Soluble and High Molecular Weight Polyaniline

Masao Abe,[a] Akira Ohtani,[a] Yasuhiro Umemoto,[b] Shinya Akizuki,[a] Minoru Ezoe,[a] Hiroyuki Higuchi,[a] Keiji Nakamoto,[a] Akitoshi Okuno,[b] and Yuzuru Noda[a]

[a] *Central Research Laboratory, Nitto Denko Corporation, 1-1-2, Shimohozumi, Ibaraki, Osaka 567, Japan*
[b] *Nitto Technical Information Center, 1-1-2, Shimohozumi, Ibaraki, Osaka 567, Japan*

Low temperature polymerization of aniline using ammonium peroxodisulphate results in a soluble, high molecular weight polyaniline which forms a very strong free-standing film.

Low-dimensional conducting polymers such as polyacetylene, polypyrrole, polyaniline (PAn),[1—4] and polythiophene have been much investigated over the past ten years. However, their practical applications have been limited because most conducting polymers do not dissolve in conventional organic solvents. Some studies of low molecular weight, soluble PAn compounds have been reported,[5—7] but the films prepared from these had low mechanical strengths. We have studied the polymerization of aniline and synthesized a soluble, high molecular weight PAn. Two aspects of soluble PAn are discussed here: (i) the effect of polymerization temperature on molecular weight, and (ii) the influence of the unit sequence on the solubility of the PAn.

Soluble PAns were prepared by chemical oxidative polymerization of aniline in an acidic aqueous solution (HCl–H_2SO_4) using ammonium peroxodisulphate as an oxidant, followed by undoping (deprotonation) with aqueous ammonia. An equimolar ratio of peroxodisulphate to aniline was used. The effects of polymerization temperature on molecular weight and conductivity of the resulting polymers are shown in Table 1.

The average molecular weight was evaluated by gel permeation chromatography (GPC) [polystyrene standard, 0.01 mol dm^{-3} LiBr/*N*-methyl-2-pyrrolidone (NMP) solution as eluent]. It is clear that the molecular weight of PAn increases as its polymerization temperature decreases. The PAn prepared in the range −5 to −3 °C, followed by the undoping treatment, [PAn(LT)], showed a high intrinsic viscosity [η] of 1.23×10^{-4} m^3 g^{-1} and a high weight-average molecular weight (M_w) of 1.6×10^5. It is assumed that the suppression of side-reactions by lowering the polymerization temperature contributed to the increase in molecular weight. The solubilities of variously prepared PAns were barely affected by the polymerization temperature. Only a small portion of undoped PAn was insoluble; undoped PAn was soluble up to a level of 12 wt%, in NMP. In contrast to previous results,[5—7] the undoped PAn studied here was insoluble in tetrahydrofuran (THF), acetonitrile, and 80% aqueous acetic acid. The as-polymerized doped PAn was likewise poorly soluble in THF, MeCN, and aqueous AcOH.

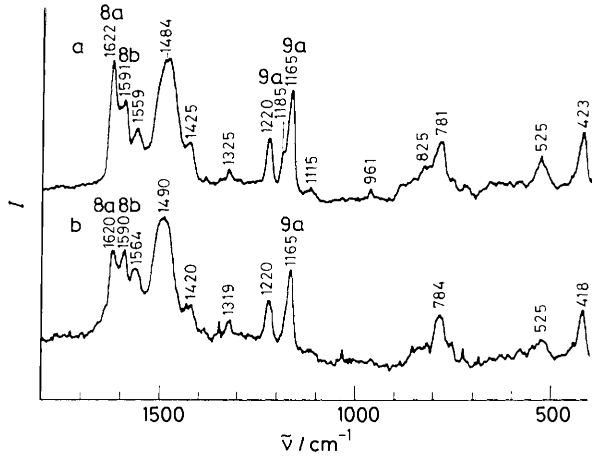

Figure 1. Raman spectra of (a) soluble PAn(LT) and (b) insoluble PAn(MnO_2), measured with 457.9 nm excitation at room temperature.

