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Synthesis and characterization of thermally stable polymers containing phenazine

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Abstract

The synthesis and characterization of two thermally stable polymers containing a polybenzimidazole and a ladder polymer structure are described. The tetraamino derivative of phenazine required for these syntheses was obtained by the reduction of the commercially available diamino, dinitro derivative of benzene. The polybenzimidazole polymer was synthesized by condensing tetraaminophenzine with terephthaldehyde in dimethylacetamide solvent. The resulting polymer had an intrinsic viscosity of 0.94 g/dl in methanesulfonic acid solvent. The TGA of the polymer showed it to be stable up to 470°C. The ladder polymer was prepared by reacting tetramainophenazine with dihydroquinone in polyphosphoric acid at a temperature of 146°C. The polymer formed a brittle, free-hanging film when cast from methanesulfonic acid. The molecule exhibited high degree of crystallinity and had a tendency to form dendritic-shaped structures. Doping with 15% iodine resulted in a conductivity of 9×10^{-7} mho/cm. It was thermally stable in air, showing a 10% weight loss at 410°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polybenzimidazole; Ladder polymer; Phenazine

1. Introduction

The synthesis of high molecular weight polyimides containing aromatic moieties was first reported [1,2] in 1962. These materials have been of interest industrially with applications in such areas as the hollow fibers, blends, composites, adhesives, foams, liquid crystalline materials and photosensitive materials. The synthesis of polyimides containing tricyclic heteroaromatic components has been a major area of interest at this laboratory for some time [3,4]. We have previously reported the synthesis and characterization of several polyimides in which the tricyclic diamines possessed one or two heteroatoms, nitrogen or nitrogen and sulfur. The rationale behind these studies was that the incorporation of nitrogen and sulfur atoms at the 9 and 10 positions of the tricyclic aromatic component would confer increased thermal stability and facile processability to the system. Such polyimides have not been extensively investigated although results have indicated that presence of nitrogen or sulfur at the 9 and 10 positions of the tricyclic heteroaromatic component would confer increased thermal stability and facile processability to the system. Some polyimides have been used in high temperature applications as conductive adhesives, and if the tricyclic heteroaromatic polymers could be made with sufficiently high conductivity, the need for significant amounts of doping additives could be reduced or eliminated. Since the heteroatom tricyclic monomers are known to from a complex with certain transition metals and metal ions, the present synthetic materials were considered to offer a promising entrée into this unique class of polymers.

Polymer thermal stability is enhanced by the presence of aromatic rings and is reduced by the presence of aliphatic groups. A key factor that governs the thermodynamic stability of macromolecular materials is the relationship between the melting temperature T_m, the heat of melting ΔH_m and the entropy of fusion $\Delta S_{f.}$ This relationship is given by the equation: $T_m = \Delta H_m / \Delta S_f$. Thus, an increase in intermolecular forces increases the heat of mixing, and an increase in chain stiffness lowers the entropy of fusion. By careful choice of the monomer components one can try to maximize these parameters and obtain synthetic polymers that have properties conforming to the needs of the application.

We report the synthesis and properties of two polymer systems whose properties are in part, a consequence of the above considerations.

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2. Experimental

2.1. Materials and reagents

Phosphorous pentoxide powder (J. T. Baker, reagent grade), 85% *o*-phosphoric acid (Fisher Scientific, reagent grade), and 1,3-diamino-4,6-dinitrobenzene (Polysciences, Inc.) were used as received. Terephthaldehyde (Aldrich) was recrystallized before use. 2,5-Dihydroxybenzoquinone was sublimed twice in vacuum before use.

2.2. Instrumentation

Solution NMR spectra were obtained on a Brucker 360 MHz NMR spectrometer. UV spectra were obtained with a Varian DMS 300 UV–Visible spectrophotometer. Infrared spectra were obtained on a Nicolet 5-DX spectrometer. Mass spectra and elemental analyses were provided by the analytical services laboratory of the chemistry department at the University of Michigan. Viscometric measurements were performed at a constant temperature of 25 ± 0.5°C using Ubbelhode viscometers with solvent efflux times greater than 100 s. DSC studies were carried out using a Perkin–Elmer-7 series differential scanning calorimeter. TGA analysis was carried out using a Shimadzu Thermogravimetric analyzer TGA-50 in air, at a heating rate of 20°C to 40°C/min.

