Polyimines from Terephthalaldehyde and Aliphatic Diamines. 3. Copolymers with Odd–Even Combinations of the Number of Methylene Units in the Flexible Spacer

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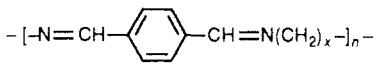
ABSTRACT: Two series of copolyimines from terephthalaldehyde and odd–even combinations of aliphatic diamines are synthesized. COPI-3-10 is formed with 1,3-diaminopropane and 1,10-diaminodecane and COPI-5-10 from 1,5-diaminopentane and 1,10-diaminodecane. The transition temperatures of the copolyimines are depressed in comparison to the homopolyimines. Copolyimines having approximately the same molar amount of the two spacers are not liquid crystalline, and they have the lowest transition temperatures. This is a proof of the isodimorphic character of the phases. Phase diagrams of the two series of copolyimines are presented. A linear correlation is established between the amount of the "cis" conformation and the enthalpy change associated with the transition from the crystalline phase to the liquid crystalline phase, confirming that this transition can be assigned to the melting of the cis conformation. The two series of copolyimines are soluble in chloroform and tetrahydrofuran.

Introduction

In our previous papers,[1,2] a series of liquid crystalline polyimines was synthesized and their structure characterized by solid-state NMR and X-ray diffraction. The polyimines with the general formula



PI-X (X = 3–10, 12)

are semicrystalline and insoluble in common organic solvents. PI-6 has been previously synthesized in *m*-cresol[3] as a polyimine with a lower crystallinity, soluble in chloroform and *m*-cresol. The polyimines with relatively short spacers (x = 3, 4, 6) decompose before melting into an isotropic phase. Those with longer spacers present multiple thermal transitions.[1] We have proposed[2] that PI-10 undergoes crystalline to S_G to S_C to isotropic transitions. The transition from the S_G phase to the S_C phase is probably overlapped by the transition to an isotropic melt. The crystalline phase in PI-10 as synthesized is made up of a mixture of the "cis" and "trans" conformations[1] (shown in Figure 1) in the crystalline phase. It changes from the crystalline phase into the smectic G (S_G) phase by melting the cis conformation at T_{k-s} and then from the S_G to the smectic C (S_C) phase by melting the trans conformation followed immediately by the S_C phase transition into an isotropic phase at T_{s-i}. PI-3 has only 3 methylene units in the flexible chain. Due to its relatively short spacer, PI-3 as synthesized exists only in the form of the trans conformation, the most extended one in the crystalline phase.[1] Upon heating, it melts from the crystalline phase into an unidentified phase which shows birefringence. Subsequently, PI-3 shows a weak transition into isotropic melt. However, PI-3 is unstable and starts to decompose around the first transition temperature. PI-5, having five methylene units on the flexible spacer, shows two first-order transitions. It exhibits a liquid crystalline phase between the two transitions.[1] PI-5 is more stable and does not decompose below the transition temperature T_{lc-i}. We had planned to study charge-transfer interactions between these polyimines and small electron acceptor molecules. This was impossible though, because all PI-X samples were insoluble in solvents for the electron-accepting molecules. Consequently we have started investigating copolymers containing the same rigid part and spacers of different lengths. The disorder thus introduced is supposed to improve the solubility of the polyimines. On the other hand, it is known[4] that copolymerization can be used to modify some transition temperatures of liquid crystalline polymers. In this paper we are investigating two series of copolyimines; one containing 3 and 10 methylene spacers and another containing spacers of 5 and 10 methylene units. An improvement in the resolution of the above-mentioned transitions was also anticipated.

Figure 1. Illustration of the "cis" and "trans" conformations.

There are quite a few reports on the relationship between copolymer composition and transition temperatures (and the associated enthalpy changes) of main-chain liquid crystalline copolymers. Papers before 1983 have been reviewed[4] by Ober, Jin, and Lenz. Those were mainly on liquid crystalline polyesters. New publications on this subject continue to appear.[5,6] Liquid crystalline copolyethers[7] have also been synthesized, and the dependence of the transition temperatures on copolymer composition was investigated. Percec and co-workers[8,9] carried out a systematic study of the properties of liquid crystalline copolyethers with a single mesogenic unit and various ratios of two or more than two kinds of spacers of different lengths.

This paper presents the synthesis of two series of copolyimines by polycondensation of terephthalaldehyde with diaminopropane and diaminodecane and, respectively, with diaminopentane and diaminodecane in various compositions. The transition temperatures of the copolyimines and the liquid crystalline temperature ranges are studied as a function of composition.

Experimental Section

Materials. Terephthalaldehyde, hexamethylphosphoramide, and all the aliphatic diamines were used as received from Aldrich.

