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SYNTHESIS OF HIGHLY CONDUCTING HETEROCYCLIC POLYCARBAZOLES BY SIMULTANEOUS POLYMERIZATION AND DOPING IN LIQUID IODINE

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ABSTRACT

Electrically conducting iodine complexes of homopolymers and copolymers of poly(N-alkyl-3,3'-carbazolyl) are prepared by simultaneous polymerization and doping of N-alkyl- and dihalo-derivatives of carbazole in liquid iodine. This represents a direct one-step chemical method of preparing doped conducting polymers from the monomers and dopants analogous to the electrochemical synthetic technique. The amorphous black polymer complexes are stable in air and can be melt cast into films with conductivity in the range 10^{-3} to 1 $ohm^{-1}cm^{-1}$. Preliminary results of Thermal Analysis, FTIR Spectroscopy, and Gel Permeation Chromatography have provided insights into the mechanism and kinetics of polymerization and polymer structures. X-ray Photoelectron Spectroscopy (XPS) data has provided evidence of transfer of charge from the carbazole unit in the polymer complexes.

INTRODUCTION

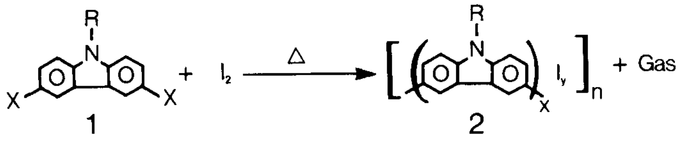
The heterocyclic polymer, poly(3,3'-N-methyl carbazolyl) (PMCZ), was recently prepared by a nickel complex-catalyzed polymerization of the Grignard reagent of 3,3'-N-methyl dibromocarbazole and shown to be solution- and melt-processible and to be highly conducting (1-10 $ohm^{-1}cm^{-1}$) and stable in air when doped with iodine.[1] In the course of chemical doping studies of PMCZ we observed that the acetone-soluble low molecular weight fractions further polymerized in liquid iodine to yield higher molecular weight materials.[1] This earlier observation prompted us to explore the feasibility of direct polymerization of carbazole monomers by iodine liquid or vapor. We have discovered that N-alkyl- and dihalo-carbazole monomers can indeed be simultaneously polymerized and doped by liquid iodine to high molecular weight conducting polymers. It was also found that some of the carbazole monomers oligomerize in the solid state upon exposure to iodine vapor.

The observed simultaneous polymerization and doping of carbazole monomers by liquid iodine is a new one-step chemical method for the preparation of electrically conducting polymers. It is analogous to the electrochemical preparation of conducting polymers, such as polypyrrole, polythiophene, and polyazule, where electrolysis of solutions of the monomers and dopants ($C10_4^-$, BF_4^-, etc.) produce the doped conducting polymers in one step.[2-4] It is also similar to the preparation of arsenic pentafluoride-doped polyphenylene by simultaneous solid-state polymerization and doping of para-phenylene oligomers[5] which have a degree of polymerization from 2 to 6, i.e. biphenyl, paraterphenyl, para-quarterphenyl, etc., by AsF_5. However, the monomer does not polymerize with AsF_5 to polyphenylene.

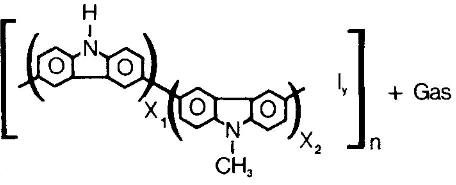
In this paper we present preliminary results of the preparation of conducting polycarbazoles by polymerization and doping in liquid iodine and characterization of the resulting doped polymers.

POLYMERIZATION AND DOPING IN LIQUID IODINE

The preparation of iodine-doped conducting polycarbazoles can be accomplished by a simple one-step process in which simultaneous polymerization and doping of the requisite monomers is carried out in liquid iodine. In the case of poly(3,3′-N-alkylcarbazolyl) structures this process can be represented by:



1a. $R=H$, $X=H$ (Cz)
1b. $R=H$, $X=Br$ (DBCZ)
1c. $R=CH_3$, $X=H$ (NMCZ)
1d. $R=CH_3$, $X=Br$ (NMDBCZ)
1e. $R=CH_3$, $X=I$ (NMDICZ)



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The above polymerization reactions have been carried out in a beaker in air, in a tube with flowing nitrogen, in a test tube in air, in an evacuated and sealed tube, or other vessels and atmospheres, by mixing the solid monomers with solid iodine (re-sublimed crystals) followed by isothermal or nonisothermal heating. Though pure solid iodine sublimes readily because of its high vapor pressure below its melting point (113.6°C), its mixtures with carbazole monomers usually melt before any appreciable sublimation. In a typical polymerization in a beaker in air the monomer-iodine mixture is heated on a hot plate at a constant temperature. Stirring with a stirring rod is initiated as soon as the mixture melts to give a homogeneous solution of monomer in liquid iodine. Evolution of a gaseous product from the solution marks the onset of polymerization and this occurs almost instantaneously with fusion of the mixture. The viscosity of the polymerizing solution increases with polymerization time, changing by orders of magnitude in minutes. The viscosity of the solution therefore provides one measure of the extent and kinetics of polymerization. Depending on the initial concentration of monomer in solution the product of polymerization may contain excess (free) iodine that may be removed by a variety of methods including heating or reaction with sodium thiosulfate solutions.

