ELSEVIER

Polymer 43 (2002) 3753–3757

polymer

www.elsevier.com/locate/polymer

Temperature dependence of photoinduced birefringence in mixed Langmuir–Blodgett (LB) films of azobenzene-containing polymers

Josmary R. Silva[a], F.F. Dall'Agnol[a], O.N. Oliveira Jr[a], José A. Giacometti[b,*]

[a]Instituto de Física de São Carlos, Universidade de São Paulo CP 369, 13560-970 São Carlos, SP, Brazil
[b]Faculdade de Ciências e Tecnologia, Universidade Estadual Paulista CP 467, 19060-900 Presidente Prudente, SP, Brazil

Received 1 October 2001; received in revised form 24 January 2002; accepted 28 January 2002

Abstract

The temperature dependence of photoinduced birefringence was investigated for mixed Langmuir–Blodgett (LB) films from the homopolymer poly[4′-[[2-(methacryloyloxy)ethyl]ethyl-amino]-2-chloro-4-nitroazobenzene] (HPDR13) and cadmium stearate (CdSt) and from the copolymer 4-[*N*-ethyl-*N*-(2-hydroxyethyl)]amino-2′-chloro-4′-nitroazobenzene (MMA-DR13) and CdSt. Birefringence was achieved by impinging a linearly polarized light on the LB films. The maximum birefringence achieved decreased with temperature as thermal relaxation of the chromophores was facilitated. The buildup curves for birefringence were fitted with biexponential functions representing distinctly different mechanisms with time constants. The first, fast process is thermally activated and may be represented by an Arrhenius process. The decay of birefringence after switching off the laser source was described by a Kohlraush–Williams–Watts (KWW) function, consistent with a distribution of relaxation times for the polymer system. Activation energies were obtained from Arrhenius plots of the rate constant of the exponential functions and KWW function, which showed that the buildup of birefringence was very similar for the two polymer systems. The decay, however, was slower for the LB film from MMA-DR13/CdSt. © 2002 Published by Elsevier Science Ltd.

Keywords: Azobenzene polymers; Langmuir–Blodgett films; Photoinduced birefringence

1. Introduction

The photoisomerization properties of azobenzene-containing polymers have been extensively exploited owing to their potential applications in optical storage [1–7], optical switching and holographic gratings [8,9]. Birefringence in azopolymer films may be created by *trans–cis–trans* photoisomerization processes produced with a linearly polarized light, with the induced orientation of the chromophores being perpendicular to the polarization direction [3]. The *trans–cis* isomerization process is induced by light while the converse *trans–cis* process may be induced by light or heat.

Photoisomerization is usually investigated in polymer films obtained by solution casting or spin coating of azobenzene-containing polymers. These may be guest–host systems, in which the azobenzene chromophore is mixed in a polymer matrix, or side-chain or main-chain azopolymers, where the chromophores are covalently attached to the polymer chain [10]. The photoinduced birefringence depends on several factors such as dipole–dipole interaction [11], size of the azobenzene [12], and temperature [3,10]. Investigations into the dynamics of the buildup and decay of birefringence have been made by many authors [13–22]. The effects of varying the temperature at which optical storage experiments are carried out have been investigated mainly for cast films and spin-coating, and no report appears to have been made for Langmuir–Blodgett (LB) films. The use of the LB technique to produce the films is motivated by the possible control over film thickness and molecular architecture, with the advantage that higher birefringence may be photoinduced in comparison to cast films of the same azopolymer [23].

In this work, we present an investigation of effects of varying the temperature in the buildup and decay of photoinduced birefringence for LB films from two distinct polymeric materials, HPDR13 and MMA-DR13. In both cases, the LB films were produced from mixtures of polymer and cadmium stearate, where the latter simply served as a means to improve the monolayer stability on the water surface and the monolayer transferability.

2. Experimental

The polymers poly[4′-[[2-(methacryloyloxy)ethyl]-ethyl-amino]-2-chloro-4-nitroazobenzene] (HPDR13) and

---

* Corresponding author.
E-mail address: giacometti@prudente.unesp.br (J.A. Giacometti).

