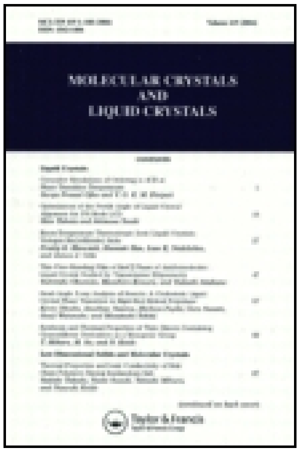

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Synthesis and Characterization of Side-Chain Liquid Crystalline (M6MPP/M6NPAP) Copolymers with NLO Properties

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Synthesis and Characterization of Side-Chain Liquid Crystalline (M6MPP/M6NPAP) Copolymers with NLO Properties

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A series of novel thermotropic side-chain liquid crystalline polymer based on polymethacrylate backbone containing electron-accepting 4-(4'-nitrophenylazo)phenoxy as nonlinear optical active group and electron-donating 4(4'-methoxyphenyl) phenoxy group as mesogen attached covalently to the backbone through the flexible spacer was prepared and characterized, respectively. The results from differential scanning calorimetry showed that these series of copolymers were enantiotropic liquid crystal with single mesophase. The melting points and the relative enthalpy change of the copolymers depressed with increasing the molar percent of 4'-nitroazobenzene monomer units over 0~50mol%, but the enthalpies change of the transition from mesophase to isotropic state increased for the copolymers containing 0~50mol% 4'-nitroazobenzene units. The texture observed under polarized optical microscope identified that the copolymers containing 24molar% or more than 24mol% 4-nitroazobenzene monomer units could form smectic mesophase with the focal-conic texture. The results detected by WAXD were in good agreement with the results observed by POM.

Keywords: synthesis; side chain liquid crystalline polymers; intermolecular electronic donor-acceptor interaction; 4-nitroazobenzene

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INTRODUCTION

Recently, much attention has been paid to a new family of side-chain liquid-crystal polymers containing intermolecular electron donor-acceptor interaction system because of their significant interests of the fundamental research and the potential application in several fields such as information storage and nonlinear optics[1-10]. A number of investigations on side-chain liquid crystal polymers with the presence of intermolecular electron donor-acceptor interaction reported in literature have shown thermal stabilization of mesophase and the formation of an induced mesophase[6-10]. Ringsdorf and his colleagues[4] reported that the first typical example for mesophase formation of side chain liquid crystal polymers which were induced by intermolecular electron donor-acceptor interaction was the mixing of discotic liquid crystalline triphenylene-containing polymer with electron acceptor - trinitrofluorenon derivatives. It was suggested that the disk-shaped portions were arranged in a thermally stable by charge transfer complexion[4,5]. For side-chain liquid-crystal copolymers, it was reported that polyesters containing both electron-donating 4-methoxyazobenzene and electron-accepting 4-cyanoazobenzene units exhibited thermal stabilization and formation of smectic phase due to the presence of intermolecular electron donor-acceptor interaction[6]. More recently, Kosaka and their coworkers[8-12] have investigated a new class of side-chain liquid crystal polymetharylate containing both (carbazol-2-ylmethylene)aniline unit as electron donor and (4'-nitrobenylidene) or and (4'-cyanobenzylidene)aniline units as an electron acceptor attached to the backbone through various length flexible spacers.

From the basic and application research point of view, in the present work, the aim was to design and prepares novel thermotropic side chain liquid crystalline copolymers by taking advantage of intermolecular electron donor-acceptor interaction for the sake of preparing materials with the nonlinear optical property. As usual, the nonlinear optical active groups are chromophore molecules with a conjugated π-electron donor-acceptor system[13], which can polarize the large molecular susceptibility. Therefore, 4'-nitroazobenzene was used as a NLO active group in this study. The attempt to synthesize side-chain liquid crystalline copolymers based on polymethacrylate backbone containing 4'-methoxybiphenyl as an electron donor and 4'-nitroazobenzene as an electron acceptor as side chain attached to the backbone of polymethacrylate through the flexible spacer for the sake of controlling the thermal stability of mesophase and enhancement of nonlinear optical properties has been made. The relationship between structure and thermal transition behavior for these series of copolymers have been studied. In this contribution, the investigation on synthesis, structure, phase transition and the texture of mesophase for this series of copolymers have been reported, respectively.

Experimental section

Materials

4,4'-biphenol, 1,6-dibromohaxane were purchased from Alderich Chemical Inc. and used as obtained. 4'-nitroaniline, methacrylate acid and phenol (Beijing Chemical Factory). 2,2'-azoisobutyronitrile (Beijing Chemical Factory) was recrystallinzed from enthanol twice. The solvents used in this study were N,N-dimethylformide(DMF), toluene, chloroform etc. These solvents were distilled vacuum just before used.

