is considerably less efficient than the Py*–TEA pair as a photoinitiator system. This lack of photoinitiation could be explained in terms of the inefficiency of processes 6 and/or 7. In agreement with this, the data given in Figure 4 show that An photobleaching is considerably less sensitive to MMA addition than Py photobleaching.

Acknowledgment. We are grateful to FONDECYT (Grant 1429/86) and DICYT (Universidad de Santiago de Chile) for financial support of this work.

Registry No. Py, 123-00-0; TEA, 121-44-8; MMA, 80-62-6.

References and Notes

(1) Ledwith, A. *Pure Appl. Chem.* **1977**, *49*, 431.
(2) Hageman, A. J. *Prog. Org. Coat.* **1985**, *13*, 123.
(3) Amirzadeh, G.; Schnabel, W. *Makromol. Chem.* **1981**, *182*, 2821.
(4) Williams, J. L. R.; Specht, D. P.; Farid, S. *Polym. Eng. Sci.* **1983**, *23*, 1022.
(5) Allen, N. S.; Catalina, F.; Green, P. N.; Green, W. A. *Eur. Polym. J.* **1983**, *22*, 49.
(6) Encinas, M. V.; Garrido, J.; Lissi, E. A. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(7) Sengupta, P. K.; Modak, S. K. *J. Macromol. Sci., Chem.* **1983**, *A20*, 789.
(8) Schnabel, W. *J. Radiat. Cur.* **1986**, *13*, 26.
(9) Capek, I.; Barton, J. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 327. Barton, J.; Capek, I.; Hrdloviv, P. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2671.
(10) Kubota, H.; Ogiwara, Y. *J. Appl. Polym. Sci.* **1985**, *28*, 2425.
(11) Lissi, E. A.; Zanocco, A. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2197.
(12) Cohn-Ginsberg, E.; Fox, T. G.; Mason, H. F. *Polymer* **1962**, *3*, 97.
(13) Encinas, M. V.; Rubio, M. A.; Lissi, E. A. *J. Photochem.* **1982**, *3*, 97.
(14) Niki, E.; Kamiya, Y. *J. Am. Chem. Soc.* **1974**, *96*, 2129.
(15) Encinas, M. V.; Guzman, E.; Lissi, E. A. *J. Phys. Chem.* **1983**, *87*, 4770.
(16) Lissi, E. A.; Encinas, M. V.; Abarca, M. T. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 19.
(17) Cohen, S.; Parola, A.; Parsons, G. *Chem. Rev.* **1973**, *73*, 141.
(18) Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1973**, *95*, 5783.
(19) Okada, T.; Tashita, N.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3398.
(20) Okada, T.; Tashita, N.; Mataga, N. *Chem. Phys. Lett.* **1980**, *75*, 220.
(21) Okada, T.; Karaki, I.; Mataga, N. *J. Am. Chem. Soc.* **1982**, *104*, 7191.
(22) Weller, A. *Z. Phys. Chem.* (*Neue Folge*) **1982**, *130*, 129.
(23) Kuzmin, M. G.; Sadovskii, N. A.; Sobolera, I. B. *Chem. Phys. Lett.* **1980**, *71*, 232.

A New Electron-Rich Network Polymer: Poly(1,3,5-triaminobenzene)

I. Johannsen,[†] J. B. Torrance,* and A. Nazzal

IBM Research Division, Almaden Research Laboratory, San Jose, California 95120-6099.
Received November 9, 1987

ABSTRACT: In the presence of acid, 1,3,5-triaminobenzene (TAB) polymerizes under mild conditions to form a new network polymer. The mechanism of this unusual, simple polymerization reaction is discussed on the basis of model reactions and the unusual ring protonation of TAB in mild acids. As an example of a model reaction, TAB is reacted with aniline in acetic acid to form 1,3,5-trianilinobenzene. Poly-TAB is a new electron-rich polymer, of special interest as a potential organic ferromagnet or a conducting polymer.

