Polymer Bulletin 22, 489–496 (1989)

**Polymer Bulletin**

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# Liquid crystalline polyethers based on conformational isomerism

## 7. Synthesis and determination of the virtual mesomorphic phase transitions of polyethers and copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane and 1,13-dibromotridecane

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## SUMMARY

This paper describes the synthesis and characterization of the polyether based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl) ethane (MBPE) and 1,13-dibromotridecane (MBPE-13) and of the copolyethers based on MBPE and 1,13-dibromotridecane with 1,5-dibromopentane (MBPE-5/13), 1,7-dibromoheptane (MBPE-7/13), 1,9-dibromononane (MBPE-9/13), and 1,11-dibromoundecane (MBPE-11/13). MBPE-13 is only crystalline while all copolymers display two monotropic nematic mesophases. The virtual averaged isotropic-nematic transition temperature of MBPE-13 determined from these copolymers is 70 ± 3 °C ($\Delta H = 1.63 \pm 0.24$ kcal/mru), while the virtual nematic-nematic transition temperature is 60 ± 6 °C ($\Delta H = 0.03 \pm 0.02$ kcal/mru).

## INTRODUCTION

In the previous papers from this series we have advanced the concept of flexible mesogenic unit or rod-like mesogenic units based on conformational isomerism (1-6). This concept was applied to the synthesis of liquid crystalline polyethers without flexible spacers (1), and of liquid crystalline polyethers based on flexible mesogenic units and flexible spacers (2-6). They represent the first examples of main chain liquid crystalline polymers which do not contain rigid rod-like mesogenic units (7-13). Presently, we are performing a comprehensive investigation of the series of polyethers (MBPE-n) based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and α,ω-dibromoalkanes (2-6). Most of these polyethers display only virtual mesophases. Exception are the polyethers based on 1,5-dibromopentane (MBPE-5), 1,9-dibromononane (MBPE-9) and 1,11-dibromoundecane (MBPE-11) which display two monotropic nematic phases (2), and the polyether based on MBPE and 1,8-dibromooctane (MBPE-8) (4, 5). MBPE-8 displays a very narrow enantiotropic nematic mesophase that overlaps the melting transition. The first monotropic nematic mesophase, Nu, was identified by X-ray scattering and DSC-experiments (14), and by kinetic DSC and X-ray diffraction experiments (15). No definitive assignment of the second monotropic nematic mesophase is yet available (14, 15). The virtual mesophases displayed by the polyethers containing up to twelve carbon atoms in their flexible spacers were determined from copolymerization experiments (2-6).

The goal of this paper is to describe the synthesis of the polyether based on MBPE and 1,13-dibromotridecane (MBPE-13) and determine its virtual phase transition temperatures and enthalpy changes from copolymerization experiments performed between MBPE and 1,13-dibromotridecane with 1,5-dibromopentane, 1,7-dibromoheptane, 1,9-dibromononane and 1,11-dibromoundecane.

## EXPERIMENTAL

### Materials

1,5-Dibromopentane (97% from Aldrich) was fractionated by vacuum distillation. 1,7-dibromoheptane (97% from Aldrich), 1,9-dibromononane (97% from Aldrich), and 1,11-dibromoundecane (97% from Aldrich) were used as received.

1,13-Tridecanediol. A solution of 13.0 g (0.053 mol) of 1,13-tridecanedioic acid (94% from Aldrich ) in 170 ml of $LiAlH_4$ dried THF, was added dropwise under nitrogen to 200 ml (0.2 mol) of $BH_3$-THF complex (1 M from Aldrich) at 0-5 °C. At the end of addition a gel-like precipitate formed. The temperature of the reaction mixture was raised to 50 °C and maintained overnight. The reaction mixture was poured into 2.5 l of water and the resulting white precipitate was filtered, washed with water, aqueous $NaHCO_3$ and water. The filtrate was dried and recrystallized from benzene to yield 8.3 g (72%) of white crystals. mp = 76-76.5 °C (ref 16, mp = 76.4-76.6 °C). $^1$H-NMR ($CDCl_3$, TMS, δ, ppm): 1.27 (m, 18H, $-(C\underline{H}_2)_9-$), 1.57 (m, 4H, $-OCH_2C\underline{H}_2-$), 3.64 (t, 4H, $-OCH_2C\underline{H}_2-$).

