MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Influence of the Molecular Structure of Comb-Shaped Photochromic Copolymers on Photoinduced Birefringence

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Abstract—A series of mesomorphic and amorphous photochromic copolymers containing azobenzene groups were prepared. The emergence of induced birefringence in films of these copolymers under the action of plane-polarized laser light was studied.

Comb-shaped photochromic mesomorphic polymers (MPs) show promise as media for information recording and storage, as well as for application in various optical elements, including filters, polarizers, switches, etc. [1–3]. Photosensitive MPs are usually obtained from compounds comprising two basic structural elements, photochromic and mesogenic. The primary role in photoorientation of photochromic MPs under linearly polarized laser light belongs, undoubtedly, to photochromic moieties. Mesogenic groups in the mesomorphic copolymers (MCs) not only participate in photoorientation but also perform the following important functions. First, they are responsible for mesomorphic ordering, which in many cases allows significant improvement of the photoinduced order (birefringence enhancement effect [4, 5]). Second, the mesomorphic order substantially enhances the thermal stability of the photoinduced birefringence [6]. This allows preparation of photochromic MCs suitable as advanced information carriers.

Much progress has been achieved in physical chemistry of MPs comprising azobenzene photochromic moieties, but the influence of the chemical structure of photochromic and mesogenic groups on the photo-optical properties of copolymers still remains to be elucidated. There are scarce published data on homologous series of comb-shaped MPs with varied length of the aliphatic spacer and invariant structure of the mesogenic units [7, 8]. At the same time, specifically studies of homologous series can provide quantitative information on how the chemical structure of comb-shaped MPs affects the magnitude and kinetic features of photoinduced birefringence.

The aim of this study was to elucidate how the molecular structure of comb-shaped photochromic MPs affects the kinetic features and magnitude of photoinduced birefringence. To this end, we synthesized comb-shaped mesomorphic and amorphous copolymers (ACS) P-1–P-6 with varied photochromic unit polarity and distance separating the azobenzene fragment and the polymer chain:
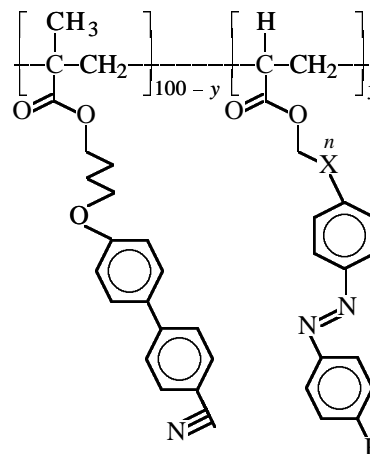
with no X, R = H , $n = 0$ (P-1); X = O, R = H, $n = 4$ (P-2); X = O, R = H, $n = 10$ (P-3); no X, R = CN, $n = 0$ (P-4); X = O, R = CN, $n = 4$ (P-5); and X = O, R = CN, $n = 10$ (P-6); and $y = 21 \pm 1$ mol%.

EXPERIMENTAL

The copolymers were prepared by radical copolymerization from appropriate monomers in absolute tetrahydrofuran with azobis(isobutyronitrile) (AIBN) as initiator. The resulting copolymers were refluxed in ethanol for a long time to exhaustively remove oligomers and low-molecular-weight products. Microcalorimetric studies were carried out on a Mettler differen-

tial scanning calorimeter (heating rate 10 deg min^{-1}), and microscopic examinations, on a POLAM-P-211 polarization microscope equipped with a Mettler FP-82 heating system. The molecular weight characteristics of the P-1–P-6 copolymers were determined by gel-permeation chromatography on a GPC-2 Waters instrument equipped with an LC-100 column and a Data Modul-370 data processing system. The measurements were made with a UV detector (solvent THF, 1 ml min^{-1}, 25°C; 100, 500, and 10^3 Å columns; calibration against polystyrene).

The kinetic features of the photoinduced birefringence were studied on the photooptical installation described in [9]. The vertically polarized "recording" beam from an argon laser (λ_{rec} = 488 nm, intensity I_0 = 0.035 W cm^{-2}) was directed toward the selected segment of the polymer film. To record the photoinduced alterations in the polymer film, the same segment of the sample was simultaneously illuminated with the probing laser beam from an He–Ne laser (λ_{sens} = 633 nm). The intensity of the probing beam that passed through the sample and analyzer was measured with a photodiode and a special recording system. The photoinduced birefringence Δn_{ind} was estimated from the phase shift $\varphi(\tau)$ between the probing beam components polarized in parallel and perpendicularly to the polarization direction of the recording beam. The absorption of the probing beam passing through the polymer was measured using the monitor channel.

