

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Polymerization of polymer/ferroelectric liquid crystal composites formed with branched liquid crystalline bismethacrylates

C. Allan Guymon; Renfan Shao; Dirk Holter; Holger Frey; Noel A. Clark; Christopher N. Bowman

Online publication date: 06 August 2010

To cite this Article Guymon, C. Allan , Shao, Renfan , Holter, Dirk , Frey, Holger , Clark, Noel A. and Bowman, Christopher N.(1998) 'Polymerization of polymer/ferroelectric liquid crystal composites formed with branched liquid crystalline bismethacrylates', *Liquid Crystals*, 24: 2, 263 – 270

To link to this Article: DOI: 10.1080/026782998207442

URL: <http://dx.doi.org/10.1080/026782998207442>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polymerization of polymer/ferroelectric liquid crystal composites formed with branched liquid crystalline bismethacrylates

by C. ALLAN GUYMON, RENFAN SHAO[†], DIRK HÖLTER[‡], HOLGER FREY[‡], NOEL A. CLARK[†] and CHRISTOPHER N. BOWMAN*

Department of Chemical Engineering, University of Colorado,
Boulder CO 80309-0424, USA

[†]Department of Physics, University of Colorado, Boulder CO 80309-0390, USA

[‡]Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum,
Albert-Ludwigs-Universität, Stefan-Meier-Str. 21/31, 79104 Freiburg, Germany

(Received 16 May 1997; accepted 19 September 1997)

Polymerization and phase behaviour of a branched liquid crystalline bismethacrylate in a ferroelectric liquid crystal (FLC) were characterized. Addition of the monomer increases the temperature range of the smectic A phase, and, at relatively low concentrations of monomer, the temperature range increases to more than 10 times that observed in the neat FLC. Other phases such as the smectic C* phase are no longer exhibited as the monomer interferes with the inherent tilt of the FLC molecules. After polymerization, the polymer network phase separates and the phase transition temperatures return to values close to those of the FLC. The monomer also shows a high degree of orientational order before polymerization, which is retained to a large extent after polymerization. The order in the polymer network results in considerable birefringence at temperatures well above the clearing point of the pure FLC. This behaviour is induced by the order of the polymer network and interactions of the FLC molecules with the network which prevent a fraction of the FLC molecules from exhibiting typical phase behaviour. In the formation of the branched liquid crystalline bismethacrylates/FLC composites, a steady increase is observed in the polymerization rate as the polymerization temperature increases and the order of the FLC phase decreases, a behaviour significantly different from that observed in other monomer/FLC mixtures for which the polymerization rate increases as the order of the FLC phase increases. Additionally, at appropriate polymerization temperatures around the clearing point, polymerization driven endothermic phase transitions may be observed.

1. Introduction

Recently, the development and application of polymer/liquid crystal composites have become areas of great interest in liquid crystal (LC) research. To produce novel LC phase behaviour and properties, a number of composites have been developed [1–5]. One group of composites that show great promise is formed by polymerization of monomer solutes in an LC solvent forming polymer/LC gels [6]. The polymer increases the inherent mechanical strength of the system [7], but may also change the phase behaviour and electro-optic properties. Conversely, the directional ordering present in the LCs may influence the polymerization behaviour and thereby change the polymer morphology.

One class of polymer/LC gels incorporates liquid crystalline cross linking monomers in a low molar mass liquid crystal [8]. When the monomer is polymerized

in the ordered LC phases, the resulting polymer network retains order imparted by the LC [9]. The anisotropy of the polymer consequently alters the optical and electro-optic properties of the composite. In fact, at temperatures well above the isotropic transition temperature, the polymer/LC mixture exhibits a large degree of anisotropy and considerable birefringence [10]. This effect is caused by the ordering of the polymer network, as well as by the induced alignment of a certain fraction of the LC. The phase behaviour, electro-optic properties [11] and the structure of the anisotropic network [12] have been studied for a variety of different systems.

Other LC/polymer composite gel materials have also been examined which are formed by polymerizing amorphous [13] and liquid crystalline [14] monomers in ferroelectric liquid crystals (FLCs). In addition to imparting mechanical strength [7], the polymer may be used to modify the phase behaviour and electro-optic properties of the FLC [15]. These polymer/FLC

*Author for correspondence.

composites have been developed with adjustable grey scales [6] as well as other electro-optic characteristics [16]. In fact, the properties are dependent not only on the type of polymer introduced, but also on the polymerization conditions and temperature [17]. Conversely, the temperature and order of the FLC phase in which polymerization occurs may dramatically affect the segregation of monomeric species [18] and consequently the polymerization behaviour [19, 20].

A new class of monomers may prove promising in understanding these effects and in producing novel phase behaviour and properties in polymer/FLC composites. These monomers, called branched LC bismethacrylates [21], contain mesogenic moieties both in the central and lateral segments of the molecule. Some of these bismethacrylates exhibit a stable nematic phase over a wide temperature range which includes typical ambient conditions. The mesogenic groups in the monomer also retain a large degree of the order during polymerization and therefore exhibit volume reductions as low as 2.5%. Because of these properties, the phase behaviour, the orientation of the polymer and the chemical structure of the monomer may induce interesting polymerization behaviour in the FLC.

