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Liquid Crystal Polymers Containing Permanent Dipole Azobenzene Chromophores

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SUMMARY: Three photochromic monomers containing a permanent dipole photochromic azobenzene group spaced from the methacryloyl moiety by a polymethylene segment were synthesized in three steps starting from 4-cyanoaniline. The monomers were homopolymerized and copolymerized with an optically active monomer, (-)-menthyl methacrylate, in the presence of AIBN as a radical initiator. Structurally similar amphiphilic polymers were obtained by homopolymerization of analogous methacrylates in which oligo(oxyethylene) segments replaced the polymethylene spacers. The polymeric materials, having a molar content of photochromic units between 5 and 100 % and molecular weights of about 15,000, were characterized by thermal analysis, X-ray diffraction, 1D and 2D NMR. Mobility and photochromic properties in solution were also investigated.

Introduction

Photochromic polymers have attracted a great deal of interest of both fundamental and applied significance mainly due to their possible application in non-linear optics and optoelectronics[1-8].

In the framework of an ongoing research line[9-12], it appeared interesting to investigate polymeric materials having liquid crystalline properties and containing both optically active groups and photoresponsive azobenzene chromophores substituted in the *para* positions with one electron-withdrawing and one electron-donating group. Indeed, these systems, having a permanent dipole moment and being intrinsically dissymmetric, could display interesting photochromic properties coupled with the possibility of generating second-order non-linear optical responses. Moreover, the presence of a liquid crystalline order could help to maintain the orientation of poled chromophores within time.

Accordingly three photochromic methacrylates containing a 4-cyanoazobenzene chromophore spaced from the methacryloyl group by polymethylene spacers of different length were prepared. Structurally similar amphiphilic monomers containing oligo(oxyethylene) segments were also synthesized.

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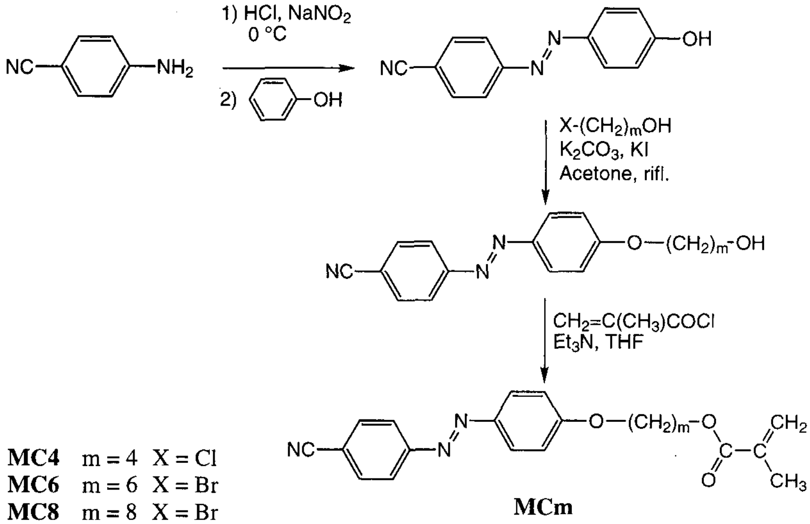
Homo and copolymerization of the above monomers was investigated in the presence of AIBN as radical initiator. Polymer thermal and liquid crystalline properties, 1D and 2D NMR spectra, molecular dynamics in solution and photochromic and photoresponsive properties were investigated. Evaluation of the potential of these polymeric materials as optical storage medium has been also performed by holographic measurements, as reported elsewhere13).

Results and Discussion

Monomer Preparation. Photochromic monomers containing push-pull azobenzene chromophores spaced from the methacrylic group by a polymethylene segment (**MCn**, n = 4, 6, 8) were synthesized in fairly good yields by following the reaction sequence outlined in Fig. 1. Phenol was coupled with the diazonium salt of 4-cyanoaniline and the resulting 4-cyanoazobenzene was reacted with linear α-hydroxy-ω-haloalkanes containing 4, 6, and 8 methylene groups, respectively. The photochromic alkanols were finally reacted with methacryloyl chloride in presence of triethylamine and the crude reaction products were recrystallized twice from *n*-hexane to yield 4-(4-oxy-4'-cyanoazobenzene)but-1-yl methacrylate (**MC4**), 6-(4-oxy-4'-cyanoazobenzene)hex-1-yl methacrylate (**MC6**); and 8-(4-oxy-4'-cyanoazobenzene)oct-1-yl methacrylate (**MC8**) as bright orange crystals.



