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The Synthesis and Characterization of a Novel Ternary Polymer Bisphenol A-4,4'-Difluorobenzophenone-*bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic Diimide Monomer

Zhiyu Dou, Xianfeng Li, Shuangling Zhong, Chengji Zhao, Hui Na (✉)

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China

E-mail: huina@jlu.edu.cn; Fax: +86-431-5168868

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Summary

A novel *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide (NTDA–OH) monomer was prepared through the condensations of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) with *p*-aminophenol. A series of ternary copolymers derived from NTDA–OH were further synthesized by the nucleophilic substitution reactions. Both the monomer and the ternary copolymers were characterized by FT–IR, ^{1}H NMR, and inductively coupled plasma (ICP). The characterization results showed that, the imide groups were successfully introduced into the prepared monomer. The differential scanning calorimetry (DSC) and the thermal gravimetry analysis (TGA) were further performed on the produced polymers. The thermal stability of the polymer increased with the content of the NTDA–OH increasing.

Introduction

Poly (ether ether ketone) (PEEK) are an important class of industrial plastic materials developed in the 1980s which have been widely used in the fields of traffics, aeronautics, astronautics, and medicines, etc., due to their advanced mechanical properties, solvent resistance, insulation properties, and flame retardation.[1-3] The glass-transition temperature (T_g), the melting point temperature (T_m), and the thermal decomposition temperature (T_d) of PEEK are 143°C, 334°C, and 530°C, respectively. To enhance the thermal stabilities of PEEKs, various functional groups have been introduced into their backbones and branched chains,[4,5] through further copolymerizations,[6-8] blends, and multiblocks.[9,10]

Polyimides are one of the most successful classes of high-performance polymers which are widely used in industries. Because of the rigidity of the imide ring, most polyimides possess high thermal resistance, high tensile strength, and high modulus.[11] Copolymerization is an effective approach to the synthesis of polymer materials, which could enhance the properties of the homopolymers and produce various polymer materials with new structures. Introduction of rigid imide rings into the PEEK backbones through copolymerizations could resist the inner-rotations in the polymer chains, which might be an effective way to increase the thermal stabilities of PEEK. Here, we describe the synthesis of a new bisphenol monomer with imide groups from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), and further a series of bisphenol A-4,4'-difluorobenzophenone-*bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide ternary polymers through copolymerizations. The purpose of this paper is to increase the thermal stability of the PEEK and explore novel thermal plastic with excellent properties.

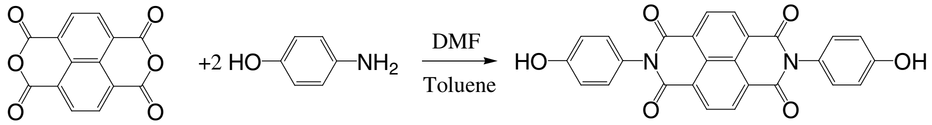
Experimental

Materials

1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA, Shanghai Institute of Resin), *p*-aminophenol (Huludao Chemical Plants), bisphenol A, and 4,4'-difluorobenzophenone (Yinsheng Chemical Plants) were used as received. Potassium carbonate was dried at 180°C for 10 hours before use. Other reagents and solvents, such as N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *m*-cresol, were obtained commercially (Beijing Chemical Plants) and used without further purification.

Synthesis of Bis(p-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic Diimide Monomer