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Table I
Number-Average Molecular Weights ($\bar{M}_n$) and Average Degree of Polymerization ($\overline{DP}_n$) of the COPI-3-10 and COPI-5-10 Series

copolymer	$\bar{M}_n$	$\overline{DP}_n$	copolymer	$\bar{M}_n$	$\overline{DP}$
COPI-3-10(10/90)	6 300	24	COPI-5-10(10/90)	10 000	38
COPI-3-10(20/80)	6 200	25	COPI-5-10(20/80)	19 900	78
COPI-3-10(30/70)	10 000	41	COPI-5-10(30/70)	13 200	59
COPI-3-10(40/60)	6 300	27	COPI-5-10(40/60)	22 400	93
COPI-3-10(50/50)	5 600	25	COPI-5-10(50/50)	16 700	71
COPI-3-10(60/40)	16 200	74	COPI-5-10(60/40)	17 500	77
COPI-3-10(70/30)	17 400	85	COPI-5-10(70/30)	20 000	90
COPI-3-10(80/20)	5 700	29	COPI-5-10(80/20)	11 000	51
COPI-3-10(90/10)	3 600	20	COPI-5-10(90/10)	9 500	46

Lithium chloride (BDH) and all the solvents (BDH) were used without further purification.

Copolymerization was carried out according to the procedure described in detail in our previous publication.[1] Since the copolymers are soluble in several solvents at room temperature, reprecipitation in a chloroform/ethanol system was used as a purification procedure. The polymers were dried in vacuo at room temperature for at least 48 h.

Characterization. IR spectra were obtained on a Bomem Michelson spectrophotometer using KBr pellets. Solution NMR spectra were obtained on a Bruker AC-F 200-MHz NMR spectrometer using chloroform-*d* as solvent. Solid-state high-resolution ^{13}C-NMR spectra were recorded on a Bruker CXP-200 spectrometer operating at a frequency of 50.307 MHz, using a standard cross-polarization/magic angle spinning/dipolar decoupling sequence with a proton 90° pulse of 3.7 μs, a contact time of 1 ms, an acquisition time of 0.102 s, and a relaxation decay of 10 s. The data were collected in 2K and zero-filled to 4K. Processing data was conducted with a 20-Hz line broadening. Molecular weights and distributions were characterized in tetrahydrofuran by gel permeation chromatography (GPC) with a Waters Associates Model 400 instrument equipped with three columns, μ-Styragel 10^4, 10^3, and 10^2 Å in series. The polystyrene GPC calibration curve was used.

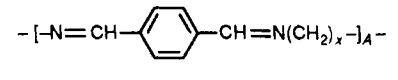
A Mettler TA-3000 differential scanning calorimeter (DSC) equipped with a Mettler TC10A data processor was used for thermal analysis. Heating and cooling scan rates were 10 °C/min in all cases. Optical observations were made on a Carl-Zeiss microscope under cross-polarized light (magnification 200×) with 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 (λ_α = 1.5418 Å).

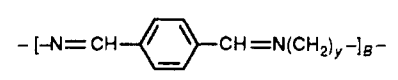
The amount of the cis conformation was obtained by deconvolution of the solid-state NMR spectra.[2] The program used for the deconvolution was Glinfit (version 3.0) provided by Bruker.

Results and Discussion

Copolymerization and Characterization. The copolyimines prepared are statistical copolymers with two different structural units whose general formulas are as follows:



R-X



R-Y

All the copolyimines have the same mesogenic units but different spacers. Throughout this paper R-*X* and R-*Y* are used to name the different structural (repeating) units, where *X* or *Y* is the number of the methylene units in the flexible chain. The two series of copolyimines synthesized are COPI-3-10(*A*/*B*) and COPI-5-10(*A*/*B*). The molar percentage (*A*/*B*) in each series is varied by 10 from *A*/*B* = 10/90 to *A*/*B* = 90/10.

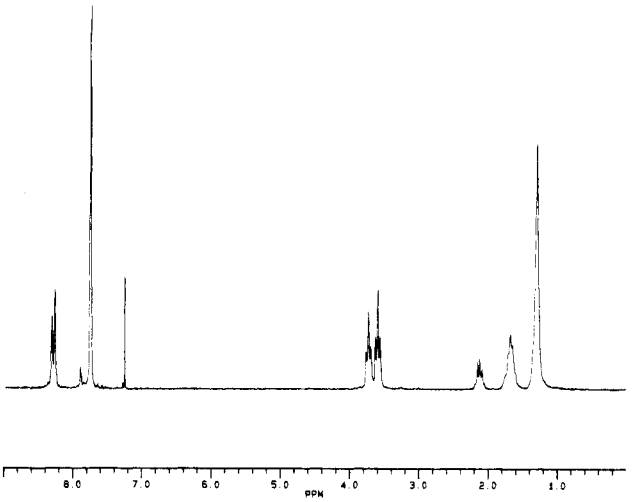


Figure 2. Solution NMR spectrum of COPI-3-10(50/50) in $CDCl_3$.