0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00122-2

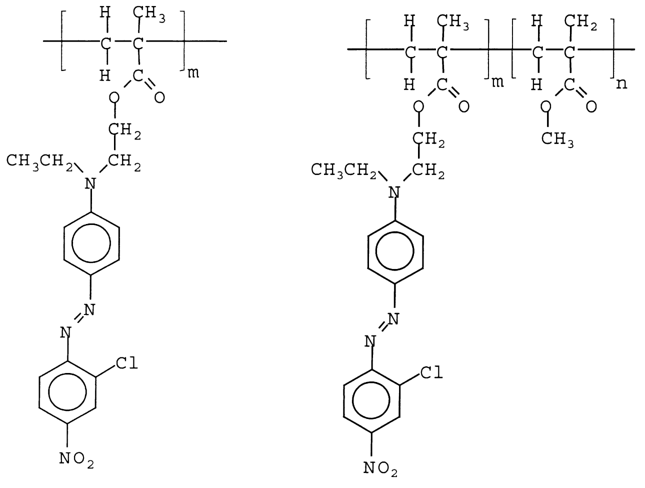

Fig. 1. Chemical structure of the two polymers used.

4-[*N*-ethyl-*N*-(2-hydroxyethyl)]amino-2′-chloro-4′-nitroazobenzene (MMA-DR13) (Fig. 1) were obtained through chemical synthesis as described in Refs. [24,25]. The glass transition temperature (T_g) of HPDR13 and MMA-DR13 are ~70 and ~120 °C, respectively. Stearic acid was purchased from Aldrich, with purity greater than 99%. The spreading solution for the Langmuir films was prepared by dissolving 1 mg of the polymer and 1 mg of stearic acid into 10 ml of chloroform (Merck, HPLC grade). Ultrapure water was supplied by a Milli-RO filter coupled to a Milli-Q system from Millipore (resistivity 18.2 MΩ cm). Cadmium chloride (Carlo Erba, AR grade, 99%) was added to the subphase at a concentration of 4×10^{-4} mol, so that the cadmium ions could complex with ionized stearic acid, thus forming cadmium stearate (CdSt). The subphase pH was kept at ca. 6.0 by adding sodium bicarbonate (LABSYNTH, AR grade, 99.7%), which caused the stearic acid to be fully ionized and consequently facilitating the complexation. Langmuir monolayers and LB films were fabricated with a KSV5000 system, mounted on an antivibration table in a class 10 000 clean room. The subphase temperature was kept at 20 °C. The mixed monolayers were transferred onto BK7 glass substrates, at a dipping speed of 2.5 mm/min for the downstrokes and 6.5 mm/min for the upstrokes. The film was dried in air for 10 min after each pair of layers had been transferred. The transfer ratio was ca. 0.9 for the upstrokes as well as the downstrokes, leading to Y-type LB films. Measurements were performed on 21-layer LB films whose thickness was estimated to be ~40 nm by atomic force microscopy (AFM). Film thickness was measured by inscribing a furrow on the film surface with the AFM tip, and then obtaining the height profile across the furrow [26].

The photoinduced birefringence of the transferred LB films was measured for the films at various temperatures, using the experimental set-up similar to that described in Ref. [10]. Briefly, photoinduced isomerization was performed by impinging a cw Nd/YAG laser beam (writing beam) at 532 nm, polarized at 45 °C in relation to the polarization direction of the reading beam. The intensity of the writing beam was 7 mW/cm^2. The reading beam was a low power He–Ne laser at 632.8 nm, which passed through crossed polarizers with the sample in between. The change in transmittance of the reading beam, indicative of birefringence, was measured with a photodiode, with the data being stored in a PC computer. The sample holder was placed in an oven whose temperature could be controlled in the range from 20 to 80 °C.

