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Photoinduced anisotropy in a series of azobenzene copolymers

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In order to optimize the parameters of the photoinduced birefringence in azopolymers, we have synthesized and studied copolymers with different weight ratios of two monomers which differ in the length of spacer between the azochromophore and the polymer backbone. The polymer P_1 based only on the first monomer is amorphous, and the polymer P_2 which contains only the second monomer is liquid-crystalline (LC). In addition to the homopolymers P_1 and P_2, five copolymers were synthesized, described by the general formula $P_1(100-x)P_2(x)$, where x gives the percent weight ratio of the second monomer in the final copolymer. As a result the following seven polymers were obtained – P_1, $P_1(75)P_2(25)$, $P_1(60)P_2(40)$, $P_1(50)P_2(50)$, $P_1(40)P_2(60)$, $P_1(25)P_2(75)$, P_2.

The main parameters of the photoinduced birefringence in these polymers, such as maximal value, response time and time stability, have been measured and compared.

Keywords: azopolymer, copolymer, photoinduced birefringence, optimization

INTRODUCTION

The first report on high-efficient polarization recording in azobenzene material appeared in 1984 by Todorov *et al*. [1]. The material was solid solution of methyl orange in poly(vinyl alcohol). The large photoinduced birefringence and dichroism are caused by the reorientation of the azomolecules via *trans-cis-trans* photo-isomerization.

The potential of the azobenzenes for reversible digital and holographic storage including also commercial applications was realized by Eich and Wendorff [2, 3]. They used a material, where the azochromophore was chemically attached to a polymer chain i.e. the first liquid crystalline (LC) azopolymer. Later, huge number of azopolymers have been studied for holographic data storage [4] – liquid crystalline [5–8] and amorphous [9–11]. As both states (LC and amorphous) have certain advantages, some researchers tried to combine them, synthesizing copolymers containing mesogenic and non-mesogenic monomers [12].

Our approach in this study is similar. Earlier, we have synthesized and investigated three side-chain azopolymers (two homopolymers and a copolymer) with similar structures of the main chain and the chromophore, but different spacer between them [13]. These azopolymers have also been used as organic matrix for recently developed photosensitive hybrid organic/inorganic materials [14–17].

Two of these polymers are amorphous and one is LC. In order to optimize the parameters of the photoinduced anisotropy in azopolymers, we have synthesized four additional copolymers with different weight ratios of two monomers and determined the main characteristics of the birefringence in the entire azopolymer family.

EXPERIMENTAL

Synthesis of the azo homopolymers and copolymers

All seven polymers (both homopolymers and copolymers) studied in this article are side-chain cyan azo polymers containing different ratios of the monomers shown in Fig. 1. They were synthesized by a three-step process: (a) synthesis of the azo dyes; (b) preparation of the chromophore monomers, and (c) radical-type polymerization of the monomers. Initially the azo dye (I) 4-(4-hydroxy-phenylazo)benzonitrile was synthesized by dissociation of 4-aminobenzonitrile and coupling

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with phenol using standard technology. Dye (II) 4-[4-(6-hydroxy-hexyloxy)phenylazo]benzonitrile was obtained from dye (I) by etherification with 6-bromo-1-hexanol. At the second step, the two azo dyes were transformed in the monomers M_1 and M_2 (see Fig. 1) by etherification with acryloyl chloride. Finally, different weight ratios of the two monomers have been combined and polymerized via radical-type polymerization.

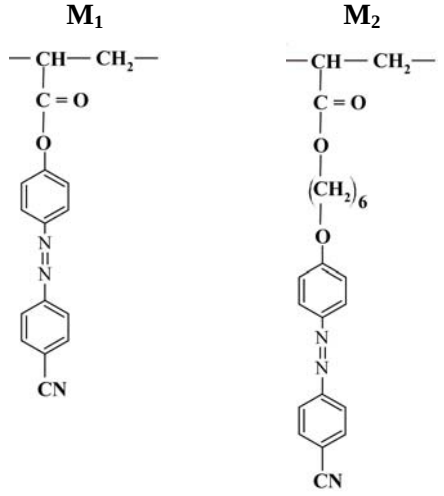

Fig. 1. Structure of the monomers used to prepare the homopolymers and copolymers.

