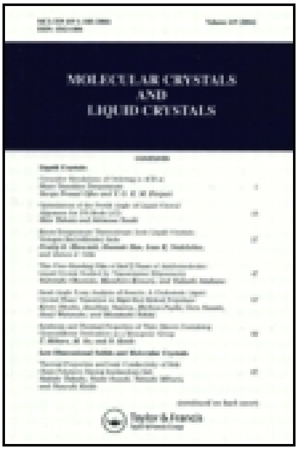

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Rubbing-Induced Side Chain Alignment at the Surface of N-Substituted Aromatic Polyamide Film as Studied by Charge-Transfer Absorption Dichroism

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Rubbing-Induced Side Chain Alignment at the Surface of *N*-Substituted Aromatic Polyamide Film as Studied by Charge-Transfer Absorption Dichroism

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Spin-coated *N*-anthrylmethyl poly(*p*-phenylene terephthalamide) (AM-PT) film, which showed good liquid crystal alignment after rubbing, was prepared on a quartz plate, and rubbing-induced side-chain alignment was studied by means of charge-transfer (CT) band dichroism. By immersing the samples in methanolic 2,4,5,7-tetranitro-9-fluorenone (TENF) solution, a CT complex between the anthrylmethyl side-chain and TENF was formed only at or near the surface. The rubbed film showed smaller CT absorption compared to film without rubbing. The CT absorbance of the rubbed film to the linearly polarized light parallel to the direction of rubbing was significantly larger than that the perpendicularly polarized light, giving a dichroic ratio of (1.34 ± 0.14 (S.D.), $n = 3$), though films without rubbing showed no dichroism (1.02 ± 0.01 (S.D.), $n = 3$). The results confirmed the rubbing-induced orientation of the anthrylmethyl side-chain, demonstrating that this method offers the direct and sensitive way to monitor rubbing-induced conformational change of the polymer at the surface.

Keywords: N-Anthrylmethylated PPTA, rubbing process, CT complex formation, side-chain alignment, Dichroism

INTRODUCTION

The rubbing technique is the most popular method to induce homogeneous alignment of nematic liquid crystals, in which a film-coated surface is rubbed unidirectionally with a fibrous material. The mechanism of liquid crystal alignment on the treated surface is not yet clarified and has been studied with considerable interest.[1–5] Several lines of evidence have suggested that alignment acts through the orientation of polymer molecules rather than through grooves or scratches induced by the rubbing process.[1,4,6]

We developed the first polyamide-type liquid-crystal alignment film that has the ability to generate a high pretilt angle.[6] In a previous report,[7] it is demonstrated that induction of good alignment and high pretilt angle is closely related to the degree of

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substitution and molecular structure of the side chain rather than the surface-free energy of the film and the importance of the rubbing-induced side chain alignment is suggested. Since the *N*-substituted polyamide is a suitable substrate to study the molecular-scale understanding of the liquid crystal alignment and pretilt generation, we conducted the study to clarify the rubbing-induced side chain alignment at the surface of this polymer by means of charge transfer band dichroism.

EXPERIMENTAL

Anthrylmethylated poly-(*p*-phenylene terephthalamide) (AM-PT) was synthesized by a reaction of 9-chloromethyl anthracene with metalated PPTA,[7] yield 85%, degree of substitution determined by elemental analysis, 78%, Tg 492 K. Thin polymer films were prepared on quartz-made flat plates (45 × 10 mm) by spin-coating from a dilute polymer/bromoform solution (0.04 M) and the solvent was removed by heating at 70°C for 2 h. Unidirectional rubbing was performed by pressing the sample down onto a rayon fiber. Charge-transfer complex formation was carried out by immersing the film-coated plate in an acceptor solution at room temperature. Electronic spectra were recorded on a Shimazu UV 2000 spectrophotometer, where the quartz plates were placed perpendicular to the light-path. For measurement of absorption dichroism, a set of polarizers (400 < λ < 700 nm) was inserted on the light-path (Figure 1).

