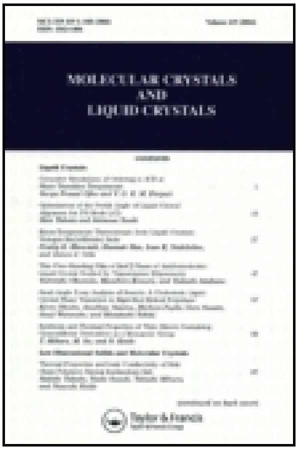


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Copolymerization Effects of Non-Mesogenic Components on the Characteristics of Liquid Crystalline Side-Chain Polymers

R. Akashi [a] & A. Inoue [a]
[a] Materials Research Laboratory, Fuji Xerox Co. Ltd., 1600 Takematsu Minamiashigara-shi Kanagawa-ken, 250-01, Japan
Version of record first published: 24 Sep 2006.

To cite this article: R. Akashi & A. Inoue (1994): Copolymerization Effects of Non-Mesogenic Components on the Characteristics of Liquid Crystalline Side-Chain Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 250:1, 269-284

To link to this article: http://dx.doi.org/10.1080/10587259408028212

Mol. Cryst. Liq. Cryst., 1994, Vol. 250, pp. 269–284
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Copolymerization Effects of Non-Mesogenic Components on the Characteristics of Liquid Crystalline Side-Chain Polymers

R. AKASHI and A. INOUE

Materials Research Laboratory, Fuji Xerox Co. Ltd. 1600 Takematsu Minamiashigara-shi Kanagawa-ken 250-01 Japan

(Received August 9, 1993; in final form November 9, 1993)

The effects of copolymerization with non-mesogenic components on liquid crystalline side-chain polymers (LCSP) were studied from the point of view of improvements of thermal and electro-optical characteristics in applications to display and recording devices. LCSPs were designed and synthesized from cyanobiphenyl acrylate monomers with two different alkyl-oxy spacer lengths (C6 or C11/abbreviated as 6CBA and 11CBA, respectively) and from various acrylate or methacrylate monomers. Micro-phase separation phenomena were observed in polymers having non-mesogenic components. The effects of copolymerization of acrylate non-mesogenic monomer (NMM) were compared with those of methacrylate NMM on these phenomena. The results indicate that the degrees and stabilities of micro-phase separation of copolymers consisting of methacrylate NMM were observed to be higher than those with acrylate NMM. Stabilities of the mesophase of individual mesomorphic droplets were found to decrease with increasing non-mesogenic monomer content. This unstabilized effect was found to be more pronounced in LCSP with acrylates as the NMM component than in those with methacrylates. All the LCSPs except the 11CBA homopolymer were found to respond to an applied electric field.

Keywords: Liquid crystalline polymer, micro-phase separation, copolymer, recording device

INTRODUCTION

Liquid crystalline side-chain polymers (LCSP) are functional materials of great interest because they have electro-optical characteristics similar to those of low molecular weight liquid crystals, they are self-supporting, and because their orientational order can be frozen in the glassy state showing a memory effect. Applications of LCSP to various fields, such as display or optical memory devices, alignment films, non-linear optics, wave-guides or to optical compensators have been proposed and demonstrated.[1–4]

It is well known that structural factors, such as the kind of mesogen, polar substituents, backbone and alkyl spacer length, affect the electro-optical properties and the mesomorphic characteristics of LCSP.[5,6] Although studies of these structural effects have mostly involved homopolmers,[6] several attempts have been reported on copolymers consisting of side chains of different mesogens, pleochroic dyes,[7,8] or photoreactive (photochromic) substituents.[9,10] In these copolymers, such substituents on the side chains were found to behave similarly to mesogens, i.e., they aligned in the same direction as mesogenic groups in an electric field or magnetic field.

In the present paper, the copolymerization effects of non-mesogenic monomers (NMM) on LCSP were studied from the point of view of phase transition behaviors and electro-optical characteristics. The idea behind the present approach using copolymers consisting of NMM comes from the analogy to polymer-dispersed liquid crystals (PDLC), where the liquid crystal (LC) domain size is controlled by the relative content of LC vs. polymers.[11,12] In LCSPs the mesogenic groups assemble and form LC domains. It is expected that the sizes of such LC domains can also be controlled by introducing NMM in the LCSP. Since the LC domain size is considered to be closely related to light scattering ability and electric field response, this attempt might be an effective method for expanding the field of applications as well as broadening the latitude of molecular design of LCSP in electro-optical applications. There are only a few reports concerning copolymers consisting of both mesogenic and NMM, and no detailed investigations have been made of the electro-optical properties of such LCSPs.[11-16]

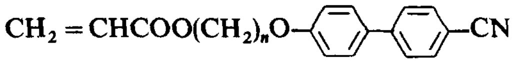
EXPERIMENTAL

(1) Preparation of Monomers and Polymers

Cyanobiphenylacrylate monomers with two kinds of alkyl spacer lengths were synthesized in a process similar to that described in the literature.[5] The molecular formulas of mesogenic monomers employed in this study are shown below. Hereafter, mesogenic monomers are abbreviated as nCBA, where n, CB, and A denote the length of the alkyl spacer, cyanobiphenyl and acrylate, respectively.

Polymers were synthesized by conventional free-radical polymerization by the following procedure: monomer concentration 0.4 g/ml; solvent THF; initiator AIBN (concentration: 8×10^{-4} g/ml); temperature 60°C; polymerization time 48 Hr. Polymers were obtained in 95% yield after purification by precipitation of the crude polymers in ethanol several times and drying in vacuo.

