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New one-step synthesis of polyimides in salicylic acid

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Abstract

A new polymerization in the melt of salicylic acid has been developed for the one-step synthesis of polyimides from various diamines and dianhydrides. The polymerization is carried out in high solid content up to 40–50 wt/v% at 200 °C and affords the completely cyclized polyimides with high molecular weights in 1–2 h. The preliminary studies on some of the polymerization variables (e.g., concentration and time) suggest that the imidization is very fast and the chain growth is likely to proceed via the addition of the growing imide segments.

Keywords: Polyimide; One-step polymerization; Salicylic acid

1. Introduction

Polyimides are a class of high-performance polymers that have many outstanding characteristics such as low dielectric constant, excellent mechanical strength, high thermal stability and chemical resistance and are being used in microelectronics, aerospace and automotive industries [1–3]. The recent trend in polyimide research seems to focus more on the development of structural and functional polyimides with new properties without addressing the limitations of the current synthetic methods. However, advances in polymer research in general are led not only by the creation of a new structure but also pushed by the invention of a new synthetic method.

There are two main synthetic routes to polyimides, namely one-step and two-step polymerizations. In the one-step polymerization, completely cyclized polyimides are obtained directly, from their corresponding teteracarboxylic acid dianhydride and diamine, using high boiling solvents, such as *m*-cresol and *p*-chlorophenol. This method is usually used when working with soluble polyimides and is considered more practical for polymerizing less reactive dianhydrides and diamines. However, this method suffers from some enormous drawbacks, such as the use of very toxic carcinogen solvents and a rather low polymerization concentration (usually less than 10 wt/v%), which hampers direct processing of the polyimides into the final products (e.g., films and fibers) from their polymerization solutions, and a long reaction time (typically over 18 h). In the two-step polymerization, the polyamic acid is first prepared from dianhydride and diamine in a polar aprotic solvent, such as *N*,*N*-dimethylacetamide (DMAc) or *N*,*N*-dimethylformamide (DMF) [1,3]. During this step, the self-catalyzed cyclization to form polyimides cannot occur due to the strong interaction between the amic acid and the basic solvent or the larger acylation equilibrium constant [1,4]. In the second step, the polyamic acid is cyclodehydrated at elevated temperatures or by adding a cyclizing agent such as acetic anhydride [1,3–5]. Main advantages of this method over the one-step polymerization are the use of less toxic solvents and direct processing of the soluble polyamic acids to form the final polyimide products such as films and fibers after thermal imidization. However, the stability of polyamic acid on storage and control of thermal imidization are still important issues.

In 2000, Kuznetsov reported the use of the melt of benzoic acid as a solvent at 140 °C in one-step polymerization for the synthesis of aromatic polyimides with reasonably high molecular weights [4]. Benzoic acid is less powerful in solvating aromatic polyimides and thus it is difficult to run the polymerization at

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a concentration more than 12 wt/v%. In addition, benzoic acid begins to sublime readily at 100 °C under ambient atmosphere, which makes it necessary to run the polymerization in a sealed tube completely immersed in a heated oil bath.

Herein, we report a new synthetic method for the one-step synthesis of completely cyclized polyimides with high molecular weights using salicylic acid as a solvent within a very short period of time. This solvent system offers many advantages for one-step polyimide synthesis, due to its high acidity, low volatility and excellent solvating power, on comparison with *m*-cresol, *p*-chlorophenol, and benzoic acid.

2. Experimental section

2.1. Materials

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 4,4′-oxidiphthalic dianhydride (ODPA) were purchased from ChrisKEV company, Inc. and purified by recrystallization from acetic anhydride. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) were purchased from Allco Chemical Corporation and Aldrich Chemicals Inc., respectively, and dried in oven at 100 °C prior to use. 2,4-Diaminophenol dihydrochloride (2,4-DAP·2HCl) was purchased from Aldrich and used as received. 3,3-Diaminodiphenylsulfone (3,3-DDS) was purchased from TCI America and purified by recrystallization from ethanol. 4,4-Oxydianiline (4,4-ODA) and *o*-tolidine were purchased from Aldrich and purified by recrystallization from THF and ethanol, respectively. 4,4′-Bis(4-aminophenoxy)biphenyl (BAPB) and bis[4-(4-aminophenyoxy)phenyl]sulfone (BAPS) were purchased form Ken Seika corporation and used with no further purification.

