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Polymer 45 (2004) 2533–2538

polymer

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Copolymerization of dichlorodiphenylsulfone with bis(chlorophthalimide) catalyzed by $NiBr_2/PPh_3/Zn$

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Received 17 January 2004; received in revised form 9 February 2004; accepted 12 February 2004

Abstract

A new high-performance material, poly(sulfone-imide) was prepared by Ni(0)-catalyzed coupling of aromatic dichlorides containing imide structure and 4,4'-dichlorodiphenylsulfone. The copolymers were produced with high yield and moderate to high inherent viscosities of 0.52–1.13 dL/g. Wide-angle X-ray diffractograms revealed that the polymers were amorphous. Most of the polymers exhibited good solubility and could be readily dissolved in various solvents such as *N*-methyl-2-pyrrolidinone(NMP) and *N*,*N*-dimethylacetamide (DMAc). These polysulfone-imides had glass-transition temperatures between 317 and 345 °C and 10% weight loss temperatures in the range of 450–476 °C in nitrogen atmosphere. The tough polymer films, obtained by casting from cresol solution, had a tensile strength range of 21–158 MPa and a tensile modulus range of 2.1–3.3 GPa.

Keywords: Bis(chlorophthalimide); Dichlorodiphenylsulfone; Coplymerization

1. Introduction

Polyimides (PIs) have been of great interest in engineering and microelectronics for a number of applications owing to their unique property combinations [1]. Conventionally, these materials are made through the condensation reaction of a diamine with a dianhydride giving soluble polyamic acids, followed by thermal or chemical imidization [2]. Other approaches involve a nitro-displacement reaction of a dinitro bisimide and a diphenoxide [3a,b], and the palladium-catalyzed carbonylation of a bis(*o*-iodo ester) and a diamine [3c,d]. But it is difficult for one component of PIs to have all the required properties such as thermo-oxidative stability, hydrolytic stability etc. Recently, considerable attention has been direct to modifying this polymer through blending to obtain inexpensive material with improved characteristics. However, some of the blends are miscible over a wide rang of compositions and structural variation [4]. And some others are immiscible [5].

In the previous paper [6], we reported a successful synthesis of biphenyl type of polyimides by nickel-catalyzed coupling polymerization of aromatic dichloride containing phthalimide. High molecular weight polymers were obtained by the polymerizations of bis(4-chlorophthalimide)s with bulky side substituents. However, the polymerization of bis(4-chlorophthalimide)s containing rigid diamine moieties gave low molecular weight polymers because of the formations of polymer precipitate. It was clear that the resulting polymer should be soluble in the polymerization solution to obtain high molecular weight polyimides.

In this article, we report a successful synthesis of copolymer of polyimide and polysulfone by nickel catalyzed coupling of aromatic dichlorides containing sulfone and phthalimide structures. The insertion of sulfone groups into the macromolecular chain generally results in an improved solubility, together with interesting properties such as increased T_g and high thermo-oxidative stability. Hence, the goal of better thermal stability together with good processability may be achieved in preparing polyimides bearing both sulfone and biphenyl units.

We believe that the combination of polyimides and other high-performance macromonomers will allow one to

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0032-3861/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2004.02.019

produce new materials that represent a balance of homopolymer properties.

2. Experimental section

2.1. Materials

Reagent grade anhydrous $NiBr_2$ was dried at 250 °C under vacuum. Triphenylphosphine (PPh_3) was recrystallized from hexane. Powdered (100 mesh) zinc was stirred with acetic acid, filtrated, washed thoroughly with diethyl ether, and dried under vacuum. 4-Chlorophthalic anhydride (99.2%) was purified by distillation. 4,4'-dichlorodiphenyl sulfone (DDS) was used as received from Aldrich. *N*,*N*-dimethylacetamide (DMAc) was stirred over phosphorous pentoxide for 5 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves. Other reagents and solvents were obtained commercially and used without further purification.

2.2. Instrumentation

The ^1H NMR spectra were measured at 300 MHz on a AV300 spectrometer. The FTIR spectra were obtained with a Bio-Rad digilab Division FST-80 spectrometer. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin–Elemer. TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. The dynamic mechanical properties of copolymer films were conducted using a dynamic mechanical thermal analyzer (DMA) equipped with a high-temperature (500 °C) head operating at a frequency of 1 Hz and a constant strain in a single-cantilever geometry. The thickness of the films was in the range of 0.1–0.2 mm. Data were collected at a heating rate of 3 °C/min in air. The X-ray diffraction data were collected on a SiemensP44-circle diffractometer at 293 K under monochromatized Cu Kα radiation. The mechanical properties of the films were measured by a material tester, Instron-1211. The inherent viscosities were determined at a 0.5%concentration of polymer in m-cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C.