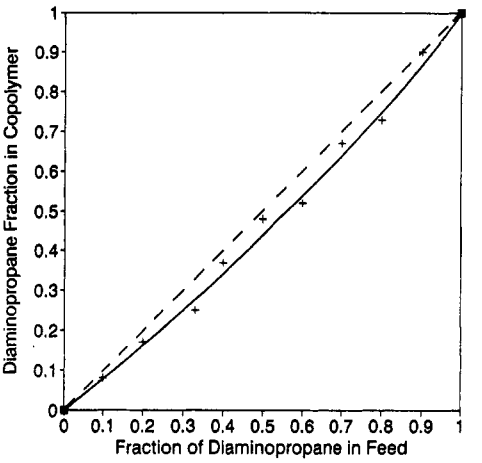


Figure 3. Copolymerization diagram of the COPI-3-10 series.

The composition of the copolyimines is determined by solution NMR spectroscopy. The IR characteristic absorptions are the same as those of the homopolyimines.[1] The average molecular weights of all the copolyimines are presented in Table I.

COPI-3-10. The NMR spectrum ($CDCl_3$) of COPI-3-10(50/50), as an example, is shown in Figure 2. Two singlet peaks at 8.30 and 8.25 ppm are due to –CH=N– protons of the R-3 and R-10 structural units, respectively. The singlet peak at 7.74 ppm is due to the aromatic protons. Two types of α-CH_2 protons of the R-3 and R-10 spacers appear at 3.72 and 3.58 ppm (triplets), respectively. β-CH_2 protons of PI-3 and PI-10 resonate at 2.11 and 1.67 ppm (quintets), respectively. The broad peak at 1.28 ppm is due to the remainder of protons of the PI-10 aliphatic chain. The differences in chemical shifts of the α-CH_2, β-CH_2, and –CH=N– protons in R-3 and R-10 allow determination of the copolyimine composition. The copolymerization diagram for COPI-3-10 is illustrated in Figure 3. Step polymerization is a purely statistic process, and one would have expected a straight diagonal line in Figure 3. However, the content of R-3 in COPI-3-10 is slightly lower than its feed composition. This occurs probably because diaminopropane is volatile and some of it escapes from the polymerization vessel.

All the COPI-3-10 samples are soluble in chloroform and tetrahydrofuran at room temperature. The solubility

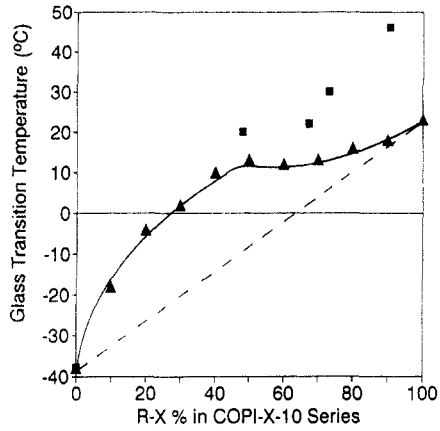


Figure 4. Relationship between glass transition temperatures and copolymer composition for (■) the COPI-3-10 series and (▲) the COPI-5-10 series.

is the lowest for COPI-3-10(90/10). Chloroform is a better solvent than THF. The solubility of the copolyimines is probably a consequence of lower crystallinity and less perfection of the crystalline phase in copolymers[7,8c] as compared to the homopolyimines.

Glass transitions are very weak. Their intensity is directly correlated to the amount of the amorphous phase in the copolymer. Glass transition temperatures (T_g) were read from the second heating scan, and transitions are observed only for four of the copolymers. The values are plotted as a function of copolymer composition in Figure 4 along with the T_gs of the COPI-5-10 series.

Table II summarizes the thermal analysis results of COPI-3-10 samples obtained by DSC. When two transitions are not well resolved, the sum of the enthalpy changes for the two peaks is given in braces { } in Table II to distinguish them from the enthalpy changes of the resolved transitions. For all the copolymers, the thermograms from the first heating scans are slightly different from those of the second heating scans. The thermograms from the second heating scans and the subsequent scans are similar. All the thermograms from the different cooling scans are the same. Table II contains thermodynamic data from the first heating and the first cooling scans. These data do not bear the effects of thermal history on the samples. COPI-3-10(10/90), COPI-3-10(20/80), COPI-3-10(30/70), and COPI-3-10(40/60), which have more R-10 component, show two transitions. Once there are approximately equal amounts of R-3 and R-10 in the copolymers, COPI-3-10(50/50) and COPI-3-10(60/40), whose actual compositions are A/B = 48.1/51.9 and 51.7/48.3, respectively, exhibit only one transition. COPI-3-10(70/30), COPI-3-10(80/20), and COPI-3-10(90/10) show three or more transitions. On the cooling scan, COPI-3-10(10/90), COPI-3-10(20/80), COPI-3-10(30/70), and COPI-3-10(40/60) show two transitions. The intensity of the transition at the higher temperature for these four polymers is strong, while that at the lower temperature is relatively weak. COPI-3-10(50/50) and COPI-3-10(60/40) still show only one transition. COPI-3-10(70/30), COPI-3-10(80/20), and COPI-3-10(90/10) exhibit only one weak shoulderlike transition or no transition at all.