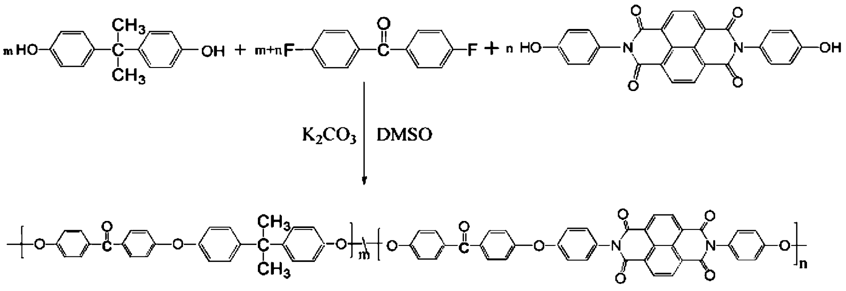
26.8 g of NTDA, 22.4 g of *p*-aminophenol, and 350 mL of DMF were added to a completely dried 3-necked flask equipped with a mechanical stirrer, a reflux condenser, and a nitrogen inlet. Toluene was used to remove the produced water. The reaction mixture was stirred at room temperature and then heated to reflux under the nitrogen flow at 120°C for 4 hours. After removing the water that produced in the reaction, the reaction mixture was reheated to 120-140°C for 5 hours. When toluene was evaporated out, the reaction mixture was cooled to room temperature. The solid product was filtered and thoroughly washed with boiling water and ethanol to remove the residual *p*-aminophenol, dried at 80°C for 10 h, and then gave 45 g of yellow powder solid, which was the *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide (Yield: 92%). Scheme 1 has illustrated this process in detail. Anal. Calcd for NTDA–OH ($C_{26}H_{14}N_2O_6$): C, 69.34%; H, 3.11%; N, 6.22%; Found: C, 69.75%; H, 3.05%; N, 6.20%. ^{1}H NMR (ppm, DMSO-*d*6): $\delta_{H1} = 9.71$, $\delta_{H2} = 8.70$, $\delta_{H3} = 7.20–7.22$, $\delta_{H4} = 6.89–6.91$. FT–IR (KBr, cm^{-1}): 1683 (–CO–), 1340(C–N), 1255 (C–O).



Scheme 1 The preparation of the *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide monomer

Synthesis of the Polymer

A typical procedure for the copolymerization is shown in Scheme 2. To a 3-necked flask equipped with a mechanical stirrer, a reflux-condenser, and a nitrogen inlet, *m* mol of bisphenol A, *n* mol of *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide, (*m*+*n*) mol of 4,4'-difluorobenzophenone, K_2CO_3, DMSO, and toluene were added. After stirred at 140°C for 4 hours, toluene was evaporated out. The reaction mixture was heated at 180°C for 6 hours, and then poured into distilled water. The product was cooled to room temperature and washed carefully with distilled water.



Scheme 2 The preparation of the copolymers

Measurements

Specific viscosity was measured at a concentration of 5.00 g/L in DMF at 25°C using Ubbelohde viscometer. IR spectra were recorded on a Nicolet Impact 410 FT–IR spectrometer for the monomer and the polymer powder as KBr pellets. ^{1}H NMR spectra were recorded on a Bruker Avance 500S spectrometer with dimethyl sulfoxide-*d*6 (DMSO-*d*6) as a solvent and with tetramethylsilane as a reference. Differential scanning calorimetry (DSC) was performed with a DuPont TA–910 instrument at a heating rate of 10°C /min in N_2 flow. Thermal gravimetry (TG) was measured with a Netzsch Sta449C instrument in air at a heating rate of 10°C /min. The inductive coupled plasma (ICP) analysis was conducted on a Jarrzall–ash 800 Mark–II ICP instrument, and the elemental analysis was performed on a Perkin–Elmer 240C element analyzer.

Results and discussion

Synthesis and Characterization of the Monomer

As shown in Scheme 1, the *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide monomer was prepared via the nucleophilic substitution condensation of NTDA with *p*-aminophenol in the DMF/toluene solvent system. The composition and structure of the resulted monomer were confirmed by the ^{1}H NMR and the elementary analysis. The elementary analysis results and their theoretical values for this synthesized monomer were in good agreement. The ^{1}H NMR spectrum of the monomer is illustrated in Figure 1. All of the hydrogen atoms were well assigned to the supposed chemical structure (δ_{H1} = 9.71 ppm; δ_{H2} = 8.70 ppm; δ_{H3} =7.20–7.22 ppm; δ_{H4} = 6.89–6.91 ppm), and the integration ratio of the peaks were in good agreement with the expected monomer compositions. No residual amide and carboxylic protons were observed, which indicated that the imidization was complete. Both the elementary analysis and the NMR spectrum result suggested that we had synthesized a bisphenol monomer with imide groups as shown in Scheme 1.