Free-standing PAn films were prepared by casting a PAn(LT)/NMP solution (10 wt%) on glass plates, followed by drying at 150 °C for 2 h; homogeneous transparent thin films were also formed on glass plates, as well as on insulating polymer films from the diluted PAn/NMP solution. These resulting free-standing and thin films, unlike the undoped PAn powder, are not soluble in NMP, probably as a result of cross-linking during drying at high temperatures. Doped (protonated) PAn films were easily obtained by immersing the undoped films in solutions of various protonic acids, *e.g.* HCl, H_2SO_4, $HClO_4$, toluene-*p*-sulphonic acid, and polyvinylsulphonic acid, as dopants. The conductivity of the doped free-standing films (10^{-2}—30 S cm^{-1}) was equivalent to that of the compressed tablets made from the as-polymerized PAn powder.

Both the undoped and doped films exhibited very high mechanical strength, in the range 500—900 kgf cm^{-2} (1 kgf = 9.80665 kg m s^{-2}). The $HClO_4$-doped PAn film could be elongated by 80%. These mechanical properties are comparable to those of common polymer films such as polyethylene, polystyrene, and Nylon. The surface resistance of the doped thin films mounted on the insulating substrate was 10^4—10^8 Ω.

Solubility can be changed by the PAn's unit sequence, which is composed of a quinonediimine (oxidized form) and a

Table 1. Effect of polymerization temperature on molecular weight of soluble PAn.

T^a /°C	$[\eta]^b$ /$\times 10^{-4}$ m^3 g^{-1}	$\bar{M}_n{}^c$ /10^4	$\bar{M}_w{}^c$ /10^5	Conductivity^d /S cm^{-1}
−5 to −3	1.23	2.3	1.6	18
5 to 20	0.56	1.4	1.3	11
25 to 50	0.48	1.2	1.2	2

[a] Polymerization temperature. [b] Intrinsic viscosity measured in NMP at 30 °C. [c] Number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights were evaluated by GPC (polystyrene standard, 0.01 mol dm^{-3} LiBr/NMP solution as eluent). [d] Conductivity of the compressed tablet of the as-polymerized PAn powder.

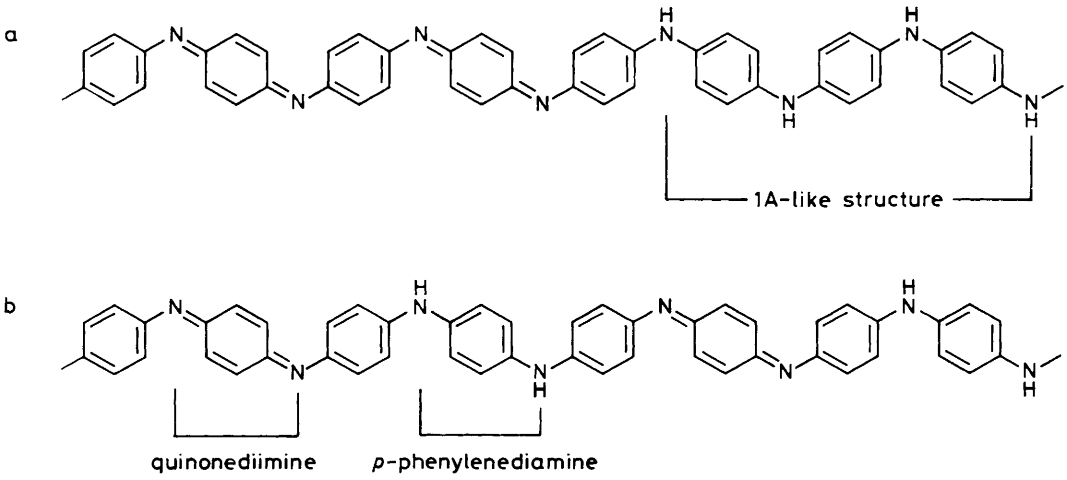

Figure 2. Presumed unit sequence of (a) soluble 2A-type PAn and (b) insoluble 2A-type PAn.

p-phenylenediamine (reduced form). We have observed that the solubility of PAn is influenced by the oxidant species used for polymerization. The PAn prepared by using MnO_2 [PAn(MnO_2)] has poor solubility in NMP.

