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Polyimines from terephthalaldehyde and aliphatic diamines

4. Copolymers with odd numbers of methylene units in the flexible spacer

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Summary

A series of liquid crystalline copolyimines based on terephthalaldehyde, 1,7-diaminoheptane and 1,9-diaminononane is synthesized. Both melting and isotropization temperatures of the copolyimines are depressed compared to homopolymers PI7 and PI9. The copolyimines show wider liquid crystalline temperature ranges than the parent homopolyimines.

Introduction

In the previous papers of this series we have reported the synthesis and characterization of a series of polyimines (1,2) and a series of copolyimines with odd-even (3) and even-even (4) combinations of the number of methylene units in flexible spacers. When one spacer of odd-numbered methylene units (1,3-diaminopropane or 1,5-diaminopentane) and another spacer of even-numbered methylene units (diaminodecane) are combined in the copolyimines (3), both the melting (T_{k-lc}) and isotropization (T_{lc-i}) transition temperatures are depressed and the liquid crystalline temperature ranges decrease to some extent depending on composition. The copolyimines having about equal amounts of the odd and even spacers do not show any liquid crystalline phase. The phase diagrams of the copolyimines with a combination of odd-even spacers show isodimorphism. The copolyimines with combination of even-even spacers (4) show a continued change of melting and isotropization temperatures with copolyimine composition. It has reported (5-7) that odd-odd, even-even and odd-even combinations of spacers produce different changes in the transition temperatures and the liquid crystalline temperature range for some liquid crystalline copolyesters. Similar results have also been obtained for some liquid crystalline copolyethers (8-12). This paper presents the synthesis of a series of copolyimines with odd-odd spacers by polycondensation of terephthalaldehyde with 1,9-diaminononane and 1,7-diaminoheptane. The dependence of the transition temperatures and liquid crystalline temperature ranges on copolymer composition is also discussed.

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

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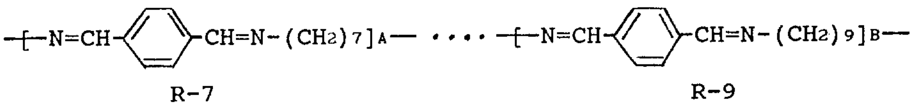

R-7 and R-9 are used to name the structural units with 7 and 9 methylene units in the flexible spacers respectively. The copolyimines are represented as COPI-7-9(A/B), where A/B is the ratio of the molar percentage of the diamines in the copolyimines and varies by 10 from A/B=10/90 to 90/10.

Experimental

Materials

Terephthalaldehyde, hexamethylphosphoramide, 1,7-diaminoheptane and 1,9-diaminononane were used as received from Aldrich. Lithium chloride (BDH) and all the solvents (BDH) were used without further purification.

Polymerization and Characterization

Copolymerization was carried out according to the procedure described in detail previously (1). The copolyimines were purified in a chloroform/ethanol system and copolymer composition was determined as described in the preceding paper (3). IR spectra were obtained on a Bomem Michelson spectrophotometer using KBr pellets. Solution NMR spectra were recorded on a Bruker AC/F-200 MHz spectrometer using chloroform-d as solvent. Average molecular weights were determined in tetrahydrofuran by GPC, using the polystyrene calibration curves. A Mettler TA-3000 differential scanning calorimeter (DSC) equipped with a Mettler TC10A data processor was used for thermal analysis. Optical observations were made on a Nikon Labophot-2 microscope under cross-polarized light using a Wild-Leitz heating stage 350. The detailed experimental conditions have been given in the previous papers (1-3).

Results and Discussion

The copolyimines of COPI-7-9 series are soluble in chloroform and tetrahydrofuran. Feed and copolymer compositions are the same (i.e, $r_1=r_2=1$) for all COPI-7-9 samples. The average molecular weights measured by GPC are about 10,000. Results from thermal characterization are summarized in Table 1. When two transitions are not well resolved, the sum of enthalpy changes for the two peaks is given in the parentheses { } to distinguish it from enthalpy changes of the resolved transitions in the parentheses ( ). The DSC thermograms of COPI-7-9 samples on heating and cooling scans are illustrated in Fig.1a and 1b respectively.It can be seen from Fig.1 that all COPI-7-9 samples show two transitions on both heating and cooling. Under cross-polarized light it can be seen that all COPI-7-9 samples melt from the crystalline phase into a liquid crystalline phase at the first endotherm upon heating as indicated on the DSC thermograms. The liquid crystalline texture of COPI-7-9(50/50), as an example, is shown in Fig.2. At the second endotherm they melt from the liquid crystalline

