A New Route to the Synthesis of a Novel Poly(phenylene) Derivative

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Study on π−conjugated polymers has been an active research area during the last decades. Poly(arylene) is an important class of conjugated polymers which have received considerable attention toward the applications to electronic devices due to their high conductivity. As one of this kind of polymer, poly(phenylene) (PP) has been synthesized by electrochemical as well as chemical oxidative polymerization of benzene.[1,2] Through reductive coupling of dihalobenzene by electrolysis or with chemical reductants, pure poly(*p*-phenylene) or poly(*m*-phenylene) with clear linear structures can also be obtained.[3] However, the insolubility of PP gives rise to great difficulties in the characterization as well as in the process. Recently, soluble PP derivatives have been synthesized by oxidative polymerization of alkoxy-substituted benzene[4] or by catalyzed polycondensation of (2,5-dialkoxy-4-bromophenyl)boronic acid.[5] The addition of side groups to the PP backbone could not only improve the solubility but also change many other properties. We think it is an effective approach to modify PP by varying the introduced substituents for the purpose of adjusting the energy band of the polymer semiconductor. In general, if donor groups such as *N*,*N*-dimethylamino groups are introduced as substituents onto the conjugated backbone, the resulting polymer would exhibit properties of a p-type semiconductor, whereas those bearing withdrawing groups would display properties of an n-type semiconductor. As for the PP derivative bearing donor groups, it cannot be synthesized through the above-mentioned direct oxidative polymerization of the related monomer because the substituents we want to introduce are likely to be destroyed under oxidative conditions. Therefore a practicable synthesis route to the PP derivative bearing such substituents should be one which can protect these substituents during the process of polymerization.

In this paper, we report a new synthetic method for the preparation of poly(*N*,*N*-dimethylaniline) (PDMA). The synthetic process involved two steps: first, the formation of a CT complex between monomer *N*,*N*-dimethylaniline (DMA) and tetrachloro-*p*-quinone (TCQ) (see Scheme 1) and, second, the transformation of the CT complex itself into PDMA and tetrachloro-*p*-hydroquinone (TCHQ). Eastman et al.[6] and Yassin et al.[7] have studied the reaction of TCQ and DMA. They did not obtain any kind of polymer but crystal violet or *p*-substituted DMA. This might be the result of the fact that the reaction systems they studied were all dilute solutions in which DMA was first oxidized by TCQ to produce active intermediates which condensed with an excess of DMA to form crystal violet or *p*-substituted DMA. However, in our experiment we studied the polymerization of a crystalline CT complex in which free DMA was not available to perform the above-mentioned condensation with an active intermediate. Therefore, we obtained a new kind of polymer rather than low molecular weight species. The formation of a CT complex is characteristic of this type of polymerizing reaction, which has played an important role in protecting the dimethylamino groups and also provided a special reaction route with a relatively low energy of activation. As a result, the polymerization was carried out rapidly and thoroughly without the presence of any catalyst.

The CT complex prepared by mixing equal mole ratios of DMA to TCQ is a deep-colored crystalline powder. When heating at a temperature of 120 °C, it quickly turned into a dark blue solid. The reaction was monitored by X-ray diffraction at 80 °C for 3 min. It was found that the process of polymerization of the CT complex was accompanied with a bulk structure change from crystalline CT complex to amorphous polymer. In addition, a DSC study confirmed that the polymerization was an exothermal reaction with $\Delta H = -125.8$ kJ/mol, recorded at a heating rate of 20 °C/min. As seen from the DSC diagram, the reaction began at 65 °C and finished at 160 °C, leaving a peak position at 100.5 °C. We also tested the possibility of polymerization of alkoxybenzene or alkylbenzene in the same way and found that no polymerization occurred without the presence of catalyst such as $AlCl_3$. It seemed that the activity of polymerization depends on the degree of charge transition between the monomer and TCQ.