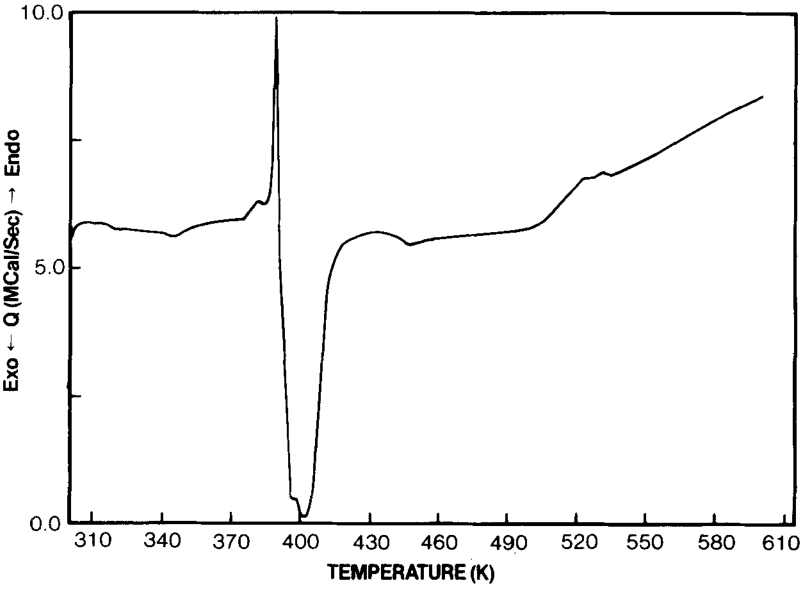


FIGURE 1 DSC Thermogram of 2% (w/w) mixture of NMDBCZ with iodine obtained at a scan rate of 10°c/min.

The iodine-doped polycarbazoles prepared by polymerization and doping in liquid iodine are readily further processed into films, fibers, or molded shapes. Films have been produced by melt casting of doped polymer complexes onto substrates and directly from the monomer-iodine solutions by polymerization onto a planar substrate. Fibers up to a meter long have been drawn from the high viscosity polymerizing melt but could also probably be obtained by melt spinning. It is also conceivable that molded shapes may be obtained by direct polymerization in a molding die.

Direct evidence for thermal polymerization of solutions of carbazole monomers in liquid iodine has been partly provided by differential scanning calorimetry (DSC) results. Figure 1 shows the DSC thermogram of 2% (w/w) mixture of monomer **1d** with iodine obtained at a scan rate of 10°C/min. in a hermetically sealed pan. Melting of the mixture occurs at 388.9K (115.7°C) with a heat of fusion of 3.77 cal/g compared to the melting points of the pure monomer (159°C) or pure iodine (113.6°C). The polymerization reaction is evidenced by the large exotherm with a peak at 400.9K (127.8°C) and a heat of reaction of ca. −63.13 cal/g or −21.4 kcal/mole of monomer. It is to be noted that polymerization followed melting of the iodine-monomer mixture. Indeed, the onset of polymerization 390.4K(117.2°C) is also the upper limit of fusion. Thus the thermal polymerization is a *solution polymerization* in which liquid iodine acts as the solvent among its other roles.

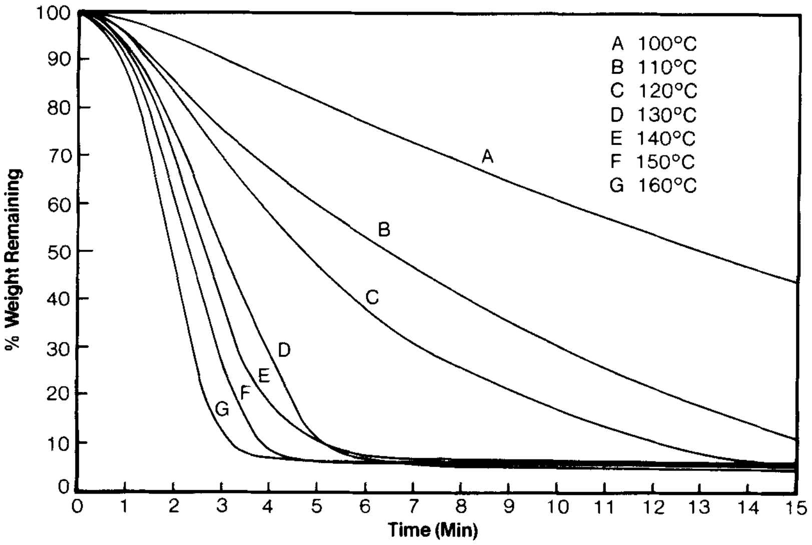


FIGURE 2 Isothermal Thermogravimetric analysis of 5% (w/w) mixture of NMDBCZ with iodine in nitrogen at different temperatures.

