Polyimines from terephthalaldehyde and aliphatic diamines: 5. Copolymers with even–even numbers of methylene units in the flexible spacer

Haixin Yang and Almeria Natansohn*
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6
(Received 24 June 1992; revised 18 December 1992)

A series of copolyimines from terephthalaldehyde and 1,8-diaminooctane and 1,10-diaminodecane is synthesized. X-ray diffraction and cross-polarized microscopic studies reveal that all the copolyimines exhibit a liquid crystalline smectic phase as does one of the parent homopolyimines, PI10. The transition temperatures and the associated enthalpy and entropy change continuously as functions of copolymer composition. The crystalline and liquid crystalline phases of the copolyimine series are isomorphic. The copolyimines are soluble in chloroform and tetrahydrofuran.

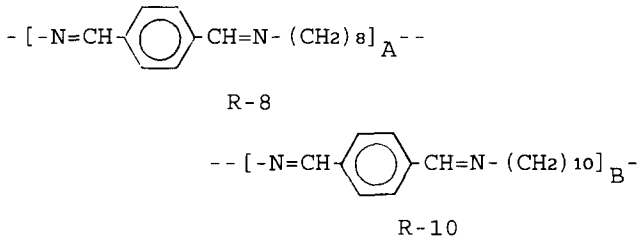
(Keywords: polyimines; copolymer; phase transition)

INTRODUCTION

In the previous papers[1–4] the synthesis and characterization of series of liquid crystalline polyimines[1,2] and copolyimines with odd–even[3] and odd–odd[4] combinations of methylene units on the flexible spacers in the main chain have been reported. Both melting and isotropization temperatures of the copolyimines with odd–even combinations of the number of methylene units in the flexible spacer are depressed and the liquid crystalline temperature ranges are narrowed compared to the corresponding homopolyimes. The copolyimines having approximately the same molar amounts of the even and odd spacers do not exhibit liquid crystalline phases and they have the lowest melting transition temperatures. Both the crystalline and liquid crystalline phases of these copolyimines have isodimorphic character. The copolyimines with an odd–odd combination of methylene units in the flexible spacer exhibit a wider liquid crystalline temperature range. This is mainly the consequence of the significant depression of the melting transition temperatures upon copolymerization. Both the crystalline and liquid crystalline phase of these odd–odd copolyimines exhibit isodimorphic character.

It has been reported[5–7] that odd–odd, even–even and odd–even combinations of the number of methylene units in the flexible spacer tend to produce different changes in the transition temperatures and liquid crystalline temperature ranges for some liquid crystalline polyesters. Various combinations of different spacers have also been investigated for some liquid crystalline copolyethers[8–12]. This paper presents the synthesis of a series of copolyimines with an even–even combination of the numbers of methylene units in the flexible spacer. The dependence of the transition temperatures and the associated enthalpy and entropy changes on copolyimine composition is also discussed.

The copolyimines prepared are statistical copolymers with general formulas as follows:



All the copolyimines have the same mesogenic unit but different flexible spacers. R-8 and R-10 are used to name the different structural (repeating) units, where 8 or 10 is the number of the methylene units in the flexible chain. Therefore the series of copolyimines is represented as COPI-8-10 (A/B). The ratio of the molar percentages (A/B) is varied by increments of 10 from A/B = 10/90 to 90/10.

EXPERIMENTAL

Materials

Terephthalaldehyde, hexamethylphosphoramide and all the aliphatic diamines were used as received from Aldrich. Lithium chloride (BDH) and all the solvents (BDH) were used without further purification.

Copolymerization and characterization

Copolymerization was carried out according to the procedure described in detail in previous papers[1,3].

* To whom correspondence should be addressed

0032-3861/93/194135-05

Purification was performed by reprecipitation in a chloroform/ethanol system as described in a preceding paper[3]. Copolymer compositions were determined by solution n.m.r. and reactivity ratios were calculated according to the method used previously[3]. I.r. spectra were obtained on a Bomem Michelson spectrophotometer using KBr pellets. Solution n.m.r. spectra were obtained on a Bruker AC-F 200 MHz n.m.r. spectrometer using chloroform-d as solvent.

Molecular weights were determined in tetrahydrofuran by gel permeation chromatography (g.p.c.) on a Waters Associates model 400 instrument equipped with three columns, μ-Styragel 10^4, 10^3 and 10^2 Å in series. The polystyrene calibration curve was used.