2.3. Monomer synthesis

2.3.1. 4,4'-Bis(4-chlorophthalimido)-3,3'dimethyldiphenylmethane)(4-BCPI)

The compound was prepared as reported in the literature [6]. Mp 126–128 °C (Lit. [6] mp 126–127 °C).

2.4. Polymer synthesis

A typical M-50 was carried out with the following method.

A 250 ml three-necked round-bottomed flask equipped with serum caps, nitrogen inlets and outlet was placed with $NiBr_2$(0.39 g, 1.8 mmol), PPh_3(3.301 g, 14.4 mmol), Zinc dust (5.2 g, 80 mmol), and 2,2'-bipyidine (0.22 g, 0.14 mmol). The flask was evacuated and filled with nitrogen three times. Then dry DMAc (20 ml) was added via syringe through the serum caps. The mixture was stirred with a magnetic bar at 80 °C. When the mixture changed into red–brown after 20 min, a nitrogen purged solution (80 ml) of 4-BCPI (5.6 g, 10 mmol) and DDS (2.87 g, 10 mmol in dry DMAc was added via syringe to the reaction mixture. The mixture was stirred at 80 °C for another 8 h. The resulting viscous mixture was poured into 300 ml of 25% HCl/methanol. The solid was collected and washed with methanol and water, and dried in vacuo at 200 °C for 10 h. The yield was 8.64 g (92%). The inherent viscosity of the polymer in cresol was 0.84 dL/g, measured at a concentration of 0.5 g/dL at 30 ± 0.1 °C.

2.5. Model compounds synthesis

2.5.1. 2,2'-Di-o-toly-[5,5']biisoindolyl-1,3,1',3'-tetraone (AA)

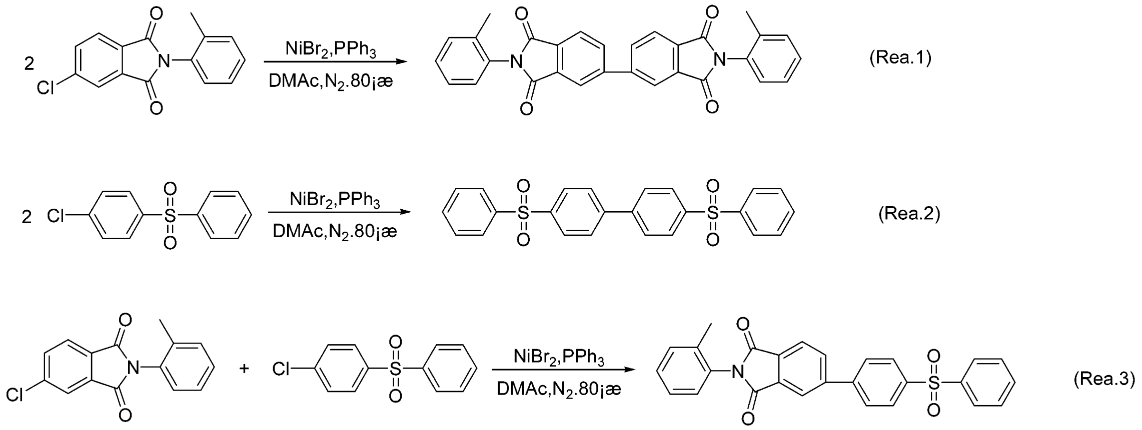
Compound AA was prepared from 2-methyl-*N*-phenyl-4-chloro-phthalimide(A) using a similar procedure as reported in the literature [7]. The yield of AA was 97%. Mp 303–304 °C. ^1H NMR ($CDCl_3$): 8.01–8.04 (2H, dd), 7.84–7.90 (2H, t), 7.75–7.78 (2H, dd), 7.11–7.34 (8H, m), 2.14 ppm (6H, s). IR: 1776 and 1725 cm^{-1} ($\nu_{C=O}$), 1375 cm^{-1} (ν_{C-N}), 742 cm^{-1} ($\delta_{C=O}$). Anal. calcd for $C_{30}H_{20}O_4N_2$: C, 76.26%; H, 4.27%; N, 5.93%. Found: C, 76.31%; H, 4.23%; N, 5.28%.