Optical microscopic studies were performed with an Olympus BH-2 UMA instrument with Mettler FP-80, 82 hot stage. Electron microscopy was accomplished with a JEOL 4000EX that was operated at 400 kV. X-ray diffraction experiments were carried out using a Rigaku rotaflex X-ray diffraction instrument. Electron paramagnetic resonance spectra were obtained with a Century line (X-band) EPR spectrophotometer. Conductivity measurements of the polymer were performed using a two-probe method, and the resistance was measured with a Keethley multimeter. Computer simulations were carried out using the Polygraf software program.

2.3. Synthesis

2.3.1. Synthesis of 2,3,6,7-tetraaminophenazine [5–10]

2.3.1.1. Synthesis of 1,2,4,5-tetraaminobenzene tetrahydrochloride. In a three-neck flask equipped with a reflux condenser was placed 0.465 g (2.35 mmol) of 1,3-diamino-4,6-dinitrobenzene and 1.547 g (23.67 mmol) of zinc powder. A solution of 20% hydrochloric acid (8.6 ml) was then added drop wise. The mixture was heated under reflux at 100°C for 1 h. The reaction mixture was then cooled to room temperature, and was saturated with gaseous hydrochloric acid. A very fine, pink-colored precipitate was obtained which was filtered and dried in vacuum oven for 24 h to give 0.307 g (46%) of the required product.

2.3.1.2. Synthesis of 2,3,6,7-tetraaminophenazine hydrochloride. In a three-neck flask fitted with a reflux condenser were placed 0.107 g (0.189 mmol) of 1,2,4,5-tetraaminobenzene tetrahydrochloride, 0.215 g (2.62 mmol, i.e. 1:14) of anhydrous sodium acetate and 5 ml of distilled water were added. Compressed air was then bubbled through the refluxing solution for 5 h. The dark brownish black precipitate obtained on cooling was collected and dried in a vacuum oven at room temperature for two days to give the product in quantitative yield.

^{1} NMR spectrum: solvent DMSO-d_6; 5.47 (8H, amine protons), and 6.78 (4H, aromatic protons).

^{13}C NMR spectrum: 104.25 (C–NH_2); 138.31 (aromatic carbon); 140.19 (aromatic bridge head carbon).

Elemental analysis for 2TAP.3HCl

Expected: %C 48.87; %H 4.61; %N 28.49;
Obtained: %C 50.50; %H 4.98; %N 28.05.

2.3.2. 2,3,6,7-Tetraaminophenazine from 1,2,4,5-tetraaminobenzene

2.3.2.1. Synthesis of 1,2,4,5-tetraaminobenzene from 1,2,4,5-tetraaminobenzene tetrahydrochloride. A solution of 1 g (3.52 mmol) of 1,2,4,5-tetraaminobenzene tetrahyrochloride was prepared in 8 ml of boiling, oxygen free, distilled water. This hydrochloride solution was added drop wise to an ice cold 15% sodium hydroxide solution with stirring. Nitrogen was continuously passed through the sodium hydroxide solution. A shiny, yellow precipitate obtained was filtered under nitrogen, washed with cold methanol and then dried in a vacuum oven to get 0.45 g of tetraaminobenzene. Yield—93%. M.P. 273–274°C

