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Synthesis and Characterization of Poly[(2,6-diaminotoluene-3,5-diyl)methylene] and Its Condensation Product, Poly(1-methylcyclohexa-1,3-diene-2,3-diyl-5,6-diylidene-5-methylidyne-6-nitrilo), a Linear Ladder Aromatic Polymer

J. Z. Ruan and M. H. Litt*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. Received June 27, 1986

ABSTRACT: 2,6-Diaminotoluene reacts with formaldehyde in aqueous solution with acid catalysis to produce a crystallizable prepolymer, poly[(2,6-diaminotoluene-3,5-diyl)methylene]. The prepolymer can be crystallized from DMF or DMSO solution. A unit cell for the crystalline polymer was determined. The reaction temperature and time substantially affect its molecular weight. The structure of the polymer was analyzed and confirmed by NMR spectra, IR spectra, and element analysis. Further condensation in poly(phosphoric acid) at high temperature (345 °C) produces a soluble linear ladder aromatic polymer, poly(1-methylcyclohexa-1,3-diene-2,3-diyl-5,6-diylidene-5-methylidyne-6-nitrilo). The condensed polymer was characterized by using UV/vis/near-IR, IR, and X-ray diffraction.

Introduction

Much effort has been devoted to conducting polymers over the past few years. This interest was created by the discovery that some conjugated organic polymers can be made highly conducting upon doping with electron donors or acceptors.[1-3] However, the majority of the conducting polymers, such as doped polyacetylene,[4] poly(*p*-phenylene),[5,6] poly(phenylene sulfide),[7] etc., are air unstable. They degrade through reaction with oxygen and/or water vapor under exposure of air.

Both theoretical and experimental studies show that ladder polymers are more resistant to degradation as well as more highly conducting than analogously structured nonladder systems.[8-10] The primary problem of ladder polymers is that conductivity compromises their mechanical properties. The inflexibility of their backbones, required for the extended conjugation, engenders rigidity in the polymer framework. This low degree of freedom for rotation makes solution difficult. In our earlier works,[11,12] we discussed the synthesis of the soluble ladder polymer poly[1-methylcyclohexa-1,3-diene-2,3-diyl-5,6-diylidene-5-(3-pyridylmethylidyne)-6-nitrilo] (PPMQ) and its electronic properties. Its large side group, 3-pyridyl, which solubilized it, probably made it difficult for free carriers to transfer from one molecular chain to another, which may have controlled its electronic conductivity. A new linear soluble ladder aromatic polymer, poly(1-methylcyclohexa-1,3-diene-2,3-diyl-5,6-diylidene-5-methylidyne-6-nitrilo) (PMQ), without the side pyridyl group, has been made. The synthesis and characterization of its prepolymer, poly[(2,6-diaminotoluene-3,5-diyl)methylene] (PM), and the ladder polymer are reported here.

Experimental Section

Chemicals. 2,6-Diaminotoluene (Aldrich Chemical Co.) was recrystallized from hot water (65 °C), and the crystals were sublimed three times at 65 °C and 0.025 Torr, mp = 106 °C.

Formaldehyde solution, 37% by weight, was bought from Fisher Scientific and used as received.

Synthesis of Prepolymer. The synthetic procedure is similar to that used to make PPMQ.[11] Finely powdered 2,6-diaminotoluene (DAT) (3.06 g, 0.025 mol) was dissolved in 50 g of water, and 2.35 mL (0.025 mol) of concentrated hydrochloric acid was added at 60 °C. The solution was cooled or heated rapidly to a predetermined temperature. Because the concentration of formaldehyde in water may change either by precipitation of paraformaldehyde or by evaporation, and because the highest molecular weight polymer may result when the mole ratio differs slightly from 1.00, different amounts of formaldehyde solution, from 2.00 (0.99 mol ratio CH_2O/DAT) to 2.12 g (1.05 mol ratio CH_2O/DAT), were added. The solution was stirred with a magnetic stirrer under nitrogen for a predetermined time (see Table I). It was then neutralized with ammonium hydroxide to pH ~9. The precipitate was filtered, washed with distilled water, and finally dried in a vacuum oven at room temperature and 0.05 Torr. Yield = 3.1 g (92.2%). The prepolymer was analyzed by NMR spectra, IR spectra, UV spectra, and element analysis. Calculated for PM13 (see Table I) $C_8H_{10}N_2 \cdot 0.5H_2O$ + 0.28% ash: C, 66.94; H, 7.67; N, 19.52; ash, 0.28. Found: C, 67.15; H, 7.59; N, 19.36; ash, 0.28.

Table I
Reaction of DAT with Formaldehyde

polymer	temp, °C	time, h	formaldehyde/DAT	[η]
PM1	20	2	0.99	0.05
PM2	20	2	1.00	0.06
PM3	20	2	1.01	0.07
PM4	20	2	1.02	0.09
PM5	20	2	1.03	0.07
PM6	20	2	1.05	0.05
PM7	65	1	1.02	0.07
PM8	65	2	1.02	0.10
PM9	65	4	1.02	0.08
PM10	5	2	1.02	0.07
PM11	5	4	1.02	0.10
PM12	5	8	1.02	0.12
PM13	5	22	1.02	0.15
PM14	5	44	1.02	0.12
PM15	5	24	1.02	0.14

Condensation to Final Polymer. Finely ground dry prepolymer powder, 15.0 g, was mixed with 400 g of poly(phosphoric acid) (PPA). The mixture was stirred under nitrogen by using a mechanical stirrer with a glass paddle at a predetermined temperature for a set time. The PPA was removed by pouring the mixture into distilled water, boiling, centrifuging, decanting the clear layer, adding more distilled water, stirring, and repeating the above process until the pH of the water layer was about 5.

