

Synthesis, Characterization and Liquid Crystalline Properties of Polyacrylates and Polymethacrylates Containing Aryl Ester Pendant Unit

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ABSTRACT: Aryloxycarbonylphenyl acrylates and methacrylates were prepared by reacting 4-acryloyloxybenzoyl chloride and 4-methacryloyloxybenzoyl chloride with different phenols. They were homopolymerized using benzoyl peroxide as the initiator at 65°C in dimethylformamide. The polymers were characterized by IR and ¹H-NMR spectra and size exclusion chromatography. Differential scanning calorimetry and polarizing optical microscopy studies revealed that the phenyl esters of poly(4-acryloyloxybenzoic acid) and poly(4-methacryloyloxybenzoic acid) did not show any liquid crystalline properties, but, the para-aryl-substituted phenyl esters did exhibit mesophase properties in the temperature range of 98–265°C depending on the nature of the aryl substituent. Polymethacrylates exhibit higher T_g , and lower T_m and T_i than the polyacrylates having the same pendant mesogen. Thermogravimetric analyses have shown that the initial decomposition temperatures of the polymers are above 230°C. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 465–474, 2000

Key words: aryloxycarbonylphenyl acrylates and methacrylates; liquid crystalline properties; differential scanning calorimetry; polarizing optical microscopy

INTRODUCTION

In recent years, side-chain liquid crystalline polymers (SCLCPs) have attracted much attention due to their potential applications in numerous areas, especially in the field of optic, opto-electronic and thermoconducting materials.^{1–6} The polymeric backbones of SCLCPs are primarily polyacrylates, polymethacrylates and polysiloxanes, and the mesogenic moieties are mainly derived from substituted benzoic acid, aromatic schiff bases, substituted biphenols, aromatic azo or azoxy compounds.^{7–9} The mesogens are usually attached to the polymeric backbone via a flexible spacer, which is generally an aliphatic hydrocarbon chain containing, normally, more than two

methylene units. The spacer decouples the mesogenic side groups from the backbone and renders the mesogens to order anisotropically to a first approximation. When the rigid mesogen is directly attached to the polymeric backbone an amorphous polymer is obtained, in most cases, because of restricted mobility of the laterally attached mesogenic unit. Poly(4-acryloyloxybenzoic acid) and poly(4-methacryloyloxybenzoic acid),¹⁰ poly(4-biphenyl acrylate),^{11,12} and poly(4-cyclohexylphenyl acrylate),¹³ are the notable SCLC polymers which exhibit mesophase properties without the presence of any flexible spacer between the polymer backbone and the pendant mesogen unit. We previously reported¹⁴ the synthesis and properties of copolymers of 4-biphenylacrylate with methyl methacrylate.

The liquid crystalline properties of SCLC polymers depend on the nature of polymer backbone, the type of mesogen, the flexible spacer and its

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length, and the nature of terminal groups.^{15–19} The relationships between the above mentioned variables and phase transition properties for SCLCPs have been discussed in depth by several researchers.^{20–22} The present paper reports the synthesis, characterization, and mesophase properties of polyacrylates and polymethacrylates in which the pendant aromatic mesogenic group is attached to the polymeric backbone either directly or via an ethyleneoxy or benzoyloxy unit.

EXPERIMENTAL

Materials

4-Hydroxybenzoic acid (HBA), 4-hydroxybenzophenone (HOBP), 4-phenoxyphenol (POP), 4-biphenol (BP), acryloyl chloride and methacryloyl chloride from Aldrich were used as received. Benzoyl peroxide (BPO) was recrystallized from chloroform/methanol mixture. All the other chemicals and solvents were of analytical grade and used without further purification.

Preparation of 2-Aryloxyethanols

2-Aryloxyethanols were prepared by reacting 4-substituted phenols with 2-chloroethanol in presence of KOH in aqueous-ethanol solution. In a typical procedure, a mixture of 4-biphenol (10.04 g, 0.059 mol), 2-chloroethanol (4.75 g, 0.059 mol) and KOH (10 g) in 25 mL of water and 50 mL of ethanol was refluxed for 10 h. The product 2-(*p*-biphenyloxy)ethanol (BOE) was isolated in ice-cold water, and recrystallized from ethanol. Similarly, 2-(*p*-benzophenoneoxy)ethanol (BPOE) and 2-(*p*-phenoxy)phenoxyethanol (PPE) were prepared by the reaction of 4-hydroxybenzophenone and 4-phenoxyphenol, respectively, with 2-chloroethanol. The yields of the compounds were around 70%. The structures of the compounds were identified by elemental analysis and IR and ¹H-NMR techniques.

