Macromolecules

Volume 24, Number 20 September 30, 1991

Polyimines from Terephthalaldehyde and Aliphatic Diamines. 1. Synthesis, CP-MAS ^{13}C NMR Spectra, and Thermal Analysis

Almeria Natansohn,* Haixin Yang, and Carolyn Clark

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

Received July 30, 1990; Revised Manuscript Received March 19, 1991

ABSTRACT: A series of semicrystalline polyimines from terephthalaldehyde and diamines with 3–10 and 12 methylene groups is synthesized, and their thermal behavior is investigated. Polyimines with short spacers (3 and 4 methylene units) are obtained only in an elongated "trans" configuration, while spacers longer than 4 allow for formation of nonplanar and a bent "cis" configuration. The cis structure, when present, melts first to create an ordered phase which may be semicrystalline or liquid crystalline and consists of ordered trans structures in a disordered amorphous background. Melting of the trans structure creates another phase, which seems to clear into an isotropic melt almost immediately. Only the polyimine with the shortest spacer (3) shows birefringence above the trans melting temperature, but the assignment of this interval to a nematic range is uncertain, due to a superimposed decomposition process. The polyimines form charge-transfer complexes with electron acceptor molecules, and the thermal behavior of these complexes is irreversible. Only complexes with 2,4,7-trinitro-9-fluorenone show some reversible thermal behavior.

Introduction

Our general area of interest is investigation of charge-transfer interactions in polymers. These interactions play a significant role in various electrical and optical phenomena in polymers. Electrical conductivity and, to a great extent, photoconductivity in organic polymers are a direct result of donor–acceptor complex formation.[1] Other interesting electronic applications of polymers, such as nonlinear optical materials, are also based on the presence of donor and acceptor groups.[2]

Our main tool to investigate charge-transfer interactions in polymer systems is solid-state high-resolution NMR spectroscopy, obtained through cross-polarization and magic angle spinning (CP-MAS). We have demonstrated that, for aromatic groups, upfield chemical shifts appear due to complexation, and they can best be understood on the basis of molecular models.[3,4] We have also shown that there is a correlation between the proton spin–lattice relaxation time in the rotating frame of a polymer sample and the extent of charge-transfer interaction in that polymer.[3–6] The next step in our investigation is to introduce some kind of ordering into our polymers and to see what effect this order would have on the charge-transfer interaction, as observed by NMR. The easiest way to build ordered polymers is to synthesize crystalline or liquid crystalline structures. The charge-transfer complexes could then be comparatively studied in the ordered and the disordered states. Formation of such complexes between amorphous polymers (with electron-donor mesogenic moieties) and small molecular electron acceptor molecules has been shown to induce liquid crystalline order and compatibilize pairs of such polymers.[7]

For NMR studies, the polymer had to be as simple as possible, and even if our aim was carbazole-containing ordered polymers, we had to choose a simpler structure for our initial NMR investigations. We present in this paper the synthesis and characterization of new polyimines based on terephthalaldehyde and aliphatic diamines. Polyimines were chosen for their potential electron-donating properties in complexes with electron-acceptor molecules. The NMR investigation of the relaxation parameters of these polymers will be the subject of another paper.

Polyimines are a class of polymers first reported in 1923[8] and intensively studied since then.[9] The first published reports on liquid crystalline main-chain polyimines and poly(imine–ethers) appeared in 1979.[10–12] More recently, there has been a renewed interest in these polymers, due to their very good engineering properties.[13,14] Harris[15,16] started a series of studies of polyimines with ethylene glycol spacers. Polyimines obtained from terephthalaldehyde and aliphatic diamines are not a "classical" type of the structure expected to generate main-chain liquid crystalline polymers.[17] The normal mesogenic structure includes at least two aromatic rings separated by some connecting structure, which in some cases can be the imine double bond. The rigid structure obtained in this polymerization is remarkably shorter (one aromatic ring extended by two imine bonds), but one can assume that its behavior can be "decoupled" by the very flexible and relatively long spacers introduced by the aliphatic amine. We will show in this paper that some first-order phase

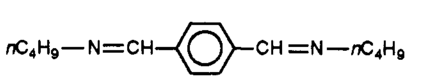
0024-9297/91/2224-5489$02.50/0

transitions are observed in this series and that the CP-MAS NMR spectra can give information on the structural significance of these transitions. The nature of the phases formed after these first-order transitions can be semicrystalline or liquid crystalline, but a definite assignment is still uncertain.

Experimental Section

The polymers were synthesized in 50-mL round-bottom three-necked flasks under nitrogen at room temperature. The basic procedure was similar to that described by Harris et al.[15] The reactions took place between equivalent amounts (0.2 mol) of terephthalaldehyde and aliphatic amines of the general formula $H_2N(CH_2)_xNH_2$, where x = 3–10 and 12, in the presence of 1.5 g of lithium chloride and 1.3 mL of hexamethylphosphoramide. The solvent was anhydrous *N,N'*-dimethylacetamide (30 mL). The reaction was stirred for 24 h, and the polyimines formed as white precipitates. They were filtrated, washed with water, and then washed twice with methanol. They were then dried in vacuo for at least 24 h prior to use.

The model compound for charge-transfer compelxation studies, bis(*N*-butyl-*p*-xylylideneimine) (BI)



was synthesized as follows. To 20 mL of dry benzene and 15 mL of dry *N,N'*-dimethylacetamide in a 50-mL round-bottom flask were added 0.015 mol of terephthalaldehyde, 0.03 mol of *n*-butylamine, and 1.5 g of lithium chloride. The solution was refluxed with a Dean–Stark water separator for 4 h. The product is a colorless oil and was isolated by vacuum distillation at 145 °C after removal of the reaction solvent by distillation. IR (KBr): 2899 (aromatic CH), 1644 (C=N stretch), 1298 cm^{-1} (CN stretch). NMR ($(CD_3)_2CO$): 8.35 (s, –CH=N), 7.80 (s, CH aromatic), 3.58 (t, NCH_2–), 1.65 (quintet, –CH_2–), 1.38 (sextet, –CH_2–), and 0.93 ppm (triplet, –CH_3).