After polymerization, the product was dissolved in ethanol and then poured into diluted NaOH aqueous solution. The produced TCHQ was water-soluble and separated with the polymer. The precipitated polymer was filtered and washed with water several times and dried in vacuum. The obtained polymer was purified by washing with ethyl acetate in a silica gel column, finally getting a yield of 87%. The polymer was soluble in ethanol, chloroform, DMF, and acetic acid and could therefore be characterized with ^{1}H NMR spectroscopy and the UV/vis spectrum in solution. Elemental analysis (Found: C, 80.9; H, 7.6; N, 11.5) is consistent with the structure shown in Scheme 1 (Calcd for C_8H_9N: C, 80.7; H, 7.5; N, 11.8). The weight-average molecular weight of polymer was measured with GPC in THF against polystyrene standards and found to be 5600. The ^{1}H NMR spectrum of the polymer is shown in Figure 1. The two resonacnes at δ 3.22 and δ 3.04 ppm should be assigned to the methyl groups of substituents located at the polymer backbone and terminal groups, respectively. The relationship between the degree of polymerization (DP) and the ratio of the intensity of these two peaks can be expressed as $DP = 2(I_{3.22}/I_{3.04}) + 2$. According to the integration of these two peaks, the DP of the polymer was calculated to be 38 and the M_n was about 4500. The peaks between δ 6.80 and δ 7.36 ppm are resonances for the aromatic protons on the polymer backbone. The total area of these peaks was nearly half of that of peaks at δ 3.22 and δ 3.04 ppm together, which supported the structure presented in Scheme 1 according to the fact that twice as many protons are on the methyl groups as are on the benzene rings if the DP is high enough. However, it is not easy to determine the structure of the polymer backbone from the resonances of the aromatic protons since the polymer backbone contains two types of structural units—one is the *meta*-linked benzene ring and the other is the *para*-linked one. Enlargement of the peak at δ 3.22 ppm showed that the chemical shift of the methyl groups attached to the *meta*-linked units was slightly different from that of the methyl groups attached to the *para*-linked units. Both IR and UV/vis data confirmed that the *meta*-linked benzene ring was the preferential structural unit in the polymer backbone, which meant that the main peak at

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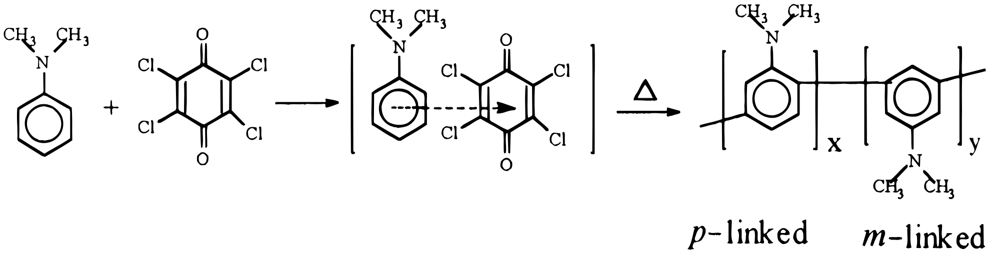
Scheme 1



around δ 3.22 ppm was the resonance of the protons of the methyl groups attached to the *meta*-linked units and the shoulder belonged to the methyl groups attached to the *para*-linked units. Calculated from the integration of these two discrete peaks, it could be determined that the polymer backbone was composed of 73% *meta*-linked unit and 27% *para*-linked unit.

