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Photopolymerization in Self-organizing Systems

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Mesogenic monomers of 4-[6-(acryloyloxy) hexoxy] benzoic acid (AHB) and 4-[[6-[(2-methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoic acid 4′-[(1-oxo-10,12-nonadecadiynyl)-oxy]-[1,1′-biphenyl]-4-yl] ester (MHNB) are prepared for polymerization in highly ordered smectic and nematic mesophases and liquid crystal solvents. AHB exhibits smectic C and nematic mesophases, whereas MHNB displays the phase sequence of smectic X, C, A and nematic phases. The highest molecular-weight polymers with the widest molecular-weight distribution were found in polymerization of the highly ordered smectic phase and using smectic solvents. Photopolymerization in nematic systems gave the narrowest molecular weight distribution polymers when compared with those in other systems.

Keywords: Photopolymerization; nematic mesophases; liquid crystal

INTRODUCTION

The use of self-organizing materials, which include liquid crystals and hydrogen-bonded materials, may lead to developing new structures and devices for electro-optical applications. The investigation of polymerization in organized or self-organizing systems has drawn extensive attention recently [1–3]. In nature, hydrogen-bonding interaction is one of the processes for molecular self-organization and molecular recognition. Self-organizing monomers may affect polymerization kinetics, polymer structure, and polymer microstructure; in all these aspects the property of a

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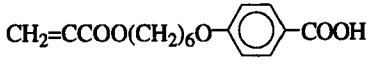
polymer or network is directly related to the organization of the reacting monomers [4–6].

Photochemically initiated polymerization of liquid-crystalline acrylates has been useful in preparing side-chain liquid-crystalline polymers [7–9]. Uniaxially oriented polymers and networks, resulting from photopolymerizing mesogenic acrylates and diacrylates, have been useful in optoelectronic and display devices [10–12]. Among new materials, polymer stabilized liquid crystals (PSLC) exhibit great potential to revolutionize conventional flat panel display technology [11, 12]. The PSLC materials consist of a low concentration of an oriented polymer network dispersed in a low molecular weight liquid crystal. The principle of operation of this type of devices is to preserve the alignment of the resulting polymers or networks in the liquid crystals. Photopolymerization induced phase separation is a very useful method in preparing these types of dispersions. With these considerations in mind, we investigated the photopolymerization of a liquid-crystalline acrylate AHB **1** in both mesophases and liquid crystal solvents.

To explore the construction of a supramolecular multidimensional film [13], we studied a multi-functional monomer MPNB **2**, which consists of a polymerizable methacrylate group, a mesogenic moiety and a diacetylene group. The molecular design targets molecular self-organization where not only methacrylate termini aggregate in space but also their reactive diacetylene groups closely pack to give a minimum distance in which the co-reaction can take place. Polymerization was carried out in the mesomorphic states of monomer **2**. By controlling the dose of photoirradiation, the locked-in macroscopically oriented structure was possible.



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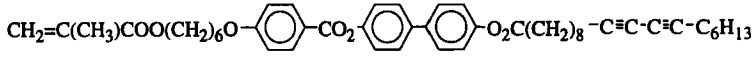

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EXPERIMENTAL

Materials and Technique

Most of the materials were obtained from Aldrich Chemical Company and used without further purification. The diacetylenic acid was purchased from

TCI America. All the intermediates, monomers and polymers were characterized using the following instruments: NMR, FI-IR, elemental analysis, HPLC, GPC, DSC, polarizing optical microscope with hot stage, and small angle X-ray diffraction (SAXD). The DSC experiments were measured at the heating and cooling rate of 10°C/min.

Synthesis

4-(6-acryloyloxyhexoxy)benzoic acid (AHB) (1)

In a 250 ml round-bottomed flask was added (10 g, 0.042 mol) of 4-(6-hydroxyhexoxy)benzoic acid, (12.01 g, 0.168 mol) of acrylic acid, (4.79 g, 0.025 mol) of *p*-toluene sulfonic acid, (2.77 g, 0.025 mol) of hydroquinone and 200 ml of benzene. The mixture was refluxed under Dean-Stark trap for 24 hrs. The resultant solution was cooled to room temperature, diluted with ethyl ether, washed two times with warm water and one time with salt water, dried over magnesium sulfate. After evaporating the solvent on a rotavap the crude product was purified with flash chromatography (100% methylene chloride). Yield: 2.2 g (18%).

