

Highly soluble and thermally stable copolyimides modified with trifluoromethyl and siloxane

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ABSTRACT: A series of highly soluble aromatic polyimides with excellent thermal properties were fabricated by traditional two-step polycondensation reaction of dianhydride monomer 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) or 4,4-(hexafluoroisopropylidene)diphthalic anhydride with diamine monomer 1,3-bis(4-aminophenoxy)benzene or 1,3-bis(3-aminopropyl) tetramethyldisiloxane in *N,N*-dimethylacetamide solvent. Results revealed that copolyimide of PI-4 containing trifluoromethyl and tetramethyldisiloxane possessed excellent solubility and remarkable thermal properties. PI-4 could dissolve well in common low boiling point solvents such as THF of up to 80 mg/mL and acetone of 40 mg/mL. Moreover, the 10% weight loss temperature of the PI-4 was 539°C and the T_g value of the PI-4 was 311°C. PI-4 might be easily cast into flexible and tough films applied in optoelectronic devices. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41713.

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INTRODUCTION

Aromatic polyimides have been widely applied as gas or solvent separation membranes, memory devices, biosensors as well as adhesives in fuel cells,^{1–3} microelectronics devices, and electroluminescent materials^{4–7} due to their outstanding thermo-oxidative stability, excellent mechanical properties, high solvent resistance, and low dielectric constant, etc.^{8–10} However, the intrinsic insolubility in most organic solvents, high melting and softening temperatures of polyimides have limited its wider application. Up to now, many methods, such as introducing flexible linkages,^{11–13} bulky substituents, and pendent groups^{14–16} to the main chain or employing non-coplanar or asymmetric monomers,^{17–19} have been proposed to improve the solubility of aromatic polyimides.

Recently, siloxane-containing polyimides have attracted considerable attention. The incorporation of siloxane into the main chain of aromatic polyimides can effectively increase the solubility, impact strength, and adhesion to metal and glass, but decline thermal stability of aromatic polyimides.^{20–22} On the other hand, the introduction of trifluoromethyl group into the main chain of aromatic polyimides can enhance the solubility, dielectric properties, and the resistance to wear and abrasion. Besides, the bulky trifluoromethyl group can also effectively improve the optical transparency and gas permeability of the polyimides.^{23–25}

To our best knowledge, the introduction of flexible linkages into the main chain of the polyimides can improve the solubility,

but reduce the thermal stability of the original polyimide obviously. The trifluoromethyl can provide high thermal stability to the aromatic polyimides. Moreover, siloxane-containing polyimides possess excellent solubility, which are easy to dissolve in organic solvents. However, the thermal properties and solubility of aromatic polyimides possessing both trifluoromethyl and siloxane are hardly reported. Besides, relative reports on the quantification of solubility in solvents are seldom found.

In our present work, a series of highly soluble aromatic polyimides with excellent thermal properties were fabricated by traditional two-step polycondensation reaction of dianhydride monomer 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA) or 4,4-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with diamine monomer diamine monomer 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) or 1,3-bis(3-aminopropyl) tetramethyldisiloxane (GAPD) in *N,N*-dimethylacetamide (DMAc) solvent. And the combined effects of flexible linkages, bulky pendent group, siloxane as well as copolymerization on the solubility and thermal properties of aromatic polyimides were investigated. What's more, the solubility of the prepared polyimides in different organic solvents was quantified.

EXPERIMENTAL

Main Materials

BPADA, 6FDA, and 1,3,4-APB were all purchased from Changzhou Sunlight Medicine Raw Material Co., China. BPADA and

Table I. Feed Ratio of Monomers for the Synthesized Polyimides

Samples	BPADA (mmol)	6FDA (mmol)	1,3,4-APB (mmol)	GAPD (mmol)
PI-1	10	-	10	-
PI-2	10	-	9	1
PI-3	-	10	10	-
PI-4	-	10	9	1

