Storage Studies of Langmuir−Blodgett (LB) Films of Methacrylate Copolymers Derivatized with Disperse Red-13

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ABSTRACT: Optical storage and photoisomerization characteristics were investigated for composite Langmuir−Blodgett (LB) films made up of methacrylate copolymers with different weight percentages of disperse red-13 and cadmium stearate. The influence of the dye content in the copolymer and number of layers of the composite LB films on the optical storage characteristics is discussed. Distance-dependent cooperative interactions between azobenzene chromophores seem to affect the time to achieve 50% of maximum birefringence and the amount of remaining birefringence after the writing beam is switched off. LB films were also characterized by UV−vis, FTIR, and XRD measurements. The LB fabrication followed a systematic investigation of monolayer properties of the dye-containing methacrylate copolymers using surface pressure and surface potential isotherms, to identify optimal deposition conditions. For instance, monolayers from pure copolymers were not amenable to transfer onto solid substrates, which was circumvented by codeposition with cadmium stearate.

Introduction

The trans−cis−trans reversible isomerization of azobenzene-functionalized polymers can be exploited in a number of applications, such as in information storage,[1−3] optical switches,[4] optical modulators,[5] nonlinear optics,[6,7] surface relief gratings,[8,9] and command surfaces for aligning liquid crystals.[10,11] In contrast to guest−host composite systems in which the azobenzene guest molecules are dispersed in a host polymer matrix, in azo-functionalized polymers the azobenzene chromophore is covalently linked to the polymer backbone, which can prevent the crystallization/aggregation of chromophores. The optical properties of azobenzene polymers can be fine-tuned through several strategies: (i) suitable choice of the polymer backbone to which the azobenzene group is attached as side chain,[1] (ii) introduction of substituents in the azobenzene group,[13] (iii) introduction of spacer groups either in the main chain or between the main polymer chain and the azobenzene side chain,[14] and (iv) change in chromophore density along the polymer chain.

Optical storage characteristics of cast films of a series of differently functionalized azo-polymers have been reported by Natansohn et al.[1,2,8,14−17] In particular, it was demonstrated that the optically induced birefringence and dichroism can be used for optical information storage.[1,2] Information is stored in the form of optically induced anisotropy resulting from the trans−cis−trans isomerization of the azobenzene group upon absorption of light and subsequent molecular reorientation. Upon exposure to linearly polarized laser light, the photoisomerization and reorientation sequence takes places until the molecule orients perpendicular to the polarization direction of the laser light. The net macroscopic anisotropy induced in the film (induced birefringence) depends on the material absorbance and hence on the chromophore content (number density) under the area of exposure to the laser light. If films with uneven, i.e., nonuniform, thicknesses are used, an irreproducible write−erase pattern is produced whose analysis is complicated.

The possibility of thickness control and surface uniformity[18,19] has prompted us to investigate ultrathin Langmuir−Blodgett (LB) films. In the present study, copolymers with different mole percentages of disperse red-13 have been synthesized, and their optical storage characteristics have been studied in the form of LB films. The LB manipulation of azobenzene functionalized polymers also permits the study of photoisomerization of the azobenzene group in the solid state. During the course of the LB film preparation, the monolayer characteristics of copolymers with different dye contents were studied through surface pressure and surface potential isotherms. Owing to the poor stability of their pure monolayers, the copolymers were transferred onto solid substrates along with cadmium stearate (CdSt).[20] The multilayer mixed LB films were characterized by UV−vis and transmission Fourier transform infrared (FTIR) spectroscopies and X-ray diffraction (XRD).

Experimental Section

Methacrylate copolymers containing 6, 29, 37, 57, and 77 wt % of disperse red-13 dye, named as CoDR6, CoDR29, CoDR37, CoDR57, and CoDR77, respectively, were synthesized using the method reported in ref 21. The general structure of these copolymers is shown in Figure 1. The corresponding mole fractions of the dye are 0.02, 0.11, 0.20, 0.29, and 0.51. To prepare the copolymers, the DR13 monomer (2.8×10^{-4} M) and 2,2′-azobis(isobutyronitrile) (AIBN, 0.005 g) were dissolved in a solvent mixture of dimethylformamide (DMF)/methyl ethyl ketone (MEK) 1/1 v/v (2 mL) and heated to 70 °C. After an interval of 4 h, 0.25 mL of 2-hydroxyethyl methacrylate (HEMA) and 0.005 g of AIBN in 2 mL of DMF−MEK solvent mixture were added to the above reaction mixture. Similar amounts of HEMA and AIBN in DMF−MEK were added after a time interval of 7, 10, and 17 h. The reaction mixture was kept at 70 °C for further 28 h after the latest addition of reactants. It was then poured into *n*-hexane, and the viscous