2.2. Characterization

Fourier Transform Infrared (FTIR) measurements were performed on a Bomen FTIR spectrophotometer. The onset temperatures for 5% weight loss of the polymers were determined using a TA thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen. Glass transition temperature (T_g) was determined on a TA DSC Q100 at a heating rate of 10 °C/min in nitrogen. Inherent viscosities of polymers were measured with an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C with a concentration of 0.5 g/dL.

2.3. Syntheses of polyimides ***PI-1*–*PI-15***

The typical procedure for the synthesis of **PI-9** is as follows: salicylic acid (3.67 g, 2.60 mL) was placed in a pressure glass tube (35 mm in outer diameter and 250 mm in length), melt and maintained at 200 °C for 10 min. 4,4′-Oxidiphthalic dianhydride (ODPA) (0.62 g, 2.00 mmol) and 4,4-oxydianiline (4,4-ODA) (0.40 g, 2.00 mmol) were introduced into the melt. The concentration of monomers in salicylic acid was 40 wt/v%, followed by addition of 8 drops of isoquinoline. Once all were dissolved, the reaction tube was closed tightly (with a crew cap) and the portion of the tube containing the reaction mixtures (about 1/3 in length) was immersed in an oil bath at 200 °C for 1.5 h. After cooling to about 150 °C, the tube cap was removed carefully and the viscous transparent pale-yellow solution was poured slowly into methanol (200 mL) with vigorous stirring. The polymer **PI-9** was collected by filtration, boiled in hot methanol for 1 h, and dried in a vacuum oven at 120 °C overnight.

PI-1: 74% yield. IR (film, cm^{-1}): 1787 (unsymmetrical C=O of imide), 1733 (symmetrical C=O of imide), 1372 (C–N of imide), 723 (C–N–C of imide).

PI-2: 94% yield. IR (film, cm^{-1}): 1785 (unsymmetrical C=O of imide), 1733 (symmetrical C=O of imide), 1382 (C–N of imide), 723 (C–N–C of imide).

PI-3: 95% yield. IR (film, cm^{-1}): 1789 (unsymmetrical C=O of imide), 1735 (symmetrical C=O of imide), 1375 (C–N of imide), 721 (C–N–C of imide).

PI-4: 95% yield. IR (film, cm^{-1}): 1785 (unsymmetrical C=O of imide), 1735 (symmetrical C=O of imide), 1380 (C–N of imide), 725 (C–N–C of imide).

PI-5: 81% yield. IR (film, cm^{-1}): 1785 (unsymmetrical C=O of imide), 1731 (symmetrical C=O of imide), 1380 (C–N of imide), 723 (C–N–C of imide).

PI-6: 85% yield. IR (film, cm^{-1}): 1785 (unsymmetrical C=O of imide), 1733 (symmetrical C=O of imide), 1382 (C–N of imide), 723 (C–N–C of imide).

PI-7: 93% yield. IR (film, cm^{-1}): 1782 (unsymmetrical C=O of imide), 1728 (symmetrical C=O of imide), 1375 (C–N of imide), 745 (C–N–C of imide).

PI-8: 67% yield. IR (film, cm^{-1}): 1784 (unsymmetrical C=O of imide), 1733 (symmetrical C=O of imide), 1375 (C–N of imide), 744 (C–N–C of imide).

PI-9: 99% yield. IR (film, cm^{-1}): 1778 (unsymmetrical C=O of imide), 1726 (symmetrical C=O of imide), 1382 (C–N of imide), 744 (C–N–C of imide).

PI-10: 85% yield. IR (film, cm^{-1}): 1775 (unsymmetrical C=O of imide), 1724 (symmetrical C=O of imide), 1380 (C–N of imide), 744 (C–N–C of imide).

PI-11: 79% yield. IR (film, cm^{-1}): 1782 (unsymmetrical C=O of imide), 1733 (symmetrical C=O of imide), 1377 (C–N of imide), 727 (C–N–C of imide).

