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Synthesis of Highly Conducting Polyaniline with Photochromic Azobenzene Side Groups

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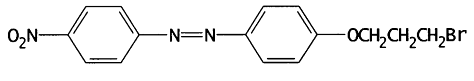
Azobenzene functionalized polymers are candidate materials for constructing various molecule-based optical devices, exploiting features from nonlinear optics, optical switching, optical storage, surface relief gratings, holograms, optical modulates, and command surfaces for aligning liquid crystals.[1] One of the main properties to be exploited is the photoinduced reversible trans−cis isomerization of the azobenzene group, which is usually accompanied by a structural change as reflected in the changes of dipole moment and geometry.[2] Various photoresponsive polymers have been extensively studied to date.[3]

Among the polymers, the conducting polymer is a new generation of polymers because of its covering the whole range from insulator to metal and retaining the attractive mechanical properties as well as processing advantages of polymers.[4] Recently, a few of papers dealing with conducting polymers containing the azobenzene moiety have been reported in the literature. Chen et al.,[5] for instance, have reported that copolymers of 3-hexylthiophene and the azobenzene moiety modified 3-hexylthiophene showed photocontrolled conductivity switching behavior, which is attributed to a generation of photoexicted in the azobenzene moiety upon irradiation of UV light. Yoshino et al.[6] have also reported that poly(*p*-phenylenevinylene) (PPV) and polyacetylene (PA) derivatives including azobenzene moieties as side chains showed optical anisotropy accompanying trans−cis isomerization of azobenzene upon irradiation of linearly polarized light. Moreover, Izumi et al.[7] have synthesized the poly(*p*-phenyleneethynylene)- and heteroaromatic-containing poly(phenylene)-based conjugated polymers having photoisomerizable azobenzene units in the main chain using the palladium-catalyzed coupling methods. Recently, Chen et al.[8] have synthesized the polypyrrole-based liquid crystals containing azobenzene mesogenic groups. Among the intensive studies of conjugated polymers, polyaniline (PANI) has attracted great attention because of its electronic, electrochemical, and optical properties and especially good environmental and thermal stability.[9] Here, we report a successful preparation of the first photoinduced polyaniline derivative, poly(aniline-*co*-*N*-propane[4-(4-nitrophenylazo)-phenyloxy]aniline) (PAPNPAPOA), which can be cast into free-standing film from its NMP solution. The free-standing thin film of PAPNPAPOA doped with 1.0 M HCl gives a conductivity of 1.2 S/cm at room temperature, which is higher than that of other N-alkyl-substituted polyanilines ($10^{-2}-10^{-7}$ S/cm).[10] In particular, the PAPNPAPOA dissolved in NMP solution shows trans−cis photoisomerization upon irradiation with UV light ($\lambda = 365$ nm).

1-Bromo-3-(4-(4-nitrophenylazo)phenyloxy)propane (represented by B3) was designed and successfully synthesized by the Williams etherification method as described in ref 11.



B3

The emeraldine base (EB) form of polyaniline was synthesized by a chemical oxidation method similar to that of MacDiarmid and co-workers.[12] The fully reduced leucoemeraldine (LEB) form of PANI was prepared by reacting the EB powders with hydrazine in ethanol for 48 h under an argon atmosphere. The light gray LEB powders were washed thoroughly with ethanol and THF to remove the excess reducing agent and the low-molecular-weight LEB species. The LEB powders were then dried under reduced pressure at room temperature.

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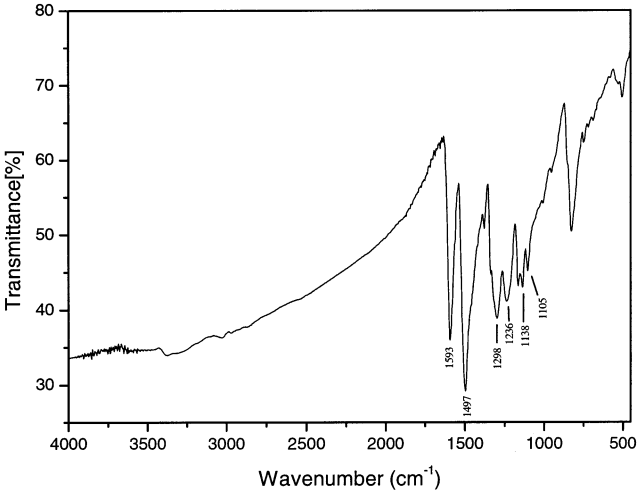

Figure 1. Typical FTIR spectra of the PAPNPAPOA.