Preparation of 4-Acryloyloxybenzoic Acid and 4-Methacryloyloxybenzoic Acid (1, 2)

To a well-stirred solution of HBA (13.14 g, 0.095 mol) and NaOH (7.7 g, 0.193 mol) in 50 mL of water and 25 mL of dioxane was added dropwise 0.1 mol of acryloyl chloride or methacryloyl chloride at 10–15°C. After stirring at room temperature for 4 h, the reaction mixture was neutralized with dilute HCl. The solid 4-acryloyloxybenzoic

acid (ABA) or 4-methacryloyloxybenzoic acid (MBA) thus precipitated was filtered, washed with warm water, dilute HCl and water, successively, and recrystallized from ethanol. The yields of ABA and MBA were about 70%. The structures of the monomers were confirmed by elemental analysis and IR and ¹H-NMR techniques (Scheme 1).

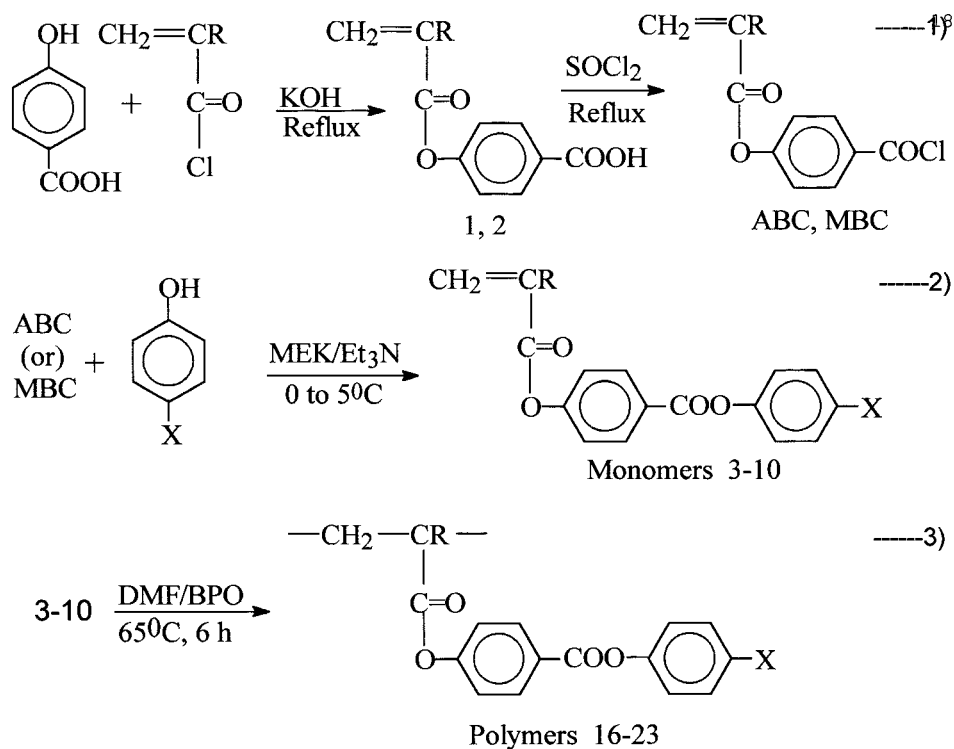
Preparation of 4-(meth)Acryloyloxybenzoyl chloride (ABC/MBC)

ABA/MBA (10 g) was refluxed with 100 mL of thionylchloride in presence of a trace amount of dimethylformamide for 8 h, and then the excess of thionylchloride was removed by vacuum distillation. The product was recrystallized from CH₂Cl₂, and identified by elemental analysis and IR spectra.

Preparation of Aryloxycarbonylphenyl acrylates and methacrylates (3–10)

A typical procedure for the preparation of phenoxy carbonylphenyl acrylate (PCPA; **3**) is described as follows. In a 100-mL three neck flask, phenol (3.58 g, 0.038 mol) and triethylamine (3.84 g, 0.038 mol) were dissolved in 25 mL of methyl ethyl ketone (MEK), and the contents were cooled to 0–5°C. Then, 4-acryloyloxybenzoyl chloride (ABC) (8.0 g, 0.038 mol) in 50 mL of MEK was added dropwise with stirring at the same temperature. After stirring at room temperature for 2 h, the solid quaternary ammonium salt was filtered off. The organic solution was washed successively with 5% aqueous NaOH solution, dilute HCl and distilled water, and dried over anhydrous sodium sulphate. The solvent was evaporated, and the solid PCPA was recrystallized from ethanol.

Similarly, the other monomers (**4–10**), namely, 4-(phenoxy)phenoxy carbonylphenyl acrylate, (PPCPA; **7**), *p*-biphenyloxy carbonylphenyl acrylate (BPCPA; **5**) and *p*-benzophenoneoxy carbonylphenyl acrylate (BPOCPA; **9**) were prepared by reacting ABC with POP, BP, and HOBP, respectively; and phenoxy carbonylphenyl methacrylate (PCPMA; **4**), 4-(phenoxy)phenoxy carbonylphenyl methacrylate (PPCPMA; **8**), *p*-biphenyloxy carbonylphenyl methacrylate (BPCPMA; **6**), and *p*-benzophenoneoxy carbonylphenyl methacrylate (BPOCPMA; **10**) were prepared by reacting MBC with phenol, POP, BP and HOBP, respectively. All the monomers were characterized by melting points, elemental analyses, and IR and ¹H-NMR techniques (Scheme 1).