PI-12: 87% yield. IR (film, cm^{-1}): 1784 (unsymmetrical C=O of imide), 1733 (symmetrical C=O of imide), 1377 (C–N of imide), 721 (C–N–C of imide).

PI-13: 80% yield. IR (film, cm^{-1}): 1780 (unsymmetrical C=O of imide), 1731 (symmetrical C=O of imide), 1380 (C–N of imide), 723 (C–N–C of imide).

PI-14: 99% yield. IR (film, cm^{-1}): 1780 (unsymmetrical C=O of imide), 1733 (symmetrical C=O of imide), 1377 (C–N of imide), 733 (C–N–C of imide).

PI-15: 80% yield. IR (film, cm^{-1}): 1776 (unsymmetrical C=O of imide), 1731 (symmetrical C=O of imide), 1382 (C–N of imide), 740 (C–N–C of imide).

2.4. Synthesis of random copolymer ***PI-16***

Salicylic acid (7.69 g, 5.3427 mL) was placed in a thick-wall pressure glass tube (35 mm in outer diameter and

250 mm in length), melted and maintained at 200 °C for a few minutes. Then, ODPA (1.24 g, 4.00 mmol), 4,4-ODA (0.40048 g, 2.00 mmol), 3,3-DDS (0.4966 g, 2.00 mmol) and a few drops of isoquinoline were added to the melt. The concentration of the reaction mixture was 40 wt/v%. The reaction tube was closed tightly and the polymerization proceeded at 200 °C for 2 h. After the reaction tube was left at room temperature for cooling for about 5 min, the viscous solution was poured slowly into methanol (200 mL) with stirring. The polymer product was collected by filtration, washed with hot methanol and dried in a vacuum oven at 120 °C overnight; 73.0% yield; IR (film, cm^{-1}): 1780 (unsymmetrical C═O of imide), 1730 (symmetrical C═O of imide), 1377 (C–N of imide), 744 (C–N–C of imide cycle).

3. Results and discussion

Salicylic acid is used as a preservative in food products, antiseptic and anti-fungal agents, starting material for various medicinal uses (e.g., aspirin). Salicylic acid contains both the acidic and phenolic groups resembling *m*-cresol and benzoic acid. Since it is more acidic (pKa = 2.97) than benzoic acid (pKa = 4.19) and *m*-cresol (pKa = 10.09), salicylic acid should be a much more powerful solvent for a variety of aromatic polyimides than those common solvents for polyimides. Furthermore, salicylic acid melts at about 160 °C, lower than its isomers, 3-hydroxybenzoic acid (mp = 200–203 °C) and 4-hydroxybenzoic acid (mp = 213–217 °C). It boils at 211 °C, being between the boiling temperatures of the two solvents for polyimide synthesis, *m*-cresol (203 °C) and *p*-chlorophenol (220 °C) and is suitable for the synthesis of the most aromatic polyimides. Thus, to test its feasibility and suitability as a solvent for polymerization, a series of dianhydrides and diamines were selected and polymerized (Scheme 1).

The polymerization was carried out in salicylic acid at 200 °C at a concentration of 30–45 wt/v% to afford a series of polyimides (Scheme 1). Once salicylic acid melted in a thick-walled glass tube (35 mm in outer diameter and 250 mm in length), a stoichiometric amount of dianhydride and diamine monomers (typically in a 3-mmol scale) were added, followed by addition of a few drops of isoquinoline. After all the monomers were dissolved in the melt of salicylic acid, the reaction tube was closed tightly (with a crew cap) and the portion of the tube containing the reaction mixtures (about 1/3 in length) was immersed in an oil bath at 200 °C for 1–2 h. The resulting polyimides remained soluble in salicylic acid during the course of polymerization. The viscosity of the polymerization solution increased rapidly, indicating the polymer chain growth and an increase in the molecular weight. After cooling to about 150 °C, the tube cap was removed. The polymerization solution could be poured directly onto a large metal or glass plate and the reaction mixture solidifies on cooling to room temperature. Salicylic acid can be easily removed by repeated washing in a Soxhlet extractor with ethanol or acetone and recovered after removal of low-boiling solvents. Alternatively, the hot polymerization solution could be poured into methanol and the precipitated polymers were collected by filtration, which were re-dissolved in DMAc (or *m*-cresol) and precipitated out from methanol.