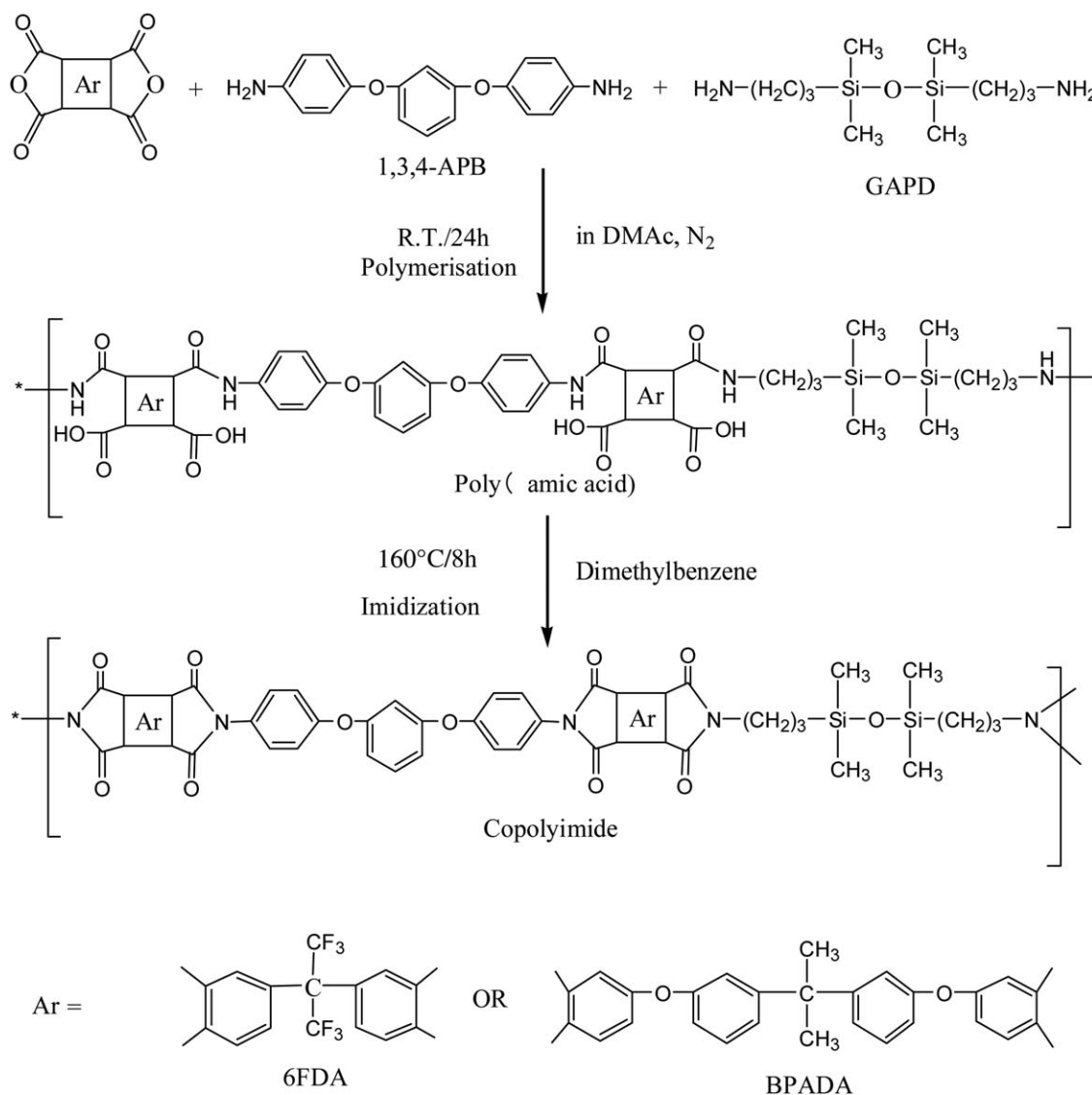
6FDA were sublimated respectively prior to use. Besides, 1,3,4-APB was dried under vacuum at 80°C for 2 h. GAPD was provided by Hangzhou Si Long Materials Technology Co. China. DMAc, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), THF, acetone, and ethanol were all received from Tianjin Fu Yu Fine Chemicals Co. China. DMAc was distilled under vacuum after being dried over phosphorus pentoxide overnight and stored over newly baked 4 Å molecular sieves,

and the others were used as received. *m*-Dimethylbenzene was provided by Tianjin Tianli Chemical Reagent Co. and used after dried over 4 Å molecular sieves for 24 h. *N*-Methyl-2-pyrrolidone (NMP) was purchased from Shanghai Sinopharm Chemical Reagent Co. China. The 4 Å molecular sieves was provided by Tianjin Kemiou Chemical Reagent Co. and dried at 600°C for 3 h before use. All the monomers were commercially available, which was cost-effective and convenient for mass production.