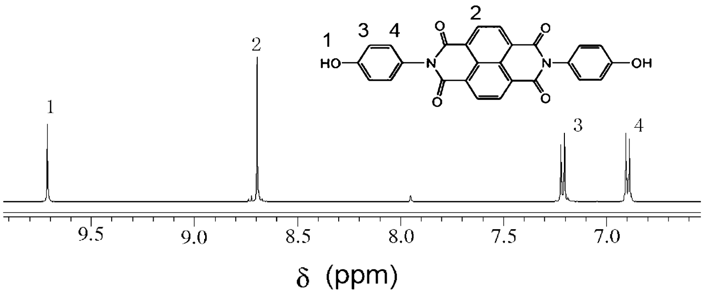


Figure 1 ^{1}H NMR spectrum of the synthesized monomer.

Synthesis and Characterization of the Polymers

A series of polymers were obtained through ternary copolymerizations of 4,4'-difluorobenzophenone and various ratios of two kinds of bisphenols by nucleophilic substitution reactions. K_2CO_3 was used as the salifying reagent, and toluene was used to remove the water produced during the reaction. The synthetic routes are showed in Scheme 2. Table 1 lists the results of elementary analysis, viscosity analysis and DSC analysis for polymers with different molar ratios of bisphenol A and *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide. Polymer 'a' denotes the homopolymer synthesized by bisphenol A and 4,4'-difluorobenzophenone; polymer 'k' denotes the homopolymer synthesized by *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide and 4,4'-difluorobenzophenone; polymer 'b' to polymer 'j' denote the ternary copolymers synthesized by 4,4'-difluorobenzophenone and different molar ratios of the two bisphenols, and the '*m*:*n*' denotes the molar ratio of bisphenol A and *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide. The viscosity factor η showed that the polymers we synthesized were of high molecular weights.

Table 1 The results of elementary analysis, viscosity analysis and DSC analysis for different polymers

Polymer	m:n*	η_{sp}/c	T_g/°C	t_5/°C	t_{10}/°C
a	10:0	1.15	146.2	510.2	535.5
b	9:1	1.08	161.8	527.0	545.3
c	8:2	0.97	170.3	536.6	557.1
d	7:3	0.92	176.5	542.3	565.9
e	6:4	0.85	184.1	550.4	577.3
f	5:5	0.80	196.6	561.4	586.0
g	4:6	0.75	214.5	574.9	597.7
h	3:7	0.77	231.0	586.0	608.4
i	2:8	0.73	248.7	598.7	615.6
j	1:9	0.68	268.2	603.6	625.2
k	0:10	0.57	283.9	620.2	644.3

*: '*m*:*n*' denotes the molar ratio of bisphenol A and *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide

The IR spectra of the polymers with different ratios of the two bisphenols are shown in Figure 2. For all the polymers from A to K, the adsorption peaks at *ca* 1235 cm^{-1} could be found, which corresponded with the –O– vibrations. For polymer A, there were adsorption peaks at 2968cm^{-1} and 1363 cm^{-1}, which could be assigned to the vibrations of $–CH_3$ groups, while no peaks at 1340cm^{-1} were found corresponding with the vibrations of N–C bonds; for polymer K, only adsorption peaks assigned to N–C bonds could be found, while no peaks could be found corresponding with $–CH_3$ groups; for polymer B to J, both the adsorption peaks corresponding with the $–CH_3$ groups and the N–C bonds could be found.

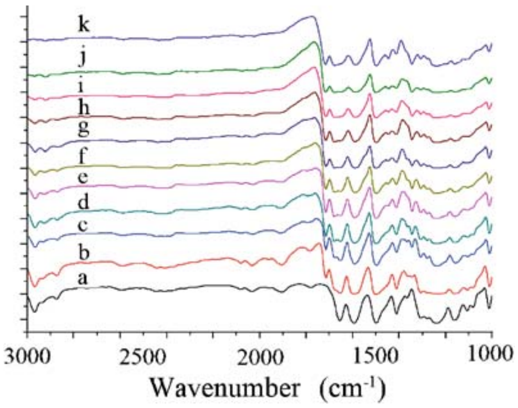


Figure 2 The FT-IR spectra of the polymers with different compositions.