The complete imidization was confirmed by IR spectroscopy, as shown for **PI-2**,**7**,**13**,**15** in Fig. 1. The IR spectra

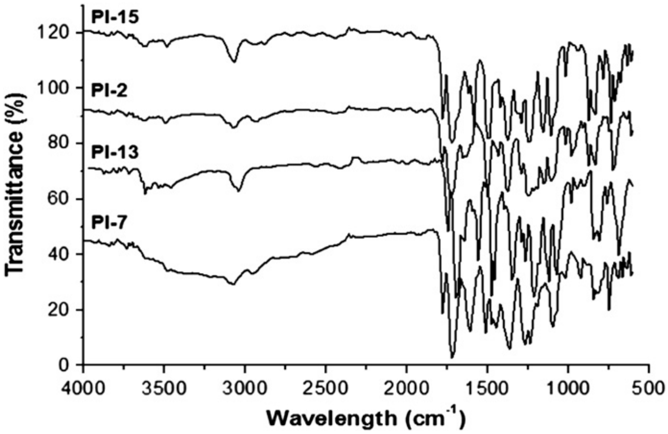
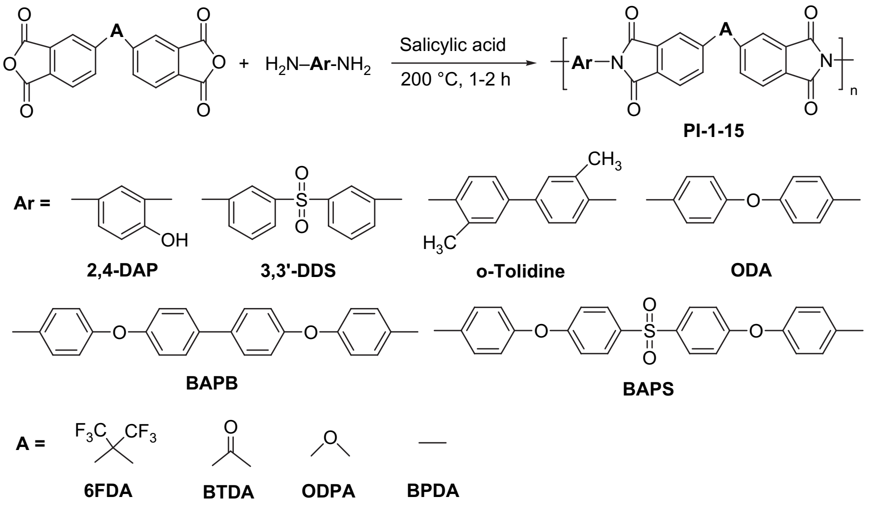


Fig. 1. IR spectra of some polyimides synthesized in salicylic acid at 200 °C for 2 h.



Scheme 1. One-step synthesis of polyimides in salicylic acid.

exhibited the imide characteristics at 1782 cm^{-1} (unsymmetrical C=O), 1730 cm^{-1} (symmetrical C=O), 1380 cm^{-1} (C–N) and 720 cm^{-1} (C–N). There are no carbonyl peaks for the amic acid.

Thermal properties of these polyimides were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The glass transition temperatures (T_g) ranged from 248 to 336 °C, depending on the chemical structures of the dianhydrides and diamines used. All the polyimides were thermally stable up to 470 °C in nitrogen, as assessed by TGA for the onset temperatures for 5% weight loss (Table 1).