FTIR, (nujor, cm^{-1}): 3840–2760 (— OH), 1735 ($CH_2 = CHCOO$ —), 1690 (Ph —COOH). ^1H NMR ($CDCl_3$, δ ppm): 1.39–1.91 (*m*, 8H, alkyl), 4.00–4.07 (*t*, 2H, $J = 6.65$, PhO —$C\underline{H}_2$), 4.15–4.22 (*t*, 2H, $J = 6.51$, COO —$C\underline{H}_2$), 5.79–5.85 (*dd*, 1H, $J_1 = 1.54$, $J_2 = 10.29$, trans to $\underline{H}CH = CHCOO$ —), 6.14–6.36 (*dd*, 1H, $J_1 = 10.4$, $J_2 = 17.36$, $HCH = C\underline{H}COO$ —), 6.37–6.46 (*dd*, 1H, $J_1 = 1.5$, $J_2 = 17.21$, cis to $HC\underline{H} = CHCOO$ —), 6.98 (*d*, 2H, $J = 8.87$, ortho to — OH), 8.06 (*d*, 2H, $J = 8.91$, ortho to — COO).

4-[6-(methacryloyloxy)hexoxy]benzoic acid (a)

The reaction was carried out with the same procedure as that of **1**.

FTIR, (nujor, cm^{-1}): 3840–2760 (— OH), 1735 ($CH_2 = CCH_3$ COO —), 1690 (Ph —COOH). ^1H NMR ($CDCl_3$, δ ppm): 1.39–1.91 (*m*, 8H, alkyl), 1.94 (*s*, 3H, C = C —CH_3), 4.00–4.06 (*t*, 2H, $J = 6.43$, PhO —$C\underline{H}_2$), 4.14–4.20 (*t*, 2H, $J = 6.52$, COO —$C\underline{H}_2$), 5.55–5.56 (*d*, 1H, $J = 1.44$, trans to COO —), 6.11 (*d*, 1H, $J = 1.1$, cis to COO —), 6.90–6.95 (*d*, 2H, $J = 8.87$, ortho to — OH), 8.04–8.08 (*d*, 2H, $J = 8.71$, ortho to — COO).

4-[(6-methacryloyloxyhexoxy)]-4′-[oxy-1′-biphenyl)]benzoate (b)

Compound **a** (3.5 g, 0.0115 mol) and oxalyl chloride (10.4 g, 0.04 mol) were stirred with a trace of inhibitor 2,6-di-ter-butyl-4-methyl phenol. Two drops of DMF were added and the reaction mixture was stirred for 3 hrs at room temperature. The solvent and excess oxalyl chloride were evaporated off using a rotavap. In a separate flask, 4,4′-biphenol (6.42 g, 0.035 mol) and triethyl amine (15.36 g, 0.152 mol) were dissolved in 1,2-dichloroethane, stirred for 20 minutes and cooled to 0 to 5 degrees Celsius. The acid chloride in 1,2-dichloroethane was added slowly via an addition funnel. The reaction mixture was stirred at room temperature for 24 hrs. The solvent was rotovapped off. The residue was dissolved in methylene chloride and washed with aqueous solution of 5% KOH, 5% HCl and water. The organic layer was dried with magnesium sulfate and filtered. Column chromatography was performed with a 9:1 volume ratio of methylene chloride to ethyl acetate (Rf = 0.65). 3.79 g were obtained with a 78.5% yield. Mp: 118–120°C.

FTIR, (nujor, cm^{-1}): 3840–3328 (— OH), 1722 (C = O), 1274.2 (Ph —OR). ^1H NMR ($CDCl_3$, δ ppm): 1.39–1.91 (*m*, 8H, alkyl), 1.94 (*s*, 3H, C = C —CH_3), 4.05 (*t*, 2H, *J* = 6.37, PhO —$C\underline{H}_2$), 4.18 (*t*, 2H, *J* = 6.54, COO —$C\underline{H}_2$), 5.66 (*d*, 1H, *J* = 1.4, HHC = C trans to COO —), 6.11 (*d*, 1H, *J* = 1.1, HHC = C cis to COO —), 5.79 (*s*, 1H, Ph —O$\underline{H}$), 6.85, (*d*, 2H, *J* = 8.67, ortho to — OH), 6.98 (*d*, 2H, *J* = 9.0, ortho to — OR), 7.23 (*d*, 2H, *J* = 8.67, ortho to — OCC), 7.42 (*d*, 2H, *J* = 8.67, meta to — OOC), 7.54 (*d*, 2H, *J* = 8.71, meta to — OH), 8.16 (*d*, 2H, *J* = 8.91, ortho to — COO).