We took the polymer C as an example to illustrate the ^1H NMR spectra of our synthesized polymers. Figure 3 shows the ^1H NMR spectrum of polymer C. The chemical shifts δ_H at 1.69–1.75 ppm were assigned to the hydrogen atoms of methyl groups; δ_H at 8.78 ppm was assigned to the hydrogen atoms of naphthalene; δ_H at 7.91–6.90 ppm were assigned to the hydrogen atoms of benzene rings; and δ_H at 2.79 ppm was assigned to the hydrogen atoms of DMSO molecules. Table 2 lists the elementary results of the synthesized polymers. The experimental compositions of the

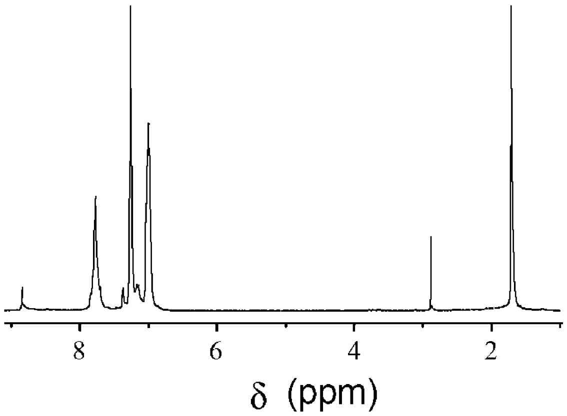


Figure 3 ^1H NMR spectrum of the polymer C.

polymers were in good agreement with the theoretical calculated values. The IR spectra, ^{1}H NMR spectra, and the elementary analysis results indicated that we had successfully synthesized a series of ternary copolymers with different ratios of bisphenol A and *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide.

Table 2 The elementary analysis results of the synthesized polymers

		C (% wt)	H (% wt)	N (% wt)
A	Exp.	82.51	5.27	0.00
	Calcd.	82.74	5.46	0.00
B	Exp.	80.98	5.03	0.62
	Calcd.	81.53	5.13	0.65
C	Exp.	80.23	4.56	1.20
	Calcd.	80.45	4.83	1.24
D	Exp.	79.15	4.42	1.59
	Calcd.	79.46	4.56	1.78
E	Exp.	78.51	4.36	2.25
	Calcd.	78.57	4.31	2.26
F	Exp.	77.71	4.05	2..65
	Calcd.	77.75	4.09	2.71
G	Exp.	76.32	3.49	3.12
	Calcd.	77.00	3.88	3.11
H	Exp.	76.21	3.56	3.41
	Calcd.	76.30	3.70	3.49
I	Exp.	75.00	3.61	3.49
	Calcd.	75.66	3.52	3.84
J	Exp.	74.56	3.22	4.03
	Calcd	75.07	3.36	4.16
K	Exp.	74.38	3.08	4.39
	Calcd.	74.52	3.21	4.46

Solubility of the Copolymers

Table 3 lists the solubility of the synthesized polymers. The solubility of the copolymer decreased rapidly when the ratio of the bisphenol A and *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide increased. This was because that, the decrease of the content of the flexible bisphenol A or the increase of the content of the rigid imide rings caused the increase of the order of the degree of the backbones. The movements of the backbones were more limited in the copolymers with lower *m*/*n* ratios, which made the solute molecules more difficult to diffuse and decreased the solubility of the copolymers.

Thermal Properties of the Copolymers

The DSC results of the copolymers are illustrated in Figure 4. The glass-transition temperature of the copolymer increased with the content of the imide rings. The T_g of the PEEK with only imide groups was high up to 290°C. This was because that, after the introduction of the *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide into the backbones, the number of rotatable single bonds in the backbones decreased, and the rigidity of the backbones increased, which raised the glass transition temperature. On the other hand, the ternary copolymerization broke the ordered arrangement of the backbones, which caused the glass transition temperatures of the copolymers lying between the homopolymers.

