide (M3) were synthesized as reported [20,23]. These compounds have been used further to synthesize chromophore functionalized maleimide model compounds M4 and M5 (Scheme 1).

Scheme 1.

The chemical structure of all the resulting maleimides was confirmed by FTIR, ¹H-and ¹³C-NMR spectroscopy. Suggestive FTIR spectra of chromophore model compounds **M4** and **M5** are presented in Fig. 1. Spectra revealed the presence of both common and specific absorption bands. Some common absorption bands follows (cm⁻¹): v =C–H (vinyl and aromatic) 3100 (M4), 3070 (**M5**); v C=O (imide II) 1700 (**M4**), 1720 (M5); v C-N (imide III) 1380 (**M4**), 1405 (**M5**); out-of-plane 1,4-phenylene ring 810 (**M4**), 845 (**M5**); bending C=O (imide IV) 750 (**M4**), 758 (**M5**). As specific absorption bands (cm⁻¹): v N-H 3410 (**M4**); v C=O (-NH–CO–) 1640 (**M4**); v C=O (–COO–) 1627 (**M5**); v -CH=N– 1625 (**M5**); v C-O asym. (–COO–) 1260 (**M5**).

Figure 1

Fig. 2 shows the ¹H-NMR spectrum for the maleimide **M4** in DMSO-d₆ at room temperature. The singlet at δ 10.67 ppm was assigned to the proton of –CONH– linkage, the multiplet at 7.45-8.23 ppm was assigned to the resonance of aromatic protons while the singlet at 7.24 was due to the protons of -CH=CH- linkage belonging the maleimide ring.

Figure 2

The molecular design of photochromic polymers can be realized mainly either by blending dye molecules with the polymer matrix, or by covalent binding the dye molecule via polymerization or chemical modification route. The second option gives polymers having chromophores chemically linked to the main chain thus avoiding the phase separation [25]. In a first step, two styrene-maleimide copolymers **P1**, **P3** having different side-chain reactive functional groups: -COOH and -CH=O, respectively were prepared. This was done by radical copolymerization in solution of styrene with N-(4-carboxyphenyl)-maleimide (**M1**) or N-(4-formylphenoxy-4'-carbonylphenyl)-maleimide (**M3**) (Scheme 2). These two intermediate copolymers were further chemically modified with *p*-aminoazobenzene (**4**), leading to the final azo-copolymers **P2** and **P4**, containing, besides the common azo (-N=N-), different chemical linkages: -CO-NH-; (**P2**) and -COO-; -CH=N-; (**P4**) (Scheme 2).

Scheme 2

An alternative method to prepare such copolymers by copolymerization of styrene with the maleimide model compounds **M4** and **M5**, failed, showing both low yields and poor molecular weight. The imide structure (Fig. 3) was confirmed by the presence of four specific absorption bands (cm⁻¹) at: imide I at 1782 (**P2**), 1775 (**P4**), imide II at 1714 (**P2**, **P4**), imide III at 1383 (**P2**), 1382 (**P4**), imide IV at 758 (**P2**), 757 (**P4**). Supplementary absorption bands illustrated the presence of particular chemical linkages (cm⁻¹): amide at 1648 (**P2**), -CH=N- at 1626 (**P4**), ester at 1207 and 1157 (**P4**).

Figure 3

Fig. 4 shows the ¹H-NMR spectrum in CDCl₃ of the copolymer **P4** with the corresponding assignments. The absence of any signal at δ 9.8 ppm due to CHO protons and the presence of a singlet at δ 8.27 ppm due to azomethine (-N=CH-) protons proves the chemical

modification reaction of the aldehyde pendent groups of the copolymer **P3**. The region from δ 6.73 to 7.85 ppm is due to the 22 aromatic protons. The multiplet at δ 3.2–4.1 ppm showed the presence of the new formed [>CH–CH<]_n linkage. Depending upon the substitution in maleimide, this signal has been reported in the δ range of 3.0–5.0 ppm, [23, 26-28]. The ethylidene protons of the styrene moiety (>CH-CH₂-)_n were assigned at δ 3.02-3.07 ppm.