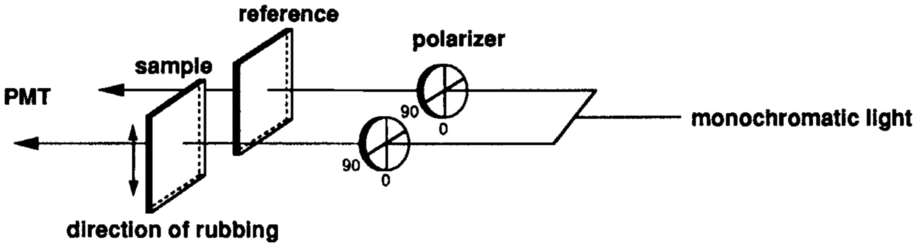
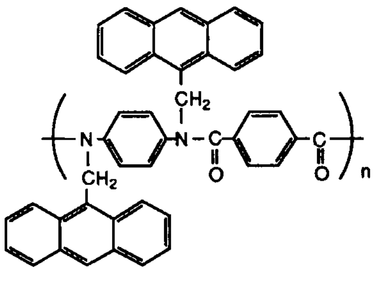


FIGURE 1 Schematic diagram for the measurement of polarized light absorption of thin polymer-films on quartz plates.



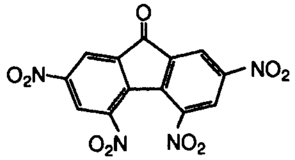
Anthrylmethylated poly(*p*-phenylene terepthalamide) (AM-PT)

RESULTS AND DISCUSSION

Formation of Charge-Transfer Complex at the Spin-Coated Film Surface

Highly *N*-aralkylated PPTA films showed homogeneous liquid crystal alignment and generation of the pretilt angle of 0.5 to 8.1 deg. depending on the side chain structure and degree of substitution. One of the *N*-aralkylated PPTAs, AM-PT also showed good rubbing induced liquid crystal alignment on its surface along the direction of rubbing, although the generated pretilt angle was 0.5deg.[7] As the anthrylmethyl unit has a high electron-donating ability to form the charge-transfer complex with nitrofluorenones,[8] we chose this polymer as a probe to study the rubbing-induced side chain alignment at the surface. The polymer was sufficiently soluble in dimethylformamide and bromoform to fabricate a thin film by the cast method, but was poorly soluble in chloroform and not at all in methanol. Nitrofluorenones have a fused aromatic ring structure with electron-withdrawing nitro groups, and are strong electron-acceptors to form the CT complex with anthracene derivatives in a face-to-face stacked mode.[8] Among them, 2,4,5,7-tetranitro-9-fluorenone (TENF) is soluble in methanol and, therefore, is the suitable acceptor for preparing the CT complex only at the surface of the AM-PT film.

Spin-coated AM-PT film on a quartz plate had a smooth suface with a slightly yellowish color. Upon immersing the plate in a methanolic TENF solution, the surface of the film became greenish. After a certain time of immersion, the plate was washed with methanol to remove the excess TENF on the surface. The electronic spectrum of the film immersed in the TENF solution for more than 3 h showed the absorption bands at around 500 and 650 nm (Figure 2(c)), though the AM-PT film or the TENF solution alone had no absorption above 450 nm. A chloroform solution of methylanthracene and TENF (Figure 1(a)) and a bromoform solution of AM-PT and TENF (Figure 2(b)) showed characteristic absorption at around 530 and 650 nm due to the CT complex formation, which are quite similar to those observed for the TENF-treated film. Therefore, the absorption bands observed above 450 nm for the TENF-treated AM-PT film are due to the CT complex between the anthrylmethyl unit of the polymer side-chain and TENF. Figure 3 shows the time-dependent increase of the CT absorption around 650 nm during immersion in the TENF solution, which indicated that formation of the CT complex was completed within 3 h and no further increase was practically observed thereafter. Absorbance of this CT band was slightly different for different samples, and the films having 0.8 to 1.7 μm thickness showed the absorbance of 0.027 ± 0.005 (S.D., $n = 4$) after 3 h of immersion. As absorbance of a TENF-treated film having 12 μm thickness was 0.018, the CT complex formation was not sensitive to