Copolymers with various compositions of mesogenic and non-mesogenic components were synthesized similarly via copolymerization of mixtures of mesogenic monomers and some acrylate or methacrylate monomers. The copolymers thus obtained are assumed to have random monomer sequences, the same as conventional acrylate-methacrylate copolymer systems.[17] Such monomers as methylacrylate(MA), ethylacrylate(EA), butylacrylate(BA), 2-ethylhexylacrylate(EHA), methylmethacrylate(MMA), ethylmethacrylate(EMA), butylmethacrylate(BMA), 2-ethylhexylmethacrylate(EHMA) and dodecylmethacrylate(DMA) were used in the copolymerization as NMM. These monomers were purchased from Tokyo-kasei Co. and purified by distillation in vacuo.



n = 6:6CBA n = 11:11CBA

Structural formula of mesogenic monomers

TABLE I

Typical Copolymer Compositions and Phase Transition Temperatures

Sample	Copolymer composition Wt-% of non-mesogenic unit	Phase transition temp. in °C
poly (6CBA)	0	g 35 s, n 122 i
6CBA-BA-5	5	g 32 n 93.4 i
6CBA-BA-10	10	g 23 meso 83 i
6CBA-BA-20	20	g 17 meso 48 i
6CBA-BMA-5	5	g 33 meso 113 i
6CBA-BMA-10	10	g 34 meso 114 i
6CBA-BMA-20	20	g 34 meso 101 i
poly(11CBA)	0	g 22 s 147 i
11CBA-EHA-5	5	g 14 s, n 131 i
11CBA-EHA-10	10	g 12 s, n 123 i
11CBA-EHA-20	20	g 5 meso 92 i
11CBA-EHMA-5	5	g 15 s, n 138 i
11CBA-EHMA-10	10	g 15 meso 135 i
11CBA-EHMA-20	20	g 13 meso 131 i

meso: mesophase (kinds of phase were not determined)
g: glassy state; i: isotropic liquid state; s: smectic state; n: nematic state

(2) Analysis

The molecular weight and composition of the copolymers were determined using TOSO HLC-802A Gell permeation chromatography (GPC) and a Varian UNITY300 ^{1}H NMR spectrometer. The molar compositions of most copolymers were analyzed to be almost the same as the initial monomer composition ratio, indicating polymerization conversions of approximately 100%. The average molecular weights (*Mw*) of most polymers were 20000–40000. Phase transition temperatures of *Tg* (glass transition temperature) and *Ti* (mesophase and isotropic liquid phase) were located by means of a Shimazu DSC (differential scanning calorimeter) and textures of mesophases were inspected by a Nikon OPTIPHOT-POLXP-11 polarized microscope with a Metller FT82HT thermal control system.

The mesomorphic properties of the homopolymers and typical copolymers employed in this study are summarized in Table 1. In this table, copolymers of mesogenic monomer (nCBA) are denoted as nCBA-BA-x or nCBA-BMA-x where x indicates the contents of BA or BMA in wt%.

(3) Electro-Optical Measurements

The LCSP cell configuration and procedure for electro-optical measurements are represented schematically in Figure 1. An LCSP layer ~30 μm thick, is laminated between two conductive ITO-coated glass plates. The electro-optical responses were evaluated using the cells as transmission changes with homeotropic alignment. The cells were heated at a temperature above the *Ti* and then cooled under AC of $5 \sim 100\ V_{rms}/50$ Hz. The orientational behavior of the mesogenic molecules was investigated by inspecting the conoscopic figures using a polarized microscope.

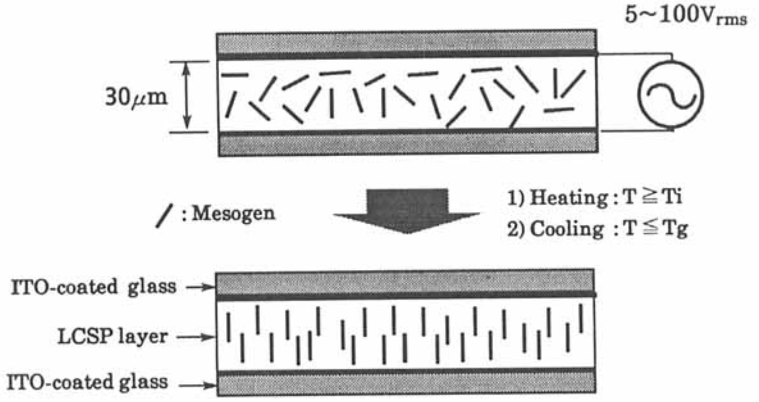


FIGURE 1 Schematic cell configuration and procedure of electrical response measurement.

RESULTS AND DISCUSSION

(1) Mesomorphic Behavior

6CBA system

Photographs through a polarized microscope of the 6CBA homopolymer and typical copolymers at temperatures immediately below the phase transition temperature from isotropic to mesophase are shown in Figures 2a–2d. In the homopolymer (Figure 2a) a multi-domain pattern is observed. Each mesomorphic domain is relatively large (~100 μm) and exhibits the Schlielen texture, indicating that they are of the nematic phase. This observation is consistent with those in the literature.[5] Upon copolymerization with NMM (Figures 2b–2d), the number of domains were found to increase drastically with a concomitant decrease in domain size as the NMM content increases. This phenomenon was observed in the cases where butyleacrylate(BA) or butylmethacrylate(BMA) were introduced as NMMs, the effect being more pronounced in the latter.