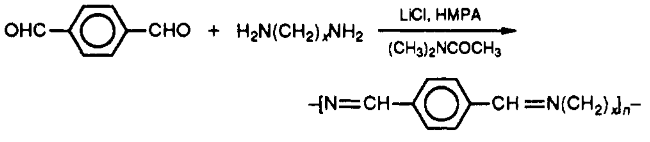
Spectral characterization of the products was performed on a Bomem Michelson infrared spectrophotometer (KBr pellets), on a Hewlett Packard 8452A UV–visible spectrophotometer (THF solutions), on a Bruker AM-400 NMR spectrometer (acetone-d_6 solutions), and on a Bruker CXP-200 NMR spectrometer (CP-MAS ^{13}C NMR spectra in the solid state). The NMR spectra in the solid state were recorded at a spectrometer frequency of 50.307 MHz, 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 delay of 10 s. The data were collected in 2K and zero-filled to 4K, and processing was done with a 20-Hz line broadening. The reference for chemical shift measurements was tetrakis(trimethylsilyl)silane (Aldrich), resonating at −1.5 ppm.

Thermal characterization was performed on a Mettler TA-3000 DSC instrument at 10K/min heating/cooling rates. The samples were observed under polarized light on a Leitz microscope (magnification 200×) at temperatures set by a Wild–Leitz heating stage 350. Samples for microscopic observation were pressed into films and mounted between two glass slides. X-ray powder diffraction patterns were registered by a CSS/STOE 2P/L two-circle diffractometer using copper radiation.

Charge-transfer complexes of the polyimines were obtained by swelling the polymers in THF solutions of the electron acceptors. The final products were obtained by evaporation of THF and drying in vacuo at room temperature for over 24 h.

Results and Discussion

The general scheme of the reaction for the synthesis of the PI-*x* polymer series is



PI-*x*

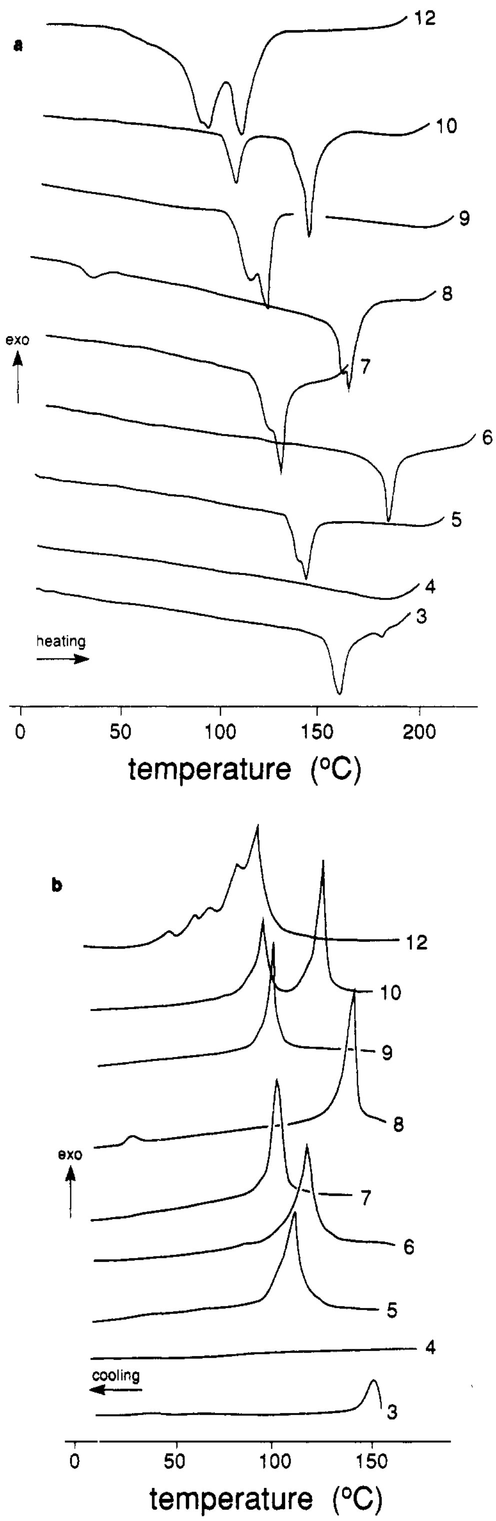


Figure 1. (a) Second heating scans for the polyimines. (b) First cooling scans.

where x = 3–10 and 12. The PI-*x* polymers are insoluble in any organic solvents; hence, their structure was characterized by IR spectroscopy and high-resolution solid-state NMR spectroscopy. Some IR characteristic absorptions for a PI sample (PI-10) are 3020 (weak) and 2932 and 2845 cm^{-1} (strong) (aromatic CH), 1642 (–C=N– stretch), 1463 (CH deformation), and 1298 cm^{-1} (–CN= stretch). Some indication of the molecular weight of the polymers can be obtained from the CP-MAS NMR spectra. Aldehyde and amino end groups are expected to be present in the polymer. The aldehyde carbon resonates at 188.7 ppm, while the imine carbon resonates at ca. 155 ppm.

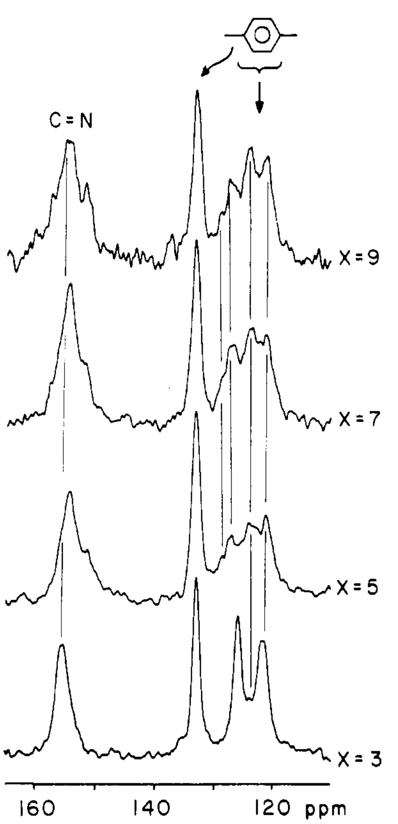


Figure 2. Aromatic region of the CP-MAS NMR spectra of PI-3, PI-5, PI-7, and PI-9.