The samples for photooptical measurements were prepared in a glass sandwich cell; the polymer layer thickness was adjusted with Teflon spacers (30 μ). We used amorphous or amorphized samples prepared by rapid cooling of the isotropic melt to the glassy state.

Phase characteristics of P-1–P-6 copolymers. Figure 1 shows the differential-scanning calorimetric (DSC) curves of the copolymers. The P-1 and P-4 copolymers are amorphous, as suggested by the absence of melting peaks of the mesomorphic phase in the DCS curves, as well as by the lack of optical anisotropy of the samples. Copolymer P-5 forms a nematic mesomorphic phase, and P-2, P-3, and P-6 copolymers, a smectic mesophase. The DCS curves of the MCs, recorded in the heating mode, exhibit an endothermic peak with the enthalpy of melting of 1.1–2.1 J g^{-1}. The glass transition points for P-1–P-6 copolymers lie within 61–74°C and are weakly dependent on the nature of the substituent in the azobenzene moiety. Table 1 summarizes the molecular-weight characteristics and phase characteristics of the copolymers.
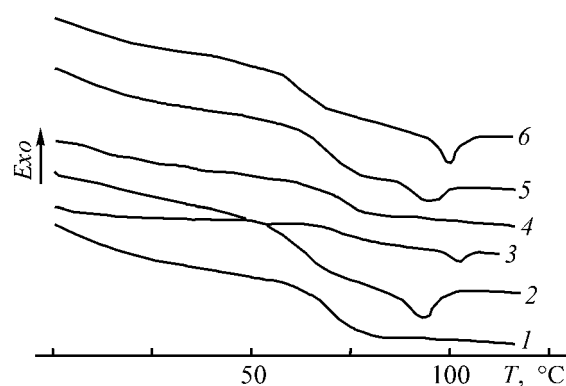

Fig. 1. (*1–6*) DCS curves of P-1–P-6 copolymers, recorded in the heating mode. (*T*) temperature.

Photooptical characteristics of the copolymers. To study the photooptical characteristics of the photochromic copolymers P-1–P-6, we recorded the curves of build-up of the photoinduced birefringence in the course of laser irradiation. Specifically, we recorded the time dependence of the phase shift φ/π between the probing beam components polarized parallel and perpendicular to the electric vector of the recording beam. Figure 2 shows a typical dependence of the phase shift on the irradiation time for the P-6 copolymer. For all the copolymers studied, the φ/π phase shift growth curves are typical of photochromic copolymers [1, 9, 10]. Laser irradiation is responsible for the emergence and build-up of the phase shift. Upon termination of irradiation, the birefringence decreases by 15–20% within 1000–3000 s, whereupon it remains unchanged for a long time.

Two segments are distinguishable in the birefringence build-up curves, namely, those corresponding to fast and a slow rise in birefringence (Fig. 2, curves *1*

Table 1. Molecular-weight characteristics, phase transition temperatures, heats of melting, and π–π^*-transition wavelengths for P-1–P-6 copolymers

Sample	$M_w \times 10^3$	M_w/M_n	Phase transition, °C (heat of melting, J g^{-1})	λ_{max}, nm
P-1	11.7	1.7	G 69 I	326
P-2	15.5	1.6	G 74 S 103 (1.2) I	346
P-3	12.4	1.7	G 59 S 88 (1.2) I	346
P-4	11.9	1.8	G 72 I	333
P-5	10.8	1.5	G 67 N 97 (1.1) I	365
P-6	16.5	1.8	G 61 S 101 (1.6) I	365

* M_w is the weight-average molecular weight; M_n, number-average molecular weight; G, glassy state; S, smectic phase; and I, isotropic melt.