1,13-Dibromotridecane Bromine (12.5 g, 0.078 mol) was added dropwise under nitrogen to an ice cooled (0-10 °C) solution of 20.5 g (0.078 mol) of triphenylphosphine in 120 ml of dried DMF. The color of bromine disappeared and the mixture turned orange. To the $PPh_3$-$Br_2$ complex was added dropwise a solution of 8.0 g (0.037 mol) of 1,13-tridecanediol dissolved in 120 ml of dried DMF, and the reaction was left stirring at room temperature overnight. DMF was distilled under vacuum and the resulting pale yellow oil was extracted two times with 200 ml of hexane. The white precipitate ($Ph_3PO$) was filtered and hexane was evaporated. Vacuum distillation of the residue gave 9.6 g (76%) of 1,13-dibromotridecane. bp = 160-162 °C / 0.5 mmHg (lit 15, bp =185-187 °C / 9mmHg ) . $^1$H-NMR ($CDCl_3$, TMS, δ, ppm): 1.27 (m, 18H, $-(C\underline{H}_2)_9-$), 1.86 (quintet, 4H, $BrCH_2C\underline{H}_2-$), 3.41 (t, 4H, $BrCH_2C\underline{H}_2-$), 3.41 (t, 4H, $BrC\underline{H}_2CH_2-$). $CH_2OH$ group could not be detected by NMR analysis.

1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) (100% purity by HPLC) was synthesized as previously reported (2).

### Techniques.

All analytical techniques used were previously described (2-6).

### Synthesis of Polyethers and Copolyethers.

Both polyethers and copolyethers were synthesized and purified as described in previous publications (2-6).

## RESULTS AND DISCUSSION

In the previous publications from this series we have developed a method for the

**Table I** Characterization of Polyethers based on MBPE and 1,5-dibromopentane (MBPE-5), MBPE and 1,13-dibromotridecane (MBPE-13) and of Corresponding Copolyethers [MBPE-5/13 (A/B)], and 1,7-dibromoheptane (MBPE-7) and of Corresponding Copolyethers [MBPE-7/13 (A/B)]

| Copolymer MBPE-5, 7/13 (A/B) 5, 7/13 Mole Ratio | Mn GPC | Mw/Mn | Thermal transition (° C), and corresponding enthalpy changes (Kcal/mru) in parentheses: Heating | Cooling |
|---|---|---|---|---|
| MBPE-5/13 | | | | |
| 100/0 | 19,000 | 1.90 | g 20 k 79(1.44) k 115(0.33) i | i 51(0.57) $n_1$ 37(0.10) $n_2$ 13 g |
| 80/20 | 12,000 | 2.25 | g 15 k 44(0.09) k 61(0.73) i | i 54(0.65) $n_1$ 38(0.07) $n_2$ 8 g |
| 60/40 | 35,500 | 1.72 | g 10 k 54(0.59) k 65(0.58) k 77(0.43) i | i 59(0.92) $n_1$ 45(0.09) $n_2$ 6 g |
| 50/50 | 20,400 | 1.70 | g 9 k 54 k 59 k 65(2.13*) k 74(0.18) i | i 59(1.03) $n_1$ 45(0.05) $n_2$ 31(0.44) k 3 g |
| 40/60 | 11,400 | 1.49 | g 8 k 60(0.79) k 69 k 77(1.98*) i | i 63(1.20) $n_1$ 52(0.05) $n_2$ 42(0.77) k 2 g |
| 20/80 | 14,300 | 2.00 | g 13 k 76 k 83 k 88(3.17*) i | i 68(1.39) $n_1$ 55(1.51) k 5 g |
| 0/100 | 12,900 | 1.91 | k 77 k 85 k 98(4.26*) i | i 69(5.24) k |
| MBPE-7/13 | | | | |
| 100/0 | 22,100 | 1.76 | g 7 k 85(2.18) i | i 66(2.01) k 0 g |
| 80/20 | 26,300 | 2.11 | g 12 k 63(0.57) k 78(1.65) i | i 64(0.83) $n_1$ 52(0.08) $n_2$ 2 g |
| 60/40 | 15,300 | 1.44 | g 8 k 51 k 57 k 70(2.39*) i | i 64(1.05) $n_1$ 52(0.09) $n_2$ 2 g |
| 50/50 | 14,400 | 1.46 | g 8 k 53(0.88) k 71(1.36) i | i 64(1.15) $n_1$ 53(0.09) $n_2$ 20(0.12) k 1 g |
| 40/60 | 11,800 | 1.74 | g 13 k 58(0.83) k 68 k 75(1.86*) i | i 66(1.23) $n_1$ 56(0.04) $n_2$ 30(0.41) k 4 g |
| 20/80 | 25,500 | 1.67 | g 7 k 67 k 80 k 87(4.59*) i | i 67(1.34) $n_1$ 55(1.99) k 5 g |
| 0/100 | 12,900 | 1.91 | k 77 k 85 k 98(4.26*) i | i 69(5.24) k |