The phenomenon in the above copolymers in which the mesomorphic domain decreases in size with increasing NMM content can be attributed to extensive micro-phase separation induced by copolymerization. In such systems of micro-phase separation, existence of two separate *Tg*'s might be observed. In the present cases, however, only single *Tg*'s were obtained, which may be because *Tg*'s are not well resolved. In the systems with large NMM content *Tg*'s become larger due to the interaction among less flexible segments. In LCSP, the mesogenic groups assemble themselves and form mesomorphic domains. These mesomorphic domains are split into smaller droplets with the introduction of NMM as is the case with PDLC.[11,12] Here the NMM plays the role of polymer network in PDLC. According to these pictures, the effect of micro-phase separation is larger when methacrylate NMM are introduced than with the acrylate type.

In copolymer systems including acrylate NMM such phase separation patterns were found to change as the specimens were annealed: Mesomorphic droplets were assem-

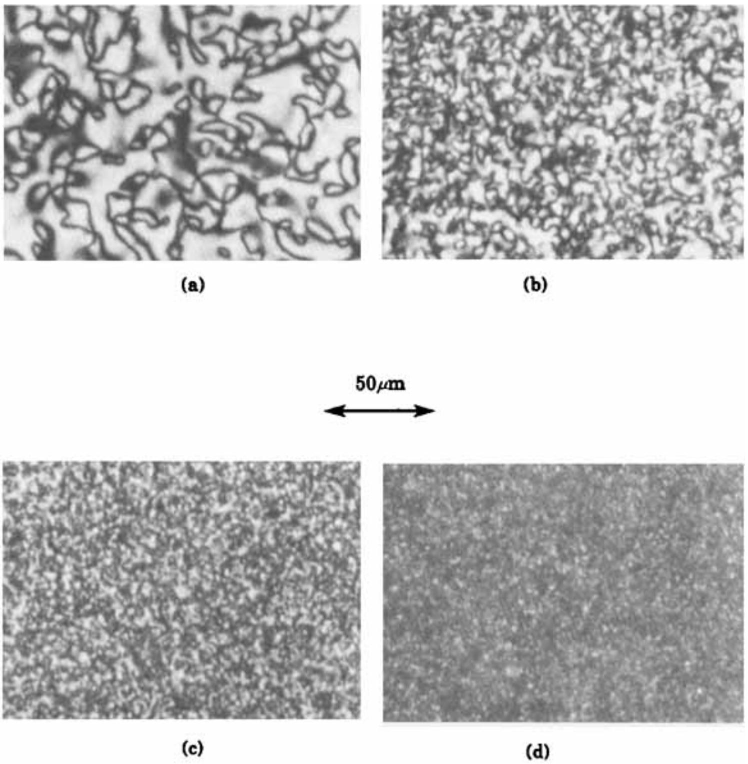


FIGURE 2 Photographs through a polarized microscope: (a) poly(6CBA), (b) 6CBA-BA-5, (c) 6CBA-BA-10, (d) 6CBA-BA-20.

bled to form larger droplets upon annealing. On the other hand, the patterns are stable in methacrylate NMM systems.

Ti's and *Tg*'s were measured in these copolymers as a function of NMM content and are shown in Figures 3a–3d. These transition temperatures vs. NMM content were plotted separately with units of molar % and weight % in order to investigate the effect of kind and size of substituent group on the NMM. These plots show the relative compositions of monomeric unit number and weight content of mesognic monomer and NMM in the copolymers respectively. Analysis of these phase diagrams leads to the following simple points:

1. In all the phase diagrams, the *Ti*'s are higher in copolymers containing methacrylate NMM than in those with the acrylate type. (see Figures 3a and 3b).
2. In the wt % plot, the *Ti* vs. NMM content curve (Figure 3a) is insensitive to the kind of NMM, i.e., the alkyl chain length in the acrylate, while in the methacrylate system (Figure 3b) there is a tendency for *Ti* to be higher with longer alkyl side chain length.
3. The molar % plot of the acrylate systems (Figure 3c) indicates that the mesophase becomes less stable (*Ti*'s are lower) as the alkyl side chain increases in size, while in

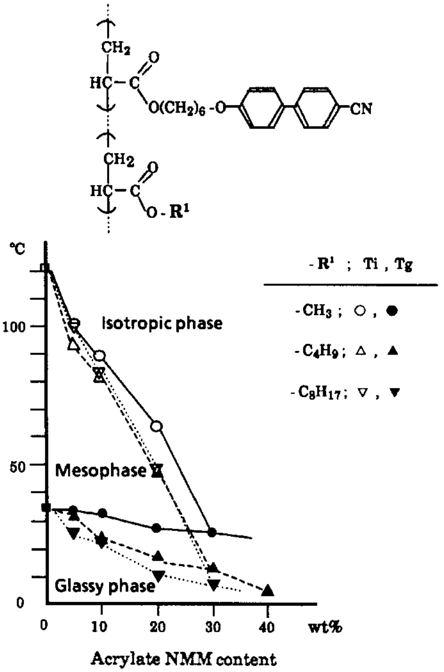


FIGURE 3a Relationships between phase transition temperature and acrylate NMM content in wt %.