X-ray diffraction and cross-polarizing microscopy were employed to investigate the characteristics of phases between the first-order transitions. The X-ray diffraction was measured for COPI-3-10(10/90), COPI-3-10(20/80), and COPI-3-10(30/70) at room temperature and between the two endotherms, respectively. At room temperature, the copolyimines are in a crystalline phase, and between the transition temperatures they show a liquid crystalline phase. As an example, the X-ray diffraction spectrum of COPI-3-10(30/70) at 102 °C is presented in Figure 5a. It shows a small-angle diffraction at about 2θ = 5.2°, one strong diffraction at a large angle around 2θ = 20° and one weak diffraction close to the strong diffraction. The X-ray diffraction spectra of COPI-3-10(10/90) and COPI-3-10(20/80) are similar to that of COPI-3-10(30/70). The X-ray diffraction spectra are very similar to that of PI-10.[2] Therefore, the liquid crystalline phase can be tentatively assigned to be a smectic G phase. Hence, upon copolymerization, the same type of liquid crystalline phase as in one of the parent homopolymers, PI-10, is obtained. The layer distances (D_{001}), calculated from the small diffraction angle,[2] of these three copolyimines and PI-10 are summarized in Table III. It can be seen from Table III that D_{001} increases with an increase in the content of the R-3 component in both the crystalline and liquid crystalline phases. This increase of the space between the layers means that both the crystalline phase and the liquid crystalline phase become more and more disordered with the increase of the R-3 component. This trend is valid up to 50% of the R-3 component in the copolymers.

Results from the microscopy confirm the above findings. COPI-3-10(10/90), COPI-3-10(20/80), COPI-3-10(30/70), and COPI-3-10(40/60) are semicrystalline below the first endotherm. They melt into a liquid crystalline phase at the first transition. The texture observed has an appearance similar to that of PI-10.[2] Above the second transition temperature these four copolyimines form isotropic melts. On cooling, they first go into the liquid crystalline phase. Then, on further cooling, they enter the crystalline phase. It should be noted that the liquid crystalline texture is preserved even to room temperature. This kind of behavior was also observed by Lenz et al.[5] for a series of copolyesters. The corresponding changes at the molecular level are similar to those noted for the homopolyimines.[1] The cis conformation melts at the first transition temperature. The higher transition temperature corresponds to the melting of the trans conformation. On cooling, the energy-favored trans conformation prevails, and once it forms it is stable to room temperature. The cis conformation still does form and exists to a lesser extent than as synthesized. Therefore, the transition from the liquid crystalline phase to the crystalline phase on cooling is weaker than the same transition on the first heating scan. On heating, the transition at lower temperature is assigned as a melting transition (T_{k-s}) and that at higher temperature as an isotropization transition (T_{s-i}).

COPI-3-10(50/50) and COPI-3-10(60/40) have almost equal amounts of R-3 and R-10. They were observed on the microscopy to melt from the crystalline phase directly into the isotropic melt without going through any liquid crystalline phase. When the copolyimines have more R-3 component, i.e., are less flexible, the transitions are more complicated. COPI-3-10(70/30) on its first heating scan shows three transitions at around 95, 118, and 150 °C. According to the microscopic observations, COPI-3-10(70/30) starts to show the liquid crystalline texture when it is heated to ca. 115 °C and becomes isotropic at ca. 145 °C. No changes are observed around 95 °C by microscopy. On cooling from the isotropic melt, almost a complete black screen with some tiny shiny spots is observed when cooled to room temperature. The sample solidifies before reaching room temperature. When this sample is left at room temperature for days, these tiny spots grow and form a crystalline phase. On the second heating scan, the crystalline phase goes into a liquid crystalline phase at T_{k-s} and then from the liquid crystalline phase into the

Table II
Thermal Characterization of the COPI-3-10 Series

COPI-3-10(*A*/*B*)	thermal transition temp[a] (°C) and corresponding enthalpy changes (kJ mol^{-1}) in parentheses	
	heating	cooling
0/100	k 107 (8.7) s 143 (13.1) i	i 123 (10.2) s 95 (6.9) k
10/90	k 99 (3.4) s 136 (9.7) i	i 115 (7.5) s 97 k 92 k {4.6}[b]
20/80	k 97 (2.6) s 131 (8.4) i	i 106 (4.2) s 94 (1.6) k
30/70	k 92 (1.6) s 112 (5.1) i	i 84 (4.2) s 56 (0.4) k
40/60	k 94 s 102 i {13.0}[b]	i 76 (5.7) s 50 (0.3) k
50/50	k 93 (12.4) i	i 47 (3.8) k
60/40	k 93 (9.0) i	i 38 (0.5) k
70/30	k 93 (0.7) k 117 (4.6) lc[c] 147 (0.7) i	i 34 (0.4) lc[c]
80/20	k 118 (4.1) k 149 lc[c] 162 i {3.3}[b]	
90/10	k 118 k 120 {7.1}[b] k 162 lc[c] 172 i {3.3}[b]	
100/0	k 157 (11.7) lc[c] 180 (2.2) i	

[a] The data in the table are represented as $T(\Delta H)$. [b] When two transitions are not well resolved, total enthalpy changes are given in braces { } to distinguish them from those in parentheses ( ). [c] "lc" stands for the unidentified liquid crystalline phase.