Table 1 Number average molecular weights ($\bar{M}_n$) and average degree of polymerization ($\overline{DP}_n$) of COPI-8-10

Copolymer	$\bar{M}_n$	$\overline{DP}_n$
COPI-8-10(10/90)	8600	23
COPI-8-10(20/80)	9200	25
COPI-8-10(30/70)	10320	29
COPI-8-10(40/60)	11200	31
COPI-8-10(50/50)	8060	22
COPI-8-10(60/40)	10700	30
COPI-8-10(70/30)	8800	25
COPI-8-10(80/20)	9530	27
COPI-8-10(90/10)	7980	23

A Mettler TA-3000 differential scanning calorimeter equipped with a Mettler TC10A data processor was used for thermal analysis. Heating and cooling scan rates were 10 K min^{-1} in all cases. Optical observations were made on a Nikon Labophot-2 microscope under cross-polarized light (magnification 200 ×) using a Wild–Leitz heating stage 350. Samples for microscopic observation were cast as films on glass slides from chloroform solutions.

X-ray powder diffraction patterns were obtained using a CSS/STOE 2P/L two-circle diffractometer with a high temperature attachment. The X-ray beam used was nickel filtered Cu radiation ($\lambda_\alpha = 1.5418$ Å).

RESULTS AND DISCUSSION

All COPI-8-10 samples are soluble in chloroform and tetrahydrofuran while the homopolyimines PI8 and PI10 are insoluble in these solvents. The solubility of the copolyimines is probably a consequence of the lower crystallinity and of the less perfect crystalline phase in copolymers[3,10,13] as compared to the homopolymers. The reactivity ratios for both R-8 and R-10 are the same ($r_1 = r_2 = 1$), as expected for a statistical step copolymerization. The average molecular weights and degrees of polymerization are summarized in *Table 1*.

The thermal characterization by d.s.c. is summarized in *Table 2*. The d.s.c. thermograms of COPI-8-10 samples

Table 2 Thermal characterization of COPI-8-10 series

COPI-8-10 (A/B)	Thermal transition temperature (°C) and corresponding enthalpy changes (kJ mol^{-1}) and entropy changes (J mol^{-1} K^{-1})[a]	
	On heating	On cooling
0/100	k 107(8.7;22.9) s 143(13.1;31.5) i	i 123(10.2;25.8) s 95(6.9;18.8) k
	k 97(8.3;22.4) s 138(19.3;52.1) i	
10/90	k 92(5.7;15.7) s 141(22.5;53.3) i	i 123(16.7;48.7) s 82(10.2;28.7) k
	k 92(5.7;15.7) s 141(22.5;53.3) i	
20/80	k 86(6.3;17.6) s 138(21.9;53.2) i	i 120(16.2;41.1) s 72(8.2;23.8) k
	k 87(6.4;17.7) s 137(18.9;46.1) i	
30/70	k 81(5.0;14.1) s 137(18.2;44.4) i	i 120(12.4;32.4) s 64(5.6;16.7) k
	k 94(3.0;8.3) s 136(16.5;40.2) i	
40/60	k 77(1.6;4.5) s 138(18.5;45.0) i	i 120(13.0;33.1) s 58(5.3;16.0) k
	k 94(3.0;8.3) s 136(16.5;40.2) i	
50/50	k 90(2.1;5.6) s 139(19.1;46.3) i	i 121(11.5;29.0) s 50(3.8;11.8) k
	k 91(2.5;6.9) s 138(14.9;36.3) i	
60/40	k 92(3.9;10.8) s 144(18.1;43.4) i	i 119(8.8;22.3) s 47(3.3;10.5) k
	k 90(0.8;2.2) s 145(14.7;34.2) i	
70/30	k 92(1.8;4.9) s 145(17.8;42.5) i	i 126(10.1;25.3) s 51(4.1;12.6) k
	k 88(0.8;2.1) s 144(14.8;35.5) i	
80/20	k 93(1.4;3.7) s 151(18.2;42.8) i	i 129(11.3;28.2) s 52(1.2;3.7) k
	k 75(0.6;1.8) s 146(14.7;35.1) i	
90/10	k 81(1.1;3.1) s 157(20.6;47.9) i	i 136(12.0;29.5) s 35(0.9;2.9) k
	k 57(1.4;4.2) s 152(15.7;36.9) i	
100/0	k 107(9.1;23.9) k_2 162(16.5;37.9) i	i 137(12.5;30.5) k_2 32(0.8;2.6) k
	k 33(1.3;4.2) k_2 155(14.6;34.1) i	

