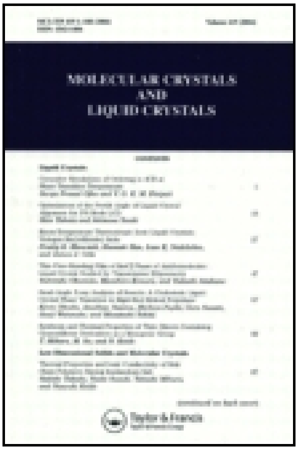

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Polyamide-Type High Pretilt Surface: Effect of Side-Chain Structure and Type of Liquid Crystals on the Generation of Pretilt Angle

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Highly *N*-aralkylated poly(*p*-phenylene terephthalamide) (PPTA) with various substituents having benzyl units in their structures were synthesized in a high yield, and their properties as a liquid crystal alignment film were studied. Good liquid crystal alignment and pretilt angles of 0.5 to 8.1 deg were observed on the spin-coated polymer films after rubbing when a nematic liquid crystal, ZLI-2293 was used. The induced pretilt angle showed no correlation with the surface-free energy of the polymer film, but was strongly dependent on the structure of the side chain. The effects of the structural difference of the side chain and type of liquid crystals are discussed in more detail.

Keywords: N-aralkylated PPTA, liquid crystal alignment film, pretilt angle generation, side chain structure

INTRODUCTION

Orientation of liquid crystals at surfaces of alignment films is usually described in terms of pretilt angle, and preparation of a high pretilt surface is the key to develop high-performance LCD devices. The rubbing technique is the most widely used method for aligning liquid crystals, and polyimide has been used predominantly as the liquid crystal alignment film. Recently Fukuro *et al.* reported generation of high pretilt angles on alkyl-branched polyimide films.[1] However, it requires annealing of the coated precursor, polyamic acid, to form a thin polyimide film.

We previously reported[2] that *N*-substituted poly(*p*-phenylene terephthalamide) (PPTA) films show good liquid crystal alignment, and they also have an ability to induce high pretilt angles when the substituent group is benzyl, methylbenzyl, or cyclohexylmethyl. This is the first report on the polyamide-type high pretilt surface, and thin films of the highly *N*-substituted polymers having various side chain structures can easily be prepared by the simple spin-coat method. The induced pretilt

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angle is suggested to depend on the degree of substitution and side chain structure rather than their surface energies.[2] Therefore, the *N*-substituted PPTAs offers a suitable probe to study the mechanism of the induction of pretilt angle at the rubbed polymer surface from the molecular basis. In this study, we prepared a series of *N*-aralkylated PPTAs having benzyl unit in their side-chain structure, and examined the effect of the structural variation of the phenyl ring of the benzyl unit on the induced pretilt angle in order to clarify the role of the side chain structure.

EXPERIMENTAL

Materials

The PPTA samples were supplied by Torey Co. in pulp form. Sodium hydride in a suspension in paraffin was a reagent grade obtained from Tokyo Kasei. 9-Chloromethyl anthracene was obtained from Aldrich Chemical Co. and bromo-substituted biphenyl derivatives were prepared by photobromination. Other halides were obtained from Tokyo Kasei. Dimethyl sulfoxide (DMSO) was fractionally distilled over calcium hydride in a vacuum and finally dried over molecular sieve 4A. Nematic liquid crystals used in the liquid crystal cells were ZLI-2293, ZLI-1132 and ZLI-3086 from Merck Japan Ltd.[3]; ZLI-1132 is an all-cyano type having cyano groups in its mesogenic units, a major component of which is 4-alkyl-4′-cyanophenylcyclohexane, and parallel and perpendicular dielectric constants (20°C, 1 KHz), $\varepsilon_{//}$ and $\varepsilon_{\perp}$ are 15.0 and 4.7, respectively; ZLI-3086, all alkoxy-type, 4-alkyl-4′-alkoxyphenylcyclohexane, $\varepsilon_{//}$ 2.9 and $\varepsilon_{\perp}$ 2.84; ZLI-2293, a mixture of cyano-type (65%) and dialkyl-type (35%), whose major structure of the mesogenic unit is phenylcyclohexane, $\varepsilon_{//}$ 14.1 and $\varepsilon_{\perp}$ 4.1.

