Conclusions

We find that the current theoretical description of motions in cross-linked polymers[4] is applicable to highly cross-linked epoxy resin systems, at least for determining the cross-link density of a material of unknown composition. We also find that ^1H NMR spin–spin relaxation times plateau above T_g in epoxy thermoset resins, and the plateau values increase linearly with the average number of bonds between cross-links, even in the most highly cross-linked systems. For the epoxy system we studied, approximately 10 backbone bonds are necessary to define a statistical segment, a portion of a chain which moves independently of the rest of the chain motions.

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Registry No. (DGEBA)(DDH)(DAB) (copolymer), 99037-53-3; (DGEBA)(DDH) (copolymer), 31832-83-4; (DGEBA)(DAB) (copolymer), 69777-26-0.

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(5) ZXSSQ and complimentary subroutines are copyrighted by IMSL, Inc., NBC Building, Houston, TX 77036-5085.
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(13) The factor of $46^{1/2}$ in eq 12 would be replaced by $\pi/2$ for a Gaussian line shape and replaced by $99^{1/2}$ for 1% cutoffs for a Lorentzian line shape.

Vibrational Spectra and Structure of Polyaniline

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ABSTRACT: Vibrational spectra have been studied on polyaniline in various forms with different electrical properties: two conducting forms, as-polymerized (2S) and doped 1A polyanilines; and three insulating forms, reduced-alkali-treated (1A), acid-treated 1A (1S), and oxygen-treated 1A [$1A(O_2)$] polyanilines. Polyaniline 1A is spectroscopically evidenced to be poly(imino-1,4-phenylene), —$(NHC_6H_4)_n$—. Polyaniline 1S consists of imino-1,4-phenylene (IP) unit (—NHC_6H_4—) and its salt unit (—$NH_2^+A^-$—C_6H_4—, (A^-, anion)). Treatment of 1A with oxygen converts part of consecutive IP units (—$NHC_6H_4NHC_6H_4$—) to nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene (NP) unit (—$N{=}C_6H_4{=}NC_6H_4$—). Semiquinone radical cations of IP units exist only in the conducting forms of polyaniline, 2S and doped 1A, indicating that semiquinone radical cations play an important role in electrical conduction in polyaniline.

Introduction

Polyaniline is an interesting material because it is not only an electrically conducting polymer[1–8] but also a good material as an electrode of a secondary battery with aqueous or nonaqueous electrolytes.[9–15] Polyaniline polymerized from aniline in aqueous acid solution is converted to several forms with different electrical properties by acid/base treatments and oxidation/reduction (see Figure 1). The as-polymerized form (2S[16]) gives high electrical conductivity (~5 S/cm).[1–7] It becomes insulating when treated with aqueous alkaline solution[2–6] (2A) or reduced electrochemically in aqueous acid solution (1S).[7] Reduced-alkali-treated polyaniline (1A) also is insulating[4,8] and it is unstable in air; its color changes from white to blue upon exposure to air. Polyaniline 1A doped with electrolyte anions[14] (doped 1A) is obtained by electrochemical oxidation and it was found, in this work, to be a new conducting form (σ = 5.8 S/cm). Recently, a secondary lithium battery with a 1A pellet (as the cathode) and nonaqueous electrolytes has been developed as a power source of memory back up and a maintenance-free power source combined with a solar battery.[9,13]

It is important to elucidate the structure of each form of polyaniline for understanding its properties. In a preceding paper[17] Furukawa et al. studied the Raman and infrared spectra of as-polymerized (2S) and alkali-treated (2A) polyanilines and electrochemical reduction process from 2S to 1S using some structural key bands. It was shown that the 2A form is a hybrid of the imino-1,4-phenylene (IP) unit (—NHC_6H_4—) and nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene (NP) unit (—$N{=}C_6H_4{=}NC_6H_4$—) containing quinone diimine structure (—$N{=}C_6H_4{=}N$—) and that high electrical conductivity in the 2S form is due to the presence of

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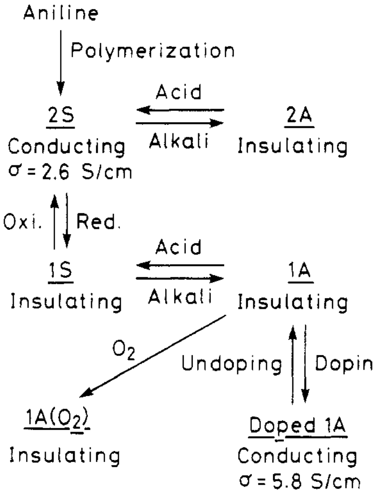

Figure 1. Various forms of polyaniline.

"modified quinone diimine" structures in which the delocalization of π-electrons occurs. Raman spectroscopy proved valuable for studying structures of this multichromophore material, polyaniline.

In this paper Raman and infrared spectra of polyaniline 1A, acid-treated 1A (1S), oxygen-treated 1A [1A(O_2)], and doped 1A are studied. Assignments of vibrational spectra are made referring to the data of ^{15}N-substituted and C-deuteriated polyanilines, *N*,*N*′-diphenyl-1,4-benzenediamine, and its derivatives. Key bands that are useful in determining the structures of various forms are elucidated and the relation between vibrational spectra, structures, and electrical properties is discussed.

Experimental Section

Reduced-Alkali-Treated Polyaniline (1A). 1A was prepared in the following modification of a previous method.[9] As-polymerized polyaniline (2S) was prepared by an electrochemical polymerization of aniline in aqueous solution containing 2 M (M = mol/dm^3) hydrofluoroboric acid and 1 M aniline under an electric current of 10 mA/cm^2. This 2S film was electrochemically reduced in 1% hydrofluoroboric acid until the color of the film became yellowish green. The resulting film was immersed in 5% hydrazine aqueous solution and the color became white. The film was immersed in degassed methanol and successively dried under dynamic vacuum (1A). Aniline-^{15}N (Merck Frosst Canada Inc., 99 atom % ^{15}N) and aniline-*2,3,4,5-d*$_4$ (Merck Frosst Canada Inc., 99.5 atom % D) were used in the syntheses of corresponding polymers (1AN and 1AD).

1A Treated with Acid (1S). 1A film was immersed in aqueous acid (HCl, HBr, or HBF_4) solution containing hydrazine (pH ≤1) and washed with degassed methanol. The resulting sample was dried under dynamic vacuum. The color was yellowish green. The samples prepared with HCl, HBr, and HBF_4 are abbreviated to 1S(HCl), 1S(HBr), and 1S(HBF_4), respectively.

1A Treated with Oxygen [1A(O_2)]. 1A film was kept in oxygen atmosphere (~1 atm) for 15 days. The color changed from white to blue by the treatment.