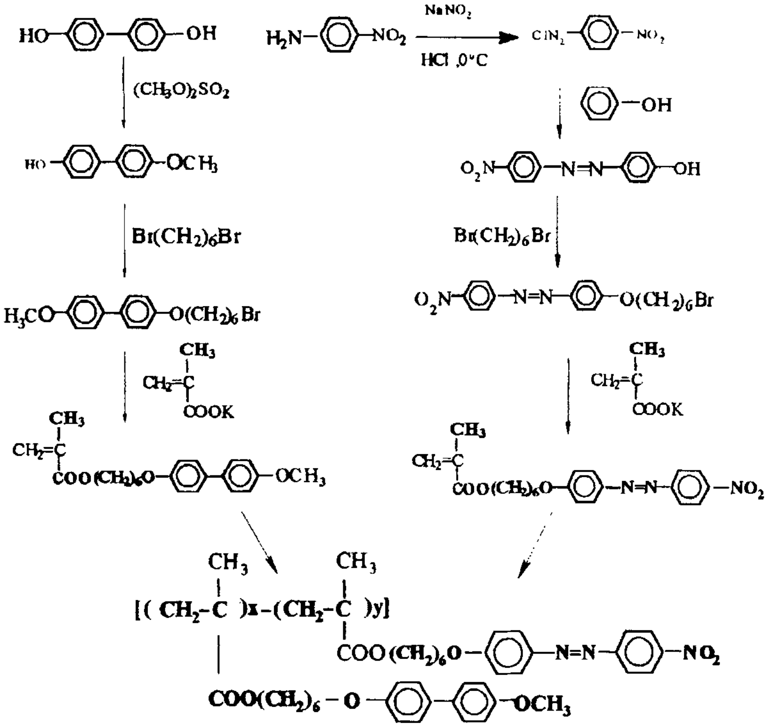
Synthesis

The synthetic route of monomers and copolymers in this study was outlined in scheme I.

4-hydroxyphenyl-4'-nitrophenylazo (1)

4-nitroaniline (0.02mol,) is added to a mixture conc. HCl (10ml) and water (10ml) in a flask with stirring. The mixture solution is cooled and kept at below 5°C using an ice/salt bath and diazotized by addition dropwise of cooled aqueous sodium nitrite (0.02mol) in water(10ml). Then, a solution of phenol (0.02mol) and sodium hydrooxide (0.02mol) in water(10ml) was cooled in ice and dropwise and added to the diazonium salt with stirring. The resultant solution was acidified with conc. HCl. Filter the red solid product with suction and recrystallise it from ethanol , The dark red crystals was dried in vacuum oven at 50°C for 48 hours. Yields: 75%, mp. 219°C (DSC), (lit. 219-220°C[14]).

FT-IR (KBr): 3440cm^{-1} (OH), 1506, 1340cm (NO_2), 854cm^{-1}(C-N) ^{1}H-NMR($CDCl_3$, 400MHz): 8.38ppm (2d, aromatic, 2H); 8.07ppm(2d, aromatic, 4H); 7.02ppm(2d, aromatic, 2H); 5.4ppm(m, OH, H).



SCHEME I Synthetic route of the titled SCLC copolymers

4-(6-bromohexoxyphenyl)-4'-nitrophenylazo(2)

To a round-bottom flask was added the compound(1) (0.01mol), 30ml acetone and excess of potassium carbonate, respectively. The mixture solution was stirred for 20min in order to make sure that the potassium salt of phenol was formed. To the solution, 1,6-dibromohaxane with 10-fold excess was added. The mixture was heated under reflux with stirring overnight. The mixture was filtered to remove the inorganic solids and the solvent was evaporated. Most of the excess of 1,6-dibromohaxane was then recovered by vacuum distillation. The residue solution was precipitated with n-hexane. The crude products were recrystallised from ethanol. Yield: 65%, mp 93°C

FT-IR (KBr): 2871, 2935cm^{-1}(CH_2); 1274cm^{-1} (Br- CH_2); 1508, 1342cm^{-1} (NO_2);

^{1}H-NMR(400Hz, $CDCl_3$): 8.38ppm(d, aromatic, 2H), 7.97ppm(d, aromatic, 4H); 7.02ppm (t, aromatic, 2H). 4.18ppm (t, 2H, CH_2O-); 3.47ppm (t, 2H, Br-CH_2); 2.08ppm (m, 2H, OCH_2CH_2-); 1.95ppm(m, 2H, $BrCH_2CH_2$-); 1.53ppm(m, 4H, - CH_2CH_2-)

