

Interfacial Polycondensation of Diphenolic Acid and Isophthaloyl Chloride

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ABSTRACT: Interfacial polycondensation of diphenolic acid (DPA) and isophthaloyl chloride (IPC) in various solvent/water systems was investigated with tetrabutyl ammonium chloride as a phase transfer catalyst. It was found that a large mass of capsules were formed at the beginning of the reaction for all solvents examined but the capsule morphology and reaction results depended on the solvents. It is believed that the capsule shells make up of the reaction zone and a mechanism of the interfacial polycondensation is proposed accordingly. The effect of the solvents on the

reaction was interpreted from the interaction between the polymer and the solvent according to the mechanism. The reaction conditions were optimized, and poly(DPA-IPC) with high intrinsic viscosity was prepared in high yield under the optimal condition. It is an amorphous polymer with glass transition temperature of about 160°C. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3586–3592, 2008

Key words: polyester; polycondensation; step-growth polymerization; interfacial polycondensation; diphenolic acid

INTRODUCTION

Diphenolic acid (DPA) ester had always been used for the synthesis of polycarbonate since the past four decades.¹ In recent years, DPA has been attracted much attention because it can be produced on large scale² from phenol and levulinic acid, a potential platform chemical from biomass.³ It has been used as a new monomer in preparation of reactive aromatic polyesters^{4–6} and polycarbonates^{7,8} bearing pendent carboxyl groups via interfacial polycondensation as well as hyperbranched polyesters via melt polycondensation.⁹ As the carboxyl groups can be converted into other useful groups,⁴ these polymers are expected for application as polymer catalyst, amphiphilic polyelectrolytes, chelating agents for metal ions, and drug delivery carriers.⁶

It has been reported that poly(DPA-IPC) can be synthesized via interfacial polycondensation of DPA and isophthaloyl chloride (IPC) catalyzed by quaternary ammonium salts,^{4,6} crown ethers,⁶ and polymeric

catalyst^{4,5} in various solvent/water systems, but the yield and the molecular weight of the produced polymer were relatively lower. It seems that there are big spaces to optimize the polymerization process. In addition, from the viewpoint of reaction engineering, the reaction locus of such a heterogeneous polymerization process needed to be elucidated because it will have great influence on the polymerization behaviors.

In this study, interfacial polycondensation of DPA and IPC in various solvent/water systems was investigated with tetrabutyl ammonium chloride (TBAC) as a phase transfer catalyst. The interaction between the polymer and the solvents was quantitatively analyzed and a reaction mechanism was proposed. The effect of the solvents on the reaction was interpreted accordingly. Then, the reaction conditions were optimized, and poly(DPA-IPC) with high intrinsic viscosity was prepared in high yield. And its thermal transition was characterized.

EXPERIMENTAL

Materials

Diphenolic acid (DPA, purity > 98%, Jiangsu Fenghuang Chemical Plant, China) was purified via recrystallization with H₂O/ethanol for twice before use. Isophthaloyl chloride (IPC, purity > 98%, Jiangxi Lianda Chemical Plant, China) was purified via vacuum distillation. Tetrabutyl ammonium chloride (TBAC, CP, Shanghai Chemical Reagent Co.,

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China), dichloromethane, acetone, and sulfuric acid (98%) were used as received.

Interfacial polycondensation of DPA and IPC

Interfacial polycondensation of DPA and IPC was carried out in a three-neck flask equipped with a thermometer, a condenser, and a stirrer. A typical process was as follows: First, sodium hydroxide (0.03 mol), DPA (0.01 mol), and TBAC (0.117 g) were added successively into 90 mL water. To the resulting aqueous solution, 50 mL dichloromethane solution containing 0.01 mol of IPC was quickly added under stirring at 400 rpm. The reaction started immediately, forming a mass of capsule particles. After reaction at 25°C for 1 h, certain amount of sulfuric acid was added, controlling the pH of the solution to be about 3, and an acidified polyester product, poly(DPA-IPC), was obtained. The polyester deposit was washed first with deionized water and then with acetone, filtered, and dried at 100°C in a vacuum oven to constant weight. FTIR (KBr): 1740 cm⁻¹ (COO), 1700 cm⁻¹ (COOH), 1505 cm⁻¹ (phenyl), 2960 cm⁻¹ (CH₃).

