Synthesis of Polynitrobenzene by Chemical Modification of Poly(*N*,*N*-dimethylaniline)

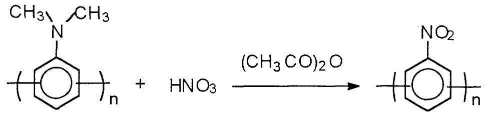
Haipeng Zheng, Ruifeng Zhang,* and Jiacong Shen
Key Laboratory for Supramolecular Structure & Spectroscopy, and Department of Chemistry,
Jilin University, Changchun, 130023, P. R. China

(Received February 25, 1997; CL-970139)

Nitrification of poly(N,N-dimethylaniline)(PDMA) was carried out to synthesize a new kind of poly(phenylene)(PP) derivative—polynitrobenzene(PNB). Characterization of PNB and the determination of another product showed that in this reaction almost all the N,N-dimethyl groups on PDMA were replaced by the nitro groups without degradation. A possible mechanism of this special reaction has been put forward.

Poly(phenylene)(PP) is one kind of conjugated polymer which possesses desirable qualities such as high mechanical strength,[1] thermol stability, and in the doped condiction, electrical conductivity.[2] However, because the polymer is infusible and insoluble in known solvents, only limited studies and functions have been made and developed. Most recent work on PP has focused on the synthesis of its soluble derivatives by adding various side chains to the phenyl groups[3-6] or by indirect synthetic methods.[7-9] To our knowledge, the introduction of side groups onto PP backbone was mainly carried out by the polymerization of the substituted monomer. Only a few works[10] have been reported on the synthesis of one PP derivative by chemical modification of another one.

Some works reported that by using plasma[11] or ultraviolet[12] excitation nitrobenzene could be homopolymerized to produce polymers or oligomers with unclear structure. However, polynitrobenzene(PNB) as one kind of PP derivative can not be synthesized by directly coupling of nitrobenzene or related monomer. In this paper we first reported a new effective method to synthsize PNB by nitrification of Poly(N,N-dimethylaniline) (PDMA)[13] in which the nitro groups completely replaced the dimethylamino groups.



PNB was synthesized according to the following procedure, that is, PDMA powder (1.2 g, 0.01 mol monomer unit) was first dissolved in hot acetic anhydride (20 mL) and excess of the concentrated HNO_3 (1mL, about 0.02 mol) was added dropwise to this solution. The reaction mixture was stirred at 70 °C for 1 h, then poured into water. The yellow precipitate appeared at once, which was filtered and washed thoroughly with water. The crude product was purified by reprecipitating from hot acetone to ethanol, then dried for 10 h. The yield of the resulting polymer is 94%. It was soluble slightly in ethanol and $CHCl_3$, but well in acetone, THF and DMF. Elemental analysis (Found: C, 57.86; H, 4.10; N, 10.92%) was consistent with the above-given structure of PNB(Calcd for $C_6H_3NO_2$: C, 58.31; H, 4.06; N, 11.30%).

The FTIR spectrum of the polymer is shown in Figure 1. The peak at 3087 cm^{-1} corresponds to the vibrational absorption of C-H bonds on benzene rings of the main chain. Two bands at 1546 and 1345 cm^{-1} should be ascribable to the asymmetric and symmetric vibration of nitro groups as the side groups. It is noted clearly that no trace of the absorptions at 2954 and 2923 cm^{-1} of the CH_3 groups on PDMA[11] could be detected in this spectrum, which means that PDMA has been thoroughly converted into PNB during nitrification.

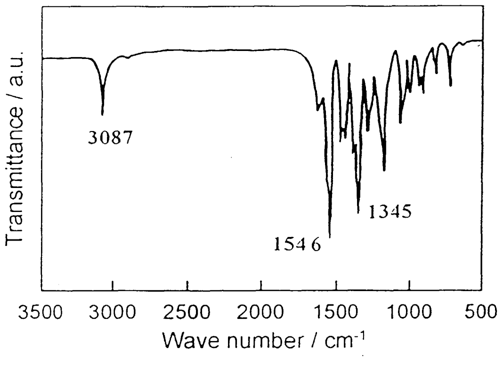


Figure 1. FTIR spectrum of PNB in KBr pellet.