* overlapping transition

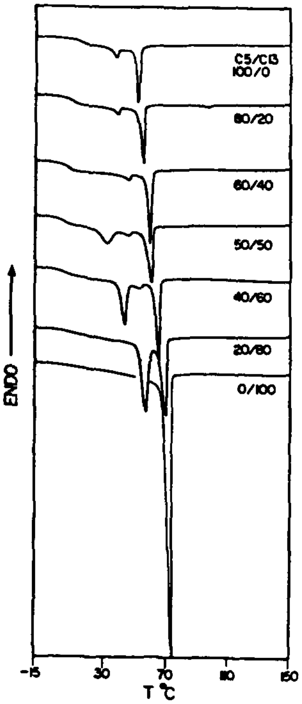

**Figure 1:** Cooling DSC traces (20°C/min) of MBPE-5/13

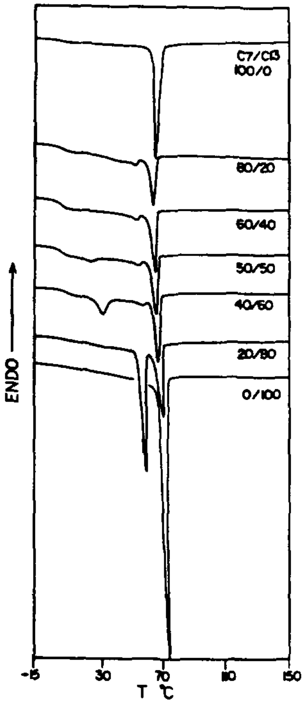

**Figure 2:** Cooling DSC traces (20°C/min) of MBPE-7/13

determination of the virtual phase transition temperatures and thermodynamic parameters of homopolymers. This method is based on the synthesis and characterization of copolymers based on a single mesogenic unit and two (2-5) or more than two flexible spacers (6). The main requirements of this technique are: 1) the molecular weights of these copolymers should be above the molecular weight which influences phase transition temperatures. For the case of MBPE-n this value is Mn ≈ 12000; 2) the copolymer composition should be well defined, 3) the compositional heterogeneity of the copolymer should be as low as possible. Upon copolymerization, the crystallization temperature gets suppressed below the isotropic-anisotropic transition temperature, and therefore the virtual mesophases of the homopolymers become monotropic or even enantiotropic in copolymers (2-6).

Most frequently, the structural units of the copolymers are isomorphic in the liquid crystalline phase but not in the crystalline phase (2-6). Therefore, the mesomorphic phase transition temperatures and their corresponding thermodynamic parameters show a linear dependence of composition which by extrapolation leads to the determination of the virtual phase transition temperatures and thermodynamic parameters of the homopolymers. This is not the case for the crystalline phase. The only crystalline phase which displays such a dependence is the intermeshed one (2-7). Combinations of spacers containing odd-odd (2, 3, 6) even-even (4) and even-odd (5) number of carbon atoms are providing copolymers which exhibit this behavior.