Synthesis of Polyimides

All polyimides were synthesized via traditional two-step polycondensation reaction from a Polyamic acid (PAA) precursor followed by thermal or chemical imidization. The former, that is, thermal imidization was adopted in our work. The feed ratio of the monomers of PI 1–4 is listed in Table I. The solid concentration ranges from 10 wt % to 20 wt % in DMAc.

Take the synthesis of PI-4 as an example. DMAc, 1,3,4-APB (9 mmol), and GAPD (1 mmol) were added into a 100-mL

**Figure 1.** Schematic diagram of polyimides synthesis and structures of monomers.

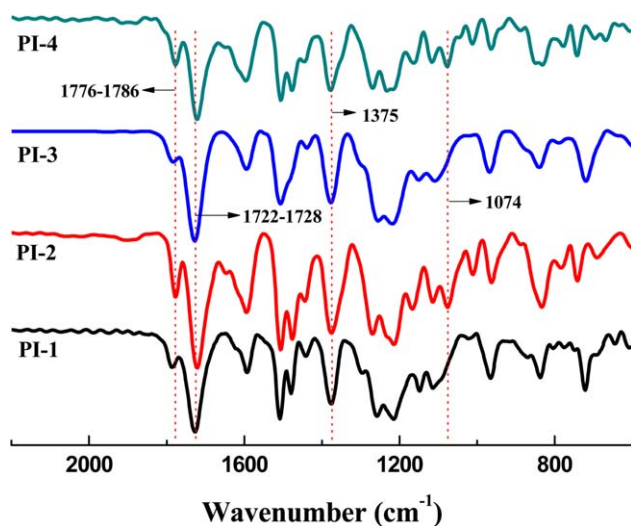


Figure 2. FTIR spectra of the synthesized polyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

four-necked round bottomed flask equipped with an inlet for nitrogen purging, a mechanical stirrer, and a Dean-Stark trap at room temperature. Then 6FDA (10 mmol) was added into the flask in several batches and stirred for 24 h at room temperature. Then stoichiometric *m*-dimethylbenzene was added into solution above. The mixture was heated to 160°C and kept for more than 8 h. The obtained products were precipitated in 300 mL absolute ethanol at room temperature, followed by washing with absolute ethanol for several times. Finally, the synthesized product was stored at 150°C in vacuum oven for 15 h to obtain light yellow granular polyimides. Figure 1 presents the schematic diagram of polyimides synthesis and structures of monomers.

Characterization

Fourier transform infrared (FTIR) spectra of the polyimides were recorded on a PerkinElmer FTIR 2000 Spectrophotometer through using KBr pellets. Wide angle X-ray diffraction (WAXD) was performed on an X'Pert MPD PRO X Diffractom-

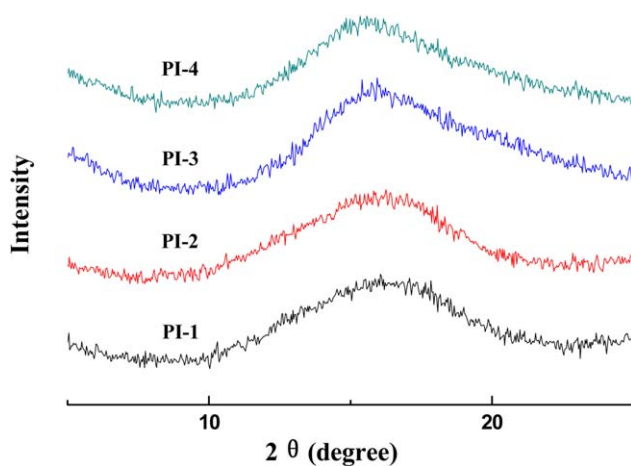


Figure 3. WAXD patterns of synthesized polyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Intrinsic Viscosity of the Synthesized Polyimides