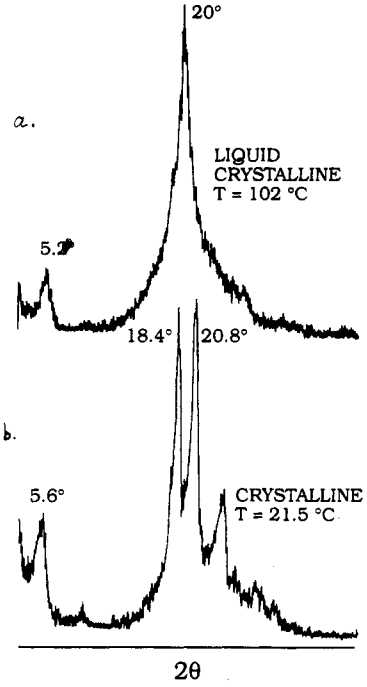


Figure 5. X-ray diffraction spectra of COPI-3-10(30/70) (a) in the liquid crystalline phase at 102 °C and (b) in the crystalline phase at 21.5 °C.

Table III
Layer Distances of PI-10 and Some COPI-3-10 in the Crystalline and Liquid Crystalline Phase

polymer	layer distances (Å)	
	crystalline phase	liquid crystalline phase
PI-10	15.48	17.07
COPI-3-10(10/90)	15.64	17.17
COPI-3-10(20/80)	16.07	17.22
COPI-3-10(30/70)	16.98	17.54

isotropic melt at T_{s-i}. COPI-3-10(90/10) and COPI-3-10-(80/20) behave in a similar way. On heating, their transition at the lowest temperature is assumed to be a crystalline–crystalline transition. The change from one crystalline phase to another crystalline phase is not observed under the microscope. The remaining two transitions are crystalline to liquid crystalline and liquid crystalline to isotropic, respectively. The liquid crystalline phase exhibited in these three copolymers cannot be identified, mainly because the samples are not stable enough to be subjected to an X-ray diffraction experiment. The first heating–cooling cycle is probably an annealing process during which big and uniform crystals may be

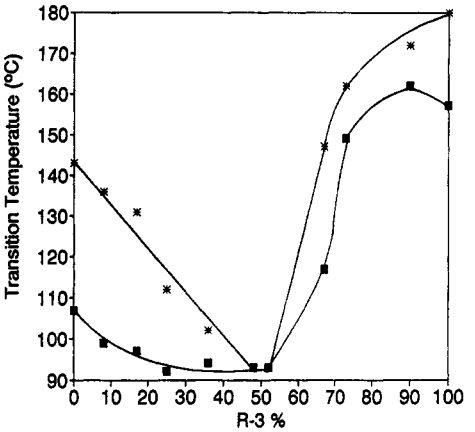


Figure 6. Phase diagram of the COPI-3-10 series: (■) transition from the crystalline phase to the liquid crystalline phase; (*) transition from the liquid crystalline phase to the isotropic melt.

obtained.[10-12] Several other research groups found similar multimelting phenomena for some copolyethers[8] and copolyesters.[5,10]

On the basis of the results above, a phase diagram of the COPI-3-10 series is obtained and shown in Figure 6. The transition temperatures, both T_{k-s} and T_{s-i}, were taken from the first heating scans. However, the basic shape of the phase diagram remains if T_{k-s} and T_{s-i} are read from the cooling or the second heating scans. It has to be noted that the phase diagram does not represent a thermodynamic equilibrium and contains kinetic effects.[6,11] The phase diagram shows that the lowest T_{k-s} and T_{s-i} are at the composition of about A/B = 50/50. This means that both the crystalline and liquid crystalline phases are isodimorphic. This type of phase diagram was also obtained by several other groups[6,9-11] for copolyesters of even–even combinations of methylene units in spacers. From the phase diagram, it is clearly seen that both the melting temperature (T_{k-s}) and the isotropization temperature (T_{s-i}) are depressed compared to homopolyimines, PI-3 and PI-10, by copolymerization. The transition temperature of the liquid crystalline phase to the isotropic melt, T_{s-i}, is depressed more than that of the crystalline to liquid crystalline phase, T_{k-s}. This depression is another indication that these copolyimines are less ordered than their parent homopolyimines, PI-3 and PI-10. According to the phase diagram, the copolyimines can be divided into three groups. On the left side of the phase diagram are those copolymers containing more R-10 component, which allows more flexibility. On the right side are those having more R-3 component and are less flexible. The properties of the copolyimines containing more R-10

