

Structure, thermal stability, electrochemical behaviors, and mechanical properties of organosoluble polyimide with pyrimidine ring in the main chain

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ABSTRACT: A novel organosoluble polyimide (PI) with pyrimidine ring in the main chain was synthesized by chemical and thermal imidization, respectively, from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 2,4-diamino-6-chloropyrimidine as raw materials and its molecular structure, solubility, UV-visible absorption characteristic, crystallinity, thermal stability, electrochemical behaviors, and mechanical properties were also studied. It was found that the introduction of pyrimidine ring in the main chain could increase the solubility of PI in polar aprotic solvents at room temperature and 60 °C, respectively, because of its molecular main chain with asymmetric structure and two polar N atoms in pyrimidine ring. Furthermore, PI had strong optical absorption peak intensity, excellent thermal stability, good redox reversibility, especially outstanding mechanical properties, which were conducive to its potential applications in adhesives, polyelectrolyte, separation membrane, and so on. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43680.

KEYWORDS: electrochemistry; mechanical properties; polycondensation; polyimides; properties and characterization

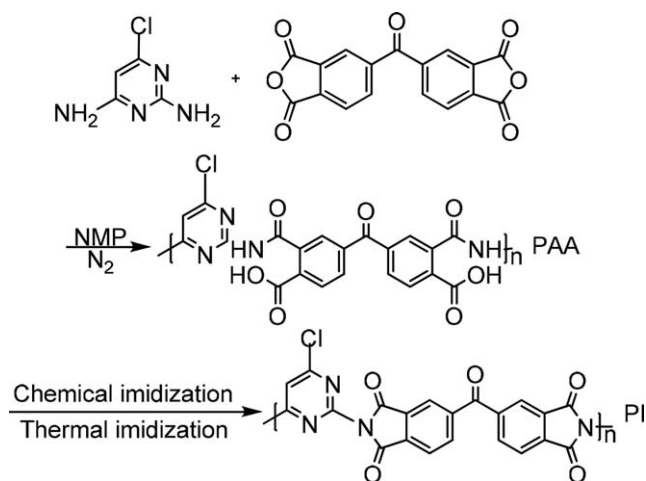
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INTRODUCTION

Polyimide (PI) a sort of polymer with imide rings in the main chain has been used widely in adhesives,^{1,2} polyelectrolyte,^{3,4} separation membrane,^{5,6} aerospace,^{7,8} and so on, because of its preeminent mechanical property, good electrical property, and excellent thermal stability. However, PI with the wholly aromatic structure has poor solubility and non-melting property attributed to its rigid main chain and strong inter-chain interaction, which limit its practical applications seriously. Fortunately, researchers have mainly concluded four aspects of structure modification by enhancing the flexibility of molecular main chain and weakening the intermolecular interaction of PI in order to improve its solubility in the past decades, which involved the incorporation of thermally stable but flexible linkages in the main chain,^{9,10} the synthesis of unsymmetrical linkages in the main chain,^{11,12} the introduction of polar or nonpolar substituent branched to the main chain,^{13–16} and the destruction of symmetrical structure of the main chain with the introduction of hyperbranched structure.^{17–19} In particular, the researchers have found that the incorporation of aromatic heterocyclic compounds into the main chain could form thermally stable and flexible linkages in PIs main chain, which would reduce the intermolecular interaction effectively

and improve the solubility remarkably.²⁰ Hariharan *et al.*¹⁰ has reported the synthesis of a series of new PIs containing pyrimidine moiety with various aromatic dianhydrides in DMF. All the PIs were soluble readily in organic solvents such as DMF, DMAc, pyridine, *m*-cresol, THF, etc. The PIs also exhibited good thermal stability with 10% weight loss temperature in the range 403–502 °C. Lin *et al.*²¹ has reported the synthesis of novel PIs containing 1,3,5-triazine rings with various aromatic dicarboxylic acids. All polymers were soluble in polar aprotic solvents such as DMF, DMAc, DMSO, NMP, and pyrimidine. These novel PIs presented high resistance against thermal decomposition up to 470 °C. This article reported a novel organosoluble PI synthesized by chemical and thermal imidization, respectively, from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 2,4-diamino-6-chloropyrimidine (DCP) as raw materials. It was found that the introduction of pyrimidine ring in the PIs main chain would increase the solubility in polar solvent as a result of the decrease of intermolecular interaction because of the protonation or alkylation of two polar N atoms in pyrimidine ring. The molecular structure, solubility, UV-visible absorption characteristic, crystallinity, thermal stability, electrochemical behaviors, and mechanical properties were also studied.