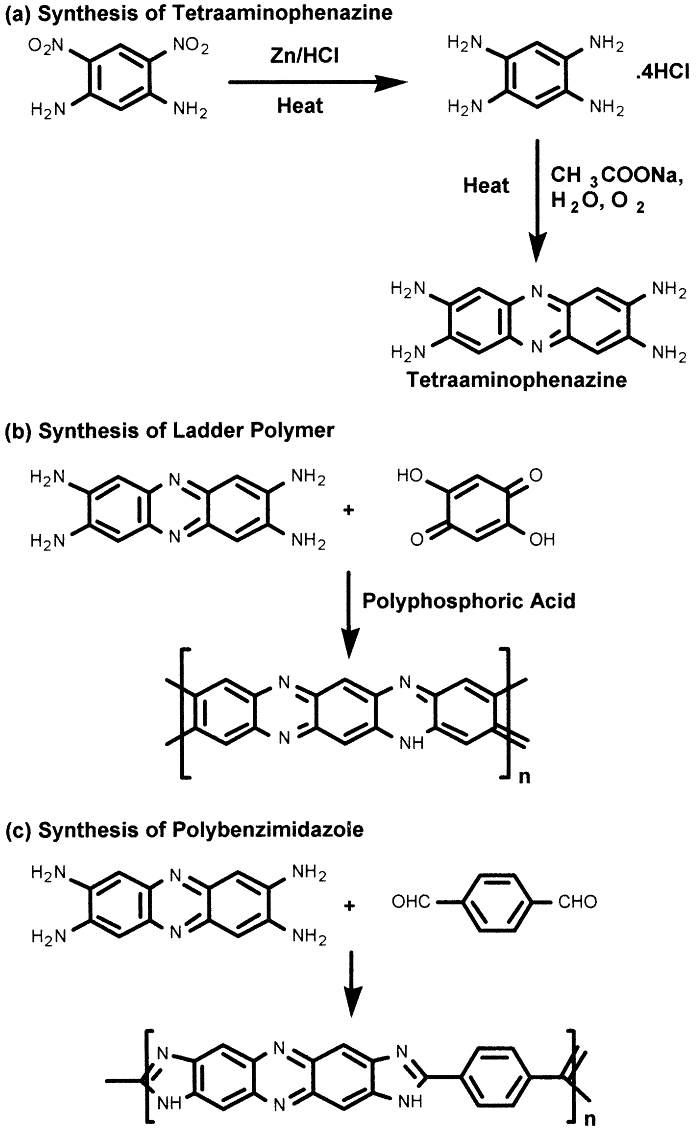
2.3.2.2. Synthesis of 2,3,7,8-tetraaminophenazine from 1,2,4,5-tetraaminobenzene. The reaction was carried out as previously described [9,10] to obtain the required material in the quantitative yield.

2.3.3. Model compound synthesis from tetraaminophenazine and benzaldehyde

Tetraaminophenazine, 0.4728 mmol, was dissolved in 4 ml of dry dimethylacetamide and then 1 ml of pyridine was added to the solution. Benzaldehyde, 0.1004 mmol, was mixed separately with 10 ml of dry dimethylacetamide. Both solutions were purged with dry nitrogen for 10 min. The benzaldehyde solution was then added drop wise over a period of 3 h to the amine solution under a nitrogen atmosphere. The solution was stirred at room temperature for 33 h. The reaction product was precipitated in 150 ml of ethyl acetate, filtered and dried at room temperature in a vacuum oven to get the required dark brown product in quantitative yield. Melting point >350°C. Mass spectroscopy—electron impact 412.

2.3.4. Polybenzimidazole from tetraaminophenazine and terephthaldehyde

Tetraaminophenazine, 0.464 mmol, was dissolved in



Scheme 1.

4 ml of nitrogen-saturated, freshly distilled, dimethylacetamide. Terephthaldehyde, 0.466 mmol, was dissolved separately in 9 ml of freshly distilled dimethylacetamide. The terephthaldehyde solution was added slowly to the tetraamine solution over a period of 1 h and then 1.5 ml of pyridine was added to the solution. The solution was stirred for 10 h at 65°C and then for an additional 12 h at room temperature. The reaction product was precipitated in 150 ml of vigorously stirred methanol. The precipitate obtained was filtered and washed with 200 ml of boiling water and with methanol. The precipitate was dried for 24 h in a vacuum oven to obtain the product in 85–87% yield.

Elemental analysis (on the product precipitated from methane sulfonic acid solution)

Expected: %C 58.60, %H 3.28 and %N 19.52 (with one molecule of methane sulfonic acid per repeat unit)

Obtained: %C 57.53, %H 4.23 and %N 18.44.

Solid state ^{13}C NMR: aromatic protons—128 ppm, nitrogen ipso carbons between 140 and 150 ppm, and benzimidazole carbon 157 ppm.

Intrinsic viscosity in methane sulfonic acid—0.943.

2.3.5. Synthesis of the ladder polymer from 2,3,7,8-tetraaminophenazine

The synthesis of the ladder polymer can be carried out as shown in Scheme 1. This reaction can be carried out in one step or in multiple steps.