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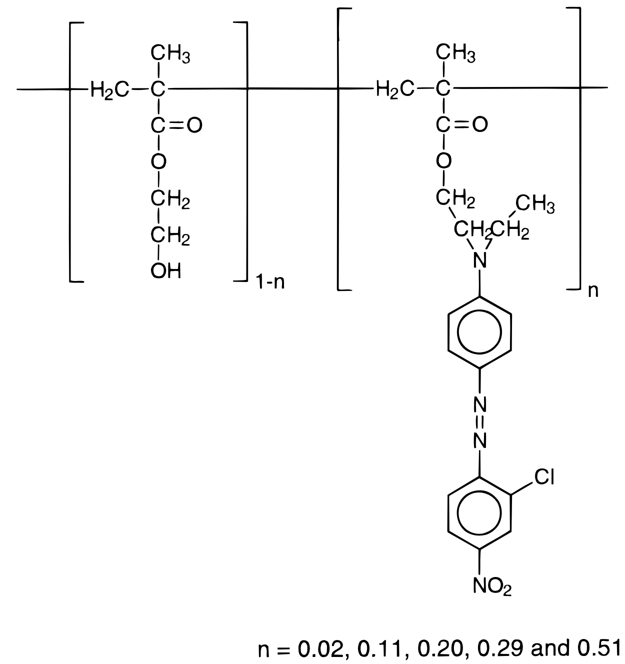

Figure 1. Chemical structure of copolymers.

mass thus separated was washed with *n*-hexane and ethyl acetate to obtain a solid product. The copolymer obtained was washed repeatedly with ethyl acetate to remove unreacted monomers and dried under vacuum. The absence of unreacted monomers in the final product has been confirmed by thin-layer chromatography (TLC) analysis.

The differential scanning calorimetry (DSC) analysis of the CoDR6 revealed a glass transition temperature of 85 °C, which is similar to that observed for the HEMA homopolymer. The actual weight percentage of dyes in the copolymer was inferred by comparing the UV−vis absorbance in a DMF solution with the calibration curve obtained with the UV−vis absorbance of a DMF solution with different concentrations of the methacrylate monomer of the DR13 dye. All copolymers were characterized by UV−vis and Fourier transform infrared (FTIR) spectroscopies, using a Hitachi U2001 spectrophotometer and a BOMEM Michelson spectrometer, respectively. In the UV−vis spectra of a DMF solution a peak at $\lambda_{max} = 506$ nm was observed. For a cast film on ZnSe, the FTIR spectra displayed the following peaks (in cm^{-1}): 3300 (broad, OH), 2917 and 2850 (CH_2), 1732 (C−O, ester), 1599 and 1500 (C=C, aromatic), 1518 and 1336 (NO_2), 1242 (C(=O)−O), 1252 and 1134 (O−C−C, ester group).

Ultrapure water supplied by a Milli-RO coupled to a Milli-Q water purification system from Millipore was used as subphase. In the case of the pure copolymer monolayer, a solution of copolymer in a mixture of DMF and chloroform (2:98 by volume) with a concentration of 0.2 mg/mL was spread on the surface of pure water. For mixed monolayers, a mixture of copolymer:stearic acid (50%:50% by weight) in a DMF−chloroform solvent mixture was spread on the water containing cadmium chloride (4×10^{-4} M) and sodium bicarbonate (5×10^{-5} M) at a subphase pH ~6.0. All LB experiments were carried out at a room temperature of 22 °C. Surface pressure and surface potential isotherms and LB deposition were carried out with a KSV-5000 LB instrument placed on an antivibration table in a class 10 000 clean room. Glass and ZnSe plates were used as substrates that were cleaned thoroughly prior to use. Isotherms were recorded by compressing the monolayer with a barrier speed of 10 mm/min. For pure copolymer monolayers, the mean molecular area axis (*X*-axis) of the isotherm is based on the average molecular weight of the repeat unit calculated using the percentage of dye substitution in the polymer. For mixed monolayers, the mean molecular area axis is based only on the number of stearic acid in the mixture. X-ray diffraction (XRD) measurements were carried out with a Rigaku Rotaflex-RU 200B X-ray powder diffractometer in the 2*θ* range of 3−20 using a Cu target.

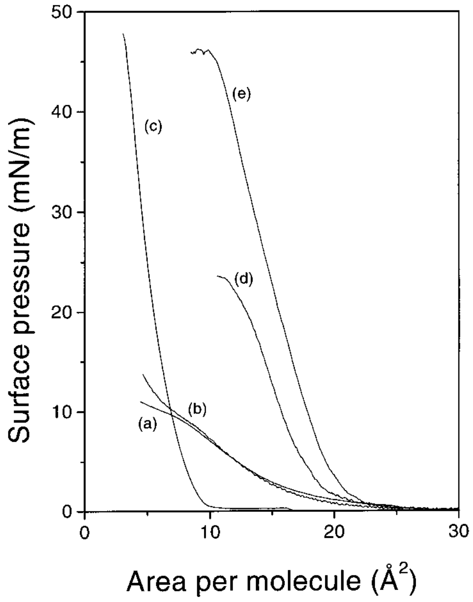

Figure 2. Surface pressure isotherms of pure copolymers: (a) CoDR6, (b) CoDR29, (c) CoDR37, (d) CoDR57, (e) CoDR77.

Photoinduced trans−cis isomerization of the azobenzene chromophores in the mixed LB film was achieved by irradiating the film with a circularly polarized unfocused 30 mW beam from an argon ion laser operating at 514 nm. Circularly polarized light was used to avoid reorientation of the azo groups, and the beam was unfocused in order to avoid heating the sample at the point of contact. Under these conditions, only the photoisomerization of azobenzene chromophores should take place. A very low-intensity probe beam at the same wavelength was passed through the sample coincident with the pump beam and into a photodiode. The intensity of the probe beam light transmitted through the polymer film was monitored and recorded to observe the time evolution of the photoisomerization.