The goal of this work is to elucidate the effects of adding (and polymerizing) a branched LC bismethacrylate into an FLC and thereby further the knowledge of polymer structure within ordered LC media during the formation of polymer/LC composites. To accomplish this goal, the LC phase characteristics, including phase transition temperatures and heats of transition, both before and after polymerization, are examined. The order of the monomeric species is also examined both before and after polymerization. Additionally, the polymerization behaviour of the branched LC bismethacrylate in the FLC is determined as a function of concentration and polymerization temperature. Through these studies greater knowledge and understanding of the interactions between polymer networks and FLC molecules, as well as the complex processes involved in the polymerization of monomeric species during the formation of polymer/FLC composite materials are obtained.

2. Experimental

2.1. Materials

The monomer used in this study was the branched liquid crystalline bismethacrylate BM5 [21]. The ferroelectric liquid crystal consists of a 1:1 mixture of W82 and W7 (Displaytech, Longmont, CO). Chemical structures and the LC phase behaviour of the monomer and liquid crystal components are shown in figure 1. Photopolymerizations were initiated with 2-methyl-1-(4-methylthiophenyl)-2-(4-morpholinyl)-1-propanone (Irgacure 907; Ciba Geigy, Hawthorne, NY). All mat-

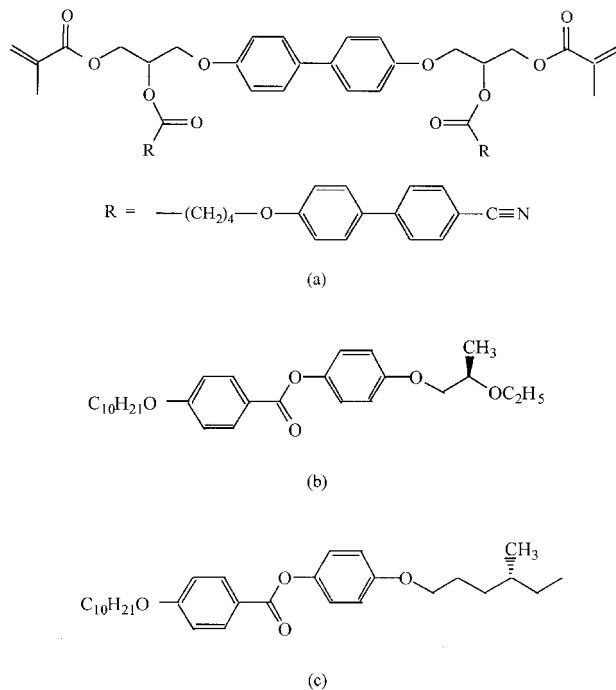


Figure 1. Chemical structures of the dimethacrylate monomer and components of the FLC mixture used in this study. Shown are (a) the branched liquid crystalline bismethacrylate BM5 (phase sequence: isotropic \rightarrow 68°C \rightarrow nematic \rightarrow 18°C \rightarrow glass); (b) W7; (c) W82 (phase sequence for 1:1 W82, W7 mixture: isotropic \rightarrow 58°C \rightarrow smectic A \rightarrow 48°C \rightarrow smectic C* \rightarrow 15°C \rightarrow more ordered smectic phase).

erials were used without further purification. The monomer/FLC mixtures were prepared with initiator concentrations approximately 10 mol % of the total monomer concentration.

2.2. Procedure

Phase transitions of the mixtures were measured using a polarizing optical microscope (Optiphot 2-pol; Nikon, Melville, NY) equipped with a temperature controlled hot stage (Instec, Broomfield, CO). For these measurements, samples were first heated above the isotropic transition and then cooled at approximately 0.3°C min⁻¹. These phase transitions were confirmed by those obtained from differential scanning calorimetry (DSC 7; Perkin-Elmer, Norwalk, CT) at a scan rate of 5°C min⁻¹. Enthalpies of transition were also obtained from the DSC measurements. To prepare polymer/FLC samples, the monomer/FLC mixtures were polymerized at temperatures 10°C below the isotropic/smectic A transition of the unpolymersed sample, unless otherwise indicated.

Polymerization rate profiles were monitored using a DSC (DSC-DPA 7; Perkin-Elmer) modified with a

photocalorimetric accessory. Polymerizations were initiated using monochromatic light of wavelength 365 nm with an intensity of 2 mW cm^{-2} , unless otherwise indicated. The DSC sample cell was also attached to a refrigerated circulating chiller (RTE-111; NESLAB, Newington, NH) to achieve isothermal reaction conditions. For rate studies, approximately 12 mg of the monomer/LC mixture were placed in an aluminium DSC pan. These samples were heated above the isotropic transition and then cooled to the appropriate polymerization temperature to ensure uniform thickness and adequate thermal contact. The DSC sample cell was flushed with nitrogen for 10 min prior to polymerization to mitigate oxygen inhibition [22]. Polymerization rate profiles and double bond conversions were determined from the heat flux measured by the DSC. For these studies, the theoretical value of $13.1 \text{ kcal mol}^{-1}$ was used as the heat evolved per methacrylate double bond reacted [23]. The complete analysis for the determination of polymerization rate and double bond conversion is described in detail elsewhere [19].

