Interactions of Linear Conjugated Polymers with Gases

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ABSTRACT: Poly(phenylacetylene) (PPA) and poly(*p*-nitrophenylacetylene) (PNPA) are linear conjugated polymers. These polymers have been shown to exhibit substantial increase in electrical conductivity in the presence of ammonia or water vapor. The present paper reports some physical studies of interactions of these polymers with ammonia and water. It has been found that the electron spin resonance spectrum of PNPA taken under vacuum exhibits a three-line hyperfine structure which in the presence of ammonia gas becomes a single line spectrum similar to that of PPA. The presence of water vapor, however, did not alter the ESR spectra of PNPA. Sorption isotherms of ammonia and water vapor on PNPA have been found to be characteristically different. UV and visible absorption spectra of PNPA taken in the presence of NH_3 indicate that the interaction between the polymer and the gas resulted in more absorption of light in the visible region which suggests the formation of a charge-transfer complex.

The semiconductive polymer has been the subject of intensive research in recent years.[1-3] Although highly conductive polymers which possess useful mechanical and thermal properties have not yet been obtained,[4] many polymers with semiconductive properties have been synthesized.[2]

Semiconductive polymers have been broadly classified as (a) conjugated polymers and (b) polymeric charge transfer complexes.[4] In simplest terms, the conjugation can be defined as a chemical structure which contains double bonds that alternate with single bonds.[5] In a highly conjugated system, delocalization of π electrons generally occurs, and the delocalization is presumably responsible for the observed electronic conductivity in the conjugated polymers. The observed electrical conductivity of *linear*, conjugated polymers is generally low, less than 10^{-10} ohm^{-1} cm^{-1} at 25 °C.[6] Although a charge carrier can move through the conjugated chain without much interruption, its movement is interrupted at the end of the chain where an intermolecular barrier constitutes a large energy gap for further charge transport. To facilitate the charge transport across the intermolecular barrier, either the polymer can be complexed with a suitable acceptor (or donor) or its structure can be modified such that extended conjugation is obtained. Enhanced conductivity is generally obtained in polymers with extended conjugation. Extended conjugation, however, usually resulted in a polymer which is insoluble or infusible and the polymer no longer possesses useful "plastic" properties.

Among various linear conjugated polymers which have been studied, poly(phenylacetylene)[7,8] and its derivatives are of considerable interest. It has been reported that NASA and HUD are supporting development of a low cost early warning fire detection system based on poly(phenylacetylene).[9,10]

The conductivity of poly(phenylacetylenes) at room temperature is low, in the order of 10^{-16} ohm^{-1} cm^{-1}.[6,11] The molecular weight of the polymers synthesized by various methods is also low, less than 20 000. The polymers are generally soluble in organic solvents in contrast to other highly conjugated polymers which are often insoluble. The polymers can be cast into film or coated as a thin layer on a suitable substrate without great difficulty. Although some of the polymers are known to exhibit measurable change in electrical conductance in the presence of certain gases,[9,10] a detailed study on such polymer–gas interactions has not been reported.

In this paper, we wish to report the syntheses and characterizations of high molecular weight poly(phenylacetylene) (PPA) and poly(*p*-nitrophenylacetylene) (PNPA) and the studies of their interaction with ammonia and water vapor.

The interactions have been studied by a variety of physical techniques. Electron spin resonance spectra of PNPA taken under vacuum exhibit a three-line hyperfine structure which in the presence of ammonia gas becomes a structureless single line similar to that of PPA. The presence of water vapor, however, did not alter the ESR spectra of PNPA. Sorption isotherms of ammonia and water vapor on PNPA have been found to be characteristically different. UV and visible absorption spectra of PNPA taken in the presence of NH_3 indicate that the interaction between the polymer and the gas resulted in more absorption of light in the visible region. The breadth of the spectra indicates the weak nature of the interaction and suggests the formation of a charge-transfer complex.

Experimental Section

Materials. Phenylacetylene was obtained from Aldrich Chemical Co. It was vacuum distilled before use. Tungsten hexachloride (WCl_6) (resublimed, 99%) was obtained from Ventron Corp., Danvers, Mass.

Polymer Synthesis and Characterization. A. Poly(phenylacetylene) (PPA). PPA was prepared by two methods: (a) thermal polymerization[7] and (b) polymerization catalyzed by WCl_6.[12] Low molecular weight PPA-t was obtained by a thermal polymerization method. In this method, 48 mL of distilled phenylacetylene was mixed with 160 mL of distilled chlorobenzene and heated under dry nitrogen atmosphere at reflux temperature for 48 h. The polymer showed a deep red color in the solvent (chlorobenzene) and became a yellow powder upon reprecipitation from the chlorobenzene solution when adding methanol.

The polymer was amorphous and the number average molecular weight of PPA-t was 800 as determined by a Wescan Model 232 vapor phase osmometer. An IR spectrum of PPA-t is shown in Figure 1. The spectrum is virtually identical with the one published by Okamoto et al.[7] At room temperature the resistivity of the polymer was reported to be 10^{16} ohm cm and has an apparent energy gap of 0.963 eV.[7] Elemental analysis of the polymer gave the carbon and hydrogen contents which were in agreement with the calculated values. The properties of PPA-t are listed in Table I.