Characterization of poly(DPA-IPC)

The yield of poly(DPA-IPC) (y) was gravimetrically determined according to eq. (1), in which m_p is the weight of the polymer, n is the molar quantity of the limited monomer (which is not excessive), and M_{DPA} , M_{IPC} , M_{HCl} are the molecular weight of DPA, IPC, and HCl, respectively.

$$y = \frac{m_p}{n * (M_{DPA} + M_{IPC} - M_{HCl})} \quad (1)$$

The intrinsic viscosity $[\eta]$ of poly(DPA-IPC) was measured with a Ubbelodhe viscometer at 30°C using a 0.5 g/dL poly(DPA-IPC) solution in tetrachloroethane/phenol mixture solvent (2 : 3 by weight) containing 4.8% (by volume) of H₂SO₄.⁴

To evaluate the affinity between the polymer and the solvent during the polycondensation process, a poly(DPA-IPC) sample was synthesized using dichloromethane as solvent and separated without acidification, dried, and then soaked in various solvents for at least 72 h at 25°C until full swelling. The degree of swelling (a , mL/g) was calculated according to eq. (2), where ρ is the density of the solvent, and m_0 and m are the weight of the dry and fully-swelled polyester, respectively.

$$a = \frac{m - m_0}{m_0 \times \rho} \text{ (mL/g)} \quad (2)$$

The FTIR spectrum of poly(DPA-IPC) was recorded with a Nicolet IR-560 infrared spectrometer using a KBr pellet sample.

RESULTS AND DISCUSSION

Mechanism of the reaction

The interfacial polycondensations of DPA and IPC were conducted in seven different solvent/aqueous media. IPC was dissolved in an organic solvent to make up the organic phase, and DPA, NaOH, TBAC, and water composed the aqueous phase. When the organic phase was in contact with the aqueous phase under stirring, a mass of white capsule-like particles were formed immediately, since the polymer was swelled but not soluble in the solvent. The capsule was composed of a solvent/monomer core and a swelled polymer shell. At the end of the reaction with stirring being stopped, the particles sedimented at the bottom of the reactor and the aqueous phase was supernatant. After washing and removing the solvent, white polyester product, poly(DPA-IPC), was obtained.

The yield (y) and intrinsic viscosity ($[\eta]$) of poly(DPA-IPC), were summarized in Table I. Among the solvents examined, a maximum $[\eta]$ of 1.77 dL/g was reached for *sym*-tetrachloroethane, and a minimum $[\eta]$ of 0.68 dL/g was obtained for cyclohexane. For dichloromethane, a maximum yield (0.95) and a high $[\eta]$ (1.71 dL/g) were obtained. The yield for *sym*-tetrachloroethane is passable, but it is very low for cyclohexane. Clearly, dichloromethane is a preferable solvent.

To know the effect of solvent better, the changes of yield and $[\eta]$ as functions of reaction time for three typical solvents were investigated and the results are shown in Figure 1. For dichloromethane, both yield and $[\eta]$ increased fast with reaction time and reached high levels in half an hour. For *sym*-tetrachloroethane, the yield increased more rapidly but the $[\eta]$ built up a little slower. In the case of cyclohexane as the solvent, both the yield and $[\eta]$ increased slowly though they reached certain levels at the beginning of the reaction.

Similar effect of solvents has always been reported and attributed to the difference of the polarity of the solvents used.⁵ In this study, we tried to elucidate the solvent effect from the miscibility between the solvent and the polymer and the consequent difference in concentration and diffusion in reaction zone.

Capsule-like particles were prepared with all the seven solvents examined, but they exhibited different morphologies, depending on the solvent used. As shown in Figure 2, the particle size increased but the thickness of the capsule shell decreased when the solvent was changed from *sym*-tetrachloroethane to dichloromethane and to cyclohexane. In the case of *sym*-tetrachloroethane, the capsule shell was fully swelled so that it was hardly observed. The swelling ratio decreased for the other two solvents and the interface between the solvent (core) and the swelled polymer (shell) was clearly observed.

