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ELECTRONIC CONDUCTION MECHANISM IN POLYCARBAZOLE IODINE COMPLEXES

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ABSTRACT

Recently we have made iodine complexes of nitrobenzene soluble polycarbazoles which are indefinitely stable in air at room temperature and have conductivities as high as 6 $ohm^{-1}cm^{-1}$. GPC analysis reveals that more than a three fold increase in molecular weight occurs upon complexing the solvent cast film with iodine gas. However, some crosslinking is suspected at the highest levels of iodine. The most rapid rise in the conductivity is coincident with the development of significant IR absorption. The increased positive charge that XPS shows developing on the carbazole nitrogen with iodine complexation is consistent with the presence of the type cations which are known to exist in model dicarbazolyl complexes. The mechanism of postpolymerization and conductivity will be discussed in the context of these cations.

INTRODUCTION

Many organic high polymers with conductivities in the semiconducting-to-metallic range (10^{-6} to $10^{4}\Omega^{-1}cm^{-1}$) have been synthesized and studied extensively (1-9). All these polymers in their native or neutral state are still insulators, except $(SN)_x$, but they become highly conducting after modification of their electronic structure by chemical or electrochemical oxidation or reduction(1-9). The electrical conductivity enhancement process is commonly referred to as molecular doping. The resulting oxidized or reduced polymer is essentially a charge-transfer complex formed between the native polymer and acceptor or donor dopants. Notable classes of polymers known to be highly conducting after doping are polyacetylene(1), poly p-phenylene(2), polypyrrole(3), and polymeric bridge-stacked phthalocyanines(4).

Unfortunately, the road to useful conducting polymers that could find practical applications and fulfill their promise is plagued by several severe problems, and none of the above polymeric materials is immune from all of the problems(5-9). Notable are the lack of long-term stability in ambient air, nonprocessibility by solvent and melt techniques, and loss of desired mechanical properties, such as flexibility, after doping. A further important consequence of intractability is that progress in characterization and understanding of structural, molecular, and physical properties of the materials is thereby hampered.

These problems of environmental instability, intractability, and degradation of mechanical properties upon doping, just as the achievable electronic properties, appear to be rooted in the structures (molecular and supra-molecular) of the undoped polymers and the doped conducting complexes. Thus, fundamental solution of these problems is to be sought in new polymer backbone structures which can circumvent the problems and thereby pave the way toward practical applications of the promising new class of electronic materials. Recently, we have undertaken a search for new polymer backbone structures which could lead to a combination of all the desired properties: (1) processibility by solution and/or melt techniques; (2) environmental stability of both doped and undoped polymer; (3) high conductivity ($>0.1\Omega^{-1}cm^{-1}$); (4) good mechanical properties; and (5) molecular design flexibility. Heterocyclic backbone organic polymers seem ideal for achieving this combination of properties. Indeed, we have achieved such a combination of properties in carbazole(10). Some other known heterocyclic conducting polymers include polypyrrole, polythiophene, and the recently reported polymer based on quinoline structure(11) which is highly conducting, and soluble in concentrated acids. However among these only polypyrrole is air stable. Features of these new classes of conducting polymers based on carbazole to be investigated are outlined below.

We have tried to surmount the twin difficulties of lack of processibility and environmental stability of currently known conducting polymers by synthesizing poly 3,3' N-methyl carbazolyl (PC). The basic synthetic outline involves Grignard arylation of a nickel catalyst(12,13) and subsequent crosscoupling to an attacking brominated monomer (Figure 1).

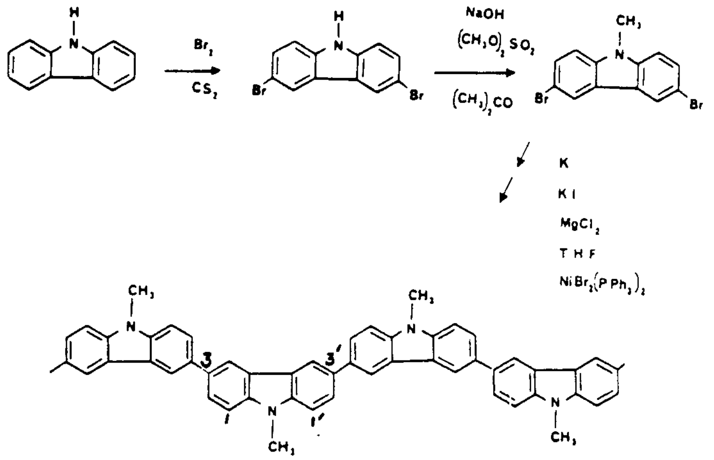


Figure 1 Synthesis of Poly N-Methyl 3,3' Carbazole.