Table I summarizes the experimental results for MBPE-5, MBPE-13, MBPE-7 and for the copolymers MBPE-5/13 and MBPE-7/13. MBPE-5 displays a monotropic nematic mesophase at 51 °C and a monotropic nematic-nematic transition at 37 °C. MBPE-7 and MBPE-13 are only crystalline. None of the synthesized copolymers display an enantiotropic mesophase. However, most of them display two monotropic nematic mesophases. Representative cooling DSC scans for the system MBPE-5/13 are presented in Figure 1 while for the system MBPE-7/13 in Figure 2. Let us follow the system MBPE-5/13. Upon inserting 20 mol% of short spacer in the structure of MBPE-13, the crystallization peak gets splitted into an isotropic-nematic peak at 68 °C and a nematic-crystalline peak at 55 °C. Increasing the content of the short spacer depresses even more the crystallization temperature until for MBPE-5/13 (60/40) it goes below Tg. Copolymers MBPE-5/13 (40/60) to MBPE-5 present also a monotropic nematic-nematic mesophase. The isotropic-nematic and nematic-nematic phase transition temperatures show linear dependence of composition. Cooling DSC scans for the system MBPE-7/13 are shown in Figure 2. Both MBPE-7 and MBPE-13 are crystalline only. However, upon copolymerization, the crystallization peaks get splitted into isotropic-nematic, nematic-nematic and nematic-crystalline peaks (Figure 2). All phase transition temperatures from the cooling DSC scans are plotted in Figures 3 and 4 while their corresponding thermodynamic parameters in Figures 5 and 6. Upon extrapolation, the isotropic-nematic and nematic-nematic phase transitions and their corresponding thermodynamic parameters were determined.

Table II summarizes all characterization data for MBPE-9, MBPE-11, MBPE-13 and the series of copolymers MBPE-9/13 and MBPE-11/13. MBPE-9 displays a monotropic isotropic-nematic phase transition (64 °C), a monotropic nematic-nematic phase transition (58 °C), and a crystallization peak (48 °C) (Figure 7). MBPE-11 displays a monotropic nematic mesophase (72 °C) and a crystallization peak (64 °C) (Figure 8). DSC scans from Figures 7 and 8 were interpreted in a similar manner as those from Figures 1 and 2. Thermal transition temperatures were plotted in Figures 9 and 10 while their thermodynamic parameters in Figures 11 and 12.

Table 3 summarizes the virtual thermal transition temperatures and thermodynamic parameters of MBPE-13 determined from various series of experiments as well as the averaged values.