4-Bromomethylbiphenyl and 4-bromomethyl-4′-methylbiphenyl were synthesized by photobromination with *N*-bromosuccinimide (NBS) according to the reported procedure.[4] A solution of biphenyl derivative and NBS was irradiated at room temperature with a 100-W high-pressure mercury, directly or through Toshiba glass filter C-39A ($\geq$390 nm) under a nitrogen atmosphere; 4-bromomethylbiphenyl: Yield 96%, Mp 106.3–106.8°C, ^{1}H NMR ($CDCl_3$) δ = 4.55 (2H, s), 7.33–7.67 (8H, m); 4-bromomethyl-4′-methylbiphenyl: Yield 69%, Mp 106.9°C (Reported value,[4] 106.1–106.7), ^{1}H NMR ($CDCl_3$) δ = 2.37 (3H, s), 4.52 (2H, s), 7.40–7.55 (8H, m). Synthesis of the *N*-substituted PPTAs were carried out according to the procedure reported previously.[5]

Measurement

Characterization of the *N*-substituted PPTAs was carried out using Perkin Elmer 1600 series FTIR and JEOL JMN-GX270 spectrometers. Glass transition temperature (Tg) was determined by a Perkin Elmer differential scanning calorimeter (DSC) DSC-2 at a heating rate of 5 K min^{-1} in a nitrogen atmosphere. Surface-free energies of the polymer films were determined from the contact-angle measurement by a Kyowa precise contact-angle meter.[2] Liquid crystal cells were composed of transparent glass electrodes covered by a spin-coated liquid crystal alignment film (1000 Å) and liquid crystals. The surface of the alignment film was rubbed with rayon fibers five times before assembling the cell, and the cell was annealed at 105°C. Alignment of liquid crystals in liquid-crystal cells was investigated by using a polarizing plate.[6] Pretilt angles were measured with the crystal rotation method.[7]