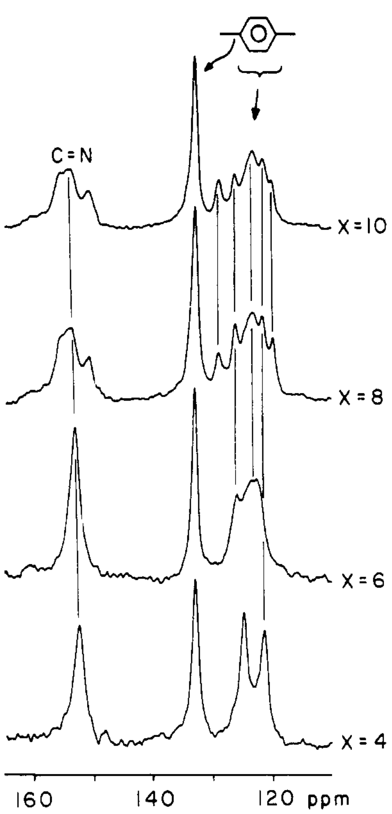


Figure 3. Aromatic region of the CP-MAS NMR spectra of PI-4, PI-6, PI-8, and PI-10.

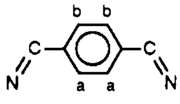
The sensitivity of the NMR method for ca. 500 scans is supposed to be such that one aldehyde group per 20 structural units should be visible in the spectrum. Since no signal was present in the aldehyde region for any of our polymers, it is reasonable to assume that the average degree of polymerization is higher than 20 for all the samples.

All polymers are semicrystalline at room temperature. DSC scans of the PI series were reproducible starting with the first cooling and the second heating scans. Figure 1a presents the second heating scans for all the polymers, extended above the polymer decomposition temperatures (the onset of the exothermal process), while the first cooling scans are presented in Figure 1b. Except for PI-4, which decomposes before anything else happens to it, every polymer presents at least one first-order transition. Some of these peaks seem to be overlaps of the two processes (in Figure 1a the higher temperature peaks of PI-5, PI-7, PI-8, and PI-9, and, less resolved, for PI-10). Also to be noted is the relatively low temperatures at which the polymers show the onset of degradation. Samples heated above this temperature become brown and the color darkens as the temperature increases. Aliphatic amines and imines are known to be relatively unstable to oxidation when heated in air. PI-3 shows a smaller endotherm at 180 °C superimposed on the irreversible exothermic oxidation process.

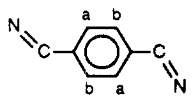
To explain the nature of the first-order processes observed by DSC, solid-state NMR spectra of the initial polymer samples were run and compared with the same samples after heating. Figure 2 shows the aromatic region of the spectra of PI with an odd number of methylene groups. The assignment of the signals is straightforward. An imine carbon resonates at ca. 155 ppm, while the aromatic carbon resonances consist of the sharp signal of the nonprotonated carbons (133 ppm) and a few signals due to the protonated carbons. The only signal that has the same shape for all samples belongs to the nonprotonated carbon of the benzene ring. With increasing the spacer length, the protonated aromatic carbon signals become rather complicated, while the imine carbon signal broadens considerably, without a lot of resolution. At $x = 3$, there are only two main signals due to the protonated aromatic carbons.

The spectra (aromatic region) for the polyimines with an even number of methylene spacers are presented in Figure 3. They are similar to the spectra in Figure 2, except for a better resolution of some of the peaks. Again, the nonprotonated aromatic carbon signal hardly changes. The C═N signal, however, broadens considerably for $x = 8$ and $x = 10$, and some splitting can be noted. The most interesting signal is that of the protonated aromatic carbons. It consists of a relatively sharp doublet for PI-4, similar to the doublet of PI-3. For PI-6 another broader signal appears in the middle. Starting with $x = 8$, another doublet appears, with a larger splitting than the doublets of PI-3 and PI-4.

The doublets in the PI-3 and PI-4 spectra indicate a relatively simple structure in which there are two types of nonequivalent protonated aromatic carbons. This suggests that the geometry of the imine–benzene–imine structure should be planar, creating a conjugated system. There are two possible arrangements of the coplanar system, which will be called here cis and trans.

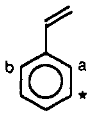


cis



trans

Both structures have nonequivalent protonated aromatic carbons, marked with a and b. It is reasonable to assume that the difference in chemical shifts of the protonated carbon is a consequence of diamagnetic ring current effects produced over the whole conjugated domain. Then, the most deshielded carbons will be those closer to a C=N double bond (a), while all carbons b will also experience deshielding to a lesser degree.



As it can be seen here, the a carbon in the ortho position experiences the strongest effect, while the b carbon in the ortho position experiences an effect similar to the carbon in the meta position on the same side as the double bond (*). The overall effect on each carbon will then be as follows:

(a) Carbons a of the cis configuration will be the most deshielded, experiencing a sum of the strong deshielding from the C=N bond in the ortho position and of the weak deshielding from the other C=N bond.

(b) Carbons a of the trans configuration, experiencing only one strong deshielding, will resonate next, with an increase in the field strength.

(c) Carbons b of the trans configuration will be next, each experiencing a sum of two weak deshielding effects from the two C=N bonds.

(d) Carbons b of the cis configuration will resonate at the highest field, because each experiences only one weak deshielding effect.

With these assumptions, the doublets of PI-3 and PI-4 can be assigned to an elongated trans configuration. It seems to be the only configuration formed during the synthesis of PI-3 and PI-4. This is not surprising, due to the rather restricted conformations allowed by such short spacers. For longer spacers (PI-5 and PI-6), the protonated aromatic carbons show three signals: two similar to those previously assigned to the trans configuration and a new one in between the two. All the protonated aromatic carbons can be equivalent if the plane of the C=N bonds is preferentially perpendicular to the aromatic ring or if there is free rotation around the C(aromatic)–C(imine) bonds.[18] Hence, it is reasonable to assign the center signal to either a perpendicular or a freely rotating structure and to assume that PI-5 and PI-6 consist of a mixture of planar trans and "perpendicular" or "freely rotating" configurations.