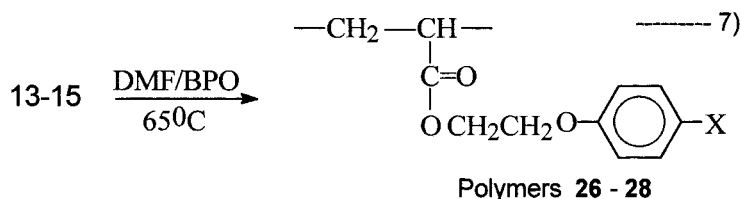
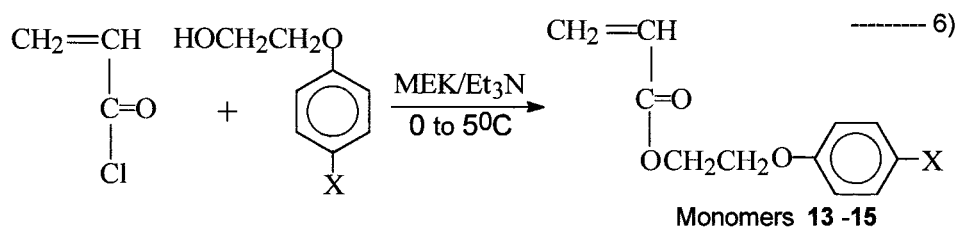
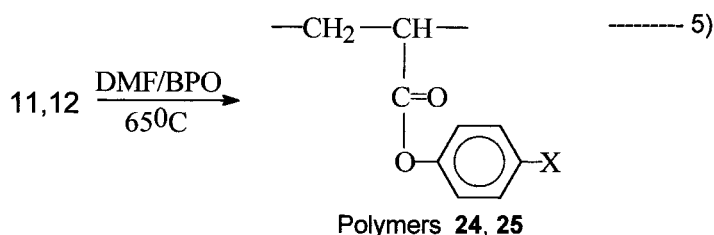
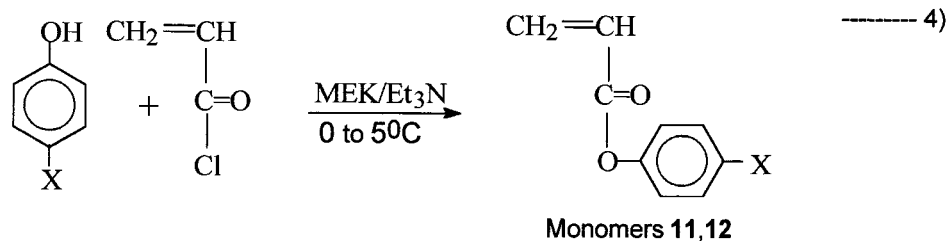
R	X	Monomer	Polymer
H		1, ABA	Poly(ABA)
CH ₃		2, MBA	Poly(MBA)
H	H	3, PCPA	16, Poly(PCPA)
CH ₃	H	4, PCPMA	17, Poly(PCPMA)
H	C ₆ H ₅	5, BPCPA	18, Poly(BPCPA)
CH ₃	C ₆ H ₅	6, BPCPMA	19, Poly(BPCPMA)
H	C ₆ H ₅ O	7, PPCPA	20, Poly(PPCPA)
CH ₃	C ₆ H ₅ O	8, PPCPMA	21, Poly(PPCPMA)
H	C ₆ H ₅ C=O	9, BPOCPA	22, Poly(BPOCPA)
CH ₃	C ₆ H ₅ C=O	10, BPOCPMA	23, Poly(BPOCPMA)

Scheme 1 Preparation of aryloxycarbonylphenyl acrylates/methacrylates and their polymers. Monomers, 1–10; polymers, 16–23.

Preparation of Aryl acrylates and Aryloxyethyl acrylates (11–15)

2-(*p*-Biphenyloxy)ethyl acrylate (BOEA, **13**), 2-(*p*-phenoxy)phenoxyethyl acrylate (PPEA, **14**), 2-(*p*-benzophenoneoxy)ethyl acrylate (BPOEA, **15**), 4-phenoxyphenyl acrylate (POPA, **11**), and 4-ben-

zoylphenyl acrylate (BOPA, **12**) were prepared by reacting equimolar amounts of acryloyl chloride with BOE, PPE, BPOE, POP, and HOBP, respectively, in presence of triethylamine in MEK solution by following the procedure described in the preparation of phenoxy carbonylphenyl acrylate (Scheme 2).