6-[4-(4'-nitrophenylazo)phenoxyl]hexyl methacrylate(M6NPAP)(3)

The methacrylate potassium(0.01mol, 1.24g) was reacted with the compound (2) (0.005mol, 2.04g) in the presence of hydroquinone (0.00005mol, 0.0055g) in DMF (15ml). The reaction was carried out in a sealed glass ampoule in N_2 atmosphere at 100 °C for 10h. Then, the solvents were dissolved in chloroform (30ml). The chloroform solution were transferred into a separating funnel and was washed with water repeatedly, and then dried on $MgSO_4$. Remove of solvent gave orange yellow crystal. The product was purified by recrystallization from methanol. Yield: 42%, mp. 86°C.

FT-IR(KBr): 1719cm^{-1}(C=O); 1638cm^{-1} (C=C)

^{1}H-NMR(400Hz, $CDCl_3$): 8.37ppm(d, aromatic, 2H), 8.02ppm(d, aromatic, 4H); 7.02ppm (t, aromatic, 2H). 6.11, 5.56ppm(2s, CH_2=, 2H), 4.19ppm (t, 2H,O CH_2); 4.09ppm(t, 2H, OCH_2); 1.95ppm(s, 3H, CCH_3); 1.86ppm(m, 2H, OCH_2CH_2-); 1.74ppm (quint, CH_2, 2H); 1.42-1.60ppm(m, 4H, -CH_2CH_2-).

4-hydroxy-4'-methoxybiphenyl(4)

The compound (4) was synthesized from 4,4'-biphenol(27.95g, 0.15mol), dimethyl sulfate(14.3ml, 0.15mol) bythe method described as Ref.20, Yield: 26.7%, mp. 183 °C(lit.182-183 °C).

4-(6-bromohexoxyphenyl)-4'-methoxybiphenyl(5)

The compound (4) (8.0, 0.04mol) and excesses of K_2CO_3 (8.3g, 0.06mol) were added to acetone (100ml) in a round-buttom flask and stirred until the purple potassium salt of the phenol was formed. 1,6-bromohexane (51g, 0.4mol, 10-fold excess) was added to the mixture mentioned above. The mixture were stirred under reflux overnight. The reaction mixture were filtered to remove inorganic solid. The solutions were cooled to room temperature and the white crystal product were recrystallised from the solution. Filtered the crystal product with suction. The white crystals were recrystallised from ethanol. Yield: 81%, mp.125 °C.

FT-IR(KBr): 2871, 2935cm^{-1} (CH_2); 1274cm^{-1} (CH_2Br)

^{1}H-NMR($CDCl_3$, 400Hz): 6.96ppm (m, aromatic, 4H); 7.47ppm(m, aromatic, 4H); 4.00ppm (t, $PhOCH_2$); 3.83ppm (s, CH_3); 3.42ppm (t, -CH_2Br, 2H); 1.81ppm(quin, Br- CH_2 CH_2-, 2H), 1,89ppm(quin, PhO CH_2 CH_2 CH_2-, 2H); 1.54-1.50ppm(m, - CH_2 CH_2-, 4H).

6-[4-(4'-methoxyphenyl)phenoxy]hexyl Methacrylate(M6MPP)(6)

The compound (6) was synthesized from the compound(5) (0.015mol) and potassium methacrylate (0.03mol) by the similar procedure according to ref[20], Yield: 35%, mp. 62 °C

FT-IR(KBr film): 1719cm^{-1} (C=O), 1638cm^{-1} (C=C)

^{1}H-NMR($CDCl_3$, 400Hz): 6.9, 7.5ppm(m, aromatic, 8H), 6.21, 5.60ppm(2s, CH_2=C, 2H); 4.16, 3.99ppm (2t, OCH_2-, 4H); 3.84ppm(s, OCH_3, 3H);

1.95ppm(s, CCH_3, 3H); 1.82, 1.73ppm)(m, OCH_2CH_2-,4H); 1.40-1.60ppm(m, - CH_2CH_2 -, 4H).

Polymerization

Radical polymerization using 2.2'-azoisobutyronitrile(AIBN)as an initiater was conducted in an ampoule under a nitrogen atmosphere at 70°C for 30h. Toluene and N,N-dimethylformade(DMF) were used as solvent for homopolymerization and compolymerization. The resultant polymer was purified by reprecipitation from chloroform solution to methanol repeatedly.