3. Results and discussion

Figs. 2 and 3 show the buildup and decay of the photoinduced birefringence at various temperatures for mixed LB films of HPDR13/CdSt and MMA-DR13/CdSt. All birefringence curves were normalized by the maximum value measured at room temperature. The two types of LB film essentially display the same behavior; though the temperature at which the decay curves become temperature independent is ca. 60 °C for HPDR13/CdSt and 80 °C for MMA-DR13/CdSt. This difference is probably associated with the distinct glass transition temperatures of the polymers, which is necessary to randomize the azobenzenes [27]. Above such temperatures, the amplitude of the signals becomes very small and independent of temperature.

The curves for the buildup of birefringence can be fitted with biexponential functions of the form

$$y = A(1 - \mathrm{e}^{-t/\tau_F}) + B(1 - \mathrm{e}^{-t/\tau_S}) \tag{1}$$

where *A* and *B* are the pre-exponential factors, *t* the time and τ_S and τ_F the time constants for writing the slow and fast processes, respectively. Biexponential functions are normally employed for representing the photoisomerization buildup process. They are related to two processes of orientation. The first is much faster and is attributed to the local movement of the azobenzene groups in the *trans–cis–trans* photoisomerization [3]. Such a fast process depends on the size of the azobenzene group, on the local free volume and on the polymer chain character [4]. The slow process is associated with the movement of the azobenzene groups linked to the polymeric chain [3].

Figs. 2 and 3 show that the saturation value for birefringence decreases with increasing temperatures. This is best shown in Fig. 4. Two competing processes define the maximum achievable birefringence: the orientation due to photoisomerization and the thermal relaxation that tends to disorientate the azobenzene groups. As the temperature is increased, the second process becomes more important than the first [27]. These two competing processes are also likely to be relevant for the kinetics of the buildup and decay of birefringence. The first, fast process for the buildup is found to be thermally activated. Fig. 5 shows the Arrhenius plot for the fast orientation process, obtained from the rate constant $k_F = 1/\tau_F$, associated with the photoisomerization for both polymeric materials. Therefore, by increasing the

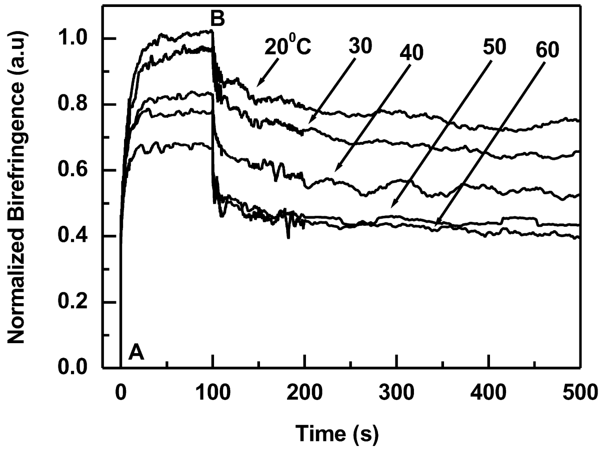

Fig. 2. Buildup and decay of the photoinduced birefringence at various temperatures for a 21-layer mixed LB film of HPDR13/CdSt. The writing laser is switched on at point A and switched off at B.

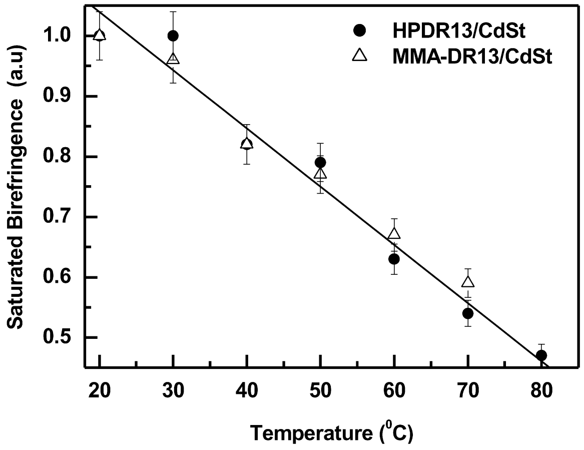

Fig. 4. Plot of the maximum (saturated) birefringence versus temperature.