The FTIR spectra of the polymer showed absorptions at 2954 and 2923 cm^{-1} for the presence of the CH_3 groups of substituents. A strong aromatic C$-$N stretching band was seen at 1361 cm^{-1}. The strong band at 1583 cm^{-1} and weak band at 1466 cm^{-1} were respectively characteristic of the stretching vibration of *meta*-linked and *para*-linked benzene rings.[8] The UV/vis spectrum of the polymer (shown in Figure 2) displays a peak at 305 nm and a shoulder at about 350 nm attributed to the $\pi-\pi^*$ electronic transition for the conjugated benzene ring in the polymer backbone. Due to the relatively poor conjugation degree of the π electrons, the *meta*-linked benzene ring exhibits a $\pi-\pi^*$ absorption much more blue-shifted than that of the *para*-linked benzene ring.[8,9] Therefore the bands at 305 and 350 nm respectively correspond to the absorption of *meta*-linked and *para*-linked structural units in the polymer backbone. The strong band at around 587 nm should be attributed to the n$-\pi^*$ transition of the substituents. Its abnormal strength was a result of the formation of a radical cation structure. ESR spectra of the polymer recorded a single-line signal at $g = 2.0056$ in either the solution or solid state, indicating the presence of delocalizing radicals on the polymer backbone. We also observed that if the radical cation was eliminated by means of chemical reduction with Zn powder in acetic acid aqueous solution, no absorption could be observed at 587 nm and that the absorption reappeared when the reduced polymer was oxidized with H_2O_2. There seemed to be a certain correlation between the delocalization of the radicals along the polymer backbone and the n$-\pi^*$ transition of the substituents. A detailed analysis of the ESR data is needed for the elucidation of the behavior of the radical cation.

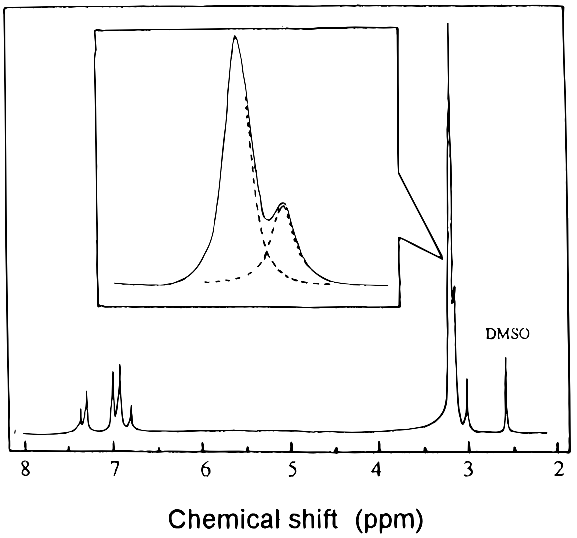


Figure 1. ^{1}H NMR spectrum of PDMA in DMSO-d_6.

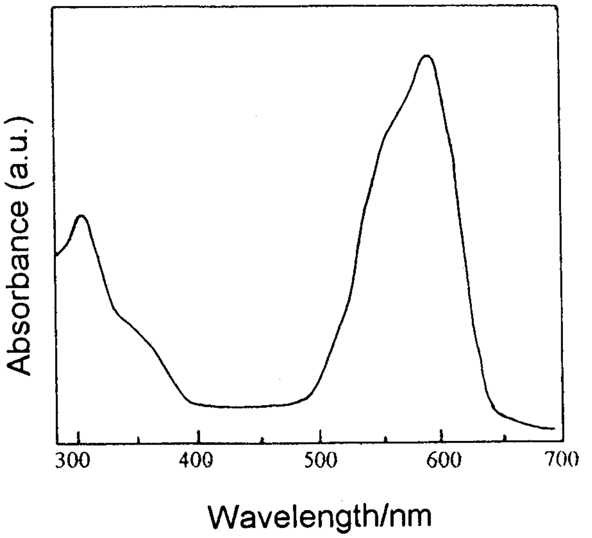


Figure 2. UV/vis spectrum of PDMA in $CHCl_3$.

In this work a new method for the synthesis of conjugated polymer based on the formation of a CT complex has been described. By using this new method a novel PP derivative bearing *N*,*N*-dimethylamino substituents has been synthesized. Some interesting properties of PDMA such as protonation, redox reaction, and chemical modification will be discussed in subsequent papers.

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