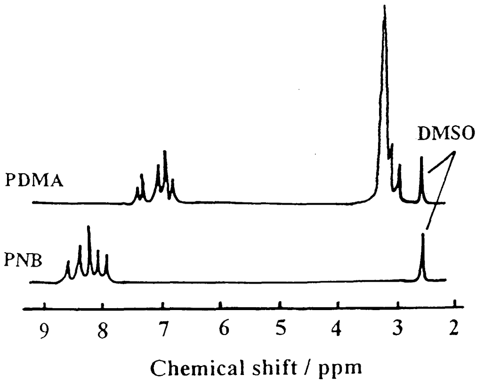


Figure 2. ^{1}H-NMR spectra of PDMA and PNB in DMSO-d_6.

Figure 2 shows the ^{1}H-NMR spectrum of PNB together with that of PDMA, which is inserted for comparison. The peak at δ=3.22 corresponds to the CH_3 groups on PDMA. In the spectrum of PNB, no peak appears in the range of high field, also supporting the structure of PNB that the CH_3 groups were substituted by the NO_2 groups completely. It is also found that in the range of low field the peaks assigned to hydrogen atoms on benzene rings of PNB are much more low-field-shifted than that of hydrogen atoms on benzene rings of PDMA. This kind of shift towards low field resulted from the effect of electron-withdrawing nitro groups on benzene rings.

The absorption spectrum of PNB in THF is shown in Figure 3. Compared with that of nitrobenzene in hexane, the π-π*

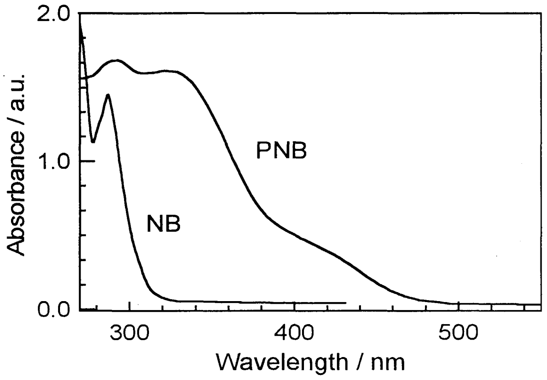


Figure 3. UV/vis absorption of PNB in THF and nitrobenzene (NB) in hexane.

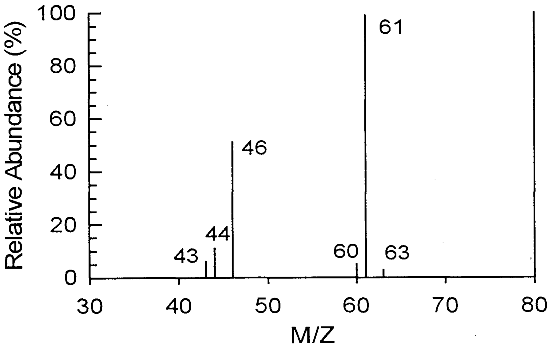
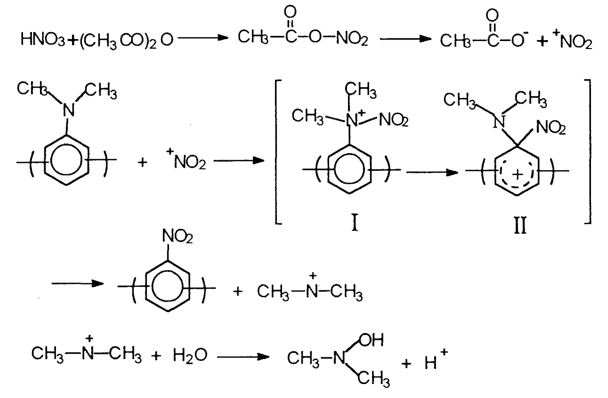