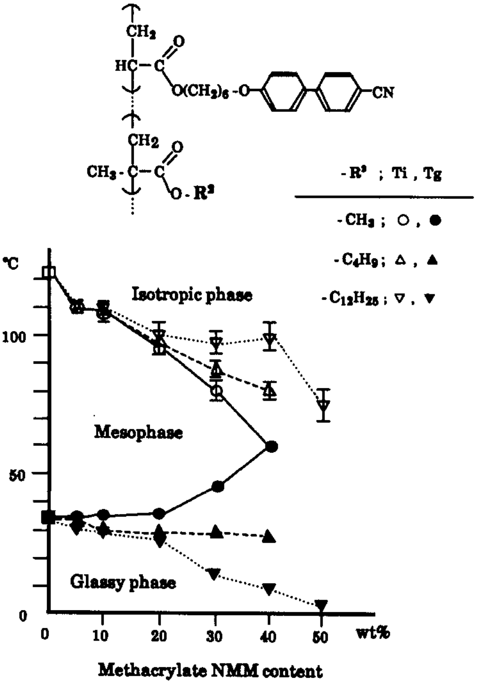


FIGURE 3b Relationships between phase transition temperature and methacrylate NMM content in wt %.

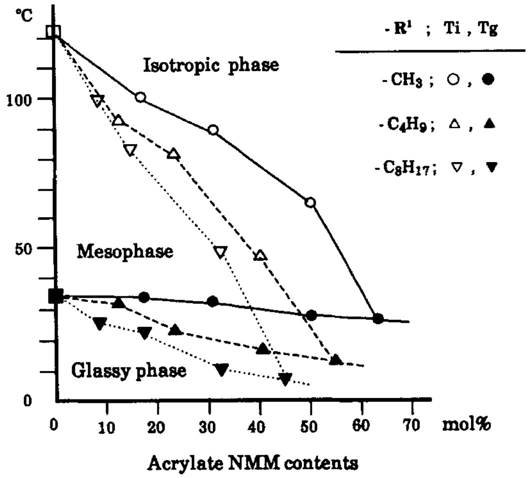


FIGURE 3c Relationships between phase transition temperature and acrylate NMM content in mol %.

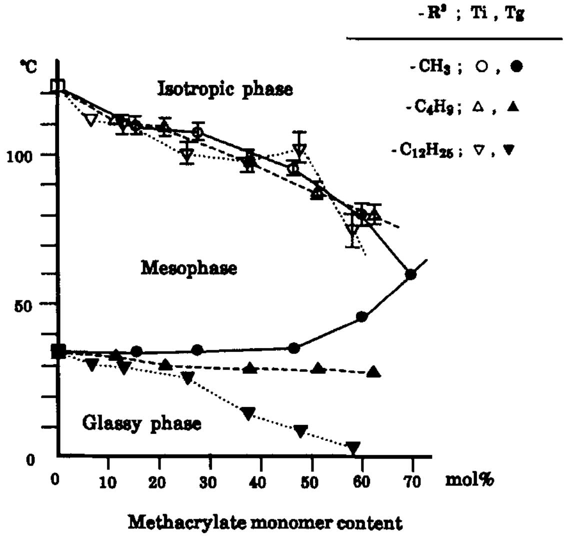


FIGURE 3d Relationships between phase transition temperature and methacrylate NMM content in mol %.

the methacrylate system, the *Ti*'s are much less sensitive to the kind of alkyl side chain in the NMM.

The above-mentioned difference in the phase diagram between copolymers composed of acrylate and methacrylate as NMM can be interpreted based on the following reasoning:

In the acrylate NMM system, micro-phase separation is highly dependent on the length of the alkyl chain, while in the methacrylate NMM system, the micro-phase

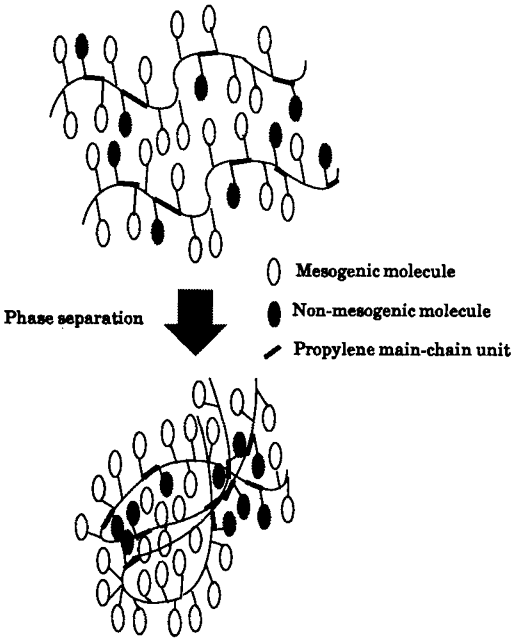


FIGURE 4a Phase separation mechanism of methacrylate NMM system.

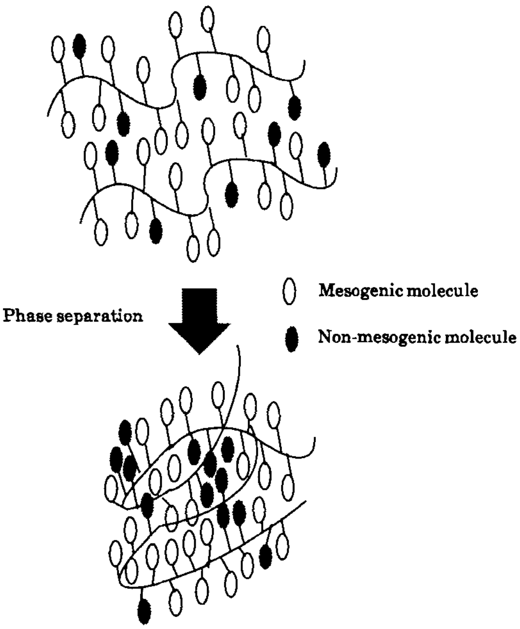


FIGURE 4b Phase separation mechanism of acrylate NMM system.