<u>X</u>	<u>Monomer</u>	<u>Polymer</u>
C ₆ H ₅ O	11 , POPA	24 , Poly(POPA)
C ₆ H ₅ C=O	12 , BOPA	25 , Poly(BOPA)
C ₆ H ₅	13 , BOEA	26 , Poly(BOEA)
C ₆ H ₅ O	14 , PPEA	27 , Poly(PPEA)
C ₆ H ₅ C=O	15 , BPOEA	28 , Poly(BPOEA)

Scheme 2 Preparation of aryl acrylates and aryloxyethyl acrylates and their polymers. Monomers, 11–15; polymers, 24–28.

Polymerization

Monomers 3–15 were polymerized as 2 M solution in dimethylformamide using benzoyl peroxide (0.50 wt % with respect to monomer) as the initiator at 65°C under nitrogen atmosphere. The polymers were isolated after 6 h of polymerization time by adding the reaction solution to excess of methanol, purified by reprecipitation from DMF solution into methanol, and dried under vacuum.

Techniques

Elemental analyses were carried out with a Carlo Erba C—H—N analyzer. IR spectra were recorded with a Hitachi 270-500 spectrophotometer as KBr pellets. ¹H-NMR spectra were obtained with a Bruker 90 MHz FT NMR spectrometer in CDCl₃ solution using tetramethylsilane (TMS) as an internal reference. Differential scanning calorimetry (DSC) measurements were performed

with a Perkin Elmer DSC-7 at a heating rate of 15°C/min. Apparent weight (M_w) and number (M_n) average molecular weights of the polymers were measured by Waters 501 size exclusion chromatography (SEC), equipped with RI-401 detector and three ultrastyrigel columns. Tetrahydrofuran was used as the mobile phase, and the calibrations were made against polystyrene standards. Optical observations were made with a Leitz Laborlux 11 POLS polarizing microscope. Samples were heated at 5°C/min, and observed under crossed polarizers. Thermogravimetric analyses (TGA) were carried out with a Mettler TA 3000 thermal analyzer at a heating rate of 15°C/min in air.

RESULTS AND DISCUSSION

Aryloxy-carbonylphenyl acrylates and methacrylates (**3–10**) were synthesized in three steps as outlined in Scheme 1. In the first step, 4-acryloyloxybenzoic acid (ABA) and 4-methacryloyloxybenzoic acid (MBA) were prepared by reacting acryloyl chloride and methacryloyl chloride, respectively, with 4-hydroxybenzoic acid (HBA) in aqueous alkaline solution. Then, 4-acryloyloxybenzoyl chloride (ABC) and 4-methacryloyloxybenzoyl chloride (MBC) were obtained by treating ABA and MBA, respectively, with thionylchloride. Finally, ABC and MBC were reacted with phenol, POP, HOBP, and BP in presence of triethylamine in MEK to obtain aryloxy-carbonylphenyl acrylates and methacrylates.

Aryloxyethyl acrylates and aryl acrylates (**11–15**) were prepared by reacting acryloyl chloride with aryloxyethanols and 4-substituted phenols, respectively, in the presence of triethylamine in MEK at 0–5°C (Scheme 2).

The elemental analysis data of the monomers were in good agreement with the calculated values for the assigned structures. The IR spectra of the monomers show characteristic bands around 1740 and 1625 cm^{-1} due to the stretchings of ester carbonyl and ethylenic double-bond, respectively. The $^1\text{H-NMR}$ spectra of the monomers show a multiplet at 8.10 to 5.75 ppm, corresponding to aromatic as well as olefinic protons. Aryloxyethyl acrylate monomers did show two triplets around 3.80 and 4.05 ppm due to the protons of ethyleneoxy unit. In addition, methacrylate monomers exhibit a singlet at about 1.90 ppm due to methyl protons.

Polymer Synthesis and Characterization

Monomers **3–15** were polymerized in dimethylformamide solution using benzoyl peroxide as the free radical initiator at 65°C. The polymerization of all the monomers, except that of *p*-biphenyloxy-carbonylphenyl acrylate (BPCPA), has proceeded in homogeneous solution. However, poly(BPCPA) was precipitated within 1 h of polymerization time. All the polymers, except poly(BPCPA), were readily soluble in polar aprotic solvents such as dimethylformamide, dimethylacetamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, tetrahydrofuran, etc., and chlorinated solvents such as chloroform, 1,2-dichloroethane, dichloromethane, etc. However, poly(BPCPA), which was precipitated within 1 h of polymerization time, was insoluble in most of the common organic solvents. All the polymers were insoluble in hydrocarbons (e.g., benzene, toluene, xylene) and the hydroxy-group containing solvents such as methanol, ethanol, propanol, and isopropanol. The apparent M_w values of the polymers were above 40,000 g/mol (40,000–75,000 g/mol), which suggests that the liquid crystalline properties of the polymers are independent of molecular weight.²³ The polydispersity index (M_w/M_n) values of the polymers are in the range of 2.1–3.0.