To separate inorganic impurities, e.g., $SiO_2P_2O_5$, as well as any insoluble fraction of the polymer, the dried black solid was dissolved in concentrated sulfuric acid. After centrifuging, the solution was filtered through a fine-fritted glass filter. The solution was poured into distilled water. The clear liquid was decanted after centrifuging and the precipitate rewashed with water until the pH rose to 6. It was dried under vacuum (0.05 Torr) at 60 °C. Yield = 11.2 g (87.0% of theory).

NMR Spectra. The prepolymer crystallizes gradually from DMSO or DMF solution. A dilute polymer solution $(5.0 \times 10^{-2}$

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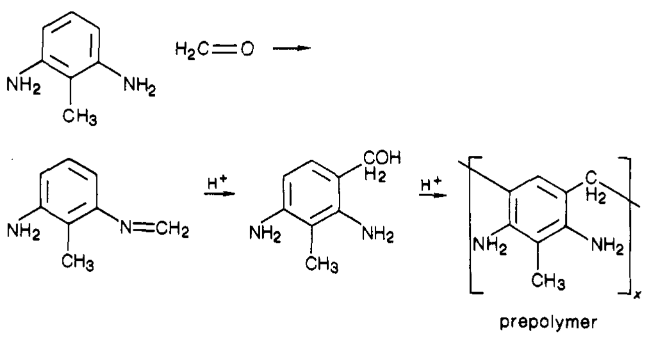
Scheme I



g/mL) in DMSO-d_6 was therefore used to avoid crystallization while running NMR spectra. ^{13}C NMR spectra were taken by using a Varian XL-200M spectrometer; ^1H NMR spectra were recorded on a Varian XL-200H spectrometer.

IR Spectra. IR spectra were obtained on a Digilab FTS-14 FTIR spectrometer at a resolution of 4 cm^{-1} with a total of 50 scans. The pellets were prepared by mixing finely powdered polymers with KBr and pressing them under vacuum. The pellets were uniform or they were reground and repressed until uniform. The spectra were stored in a computer for further analysis.

UV/Vis Spectra. Ultraviolet spectra were taken by using a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrometer. Spectra of the prepolymer were run in DMF solution at 5.0×10^{-5} g/mL concentration with 1% trifluoroacetic acid (TFA) added to prevent the prepolymer from crystallizing. The final polymer spectra were run in concentrated sulfuric acid at a concentration of 1.0×10^{-5} g/mL.

X-ray Diffraction. X-ray diffraction patterns of powdered polymers pressed in the diffraction holder were recorded on a Phillips automated powder diffractometer with monochromatized Cu Kα radiation and scanned at 1.2 deg/min with an 0.02-deg step. The diffraction patterns were transferred to system memory for further manipulation and spectrum plotting.

Electron Microscopy. A very small amount of polymer powder was put into distilled water. The solution was then subjected to ultrasonic vibration in a Bransonic 220 to break down the particles further. One drop of the suspension was put on a carbon-coated copper grid. After evaporating the water, the grid was shadowed with carbon–platinum. Electron micrographs and diffraction patterns were taken by using a JEOL LTD JEM-100SX electron microscope.

General. Intrinsic viscosities were measured in an Ubbelohde-type capillary viscometer (Cannon 50 M120) starting with a 1% (g/mL) polymer solution in DMSO plus 3% of TFA. The temperature was maintained at 30 ± 0.1 °C.

Elemental analyses including ash content were performed by Galbraith Laboratories, Inc. Duplicate analyses were requested for better accuracy. The prepolymers and condensed polymers were dried for 30 h under vacuum at 22 and 100 °C, respectively, before the analyses. Strong reaction conditions were requested for the condensed polymer because of the polynuclear heterocyclic structure.

Results and Discussion

The expected prepolymer was readily obtained (Scheme I) as a yellow solid by the reaction between equivalent amounts of DAT and formaldehyde with hydrochloric acid catalysis. The proposed reaction mechanism is shown in Scheme I.[13] The Schiff base, formed between the diamine and formaldehyde, rearranges with acid catalysis to the corresponding benzyl alcohol. The benzyl group may also react reversibly with an amino group to give a benzyl amine intermediate. In the presence of acid, there is eventual reaction on the 5-carbon of DAT to generate the prepolymer shown.

The agreement between calculated and found (elemental analysis) values was excellent. For some polymers, which were brown in color, internal ring closure and oxidation with loss of NH_3/H_2 seems to have occurred (see later discussion). The closure results in the formation of 2,7-diaminoacridine moieties (Scheme II).[13,14] The ring closure of bis(2,4-diaminophenyl)methane to 2,7-diaminoacridine in the presence of HCl was first described by Elbs et al.[15] Concentrated HCl effected complete ring closure at 180–190 °C. The polymer ring-closed rapidly when heated with dilute HCl.[13]