4-[(6-(2-methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic acid 4′-[(1-oxo-10,12-nonadecadiynyl)oxy][1,1′-biphenyl]-4-yl ester (MHNB) 2

1-oxo-10,12-nonadeca-diynyl (0.15 g, 0.0057 mol) and oxalyl chloride (1.7, 0.013 mol) were dissolved in methylene chloride along with a trace of inhibitor 2,6-ditert-butyl-4-methyl-phenol. Two drops of DMF were added and the reaction mixture was stirred for 3 hrs at room temperature. The solvent and the excess oxalyl chloride were evaporated using a rotovap. In a separate flask, compound **b** (0.25 g, 0.52 mmol) and triethyl amine (0.06 g, 0.57 mmol) were dissolved in methylene chloride, stirred for 20 minutes and cooled to 0 to 5 degrees Celsius. The acid chloride in methylene chloride was added slowly via an addition funnel. The reaction mixture was stirred at room temperature for 24 hrs. The solvent was rotovapped off. The residue

was dissolved in methylene chloride and washed with aqueous solution of 5% KOH, 5% HCl and water. The organic layer was dried with magnesium sulfate and filtered. A flash chromatography column was run with methylene chloride as the eluent. Recrystallization from a mixture of ethanol and ethyl acetate (2:1) the result was 0.21 g with a 56% yield. HPLC: > 99.5%. Transition temperatures (°C):K 67.8 S_X 89 S_C 102 S_A 136.7 I. Anal. Calcd. for $(C_{48}H_{58}O_7)_n$: C, 77.18; H, 7.8. Found:C, 76.47; H, 7.65. FTIR, (nujor, cm^{-1}): 1748, 1725, 1719 (C = O), 1602 (C = C of benzene), 1256 (Ph —OR). ^1H NMR ($CDCl_3$, δ ppm): 0.88 *t*, 3H, J = 6.60, CH_3), 1.21–1.91, (*m*, 22H, alkyl), 1.94 (*s*, 3H, C = C —CH_3), 2.20–2.27 (*t*, 4H, J = 4.9, two acetylene — $C\underline{H}_2$), 2.58 (*t*, 3H, L = 7.43, $C\underline{H}_2$ —COO —Ph), 4.02–4.08 (*t*, 2H, J = 6.35, PhO —$C\underline{H}_2$), 4.14–4.20 (*t*, 2H, J = 6.55, COO —$C\underline{H}_2$), 5.56–5.58 (*d*, 1H, J = 1.61, HHC = C trans to COO —), 6.10–6.11 (*d*, 1H, J = 1.7, HHC = C cis to COO —), 6.95–7.00 (*d*, 2H, J = 9.0, ortho to — OR), 7.13–7.17, (*d*, 2H, J = 8.72, ortho to — OOCR), 7.25–7.28 (*d*, 2H, J = 8.67, ortho to — OOCPh), 7.56–7.58 (*d*, 2H, J = 3.40 meta to — OOCPh), 7.59 (*d*, 2H, J = 3.42, meta to — OOCR), 8.14–8.18 (*d*, 2H, J = 8.95, ortho to — COOPh). ^{13}C NMR ($CDCl_3$, δ ppm): 14.06 (CH_3), 18.35 (CH_3), 19.20, 22.52, 24.92, 25.63, 25.70, 25.79, 28.30, 28.41, 28.55, 28.75, 28.91, 29.0, 29.09, 31.30, 34.39, 64.60, 68.09, 76.41, 77.04 (CH_2), 112.31, 114.29, 121.55, 121.92, 122.13, 128.13, 132.33, 136.47, 138.02, 138.09, 150.19, 150.54, 163.48, 164.95, 172.32.