2,4,5,7-Tetranitro-9-fluorenone (TENF)

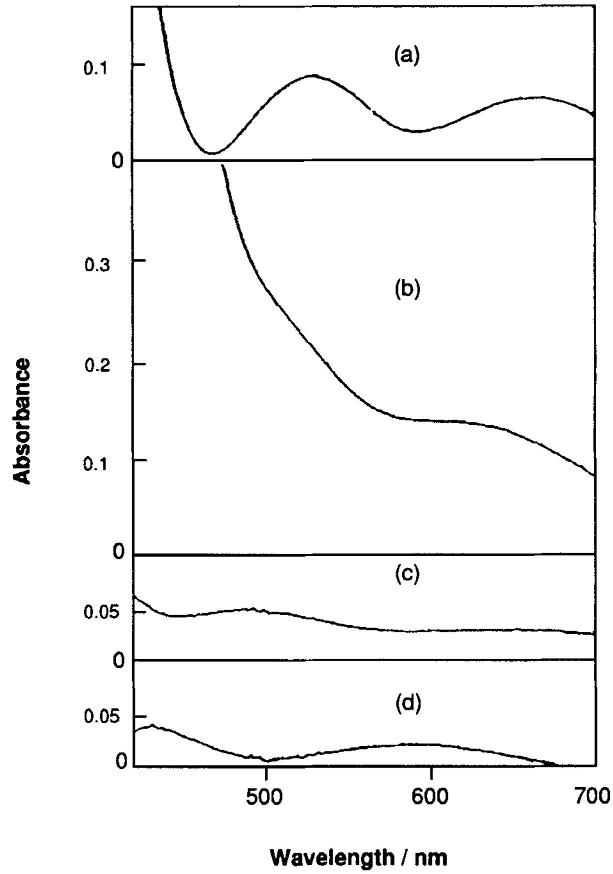


FIGURE 2 Absorption spectra of (a) mehylanthracene (12 mM) and TENF (2 mM) in chloroform, (b) AM-PT (4 mM) and TENF (4 mM) in bromoform, (c) spin-coated film without rubbing after TENF treatment, and (d) spin-coated after rubbing and TENF treatment.

the film thickness. Use of a chloroform or dichloromethane solution of TENF instead of the methanolic solution resulted in much larger absorbance of more than 0.1 with occasional crack formation. Though chloroform and dichloromethane are poor solvents for the AM-PT polymer, they might cause swelling of the polymer leading to the increased CT complex formation and crack formation. These results confirmed that the CT complex formation, by immersing in the methanolic TENF solution, took place only at or near the surface of the films, and therefore, the CT absorption can be used to monitor the surface alignment of the anthrylmethyl unit of the side chain.

To test the effect of rubbing, two film-coated samples were prepared at the same time and only one of them was subjected to the unidirectional rubbing. A set of samples was treated by the same procedure in order to minimize variation of the sample preparation. The rubbed films also showed characteristic CT absorption by immersing in the methanolic TENF solution (Figure 2(d)), but their absorption was smaller and blue-shifted by approximately 50 nm compared to that of the film without rubbing. The

