

# Chemical synthesis of cross-linked polyaniline by a novel solvothermal metathesis reaction of *p*-dichlorobenzene with sodium amide

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Received 3 December 2004; received in revised form 10 January 2005; accepted 14 January 2005

Available online 26 February 2005

## Abstract

We reported the chemical synthesis of cross-linked polyaniline (PANI) by a novel solvothermal metathesis reaction of *p*-dichlorobenzene (C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>) with sodium amide (NaNH<sub>2</sub>) in benzene at 220 °C. In this method, the aniline monomer and complicated treatment were needless and the yield of final products was over 50%. The as-synthesized brown samples were NMP-soluble but water-insoluble; and they were characterized by XRD, FT-IR, UV–vis absorption, XPS, elemental analysis, TGA, and TEM. It was found that solvents have significant influence on the final product. The predominant mechanism of chain growth in PANI polymerizations was proposed as the ionic S<sub>N</sub>Ar process; however, further theoretical and experimental investigations are needed to obtain the undoubted evidences. We believe that this novel solvothermal metathesis reaction will give us a new guideline for the synthesis of some polymers.

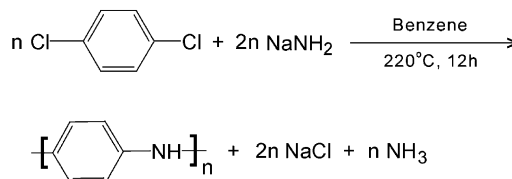
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**Keywords:** Polyaniline; Polymer synthesis; Metathesis reaction

## 1. Introduction

The discovery of conducting polymers has opened up a new promising field in materials science and engineering. The most widely studied conducting polymers include polyaniline (PANI), polypyrrole, and polythiophene. Among them, PANI is appealing due to its environmental stability, high degree of processability and interesting redox properties associated with its chain heteroatom [1–3]. Recently, remarkable progress in the field of nanostructured PANI has been made [3–8]. Exploring new methods to synthesize PANI and its nanostructures is significant for both fundamental research and practical application. In the past few years, considerable methods have been performed for the synthesis of PANI, including oxidative polymerization [9,10], emulsion polymerization [11], interfacial polymerization [3,4,12], electrochemical polymerization [13], and enzymatic polymerization [14,15]. In the traditional methods, the aniline monomer is a prerequisite to

the synthesis of PANI. Herein, we describe a novel solvothermal metathesis reaction of *p*-dichlorobenzene with sodium amide for the chemical synthesis of PANI in benzene. In our strategy, the aniline monomer is needless. The reaction scheme can be formulated as follows:



It is well known that alkali metal amides are strong bases and they have significant application in chemical synthesis [16–18]. It was reported that imide salt (or ionic nitride) can be prepared by loss of ammonia from amide salt on heating [19], which enlightened us on attempting to make NaNH<sub>2</sub> transform to Na<sub>2</sub>NH by loss of ammonia on heating under suitable conditions. The renescent Na<sub>2</sub>NH can be used as a good kind of –NH– source due to its high reactivity. In the above metathesis reaction, PANI is readily formed via elimination of NaCl. We note that our reaction strategy is similar to the reaction for commercial synthesis of poly(*p*-phenylene sulfide) (PPS) from a sodium sulfide equivalent (e.g., an equimolar mixture of sodium hydrosulfide and

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sodium hydroxide) and *p*-dichlorobenzene (DCB) in *N*-methylpyrrolidinone (NMP) at 200–280 °C [20].