The additional rationale for choosing this polymer was first that N-methyl carbazole forms charge transfer complexes with a wide variety of acceptors. The electrochemical oxidation of disubstituted 3,3' N-dimethyl bicarbazolyls produces air stable radical cations and dications(14,15) which, of course, would be the source of charge transport in any solid complex. The most likely explanation for the stability of the charged species is that unpaired electrons will localize on the nitrogen and on positions ortho (1,1') and para (3,3') to the nitrogen(16). These positions are all blocked from reaction with O_2, H_2O, or other carbazole molecules by replacement of the hydrogen by halogen or alkyl group or by steric hindrance by the N-CH_3 group as, for example, on the 1,1' positions.

An additional feature of the polymer would also be the solubility and melt processibility promoted by the conformational flexibility characteristic of the 3,3' linkages. However, processibility most often will be at odds with high intrachain carrier mobilities which require long un-interrupted lengths of π orbital which require rigid rod molecules; clearly polymers with significant intrachain conformational disorder must exhibit high conductivities through interchain hopping. Although the randomness of the amorphous state precludes the high hopping mobilities achieved in a partially oxidized donor stack(17) (e.g. as in TTF-Br), the stringent requirements for the correct π orbital overlap symmetry between neutral molecule and radical cation(18), which might not be met in the thermodynamically most stable crystal form, can be satisfied, at least some of the time, in the amorphous state. Some preliminary evidence suggesting this as a possiblility has been recently obtained(19).

PROPERTIES OF POLY N-METHYL 3,3' CARBAZOLYL

Recently we have demonstrated that poly N-methyl 3,3' carbazolyl (PC) will form charge transfer complexes with iodine in the ratio of one iodine per carbazole monomer unit(10). Both I_3^- and I_5^- species have been found by Resonance Raman. PC films can be cast from nitrobenzene solution and subsequently exposed to iodine vapor to produce black shiny films of conductivity $1\text{-}10\Omega^{-1}cm^{-1}$. This p-type electrical conductivity is stable in air for many months and shows an Eyring type semiconducting temperature dependence with an activation energy of 0.17 eV. (Figures 2,3) The very low activation energy for conduction is consistent both with a fixed range hopping mechanism (at least in the temperature range -78°C to 100°C) and the strong electronic absorbance that extends well into the mid infrared.

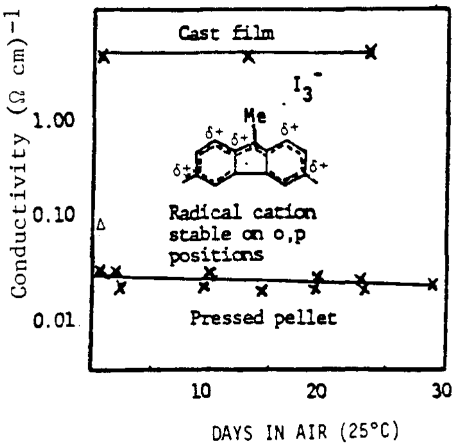


Figure 2 The Environmental Stability of Cast Films and Pressed Pellets of Iodine-Doped Polycarbazole at 25°C. Δ = inductive, x = 4-point probe.