Figure 4

Figure 5

A representative ¹³C-NMR spectrum of the copolymer P2 is plotted in Figure 5. The two types of carbonyl carbon atoms appeared around 177 ppm (succinimide) and at 167 ppm (amide). The aromatic carbons ranged between 154 ppm and 120 ppm, and the aliphatic carbons are present in the range 55-20 ppm. The copolymers showed good solubility in common aprotic dipolar solvents like DMF, NMP, DMAc, DMSO and also in THF. This behavior could be the result of the presence of voluminous side-chain units which, by steric hindrance, prevents the close packing of the polymer chains. Their molecular weights have been determined by GPC measurements on THF solutions. The obtained results are listed in Table 1. As can be seen from Table 1, reasonable molecular weights were obtained, even little higher than other side-chain azobenzene containing polymers [29a].

Table 1

Thermal stability and liquid crystalline properties

The thermal stability of the copolymers was evaluated by TGA under nitrogen atmosphere. The obtained results are summarized in Table 1 and Figure 5. The temperature for 10 % weight loss (T_{10}), comprised between 329 and 355 °C was selected as criterion of thermal stability of copolymers. The lowest T_{10} value of the copolymer P1 could be explained by

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the poor thermal stability of aldehyde functional group. The azobenzene containing copolymers P2 and P4 have T_{10} values intermediary between copolymers P1 and P4. The highest T_{10} value of copolymer P4 could be due to an extension of thermal stability in the initial step due to hidrogen bonds. Also, literature data showed that copolymers having pendant carboxyl groups exhibited T_{10} values above 450 °C [29b].

Figure 6

Two stages were observed during decomposition process. The first stage, ranging between 353 and 365 °C, was assigned to the gaseous nitrogen release due to cleavage of -N=N-linkages [30]. The second stage comprised between 492 and 517 °C incorporates the decomposition of the rest of chemical moieties. The thermotropic liquid crystalline behavior of the copolymers was studied by polarizing optical microscopy (POM) of thin layer specimen between glass slides, as qualitative observation of textures, and also by differential scanning calorimetry (DSC) to record temperature of phase transitions. The obtained results are presented in Table 2 and Figure 7. The transition temperatures listed in Table 2 were recorded only during the first heating cycle, because of possible affectation of the mesophase by the occurring of the thermal degradation.

Table 2

All the investigated samples exhibited enantiotropic liquid crystalline behavior, excepting sample **P1**, which was isotropic. In Fig. 7 the DSC thermograms are related with the corresponding POM microphotographs of the observed texture. Two endothermal peaks have been recorded in all cases and were assigned: first to crystal-nematic phase transition and second to nematic-isotropic phase transition. In all cases the second endothermal peak is more or less affected by an exothermal peak which follows. Only the sample **M4** has the isotropization peak blended with the exothermal one with maximum at 266 °C. This overlapping phenomenon is known in case of low molecular compounds, especially of

maleimide type [33]. This exo peak is due to the polymerization process of ethylenic maleimide double bond. For the remaining samples there is an overlap between the polymerization and thermal degradation.

Figure 7

As can be seen from Fig. 5, only the sample **P3** showed a banded texture under shear stress, while the other samples presented a fine grainy texture, as reported for other sidechain liquid crystalline polymers [29,34-36]. Noël explained that such fine grainy textures have been investigated by transmission electron microscopy, which revealed that they correspond to regions of uniform orientation correlation within nematic structures [37]. The reason for the generation of such texture was supposed to be the low level of interchain attraction [29]. We observed that, since our copolymers had the side chain mesogenic moieties directly coupled to the main chain, without any flexible spacer, the interchain attraction became disfavored. In case of samples M3, M4 and M5 we tried to correlate the thermotropic behavior with their molecular features like: ovality (O_v) [38], molecular polarizability (α) [31] and mesogenic index (MI) [32]. As Villanueva-Garcia pointed out [38], in case of cylinder-shape (calamitic) molecules like ours, the ovality (O_v) can be related with the aspect ratio (length/diameter) of the molecule, by the equation:

$$O_v = (3/54)^{1/3} \cdot (2x+1)/(x)^{2/3}$$

where: x = length/diameter ratio. Looking at the O_v values, the following shape domains could be described:

 $O_v \ll 1$ oblate spheroid; $O_v = 1$ perfect sphere; $O_v > 1$ prolate spheroid;

By using Hyperchem [39] the geometry optimization of compounds M3, M4 and M5 was performed (Fig. 8).