temperature, one increases the mobility of the chromophore and the process becomes faster. The activation energy was $E = 9.0 \pm 0.7$ kJ/mol for HPDR13/CdSt and 14.0 ± 0.9 kJ/mol for MMA-DR13/CdSt. Song et al. [10] reported $E = 27.6$ kJ/mol for cast films of an amorphous polymer derivative with side chains containing DR19, while Wu et al. [15] reported an $E = 520.5$ kJ/mol for a liquid-crystalline cast polymer. The large difference between liquid-crystalline and amorphous polymers is explained by the tendency of the chains of the former polymers to align cooperatively. A higher energy is required to overcome such tendency. As expected, the activation energies are similar for the amorphous polymers, either in the form of cast or LB films. Nevertheless, a lower energy should be expected for the more organized LB film, in which relatively larger birefringences may be achieved [23]. This is indeed observed experimentally.

We also analyzed the second process for the birefringence buildup. Here, there was no clear dependence of the characteristic constants for the process on the temperature. Within the dispersion of the experimental data, the characteristic time for this second process is practically independent of the temperature. Since the second process is associated with the mobility of chains, the disorientation caused by the increase in temperature seems to be more important than in the first kinetics process. The temperature dependence for the disorientation apparently compensates the dependence on the chain mobility. The temperature-independent nature of the slow process may indicate that another mechanism, such as optical erasure during probing, dominates [27].

Table 1 summarizes the results for the two polymer systems. The parameters E_F and τ_F were calculated from the fast component of the biexponential function given in Eq. (1). The activation energy and time constant for the fast process during the buildup of the birefringence is close to each other for the two systems, which suggests similar

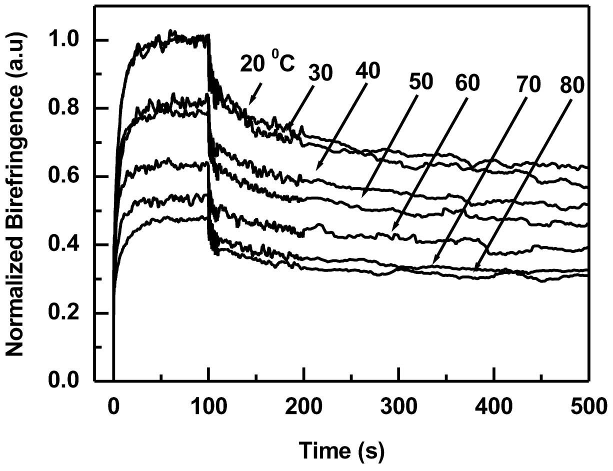

Fig. 3. Buildup and decay of the photoinduced birefringence for a 21-layer LB film of MMA-DR13/CdSt at various temperatures.

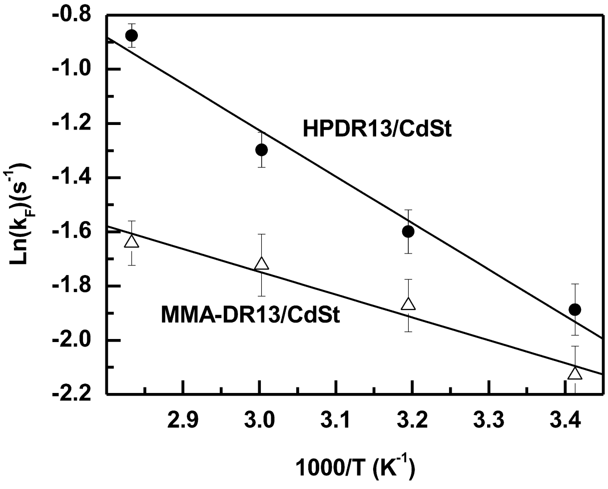

Fig. 5. Arrhenius plot for the fast rate constant, $1/\tau_F$, in the buildup of birefringence obtained from the fitting of the experimental results with a biexponential function.