Still increasing the spacer lengths, starting probably with PI-8 (the resolution of PI-7 is not good enough to decide if more signals are present), two more lines appear in the region of protonated aromatic carbons. They can be assigned to the planar cis configuration, having a greater nonequivalence (translated into a greater spacing between signals) of the two protonated carbons. Though the spectra presented here are not quantitative, a rough comparison in Figure 3 indicates that the amount of cis configuration increases with an increase in the spacer length. This seems to suggest that formation of the cis structure is kinetically preferable but is sterically restricted at lower spacer lengths.

A solid-state NMR spectrum of terephthalaldehyde shows four sharp signals: at 188.7 ppm the aldehyde carbon, at 132.9 ppm the nonprotonated aromatic carbon, and at 127.7 and 119.3 ppm two signals for the protonated aromatic carbons. These last two signals correspond to the cis configuration resonances of the polyimines. Formation of an imine is an addition–elimination reaction with opening of the C=O double bond and formation of a quaternary intermediate. Re-formation of the C=N double bond takes place with no configurational preference. Starting with a cis terephthalaldehyde, a mixture of cis and trans products are expected. This is indeed what happens if the spacer is long enough.

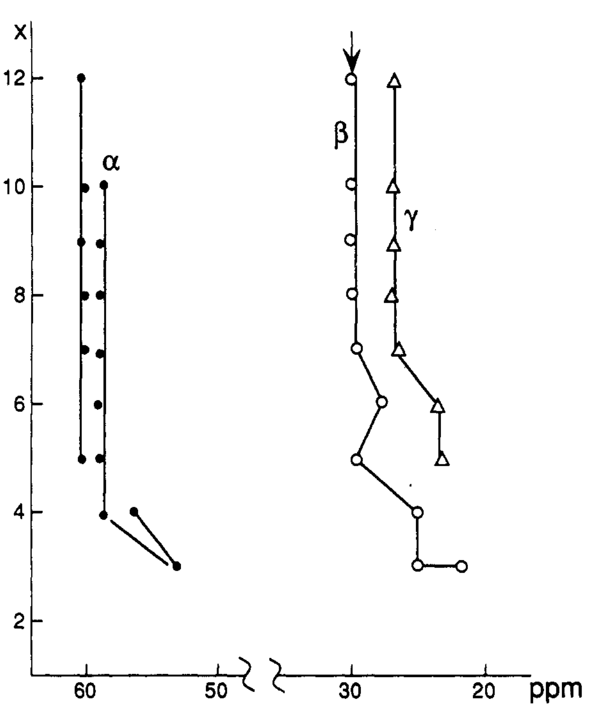


Figure 4. Chemical shift diagram for the aliphatic region of the PI series. The arrow indicates the position of the signal for the "internal" methylene carbons with $x > 7$.

It is apparent from the spectra that the resolution of the cis and trans signals is much better for the polyimines with even spacers. This results from a comparison of the protonated aromatic carbon signals in Figures 2 and 3. The overall resolution of both series of spectra is about the same, and this can be seen from the comparable width at half-height of the nonprotonated aromatic carbon signal. This difference in resolution might be an effect of better packing and higher crystallinity in the polyimines with even spacers. Another conclusion that can be drawn from the spectra in Figure 3 is that the C=N carbon is also sensitive to configuration, and most probably the higher field part of this signal belongs to the cis configuration.

The aliphatic region of the CP-MAS NMR spectra is summarized in Figure 4. The methylene carbons directly bonded to the nitrogen (α-C) resonate at the lowest field and are normally split into two signals. It is reasonable to assume that the split is due to the relative position of this methylene group to the C=N double bond rather than to the cis or trans configurations of the extended conjugated system. This methylene group can assume a cis or trans position with respect to C=N. The higher chemical shift of these α-C belongs to PI-3. This is not surprising, because, for a spacer of three methylene groups only, the second nitrogen atom will exert a γ effect on the carbon bonded to the first nitrogen atom. Any gauche conformation would induce a high-field shift of the signal.[19] From the position of this peak for PI-3, it seems that the gauche conformation component is significant. The fact that there is only one signal for the α-C in PI-3 seems to confirm that PI-3 as is formed has a rather simple ordered structure. PI-4 already presents the two α-C signals, at a lower field than PI-3, and starting with PI-5 the position of these signals is constant. The β-C signal also includes the "internal" methylene groups for spacers longer than $x = 7$. It is split into two signals for PI-3, indicating at least two conformations for this polymer. It has the highest chemical shift for PI-4. This is due to the second nitrogen

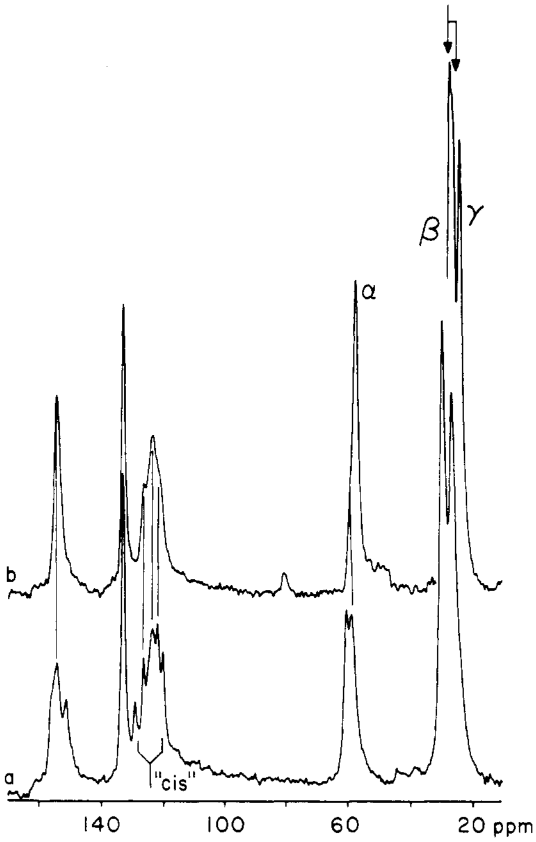


Figure 5. CP-MAS NMR spectra of (a) PI-8 as synthesized and (b) PI-8 heated at 140 °C for 2 h and then quenched in liquid nitrogen.