Characterization

Chemical structure of the intermediates, monomers, homopolymers and copolymers were characterized with FT-IR spectrum using FTS-7 spectrometer (BIO-RAD) and ^{1}H-NMR spectrum using Unity-400MHz spectrometer (Varian) in chloroform-d-solution). A differential scanning calorimeter (DSC)(Perkin-Elmer DSC-7) calibrated with Indium was used to determined the phase transition temperature of the polymers at the heating and cooling rates of 10°C /min. The texture for the copolymers and homopolymers were observed under a polarized optical microscope (Carl-Zeiss) mounted with a hot-stage. X-ray diffraction was measured on a PW-1700X diffractometer (Philips) equipped with a hot-stage.

RESULTS AND DISCUSSION

The structural analysis of(M6MPP/M6NPAP) copolymers

FT-IR spectra for the series of (M6MPP/M6NPAP) copolymers showed that 1638 cm^{-1} characteristic absorption which is assigned to the stretching vibration of carbon-carbon double bond disappears after polymerization. The absorption band at 1720 cm^{-1} is attributed to the stretching vibration of C=O group. 2850 cm^{-1} characteristic absorption band of hydrogen-carbon bond of methoxy group was depressed with the decrease of M6NPAP component.

TABLE I Molecular weight and thermal properties of the copolymers and the relative homopolymers

dye contents mol%	M_n ($\times 10^3$)	M_w ($\times 10^4$)^b	Phase transition / ^oC ^{c}	ΔH ^{d} ($J\times g^{-1}$)
0	5.22	2.09	g82c121n133i	7.35
11	4.10	1.7	g75c108n131i	8.25
24	11.1	2.44	g66c94s138i	7.59
43	6.22	1.28	g63c68s130i	6.16
85	1.65	6.81	g48s129i	2.48
100	4.95	0.89	g45s127i	1.56

a: Composition ratios of the M6MPP in copolymers were calculated by ^{1}H-NMR. b: Molecular weight of the copolymers were determined by GPC with respect to polystyrene standard sample. c: The melt point and clear point were measured at the heating rate of 20°C/min for the second heating process. d: The value of enthalpy at the transition from mesophase to isotropic state.

The composition ratios of two monomer units in the copolymers were estimated by a comparison of integration of the phenyl resonance at 7.9ppm for M6NPAP unit with the another phenyl resonance at 6.9ppm for M6MPP unit according to ^{1}H-NMR spectra. The results were listed in TABLE I. The stereoregular structure of M6MPP/M6NPAP copolymers were detected by ^{1}H-NMR spectra. It is well known that radical polymerization of a number of methacrylate formed polymers with rich in syndiotacticity[15, 16]. For this series of copolymers, the resonance peak due to the proton of α-methyl group in polymethacrylate backbone appeared at 0.91-1.29ppm. The resonance related to α-methyl split into three peaks owing to the existence of various stereotacticity.

Phase transition behavior and liquid crystallinity of (M6MPP)/(M6NPAP) copolymers

It was well known that polymer of [6-4-(4'-methoxyphenyl) phenyl) hexyl-methacrylate] (M6MPP) had been investigated extensively investigated by many researchers[15,17]. As shown in TABLE I, the transition temperature from mesophase to isotropic state, i.e. clear point of the homopolymer of (M6MPP), was lower than that reported in literature because the sample of PM6MPP in this study has a lower molecular weight.

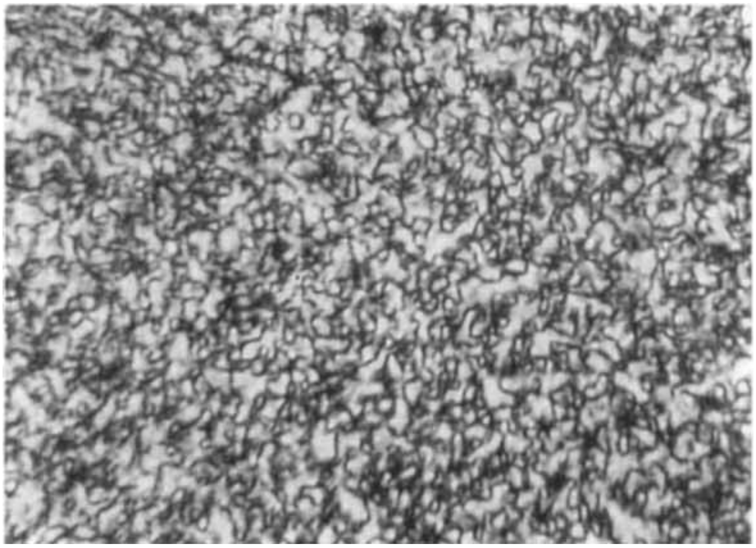


FIGURE 1 Optical polarized micrograph of the homopolymer of M6MPP at 128°C

As for the texture of PM6MPP, the thread and schileren texture was observed under polarized optical microscopy as shown in Fig. 1 exhibited the characteristics of nematic phase between 121°C and 133°C, which was in agreement with the result reported by Nakano[15].