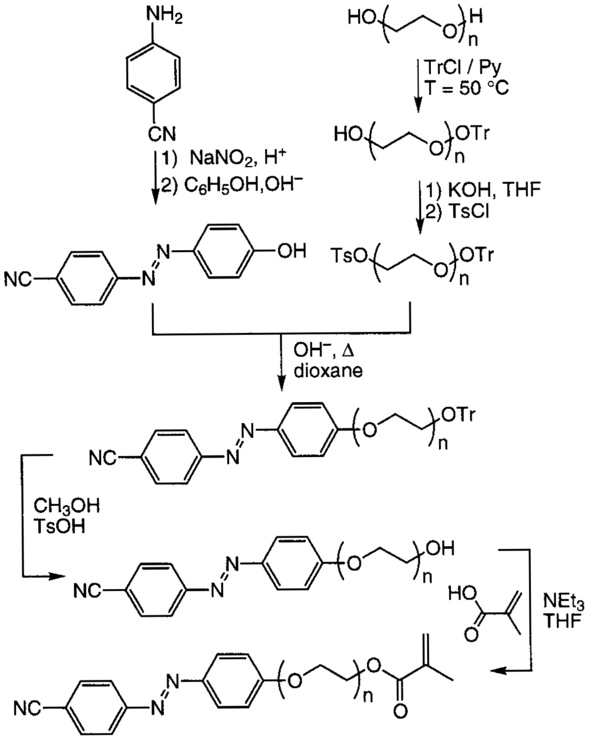
MC4 m = 4 X = Cl
MC6 m = 6 X = Br
MC8 m = 8 X = Br

MCm

Fig. 1: Preparation 4-(ω-methacryloyloxyalkylene)-4'-cyanoazobenzenes.

The low molecular weight structural model of polymers containing MCn units, 6-(4-oxy-4'-cyanoazobenzene)hex-1-yl 2-methylpropanoate (**IC6**), was prepared according to the same reaction sequence by using 2-methylpropanoyl chloride instead of methacryloyl chloride.

Photochromic monomers containing azobenzene chromophores spaced from the methacrylic group by an oligo(ethylene glycol) segment (**MEn**, n = 3, 4) were prepared by common synthetic procedures according to the reaction scheme depicted in Fig. 2.



ME3 n = 3
ME4 n = 4

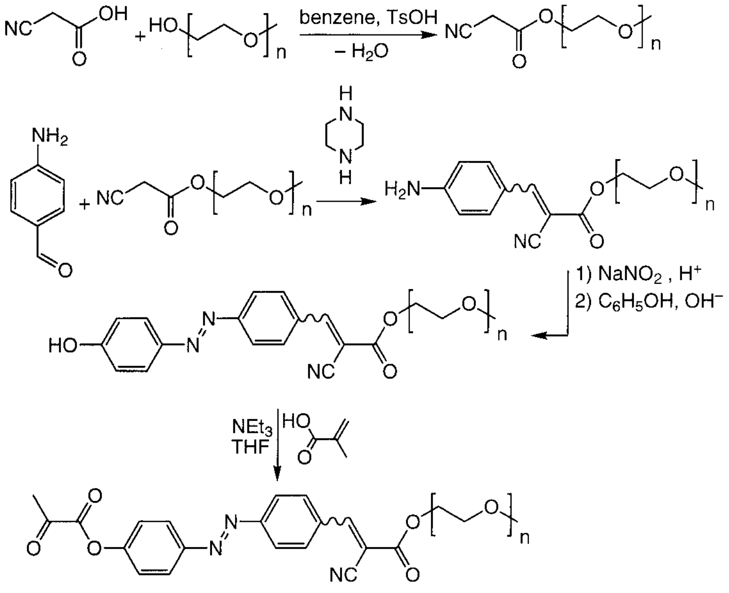
Ts = Tosyl; Tr = Trityl

Fig. 2: Preparation of 4-(ω-methacryloyloxyoligo(oxyethylene))-4'-cyanoazobenzenes.

Photochromic monomers containing azobenzene chromophores linked to the methacrylic group from the one side and to a monomethoxyoligo(ethylene glycol) segment from the other side (**MEnM**, n = 3, 8) were prepared by common synthetic procedures according to the reaction scheme depicted in Fig. 3.