The kinetics of polymerization of carbazole monomer in liquid iodine can be studied by several methods including the viscosity of the polymerizing solution, the amount of gas evolved, extraction and chemical analysis of monomer/polymer/iodine mixtures at different times, and thermal analysis. DSC techniques can be used because of the significant thermal effects accompanying polymerization as seen in Figure 1. Thermogravimetric Analysis (TGA) can also be used because of the weight loss accompanying gaseous product evolution. Figure 2 shows isothermal TGA curves of 5% (w/w) mixture of monomer **1d** with iodine in flowing nitrogen atmosphere at different temperatures between 100-160°C. The same sample size (40.0±0.4 mg) was used at each temperature. The residue samples removed after 15 minutes polymerizations at 120-160°C were black shining electrically conducting polymer films apparently free of any excess iodine. As would be expected from DSC melting point data residue of samples run at 100°C and 110°C had not fused after 15 min. but nevertheless had changed color and apparently polymerized to some extent.

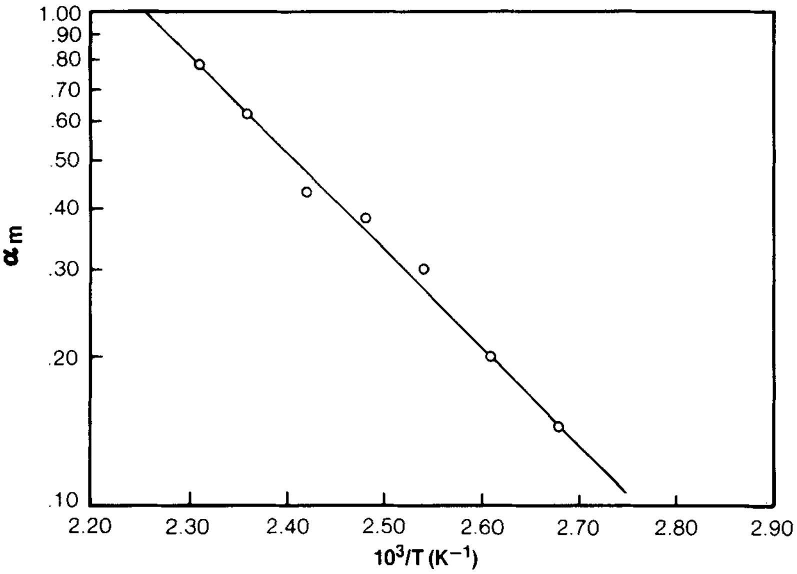


FIGURE 3 Arrhenius plot of fractional weight loss at maximum rate of reaction versus temperature.

Figure 3 shows an Arrhenius plot of the fractional weight loss (α_m) at the maximum rate of reaction, $(d\alpha/dt)_{max}$, derived from Figure 2, versus reciprocal absolute temperature. It is interesting that the data points at

100 and 110°C both fit in a line with those at the higher temperatures. This suggests that a similar process is taking place in the solid state at 100 and 110°C as in solution polymerization at the higher temperatures. This will be confirmed in future studies of isothermal polymerization by DSC. The apparent activation energy for the overall polymerization process of monomer **1d** by iodine is 9.0 kcal/mole. This apparent activation energy of 9.0 kcal/mole describes the overall process including polymerization, complexation of monomer/polymer with iodine, and evaporation of iodine and not solely due to evaporation of pure iodine.

The precise details of the roles of iodine in the observed simultaneous polymerization and doping of carbazole monomers by iodine are yet to be fully elucidated. However, some points are clear from our studies to date. Iodine is an electron acceptor that forms charge transfer complexes with the carbazole polymers[1] and monomers. In its liquid state (113.6-184°C) it is an excellent solvent for carbazole monomers and polymers. Indeed, liquid iodine is known to be a good solvent for many other organic and inorganic substances and its salt solutions are good conductors of electricity.[6] Thus it is a highly polarizable solvent and it ionizes mostly as $2I_2 = I^+ + I_3^-$. Fused carbazole monomers at or above their melting points do not polymerize thus precluding thermal initiation. Iodine is clearly the initiator of polymerization.