Polymer	PI-1	PI-2	PI-3	PI-4
η (dL/g) ^a	1.112	0.8325	0.7781	0.3917

^a Measured in 0.5 g/dL NMP at 25°C.

eter, using the Ni-filtered Cu-K α radiation ($\lambda = 0.1541$ nm). Initial samples for X-ray measurements were powders. The inherent viscosities of the polyimides were determined at 25°C in NMP–polymer solutions of 0.5 g/dL concentration with an Ubbelohde viscometer. The quantified solubility of the polyimides was measured in 1 mL different organic solvents by dissolving 20 mg, 40 mg, 60 mg, 80 mg, and 100 mg polymers at room temperature, respectively. The thermal stability of the polyimides was investigated by thermogravimetric analysis (TGA) using TA SDTQ600 apparatus operating in nitrogen at a heating rate of 10°C/min from room temperature to 800°C. The glass transition temperature (T_g) of the polyimides was obtained by using a DSC 2910 (TA, America) equipment operating in nitrogen at a heating rate of 10°C/min from room temperature to 400°C.

RESULTS AND DISCUSSION

Infrared Analysis

FTIR spectra of the obtained polyimides (PI-1, PI-2, PI-3, and PI-4) are shown in Figure 2. All the polyimides presented strong characteristic absorption peaks in the bands of 1776–1786 cm^{-1} (C=O), 1722–1728 cm^{-1} (C=O), 1375 cm^{-1} (C–N–C) and 720–740 cm^{-1} (imide ring), indicating the formation of imide ring. The absorption bands around 3300 cm^{-1} (N–H) and 1670 cm^{-1} (C=O) in PAA were almost disappeared, which revealed that the polyimides were synthesized successfully. Meanwhile, the FTIR spectra of PI-2 and PI-4 exhibited clear absorption peaks around 1074 cm^{-1} (Si–O–Si), suggesting the successful incorporation of siloxane.

Wide Angle X-ray Diffraction

WAXD spectra were carried out and presented in Figure 3. All polyimides exhibited broad peaks, which revealed the resulting polyimides were all amorphous. It could be attributed to the introduction of flexible tetramethylsiloxane and bulky trifluoromethyl pendent group. Common function in above both sides together with copolymerization could available break the regularity and stiffness of the main chain of aromatic polyimides, and then the interchain interactions were decreased, resulting in losing the pack of polymer chain. And the crystallinity of the polyimides was reduced accordingly, to effectively improve the solubility of the polyimides.

Intrinsic Viscosity

Intrinsic viscosities of the synthesized polyimides are shown in Table II. PI-1 had the highest intrinsic viscosity of 1.112 dL/g, while PI-4 had the lowest intrinsic viscosity of 0.3917 dL/g. Compared with that of PI-1 and PI-4, the viscosity of PI-2 and PI-3 was moderate. The reason was that PI-1 might have long molecular chain with relative good chain regularity, to tangle easily with each other. Hence, the interchain interactions might be the strongest and the corresponding intrinsic viscosity was

Table III. Solubility of the Synthesized Polyimides

	NMP	DMAc	DMF	DMSO	THF	acetone
Solvents (20 mg/mL)						
PI-1	++	++	++	++	+-	+-
PI-2	++	++	++	++	++	++
PI-3	++	++	++	++	++	++
PI-4	++	++	++	++	++	++
Solvents (40 mg/mL)						
PI-1	++	++	++	++	+-	+-
PI-2	++	++	++	++	++	+-
PI-3	++	++	++	++	++	+-
PI-4	++	++	++	++	++	++
Solvents (60 mg/mL)						
PI-1	++	++	++	++	+-	+-
PI-2	++	++	++	++	+-	+-
PI-3	++	++	++	++	+-	+-
PI-4	++	++	++	++	++	+-
Solvents (80 mg/mL)						
PI-1	+-	+-	+-	+-	+-	+-
PI-2	+-	+-	+-	+-	+-	+-
PI-3	+-	+-	+-	+-	+-	+-
PI-4	++	++	++	++	++	+-
Solvents (100 mg/mL)						
PI-1	+-	+-	+-	+-	+-	+-
PI-2	+-	+-	+-	+-	+-	+-
PI-3	+-	+-	+-	+-	+-	+-
PI-4	+-	+-	+-	+-	+-	+-