γ-effect, an effect similar to that on α-C in PI-3. Then, for longer spacers, the β-C resonates at the same position, with the exception of PI-6, which has a slightly higher shift. Finally, all γ-C resonate at the highest field, due to the γ gauche effect. This time PI-5 will show a double γ effect and will be shifted upfield. Again PI-6 is an exception by resonating at slightly higher fields than all other polymers. There are not enough data present to decide why PI-6 has such a different aliphtic spectrum than one would expect by looking at the other polymers. One possibility is that PI-6 is formed in a single preferred configuration of CH_2 with respect to C=N (one signal is apparent for the α-C) and that this affects the overall conformation of the spacer.

For samples with two distinct DSC peaks and with a relatively large temperature interval between these peaks (PI-3, PI-8, and PI-10), CP-MAS NMR spectra were also run after some thermal treatment. The sample was heated to a temperature in between the two transitions, held there for a few minutes, and then rapidly thrown in liquid nitrogen, in the hope of "freezing" the configuration existing at that temperature. Figure 5 shows the results for PI-8. The same conclusions can be drawn for PI-10, with the CP-MAS NMR spectral effects being similar. The spectral resolution is unchanged for PI-8 as synthesized (Figure 5a) and for quenched PI-8 (Figure 5b), because the width is half-height of the nonprotonated aromatic carbon signal is not changed. However, there are important changes for all other signals. The protonated aromatic carbon region now shows only signals previously assigned to the trans planar configuration and to the nonplanar structures (central signal). This central signal has increased in intensity when compared to the trans peaks. The cis configuration signals have completely disappeared. The C=N signals narrowed, and the upper field part of this signal, also previously assigned to the cis configuration, disappeared. It seems that the first DSC transition for PI-8 and PI-10 is a melting of the cis structures, which become nonplanar, amorphous (the central signal). The structure of PI-8 and PI-10 in between the two DSC transitions thus consists of ordered trans domains within a background of disorder. All the aliphatic carbons show some upfield shifts. The α-C is not split anymore, confirming that some rotations and configurational changes have taken place. The β-C seem to present a new splitting. The upfield shift of the γ-C is the easiest to interpret. It indicates an increase of the more disordered gauche conformation, as opposed to the more ordered trans.[18] It is interesting to note that the quenched PI-8 sample as a spectrum that is very similar to the as-synthesized PI-6 sample, including all the "anomalous" upfield shifts in the aliphatic region. The PI-6 sample did not have any cis configuration, it only contained a mixture of trans and amorphous, the same configuration as the quenched PI-8 but probably in different proportions.

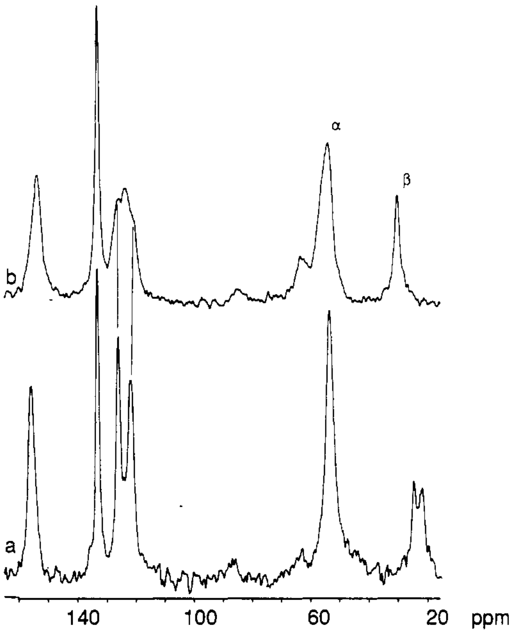


Figure 6. CP-MAS NMR spectra of (a) PI-3 as synthesized and (b) PI-3 heated at 160 °C for 15 min and then quenched in liquid nitrogen.

PI-3 has no cis structure according to the NMR spectrum but still presents two DSC transitions, though the last one is much less intense than those of PI-8 and PI-10. Figure 6 presents the spectra of PI-3 as synthesized and PI-3 after being heated above the first transition for 15 min and then quickly dipped into liquid nitrogen. Comparison of these two spectra demonstrates that the first DSC transition is also a melting, this time a melting of trans structures into nonplanar ones (the central signal of the protonated aromatic carbons—absent in the sample as synthesized). The fact that some trans signals are still present could mean either an incomplete melting or recrystallization when cooled (even if the cooling is done very fast to avoid any recrystallization). The only experiment that would allow us to decide between these two possibilities would be to run the NMR spectra at higher temperatures and not on quenched samples. We are currently attempting to perform these experiments on all samples, but a major impediment is the PIs high tendency to oxidize at high temperatures, and a good NMR spectrum requires keeping the sample for a few hours at the set temperature. There are some changes in the aliphatic region of the spectrum as well. The appearance of a side

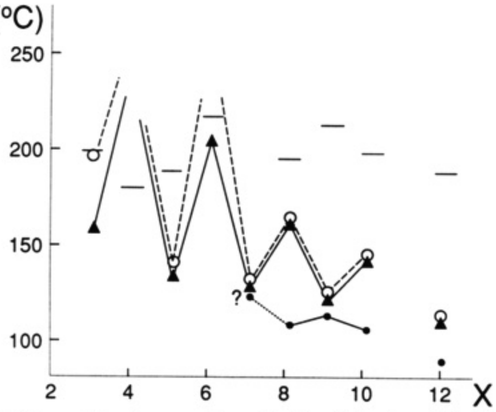


Figure 7. Transition temperatures for the PI series with different spacer lengths. X = number of methylene units in the spacer; (●) cis melting; (▲) trans melting; (○) clearing; (—) decomposition. For PI-8, the cis melting temperature is that obtained in the first scan (sample taken as synthesized).

peak of the α-CH_2 signal (about 60 ppm), as well as broadening of this signal, is probably due to partial oxidation of the sample. This is also visible from the light brown color the sample acquires after being thermally treated. The lower field shift of the β-CH_2, accompanied by the collapse of the doublet can only be explained by some conformational changes. This is unlike all other aliphatic shifts, which were upfield (Figure 5). The downfield shift cannot be associated with a γ effect; therefore, there is no simple explanation for it. An ab initio calculation of the expected shifts with the aliphatic chain conformation is feasible here, due to the relatively short spacer.