2.5.2. 4,4'-Bis-benzenesulfonyl-biphenyl (**BB**)

This compound was prepared from 4-chlorodiphenyl sulfone(B) using the same procedure as described above and recrystallized from dichloromethane and hexane (2:1, v/v). The yield was 62%, mp 242 °C (based on DSC, 5 °C/min). ^1H NMR (DMSO): 8.03–8.06 (4H, d), 7.98–8.00 (4H, d), 7.93–7.97 (4H, d), 7.67–7.69 (2H, d), 7.60–7.65 (4H, t). IR (KBr): 1155 and 1347 cm^{-1}($\nu_{S=O}$). Anal. calcd for $C_{24}H_{18}O_4S_2$: C, 66.36%; H, 4.15%; S, 14.75%. Found: C, 66.45%; H, 4.18%; S, 14.52%.

2.5.3. 5-(4-Benzenesulfonyl-phenyl)-2-o-tolyl-isoiodole-1,3-dione (**AB**)

This compound was prepared from A and B using the same procedure as described above and the crude products was chromatographed on silica gel with 15:1 hexane–acetone to afford **AB**. The yield was 52%. ^1H NMR (DMSO): 8.29 (H, s), 8.25–8.23 (2H, dd), 8.10 (4H, s), 8.09–8.07 (1H, d), 8.04–8.02 (2H, dd), 7.72–7.70 (1H, m), 7.67–7.64 (2H, m), 7.43–7.40 (4H, m), 2.14 (3H, s). IR (KBr): 1776 and 1725 cm^{-1} ($\nu_{C=O}$), 1375 cm^{-1}(ν_{C-N}), 742 cm^{-1}($\delta_{C=O}$), 1155 and 1347 cm^{-1}($\nu_{S=O}$). Anal. calcd for $C_{27}H_{19}O_4NS$: C, 71.52%; H, 4.19%; N, 3.09%; S, 7.06%. Found: C, 71.42%; H, 4.22%; N, 3.18% S, 7.04%.



Scheme 1. Model reactions.

2.6. Kinetic data

Kinetic analysis of the model reactions was made by removing 0.15 ml aliquots of the reaction mixture by syringe quenching with aqueous acid and shaking in the presence of air to yield light green solution, added 1.5 ml deionized water, precipitate was appeared, then dissolved and extracted with CH_2Cl_2, the organic layer was washed with water for several times, then removed CH_2Cl_2, the residues were resolved with THF. The samples were then analyzed by HPLC. Observed rate constants were determined from the slope of the initial linear portion of the plots of percent conversion of the model monomers vs. time.

2.7. Preparation of films

Films were prepared by casting on 5% solution of polymers in cresol on a glass plate in a dust-free room, and dried at 70 °C overnight, then at 200 °C for 48 h in vacuum oven.

2.8. Water uptake and contact angle

The films were dried at 150 °C for 8 h and the dried samples of 4 × 4 cm size were dipped into 100 ml of double distilled water in a beaker at 30 °C. The water uptake at different intervals of time till the equilibrium conditions were recorded [8]. The weight were taken by Sartorius microbalance with accuracy up to 10 μg. Contact angles of films and water were tested by Drop Shape Analyzer-112. The films were obtained by spin-coated 5 wt% polymer solution onto a freshly cleaved Mica substrate.

2.9. Alkaline hydrolytic stability

The films prepared from M-0, M-25, M-50 and Kapton were heated in 10% NaOH aqueous for 3 h at 70 °C, then the mechanical properties were tested. For each tensile strength and maximum elongation reported at least three measurements were taken and an average result was calculated.

3. Results and discussion

3.1. Model reaction

In this work, we set up three model reactions. These reactions are designed to gain a better understanding of the capacity of the two monomers to cross polymerization (Scheme 1).