Doped 1A. 1A film was electrochemically oxidized in propylene carbonate containing 1 M $LiBF_4$ (Mitsubishi Petrochemical Co. Ltd.). An Al–Li alloy was used as the counter electrode and 3.8 V was applied between working and counter electrodes. The amount of charge-transfer (i.e., doping level) at this oxidation level is calculated to be 0.48 per one aniline unit from the discharge capacity.[28] The resulting film was washed with dry acetonitrile and dried under dynamic vacuum. The color of the film was bluish green.

As-Polymerized Film (2S). 2S(Pt) was prepared electrochemically according to a previous method[17] using platinum electrodes.

***N*,*N*′-Diphenyl-1,4-benzenediamine,** $C_6H_5NHC_6H_4NHC_6H_5$ (BBB, B denotes benzenoid),[18] was purchased from Wako Pure Chemical Industries, Ltd. (practical grade), and recrystallized from the ethanol solution several times until the crystals became colorless. *N*,*N*′-Diphenyl-1,4-benzenediamine dihydrochloride (BBB-2HCl) was obtained by bubbling of HCl vapor into ether solution of BBB. *N*,*N*′-2,5-Cyclohexadiene-1,4-diylidenebis(benzenamine), $C_6H_5N{=}C_6H_4{=}NC_6H_5$ (BQB, Q denotes quinoid),[19] was synthesized by oxidation of BBB.[20] Semiquinone radical cation of BBB ($BBB^{\bullet+}$) was prepared by adding aqueous HCl solution to the methanol solution of BQB until the color turned to blue.[21] Formation of $BBB^{\bullet+}$ was checked by visible absorption.[21]

Table I
Electrical Conductivity of Polyanilines at Room Temperature

polyanilines	state	σ, S/cm
2S(chem)[a]	compressed pellet of powder	2.6
2A(chem)[a]	compressed pellet of powder	$<10^{-6}$
1A	compressed film	$<10^{-5}$
1S(HCl)	compressed film	$<10^{-5}$
1A(O_2)	compressed film	$<10^{-5}$
doped 1A	compressed film	5.8

[a] Data from ref 17.

Electrical conductivity was measured by the four- or two-probe technique for pressed films of 1A, 1S(HCl), 1A(O_2), and doped 1A at room temperature.

Infrared spectra were recorded on a JASCO IR-810 spectrophotometer. Spectra were measured at room temperature for pressed KBr disks in which samples were dispersed. Raman spectra were measured on a JEOL 400D double monochromator equipped with a photon-counting system or a JASCO CT-80D polychromator (two 600 groove/mm gratings, 500-nm blaze) equipped with a multichannel detector (Princeton Instruments, Inc., IRY/700). Excitation light was provided from an NEC GLG 3300 Ar ion laser, a Coherent Radiation Model 52 Ar ion laser (457.9, 488.0, and 514.4 nm), or a JEOL He–Ne laser (632.8 nm). Raman spectra of polyanilines were measured for the films at liquid nitrogen temperature by using a cryostat (Oxford Instruments Ltd., DN754).

Results

Electrical Conductivity. Measured electrical conductivities at room temperature are listed in Table I. Doped 1A shows high conductivity, similar to that of 2S. Doped 1A is a new conducting form of polyaniline.

Reduced-Alkali-Treated Polyaniline (1A). The Raman spectrum of white 1A excited with 488.0-nm light is shown in Figure 2a. Those excited with 457.9- and 514.5-nm light are similar to this spectrum. The spectral pattern is that of para-disubstituted benzene rings.[22] The strong band at 1621 cm^{-1} is assigned to a ring stretching vibration (8a mode[23]). The band at 1221 cm^{-1} is assigned to a mixed mode of the CN and ring stretching vibrations because the band shifts to 1217 and 1202 cm^{-1} on ^{15}N-substitution (Figure 2b) and C-deuteriation (Figure 2c), respectively. The strong band at 1181 cm^{-1} is assigned to a CH in-plane bending vibration (9a) because of the 316-cm^{-1} downshift on C-deuteriation (Figure 2c). The bands at 820 and 603 cm^{-1} arise from the ring symmetric stretching and ring in-plane deformation vibrations characteristic of para-disubstituted benzene, respectively.

It was reported in the preceding paper[17] that polyaniline 2A is composed of para-disubstituted benzene and quinone diimine structures and gives a ν_Q Raman band (ν_Q being a mixed mode of the C=N and CH=CH stretching vibrations) in the 1485–1471 cm^{-1} range whose wavenumber changes with excitation wavelength, indicating the presence of various quinone diimine structures of different bond orders. These bands are not observed in the spectra of 1A with 457.9–514.5-nm excitation. Therefore, 1A has no quinone diimine structure and consists solely of para-disubstituted benzene rings; i.e., all the —N= groups at the quinone diimine parts in 2A are hydrogenated in 1A

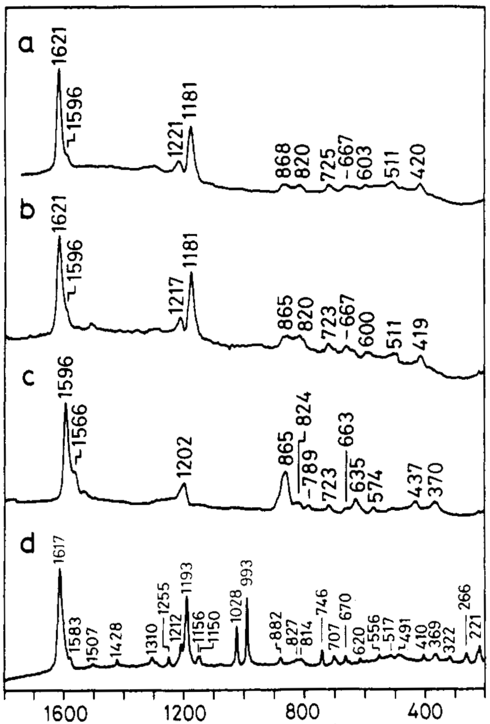

Figure 2. Raman spectra of (a) polyaniline 1A film (with 488.0-nm excitation), (b) the ^{15}N-substituted analogue (1AN, 488.0 nm), (c) the C-deuteriated analogue (1AD, 488.0 nm), and (d) *N,N'*-diphenyl-1,4-benzenediamine (BBB, solid, 514.5 nm).