Table 2. Characteristics and major kinetic parameters of P-1–P-6 copolymers used in photooptical experiments (laser light intensity 0.04 W cm^{-2}, 25°C)

Sample	Fast build-up segment			Slow build-up segment		
	C, J cm^{-2}	β	$\Delta n \times 10^4$	β	B, s$^{-\beta}$	$\Delta n \times 10^3$
P-1	0.21 ± 0.02	1 ± 0.01	8.8 ± 0.2	0.97 ± 0.05	0.0005 ± 0.0001	9.0 ± 0.3
P-2	0.13 ± 0.01	1 ± 0.01	4.7 ± 0.1	0.50 ± 0.03	0.0037 ± 0.0003	3.8 ± 0.2
P-3	0.22 ± 0.02	1 ± 0.01	11.6 ± 0.2	0.50 ± 0.03	0.01 ± 0.003	12.3 ± 0.4
P-4	0.18 ± 0.02	1 ± 0.01	5.3 ± 0.2	0.73 ± 0.04	0.0025 ± 0.001	4.0 ± 0.2
P-5	0.09 ± 0.01	1 ± 0.01	16.0 ± 0.3	0.66 ± 0.03	0.019 ± 0.001	30.7 ± 0.8
P-6	0.08 ± 0.01	1 ± 0.01	5.9 ± 0.2	0.52 ± 0.03	0.018 ± 0.0005	10.0 ± 0.4

Note. The birefringence Δn is given for the irradiation time of 2400 s.

and *2*). The first segment (Fig. 2, curve *1*) can be closely approximated by the exponential curve [9]

$$\varphi(\tau) = \frac{2\pi}{\lambda_{\text{sens}}} \frac{\Delta n_{\text{max}}}{\alpha} \left\{ \ln K - \int_1^K \exp\left[-\left(\frac{\hat{\tau}}{z}\right)^\beta \right] \frac{dz}{z} \right\}, \quad (1)$$

$$\hat{\tau} = \tau/t_0, \quad C = t_g I,$$

where $\lambda_{\text{sens}} = 633$ nm is the probing beam wavelength; t_g, characteristic time of birefringence growth on the sample surface; α, absorption coefficient of the polymer film for the probing beam ($\ln K = \alpha d$); d, sample thickness; and β, constant in the Kohlrausch–Williams–Watts function

$$\Delta n = \Delta n_{\text{max}}\{1 - \exp[-(\tau/t)^\beta]\}. \quad (2)$$

We described the second segment of the birefringence build-up curve, corresponding to slow, linear, build-up of φ/π (Fig. 2, curve *2*), by the same function (1) for $\hat{\tau} \ll 1$:

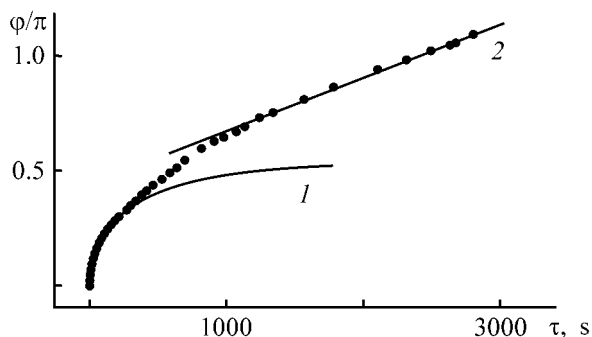$$\varphi/\pi = B\tau^\beta, \quad (3)$$

where B is a constant.

Fig. 2. Variation of the phase shift φ/π for P-6 copolymer in the course of laser irradiation (0.025 J cm^{-2} power). (τ) Time. Approximation of the segments corresponding to (*1*) slow and (*2*) fast birefringence build-up.

Table 2 summarizes the kinetic parameters of P-1–P-6 copolymers, calculated by Eqs.(1)–(3).

Data in Table 2 allow certain conclusions about the kinetic features of the photooptical behavior of the copolymers studied.

It is seen that, for copolymers whose molecules contain the cyano group (R = CN) of the azobenzene moiety (P-4–P-6), the rates in the fast and slow build-up segments of the birefringence curves exceed those of the copolymers with the substituent R = H (P-1–P-3). For example, the constant C [Eq. (1)] for P-3, which is inversely proportional to the birefringence build-up rate, was estimated at 0.22 J cm^{-2}. At the same time, for P-6 containing a polar substituent the constant C is much lower (0.08 J cm^{-2}). Similar trends were observed for the rates B in the slow build-up segments of the kinetic curves of the birefringence. The constants B of copolymers P-4–P-6 exceed those of P-1–P-3, for example, fivefold in the case of P-4 vs. P-1.

Broadening of the spectrum of the relaxation time β in the slow build-up stage suggests gradual complication of the photoorientation process with lengthening of the methylene spacer n. At the same time, β in the fast build-up stage is independent of n, which suggests only one birefringence build-up process in the initial stage of irradiation (up to 100 s). Most probably, this is photoorientation of the dye molecules in defective domains of the sample.