The IR spectra of the polymers show strong characteristic bands at about 1735 cm^{-1} due to ester C=O stretchings, around 1605 cm^{-1} due to aromatic C=C stretchings, and at about 1265 cm^{-1} , corresponding to ester C—OC stretchings. In addition, polymers **22**, **23**, **25**, and **28** show strong bands around 1645 cm^{-1} due to ketone C=O stretchings of the pendant benzophenone moiety.

$^1\text{H-NMR}$ spectra (Fig. 1) of the polymers show a singlet at about 8.05 ppm due to the two aromatic protons at an ortho-position to the carboxylate group of HBA moiety. The signals due to the other aromatic protons are coalesced and observed as a multiplet at 6.95–7.27 ppm. All the polyacrylates show broad signals at 2.32–1.60 ppm due to backbone methylene and methine protons. In addition, polymers **26–28** show two triplets at 3.84 and 4.02 due to an ethyleneoxy (—O—CH₂—CH₂—O—) unit. Polymethacrylates exhibit a group of signals at 1.27 to 0.86 ppm due to α -methyl protons, thus indicating the presence of conformational tacticity. The $^1\text{H-NMR}$ analysis has shown that the polymers contain 59–76% heterotacticity, 22–40% syndiotacticity, and 1–3% isotacticity. The lower syndiotacticity and

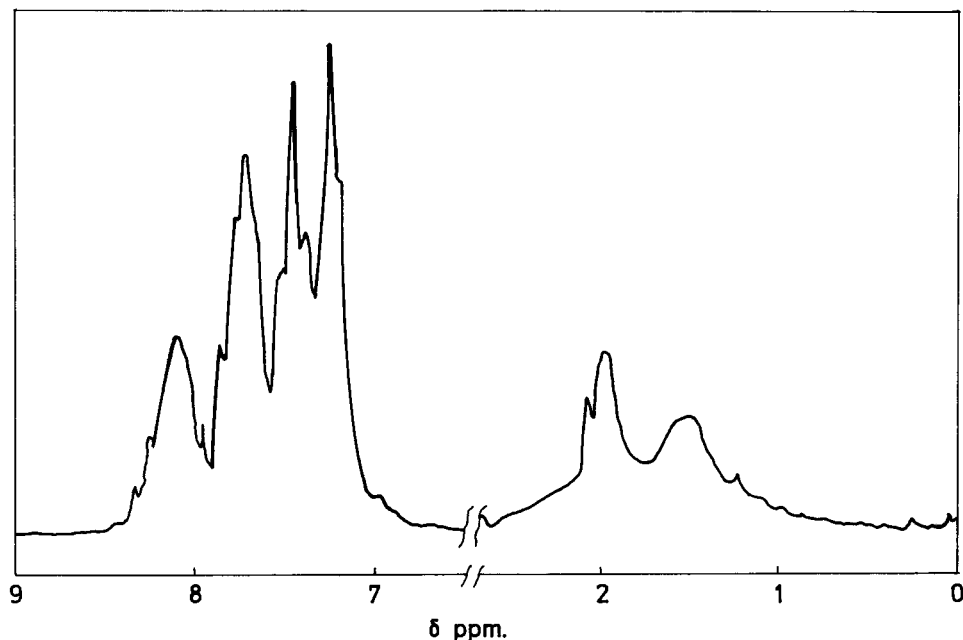


Figure 1 $^1\text{H-NMR}$ spectrum of poly(BPOCPMA).

higher heterotacticity ratios may be due to the presence of bulky pendant group. Similar observations have been reported for the free radical polymerization of methacrylate monomers with large side groups, such as phenyl methacrylate and trityl methacrylate.^{24–26}

Liquid Crystalline Properties

The phase transition temperatures and optical textures of the polymers were examined by DSC and polarizing optical microscopy (POM), and the data are given in Table I. Poly(ABA) and

poly(MBA) exhibit T_g values of 95 and 105°C, respectively. The glass transition temperatures of polymers **16–23** are in the range of 60–100°C, depending on the nature of the pendant group. Polymer **20** has the lowest T_g value of 60°C, whereas polymer **19** exhibits the highest T_g value of 100°C. The T_g values of polymethacrylates are higher, by about 5–20°C, than the polyacrylates with the corresponding pendant moiety. It may be appropriate to mention here that poly(methyl acrylate) has a T_g of about 10°C, whereas poly(methyl methacrylate), which contain α -methyl group, has very high T_g of about 110°C. However,

Table I TGA, DSC and Polarizing Optical Microscopy Data of the Polymers

Polymer No.	IDT (°C)	DSC			POM	
		T_g (°C)	T_m (°C)	T_i (°C)	LC Phase (°C)	Texture
16	260	95	—	—	—	—
17	243	99	—	—	—	—
18	265	81	195	263	192–265	S
19	260	100	162	250	160–255	S
20	259	60	144	239	145–247	N
21	230	74	98	180	94–181	N
22	255	69	—	202	145–199	N
23	232	72	121	168	116–166	N

IDT, initial decomposition temperature (determined by TGA).

the relatively smaller differences in the T_g values between polyacrylates and polymethacrylates in the present case may be due to the presence of bulky pendant aromatic ester group, which greatly influences the T_g of the polymer.