## 2. Experimental part

### 2.1. Materials

In a typical experiment, about 45 mL benzene (dehydration by metal sodium for several hours in advance) was placed into a Teflon-lined stainless steel autoclave with 60 mL capacity; then nitrogen stream was injected into benzene to drive off the oxygen for 10 min. And then 1.47 g  $C_6H_4Cl_2$  (*p*-dichlorobenzene) and 0.78 g  $NaNH_2$  (sodium amide, m.p. 210 °C) were added. The autoclave was sealed under a nitrogen atmosphere and heated from room temperature to 220 °C with a speed of about 10 °C/min in a furnace, then kept at 220 °C for 12 h, and finally cooled to room temperature in the furnace naturally. After filtration, the obtained brown coherent product was rinsed with distilled water to remove the residual benzene, then ground in an agate mortar for a few seconds. After that, it was washed with distilled water to remove the byproduct NaCl, and then dried in vacuum at 60 °C for several hours. Finally, about 0.50 g water-insoluble but NMP-soluble brown powders were obtained for characterization.

### 2.2. Characterization

XRD patterns were collected with a  $2\theta$  range from 5 to 60° with a scan speed of about 2° ( $2\theta$ )/min on a Phillips X'Pert SUPER powder X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), using a silicon waver as the underlay. TEM images were recorded on a Hitachi-800 TEM at an acceleration voltage of 200 kV. Samples were deposited from ethanol suspensions of the products onto thin amorphous carbon films supported by copper grids. XPS were recorded on an ESCALab MKII instrument with Mg  $K\alpha$  radiation as the exciting source. Ion beam cleaning was not carried out before the XPS analysis because many studies have shown that this high energy process results in preferential nitrogen loss and changes in nitrogen chemical environment. Bulk elemental analysis (from C–N–H combustion) was taken on a Elementar Vario EL-III elemental analyzer. Oxidation and reduction temperatures are 950 and 500 °C, respectively. FT-IR was recorded with a Nicolet Model 759 Fourier transform infrared spectrometer, in transmission mode in a KBr pellet. UV–vis spectrum was obtained from powders dissolved in NMP using a Shimadzu UV–visible Recording Spectrophotometer (UV-240). TGA was run on a Shimadzu DT-50 thermalizer system with a rate of 10.0 °C/min up to 800 °C under argon flow with a rate of 20.00 mL/min.

## 3. Results and discussion

The XRD patterns (Fig. 1) show a broad peak centered at about 19.0° ( $d = 4.67 \text{ \AA}$ ), which is mainly ascribed to the periodicity parallel to the polymer chain [21]. Suppose that an N–Ph–N length is about 5.52 Å and a Ph–N–Ph angle is about 120° [21], the half-length of a periodicity parallel to the polymer chain will be 4.78 Å ( $5.52 \times \sin 60^\circ = 4.78$ ). This value is very close to the experimental value of 4.67 Å and the result supports the existence of the repeat unit of N–Ph–N in the product. From the XRD patterns, one can see that the product is almost amorphous and the periodicity perpendicular to the polymer chain is completely missing. Ding et al. ever reported that polyaniline (EB) would become completely amorphous from partially crystalline after annealing at 215 °C because of a non-reversing chemical cross-linking reaction [22]. Considering that our reaction temperature (220 °C) and the XRD patterns are comparable to those of Ding et al., we conclude that the amorphousness of the product is attributed to the cross-linking reaction in our synthesis.

The FT-IR spectra are shown in Fig. 2. All the peaks and bands can be well assigned to the vibration modes of PANI. The bands at 3370 and 3026  $cm^{-1}$  can be assigned to the N–H and C–H stretching modes, respectively. The bands at 1598, 1488, and 1150  $cm^{-1}$  are attributed to the C=C and C–C stretching and bending modes for the benzenoid units, and 1306  $cm^{-1}$  is attributed to C–N stretching mode for N–Ph–N units. The band at 746  $cm^{-1}$  is attributed to the C–H out-of-plane bending mode [1]. The FT-IR spectra suggested that the as-synthesized sample is the fully reduced Leucoemeraldine.