[a] The data are presented as $T(\Delta H;\Delta S)$. The entropy values were not calculated by extrapolating to zero scanning rates. Data on the first lines are from the first heating and the first cooling scans. Data on the second lines are from the second heating scans. k and k_2 represent crystalline phases, s the liquid crystalline phase and i the isotropic melt

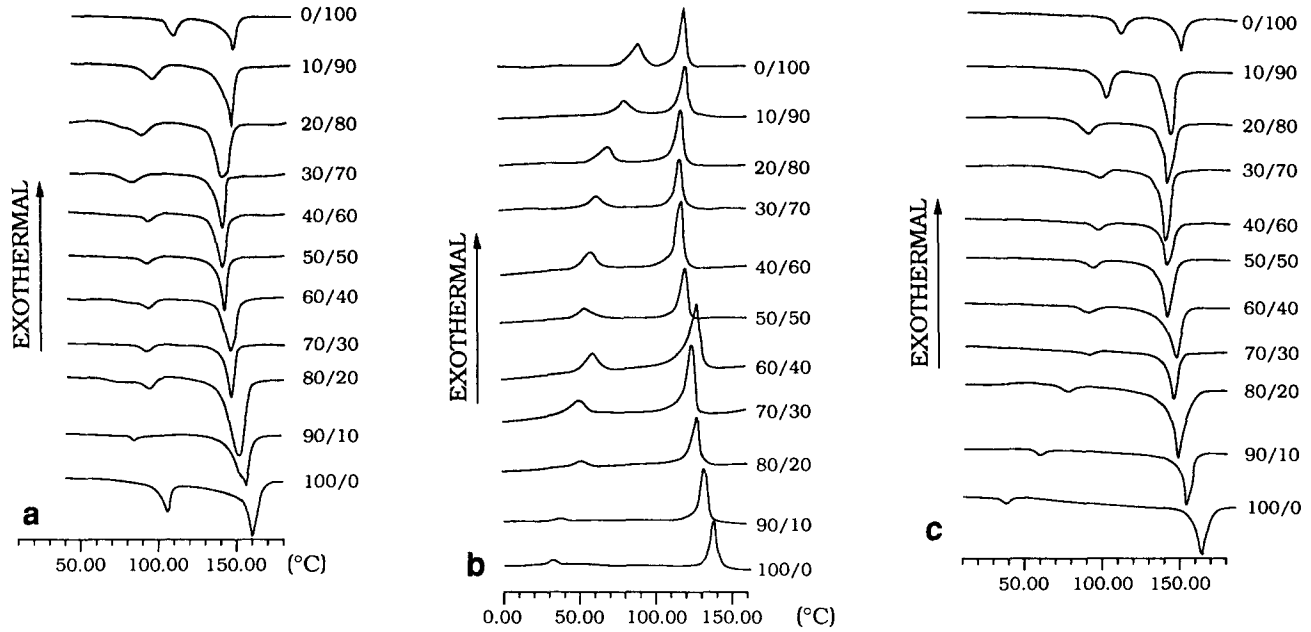


Figure 1 D.s.c. thermograms of COPI-8-10: (a) first heating scan; (b) first cooling scan; (c) second heating scan

along with those of PI8 and PI10 are shown in *Figure 1*. For all the copolyimines, the thermograms of the first heating scans are different from those of the second heating scans. The thermograms of the second heating scans and the subsequent scans are similar. All the thermograms of the different cooling scans are the same. *Table 2* contains thermodynamic data for the first heating, the second heating and the first cooling scans. Transition temperatures are taken at the maximum or minimum of the exothermic or endothermic peaks. The calculation of entropy values is not extrapolated to zero heating (cooling) rate. This means that the apparent values do not represent thermodynamic equilibrium and contain kinetic effects. It can be seen in *Figure 1a* (the first d.s.c. heating scans) that there are two endothermic transitions for each COPI-8-10 sample. This is different from the case of COPI-3-10 and COPI-5-10 series[3], which showed only one transition (the transition from crystalline state to isotropic liquid) at approximately equal amounts of odd and even numbered spacers in the copolyimines, such as in COPI-3-10 (50/50). The transition temperatures of the polyimines are not depressed, as compared to the transitions of the homopolyimines, PI8 and PI10. The transition at the lower temperature on each d.s.c. thermogram of the copolyimines is weaker than that of the homopolyimines. On the cooling scans (*Figure 1b*), there are two corresponding exothermal transitions for each sample. The transition at the lower temperature shifts to even lower temperature and the transition at the higher temperature shifts to higher temperature with the increase of R-8 component in the copolymers. Also, the transition at the lower temperature becomes weaker with the increase of R-8. On the second heating scans, all the copolyimines again show two transitions. The transition at the lower temperature is even more depressed and is weaker than on the first heating scan.