3. Results and discussion

3.1. Phase behaviour

The phase behaviour of ferroelectric liquid crystals may be substantially altered upon addition of monomer and then changed again after polymerization [9]. It is important to elucidate any changes induced both before and after polymerization to predict the interactions between the polymer and FLC and thereby understand the ultimate performance behaviour of the polymer stabilized ferroelectric liquid crystal (PSFLC). To examine the effects that the addition of BM5 has on the phase transitions of W82, W7, the phase diagram of the monomer/FLC mixtures was determined (see figure 2). It appears that the transition temperatures from isotropic to smectic A ($I \rightarrow \text{SmA}$) phase are only changed slightly. In contrast to other monomer/LC mixtures which typically show decreases upon addition of monomer [13], the $I \rightarrow \text{SmA}$ transition temperature actually increases slightly with increasing concentration of BM5 monomer. The increase is monotonic and approaches the isotropic to nematic phase transition (68°C) of the pure BM5 monomer at higher concentrations.

More dramatic deviations, however, are observed for the smectic A to smectic C* ($\text{SmA} \rightarrow \text{SmC}^*$) transition. This transition drops over 5°C for only 2 wt % monomer, broadening the smectic A range considerably. The range increases to over 30° at 5 wt % BM5, and at slightly higher concentrations both the smectic C* and semi-crystalline phases disappear completely. In fact with only 9 wt % BM5, the smectic A phase is observed at temperatures as low as -42°C . Therefore, by adding this monomeric species to the FLC, the smectic A

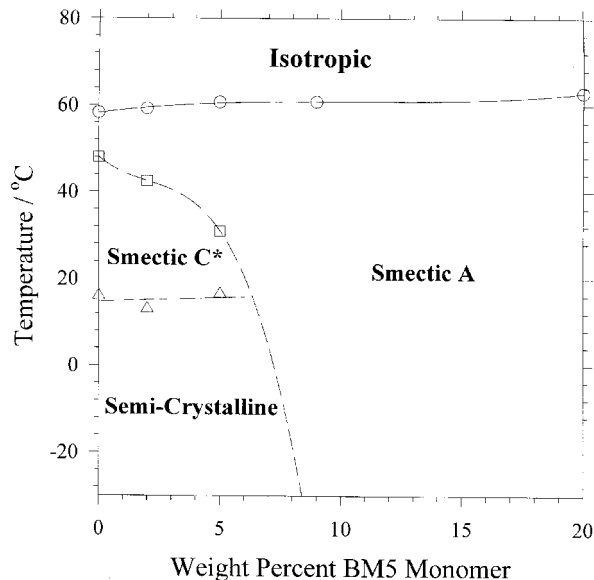


Figure 2. Phase diagram of W82, W7 with varying percentages of BM5 monomer. The transition temperatures from the isotropic-smectic A phase (○), the smectic A-smectic C* phase (□) and the smectic C*-more ordered smectic phase (△) are indicated.

temperature range increases from 10°C to over 100°C . The bulkiness of the monomer appears to interfere significantly with the preferred alignment of the neat FLC. In fact, these molecules prevent the liquid crystals from tilting at very low concentrations, eliminating the smectic C* and semi-crystalline phases entirely.

The phase behaviour of the BM5/W82, W7 mixtures changes considerably after polymerization (see figure 3). Transition temperatures return very closely to those observed for the pure FLC, thereby showing phase behaviour similar to other polymer/FLC systems [13]. The transitions are reduced a few degrees at higher concentrations of polymer, but far less than the dramatic changes observed prior to polymerization. The polymerization, however, does appear to alter other properties of the system. Even at very low concentrations the system remains somewhat birefringent at very high temperatures. When samples with BM5 concentrations as low as 2 wt % are polymerized in the smectic A phase, the PSFLC shows a birefringent smectic A texture until temperatures above 180°C . Such birefringence has also been observed for other polymer/LC composites formed by polymerization of LC monomers in ordered LC phases [10]. The birefringence increases as the temperature approaches the clearing point and, despite the presence of these ordered domains, distinct phase transitions (figure 3) are still observed. As the concentration increases, so does the birefringence at temperatures above the clearing point until it is quite difficult to