The UV–vis absorption spectra (Fig. 3) showed strong blue-shift absorption band centered at about 290 nm, which can be assigned to the  $\pi \rightarrow \pi^*$  electronic transition [1,23]. The absorption band related to charge-transfer excitation-like transition disappears in the range from 450 to 650 nm, which suggests that the oxidation state of the synthesized

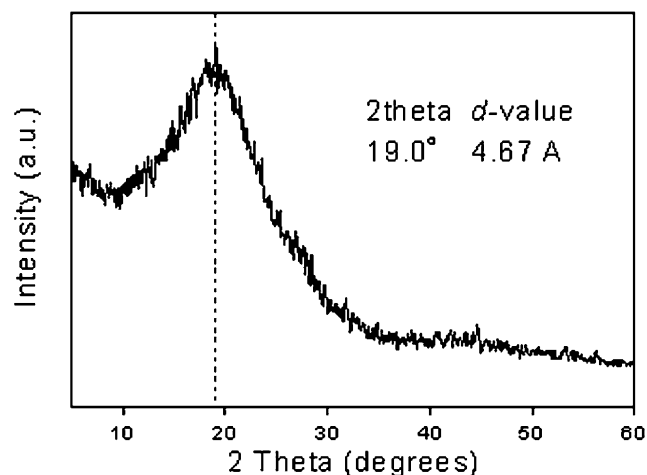


Fig. 1. XRD patterns of the sample.

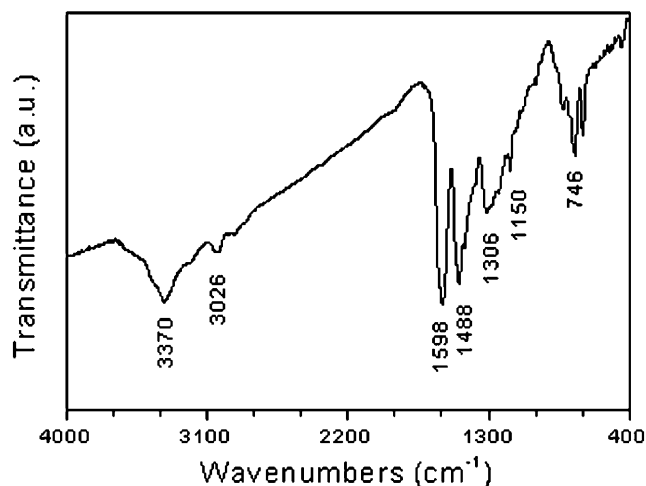


Fig. 2. FTIR spectra of the sample.

polyaniline is very similar to that of the fully reduced Leucoemeraldine [1], and it is in agreement with the FT-IR results. The electrical conductivity measurement (by a two-probe method) of compressed pellet shows the sample is dielectric, which further supports that the sample is the fully reduced Leucoemeraldine. It is well known that the fully reduced Leucoemeraldine can be readily oxidized by oxidants such as bubbling oxygen,  $\text{H}_2\text{O}_2$ , and APS [24], but our synthesized Leucoemeraldine is difficult to be oxidized by common oxidants. Why? It is reported that the annealing of dilute EB/NMP solution resulted in cross-linking reaction instead of reductive reaction and the obtained cross-linked polyaniline could not be oxidized [25]. According to this result, we conclude that the cross-linking causes that our synthesized Leucoemeraldine is difficult to be oxidized. It should be noted that the two cross-linking reactions of lee's [25] and ours may be not the same, but they have the same effects on the oxidation of PANI.

XPS was performed to address the chemical bond nature of the prepared sample. No peaks of other elements except C, N, and O are observed on the survey spectra (Fig. 4a).

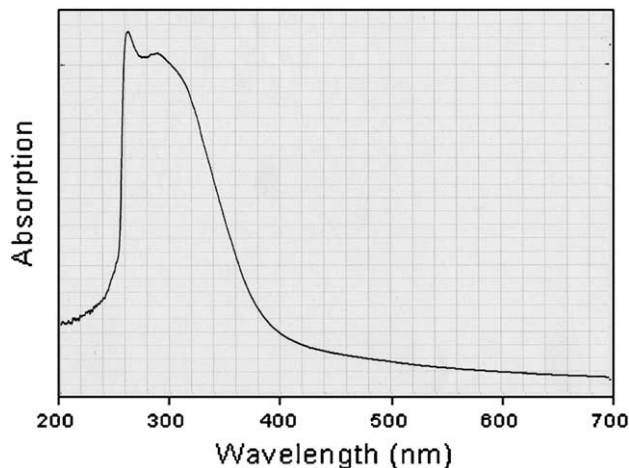


Fig. 3. UV-vis absorption of the NMP solutions of the sample.