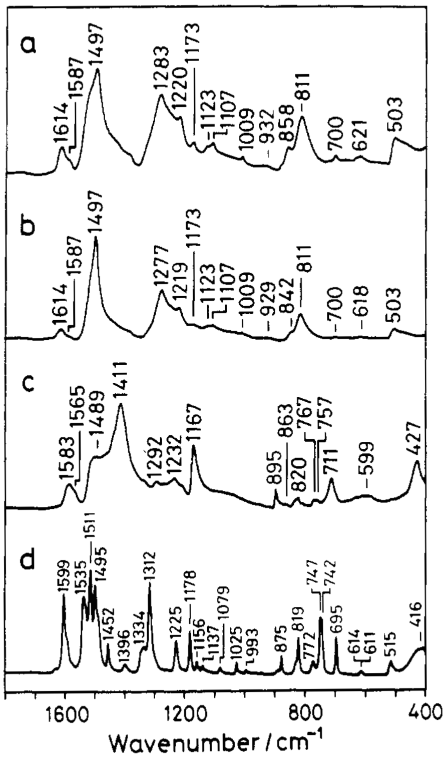

Figure 3. Infrared spectra (1800–400 cm^{-1}) of (a) polyaniline 1A, (b) 1AN, (c) 1AD, and (d) BBB in KBr disks. See the caption of Figure 2b–d.

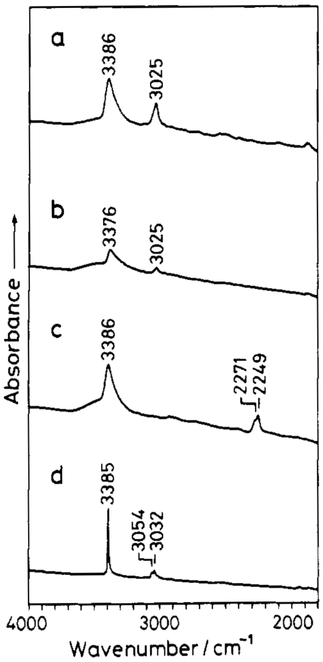

Figure 4. Infrared spectra (4000–1800 cm^{-1}) of (a) polyaniline 1A, (b) 1AN, (c) 1AD, and (d) BBB in KBr disks. See the caption of Figure 2b–d.

to yield consecutive —NHC_6H_4— structures. This observation is consistent with the optical absorption spectrum in which the visible absorption associated with quinone diimine structures[17] is absent.[12]

In the Raman spectrum of BBB (Figure 2d) two strong bands are observed at 1617 and 1193 cm^{-1}, corresponding respectively to those at 1621 and 1181 cm^{-1} of 1A. The additional strong bands at 1028 and 993 cm^{-1} arise from a CH in-plane bending and the ring breathing vibrations of monosubstituted benzene rings at both ends of the molecule, respectively.[22] Since the bands due to these vibrations are not observed in the spectra of 1A, the degree of polymerization is quite large. These bands would be useful markers of degree of polymerization of aniline oligomers.

Infrared spectra of 1A, its isotope-substituted analogues, and BBB are shown in Figures 3 (1800–400 cm^{-1}) and 4 (4000–1800 cm^{-1}). The band at 1614 cm^{-1} is attributed to the ring stretching 8a mode of the benzene ring. The band at 1497 cm^{-1} with a shoulder on the high wavenumber side is assigned to an overlap of 19a and 19b ring stretching vibrations, because this band splits and shifts down to 1489 and 1411 cm^{-1} on C-deuteriation. Of the two infrared bands of 2A around 1590 and 1500 cm^{-1} [5,24,25] the former arises mainly from the quinoid ring and the latter from the benzenoid ring.[24] The negligible intensity around 1590 cm^{-1} in spectrum 1A indicates that 1A does not contain a quinone diimine structure. The shoulder at 1587 cm^{-1} is assigned to the ring stretching 8b mode of benzene rings.

The band at 1283 cm^{-1} is due to a mixed mode of the CH bend and the CN stretch because the peak disappears on C-deuteriation and shifts down by 6 cm^{-1} on ^{15}N-substitution.

The wavenumbers of CH out-of-plane bending vibrations of a benzene ring reflect the substitution. The band at 811 cm^{-1} in 1A (711 cm^{-1} in the C-deuteriated analogue) is characteristic of para-disubstitution. This is consistent with the previous result that aniline polymerizes through head-to-tail coupling at the C_4 and N positions in aqueous acid electrolytes.[17,26]

In the infrared spectrum of BBB (Figure 3d), the band at 819 cm^{-1} is assigned to the CH out-of-plane in-phase bending vibration of the para-disubstituted benzene ring in the BBB molecule.[22] In addition, the band around 745 cm^{-1} (peak wavenumbers, 747 and 742 cm^{-1}) is assigned to the CH out-of-plane in-phase bending vibration of monosubstituted benzene rings at both ends of the molecule and the band at 695 cm^{-1} is also ascribed to these rings.[22] In the spectrum of 1A the corresponding CH

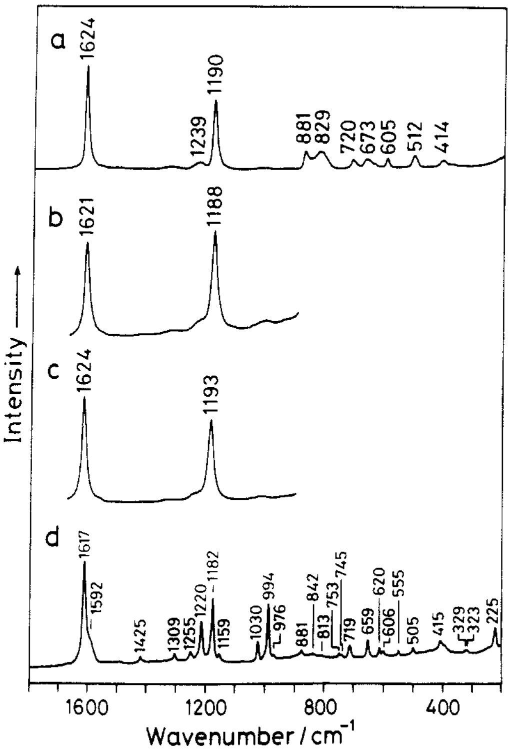

Figure 5. Raman spectra of (a) HCl-treated, (b) HBr-treated, and (c) HBF_4-treated polyaniline 1A films (to be called 1S(HCl), 1S(HBr), and 1S(HBF_4), respectively) and (d) *N*,*N*′-diphenyl-1,4-benzenediamine dihydrochloride (BBB-2HCl) in solid form with 488.0-nm excitation.

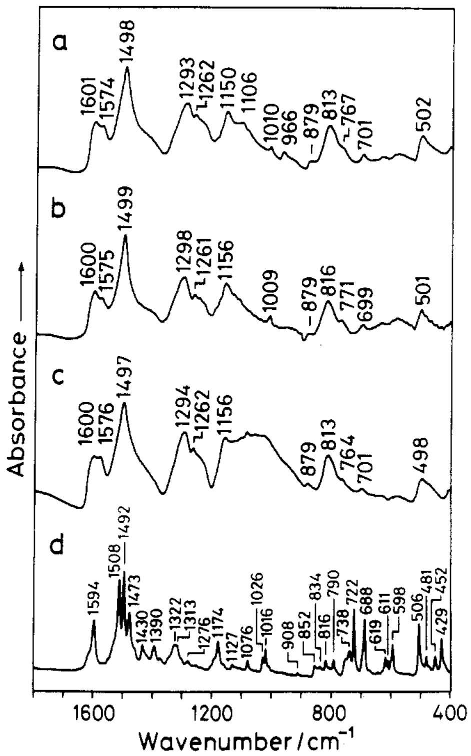

Figure 6. Infrared spectra (1800–400 cm^{-1}) of (a) 1S(HCl), (b) 1S(HBr), (c) 1S(HBF_4), and (d) BBB-2HCl in KBr disks. See the caption of Figure 5a–d. The band around 1050-cm^{-1} in (c) is due to BF_4^- ion.

out-of-plane bending band is not observed, which is consistent with the Raman observation that the degree of polymerization is quite large.