Optical storage experiments were carried out at room temperature and under ambient conditions. Mixed LB films containing copolymers with different mole percentages of dye substitution and CdSt were studied. The optical birefringence was induced in the LB film using a polarized Nd:YAG continuous laser operating at 532 nm (writing beam) with a polarization angle of 45° with respect to the polarization direction of the probe beam. The power of the writing beam was 6.8 mW for a spot of 2 mm. The change in transmission of a low-power He−Ne laser (probe beam) operating at 632.8 nm that passes through two crossed polarizers and the sample was measured with the aid of a photodiode.

Results and Discussion

Langmuir Monolayers. Surface pressure−mean molecular area isotherms of copolymers with different weight percentages of dye substitution are shown in Figure 2. For low dye contents, i.e., CoDR6 and CoDR29, the monolayers were considerably expanded and collapsed at low surface pressures, close to 10 mN/m. Further hysteresis experiments revealed the formation of metastable monolayers that probably comprised aggregates of polymer molecules. In contrast, the copolymers CoDR37, CoDR57, and CoDR77 yielded condensed isotherms with the limiting molecular area (obtained by extrapolation of the steep part of the isotherm curve) increasing with the amount of dye substitution (8, 18.5, and 20 Å² for CoDR37, CoDR57, and CoDR77, respectively). The reason the collapse

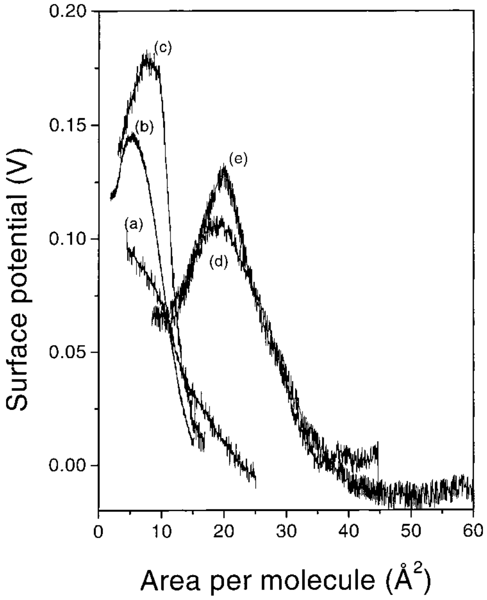

Figure 3. Surface potential isotherms of pure copolymers: (a) CoDR6, (b) CoDR29, (c) CoDR37, (d) CoDR57, (e) CoDR77.

pressure for CoDR57 is lower (about 24 mN/m) than for CoDR37 and CoDR77 (in the range 45−47 mN/m) is probably associated with interactions of neighboring similar groups, between either azo groups or HEMA groups, in the copolymer chain,[17] and these interactions need not be directly proportional to the number of chromophores. Despite the high collapse pressures, in stability experiments, where the monolayers are kept at a fixed pressure and the changes in area per molecule are monitored, we noticed that the monolayers for the copolymers are relatively less stable than for the corresponding homopolymer, HPDR13. The latter, for which the dye substitution is 100%, displays a condensed isotherm with a limiting area of ca. 22 Å^2.[22] It should be mentioned that poly(2-hydroxyethyl methacrylate) (PHEMA), a polymer with no dye substitution, did not form a monolayer at the air−water interface.[21]

Monolayers were also characterized using the surface potential technique, as shown in Figure 3. It should be stressed that, for complex molecules such as preformed polymers, measured surface potentials cannot be related to group dipole moments, unlike the case of model amphiphilic molecules,[24] and can only serve for probing effects such as change of composition in a mixed monolayer and of subphase pH.[25,26] Hence, only a qualitative analysis has been attempted for the surface potential isotherms. For large areas per molecule, the surface potential was close to zero for monolayers of all weight percentages of dye investigated. This is in contrast to most preformed polymers,[23] which present an initial nonzero surface potential owing to aggregation. The rise in surface potential at a particular area can be related to the approaching of molecules to form large domains that are not detected by the surface pressure measuring system.

For CoDR6, the surface potential increased monotonically from ca. 25 Å^2 until a noticeable slope change at a surface potential of 70 mV. This may indicate the formation of expanded-type aggregates with no specific interaction between the polymer molecules, consistent with the surface pressure isotherms and also observed with methacrylic copolymers of disperse red-1 with low dye content.[21] For CoDR29 and CoDR37, the surface potential onset occurred at ca. 15 Å^2. The maximum surface potential ($\Delta V_{\max}$) for CoDR29 and CoDR37 was about 140 and 180 mV, respectively. It is interesting to compare the characteristics of the copolymers with lower weight percentages (6−37) of dye substitution. A comparison of Figures 2 and 3 reveals that though the surface pressure isotherms of CODR6 and CoDR29 were similar, their surface potential isotherms differ with the one of CoDR6 being similar to that of CoDR37. This may be due to the difference in interaction between polymer molecules at the initial stages of compression, which seems to depend on the dye content in the polymer chain.