Table IV
Thermal Characterization of the COPI-5-10 Series

COPI-5-10(A/B)	thermal transition temp[a] (°C) and corresponding enthalpy (kJ mol^{-1}) changes in parentheses	
	heating	cooling
0/100	k 107 (8.7) s 143 (13.1) i	i 123 (10.2) s 95 (6.9) k
10/90	k 95 (6.1) s 136 (13.8) i	i 104 s 87 k {12.53}[b]
20/80	k 93 (4.1) s 126 (9.2) i	i 94 s 86 k {11.70}[b]
30/70	k 91 (2.9) s 115 (8.0) i	i 89 (8.2) s 61 (0.4) k
40/60	k 92 s 108 i {13.4}[b]	i 76 s 50 i {7.9}[b]
50/50	k 92 s 97 i {12.6}[b]	i 63 (6.3) s
60/40	k 89 (12.2) i	i 47 (4.1) k
70/30	k 92 (10.4) i	i 32 (3.3) k
80/20	k 113 (9.6) i	i 38 (0.8) k
90/10	k 123 lc[c] 132 i {9.3}[b]	i 85 (4.6) lc[c]
100/0	k 134 lc[c] 142 i {10.3}[b]	i 114 (6.4) lc[c]

[a] The data in the table are represented as $T(\Delta H)$. [b] When two transitions are not well resolved, total enthalpy changes are given in braces { } to distinguish them from those in parentheses ( ). [c] "lc" stands for the unidentified liquid crystalline phase.

component are dominated by the properties of R-10. Their transition temperatures are similar to those of PI-10. On the other hand, properties of the polyimines having more R-3 component are determined by R-3, and their transition temperatures are more similar to those of PI-3. When almost equal amounts of the R-10 and R-3 components are present in the copolymers, such as in COPI-3-10(50/50), the copolymers show quite different thermal behavior. The crystalline to liquid crystalline transition disappears. It has been reported[11] that a high degree of cocrystallization is unlikely to be achieved with structural units which differ so much. The shape of the curve of T_{s-i} versus copolymer composition can be explained by the modified Schroeder–van Laac equation.[12] In our case, similar to what was described by van Hecke,[13] the binary system (liquid crystalline and istropic phases) can be treated as a nonideal solution.

It can be seen from the phase diagram (Figure 6) that the isotropization temperature (T_{s-i}) decreases approximately linearly with an increase in the content of the R-3 component for those COPI-3-10 samples having less than 50% R-3. The T_{s-i} transition temperature does not vary linearly with changes of copolymer compositions over the entire composition range. For the samples with less than 50% R-3, the decrease in T_{s-i}, ΔT_{s-i}, can be described using the equation

$$\Delta T_{s-i} = km \quad (1)$$

as if the isotropization temperature were depressed by an impurity, R-3. In eq 1, k is a constant and m is the molar fraction of the R-3 component in the copolyimines. The liquid crystalline temperature range ($T_{s-i}-T_{k-s}$) is also narrowed approximately linearly with the increase in the content of the R-3 component for these four copolyimines. This can be described by a similar equation

$$\Delta(T_{s-i}-T_{k-s}) = k'm \quad (2)$$

where k' is also a constant. For the COPI-3-10 series with over 50% R-10, k and k' are −0.75 (°C) and −0.54 (°C), respectively. The effects of the copolymerization on the melting temperature (T_{k-s}) are relatively small. It can be seen from the phase diagram that the depression of T_{k-s} is not as significant as the depression of T_{s-i} and that the depression is not linear. Enthalpy changes (ΔH) for both T_{k-s} and T_{s-i} in Table II also show such a trend: ΔH decreases with an increase in the content of the R-3 component. The lower ΔH values of the copolyimines (as compared to those of PI-10) mean that both the crystalline and the liquid crystalline phases are less ordered. These results are in accord with the depression of the transition temperatures. On the right side of the phase diagram, the copolymers have more than 60% R-3. As discussed in the previous paragraphs, their transitions are more complicated. Only the transition temperatures of the crystalline phase to the liquid crystalline phase and the liquid crystalline phase to the isotropic melt are shown. On this side both transition temperatures increase with the increase of the amount of R-3.

In conclusion, upon copolymerization all transition temperatures are depressed. The copolymers in this series are more stable than PI-3. Contrary to what we expected, the transition from the S_G phase to the S_C phase is not resolved from the transition of the S_C phase to the isotropic melt. It is reasonable to believe the S_C phase still exists between the S_G phase and the isotropic melt, since the appearance of the S_G phase observed on cooling by the microscopy is similar to that of the S_C phase. As reported[14] and as we discussed previously,[2] this is usually taken as an indication of the existence of the S_C phase.