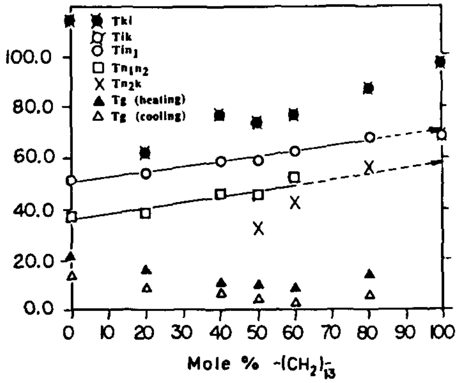

**Figure 3:** Thermal transitions of MBPE-5/13

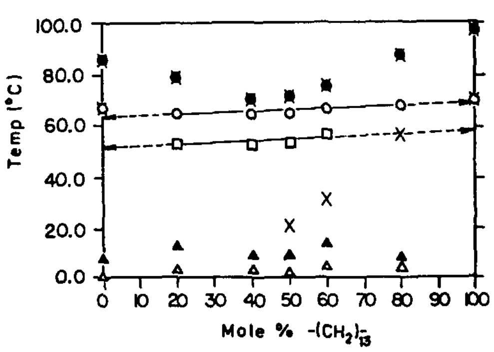

**Figure 4:** Thermal transitions of MBPE-7/13 (symbols as in Fig. 3)

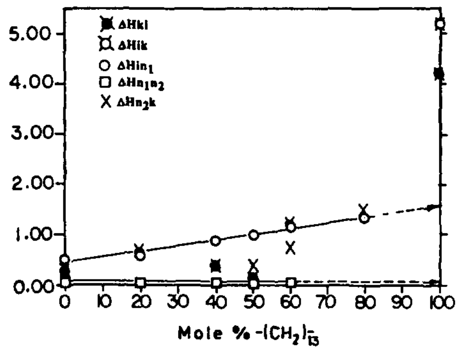

**Figure 5:** Enthalpy changes associated with phase transitions of MBPE-5/13

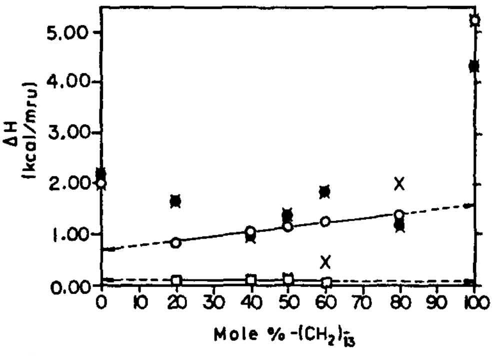

**Figure 6:** Enthalpy changes associated with phase transitions of MBPE-7/13 (symbols as in Fig. 5)

**Table II** Characterization of Polyethers based on MBPE and 1,9-dibromononane (MBPE-9), MBPE and 1,13-dibromotridecane (MBPE-13) and of Corresponding Copolyethers [MBPE-9/13 (A/B)], and 1,11-dibromoundecane (MBPE-11) and of Corresponding Copolyethers [MBPE-11/13 (A/B)]

| Copolymer MBPE-9, 11/13 (A/B) 9, 11/13 Mole Ratio | Mn GPC | Mw/Mn | Thermal transition (°C), and corresponding enthalpy changes (Kcal/mru) in parentheses: Heating | Cooling |
|---|---|---|---|---|
| MBPE-9/13 | | | | |
| 100/0 | 20,600 | 1.38 | g 6 k 75 k 80 k 91(2.67) i | i 64(1.05) $n_1$ 58(0.06) $n_2$ 48(2 .13) k 0 g |
| 80/20 | 21,900 | 1.72 | g 11 k 49(0.47) k 73(0.08) k 85 (2.38) i | i 73(1.26) $n_1$ 64(0.14) $n_2$ 4 g |
| 60/40 | 22,000 | 1.99 | g 14 k 50(0.32) k 80(2.26) i | i 69(1.17) $n_1$ 62(0.04) $n_2$ 8 g |
| 50/50 | 22,700 | 1.53 | g 11 k 46 k 48 k 77(3.52) i | i 68(1.34) $n_1$ 58(0.12) $n_2$ 25(0.51) k 4 g |
| 40/60 | 17,600 | 2.29 | g 16 k 53(0.58) k 79 (2.27) i | i 70(1.34) $n_1$ 60(0.08) $n_2$ 34(0.39) k 9 g |
| 20/80 | 15,100 | 1.70 | g 13 k 72(0.16) k 90(3.58) i | i 72(1.65) $n_1$ 68(0.01) $n_2$ 57(1.61) k 4 g |
| 0/100 | 12,900 | 1.91 | k 77 k 85 k 98(4.26*) i | i 69(5.24) k |
| MBPE-11/13 | | | | |
| 100/0 | 28,500 | 2.02 | g 5 k 101(4.49) i | i 72(1.09) $n_1$ 64(2.66) k |
| 80/20 | 13,700 | 1.92 | g 5 k 74(0.24) k 83 k 88(3.07*) i | i 72(1.44) $n_1$ 63(0.06) $n_2$ 51(1.67) k |
| 60/40 | 16,800 | 1.80 | g 7 k 51 k 74 k 80 k 84(4.01*) i | i 73(1.59) $n_1$ 66(0.10) $n_2$ 48(1.38) k |
| 50/50 | 22,300 | 1.66 | g 10 k 56 k 77(3.91) i | i 68(1.59) $n_1$ 58(0.04) $n_2$ 42(1.56) k |
| 40/60 | 17,800 | 1.76 | g 12 k 79(3.67) i | i 70(1.51) $n_1$ 60(0.03) $n_2$ 49(1.24) k |
| 20/80 | 13,600 | 1.92 | g 12 k 81 k 87(4.79) i | i 71(1.71) $n_1$ 61(2.02) k |
| 0/100 | 12,900 | 1.91 | k 77 k 85 k 98(4.26*) i | i 69(5.24) k |