All the copolyimines exhibit a crystalline phase below the transition at the lower temperature and a liquid crystalline phase in between the two transitions. Above the transition at the higher temperature, all copolyimines from isotropic melts. The liquid crystalline textures of COPI-8-10 (10/90), COPI-8-10 (50/50) and COPI-8-10 (90/10), as examples, are presented in *Figures 2a–c*, respectively. The textures of the three are alike and similar to the texture of PI10, which was assigned to a liquid crystalline smectic G phase. PI8 exhibited another crystalline phase in between the two transitions[2].

To confirm the type of the liquid crystalline phase observed under the cross-polarizing microscope, X-ray powder diffraction was carried out on one of the copolyimines, COPI-8-10 (50/50), as a function of temperature. The X-ray diffraction patterns of COPI-8-10 (50/50) in the crystalline phase at 23°C and liquid crystalline phase at 129°C are shown in *Figure 3*. Diffraction peaks are indexed based on our previous X-ray diffraction results of PI8 and PI10[2]. *Figure 3B* shows that there are only two sharp diffraction peaks for COPI-8-10 (50/50) at 129°C, a temperature between the two transitions on heating. The peak at $2\theta = 5.58°$ is the diffraction by plane (0 0 1) which is the layer plane[2]. Another at $2\theta = 20.23°$ can be indexed as (1 1 1) diffraction. The angle between the c axis and the layer plane is tilted about 60°. This kind of diffraction pattern can be assigned to a liquid crystalline smectic G phase[2,14]. It is reasonable to believe that the nature of the liquid crystalline phase in all the copolyimines is similar. Hence the two transitions on the heating scan can be obtained as T_{k-s} and T_{s-i}, respectively, and on cooling they are correspondingly T_{s-k} and T_{i-s}; subscript k represents the crystalline phase, s the liquid crystalline phase and i the isotropic melt.

The percentage crystallinity obtained by X-ray diffraction for COPI-8-10 (50/50) is 34%, while the crystallinity of PI10 and PI8 as synthesized is 36% and 42%, respectively[2]. The layer distance D_{001} at room temperature for COPI-8-10 (50/50) is 15.65 Å, which is larger than $D_{001} = 15.48$ Å for PI10 and $D_{001} = 13.09$ Å for PI8. This means that the crystalline phase of the copolyimine is more disordered when compared to that of the homopolyimines[2,3]. This agrees with the explanation for the solubility of the copolyimines.