Poly[4-[(6-(2-methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]benzoic acid 4′-[(1-oxo-10,12-nonadecadiynyl)oxy][1,1′-biphenyl]-4-yl ester]

In a side-armed polymerization tube was added the MHNB **2** (0,30 g, 0.40 mmol), the initiator AIBN (4 mg) and 1 ml of toluene. A freeze-thaw technique was used to purified the monomer. The polymerization tube was placed in an oil bath at 75°C and maintained at that temperature for 24 hrs. The solution was then cooled to room temperature, concentrated, and redissolved in dichloromethane and precipitated into methanol. This polymer was further purified by dissolution in methylene chloride followed by reprecipitation with hexane and methanol until the TLC in dichromethane showed one spot at the baseline. The solid was dissolved in dichromethane and filtered through a 0.5 micron filter. After drying at 60°C for 48 hrs in *avacuo* the result was 0.99 g with 33% yield. Molecular weight: Mn = 30,200, Mw = 59,000, MWD = 1.95. Transition temperatures; g 83.7 S_C 190.4 S_A 228.3 I.

^{1}H NMR ($CDCl_3$, δ ppm): 0.88 (*b*, 3H, CH_3), 1.05–1.88, (*b*, alkyl), 2.12–2.30 (*b*, acetylene— $C\underline{H}_2$), 2.41–2.60 (*b*, $C\underline{H}_2$ —COO —Ph) 3.90–4.05 (*b*, PhO —$C\underline{H}_2$), 4.14–4.20 (*b*, COO —$C\underline{H}_2$), 6.84–7.00 (*d*, ortho to — OR), 7.05–7.29 (*d*, ortho to — OOCR), 7.25–7.28 (*d*, ortho to — OOCPh), 7.56–7.58 (*d*, meta to — OOCPh), 7.61 (*d*, meta to — OOCR), 8.01–8.19 (*d*, ortho to — COOPh).

Photopolymerizations

Photopolymerization of AHB **1** was performed using a Perkin Elmer DPC 7 in both mesophases and liquid crystal solvents. The photopolymerization of monomer **2** was carried out in its mesophases. The samples for polymerization in mesophases were prepared by dissolving a monomer and photoinitiator, benzoin methyl ether (2% by the weight of monomer), in THF and then evaporating the solvent. Samples of monomer **1** for polymerization in the liquid crystal solvents were prepared as follows: 20 wt% of **1** was dissolved in either K15 or K24 and 45% of **1** was dissolved in either E48 or OS35. For DPC experiments, the mixtures were weighted 3 mg into each unsealed DSC pan. All the experiments were carried out isothermally at desired temperatures. The intensity of the UV is 40 mW cm^{-2}. After photopolymerization, the samples were dissolved in THF and their molecular weights were evaluated using a Waters GPC calibrated with polystyrene standards.

RESULTS AND DISCUSSION

Mesomorphic Behaviour of Monomers and Polymers

The phase transition temperatures of monomers **1** and **2** are summarized in Table I. Both monomers were found to exhibit liquid crystallinity, identified by a differential scanning calorimeter (Figs. 1a and 1b) and polarizing optical microscope. Monomer **1** exhibited the smectic S (S_C) and nematic

TABLE I The transition temperatures of monomers **1** and **2** and polymer **1** and **2**

Compound	*Transition Temperature °C (Kcal/mol)*
m1	K 93 (9.95) S_C 102 (0.1) N 110 (0.24)
m2	K 68 (11.35) S_X 89 (0.52) S_C 102 (0.03) S_A 110 (1.44) I
p1	g 66 S_C 141 N 155 I
p2	g 84 S_C 190 S_A 228 I