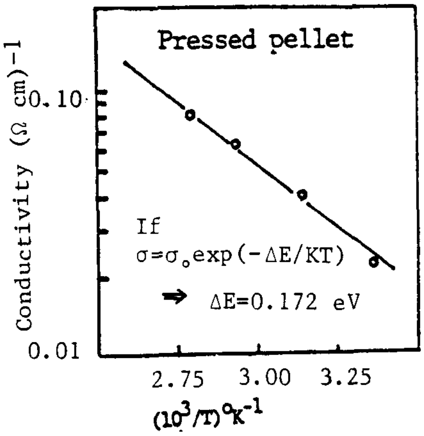
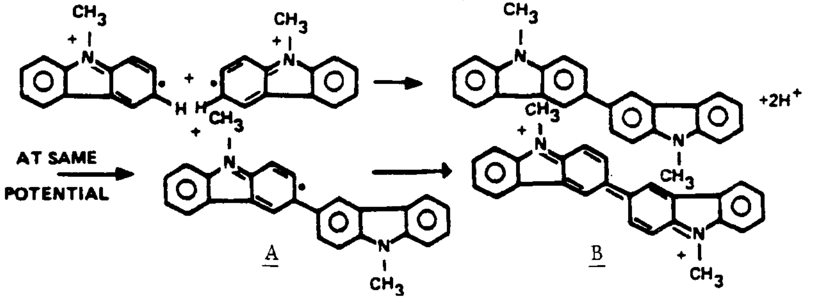


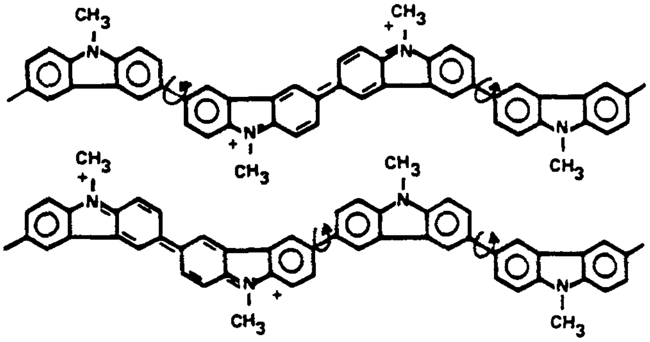
Figure 3 Conductivity as a Function of Temperature for Iodine-Doped Polycarbazole. Small thermoelectric voltage at 25°C indicates p-type carrier.

POSSIBLE CHARGE TRANSPORT MECHANISM

X-ray diffraction reveals that the complexes are quite amorphous. Thus conformational disorder would probably limit π orbital delocalization to only a few adjacent monomer units. With these structural constraints the intermolecular hopping contribution to the conductivity should be quite large. Species similar to the radical cations and dications seen in bicarbazolyl complexes should be responsible for the charge transport. Electrochemical experiments have shown that the disubstituted 3,3' N-methyl bicarbazolyl is oxidized to both radical cation and dication at less anodic potentials than N-methyl carbazole is oxidized to radical cation(15).



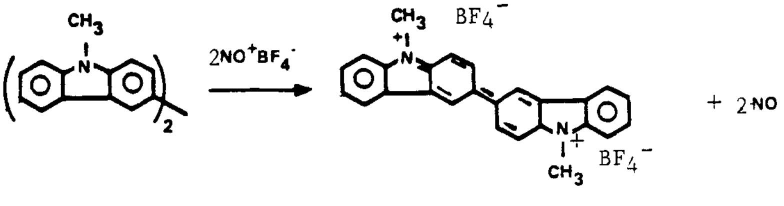
The diimine dication(B) could propagate down the chain bv a hopping process activated by torsional vibrations around biphenyl bonds.



This process is similar to the bipolaron transport mechanism envisioned for a number of polymers(20). Hopping between chains would be facilitated by the close stacking expected between adjacent flat aromatic chains. The most likely possibility here is that intermolecular hops would involve a neutral section of the chain molecule and a cationic section in order to avoid electrostatic repulsion between like cationic sections. If fact even in solution strong bonding forces are known to exist between, for example, TTF^+ and neutral TTF where a distinct intermolecular charge transfer band arises in the spectrum below 1 eV(17).

MODEL COMPOUNDS - PREPARATION AND SPECTROSCOPY

Considering the extensive electrochemical data already available for bicarbazolyl derivatives we decided to undertake a detailed spectroscopic analysis of these model compounds in order to understand the polymer complexes. Wishing to avoid any spectroscopic contributions due to I_x^- we prepared the BF_4^- salts of dicarbazolyl(14).



The blue green bicarbazolyl cation radical salt was easily reduced to neutral bicarbazolyl by $Na_2S_2O_4$ reduction in oxydiethanol to a yellow solid completely soluble in DMF that showed only a single narrow GPC peak at the position expected. Clearly no polymerization beyond dimer had occurred either upon the original oxidation of the neutral material or later in the oxydiethanol solution.