Synthesis based on the one-step addition of phosphorous pentoxide: to a hot polyphosphoric acid (containing 35.88% phosphorous) solution (184 g) at 120°C was added 4.175 mmol of TAP (or TAP.xHCl). After 10 min, 4.177 mmol of 2,5-dihyroxybenzoquinone was added to the above solution. The solution was heated to 180°C over 30 min and then brought back to 146°C and maintained at that temperature for 10 h. The solution temperature was again raised to 180°C and maintained at that temperature for 2 h. At the end of the reaction, the hot solution was added drop wise to 1000 ml of stirred distilled water. The solution was then filtered using a fritted glass filter and the precipitate was washed with 400 ml of 15% ammonium carbonate solution followed by 200 ml of boiling distilled water. The precipitate was dried in a vacuum oven at 60°C for 24 h to yield 103% of the product. The higher percentage yield was due to the binding of phosphoric acid onto the polymeric backbone.

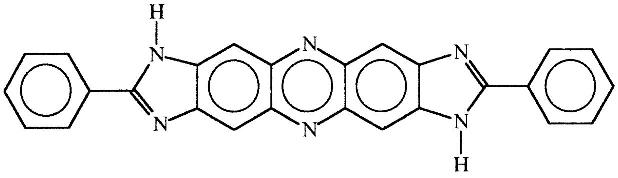
Elemental analysis

Expected: %C 53.21; %H 2.73; %N 20.68 (with one molecule of phosphoric acid per repeat unit)
Obtained: %C 54.56; %H 2.65; %N 19.20.

Synthesis of the polymer via multi-step addition of phosphorous pentoxide: The polymer was synthesized by the stepwise addition of phosphorous pentoxide to compensate for the decrease in the phosphorous content of the reaction due to the water of reaction. The reaction was started in polyphosphoric acid solution having 31% phosphorous. The solution was then made 36% in phosphorous by the addition of phosphorous pentoxide in two hours. After 7 h of reaction, an additional 1 g of phosphorous pentoxide was added to compensate for any water of reaction. The product was treated as described earlier to obtain the product in 103% yield.

3. Results and discussion

The reactivity of 2,3,6,7-tetraaminophenazine with an aldehyde was probed by the reaction of benzaldehyde with the tetraaminophenazine. The product of the reaction had an atomic mass of 412 Da that corresponds to the expected benzimidazole shown in the following structure.



This result then allowed the next reaction sequence in which 2,3,6,7-tetraaminophenzaine and terephthaldehyde were condensed. The products of this and similar reactions yielded compounds that gave poor infrared spectra from 400 to 4000 cm^{-1} irrespective of the method of measurements. These compounds either absorbed most of the radiation or scattered the radiation resulting in weak and poorly resolved intensities. Equally poor ^{1}H NMR spectra were obtained on the polymer solutions due to overlapping and unresolved peaks and poor solubility. The solid state ^{13}C NMR spectrum of the polymer showed a band at 157 ppm that is assigned to the benzimidazole carbon atom. The band assigned to the nitrogen ipso carbon atoms appeared between 140 and 150 ppm, and the remaining aromatic protons were present in the band at 128 ppm.

The solubility of the polymers was limited to solvents that are strong acids such as methanesulfonic acid and sulfuric acid. Solutions of the polymer in methanesulfonic acid could be used to cast strong films.

Thermogravimetric analyses of the polymer in air indicated that polymer decomposition commences at 305°C and results in a 10% weight loss when the temperature rises to 470°C. Degradation proceeds in a stepwise manner with the maximum rate occurring at 630°C. Polymer decomposes completely by 710°C leaving no residue at 850°C.

Synthesis of the ladder polymer was achieved by condensing 2,3,6,7-tetraaminophenzaine with 2,5-dihydroxybenzoquinone in polyphosphoric acid at 180°C and 140°C for selected time intervals. The ladder polymer obtained by this technique differs from the previously reported ladder polymers [6–30] in the expected structure of the repeat unit. The previously reported similar ladder polymers were synthesized from tetraaminobenzene unlike tetraaminophenazine. The condensation reaction is facilitated by the removal of the water formed by the polyphosphoric acid. The polyphosphoric acid maintains the homogeneous solution of reactants and products and provides for in situ doping of the ladder polymer. The resulting polymer upon precipitation always contains one molecule of phosphoric acid per repeat unit.