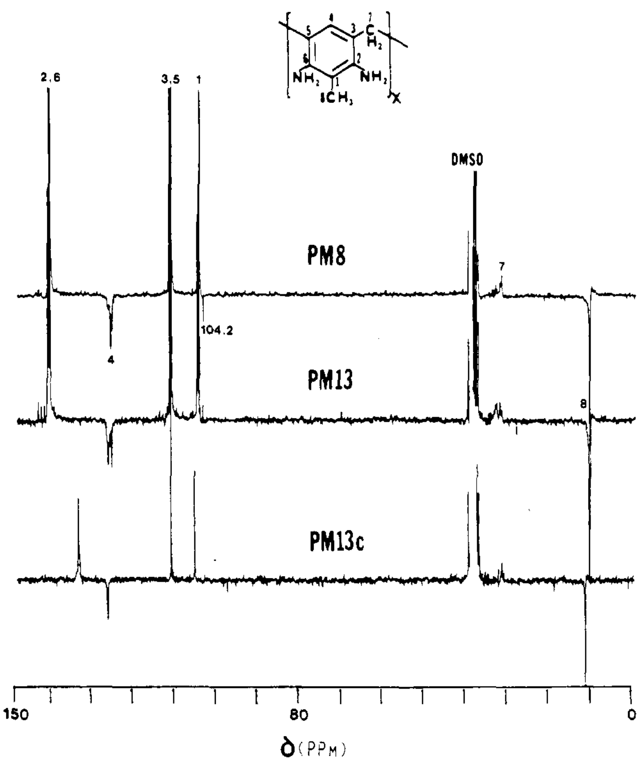
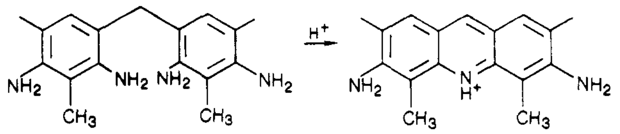


Figure 1. ^{13}C NMR spectra of PM8, PM13, and PM13c.

Scheme II



The prepolymer, yellow in color, dissolved in DMF or DMSO and gradually crystallized from solution as a white solid. The white color indicates that the crystalline polymer has almost no fused rings. This was also supported by NMR and UV spectra.

The influence of reaction temperature, time, and the ratio between DAT and formaldehyde were studied. The results are summarized in Table I.

It turns out that 2% more formaldehyde than as labeled is needed for the highest viscosity polymer. The intrinsic viscosity, shown in Table I, depends on both the reaction temperature and time. Above room temperature, the polymerization is complete in about 2 h; the intrinsic viscosity no longer increases. At 5 °C, the polymerization takes about 1 day. The maximum intrinsic viscosity found was 0.15. The molecular weight of this prepolymer was estimated to be in the range of 5,400 (DP = 40) to 13,400 (DP = 100) from its intrinsic viscosity by using the data from a linear *o*-chlorophenol–formaldehyde polymer,[16] which has a molecular structure similar to that of the prepolymer (meta reaction of formaldehyde).

NMR Spectra. Typical ^{13}C NMR spectra of three prepolymers, PM8, PM13, and PM13c, are shown in Figure 1. PM13c is the prepolymer crystallized from PM13 in DMF solution. Its spectrum was obtained in DMSO containing 1% deuteriated TFA. All peaks from TFA were

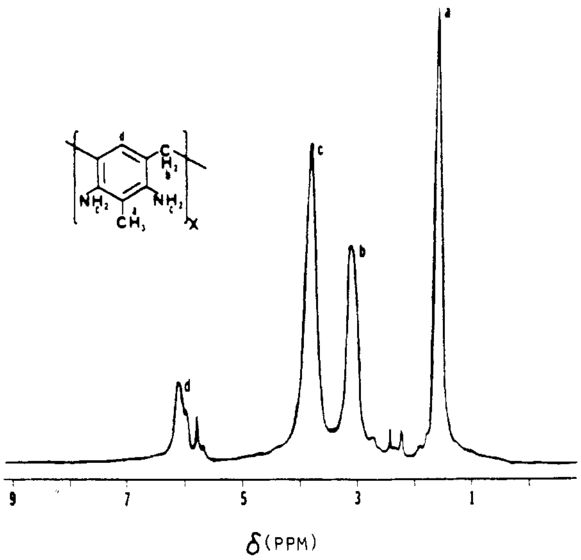
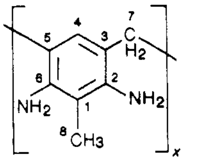


Figure 2. ^{1}H NMR spectra of PM13c.

Table II
Predicted and Observed Chemical Shifts of C for Prepolymer PM13



carbon	predicted^{18}	obsd	carbon	predicted^{18}	obsd
C-1	110.6	105.9	C-4	128.8	127.4
C-2,6	145.9	142.1, 141.9	C-7		32.5
C-3,5	114.1	113.0, 112.6	C-8		11.3

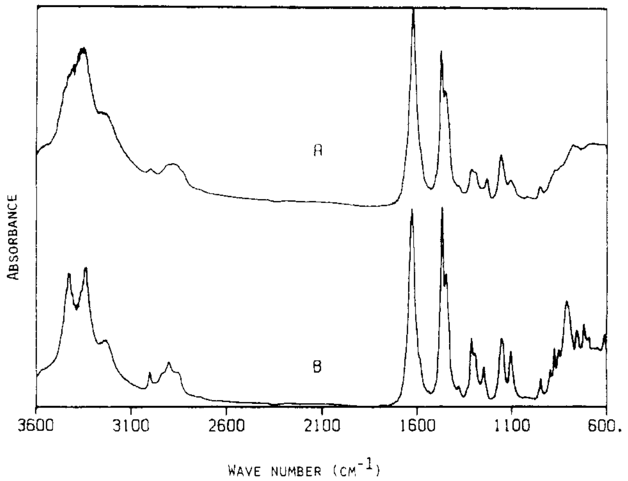


Figure 3. IR spectra of PM13 and PM13c: (A) from PM13; (B) from PM13c.