separation process is not sensitive to the size of the alkyl chain. This difference can be attributed to the difference in the micro-phase separation mechanism. Models for the micro-phase separation are schematically represented in Figures 4a and 4b for the cases of copoly-merization between 6CBA and methacrylate or acrylate as the NMM. When metha-crylate NMMs are copolymerized, The LCSP has a main chain composed of acrylate and methacrylate. Since the ester group is common to both main chain components, the interaction of ethylene and propylene units is considered to play an essential role in main chain dynamics (the propylene unit is shown by thick lines in Figure 4a). Thus, these two kinds of units are very different in chain dynamics, manifesting, e.g., the large difference in the Tg of poly(methylmethacrylate) and poly(methylacrylate), 383 K and 300 K respectively.[18] The characteristics of micro-phase separation will be mainly determined by main-chain dynamics in copolymers composed of methacrylate as the NMM (Figure 4a). On the other hand, when only the acrylate monomer is copolymerized, the main chain is comprised simply of a polyethylene backbone, and the micro-phase separation process may be controlled by interaction among mesogenic and non-mesogenic alkyl side chains (Figure 4b). In this case, only the instability of the mesophases (decrease in *Ti*) is supposed to take place due to the interaction of the NMM side chains with mesogenic molecules (a solution of the non-mesogenic moiety into mesomorphic droplets).

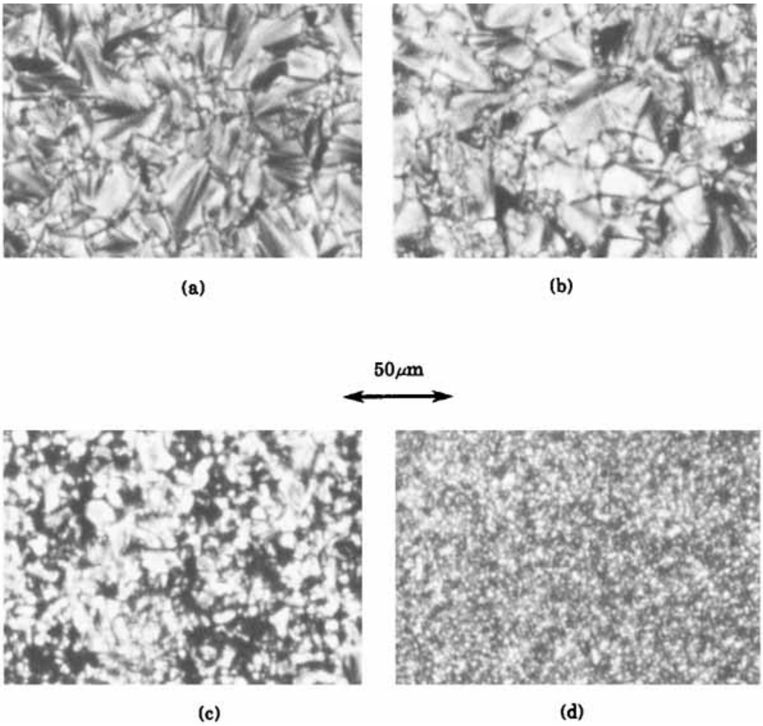


FIGURE 5 Photographs through a polarized microscope: (a) poly(11CBA), (b) 11CBA-EHA-5, (c) 11CBA-EHA-10, (d) 11CBA-EHA-20. See Color Plate XI.

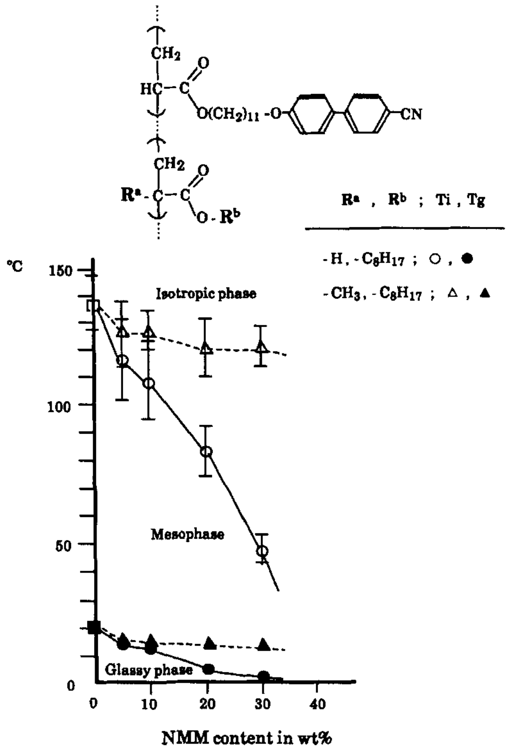


FIGURE 6 Relationships between phase transition temperatures and NMM content in wt % on 11CBA system.

11CBA system

Polarized microscopic pictures of 11CBA copolymers (11CBA-EHA, where EHA stands for ethylhexylacrylate) and homopolymer at temperatures immediately below *Ti* are shown in Figures 5a–5d. The homopolymer of 11CBA shows a typical focal conic fan texture and was determined to be of the smectic phase[5] (Figures 5a). Similar to the 6CBA system, introduction of a non-mesogenic component induces micro-phase separation (Figures 5b–5d). The domain sizes of the mesomorphic droplets seemed to be small, maintaining the smectic phase. In the case of copolymers consisting of large amounts of NMM, it was difficult to determine the kind of mesophase since the droplet sizes were very small.

In the 11CBA system, the degrees and stabilities of micro-phase separation were also found to be more pronounced in copolymers with methacrylate NMM than with acrylate NMM as was true of the 6CBA system.