In addition to the homopolymers P_1 (obtained from monomer M_1 only) and P_2 (containing only M_2), five copolymers were synthesized, described by the general formula $P_1(100-x)P_2(x)$. Here x gives the percent weight ratio of the second monomer (M_2) in the final copolymer and has values x = 0, 25, 40, 50, 60, 75, 100. As a result the following seven polymers were obtained – P_1, $P_1(75)P_2(25)$, $P_1(60)P_2(40)$, $P_1(50)P_2(50)$, $P_1(40)P_2(60)$, $P_1(25)P_2(75)$, P_2.

The polymers P_1, $P_1(50)P_2(50)$ and P_2 have been studied earlier and it has been established that P_1 and $P_1(50)P_2(50)$ are amorphous, P_2 is liquid crystalline [13, 16]. Their molecular weights and glass transition temperatures are also known: P_1 – $M_w = 1.46\times10^4$ g/mol, T_g = 106 °C, $P_1(50)P_2(50)$ – $M_w = 3.60\times10^3$ g/mol, T_g = 102 °C and P_2 – $M_w = 2.05\times10^3$ g/mol, T_g = 35 °C. The other four copolymers are newly synthesized.

Thin films preparation and FTIR characterization

In order to prepare thin films for optical testing, 20 mg of the polymer were dissolved in 200 µl of 1,2-dichloroethane, i.e. at concentration of 100 g/L. Then the solutions were spin coated at 1500 rpm on glass substrates to produce films with uniform thickness. The thicknesses of the films were measured by high-precision Talystep profilometer. Fourier transform infrared spectra (FT-IR) were measured by Bruker IR spectrometer for the homopolymers P_1 and P_2, and also for their "closest" copolymers: $P_1(75)P_2(25)$ and $P_1(25)P_2(75)$, respectively. They are given in Fig. 2. As seen, the characteristic peaks of absorption of the corresponding polymers are similar that indicates the correct composition of the copolymers.

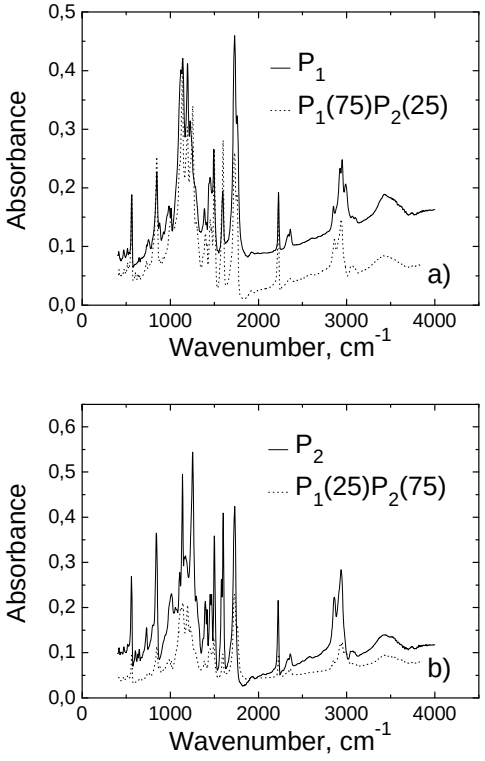

Fig. 2. FT-IR spectra of: a) P_1 and $P_1(75)P_2(25)$; b) P_2 and $P_1(25)P_2(75)$.

Photoinduced birefringence measurement

Birefringence is induced in the samples by a vertically polarized beam from a DPSS laser at 473 nm (I = 400 mW/cm^2), inside the absorption band of the azochromophores. The sample is placed between crossed polarizers oriented at ±45° with respect to the vertical. The intensity I of a probe beam (λ_{probe} = 633 nm) passing through the system is measured and the value of the photoinduced birefringence Δn is determined by the equation $\Delta n(t) = (\lambda_{probe}/\pi d)\arcsin\sqrt{I(t)/I_0}$, where d is the film thickness, I_0 is the intensity of the probe beam before the start of the recording and at parallel polarizers.

RESULTS AND DISCUSSION

Using the optical scheme described in Section 2.3, for each sample we have made a 15 min measurement, consisting of three stages: (*i*) 1 min to estimate the background optical noise; (*ii*) 5 min of recording by which we find the response time τ and the maximal birefringence Δn_{max}, and (*iii*) 9 min of relaxation after the end of the recording to determine the stability *r*. A typical measurement is presented in Fig. 3a for the copolymer $P_1(75)P_2(25)$. The data for all the polymers from the series are given in Table 1. The correlation between Δn_{max} and the polymers composition is shown in Fig. 3b. From the tabulated data is seen that the LC polymer P_2 has highest value of the photoinduced birefringence and it is also most stable, even some increase is observed after the end of the recording. This is most likely due to a relaxation from *cis* to *trans* state of some of the chromophores, which tend to orient in line with the already optically oriented majority of the azomolecules. On the other hand, the copolymer $P_1(75)P_2(25)$ has fastest response. The choice of particular polymer from these series can be done depending on the application.

