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Synthesis and properties of new organosoluble aromatic polyamides with cyclic bulky groups containing phosphorus

Ying-Ling Liu*, Shr-Hau Tsai

Department of Chemical Engineering and R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli, Taoyuan 320, Taiwan, ROC

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Abstract

Aromatic polyamides were prepared from various diacids with a new diamine bearing two 9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl (DOPO) substituents. The polyamides possessed inherent viscosities of 0.33–0.81 dl/g and glass transition temperatures of 230–251 °C measured with DSC. All the polyamides were amorphous and readily soluble in NMP, DMAc, DMF, and DMSO. Incorporating DOPO groups into polyamides resulted in polymers with low initial decomposition temperatures (IDT, 310–362 °C), deriving from the decomposition of the DOPO groups. With thermogravimetric analysis (TGA), the DOPO-containing polyamides exhibited high integral procedure decomposition temperatures (IPDT) of 928–1086 °C, to indicate improvement on polyamides' weight loss rate, thermal stability, and heat insulating property at high temperature region. High tensile strength of 42.0–52.8 MPa and Young's modulus of 506–869 MPa measured with stress–strain tests were observed for the polyamides to indicate these polymers possessing good mechanical properties. © 2002 Published by Elsevier Science Ltd.

Keywords: Polyamide; Phosphorus; Thermal properties

1. Introduction

Aromatic polyamides have received notable attention in research owing to their useful properties, like thermal stability, flame retardant characteristic, and excellent mechanical properties [1]. However, most of the aromatic polyamides show poor processing properties owing to their high melting points and poor solubility in organic solvents. Therefore, research effort has been devoted to improve this drawback of aromatic polyamides in the last decade. Some approaches, such as incorporation of bulky groups into the polymer chain [2–4], introducing flexible linking groups into the rigid backbones of the polymers [3–6], using fluorinated monomers [4], introduction of highly polar groups into the polymers [7], and bringing non-coplanar and alicyclic monomers into the polymerization systems [8], have shown their success in preparation of organosoluble polyamides.

Phosphorus-containing groups were considered to bring improved organosolubility to high performance polyamides and polyimides [8–12]. Polyamides [8–10] and polyimides [12] with triphenylphosphine oxide groups in the polymer backbones have shown good organosolubility, good thermal and oxidative stability, and high glass transition temperatures. Moreover, phosphorus-containing groups were also incorporated into polymers for increasing the polymers' adhesive properties [12,13]. On the other hand, the cyclic phosphorous group, 9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl (DOPO), was widely incorporated into polymers for improving the polymer's flame retardant properties and thermal stability [15,16]. Moreover, incorporation of DOPO groups onto polymers also brought improved organosolubility to the polymers, due to the DOPO group's bulk structure and polarity [11,14]. In the previous work [14,17], a novel aromatic diamine possessing two DOPO pendent groups (2DOPO-A) was synthesized through a simple preparation route. The diamine, naturally possessed bulk structures, polar groups, non-coplanarity, and cardo structure [18,19], was demonstrated to bring enhancement on polyaspartimides' organosolubility [17]. Therefore, in this work, 2DOPO-A was polymerized with various diacids to prepare aromatic polyamides. The characterization, organosolubility, thermal properties, and mechanical properties of the resulted polyamides were discussed.

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* Corresponding author. Tel.: +886-3-2654130; fax: +886-3-2654199.
E-mail address: ylliu@cycu.edu.tw (Y.L. Liu).

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2. Experimental section

2.1. Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) from ADD APT Chemical AG, The Netherlands, was recrystallized from tetrahydrofuran prior to use. 4,4′-Diaminobenzophenone (DABP) was purchased from Aldrich Co. 2DOPO-A was prepared by reacting DOPO with DABP according to the reported method [14,17]. All of the dicarboxylic acids (Tokyo Kasei Kogyo Co.) were used as received.