(-)-Menthyl methacrylate (**MnMA**), having optical purity larger than 99 %, was prepared by reacting natural (-)-menthol with methacryloyl chloride$^{14)}$.

Polymer synthesis. Photochromic polymers were prepared by homo and copolymerization of **MCn** monomers with **MnMA**. The choice of MnMA as a comonomer was suggested by the need of polymeric materials endowed with optical activity and a rather high glass transition temperature. Polymerization experiments were carried out in benzene at 60 °C for 35 h, in the presence of 1 % AIBN as radical initiator. The reaction products were coagulated in methanol and dried under vacuum to yield fairly good conversions to orange polymeric products having 10-30 kD number average molecular weight and 1.5-2.5 polydispersity index (Tab. 1). For comparison, a poly(**MnMA**) sample (PMM) was prepared under the same experimental conditions. **MCn** monomers displayed a larger reactivity as compared to **MnMA**, very likely due to the steric hindrance exerted by the bulky menthyl group on the double bond.



ME3M n = 3
ME8M n = 8

Fig. 3: Preparation of 4-methacryloyloxy-4'-(2-cyano-3-oxy-3-(ω-methoxyoligo(oxyethylene))prop-1-en-1-yl)azobenzenes.

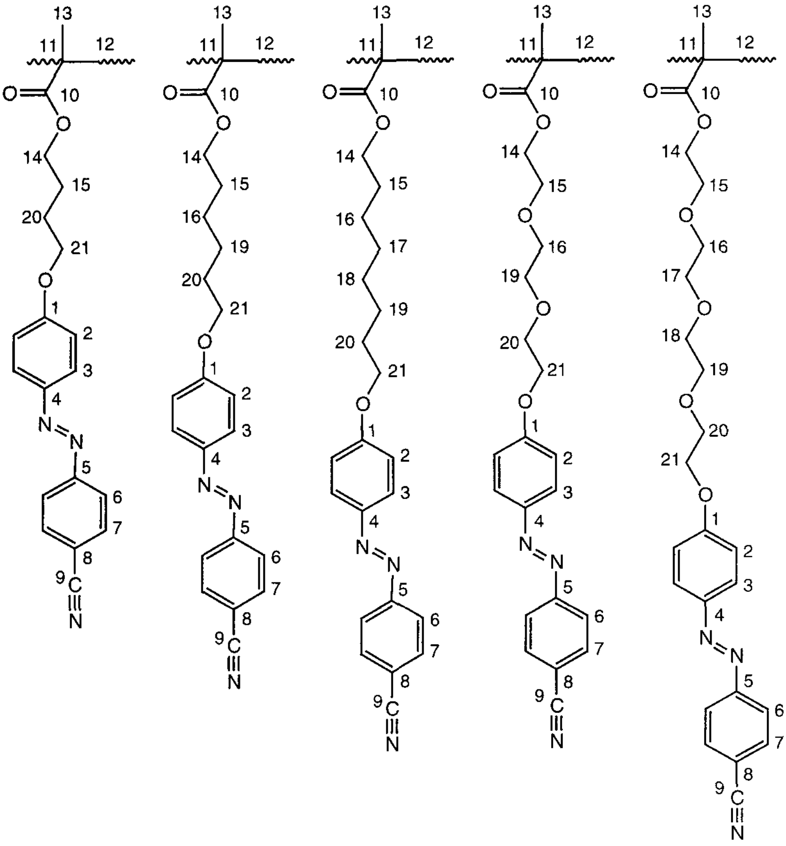
Polymerization of **MEn** monomers, carried out in benzene at 60 °C in the presence of AIBN as radical initiator, gave fairly good yields of red-orange polymeric products having an average molecular weight of 40-45 kD and a polydispersity index of 1.5. On the contrary, only oligomeric products were obtained in low yields when the polymerization of **MEnM** methacrylates was attempted in benzene or DMSO at 60 and 70 °C for 24 h, in the presence of 1-5 % AIBN as initiator. This unexpected behavior was tentatively attributed to the presence of the 2-cyano-2-carboxypropenyl group that may interfere with the radical chain propagation reaction.