Figure 8

The calculated values of O_v are presented in Table 3, together with values of molecular polarizability (α), calculated with program ACD/Chemsketch and the mesogenic index MI [32]. The last one represents an empirical method for predicting the capability of forming mesophase for copolymers in relation with their chemical composition [32] but we observed that it works also for low molecular compounds. If the condition MI > 10 is satisfied, then thermotropic behavior is expected. As can be observed from Table 2 all the O_v values are greater than 1 which indicate a prolate spheroid shape, as a consequence of the aspect ratio values depicted in Fig. 6. The MI values of all the compounds are greater than 10 which suggested a thermotropic behavior as expected (Table 3).

Table 3

Considering both the Cr-N and N-I phase transitions, the following series of increasing transition temperatures can be written: M5<M3<M4. Although sample M5 has greater polarizability value than samples M3 and M4, the greater transition temperatures in case of sample M4 can be explained by the high content of hydrogen bonds of amide linkage. The mesophase range, comprised between 18 and 43 °C, increases with the increasing of all discussed parameters, polarizability, ovality and mesogenic index. By comparing the transition temperatures, the mesophase range and the texture aspect of the model compounds M4, M5 with those of corresponding pair copolymers P2, P4, respectively, one can observe that transition temperatures of copolymers are higher than those of model compounds, as expected. The mesophase range is equal in case of pair M5-P4, while copolymer P2 had a better mesophase stability than corresponding model M4, probably due to hydrogen bonds. No significant differences of texture features were observed for both models M4,M5 and copolymers P2, P4. The copolymer P1, having no mesogenic pendant groups, showed no mesophase, while P2-P4 having pendant mesogenic groups of variable length, exhibited nematic phases. As can be seen from Fig. 5, the samples

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containing azobenzene moiety showed textures orange-red colored. The copolymer P3 and maleimide M3, both without azobenzene moiety, exhibited different colored textures: a black-white banded texture for sample P3 but orange grainy texture for sample M3. Analyzing the transition temperatures of the copolymers P3-P4 one can obtain the increasing temperature order series: P3 < P4 < P2. While the copolymers P2 and P4 had similar molecular weights, the lower transition temperatures of sample P3 can be explained by its lower molecular weight. The copolymer P2 had superior transition temperatures to those of P4, probably due to the same reason of hydrogen bonds. An investigation of copolymers by powder X-ray diffraction at room temperature revealed an amorphous behavior. Fig. 9 showed two suggestive diffractograms of samples P2 and P4.

Figure 9

One can observe that, although both samples exhibited crystalline-like melting endothermal peaks in DSC thermogram, however their X-ray diffraction patterns are almost amorphous, with a broad reflection around 17-18°. Similar results were reported for liquid crystalline copolymers having side chain azobenzene mesogenic units [36, 40, 41].

Optical properties of the polymers in solution

UV-VIS absorption spectroscopy was used to characterize the *trans-cis-trans* isomerization process of azobenzene chromophores in maleimide derivatives. Fig. 10 exhibits the electronic absorption spectra of **M4** in DMF solution after exposure at different times of UV irradiation at 365 nm. The strong absorption band at about 360 nm is assigned to the $\pi - \pi^*$ transition of the *trans* form of the azo bond and the band at 440 nm is due to n - π^* transition of the *cis* form of the azo bond. [42, 43]. As shown, the absorption band at around 360 nm decreases gradually in intensity, while the maximum absorbance at 440 nm increased with light irradiation time, indicating formation of the *cis* isomers in system. Two isosbestic points are seen at about 320 and 422 nm suggesting that the *trans*-