In the homo-coupling reaction, the reaction rate was first order in nickel and bromide ion [7,9]. We have observed that the homo-coupling reaction of 1 was completed in about 30 min at 80 °C with reaction rate $k_1 = 3.11\ \mathrm{min}^{-1}$. In reaction 2 about 60% of B was conversed in about 3.5 h with the reaction rate $k_2 = 0.29\ \mathrm{min}^{-1}$. Reaction 1 was about 10 times faster than reaction 2. Simultaneous coupling of two different aryl chlorides gave a mixture of biaryl products. In this cross-coupling process, the cross polymerization capacity was determined by the formation rate of these three model products (see Fig. 1). With reasonable reliance we can state that in the model reaction the formation rate of AB is faster than AA and BB (in DMAc, at 80 °C). In the

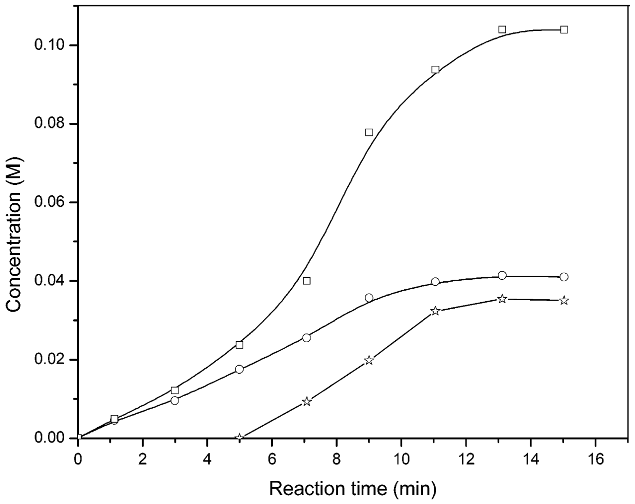
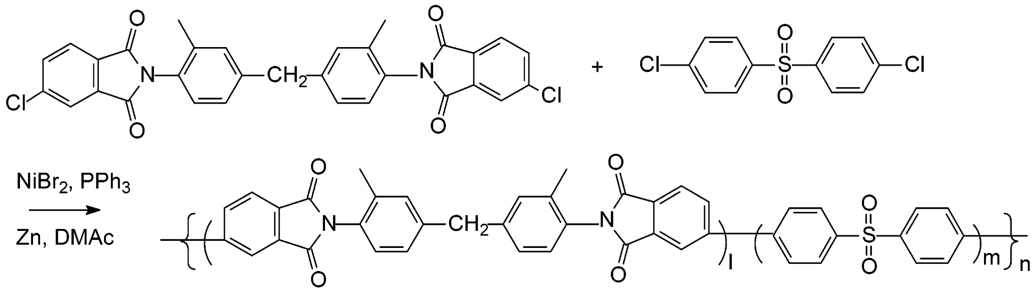


Fig. 1. Comparison of the formation rate of the model products AA (circles) BB (stars) and AB (squares) in cross-coupling reaction in DMAc at 80 °C.



Scheme 2. Cross-coupling copolymerization reaction.

final products, we found the mol ratio of the three model products is 4.1:10.4:3.1 (AA:AB:BB)

3.2. Polymer syntheses

All polymerization results were carried out with our original reaction conditions [6], which were not optimized. A series of copolymers were synthesized by the Nickel (0)-catalyzed coupling copolymerization of 4-BCPI and DDS (Scheme 2). The compositions of the copolymers were varied by changes in the molar fractions of 4-BCPI and DDS in the feed, and the copolymers were denoted $M - x$, where x is the molar fraction of DDS in the feed. The polymers were yellowish solid, and soluble in phenolic solvents and dipolar aprotic solvents at room temperature (Table 1). Polymerization results and elemental analytical data were summarized in Table 2. The inherent viscosity of the polymer is over 0.84 till the content of the sulfone group up to 50%, which indicated that high molecular weight of the copolymers. And the elemental analysis results the polymer M-0, 25, and 50 were in good agreement with the calculated values, indicating that the DDS were successfully coupled with the 4-BCPI. However, that of M-75 is very different from the calculated value, especially in the amount of sulfur and carbon. This imply that the content of the sulfone in copolymer is below 75%.

The chemical structures of the samples were confirmed by FTIR. The characteristic sulfone group absorption bands at 1155 and 1317 cm^{-1} ($\nu_{S=O}$) appeared in the IR spectra of the copolymers (Fig. 2), and the intensity of these absorption bands increased as the amount of DDS increased. The characteristic absorption bands of imide group at 1776 and 1725 cm^{-1} ($\nu_{C=O}$) and 1371 cm^{-1} (ν_{C-N}) also appeared in the spectra. Therefore, the IR spectra indicated that the copolymers were formed from 4-BCPI and DDS units.