What is not yet clear is the true mechanism of polymerization (initiation and propagation) considering that there are many possibilities. One possibility is suggested from the well-known iodine-initiated solution and bulk (liquid and solid state) polymerization of various monomers including N-vinylcarbazole and vinyl alkylethers. In these polymerizations the active initiation species is the iodonium ion (I^+) giving rise to conventional cationic initiation and propagation mechanisms:[7-8]

$$2I_2 = I^+ + I_3^-$$

$$I^+ + M \rightarrow I\text{-}M^+$$
$$M_n^+ + M \rightarrow M_{n+1}^+$$

where M stands for a monomer. Although the concentration of iodonium ions in our polymerization mixtures are not known cationic initiation is not very likely. A more likely possibility is initiation involving a charge-transfer (CT) complex and a monomer cation radical formation. It is well-known that some donor monomers (M) which form CT complexes with acceptor (A) molecules may be polymerized according to the scheme:[8-10]

$$M + A = MA(\text{CT Complex}) = {}^{\bullet}M^+ + {}^{\bullet}A^-$$
$${}^{\bullet}M^+ + nM \rightarrow {}^{\bullet}M_{n+1}^+$$

where • denotes an unshared electron. The requirement in the above initiation step that the monomer (M) be sufficiently nuclophilic in character with respect to the acceptor (A) is met by all the carbazole monomers and iodine. Prior chemical[11-13] and electrochemical[14] oxidation studies of carbazole monomers suggest monomer cation radical intermediates in the formation of oligomers[11-14] and probably polymers.[4] The electrochemical studies[14] in particular show the loss of one electron per carbazole monomer cation radical formed. Propagation of the proposed cation radical-initiated polymerization most likely involves addition of monomer molecules to the charged site, the charge being accompanied by a counter ion which is most likely I_3^-. Detailed studies with the goal of elucidating the true mechanism of polymerization are in progress.

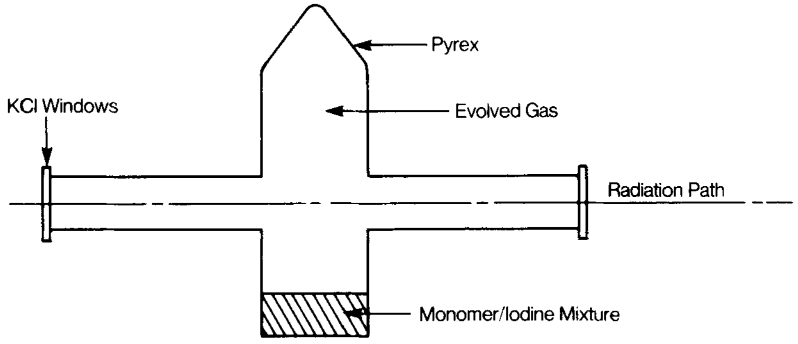


FIGURE 4 FTIR Spectroscopy Gas Absorption Cell for analysis of evolved gas during polymerization in liquid iodine.

The gas evolved during polymerization of the mixtures of monomers and iodine and the solid polymer complexes were studied by Fourier Transform Infrared (FTIR) spectroscopy in order to gain further insights into the mechanism of polymerization and the structures of the polymer products. A special FTIR gas absorption cell was constructed of pyrex glass as shown in Figure 4. Two KCl windows were attached to provide a path length of 12.70 cm. FTIR spectra in the range 400 to 4000 cm^{-1} were taken before heating the samples (iodine-monomer mixtures), after heating to 120-125°C for 5 minutes, and after opening the cells. Films of polymer products were melt-cast onto KCl windows and their spectra taken. Figure 5 and 6 show the spectra of reaction products from iodine mixtures of monomers **1d** and **1b** respectively. As seen in Figure 5 and 6 HBr gas with bands in the range 2400-2800 cm^{-1} was clearly revealed. HBr gas was observed in all polymerizing mixtures containing dibromomonomers, either as single monomer mixtures with iodine such as **1b** or **1d**, or in iodine mixtures with monomer pairs such as **1a** and **1b**, **1a** and **1d**, or **1c** and **1d**. The spectra of one or two other gases are present, as seen in Figures 5 and 6, but have as yet not been positively identified. However, HI which could be present in the gas evolved was not seen in the FTIR spectra perhaps because the sensitivity, path length, and concentration were not high enough for detection. Other suspect gases such as IBr, I_2, Br_2, CH_3I and CH_3Br are either not infrared active or have not been positively identified as reaction products. The strong electronic absorption of the polymer complexes was featureless except for some superimposed vibrational structure in the 1600-800 cm^{-1} region. The FTIR spectroscopy results suggest the poly (3,3'-N-alkylcarbazolyl) structures 2 and 3 as the main products of polymerization. However, some crosslinking through the 1,1' positions is suggested by the insolubility of a small portion of the polymer complexes in sulfuric acid.