Introduction

In the field of conducting organic solids, polymers have played a critical role.[1] Examples of such polymers include polyacetylene, polypyrrole, polyphenylene, and polyaniline. In the virgin field of ferromagnetic organic solids, polymers are expected to be correspondingly important. The major theories for ferromagnetic interactions in organic solids include orbital degeneracy as the key element.[2–7] In one approach, these degenerate orbitals are nonbonding orbitals.[3,4] Recent work[8] on isolated oligomers of phenylcarbenes has shown ferromagnetic interactions between eight neighboring unpaired spins. In addition, a preliminary Russian report[9] of a ferromagnetic polymer is presumed to involve such types of orbitals. The second approach[2,5–7] involves orbitals whose degeneracy orginates because of high molecular symmetry. Recent work following this approach has involved crystalline charge-transfer salts,[5,10,11] as well as a polymer made from 1,3,5-triaminobenzene, which has been reported[6,12] to be ferromagnetic. These latter two ferromagnetic polymers[6,9] are obtained in extremely poor yield and are very poorly understood in terms of their structure, chemistry, and mechanism of polymerization. For these reasons, there are major problems in reproducibly preparing these organic ferromagnetic materials. More work is clearly necessary to understand these polymers.

In this paper, we report a study of a polymer based on 1,3,5-triaminobenzene (TAB). The initial reports[6,12] described a mterial obtained from a reaction of TAB with iodine in acetic acid and other solvents at room temperature. Chemical analysis of the resulting solids showed a loss of nitrogen and hydrogen. It was speculated that the polymer in Figure 1 (poly-TAB) was produced and was responsible for the ferromagnetic behavior which was found on rare occasions. Note that, in Figure 1, the local structure of these polymeric subunits has the high (three-fold) molecular symmetry necessary to give orbital degeneracy, as required by the appropriate model[6] for organic ferromagnetism. However, if the polymer synthesized from TAB was indeed poly-TAB, its synthesis would have involved a rather unusual reaction: room temperature condensation of two arylamines to form a diarylamine. Although such reactions are known, they normally require very harsh conditions. For instance, aniline can be converted[13] into diphenylamine in moderate yield by heating it with phosphoric acid and zinc chloride for 10 h at 250–270 °C. Previous studies of TAB have focused on the way in which this molecule is protonated (Figure 2): it has been shown[14–16] that the first protonation of TAB occurs not on the amino group but on the ring

---

[†] Permanent address: Chemistry Lab II, H. C. Oersted Institute, University of Copenhagen, Copenhagen, Denmark.

0024-9297/89/2222-0566$01.50/0 © 1989 American Chemical Society

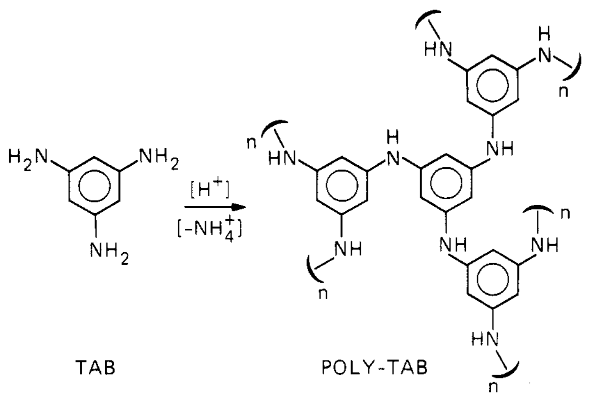

Figure 1. Structure of poly(1,3,5-triaminobenzene) (poly-TAB) and the polymerization reaction reported here.

carbon (IIa,b). This results in a breakdown of aromaticity, as seen by the appearance of a yellow color (λ_{max} (HOAc) 365, 272 nm). This ring protonation is favored because the positive charge can be stabilized by delocalization over the three amino groups in II. Subsequent protonation, on the other hand, places the protons on the amino groups, restoring aromaticity. We recognized that a further conseqence of this is that the reactivity of TAB would be very dependent on the acid strength used in the condensation. The $=NH_2^+$ group in the monoprotonated TAB (II) would be now vulnerable to nucleophilic attack (III) by another amine, potentially leading to the desired condensation (V, VI). Reports on this type of nucleophilic attack on iminium ions are rare, but it has been mentioned as an intermediate step in the reaction of imido esters with amines,[17] in the oxidative deamination of benzylamines,[18] and in reactions between methyleneiminium ions and amines.[19] It was difficult to see how iodine could promote this rather unusual condensation and therefore it was assumed that iodine mainly played a role in oxidizing the formed polymer, and we concentrated on studying the polymerization reaction in the absence of iodine.