All these data suggest that polyimines with longer spacers are being obtained as a mixture of nonplanar cis and trans configurations. When the spacer has 5–7 methylene groups, a mixture of nonplanar and trans configurations is obtained by synthesis, while with 3 and 4 methylene groups, the polymer is more ordered, with a predominantly trans configuration. Those polyimines that contain cis structures, when heated, will undergo first a melting of the cis structures, which will generate a less ordered phase consisting of nonplanar and trans configurations. The amount of nonplanar, disordered domains is greater than any obtained by direct synthesis. Samples that underwent cis melting, as well as samples that did not contain any cis by synthesis, when heated, undergo a melting of the trans domains to create a mainly amorphous structure. Except for PI-3, this amorphous structure seems to be isotropic. PI-3 is the only sample showing an endotherm, which cannot be assigned to either cis or trans melting. Because a film of this sample still presents birefringence above the trans melting endotherm, we are tentatively assigning the interval above the trans melting to a nematic range; hence, the small endotherm would be a clearing process. This assignment is tentative at best, because in that temperature range PI-3 starts oxidizing. Figure 7 summarizes the transitions described above. Since the melting of trans structures appears as a double peak in most polyimines (see Figure 1a), we are proposing that it is accompanied by a clearing of some partly ordered domains. This would mean that most polyimines present a virtual nematic interval, which is slightly larger only for PI-3. Even for PI-3, the clearing endotherm takes place just as the sample starts oxidizing. This makes it impossible to obtain a picture of the nematic texture, as these are best observed on the cooling scan.

Starting with PI-7 or PI-8, the polyimines exhibit a temperature range where a significant degree of order is present. Figure 8 shows the textures observed for PI-8 and PI-10 on cooling from the isotropic phases. These microscopic textures are similar to those observed for smectic phases. An attempt to characterize these phases was made by using the X-ray diffraction patterns, which are presented below and above the cis melting temperature in Figure 9 for PI-8 and in Figure 10 for PI-10. Goodby[20] attempted a classification of some higherly ordered phases, similar to these obtained here, in more ordered (crystal) and more fluid (liquid crystal). He suggested that, if no more than 5 orders of reflections are observed in the X-ray diffractogram and if there is intense diffuse scattering, the layer distribution function is not sharp and is therefore different from that of a typical crystal. Consequently, using Goodby's definitions, the phase obtained by cis melting in PI-8 seems to be a smectic crystal phase, a disordered solid, while the one in PI-10 seems to be a smectic liquid crystal phase. Visual inspection under the microscope seems to confirm that the first melting of PI-10 generates a fluid substance. The X-ray diffraction pattern of PI-10 has only three peaks and intense diffuse scattering, indicating considerable disorder. PI-9 and PI-12 do not show large enough intervals after the cis melting to allow for an X-ray diffraction pattern to be recorded. One explanation for the difference between PI-8 and PI-10 is a higher proportion of cis configuration in PI-10, which, when it melts, produces a higher proportion of "disorder".

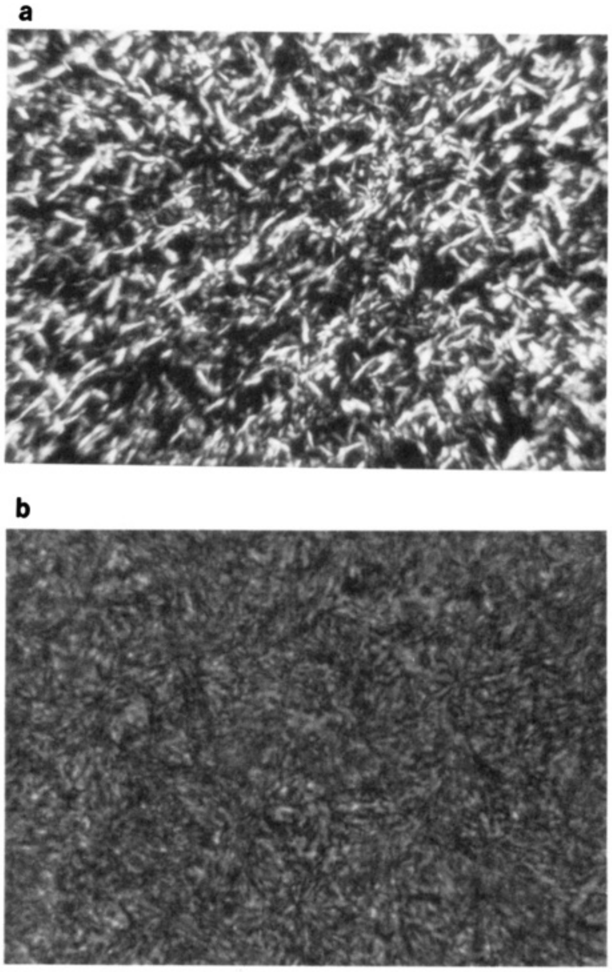


Figure 8. Sample of PI-8 (a) and one of PI-10 (b) photographed with polarized light. The samples were heated above the isotropic transition, and the picture was taken on cooling, just after the birefringence appeared.

Table I presents the enthalpies of transition for the poly-

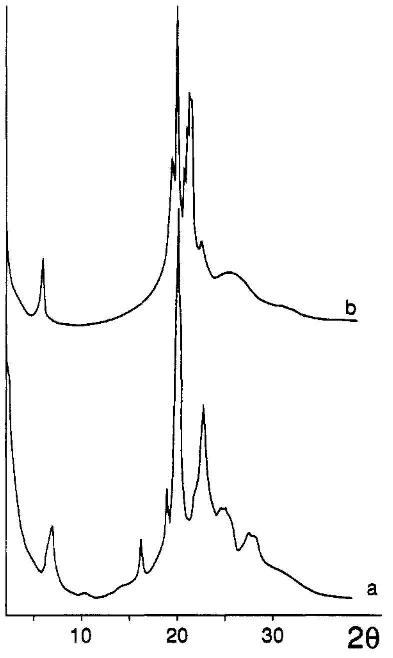


Figure 9. X-ray powder diffraction patterns for PI-8 as synthesized (a) and at 95 °C after cooling from the isotropic melt (b).