The N,N' dimethyl 3,3' dicarbazolyl tetrafluoroborate was initially thought to be the radical cation salt since the literature preparation was used with one $NOBF_4$ per two N-methyl carbazole molecules. In agreement with B. Bandlish et al.(21) we found a singlet ESR signal. However quantitative double integration of the derivative line and subsequent comparison with a 1,1 diphenyl 2-picrylhydrazyl standard diluted with N-methylcarbazole revealed that only 1.3% of the bicarbazolyl molecules possessed an unpaired spin. The only explanation for this observation is that the salt must be a mixture of neutral molecules and dicationic species.

If the oxidation potential of NO^+ is sufficient to oxidize N-methylcarbazole monomer, dimer can be easily oxidized to the dication as discussed above. Conceivably the solid consists of separate stacks of mixed neutral and dicationic molecules with columns of BF_4^- anions. The usual requirement for the existence of such a salt is that a solution complex can form between the neutral and charged molecules.

This hypothesis was checked by obtaining both the solid state and solution spectra of N,N dimethyl 3,3' bicarbazolyl on a Cary 17 spectrophotometer in the range of 200nm to 2500nm (Figure 4). Both Nujol hydrocarbon with which the solid complex was mixed to form a mull and oxydiethanol solvent did not react with the complex and did not interfere with the complex spectra. The most noticeable features of the visible and near IR spectra of both the solid complex and solution are the two absorbances at 850nm and 1900nm. The neutral molecule displays no absorbance in this region. As suspected the 850nm corresponds to 800nm absorbance found by Ambrose et al(15) for the dication electrochemically generated in acetonitrile solution. Ambrose apparently made no attempt to analyze the near IR transitions of his compound. Since its intensity is proportional to concentration in the fixed path length NaCl solution cell we assume that the transition is associated with an intramolecular charge transfer process.

The 1900nm transition behaves quite differently though in that its intensity increases continuously relative to the 850nm absorbance with increasing solution concentration. Clearly the concentration behavior and the long wavelength of the band associates it with an intermolecular charge

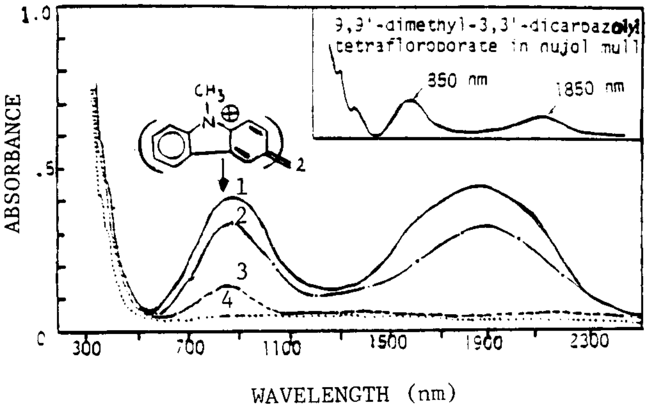


Figure 4 UV-Visible-Near IR spectra of 9,9'-dimethyl-3,3'-dicarbazolyl tetrafloroborate solution in oxydiethanol with same pathlength (0.05 mm), compare to that of 9,9'-dimethyl-3,3'-dicarbazole. (1) 0.035 g/ml; (2) 0.023 g/ml; (3) 0.014 g/ml; (4) 9,9'-dimethyl-dicarbazole, 0.023 g/ml.

transfer process, most probably between neutral and dicationic molecules.. The long wavelength absorbance is not connected with an intramolecular radical cation transition since there is no reason to expect such an entity to be preferred in concentrated solution.

Thus, as hoped for, we have by extrapolation, evidence that short charged and neutral sections of the polycarbazole chain can exchange charge.