++:soluble; +-: partially soluble.

the highest. PI-4 might have the largest fractional free volume and worst intermolecular forces derived from combined effects of bulky trifluoromethyl, flexible tetramethylsiloxane, and ether bond in the main chain. The different intrinsic viscosities of PI 1-4 further verified that the regularity of polymer chain and interchain interactions of polyimides could affect the intrinsic viscosities.

Solubility

The proposed quantified solubility of the polyimides was measured in 1 mL different organic solvents by dissolving 20 mg, 40 mg, 60 mg, 80 mg, and 100 mg polymers at room temperature, respectively. And the solubility of the synthesized polyimides is summarized in Table III.

All the synthesized polyimides were able to dissolve completely in aprotic polar solvents such as NMP, DMSO, DMAc, and DMF up to the level of 60 mg/mL. Ghaemy *et al.*²⁶ reported that the polyimides containing bulky side chain and unsymmetrical structure exhibited good solubility in the above solvents by 10 mg/mL. Anannarukan *et al.*²⁷ introduced porphyrin into the backbone of polyimides and the solubility was increased to 40 mg/mL.

In our work, the solubility of the polyimides in THF or acetone was quite different. PI-1 could partially dissolve in THF or ace-

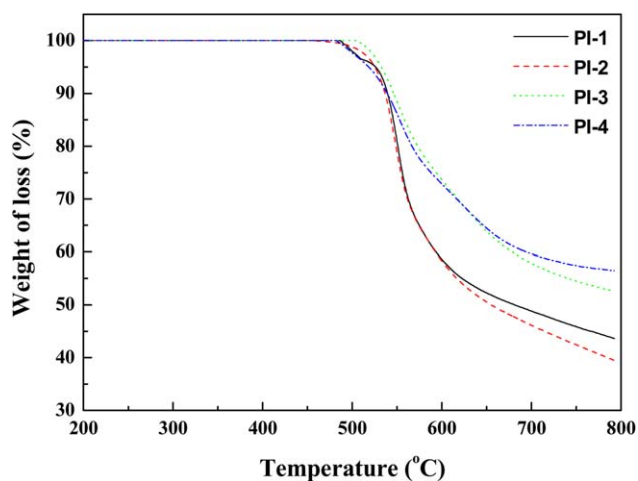


Figure 4. TGA curves of synthesized polyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tone of 20 mg/mL. It can be attributed that the introduction of ether linkage to the backbone could improve the flexibility of polyimides. The solubility of PI-2 and PI-3 was significantly improved and both of them could dissolve thoroughly in THF of 40 mg/mL and acetone of 20 mg/mL. In comparison, the solubility in THF of the hyperbranched 6FDA-based copolyimide was 20 mg/mL reported by Chen and Yin²⁸.

The bulky trifluoromethyl group could further loose the chain packing and reduce the interactions among chains, to increase the solubility of PI-3. For PI-2, the presence of tetramethylsiloxane group could also reduce the interactions among chains.²⁹ Besides, with the introduction of aliphatic group, the molecular chain became more flexible in GAPD, resulting in higher solubility of PI-2 than that of PI-1. PI-4 possessed the most excellent solubility, which could well dissolve in THF of up to 80 mg/mL and acetone of 40 mg/mL. The reason was that PI-4 possessed the flexible ether bond, bulky trifluoromethyl, tetramethylsiloxane, which were beneficial to increase the solubility. Additionally, the solubility of PI-4 could be further improved via copolymerization, which would incorporate molecular structures above, finally to disturb the regularity of homopolymers.³⁰ It is also interesting to note that the solubility of PI-4 in low boiling point solvents was excellent, which is critical for preparing polyimide films or coatings at a relatively low processing temperature, which is desirable for optoelectronic devices.³¹

Table IV. Thermal Data of Synthesized Polyimides from TGA Analysis

Polyimides	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
PI-1	526	539	49
PI-2	525	537	46
PI-3	532	546	58
PI-4	518	539	60

^a Temperature at 5% weight loss.