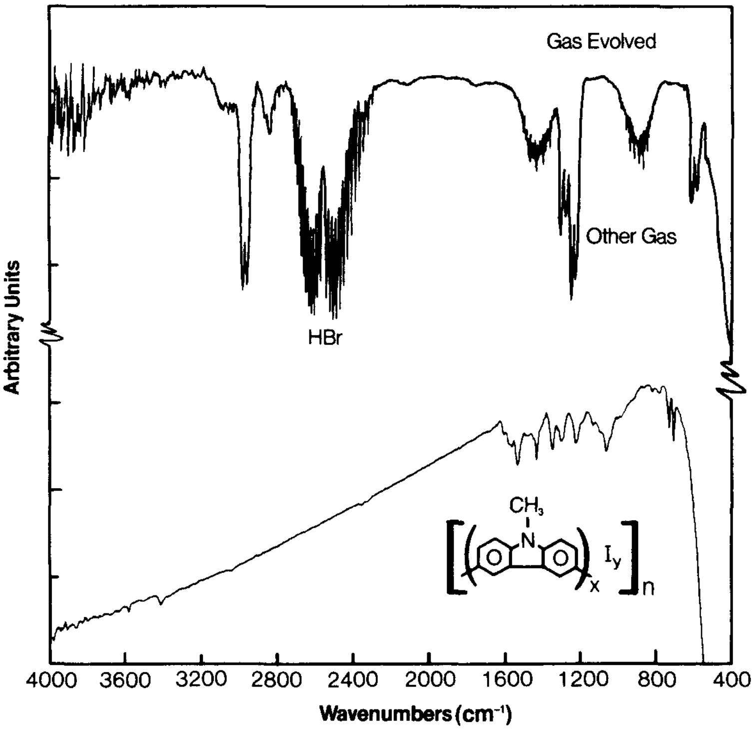


FIGURE 5 FTIR Spectra of Reaction Products of NMDBCZ with iodine at 120-125°C for 5 min.

One wonders how general the observed simultaneous polymerization and doping in liquid iodine may be and its implication for synthesis of other electrically conducting polymers. In the absence of a full understanding of the precise mechanism of polymerization generalization may be out of the question at this time. More recently, we have observed that other heteroaromatic monomers including phenothiazines and N-alkyldiphenylamines do indeed undergo simultaneous polymerization and doping in liquid iodine similar to carbazole monomers to yield conducting polymer products.

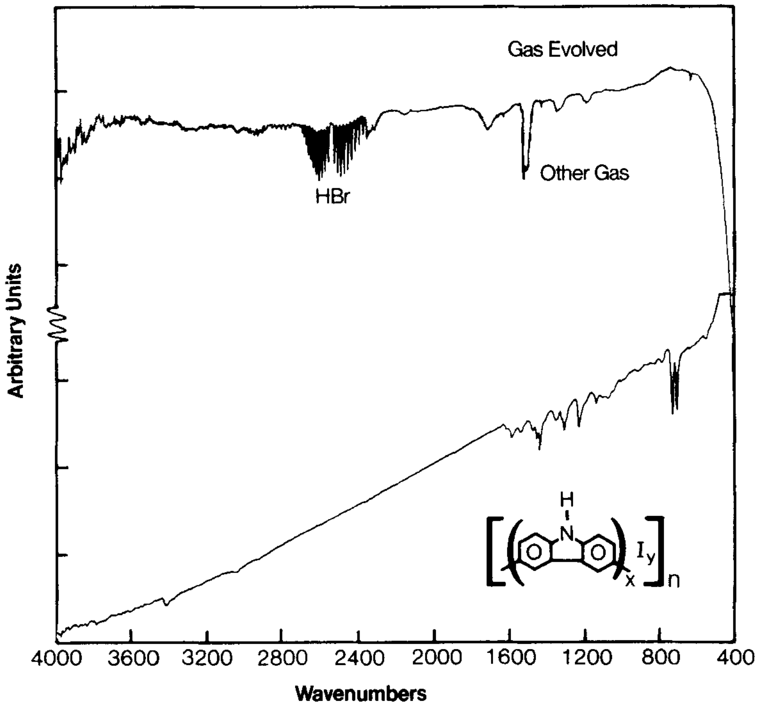


FIGURE 6 FTIR Spectra of Reaction Products of DBCZ with Iodine at 120-125°C for 5 min.