For the homopolymer of M6NPAP, it displayed a second-order transition and only one first-order phase transition that is corresponding to clear point temperature on the heating and cooling trace of DSC, the data were summarized in TABLE I. Microphotograph shown in Fig.2 exhibited that the focal-conic and broken-fan texture appeared for homopolymer of M6NPAP annealed at 112°C. The focal-conic and broken-fan texture was the characteristic of smectic phase[18], indicating the polymer can form smectic phase at the temperature range of mesophase.

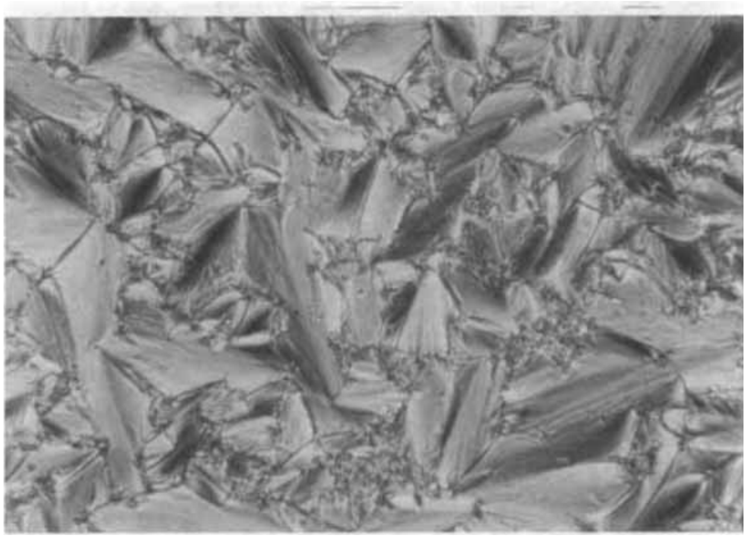


FIGURE 2 Optical polarized micrograph of homopolymer of M6NPAP annealed at 112°C (See Color Plate III).

Phase transition temperature and thermal parameter of (M6MPP/ M6NPAP) copolymers were listed in TABLE I. The results obtained from DSC showed that all of the copolymers could form mesophase and the first order phase transition of the copolymer at the clear points appears on both cooling and heating trace which indicate that this series of the copolymers are the enantiotropic liquid crystal polymers[19]. For example, Fig.3 showed DSC trace for the copolymers of M6MPP/ M6NPAP(24/76) had two first order phase transition on both cooling and heating trace.

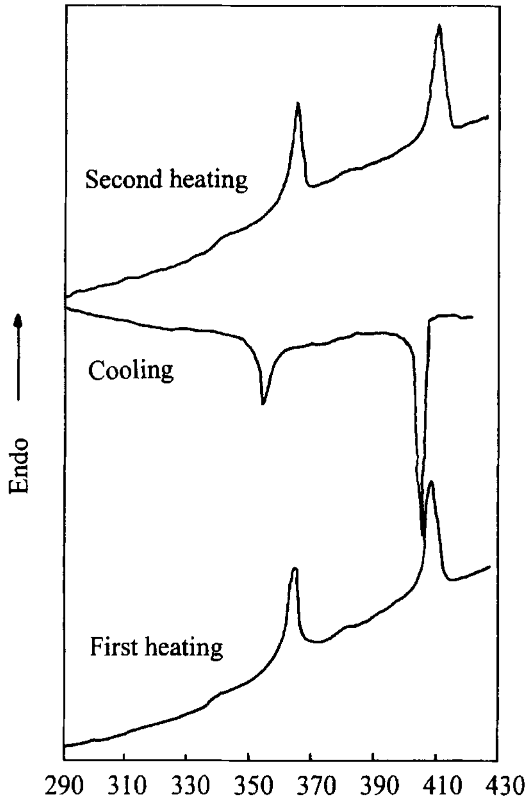


FIGURE 3 DSC trace of M6MPP/ M6NPAP (76/24) copolymer on heating and cooling cycle.

Furthermore, the phase transition temperatures were plotted as a function of the composition ratio of M6NPAP units. Diagram of this series of copolymers was presented in Fig 4. When the content of M6NPAP units contained in the copolymers is below ca.50mol%, the copolymers exhibited two first-order phase transitions which were corresponding to the melting and clear point, respectively as well as second order transition, i.e. glass transition.