The band around 3386 cm^{-1} in the spectrum of 1A (Figure 4a) is assigned to the NH stretching vibration of the $-C_6H_4NHC_6H_4-$ groups based on the 10-cm^{-1} downshift on ^{15}N-substitution. This band is tailed at the low wavenumber side. The NH stretching wavenumber is known to be lowered by H-bonding. The wavenumber of BBB is 3385 cm^{-1} in the solid state and 3429 cm^{-1} in dry CCl_4 solution (5 mM) in which BBB molecules are considered to be free of H-bonding. Accordingly, BBB in the solid state and most of the NH groups in 1A are involved in H-bondings of similar strengths. The low-wavenumber tail in 1A indicates that some of the NH groups form stronger H-bondings. In contrast to this observation 2A gives three NH stretching bands at 3380, 3254, and 3168 cm^{-1},[17] the latter two arising from the NH groups with H-bonds much stronger than those giving rise to the 3380-cm^{-1} band in 2A and the 3386-cm^{-1} band in 1A. These strong H-bonds are possibly formed between the —NH— and —N= groups in adjacent polymers. Anyway, it is important to note that the nitrogen atoms in neighboring polymer chains in 1A (as well as in 2A) are closely connected to one another through H-bondings.

The band at 3025 cm^{-1} is assigned to a CH stretching vibration of the benzene rings because it shifts to 2249 cm^{-1} on C-deuteriation.

Spectroscopic data described above give the evidence that white polyaniline 1A is poly(imino-1,4-phenylene), —$(NHC_6H_4)_n$—. It is reasonably understood that the nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene part (—$N{=}C_6H_4{=}NC_6H_4$—) in 2A is changed to imino-1,4-phenylene (—$NHC_6H_4NHC_6H_4$—) upon reduction.

Acid-Treated Polyaniline 1A (1S). Raman spectra of 1S films are shown in Figure 5a–c. Although their spectral pattern is similar to that of 1A, the peak wavenumbers are more or less different. The ring stretching vibrations at 1621 and 820 cm^{-1} in 1A are upshifted by 3 and 9 cm^{-1}, respectively, in 1S. The ring deformation at 603 cm^{-1} in 1A is upshifted by 2 cm^{-1}. The vibration with the CN stretching contribution (1221 cm^{-1} in 1A) and the CH bending one (1181 cm^{-1} in 1A) are also upshifted by 18 and 9 cm^{-1}, correspondingly.

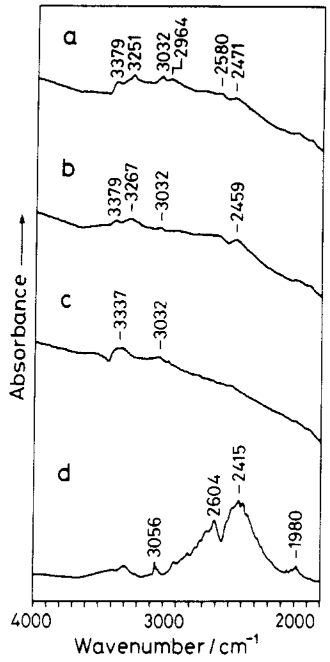

Figure 7. Infrared spectra (4000–1800 cm^{-1}) of (a) 1S(HCl), (b) 1S(HBr), (c) 1S(HBF_4), and (d) BBB-2HCl in KBr disks. See the caption of Figure 5a–d.

Infrared spectra in the range 1800–400 cm^{-1} (Figure 6a–c), as well, show similar small changes by treatment

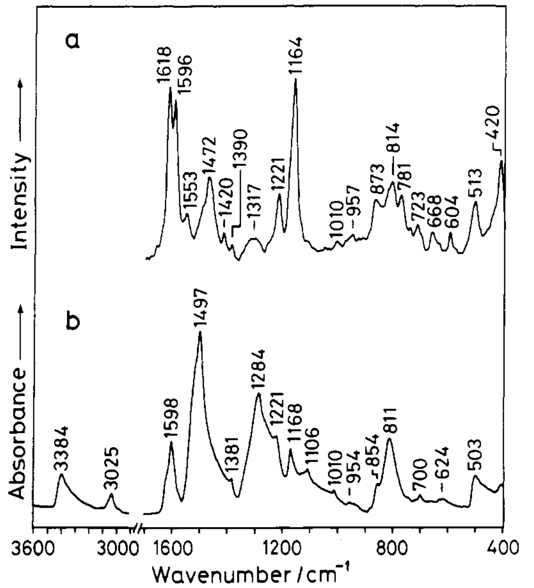

Figure 8. Raman (upper) and infrared (lower) spectra of polyaniline 1A treated with oxygen [1A(O_2)]. Raman spectrum is taken with 488.0-nm excitation in a film and infrared spectrum is taken in a KBr disk.

with acid. On the other hand, a remarkable difference is observed in high-wavenumber region (Figure 7a–c). The broad band with two or three peaks in the 3400–3100-cm^{-1} region is assigned to an overlap of the NH stretching vibrations of $-C_6H_4NHC_6H_4-$ groups. The bands ranging from 3000 to 2200 cm^{-1} are assigned to vibrations associated with the NH_2^+ part in $-C_6H_4NH_2^+C_6H_4-$ groups because *N,N'*-diphenyl-1,4-benzenediamine dihydrochloride (BBB-2HCl) gives absorption in the range 2900–1900 cm^{-1} (Figure 7d) and $-NH_2^+-$ groups show broad bands around 2700–2250 cm^{-1}.[27] Therefore, part of the NH group is protonated by the acid treatment and converted to NH_2^+. Thus 1S consists of a imino-1,4-phenylene unit ($-NHC_6H_4-$) and its salt unit ($-NH_2^+A^-C_6H_4-$, (A^-, anion)). A large number of NH groups become strongly hydrogen bonded by the acid treatment, because the absorbance at 3386 cm^{-1} is smaller than those of lower wavenumber NH stretching bands. The degree of protonation depends on acids because shapes of the bands attributed to NH and NH_2^+ groups are different for the acids used (Figure 7a–c).