Table 1
Solubility of polymers

Sample	Solvent			
	DMAc	NMP	DMSO	*m*-Cresol
M-0	+	+	+	+
M-25	+	+	+	+
M-50	+	+	+	+
M-75	±	±	±	±

(+), Soluble on heating; (±), partially soluble or swelling.

3.3. Polymer properties

The thermal properties of the polyimides were evaluated by differential scanning calorimetry(DSC) and thermogravimetry (TG). The results are tabulated in Table 3. Glass transition temperatures (T_g's) of polyimides were found in the range 317–345 °C. As can be expected, the sulfone containing polyimide exhibited the higher T_g due to its higher intermolecular force. This result may be contributed to the higher interchain interaction due to the polar sulfone group.

Fig. 3 shows the temperature dependence of the loss factor (tan δ) for copolymers. It is clear that a well defined tan δ relaxation peak was obtained for each polymer and the maximum in tan δ (associated with T_g) was shift to higher temperature as the DDS content increased. But it decreased as the DDS content attained 75%. In Fig. 2 a small wide β transition also appeared in these polymers and it was clearer with increasing the amount of DDS. These changes duo to the introduction of the sulfone groups to the main chain, and the independent mobility of the sulfone group led to the secondary transition which will endow the polymers with excellent anti-impacting properties between glass transition temperature and β transition temperature.

Crystallinity of the polymers was evaluated by wide-angle X-ray diffraction experiments. Increase in the amount of sulfone groups resulted in an increase in crystallinity of the chain. This followed from the fact that the X-ray

Table 2
Preparation of copolymers

Sample	Yield (%)	η_{inh} (dL/g)	Elemental analysis (%)			
			N		S	
			Calcd	Found	Calcd	Found
M-0	100	0.98	5.78	5.59	–	–
M-25	95	1.13	5.03	5.03	1.91	1.84
M-50	92	0.84	4.00	4.07	4.57	4.50
M-75	81	0.52	2.47	4.67	8.48	6.20

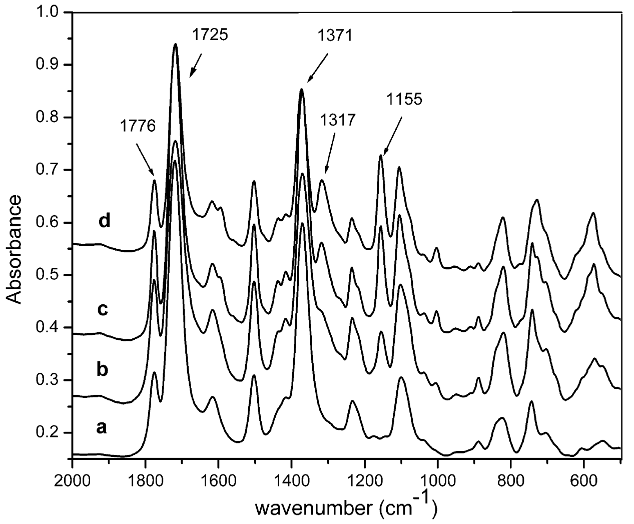


Fig. 2. FTIR spectra of copolymers. (a) M-0; (b) M-25; (c) M-50; (d) M-75.

diffraction results were determined for that M-0 and M-25 were amorphous polymers, M-50 and M-75 were low crystalline polymers, and the crystallinity increased with increase in the amount of DDS (Fig. 4). The main reason lied in the regular packing of the moieties containing sulfone group.

Table 4 shows water uptake and contact angle of the films and water. These two results are consistent well with each other. Because the hydrophilicity of the sulfone groups, the more sulfone groups there were in the chain, the more water the films absorbed, and the smaller the contact angle is. This kind of film should be used to remove humidity from gas as a membrane.

The films cast from polymer solutions appeared as free-standing, semitransparent yellowish. Films prepared from M-0, M-25, M-50 exhibited good mechanical properties as displayed in Table 5. High crystallinity would make the film too brittle to be tested (for example M-75).

Partial disintegration of Kapton film occurred after heated 1 h in the alkaline solution. The films prepared from M-0, M-25, M-50 slightly swelled while retaining strength and flexibility after heated 3 h.