COPI-5-10. Like COPI-3-10, all COPI-5-10 samples are soluble in chloroform and tetrahydrofuran. The feed and copolymer compositions are the same as expected for a statistical step copolymerization process.

Like in the case of the COPI-3-10 series, the glass transitions of the COPI-5-10 series are rather weak and their intensity depends on the amount of amorphous material present. They are shown in Figure 4. The glass transition temperature increases with an increase in the R-5 composition in the copolyimines, and it is always lower than the T_g of the COPI-3-10 sample of similar composition.

Thermal data from DSC for the COPI-5-10 samples are summarized in Table IV. They are also taken from the first heating and the first cooling scans. COPI-5-10(10/90), COPI-5-10(20/80), COPI-5-10(30/70), COPI-5-10(40/60), and COPI-5-10(50/50) have two first-order transitions on both the heating and the cooling scans. These copolyimines are also semicrystalline. Between the two transitions they exhibit a liquid crystalline phase, and above the transition at the higher temperature they become an isotropic melt. The texture observed for those COPI-5-10 having less than 60% R-5 is the same as that for PI-10 and COPI-3-10 having less than 50% R-3. The liquid crystalline phase is believed to be the S_G phase based on the microscopic observation. COPI-5-10(60/40), COPI-5-10(70/30), and COPI-5-10(80/20) only show one transition from the crystalline phase to the isotropic melt. COPI-5-10(90/10), having 90% R-5, shows two transitions on the heating scans and on the cooling scan. This copolyimine exhibits a liquid crystalline phase between

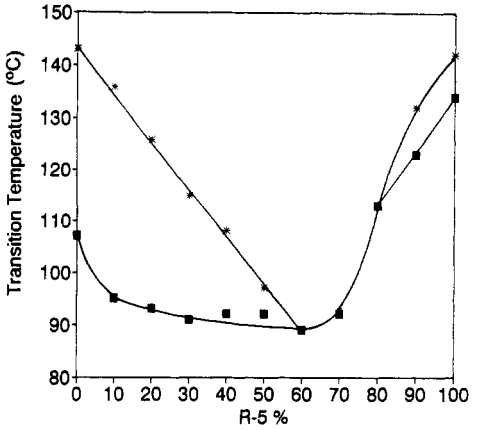


Figure 7. Phase diagram of the COPI-5-10 series: (■) transition from the crystalline phase to the liquid crystalline phase; (*) transition from the liquid crystalline phase to the isotropic melt.

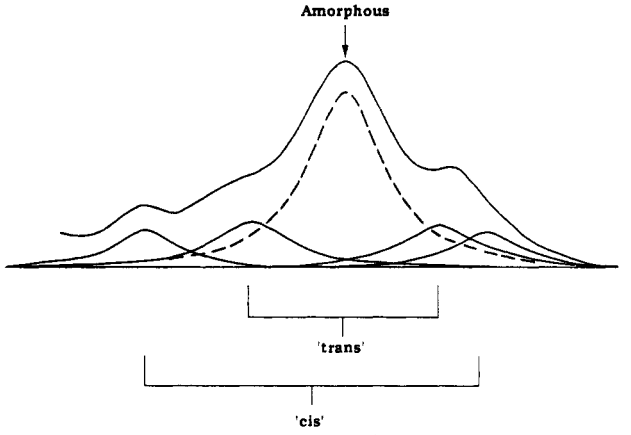


Figure 8. Aromatic part (protonated carbons) of the solid-state ^{13}C-NMR spectrum of COPI-5-10(10/90).

the two transitions. COPI-5-10 samples do not show multiple transitions on the first heating scans as the COPI-3-10 series does. On cooling, COPI-5-10(90/10) shows two transitions instead of the straight line COPI-3-10(90/10) exhibited. This happens probably because R-5 is more flexible than R-3 so that it is easier for segments of COPI-5-10(90/10) to move. Consequently, it is easier for COPI-5-10(90/10) to crystallize during the cooling process.

A phase diagram of COPI-5-10 is presented in Figure 7. Again it should be noted that the phase diagram does not represent a thermodynamic equilibrium. The pattern of the diagram is similar to that of COPI-3-10. COPI-5-10(60/40) has the lowest melting temperature (T_{k-s}). Both the crystalline and the liquid crystalline phases are isodimorphic. The depression of the T_{k-s} and the $\Delta(T_{k-s}-T_{s-i})$ with the increase in the R-5 component is linear within the region of the R-5 component less than 60%. It can also be described by eqs 1 and 2. In this case, k and k' are −0.89 (°C) and −0.9 (°C), respectively.