High molecular weight PPA-C was obtained by polymerization of phenylacetylene catalyzed by WCl_6.[12] In this method, 86 mL of distilled phenylacetylene was mixed with 430 mL of distilled benzene at 30 °C and 2.43 g of WCl_6 and 0.06 mL of H_2O were also added to the monomer/solvent mixture. Polymerization was carried out under a dried nitrogen atmosphere at 30 °C for 1 h. After polymerization, the polymer was twice precipitated from benzene with methanol and dried in a vacuum oven at 45 °C for 3 days and stored at −10 °C. Since WCl_6 is soluble in methanol,[13] most of the WCl_6 was removed from the polymer when the polymer was twice precipitated from benzene with methanol. An emission spectrographic analysis of the PPA-C indicated that less than 50 ppm of WCl_6 remained in the polymer. An IR spectrum of PPA-C is shown in Figure 2. The spectrum is virtually identical with the one published by Masuda et al.[14] Characterization of PPA-C is shown in Table I.

B. Poly(*p*-nitrophenylacetylene) (PNPA). PNPA-t and PNPA-C were obtained by nitration of PPA-t and PPA-C respectively. The nitration of PPA has been carried out by reacting the polymer with nitric acid in nitromethane.[15] In the present work, nitration of both PPA-t and PPA-C was carried out by reacting the polymers with a mixture of H_2SO_4 and HNO_3. It was found that the

Table I
Characterization of PPA and PNPA

Polymer	Composition, wt %				No. av mol wt	Deg of polymerization
	C	H	N	O		
PPA-t	93.8	6.2	0	0	800	8
PPA-C	93.5	5.8	0	0.7	12300	120
PNPA-t	57.8	3.2	9.7	29.3	1200	8
PNPA-C	71.7	4.1	6.4	17.8	2000	14

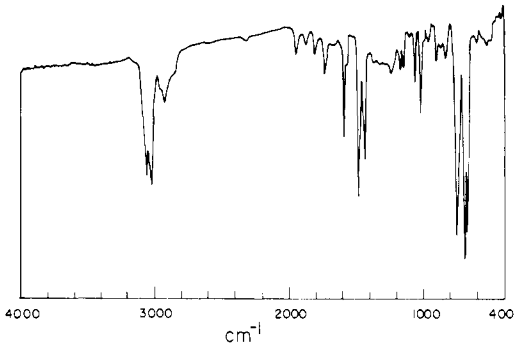

Figure 1. Infrared spectrum of poly(phenylacetylene)-t.

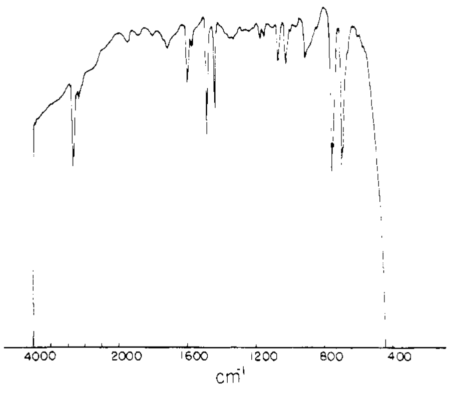

Figure 2. Infrared spectrum of poly(phenylacetylene)-C.

polymers obtained from the nitration of PPA-t all showed brown color. The deepness of the color, however, depends on the experimental conditions. In Table II, the experimental conditions (nitration procedure) of the polymers obtained are described. The polymers obtained were characterized by IR spectroscopy. IR spectra of polymers taken after nitration show major absorption bands occurring in the range 2900–3100 cm^{-1} (aromatic C–H stretching), at 1600, 1560, and 1440 cm^{-1} (C=C skeletal in-plane vibration), and at 1350 (NO_2 symmetric stretching) and 1520 cm^{-1} (NO_2 asymmetric stretching). It was found that IR spectra of all nitrated polymers are virtually identical except that the absorption intensity at 3000 cm^{-1} (aromatic C–H stretching) and at 1350 and 1520 cm^{-1} varied from sample to sample. This indicates that the polymers vary in the degree of nitration. The IR sepctra of PNPA-4 is virtually identical with that of poly(*p*-nitrophenylacetylene) synthesized by Simionescu et al.[16]

PNPA-4 was found to be soluble in acetone and butanone. When PNPA-4 was further reacted with the acid mixture for 30 min, its IR spectra showed a very weak band at 3000 cm^{-1} probably an indication of formation of poly(2,4-dinitrophenylacetylene). Both PNPA-t and PNPA-C were prepared under the experimental conditions used in preparing PNPA-4. IR spectra of PNPA-t and PNPA-C are shown respectively in Figures 3 and 4.

Elemental analyses of both PNPA-t and PNPA-C were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. The results of elemental analysis indicated that PNPA-t contained slightly more than one NO_2 group (1.15) per monomer unit, but PNPA-C contained less than one NO_2 group (0.61) per monomer unit. The carbon, hydrogen, nitrogen, and oxygen contents of PNPA-C determined from elemental analysis are in agreement with calculated values. However, PNPA-t contains 6.5% more of oxygen than the calculated value. The "extra" amount of oxygen is probably due to the oxidation of an end group during nitration, but its exact nature is not known. The molecular weight of PNPA-C is much lower than PPA-C. This indicates that degradation occurred in PPA-C during nitration. The properties of both PNPA-C and PNPA-t are listed in Table I.

