Inverse miniemulsion copolymerisation of aniline with p-phenylenediamine

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Polyaniline/poly(p-phenylenediamine) (PAN/PAPPD) copolymer was prepared in an inverse miniemulsion by the copolymerisation of p-phenylenediamine and aniline using $(NH_4)_2S_2O_8$ as an oxidant in the presence of surfactant sodium dodecylbenzenesulfonate. The PAN/PAPPD copolymers were characterised in terms of X-ray diffraction diagrams, Fourier transform infrared and dynamic light scattering, respectively. The effect of a monomer molar ratio, the content of the surfactant, the concentration of the oxidising agent and the temperature on the yield and the intrinsic viscosity of the copolymer were investigated. In this system, the apparent value of the energy of activation (E_a) was calculated to be −16.1 kJ/mol from 5 to 30°C. The conductivity of the copolymer obtained in the miniemulsion was higher than that in the solution.

1. Introduction: Polyaniline (PAN) has been widely applied in the areas of batteries, sensors, electrochromic devices, capacitors, photochemical cells and light emitting diodes because of its environmental stability, high conductivity, good redox reversibility and various application potentials [1, 2]. Traditionally, PAN is typically synthesised via a chemical-oxidation polymerisation with oxidising agents such as ammonium persulfate (APS) or electrochemical preparation; production can be carried out as solution [3–5], emulsion [6–8], microemulsion [9–11] or miniemulsion free-radical polymerisation [12–14]. However, PAN is difficult to process because of its rigidity, large polar, poor mechanical properties, insolubility and infusibility, causing limitations in its industrial applications and further research [15, 16]. The solubility, the processability and the electrical properties of PAN can be improved by the copolymerisation of a series of derivatives of aniline and particularly by the choice of the substituents [17, 18]. This has been established as a convenient method for the preparation of novel conducting materials with desired properties superior to those of individual homopolymers.

A number of alky [19, 20] or alkoxyl ring-substituted polyanilines [21], such as o-toluidine [19], o-ethoxy aniline [20] and o-aminobenzoic acid [21] are used; the properties of such copolymers are controlled by adjusting the molar feed ratio of the comonomers.

Poly(aniline-co-PPD) (PAPPD) has been paid less attention until now. Only a few studies about the copolymerisation of aniline and p-phenylenediamine have been reported [22].

Miniemulsions, which are prepared via ultrasonication, combine the bulk reaction in nanosized droplets and the advantages of emulsion polymerisation. The miniemulsion polymerisation is known to be a powerful technique to produce a whole variety of new polymer latexes. By now, no report concerning the miniemulsion copolymerisation of aniline (AN) with p-phenylenediamine has been found. The effect of the miniemulsion copolymerisation on the properties of PAPPD has not yet been studied, particularly with nanoscale synthesis.

The aim of the work reported in this Letter was to investigate the effect of the miniemulsion copolymerisation of the PAPPD. With the further aim of enhancing the processibility and the conductivity, the synthesis of PAPPD was achieved by the inverse miniemulsion polymerisation method in the presence of a cationic surfactant. The synthesised copolymers were characterised with Fourier transform infrared (FTIR), ultraviolet-visible (UV–vis), thermogravimetric analysis (TGA), X-ray diffraction techniques. The effect of the copolymerisation on the morphological, the thermal and the conductivity characteristics of the resulting copolymers was analysed.

2. Experimental

2.1. Chemicals: Aniline (AR) was obtained from the Tianjin Tianli Chemical Reagent Co. Ltd, Tainjin, China. It was distilled under reduced pressure prior to use. p-phenylenediamine (AR) was purchased from the Shanghai Jinshanting Chemical Reagents Factory, China. APS (AR) and sodium dodecyl benzenesulfonate (SDBS) (AR) were purchased from the Tianjin Fuchen Chemical Reagents Factory, China and used as received. Hexadecane (HD) (AR) was obtained from Shanghai Chemical Reagent Corporation, China and used as received. Other reagents were used as received. All the solutions were prepared by using bidistilled water.

2.2. Inverse miniemulsion copolymerisation of p-phenylenediamine with aniline: The inverse miniemulsions were prepared according to the following procedure. As an example, a mixture of 0.9313 g aniline (0.01 mol) and 3 g of concentration aqueous HCl was dispersed in a solution of 6.9696 g SDBS (0.02 mol) in 80 ml of cyclohexane. 1.0814 g solution of p-phenylenediamine (0.01 mol) was mixed with aniline in a reaction. 2.2818 g APS (0.02 mol) was dissolved in 10 ml bidistilled water and was introduced. The above procedure was performed under stirring and nitrogen at room temperature for 1 h. The coarse inverse emulsion was then sonicated with a Fisher Model 30 sonic dismembrator operated at 70% power output for 5 min. The obtained miniemulsion was transferred into a 100 ml flask with a magnetic stirring bar. The reaction mixture was kept in a water bath at a desired temperature range of 5–30°C.