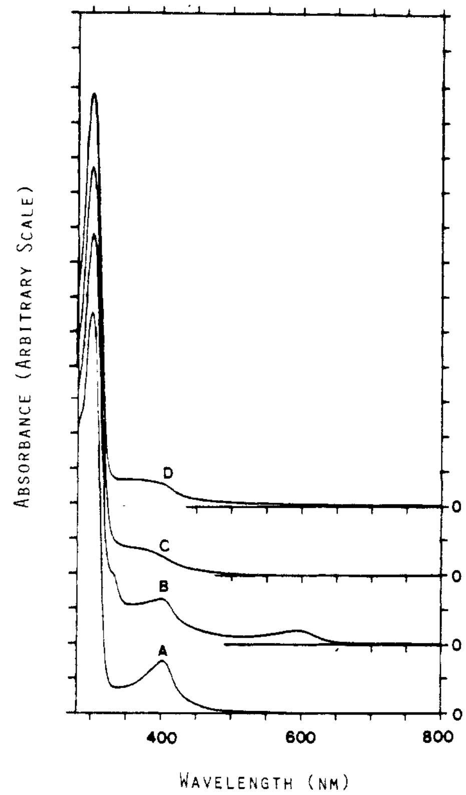


Figure 4. UV/vis spectra of PM4, PM8, PM10, and PM13 in DMF: (A) from PM4; (B) from PM8; (C) from PM10; (D) from PM13.

carefully removed for better resolution.

A normal APT method[17] was used for the simplification of the spectra and peak assignment. Peaks up are attributed to even-proton-bearing carbons; while peaks down correspond to odd-proton-bearing carbons. Chemical shifts for the carbon in the benzene ring were assumed to be additive for a substituted benzene with methyl groups on C-3 and C-5. The predicted[18] and observed chemical shifts are listed in Table II.

The peak corresponding to singly protonated C-5 at the chain end is predicted at 105.2 ppm with the peak down. It appears at 104.2 ppm only in the spectrum of PM8, indicating that PM13 has reasonably high molecular weight. In the spectrum of PM13c, the peaks corresponding to C-2,6 and C-1 are shifted toward 128.5 ppm, the absorption of nonsubstituted benzene, due to the addition of TFA to the solution. The amino group is protonated and hence there is a reduced substituent effect. The spectrum of PM13c is much cleaner than that of PM13 and suggests that the crystallized prepolymer has a regular structure.

Figure 2 shows the proton NMR spectrum of PM13. The band at 6.1 ppm is from proton d. The big peak near 4 ppm arises from the two amino groups. The resonance corresponding to the CH_2 group appears at 3.3 ppm. The sharp peak at 1.8 ppm is assigned to the methyl group. The extra peaks at 5.8 and 2.2 ppm could arise from diaminoacridine residues in the polymer.

IR Spectra. Figure 3 shows that IR spectra of two prepolymers: (A) is from PM13; (B) is from PM13c. The peaks in spectrum B are sharper than that of spectrum A because PM13c is purer and more crystalline. The two split sharp peaks at 3430 and 3344 cm^{-1} are from asymmetrical and symmetrical N–H stretching, respectively.[19] The sharp peaks at 1630 and 1474 cm^{-1} are due to skeletal vibration and C═C and C—N stretching. The C—H bend of CH_2 and CH_3 shows as a shoulder at 1451 cm^{-1} which overlaps with the peak at 1474 cm^{-1}. All is consistent with the expected structure.

UV/Vis Spectra. UV/vis spectra were used to study the polymer structure. Figure 4 shows the UV spectra of PM4, PM8, PM10, and PM13, separately. The absorption peak at 300 nm is due to the B band of diaminotoluene; the corresponding molar extinction coefficient is 3200. There are two extra bands in the spectrum of the prepolymer prepared at higher temperature. The band at 405 nm is similar to that found for diaminoacridine.[20,21] Another band near 600 nm could be from small amount of derivatives with five condensed rings.[21] It suggests that

Table III
Observed and Calculated d-Spacing and Indices of PM13c[a]

no.	d(exptl), Å	intensity	d(calcd), Å	h	k	l	% δ
1	7.93	367.0	7.94	0	1	1	−0.075
2	6.86	223.0	6.91	0	2	0	−0.795
3	5.16	124.0	5.15	1	2	1	0.119
4	4.70	37.0	4.70	2	2	0	−0.020
5	4.55	38.0	4.53	1	0	2	0.394
			4.57	0	1	2	−0.493
6	3.78	12.3	3.79	1	2	2	−0.278
			3.76	3	1	1	0.465
7	3.28	28.0	3.26	0	4	1	0.724
8	2.99	32.0	2.98	3	3	1	0.272
			2.97	4	1	1	0.613
9	2.76	60.0	2.75	1	4	2	0.404
10	2.45	33.0	2.45	2	3	3	0.194
			2.46	2	5	1	−0.271
			2.44	5	1	1	0.417
11	2.24	28.0	2.24	5	3	0	−0.033
			2.24	0	6	1	−0.108
			2.24	5	1	2	0.161

[a] a = 12.82 ± 0.01 Å; b = 13.83 ± 0.10 Å; c = 9.69 ± 0.02 Å; σ = 0.017 Å.