Polyimides are known for their poor solubility, due to the rigidity of the polyimide backbone and strong interchain interaction [1,2]. Thus, polymerization in *m*-cresol is usually carried out at the concentration less than 15 wt/v% to prevent physical gelation. In comparison, four dianhydrides, 6FDA, BTDA, BPDA and ODPA, were readily polymerized with various diamines in salicylic acid without gelation (except for **PI-4**) at a concentration up to 45 wt/v% during the course of polymerization (Table 1), demonstrating the solvating power of salicylic acid. Some polyimides such as **PI-12** derived from BTDA and 3,3′-DDS can even be polymerized at a concentration as high as 50–60 wt/v%. The polyimides derived from PMDA and the diamines as listed in Table 1 were obtained in low molecular weights, due to their limited solubility in the melt of salicylic acid. It should be noted that one-step polymerization in salicylic acid also allows for the direct use of the HCl salt of 2,4-diaminophenol (2,4-DAP) as a monomer, which implies that many other air-sensitive diamines could be converted to the corresponding more air-stable HCl salts as monomers for making polyimides. Furthermore, the one-step polymerization at high concentration allows for direct processing of the resulting polyimides from the polymerization solution. In our case, the preliminary tests confirmed that a tough, flexible film could be directly cast from the viscous polymer solution right after polymerization (e.g., **PI-12**). Because salicylic acid is volatile and can be effectively evaporated off during the film preparation at the elevated temperatures, such as 200 °C, hair-like fibers could also be drawn from the hot viscous "honey-like" polymer solution. The washing was necessary to remove salicylic acid. No further treatment such as thermal cure was done on the fibers and the fiber property was not evaluated.

High molecular weight polyimides were readily obtained within 2 h, as evident from their high viscosity values. The inherent viscosities of the synthesized polyimides ranged from 0.43 to 1.0 dL/g, which are higher or comparable to those of the same polyimides synthesized by other one-step methods. For example, St. Clair and Slemp reported **PI-2** and **PI-8** with the viscosity of 0.47 dL/g in DMAc [1,6], which are quite similar to what we have obtained after polymerization in only 2 h. In 2000, Kuznetsov reported **PI-9** with a viscosity of 0.42 dL/g in DMAc [4], while the same polyimide made in the melt of salicylic acid had an inherent viscosity of 0.95 dL/g. **PI-12** was reported before for a viscosity of 0.42 dL/g in DMAc [1], which is much lower than what we have obtained (1.0 dL/g) but using *m*-cresol due to the insolubility of **PI-12** in DMAc. No direct comparison was made for the rest of the polyimides, as they were previously synthesized in a two-step process.

The new method can be applied for the synthesis of copolyimides. For example, a copolymer was prepared from ODPA and ODA and 3,3′-DDS under the same conditions as for the homopolymers. The copolymer had an inherent viscosity of 0.67 dL/g and a T_g of 263 °C between those of **PI-8** (257 °C) and **PI-9** (273 °C). Its IR spectrum also indicated the complete imidization with the characteristic peaks at 1782 and 1730 cm^{-1}.

The effect of polymerization concentration on the chain growth or molecular weight was probed by varying the concentration from 20% to 60 wt/v% in salicylic acid for the synthesis of **PI-12** derived from BTDA and 3,3′-DDS within

Table 1
Characterizations of the polyimides made in salicylic acid at 200 °C within 2 h

Dianhydride	Diamine	PI	Concentration (wt/v%)	η_{inh} (dL/g)	T_d[d] (°C)	T_g[e] (°C)
6FDA	2,4-DAP (2HCl)	**PI-1**	35	0.65[a]	567	349
	3,3′-DDS	**PI-2**	45	0.50[a]	495	280
	ODA	**PI-3**	45	0.55[a]	536	317
	o-Tolidine	**PI-4**	16	0.95[a]	534	248
	BAPB	**PI-5**	40	0.51[a]	518	296
	BAPS	**PI-6**	40	0.46[a]	538	299
ODPA	2,4-DAP (2HCl)	**PI-7**	30	0.66[a]	572	248
	3,3′-DDS	**PI-8**	45	0.49[a]	553	257
	ODA	**PI-9**	40	0.99[c]	558	273
	BAPS	**PI-10**	40	0.87[b]	527	297
BTDA	2,4-DAP (2HCl)	**PI-11**	40	0.97[a]	470	336
	3,3′-DDS	**PI-12**	45	1.00[a]	550	276
	BAPS	**PI-13**	30	0.73[c]	556	289
BPDA	3,3′-DDS	**PI-14**	40	0.45[b]	527	293
	BAPS	**PI-15**	40	0.70[b]	573	294

[a] Inherent viscosity measured in DMAc at 30 ± 0.1 °C with a concentration of 0.5 g/dL.
[b] Inherent viscosity measured in NMP at 30 ± 0.1 °C with a concentration of 0.5 g/dL.
[c] Inherent viscosity measured in *m*-cresol at 30 ± 0.1 °C with a concentration of 0.5 g/dL.
[d] Onset temperature for 5% weight loss by TGA in nitrogen with a heating rate of 10 °C/min.
[e] Glass transition temperature by DSC in nitrogen at a heating rate of 10 °C/min.