Results and Discussion

Dissolving TAB in acetic acid gives a clear yellow solution, indicating the presence of appreciable amounts of monoprotonated TAB. As discussed above, this mixture should be prone to self-condensation between iminium and amino groups on neighboring molecules. In order to test this conjecture, we heated TAB in acetic acid to 40–60 °C under an inert atmosphere. After several hours, a yellow/orange precipitate was formed. This partially protonated polymer could be neutralized with triethylamine or by simply washing with acetonitrile, giving an almost colorless product, which was insoluble in common solvents. Elemental analysis of this polymer indicated loss of nitrogen and hydrogen corresponding to net elimination of 1.3 NH_3 units per benzene ring during the polymerization.

In order to obtain more information about the mechanism of this polymerization reaction and about the structure of the resulting polymer, a number of model reactions were studied. For example, TAB was reacted with a large excess of aniline in acetic acid. Apart from small amounts of acetanilide, the only product that could be isolated was 1,3,5-trianilinobenzene. The yield based on triaminobenzene was almost quantitative, showing that the reaction with aniline under these conditions was faster than the polymerization. The fact that only the symmetrical trianilinobenzene was formed suggested that the substitution reaction took place only at the amino-substituted carbons of TAB. In order to prove this point, TAB was reacted with 1 equiv of *p*-methoxyaniline in the presence of about 2 equiv of acetic acid. The major product from this reaction was (4-methoxyphenyl)(3,5-diaminophenyl)amine as identified by means of combined mass, 1 H NMR, and ^{13}C NMR spectroscopies. Under similarly mild conditions, mono- or diaminobenzenes appear not to undergo similar reactions.[13,20]

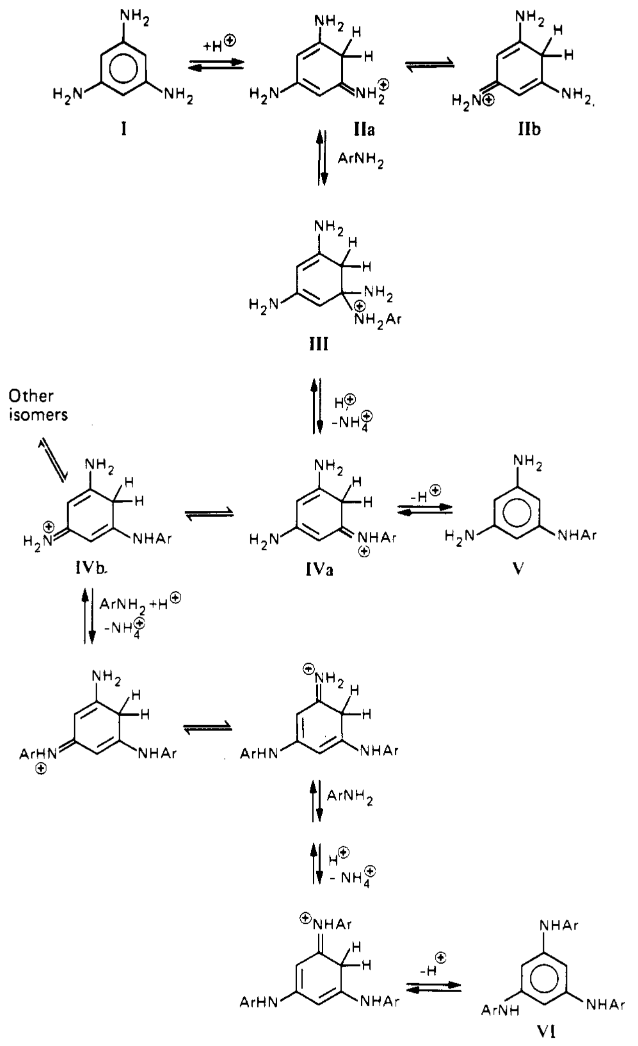

Figure 2. Mechanism of protonation of TAB and the simple condensation reaction responsible for model reactions and synthesis of poly-TAB.