Let us discuss how the polarity of the terminal group R, as well as the length of the aliphatic spacer between the polymer chain and azobenzene moiety, affect the birefringence Δn. Notably, for both fast and slow build-up processes, the photoinduced birefringence of P-4–P-6 copolymers passes through a maximum. The largest birefringence is characteristic of

P-5. This unambiguously suggests a strong influence of the steric factor on the photoorientation process.

To explain the relationships revealed in this study, we will refer to papers by Ho *et al.* [11] and Meng *et al.* [12]. These authors noted that the polarity of the photochromic and mesogenic moieties of macromolecules strongly affect the parameters of the photoorientation process. This influence is the strongest when both the mesogenic and photochromic moieties in the copolymer contain polar cyano groups. Strong Coulomb interaction of the polar fragments increases the efficiency of transfer of the orienting action from the azonbenzene to mesogenic moiety, which suggests cooperativity of the motions of the photoactive groups of the dye and inert mesogenic moieties. At the same time, the birefringence of comb-shaped photochromic copolymers containing both polar and nonpolar side moieties was not enhanced. This allowed Natansohn *et al.* [11, 12] to conclude that, in the copolymer series studied, the deciding influence on the photoinduced birefringence is exerted by specifically dipole interactions between the side groups of the copolymer. The contribution from the cooperativity of the motions of these moieties is less significant.

As mentioned above, our results agree with the conclusions made in [11, 12] and also suggest the importance of dipole interactions between polar photochromic and mesogenic groups. Indeed, the strength of interaction of dipoles is inversely proportional to the cubed distance. Thus, with increasing distance between the photochromic and mesogenic moieties, the strength of their interaction and, hence, the efficiency of transfer of the orienting action from the photochrome to the mesogene will sharply decrease. Therefore, for P-5 copolymer comprising spacers with $n = 4$, the cooperative interaction between the photochromic azobenzene and mesogenic cyanobiphenyl moieties is the strongest, and P-5 is characterized by the largest birefringence. A decrease in the efficiency of interactions because of the less favorable steric arrangement of the interacting polar groups is responsible for much smaller birefringences in the case of P-4 and P-6 copolymers.

For another series of copolymers, P-1–P-3, containing a nonpolar azobenzene moiety we obtained unexpected results. In these copolymers, photoorientation is also strongly affected by the spacer length. However, in contrast to the above-mentioned relationships, the birefringence for P-2 ($n = 4$) copolymer is the smallest for both fast and slow build-up processes. This once again suggests the importance of dipole
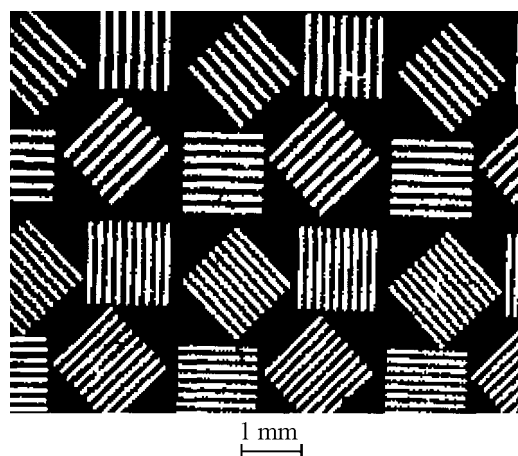

Fig. 3. Image of a standard array recorded on the copolymer P-3 film.

interactions and the predominance of the dipole factor over the steric factor. Moreover, we found that the maximum birefringence can be achieved for P-5 copolymer in which both factors are favorably combined.

Let us discuss whether the mixtures studied by us are suitable, in principle, as media for optical recording and storage of information. Figure 3 shows as an example the image of a standard test-array obtained upon irradiation of the P-3 copolymer film with unfiltered light from a mercury lamp through a template. The image exhibits reasonable contrast and stability at room temperature.

CONCLUSIONS

(1) A series of comb-shaped photochromic copolymers were synthesized, which contain cyanobiphenyl mesogenic and azobenzene groups differing in the polarity and length of the aliphatic spacer ($n = 0, 4, 10$) between the azobenzene moiety and the polymer backbone.

(2) Kinetic parameters of the birefringence build-up depend on the mutual arrangement of the azobenzene and mesogenic groups, which is manifested in a noticeable influence of the spacer length n on the induced birefringence. For copolymers containing 4-cyanoazobenzene photochromic moieties, the greatest birefringence is achieved for a copolymer in which the mesogenic and photochromic groups are equidistant from the polymer backbone.

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