Table II
Experimental Conditions for Nitration of PPA-t

Polymer	HNO_3:H_2SO_4 vol ratio, total volume, mL	PPA-4 used, g	Reaction temp, °C	Reaction time, min
PNPA-1	5:3, 80	9.28	10	20
PNPA-2	5:3, 80	9.28	10	10
PNPA-3	13:17, 30	1.5	0	17
PNPA-4	9:5, 70	7.0	0	10
PNPA-5	5:3, 40	5.39	0	11

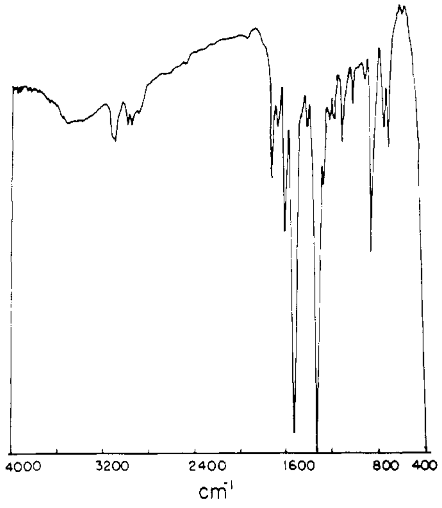

Figure 3. Infrared spectrum of poly(*p*-nitrophenylacetylene)-t.

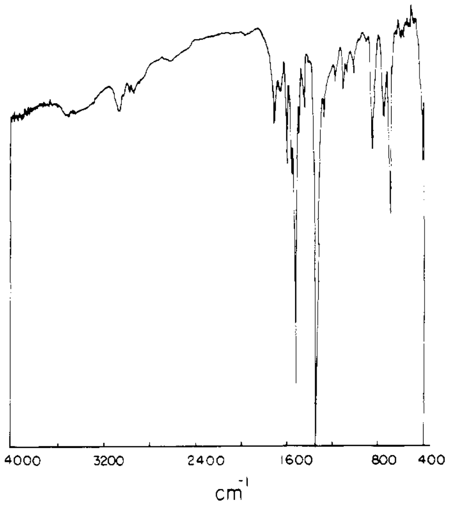

Figure 4. Infrared spectrum of poly(*p*-nitrophenylacetylene)-C.

Preparation and Characterization of Polymer Films. The

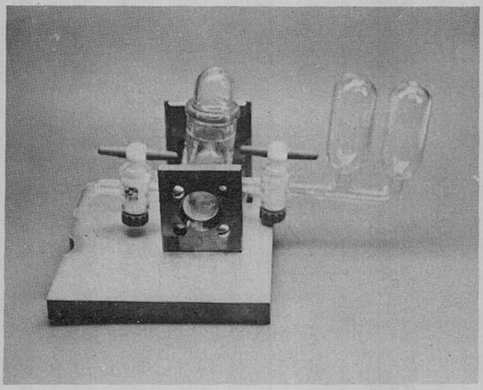

Figure 5. Photograph of the cell used for UV–visible spectroscopy.

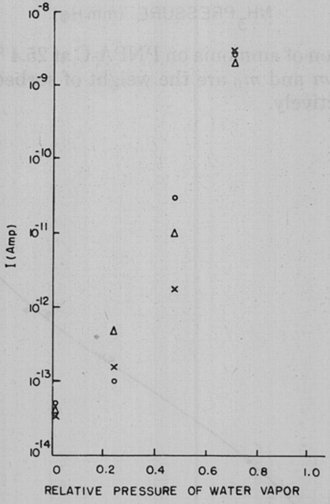

Figure 6. Dc current vs. relative pressure of water vapor at 23 °C and 6 V of applied voltage. (X) electrode without polymer coating; (△) electrode coated with 1.8-μm PPA-C film; (○) electrode coated with 0.9-μm PPA-C film.

polymer films coated on the sapphire substrate were prepared from a polymer solution by spin coating. The film thickness was measured by a Bendix proficorder. It has been observed that low molecular weight PPA-t and PNPA-t films prepared by spinning 5% polymer solution in butanone at 1500 rpm have many cracks, but high molecular weight PPA-C and PNPA-C films prepared by the same method are virtually crack free.

Electrical Measurement. To measure the conduction current of polymer films exposed to gases, a sensing device similar to the lateral resistor of McClure[17] has been used. The device mainly consists of interdigitated gold fingers deposited on a sapphire substrate. The width of a finger is 1 mil and the spacing between two fingers is 2 mil. There are approximately 300 fingers in a sensor and the thickness of the electrode is 500 Å. Polymer films were coated over the electrode by spin coating. After coating, the films were dried in a vacuum oven at 50 °C for more than 24 h. The electrode was placed inside a bell jar and the device current was measured before and after exposure to selected gases at different pressures.

Before a gas was introduced into the system for testing, the system was evacuated to 10^{-3} mm of Hg. Testing was conducted at room temperature (23–25 °C). The polymer films tested ranged from 0.5 to 2.0 μm. The voltage across the resistor was usually 10 V. A Keithley Model 616 digital electrometer was used to measure the conductance of the electrode.

Mass Sorption Experiment. The gas sorption apparatus is basically a quartz spring balance (Worden Quartz Products, Inc.). The spring and balance pan are suspended in a glass vacuum chamber which is jacketed by a constant temperature water bath (±0.1 °C). Two quartz springs used in the present work were calibrated with known weights and had sensitivities of 1.97 and 0.66 mg/mm. The pressure of the chamber was measured with an MKS Baratron capacitance manometer. The mass sorption apparatus was attached to a vacuum line connected to the polymer conductance measurement chamber, and the mass sorption data were taken concurrently with the electrical current measurement. In the mass sorption experiment, 50.0 mg of polymer powder was placed in a quartz pan, and the weight increase due to gas sorption was determined by measuring the elongation of the spring with a cathetometer.