POLYMER SPECTROSCOPY

The core level electronic structure of poly N-methyl 3,3' carbazolyl and its saturated iodine complex were examined by x-ray photoelectron spectroscopy (XPS). The neutral polymer was cast onto a glass slide in the form of a thin 2000-3000Å thick film from nitrobenzene solution and then decorated with gold layer thin enough to expose at least some of the surface. The $4f_{7/2}$ peak of Au was used to calibrate the binding energy spectrum of the polymer. The uniformity of surface charging was verified by observing a uniform shift in the Au $4f_{7/2}$ and C 1s upon flooding with thermal electrons. The conducting complex was made in the same thin film form by complexing the thin neutral film with

I_2. Surface charging was not a problem in this sample. A Perkin-Elmer 555 operating at a vacuum of 10^{-8} to 10^{-9} torr and using MgK_α excitation was employed for the XPS analysis. The spectrum was obtained with sample at liquid N_2 temperatures.

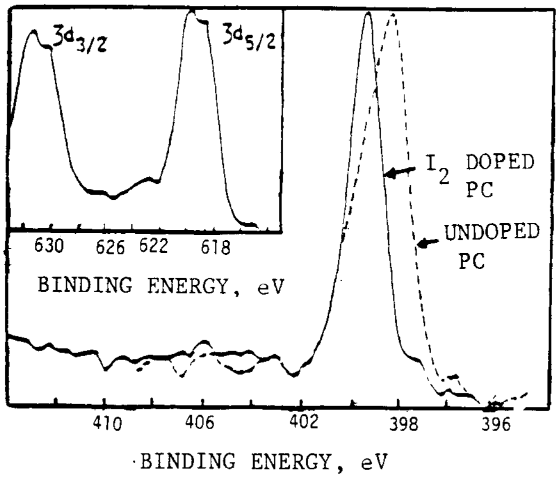


Figure 5 XPS N 1s multiplex of the doped and the undoped poly(3,3'-N-methylcarbazole). The inserted figure is the I 3d mutiplex of the doped polymer.

As expected for charge transfer from the carbazole ring the binding energy of the N-1s increased from 398.6 eV to 399.4 eV upon complexing with iodine (Figure 5). This binding energy difference is reproducible and more than the 0.5 eV resolution of the instrument. The shape of the single component nitrogen peak was quite symmetric suggesting considerable delocalization of the charge evenly among all the nitrogens similar to what has been found in polypyrrole(22).

Both the iodine $3d_{3/2}$ and $3d_{5/2}$ peaks were two component (Figure 5), the lower energy component corresponding to I_x^- and the higher energy peak to adsorbed I_2. Unfortunately separation of various iodine oligomer spectral components is not possible(23) but Resonance Raman clearly shows I_3^- and I_5^-.

The polymer spectra was obtained from a thin film cast onto a NaCl salt plate from 2-chloronitrobenzene solution. After each measurement the same film was complexed with more iodine by exposure to a dilute solution of iodine in CCl_4 at 50°C. Figure 6 shown the evolution of the film spectrum with increased iodine up to the maximum level.

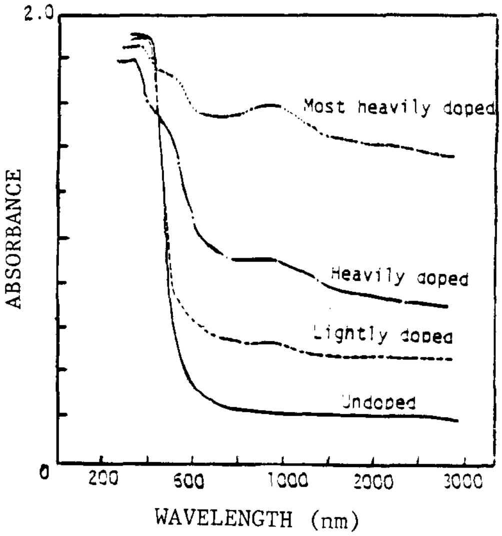


Figure 6 UV-Visible-Near IR spectra of poly(3,3'-N-methylcarbazole) from the same sample with different doping levels.

The polymer complex spectra are much less well defined than the dimer spectra but several features can be identified in addition to the featureless background absorbance. Distinct peaks develop at about 900nm and 550nm and grow more intense with increased iodine content. The 550 nm peak is in a range where there could be significant I_x^- absorbance(24), however the 900nm peak is likely to be related to the 850nm transition found in the dimer complex. If this were true it would be suggestive of the presence of rather localized dicationic structures.