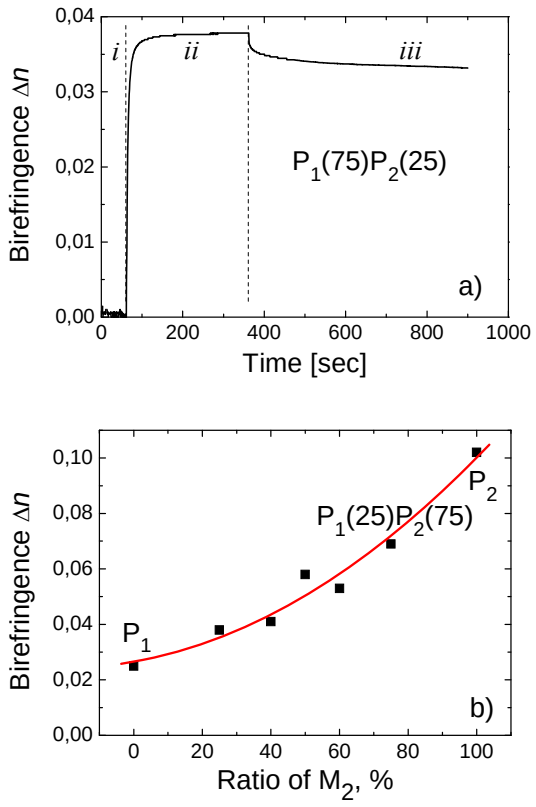

Fig. 3. a) kinetics of Δn for $P_1(75)P_2(25)$; b) Δn_{max} vs. ratio of the monomer M_2.

Table 1. Summary of data for the series of azobenzene copolymers P_1–P_2.

Azopolymer	Maximal Birefringence Δn_{max}	Stability[a] *r*, %	Response time τ, sec
P_1	0,025	84	25
$P_1(75)P_2(25)$	0,038	82	**6**[b]
$P_1(60)P_2(40)$	0,041	85	11,5
$P_1(50)P_2(50)$	0,058	89	12
$P_1(40)P_2(60)$	0,052	88	10
$P_1(25)P_2(75)$	0,069	86	19
P_2	**0,102**[b]	**110**[b]	25,5

[a] Stability is evaluated as ratio of birefringence 9 min after the end of recording to Δn_{max}.

[b] The highest values of the maximal birefringence and stability as well as the shortest response time are outlined in bold.

CONCLUSIONS

We have synthesized a series of seven azopolymers described by the general formula $P_1(100-x)P_2(x)$, namely P_1, $P_1(75)P_2(25)$, $P_1(60)P_2(40)$, $P_1(50)P_2(50)$, $P_1(40)P_2(60)$, $P_1(25)P_2(75)$, P_2. The main parameters of the photoinduced birefringence in these polymers, such as maximal value, response time and time stability, have been measured and compared. The highest birefringence is obtained in the homopolymer P_2 (Δn_{max} = 0,102) and the copolymer $P_1(75)P_2(25)$ has shortest response time – 6 s.

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ФОТОИНДУЦИРАНА АНИЗОТРОПИЯ В СЕРИЯ АЗОБЕНЗЕН-СЪДЪРЖАЩИ СЪПОЛИМЕРИ

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(Резюме)

С цел оптимизиране параметрите на фотоиндуцираното двулъчепречупване в азополимери, бяха синтезирани и изследвани съполимери с различни тегловни отношения на два мономера, които се различават по дължината на страничната верига, свързваща азохромофора с главната полимерна верига. Полимерът P1 изграден само от единия мономер е аморфен, докато полимерът P2, който е съставен само от втория мономер е течнокристален. Освен това са синтезирани още пет съполимера, описани от общата формула P1(100–x)P2(x), където x задава тегловното съдържание в проценти на втория мономер в крайния съполимер. В резултат на това са получени следните седем полимера – P1, P1(75)P2(25), P1(60)P2(40), P1(50)P2(50), P1(40)P2(60), P1(25)P2(75), P2.

Измерени са основните параметри на фотоиндуцираното двулъчепречупване в тези полимери – максималната му стойност, времето на отклик и стабилността във времето – и е направено сравнение между тях.