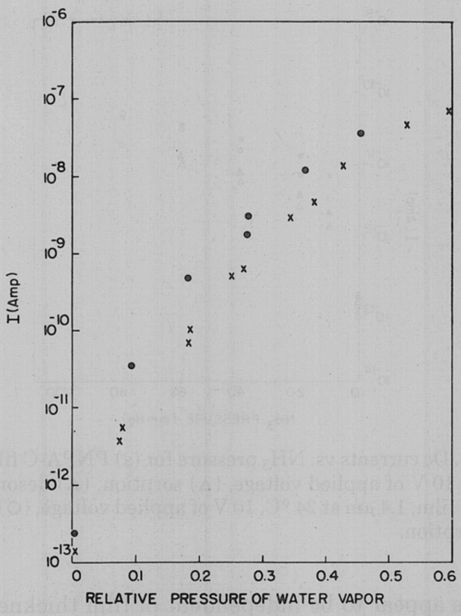

Figure 7. Dc currents vs. water vapor pressure for PNPA-C film, 0.9 μm, at 24 °C: (X) sorption, (●) desorption.

Electron Spin Resonance. ESR spectra were recorded on a Varian E-3 spectrometer at room temperature. To obtain ESR spectra of polymers with and without the presence of NH_3 gas, a small gas chamber was attached to a Pyrex tube 5-mm o.d. which contained the polymer. The gas chamber is separated from the polymer by two vacuum stopcocks and a three-way connector.

To fill the gas chamber with NH_3 gas, the apparatus was attached to a vacuum line and the polymer was dried under a reduced pressure of 10^{-2} mm of Hg for 20 h. After drying, the polymer was isolated from the chamber and the chamber was filled with gas. After filling, the chamber stopcock was closed, and the tubing between the stopcocks was evacuated and sealed off. The ESR spectra of dried polymers under vacuum were taken while both stopcocks remained closed. The ESR spectra of polymer in the presence of the gas were taken after both stopcocks were opened.

UV and Visible Spectroscopy. A test cell was designed and built so that UV and visible transmission spectra of a quartz substrate coated with the polymer film could be taken in the presence of NH_3 or water vapor. The cell was constructed from 2.5-cm i.d. Pyrex tubing, 4.0-cm long, with 1-mm thick quartz windows cemented to the both ends. The substrate was inserted into the cell through a ground glass standard taper joint and supported on a stainless steel frame which is held by spring tension in the sealed off male half of the joint. A gas reservoir with a stopcock is sealed to one side of the cell and the other side of the cell is connected to a tube with a stopcock. The cell is mounted on a brass plate with a kinematic mounting for positive positioning in the spectrometer. (See Figure 5.)

A Cary 14 recording spectrophotometer was used to determine the spectral transmission of the samples. The instrument was adjusted to read 100% transmission without the test cell. The transmission of the substrate without polymer coating inside the test cell and the transmission of the substrate with polymer coating were determined under vacuum, in the presence of ammonia or in the presence of water vapor.

Results and Discussion

Electrical Measurements. The results of electrical measurements are shown in Figures 6–8. In Figure 6, the dc conduction currents vs. relative pressure of water vapor are plotted for two PPA-C films of different thickness (1.8 and 0.9 μm, respectively) coated on the electrode and for the electrode without polymer coating. It is seen that water vapor has a significant effect on the conductance of each material and at high relative pressure ($P/P \geq 0.7$), the measured dc

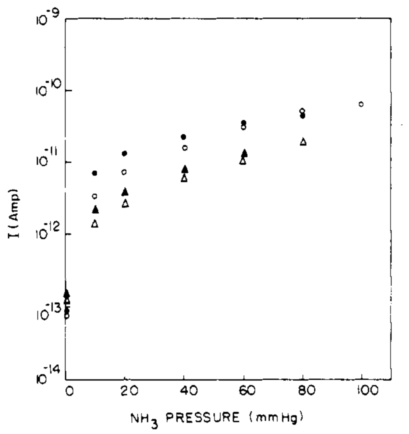

Figure 8. Dc currents vs. NH_3 pressure for (a) PNPA-C film, 0.9 μm at 25 °C, 10 V of applied voltage, (△) sorption, (▲) desorption; (b) PNPA-C film, 1.4 μm at 24 °C, 10 V of applied voltage, (○) sorption, (●) desorption.

currents appear to be independent of film thickness or the nature of the materials. In Figure 7, dc currents vs. relative vapor pressure of water are plotted for a 0.9-μm PNPA-C film. It is seen that the conductance of the polymer film is also affected significantly by the presence of water vapor and at the same relative pressure of water vapor, the conductance of the PNPA-C film is seen to be larger than that of the PPA-C film shown in Figure 7.

Although the presence of 80-mm NH_3 appears to have negligible effect on the conductance of both PPA-C films and the electrode without polymer coating, it has been found that NH_3 gas has a significant effect on the conductance of both PNPA-C and PNPA-t films. In Figure 8, dc currents vs. NH_3 pressure are plotted for two PNPA-C films, being 1.4 and 0.9 μm, respectively. It is seen that the presence of NH_3 gas has a significant effect on the conductance of PNPA-C films and the measured currents increase with (a) increase in polymer film thickness and (b) increase in ammonia gas pressure. At 80-mm NH_3, the ratio of dc current measured after exposure to NH_3 gas to the current measured before exposure is approximately 600.