Figure 4. Mass spectrum of N,N-dimethylhydroxylamine.

absorptions of PNB is more red-shifted due to the effect of conjugation and this wide band with a small shoulder also shows the different-degree conjugation of the *p*-linked and *m*-linked benzene rings. Furthermore, the weight-average molecular weight of PDMA and PNB were calculated respectively to be 5600 and 5400 with GPC in THF against polystyrene standards. So we can infer that degradation reaction hardly took place during the process of nitrification, based on the fact that each repeat unit of PNB or PDMA has almost the same molecular weight.

The above characterization of PNB showed that the nitrification of PDMA was quite different from the traditional nitration reaction of arene. The nitro groups tended to replace all the N,N-dimethylamino groups on PDMA but not the hydrogen atoms on benzene rings. In order to determine other products of this reaction, the above-mentioned filtrate was first neutralized with KOH to pH=10 and then extracted with $CHCl_3$. The obtained solution was analysized with Gas Chromagraph Mass Spectrograph(Finnigan 4510P) after being dried with anhydrous Na_2SO_4, which exhibited only one component in the $CHCl_3$ solution. After analyzing this product by means of Mass Spectrum (see Figure 4), we confirmed the presence of N,N-dimethyl hydroxy amine in the reaction system and put forward the following reaction mechanism:



The nitronium ion which was generated from the reaction of Ac_2O and concentrated HNO_3[14] first attacked the nitrogen atom on each PDMA unit to form the intermediate I , then it might convert into the intermediate II by rearrangement. The replaced $N(CH_3)_2$ group finally produced in the form of N,N-dimethyl hydroxylamine as a by-product. In our opinion, there are two factors effecting this unusual reaction. Low-degree protonation of $N(CH_3)_2$ group in Ac_2O medium make it possible for $^+NO_2$ to interact with nitrogen atom on PDMA, while in concentrated H_2SO_4 medium this kind of nitrification could not occur as a result of high-degree protonation of $N(CH_3)_2$ group. The chain structure may prevent $^+NO_2$ from attacking benzene ring because of steric hindrance, which means that this special nitrification can not be extensively applied to low molecular weight species.

References

1 D. M. Gale, *J. Appl. Polym. Sci.*, **22**, 1971 (1978).
2 P. Kovacic and M. B. Jones, *Chem. Rev.*, **87**, 357 (1987).
3 M. Rehahn, A.-D. Schluter, G. Wegner, and W. Feast, *J. Polymer*, **30**, 1054 (1989) .
4 T. Wallow and B. M. Novak, *Polym. Prepr.*, **33**, 908(1992).
5 J. M. Tour, *Adv. Mater.*, **6**, 190 (1994).
6 J. R. Reynolds, J. P. Ruiz, and A. D. Child, *Macromolecules*, **24**, 678 (1991).
7 V. Chaturvedi, S. Tanaka, and K. Kaeriyama, *Macromolecules*, **26**, 2607 (1993).
8 D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.*, **116**, 10507 (1994).
9 D. G. H. Ballard, A. Courtis, I. M. Shirley, and S. C. Taylor, *J. Chem. Soc., Chem. Commun.*, **1983**, 954.
10 M. Hamaguchi, H. Sawada, J. Kyokane, and K. Yoshino, *Chem. Lett.*, **1996**, 527.
11 K. Inagaki, Jpn. Kokai Tokkyo Koho JP 62243617, *Chem. Abstr.*, **108**, P77207d (1988).
12 T. Shiota, T. Kanayama, and K. Hayashi, *Kobunshi Ronbunshu*, **38**, 183 (1981).
13 R. Zhang, H. Zheng, and J. Shen, *Macromolecules*, **29**, 7627 (1996).
14 Henry Feuer, in "The Chemistry of the Nitro and Nitroso Groups," John Wiley & Sons, New York, Part I (1969); Part II (1970).