A 40 mL aliquot of dimethyl sulfoxide (DMSO) and 2.6×10^{-2} g (1.1×10^{-3} mol) of NaH were added to a 100 mL round-bottom flask. The reaction flask was kept under an inert atmosphere throughout the subsequent reactions by a constant flow of argon. The mixture was stirred at 60 °C until the NaH was completely dissolved. A solution of methylsufinyl carbanion in DMSO was formed as described in the literature.[13] 0.1 g (1.1×10^{-3} mol) of LEB powder was added to the sodium methylsufinyl carbanion solution at 60 °C. A dark-yellow anion solution formed after reaction for 4 h. The solution was cooled to 40 °C, and 0.20 g (5.5×10^{-4} mol) of B3 was added with vigorous stirring. The reaction was allowed to continue for another 24 h, and then the reaction mixture was poured into a 10 times excess volume of doubly distilled water, under vigorous stirring, to precipitate the copolymer. The precipitate was recovered by filtration and washed exhaustively with doubly distilled water, ethanol, and acetone to remove the residual amount of unreacted species. The product so obtained was dried under reduced pressure at ambient temperature for 48 h.

The FTIR spectrum of the PAPNPAPOA shows that all characteristic bands of PANI at the 1593 cm^{-1} (assigned as C=C stretching of the quinoid rings), 1497 cm^{-1} (C=C stretching of benzenoid rings), 1298 cm^{-1} (C−N stretching mode), and 1138 cm^{-1} (N=Q=N, Q representing the quionoid ring) were observed (Figure 1). This indicates that the structure of PAPNPAPOA is identical to that of the main chain of PANI.[14] However, the presence of absorption peaks at 1105 cm^{-1}, 1150 cm^{-1} (characteristic of C−O−C stretching mode), and 1236 cm^{-1} (characteristic of C−O−Ar stretching mode)[15] shows the alkaneoxynitroazobenzene side groups are linked on the PANI.

The ^{1}H NMR spectrum (Figure 2) of the PAPNPAPOA shows three broad peaks around 6.9 (c), 7.9 (b), and 8.3 ppm (a), characteristic of the aromatic protons of the PANI backbone, the bound to the N=N group, and the bound to the NO$_2$ group, respectively, while peaks at 4.2 (e) and 2.1 ppm (g) are characteristic of the protons of the bound to the oxygen atom and the next methylene group, and a peak at 3.6 ppm (f) is characteristic of the protons of methylene group directly bonded to nitrogen. Another feature in the spectra for the N-alkylated polymer is the very weak peak of N−H amine hydrogen resonance near 5.3 ppm (d). These results indicate the presence of alkaneoxynitroazobenzene groups in the resulting PANI derivative, which is consistent with the FTIR results.

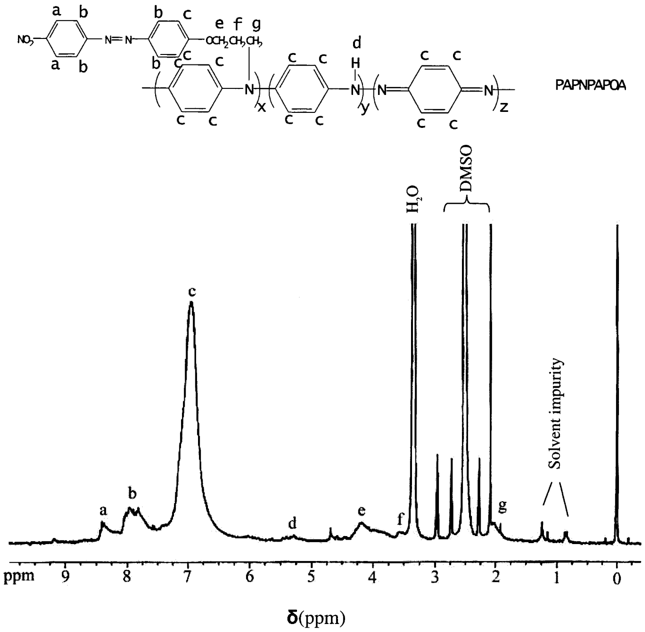

Figure 2. Typical ^{1}H NMR spectra of the PAPNPAPOA in d_6-DMSO.

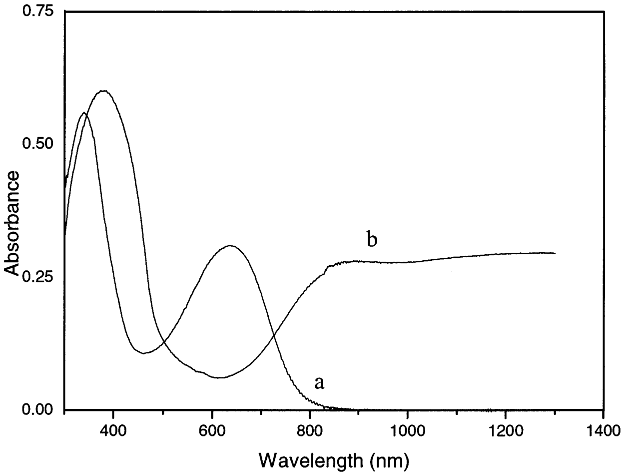

Figure 3. UV−vis spectra of PAPNPAPOA: (a) in NMP; (b) thin film coated on a quartz glass plate with 1.0 M HCl solution doping.