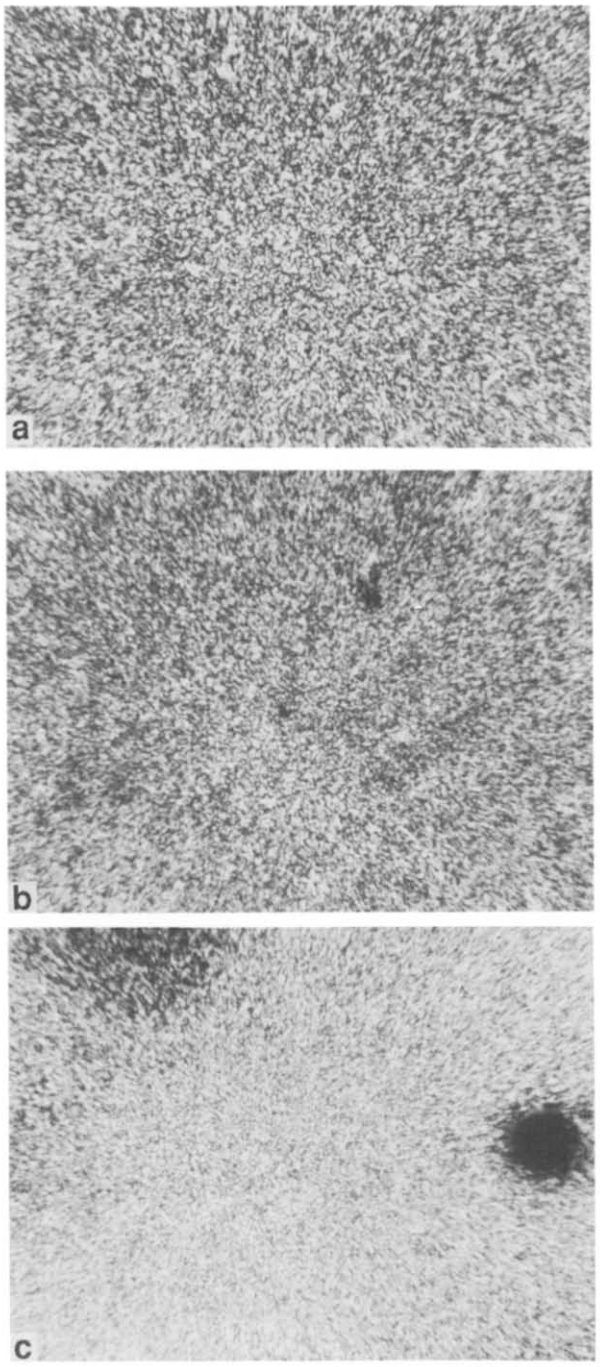


Figure 2 Liquid crystalline textures obtained on cooling from isotropic melt: (a) COPI-8-10(10/90) at 102°C; (b) COPI-8-10(50/50) at 99°C; (c) COPI-8-10(90/10) at 96°C. Magnification 140 ×

Based on the results above, the phase diagrams of COPI-8-10 are obtained and shown in *Figures 4a* and *b*, using the data from the second heating scan and the first cooling scan, respectively. It should be noted that the phase diagrams do not represent a thermodynamic equilibrium and contain kinetic effects[15,16]. The transition temperature from the liquid crystalline phase to isotropic melt (T_{s-i}) stays approximately constant when R-8 content is below 50%. Then T_{s-i} increases slightly in the R-8 range from 60 to 100%. The transition temperature from the crystalline phase to the liquid crystalline phase, T_{k-s}, decreases slightly with the increase of R-8 component up to 70% R-8. Above 70%, T_{k-s} decreases significantly. On cooling (*Figure 4b*), T_{i-s} exhibits a similar trend to T_{s-i} on heating, while T_{s-k} decreases gradually with the increase in R-8.

It can be seen from *Figures 5* and *6*, respectively, that the enthalpy change (ΔH) and the entropy change (ΔS) associated with the transitions on the second heating scans decrease gradually with the increase in R-8 component up to 50% then stay unchanged with further increase in R-8 to 100%.

From the phase diagrams (*Figure 4*) and the relationship between ΔH, ΔS and copolyimine composition, no obvious minimum point of any transition temperature or of ΔH or ΔS is observed. Therefore the COPI-8-10 series has no isodimorphic character[3,15–18] of either the crystalline or the liquid crystalline phases. According to the results above, it is reasonable to believe that the crystalline and the liquid crystalline phases of the COPI-8-10 series are isomorphic[8,19]. In this case, R-8 and R-10 coexist uniformly in both the crystalline and liquid crystalline phases.

The isomorphic character of the copolyimines in the liquid crystalline phase is also reflected by the layer distance (D_{001}) obtained by X-ray diffraction. The layer distance of COPI-8-10 (50/50) in the liquid crystalline phase at 129°C is $D_{001} = 15.83$ Å, which is approximately the average value, 15.93 Å, of $D_{001} = 14.80$ Å of PI8 and