RESULTS AND DISCUSSION

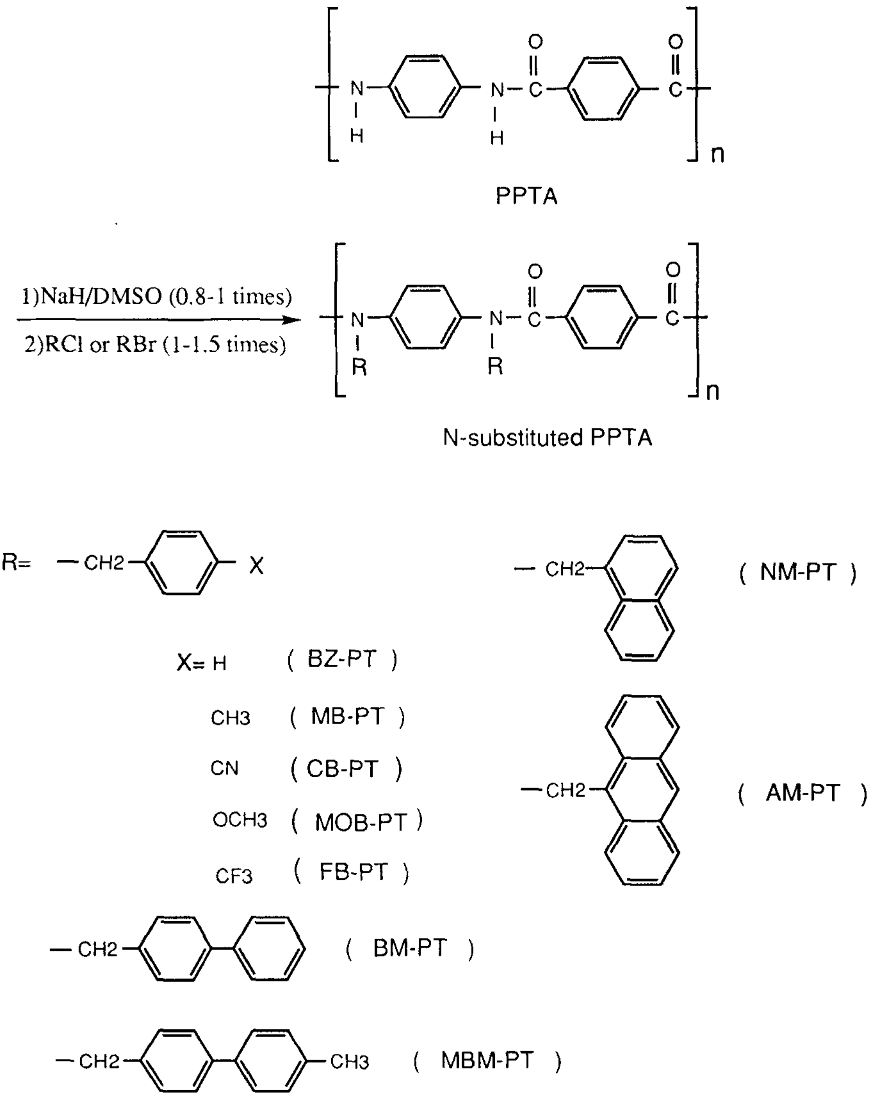
N-Substituted PPTA

Previously it was suggested that the *N*-substituted PPTAs having rigid side chains show high pretilt angles.[2] In this study, we prepared various *N*-aralkylated PPTAs having benzyl unit in their side chain structure in order to clarify the role of the side chain structure further. The *N*-aralkylated PPTAs were synthesized by reaction of metalated PPTA and corresponding halides. Their structures and abbreviated codes are shown (Scheme I). The degree of substitution was determined from the carbon:nitrogen molar ratio of the polymers (Table I). It is worth noting that highly *N*-substituted PPTAs were easily obtained in high yields. For the preparation of the FB-PT(II), excess amounts of NaH (2.5 times) and halides (5 times) were used in order to attain a high degree of substitution. Methylbiphenylmethyl-substituted samples of different degrees of substitution were also synthesized by controlling the extent of metalation.

The absence of NH stretching and amide II peaks in the IR spectra of the *N*-substituted polymers were essentially the same as those reported previously.[2] Their structures were further confirmed by ^{1}H NMR spectra. Table I shows the Tg values of the polymers determined by DSC under a nitrogen atmosphere. Although hydrogen bonds in between amide units of the polymer are diminished by *N*-substitution, their Tg values are above 160°C, showing the high thermal stability of these polymers. Solubilities of the polymers in various solvents are shown in Table II. All the *N*-substituted PPTAs were soluble in a number of organic solvents, and they showed good film-forming ability.

N-Substituted PPTAs as Liquid Crystal Alignment Film

The liquid-crystal cells were prepared using these polymers as the alignment films. In this and previous studies, we used one of the popular nematic liquid crystals, ZLI-2293. All the *N*-aralkylated PPTAs, after being rubbed with rayon fibers, showed good liquid-crystal alignment. Observed pretilt angles are shown in Table III, which range from 0.5 to 8.1 deg. Their surface-free energies (γ) obtained from the contact-angle measurements are also included in the Table. A decrease of the surface-free energy upon *N*-substitution (γ for PPTA is 54.6 erg cm^{-2})[2] indicated that the side chain is exposed to the surface. It is apparent from the Table that the pretilt angle has no immediate correlation with the surface-free energy. For example, MBM-PT(III) and AM-PT have similar surface-free energies of 44.1 and 44.2 erg cm^{-2}, but the induced pretilt angles are 7.3 and 0.5, respectively. Previously we concluded from the *N*-alkylated and *N*-aralkylated PPTAs that the surface-



SCHEME I Synthesis of *N*-aralkylated PPTAs.