The electrical conduction mechanism in the polymers is complicated and not quite understood. The theoretical description of the observed behaviors shown in Figures 6–8 is difficult and has not been attempted. However, present electrical measurements clearly have shown that (a) the conductivity of PNPA-C is greatly increased in the presence of NH_3 or water vapor, (b) the increase in conductance in the presence of NH_3 cannot be totally attributed to the surface conduction but must involve bulk reaction, and (C) since NH_3 has a negligible effect on the electircal properties of PPA but has significant effect on that of PNPA, the interaction between NH_3 and the NO_2 group of PNPA must be responsible for the change in conductivity.

To understand the nature of interaction which is responsible for increase in electrical conductivity, the interactions between the polymers and the gases have been studied by a number of physical techniques including gas sorption, UV and visible spectroscopy, and electron spin resonance. Since PNPA-t obtained in the present work contains some extra oxygen whose nature and status has not yet been clarified, the interaction studies have been carried out mainly on PNPA-C.

Gas Sorption. Sorption isotherms for NH_3 and for water vapor on PNPA-C are shown in Figures 9 and 10, respectively. The sorption isotherm of NH_3 on PNPA-C is similar to that of type I and the isotherm for water vapor is similar to that of type II according to BET classification.[18,19] Type I generally

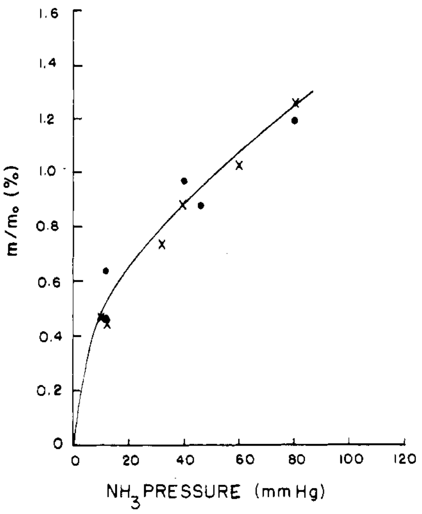

Figure 9. Sorption of ammonia on PNPA-C at 25.4 °C: (X) sorption, (O) desorption. m and m_0 are the weight of sorbed molecules and polymers, respectively.

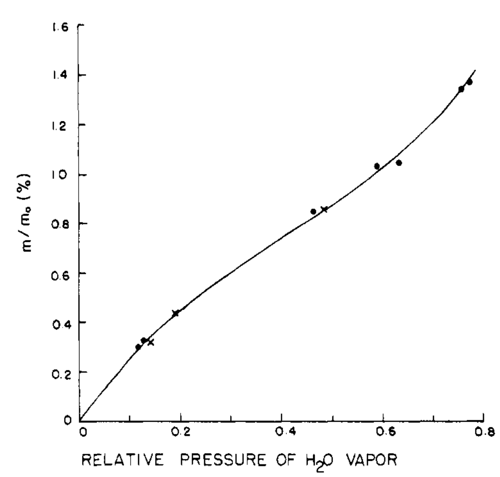

Figure 10. Sorption of water on PNPA-C at 25.4 °C: (●) sorption, (X) desorption. m and m_0 are the weight of sorbed molecules and polymers, respectively.

represents initial sorption on some kind of specific sites in the polymer. When the sites are nearly all occupied, a small amount of penetrant dissolves in the polymer with a more or less random distribution. Type II generally represents initial sorption on specific sites at low pressure; however, at high pressure, association or clustering of sorbed molecules predominates.[19] Since NH_3 is chemically basic with one lone pair of electrons and the NO_2 group is a strong electron-withdrawing substituent, NO_2 groups in PNPA represent specific sites for sorption of NH_3. Since both H_2O molecules and NO_2 groups are polar, NO_2 groups in the polymer also represent specific sorption sites for H_2O water molecules.

The sorption isotherms determined in the present work have been analyzed according to BET equation for multilayers of sorption

$$\frac{x}{m(1-x)} = \frac{1}{CM_m} + \frac{(C-1)x}{CM_m}$$

where m is the weight of sorbed molecules, M_m is the weight of the monolayer, x is the relative pressure of gas, and C is a constant. A plot of $x/(1-x)m$ vs. x should yield a linear line if the isotherm can be represented by BET isotherm. The plots for NH_3 and water vapor sorption isotherm for water can be satisfactorily represented by the BET equation up to $P/P_0 \sim 0.5$. The monolayer sorption for water vapor on PNAP-C, as

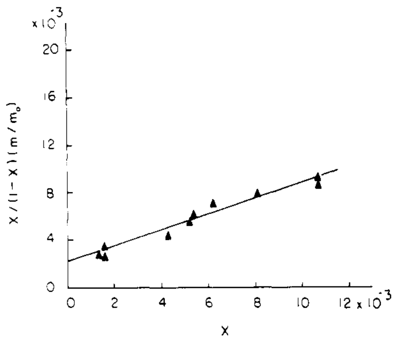

Figure 11. BET equation plot for sorption of ammonia on PNPA-C.