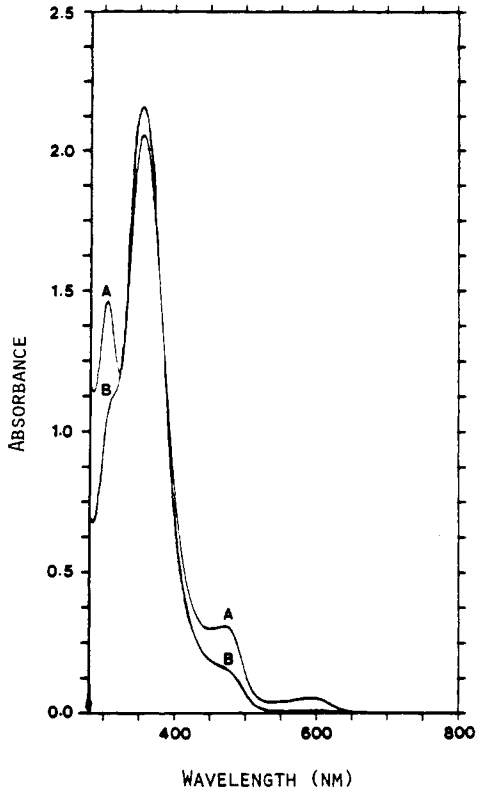


Figure 5. UV/vis spectra of PM13 and PM13c in DMF plus 1% TFA: (A) from PM13; (B) from PM13c.

the higher reaction temperature favors a cyclodeamination oxidation reaction as was shown in Scheme II.[13]

Figure 5 shows the UV spectra of PM13 and PM13c. The original peak at 300 nm is replaced by one at 355 nm due to the addition of TFA to the solution. The other two bands at longer wavelength are considerably reduced after crystallization, which agrees with the NMR data.

Electron Micrograph. The main difficulty for electron diffraction is that the polymer degraded rapidly upon electron irradiation. The spots disappear so quickly there is little time to take a picture, even at very low intensity. However, a selected area electron diffraction pattern of PM13c was obtained, which displays a rectangular diffraction pattern, even though it is not quite clear. Lattice constants a = 12.9 Å and b = 13.7 Å were obtained. The diffractions (0,k,0) with k = odd are systematically absent. Figure 6 shows its schematic diffraction pattern.

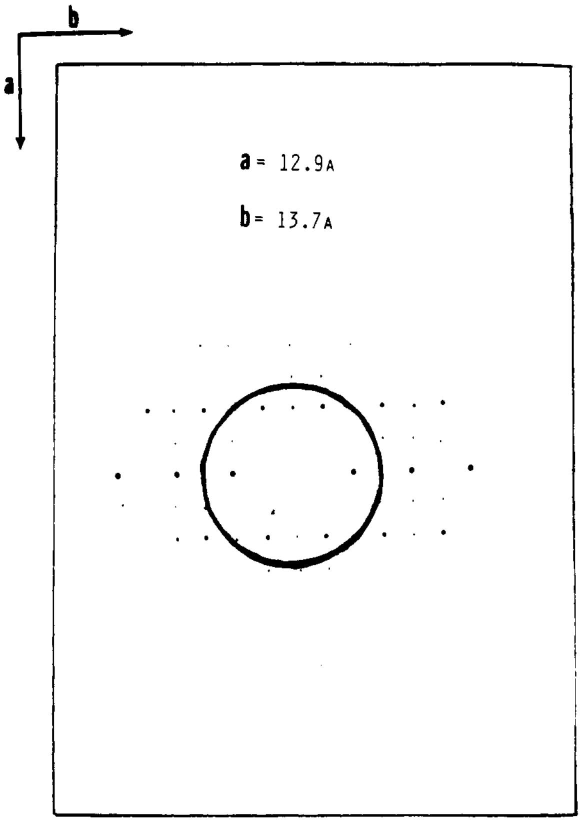
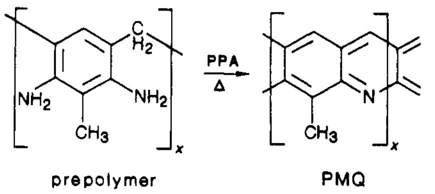


Figure 6. Schematic electron diffraction pattern of PM13c.

Scheme III



X-ray Diffraction of PM. A WAXD spectrum of PM13c is given in Figure 7. The data can be indexed in an orthogonal unit cell by using a c dimension of 9.69 Å plus the two dimensions found from electron diffraction (Figure 6). d-Spacings and their indices are listed in Table III together with the d-spacings calculated by using the lattice constants a = 12.82, b = 13.83, and c = 9.69 Å. The fit is excellent.

Table IV
Element Analysis of Final Polymers

	C	H	N	P	S	O	ash
PMQ1 found	63.74	5.74	10.85	0.70	2.77	15.02	1.25
$C_8H_{6.5}N_{1.17}\cdot 0.035HPO_3\cdot 0.13H_2SO_4\cdot 0.8H_2O$ + 1.25% ash	63.74	5.47	10.79	0.72	2.76	15.21	1.25
PMQ2 found	66.81	4.82	7.05	0.84	3.95	16.53	1.38
$C_8H_5N_{0.73}\cdot 0.04HPO_3\cdot 0.18H_2SO_4\cdot 0.7H_2O$ + 1.38% ash	65.45	4.64	6.97	0.85	3.93	16.80	1.38
PMQ3 found	64.07	4.79	6.75	0.55	4.51	19.21	
$C_8H_5N_{0.72}\cdot 0.024HPO_3\cdot 0.21H_2SO_4\cdot 0.9H_2O$	64.02	4.83	6.72	0.50	4.48	19.33	
PMQ4 found	65.35	2.90	5.14				5.9
73.4% $C_8H_5N_{0.54}$ + 5.9% ash	64.91	3.38	5.11				5.9