free energy, a macroscopic index, does not explain the induced pretilt angle. The present study confirmed further that the conclusion is true even among the *N*-aralkylated PPTAs. The degree of substitution also affected the pretilt angle, and a higher degree of substitution resulted in higher pretilt angles in the case of MBM-PT, coinciding with the previous results for BZ-PT and MB-PT. The only exception is FB-PT, where FB-PT(II) showed lower pretilt angles than FB-PT(I). In this case excess amounts of NaH were used to prepare the FB-PT(II), and this may be the reason for the generation of the low pretilt angle. The use of excess amounts of NaH sometimes resulted in low solvent solubility of the obtained polymer.

TABLE I

N-substituted PPTAs

Code	Substitutent(R)	Yield /%	Degree of substitution /mole%	Tg /K
CB-PT	cyanobenzyl	86	98	490
MOB-PT	methoxybenzyl	76	87	448
FB-PT(I)	trifluoromethylbenzyl	85	85	-[a]
(II)		82	99	-[a]
BM-PT	biphenylmethyl	78	78	471
MBM-PT(I)	methylbiphenylmethyl	79	84	474
(II)		78	90	478
(III)		78	95	472
NM-PT	naphtylmethyl	91	99	466
AM-PT	anthrylmethyl	88	91	546

a; not detected

TABLE II

Solubilities of the *N*-substituted PPTAs[a]

Polymer	Solvent				
	Chloroform	NMP[b]	THF	DMSO	o-Chlorophenol
CB-PT	-	+	-	-	+
MOB-PT	-	-	-	-	+
FB-PT(I)	-	+	-	+	+
(II)	-	+	-	+	+
BM-PT	+	+	-	-	+
MBM-PT(I)	-	-	-	-	+
(II)	-	-	-	-	+
(III)	-	-	-	+	+
NM-PT	+	+	+	+	+
AM-PT	-	-	-	+	-

a; + : soluble, - : insoluble

b; NMP: N-Methyl-2-pyrrolidone

Unlike the *N*-alkyl-substituted PPTAs which have no ability to induce the pretilt angle,[2] all the polymers used in this study have induced the pretilt angle. They have the benzyl unit in their side chain structures which are connected to the same main-chain structure, and the degree of substitution is high enough for most of the polymers. But the induced pretilt angle was found to be quite sensitive to the structural difference of the side chain. The results indicate that generation of the pretilt angle on the rubbed *N*-substituted PPTA film should be discussed in terms of microscopic or molecular-scale indices that reflect the structural variation of the phenyl ring of the benzyl unit at the side-chain rather than the surface-free energy. This is the marked difference from those reported for the alkyl-branched polyimide films, where direct correlation of the pretilt angle with surface-free energy is indicated.[1]

The substituent group at the para-position of the benzyl side chain showed a large effect on the pretilt angle, and the methyl group, a weak electron-donating group (Hammett substituent constant, $\sigma_{\text{para}} = -0.17$) is most effective among the para-substituted benzyl structures. The strong electron-withdrawing cyano group ($\sigma_{\text{para}} = +0.66$) is ineffective for generating high pretilt angles, though the degree

TABLE III

Surface free energies and pretilt angles (ZLI-2293) of the *N*-substituted PPTA films

Code	Degree of substitution /mole%	surface free energy/ erg/cm^2	pretilt angle /deg
BZ-PT[a]	93	50.2	4.5
MB-PT(I)[a]	89	40.0	0.5
(II)[a]	95	40.9	5.3
(III)[a]	99	41.3	8.1
CB-PT	98	41.0	1.1
MOB-PT	87	47.9	2.0
FB-PT(I)	85	35.1	5.2
(II)	99	35.0	2.0
BM-PT	78	39.3	2.9
MBM-PT(I)	84	43.9	3.4
(II)	90	43.9	6.3
(III)	95	44.1	7.3
NM-PT	99	50.4	0.8
AM-PT	91	44.2	0.5

a; Ref. 2

of substitution of CB-PT is as high as 98%. The methoxy group ($\sigma_{para} = -0.27$) is not so effective either, but the low pretilt angle observed for MOB-PT might be due in part to the low degree of substitution.