^b Temperature at 10% weight loss.

^c Percentage of weight residue at 700°C.

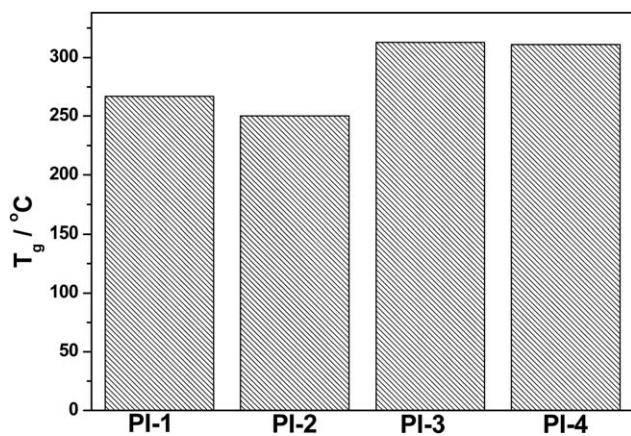


Figure 5. T_g value of polyimides from DSC analysis.

Thermal Properties

TGA curves of polyimides are shown in Figure 4. The weight loss of the PI-1 was below 1 percent before 480°C, which was mostly due to the loss of absorbed water and the volatilization of other small molecules. The weight loss of the PI-1 reached 56.4% till 790°C, the moment could be contributed that the PI-1 began to fuse and further decompose. It could be also seen that there was no obvious thermal degradation of the polyimides until 510°C. T_{10} (10% weight loss temperature) of the polyimides was from 537°C to 546°C. The residue mass of the polyimides at 700°C was from 46 wt % to 60 wt %. And the corresponding thermal data of these polyimides are summarized in Table IV. All the polyimides had excellent thermal stability, and the incorporation of trifluoromethyl and tetramethylsiloxane had no remarkable effects on the thermal stability of polyimides.

Figure 5 presents the T_g value of polyimides from Differential Scanning Calorimetry (DSC) analysis. PI-3 possessed the highest T_g value of 313°C, while PI-2 had the lowest one of 250°C. The T_g of PI-1 and PI-4 was 267°C and 311°C, respectively. The results revealed that the introduction of tetramethylsiloxane could decrease the T_g of polymers, which was ascribed to increasing flexibility of the chain and improving space between chains.³² However, the bulky trifluoromethyl could enhance the steric hindrance, to hinder the internal rotary of the molecules. As a result, the introduction of bulky trifluoromethyl could improve T_g of the polyimides.

CONCLUSION

Highly soluble aromatic copolyimide of PI-4 with excellent thermal properties was successfully synthesized from 6FDA with 1,3,4-APB and GAPD in DMAc solvent via two-step polycondensation reaction. PI-4 containing trifluoromethyl and tetramethyldisiloxane could dissolve well in common low boiling point solvents such as THF of up to 80 mg/mL and acetone of 40 mg/mL. Moreover, the 10% weight loss temperature of the PI-4 was 539°C and the T_g value of the PI-4 was 311°C. PI-4 might be easily cast into flexible and tough films applied in optoelectronic devices.