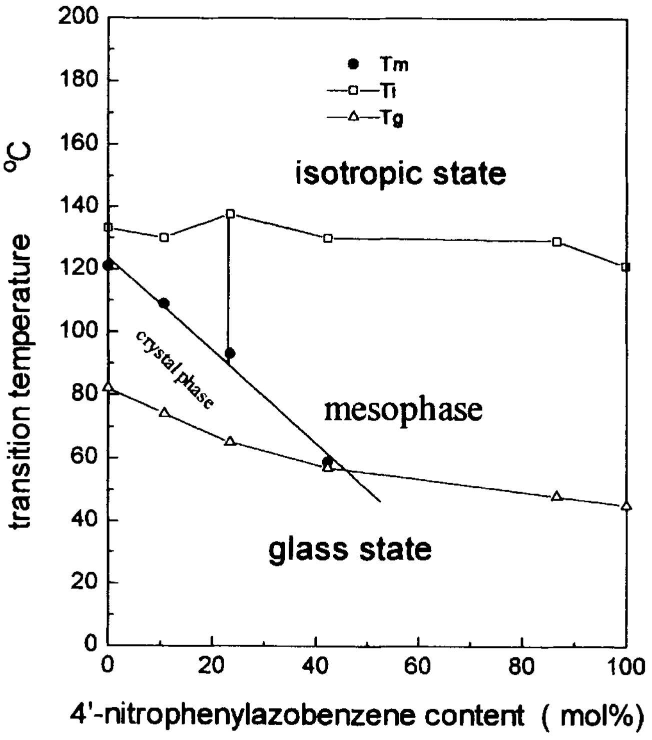


FIGURE 4 Diagram of (M6MPP/M6NPAP) copolymers

It was worthy noting that the copolymers possessed the broader temperature of mesophase. For instant, as shown in TABLE I, the mesophase temperature range of the copolymers M6MPP/ M6NPAP(89/11) had a broader range of mesophase temperature than that of the homopolymers of M6MPP. Meanwhile, the value of enthalpy corresponding to clear point increase with the content over 0~50mol%. Thus, the ranges of mesophase temperature of M6MPP/ M6NPAP copolymers were broadened due to the incorporation of an electron-acceptor, 4-nitroazobenzene group, as pendant side chain group attached to the backbone with respect to homopolymer of M6MPP. It is well known that 4-(4'-methoxypnenyl)phenoxy) group was an electron donor and 4-nitroazobenzene was electron acceptor[3]. Therefore, the existence of intermolecular electron-donor and acceptor interaction between side chain groups like 4-(4'-nitrophenylazo)phenoxy and 4-(4'-methoxypnenyl)phenoxy) group is no exception.

For side-chain liquid crystalline copolymers with electron donor-acceptor interaction, a number of investigators[1-12] has demonstrated that thermal stabilization and formation of a smectic phase could be induced by the existence of intermolecular electron donor-acceptor interaction. In this study, the copolymers with 11mol% M6NPAP unit exhibit a broader mesophase temperature range and the higher enthalpy of isotropilization than that of homopolymer of M6MPP. It was found that the formation of smectic phase for the copolymer containing 24mol% M6NPAP may be induced by intermolecular electron donor-acceptor interaction between 4- (4' -methoxypnenyl)phenoxy)(MPP) and 4-(4'-nitrophenyl)azophenoxy) (NPAP) group. According to the concept for the intermolecular charge transfer complexation or intermolecular electron donor-acceptor interaction[6], these results mentioned above indicated that the intermolecular electron donor-acceptor interaction existed between 4-(4'-methoxy-phenyl)phenoxy)(MPP) 4-(4'-nitrophenyl) azophenoxy) (NPAP) group. Seeing from the data in TABLE I, a comparison of the enthalpy value of the isotropilized transition for the copolymers with the relative homopolymers reveal further that the existence of the interaction between electron donor, 4-(4'-methoxypnenyl)-phenoxy) group and electron acceptor, 4-(4'-nitrophenyl)-azophenoxy).

Fig.5 (a~b) shows mesophase textures of this series of M6MPP/ M6NPAP copolymers with the film sample in liquid crystal state observed under polarized optical microscopy.