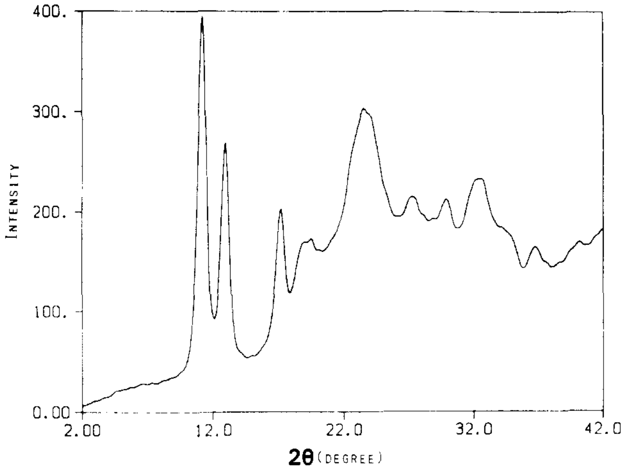


Figure 7. X-ray diffraction pattern of PM13c.

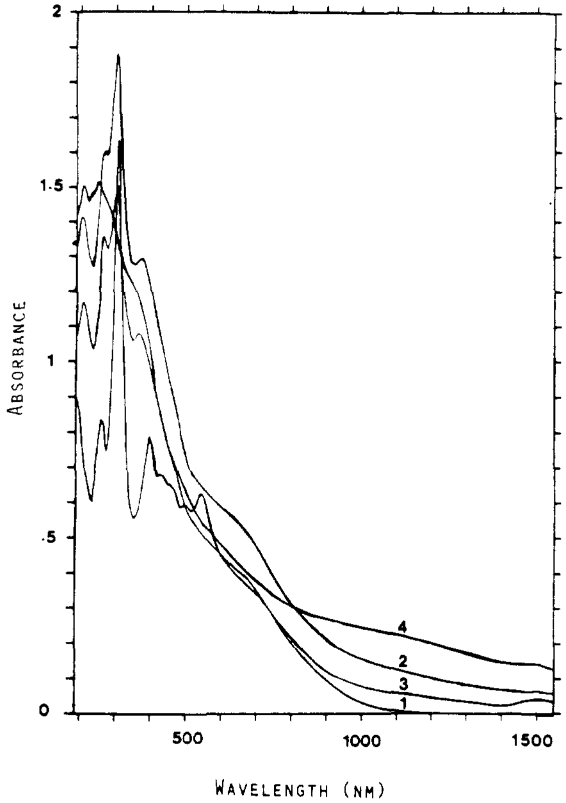


Figure 8. UV/vis spectra of PMQ1, PMQ2, PMQ3, and PMQ4: (1) from PMQ1; (2) from PMQ2; (3) from PMQ3; (4) from PMQ4.

Polycondensation Reaction. The condensation reaction (Scheme III) was carried out at various temperatures in poly(phosphoric acid) (PPA), which has been extensively used as for cyclodeamination because of its exclusive cyclizing function.[14,22,23] The final polymer is soluble in sulfuric acid if it is condensed below 385 °C. The polymer condensed at 385 °C is only about 1% soluble. The insoluble part swells in sulfuric acid. It is not certain whether cross-linking occurred or the condensed molecular chain has become too long to be dissolved. Four polymers, PMQ1 condensed at 250 °C, PMQ2 at 310 °C, PMQ3 at 345 °C, and PMQ4 at 385 °C, were investigated here. The purification of PMQ4 is the same as described in the experimental section except that the solution was filtered through a coarse instead of fine fritted glass filter after centrifuging. Table IV shows element analyses for the final polymers.

The high value of nitrogen for PMQ1 found from element analysis may indicate that rings were not completely fused; the hydrogen value found from element analysis is also high, suggesting that some rings were closed but may not have been oxidized. This is confirmed by the UV/vis spectrum (see below) which shows the presence of many three and five fused ring moieties. Any finite ring structure has one extra amine group per ring. Therefore, $(^1/_6)[3\text{-}(C_8H_5N + C_8H_7N) + NH_3]\cdot 0.035HPO_3\cdot 0.13H_2SO_4\cdot 0.8H_2O$ was used to fit the found values. This means that on average only 50% of the closed rings were oxidized and one ring in every six repeat units was still open. However, the nitrogen values found for PMQ2, PMQ3, and PMQ4 are lower than that expected for C_8H_5N. It is very difficult to get the correct analysis of nitrogen in polynuclear heterocyclic structures. Nitrogen may also be lost from the polymer, but the WAXD patterns (vide infra) and solubility make this unlikely.

PMQ2 elemental analyses, done in duplicate, add up to 101.4% including ash, even with the low nitrogen analysis. After discussion with Galbraith Laboratories, PMQ2 was carefully reanalyzed. Anal. Found, calcd: C (58.55, 58.32), H (5.28, 5.21), N (9.87, 9.95), P (0.85, 0.83), S (4.85, 4.86%), O (18.82, 19.12), ash (1.32, 1.41). These add up to about 100%. There is almost no correspondence between these values and those in Table IV. The C/N ratio here is 8/1.16. Thus, the best that element analyses can say is that the proposed structure is possible. Inaccuracies in analysis due to adsorption of H_2O and NH_3 on high internal surface area and intractability of the material make quantitative agreement impossible. The presence of sulfur even after extensive washing implies that some sulfate or bisulfate salts are present. These could be associated with 1,4-dihydroquinolino groups.