Solubility of the polymer in common organic solvents with or without lithium chloride is very low. The most effective solvents are strong acids such as methanesulfonic acid and sulfuric acid. The proton NMR spectrum of the polymer in deuterated sulfuric acid containing tetramethylsilane as an external reference exhibited only four weak singlet bands between 2.3 and 5.4 and a broad band at 2.7 ppm. These band positions are ascribed to aliphatic protons rather than aromatic resonances although abnormally high chemical shifts have been reported for some paramagnetic compounds.

The esr spectrum showed the presence of unpaired electrons and an absence of hyperfine splittings. We interpret this as being indicative of electron delocalization in a completely conjugated aromatic ladder polymer. The unusual band positions observed in the solution proton NMR spectrum is attributed to the electron delocalization and the presence of a significant number of free radical centers.

A powder polymer sample gave a poor infrared spectrum with weak bands. Either this polymer system absorbs most of the infrared radiation or it scatters a significant component of the incident beam. It was possible to confirm the presence of the bound phosphoric acid to the polymer.

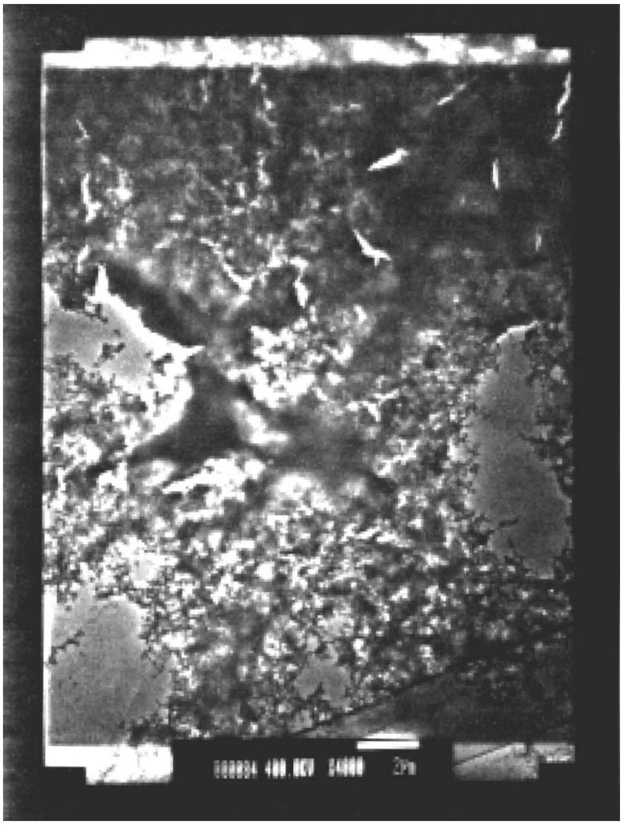


Fig. 1. Electron micrograph of the precipitated ladder polymer on a copper grid.

Electron micrographs were obtained on polymer films prepared by the precipitation of a 0.15% (w/w) methanesulfonic acid solution of the polymer. The solution was precipitated in film form in water and collected on carbon covered copper grids. Electron micrographs exhibited structures of the polymer network as shown in Fig. 1.

Wide angle X-ray diffraction was obtained on polymer films prepared as described. These films showed sharp rings in addition to an amorphous halo. Upon annealing the films at 200°C for 2 h the ring pattern intensified indicative of increased crystallinity.

A similar film formed on a glass slide by evaporating the solvent in a vacuum oven at 60°C for 24 h exhibited the dendritic-shaped crystal as shown in Fig. 2.

DSC experiments carried out with the polymer kept under nitrogen revealed that the polymer was stable up to approximately 350°C. There appeared to be a transition at approximately 150°C, that we ascribe to some modification of the chain mobility. Support for this view was present in the electron micrographs of the annealed sample. It would appear that complete cyclization does not occur under the reaction conditions. The TGA analysis revealed that a 10% weight loss occurred at 410°C with complete decomposition occurring at 790°C with a heating rate of 20°C/min in air. A char residue of 6.5% is present at 850°C. Polymer decomposition appears to progress via two competitive steps.