Scheme 1. Synthetic route to PI.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), *N*-methylpyrrolidone (NMP), metacresol (*m*-cresol), tetrahydrofuran (THF), and chloroform (CHCl_3) were purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China and purified by vacuum distillation before use. BTDA and DCP obtained from Aladdin Chemical Co. Ltd, Shanghai, China were dried at 100 °C overnight in vacuum prior to use. Other reagents were used as supplied.

Synthesis

The novel organosoluble PI with pyrimidine ring in the main chain was synthesized by chemical and thermal imidization according to refs. 22–24 and the synthetic route is outlined in Scheme 1. For the convenience of discussion, the resulting PI was designated as PI-C for chemical imidization and PI-T for thermal imidization, respectively.

DCP (10 mmol) and NMP (20 mL) were added in a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, condenser, and N_2 gas inlet. After DCP dissolved, 10 mmol BTDA was added drop by drop, and the mixture was stirred at room temperature for 5 h under N_2 atmosphere to form polyamic acid (PAA) solution. The PAA solution was then poured into deionized water and a pale white PAA precipitate was filtered and dried at 60 °C under vacuum (Yield = 94%). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ): 11.2 (s, 1H, COO-H), 8.4–7.54 (m, 6H, Ar-H), 6.87 (s, H, DCP-H), 5.79 (s, 1H, N-H). IR (KBr, cm^{-1}): 3350 ($\nu_{\text{N-H}}$, stretching vibrations), 1790 ($\nu_{\text{C=O}}$, symmetric stretching vibrations), 1715 ($\nu_{\text{C=O}}$, asymmetric stretching vibration), 1260 ($\nu_{\text{C-N-C}}$, stretching vibration). GPC (DMF, 2 mg/mL): $M_n = 4.63 \times 10^4$; PDI = 1.35.

The mixture solution of 8.5 mL acetic anhydride and 12.54 mL triethylamine was dropped slowly in the above PAA solution. Then the reaction mixture was poured into ethanol after further stirring for 24 h at 75 °C to form fiber-like precipitate. After filtration and washing, brown PI-C was dried at 60 °C under vacuum (yield = 95%). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ): 8.4–7.54 (m, 6H, Ar-H), 6.97 (s, H, DCP-H). IR (KBr, cm^{-1}): 1788

Table I. Solubility of PI

Solvent	DMF	DMAc	DMSO	NMP	<i>m</i> -Cresol	THF	CHCl_3
PI-C	++	++	++	++	++	+	h++
PI-T	++	++	++	++	+	+	h+

++: Soluble at room temperature; +: Partially soluble at room temperature; h++: Soluble at 60 °C; h+: Partially soluble at 60 °C.

($\nu_{\text{C=O}}$, symmetric stretching vibrations), 1718 ($\nu_{\text{C=O}}$, asymmetric carbonyl stretching vibration), 1250 ($\nu_{\text{C-N-C}}$, stretching vibration). GPC (DMF, 2 mg/mL): $M_n = 4.39 \times 10^4$; PDI = 2.08.

The above PAA solution was poured on a clean glass plate, and then heated step by step in the oven, specific steps: 80 °C overnight, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C for 1 h. Brown PI-T was obtained after cooling to room temperature (yield = 85%). $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ): 8.4–7.54 (m, 6H, Ar-H), 6.97 (s, H, DCP-H). IR (KBr, cm^{-1}): 1780 ($\nu_{\text{C=O}}$, symmetric stretching vibrations), 1720 ($\nu_{\text{C=O}}$, asymmetric stretching vibration), 1275 ($\nu_{\text{C-N-C}}$, stretching vibration). GPC (DMF, 2 mg/mL): $M_n = 4.00 \times 10^4$; PDI = 2.87.