Polyaniline 1A Treated with Oxygen [1A(O_2)]. A Raman spectrum of 1A(O_2) is shown in Figure 8a. The spectral pattern is different from that of 1A but similar to that of 2A, because the bands at 1596, 1553, 1472, 1164, 814, and 781 cm^{-1} characteristic of 2A are observed. The bands at 1618, 1596, 1221, 1164, 814, and 604 cm^{-1} are assigned to the ring stretching (8a), ring stretching (8b), CN stretching (7a), CH in-plane bending (9a), ring symmetric stretching (1), and ring in-plane deformation (6a) of para-disubstituted benzene, respectively, corresponding to those of 2A at 1614, 1595, 1222, 1162, 817, and 606 cm^{-1}. The band at 1472 cm^{-1} is assigned to ν_Q of the quinone diimine structure.[17] Accordingly, the quinone diimine structure is formed by oxygen treatment. The relative intensity, I_{1480}/I_{1590} (I_{1472}/I_{1596} in the present case), reflects the content of the para-disubstituted benzene ring and quinone diimine structure.[17] Since the I_{1472}/I_{1596} value in 1A(O_2) is smaller than that in 2A, the content of the quinone diimine structures in 1A(O_2) is less than that in 2A.

The infrared spectrum of 1A(O_2) is shown in Figure 8b. The area intensity of NH stretching vibration observed around 3380 cm^{-1} is 25% of that of 1A. The decrease of NH stretching intensity is reasonably understood because the formation of quinone diimine from benzenoid structure is accompanied by loss of NH bonds. Furthermore, the increase of the relative intensity of the band around 1598 cm^{-1} to that around 1497 cm^{-1} as compared to that in 1A (Figure 3a) is noticed. As mentioned earlier, the former band arises mainly from the quinoid rings and the latter mainly from the benzenoid rings and the relative intensity of such bands reflects the content of quinoid rings.[24] Thus, the increase of I_{1598}/I_{1497} is explained by the formation of quinone diimine structures by exposure to oxygen. It must be noticed that the origin of the Raman band at 1596 cm^{-1} is different from that of the infrared band at 1598 cm^{-1}. The Raman band arises mainly from para-disubstituted benzene rings, because the band intensity is preresonantly enhanced with excitation at wavelengths close to the UV absorption due to the benzene rings.[17]

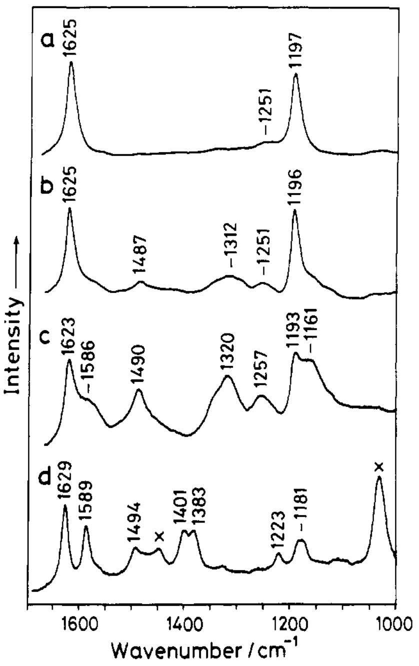

Figure 9. Raman spectra of (a)–(c) polyaniline 1A film oxidized electrochemically at 3.8 V in propylene carbonate containing 1M $LiBF_4$ (doped 1A) and (d) semiquinone radical cation of *N,N'*-diphenyl-1,4-benzenediamine ($BBB^{•+}$) in methanol. Excitation wavelengths are 457.9, 488.0, 514.5, and 632.8 nm for (a), (b), (c), and (d), respectively. The bands with × are due to methanol.

Polyaniline 1A Oxidized in Nonaqueous Solution (Doped 1A). The Raman spectra of doped 1A are shown in Figure 9a–c. When excited with the 457.9-nm light, the spectral pattern is that of para-disubstituted benzene rings. The ring stretching vibration (8a) at 1621 cm^{-1} and the CH in-plane bending vibration (9a) at 1181 cm^{-1} in 1A are upshifted by 4 and 16 cm^{-1} in doped 1A, respectively. The CN stretching band (1221 cm^{-1} in 1A) is also upshifted by 30 cm^{-1}. In polyanilines studied so far, para-disubstituted benzene exists as an imino-1,4-phenylene (IP) unit ($-NH-C_6H_4-$) and/or its salt (IP^+) unit ($-NH_2^+A^-C_6H_4-$). Since protonation does not occur and the IP^+ unit cannot exist in non-aqueous electrolytes, para-disubstituted benzene in doped 1A must take the form of IP. An XPS study has shown the presence of IP units and the absence of IP^+ units.[28]

When excited with the 514.5-nm light (Figure 9c), new bands are observed at 1586, 1490, 1320, 1257, and 1161 cm^{-1}. The spectrum is different from those of 2A,[17] 1A, 1S, and 1A(O_2). Thus, new structures except the IP, IP^+, and NP units are formed by oxidation in nonaqueous solution. Figure 9d shows the Raman spectrum of semi-

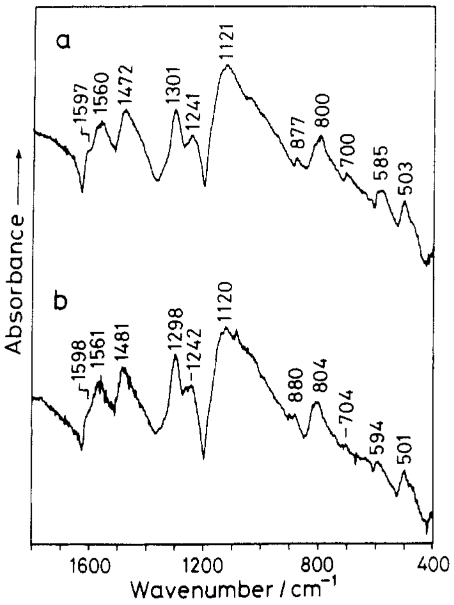

Figure 10. Infrared spectra of (a) as-polymerized polyaniline (2S(Pt)) and (b) doped 1A (see the caption of Figure 9a–c) in KBr disks.

quinone radical cation of BBB (BBB$^{\bullet+}$) with 632.8-nm excitation, which is in resonance with a broad absorption around 710 nm.[21] This spectrum is similar to Figure 9c except for the difference between the bands in the range 1300–1400 cm^{-1}: doped 1A, 1320 cm^{-1}, and BBB$^{\bullet+}$, 1401 and 1383 cm^{-1} (peak wavenumbers). The wavenumber of these bands probably depends on electron delocalization, because the degree of polymerization of polyaniline is much larger than that of BBB. Thus it seems that semiquinone radical cations of IP units (IP$^{\bullet+}$) are formed in doped 1A. This is consistent with the results of the ESR,[12] electronic absorption,[12] and XPS[28] studies.