For the copolymers with higher weight percentages of dye substitution (CoDR57 and CoDR77), the surface potential onset occurred at ca. 40 Å^2, which is nearly twice the mean molecular area for the onset in surface pressure. Though $\Delta V_{\max}$ for CoDR57 (130 mV) was slightly higher than for CoDR77 (110 mV), they are lower than for CoDR37. $\Delta V_{\max}$ for the homopolymer of the methacrylate derivative of DR13 was ca. 160 mV. The reproducibility of surface potential isotherms is good (the variation in the maximum surface potential is ±10 mV), provided the initial surface potential is zero. We do observe irreproducibility in the maximum surface potentials and critical areas, if the initial surface potential is nonzero due to the spreading of excess material. The observed nonlinear trend in $\Delta V_{\max}$ with respect to the weight percentage of dye substitution corroborates with the observation in the surface pressure isotherms in that cooperative interactions between neighboring azobenzene monomeric units influence the organization of polymer chains in the monolayer.

As mentioned before, pure copolymer monolayers were not completely stable, and attempts to transfer such monolayers onto solid substrates led to Z-type LB films that were visually nonuniform. We then employed the mixed monolayer approach in which the copolymer was cospread with stearic acid on an aqueous subphase containing cadmium ions. It is known that the addition of builder materials usually enhances both stability and transferability of poorly stable polymeric monolayers.[20] The properties of these LB films will be reported below. Before proceeding to the LB transfer experiments, the mixed monolayers of CdSt and copolymers with the various dye contents were characterized. The mixtures were always 50%:50% by weight of copolymer and stearic acid. Figure 4 shows that mixed monolayers are progressively condensed for copolymers with increasing dye contents. For the higher dye contents, viz. 37, 57, and 77 wt %, the extrapolated area of the condensed monolayers increased with the dye content.

LB Film Transfer and Characterization. Hereafter we shall always be dealing with LB films from mixed monolayers, since those from pure copolymer were not uniform, as already mentioned. Except for the mixed monolayer of CoDR6, all other monolayers were transferred as Y-type LB films at a constant surface pressure of 20 N/m. The mixed monolayer with low dye content was transferred as Z-type LB films at a target surface pressure of 12 mN/m. Attempts to transfer at still lower surface pressures were not successful. The transfer ratios of mixed monolayers of copolymer and CdSt were close to unity, and the transferred LB films were visually uniform.

The UV−vis spectrum of a 15-layer mixed LB film of CoDR57 and CdSt is shown in Figure 5. Also shown for

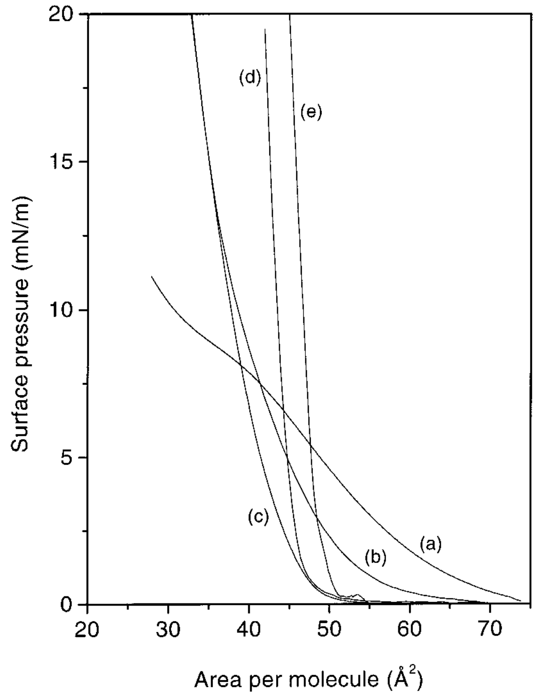

Figure 4. Surface pressure isotherms of copolymers mixed with cadmium stearate: (a) CoDR6, (b) CoDR29, (c) CoDR37, (d) CoDR57, (e) CoDR77.

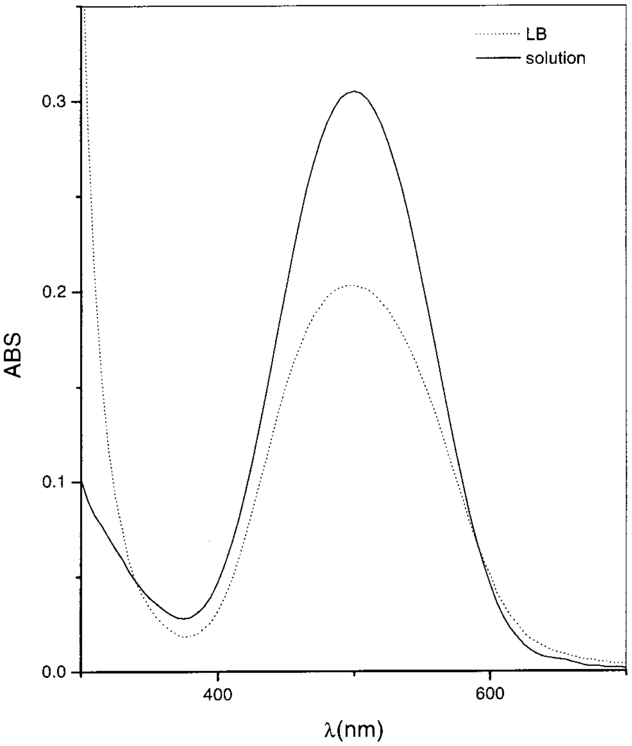

Figure 5. UV−vis spectra of a LB film of CoDR57 and of a solution of the same copolymer in DMF.