The copolymers PAPPD was synthesised with the aforementioned procedure with different monomer feed ratios of p-phenylenediamine to aniline. The samples were dedoped by washing with a 5% ammonium hydroxide solution. Then, the samples were sequentially washed three times with water and clyclohexane to remove a possible soluble fraction. The powders of the copolymers were then dried in vacuum at 65°C for 18 h.

2.3. Characteristics of the copolymer: The dried copolymer samples were used to measure the spectra and the conductivity. The FTIR spectra of the powdered copolymers were taken in the form of KBr pellets using a Thermo Nicolet 370 FTIR spectrophotometer.

The intrinsic viscosities of the PAPPD copolymers were determined using an Ubbelohde viscometer at 30 ± 0.1°C. The solvent was NMP.

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For the X-ray diffraction analysis, X-ray diffractograms were recorded with an XRD-6000 (Shimadzu, Japan) crystallographic unit and a Cu Kα ($\lambda = 1.541$ Å) radiation mode was used (40 kV, 30 mA) for recording data in the range of $2\theta = 10$–$80°$ at a scan rate of 8°/min with 0.02° steps.

Final latex particles were measured with a Zetasizer (3000 HSA, Malvern) at a fixed scattering angle of 90°. The basic principle for measuring the size distribution is based on the technique of dynamic light scattering.

The electrical conductivities of the resulting PAPPD were measured on dried pressed pellets at room temperature by using the four-point probe technique and the calculation of the conductivity σ of the PAPPD samples was as described in the literature [23]. σ was calculated according to the formula: σ(electrical conductivity) = L/RS (L, R and S refer to the thickness, the resistance and the touching area of the sample, respectively).

The yield of the polymer was determined by the formula: yield (%) = $W_2/W_1 \times 100\%$ where W_1 is the initial weight of the comonomers and W_2 is the weight of the resultant polymer.

3. Results and discussion

3.1. Synthesis of PAPPD in the miniemulsion: PAPPD copolymers were prepared by chemical oxidation copolymerisation of p-phenylenediamine and aniline at room temperature in the miniemulsion using APS as the oxidising agent as described in Fig. 1.

The obtained PAPPD copolymer was characterised by FTIR, and the FTIR spectrum is shown in Fig. 2. As indicated, the band at 817 cm^{-1} was assigned to the deformation of the CH out of the plane. A medium peak at 1307 cm^{-1} is due to the C–N stretching vibration in an alternative unit of quinoid–benzenoid–quinoid. The much stronger absorption peak at 1508 cm^{-1} was attributed to the benzenoid unit. The stretching vibration of the benzene ring of the PPD portion appeared at 1585 cm^{-1}. The band at 2801 cm^{-1} was assigned to the oligomers of aniline, as reported by Kang *et al.* [24].

The PAPPD copolymers were further analysed by X-ray diffractograms. In the X-ray diffractograms (Fig. 3), two polymers with AN/PPD ratios of 7:3 and 3:7, respectively, exhibit their strongest peak at $2\theta = 20.8°$ and 24.4°, their second strongest peak at 19.3° is attributed to the momentum transfer and the periodicity parallel to the polymer chain. A medium peak appeared at 16.7°. The results were similar to [22]. However, the X-ray diffractograms of the copolymers obtained were almost identical in the presence of different molar ratios.

Fig. 4 presents a plot of the particle size distribution for the PAPPD particles synthesised with AN and PPD molar ratios of 7:3 in the miniemulsion system. As can be seen from Fig. 4, the particle size distribution centred at 216, 92 and 28 nm, respectively.