Poly(ABA) and poly(MBA) have shown phase transitions in the temperature range of 200–255°C and 174–195°C, respectively. Among the polymers **16–23**, poly(PCPA) and poly(PCPMA), the phenyl esters of poly(ABA) and poly(MBA), did not show any mesophases. However, polymers **18–23**, the para-phenyl, phenoxy, and benzoyl group substituted phenyl esters of poly(ABA) and poly(MBA), have shown LC properties in a broad range of temperature. The temperature range of mesophases depends on the nature of the aryl substituent. These observations clearly indicate that the phenoxy-carbonylphenyl [$\text{C}_6\text{H}_5\text{—O—C(=O)—C}_6\text{H}_4\text{—}$] group itself does not act as a mesogen when directly attached to polyacrylate or polymethacrylate backbone. But, the para-arylphenoxy-carbonylphenyl group, [i.e., $\text{Ar—C}_6\text{H}_4\text{—O—C(=O)—C}_6\text{H}_4\text{—}$, where $\text{Ar} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{—O}$ or $\text{C}_6\text{H}_5\text{—C=O}$], acts as a mesogen when attached to polyacrylate and polymethacrylate backbones, even in the absence of a flexible spacer. The crystal–liquid transition temperatures (T_m) of these polymers are lowered by 40–70°C, compared to those of poly(ABA) and poly(MBA). The decrease in the T_m of the ester derivatives may be attributed to the presence of a flexible ester linkage in the pendant unit.

It may be interesting to compare the properties of polymers in which para-aryl-substituted phenyl group is attached to the polymer backbone in different ways. Polymers **18**, **19**, and **26** contain biphenyl unit in the pendant. As such, the rigid biphenyl moiety does not have any propensity to form liquid crystalline phases on its own, as was observed by DSC. It is well known that poly(biphenyl acrylate) and poly(biphenyl methacrylate), in which the biphenyl moiety is directly attached to the poly(meth)acrylate backbone, show liquid crystalline properties. In the present investigation, it was observed that polymer **26**, in which the biphenyl moiety is attached to the polymer backbone via an ethyleneoxy ($\text{—CH}_2\text{CH}_2\text{O—}$) unit, softens at about 95°C and becomes an isotropic liquid at about 175°C without showing any LC phase transitions. However, polymers **18** and **19**, the biphenyl esters of poly(ABA) and poly(MBA), respectively, did exhibit mesophase properties. The DSC thermogram of polymer **19** shows an endotherm at 162°C due to crystal–

liquid crystal phase transition (T_m), and a second endotherm at 250°C corresponding to liquid crystal–isotropic transition (T_i). The transition temperatures noted in DSC thermograms agree well with the mesomorphic transition temperature range (160–255°C) observed with hot-stage coupled polarizing microscopy. The photomicrographs (Fig. 2) taken at different temperatures during the heating cycle of the polymer indicate the smectic texture of the liquid crystals. These observations clearly indicate that the presence of a short ethyleneoxy spacer between the biphenyl unit and polymer backbone hinders the LC arrangements of the laterally substituted biphenyl unit. The DSC and POM studies have shown that poly(BPCPA) (**18**) exhibits LC properties at 192–265°C with T_m and T_i values of 195 and 263°C, respectively. Polymer **19** possesses higher T_g and lower T_i values than polymer **18** with same pendant mesogen group. This may be due to the somewhat rigid nature of the polymethacrylate backbone. Higher T_g , and lower T_m and T_i values for polymethacrylates than the polyacrylates containing the similar pendant mesogenic group have been reported.^{27–29}

Polymers **20**, **21**, **24** and **27** have diphenyl ether unit in the side chain. DSC and POM have shown that polymers **24** and **27**, in which the biphenyl ether unit is attached to the polyacrylate backbone either directly or through an ethyleneoxy unit, did not exhibit mesophase properties. However, polymers **20** and **21**, in which the biphenyl ether moiety is attached as an ester linkage of poly(ABA) or poly(MBA), did show LC properties. The DSC thermogram of polymer **20** shows, in addition to the T_g value of about 60°C, an exotherm at 141°C corresponding to crystallization, and two endotherms at 144 and 239°C due to crystal–liquid crystal transition (T_m) and liquid crystal–isotropic transition (T_i), respectively. POM observations clearly indicate that the polymer shows phase transitions at 145–247°C with nematic texture (Fig. 3). Polymer **21** exhibits LC properties at 94–181°C. The DSC trace of the polymer shows two endotherms at about 98 and 180°C due to crystal–liquid crystal transition (T_m) and liquid crystal–isotropization transition (T_i), respectively.