Conductivities of the undoped and doped polymer were carried out on the polymer powder using the two-probe method. The undoped sample had a conductivity of 1.5×10^{-8} mho/cm. However, although the sample was not doped with iodine, it did contain one molecule of phosphoric acid per monomer repeat unit. When this polymer was doped

Fig. 2. Optical micrograph of a film of the ladder oligomer showing the dendritic crystal structure.

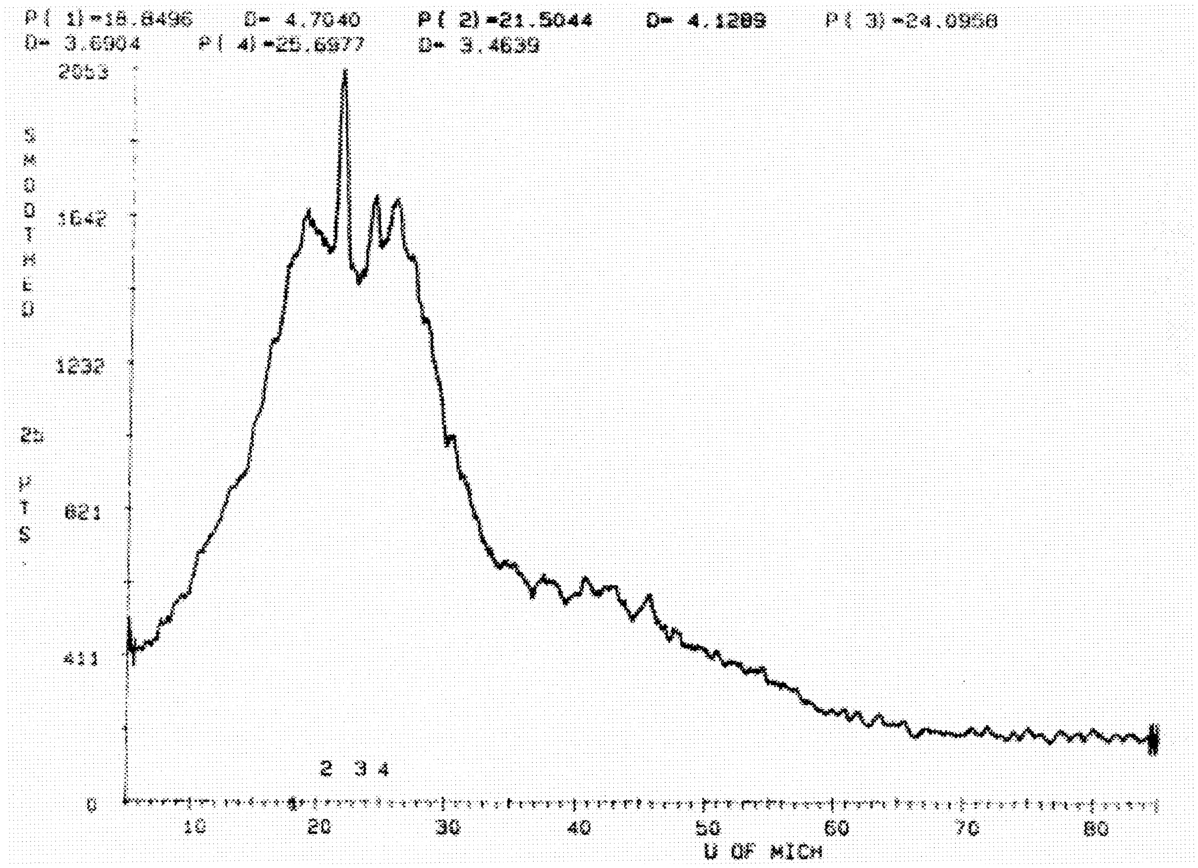


Fig. 3. WAXD of the ladder oligomer.

with 15% iodine the conductivity increased to 9 × 10^{-7} mho/cm, a conductivity increase of 60 fold. This small increase in conductivity on doping is in line with other heterocyclic ladder polymers [25].