TABLE I
Interfacial Polycondensation of DPA and IPC in Various Solvent/Aqueous Media^a

Solvent in organic phase		Polymer		
Name	δ (J/cm ³) ^{1/2}	y (%) ^b	$[\eta]$ (dL/g) ^b	a (mL/g) ^c
<i>sym</i> -Tetrachloroethane	21.3	87.4	1.77	4.25
Chloroform	19.0	75.6	1.71	3.91
Dichloromethane	19.8	95.0	1.71	3.71
1,2-Dichloroethane	20.1	82.1	1.46	2.27
Toluene	18.2	69.8	1.44	1.72
Tetrachloromethane	17.6	52.7	0.95	1.59
Cyclohexane	16.8	35.9	0.68	0.78

^a Polycondensation conditions: $n_{\text{DPA}}/n_{\text{IPC}} = 1$, 4% TBAC as catalyst, 25°C, 1 h.

^b Interfacial polycondensation was conducted with various solvents.

^c Swelling ratio of fresh poly(DPA-IPC) separated before acidification (namely, poly(DPA-IPC) with a pendent carboxylate salt group rather than a carboxyl group) in various solvents. The fresh poly(DPA-IPC) sample was prepared using dichloromethane as the solvent.

The results implied that the miscibility between solvents and polymer have clear influence on the reaction. To better understand the miscibility between the solvent and the polymer, the swelling

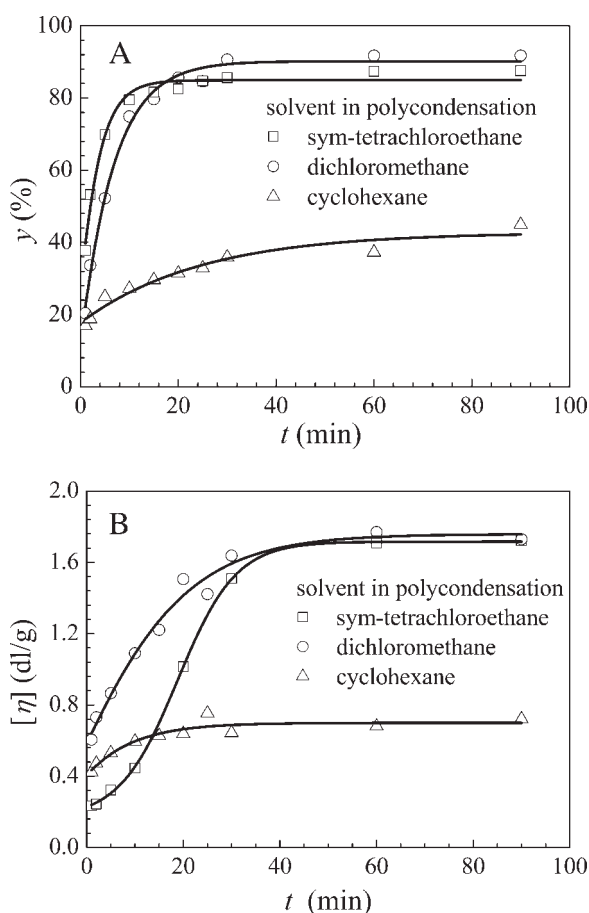


Figure 1 Evolution of the yield (A) and $[\eta]$ (B) of poly(DPA-IPC) with reaction time in the interfacial polycondensation of DPA and IPC with three different solvents: *sym*-tetrachloroethane, dichloromethane, and cyclohexane. ($[\text{IPC}] = 0.2$ mol/L, $n_{\text{DPA}}/n_{\text{IPC}} = 1$, $n_{\text{NaOH}}/n_{\text{DPA}} = 3$, $n_{\text{TBAC}}/n_{\text{DPA}} = 4\%$, $V_o/V_a = 5/9$, 25°C, 400 rpm).