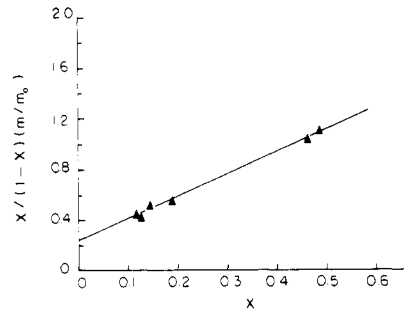

Figure 12. BET equation plot for sorption of water on PNPA-C.

deduced from the linear plot, is 0.5 wt %. The monolayer sorption for NH_3 on PNPA-C as deduced from the linear plot is found to be 1.3 wt %. The former value corresponds to equilibrium uptake of water by PNPA-C at 0.23 relative pressure. The later value corresponds to equilibrium uptake of NH_3 by PNPA-C at a pressure of 90 mm of Hg.

UV and Visible Spectroscopy. Both PNPA and PPA are linear conjugated polymers with aromatic side groups attached to the main chain. In addition to this, PNPA also contains NO_2 groups which have nonbonding electrons in both nitrogen and oxygen atoms. Both polymers contain many chromophores which can absorb ultraviolet and visible radiation originating from electronic transitions. The results of present optical absorption studies are shown in Figures 13 and 14 where percent transmittance of PNPA-C and PPA-C films in vacuum and in NH_3 is plotted against wavelength. In the UV–visible region, from 3000 to 8000 Å, where the optical absorption studies were carried out, it has been found that the presence of NH_3 (90 mm) or water vapor (7 mm) inside the test cell without polymer coatings did not induce any detectable change in light transmittance. However, both PNPA-C and PPA-C films absorb UV and visible light strongly. It is seen from Figure 14 that the cut-off wavelengths for PNPA-C and PPA-C are 4600 and 3000 Å, respectively. Since λ_{max} for the nitro group occurs at 2800 Å,[20] the introduction of the NO_2 group into PPA apparently has the hypsochromic effect of shifting $\pi \rightarrow \pi^*$ transition to shorter wavelength.

Of special interest is the effect of NH_3 on absorption spectra of the PNPA-C film. It has been found that the presence of water vapor did not alter the absorption spectra of either the PNPA-C film or the PPA-C film; nor was the spectra of the PPA-C film affected by NH_3. However, it has been found that the optical absorption of the PNPA-C film is noticeably increased by the presence of NH_3. In Figure 13 the absorption spectra of PNPA-C in the presence of 93-mm NH_3 is shown along with the spectra of PNPA-C under vacuum. The difference between the two spectra is plotted as a function of wavelength in Figure 14. It is seen that the difference occurs at 5200 Å which corresponds to maximum absorption of light originating from polymer–gas interaction.

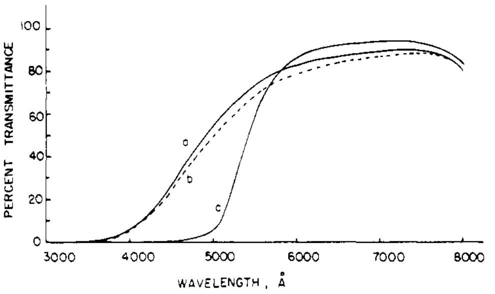

Figure 13. Ultraviolet and visible spectra: (a) PNPA-C under vacuum (b) PNPA-C in 93-mm NH_3, (C) PPA-C under vacuum.

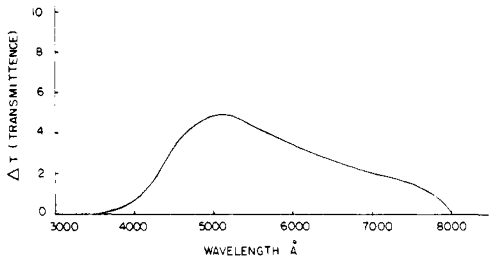

Figure 14. Difference between the transmittance spectra of PNPA-C taken under vacuum and in 93-mm NH_3.

It is well known that a charge-transfer complex is formed between a doner, an electron rich molecule, and an acceptor, an electron attracting molecule. The formation of a charge-transfer complex is usually characterized by an electronic absorption band associated with the transfer of an electron from the doner to the acceptor.[21] Since the NO_2 group is an electron-withdrawing group and NH_3 is an electron-rich molecule with a lone pair of electrons, one must conclude that the UV–visible absorption band of PNAP-C associated with the presence of NH_3 is most probably a charge-transfer absorption band attributable to the formation of the charge-transfer complex. The breadth of the band suggests the loose nature of binding in the ground state of the complex.[21]

Electron Spin Resonance. The results of ESR experiments at room temperatures are shown on Figures 15 and 16. ESR spectra of both PPA-C and PPA-t are broad single-line spectra with a peak-to-peak width of ~10 G (Figure 15). The peak-to-peak width of PPA-C is 10.7 G which is somewhat broader than that of PPA-t, 9.5 G. ESR spectra of PNPA-C under vacuum and in 94 mm NH_3 are shown in Figure 16. The ESR spectrum of PNPA-C under vacuum (Figure 16a) is a three-line hyperfine structure similar to the rigid glass spectrum of nitroxides.[22] It was found that when the polymer was exposed to NH_3 (94 mm of Hg), the three-line hyperfine structure of PNPA-C disappeared. When NH_3 was removed from the polymer, the ESR spectrum again showed the three-line hyperfine structure. A close inspection of the ESR spectrum of PNPA-C under vacuum revealed that the spectrum actually consisted of two spectra superimposed, a three-line structure and a single-line spectrum similar to that of PPA.

The paramagnetism in poly(phenylacetylene) has been observed by many workers.[23-25] Although impurities in the polymer, creation of radicals by heat, or radiation during the synthesis could be the source of paramagnetism in PPA, it has been demonstrated[26] that the paramagnetism in thermally polymerized PPA cannot be due to interaction with oxygen but rather to a property of the chemically uncontaminated polymer.