2.2. Equipment

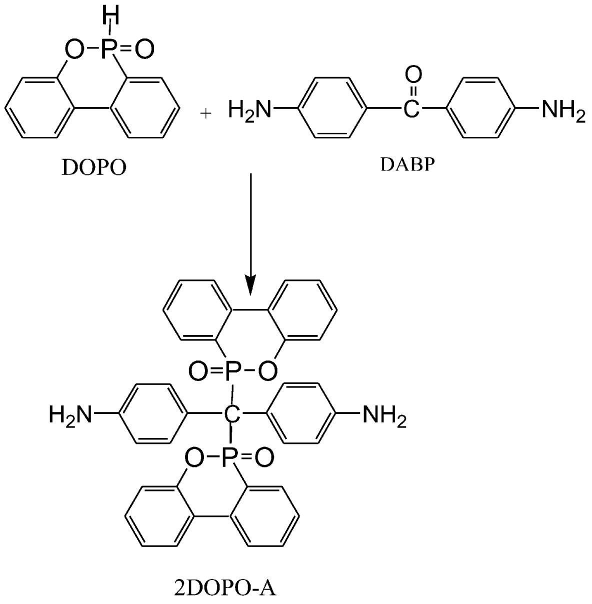
Infrared spectra (FTIR) were obtained with a Perkin–Elmer 2000 FTIR. ^{1}H and ^{31}P NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer. Wide-angle X-ray diffraction was performed with a Rigaku X-ray diffractometer using Nickel filtered Cu Kα radiation. DSC thermograms were recorded with a thermal analysis (TA) DSC-2900 at a heating rate of 20 °C/min in nitrogen. TGA was performed by a TA TGA-2050 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere. Thermal mechanical analysis was performed with a Perkin–Elmer DMA 7e thermal mechanical analyzer with a TAC 7/DX thermal analysis controller, at a heating rate of 10 °C/min and a frequency of 1 Hz. Mechanical property measurements were conducted with an Instron 5544 with an elongating rate of 5 cm/min at ambient temperature.

2.3. Preparation of polyamides

A general procedure for preparation of PA-1 was given. A mixture of diamine 2DOPO-A (3 g, 5.0 mmol), diacid ADA-1 (0.83 g, 5.0 mmol), calcium chloride (0.4 g), triphenyl phosphite (16 ml), pyridine (16 ml), and NMP (15 ml) was charged into a 50 ml round bottom flask. The mixture was heated to 100 °C with stirring for 4 h. After cooling to room temperature, the reaction mixture was poured into a large amount of methanol. The precipitate was washed with methanol and hot water, and then dried at 150 °C under vacuum for 24 h. The obtained polymer was continuously extracted with acetone for 4 h. After drying, polyamide with an inherent viscosity of 0.57 dl/g (measured at a concentration of 0.5 g/dl in NMP at 25 °C) was obtained (yield: 97%). The other polyamides were prepared with the similar procedure.

3. Results and discussion

3.1. Preparation of monomer

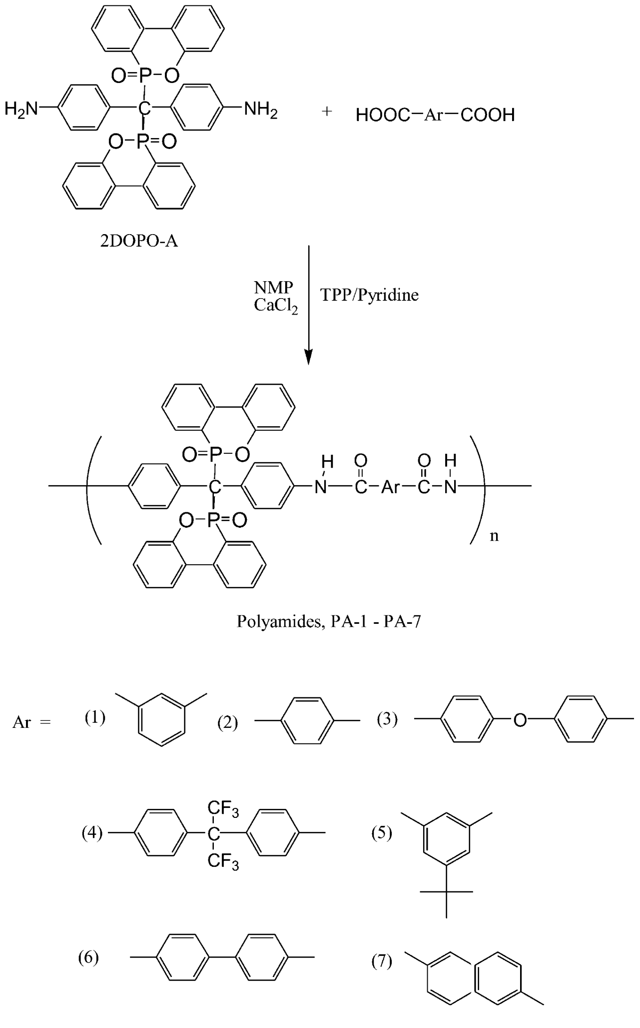


Scheme 1. Synthesis of phosphorus-containing diamine 2DOPO-A.