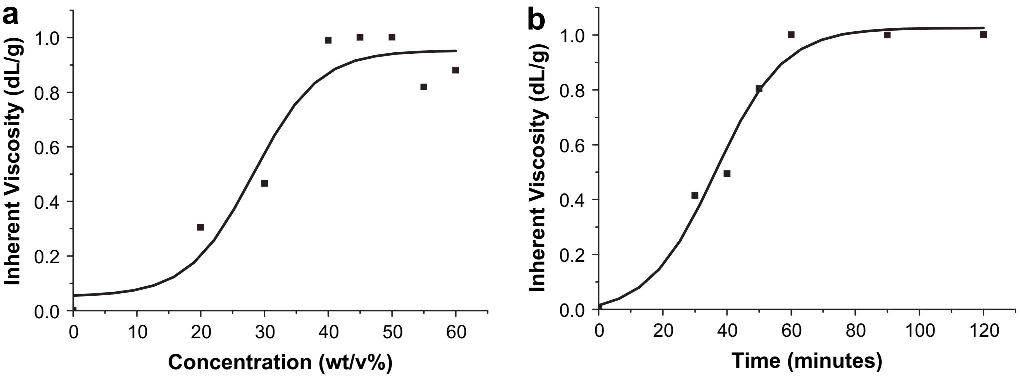


Fig. 2. Formation of **PI-12** in salicylic acid at 200 °C (a) inherent viscosity taken at 2 h vs. polymerization concentration (b) inherent viscosity vs. polymerization time at a concentration of 50 wt/v%.

a given time of 2 h (Fig. 2a). A rapid increase in viscosity was found when the concentration reached 40 wt/v%. At lower concentrations (20–30%), the polymerization was obviously slower; while at the concentration over 50 wt/v%, a slight decrease in inherent viscosity was also observed, mainly due to partial gel formation. A kinetic study on the formation of **PI-12** in salicylic acid was further done at a concentration of 50 wt/v% by measuring the inherent viscosity at different polymerization times (Fig. 2b). The inherent viscosity increased rapidly and reached a maximal value of 1.0 dL/g in 1 h. No further increase was observed after another 1 h. Thus, the polymerization is complete within 1–2 h and the chain growth in this polymerization system is believed to proceed via the addition of the completely cyclized polyimide, similar to the one done in benzoic acid with the evidence from the IR analysis for the collected samples at early stage of the reaction [4].

The addition of some inert co-solvents such as 1,2-dichlorobenzene and *m*-cresol in the polymerization was examined and resulted in lowering the molecular weights of the polyimides. The polymerization of BTDA and 3,3′-DDS was also carried out in absence of isoquinoline for 2 h and afforded **PI-12** in much lower molecular weight (inherent viscosity of 0.2 dL/g) than the one made in the presence of a small amount of isoquinoline (inherent viscosity of 1.0 dL/g). The use of carboxylic acid as a catalyst for imidization has been studied and the study shows that the more acidic catalyst of salicylic acid (pKa = 2.97) is less effective than other less acidic catalysts, e.g., benzoic acid (pKa = 4.19) and *p*-hydroxybenzoic acid (pKa = 4.48) [3]. Isoquinoline is often used in small amount in one-step polymerization and as a base with acetic acid in the chemical imidization. However, the actual role that isoquinoline may play in this one-step polymerization and its exact nature in salicylic acid at 200 °C are still unclear. It seems that the more acidic nature of salicylic acid is in favor of solvating the polyimides, while isoquinoline facilitates the imidization and thus the rapid chain growth.

4. Conclusion

Salicylic acid is a powerful solvent for one-step synthesis of a variety of aromatic polyimides. The completely cyclized polyimides with high molecular weights are readily formed in less than 2 h. The polymerization is easy to run and the solid solvent can be recovered and re-used. The preliminary studies on the effect of reaction concentration and time on the polymerization suggest that the imidization is very fast and the chain growth is likely to proceed via the addition of the growing imide segments.

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