The featureless background must arise from a significant density of states in the band gap. The exact nature of these states is uncertain. However, the model compound work already tells us that strong intermolecular charge transfer between neutral and charged segments already takes place. With only one anion per three carbazole units in the iodine complex such neutral - charged interactions are definitely possible(10). The greater range of possible intermolecular overlaps and the increased chain length of the amorphous polymer would contribute to a range of discreet states, some of which could have an energy difference of only a few hundredths of an eV which is consistent with the mid infrared electronic band seen in Figure 7.

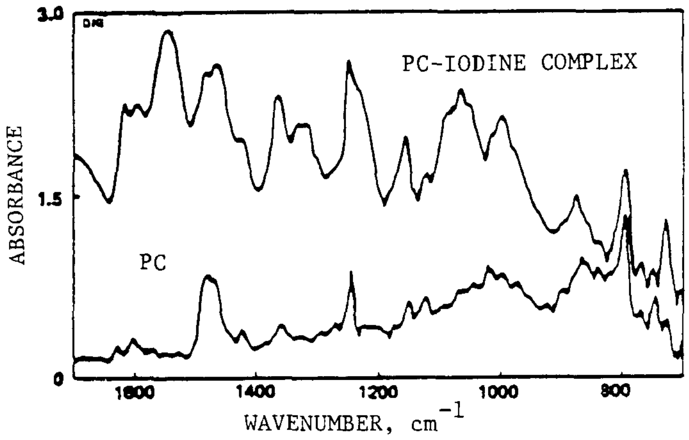
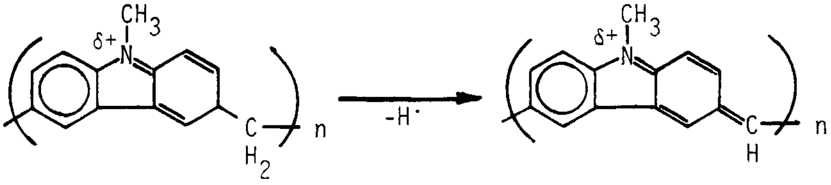


Figure 7 IR absorbtion spectra of lightly doped (iodine) and undoped poly(3,3'-N-methylcarbazole).

The electronic absorbance in the mid IR range is so strong that the vibrational structure is often obscured. However with sufficiently thin films the vibrational structure is obvious. Many of the same bands present in the undoped polymer are present but quite broadened(23). New bands also arise due to the change of force constants and bond symmetry upon doping. For example a new band associated with the aromatic nitrogen carbon stretching arises at 1550cm^{-1}. Many more bands appear in the Raman spectrum in this frequency range (Figure 8). The imine dication structure could reduce the symmetry of the normally Raman active and infrared inactive neutral carbazole bands enough to provide IR activity in the complex.

We attempted to prepare the radical cation of the carbazole by reacting a poly N-methyl carbazolyl 3'3 methylene bis(25), PCMb, in nitrobenzene solution with $NOBF_4$ in a ratio of one oxidant molecule per carbazole unit. The methylene was used to block the formation of diimine dication. The oxydiethanol solution of both the neutral and BF_4^- complex is shown in Figure 9. The transition at 680nm certainly is not representative of the dication. However quantitative ESR reveals that there is a spin on only one in ten thousand carbazole units. The spontaneous decomposition of the radical ion by the following reaction might explain the spectroscopy.



The sp^2 hybridized bridge carbon structure would have a smaller conjugation length than the dimine dication and thus the π-π transition would occur at a shorter wavelength. Conjugation through the bridge carbon is also compatible with the 10^{-3}-10^{-2} ohm^{-1}cm^{-1} conductivities we have observed for iodine complexes of PCMb films.

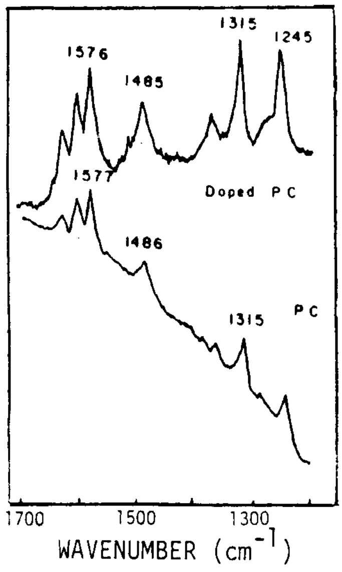


Figure 8 Resonance Raman Spectra of Iodine-doped and Undoped Poly 3,3'-N-methylcarbazole.