Polymers **22**, **23**, **25** and **28** contain the benzophenone moiety in the side chain. It was observed that polymers **25** and **28**, in which the benzophenone unit is attached to the polyacrylate backbone either directly or through an ethyleneoxy unit, did not show LC properties. However, when

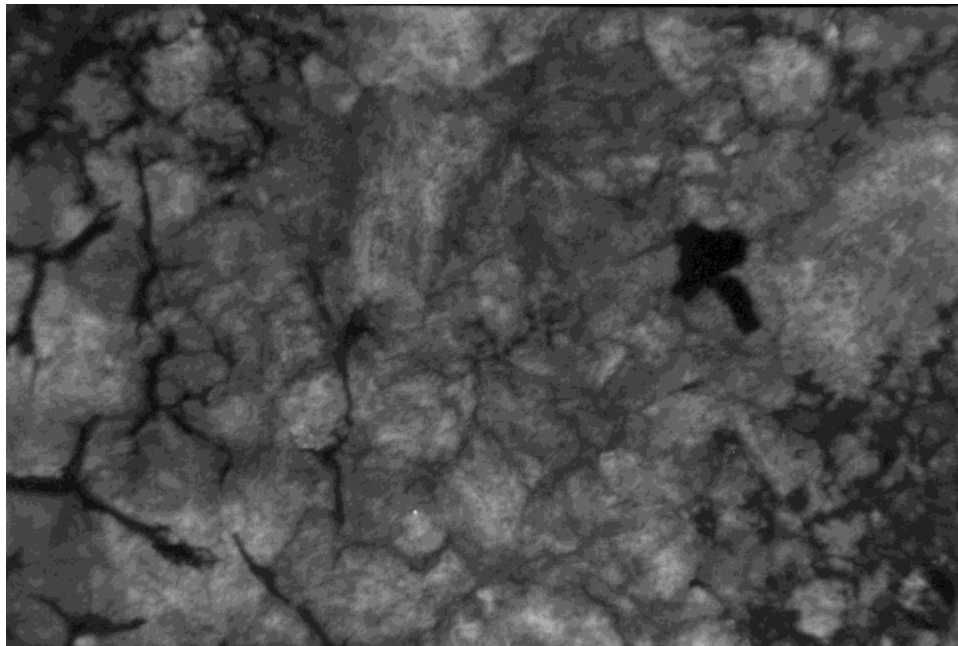


Figure 2 Polarized optical micrograph of poly(BPCPMA) at 210°C.

the same benzophenone unit is attached as an ester linkage of poly(ABA) or poly(MBA) the resulting polymers (**22** and **23**) did show LC properties. The DSC thermogram of polymer **22** shows T_g at 69°C, and an endotherm at 202°C corresponding to liquid crystal-isotropization transi-

tion (T_i). The presence of T_g and absence of crystal- to melting transition (T_m) in the DSC thermogram indicates that the polymer is non-crystalline, more specifically, glassy nematic order. The visual observations under POM (Fig. 4) have revealed that this polymer exhibits phase