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REFERENCES

- Kuorosawa, T.; Chueh, C. C.; Liu, C. L.; Higashihara, T.; Ueda, M.; Chen, W. C. *Macromolecules* **2010**, *43*, 1236.
- Jiang, L. Y.; Wang, Y.; Chung, T. S.; Qiao, X. Y.; Lai, J. Y. *Prog. Polym. Sci.* **2009**, *34*, 1135.
- Paşahan, A.; Köytepe, S.; Ekinçi, E. *Polym. Plast. Technol.* **2011**, *50*, 1239.
- Alcaide, F.; Alvarez, G.; Ganborena, L.; Iruin, J. J.; Miguel, O.; Blazquez, J. A. *Polym. Bull.* **2009**, *62*, 813.
- Tsai, M. H.; Lin, Y. K.; Chang, C. J.; Chiang, P. C.; Yeh, J. M.; Chiu, W. M.; Huang, S. L.; Ni, S. C. *Thin Solid Films.* **2009**, *517*, 5333.
- Gao, H.; Yan, C.; Guan, S.; Jiang, Z. *Polymer* **2010**, *51*, 694.
- Liaw, D. J.; Wang, K. L.; Huang, Y. C.; Lee, K. R.; Lai, J. Y.; Ha, C. S. *Prog. Polym. Sci.* **2012**, *37*, 907.
- Chu, H. J.; Zhu, B. K.; Xu, Y. Y. *J. Appl. Polym. Sci.* **2006**, *102*, 1734.
- Purushothaman, R.; Bilal, I. M.; Palanichamy, M. *J. Polym. Res.* **2011**, *18*, 1597.
- Ragosta, G.; Abbate, M.; Musto, P.; Scarinzi, G. *J. Mater. Sci.* **2012**, *47*, 2637.
- Li, Y.; Xu, H.; Tao, X.; Qian, K.; Fu, S.; Shen, Y.; Ding, S. *J. Mater. Chem.* **2011**, *21*, 1810.
- Koohmareh, G. A.; Mohammadifard, N. *J. Polym. Res.* **2011**, *18*, 983.
- Qi, H.; Liu, F.; Zhang, N.; Chen, Y.; Yang, H.; Wang, Z. *Prog. Org. Coat.* **2012**, *73*, 33.
- Kim, S. D.; Lee, S.; Heo, J.; Kim, S. Y.; Chung, I. S. *Polymer* **2013**, *54*, 5648.
- Calle, M.; García, C.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J.; Álvarez, C. *J. Membr. Sci.* **2013**, *434*, 121.
- Nasab, S. M. A.; Ghaemy, M. *J. Polym. Res.* **2011**, *18*, 1575.
- Wang, C.; Zhao, X.; Li, G. *Chin. J. Chem.* **2012**, *30*, 2466.
- Yang, F.; Li, Y.; Bu, Q.; Zhang, S.; Ma, T.; Zhao, J. *Polym. Degrad. Stab.* **2010**, *95*, 1950.
- Lin, C. H.; Chang, S. L.; Peng, L. A.; Peng, S. P.; Chuang, Y. H. *Polymer* **2010**, *51*, 3899.
- Damaceanu, M. D.; Musteata, V. E.; Cristea, M.; Bruma, M. *Eur. Polym. J.* **2010**, *46*, 1049.
- Ghosh, A.; Banerjee, S.; Komber, H.; Schneider, K.; Häußler, L.; Voit, B. *Eur. Polym. J.* **2009**, *45*, 1561.
- Adhikari, R.; Dao, B.; Hodgkin, J.; Mardel, J. *Eur. Polym. J.* **2011**, *47*, 1328.
- Dhara, M. G.; Banerjee, S. *Prog. Polym. Sci.* **2010**, *35*, 1022.
- Jin, H. S.; Chang, J. H.; Kim, J. C. *Macromol. Res.* **2008**, *16*, 503.

25. Cui, L.; Qiu, W.; Paul, D. R.; Koros, W. J. *Polymer* **2011**, *52*, 3374.
26. Ghaemy, M.; Alizadeh, R.; Behmadi, H. *Eur. Polym. J.* **2009**, *45*, 3108.
27. Anannarukan, W.; Tantayanon, S.; Zhang, D.; Alema'n, E. A.; Modarelli, D. A.; Harris, F. W. *Polymer* **2006**, *47*, 4936.
28. Chen, H.; Yin, J. *Polym. Bull.* **2003**, *50*, 303.
29. Pei, X.; Chen, G.; Fang, X. *J. Appl. Polym. Sci.* **2013**, *129*, 3718.
30. Yen, H. J.; Liou, G. S. *Polym. Chem. U.K.* **2012**, *3*, 255.
31. Zhang, H.; Li, J.; Tian, Z.; Liu, F. *J. Appl. Polym. Sci.* **2013**, *129*, 3333.
32. Lei, X. F.; Chen, Y.; Zhang, H. P.; Li, X. J.; Yao, P.; Zhang, Q. Y. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10207.