Table 1
Parameters obtained by fitting the birefringence data (for temperatures above room temperature) for LB films from HPDR13/CdSt and MMA-DR13/CdSt. The subscript F refers to the time constant τ_F of the fast process during buildup of the birefringence

	Buildup (biexponential function)		Decay (KWW function)		Remaining birefringence after 1000 s (20 °C) (%)
	E_F (kJ/mol)	τ_F (s) (20 °C)	E (kJ/mol)	τ (s) (20 °C)	
HPDR13/CdSt	14.0 ± 0.9	7.0 ± 0.2	25.0 ± 0.4	277 ± 24	60
MMA-DR13/CdSt	9.0 ± 0.7	8.0 ± 0.4	120 ± 7.0	784 ± 35	70

mechanisms for isomerization and molecular orientation. The similar behavior can be explained considering that the fast process is attributed only to side groups. There is no influence of the chain motion, which indeed depends on T_g.

Attempts to fit the decay curves for the birefringence in the LB films with biexponential functions were not successful. Much better fittings could be obtained with the stretched exponential Kohlrausch–Williams–Watts (KWW) function, which is an empirical function that has also been used to describe the dielectric relaxation of dipoles in polymers [28],

$$y = A\,\mathrm{e}^{-(t/\tau)\beta} \tag{2}$$

where A is a constant, τ the relaxation time and β the parameter that determines the width of the distribution of relaxation times. Values of β lie in the range 0.18–0.36 for MMA-DR13/CdSt and 0.04–0.06 for HPDR13/CdSt. Such small values indicate a wide distribution of relaxation times [29]. The decay process is usually associated with the motion of side azobenzene groups due to *cis–trans* thermal relaxation and chain motion [10], but in our results, these two mechanisms could not be resolved owing to the large distribution of relaxation times. As shown in Fig. 6, the activation energy obtained from an Arrhenius plot of $k = 1/\tau$ versus $1/T$ was $E = 25.0 \pm 0.4$ kJ/mol for HPDR13/CdSt and $E = 120 \pm 7$ kJ/mol for MMA-DR13/CdSt (Table 1). The large difference in activation energy may be due to the larger T_g of MMA-DR13 (~120 °C) in comparison to HPDR13 (~70 °C). Therefore, the MMA-DR13 is more rigid. It means that the segmental motion of chain is restrained, leading to higher activation energy. The azobenzene orientation in MMA-DR13/CdSt is more stable than in HPDR13/CdSt, which is confirmed by the remaining birefringence after 1000 s, as listed in Table 1.

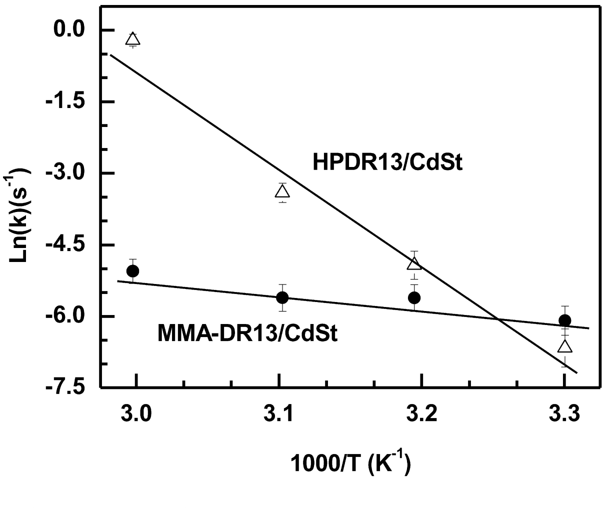

Fig. 6. Arrhenius plot for the inverse of the rate constant in the decay of birefringence obtained by fitting the data with the KWW function.

The time constants in Table 1 could not be compared to data in the literature, since their values depend on various parameters such as the laser power and sample thickness [10]. The amplitudes cannot be compared either, as works in the literature quote figures in arbitrary units.

