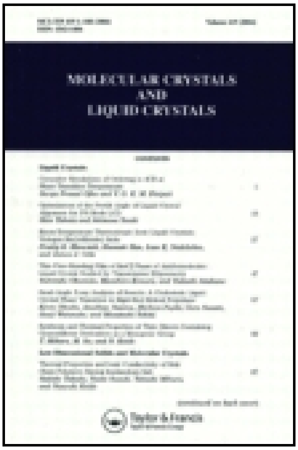

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The Role of Polymer Cations in The Polymerization and Electrical Conductivity of Polycarbazole

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THE ROLE OF POLYMER CATIONS IN THE POLYMERIZATION AND ELECTRICAL CONDUCTIVITY OF POLYCARBAZOLE

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Abstract The high electrical conductivities ($1 ohm^{-1}cm^{-1}$) in 3,3´ polycarbazole charge transfer complexes originate from hopping of radical cations delocalized over only two carbazole units. Although some intramolecular transport must occur a significant intermolecular hopping component must be present. In fact there is significant evidence from model compound studies that distinct bound states exist between radical cations on adjacent chains. The radical cations in the N-methyl substituted polymers are so stable that the conductivity remains unchanged for months in air. These same radical cations can propagate a polymerization reaction through exposed chain ends in molten iodine or bromine solvents. Polymerizations, charge transfer doping, solvent casting thus can be carried out by simply dissolving monomer in the molten halogen. The polymerizing liquid iodine solutions can be reduced by $S_2O_4^{=}$ to produce neutral polymer.

INTRODUCTION

Many polymers can be oxidized or reduced either chemically[1] or electrochemically [2] to produce semiconductor or metallic charge transfer complexes. In the case of oxidation, which is of concern in the present paper, the polymeric cation or radical cation can be delocalized over many monomer units as for instance in a rigidly planar crystalline structure such as polyacetylene[3]. This delocalization serves two purposes. First, it decreases the probability of nucleophilic attack on what would normally be a very reactive ionic species, and, second, trapping of the polymeric change carrier by the counteranion is minimized, thus increasing mobility. Environmental stability can be achieved in these materials if the polymer can be oxidized to a low electron potential before nucleophilic attack can occur[4].

Unfortunately the rigidity of these molecules is a natural barrier to fusability and solubility, even though some rigid phthalocyanine based polymers can be dissolved in flurosulfonic acid[5]. However the absence of crystallinity is not necessarily an impediment to conductivity. For instance relativily amorphous polypyrrole[6], polybenzothiophene and polythiophene[7] complexes are as conductive as 1-100 $ohm^{-1}cm^{-1}$. The predominant charge transport process in this case is most likely intermolecular hopping of aromatic ions delocalized over only a few monomer units[8]. In this respect aromatic polymers have an advantage since even though the charge might not be extensively delocalized down the chain, smearing of the charge lateral to the chain direction facilitates intermolecular charge dispersion through π-π complex formation[9] and minimizes the effect of intramolecular disorder on carrier mobility.

Making use of these concepts we have developed a series of processible carbazole[10] and phenothiazene[11] based polymers that behave as amorphous, environmentally stable, semiconductors having conductivities of 1-10 $ohm^{-1}cm^{-1}$. The carbazole structure is a good synthetic starting point since the oxidation potential can be readily tuned by substitution at the nitrogen atom. For example poly 3,6 N-methylcarbazole is oxidized by I_2 [12]

while the ummethylated derivative requires a stronger oxidizing agent such as Br_2 or $NOBF_4$.[13] Extensive electrochemical work on substituted 3,3′carbazole dimers reveals that blocking the nitrogen position along with positions ortho and para to it results in air stable dimeric radical cations and dications[14,15]. These positions all have high charge and spin density[16] and thus would normally be sites for nucleophilic attack or radical coupling.

Another interesting feature of this systems is that radical cations of 3,6 dihalogen and dihydro carbazoles are unstable to dimerization through the 3 or 6 position. This dimer is easily oxidized to both radical cation and dication at the same potential required to oxidize the monomer to radical cation. An electrochemical polymerization of the N-H derivative in acetonitrile was unsuccessful[17]. Precipitation of dimer salts on the electrode was likely to be responsible for this.