Elemental analysis of PAPNPAPOA gives an O/N atomic ratio of 0.56.[16] The graft concentration can be defined as the number of B3 units per aniline unit of PANI. It is determined from the O/N molar ratio of each copolymer, taking into account that the O/N molar ratio for B3 is 1 and there are 3 oxygens per B3 unit. Thus, the graft concentration can be calculated from the expression [(O/3)/(N−O)] to obtain a graft concentration of 0.42.

The UV−vis spectrum of the PAPNPAPOA dissolved in NMP solution has two absorption peaks at 338 and 638 nm as shown in Figure 3 (curve a). The first absorption peak corresponds to the overlap of the $\pi-\pi^*$ transition of the benzenoid rings of PANI[17] and the *trans*-azobenzene moiety of the B3 ($\lambda_{max} = 380$ nm),[18] while the latter is assigned as excition absorption of the quinoid rings of PANI.[17] As depicted in Figure 3 (curve b), the thin film of the PAPNPAPOA doped by 1.0 M HCl indicates that the absorption peak at 638 nm

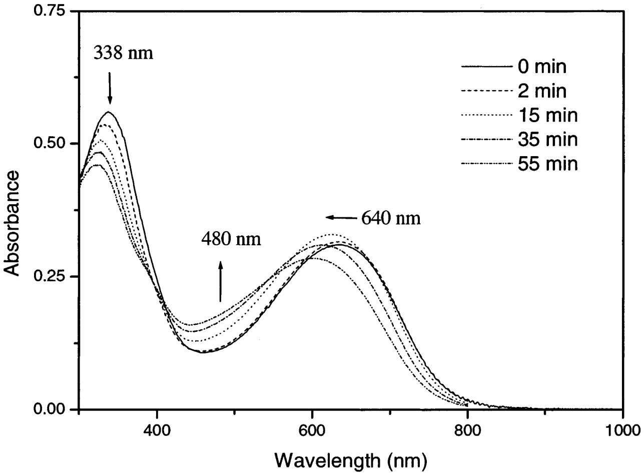

Figure 4. Photoisomerization of PAPNPAPOA dissolved in NMP solution upon irradiation with UV light ($\lambda = 365$ nm, 8 W).

disappeared; however, a new absorption peak at 800 nm was observed, which is identical to the emeraldine salt form (ES) of PANI.[19] Furthermore, the photoisomerization of PAPNPAPOA dissolved in NMP solution upon irradiation with UV light ($\lambda = 365$ nm) is shown as Figure 4. Interestingly, we found the absorption peak at 338 nm, attributed to the $\pi-\pi^*$ transition of the *trans*-azobenzene units, rapidly decreased. However, the weak absorption peak at 480 nm, attributed to the $n-\pi^*$ transition of the *cis*-azobenzene units, increased, which is more obvious compared with that of azobenzene moiety.[20] Meanwhile, the absorption peak at 640 nm, attributed to the exciton absorption of the quinoid rings of PANI, is largely blue-shifted to 605 nm upon irradiation with UV light due to effect of photoisomerization of the azobenzene units. It is known that the ionization potential, band gap, and bandwidth of PANI are affected by the torsion angles between adjacent rings.[21] According to the blue shift (from 640 to 605 nm) in the UV absorption spectrum, the alkaneoxynitroazobenzene groups attached on the N sites in the backbone can be expected to increase the torsional angle twisted by the *trans*−*cis*-azobenzene photoisomerization between adjacent rings. This will cause the degree of orbital overlap between the phenyl π electrons and the nitrogen lone pairs to decrease. This will further decrease the extent of π conjugation, resulting in increasing the energy lever of LUMO π_q. The above results proved again that the photochromic azobenzene side groups are linked on the PANI, and the resulting PAPNPAPOA can be photoisomerized upon UV irradiation.

In conclusion, we have successfully synthesized the first highly conducting PANI derivative PAPNPAPOA through an N-alkyl-substituted reaction. The freestanding film of PAPNPAPOA doped with 1.0 M HCl gives a conductivity of 1.2 S/cm at room temperature, which is higher than that of other N-alkyl-substituted PANI ($10^{-2}-10^{-7}$ S/cm). In particular, its solution in NMP shows trans−cis photoisomerization upon irradiation with UV light. Moreover, a blue shift of the exciton absorption of the quinoid rings of the PANI induced by the photoisomerization of the azobenzene moiety was observed. Further investigations into the photoisomerization and function of the obtained polymers are now in progress.

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