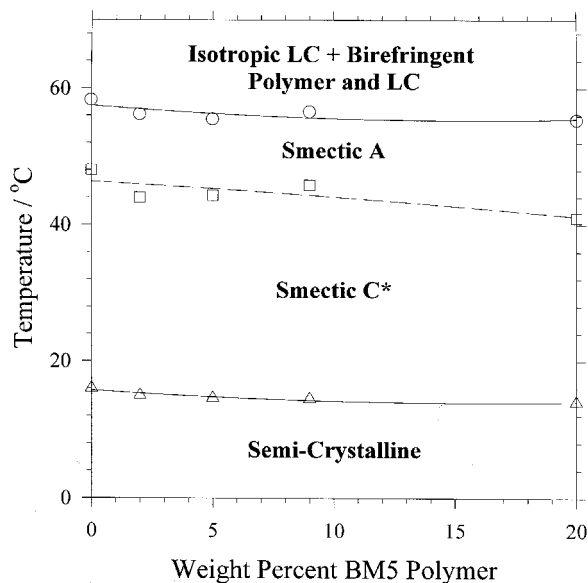


Figure 3. Phase diagram of W82, W7 with varying percentages of BM5 polymer. Polymerizations were performed at 10°C below the isotropic–smectic A transition of the monomer/FLC mixtures.

observe the isotropic to smectic A phase transition for higher concentrations of polymer.

It is reasonable to suspect that a substantial part of the birefringence at higher temperatures is caused by the order of the polymer network itself. The high degree of birefringence seen at low concentrations of polymer indicates, however, that the network itself might not be the only contributing factor. To determine if the network is also influencing the FLC molecules, the characteristics of the I → SmA transition were examined using differential scanning calorimetry. Figure 4 shows the cooling curves for 9 wt % BM5 both before and after polymerization and for neat W82, W7. These cooling curves confirm the results from the phase transition behaviour observed earlier. The addition of BM5 increases the LC phase transition temperature by a few degrees, but after polymerization the transition temperature is very close to that observed in the neat FLC. The exotherms also provide interesting additional information. The exotherm peak is much broader for the monomer/FLC system than for either the FLC or the polymerized system.

To obtain direct information on the total heat of the isotropic/smectic A transition, the exotherm peaks were integrated for different concentrations of BM5 both before and after polymerization. The resulting enthalpy changes are presented in figure 5. The data for the monomer/FLC mixtures are normalized by the total mass of the sample, including the mass of both BM5

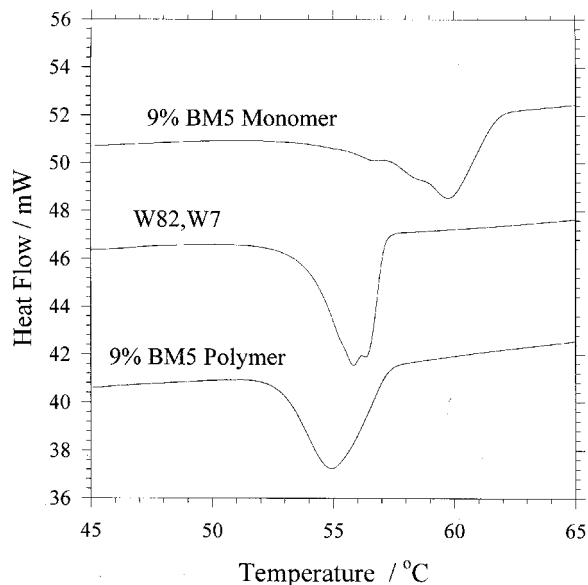


Figure 4. Cooling curves of W82, W7, as well as 9 wt % BM5 in W82, W7 before and after polymerization. Exotherms are indicated by negative peaks.

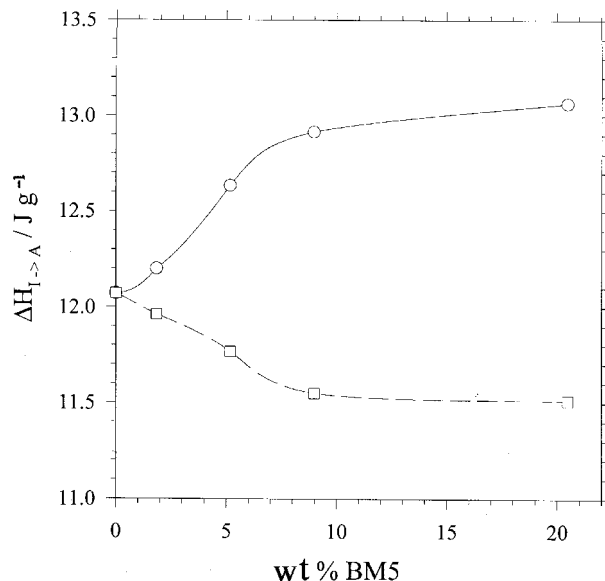


Figure 5. Heat released during the isotropic–smectic A transition for BM5 monomer (○) and BM5 polymer (□) in W82, W7. For polymer samples the heat is calculated per gram of W82, W7, whereas for monomer mixtures the heat is calculated per gram of total sample.

and W82, W7. On the other hand, the heat released for the polymer/FLC mixture is normalized by the mass of only the W82, W7, as only the low molar mass components of these systems will participate in the transition. Interestingly, the enthalpy change for the monomer/FLC

mixtures actually increases as the concentration of BM5 increases, indicating that the BM5 molecules undergo the transition and, in fact, augment the enthalpy change. Conversely, after polymerization, the heat of the transition decreases substantially even when the heat is normalized only by the amount of the FLC. The network, therefore, prevents a certain fraction of the FLC molecules from changing orientation during the transition. This 'bound' fraction can be calculated from the decrease in the heat of transition as shown elsewhere [24] and approaches 5% at higher BM5 polymer concentrations. The FLC molecules could be 'bound' in one of two ways. First, the network could keep the molecules in an isotropic state even at temperatures below the clearing point or the network could 'freeze-in' the order of the molecules at temperatures well above the clearing point. The second scenario seems to be the more reasonable explanation. The monomer/FLC mixture is polymerized in an ordered state (smectic A). If a specific orientation is to be retained, it is logical to assume that it would most resemble the order of the anisotropic network.