comparison is the UV−vis spectrum of the corresponding solution of copolymer in DMF, which indicates that there is no shift in the peak. This can be taken as evidence of a negligible aggregation of chromophores, since a significant shift would be expected otherwise. For instance, for HPDR13 a red shift of about 20 nm in the LB films in comparison to the polymer in solution was attributed to J-type aggregation of chromophores in the LB film structure.[22] In addition, for the copolymers investigated here the spectrum is not shifted when the amount of dye content is changed, either in solution or in the LB films (results not shown). This is in contrast to the results by Natansohn et al.[16,27] where a blue shift in the absorption maximum (λ_{max}) by ca. 35 and 20 nm was observed for cast films of DR1M−BEM and DR1A−MMA, respectively, as the dye content along the polymer chain was increased. This shift was related to the cooperative neighboring dipolar interactions between the azo dye and spacer groups (methacrylate derivative of nitrophenyl benzoate and methyl methacrylate for BEM and MMA, respectively) in the polymer chain.[16,27] For a given copolymer, the shift of λ_{max} was more pronounced for cast films in comparison to the solution of the copolymers. However, no such shift in λ_{max} was observed for the DR1M−MEA copolymer (MEA−methacrylate derivative of ethylazobenzene), which was interpreted as the absence of neighboring dipolar interactions between the DR1 and MEA groups.[28] The absence of a shift in our results may be attributed to either the dye component, which is different from those of refs 16 and 27, or to the nature of the side chain spacer groups. The latter reason can be ruled out, however, since the copolymer CoDR1−HEMA did not exhibit a significant shift in λ_{max} with the variation of dye content, either. In conclusion, the presence of neighboring HEMA spacer groups does not seem to affect the absorption energy of the azo groups and hence λ_{max}.

For the LB films with the same number of layers (15 layers), the absorption maximum at 497 nm increased linearly with the weight percentage of dye content in the copolymer. For the copolymer with a given dye content, the absorption maximum increases with increasing number of layers (results not shown here), indicating an equal amount of transfer of the copolymer during each transfer step. The absorption maximum at 497 nm was not affected by the change in dye content, as mentioned above, and neither by the variation in the number of layers.

The transmission FTIR spectrum of a mixed LB film of copolymer CoDR77 and CdSt on ZnSe substrate and, for comparison, the spectrum of the pure copolymer as a cast film were recorded. The characteristic peaks of copolymer presented in the cast film spectrum (3300 cm^{-1} for O−H stretching, 2960, 2850 cm^{-1} for C−H stretching, 1732 cm^{-1} for C−O stretching of ester groups, 1599 and 1500 cm^{-1} for C=C stretching in benzene rings, 1518 cm^{-1} for NO_2 asymmetric stretching, 1336 cm^{-1} for NO_2 symmetric stretching, 1242, 1252, and 1134 cm^{-1} for asymmetric and symmetric C(=O)−O and O−C−C stretching vibrations of ester group) also appear in the LB film. Characteristic vibrational absorption peaks for CdSt (2917 cm^{-1} for asymmetric C−H stretching, 2850 cm^{-1} for symmetric C−H stretching, 1548 cm^{-1} for C−O stretching of carboxylate group, and 1465 cm^{-1} for CH_2 bending vibrations) could also be visualized in the LB film spectrum. Absorption peaks corresponding to C−H symmetric and asymmetric vibrations of CH_2 group in the copolymer were overlapped by the strong CH absorption of CdSt. The broad OH absorption in the region of 3300 cm^{-1} is not obvious due to the strong CH stretching vibration of CH_2 groups from CdSt and from the copolymer. The absence of an absorption peak at ca. 1700 cm^{-1} revealed the complete ionization of COOH headgroups of stearic acid under the subphase conditions indicated in the Experimental