ratios of poly(DPA-IPC) in various solvents were quantitatively measured. Since the polycondensation was carried out in alkaline aqueous media, the sample used for swelling ratio measurement was that synthesized with dichloromethane as solvent and directly separated without acidification. The results are listed in Table I. The solubility parameters of the solvents¹⁰ and the polymer are also provided. The solubility parameter of poly(DPA-IPC), 20.6 (J/cm³)^{1/2}, was calculated using the well-known group-contribution method. According to the "like dissolves like" rule, the solvents that have solubility parameters [18.2–21.3 (J/cm³)^{1/2}] close to the polymer swelled the polymer well. Higher swelling ratio resulted in higher intrinsic viscosity. The clear dependence of intrinsic viscosity on the swelling ratio indicates that a high affinity of the polymer to the solvent or a good miscibility between them is conducive to growth of molecular weight.

The effect of the solvent was interpreted as follow based on the understanding of the reaction mechanism. DPA was basified with NaOH in water to form a sodium phenoxide with pendent sodium carboxylate and further reacted with TBAC to form quaternary amine phenoxide with pendent carboxylate (C_a) in aqueous phase. C_a diffused into the organic phase (denoted as C_o in organic phase)

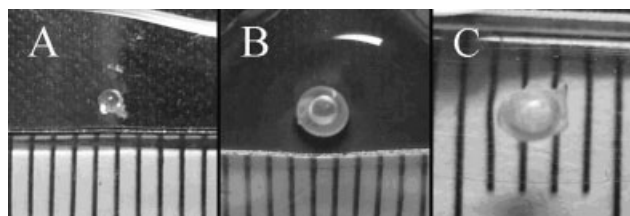
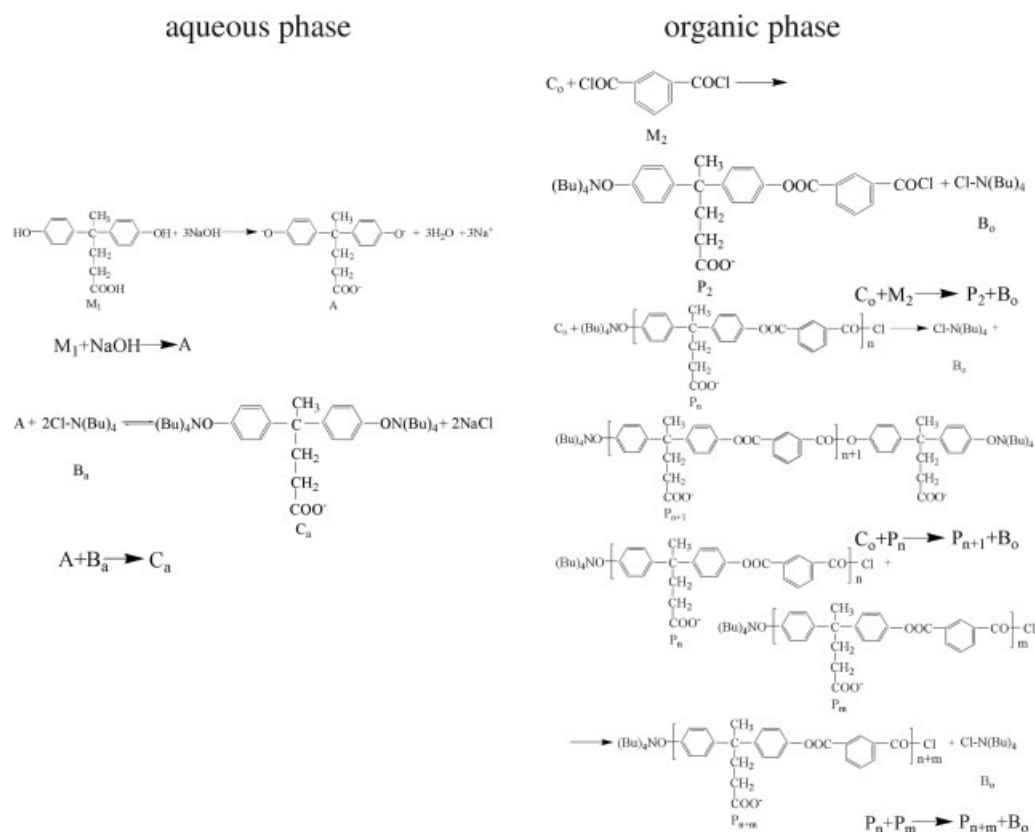


Figure 2 Morphology of the capsule-like particles of poly(DPA-IPC) prepared with three different solvents. (A) *sym*-tetrachloroethane, (B) dichloromethane, and (C) cyclohexane.