The DOPO-containing diamine (2DOPO-A) was obtained from DOPO and 4,4′-diaminobenzophenone (DABP) through addition and dehydration reactions between DOPOs P–H group and DABPs carbonyl group [14]. Under proper reaction condition, the addition and dehydration reactions could be performed in the one-pot process (Scheme 1). The –P=O group in DOPO provided 2DOPO-A a high polarity. The two bulky DOPO groups blocked the phenyl group passing through the symmetric conformation, to result in a steric hindrance. This steric hindrance made the two phosphorus atoms in 2DOPO-A to have chirality. Furthermore, the non-coplanarity of 2DOPO-A was reasonably expected from its sp^3 carbon center, and was demonstrated with modeling 2DOPO-As configuration of least energy state through computer simulation (Software: MSI Cerius^2 4.0, Amorphous Builder). Moreover, 2DOPO-A has a cardo structure, which was demonstrated to bring enhancement on aromatic polyamide's solubility [18, 19]. Based on the above-mentioned characteristics, 2DOPO-A was expected to be a good monomer for preparing organosoluble aromatic polyamides.

3.2. Preparation and characterization of polyamides

Polyamides were prepared through direct polycondensation of 2DOPO-A with various aromatic dicarboxylic acids (ADA-1 to ADA-7). The reactions were carried out in NMP with triphenyl phosphite (TPP) and pyridine as condensing agents [18–20] (Scheme 2). All of the resulting polyamides were characterized with FTIR, ^{1}H NMR, ^{31}P NMR, and elemental analysis to confirm their chemical structures (Table 1). Absorption peaks of FTIR spectra at around 1595 (P–Ph), 1204 (P=O), and 930 cm^{-1} (P–O–Ph), and peaks of ^{31}P NMR spectra at around $\delta = 29.1$ and 30.7 ppm demonstrate the resulted polyamides maintaining the cyclic DOPO groups. Moreover, the absorption peaks due to the



Scheme 2. Preparation of polyamides.

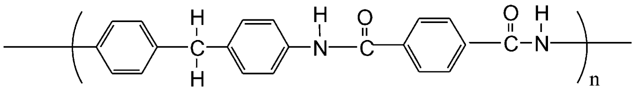
amide proton (–N–H) was also observed in the FTIR spectra (3808–3354 cm^{-1}) and in the ^{1}H NMR spectra (around $\delta = 10.32$ ppm) of the polyamides. The polyamides' inherent viscosity was measured to be 0.33–0.81 dl/g at 25 °C in NMP. For PA-2 (inherent viscosity = 0.81), the number-average and weight-average molecular weights measured with gel permeation chromatography with DMF as a solvent were 53,000 and 115,000, respectively. With the high molecular weight, all the polyamides films could be obtained by casting their NMP solutions and dried at 150 °C under vacuum. All the polyamides' films were transparent to imply that the polyamides should be amorphous. With wide-angle X-ray diffraction measurements, all of the polymers showed amorphous patterns. The bulky pendent DOPO groups of the polyamides increase the chain distance, inhibit the chain packing, and decrease the interaction of the polymer chains, therefore to result in disappearance of crystallinity [11]. The amorphous nature of the polyamides was also reflecting their good organosolubility.

The synthesized polyamides were soluble in polar solvents like NMP, DMF, DMSO, and DMAc at room