Characterization

$^1\text{H-NMR}$ spectra were obtained with a Bruker Advance III 500 spectrometer, Karlsruhe, Germany, $\text{DMSO-}d_6$ was used as a solvent and TMS as an internal standard. Fourier transform infrared (FTIR) spectra were measured with KBr pellet by a Perkin-Elmer Lambda 900 FTIR spectrometer, Norwalk, California. The molecular weight was determined by gel permeation chromatography (GPC) using a Waters 1515, Milford, Massachusetts with DMF as an eluent and PMMA as a standard. The solubility of PI was tested in NMP, DMAc, DMF, DMSO, THF, and *m*-cresol, and the concentration was 10 mg/mL. UV-visible absorption spectra were recorded on a Hitachi U-2001 UV-visible spectrometer, Tokyo, Japan and the concentration of PAA or PI in DMF solution was 0.08 mg/mL. X-ray diffraction (XRD) measurements were conducted on X'Pert Pro MPD, Almelo, Netherlands using $\text{Cu K}\alpha_1$ ($\lambda = 0.154056$ nm) irradiation at a rate of 2°/min from 5° to 60°. TGA was performed by a Seiko SSC5200

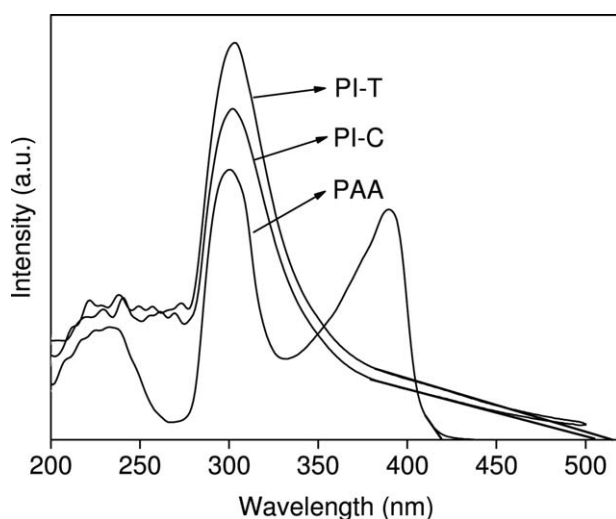


Figure 1. UV-visible spectra of PAA and PI.

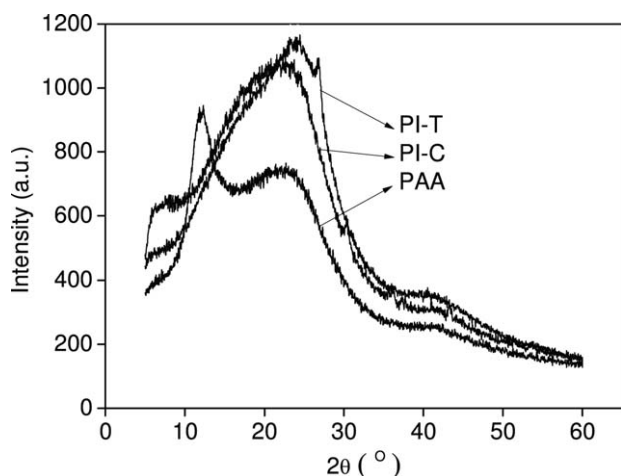


Figure 2. XRD patterns of PAA and PI.

thermal analyzer, Tokyo, Japan at a heating rate of 10 °C/min under flowing N₂ gas and the sample was dried at 90 °C for 1 h before the experiment. CV was performed with a CHI660D Electrochemical Workstation, Shanghai, China in a conventional three-electrode cell, where glassy carbon electrode (GC) was used as a working electrode, a platinum wire as an auxiliary electrode, and a saturated calomel electrode (SCE) as a reference electrode. PI-C or PI-T was dissolved in NMP, DMAc, or DMSO solution of 0.1 mol/L tetrabutylammonium perchlorate (TBAP) to prepare working solution for CV and the concentration of PI in TBAP solution was 0.01 mol/L. High purity N₂ gas was passed into the solution to remove oxygen dissolved in the solution before the CV measurement. The mechanical properties were measured at room temperature on an Instron Model 3367 universal testing machine, Norwood, MA according to ASTM D882.