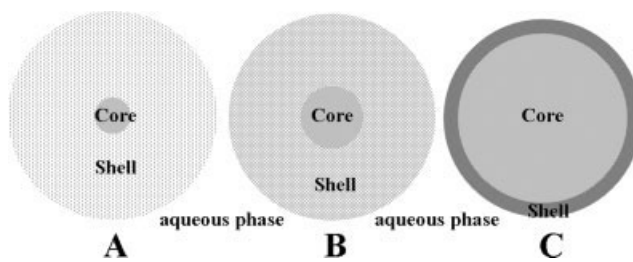


where it reacted with IPC to start polycondensation to generate a dimer (P_2). Condensation reaction among oligomers, IPC and C_0 led to chain growth and regenerated the phase transfer catalyst TBAC (B_0), which return into the aqueous phase (B_a) via diffusion. TBAC and C (C_a and C_0) diffused between the two phases until the consumption of the monomer in the aqueous phase. The elementary reactions are shown in Scheme 1.

At the very beginning of the reaction, the polycondensation took place undoubtedly at the very interface between the two phases. The formed oligo (DPA-IPC) has a hydrophobic backbone but a hydrophilic pendant carboxylate group. Therefore, the oligomer tended to locate at the interface and capsules with an oligomer shell swelled with solvent and monomer and with a core containing monomer and solvent were formed. The capsule shell made up of the reaction zone. The monomers diffused, respectively, from the aqueous phase and the capsule core into the shell to react there each other. The shell grew toward the core and thickened gradually, and the yield and molecular weight increased with the reaction time.

The miscibility between the solvent and the polymer had clear effect on the oligomer concentration and the thickness of the capsule shell (Scheme 2), as well as the viscosity of the reaction zone and diffu-

sion rate of monomers and oligomers. Therefore, polymerization using different solvent exhibited different results. For a poor solvent such as cyclohexane, the oligomer tended to concentrate at the interface other than to diffuse toward the center the organic phase. In this way, the capsule shell was thin and viscous with concentrated oligomers. As a result, the monomers were difficult to diffuse through the shell to meet together. The oligomers in the shell were also difficult to diffuse to react with each other or with the monomers. Consequently, both the intrinsic viscosity and yield increased slowly and capsules with thin shell were obtained.



Scheme 2 Schematic diagram of the structures of capsules prepared using solvents with different affinity with poly(DPA-IPC). A: good solvent; B: moderate solvent; C: poor solvent. Components in shell: polymer, oligomer, monomers and solvent; in core: IPC and solvent.