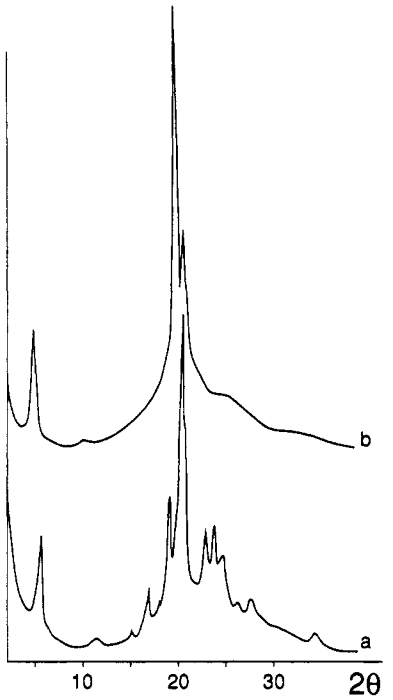


Figure 10. X-ray powder diffraction patterns for PI-10 as synthesized (a) and at 117 °C while cooling from the isotropic melt (b).

Table I
Transition Enthalpies for the Polyimines

	ΔH, kJ/mol			
sample	cis melting	trans melting	clearing	total ΔH
PI-3		11.7	2.2	13.9
PI-4				
PI-5		← 10.3 →		10.3
PI-6		← 12.3 →		12.3
PI-7	?	← 16.4 →		16.4
PI-8	1.3	← 14.6 →		15.9
PI-9	← 16.6 →			16.6
PI-10	8.7	← 13.1 →		21.8
PI-12	10.1	← 9.9 →		20.0

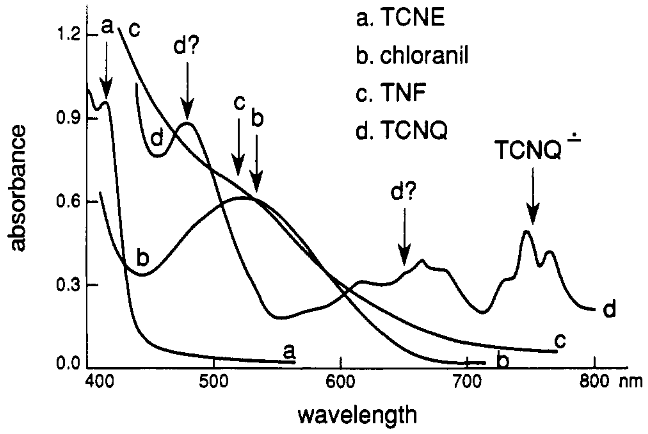


Figure 11. Electronic spectra of equimolar mixtures of BI with (a) TCNE, (b) chloranil, (c) TNF, and (d) TCNQ, registered in TNF. The spectrum of the electron acceptor solution was subtracted from the spectrum of the mixture.

imines, grouped according to the assignments made above. For most polyimines the trans melting and clearing transitions cannot be integrated separately, so the values in Table I are a sum of the enthalpies of these two processes (except for PI-3). PI-9 is also an exception, because all three processes are believed to occur at very close temperatures; hence, the peak integration measures the total effect. The ΔH values are calculated per mole of structural unit. The increasing values of cis melting enthalpies reflect the fact that, as the spacer becomes longer, the proportion of cis structures in the polymer increases. This can be seen, approximately, in the NMR spectra presented in Figures 2 and 3. When the total enthalpic effect of the transition between the semicrystalline and isotropic states is used, the polyimines can be grouped into three groups. PI-3 to PI-6, which consist mainly of trans structures and some amorphous parts, show values between 10 and 13 kJ/mol. As the transition temperatures for these polyimines are higher, it is reasonable to assume that some of the clearing processes (maybe nematic to isotropic) would occur above the decomposition temperatures. This would be an explanation for differences of ca. 3 kJ/mol between the polymers in this group. PI-7 to PI-9 show a total enthalpy of transition of ca. 16 kJ/mol. These polymers already contain some cis structures, though in a rather low proportion, and the melting of these minor cis components generates the smectic crystal phase, which itself is ordered enough to require a high enthalpy for the transition to the isotropic state. Starting with PI-10, the enthalpy of the cis melting increases to become the major process. Here, the overall enthalpy is the highest, around 20 kJ/mol. Melting of cis structures still generates a highly ordered phase; however, this is probably a smectic liquid crystalline phase according to Goodby's definitions,[20] which is slightly less ordered than the smectic crystalline phase of PI-8.

Charge-Transfer Complexes. Although the aromatic imine moiety is not a strong electron donor, a preliminary investigation on the charge-transfer complexes of the PI series with electron acceptor molecules has been undertaken. To prove the presence of a charge-transfer complex, the electron spectra of equimolar mixtures of BI with tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ), tetrachloro-1,4-benzoquinone (*p*-chloranil), and 2,4,7-trinitro-9-fluorenone (TNF) in THF are presented in Figure 11. Of the four electron acceptors, TCNQ induces total electron transfer to form the recognizable radical anion at 750 nm.

As described in the Experimental Section, it is difficult to prepare charge-transfer complexes of the polymers, due

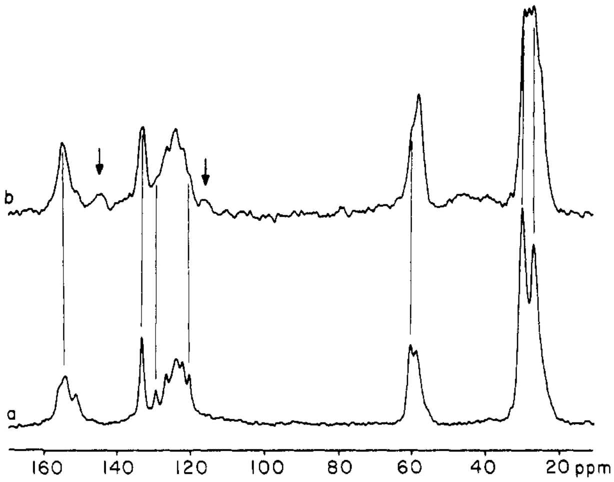


Figure 12. CP-MAS NMR spectra (0.25-ms contact time) of (a) PI-8 as synthesized and (b) PI-8 doped with TNF.

