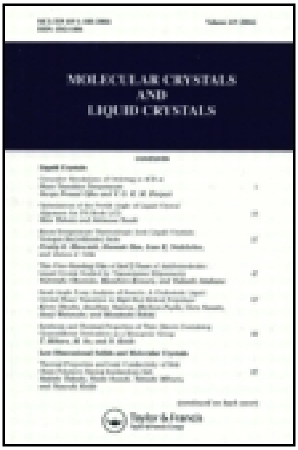

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Side Chain Copolymers Containing Liquid Crystalline and Photoactive Chromophore

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Side Chain Copolymers Containing Liquid Crystalline and Photoactive Chromophore

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Liquid crystalline monomer and photoactive monomers with various structures were synthesized and copolymerized. The resulting copolymers contain fixed LC unit and varying photoactive units. The phase transition temperatures are found to be affected by both comonomer structure and spacer length. The transition temperatures of itaconate bearing copolymer are found to be higher at smaller spacer length.

Keywords: photoactive, liquid crystal, methacrylate, itaconate

INTRODUCTION

Thermotropic side chain liquid crystalline polymers are being studied with great attention due to their potential use as material for data storage systems, piezo-, pyro-, ferro-electric devices and for systems requiring nonlinear optical characteristics[1]. Photoactive materials have unique property of inducing phase transition in adjacent liquid crystals due to their photoisomerization. It was demonstrated that reversible alternation between homeotropic and parallel modes of nematic crystals can be attained by the photoisomerization of azobenzene[2] and stilbene[3] monolayer. Among various approaches to combine the liquid crystalline and photoactive properties the most advantageous one is the synthesis of copolymers. The aim of this work is to synthesize and characterize copolymers based on methacrylate mesogenic monomer and methacrylate/itaconate photoactive monomers and study the phase transitions.

EXPERIMENTAL

p-Methoxyphenyl, p'-methacryloyloxy hexyloxy benzoate (M I): This monomer was synthesized by following the method of Horvath et. al.[14].

2-Methyl-acrylic acid 6-{methyl-[4-(4-nitro-phenyl azo)-phenyl]-amino}-hexyl ester (M II): This was synthesized by first reacting N-methyl aniline with 6-chloro-1-hexanol in presence of K_2CO_3/KI in ethanol. The product was then reacted with 4-nitrobenzenediazonium tetrafluoroborate in acetic acid medium. The azo alcohol so obtained was reacted with methacryloyl chloride in presence of triethylamine in THF to get the final monomer.

2-Methylene-succinic acid bis (2-{4-[2-(4-nitrophenyl)-vinyl]-phenoxy}-hexyl) ester (M III): It was synthesized by first reacting 4-hydroxy benzaldehyde with 6-chloro-1-hexanol in presence of K_2CO_3/KI in ethanol. The product was further reacted with 4-nitrophenyl acetic acid in presence of piperidine in ethanol. The monomer was synthesized from this product by direct esterification of itaconic acid in toluene using Dean-Stark apparatus in presence of sulphuric acid/p-toluene sulfonic acid as catalyst.

2-Methylene-succinic acid bis[2-(methyl-{4-[2-(4-nitrophenyl)-vinyl]-phenyl}-amino)-ethyl] ester (M IV): This monomer was synthesized by first reacting N-methyl ethanol amine with 4-fluoro benzaldehyde in presence of K_2CO_3/Aliquat 336 in DMSO. The product so obtained was reacted with 4-nitrophenylacetic acid in presence of piperidine in ethanol. Finally the monomer was obtained from this product after reacting with itaconic acid in THF by using Mitsunobu reaction. The catalyst used were diisopropyl azodicarboxylate (DIAD) and triphenyl phosphine.

Copolymers were prepared by radical polymerization in the presence of AIBN at feed mole ratio of 1:1. FT-IR, NMR, DSC, and optical microscope were used for characterization.

RESULTS AND DISCUSSION

All the copolymers are freely soluble in common organic solvents such as THF, chloroform, acetone etc. The phase transition data are presented in Table I.