At this point we thought that a more powerful solvent such as molten iodine might prevent precipitation at the dimer stage. In fact a facile cationic polymerization of carbazole monomers in this solvent yielded a solution of polycations from which could be cast flexible films having air stable conductivities of 1 $ohm^{-1}cm^{-1}$.[18] This concept is quite similar to the AsF_3-AsF_5 oxidizing solvent system that has been recently developed for thiophene and polyphenylene sulfide polymers[19].

Out objective in what follows is to summarize our more recent efforts 1) to characterize the mechanism of liquid iodine polymerization and the chemical structure of the films cast from this solution 2) to probe deeper into the mechanism of charge transport in polycarbazole charge transfer complexes.

POLYMERIZATION IN LIQUID IODINE

A typical reaction in liquid iodine initiates by oxidation to the radical cation, dimerization, and then oxidation to dication.

Attack on a neutral molecule at a position ortho or para to the nitrogen can then occur. The release of HBr from the polymerization of 3,6 dibromo N-methyl carbazole suggests some coupling through the ortho positions. In some cases the quality of the resultant film was poor because of bubbles of HBr that were incorporated into the film as the solution thickened during polymerization.

In order to avoid such difficulty we prepared both 3,6 diiodocarbazole and its N-methyl derivative (NMDICZ)[20] so that the possible small molecule condensates, I_2 and HI, would be soluble in the solvent. In a typical reaction 0.1g monomer was ground with ~1cc iodine and subsequently melted at 130°C initiating the polymerization. A gradual thickening of the mixture was observed in the absence of any bubbling. This same reaction could be carried out in an NMR tube to follow the polymerization over time in a FTNMR NT-300XB (Nicolet). Tetramethylsilane which did not react with I_2 was added as an internal chemical shift standard. The evolution of the reaction is easiest to follow in the case of N-methyl 3,6 diiodocarbazole (Figure 1a,b). At five minutes after fusion a mixed spectrum, most probably consisting of monomer (hatched region) and oligomers, is present. At ten minutes the simple spectrum of only the oligomer was present. A number of features should be emphasized. Firstly, the simplicity of the oligomer spectrum suggests that only one type of coupling, probably 3,3′ is predominant and also that there is very little coupling of any paramagnetic radical cation with the protons. The oligomers evidently remain suspended in solution throughout the polymerization since no loss in integrated signal strength is observed This high solubility in the solvent is undoubtedly responsible for the high quality films that can be cast from liquid I_2.

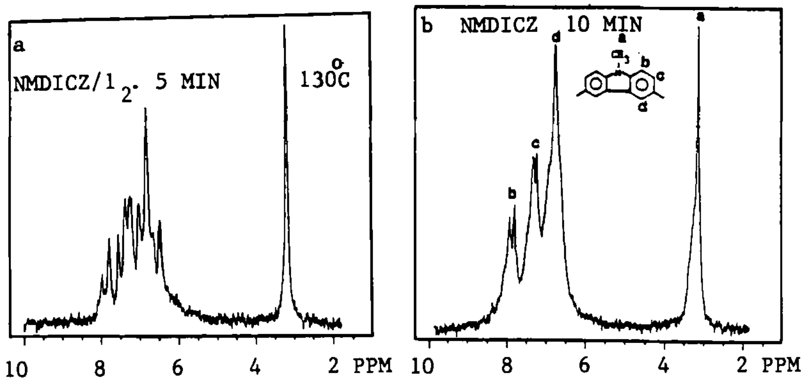
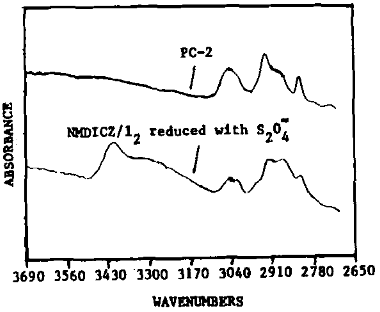


Figure 1 NMR spectra of polymerizing NMDICZ liquid I_2 mixtures.