Figure 15. Electron spin resonance spectra of PPA-t.

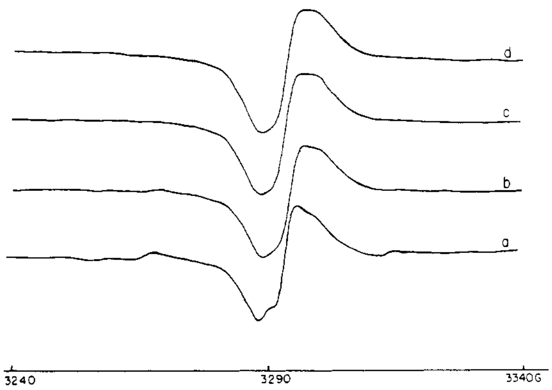

Figure 16. Electron spin resonance spectra of PNPA-C: (a) under vacuum; (b) 10 min after 94-mm NH_3 was introduced; (c) 30 min after 94-mm NH_3 was introduced; (d) 1 h after 94-mm NH_3 was introduced.

Simple concepts of the electronic structure of the conjugated systems do not predict paramagnetism in PPA.[26] Paramagnetism in PPA often has been explained by the "bond alternation defect" model of Pople and Walmsley.[27] Recent experimental work by Byrd et al.[23] appears to have substantiated the theoretical prediction of Pople and Walmsley. Byrd et al. have measured the electrical conductivity and ESR absorption of poly(phenylacetylene) and its derivatives which have a nitrogen-containing group (NH_2, NO_2, and NHCO) in the phenyl ring, i.e., poly(*p*-aminophenylacetylene), poly(*p*-nitrophenylacetylene), and poly(*p*-formamidophenylacetylene). They have observed that the introduction of the nitrogen-containing groups results in an increase in the number of unpaired electrons, an increase in the electronic conduction and activation energy of the polymer, and the appearance of a three-line hyperfine structure in the ESR spectra of poly(*p*-nitrophenylacetylene) and poly(*p*-formamidophenylacetylene) (PFPA). They believed that these observations are consistent with the "bond alternation defect" model of Pople and Walmsley. In PNPA and PFPA polymers, the high electronegative nature of the NO_2 and the NHCO groups causes the localization of the unpaired electrons and results in a three-line hyperfine structure. It was also suggested that localization of the unpaired electrons by the nitrogen group in the phenyl ring would prevent coupling of some unpaired electrons and, therefore, increase the spin concentration and electric conductivity. ESR spectra of solid polymer PPA and of the PPA solution have been published.[23,26,28] The spectra taken at room temperature all show a structureless single line of peak-to-peak width of 10 G which are in agreement with the present observations. ESR spectra of PNPA-C taken under vacuum at room temperature consist of two spectra superimposed, a three-line structure and a single line. It is believed that the three-line structure originates from the localization of unpaired electrons by NO_2 groups resulting in the interaction of the electron with the nitrogen nucleus (N,[14] $I = 1$) giving the three-line structure as suggested by Byrd et al.[23] However, since PNPA-C has an average of 0.6 NO_2 group per monomer unit (see Table I), its ESR spectra consequently possess both a three-line structure of PNPA and a single-line structure of PPA. The broadness of the spectra obviously is due to the slow motion of polymer molecules at room temperature.

The disappearance of a three-line structure in the PNPA-C spectra when the polymer is exposed to NH_3 can be interpreted as follows. When PNPA-C is exposed to NH_3 gas, the highly electronegative NO_2 groups of PNPA-C interact with NH_3 to form a charge-transfer complex $P^-NH_3^+$, where P^- designates the electron acceptor, the polymer (PNPA-C). The electronegativity of NO_2, apparently reduced by the formation of a charge-transfer complex with electron doner, is no longer powerful enough to induce the localization of the unpaired electron resulting in the disappearance of the nuclear hyperfine structure. It should be pointed out that according to the "bond alternation defects" model, the motion of nonlocalized unpaired electrons may result in coupling of some unpaired electron and, therefore, decrease the spin concentrations and perhaps conductivity as well, as suggested by Byrd et al.[23] This implied that when the polymer is esposed to NH_3, the spin concentration and conductivity of PNPA-C could be decreased. However, we have not observed any significant change in spin concentration when the polymer is exposed to NH_3 gas. The conductance of the polymer film, as noted previously, increases significantly with the presence of NH_3 gas. It is generally recognized[29] that the spin concentration and the charge carrier concentration in many conjugated polymers do not correlate. The spin concentration may be due in part to an impurity and a defect structure of the polymer as well as due to charge carriers. In a conjugated polymer where the change carrier can move freely within the chains, the macroscopic conductivity may reflect primarily the transitions between chains.[30] It is clear, therefore, that the interaction between PNPA-C and ammonia has facilitated the intermolecular charge transport and has done so without a significant increase in the spin concentration.

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Selective Complexation of Macromolecules

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ABSTRACT: It is well known that different macromolecules may interact with each other to form an interpolymer complex. A study is made of the inter-chain macromolecular selective complexation of the type of $P_1 + P_2 + P_3 \rightarrow (P_1\text{–}P_2)$complex $+ P_3$ (where both P_1 and P_3 are able to interact with P_2 individually), taking as an example: P_2 is poly(methacrylic acid) and P_1 and P_3 are chosen at will among poly(4-vinylpyridine), poly(2-vinylpyridine), poly(*N*-vinylpyrrolidone), poly(vinyl alcohol), poly(acrylamide), poly(ethylene oxide), oligo(ethyleneimine), and an integral type polycation. Selective interpolymer complexation is realized through such factors as interaction forces, solvents, ionic strength, chain length, and so on. Moreover, a substitution reaction of the type $(P_2\text{–}P_3)$complex $+ P_1 \rightarrow (P_1\text{–}P_2)$complex $+ P_3$, taking the same samples as mentioned above, progresses through two different paths.