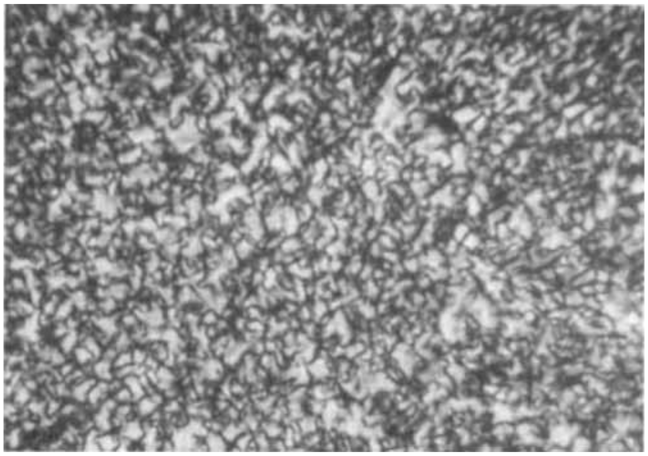


FIGURE 5a Optical polarized micrograph of the copolymers of M6MPP/ M6NPAP (89/11) in the mesophase(128°C)

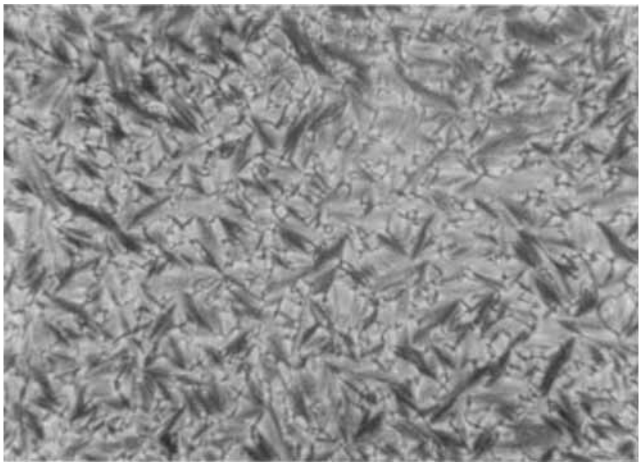


FIGURE 5b Optical polarized micrograph of the copolymer of M6MPP/ M6NPAP(76/24) in the mesophase(125°C) (See Color Plate IV).

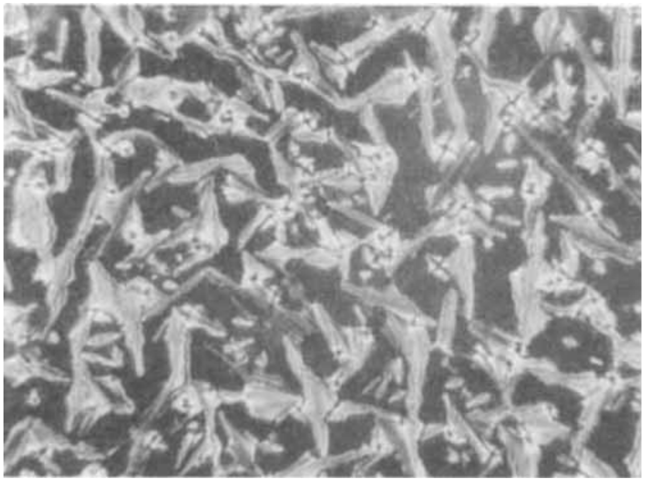


FIGURE 5c Optical polarized micrograph of the copolymer of M6MPP/M6NPAP(57/43) in the mesophase(125°C) (See Color Plate V).

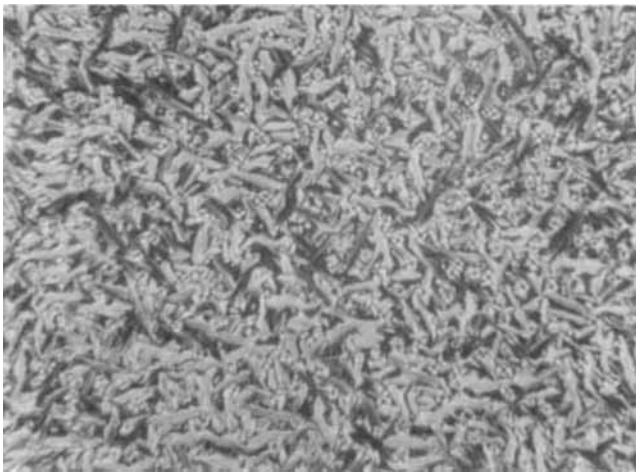


FIGURE 5d Optical polarized micrograph of the copolymer of M6MPP/ M6NPAP(25/85) in the mesophase(120°C) (See Color Plate VI).