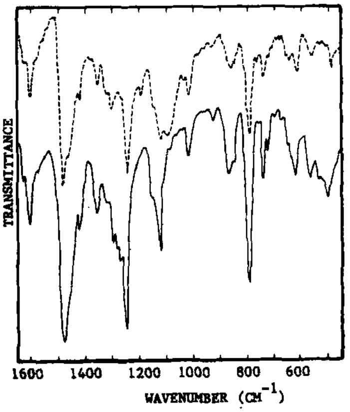
The elemental analysis of the final cast film is consistent with 4 I_3^- per three monomer units (Observed: $C_{13}H_{0.98}I_{1.33}$; Expected: $C_{13}H_9NI$), slightly high than the maximum doping level achievable with cast films of N-methyl polycarbazole doped by gaseous iodine, e.g. $3I_3^-$ per three monomer units[20].

The IR spectrum of the liquid I_2 cast film was obscured by a strong electronic band and, since only a fraction of this partially crosslinked film was soluble, we decided to quench the reaction before complete evaporation of the solvent. Our hope was to obtain in this way soluble materials which could be more adequately characterized. Thus, a 5wt % NMDICZ - iodine mixture was reacted 15 minutes at 125°C and poured directly into diglyme. No precipitation was observed at this stage. This black solution was then reduced under N_2 with a mixture of $Na_2S_2O_4$ and $NaHCO_3$ with gradual addition of H_2O to produce a light brown-yellow precipitate which turned a light green over time in air. A large portion of this powder was insoluble in hot nitrobenzene most probably because of high molecular weight or some crosslinking during reduction. The powder readily redoped with gaseous iodine to a pressed pellet conductivity of 0.01 $ohm^{-1}cm^{-1}$ at 25°C.

The FTIR spectra of the reduced product is compared with the Grignard coupled material in Figures 2a and 2b. The spectra are similar except for the presence of what appears to be an N-H vibration at 3430 cm^{-1} and extra absorbances at 1290 cm^{-1}, and in the C-H out of plane region at 835 cm^{-1}. Apparently some demethylation of the nitrogen has occurred during the reduction process. Demethylation in molten iodine seems unlikely since the elemental analysis of the liquid I_2 cast film fits so closely with that for poly N-methylcarbazole. Some minor amounts of polymerization ortho to the nitrogen is probably responsible for the slightly more complicated C-H out of plane region. The important conclusion to come away with is that the structure of the liquid iodine polymerized material is very similar to the polymer prepared by Grignard coupling.



2a. FTIR spectra of Grignard polymerized PC-2 and NMDICZ/I_2 polymer which is $S_2O_4^=$ reduced.



2b. Same as 2a except mid IR range.

IDENTIFICATION OF THE CHARGE CARRIER

Previous work with the dimeric model compound 9'9 dimethyl 3'3 dicarbazolyl tetrafluoroborate both in solution and the solid state has shown the presence of a cationic intramolecular transition at 850 nm and a non-linear concentration dependent, intermolecular transition involving a sandwich complex between two molecules at 1850 nm[10]. The solid state thin film spectra of the $NOBF_4$ oxidized poly N-methylcarbazole contains the same two transitions. However the intermolecular transition is considerably broadened in the case of polymer (Figure 3). The room temperature conductivity of this film was an air stable 10^{-1} $ohm^{-1}cm^{-1}$.

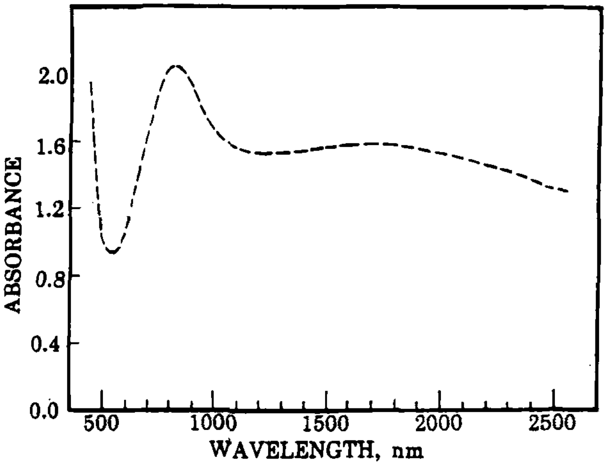


Figure 3. Visible-Near IR spectra for poly N-methylcarbazole doped with I_2-CCl_4 solution and then further oxidized with $NOBF_4$-Acetonitrile solution.