A phase diagram for the 11CBA copolymer system with EHA and EHMA as NMM is shown in Figure 6. This figure shows that the tendency is similar to those of 6CBA systems.

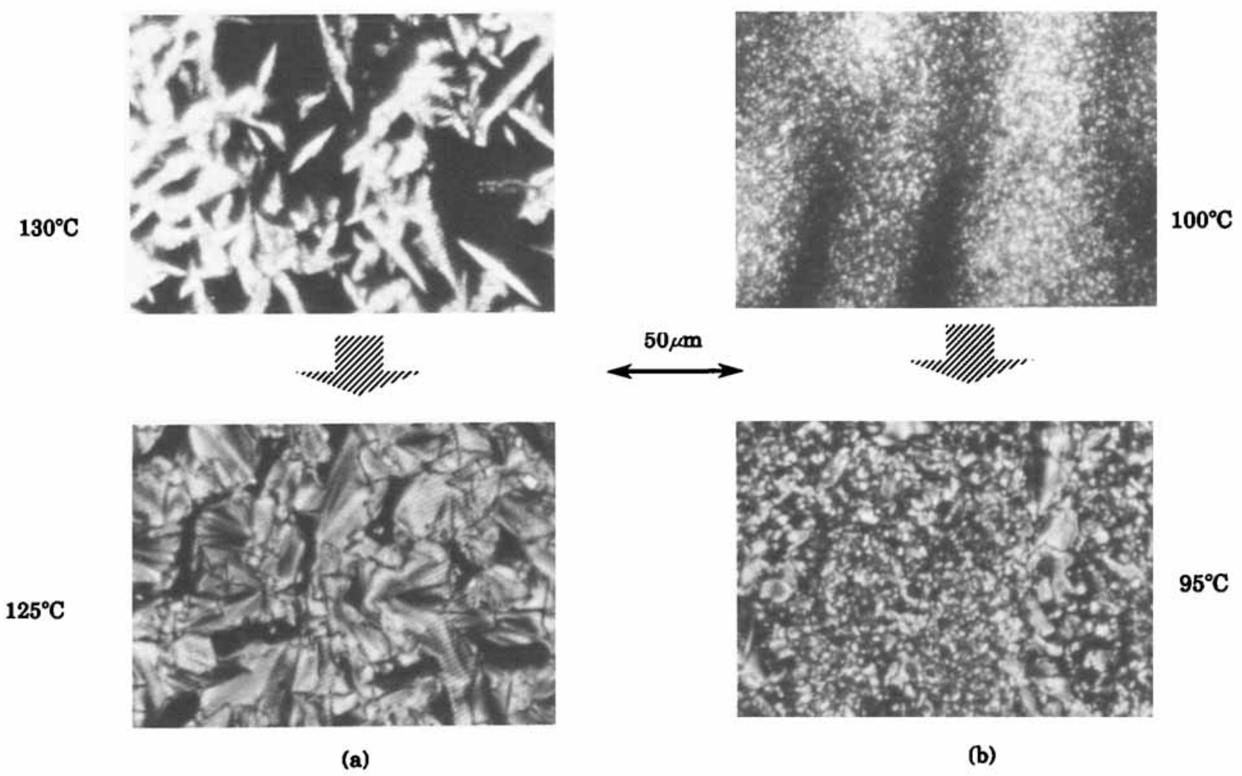


FIGURE 7 Changes of textures of LCSPs of 11CBA system by lowering temperature from immediately below Tis to lower temperatures: (a) poly(11CBA); (b) poly(11CBA-EHA-10). See Color Plate XII.

Changes in the mesophases of homopolymers and copolymers (11CBA-EHA-10) were carefully inspected at temperatures from immediately below *Ti* down to lower temperatures. Figures 7a and 7b depict photographs taken with a polarized microscope. In the homopolymer system (Figure 7a), the transition from a batonnet texture to a focal conic fan texture was observed, indicating that the smectic phase is formed just below the *Ti*. On the other hand, in the copolymer a transition from schlielen to focal conic fan texture was observed (Figure 7b), indicating that the transition takes place from the isotropic to the smectic phase through the nematic phase. The region of the nematic phase, however, is so narrow that we could not locate definite transition temperature of T_{SN}. In the case of copolymers having NMM content more than 10%, mesophase regions were so small that we could not observe clear nematic phase. Precise measurements of transition temperature is needed.

(2) Electro-Optical Responses

6CBA system

Figure 8 depicts a plot of transparency vs. NMM content measured with the method mentioned in the experimental section. In the 6CBA system, relatively high saturated transparencies were observed at NMM content up to 20 wt %. Conoscope images of LCSP at NMM concentration from 0 to 20 wt % show isogya images, which indicate that these LCSPs are of homeotropic alignment. However, the conoscopic images of copolymers with NMM were found to be somewhat disturbed (Figure 9b) compared with those of the homopolymer (Figure 9a). In spite of these disturbances of alignment, the copolymers showed high optical transparency. This phenomenon can be attributed either to interfacial disorder caused by micro-phase separation or to internal microscopic disorder within the mesomorphic droplets.