Table 1. Thermal Characterization of the Copolyimines

COPI-7-9 (A/B)	Thermal Transition Temperature (°C) and Corresponding Enthalpy Changes (KJ/mol) in ( )
	On Heating
0/100	k 113 lc 121 i {16.6}
10/90	k 98 lc 111 i {14.7}
20/80	k 95 lc 107 i {14.4}
30/70	k 100 lc 109 i {13.4}
40/60	k 98 (4.8) lc 119 i(9.5)
50/50	k 93 (4.5) lc 112 i(8.0)
60/40	k 95 (4.2) lc 113 i(7.0)
70/30	k 100 lc 113 i {13.9}
80/20	k 106 lc 111 i {11.3}
90/10	k 105 lc 127 i {45.6}
100/0	k 123 lc 130 i {16.4}
	On cooling
0/100	i 85 k
10/90	i 81 (6.7) lc 50 (1.0) k
20/80	i 75 (6.5) lc 49 (0.6) k
30/70	i 89 (7.0) lc 70 (1.6) k
40/60	i 74 lc 62 k {2.9}
50/50	i 83 (6.7) lc 33 (1.9) k
60/40	i 80 (6.1) lc 50 (1.3) k
70/30	i 79 (5.7) lc 46 (2.3) k
80/20	i 80 (6.7) lc 46 (1.0) k
90/10	i 105 (11.2) k
100/0	i 99 k

phase into an isotropic melt. On cooling, the isotropic melt starts displaying the liquid crystalline texture at the first exotherm and then crystallizes at the second exotherm at the lower temperature. Similar to that observed for other copolyimines with spacers of odd-even and even-even combinations (3,4) and some copolyesters (7), the liquid crystalline texture of COPI-7-9 samples is preserved to some extent on cooling below the second exotherm and stable at room temperature. A phase diagram showing the relationship between the transition temperature and composition of COPI-7-9 samples is presented in Fig.3. It should be noted that this phase diagram does not represent a thermodynamic equilibrium and contains kinetic effects (13,14).

The liquid crystalline temperature range of the parent homopolyimines, PI7 and PI9 is about 7 °C. COPI-7-9(40/60), COPI-7-9(50/50) and COPI-7-9(60/40) have liquid crystalline temperature ranges of around 18 °C to 20 °C. The copolyimines exhibit lower melting (T_{k-lc}) and isotropization temperatures (T_{lc-i}) as compared to the parent homopolymers PI7 and PI9. The depression of the isotropization temperature is not as significant as the depression of the melting temperature.

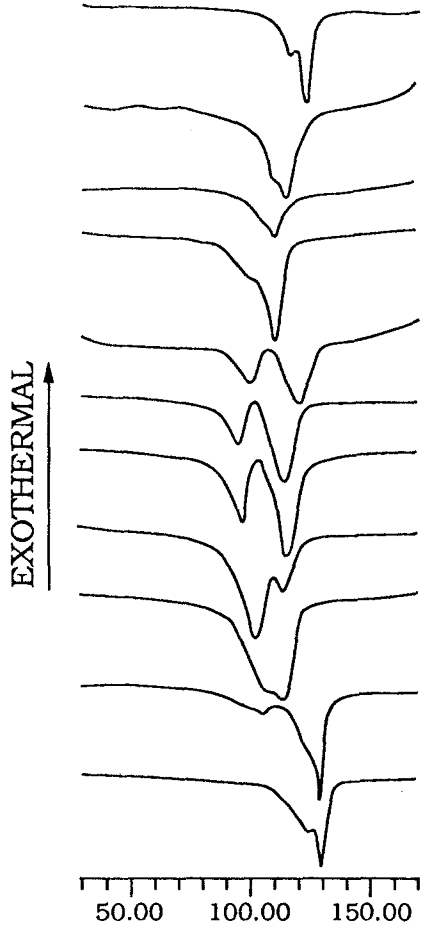

Figure 1a: DSC thermograms of COPI-7-9 on the first heating scans (10k/min.)