When doped 1A is washed with sodium hydroxide solution, the band at 1320 cm^{-1} disappears and a band at 1480 cm^{-1} appears with 514.5-nm excitation. The band is assigned to the ν_Q mode of quinone diimine structures.[17] Thus, semiquinone radicals are converted to quinone diimine structures by treatment with sodium hydroxide.

As-Polymerized Polyaniline (2S). In the preceding paper[17] it was reported that para-substituted benzene rings and "modified quinone diimine" structures exist in 2S. In this work Raman and infrared spectra of 2S are compared with those of doped 1A. The 457.9-nm Raman spectrum of 2S was attributed to disubstituted benzene:[17] 1626 cm^{-1}, ring stretching (8a); 1263 cm^{-1}, CN stretching (7a); 1193 cm^{-1}, CH in-plane bending (9a); 830 cm^{-1}, ring symmetric stretching; and 634 cm^{-1}, ring in-plane deformation. An XPS study has shown that imino-1,4-phenylene (IP) and its salt (IP$^+$) units exist in 2S.[28]

As the excitation wavelength becomes long, new bands are observed for both doped 1A and 2S with the wavenumbers similar to each other: 2S, 1583, 1513, 1484, 1344, 1324, and 1257 cm^{-1}; and doped 1A, 1586, 1490, 1320, and 1257 cm^{-1}. Such bands of 2S were considered to be due to the structure transformed from quinone diimines by treatment with acid.[17] On the other hand, such bands of doped 1A are attributed to semiquinone radical cations of IP units. Therefore, "modified quinone diimine" structures are proved to be semiquinone radical cations. The infrared spectrum of 2S is almost the same as that of doped 1A (see Figure 10) and is different from those of 1A, 1S, 1A(O_2), and 2A. Accordingly, in the infrared spectra the bands of semiquinone radical cations of IP units are dominant. Presence of semiquinone radical cations in 2S is consistent with the experimental results of ESR,[29,30] magnetic susceptibility,[31] and XPS.[28]

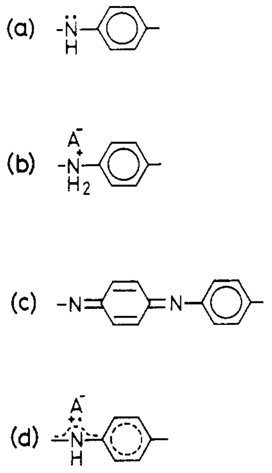

Figure 11. Constitutional units of polyanilines: (a) imino-1,4-phenylene (IP); (b) imino-1,4-phenylene salt (IP$^+$); (c) nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene (NP); (d) radical cation of imino-1,4-phenylene (IP$^{\bullet+}$). A$^-$, anion.

Discussion

Vibrational Key Bands and Structures of Polyanilines. It has turned out that polyanilines can take structures consisting of four types of constitutional units: imino-1,4-phenylene (IP), its salt (IP$^+$), nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene (NP), and radical cation of IP (IP$^{\bullet+}$) (see Figure 11). The elucidated constitutional units of polyanilines are summarized in Figure 12 with vibrational key bands that are useful in determining structures of polyanilines.

Para-disubstituted benzene rings of polyaniline exist in all the forms. Para-disubstituted benzene rings except for those of 2A and 1A(O_2) give rise to two strong Raman bands with 457.9–514.5-nm excitation: ring stretching (8a), 1626–1621 cm^{-1}, and CH in-plane bending (9a), 1197–1181 cm^{-1}. These bands are markers of the presence of para-disubstituted benzene rings with the simultaneous absence of NP units (quinone diimine structure). Para-disubstituted benzene rings of 2A and 1A(O_2) give rise to strong Raman bands in the regions 1618–1614 (8a), 1596–1595 (8b), and 1164–1162 cm^{-1} (9a) with 457.9–514.5-nm excitation. The 8b band is preresonantly enhanced because electronic absorption of para-disubstituted benzene shows the bathochromic shift owing to the formation of quinone diimines.[17] Thus, these bands indicate coexistence of *p*-disubstituted benzene rings and quinone diimine structures. Although the 1595-cm^{-1} band is attributed to para-disubstituted benzene, the band also is an indicator of the presence of quinone diimines. Strong intensity of the 9a mode and weak intensities of the CN stretching (vide infra) and ring symmetric stretching (830–814 cm^{-1}, benzene 1 mode) vibrations are peculiar to benzenoid of polyanilines. The symmetric stretching and in-plane ring deformation (6a, 634–603 cm^{-1}) vibrations characteristic of para-disubstituted benzenes are additional key bands.

Raman bands contributed mainly by the CN stretch show wavenumber differences. The additional presence of an IP$^+$ unit induces high-wavenumber shifts: 1A (IP, 1221 cm^{-1}) versus 1S (IP and IP$^+$, 1239 cm^{-1}) and doped 1A (IP and IP$^{\bullet+}$, 1251 cm^{-1}) versus 2S (IP, IP$^{\bullet+}$, and IP$^+$, 1263 cm^{-1}). Although a difference between IP and IP$^+$ units is not apparent in Raman spectra, two such structures can be differentiated by infrared NH stretching bands in insulators: NH (IP), 3400–3100 cm^{-1}, and NH$_2{}^+$ (IP$^+$), 3000–2200 cm^{-1}. However, in conductors (doped 1A