On the basis of the results given above, a reaction mechanism outlined in Figure 2 is suggested. The first step is a protonation of the TAB (I) to give a ring-protonated, nonaromatic intermediate (II). In the next step, the monoprotonated TAB is attacked nucleophilically by an arylamine to form the addition product (III), which in acetic acid eliminates ammonium ions to give IV. IV is already set up for the next nucleophilic attack by a second arylamine, etc., until the trianilinobenzene (VI, Ar = benzene) or the network polymer poly-TAB (Figure 1) is formed. The attack may occur either at the α-position as shown in the figure (1,2-addition) or at the next amine-bearing carbon, corresponding to a 1,4-addition. The resulting products after elimination are, however, undistinguishable.

This mechanism can account for several other observations. For example, the reaction depends strongly on the acid strength of the acid used: without acid, no reeaction would be expected and indeed heating TAB either neat or in acetonitrile does not produce any polymer. Also, if excess of a strong acid is used, di- and eventually triprotonated TAB is formed. In these cases, TAB is protonated[14-16] on the amino groups (not on the ring carbons).

Thus, the aromaticity is maintained and the reactivity of these molecules is drastically changed (compared with the monoprotonated TAB). If TAB is dissolved in the slightly stronger acid, formic acid, a colorless solution is formed, indicating di- or triprotonation. Heating this solution does not give a polymer. Thus, the acid strength of acetic acid apparently perfectly matches the basicity of TAB, giving mainly monoprotonated TAB in equilibrium with neutral TAB, as seen in the UV–vis spectrum which is dominated by the yellow color of the monoprotonated species.[14,15]

These reactions can also be run by using the reagent TABH$^+$BF$_4^-$, in which TAB is protonated once on the ring carbon using 1 equiv of tetrafluoroboric acid. Heating this salt alone in acetonitrile gives no polymer, in accordance with the lowered nucleophilicity of TAB upon protonation and suggesting that some unprotonated TAB is necessary for the polymerization. Heating a neat mixture of the monoacid (HBF$_4$) salt of TAB and TAB itself results in the formation of poly-TAB (indicating that the acetate ion itself is not critical). The polymer can also be synthesized by heating TAB in 3–6 equiv of acetic acid, in which case colorless crystals identified as ammonium acetate sublime from the reaction mixture.

The unusual condensation reaction described above is associated with the unusual feature of 1,3,5-triaminobenzene (TAB): that protonation occurs initially on the ring carbon. The subsequent nucleophilic attack resembles the addition of common nucleophiles to ketones or iminium ions.[17–19,21]

Note further that the ammonia (pK_b = 4.8) eliminated in the reaction is a stronger base than[22] TAB (pK_b = 8.5) and hence will remove a proton from the reaction. This fact explains why the reaction cannot be performed with only catalytic amounts of acid.

The polymerization reaction was also carried out in refluxing acetic acid, with precipitate forming after a few minutes. At 25 °C, the reaction took about 48 h before any polymer could be seen. These reaction times give a very crude estimate of the activation energy of 75 kJ/mol.

Properties of Poly-TAB

The light tan product is completely insoluble in the usual laboratory solvents, including concentrated sulfuric acid. It gave an X-ray powder diffraction spectrum with no evidence of crystallinity. We conclude that this solid is indeed an amorphous polymer. Scanning electron micrographs (Figure 3a,b) show that when synthesized in less than about 24 h, the polymer is in the form of quasi-spherical particles of diameter 1–10 μm. When the polymerization reaction occurred very slowly (at 25 °C in acetic acid or at 50 °C diluted with acetonitrile) the precipitation of the polymer occurred mainly on the glass surfaces, giving rise to rather dense films (Figure 3c,d). In both cases, the highest magnification shows typical cauliflower-like structure on the surfaces, with a porosity of the polymer apparently less than about 100 Å.