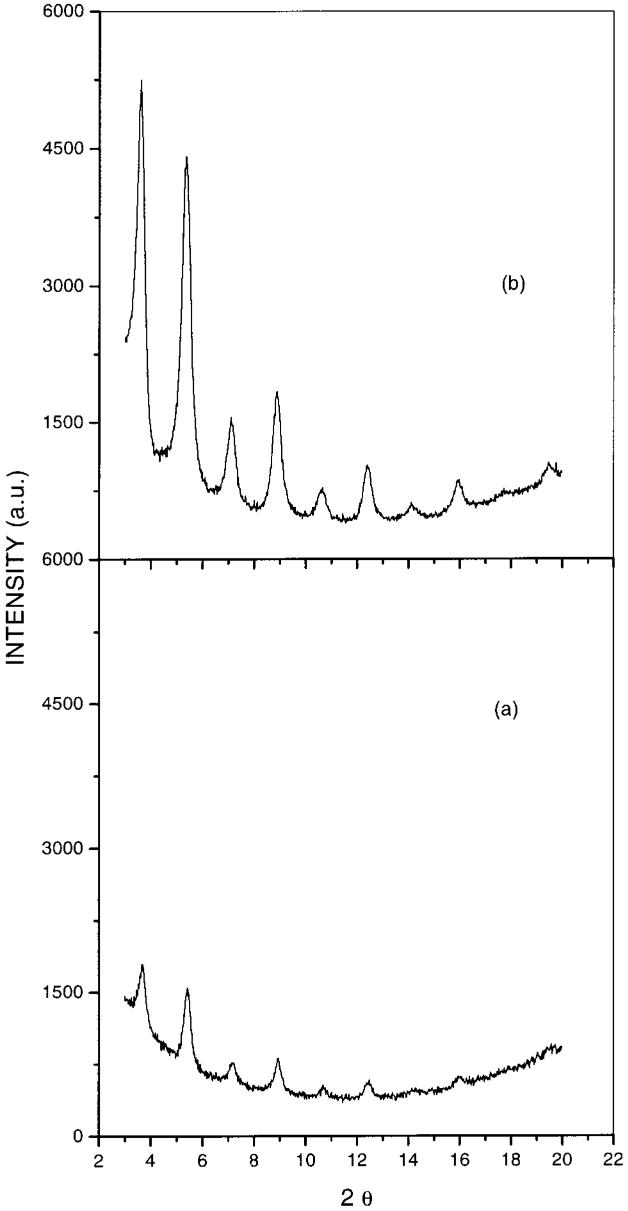

Figure 6. XRD diffraction patterns for the LB mixed films of copolymer and cadmium stearate: (a) CoDR6, (b) CoDR77.

Section. The appearance of absorption peaks corresponding to CdSt and the copolymer can be considered as conclusive that both components are transferred in the mixed LB film. Similar FTIR spectral features could be seen for mixed LB films of copolymers with other weight percentages of dye.

It is of interest to learn how CdSt and the copolymer molecules are packed in the mixed LB film, which has been done employing X-ray diffraction (XRD). For illustration, the XRD patterns of as-deposited mixed LB films containing copolymers with two weight percentages of dye (6 and 77%) and CdSt (15 layers) are shown in Figure 6. Irrespective of the dye content of the copolymer, a set of diffraction peaks is seen with the corresponding bilayer spacing of 50 ± 0.2 Å for all mixed LB films studied here. However, the intensities of the diffraction peaks, which is indication of the degree of stacking order present in the CdSt domains, depend on the dye content of the copolymer. The bilayer spacing is close to that of pure CdSt LB films which points to phase-separated CdSt domains in the mixed LB film. The weak diffraction peaks in the mixed LB film containing the copolymer CoDR6 may also be due to the Z-type transfer of the monolayer. The bilayer spacing of ca. 50 Å indicates that significant reorganization occurred in the CdSt molecules during or immediately after the transfer process.

Optical Storage Experiments. We have previously studied the optical storage characteristics of mixed LB films containing disperse red-19 isophorone polyurethane and CdSt[29] and also mixed LB films of HPDR13 and CdSt.[30] In these studies, it was shown that the birefringence induced in the mixed LB film by a linearly polarized light increases linearly with the weight percentage of the azobenzene polymer in the mixed LB film and decreases with the number of layers. The time to achieve 50% of maximum birefringence was independent of either the number of layers or the weight percentage of the azobenzene polymer. In the present work, the optical storage characteristics of mixed LB films (50:50 wt %) are first investigated by keeping the number of layers constant (15 layers) and varying the amounts of dye substitution in the copolymer. Since the number of layers of the mixed LB film is fixed (15 layers), it is reasonable to assume that the thickness is approximately the same for all films, as the thickness per layer is usually dictated by the length of the builder material.[31]

Prior to studying the optical storage characteristics, the trans-to-cis photoisomerization of the azobenzene chromophores and the thermal cis-to-trans isomerization in the mixed LB films were investigated. The level of photoisomerization in a stationary state can be monitored by the change of the probe beam transmission due to the isomerization induced by the pump beam. The probe transmission increased with the dye content of the copolymer. A similar dependence on dye concentration was observed for the copolymers in solution. Parts a and b of Figure 7 show the time evolution of the photoisomerization (trans−cis) and thermal relaxation (cis−trans), for the mixed LB film containing the copolymer CoDR57. Both photo trans−cis isomerization and thermal cis−trans relaxation exhibited a biexponential behavior, similarly to reported in the literature.[32] An initial fast process followed by a slow process could be visualized during photoisomerization and thermal relaxation. A similar characteristic has been observed with mixed LB films containing the copolymer CoDR37.

Typical optical writing sequences for mixed LB films containing copolymers with different weight percentages of dye are shown in Figure 8. They represent the time evolution of the probe transmittance, which is related to the induced birefringence. Initially, the LB film was placed between crossed polarizers, and no transmission of the probe beam was observed. At point A, the linearly polarized writing laser was turned on, and the transmission of the probe beam increased, reaching 50% of saturation value in the range 0.5−1.0 s for all copolymers. Such an increase in transmission can be related to the induced birefringence due to the orientation of the azobenzene chromophores in the direction perpendicular to the laser polarization direction in the exposed area of the LB film. Upon turning the laser light off at point B, at 25 s, the birefringence decreases by about 50% of the saturation value within 30 s, and this can be associated with thermal reorientation of some azobenzene groups. The remaining birefringence indicated that