Further understanding of the ordering of the network is obtained from polarized infrared (IR) spectroscopy. This method has been used extensively to probe the orientation of specific bonds [25]. In BM5/W82, W7 mixtures the band corresponding to the BM5 $C\equiv N$ stretch at 2225 cm^{-1} is easily isolated in the IR spectrum. This band also provides an accurate measure of the order of the polymer network. Figure 6 shows polar plots for this band in a 9 wt % BM5/W82, W7 mixture both before and after polymerization. If the BM5 cyano

groups were randomly distributed throughout the LC, then the absorbance for all different polarization angles would be the same. This situation obviously does not occur for the monomer mixture. The absorbance for the cyano band exhibits a maximum at approximately 0° , corresponding to light polarized parallel to the normal (z) layer or perpendicular to the smectic layers. In fact, this maximum is approximately 1.8 times the minimum absorbance observed for light polarized perpendicular to the normal layer, indicating a high degree of order. The same basic behaviour is also observed after polymerization. The ratio of the maximum to minimum absorbance decreases slightly to 1.6, but the order from the monomer is retained to a great extent even after polymerization. These results indicate that the resulting network is highly anisotropic and therefore may significantly influence the phase behaviour as discussed previously.

3.2. Polymerization behaviour

To understand more fully the effects that the order of the monomer induces in the ultimate behaviour of the PSFLC, and on the formation and morphology of the polymer, it is also important to investigate the polymerization behaviour of BM5 in the FLC. Figure 7 shows the polymerization rate as a function of the double bond conversion when the concentration of BM5 is increased. The polymerization rate presented is normalized by the initial monomer concentration, thus having units of s^{-1} .

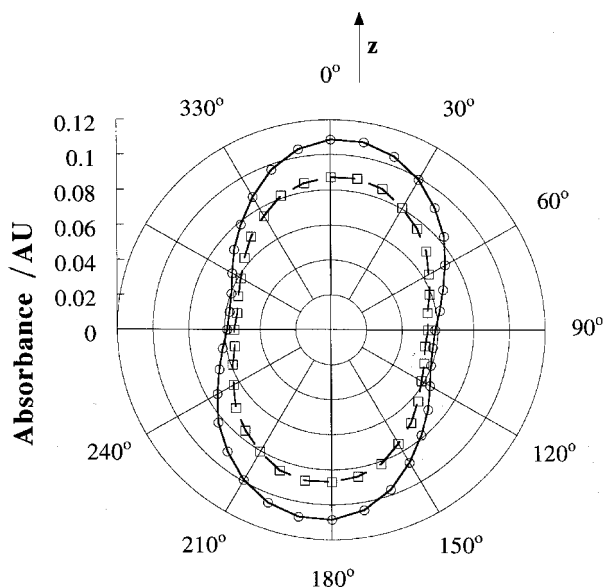


Figure 6. Polar plot of the absorbance of the $C\equiv N$ stretch from the BM5 monomer both before (\circ) and after polymerization (\square) in W82, W7.

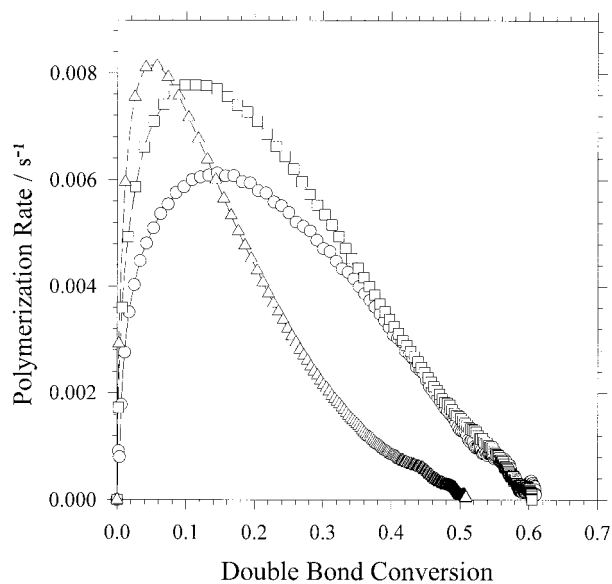


Figure 7. Polymerization rate as a function of double bond conversion for 5 wt % (\circ), 9 wt % (\square), and 20 wt % (\triangle) BM5 in W82, W7. Polymerizations were performed at 10°C below the isotropic-smectic A transition of the monomer/FLC mixtures.