* overlapping transition

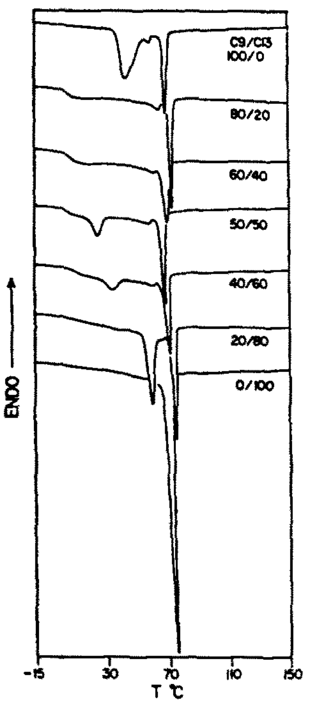

Figure 7: Cooling DSC traces (20°C/min) of MBPE-9/13

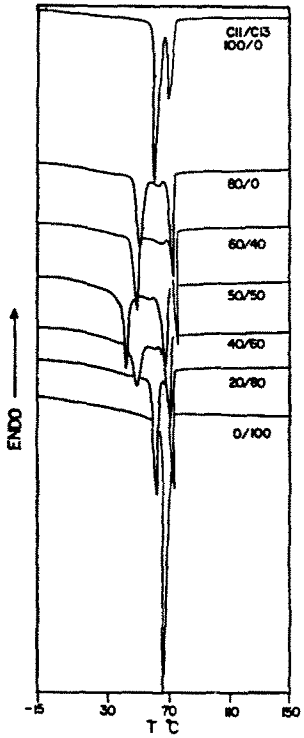

Figure 8: Cooling DSC traces (20°C/min) of MBPE-11/13

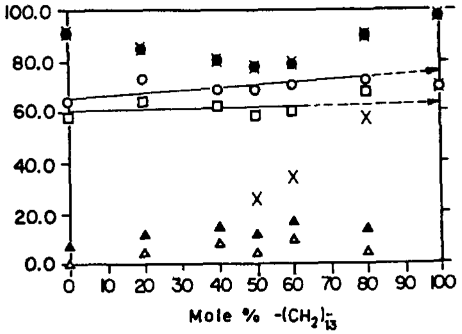

**Figure 9:** Thermal transitions of MBPE-9/13 (symbols as in Fig. 3)

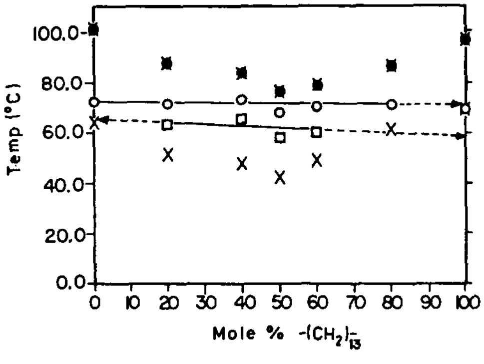

**Figure 10:** Thermal transitions of MBPE-11/13 (symbols as in Fig. 3)

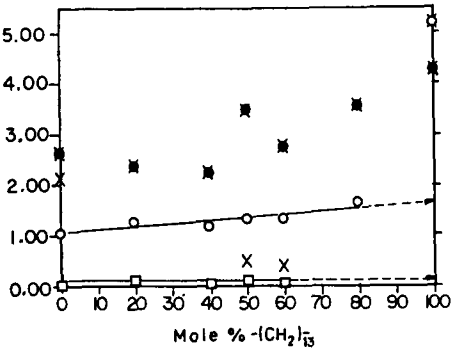

**Figure 11:** Enthalpy changes associated with phase transitions of MBPE-9/13 (symbols as in Fig. 5)

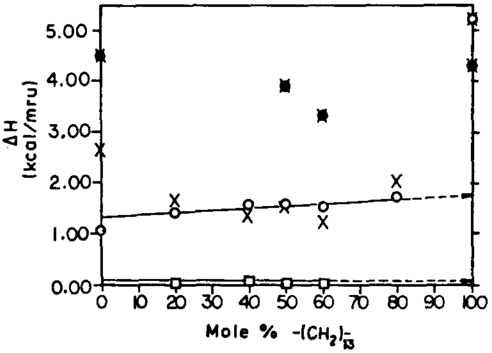

**Figure 12:** Enthalpy changes associated with phase transitions of MBPE-11/13 (symbols as in Fig. 5)

Table III Virtual Phase Transition Temperatures and Thermodynamic Parameters [ ] of MBPE-13

| MBPE-13 | Thermal transitions ( °C), and the corresponding enthalpy changes (kcal/mru) in parentheses |
|---|---|
| | cooling |
| determined from | |
| MBPE-5/13 | i [71(1.60)] $n_1$ 69(5.24) k 59(0.02) $n_2$ |
| MBPE-7/13 | i 69(5.24) k [68(1.54)] $n_1$ 58(0.03) $n_2$ |
| MBPE-9/13 | i [73(1.67)] $n_1$ 69(5.24) k 66(0.04) $n_2$ |
| MBPE-11/13 | i 69(5.24) k, [69(1.87)] $n_1$ 55(0.01) $n_2$ |
| MBPE-13 (averaged) | i [70±3(1.63±0.24)] $n_1$ 69(5.24) k 60±6(0.03±0.02) $n_2$ |