Tab. 1. Characterization of homo and copolymers of **MCn** photochromic monomers with (-)-menthyl methacrylate

Sample	**MCn** in feed mol %	Polymer yield %	Polymeric Product				
			MCn mol %	M_n/kD	M_w/M_n	T_g/°C	T_i/°C
PC4	100	43	100	20	1.4	80	165
PC4M1	86	30	91	25	1.4	83	131
PC4M2	35	43	36	18	1.7	108	–
PC4M3	26	48	26	24	1.9	108	–
PC6	100	51	100	34	1.5	60	168
PC6M1	87	74	92	13	1.5	57	123
PC6M2	75	82	76	20	2.7	69	92
PC6M3	51	89	51	14	2.5	80	–
PC6M4	25	77	27	16	2.6	104	–
PC6M5	5	71	7	11	2.3	131	–
PC8	100	58	100	15	1.4	35	160
PC8M1	91	64	95	11	1.5	35	141
PC8M2	75	60	79	12	1.6	58	99
PC8M3	50	58	51	10	1.6	65	–
PC8M4	25	48	30	10	1.5	65	–
PC8M5	6	38	7	11	1.6	124	–
PMM	0	68	0	27	2.3	147	–

NMR characterization. Poly(**MCn**) and poly(**MEn**) samples (Fig. 4) were characterized by ^{1}H-NMR, 2D COSY and 2D HETCOR analysis. In particular, the off-diagonal resonances in the aromatic proton region of the COSY spectrum evidenced a coupling between the signal at 7.9 ppm and those at 7.7 and 6.9 ppm. By taking into account also their relative intensities and coupling constants, these signals were attributed to the aromatic protons bonded to C_2 (6.96 ppm), C_7 (7.71 ppm), C_6 (7.87 ppm) and C_3 (7.88 ppm). Therefore, the most deshielded protons are those in *meta* position to the oxygen atom, indicating a contribution of internal charge transfer mesomers to the electronic distribution of the 4-alkoxy-4'-cyanoazobenzene chromophore. This effect is smaller than that observed in 4-amino-4'-

cyanoazobenzene derivatives[15], in accordance with the lower electron-donor characteristic of ethereal oxygen as compared to amino nitrogen.



PC4 **PC6** **PC8** **PE3** **PE4**

Fig. 4: Structures of the azobenzene polymers.

The multiplicity of the ^{13}C-NMR signals of the methacrylic carbons (C_{10}-C_{13}) allowed to assign a mainly atactic structure to the investigated poly(methacrylate)s with P_m values included between 0.20 and 0.24, by assuming a Bernoullian statistics[16].

Comparison of the ^{13}C-T_1 relaxation times of **MCn** homopolymers (**PCn**) with those of the corresponding **IC6** model compound evidenced as expected a much larger mobility of the low molecular weight compound (Tab. 2)[17].

The carbon atom mobility increased on increasing the distance from the stiff aromatic chromophore in **IC6** whereas an opposite behavior was observed in polymers, in which carbons farther from the azobenzene groups are closer to the more rigid polymer backbone. Moreover, in **MCn** homopolymers, a 30 % increase of azobenzene mobility was observed on increasing the spacer length from 4 to 6 methylene groups.

Comparison of ^{13}C-T_1 relaxation times of **PEn** homopolymers with those of the corresponding **MEn** monomers evidenced an analogous decrease of molecular mobility. In this case however, relaxation times of the spacer chain carbon atoms (C_{14}-C_{21}) increased with the increasing distance from the aromatic chromophore in **MEn** monomers, whereas an opposite trend was observed for **PEn** polymers. This behavior can be attributed to the significant flexibility of the oligo(oxyethylene) chain and the different stiffness of the azobenzene group and of the polymer backbone.

Tab. 2. ^{13}C NMR relaxation times (T_1) of carbon atoms present in azobenzene derivatives