This normalization facilitates comparison of the polymerization for different concentrations of monomer. As seen in the figure, the polymerization is quite similar for all three concentrations. The maximum polymerization rate and consequently the speed of the reaction do, however, increase slightly as the monomer concentration increases. This behaviour is consistent with previous results [13] that indicate that this effect is induced simply by dilution of the monomeric species. In a more dilute system the reacting species, especially the growing polymer chains, are more mobile, thereby reducing auto-acceleration of the polymerization rate [26]. As the BM5 concentration increases, the mobility during the reaction decreases, and autoacceleration is more pronounced. Interestingly, the double bond conversion is lower for the 20 wt % BM5 polymerization than for the two lower BM5 concentrations, suggesting that the mobility limitations that increase the rate also limit the number of double bonds that are allowed to react.

Interesting results are also observed when the polymerization rate is examined for different polymerization temperatures. Figure 8 shows the normalized polymerization rate plotted versus double bond conversion for three different polymerization temperatures. The highest temperature corresponds to a polymerization in the isotropic phase, the 50°C polymerization will remain in the smectic A phase throughout the polymerization, and the 25°C polymerization will remain in the smectic C* phase during the polymerization (see figures 2 and 3). As the temperature increases, the polymerization rate

also increases despite the decrease in the order of the phases. These results indicate that, in this system, the LC phase does not have a significant effect on the polymerization behaviour.

This effect becomes even more striking when the maximum heat release rate during polymerization per gram of BM5 monomer is examined as a function of the polymerization temperature for BM5/W82, W7 systems. Figure 9 shows this maximum for polymerizations of both 5 and 9 wt % BM5. The maximum heat release rate per gram of monomer is also plotted for polymerizations of 2 wt % hexandiol diacrylate (HDDA) in W82, W7 for comparison [19]. For the 9 wt % BM5 polymerizations the maximum heat release rate increases steadily as the temperature increases and almost doubles with a 50°C temperature increase. The same basic trend is also observed for the 5 wt % BM5 polymerizations, despite increased scatter due to the slightly lower polymerization rates. As the temperature increases, the heat release increases concomitantly, exhibiting typical polymerization behaviour. These results are in stark contrast to those observed for the polymerization of other LC and amorphous monomers [19] for which the polymerization and maximum heat release rates decrease with increasing temperature as the order of the LC system decreases. The HDDA polymerizations in figure 9 exhibit this enhanced rate behaviour, and in fact the

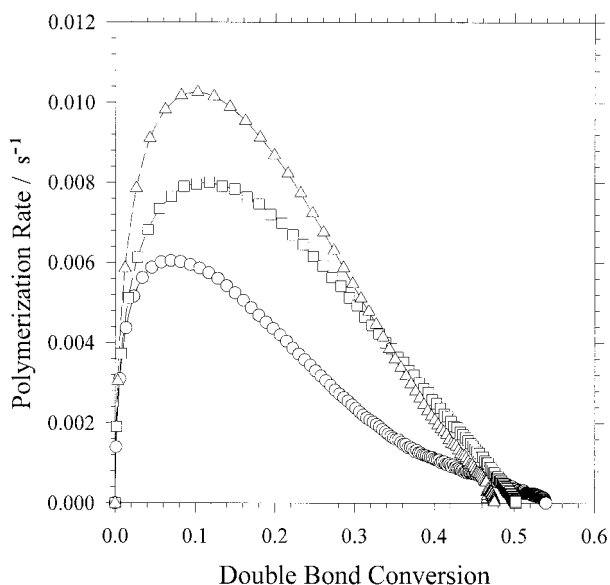


Figure 8. Polymerization rate as a function of double bond conversion for 5 wt % BM5 polymerizing in W82, W7 in the smectic C* at 25°C (○), in the smectic A at 50°C (□), and in the isotropic phase at 70°C (△).

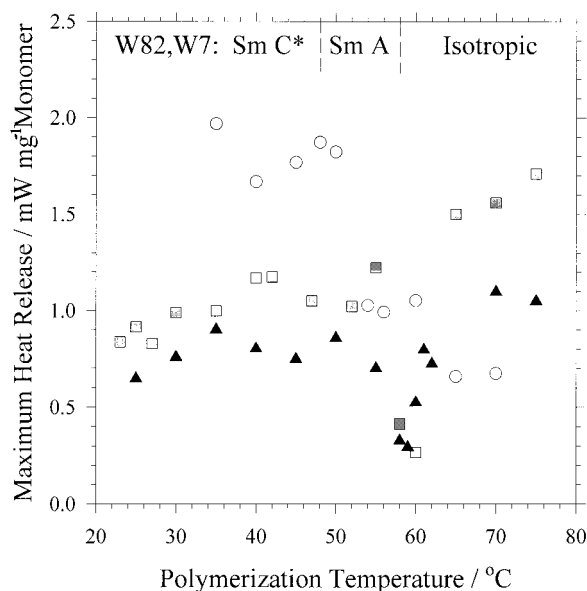


Figure 9. Maximum heat release per mg of monomer during polymerizations of 5 wt % BM5 (▲) and 9 wt % BM5 (■) as a function of polymerization temperature. The scaled (1:8) heat release per mg of monomer for polymerizations of 2 wt % HDDA (○) in W82, W7 is shown for comparison [19]. Phase transitions for neat W82, W7 are also indicated.

maximum heat release rate decreases by more than a factor of 3 when the polymerization temperature is increased 35°C. This behaviour has previously been attributed to segregation and ordering of the HDDA monomer [18, 20]. But for BM5, despite the apparent order both before and after polymerization in the LC phases (figure 6), no increase in the heat release rate in these ordered phases during polymerization is observed.