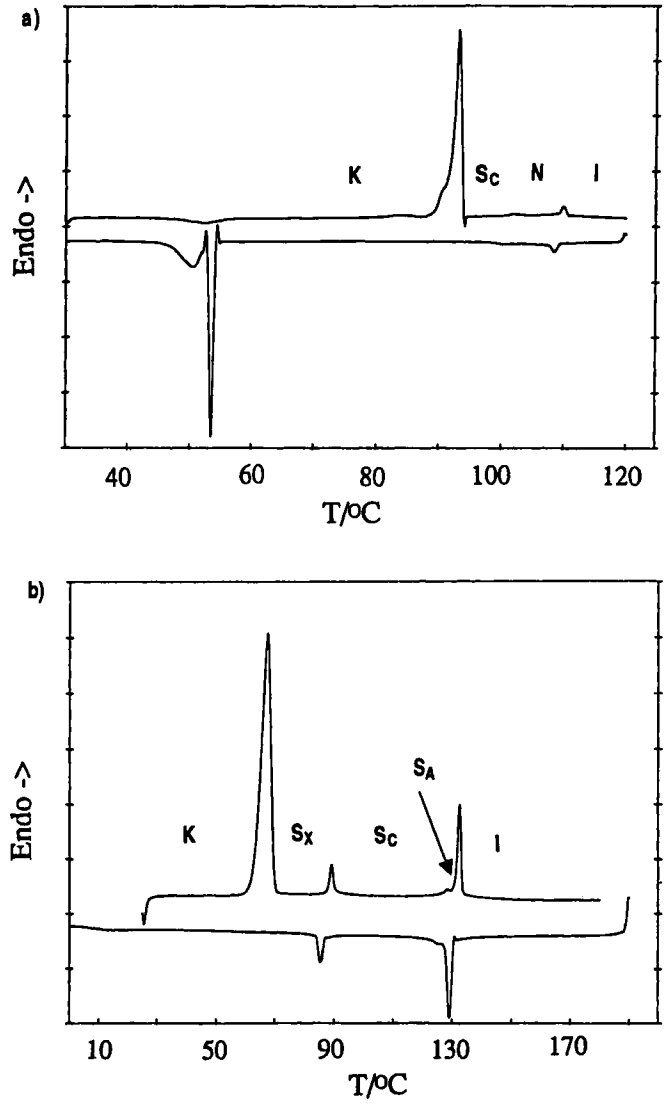

FIGURE 1 a) The DSC curves of AHB **1**; and b) the DSC curves of MPNB **2**.

phases and had broad temperature range of transitions. This phenomenon is common for hydrogen bond induced mesophases because of the strong molecular interactions. Upon cooling, the isotropic liquid of AHB **1** went through a nematic phase settling into a spontaneous twist and bifurcation of the surface orientation, a surface induced texture instability [10]. By further

cooling to the S_C phase, the texture transformed into a band texture before the appearance of schlieren texture of S_C phase (Figs. 2a and 2b). Polarizing optical microscopy showed that MHNB **2** had the focal conic fan texture for S_A phase and broken fan textures for S_C. The S_X phase, an unidentified mesophase, exhibited the schlieren texture corresponding to the higher ordered smectic phase, a characteristic of lamellar structure. The smectic structure was further studied using a DSC and a SAXD. The SAXD was studied by cooling the sample from isotropic melt into mesophases. The layer spacing for the S_A, S_C and S_X phases are 44.28 Å, 41.59 Å, and 43.67 Å, respectively. A diffraction pattern (Fig. 3) of the S_X phase measured at the temperature of 84°C is shown in Figure 3. Compared with the calculated

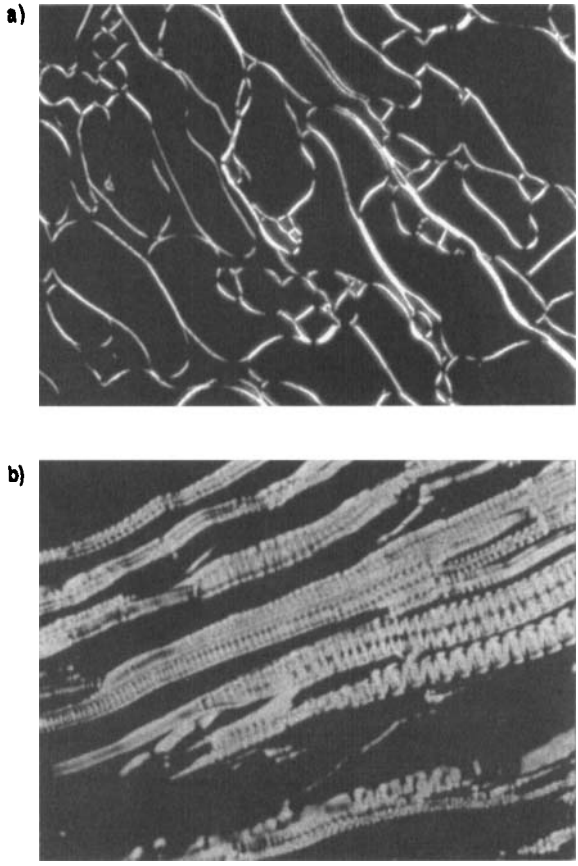

FIGURE 2 The spontaneous twist and bifurcation of the surface induced textures a) the ribbon-like texture (I- > N); b) the bond texture (N- > S_C). (See Color Plate X).