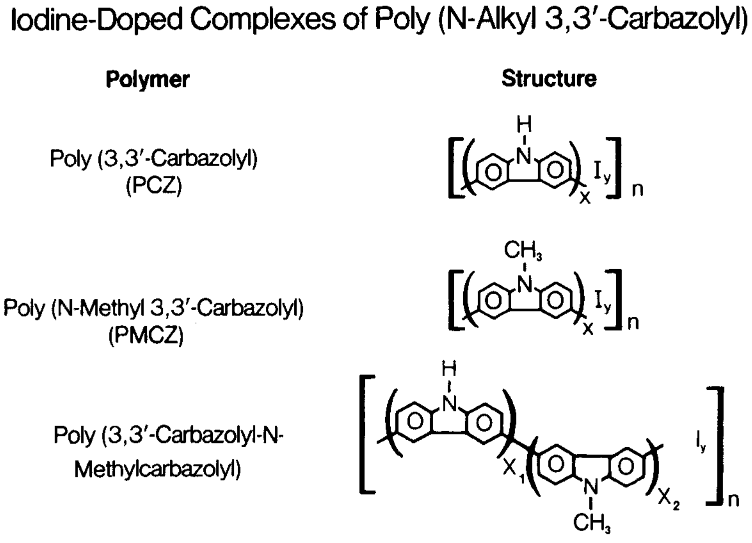
PROPERTIES OF POLYMER COMPLEXES

Homopolymers poly (3,3′-carbazolyl) (PCZ) and poly(3,3′-N-methyl carbazolyl) (PMCZ) were prepared by polymerization of equimolar amounts of monomers **1a** and **1b** and **1c** and **1d** respectively. The random copolymer with the structure **3** was obtained by polymerizing equimolar amounts of either **1a** and **1d** or **1b** and **1c**. The room temperature dc conductivity values obtained with standard four-point probe techniques for films of these samples are shown in Table 1. Other samples of polycarbazoles including those of unknown structures also exhibited conductivities in the range 10^{-3} to 1 $ohm^{-1}cm^{-1}$. These values of the conductivity of as-synthesized samples are probably not the maximum obtainable considering that the maximum doping levels have not yet been established. The value of 1 $ohm^{-1}cm^{-1}$ obtained with PMCZ is comparable with 1-10 $ohm^{-1}cm^{-1}$ previously observed with samples prepared by Grignard synthesis[1] followed by vapor phase doping. However, the conductivity of PCZ is also comparable even though we were expecting it to be higher because of the possible closer approach of the aromatic rings increasing the probability of intermolecular hopping. Most unusual was the order of magnitude lower conductivity of the PCZ/MCZ copolymer which is at present unexplained.

TABLE 1

Electrical Conductivity of Polymer Complexes

Sample	Structure	$\sigma(ohm^{-1}cm^{-1})$
PCZ	2	~1.0
PMCZ	2	~1.0
PCZ/MCZ	3	$\sim 4.8 \times 10^{-3}$



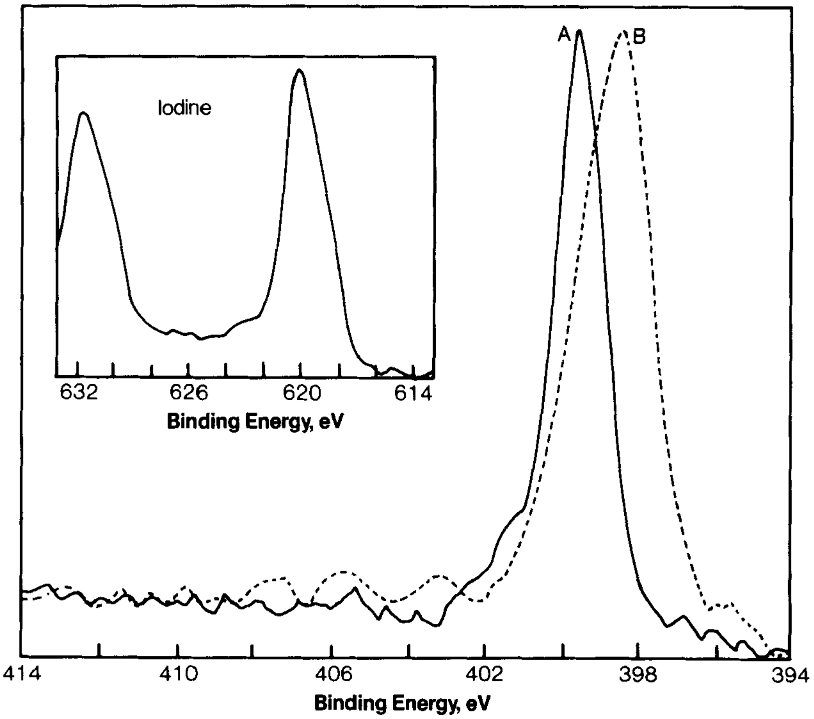


FIGURE 7 X-Ray Photoelectron Spectra (XPS) of N 1s.
A - Iodine-doped poly(3,3'-carbazolyl-N-Methyl carbazolyl)
B-Undoped poly(3,3'-N-Methyl carbazolyl). Inset shows XPS spectrum of iodine multiplex of sample A, $4d_{3/2}$ (~632 eV) and $4d_{5/2}$ (~620 eV).

X-ray photoelectron spectroscopy (XPS) data were recorded using a Physical Electronics model 555 instrument employing MgKα radiation (1253.6 eV photons, approximately 0.5 eV resolution). The neutral polymer (PMCZ) obtained from the Grignard reaction was cast in a film on a gold coated glass slide and then the sample was decorated with gold on top. Any electrostatic charging of the polymer was neutralized with thermal electrons. Calibration was checked by using the gold $4f_{7/2}$ peak at 83.8 eV. The iodine reacted random copolymer PCZ/MCZ was also cast on a glass slide, however, no gold coating was used. Since iodine sublimation was a problem, a liquid nitrogen cold stage was used to obtain a reasonable vacuum (10^{-8} to 10^{-7} torr). Electrostatic charging was not a factor with this thin film because it was highly conducting. As can be seen in Figure 7, the Nitrogen (1s) peak for the undoped polymer is at an energy of 398.6 eV while the doped polymer has the N(1s) peak at 399.6 eV. This

1 eV increase in binding energy upon doping indicates the withdrawal of charge by the I_3^- ions from the carbazole unit. Similar results showing XPS spectra changes upon oxidation are known in other conducting polymer systems.[15-17] The $4d_{3/2}$ and $4d_{5/2}$ spectra of iodine were clearly asymmetric suggesting the presence of two species, most probably surface adsorbed iodine at the high binding energy side of each peak and I_x^- at the lower energy side.