RESULTS AND DISCUSSION

Solubility

In general, the wholly aromatic PI usually showed poor solubility in organic solvent. However, PI containing pyrimidine ring in the main chain exhibited excellent solubility at room temperature and the results were listed in Table I. It was found that PI was soluble readily in polar aprotic solvents such as DMF, DMAc, DMSO, NMP, and PI-C could be dissolved even in CHCl₃ under heating condition.

It is well known that the solubility of polymer is closely relevant to its relative molecular mass, molecular packing state, and intermolecular interaction. The wholly aromatic PI with rigid main chain shows large polarity, good molecular order, and high molecular packing density resulting in the improvement of intermolecular interaction and its poor solubility. PI reported in this article had the molecular main chain with asymmetric structure and two polar N atoms in pyrimidine ring, which led to the decrease of cohesive energy density and the reduction of intermo-

Table II. Degrees of Crystallinity of PAA and PI

Sample	PAA	PI-C	PI-T
Degree of crystallinity	12.21%	0.02%	0.91%

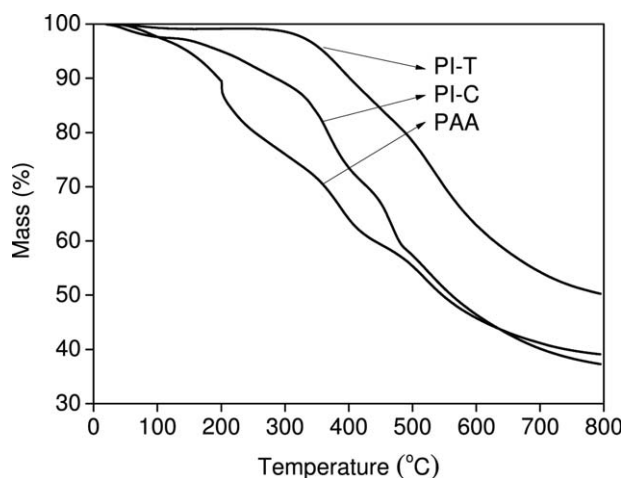


Figure 3. TGA curves of PAA and PI.

lecular or intramolecular interaction, therefore, it is easier for solvent molecules to penetrate into the molecular chains and PI exhibited excellent solubility in polar aprotic solvents. It was noteworthy that PI-T was poorer in solubility than PI-C, which might be due to the enhancement of the interchain interaction as a result of high imidization degree and intermolecular chemical crosslinking during the course of the thermal imidization.

UV-Visible Absorption Characterization

The UV-visible absorption spectra of PAA and PI in DMF solution are presented in Figure 1. It was found that PAA had two absorption peaks at 299 nm and 388 nm, respectively. The former absorption peak was ascribed to the combination of $\pi-\pi^*$ transitions arising from the benzenoid ring and the pyrimidine ring, and the later was attributed to $n-\pi^*$ transition resulting from the pyrimidine ring.²⁵ Compared with PAA, PI had only one obvious absorption peak, which might be due to the combinations of $\pi-\pi^*$ transitions arising from the benzenoid ring and the pyrimidine ring, and $n-\pi^*$ transitions resulting from the pyrimidine ring and the imide ring.²⁵ Furthermore, the absorption peak of PI-T red-shifted from 301 nm to 304 nm with stronger intensity compared to PI-C, which may be ascribed to the higher imidization degree of PI-T than that of PI-C and the intermolecular chemical crosslinking during the course of the thermal imidization. In addition, the UV-visible absorption spectrum of PI exhibited the raised optical absorption in the range of 400–500 nm followed by a red-shift of optical absorption threshold compared with PAA. The optical bandgap values of PAA, PI-C, and PI-T estimated from the absorption edges in Figure 1 were about 2.96 eV, 2.47 eV and 2.43 eV, respectively. Thus, the raised optical absorption might be consistent with the conclusion that the high imidization degree could reduce the optical bandgap.²⁶

Table III. TGA data of PAA and PI

Sample	T_d (°C)	T_d^5 (°C)	T_d^{10} (°C)
PAA	100.2	140.2	200.2
PI-C	190.6	230.2	302.2
PI-T	325.6	370.5	401.8