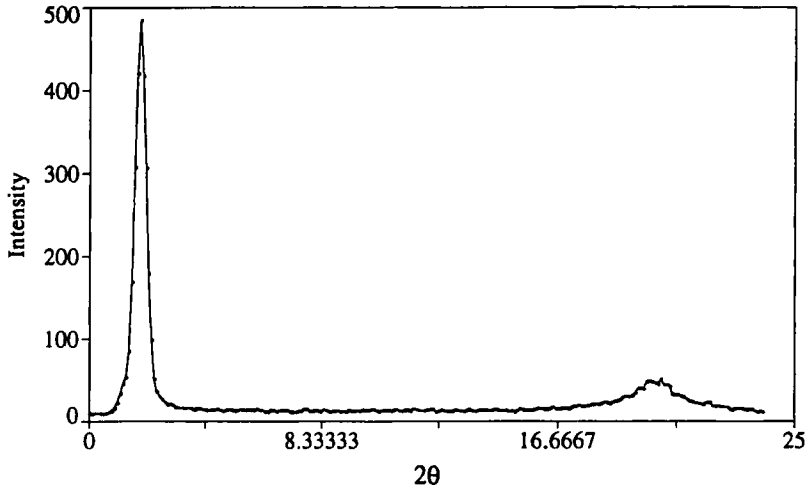

FIGURE 3 The SAXD pattern of MPNB **2** at the temperature of 84°C.

molecular length 49.1 Å, the result led to a monolayer of tilted smectic structure.

The transition temperatures of polymer **1** and **2** are summarized in Table I. Both samples of polymer **1** showed the mesomorphic property of a glass transition, S_C and nematic phases, while polymer **2** exhibited a glass transition, S_C and S_A phases (Figs. 4a and 4b).

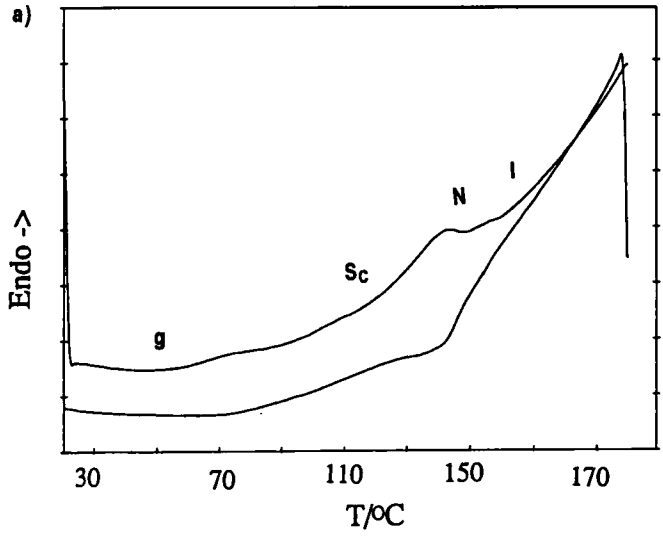

FIGURE 4 a) The DSC curves of polymer **1**; and b) the DSC curves of polymer **2**.

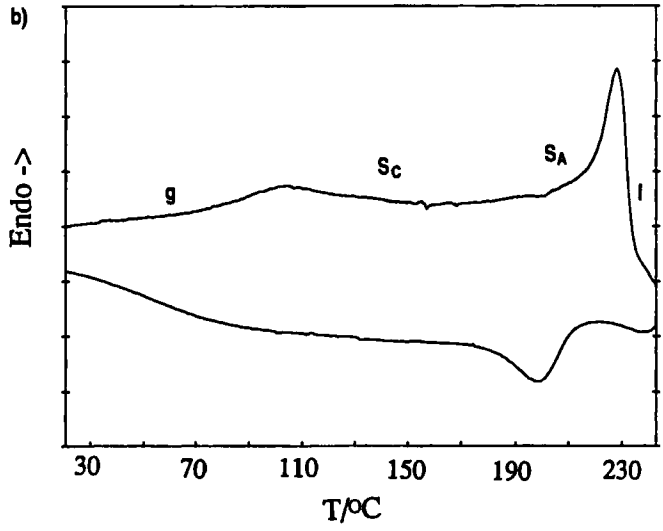

FIGURE 4 (Continued).