The X-ray diffraction of the polymer powder is given in Fig. 3. The diffraction pattern is indicative of the presence of a significant crystallinity content. The polymer molecules appear to stack one above the other as the overlapping regions correspond to a spacing of some 3 to 5 Å. A computer model simulation yielded intermolecular distances of 3.58–3.59 Å. These results also provide support for the stacking of the ladder polymer in analogy with the stacking of tetraaminophenazine.

4. Conclusion

The condensation of 2,3,6,7-tetraaminophenzine with terephthaldehyde yielded a polybenzimidazole polymer with good thermal stability and semi-conductive properties. Condensation of 2,3,6,7-tetraaminophenzine with 2,5-dihydroxybenzoquinone at elevated temperatures yielded a ladder polymer with enhanced thermal stability and good semi-conductor properties when doped with iodine. These reactions demonstrate that the incorporation of the aromatic tricyclic ring system into polybenzimidazoles and ladder polymers yields materials of enhanced thermal stability and interesting semi-conductive properties. The enhanced thermal stability is attributed to the substantial crystallinity of the polymer as revealed by wide angle X-ray diffraction. Although these polymers are not readily soluble in organic solvents they can be dissolved in strong acids and those solutions can be used to cast films and other useable forms of the polymers.

References

[1] Endrey AL. Canadian Patent 645,073 to E. I. DuPont and Co., 1962.
[2] Endrey AL. Canadian Patent 659,328 to E. I. DuPont and Co., 1963.
[3] Gajiwala HM, Zand R. Macromolecules 1993;26(22):5976–83.
[4] Gajiwala HM, Zand R. Macromolecules 1995;28:481–5.
[5] Nietzki E, Muller A. Berichte 1889;22:440.
[6] Hedberg FL, Arnold FE. J Polym Sci, Polym Chem Ed 1974;12:1925.
[7] Sicree AJ, Arnold FE, Van Deusen RL. J Polym Sci, Polym Chem Ed 1974;12:265.
[8] Vogel HA, Marvel CS. J Polym Sci 1961;50:511.
[9] Nietzki R, Schadler A. Berichte 1897;30:1666.
[10] Stille JK, Mainen EL. Macromolecules 1968;1:36.
[11] Van Deusen RL. J Polym Sci, Polym Lett 1966;B14:211.
[12] Arnold FE, Van Deusen RL. Macromolecules 1969;2:497.
[13] Arnold FE, Van Deusen RL. J Appl Polym Sci 1971;15:2035.
[14] Arnold FE. J Polym Sci, Part A-1 1970;8:2079.
[15] Bailey WJ. Encyclopedia of polymer science and technology, vol. 8. New York: Wiley, 1997.

[16] Stille JK, Mainen EL. J Polym Sci, Polym Lett Ed 1966;4:39.
[17] Stille JK, Mainen EL. J Polym Sci, Polym Lett Ed 1966;4:665.
[18] Stille JK, Freeburger ME. J Polym Sci, Polym Lett Ed 1967;5:989.
[19] Kim OK. J Polym Sci, Polym Lett Ed 1985;23:137.
[20] Imai K, Kurihara M, Matias L, Wittman J, Alston WB, Stille JK. Macromolecules 1973;6:158.
[21] De Scheryver F, Marvel CS. J Polym Sci, Part A-1 1967;5:545.
[22] Kellman R, Marvel CS. J Polym Sci, Polym Chem Ed 1975;13:2125.
[23] Lee BH, Marvel CS. J Polym Sci, Polym Chem Ed 1983;21:83.
[24] Jenekhe SA. Macromolecules 1991;24(1):1.
[25] Hong SY, Kertesz M, Lee Y, Kim O-K. Chem Mater 1992;4:378.
[26] Hong SY, Kertesz M, Lee Y, Kim O-K. Macromolecules 1992;25:5424.
[27] Dalton LR, Thomson J, Nalwa HS. Polymer 1987;28:543.
[28] Cassidy PE. Thermally stable polymers: synthesis and properties, New York: Marvel Dekker, 1980.
[29] Critchley JP, Knight GJ, Wright WW. Heat resistant polymers—technologically useful materials, New York: Plenum Press, 1983.
[30] Luise RR, editor. Applications of high temperature polymers Boca Raton, FL: CRC Press, 1997.