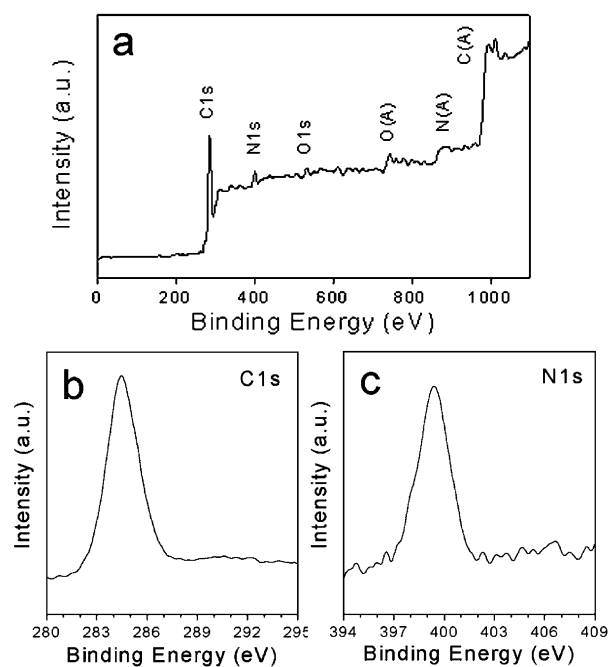


Fig. 4. XPS spectra of the sample.

The XPS does not show signals of Cl and Na, which indicates the atomic proportions of Cl and Na in the final product are less than 1%. The peaks for O1s can be attributed to the trace  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , or  $\text{CO}_2$  adsorbed on the surface of the samples. Higher resolution spectra were taken on the C1s and N1s regions. The binding energy of C1s is 284.40 eV (Fig. 4b). The N1s peak (Fig. 4c) at 399.50 eV shows an asymmetry in the left part. The nitrogen atoms mainly have one chemical state in the speculative Leucoemeraldine, namely benzenoid amine  $\text{NH}(-\text{Ph})_2$ . It should be noted that the product is a coherent mass before grinding, which can be attributed to the following two factors. First, PANI is insoluble in benzene; second, cross-linking and branch joint occur in PANI, which can produce  $\text{N}(-\text{Ph})_3$  unit. There are three  $\sigma$  bonds in both  $\text{NH}(-\text{Ph})_2$  and  $\text{N}(-\text{Ph})_3$  for N atom, but the latter has a larger  $\pi$ -conjugated system. So the latter N atom has more negative charge than the former one. Therefore, the left and right parts of the peaks are attributed to  $\text{N}(-\text{Ph})_3$  and  $\text{NH}(-\text{Ph})_2$ , respectively. Our observed C1s and N1s binding energies are comparable to the previously reported XPS data of the fully reduced Leucoemeraldine [1]. The surface N/C atomic ratio of the sample from XPS analysis is about 0.13, which is comparable to the value of 0.15 by bulk elemental analysis ( $\text{C}_{6.6}\text{NH}_{5.2}$ ) and the calculated value of 0.17 for polyaniline ( $\text{C}_6\text{NH}_5$ ). Considering the experimental N/C atomic ratio is a little smaller than the calculated value, we think that a small amount of polybenzene units may exist in the synthesized PANI chains. Because  $\text{NaNH}_2$  is a very strong base, it is possible that some polybenzene or m-PANI could be produced in the reaction.