UV/Vis Spectra of PMQ. The UV/vis spectra of the PMQ polymers are given in Figure 8. The absorptions near 260 and 397 nm are due to the E_1 band and the E_2 band of three condensed rings, respectively. The other two bands at 306 and 544 nm are characteristic of absorption from five condensed rings. The structureless spectrum of PMQ4 implies the presence of free electrons. After plotting the absorbance versus wavenumber and extrapolating to zero (Figure 9), the absorption threshold of PMQ1 was found at 1.0 eV, while that for PMQ2, 0.6 eV, is about the same as that of PMQ3. This also suggests that most rings must be closed and oxidized at a reaction temperature region between 250 and 310 °C. The threshold of PMQ4 decreased again to 0.3 eV, indicating further ring fusion

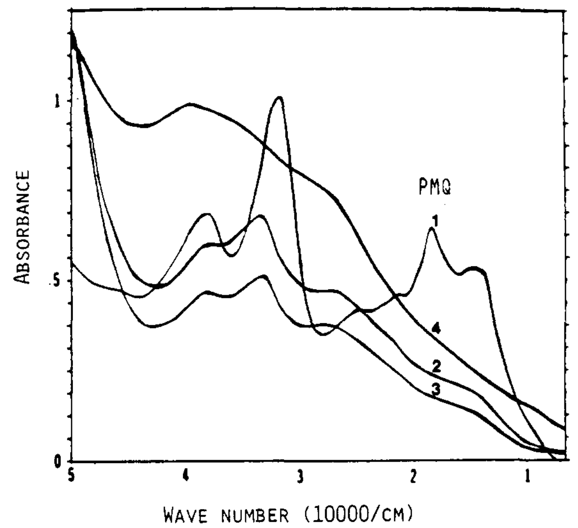


Figure 9. UV/vis spectra of PMQ1, PMQ2, PMQ3, and PMQ4: (1) from PMQ1; (2) from PMQ2; (3) from PMQ3; (4) from PMQ4.

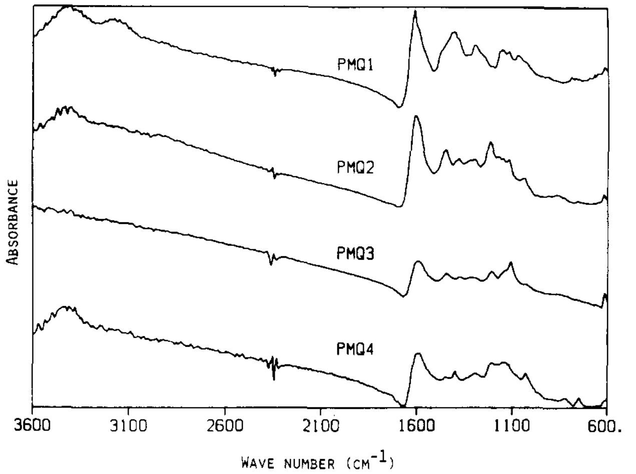


Figure 10. IR spectra of PMQ1, PMQ2, PMQ3, and PMQ4.

and/or oxidation to longer conjugated chains.

IR Spectra of PMQ. Figure 10 shows IR spectra of PMQ1, PMQ2, PMQ3, and PMQ4. The broad band near 3430 cm^{-1} is probably due to hydrogen-bonded water; even after extensive drying of the KBr pellet, water persists. No sharp peaks appear in the C—H stretching region due to scattering. The peak at 1612 for PMQ1, 1609 for PMQ2, 1595 for PMQ3, and 1594 cm^{-1} for PMQ4 is attributed partially to water and partially to aromatic C=C and C=N vibration modes. When compared with the absorption at 1630 cm^{-1} in the prepolymer, the band progressively shifts to lower wavenumbers due to the extended conjugation of the polymer.[24] The C—H bending of the methyl group and some remaining CH_2 appears at about 1450 cm^{-1} for the polymers. The band intensity decreases as condensation temperature increases, which suggests that CH_2 in unclosed or unoxidized rings at lower reaction temperatures was aromatized at the higher reaction temperatures. This is consistent with hydrogen values higher than the calculated values for the lower temperature condensed polymers (see Table IV). The peak near 1110 cm^{-1} is attributed to in-plane bending of the ring C—H. The peaks are broader as reaction temperature increases, implying more free electrons in the materials prepared at higher temperature, as is also seen in UV spectra. The peak near 1400 cm^{-1} is due to the P—O stretch from a small amount of $SiO_2 \cdot P_2O_5$ residue.

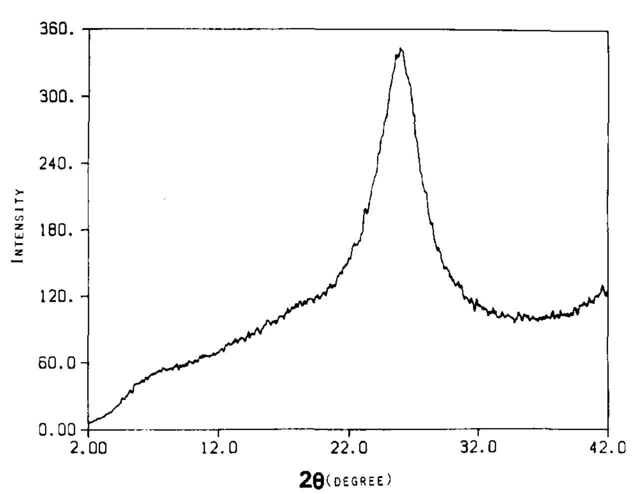


Figure 11. X-ray diffraction pattern of PMQ3.