Carbon atom	T_1 / s							
	IC6	**PC4**	**PC6**	**PC8**	**ME3**	**PE3**	**ME4**	**PE4**
C_1	>15	2.03	2.66	3.8	> 33	3.4	> 11	> 5.4
C_2	1.14	0.31	0.32	0.45	0.90	0.40	1.57	0.45
C_3	1.15	0.31	0.33	0.46	0.93	0.40	1.55	0.48
C_4	>17	3.2	2.93	4.2	> 21	3.5	> 16	> 5.0
C_5	>16	3.8	3.2	4.3	> 19	3.3	> 11.8	> 5.7
C_6	1.48	0.51	0.53	0.70	1.20	0.56	1.99	0.71
C_7	1.48	0.51	0.53	0.71	1.18	0.56	2.00	0.73
C_8	4.3	1.02	0.98	1.20	3.57	1.18	> 5.7	1.41
C_9	2.10	2.85	3.0	4.6	> 7.4	3.4	> 9.4	4.6
C_{10}	>45	1.67	2.57	1.95	> 33	3.0	> 51.4	2.07
C_{11}	0.76	0.99	1.47	1.28	> 15	1.61	> 58.9	1.38
C_{12}	3.2	0.07	0.13	0.11	1.46	0.12	1.95	0.12
C_{13}	–	0.07	0.07	0.07	> 6.3	0.07	> 5.7	0.07
C_{14}	1.20	0.11	0.14	0.14	1.31	0.14	1.89	0.12
C_{15}	1.12	0.13	0.14	0.17	1.32	0.13	1.88	0.13
C_{16}	0.96	–	0.17	0.25	1.19	0.28	1.59	0.25
C_{17}	–	–	–	0.26	0.87	0.30	1.43	0.26
C_{18}	–	–	–	0.26	1.19	0.28	–	–
C_{19}	0.96	–	0.19	0.25	1.19	0.28	–	–
C_{20}	0.68	0.13	0.18	0.26	0.56	0.25	0.91	0.25
C_{21}	0.65	0.16	0.18	0.25	0.51	0.23	0.85	0.26

Mesophase characterization. DSC analysis of the photochromic poly(**MCn**) homopolymers evidenced that the glass transition temperature (T_g) decreased from 80 to 35 °C on increasing the spacer length from 4 to 8 methylene units (Tab. 1). In all cases the copolymerization products exhibited only one glass transition at temperatures included between the T_g values of the two corresponding homopolymers (Fig. 5).

The DSC curves of **MCn** homopolymer samples were characterized by an endothermic peak with maximum (T_i) included between 160 and 168 °C, attributable to the isotropization (clearing) process. An analogous behavior was observed for copolymers containing more than 75 % aromatic units. T_i values decreased with the content of **MnMA** units, no first order transition being detectable at aromatic unit contents lower than 75 %.

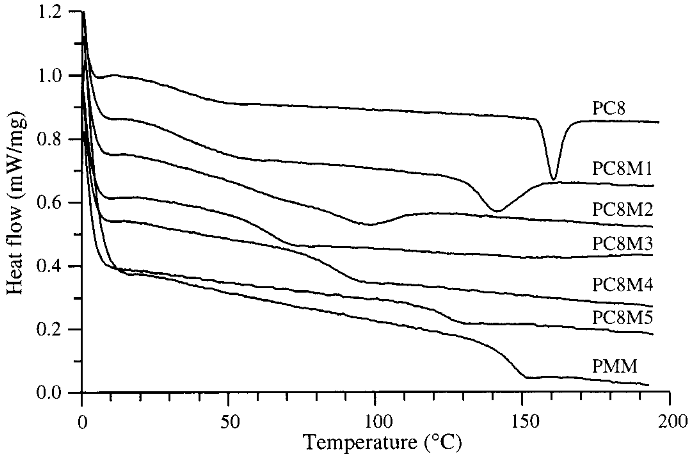
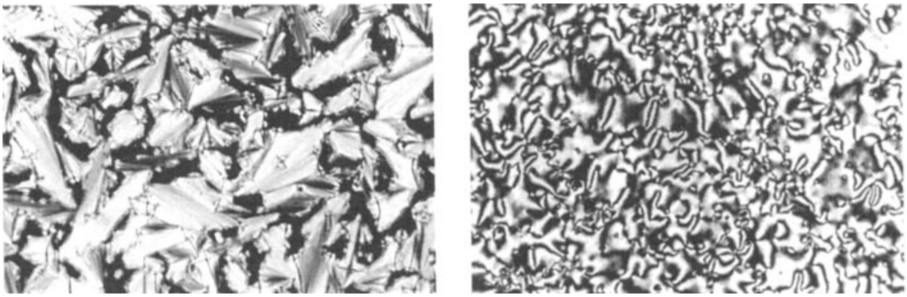


Fig. 5: DSC curves of **MC8** containing polymers.