Information about some aspects of this polymer and the polymerization process can be inferred from the elemental analysis. For the yellow/orange polymer, when washed with acetic acid, we assume that the percentage unaccounted for after C, H, N is all due to the oxygen from the acetic acid remaining in the protonated (yellow/orange) polymer. Extreme care was taken not to expose the polymer to other oxygen sources (air, humidity, etc.) prior to analysis, and the analysis showed no residual ash. On the basis of the above analysis, we find a molecular formula of $C_6H_{5.1}N_{1.7}(CH_3COOH)_{0.43}$, suggesting that the polymer is approximately half-protonated. Upon washing with acetonitrile or triethylamine and acetonitrile the polymer becomes tan (unprotonated). Drying the polymer in vacuum for several days results in a material whose analysis gives a molecular formula of $C_6H_{5,1}N_{1,7}(CH_3COOH)_{0,13}$. Even after prolonged washing with acetonitrile/triethylamine the polymer retained some acetic acid probably due to entrapment in the polymer matrix. More vigorous treatment of the polymer in order to remove the last traces of acetic acid was not undertaken because of high air sensitivity of the polymer necessitating handling in a high-purity glovebox. These analysis indicate an average loss of 1.3 NH$_3$ per ring.[23] Note that there are two simple compositions which we can compare with this result. If the polymer grew as a linear chain (with one amino group per ring remaining unreacted) or if the polymer grew by reacting only with unreacted TAB in solution, there would be a large number of unreacted amino groups and the composition would be $C_6H_6N_2$. On the other hand, if the amino groups of the polymer as it grew reacted with others on the same polymer one would obtain an extremely cross-linked polymer, with few free amino groups. In the limit of no free amino groups, the composition would be $C_6H_{4.5}N_{1.5}$. The measured analysis of $C_6H_{5.1}N_{1.7}$ indicates that the real polymer lies in between these extreme cases, with extensive internal cross-linking and numerous free amino groups.

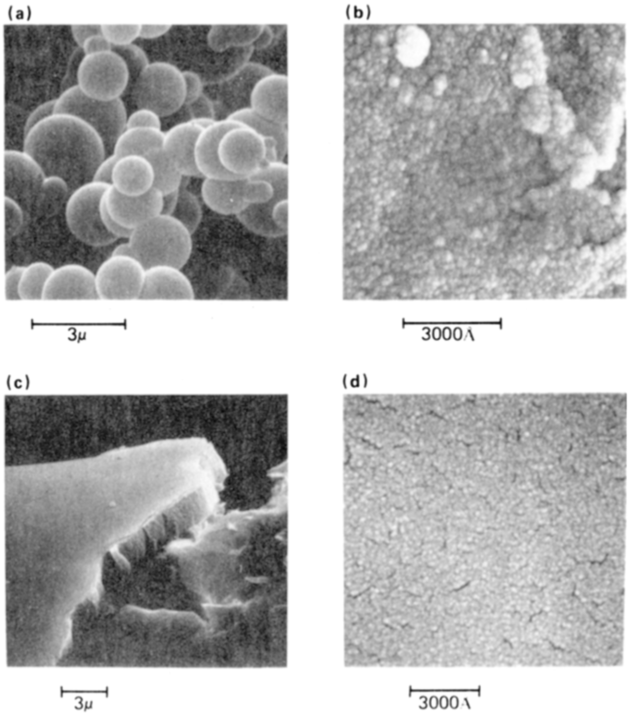

Figure 3. SEM micrographs of samples of poly-TAB: (a, b) samples grown in less than 24 h; (c, d) typical of films obtained when polymer is grown more than 24 h.

Some information of the molecular structure of the polymer can also be inferred from the chemical behavior of the polymer. The fact that the polymer can be reversibly cycled between the protonated (yellow/orange) state and the neutral (tan) state strongly suggests symmetrical triaminobenzene-like subunits, since the yellow-orange color is characteristic of ring protonation on such species.[14,15] The fact that these polymers turn dark in color over a period of hours when exposed to air is an indication of the ease of oxidation of the poly-TAB polymer (as with other aromatic amines).

The cross-polarization magic angle spinning ^{13}C NMR spectrum of solid poly-TAB is shown in Figure 4. This particular sample contained approximately 0.2 acetic acid molecules per ring and it can therefore be assumed that

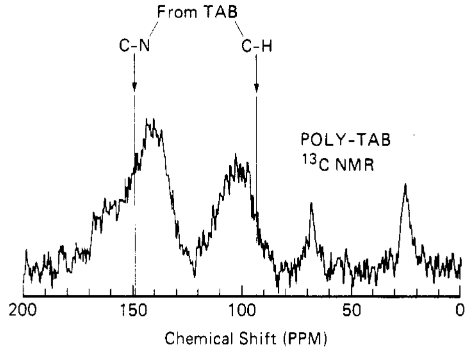

Figure 4. ^{13}C NMR spectrum (CP-MAS) of poly-TAB. Arrows indicate corresponding C–N and C–H peaks in TAB itself.