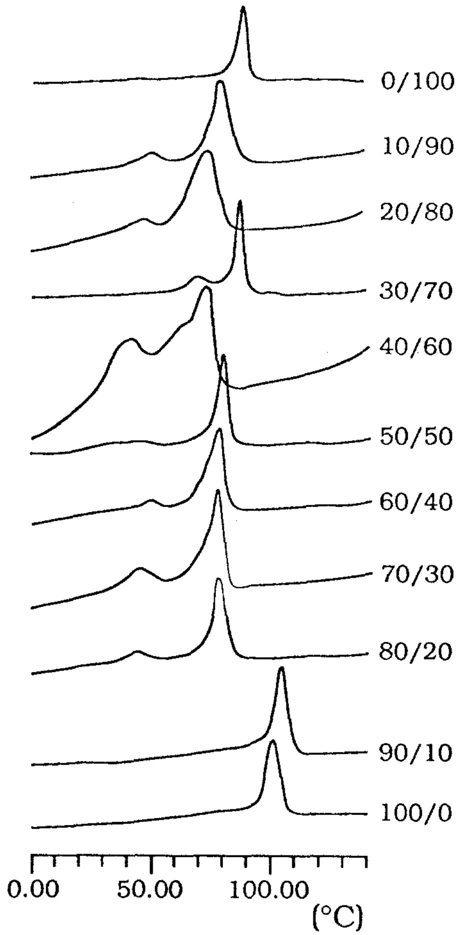

Figure 1b: DSC thermograms of COPI-7-9 on the cooling scans (10k/min.)

This produces a wider liquid crystalline temperature range for these odd-odd copolyimines. This wider liquid crystalline temperature range is probably not due to an intrinsic increase in the thermal stability of the liquid crystalline phase, but to the greater degree of depression in melting temperature (T_{k-lc}) than in the isotropization temperature (T_{lc-i}) (5). For the odd-even copolyimines (3) the depression of T_{lc-i} is more significant than the depression of T_{k-lc}. There, the liquid crystalline temperature range is narrowed compared to the corresponding homopolymers. The relationship between T_{k-lc} and the composition of COPI-7-9 samples shows isodimorphism (15) in the crystalline phase. The lowest T_{k-lc} is at the composition of 50/50 of R-7 and R-9 components in the copolyimine. Isodimorphism exist in the liquid crystalline phase since there is also a lowest point on the curve of T_{lc-i}

vs copolyimine composition. It is reasonable to believe that the R-7 and R-9 structural units, despite their similarity, do not cocrystallize into a uniform crystalline phase (14) nor in a liquid crystalline phase.

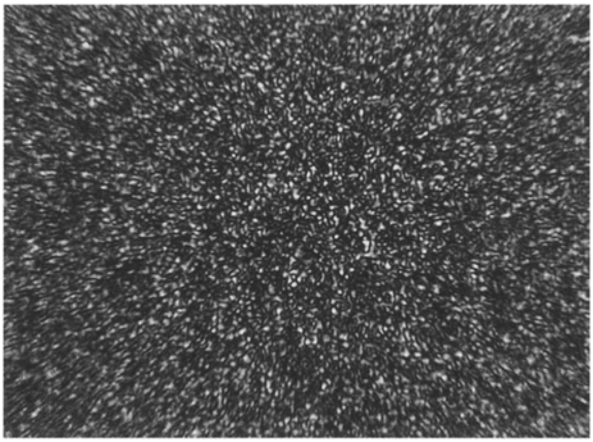

Figure 2:. Liquid crystalline texture of COPI-7-9(50/50) taken under cross-polarized light on cooling at 75 °C.

X200

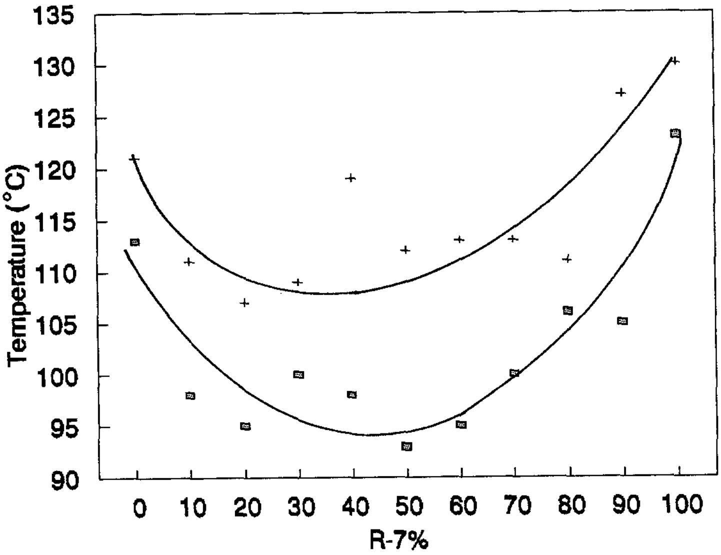

Figure 3: Phase diagram of COPI-7-9 series
▨ : Transition from crystalline to liquid crystalline; + : Transition from liquid crystalline to isotropic melt.
(Data from the first heating scan)

Conclusions

Copolymerization of one kind of mesogenic unit with two kinds of flexible spacers of odd-numbered methylene units in the main chain produces copolyimines having wider liquid crystalline temperature ranges compared to their parent homopolyimines. Based on the results presented in this paper and in previous papers (3,4), it seems possible to modify the transition temperatures of the liquid crystalline polyimines by variation of combinations of different spacers in the copolymers.

Acknowledgements

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