Optical microscopy observation with crossed polarizers of polymer films evidenced the development of fan textures typical of the smectic A phase (Fig. 6a) on slowly cooling from the melt of PC8 (158 °C), PC8M1 (140 °C) and PC6 (164 °C). PC4 (164 °C), PC4M1 (130 °C) and PC6M1 (123 °C) samples showed typical nematic textures (Fig. 6b). Only fine grained textures were observed for PC6M2 (90 °C) and PC8M2 (98 °C) samples.

None of the investigated copolymer samples containing less than 75 % of azoaromatic units exhibited the formation of optical textures attributable to the presence of liquid crystalline phases.

X ray diffraction patterns allowed to attribute an interdigitated smectic A structure to the mesophases of PC8, PC8M1, PC8M2 and PC6 polymer samples (Fig. 7a) and a nematic structure to PC6M1, in agreement with optical microscopy assignments.



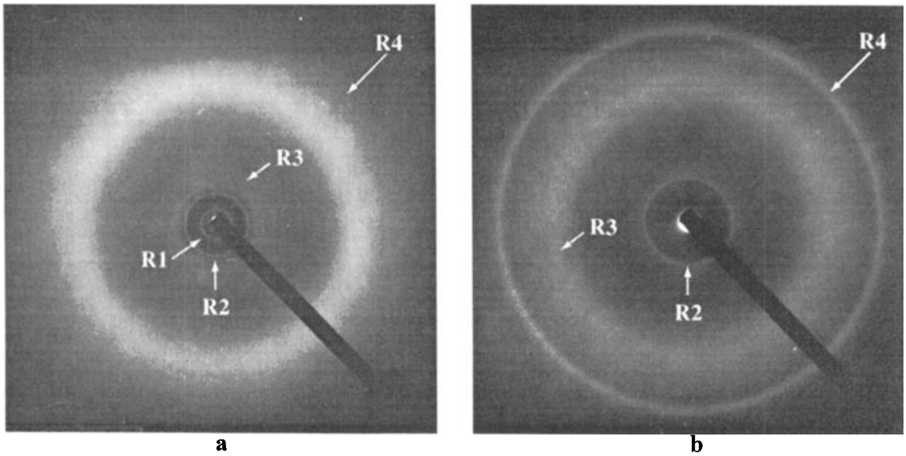
a

b

Fig. 6: Micrograph of poly(**MC8**) at 80 °C (**a**) and poly(**MC4**) at 162 °C (**b**).

DSC analysis of poly(**ME3**) evidenced the glass transition at 37 °C and an isotropization at 88 °C, whereas only a glass transition at 20 °C was observed in the case of poly(**ME4**), the isotropization process being very likely masked by the glass transition.

Hot stage optical microscopy and X ray diffraction patterns (Fig. 7b) allowed to assign a metastable smectic A_1 mesophase (interchromophore distance 5.0 Å, lamellae thickness 28.5 Å) between 20 and 55 °C and a smectic A_d mesophase (interchromophore distance 5.0 Å, lamellae thickness 33.7 Å) between 55 and 80 °C to poly(**ME3**). Poly(**ME4**) was characterized by a smectic A_1 mesophase (interchromophore distance 4.7 Å, lamellae thickness 32.4 Å) at temperatures below 15 °C.



a

b

Fig. 7: X-ray diffraction patterns of poly(**MC8**) (**a**) and poly(**ME3**) (**b**) powders.

Photochromic properties. On irradiation between 360 and 405 nm, the *trans*-azobenzene chromophores underwent a *trans* → *cis* photoisomerization process. Correspondingly shape, intensity and position of the UV absorption bands were modified (Fig. 8a). The presence of three isosbestic points at about 260, 360 and 430 nm confirmed that only two absorbing species, namely *cis*- and *trans*-azobenzene, were present in solution.

In all cases photoisomerization kinetics resulted in agreement with a monoexponential decay (Fig. 8b)[18]. Photoisomerization kinetic constants of **MCn** homopolymers and copolymers irradiated at 405 nm resulted included between 2.5 and $3.1 \cdot 10^{-3}$ s^{-1}. These values compare rather well with that ($3.0 \cdot 10^{-3}$ s^{-1}) of **IC6**, the low molecular weight model compound.

Kinetic constants of **MEn** monomers and homopolymers irradiated at 360 nm resulted included between 0.98 and $1.04 \cdot 10^{-3}$ s^{-1}.