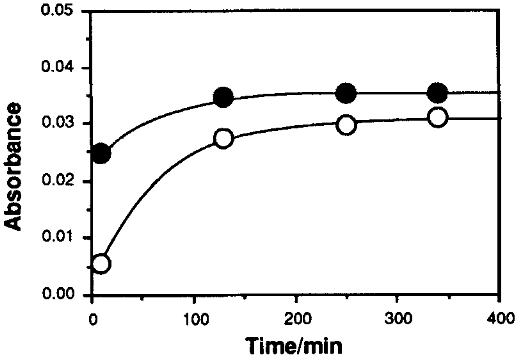


FIGURE 3 Time-course of the second band maxima of the CT complex absorption during immersion in methanolic TENF solution (0. 04 M):(○) rubbed (absorbance at 630 nm) and (●) non-rubbed (absorbance at 650 nm) film having 0.8 μm thickness.

relative intensity of the absorption at the second band maximum (590–690 nm) $A_{\mathrm{rub}}/A_{\text{non-rub}}$, was found to be 0.71 ± 0.10 (S.D., $n = 5$), confirming the decrease of the absorption significantly ($P < 0.005$). This can be the indication of rubbing-induced change in the conformation of the polymer at the suface, which might restrict the orientation of the anthrylmethyl unit less favorably to form the CT complex with TENF. However, compression of the film during the rubbing process can be another explanation, which is thought to suppress the penetration of TENF into the film. Though the effect of rubbing is clearly manifested in the relative intensity of the absorption, it is difficult to deduce any further molecular-scale information in regard to the rubbed surface.

CT Absorption Dichroism at the Surface of Rubbed Films

To monitor the rubbing-induced alignment of the side-chain at the surface, we have measured absorption dichroism of the CT complex formed only at or near the surface. Absorption spectra of the samples to the linearly polarized light parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the rubbing direction were recorded (Figure 1). The sample without rubbing showed essentially the same spectra to the parallel and perpendicularly polarized light. The dichroic ratio is defined as $A_{\parallel}/A_{\perp}$ where $A_{\parallel}$ and $A_{\perp}$ represent the absorbance of the second CT band maximum to the parallel and perpendicularly polarized light, respectively, to the rubbing direction. The dichroic ratio of the films without rubbing was 1.02 ± 0.01 (S.D., $n = 3$), confirming that the anthrylmethyl side-chain was randomly oriented at the surface. However, the rubbed film showed larger absorption to the polarized light parallel to the direction of rubbing, and the dichroic ratio was 1.34 ± 0.14 (S.D., $n = 3$) showing a significant difference. The results are a clear indication of the ordered orientation of the CT complex and, therefore, of the anthrylmethyl-side chain at the rubbed surface. Since CT absorption is the transition to the excited state of the dominant "charge-transfer" configuration,[9] transition of the anthracene-TENF complex in the face-to-face stacked mode is thought to be perpendicular to the plane of the fused aromatic ring plane. Therefore, present results suggest that the long axis of the anthracene ring is placed perpendicular rather than parallel to the direction of rubbing at the surface.

Geary *et al.* showed rubbing-induced main-chain alignment by observing birefringence, and they suggested that the orientation of polymer chains, but not scratching or grooving of the surface is responsible for induction of liquid crystal alignment on the surface,[1] while, our previous results suggested the importance of the rubbing-induced side-chain alignment for induction of liquid crystal alignment and pretilt generation.[6,7] In this case, however, *n*-alkyl-side chains are ineffective and a more rigid side-chain structure such as benzyl or cyclohexylmethyl is required. The results presented here are the direct experimental evidence to show that alignment of the side-chain at the surface does occur by rubbing of the film. This side-chain alignment might be associated with the rubbing-induced main-chain alignment, as indicated by Geary *et al.*[1] and Sugiyama *et al.*[4]

CONCLUSION

In this study, we demonstrated that the charge-transfer complex formed at the surface of the polymer film is a direct and sensitive probe to detect rubbing-induced conformational change of the polymer side chain at the surface. The dichroic ratio of the rubbed film confirmed the rubbing-induced side-chain alignment at the surface of the spin-coated AM-PT film, and it is suggested that the long axis of the anthracene ring is placed perpendicular to the direction of rubbing rather than parallel.

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