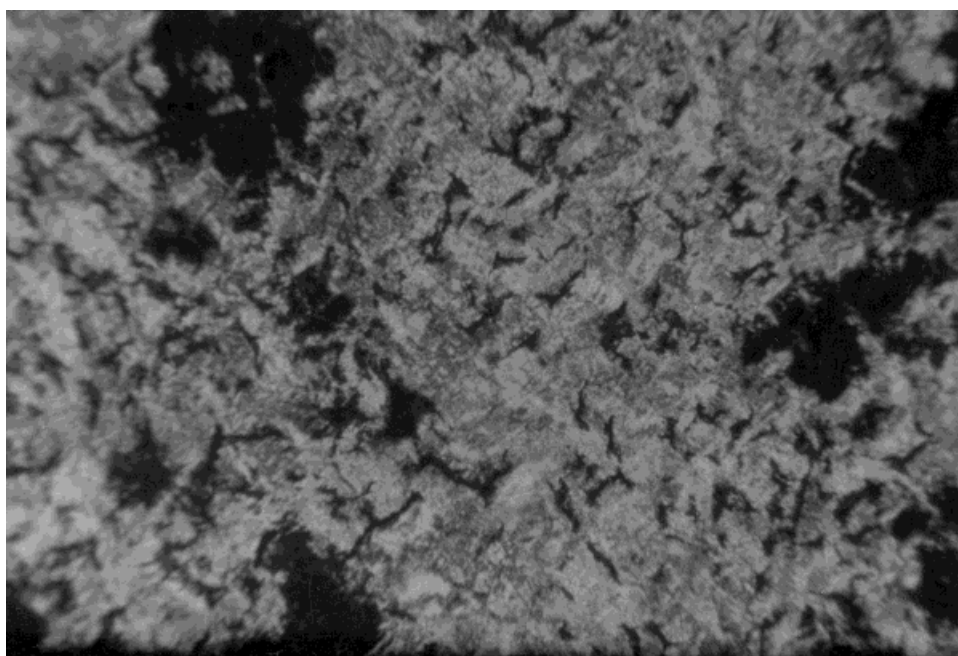


Figure 3 Polarized optical micrograph of poly(PPCPA) at 193°C.

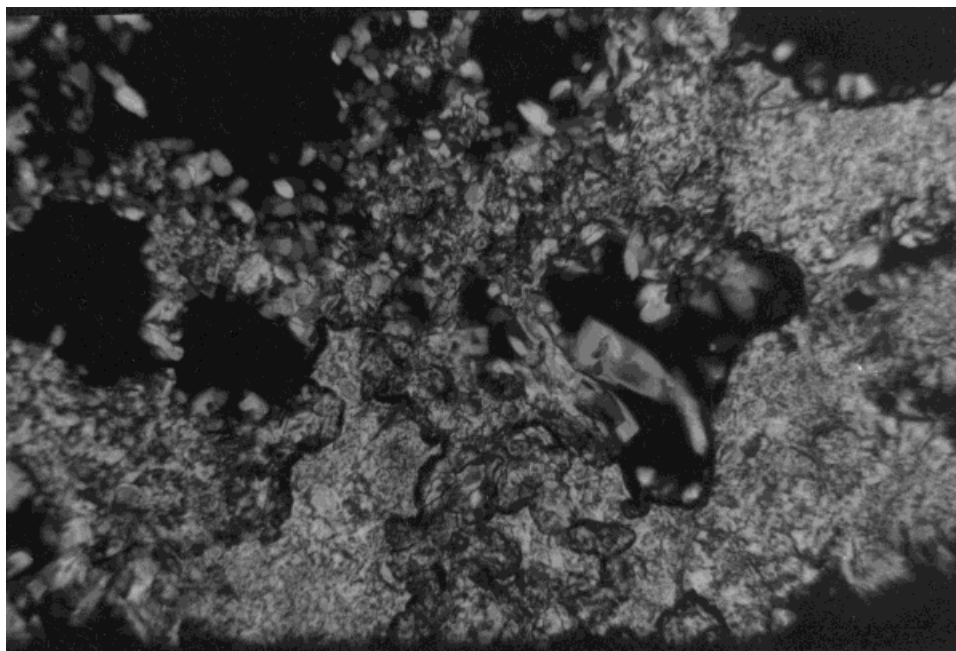


Figure 4 Polarized optical microphotograph of poly(BPOCPA) at 162°C.

transitions at 145–199°C, which clearly supports the DSC data. The DSC trace of polymer **23** contains two endotherms, the first one at 121°C is due to T_m , and the second endotherm at 168°C corresponds to T_i . Consistent with the DSC data, POM observations have clearly indicated LC properties of the polymer at 116–162°C with nematic texture.

Thermogravimetric Analysis

The thermal stability of the polymers was measured by thermogravimetric analysis in air. The thermal decomposition of the polymers starts after the isotropization temperature (T_i). They decompose in a single stage, and the initial decomposition temperatures (IDT) are above 230°C. Polymer **24** has the lowest IDT value of 230°C, where as, polymer **21** possesses the highest IDT value of 265°C.

CONCLUSIONS

The phenoxy-carbonylphenyl [$C_6H_5-O-C(=O)-C_6H_4-$] group does not act as a mesogen when directly attached to polyacrylate or polymethacrylate backbone. But, the para-arylphenoxy-carbonylphenyl [$Ar-C_6H_4-O-C(=O)-C_6H_4-$, where $Ar = C_6H_5, C_6H_5-O,$ or $C_6H_5-C=O$]

group acts as a mesogen when attached to poly-(meth)acrylate backbone, even in the absence of a flexible spacer. The polymers did exhibit phase transitions in a broad range of temperatures compared to those of poly(ABA) and poly(MBA). The crystal-liquid transition temperatures (T_m) of these polymers are lowered by 40–70°C, compared to those of poly(ABA) and poly(MBA), depending on the nature of the aryl substituent. For the same pendant mesogen group, polymethacrylates contain higher T_g and lower T_i compared to the corresponding polyacrylates, owing to the somewhat rigid nature of the polymethacrylate backbone.

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