A typical TEM images is shown in Fig. 5. It is interesting

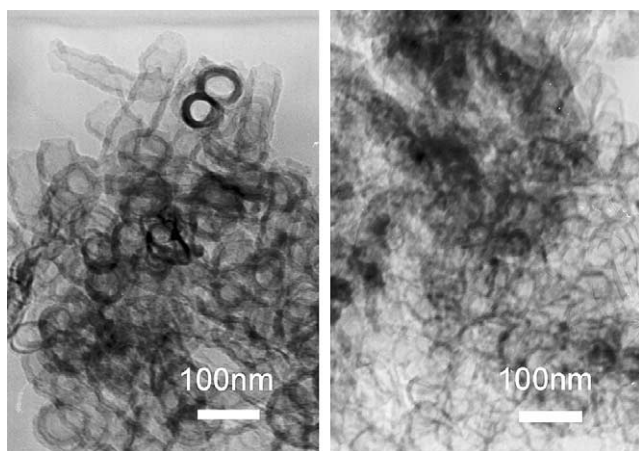


Fig. 5. TEM images of the sample.

that the prepared polyaniline has various morphologies, such as fibers, tubes, and hollow spheres, which are different from the reported results of forming approximately linear bundles [4]. The formation mechanism of various morphologies is not clear at present and needs further investigation.

TGA curves (Fig. 6) reveals that the product was very robust under an argon flow. Rate of weight-lossing was small at 30–450 °C. The weight-lossing at 100–300 °C was due to the evaporation or decomposition of a few unstable oligoaniline. At 300–450 °C the rate of weight-lossing decreased. The sharp weight lossing beginning at 500 °C presumably corresponded to the large-scale thermal degradation of PANI chains [12]. It is obvious that the evaporation or decomposition of the product did not complete even by 800 °C, which can be attributed to the good thermal stability of the PANI main chain and the cross-linking effect.

Many different mechanisms have been proposed in the literature for PPS growth by the mentioned process in Section 1 [26]. D. R. Fahey and co-worker concluded that the mechanism in PPS polymerizations was the ionic  $S_NAr$

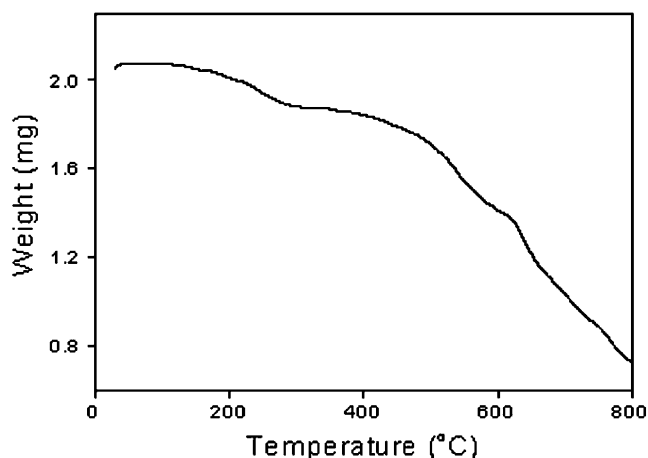


Fig. 6. TGA curves of the sample.

process on the basis of a lot of experimental evidence [26]. Considering that our synthesis strategy is very similar to that of PPS, the predominant mechanisms of chain growth in PANI polymerization could be proposed as the ionic  $S_NAr$  process; however, further theoretical and experimental investigations are needed to obtain the undoubted evidences. In addition, it should be pointed out that solvents have significant influence on the final product. According to our experiments, benzene (or toluene) is a suitable solvent for PANI synthesis, but pyridine (or NMP) is not, which could be attributed to the side reactions of strong base  $NaNH_2$  with pyridine or NMP.

#### 4. Conclusion

In summary, we first report the chemical synthesis of polyaniline by a novel solvothermal metathesis reaction of *p*-dichlorobenzene with sodium amide in benzene. We believe that this novel metathesis reaction will give us a new guideline for the synthesis of some polymers.

#### Acknowledgements

The authors acknowledge support from National Natural Science Foundation of China, Chinese Ministry of Education, and Chinese Academy of Sciences. We are also thankful to Dr. J. X. Huang from UCLA for his helpful discussion.

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