Figure 1 shows Raman spectra of (a) the soluble PAn(LT), and (b) the insoluble PAn(MnO_2). The insoluble PAn was prepared by excluding the soluble part of the undoped PAn(MnO_2) with NMP. These spectra are similar to those of the oxidized and undoped PAn (called 2A-type in MacDiarmid's notation[1]), measured at liquid N_2 temperature by Furukawa *et al.*[8] Comparing the spectra of (a) and (b) in detail, the intensity ratio of the 8a band to the 8b band (I_{8a}/I_{8b}) for the soluble PAn was larger than that for the insoluble PAn. Moreover, a shoulder band at 1185 cm^{-1} appears only on the spectrum of the soluble PAn. The 8a band [(a) 1622 cm^{-1}, (b) 1620 cm^{-1}] and the 8b band [(a) 1591 cm^{-1}, (b) 1590 cm^{-1}] indicate the ring stretching vibration of the *para*-substituted benzene.[8] These differences in the Raman spectra are believed to result from the structural differences between the soluble and insoluble PAns.

We have prepared the reduced and undoped PAn (1A-type in MacDiarmid's notation) by the chemical reduction of the 2A-type PAn with phenylhydrazine, and have found that the 1A-type PAn has a higher solubility than the original 2A-type PAn. In the Raman spectrum of the 1A-type PAn, the 8a band (1621 cm^{-1}) is very strong but the 8b band is very weak. The I_{8a}/I_{8b} ratio is therefore very large. Moreover, at 1182 cm^{-1}, the 1A-type PAn has a 9a band that indicates a CH in-plane bending vibration of the *para*-substituted benzene. The shoulder at 1185 cm^{-1} for the soluble PAn, shown in Figure 1(a), corresponds exactly to the 9a band of this 1A-type PAn.

The large I_{8a}/I_{8b} intensity ratio and the existence of the 1185 cm^{-1} shoulder band in the Raman spectrum of the soluble PAn reflect the soluble PAn's 1A-like structure. Accordingly, we speculate that: (i) the structure of the soluble 2A-type PAn partially contains the 1A-like structure, which consists of *p*-phenylenediamine, as shown in Figure 2(a), and (ii) the structure of the insoluble 2A-type PAn consists of two alternating repeat units, quinonediimine and *p*-phenylenediamine, as shown in Figure 2(b).

We conclude that these differences between the two PAn structures affect interchain hydrogen bond formation and hence their solubilities. It appears that the high solubility of the PAn studied here results from the 1A-like structure being present in the 2A-type PAn.

Received, 5th June 1989; Com. 9/02359C

References

1 A. G. MacDiarmid, J.-C. Chiang, M. Halpern, W.-S. Huang, S.-L. Mu, N. L. D. Somasiri, W.-Q. Wu, and S. I. Yaniger, *Mol. Cryst. Liq. Cryst.*, 1985, **121**, 173.

2 E. M. Genies, A. A. Syed, and C. Tsintavis, *Mol. Cryst. Liq. Cryst.*, 1985, **121**, 181.

3 J.-C. Chiang and A. G. MacDiarmid, *Synth. Metals*, 1986, **13**, 193.

4 W.-S. Huang, B. D. Humphrey, and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2385.

5 M. Angelopoulos, A. Ray, A. G. MacDiarmid, and A. J. Epstein, *Synth. Metals*, 1987, **21**, 21.

6 J.-S. Tang, X.-B. Jing, B.-C. Wang, and F.-S. Wang, *Synth. Metals*, 1988, **24**, 231.

7 R.-Z. Jiang and S.-J. Dong, *Synth. Metals*, 1988, **24**, 255.

8 Y. Furukawa, T. Hara, Y. Hyodo, and I. Harada, *Synth. Metals*, 1986, **16**, 189.