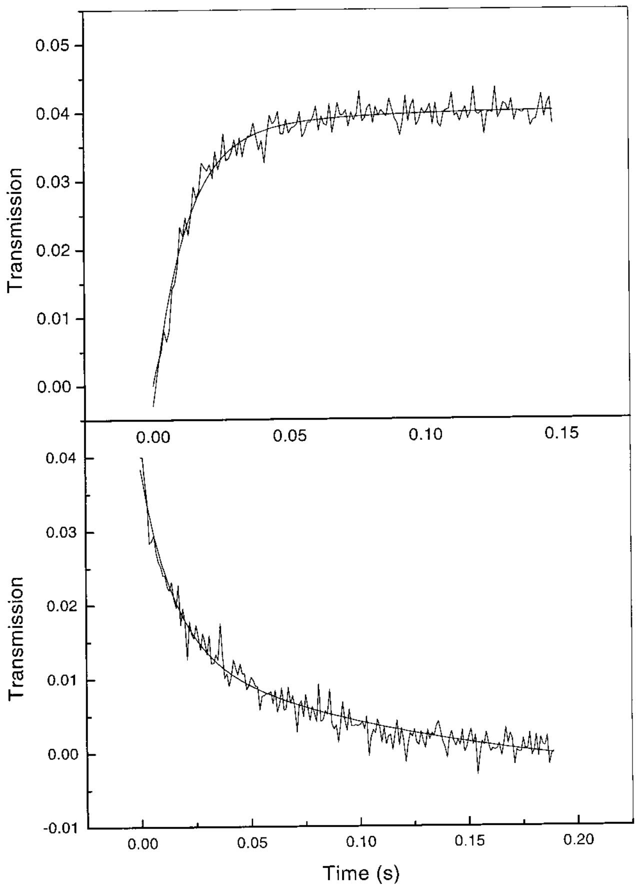

Figure 7. (a) Time evolution of the photoisomerization (trans−cis) and (b) thermal relaxation (cis−trans). The solid lines are the biexponential fittings.

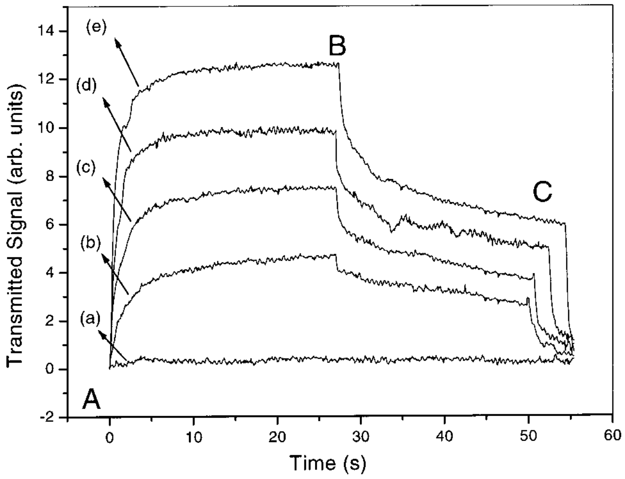

Figure 8. Writing and erasing sequences on copolymer LB films (15 layers) with different dye contents: (a) CoDR6, (b) CoDR29, (c) CoDR37, (d) CoDR57, (e) CoDR77.

a significant number of molecules remained oriented, with such birefringence being stable for several months. At point C, the birefringence was optically "erased" by overwriting the test spot with circularly polarized light. This writing beam randomizes the azo molecules, thus removing the macroscopic orientation of dipoles in the film.

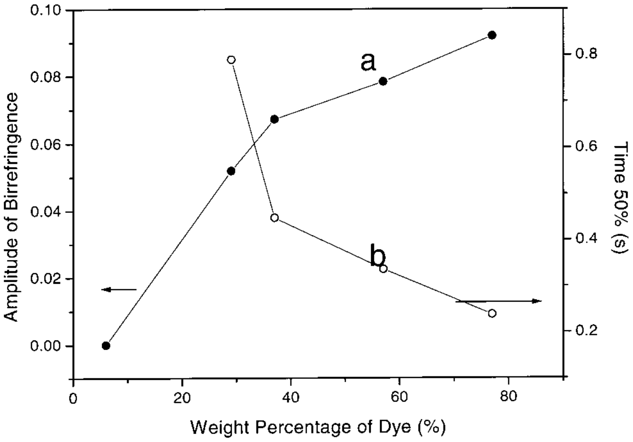

Figure 9. (a) Maximum induced birefringences. (b) Time to achieve 50% of saturated birefringence as a function of the weight percentage of dye in the copolymer.

A comparison of the maximum induced birefringence revealed a nonlinear increase with the azo group concentration in the copolymer, as shown in Figure 9 (curve a).[28] This behavior may be related to the increase in the writing beam absorption as more dye is incorporated in the copolymer. The absorption increase induces a sample heating, which counteracts the process of orientation. For lower dye contents, the orientation process has a linear behavior because the heating is small and a larger number of photoactive azobenzene chromophores in the polymer chain will generate a higher birefringence. On the other hand, for higher dye contents the thermal process begins to influence the orientation. The temperature dependence of the birefringence is currently being investigated to understand this process completely.