## ACKNOWLEDGEMENTS

Financial support of this work by the National Science Foundation, Polymer Program (DMR-86-19724), is gratefully acknowledged.

## REFERENCES

1) V. Percec and R. Yourd, Macromolecules, 21, 3379 (1988)
2) V. Percec and R. Yourd, Macromolecules, 22, 524 (1989)
3) V. Percec and R. Yourd, Macromolecules, 22, 3229 (1989)
4) V. Percec and R. Yourd, Makromol. Chem., in press
5) V. Percec and R. Yourd, Makromol. Chem., in press
6) V. Percec and Y. Tsuda, Macromolecules, in press
7) C. K. Ober, J. I. Jin and R. W. Lenz, Adv. Polym. Sci., 59, 130 (1984)
8) H. Finkelmann, Angew. Chem. Int. Ed. Engl., 26, 816 (1987)
9) H. Ringsdorf, B. Schlarb and J. Venzmer, Angew. Chem. Int. Ed. Engl., 27, 113 (1988)
10) J. Economy, Mol. Cryst. Liq. Cryst., 169, 1 (1989)
11) W. J. Jackson, Jr., Mol. Cryst. Liq. Cryst., 169, 23 (1989)
12) M. Ballauff, Angew. Chem. Int. Ed. Engl., 28, 253 (1989)
13) C. Noel, Makromol. Chem., Macromol. Symp., 22, 95 (1988)
14) G. Ungar, J. L. Feijoo, A. Keller, R. Yourd and V. Percec, Macromolecules, submitted
15) S. Z. D. Cheng, M. A. Yandrasits and V. Percec, Polymer, submitted
16) P. Chuit, Helv. Chim. Acta., 9, 271 (1929)
17) J. L. Feijoo, G. Ungar, A. J. Owen, A. Keller and V. Percec, Mol. Cryst. Liq. Cryst., 155, 487 (1988)

Accepted November 20, 1989 C