After heated in alkaline solution, the mechanical property of the M-0 film decreased slower than the M-25, M-50 films (Table 5, before the mechanical properties were tested the films were heated at 150 °C for 8 h to remove absorbed water in the films).This may be the case for the good hydrophilicity of the sulfone groups. The presence of the sulfone groups in the chain increased the amount of water that the films absorbed, and it was this kind of water that accelerated the hydrolyzation of the imide groups [10]. The decrease in hydrolytic stability of the polymers corresponded to the corporation of the sulfone groups into the chain.

Table 3
Thermal stability of polymers

Sample	T_g (°C)[a]	10% Weight loss (in N_2) (°C)[b]
M-0	307	456
M-25	317	450
M-50	341	452
M-75	345	476

[a] Measured by DMA at a heating rate of 3 °C/min.

[b] Measured by TGA at a heating rate of 10 °C/min in nitrogen.

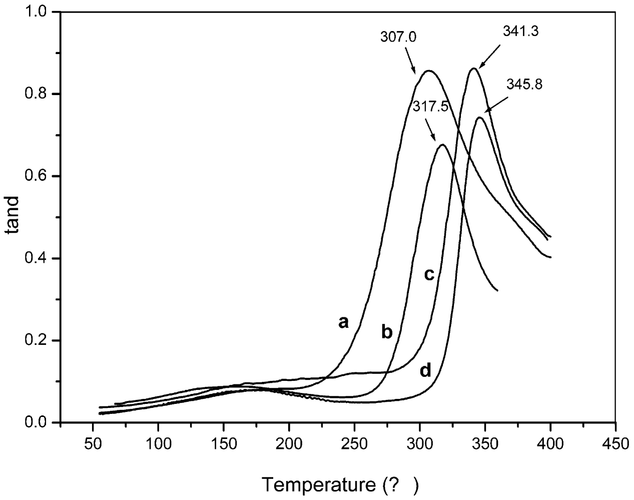


Fig. 3. DMA results for the polymers. *T* as a function of temperature for the polymers. Curves are labeled as in Fig. 2.

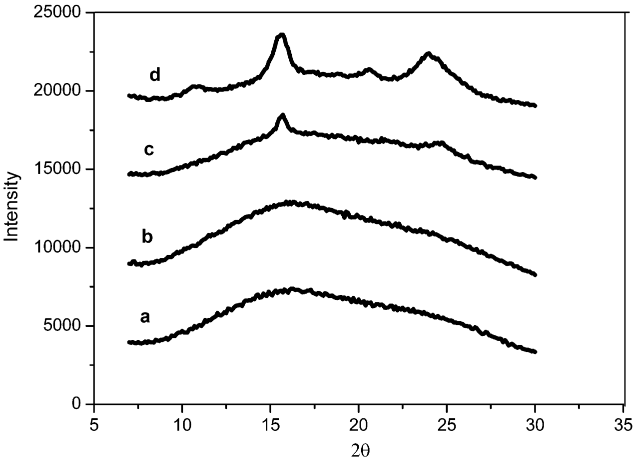


Fig. 4. X-ray results for the polymers. Curves are labeled as in Fig. 2.

4. Conclusion

In this study, we obtain a high yield of poly(sulfone-imide) copolymer by nickel catalyzed cross-coupling under

Table 4
Water uptake and contact angle

Sample	Water uptake (wt%)	Contact angle[a]
M-0	0.8	82.4
M-25	1.3	72.3.
M-50	3.4	66.3

[a] Measured at 18 °C.

Table 5
Mechanical properties before and after heated in NaOH aqueous

Samples	Before			After		
	Tensile strength/MPa	Maximum elongation/%	Tensile modulus GPa	Tensile strength/MPa	Maximum elongation/%	Tensile modulus/GPa
Kapton	104	18.7	1.9	–	–	–
M-0	144	5.9	3.0	137.5	5.4	3.2
M-25	158	7.1	3.3	109	3.7	3.4
M-50	21.3	1.1	2.1	10.4	0.57	1.9

mild conditions. The copolymerizations of aromatic dichlorides containing sulfone and phthalimide structure give polymers with high inherent viscosities. The insertion of sulfone group into the polyimide chain can not only improve the properties of the polymer such as solubility, thermal stability but also decrease the cost of the PIs materials. However, high content of sulfone group will lead to crystalline which give the polymer poor solubility and bad film-formability.

Acknowledgements

We thank the National Basic Research Program of China for the financial support.

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