3.2. Effect of the PPD content on the copolymerisation yield and the intrinsic viscosity of the copolymer: An investigation was conducted to determine the effect of the varying molar ratio of the AN/PPD on the copolymerisation yield. The reaction time of the copolymerisation was kept at 6 h with the molar ratios of aniline and p-phenylenediamine varying from 10:0 to 0:10. A series of experiments were performed. The results of the experiments are shown in Fig. 5. The yield decreased with an increasing PPD content and reached the minimum value of 27.92% at the PPD content of 90 mol%. The effect of the monomer molar ratios of the PPD and the AN on the intrinsic viscosity of the copolymers of PPD with AN is depicted in

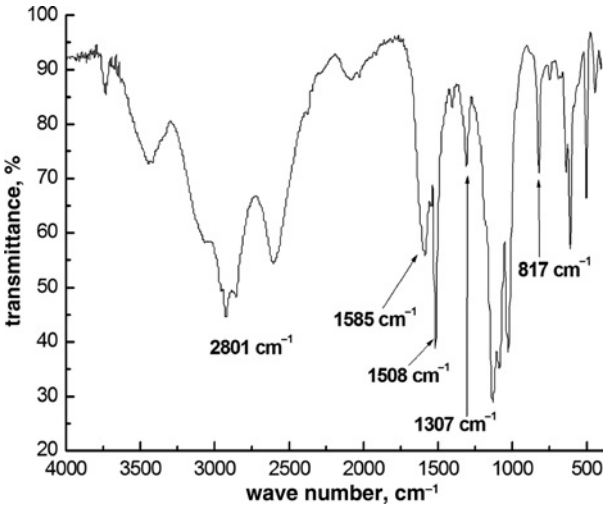


Figure 2 *FTIR absorption spectra of the copolymers with an AN/PPD molar ratio of 5/5*

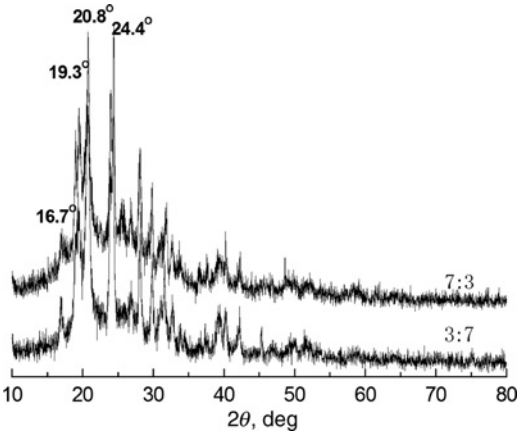


Figure 3 *X-ray diffraction diagrams of the copolymers with AN/PPD molar ratios of 7:3 and 3:7*

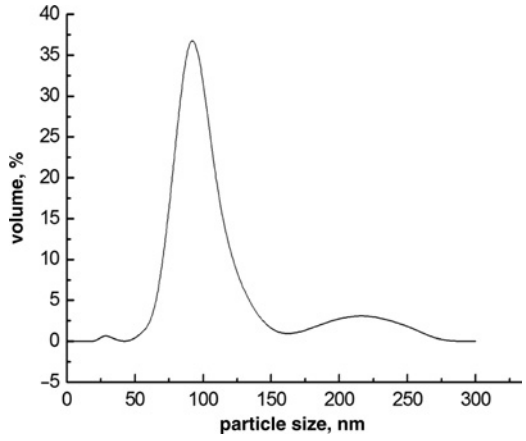


Figure 4 *Particle size distribution of the PAPPD for the oxidation copolymerisation of AN and PPD in the miniemulsion system with AN and PPD molar ratios of 7:3*

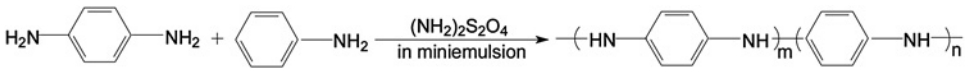


Figure 1 *Preparation of the PAPPD copolymer in reverse miniemulsion*

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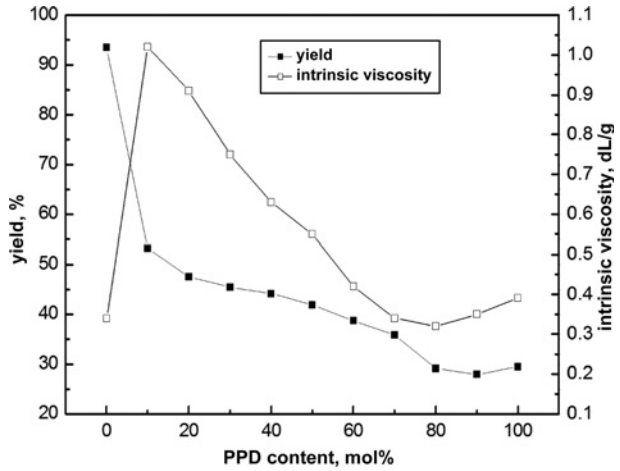