Photopolymerizations of AHB 1 in Mesophases and Liquid Crystals

The results of photopolymerization of AHB **1** in mesophases are summarized in Table II. As a consequence of a higher order and translational viscosity, bulk polymerization in the S_C phase resulted in a polymer with the highest molecular weight and wider molecular weight distribution, compared with those of samples of polymerization in nematic and isotropic phases. Differential photo calorimetry (DPC) studies showed that the rate of polymerization in LC states was $S_C > N > I$ (Fig. 5a). Photoinitiated polymerization at the isotropization temperature resulted in a slightly higher molecular weight polymer and a narrower molecular weight distribution compared with that of the nematic phase. The speculation of this result is that in bulk polymerization higher temperature gives rise to a lower viscosity.

TABLE II The molecular weight and molecular weight distribution of polymerization of AHB **1** in liquid-crystalline states

LC State	T_{poly}/°C	*Mn(g/mol)*	*MWD**
S_C	94	27, 800	4.65
N	104	24, 700	3.90
I	114	24, 900	3.47

* MWD: molecular weight distribution (= Mw/Mn).

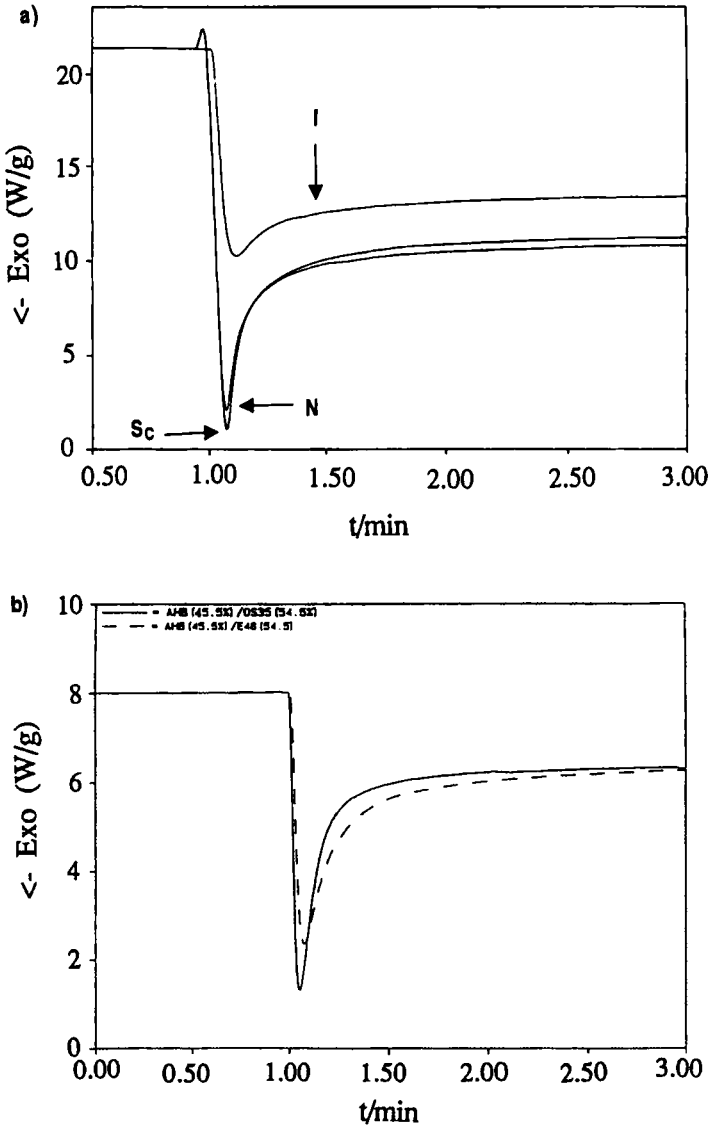

FIGURE 5 a) The DPC thermogram of AHB **1** polymerized in S_C, N and I states; b) the DPC thermogram of AHB **1** polymerized in E48 (dotted line) and OS 35 (filled line).

Photopolymerization of AHB **1** in several liquid crystal solvents is summarized in Table III. Photopolymerization in smectic solvents such as K24 (S_A) and OS35 (S_B) resulted in polymers with higher molecular weight and wider molecular weight distributions. Compared with polymerization in

TABLE III The molecular weight and molecular weight distribution of monomer **1**, photopolymerized in liquid-crystal solvents

LC	*LC State*	**1** (*Wt %*)	*Mn*	*MWD*
K15	N	20	28, 500	2.65
K24	S_A	20	31,700	3.22
E48	N	45	40,600	3.20
OS35	S_B	45	49,100	3.90

TABLE IV The molecular weights and molecular weight distributions of monomer **2**, photopolymerized in liquid-crystalline states

LC State	T_{poly}/°C	*Mn* (*g/mol*)	*MWD*
S_X	80	109, 500	3.57
S_C	110	104, 800	2.70
S_A	130	58, 500	1.43
I	145	24, 900	1.92

higher ordered liquid crystalline solvents, K24 and OS35, nematic solvents (K15 and E48) produce lower molecular weight and narrower molecular weight distribution polymers. A DPC thermogram of polymerization in E48 and OS35 (Fig. 5b) indicated that the polymerization rate in OS35 was faster than that in E48.