Again the same two transitions are observed in a dilute nitrobenzene solution of the polymer BF_4^- complex. As expected for a given mole ratio of $NOBF_4$ to monomer units (1:2) the 800 nm peak exhibits a linear concentration dependence while the

1600 transition has a faster than linear increase in concentration (Figure 4a). Upon oxidation of a polymer of given concentration (5 mg/ml) from a ratio of NOBF$_4$ to monomer units of 1:3 to a ratio of 1:2, a Beer's law concentration dependence holds for both transitions. Upon attempted further oxidation from 1:2 to 1:1, however, a slower than linear increase the 800 nm peak suggests the polymers propensity for NOBF$_4$ oxidation is saturating.

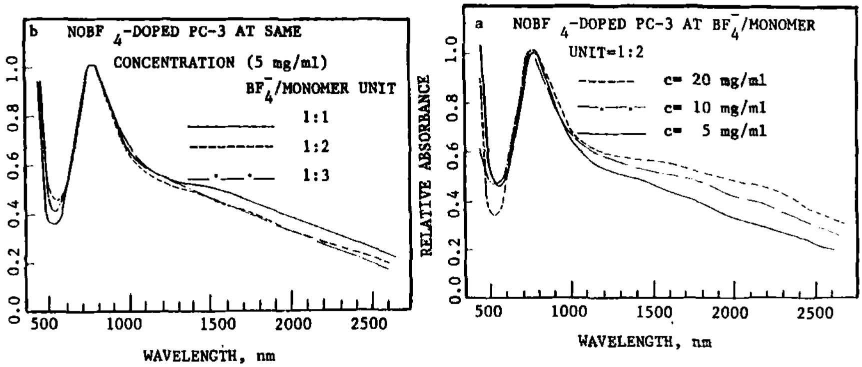


Figure 4. UV-visible-near IR spectra of poly N-methyl carbazole tetrafluoroborate complexes in nitrobenzene (a) as a function of polymer concentration (b) as a function of oxidant concentration.

The peak shape of the 800 nm transition is unaffected by either oxidation level or concentration. Clearly these observations coupled with the presence of an almost identical transition in the dimer model compound suggests that polymer chain length has little effect on the type of ion present. The same dimeric ion appears to exist in the amorphous solid state and undoubtedly is responsible for the conduction process. Even in dilute solution, the polymer intermolecular transition in the near IR is considerably broader than that found for the model compounds. This is not unexpected since the hindered approach of two polymer coils could generate a range of more distorted sandwich configurations than found in solutions of dimer radical cations.

At this point the question arises as to the nature of the carrier spin. An E-4 spectrometer in conjuction with a computer for double-integration was used in the EPR investigation of magnetic properties of model compounds and N-methyl polycarbazole iodine complexes. The first derivative absorption spectra were taken and then double-integrated to give a quantitative analysis of spin concentration in these complexes. Both solid and solution samples were analyzed quantitatively with a calibration standard of 1,1-diphenyl 2-picrylhydrazyl (DPPH) diluted in either N-methylcarbazole or nitrobenzene. Unoxidized poly N-methylcarbazole gave a synmetrical ESR first derivative signal of peak to peak width, ΔHpp. of 10.5 gauss. Oxidizing the polymer with iodine to one I_3^- per three monomer units increased ΔHpp to 18.5 gauss and the spin concentration from one spin/ 5.0×10^4 monomer units to one spin/5.0×10^2 monomer units. A polymer oxidized only to an intermediate green colored state had same spin concentration but a slightly lower ΔHpp of 12.5 gauss. In all cases the ESR signal remained unchanged when exposed to air. Intramolecular collapse of most radical cations into dimeric dications or intermolecular coupling of radical cation to form a diamagnetic ground state are two possible explantions for the low spin concentration. The 10-20 guass signal width is certainly suggestive of a localized spin.

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