We have also performed optical storage experiments with mixed LB films containing different numbers of layers, by keeping the dye concentration in the copolymer fixed. In this case, the maximum induced birefringence per layer decreased with the number of layers (results not shown here). This is probably related to the loss of ordering in the LB film as the number of layers is increased, as reported in ref 30. Meng et al.[27] found a nonlinear increase of induced birefringence with the weight percentage of dye content for the copolymers DR1M−MMA and DR1M−BEM, which was related to dipolar interactions between different neighboring groups. The observed nonlinear increase of induced birefringence has been explained on the basis of a sequence distribution of the triads DDD, MDM, and MDD (M, spacer group; D, azo group) along the polymer chain. However, our results cannot be explained by the dipolar interaction between HEMA and dye groups because the absorption results presented no significant dipolar interaction among dye groups and spacer HEMA groups, as discussed in connection with Figure 5.

Figure 9, curve b, shows the time interval necessary to achieve 50% of saturated birefringence as a function of the dye concentration in the copolymer. A decrease in the time necessary to reach the maximum birefringence is observed with the increase in dye concentration in the copolymer. In Figure 8, it was shown that, upon switching off the pump beam, the probe beam transmitted signal decreased to a fraction of the saturation value in about 30 s. The remaining birefringence seems to depend on the dye concentration in the copolymer, as shown in Figure 10. Again, a nonlinear decrease in the remaining birefringence is observed as the dye content increases.

In general, the growth and relaxation of the induced birefringence was explained by a biexponential function,

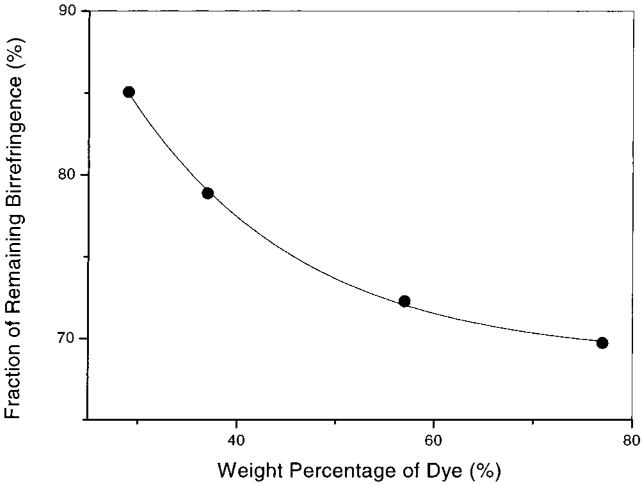

Figure 10. Fraction of remaining birefringence as a function of the weight percentage of dye in the copolymer.

comprising a fast process involving the movement of azobenzene groups and a slow process involving the movement of the main polymer chain.[28] Among the different parameters that influence the growth of induced birefringence, the availability of free volume around the azobenzene group, i.e., steric factor, can be considered as one of the most important factors. The behavior shown in Figure 9 (curve b) can be understood in terms of a thermal effect. The increase in the sample absorption induces higher heating for samples with higher dye contents. This sample heating allows a higher molecular mobility, which results in a faster writing process. However, the thermal effect causes the amplitude of the induced birefringence to decrease, as already discussed in connection with Figure 9 (curve a). The decrease in the remaining birefringence upon increasing the dye content in our films (Figure 10) may imply that the relaxation of more azo groups to the original state is facilitated in copolymers with higher dye concentration. The latter samples would be heated to a higher extent when the writing laser was turned off, which facilitated the molecular randomization and led to a lower fraction of remaining birefringence. Natansohn et al.[28] reported an increasing trend of the remaining birefringence with the dye content, in the case of a DR1M−MEA copolymer, and such a trend was ascribed to an increased dipolar interaction between the DR1 dye and unsubstituted azo dye moieties. However, no such dipolar interaction between the azo group and the HEMA spacer group is expected for the copolymer studied here. Despite the plausibility of the explanation in terms of thermal effects, a dipolar interaction between azo groups may occur in copolymers with higher dye concentration, in which there is a higher probability of DDD azo-dye sequences along the polymer chain, analogously to reported in ref 32. Therefore, the effects from interactions between azo groups cannot be completely ruled out, though the thermal effect seems to predominate in our experiments.

Conclusions

A successful and uniform transfer was obtained for mixtures of CdSt and methacrylate copolymers with different weight percentages of disperse red-13 onto solid substrates in the form of LB films. For optimized conditions to be obtained for LB manipulation, the monolayer characteristics of copolymers with different dye contents were studied through surface pressure and surface potential isotherms. FTIR results indicated the transfer of both CoDR13 and CdSt in the mixed LB film. UV−vis studies revealed no aggregation of DR13 molecules in the LB film structure and no interaction between DR13 and the HEMA spacer group. The presence of CdSt domains could be inferred from XRD patterns.

The influence of spacer groups in Langmuir−Blodgett films of methacrylate copolymers derivatized with disperse red-13 in the optical storage processes was investigated. The amplitude and time to achieve 50% of the optically induced birefringence, and the fraction of the remaining birefringence, were studied in LB films from copolymers with different dye contents. It is proposed that the cooperative interaction among neighboring azo groups and mainly the thermal effect are the processes that govern the orientation mechanism and therefore the optical storage capability of these LB films.

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