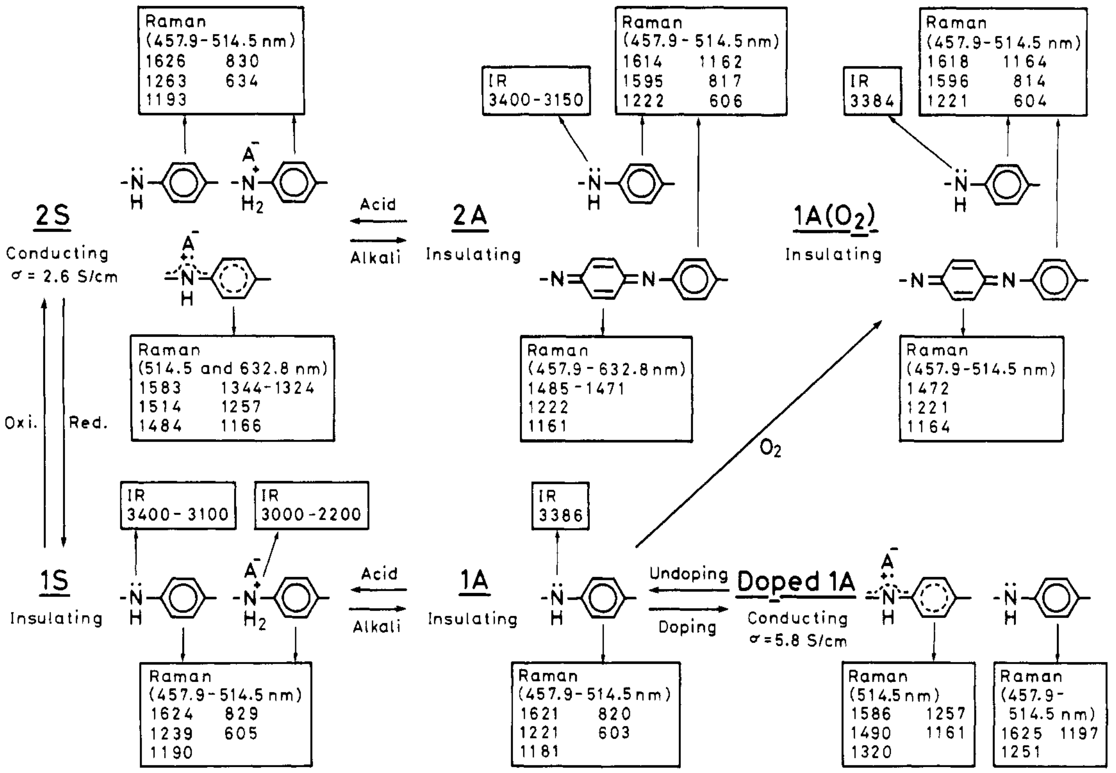

Figure 12. Constitutional units and vibrational key bands of polyaniline at various forms. A^-, anion. The content of NP unit in $1A(O_2)$ is less than that in 2A.

and 2S) these bands are obscured by strong background absorption in the infrared region.

Quinone diimine structures give rise to a strong Raman band between 1485 and 1471 cm^{-1} with 457.9–632.8-nm excitation. The strong Raman bands of semiquinone radical cation structures appear in the range 1344–1312 cm^{-1} as well as in the range 1513–1484 cm^{-1} with 514.5- and 632.8-nm excitation. Thus, the bands in the region 1344–1312 cm^{-1} are characteristic of semiquinone radical cations. The bands around 1513–1471 cm^{-1} commonly observed for the two structures are of different origins because of large ^{15}N shifts in quinone diimines and the negligible ^{15}N shift in semiquinone radical cations. Thus, these bands also are markers of the presence of quinone diimine and semiquinone radical cation structures. These key bands are practically useful in monitoring the properties (electrical conductivity, capacity when used as the electrode of batteries, etc.) of polyaniline.[32]

The CN stretching Raman wavenumbers of polyanilines are listed in Table II together with those of some aromatic amines, their hydrochlorides, and a quinone diimine, which have the common structure, $C_6H_4NC_6H_4$. The wavenumbers lie in the wide region 1200–1521 cm^{-1}. Such variety is considered to arise mainly from the difference in the nature of $C_6H_4NC_6H_4$ links. The C—N—C symmetric stretch in the C_6H_4—N—C_6H_4 group lies in the range 1200–1263 cm^{-1}. The C═N double bond stretch in the C_6H_4═N—C_6H_4 group appears in the range 1471–1521 cm^{-1} for 2A and at 1521 cm^{-1} for BQB. The wavenumber difference between 2A and BQB is explained by the difference in the C═N bond order.[17] The variety of the wavenumber in 2A indicates the presence of various C_6H_4═N—C_6H_4 groups with different bond orders.[17] The wavenumbers in radical cations, 1312–1401 cm^{-1}, lie between the two extremes, the C—N—C symmetric stretch and the C═N stretch. This is presumably because the electron on the cationic nitrogen is exchangeable with the π-electrons in the neighboring quinone ring and as a result the CN bond orders increase. On the basis of small ^{15}N shifts the bands at 1324 and 1344 cm^{-1} of radical cations in 2S have been assigned to almost symmetric CNC stretching vibrations at two slightly different C⫶N⫶C parts whose bond orders are between those of C—N and C═N bonds and nearly equal.[17] The mode of the corresponding band of $BBB^{•+}$ (1383 and/or 1401 cm^{-1}) is considered to be similar to that of 2S. However, the CN bond orders in $BBB^{•+}$ are slightly higher than those of radical cations in 2S and doped 1A, because the wavenumber of the former is about 65 cm^{-1} higher than those of the latter. In this manner, the CN stretching wavenumber reflects the difference in the nature of CNC links.

Table II
Raman Wavenumbers of the CN Stretching Vibrations of Polyaniline at Various Forms and Model Compounds

compounds	ν_{CN}, cm^{-1}	ref
Aromatic Amines and Their Hydrochlorides		
N-phenylbenzamine hydrochloride	1200	this work
N,*N*′-diphenyl-1,4-benzenediamine (BBB)	1212	this work
N-phenylbenzenamine	1219	33
N,*N*′-diphenyl-1,4-benzenediamine dihydrochloride (BBB-2HCl)	1220	this work
1A	1221	this work
$1A(O_2)$	1221	this work
2A	1222	17
1S(HCl)	1239	this work
doped 1A	1251	this work
2*S*	1263	17
Radical Cations		
doped 1A	1312–1320	this work
2S	1324–1344	17
radical cation of BBB ($BBB^{•+}$)	1383 and/or 1401	this work
Quinone Diimines		
$1A(O_2)$	1472	this work
2A	1471–1485	17
NN′-2,5-cyclohexadiene-1,4-diylidenebis(benzenamine) (BQB)	1521	17

Relation between Structures and Electrical Conductivity. Polyaniline shows three types of conductor/

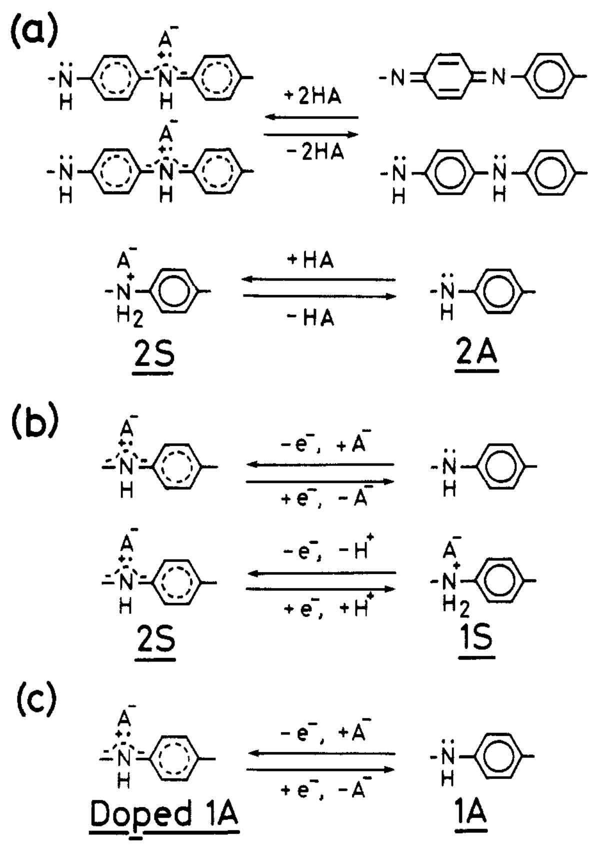

Figure 13. Reaction schemes concerning conductor/insulator transitions: (a) 2S–2A; (b) 2S–1S; (c) doped 1A–1A. A^-, anion; e^-, electron; H^+, proton.

insulator transitions: 2S–2A, 2S–1S, and doped 1A–1A. Structural changes accompanied by such transitions will be discussed on the basis of the obtained structures.