approximately every fifth ring is protonated. The major features consists of two broad but well-separated lines at approximately 150 and 100 ppm. The chemical shifts of C–N and C–H in triaminobenzene itself are indicated by the arrows in the figure. From this comparison, we assign the two broad lines to the carbons of the aromatic ring bearing nitrogen and hydrogen, respectively. The chemical shifts and the large separation of these lines strongly support the conclusions from the model reactions, i.e., that the substitutions of the aromatic rings in the polymer are on the 1,3,5-positions. Other substitution patterns, e.g., 1,2,4, would have given one broad peak, centered arount 120 ppm. The peak at approximately 22 ppm can be assigned to the methyl group of the acetate ions present, whereas the carboxylate signal may contribute to the shoulder near 170 ppm. The signal around 70 ppm is tentatively assigned to the CH_2 unit in the ring-protonated subunits.

Due to insolubility, attempts to obtain further analytical information on the polymer were hampered.

Experimental Section

1,3,5-Triaminobenzene was prepared[14-16] by catalytic hydrogenation of 3,5-dinitroaniline[24] (Pd on carbon, H_2, refluxing ethyl acetate). The triaminobenzene (TAB) was obtained as colorless crystals after recrystallization under nitrogen from ethyl acetate. Acetic acid and acetonitrile were distilled and degassed before use. All reactions were carried out in a glovebox filled with high-purity argon.

The ^{13}C NMR spectra were recorded on a Brucker FT-NMR at 20 MHz, ^{1}H NMR spectra on a Varian CW instrument at 60 MHz, and ^{13}C solid-state NMR spectra on a Nicolet TT-14 spectrometer modified for CP-MAS as described in ref 25. Mass spectra were obtained on a HP 5595A GC-MS using the direct inlet probe.

Poly(1,3,5-triaminobenzene). A typical polymerization was carried out as follows: 0.25 g (2 mmol) of TAB was dissolved in 20 mL of acetic acid to give a clear yellow solution characteristic of the monoprotonated TAB. After approximately 4 h at 50 °C, the bright yellow/orange polymer started precipitating, and the reaction was left overnight at 50 °C. If the reaction is carried out at 25 °C, the precipitate starts to appear slowly after about 48 h. At 110 °C, it comes out after 5 min. The polymer was filtered off, washed with acetic acid, and dried. Chemical analysis found: C, 64.97; H, 5.26; N, 18.87. Calculated for $C_6H_{5.1}N_{1.7}(CH_3COOH)_{0.43}$: C, 64.96; H, 5.42; N, 18.77. The almost neutral polymer was obtained as a slightly tan-colored powder upon prolonged washing with acetonitrile or by neutralizing with a 2% solution of triethylamine in acetonitrile, followed by washing with acetonitrile. The yield was essentially qualitative. Prior to chemical analysis, the polymer was dried for several days at 0.01 Torr, 25 °C. Chemical analysis found: C, 68.76; H, 5.15; N, 22.14. Calculated for $C_6H_{5.1}N_{1.7}(CH_3OOH)_{0.13}$: C, 69.09; H, 5.21; N, 21.88.

1,3,5-Trianilinobenzene. TAB (0.12 g, 1 mmol) and 1.86 g of aniline (20 mmol) in 10 mL of acetic acid were heated to 50 °C overnight with stirring. Excess acetic acid was removed under vacuum and the resulting mixture was separated by column chromatography (silica gel/ethyl acetate). In this way approximately 0.3 g of acetanilide (10% based on aniline) and 0.32 g of 1,3,5-trianilinobenzene (90% based on TAB) were isolated. Proton NMR on both compounds were in agreement with that expected: NMR ($CDCl_3$): NH at 5.55 ppm (broad); CH of central ring at 6.29 ppm (single); Ar at 6.8–7.2 ppm. Mp (trianilinobenzene) 193–194 °C (ethanol); lit.[26] 196 °C.