Biological systems are so skillful that a macromolecular chain may effectively select a complementary one to form an interpolymer complex in order to operate very specific functionalities. Synthetic polymers can also form interpolymer complexes,[1–4] but the ability of a synthetic polymer to select only one component polymer as in biological systems has not yet been realized except in the several specific systems of a pair of polymers which include one of a complementary base pair of nucleic acid individually, e.g., poly(A)–poly(U) and poly(I)–poly(C).[5,6] The authors have already reported the complexation mechanisms in various systems composed of synthetic polymers.[7–9] The interpolymer complex formation of synthetic polymers is controlled by many factors, such as interaction forces, solvents, ionic strength, temperature, and so on. These factors suggest that the selective interpolymer complexation can be realized under suitable conditions.

Experimental Section

Materials. Poly(methacrylic acid)(PMAA). Purified methacrylic acid (MAA) (distilled twice in vacuo, bp 63 °C (12 mm Hg)) was polymerized with $K_2S_2O_8$ as an initiator in aqueous solution. The monomer concentration was 0.2 mol/L and the polymerization time was 5 h in nitrogen atmosphere at 50 °C. The reaction mixture was evaporated and dissolved into methanol and then reprecipitated twice from ethyl acetate. The molecular weight of the polymer was calculated from viscosity data,[10] and $\overline{M}_w$ was calculated to be 6.8×10^4.

Poly(L-glutamic acid) (PGA). A 0.5–1.0 wt % aqueous solution of poly(sodium L-glutamate) ($\overline{M}_w$ = 50 000) was passed through a column, 3 cm in diameter and 30 cm in length, filled with an ion-exchange resin, Dow Chemical IR-120, and the pH of the eluent was 3.3. The pH of the solution was then adjusted by partially neutralizing PGA with 0.1 N NaOH aqueous solution.

Poly(4-vinylpyridine) (P4VP) and Poly(2-vinylpyridine) (P2VP). P4VP and P2VP were prepared by the radical polymerization of 4-vinylpyridine and 2-vinylpyridine respectively under the following conditions: [monomer] = 2.0 mol/L, [AIBN] = 0.05 mol/L, in methanol at 70 °C for 6 h under nitrogen atmosphere. The monomers and the initiator were purified by distillation or recrystallization according to the usual manner. The resulting polymers were reprecipitated twice from ethyl ether. The degrees of polymerization ($\overline{P}_n$) of the polymers obtained were 49 for P4VP and 108 for P2VP, respectively, by means of vapor-pressure osmometry in methanol.

Poly(*N*-vinylpyrrolidone) (PVPo) and Poly(acrylamide) (PAAm). Purified monomers (bp 94–96 °C (13 mm Hg) for *N*-vinylpyrrolidone and mp 84–85 °C for acrylamide) were polymerized by radical polymerizations in methanol under nitrogen atmosphere at 70 °C for 5 h ([monomer] = 2.0 mol/L, [AIBN] = 0.02 mol/L). The products were diluted with methanol and then reprecipitated from ethyl acetate. The degrees of polymerization of the polymers thus obtained were 96 for PVPo and 82 for PAAm, respectively, by means of vapor-pressure osmometry in methanol.

Poly(vinyl alcohol) (PVOH) and Poly(ethylene oxide) (PEO). PVOH used was a commercial one reprecipitated twice from methanol, having a degree of polymerization about 1000. PEO used were commercial materials with different chain lengths. These samples were reprecipitated twice from ethyl ether, and their molecular weights ($\overline{M}_w$) were given as 1 400, 2 900, 8 000 and 140 000.

Poly(sodium styrenesulfonate) (NaSS), poly(*N,N,N′,N′*-tetramethyl-*N*-*p*-xylyleneethylenediammonium dichloride) (2X), and Oligo(ethyleneimine) (OEI). These polymers were prepared in the same manners as those in a previous paper.[11] The degree of sulfonation of NaSS was 77.1%. OEI used was a pentaethylenehexamine.

Complexation and Measurement. The solutions of three-component polymers (10^{-2}–10^{-1} unit mol/L) were mixed together, and the precipitates were separated from the solutions by means of a centrifuge (12 000 rpm for 1 h) or filtration. The precipitates were dried in vacuo to constant weights, and then they were subjected to elemental analyses, infrared spectroscopy, and weighing. The supernatant solutions were subjected to ultraviolet spectroscopy, circular dichroism, and viscosity measurements (30 ± 0.05 °C). These supernatant solutions were dried and then recovered materials were subjected to the elemental analyses and infrared spectroscopy.

The transmittancy of the complex solutions (one of the parameters of the ability of the complex formation) was measured in the systems of two or three component polymers (2.5×10^{-3}–5×10^{-3} unit mol/L) at room temperature using a Shimadzu spectronic 20-type photoelectric colorimeter at 420 nm.

Results and Discussion

Selective Interpolymer Complexation. Macromolecules can interact with each other through such secondary binding forces as Coulombic force, hydrogen bond, van der Waals