The ring structure of the side chain also affected the induced pretilt angle. The biphenylmethyl structure extending along the side-chain axis contributed to induce higher pretilt angles than the benzylmethyl structure when the polymers having a similar degree of substitution were compared, while the PPTAs having a wider naphtylmethyl or anthrylmethyl structure induced much smaller pretilt angles. As the liquid crystals were aligned parallel to the direction of rubbing in the liquid crystal cell, the major mesogenic unit of the nematic liquid crystal, the phenylcyclohexane ring placed along its molecular axis, was also aligned along this direction. As the biphenyl structure in the side chain is effective in the generation of the pretilt angle, it is likely that the side chain is also aligned along the direction of the liquid crystal alignment. Since the rigid aromatic ring is connected to the main chain through the single methylene unit, the orientation of the aromatic ring is considerably restricted by the main chain. Therefore, alignment of the rigid polyamide main chains along the direction of the rubbing induced by the rubbing of the surface will result in concomitant alignment of the side chains, which might contribute to the induction of the pretilt angle.

Pretilt Angles of the Different Liquid Crystals

In order to clarify the role of the side chain structure further, we studied the effect of the structure of the liquid crystal molecules. For this purpose, we used ZLI-1132, an all cyano-type nematic liquid crystal having a high dielectric constant, and ZLI-3086, all alkoxy-type having a low dielectric constant, instead of ZLI-2293, a mixture of different types of liquid crystal. As shown in Table IV, MB-PT showed the highest pretilt angle. The use of more polar ZLI-1132 instead of less polar ZLI-

TABLE IV

Pretilt angles of various liquid crystals on the *N*-substituted films

polymer[a]	Degree of substitution/ mole%	liquid crystal ZLI-1132 (15.0)[b]	ZLI-2293 (14.1)[b]	ZLI-3086 (2.9)[b]
MB-PT(III)(0.36)[a]	99	8.2	8.1[c]	5.5
MOB-PT (1.38)[a]	87	2.8	2.0	0.5
CB-PT (4.18)[a]	98	5.7	1.1	0.4

a; Dipole moment of X-phenyl group is given in parenthesis[8].
b; $\varepsilon_{//}$- parallel dielectric constant of the liquid crystal[3].
c; Ref.2

3086 increased the pretilt angle moderately from 5.5 to 8.2 deg on the MB-PT film having a small dipole moment at its side chain. When the film was CB-PT having a large dipole moment at its side chain (the dipole moment of the cyanophenyl group is 4.18/Debye[8]), ZLI-1132 showed a much higher pretilt angle than ZLI-3086. Therefore this large increase of the pretilt angle may be due to the dipole interaction between the side chain and the mesogenic unit of the liquid crystal.

However, the effect of the side chain structure on the *N*-substituted PPTAs cannot be explained simply from the dipole interaction between liquid crystals and the side chain. The dipole moment of the methylphenyl group is much smaller than that of cyanophenyl group, but MB-PT showed its best performance in the generation of pretilt angles among the para-substituted benzyl derivatives. Therefore, steric and other factors should be taken into account in order to understand the observed results, and still has to be studied.

CONCLUSION

All the *N*-substituted PPTAs having the benzyl unit at their side chain structures showed good liquid-crystal alignment and induced moderate to high pretilt angle. The induced pretilt angle was quite sensitive to the structural difference of the phenyl ring of the benzyl unit and also dependent on the types of liquid crystals. Until now, generation of the pretilt angles on the rubbed polymer surface has been discussed[9] in terms of surface free energy,[10,11] anisotropic dispersion force,[12] and so on, all of which are a rather macroscopic approach to the pretilt angle generation. The results presented in this study have indicated the importance of the molecular-scale understanding of the pretilt angle generation. *N*-Substituted PPTAs are proven to serve as excellent polymers for this purpose.

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