cis photoisomerization is the only photochemical modification and no side reactions are involved. The *cis* isomer content in the photostationary state was found to be 0.86 for **M4**. The photoisomerization process in the polymer containing azo chromophore **P2** was also followed spectrally monitoring the $\pi - \pi^*$ absorption band located at about 360 nm. The spectral pattern was similar to the azomaleimide derivative **M4** including the isosbestic points at 323 and 421 nm, respectively, in DMF solution. The photoisomerization kinetics of azobenzene chromophore in **M4** and **P2** was determined by monitoring the absorbance which corresponding to absorption maximum of *trans isomer*. Kinetic data were fitted to the following equation: $\ln[(A_0 - A_{\infty})/((A_1 - A_{\infty}))] = k_1 t$, were A_0 , A_t and A_{∞} are the absorbance at time 0, t and at the photostationary state, respectively, and the k_1 is the rate constant of photoprocess [44, 45].

Figure 10

The plots of $\ln[(A_o - A_\infty)/(A_t - A_\infty)]$ versus irradiation time are linear for both sample **M4** and sample **P2**, as expected (Fig. 11). The corresponding first-order rate constants k_1 were of 5.77×10^{-2} and 4.95×10^{-2} s⁻¹ for **M4** and **P2** derivatives, respectively.

Figure 11

Fig. 12 illustrates the changes in absorbance during *cis-trans* thermal isomerization in DMF solution at 50°C for **P2**. As a result, the absorption band at 360 nm increases in intensity and the spectrum was restored to that value of the nonirradiated sample after 200 min.

Figure 12

The kinetics of thermal recovery of azo chromophores was described by a firstorder equation $\ln[(A_{\infty} - A_0)/(A_{\infty} - A_t)] = k_2 t$, where k_2 is the *cis-trans* isomerization rate constant. First-order plots for *cis-trans* relaxation for **M4** and **P2** are given in Fig. 13. It is

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observed that the values of *cis-trans* isomerization constants are too close and thus the polymer matrix have a little influence on the relaxation of azoaromatic moieties. The rate constants of thermal isomerization were 3.22×10^{-4} s⁻¹ for **M4** and 3.13×10^{-4} s⁻¹ for **P2**.

Figure 13

The photobehavior of **M5** was different by comparison with **M4** derivative. During UV irradiation in DMF solution the absorption band at about 366 nm decreases progressively in intensity but the *cis* isomer content was much smaller (40%) after 200 s, when the photostationary state was achieved. Further irradiation does not modify the spectral pattern. Thermal recovery at 70 °C of **M5** solution determines the return to the starting spectrum after 105 min. The same behavior was also applicable to polymer **P4**. In this case the transformation degree is only 0.34 after 400 sec. However, back isomerization occurs faster, in 80 min, relating to low weight molecular compound **M5**.

Conclusions

New maleimide/styrene copolymers bearing side chain azobenzene moieties as well as functionalized maleimide model compounds were synthesized. The polarizing optical microscopy and DSC measurements were shown important and interesting characteristics of liquid crystalline properties. The azo maleimide derivatives exhibit enatiotropic crystalline behavior. The azo maleimide/styrene copolymers and their corresponding maleimide model compounds were investigated for *trans-cis* isomerization under UV light irradiation and their recovery was studied thermally. The results revealed that the azo model compound **M4** and copolymer **P2** have a fast response to UV irradiation by comparison with **M5** and **P4** derivatives.

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Legend of figures

Fig. 2. ¹H-NMR spectra with assignments of maleimide model compound **M4**.

Fig. 3. FTIR spectra with assignments of copolymers P2 and P4.

Fig. 4. ¹H-NMR spectra with assignments of copolymer **P4**.

Fig. 5. ¹³C-NMR spectra with assignments of copolymer **P2**.

Fig. 6. TGA curves of copolymers P1-P4.

Fig. 7. DSC thermograms of maleimide monomer M3, model compounds M4, M5 and copolymers P2 and P4.