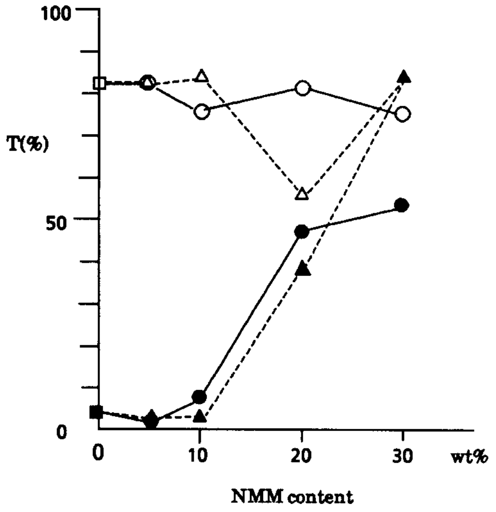


FIGURE 8 Electrical responses as function of NMM content: 6CBA-BA system (▲: initial; △: after application of electric field of 30 V) 6CBA-BMA system (●: initial; ○: after application of electric field of 30 V).

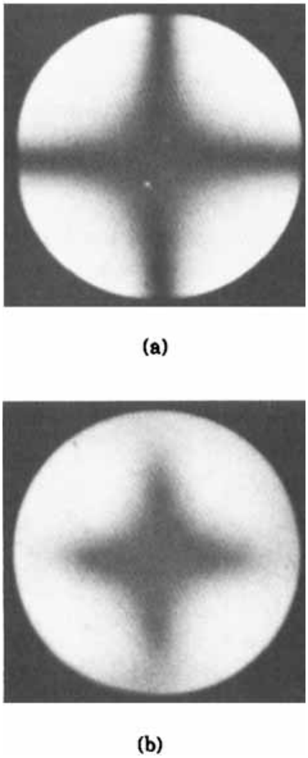


FIGURE 9 Conoscopic images of: (a) poly(6CBA), and (b) 6CBA-BMA-10. See Color Plate XIII.

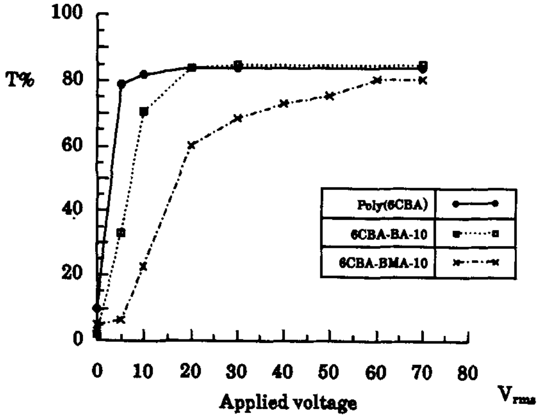


FIGURE 10 Relationships between light transmittance and applied voltage. See Color Plate XIII.

The electric field dependence of transparency in 6CBA systems (poly(6CBA), 6CBA-BA-10, and 6CBA-BMA-10) was measured. Typical field dependence curves of 6CBA systems are shown in Figure 10. The electric field strength attaining saturated transmission was found to be higher for the copolymer than for the homopolymer, especially in the case of the methacrylate NMM system, where much higher voltage was necessary for alignment. This behavior may be attributable to higher viscosity in the mesomorphic state. In the case of acrylate systems, a decrease in dielectric anisotropy or steric hindrance of NMM may be another cause. Further investigations are needed in order to elucidate the causes of the changes in the electro-optical behavior of the LCSPs.

11CBA system

The electric field responses of transparency in the 11CBA system were also measured and are shown in Figures 11 and 12. The homopolymer of 11CBA was *found not to be aligned* by the external electric field at electric fields up to 100 V. Copolymers with

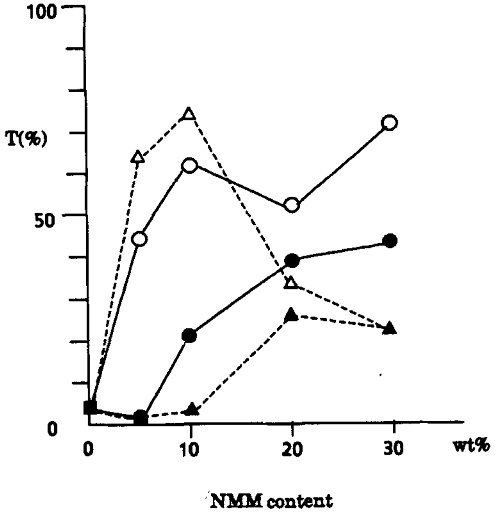


FIGURE 11 Electrical responses as function of NMM content in 11CBA system: 11CBA-EHA system (▲: initial; △: after application of electric field of 60 V), 11CBA-EHMA system (●: initial; ○: after application of electric field of 60 V).

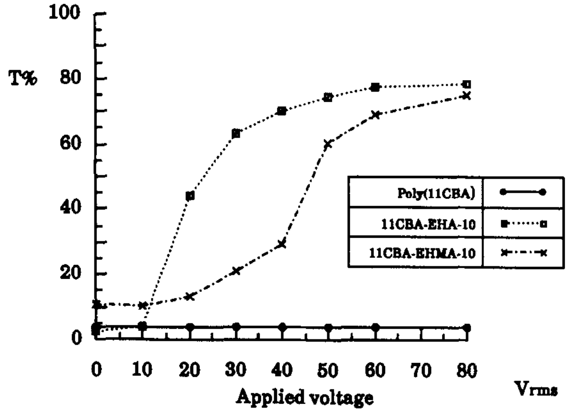


FIGURE 12 Relationship between light transmittance and applied voltage.

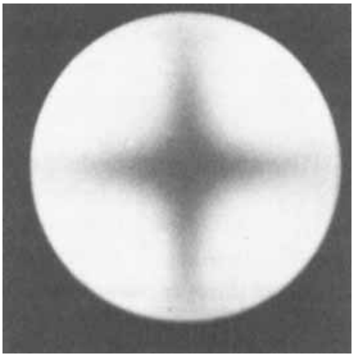


FIGURE 13 Conoscopic image of 11CBA-EHA-10. See Color Plate XIV.