The BM5 polymerizations, therefore, do not exhibit the same accelerated behaviour as the HDDA polymerizations and do not appear to be significantly influenced by the order of the system. Some of these polymerization characteristics may be attributed to the change in the order of the system during polymerization, but the rate profile for this polymerization is continuous and does not exhibit the anomalous behaviour that would be expected with a change in media if the order of the phase played a significant role [27]. The explanation lies more likely in the monomer itself. As evidenced by the molecular structure (figure 1), the molecules are quite bulky [21]. This characteristic will severely limit the mobility of the monomeric species. Additionally, the reactive double bond is sterically hindered which may reduce the ability of the double bonds to propagate. Therefore, despite the fact that the monomer is ordered within the LC, other features associated with this branched monomer prevent this ordering from influencing the polymerization rate significantly.

Another interesting feature of these polymerizations is seen for polymerization temperatures around the isotropic/smectic A transition. The maximum heat release rate drops significantly for both BM5 concentrations at temperatures between 58 and 60°C. To understand this phenomenon further, it is important to examine these polymerizations in more detail. To do so, the heat release profile during polymerization, normalized for the mass of sample, is presented in figure 10. The profiles for 9 wt % BM5 polymerized in W82, W7 at 58 and 60°C as well as for other nearby temperatures are shown. The exotherms for the 55 and 65°C polymerizations show behaviour that would be expected for these polymerizations. After the polymerization is initiated, a substantial heat release is observed, and then the heat gradually decreases until polymerization is complete. The other two polymerizations begin with the expected exotherm, but before the expected maximum is reached, the heat release dramatically decreases and a definite endotherm is seen. The mechanisms behind this behaviour become evident after re-examining figures 2 and 3. As monomer is introduced into the FLC, the isotropic/smectic A phase transition increases above that observed in neat W82, W7. After polymerization, however, these transitions decrease to temperatures slightly below those of the FLC. Therefore, during the polymer-

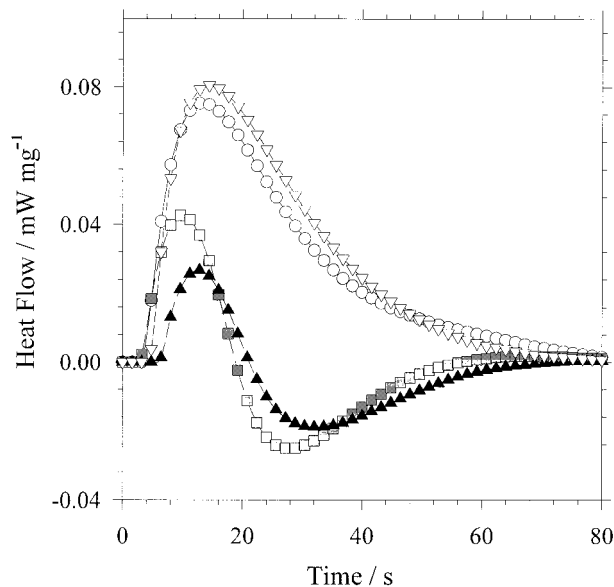


Figure 10. Heat flow during polymerization of 9 wt % BM5 at 55°C (○), 58°C (■), 60°C (▲), and 65°C (▽). Exotherms are indicated by positive peaks.

ations at 58 and 60°C, the polymerization begins in a smectic A phase, but as the polymerizations proceed, the transition temperature decreases. Consequently, the mixture undergoes the endothermic phase transition from smectic A to the isotropic phase, producing the observed endothermic polymerization behaviour.

4. Conclusions

The addition and polymerization of a branched LC bismethacrylate in an FLC produces novel phase and polymerization behaviour. At relatively low monomer concentrations the temperature range of the smectic A phase increases dramatically. As the concentration increases, the smectic A phase becomes the only observable anisotropic phase and exhibits a temperature range of over 100°C. These transitions return close to those of the neat FLC after polymerization, but some birefringence is observed at temperatures well above the isotropic to smectic A transition temperature. Additionally, the order of the network is quite substantial and not much changed from the order of the monomer before polymerization. The heat of this transition provides information to help understand this phenomenon. The heat released decreases considerably as the concentration of BM5 polymer increases, indicating that the interactions between the FLC molecules and the ordered polymer network prevent a fraction of the molecules from exhibiting typical phase behaviour.