Table 1
Synthesis and characterization of polyamides

Samples	Elemental analysis found% (calculated%)			NMR analysis (chemical shift, ppm)		FTIR absorption peaks (cm^{-1})							
	C	H	P	^{1}H NMR, amide proton	^{31}P NMR	N–H	C=O	P–Ph	P=O	P–O–Ph	C–O–C	–CF$_3$	–CH$_3$
PA-1	71.29 (71.43)	3.92 (3.97)	8.09 (8.20)	10.28, 10.36	29.16, 30.77	3296	1663	1595	1206	931	–	–	–
PA-2	71.23 (71.43)	3.92 (3.97)	8.11 (8.20)	10.30, 10.35	29.05, 30.69	3280	1666	1594	1204	925	–	–	–
PA-3	72.02 (72.17)	3.95 (4.01)	7.10 (7.31)	10.27, 10.34	29.08, 30.71	3354	1671	1595	1207	924	1237	–	–
PA-4	66.11 (65.99)	3.51 (3.46)	6.22 (6.31)	10.27, 10.36	29.08, 30.65	3307	1671	1595	1209	930	–	1175	–
PA-5	72.50 (72.41)	4.72 (4.68)	7.51 (7.64)	10.28, 10.33	29.03, 30.76	3296	1660	1594	1204	928	–	–	2963
PA-6	73.70 (73.56)	4.20 (4.09)	7.40 (7.45)	10.28, 10.36	29.01, 30.75	3280	1660	1594	1194	924	–	–	–
PA-7	73.61 (73.73)	3.77 (3.86)	7.33 (7.47)	10.27, 10.36	29.03, 30.74	3280	1658	1594	1207	923	–	–	–

temperature or upon heating at 70 °C. PA-4 (containing hexafluoroisopropylidene linkage) and PA-5 (containing *t*-butyl pendent group) were soluble in pyridine and hot 1,4-dioxane to show the greatest solubility among the polymers. However, polymer PA-6 exhibited less solubility than the others (not soluble in DMF and DMAc at room temperature) owing to that PA-6 contains the rigid and symmetric biphenyl unit [20]. Since the reference polyamide PA-2′ synthesized from diaminodiphenymethane (DDM) and ADA-2 showed no solubility in the above-mentioned solvents, the DOPOs significant effect on improving polyamides' solubility and processing properties was demonstrated.



Polyamides, PA-2'

3.3. Thermal and mechanical properties of polyamides

The thermal properties of the polyamides were estimated with DSC and TGA, and the analysis results are given in Table 2. All of the polymers except PA-3 showed a distinct glass transition temperature (T_g) at 230–251 °C on the second DSC heating scans. PA-6 exhibited the highest T_g value among the polyamides, since PA-6 bears the rigid biphenyl units. The T_gs of the polyamides were comparable with those of 2DOPO-A based polyaspartimides [14] and other aromatic polyamides [18–20], and were a little lower than the T_gs of the DOPO-containing poly(ester–amide–imide)s [11]. However, the 2DOPO-A based polyamides exhibited relatively lower T_g than did the DDM based polyamide (PA-2′). Introduction of the DOPO groups into the polymer chains provided inhibition on polymer chain motion to increase the polymers' T_g. On the other hand, the bulk DOPO group, however, also enlarged the polymers' free volume to bring a counteraction on polyamides' T_g. On the other hand, the T_g values of the polyamides obtained from DMA measurement are about 30–35 °C higher than that from DSC measurements. Storage modulus and tan δ measured with DMA were found to be 0.76–1.00 GPa, and 0.64–1.65, respectively.

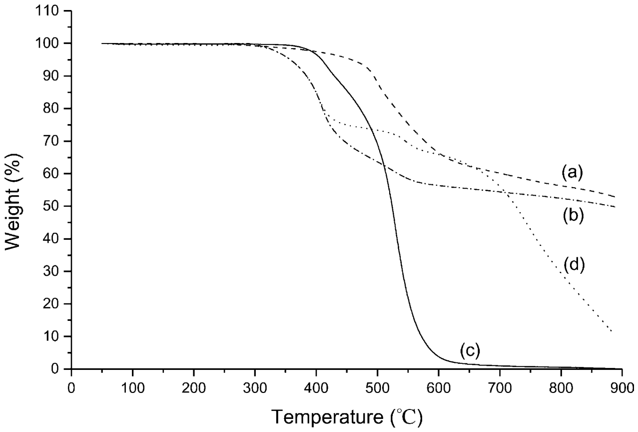


Fig. 1. TGA thermograms of polyamides: (a) PA-2′ in nitrogen; (b) PA-2 in nitrogen; (c) PA-2′ in air; (d) PA-2 in air.