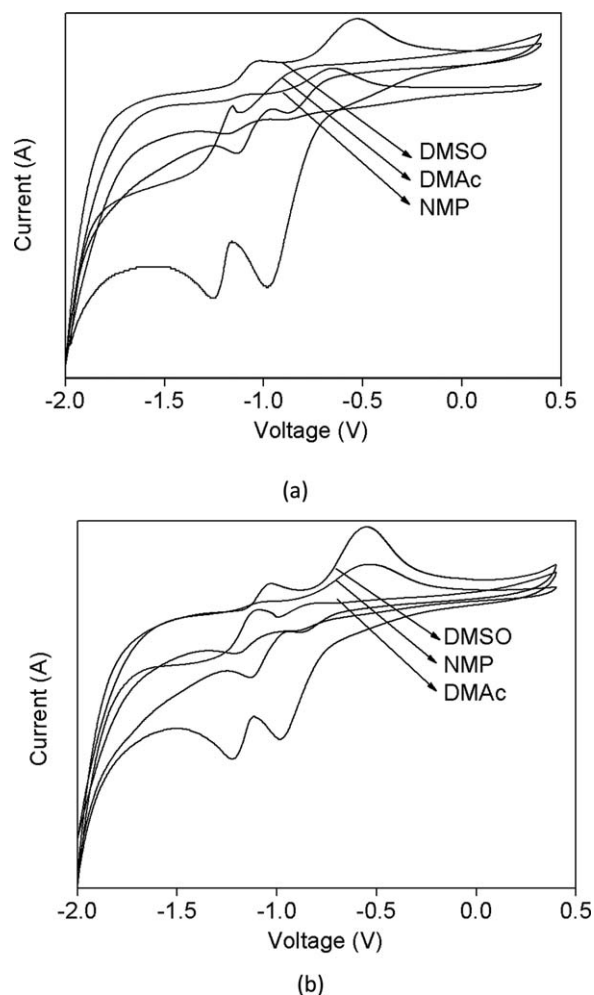
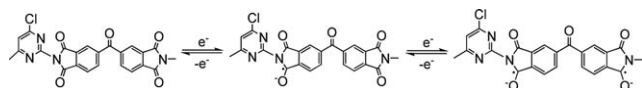


Figure 4. CV curves of PI in various solutions (a) PI-C; (b) PI-T.



Scheme 2. Progress of redox reaction of PI.

Powder X-ray Analysis

XRD patterns of PAA and PI are shown in Figure 2 and the corresponding degrees of crystallinity obtained by the software MDI Jade 6.5 are listed in Table II. Each sample showed a broad peak, which was the characteristic diffraction peak of amorphous polymer. However, PAA showed two intense peaks cen-

tered at about 24° mainly ascribed to the periodically parallel alignment to the direction of orientation of the molecular main chain and 13° corresponding to the periodically perpendicular alignment to the direction of orientation of the molecular main chain.^{25,27} Compared with PAA, PI showed only a broad peak at about 24° and the diffraction peak at about 13° disappeared, which indicated that it was difficult to form the periodic alignment perpendicular to the molecular main chain because of the improvement of imidization degree and the reduction of flexibility after the generation of complete imide structure in the main chain. Besides, PI-C had relatively lower crystallinity than PI-T owing to PI-Ts high imidization degree and intermolecular chemical crosslinking during the course of the thermal imidization.

Thermal Stability

The TGA curves of PAA and PI are shown in Figure 3 and the corresponding data are summarized in Table III. Compared with PI, PAA had the poor thermal stability and the initial decomposition temperature (T_d), 5% and 10% weight loss temperatures were only 100.2°C , 140.2°C , and 200.2°C on account of its low imidization degree and poor thermal stability of amino groups and carboxyl groups in the molecular chain. After imidization, the formation of complete imide structure in the main chain resulted in the remarkable improvement of thermal stability of PI. It was also found distinctly that the thermal stability of PI-T was superior to that of PI-C by virtue of the high imidization degree and intermolecular chemical crosslinking of PI-T, which was in accordance with its worse solubility, stronger absorption intensity, and relatively higher crystallinity than PI-C. Besides, the slight weight loss below 100°C was due to the evaporation of loosely bounded water and solvent from the polymer chain.

Electrochemical Studies

The electrochemical behaviors of PI in various solutions investigated by CV with a scan rate of 200 mV/s are shown in Figure 4, and the progress of redox reaction of PI is also shown in Scheme 2. PI could undergo the reversible redox reaction in electrolyte solution, and the imide functional groups were the centers for the electron transfer processes.