4. Conclusion

The buildup of photoinduced birefringence was explained using biexponential functions, representing a fast and a slower process. The birefringence decay was fitted with the KWW function, which is related to a distribution of relaxation times. The maximum achievable birefringence decreases almost linearly with increasing temperature. The time constant for the fast process in the buildup of the birefringence, τ_F, displays a typical Arrhenius behavior. The same does not apply to τ_S, which is practically independent of the temperature. The activation energies for the fast orientation during the buildup of the birefringence were close to each other for the two polymer systems, i.e. the orientation mechanisms are similar. The activation energy for the decay process, however, was higher for MMA-DR13/CdSt, which indicates that this system has a more stable birefringence than HPDR13/CdSt.

Acknowledgements

The authors acknowledge the financial assistance of FAPESP, CAPES and CNPq (Brazil).

References

[1] Ho MS, Natansohn A, Rochon P. Macromolecules 1995;28:6124.
[2] Natansohn A, Rochon P, Gosselin J, Xie S. Macromolecules 1992;25:2268.
[3] Meng X, Natansohn A, Rochon P. J Polym Sci, Polym Phys 1996;34:1461.

[4] Ho M-S, Natansohn A, Barret C, Rochon P. Can J Chem 1995;73:1773.

[5] Ho M-S, Natansohn A, Barret C, Rochon P. Macromolecules 1996;29:44.

[6] Natansohn A, Rochon P. Macromolecules 1992;25:5531.

[7] Iftime G, Fisher L, Natansohn A, Rochon P. Can J Chem 2000;78:409.

[8] Natansohn A, Barret C, Rochon P. Adv Mater 1999;11(16):1387.

[9] Hvilsted S, Andruzzi F, Ramanujam PS. Opt Lett 1992;17(17):1234.

[10] Song OK, Wang CH, Pauley MA. Macromolecules 1997;30:6913.

[11] Brown D, Natansohn A, Rochon P. Macromolecules 1995;28:6116.

[12] Tawa K, Kamada K, Sakaguchi T, Ohta K. Polymer 2000;41:3235.

[13] Natansohn A, Rochon P. Macromolecules 1998;31:7960.

[14] Hore D, Natansohn A, Rochon P. Can J Chem 1998;76:1648.

[15] Wu Y, Kanazawa A, Shiono T, Ikeda T, Zhang Q. Polymer 1999;40:4787.

[16] Cha SW, Choi DH, Jin J-I. Adv Funct Mater 2001;11(5):355.

[17] Markava E, Gustina D, Matisova G, Kaula I, Mazikante I, Rutkis M, Gerca L. Supramol Sci 1997;4:369.

[18] Lee GJ, Kim D, Lee M. Appl Opt 1995;34(1):138.

[19] Imamura Y, Yamaguchi Y, Tran-Cong Q. J Polym Sci, Part B: Polym Phys 2000;38:682.

[20] Yokoyama S, Kakimoto M-a, Imai Y. Masa-aki. Thin Solid Films 1994;242:183.

[21] Maack J, Ahuja RC, Möbius D. Thin Solid Films 1994;242:122.

[22] Ono H, Kowatari N, Kawatsuki N. Opt Mater 2000;15:33.

[23] Mendonça CR, dos Santos Jr DS, Balogh DT, Dhanabalan A, Giacometti JA, Zílio SC, Oliveira Jr ON. Polymer 2001;42:6539.

[24] Dhanabalan A, Balogh DT, Riul Jr A, Giacometti JA, Oliveira Jr ON. Thin Solid Films 1998;323:257.

[25] Nahata A, Shan J, Yardley JT, Wu C. J Opt Soc Am B 1993;10:1553.

[26] Lobo RFM, Pereira-da-Silva MA, Raposo M, Faria RF, Oliveira Jr ON. Nanotechnology 1999;10:389.

[27] Xu G, Si J, Liu X, Yang QG, Ye P, Li Z, Shen Y. J Appl Phys 1999;85(2):681.

[28] Dureiko RD, Schuele DE, Singer KD. J Opt Soc Am B 1998;15(1):338.

[29] Shane CB, Hayden LM. J Polym Sci, Part B: Polym Phys 1998;36:1013.