Figure 5 *Variation of the polymerisation yield and the intrinsic viscosity with the PPD feed content in the PPD/AN copolymers*
Oxidising agent/monomer ratio = l/1, surfactant/monomer ratio = l/1 and polymerisation time = 6 h

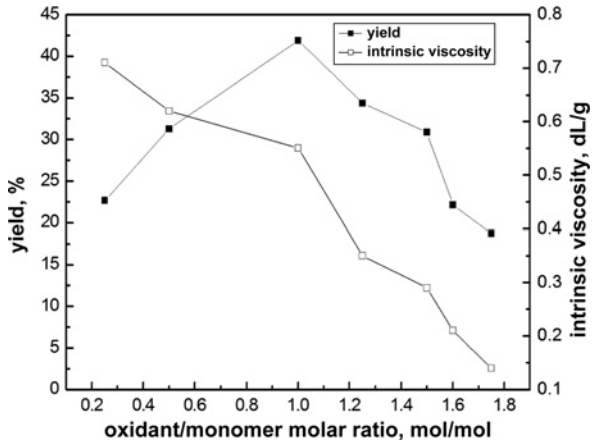


Figure 7 *Variation of the polymerisation yield and the intrinsic viscosity of the PPD/AN (5/5) copolymers with the oxidant/monomer ratio during the miniemulsion polymerisation of PPD and AN*
Surfactant/monomer ratio = l/1, PPD/AN = 5/5 and polymerisation time = 6 h

Fig. 5. The maximal intrinsic viscosity was observed with a molar ratio of 1:9. The intrinsic viscosity decreased with the molar ratio from 1:9 to 8:2. This was because the inhibition effect between the two monomers increased with increasing content of the PPD resulting in a hindrance to the polymerisation process.

3.3. Effect of the surfactant content on the copolymerisation yield and the intrinsic viscosity of the copolymer: The surfactant plays an important role in the miniemulsion polymerisation. The surfactant was used as both the formation micelles and a dopant of the polymer in the miniemulsion polymerisation of aniline.

As depicted in Fig. 6, the copolymer yield increased with the molar ratio of the surfactant/monomer, reaching the maximum value of 41.88% at the molar ratio of 1. With an increase in the molar ratio of the surfactant/monomer from 1 to 12, the yield decreased monotonically from 41.88 to 21.91%. Meanwhile, the intrinsic viscosity reached the maximum value at the molar ratio of 0.5. The above results showed that the surfactant had a vital influence on not only the yield but also the intrinsic viscosity of the copolymerisation of PPD and AN in the miniemulsion.

3.4. Effect of the amount of the oxidising agent on the copolymerisation yield and the intrinsic viscosity of the copolymer:

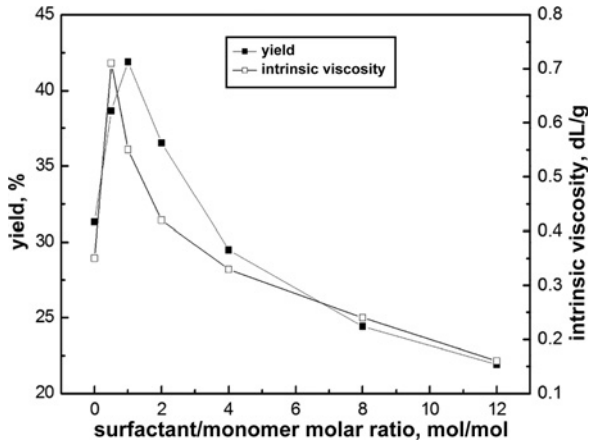


Figure 6 *Variation of the polymerisation yield and the intrinsic viscosity of the PPD/AN (5/5) copolymers with the emulsifier/monomer ratio*
Oxidising agent/monomer ratio = l/1, PPD/AN = 5/5 and polymerisation time = 6 h

The effect of the molar ratio of the oxidant $(NH_4)_2S_2O_8$/monomer on the copolymerisation of PPD/AN (5/5) at room temperature in the miniemulsion was studied.

As can be seen from Fig. 7, the copolymerisation yield increased with increasing molar ratio of the oxidant content from 0.2 to 1 and exhibited a maximum at the oxidant/monomer molar ratio of 1. However, the copolymerisation yield decreased when the molar ratio of the oxidant content increased from 1 to 1.75. It is probable that some comonomers could not be oxidised to polymerise, which reduced the polymerisation when less oxidising agent was added. However, the intrinsic viscosity of the resulting copolymer decreased with increasing of the molar ratio of the oxidant/monomer from 0.2 to 1.75. Two comonomers could be oxidised to the radical cation when more oxidising agent was added, leading to the inhibition effect increasing. The intrinsic viscosity of the copolymer was higher when the concentration of the oxidising agent was less. This might be because of the priority of the chain propagation from the monomer compared with the chain initiation because the probability of chain propagation was larger than the possibility of chain ending.