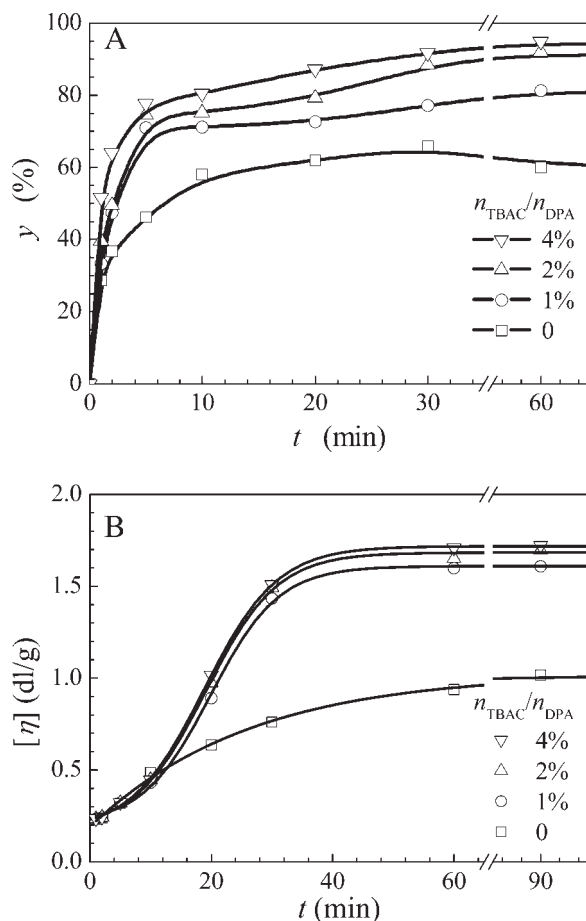


Figure 3 Evolution of the yield (A) and $[\eta]$ (B) with reaction time for the interfacial polycondensation of DPA and IPC with various amount of TBAC. ($[IPC] = 0.2 \text{ mol/L}$, $n_{DPA}/n_{IPC} = 1$, $n_{NaOH}/n_{DPA} = 3$, $V_o/V_a = 5/9$, 25°C , 1 h, 400 rpm).

However, for a good solvent such as *sym*-tetrachloroethane, the oligomer formed at the beginning was prone to diffuse toward the organic phase because of its better miscibility to the solvent. Therefore, the capsule shell was thicker but less viscous with less concentrated oligomers. The monomers diffused more easily to the shell and reacted there each other. The diffusion of the oligomers in the shell was easier, too. As a result, both the intrinsic viscosity and yield increased fast and capsules with thick shell were obtained.

The difference in the time-evolution of the yield and $[\eta]$ of poly(DPA-IPC) prepared with *sym*-tetrachloroethane and dichloromethane (see Fig. 1) can be interpreted from the relative importance of concentration and diffusion in the shell. The better miscibility between the polymer and *sym*-tetrachloroethane made the diffusion of the monomers easier, so the yield increased faster for *sym*-tetrachloroethane. On the other hand, the concentration of the oligomers might play more significant role than the diffusion for molecular weight growth. Therefore,

the higher concentration of oligomers in dichloromethane caused more rapid molecular weight growth.

Optimization of reaction conditions

Dichloromethane was used as solvent in the following experiments. TBAC played a role as phase transfer catalyst to transfer the aqueous monomer to the reaction locus. Both the yield and $[\eta]$ clearly increased in the presence of a small amount of TBAC, though the polymerization could also take place with low yield (60%) and intrinsic viscosity (1.01 dL/g) in the absence of TBAC, as shown in Figure 3. Increasing TBAC dose from 1 to 4% resulted in a clear increase in the yield and nearly constant $[\eta]$. The yield reached 95% and the intrinsic viscosity reached 1.71 dL/g, respectively, at 4 mol % TBAC.

Since DPA has two phenolic hydroxyls and one more active carboxyl, 3-fold equivalent amount of NaOH was necessary for complete conversion of the phenolic hydroxyls to phenolates to ensure high yield and intrinsic viscosity, as shown in Figure 4. On the other hand, excessive NaOH made both the yield and intrinsic viscosity to decrease clearly. This is attributed to the presence of the hydrophilic pendent carboxylate groups, which made the oligomers apt to enrich at the interface and thus some of the terminal acyl chloride group(s) hydrolyzed. This is different from other interfacial polycondensation systems, for an instance, of 3,3',5,5'-tetrabromobisphenol A (TBBPA) and IPC,¹¹ in which the oligomer is fully hydrophobic, with little chance to undergo hydrolysis.