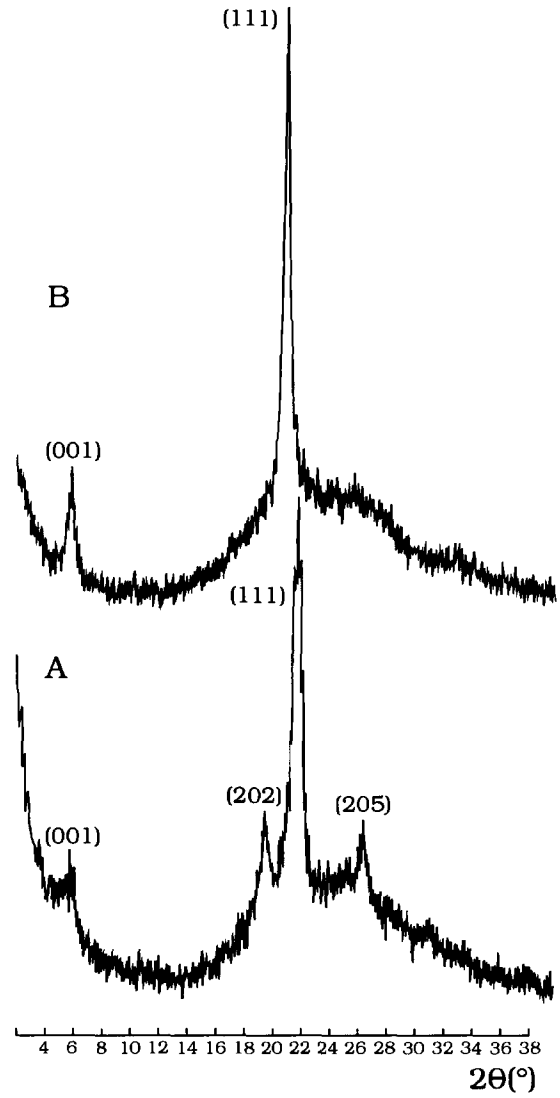


Figure 3 X-ray diffraction patterns of COPI-8-10(50/50): A, in the crystalline phase at 23°C; B, in the liquid crystalline phase at 129°C

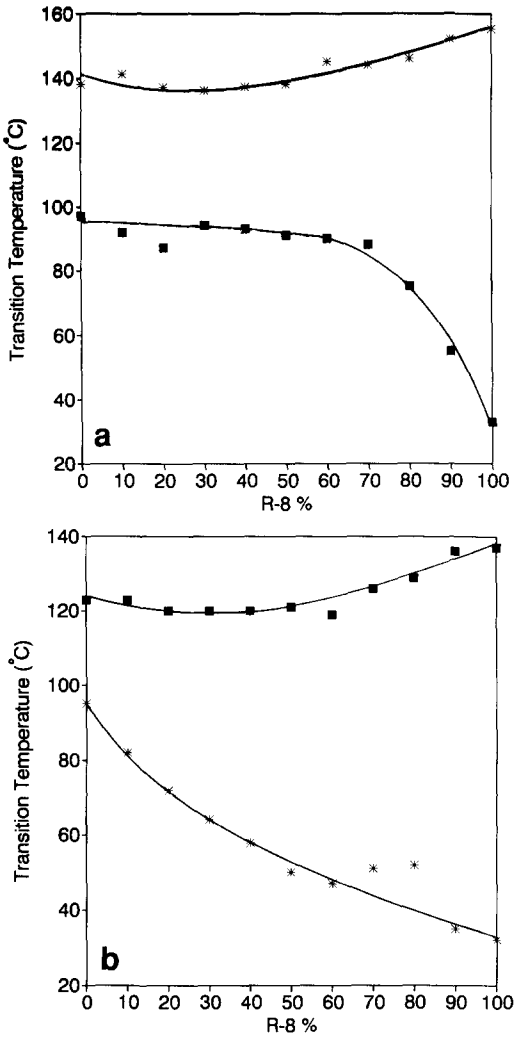


Figure 4 Phase diagrams of COPI-8-10: (a) data from the second heating scan (*, T_{s-i}; ■, T_{k-s}); (b) data from the first cooling scan (*, T_{s-k}; ■, T_{i-s})

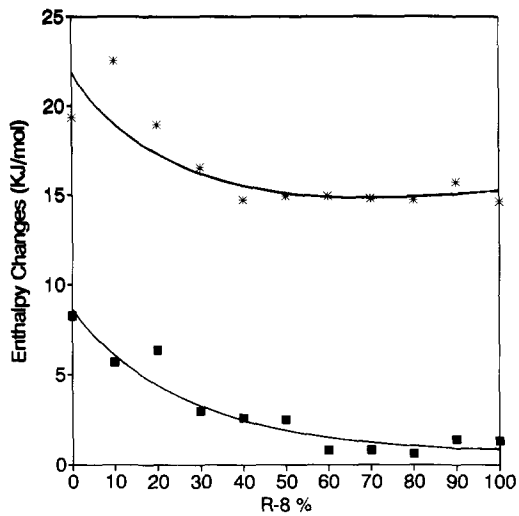


Figure 5 Relationship between the enthalpy change ΔH obtained on heating and copolyimine composition (*, ΔH_{s-i}; ■, ΔH_{k-s})

$D_{001} = 17.07$ Å of PI10 in the corresponding phase[2]. The layer distance of COPI-8-10 (50/50) in the crystalline phase is obtained on a sample as synthesized for comparison purposes. The actual D_{001} is fairly close to the average value of D_{001} of PI8 and PI10.