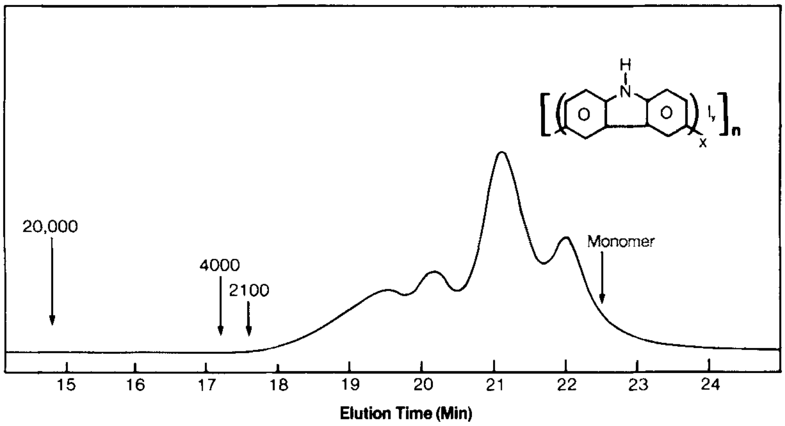


FIGURE 8 Gel Permeation chromatographic (GPC) analysis of THF-soluble fraction of as-synthesized iodine-doped poly(3,3′-carbazolyl). Elution rate - 1 ml/min. Arrows indicate monomer and polystyrene standards.

Molecular weight distribution (MWD) of polymer complexes was obtained by Gel Permeation Chromatography (GPC). GPC analysis was performed on two instruments, a Waters Model ALC/GPC-501 packed with 10^5, 10^4, 10^3, and 500 Angstrom microstyrogel columns and run at room temperature and Waters Model 150-C GPC packed with DuPont ZORBAX PSM60 columns with a molecular weight range of 200-10,000 and run at higher temperatures. Figure 8 shows the MWD of the THF-soluble fraction of as-synthesized iodine-doped PCZ sample prepared by reaction of equimolar mixtures of monomers **1a** and **1b** in liquid iodine and run at room temperature on the GPC. A multimodal MWD corresponding to oligomers is revealed. This low molecular weight fraction was about 30% of the polymer product. The remaining THF-insoluble fraction presumably of higher molecular weight and probably crosslinked. Two samples of PCZ/MCZ copolymers were similarly prepared, first by reaction of 10% (w/w) equimolar amounts of monomers with iodine in a test tube and secondly by reaction of the same solution on a watch glass from which iodine could readily be evaporated. These samples were dissolved in nitrobenzene 3mg/3ml and run on the GPC at 100 °C, Figure 9. High molecular weight polymer fractions were found in each case. However, the proportion of low molecular weight oligomers in the sample prepared by reaction on a watch glass was less. The increased surface area of this reaction vessel assures higher molecular weight due to faster kinetics at the higher polymer concentrations generated during evaporation of iodine and gaseous products from the surface.

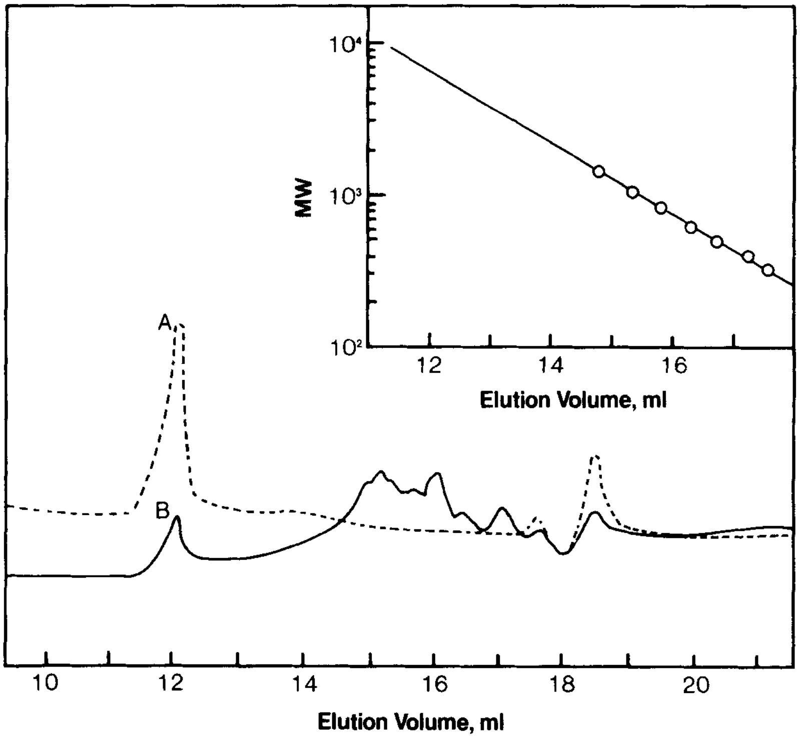


FIGURE 9 GPC Analysis of as-synthesized iodine-doped poly(3,3′-carbazolyl-N-methyl carbazolyl) in nitrobenzene at 100°C. Inset - Model compound standards. A - Reaction on a Watch glass; B - Reaction in a test tube.