Table 3 The solubility of the copolymers

	A	B	C	D	E	F	G	H	I	J	K
Water	–	–	–	–	–	–	–	–	–	–	–
Chloroform	+h	+h	–	–	–	–	–	–	–	–	–
Acetone	–	–	–	–	–	–	–	–	–	–	–
Toluene	+h	+h	+h	–	–	–	–	–	–	–	–
Methanol	–	–	–	–	–	–	–	–	–	–	–
THF	+	+	+	+h	+h	+h	+h	+h	+h	–	–
DMF	+	+	+	+	+	+	+	+h	+h	–	–
DMAC	+	+	+	+	+	+	+	+h	+h	+h	–
DMSO	+	+	+	+h	+h	+h	+h	+h	–	–	–
NMP	+	+	+	+	+	+	+	+	+h	+h	+h
HCl	–	–	–	–	–	–	–	–	–	–	–
NaOH	–	–	–	–	–	–	–	–	–	–	–

(+):soluble at room temperature , (+h):soluble under heating , (–):insoluble

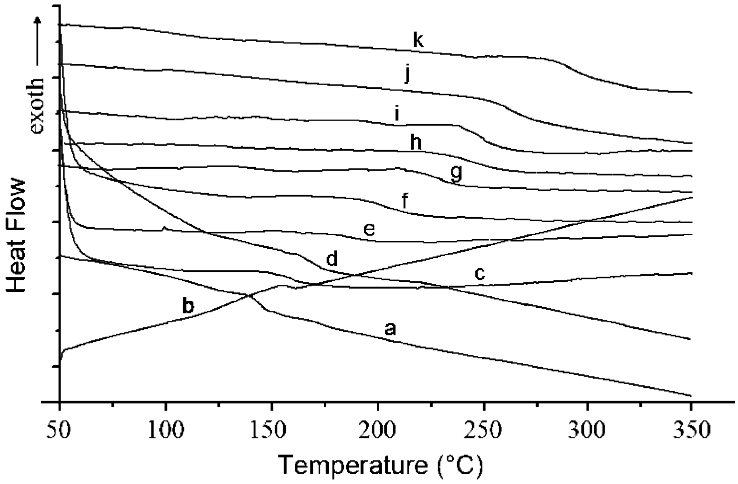


Figure 4 The DSC results of the synthesized copolymers.

The thermal gravimetry results of the synthesized copolymers are illustrated in Figure 5. The temperatures of 5% and 10% weight loss were all above 520°C and 540°C, respectively. The thermal stability of the copolymer increased with the content of the imide rings. The temperatures of 5% and 10% weight loss for the PEEK with only imide groups were at 620.2°C and 644.3°C, respectively. Both the DSC and the TGA analysis results indicated that we synthesized a series of copolymers with high glass transition and thermal decomposition temperatures.

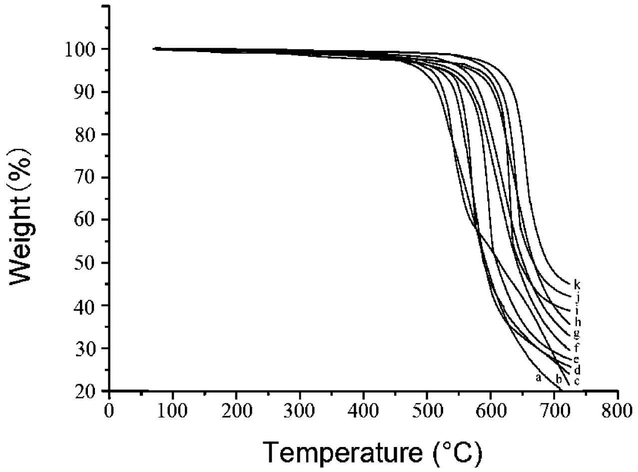


Figure 5 Thermal gravimetry of the synthesized copolymers

Conclusions

A new *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide monomer were prepared. A series of copolymers were further synthesized by the ternary copolymerization of the synthesized *bis*(*p*-hydroxylphenyl)-1,4,5,8-naphthalenetetracarboxylic diimide, bisphenol A, and 4,4'-difluorobenzophenone. The compositions of the copolymers were confirmed by the elementary analysis, FT-IR, and ^{1}H NMR spectra. The DSC and TG results indicated that the PEEK we synthesized had high glass transition and thermal decomposition temperature. The introduction of the imide groups increased the thermal stabilities of the polymers, and gave them potential applications in more fields.

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