Fig. 8. Hyperchem models of M3-M5

Fig. 9. X-ray powder diffraction curves of copolymers P2 and P4 at room temperature.

Fig. 10. Change of the electronic absorption spectra of M4 in DMF on UV irradiation;

irradiation time: 0; 2; 5;10; 20; 25; 35; 45; 60; 120; 240 s.

Fig. 11. First-order kinetic plots for photoisomerization process in M4 and P2

Fig. 12. Variation of UV-Vis absorption spectra during thermal recovery for P2 in DMF

solution at 50 °C; recovery time: 0; 3; 6; 19; 25; 35; 50; 80; 110; 230 min.

Fig. 13. Cis-trans isomerization kinetics of azoaromatic chromophores at 50 °C for M4 and

P2

Scheme 1. Synthesis of maleimide monomers (M1-M3) and azo maleimide model compounds (M4, M5).

Scheme 2. Synthesis of copolymers P1-P4.



FTIR spectra with assignments of maleimide model compounds M4, M5.

411x527mm (96 x 96 DPI)



1H-NMR spectra with assignments of maleimide model compound M4.

422x183mm (96 x 96 DPI)



FTIR spectra with assignments of copolymers P2 and P4.

422x500mm (96 x 96 DPI)





314x177mm (96 x 96 DPI)





422x169mm (96 x 96 DPI)













398x208mm (96 x 96 DPI)



X-ray powder diffraction curves of copolymers P2 and P4 at room temperature.

319x144mm (96 x 96 DPI)



Change of the electronic absorption spectra of M4 in DMF on UV irradiation; irradiation time: 0; 2; 5;10; 20; 25; 35; 45; 60; 120; 240 s.

217x169mm (96 x 96 DPI)









193x153mm (96 x 96 DPI)





Table 1

General and thermal properties of the copolymers P1-P4.

Copolymer	M_n^{a}	$M_w\!/M_n$	T _g (°C)	TGA (under N ₂ , 10 °C/min; °C)			
				T_{10}^{b}	$T_{d max1}^{c}$	$T_{d max2}^{d}$	Residue (%) ^e
P 1	5200	1.30	238	347	355	517	24.8
P 2	6700	1.70	216	337	360	500	32.0
P3	4800	1.25	177	329	353	492	20.7
P4	6800	1.80	190	341	365	505	32.8

^a GPC measurements of THF solutions, using polystyrene standards;

^b Temperature corresponding to 10 % weight loss;

^{c,d} Temperatures corresponding to maxima of DTG peaks;

^e Weight residue at 700 °C.

Table 2 Phases, transition temperatures and mesophase range of monomer M3, model

compounds M4,	M5	and	copolymers	P1-P4
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Compounds	Transition temperatures ^a (°C)	Mesophase range (°C)	$O_v^{\ c}$	$\alpha \pm 0.5 \cdot 10^{24}$ $(cm^3)^d$	MI ^e
M 3	Cr 217 N 235 I	18	1.29	33.58	14.0
M 4	Cr 220 N 263 I	43	1.36	45.20	12.0
M 5	Cr 184 N 214 I	30	1.37	57.53	18.5
P 1	Cr 280 I	-	-	-	-
P 2	Cr 223 N 276 I	53	-	-	-
P 3	C r 203 = 242 I	37	-	-	-
P 4	Cr 220 N 250 I	30	-	-	-

^a Phases: Cr – solid crystalline; N - nematic; I - isotropic;

^b Poor birefringence in the melting state;

^c Ovality, calculated as described in text;³¹

^d Molecular polarizability, calculated with program ACD/Chemsketch;

^e Mesogenic index.³²

Table 3

Structures with increments used in MI calculation for samples M3-M5.

Sample	Structure and MI increments ^a	MI	Thermotropic behavior
M 3	о о 3 3 3 3 3 3 3 3 3 3 3 2	14.0	Nematic
M 4		12.0	Nematic
M 5	$ \begin{array}{c} $	18.5	Nematic

^aAccording to reference.³²



Graphical Abstract 111x87mm (96 x 96 DPI)