Conducting 2S is converted to insulating 2A by alkali treatment and 2A is reversibly converted to 2S by acid treatment. 2S consists of IP, IP^+, and $IP^{\bullet +}$ units and 2A consists of IP and NP units. Semiquinone radical cations of 2S are considered to be converted to quinone diimine structures by a disproportionation reaction similar to the corresponding reaction concerning BBB and BQB.[21,34] An example of such reaction is shown in Figure 13a. Disproportionation may take place between semiquinone radical cations on the same chain.[29,31] Those on the adjacent polymer chains also are possibly converted to quinone diimine structure because the polyaniline chains are associated through hydrogen bonding. IP^+ units of 2S are simply converted to IP units (see Figure 13a).

Conducting 2S is also converted to insulating 1S upon electrochemical reduction and 1S is reversibly converted to 2S. 1S consists of IP and IP^+ units. Thus, semiquinone radical cation ($IP^{\bullet +}$) units are reduced to IP and IP^+ units as shown in Figure 13b. One of such reactions (upper scheme of Figure 13b) is concerned with an electron and an anion. This is called the electrochemical doping/undoping process of an anion. The other reaction (lower scheme of Figure 13b) relates to an electron and a proton. This is the doping/undoping process of a proton. Electrochemical studies[35,36] have shown that the electrochemical reactions are concerned with anion insertion/elimination and proton addition/elimination.

Insulating 1A is converted to doped 1A by electrochemical oxidation in nonaqueous solution; the process also is reversible. In the oxidation process IP units are transformed to $IP^{\bullet +}$ units (see Figure 13c). This process might be considered to be the same as the well-known electrochemical doping/undoping process in conjugated polymers (polyacetylene, polypyrrole, polythiophene, etc.). However, the process in polyaniline is different from that in conjugated polymers, because in the case of polyaniline, insulating 1A is not a conjugated polymer and it is converted to a conjugated polymer by doping.

Electrical conductivities of 2S and doped 1A were 2.6 and 5.8 S/cm, respectively. The structural characteristic of these conducting forms is the presence of semiquinone radical cations which are absent in the insulating polyanilines. Therefore, semiquinone radical cations play the decisive role in electrical conduction in polyanilines.

Conclusion

The structure of polyaniline at various forms were elucidated on the basis of vibrational key bands derived by analyzing the data of isotope-substituted derivatives and model compounds. Obtained structures are as follows: (1) Reduced-alkali-treated polyaniline (1A) is poly(imino-1,4-phenylene), —$(NHC_6H_4)_n$—. (2) Acid-treated 1A (1S) consists of imino-1,4-phenylene (IP) unit (—NHC_6H_4—) and its salt unit (—$NH_2^+A^-C_6H_4$—, (A^-, anion)). (3) Oxygen-treated 1A [1A(O_2)] is a mixture of IP unit and nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene (NP) unit (—$N{=}C_6H_4{=}NC_6H_4$—). However, the content of the NP unit in 1A(O_2) is less than that in alkali-treated polyaniline (2A). (5) Radical cations of IP units are present in conducting as-polymerized polyaniline (2S) and doped 1A.

Semiquinone radical cations existing in conducting 2S and doped 1A, but not in insulating 2A, 1A, 1S, and 1A(O_2), are responsible for high electrical conduction in polyaniline.

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Static and Dynamic Scattering from Block Copolymeric Ring Molecules

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ABSTRACT: Some conformational properties of diblock Gaussian ring copolymers are investigated. Explicit expressions are derived for the apparent mean-square radius of gyration, the apparent diffusion coefficient, and the angular dependence of the first cumulant of the dynamic structure factor. The results are discussed for rings of different relative block size and varying optical contrast among monomers and solvent.

Introduction

Various theoretical effects have been undertaken to describe the scattering behavior of linear[1-3] and branched[4,5] copolymers. The technique of anionic polymerization offers a powerful method to synthesize well-defined block copolymers of various structures.[6-8] Since the synthesis of ring polymers by anionic polymerization is now well developed,[9-11] extension of the technique to block copolymeric rings can be expected in the near future. In order perhaps to encourage such development, some scattering properties of diblock ring polymers are considered here.

The properties discussed are the mean-square radius of gyration, the particle scattering function, the diffusion coefficient, and the first cumulant of the dynamic structure factor. Two particular questions are investigated in some detail: (i) the influence of the ring constraint on homopolymeric parts of the molecules; (ii) the scattering behavior of chemically heterogeneous ring polymers in comparison to the corresponding homopolymers.

The calculation of the particle scattering function as well as of the first cumulant from block copolymeric rings involves some integrations which could only be treated numerically. These were performed by using the Dartmouth IMSL programs DCADRE, DBLIN, and DMLIN.

Model

The polymer model used is based on the Gaussian distribution of distances between any two monomers of the same polymer. We consider rings which consist of two blocks (A and B) with monomers differing in one or more of the following properties: length of a monomeric unit, hydrodynamic friction coefficient (ζ), refractive index increment (ν), and weight of the monomeric unit (M_0). The number of monomers in block A is n, each of length a; block B contains m monomers, all of length b. We write

$$N = n + m \qquad (1)$$

for the total number of monomers in the ring. Thermodynamic interactions between chemically different monomers are not taken into account. Under this assumption, the scattering behavior from monodisperse copolymers can be described by[1-3]

$$S(q,t) = \nu^{-2}\sum_{l=1}^{N}\sum_{j=1}^{N} \nu_l \nu_j M_{0_l} M_{0_j} \langle \exp(i\boldsymbol{q}\cdot\mathbf{r}_{lj}(t))\rangle \qquad (2)$$

where $S(q,t)$ is the dynamic structure factor, $\mathbf{r}_{l_j}(t)$ the distance vector between the location of monomer l at time 0 and monomer j at time t, $\mathbf{q}$ the scattering vector, M the overall molecular weight, and ν the average refractive index increment of the copolymer in solution.

$$\nu = \sum_k w_k \nu_k \qquad (3)$$

Here w_k is the weight fraction and ν_k the refractive index increment of the kth component.

The initial part of the dynamic structure factor, which is a decaying function of t, can be characterized by the first cumulant,

$$\Gamma = \lim_{t\to 0}\,[-\partial \ln S(q,t)/\partial t] \qquad (4)$$

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