3.5. Effect of temperature on the copolymerisation yield and the intrinsic viscosity of the copolymer: The effect of the changing temperature on the copolymerisation was examined in the range of 5–30°C. All the copolymerisation reaction times were kept at 6 h. The results were listed in Table 1. As can be seen from Table 1, the yield of the copolymer decreased with increasing temperature in the range of 5–30°C. The rate of the decomposition of the oxidising agent was slower at a low temperature. The radical cations were of higher stability in this system. Furthermore, the surfactant made the chain termination reaction rate lower. Thus, it would favour chain propagation under these conditions. However, the intrinsic viscosity exhibited the highest value at 20°C.

3.6. Conductivity studies: The conductivity values of the samples of the PAPPD obtained from the miniemulsion and obtained in the HCl solution are given in Table 2. The conductivity of the sample of the PAPPD obtained in the miniemulsion and obtained in the solution was found to be 4.44×10^{-5} and 2.12×10^{-5} S/cm^{-1}, respectively. The conductivity of the copolymer obtained in the miniemulsion was found to be higher than that of the copolymer obtained in the solution.

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Table 1 Effect of temperature on the copolymerisation yield and the intrinsic viscosity of the copolymer

Run	T, °C	Yield, %	k_P^{app}, s^{-1} [b]	Intrinsic viscosity, dL/g
1	5	67.85	−5.76	0.35
2	10	58.48	−5.91	0.48
3	15	52.52	−6.02	0.53
4	20	48.14	−6.11	0.63
5	25	41.88	−6.25	0.55
6	30	37.05	−6.34	0.51

Surfactant/monomer ratio = l/1, PPD/AN = 5/5, oxidising agent/monomer ratio = l/1, polymerisation time = 6 h. k_P^{app} was determined from the kinetic slope

Table 2 Conductivity values of the PNA and its copolymers

Sample	Conductivity, S/cm
PAPDD obtained in the miniemulsion	4.44×10^{-4}
PAPDD obtained in the solution [22]	2.12×10^{-5}

Fig. 8 for aniline and PPD shows the Arrhenius plot of the logarithmic rate of the polymer formation against $1/T$. The apparent value of the energy of activation (E_a) for the copolymerisation of aniline and PPD is determined to be −16.1 kJ/mol

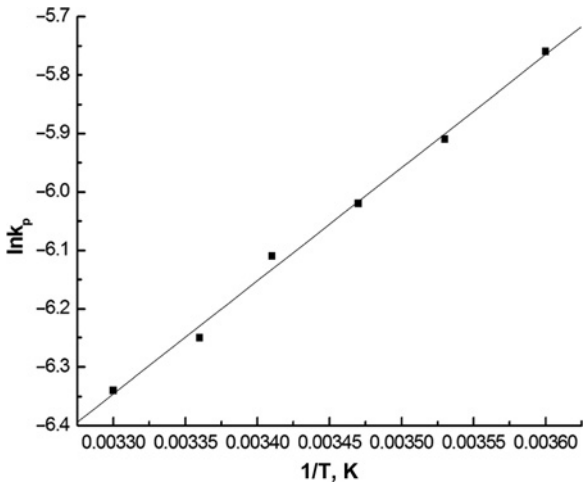


Figure 8 *Plot of log k_p against 1/T*

4. Conclusions: The chemical oxidation copolymerisation of PPD and AN at room temperature in the miniemulsion was successfully achieved with APS as the oxidising agent. The effects of the monomer molar ratio, the content of the surfactant and the concentration of the oxidising agent on the conducting copolymers of PAPPD were studied. The FTIR and the X-ray diffraction diagrams confirmed copolymerisation. The particle sizes of the copolymer were in the nanoscale range as observed by dynamic light scattering. The yield and the intrinsic viscosity of the copolymer were influenced by the monomer molar ratio, the content of the surfactant, the concentration of the oxidising agent and the temperature. The apparent value of the energy of activation (E_a) was calculated for the copolymerisation of aniline and the PPD was determined to be −16.1 kJ/mol in the range of 5–30°C. The PAPPD sample obtained in the miniemulsion exhibited increased conductivity in comparison with the PAPPD in the solution.

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