Photopolymerization of MHNB 2 in Mesophases

Samples of MHNB **2** were irradiated at different temperatures with the UV dose of 2.4 J/cm^2 (irradiation with 40 mW/cm^2, 60 s). The results of bulk photopolymerization in different liquid-crystalline phases are summarized in Table IV. Those polymers obtained from polymerizing in the S_X phase have the highest molecular weight and widest molecular weight distribution, with results similar to those of AHB **1**. The order of polymer molecular weight is $S_X > S_C > S_A > I$, while the molecular weight distribution follows the order of $S_A > I > S_C > S_X$. As a result of crosslinking, insoluble polymers were obtained when a UV dose exceeded 2.4 J/cm^2. Therefore, with higher UV dose the spontaneous lock-in of ordered network structures is possible by photopolymerizing MHNB **2** in its mesophases.

CONCLUSION

We have demonstrated the influence of degree of order on the photopolymerization and the construction of a multi-dimensional polymer network

via a self-organization. In general, photopolymerization of a mesogenic acrylate monomer in a highly ordered state or highly ordered media resulted in polymers having higher molecular weight and wider molecular weight distribution. A multifunctional mesogenic acrylate monomer allows the construction of a polymer network with a locked-in ordered structure. Photopolymerization of monomers **1** and **2** in their higher ordered mesophases result in polymers with higher molecular weights and wider molecular weight distributions than those of lesser ordered mesophases. Photopolymerization of AHB **1** in high-ordered solvents results in polymers with higher molecular weights and wider molecular weight distributions than those of less-ordered solvents. MHNB **2** has a potential of forming ordered multi-dimensional polymers because of the nature of its smectic lamellar structure and multifunctional reactive groups.

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References

[1] H. Ringsdorf, B. Schlab and J. Venzmer, *Angew Chem. Int. Ed. Engl.*, **27**, 113 (1988).
[2] M. Alhev, W. Müller, A. Reidert, H. Ringsdorf and J. Venzmer, *Angew. Chem. Int. Ed. Engl.*, **29**, 1269 (1990).
[3] J. H. Fendler, *Membrane Mimetic Chemistry*, John Wiley and Sons, New York (1982).
[4] D. J. Broer, H. Finkelmann and K. Kondo, *Makromol. Chem.*, **189**, 185 (1988).
[5] L. Strelecki and L. Liebest, *Bull. Soc. Chim. Fr.*, 597 (1973).
[6] (a) D. J. Broer, G. N. Mol and G. Challa, *Makromol. Chem.*, **190**, 19 (1989); (b) D. J. Broer, A. M. Hikmet and G. Challa, *Makromol. Chem.*, **190**, 3201 (1989).
[7] Y. Imanishi, K. Kondo and T. Kitamura, *Japan J. Appl. Phys.*, **29**, L1447 (1990).
[8] D. Braun, G. Frick, M. Grell, M. Kilms and J. H. Wendorff, *Liquid Crystals*, **11**, 929 (1992).
[9] K. Geibel, A. Hammerschmidt and F. Strohmer, *Adv. Mater.*, **5**, 107 (1993).
[10] L. C. Chien, M. N. Boyden, A. J. Walz and C. M. Citano, *ACS Symposium Series 632*, "*Liquid-Cryastalline Polymer Systems Technological Advances*," Ed. by A. I. Isaayev, T. Kyu and S. Z. D. Cheng, ACS, Washington, DC, p.182 (1996).
[11] J. W. Doane, D. K. Yang and L.-C. Chien, *Proceedings of Int. Display Research Conf. SID*, p. 49 (1991).
[12] D. K Yang, L.-C. Chien and J. W. Doane, *Appl. Phys. Lett.*, **60**, 3102 (1992).
[13] S. I. Stuppe, S. Son, H. C. Lin and L. S. Li, *Science*, **259**, 59 (1993).