In general, stoichiometric addition of monomers is necessary to get high molecular weight in polycon-

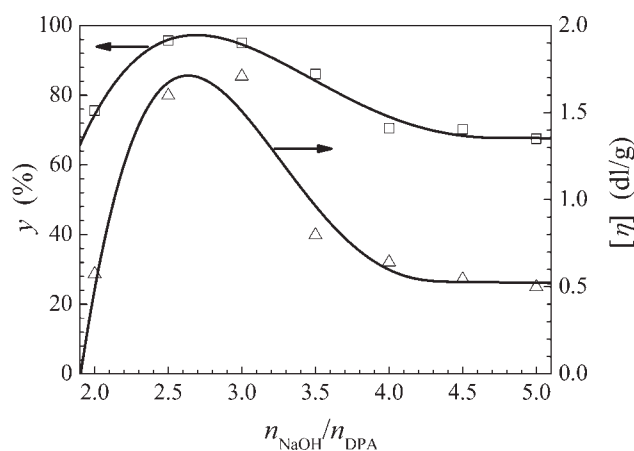


Figure 4 Effect of molar ratio of NaOH to DPA (n_{NaOH}/n_{DPA}) on the yield and $[\eta]$ of poly(DPA-IPC) prepared via interfacial polycondensation of DPA and IPC. ($[IPC] = 0.2 \text{ mol/L}$, $n_{DPA}/n_{IPC} = 1$, $n_{TBAC}/n_{DPA} = 4\%$, $V_o/V_a = 5/9$, 25°C , 1 h, 400 rpm).

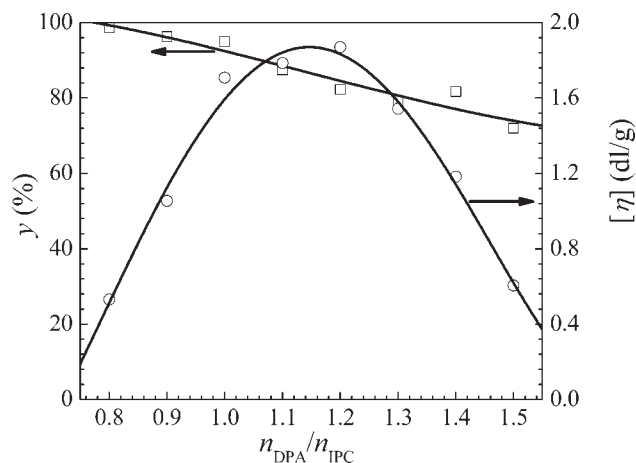


Figure 5 Changes of the yield and $[\eta]$ with n_{DPA}/n_{IPC} in the interfacial polycondensation of DPA and IPC with different n_{DPA}/n_{IPC} ratio. ($[IPC] = 0.2$ mol/L, $[DPA] = 0.11$ mol/L, $n_{NaOH}/n_{DPA} = 3$, $n_{TBAC}/n_{DPA} = 4\%$, 25°C , 1 h, 400 rpm).

densation. However, in the interfacial polycondensation, the monomer in the aqueous phase can not be completely transferred into the organic phase and certain amount of the monomer still remains at the end of the reaction. Therefore, a little excessive monomer in the aqueous phase is necessary for high molecular weight. In the interfacial polycondensation of DPA and IPC, the maximum intrinsic viscosity was reached at n_{DPA}/n_{IPC} of 1.2, as shown in Figure 5. Similar phenomenon was also found in other interfacial polycondensation systems.^{12,13} But on the other hand, excessive DPA is not conducive to the yield of the polymer.

The concentration of the monomers in both phases had clear effect on the reaction. Figure 6 shows the

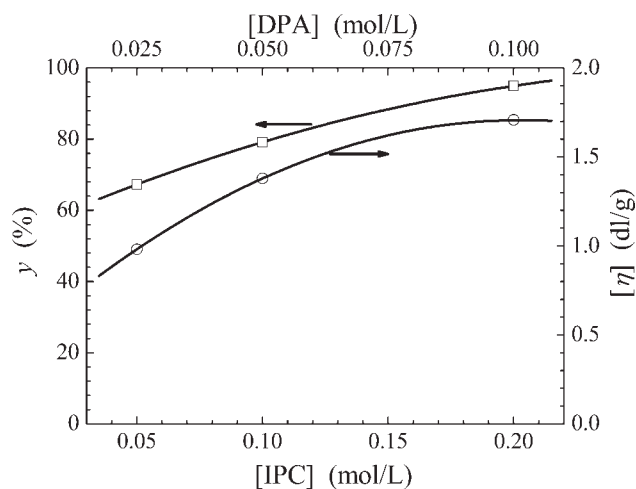


Figure 6 Effect of the concentration of DPA and IPC on the yield and $[\eta]$ of poly(DPA-IPC) in the interfacial polycondensation of DPA and IPC. ($n_{DPA}/n_{IPC} = 1$, $n_{NaOH}/n_{DPA} = 3$, $n_{TBAC}/n_{DPA} = 4\%$, $V_o/V_a = 0.5$, 25°C , 1 h, 400 rpm).