4′-Methoxy-3,5-diaminodiphenylamine. TAB (0.12 g, 1 mmol), 0.12 g of 4-methoxyaniline (1 mmol), and 0.12 g of acetic acid (2 mmol) were refluxed in acetonitrile (10 mL) overnight. The solvent and excess acid were removed under vacuum and the resulting mixture was separated by column chromatography (silica) using ethyl acetate as eluent. Apart from unreacted starting materials and 4-methoxyacetanilide the only product eluted in appreciable amounts (0.04 g, 17%) was (4-methoxyphenyl)(3,5-diaminophenyl)amine: TLC R_f 0.45 (silica gel/ethyl acetate); MS, z/e 229; ^{13}C NMR (assignments and calculated values in brackets) σ ($CDCl_3$) 55.5 (OCH_3, 55), 93.7 (C2, C6, 94), 94.4 (C4, 94), 114.5 (C3′, C5′, 116), 123.0 (C2′, C6′, 124), 135.7 (C4′, 138), 147.5 (C1, 150), 148.4 (C3, C5, 150), 155.3 (C1′, 155). No presence of the other isomers found.

Summary

We have prepared the electron-rich network polymer 1,3,5-triaminobenzene by mildly heating TAB in acetic acid. The mechanism of this unusual reaction is shown to be related to the unusual ring protonation of TAB in mild acids. Work is now in progress to oxidize (dope) this polymer in order to introduce unpaired electronic spins. This will allow us to compare the magnetic properties of this known doped polymer with those of whatever may have resulted from the reaction of TAB and iodine which was previously reported.[6,12]

Acknowledgment. We are grateful for the skillful assistance of Bill Fleming and Ron Herbold for the ^{13}C NMR measurements and John Duran for the SEM pictures. We acknowledge several insightful and helpful discussions with K. Bechgaard, F. Effenberger, and C. A. Brown. We also acknowledge the valuable technical assistance of Mike Pylman, Keith Dveirin, and Blair Romer.

Registry No. TAB, 108-72-5; TAB (homopolymer), 117162-54-6; aniline, 62-53-3; 1,3,5-trianilinobenzene, 102664-66-4; *p*-methoxyaniline, 104-94-9; 4′-(methoxyphenyl)-3,5-diaminophenylamine, 117162-53-5.

References and Notes

(1) *Synth. Met.* **1987**, *18*.
(2) McConnell, H. M. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1967**, *11*, 144.
(3) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372.
(4) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.
(5) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927. Breslow, R.; Jaun, B.; Kluttz, R. Q.; Xia, C.-Z. *Tetrahedron* **1982**, *38*, 863. Breslow, R.; Maslak, P.; Thomaides, J. *J. Am. Chem. Soc.* **1984**, *106*, 6453.
(6) Torrance, J. B.; Oostra, S.; Nazzal, A. *Synth. Met.* **1987**, *19*, 709.
(7) Bagus, P. S.; Torrance, J. B., to be submitted for publication.
(8) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. Iwamura, H.; Sugawara, T.; Itoh, K.; Takui, T. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 251.
(9) Korshak, Y. Y.; Medvedeva, T. V.; Ovchinnikov, A. A.; Spector, V. N. *Nature (London)* **1987**, *326*, 370.
(10) LePage, T. J.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 6412.
(11) Torrance, J. B.; Johannsen, I.; Batail, P.; Nazzal, A.; Parkin, S. S. P. *J. Appl. Phys.* **1988**, *63*, 2962.
(12) First reported by: Oostra, S.; Torrance, J. B. *Symposium on Horizons in the Properties of Low Dimensional Compounds*, Honolulu, Dec 20, 1984.
(13) Gruzdev, V. G. *Zh. Org. Khim.* **1971**, *7*, 1085; *Chem. Abstr.* **1971**, *75*, 63277.
(14) Koehler, H.; Scheibe, G. *Z. Anorg. Allg. Chem.* **1956**, *285*, 221.
(15) Yamaoka, T.; Hosoya, H.; Nagakura, S. *Tetrahedron* **1968**, *24*, 6203.

(16) Effenberger; Niess, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1067.

(17) Hand, E. S.; Jenks, W. P. *J. Am. Chem. Soc.* **1962**, *84*, 3505.

(18) Castedo, L.; Riguera, R.; Rodriguez, M. J. *Tetrahedron* **1982**, *38*, 1569.

(19) Boehme, H.; Bomke, U.; Dennis, J.-P. *Arch. Pharm. (Weinheim, Ger.)* **1982**, *315*, 40.

(20) The condensation of arylamines to diphenylamines requires high pressure and temperatures in the presence of strong acids: *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. E., Eds.; Pergamon: Oxford, 1979; Vol. 2, pp 131–184.

(21) See, for instance: Cook, A. G. *Enamines*; Marcel Dekker: London, 1969.