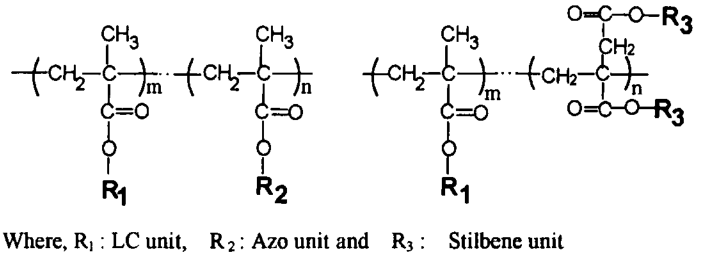

FIGURE 1. Representative copolymer structures.

TABLE I. Phase transition temperatures of monomers and copolymers.

Sample	Monomer/copolymer type	Spacer length (no. of CH_2 unit)	Phase transition Temperature (°C)
M I	Methacrylate LC	6	K 37 N 50 I
M II	Methacrylate Azo	6	K 50 S 103 I
M III	Itaconate Stilbene	6	K 70 N 110 I
M IV	Itaconate Stilbene	2	K 112 S 141 I
CP I	Meth. LC/Meth. Azo	6/6	G 40 S 72 I
CP II	Meth. LC/Itaco. Stilbene	6/6	G 65 N 108 I
CP III	Meth. LC/Itaco. Stilbene	6/2	G 75 N 118 I

It can be observed that LC monomer has narrow temperature range of LC phase whereas that of photoactive monomers are relatively wide. The transition temperatures of itaconate bearing copolymers are found to be higher than that of methacrylate bearing copolymers. As expected, T_g and T_i of the copolymer, having stilbene attached via short spacer, are higher than that attached via long spacer. However, there is drastic reduction of T_i in the case of short spacer. This may be due to dissimilar structure and spacer length of LC and photoactive units. Figure 2 shows the representative LC textures of the monomers and polymers. Methacrylate azo and Itaconate stilbene monomers have shown smectic texture. The copolymer containing short spacer has shown nematic LC phase. The appearance of LC phase may be due to influence of LC nematic comonomer. The LC textures remain embedded in the glassy phase. LC temperature span of CP II and CP III are similar in spite of the difference in spacer length. However, the span is higher than CP I.

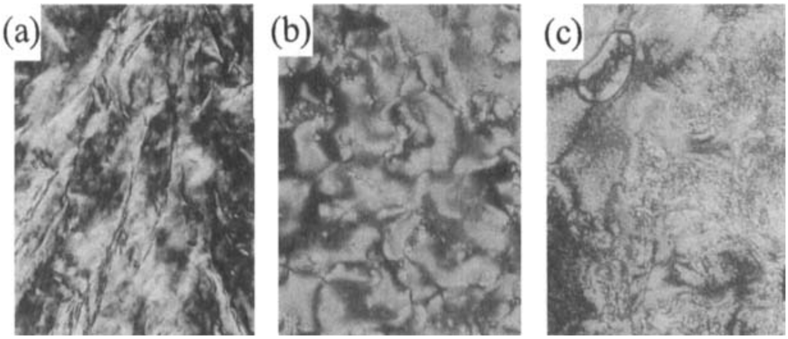

FIGURE 2. Optical micrographs of monomer and copolymer
(a) M I at 31°C; (b) M III at 35 °C; (c) CP II at 70 °C.
(See Color Plate I).

Acknowledgments

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Reference

[1.] C. B. McArdle in Side-chain Liquid Crystal Polymers, (ed), Blackie, Glasgow, 1989.

[2.] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, and K. Aoki, *Langmuir*, 4, 1214 (1988)

[3.] K. Aoki, K. Ichimura, Y. Suzuki, T. Seki, Y. Kwanishi, and T. Tamaki, *Kobunshi Ronbunshu*, 47, 771 (1990)

[4.] J. Horvath, K. Nyitrai, F. Cser, and GY. Hardy, *Eur. Polym. J.*, 21(3), 251 (1985).