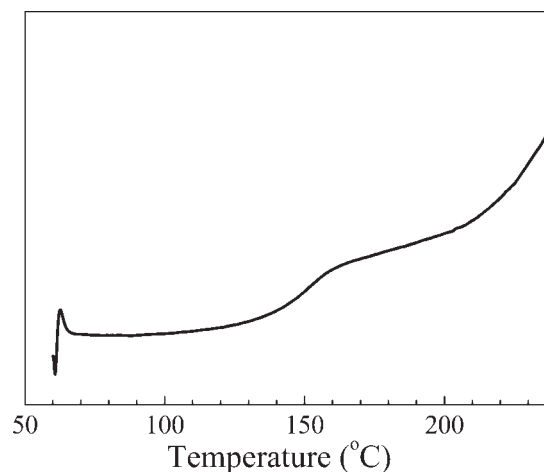


Figure 7 DSC thermogram of Poly(DPA-IPC).

changes of yield and $[\eta]$ of poly(DPA-IPC) with the concentrations of DPA and IPC, keeping the volume of the two phase unchanged. It suggested that higher concentration are beneficial to the growth of the yield and $[\eta]$, possibly because the impact of the remaining monomer in aqueous phase weakened at higher concentration of the monomers.

On the basis of the above experimental results, the interfacial polycondensation of DPA and IPC under a relatively optimal condition (dichloromethane, $n_{DPA}/n_{IPC} = 1$ –1.2, $n_{NaOH}/n_{DPA} = 3$, $n_{TBAC}/n_{DPA} = 4\%$, $V_o/V_a = 0.5$) gave poly(DPA-IPC) with satisfactory yield (95%) and intrinsic viscosity (1.71 dL/g).

Thermal properties

Aromatic polyesters are usually heat resistant polymers. For instance, the polycondensate of BPA and IPC, poly(BPA-IPC), is an amorphous polymer with glass transition temperature (T_g) as high as 180°C and thermal decomposition temperature (T_d) over 400°C .¹⁴ The DSC characterization shown in Figure 7 indicates that poly(DPA-IPC) is an amorphous polymer, too, with T_g of 159°C . And it started to decompose at about 200°C in thermal gravimetric analysis (data not shown). So, poly(DPA-IPC) is less heat-resistant and thermostable than the traditional aromatic polyester. The decrease in T_g and T_d may arise from the existence of flexible side groups and end carboxyls. Detailed research on the decomposition mechanism of poly(DPA-IPC) will be reported later.

CONCLUSIONS

Interfacial polycondensation of DPA and IPC was conducted in various solvent/water systems with TBAC as a phase transfer catalyst and poly(DPA-IPC), an aromatic polyester bearing pendant carboxyl groups, was synthesized. A large mass of

capsules were formed at the beginning of the reaction and the capsule shells with oligomers swelled with the solvent and monomers made up of the reaction zone. The shells grew toward the core and thickened gradually during the reaction. The oligomer concentration in and the thickness of the capsule shell as well as the viscosity of the reaction zone and diffusion rate of monomers and oligomers depended on the miscibility between the solvent and the polymer. As a result, the intrinsic viscosity and yield increased fast and the capsule shells were thick for good solvent, but they increased slowly and the capsule shells were thin for poor solvent. Dichloromethane seemed to have proper interaction with the polymer and behaved most favorable among the solvent examined. Poly(DPA-IPC) with high intrinsic viscosity was prepared in high yield in the dichloromethane/water system under relatively optimal conditions: complete conversion of the phenolic hydroxyls, a little excessive DPA, sufficient catalyst amount, and high enough monomer concentration. It is an amorphous polymer with a T_g of about 160°C.

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