X-ray Diffraction of PMQ. The backbone is locked into a planar configuration after condensation; the aromatic rings tend to force coplanar packing in order to favor π-interaction between segments in neighboring chains. However, the backbone is bent in the plane because the C=N bond length is shorter than that of the C=C by about 0.05 Å.[25] Therefore, while the molecules can stack well, the stacks cannot pack well side by side and the only strong diffraction that can be expected is from the layer packing. Figure 11 displays the X-ray diffraction pattern of PMQ3. The diffractions for the other three polymers show the same patterns as PMQ3; only one strong broad diffraction band at d = 3.42 Å appears. This is almost certainly from the layer diffractions. The spacing is close to the distance, 3.35 Å, between adjacent carbon planes of graphite[26] and is characteristic of the interplanar separation of aromatic molecules with planar, or nearly planar, symmetry.[27,28] The line broadening is due to the small crystallite size which can be estimated by using the Scherrer formula:[29]

$$t = 0.9\lambda/(B \cos \theta_B)$$

where

$$\theta_B = (\theta_1 + \theta_2)/2$$

where B is the half-width in terms of the diffraction angle 2θ, and $2\theta_1$ and $2\theta_2$ ($<2\theta_1$) are the angles at which the intensity is zero. The calculated stack size, t, is about 5–6 layers, 18–21 Å.

PMQ1 and PMQ2 show the same large peak at 26° of 2θ with the same half-width as PMQ3. The center of the peak gives a d-spacing of 3.44–3.45 Å, slightly larger than that of PMQ3. PMQ4 shows the effects heating to high temperature. The peak is broader toward the larger d-spacing, showing that part of the material packs poorly. However, the small d-spacing side of the peak remains exactly like that of PMQ3. Much of the material of PMQ4 packs with the same d-spacing and stack size as PMQ3.

Conclusions

A linear prepolymer, PM, can be readily obtained by reaction between 2,6-diaminotoluene and formaldehyde in acidic medium. Its molecular weight depends on the reaction temperature and time. At lower temperature (e.g., 5 °C), the polymerization takes about 1 day to reach completion. The prepolymer is soluble in DMF and DMSO and gradually crystallizes from the solution.

Condensation to an almost fully aromatic ladder polymer needs a significant period of time (e.g., 4 h) at high temperature (e.g., 385 °C). During this period, crosslinking or association could also occur. Probably, all of the rings are closed at condensation temperature in the range 310–345 °C after 4 h but are not completely aromatized. However, a large number of rings remain open if the polymer is condensed at 250 °C. The final ladder polymer is very stable toward temperature, air, acids, and base. It is soluble in strong acid if it is polycondensed below 385 °C and partly soluble when condensed at that temperature.

The regular one-dimensional packing of PMQ when precipitated from H_2SO_4 implies that it has a regular structure. If nitrogen were lost, ring closure would give five-membered rings which would change the polymer shape and inhibit stacking. Loss of nitrogen without ring closure would prevent all stacking. It seems probable then that nitrogen is not lost but that the element analysis cannot recover all of it in this refractory polyaromatic compound. We conclude that we probably have truly synthesized PMQ.

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Registry No. PMQ, 104491-01-2; $((2,6\text{-}NH_2)_2C_6H_3CH_3)(CH_2O)$ (copolymer), 112265-13-1; $((2,6\text{-}NH_2)_2C_6H_3CH_3)(CH_2O)$ (copolymer, SRU), 112265-22-2.

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Electronic Properties of Poly(1-methylcyclohexa-1,3-diene-2,3-diyl-5,6-diylidene-5-methylidyne-6-nitrilo)

J. Z. Ruan and M. H. Litt*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. Received June 27, 1986

ABSTRACT: Poly(1-methylcyclohexa-1,3-diene-2,3-diyl-5,6-diylidene-5-methylidyne-6-nitrilo) (PMQ), prepared at four different temperatures from 250 to 385 °C, was studied. There is 1 spin per 200 to 400 repeats. The temperature dependence of unpaired spin concentration for PMQ4 condensed at 385 °C implies that a phase transition from magnetic disorder to order may occur near 74 K. PMQ3 condensed at 345 °C was doped with nitrosyl hexafluorophosphate (NFP) and iodine. Iodine intercalated between the layers but hexafluorophosphate did not. EPR studies suggest that NO^+ oxidized the polymer to produce charged spinless species. There is strong coupling between iodine nuclei and the spin system. The as is conductivities at 25 °C range from about 10^{-11} S/cm for PMQ1 condensed at 250 °C to 2×10^{-5} S/cm for PMQ4 condensed at 385 °C. The conductivity of PMQ3 increases by 6 and 7 orders of magnitude upon doping with NFP and iodine, respectively, to a high of 2.4×10^{-2} S/cm at 21 °C.

Introduction

Although a large number of conducting polymers have been discovered in recent years,[1-4] the electronic structures of the doped polymers are not well understood. Perhaps the most important difference between organic and inorganic semiconductors is the influence of the lattice structure on charge transport. Polyacetylene is a typical example of the Peierls distortion in a linear chain[5,6] involving the π-electrons at half-filled band level. An additional hole or electron will be accommodated by soliton distortion[7,8] in the bond alternation of the polyacetylene chain. As a carrier or soliton moves through the polymer