Polymerization behaviour is also considerably different from that seen in other polymerizations of amorph-

ous and liquid crystalline monomers. In contrast to the decrease in polymerization rate with temperature seen for other systems, the polymerization rate increases as the temperature is increased. This behaviour indicates that the order of the monomeric system does not influence the polymerization behaviour because of the bulkiness of the monomer and the steric hindrance of the polymerizable double bond. Additionally, at appropriate temperatures, endotherms are observed during polymerization. This effect becomes prevalent at temperatures slightly above the clearing point of the neat FLC and arises as the monomer/FLC mixture is initially in an ordered phase; as the polymerization proceeds, the mixture becomes isotropic, thereby producing an endothermic transition which is larger than the exotherm produced from the polymerization.

The authors would like to thank the Department of Defense for its support of this work through a fellowship to C. A. G. The financial support of the National Science Foundation through grants (DMR-9224168 and CTS-9453369) is also gratefully acknowledged.

References

- [1] CRAWFORD, G. P., and ZUMER, S., 1996, *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks* (London: Taylor & Francis).
- [2] DOANE, J. W., GOLEMME, A., WEST, J. L., WHITEHEAD, J. B., and WU, B.-G., 1988, *Mol. Cryst. liq. Cryst.*, **165**, 511.
- [3] KITZEROW, H.-S., 1994, *Liq. Cryst.*, **16**, 1.
- [4] SERBUTOVIEZ, C., KLOOSTERBOER, J. G., BOOTS, H. M. J., PAULISSEN, F. A. M. A., and TOUWSLAGER, F. J., 1997, *Liq. Cryst.*, **22**, 145.
- [5] DRZAIĆ, P. S., 1995, *Liquid Crystal Dispersions* (Singapore: World Scientific).
- [6] HIKMET, R. A. M., and MICHIELSEN, M., 1995, *Adv. Mater.*, **7**, 300.
- [7] LESTER, G., COLES, H., MURAYAMA, A., and ISHIKAWA, M., 1993, *Ferroelectrics*, **148**, 389.
- [8] HIKMET, R. A. M., LUB, J., and MAASSEN V D BRINK, P., 1992, *Macromolecules*, **25**, 4194.
- [9] HIKMET, R. A. M., 1991, *Liq. Cryst.*, **9**, 405.
- [10] BRAUN, D., FRICK, G., GRELL, M., KLINES, M., and WENDORFF, J. H., 1992, *Liq. Cryst.*, **11**, 929.
- [11] HIKMET, R. A. M., 1990, *J. appl. Phys.*, **68**, 4406.
- [12] HIKMET, R. A. M., and BOOTS, H. M. J., 1995, *Phys. Rev. E*, **51**, 5824.
- [13] GUYMON, C. A., HOGGAN, E. N., WALBA, D. M., CLARK, N. A., and BOWMAN, C. N., 1995, *Liq. Cryst.*, **19**, 719.
- [14] HIKMET, R. A. M., and LUB, J., 1995, *J. appl. Phys.*, **77**, 6234.
- [15] HIKMET, R. A. M., BOOTS, H. M. J., and MICHIELSEN, M., 1995, *Liq. Cryst.*, **19**, 65.
- [16] HIKMET, R. A. M., BOOTS, H. M. J., and MICHIELSEN, M., 1996, *J. appl. Phys.*, **79**, 8098.
- [17] GUYMON, C. A., DOUGAN, L. A., and BOWMAN, C. N., 1997, in *Advances in Photopolymerization: Fundamentals and Applications*, edited by C. N. Bowman, A. B. Scranton and R. W. Pfeiffer (Washington: American Chemical Society), Vol. 673 (in press).
- [18] GUYMON, C. A., HOGGAN, E. N., CLARK, N. A., RIEKER, T. P., WALBA, D. M., and BOWMAN, C. N., 1997, *Science*, **275**, 57.
- [19] GUYMON, C. A., and BOWMAN, C. N., 1997, *Macromolecules*, **30**, 1594.
- [20] GUYMON, C. A., and BOWMAN, C. N., *Macromolecules*, **30**, 5271.
- [21] HÖLTER, D., FREY, H., MUELHAUPT, R., and KLEE, J. E., 1996, *Macromolecules*, **29**, 7003.
- [22] ANSETH, K. A., KLINE, L. M., WALKER, T. A., ANDERSON, K. J., and BOWMAN, C. N., 1995, *Macromolecules*, **28**, 2491.
- [23] MOORE, J. E., 1977, in *Chemistry and Properties of Crosslinked Polymers*, edited by S. S. LABANA (New York: Academic Press), p. 535.
- [24] RUSSELL, G. M., PATERSON, B. J. A., and IMRIE, C. T., 1995, *Chem. Mater.*, **7**, 2185.
- [25] JANG, W. G., PARK, C. S., MACLENNAN, J. E., KIM, K. H., and CLARK, N. A., 1996, *Ferroelectrics*, **180**, 213.
- [26] ODIAN, G., 1991, in *Principles of Polymerization* (New York: John Wiley), p. 207.
- [27] HOYLE, C. E., CHAWLA, C. P., KANG, D., and GRIFFIN, A. C., 1993, *Macromolecules*, **26**, 758.