(22) Yamaoka, T.; Hosoya, H.; Nagakura, S. *Tetrahedron* **1970**, *26*, 4125.

(23) If the unaccounated for percentage arose from $NH_4^+CH_3COO^-$, the analyses would correspond to a larger loss of NH_3 from the polymer.

(24) Used as obtained from Aldrich without further purification.

(25) Lyerla, J. R.; Fyfe, C. A.; Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 208.

(26) Buu-Hoi, S. *J. Chem. Soc.* **1952**, 4346.

Thermodynamics of Hydrogen Bonding in Polymer Blends. 1. Application of Association Models

Paul C. Painter,* Yung Park, and Michael M. Coleman

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802.

Received February 4, 1988

ABSTRACT: The application of association models to the description of the free energy changes related to hydrogen bonding between components of binary polymer blends is discussed for a system where one polymer self-associates while the second does not but is capable of forming a hydrogen bond with the first. A previous model is generalized, and the proper definition of equilibrium constants is considered. It is demonstrated that a definition of these equilibrium constants in terms of chemical repeat units is useful and allows equilibrium constants to be defined and experimentally determined for interactions of a particular generic type (e.g., urethane–urethane, urethane–ether), provided that the polymers considered are structurally similar. The equilibrium constants are simply adjusted by accounting for the difference in molar volume of the chemical repeat units.

Introduction

It is well-known that most hydrocarbon homopolymers do not mix; that is, they form so-called immiscible blends. This follows directly from a simple Flory–Huggins description of the thermodynamics of mixing, which predicts a negligibly small combinatorial entropy and a positive enthalpy term, if simple van der Waals or London dispersion forces are the only intermolecular interactions operating between segments. To obtain miscible homopolymer blends, therefore, it is usually necessary to have some sort of attractive force between unlike segments. If these attractive forces are due to dipole moments that are not localized on the surface of the polymer segment, then it would seem reasonable to treat the system in a conventional manner and simply introduce a negative interaction term. Strictly speaking, the system would not be random, in that unlike segments would have an increased propensity to be adjacent to one another. They are not in the usual sense of the word associated, however, and Flory[1] has argued that for such weak interactions the modification in the calculated entropy of mixing due to nonrandomness is not significant (compared to the effects of other approximations).

Stronger interactions, particularly hydrogen bonds, are different and cannot be dealt with by a simple approximation. Polymer segments that interact in this manner are truly associated, and above the T_g there is a dynamic equilibrium distribution of (hydrogen) bonded species. For example, in ethylene–methacrylic acid copolymers containing only 5% acid units, practically all of the carboxyl groups are present as hydrogen-bonded pairs. This number of contacts could not be predicted on the basis of random mixing.

There are other problems in treating hydrogen-bonding polymer mixtures, apart from formulating a nonrandom arrangement of certain units on a lattice. The forces between interacting functional groups are a complex combination of electrostatic, dispersion, and repulsive terms, and the description of a potential function requires a knowledge of the charge distribution and the specific arrangement of molecules. Furthermore, usual lattice treatments are based on the assumption that the internal degrees of freedom of each molecule (or segment) are not seriously disturbed by the proximity of other molecules in the mixture. The system can then be treated as an assembly whose partition function is the product of a partition function for translations of the molecules and partition functions for the internal degrees of freedom of each single molecule.[2] When molecules or polymer segments become associated by hydrogen bonds, the rotational and vibrational degrees of freedom of each become seriously modified. This effect is clearly observed in the infrared spectrum, where the vibrational modes of the interacting functional groups are strongly perturbed. This is particularly true of –OH and –NH stretching vibrations, which display significant frequency shifts and large changes in intensity as a consequence of intermolecular hydrogen bonding.[3]

A number of theoretical approaches have been developed to account for the difficulties in describing specific directional interactions. For example, Barker[4,5] and Tompa[6] used a treatment in which the surface of a molecule is divided into several contact points and the energy of nearest-neighbor interactions depends upon the relative orientations of the molecules concerned. This approach is (at least to us) mathematically complicated and introduces a number of parameters that cannot be determined independently, but only estimated by a fit to thermodynamic data. As Tompa[6] pointed out, it is uncertain how

---

* To whom correspondence should be addressed.

0024-9297/89/2222-0570$01.50/0