The aromatic part (protonated carbons) of the solid-state ^{13}C-NMR spectrum of COPI-5-10(10/90), as an example, is shown in Figure 8. The amounts of the cis and trans conformations for these COPI-5-10 samples can be obtained by deconvolution of their NMR spectra. The intensities of the signals of the cis conformation decrease with an increase in the content of the R-5 component in the copolymers. The cis signals disappear completely in COPI-5-10(60/40). The amount of the cis conformation is plotted against the enthalpy change (ΔH) at T_{k-s} of the COPI-5-10 samples. A linear relationship is obtained, as is shown in Figure 9. A hypothetical sample with 100% cis conformers would have a ΔH of 31 kJ/mol. This

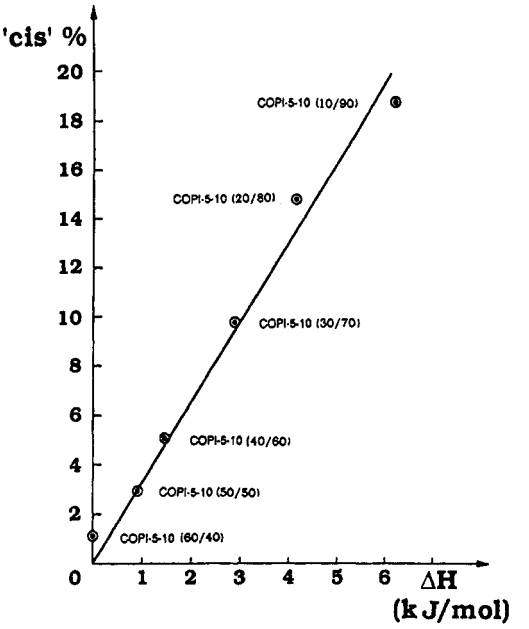


Figure 9. Correlation of the amount of the cis conformers with the enthalpy change associated with the transition from the crystalline phase to the liquid crystalline phase of the COPI-5-10 series.

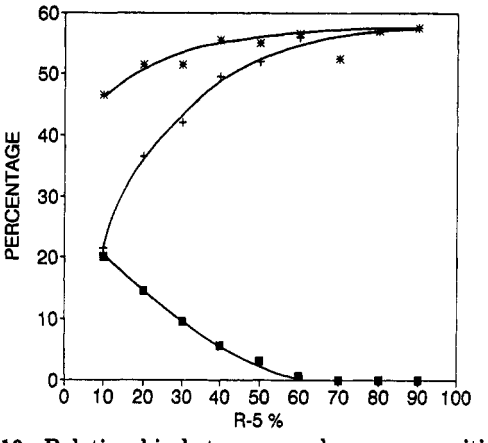


Figure 10. Relationship between copolymer composition and amounts of trans and cis conformers of the COPI-5-10 series: (*) cis + trans; (+) trans; (■) cis.

compares well with values reported for a series of polyesters[15] which undergoes crystalline to smectic G transitions. For the series of polyesters, an average of ca. 36 kJ/mol could be obtained by extrapolating to 100% crystallinity.

A correlation of the amount of the trans conformation with the enthalpy changes (ΔH) at T_{s-i} could not be obtained. The ΔH at T_{s-i} is the enthalpy change from the liquid crystalline phase, and it cannot be correlated with the amount of the trans conformation which exists in the crystalline phase.

As we proposed previously,[1,2] both the cis and trans conformations exist in the crystalline phase and the total amount of the cis and trans conformations obtained by the NMR spectroscopy is comparable to the crystallinity by X-ray diffraction. The relationship between the amounts of the trans and cis conformations and the composition of the COPI-5-10 is given in Figure 10. It can be seen from Figure 10 that the amount of the cis conformation decreases while the trans conformation increases with an increase in the R-5 component in the copolymers. We already know that the total amounts of the cis and trans conformations can be taken as the

crystallinity[2] and that in our series of polyimines those with shorter spacers have generally a greater amount of cis and trans conformations[1,2] and larger crystallinity.[2] This happens because there is a large number of possible conformations available to a longer spacer. Hence, a broad distribution of structure dimensions is obtained. This may inhibit crystallization because the regularity necessary for close packing is more difficult to achieve. In the case of the COPI-5-10, with the introduction of more and more R-5 component, there are more and more shorter structural units, which gives a narrower distribution of structure dimensions so that the total crystallinity (cis + trans) increases.

Conclusions

Copolymerization of odd–even combinations of two flexible spacers of different length with a single rigid unit generates copolymers soluble in chloroform and tetrahydrofuran. Some of the copolyimines exhibit a smectic G liquid crystalline phase as PI-10 does. The copolyimines with almost equal amounts of the two different spacers are not liquid crystalline. Both the melting and isotropization temperatures are depressed and the liquid crystalline temperature range decreases upon copolymerization. The phase diagrams of the two series of copolyimines display the minimum melting and isotropization transition temperatures when the copolymer composition is about 50/50. A correlation between the cis conformations and the enthalpy change at the first melting transition is established.

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