to the insolubility of the PI series. By following the described procedure, colored powders of the polymers are obtained after drying. The color is yellow with TCNE, light purple with TNF, brown with *p*-chloranil, and dark brown with TCNQ. Thermal analysis of these powders shows that they are quite different from the initial polymers. Complexes with TCNE and *p*-chloranil show one melting followed by decomposition, while complexes with TCNQ decompose before anything else happens. Only the complexes with TNF show multiple transitions, some of them reversible. TNF is a very large molecule, and a weaker acceptor, so its role is probably mainly to create some disruptions in the crystalline and liquid crystalline structures of the polymer. To illustrate what the effect of TNF is on the polymer upon doping, Figure 12 shows the CP-MAS NMR spectra of PI-8 and doped PI-8 (0.25 mol of TNF for each 1 mol of structural unit). The contact time was of only 0.25 ms, to avoid seeing any "free" TNF.[3] The arrows indicate signals appearing from complexed TNF. The effect of doping seems to be a narrowing of the CH= signal and an apparent decrease of the cis configuration signals. Also, some of the methylene carbon signals shift upfield, suggesting increased disorder.

Actually, things are more complicated than they seem. Microscopical observations of the samples demonstrate that they are indeed heterogeneous. Distinct regions of very intense purple color are observable above 150 °C. In this region, the DSC curve shows a continuum of endothermal peaks. These endothermic processes are irreversible and they may be assigned to decomplexation, as suggested previously for a similar system.[21] More studies are necessary for a definite answer.

It is not within the scope of this paper to study what happens with the polymer complexes. Charge-transfer complexes of the carbazole-containing polyimines will offer more insight into these processes, because much more is known about the carbazole–TNF complexes in general. The series of polyimines presented here constitute a simple model for these polymers, and investigations are in progress on the phase structure of the PI polymer series and on the differences in mobility for various parts of the molecule. These studies are being performed by CP-MAS NMR, by measuring different relaxation parameters. Also, to confirm the assignments of various crystalline or liquid crystalline phases, especially the virtual phases, work is in progress on copolymers of terephthalaldehyde with pairs of spacers of different lengths. These kinds of investigations have been shown to be very successful in resolving transitions and extrapolating transition temperatures for virtual liquid crystalline phases.[22]

Acknowledgment. This research was funded by a NSERC Canada operating grant (A.N.). The heating stage was purchased with an equipment grant from the Ontario Centre of Materials Research (A.N.). C.C. acknowledges a summer research assistantship partly funded by NSERC Canada. We thank Prof. D. Heyding for running the X-ray diffraction instrument and for helpful discussions.

References and Notes

(1) Bloor, D. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: New York, 1989; Vol. 2, p 687.

(2) Sasabe, H.; Wada, T. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: New York, 1989; Vol. 7, p 179.

(3) Natansohn, A. *Macromolecules* **1991**, *24*, 1662.

(4) Simmons, A.; Natansohn, A. *Macromolecules* **1991**, *24*, 3651.

(5) Natansohn, A.; Simmons, A. *Macromolecules* **1989**, *22*, 4426.

(6) Simmons, A.; Natansohn, A. *Macromolecules* **1990**, *23*, 5127.

(7) Ringsdorf, H.; Wustefeld, R.; Zerta, E.; Ebert, M.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 914.

(8) Adams, R.; Bullock, J. E.; Wilson, W. C. *J. Am. Chem. Soc.* **1923**, *45*, 521.

(9) Delman, A. D.; Stein, A. A.; Simms, B. B. *J. Macromol. Sci., Chem.* **1967**, *A1*, 147.

(10) Guillon, D.; Skoulios, A. *Mol. Cryst. Liq. Cryst.* **1979**, *49*, 119.

(11) Blumstein, A.; Sivaramakrishnan, K. N.; Clough, S. B.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1979**, *49*, 255.

(12) Millaud, B.; Thierry, A.; Strazielle, C.; Skoulios, A. *Mol. Cryst. Liq. Cryst.* **1979**, *49*, 299.

(13) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729.

(14) Wojtkowski, P. W. *Macromolecules* **1987**, *20*, 740.

(15) Cheng, S. Z. D.; Janimak, J. J.; Sridhar, K.; Harris, F. W. *Polymer* **1989**, *30*, 494.

(16) Cheng, S. Z. D.; Janimak, J. J.; Lipinski, T. M.; Sridhar, K.; Huang, X. Y.; Harris, F. W. *Polymer* **1990**, *31*, 1122.

(17) Gray, G. W. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1982; p 5.

(18) Uryu, T.; Kato, T. *Macromolecules* **1988**, *21*, 378.

(19) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.

(20) Goodby, J. W. *Mol. Cryst. Liq. Cryst.* **1983**, *92*, 171.

(21) Pugh, C.; Percec, V. *Polym. Bull.* **1990**, *23*, 177.

(22) Percec, V.; Tsuda, Y. *Macromolecules* **1990**, *23*, 3509.

Registry No. BI, 30862-11-4; PI-3 (copolymer), 88684-45-1; PI-3 (SRU), 88689-94-5; PI-4 (copolymer), 29036-86-0; PI-4 (SRU), 31807-93-9; PI-5 (copolymer), 115673-96-6; PI-5 (SRU), 115673-94-4; PI-6 (copolymer), 29036-87-1; PI-6 (SRU), 31987-41-4; PI-7 (copolymer), 135506-19-3; PI-7 (SRU), 135506-14-8; PI-8 (copolymer), 135506-20-6; PI-8 (SRU), 135506-15-9; PI-9 (copolymer), 135506-21-7; PI-9 (SRU), 135506-16-0; PI-10 (copolymer), 135506-22-8; PI-10 (SRU), 135506-17-1; PI-12 (copolymer), 135506-23-9; PI-12 (SRU), 135506-18-2; $OHCC_6H_4$-*p*-CHO, 623-27-8; $NH_2(CH_2)_4H$, 109-73-9.