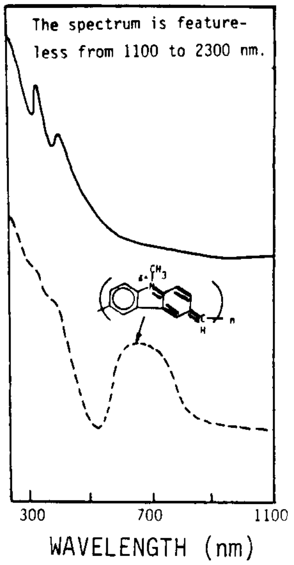


Figure 9 UV-Visible-Near IR spectra of (a) Undoped (b) BF$_4^-$-doped Poly N-methylcarbazole-3,3'-methylene.

RADICAL CATION INDUCED POLYMERIZATION OF CARBAZOLES

Elemental analysis reveals that all bromine end groups which were present in a polymer made from N-methyl dibromocarbazole are removed by complexing the polymer film with iodine. Substantial polymerization clearly occurs when oligomeric carbazole film is exposed to iodine vapor at 50°C

(Figure 10). In fact, as will be reported on in another paper in more detail, carbazole oligomers can polymerize in liquid iodine(26). Significant quantities of HBr gas are released when a mixture of unsubstituted and 3-bromosubstituted carbazoles are mixed. Radical cations of 3,6 disubstituted carbazoles are very reactive and rapidly couple

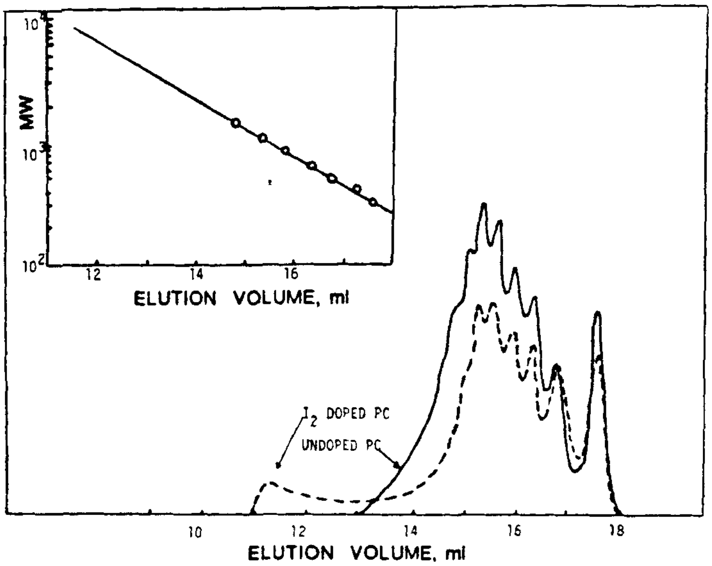
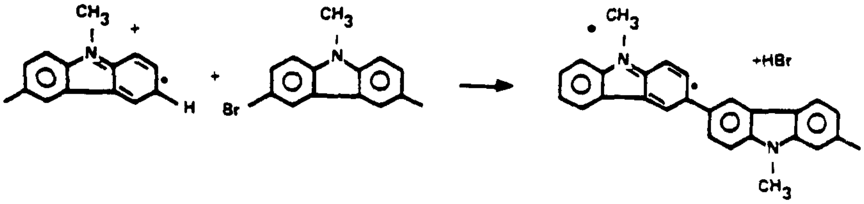


Figure 10 GPC elution curves for undoped and iodine-doped poly 3,3'-N-methylcarbazole, run in the solvent of nitrobenzene at 100 C.
The inserted figure is the calibration curve for the polymer in nitrobenzene.

through the 3,3' positions(15) when the 1,1' positions are blocked by, for example, an N-methyl group. Our polymer originally contains both unsubstituted end groups derived from hydrogenation of unreacted -MgBr ends by reaction with dilute HCl at the end of the reaction. These will then react with any remaining Br ends with the release of HBr gas.



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