The as-synthesized iodine-doped conducting polymers can be reduced to the neutral polymers by reaction with sodium dithionite. The latter reducing agent has been used in the reduction of aromatic nitro compounds[18], imines[19], and other nitrogen containing molecules. We have used sodium dithionite solutions in dimethyl formamide (DMF), 2,2'-oxidiethanol, and diethylene glycol methyl ether (Diglyme) to reduced black iodine-doped polycarbazoles, prepared by simultaneous polymerization and doping in liquid iodine, to apparently neutral yellowish-green polymers. Preliminary GPC analysis of the reduced samples show high MW fractions and MWD similar to those in Figure 9.

CONCLUSION

We have successfully prepared highly conducting heterocyclic polycarbazoles by simultaneous polymerization and doping of the heterocyclic carbazole monomers in liquid iodine. The amorphous black iodine-doped polycarbazoles are stable in air and can be further processed into films or other forms or reduced to the neutral polymers. Our preliminary results of thermal analysis, FTIR spectroscopy, and GPC analysis have provided important insights into the novel polymerization process and polymer structures. The one-step chemical synthesis of doped conducting polymers may be applicable to other heteroaromatic monomers.

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REFERENCES

1. S.T. Wellinghoff, T. Kedrowski, S. Jenekhe, and H. Ishida, Int. Conf. on Phys. and Chem. of Conducting Polymers, Les Arcs, France, Dec. 1982; J. de Phys., in press.
2. A.F. Diaz, K.K. Kanazawa, and G.P. Gardini, J.C.S. Chem. Commun., 635 (1979); K.K. Kanazawa, A.F. Diaz, W.D. Grill, P.M. Grant, G.B. Street, G.P. Gardini, and J.P. Kwak, Synthetic Metals 1, 329 (1980); A.F. Diaz, Chemical Scripta, 17, 145 (1981).
3. K. Kaneto, K. Yoshino, and Y. Inuishi, Jpn. J. Appl. Phys. 21, L-567 (1982); Solid State Comm. 46, 389 (1983).
4. J. Bargon, S. Mohmand, and R.J. Waltman, IBM J. Res. Dev. 27, 330 (1983).
5. L.W. Shacklette, H. Eckhardt, R.R. Chance, G.G. Miller, D.M. Ivory, and R.H. Baughman, J. Chem. Phys., 73, 4098 (1980).
6. C.J. Mazac, in: Kirk-Othmer Encyclopedia of Chemical Technology 3rd ed., Vol. 13, (John Wiley: New York, 1981) p. 649.

7. D.D. Eley and A.W. Richards, Trans. Faraday Soc. (London), 45, 425 (1949); D.D. Eley and J. Saunders, J. Chem. Soc. (London), 4167 (1952); 1672 (1954); D.D. Eley and A. Seabrooke, J. Chem. Soc. London, 2226 (1964); D.D. Eley, F.L. Isack, and C.H. Rochester, J. Chem. Soc. A London, 872 (1968).
8. L.P. Ellinger, Polymer, 5, 559 (1964); 6, 549 (1965); Adv. Macromol. Chem., 1, 169 (1968); and references therein.
9. H. Scott, G.A. Miller, and M.M. Labes, Tetrahedron Letters, 17, 1073 (1963).
10. N.G. Gaylord, Macromol. Rev., 4, 183 (1970); and references therein.
11. P. Maitland and S.H. Tucker, J. Chem. Soc. (London), 1388 (1927).
12. W.A. Waters and J.E. White, J. Chem. Soc. Chem. Commun. 740 (1968).
13. B. Robinson, Nature 210, 520 (1966).
14. J.F. Ambrose and R.F. Nelson, J. Electrochem. Soc. 115, 1159 (1968); J.F. Ambrose, L.L. Carpenter, and R.F. Nelson, J. Electrochem. Soc. 122, 876 (1975).
15. P. Pflunger and G.B. Street, J. Chem. Phys., in press.
16. P. Pflunger, M. Krounbi, and G.B. Street, J. Chem. Phys., in press.
17. W.R. Salaneck, R. Erlandsson, J. Prejza, I. Lundstrom, and O. Ignanas, Synthetic Metals 5, 125 (1983).
18. E. Grandmougin, J. Prakt. Chem. 76, 124 (1907).
19. P.M. Pojer, Austr. J. Chem. 32, 201 (1979).