The redox peak potentials, peak potential differences, LUMO energy levels (E_{LUMO}), HOMO energy levels (E_{HOMO}), and electrochemical bandgaps (E_g) of PI in various solvents are outlined in Table IV, in which E_{pc} and E_{pa} represented reduction and oxidation peak potentials, respectively, E referred to the peak

Table IV. Electrochemical Data of PI in Various Solvents

Sample	Solvent	E_{pa1} (V)	E_{pa2} (V)	E_{pc1} (V)	E_{pc2} (V)	E_1 (V)	E_2 (V)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g (eV)
PI-C	DMSO	-1.14	-0.86	-1.01	-0.54	0.13	0.32	-3.52	-4.43	0.91
	DMAc	-1.27	-1.03	-1.13	-0.69	0.13	0.34	-3.34	-4.12	0.98
	NMP	-1.20	-0.91	-1.05	-0.56	0.15	0.35	-3.44	-4.42	0.98
PI-T	DMSO	-1.12	-0.88	-1.02	-0.66	0.10	0.22	-3.53	-4.40	0.87
	DMAc	-1.27	-0.99	-1.15	-0.72	0.12	0.27	-3.35	-4.21	0.86
	NMP	-1.17	-0.87	-1.07	-0.64	0.10	0.23	-3.46	-4.34	0.88

Table V. Mechanical Properties of PI

Sample	Tensile strength (MPa)	Elongation at break (%)
PI-C	89	10.6
PI-T	93	10.3

potential differences, E_{LUMO} and E_{HOMO} were calculated from the onset potentials of oxidation and reduction by assuming the energy level of ferrocene/ferrocenium (Fc/Fc^+) to be 4.8 eV below the vacuum level. The formal potential of Fc/Fc^+ was measured as 0.06 V against SCE.²⁸

It was obvious that the E_2 value was larger than E_1 value for PI in various solvents because of the reduction of reversibility of the second pair of redox peak.²⁹ Moreover, though the shape of CV curve of PI-T was similar to that of PI-C in the same solvent, the E_1 or E_2 value of PI-T was smaller than that of PI-C. It might be due to the fact that PI-T had better redox reversibility than PI-C on account of its higher imidization degree and lower LUMO energy level²⁶ than PI-C as shown in Table IV. Besides, it could be easily found that the E_g value of PI-T was smaller than that of PI-C in various solvents, which also indicated that PI-T had higher imidization degree than PI-C.

Mechanical Properties

The mechanical properties of PI are shown in Table V, which indicated that it had excellent mechanical properties. The tensile strength and the elongation at break of PI-C were 89 MPa and 10.6%, respectively. Compared with PI-C, the tensile strength of PI-T increased to 93 MPa and the elongation at break decreased to 10.3%, which were mainly related to its relatively high imidization degree and crystallinity.

CONCLUSIONS

A novel organosoluble PI containing pyrimidine ring in the main chain was synthesized successfully by chemical and thermal imidization, respectively. The results showed that the introduction of pyrimidine ring in the PIs main chain could increase the solubility greatly in polar aprotic solvents, and PI could be soluble readily in DMF, DMAc, DMSO, and NMP. PI had strong optical absorption in the range of 280–320 nm, and the absorption peak of PI-T had slight red-shift and strong intensity compared with PI-C. PI was an amorphous polymer and PI-T had relatively higher crystallization degree than PI-C. PI had excellent thermal stability, and the 10% weight loss temperatures of PI-C and PI-T were 302.2 °C and 401.8 °C, respectively. PI had obvious electrochemical redox behaviors in DMSO, DMAc, and NMP solutions and PI-T had better redox reversibility and smaller electrochemical bandgap than PI-C because of its higher imidization degree and lower LUMO energy level. Furthermore, PI had preeminent mechanical properties and the tensile strength of PI-C and PI-T were 89 MPa and 93 MPa, respectively. It was demonstrated that the novel organosoluble PI containing pyrimidine ring in the main chain not only exhibited excellent solubility in polar aprotic solvents but also possessed outstanding properties, which were conducive to its

potential applications in adhesives, polyelectrolyte, separation membrane, and so on.

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