In all cases, either on standing in the dark at room temperature or under irradiation at 437 nm, the absorbance of samples at the photostationary state steadily increased up to the starting value before irradiation, thus confirming the reversibility of the isomerization process. Also in this case, the process obeyed a first order kinetics.

The absence of an influence of the polymethylene spacer length, chemical composition and molecular weight on the rate of photoisomerization can be attributed to the flexibility of the spacer that effectively decouples the azobenzene chromophores from the polymer chain. The occurrence of the isomerization process by in-plane translation rather than by out-of-plane rotation could also contribute to cancel structural effects[19-22].

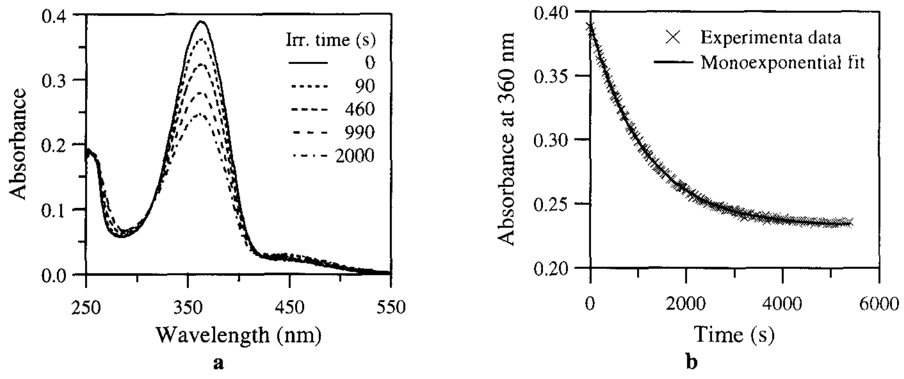


Fig. 8: Variation of the UV spectrum of poly(**MC4**) (**a**) on irradiation at 405 nm, in chloroform solution at 25 °C, and corresponding kinetic plot (**b**).

Optical storage properties. **MCn** homopolymers and copolymers with **MnMA** were examined for optical storage. After irradiation at 488 nm with a polarized laser beam, these materials presented a fairly large diffraction efficiency that resulted stable at room temperature[9]. A strong surface relief was observed in the area irradiated with two orthogonally circularly polarized beams, analogously to what reported for other azobenzene containing systems[23,24].

Monolayers and LBK films. On water subphase **MEn** monomers did not show any tendency to form monolayers, whereas thermodynamically stable films that collapsed to bidimensional solids at a surface area of about 17 Å^2/monomeric unit were obtained with **MEnM** monomers. Also **MEn** homopolymers gave thermodynamically stable monolayers that collapsed at a surface area of about 16.5 Å^2/monomeric unit (Fig. 9). In all cases a small reproducible peak was observed at about 45 Å^2/monomeric unit. This transition was tentatively attributed to a conformational rearrangement of macromolecules from a loose distribution on the water surface to a more ordered conformation in which hydrophobic groups point out of the water.

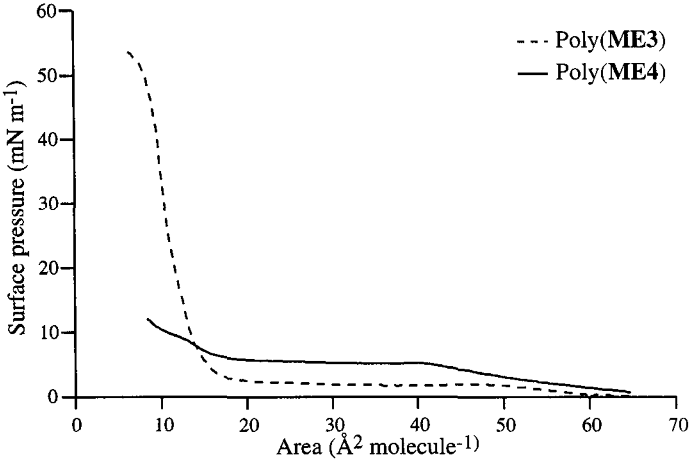


Fig. 9: Compression isotherm of poly(**ME3**) and poly(**ME4**) on water subphase.

Deposition of Langmuir-Blodgett-Kuhn (LBK) films was performed at a dipping rate of 1-20 mm/min at a surface pressure of about 10 mN/m.