As shown in Fig.5a, copolymer containing11mol% M6NPAP unit exhibits thread and schlieren texture after the sample was annealed at 128 °C for 10 hours. The thread and schlieren texture indicated that the copolymer containing 11mol% M6NPAP units can form nematic phase with the characteristics of the nematic liquid crystals. The focal-conic and broken-fan texture in the range of the mesophase temperature presented in Fig. 5b appeared for the copolymers containing 24mol% M6NPAP units, indication of the characteristics of smectic mesophase. Since the homopolymers of M6MPP and M6NPAP had nematic and smectic liquid crystallinities, respectively, it was reasonable to consider that the smectic phase would appear for M6MPP/ M6NPAP copolymers among the wide range of intermediate compositions because of the presence of intermolecular electron donor-acceptor interactions between 4-nitoazobenzene and 4-methoxybiphenyl group. It has been expected that the copolymers containing 43mol% and 85mol% M6NPAP monomers units shown the focal-conic texture exhibited in Fig.5(c ,d) which was smectic A or C mesophase.

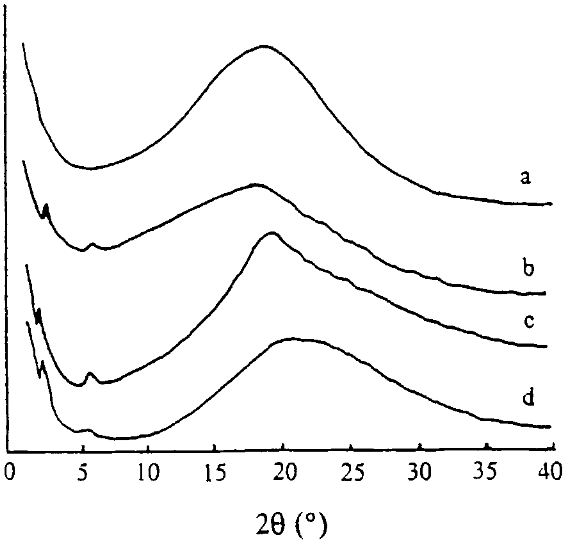


FIGURE 6 Wide Angle X-ray diffraction (WAXD) curve for the series of M6MPP/M6NPAP copolymers in the mesophase

As mentioned above, copolymers containing 4'-nitroazobenzene over 24mol%~100mol% showed focal-conic texture at the temperature range of liquid crystal state that correspond to smectic mesophase. Fig.6 presented X-ray diffraction curves for this series of (M6MPP/M6NPAP) copolymers. As shown in Fig.6a, (M6MPP/ M6NPAP) (89/11) copolymer at the mesophase temperature gave only one diffusive diffraction at 4.9Å that corresponds to lateral space of mesogenic side group, which indicated the formation of nematic phase[20]. For copolymer containing 24mol% 4'-nitroazobenzene units, the curve (b) exhibited a sharp first-order diffraction at about 27.48Å and a second-order diffraction at about 13.49Å that indicated the formation of smectic mesophase. Analogously, copolymers containing 4'-nitroazobenzene units over 24mol%~100mol% have a first-order sharp and second -order diffraction. The results obtained from X-ray diffraction were listed in TABLE II. These results identified that the copolymers containing 4' -nitroazobenzene unit over 24mol%~100mol% can form smectic phase at the temperature range of mesophase.

TABLE II. WAXD Data for (M6MPP/M6NPAP)copolymers and the homopolymer of M6NPAP

Content of dye/ mol%	$^{a}d_1$	$^{b}d_2$	$^{c}d_3$
11			4.55
24	27.48	13.49	4.52
43	27.58	13.68	4.33
85	33.53	15.37	4.68
100	34.65		4.69

a:first-order diffraction; b: second-order diffraction; c: diffuse diffraction.

CONCLUSIONS

A new series of side-chain liquid crystal copolymers (M6MPP/ M6NPAP) containing intermolecular electron donor-acceptor interaction system was prepared successfully by free radical polymerization. Both the homopolymers of M6MPP and M6NPAP exhibited liquid crystallinity, respectively. The focal-conic textures were observed under polarized optical microscopy for the homopolymer of M6NPAP which indicated that the formation of smectic phase in liquid state. The copolymers of (M6MPP / M6NPAP) exhibited the various textures at liquid crystal state for the copolymers. With comparison to the homopolymers of M6MPP and M6NPAP, the copolymers have the broader temperature of mesophase because of the presence of intermolecular electron donor-acceptor interaction. It proved that the thermal stabilization of mesophase induced by intermolecular electron donor-acceptor interaction between electron donating 4'-methoxybiphenyl group and electron accepting 4'-nitroazobenzene group attached to the backbone of polymethacrylate through flexible spacer.

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