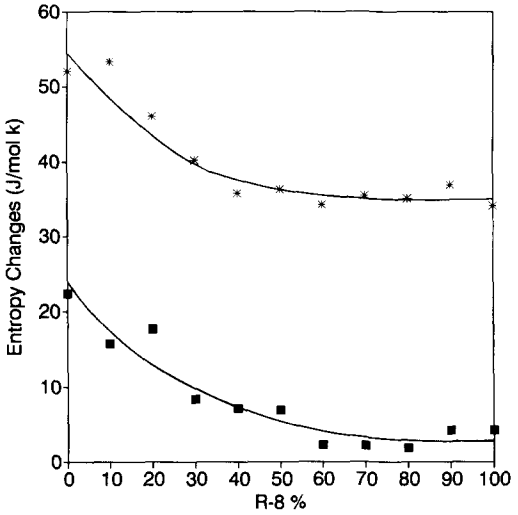


Figure 6 Relationship between the entropy change ΔS obtained on heating and copolyimine composition (*, ΔS_{s-i}; ■, ΔS_{k-s})

CONCLUSIONS

Copolymerization of one kind of mesogenic unit with two kinds of flexible spacers having different lengths of even-numbered methylene units produces copolymers soluble in chloroform and tetrahydrofuran. All the copolyimines exhibit a liquid crystalline smectic G phase as PI10 does. Both transition temperatures T_{k-s} and T_{s-k} and the associated enthalpy change (ΔH) and entropy change (ΔS) vary continuously with the copolymer composition. Both the crystalline and liquid crystalline phases of the copolyimines are considered to be isomorphic.

ACKNOWLEDGEMENTS

The authors thank Professor D. Heyding for running the X-ray diffraction instrument and NSERC Canada for financial support.

REFERENCES

1 Natansohn, A., Yang, H. and Clark, C. *Macromolecules* 1991, **24**, 5489
2 Yang, H. and Natansohn, A. *Macromolecules* 1992, **25**, 5331
3 Yang, H. and Natansohn, A. *Macromolecules* 1992, **25**, 5798
4 Yang, H. and Natansohn, A. *Polym. Bull.* 1992, **29**, 159
5 Ober, Ch. K., Jin, J. and Lenz, R. W. *Adv. Polym. Sci.* 1984, **59**, 130
6 Roviello, A. and Sirigu, A. *Eur. Polym. J.* 1979, **15**, 61
7 Reddy, C. M. and Lenz, R. W. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 1015
8 Percec, V. and Tsuda, Y. *Polymer* 1991, **32**, 661
9 Percec, V. and Tsuda, Y. *Macromolecules* 1990, **23**, 3509
10 Percec, V. and Tsuda, Y. *Polymer* 1991, **32**, 673
11 Percec, V. and Tsuda, Y. *Polym. Bull.* 1989, **22**, 489
12 Percec, V. and Tsuda, Y. *Polym. Bull.* 1991, **22**, 497
13 Misyan, A. and Ober, Ch. K. *Polym. Bull.* 1990, **23**, 535
14 Gray, G. W. and Goodby, J. W. G. 'Smectic Liquid Crystals: Textures and Structures', Leonard Hill, Glasgow, 1984
15 Cheng, S. Z. D., Johnson, R. L., Wu, Z. Q. and Wu, H. H. *Macromolecules* 1991, **24**, 150
16 Cao, M. Y. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 521
17 Bloembergen, S., Holden, D. A., Bluhm, T. L., Hamer, G. K. and Marchessault, R. H. *Macromolecules* 1989, **22**, 1663
18 Bluhm, T. L., Hamer, G. K., Marchessault, R. H., Fyfe, C. A. and Veregin, R. P. *Macromolecules* 1986, **19**, 2871
19 Allegra, G. and Bassi, I. W. *Adv. Polym. Sci.* 1969, **6**, 549