Deposition of LBK films on hydrophobic substrates failed, as the film deposited during the immersion was removed when the substrate was pulled out of the subphase.

On the contrary, irregular LBK multilayers were deposited on hydrophilic substrates and their thickness increased with the number of dipping cycles, as evidenced by the progressive increase of their UV absorbance (Fig. 10). The irregularity of the films, evidenced by the random formation of microfractures on the film surface, can be tentatively attributed to the large viscosity of the polymer film that limited mass transportation[25)]. The independence of UV spectra from the polarization of the light demonstrated that the aromatic chromophores assumed a random orientation within the multilayers.

Non Linear Optical Properties. Preliminary evaluation of the second order NLO properties of some *trans* polymer samples was performed by second harmonic generation (SHG) measurements. Spin coated thin films of the **PCn** homopolymer samples were heated above the isotropization temperature and then slowly cooled down at room temperature under electric poling (corona poling), in order to induce a polar order in the liquid-crystalline phases. In no case, however, a SHG signal was detected by 1542 nm laser excitation, thus indicating that interchromophore interactions are stronger than dipolar forces induced by the external electric field. This finding can be at least in part attributed to the interdigitated structure of some of the investigated polymers liquid crystalline phases, that results in a null macroscopic dipole moment.

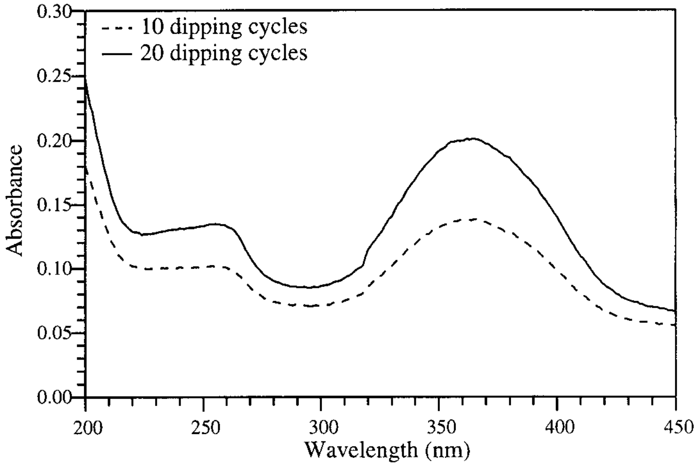


Fig. 10: UV spectra of LBK multilayers of poly(**ME4**) deposited on hydrophilic substrate.

Concluding Remarks

New photochromic polymers were obtained by radical homo- and copolymerization of monomers containing a permanent dipole photochromic azobenzene group spaced from the methacryloyl moiety by a polymethylene spacer of different length with (-)-menthyl methacrylate (MnMA).

All polymer samples containing more than 75 % of photochromic units exhibited a thermotropic behavior. Assignment of the liquid crystalline phases, performed by DSC, optical microscopy, and X-ray diffraction, evidenced that the LC order shifted from smectic A to nematic on both decreasing the length of the polymethylene spacer and increasing the content of MnMA units.

2D-NMR spectroscopy allowed to unequivocally attribute the signals in the NMR spectra of polymer samples and to highlight an appreciable contribution of charge transfer mesomers to the electronic distribution of the photochromic chromophore. Polymer tacticity was evaluated from the multiplicity of main chain ^{13}C-NMR signals.

Evaluation of ^{13}C T_1 relaxation times evidenced a rather limited mobility of the azobenzene chromophores when inserted in the macromolecules. As expected, mobility of the chromophores increased with the length of the polymethylene spacer that effectively decouples the photoresponsive groups from the stiff polymer backbone.

Irradiation at 405 nm induced a *trans* to *cis* isomerization of azobenzene chromophores. This process was thermally reversible in the dark. Both photoisomerization rate and thermal back isomerization showed a small but definite dependence on molecular weight, spacer length and chemical composition of the investigated photochromic polymers. This behavior was attributed to the variation of the polarity of the solvation shell around the azobenzene chromophore. The observed limited influence of sample structure and hence chromophore mobility on the isomerization rate has been tentatively attributed to a contribution by the azobenzene isomerization mechanism based on the in-plane inversion of the phenyl ring most removed from the main chain .

In the solid state, corona poling and hence second harmonic generation efficiency are almost completely suppressed by the strong interchromophore interactions present in interdigitated structure of the polymer mesophases.

Acknowledgments

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