NMM, on the other hand, could be aligned at electric fields as low as 50 V. Conoscopic images of the copolymer samples with NMM content of 5–20 wt % indicate that uniform homeotropic alignment is attained in these copolymers, a typical conoscopic image being shown in Figure 13. The electric field dependence on optical transmission in the 11CBA system shows that the electric field strength needed for saturated transmission of 11CBA systems was found to be much higher than those of 6CBA systems (Figure 12). Also, similar to the 6CBA system, the applied voltage was higher in copolymers, including methacrylate as the NMM than in the acrylate type.

The absence of electric field response of the 11CBA homopolymer is attributed to the large viscosity of the smectic A phase. A relatively large electric alignment effect in the copolymer system may be due to the existence of the nematic phase (Figure 7b), which is of lower viscosity, and/or to relaxation of packing of the mesogenic moiety. However, the electrical responses of the 11CBA systems were lower than those of 6CBA and are thus attributed to the above mentioned factors.

In a low molecular weight liquid crystal system, several mesogenic compounds are mixed in order to improve the electro-optical properties. In the case of LCSPs, low molecular weight liquid crystals were sometimes added to improve their electro-optical characteristics.[19] To the best of our knowledge, no attempts have been reported in which LCSP properties especially in electro-optical responses, can be improved by copolymerization of a non-mesogenic component, i.e., mesomorphic properties can be controlled by the kinds and contents of non-mesogenic molecules. We believe that the present approach of designing LCSPs will result in LCSPs with improved performance for applications to various devices.

CONCLUSION

The effects of copolymerization with non-mesogenic components on LCSP were investigated from the point of view of mesomorphic properties and electrical responses.

An extensive micro-phase separation effect was found to occur upon introduction of the NMM. The micro-phase separation behavior and mesomorphic stability were found to depend critically on the kind and content of the NMM employed. Copolymers consisting of methacrylate NMM showed a higher degree of phase separation and stability of the mesophase than those including acrylate NMM. These differences were interpreted in terms of differences in the phase separation mechanism of these two copolymer systems.

Electrical alignment of LCSP homopolymers and copolymers were investigated and analyzed from the viewpoint of mesomorphic characteristics. All the LCSPs except the 11CBA homopolymer were found to respond to an external electric field in the mesomorphic phases. Because copolymers of 11CBA including NMM respond to a moderate external electric field, we think copolymerization with NMM is a powerful tool for improving the electro-optical characteristics of LCSPs.

The above-mentioned results indicate that chemical modification of LCSP by the introduction of non-mesogenic components is an effective method for improving their properties and to providing more latitude for molecular design of LCSPs.

References

1. V. P. Shibaev, S. G. Kostrimin, N. A. Plate, S. A. Ivanov, V. Yu. Vetrav and I. A. Yakovlev, *Polym. Commun.*, **24**, 364 (1983).
2. T. Nakamura, T. Ueno and C. Tani, *Mol. Cryst. Liq. Cryst.*, **169**, 167 (1989).
3. T. Ueno, T. Nakamura and C. Tani, *Preprints Japan Display' 86*, 290 (1986).
4. H. Finkelmann, D. Naegele and H. Ringsdorf, *Makromol. Chem.*, **180**, 803 (1979).
5. V. P. Shibaev, S. G. Kostromin and N. P. Plate, *Eur. Polym. J.*, **18**, 651 (1982).
6. G. W. Gray, W. D. Hawthorne, J. S. Hill, D. Lacey, M. S. K. Lee, G. Nestor and M. S. White, *Polymer*, **30**, 964 (1989).
7. H. Ringsdorf and H.-W. Schmidt, *Makromol. Chem.*, **188**, 1355 (1987).
8. H.-W. Schmidt, *Angew. Chem. Int. Ed. Engl. Adv. Mater.*, **28**, 940 (1989).
9. I. Cabrera, V. Krongauz and H. Ringsdorf, *Mol. Cryst. Liq. Cryst.*, **155**, 221 (1988).
10. M. Eich and J. H. Wendorff, *Makromol. Chem. Rapid. Commu.*, **8**, 59 (1987).
11. J. L. Fergason, A. Dalisa, S. Lu and P. Drzaic, *SID'86 Tech. Digest*, 126 (1986).
12. Paul S, Drzaic, *J. Appl. Phys.*, **60**, 2142 (1986).
13. A. Hirai, G. R. Mitchell and F. J. Davis, *New Polymeric Mater.*, **1**, 251 (1990).
14. K. H. Al-Ammar and G. R. Mitchell, *Polymer*, **33**, 11 (1992).
15. M. Hefft and J. Springer, *Makromol. Chem., Rapid Commun.*, **11**, 397 (1990).
16. H. Richard, M. Mauzac, G. Sigaud, M. F. Achard and F. Hardouin, *Liquid Crystals*, **9**, 679 (1991).
17. Monomer reactivity ratios (MRR) of methyl acrylate and methacrylate in the typical copolymerization, are 0.37 and 1.8, respectively (taken from Ref. 18). Contribution of blocked copolymerization may not be important, instead, alternate copolymerization is expected to occure preferentially in the view of these ratios.
18. J. Brandrop and E. H. Immergut, Polymer handbook, III-146, 148 (Wiley Interscience, New York, 1975).
19. H. Ringsdorf, H.-W. Schmidt and A. Schneller, *Makromol. Chem., Rapid Commun.*, **3**, 745 (1982).