TGA thermograms revealed that all the polyamides begin to degrade at about 310 °C. The decomposition temperatures of the polymers at 10% weight loss were 340–390 °C (Table 2). As shown in Fig. 1, the thermal stability of the DOPO-containing polyamide PA-2 in nitrogen was found to be about 100 °C lower than that of the common phosphorus-free polyamide PA-2′. However, while heated in air, PA-2′ showed a 20 °C decrease in thermal stability compared with heating in nitrogen, and PA-2 did not. The weight loss for PA-2 at low temperature region should come from the decomposition of the pendent DOPO group. The decomposition of DOPO group was independent of existence of oxygen. Moreover, the DOPO-containing PA-2 showed higher heat resistance and retarded weight loss behavior at temperatures higher than 400 °C. The weight loss retarding behavior was especially dominant in air. Owing to the oxidation effect, PA-2′ showed almost no char residue at temperature higher than 600 °C in air. On the other hand, the

Table 2
Basic property data of polyamides

Samples	Yields (%)	Inherent viscosity (dl/g)	T_g (°C)	T_d[a] (°C)		Char residue at 700 °C (%)		Char residue at 800 °C (%)	
				N$_2$	Air	N$_2$	Air	N$_2$	Air
PA-1	97	0.57	230	359	355	51.5	43.7	48.6	15.9
PA-2	86	0.81	245	385	384	54.4	55.9	52.4	29.3
PA-3	97	0.33	243	341	345	40.8	3.8	37.6	2.8
PA-4	92	0.38	235	377	391	43.9	49.8	42.1	25.4
PA-5	85	0.52	235	390	392	48.0	50.3	46.4	29.9
PA-6	98	0.47	251	336	343	44.3	5.4	41.1	2.1
PA-7	90	0.67	241	400	402	57.2	57.8	55.5	34.9
PA-2′	98	–[b]	289	430	452	60.0	0.0	56.1	0.0

[a] Temperature at 10% weight loss.
[b] Not soluble.

Table 3
Thermal stability parameters for polyamides

Sample	IDT (°C)	1st Stage weight loss		2nd Stage weight loss		Thermal stability parameters for overall polymer degradation				Thermal stability parameters for degradation from DOPO groups			
		$T_{\max1}$ (°C)	$R_{\max1}$ (%/°C)	$T_{\max2}$ (°C)	$R_{\max2}$ (%/°C)	A*	K*	AK*	IPDT (°C)	A*	K*	AK*	IPDT (°C)
PA-1	309	407	0.38	530	0.08	0.7367	1.5672	1.1545	974	0.9544	1.0671	1.0185	427
PA-2	335	407	0.50	534	0.11	0.7976	1.3761	1.0977	928	0.9679	1.0442	1.0107	424
PA-3	311	364	0.53	470	0.16	0.6813	1.9001	1.2946	1086	0.9549	1.0656	1.0176	426
PA-4	337	407	0.40	515	0.27	0.7163	1.6816	1.2046	1014	0.9613	1.0530	1.0122	425
PA-5	350	407	0.55	509	0.24	0.7323	1.5876	1.1626	980	0.9715	1.0386	1.0091	423
PA-6	310	348	0.43	475	0.18	0.6949	1.8041	1.2537	1053	0.9464	1.0770	1.0193	427
PA-7	362	407	0.40	504	0.16	0.7777	1.4168	1.1018	931	0.9788	1.0265	1.0047	422
PA-2′	426	–	–	498	0.33	0.8769	1.1846	1.0389	881	–	–	–	–

Measured with TGA at a heating rate of 10 °C/min in nitrogen.

phosphorus-containing PA-2 exhibited highly anti-oxidative property at high temperature region. After the decomposition of the DOPO group at about 410 °C, the DOPO-containing polyamides' exhibited their excellent thermal stability at 450–650 °C. Very slow weight loss rate and small amount of weight loss were observed in this temperature region. At temperature higher than 700 °C, weight loss due to char oxidation occurred. However, the weight loss rate was still low. High char yields at 700 and 800 °C were observed for the DOPO-containing polyamides as a reasonable result, to imply that the anti-oxidant stability of polyamides improved with the incorporation of DOPO groups. However, the low char yield of PA-3 and PA-6 heated in air were unusual. Moreover, the high char yields at high temperature region in air also imply the high flame retardance of the DOPO-containing polyamides [11]. This could be demonstrated with the high LOI values (from 61 to 70) measured for the polyamides.

Besides the initial decomposition temperature (IDT), other reliable degradation temperature, such as the temperature ($T_{\max}$) of maximum rate of weight loss ($R_{\max}$) and integral procedure decomposition temperature (IPDT) [21–23], were used to assess the polyamides' thermal stability (Table 3). As mentioned-above, the low IDTs of the DOPO-incorporated polyamides were derived from the decomposition of DOPO group. Similar results were observed for 2DOPO-based polyaspartimides [14]. However, the IDTs of the DOPO-containing polyamides were lower than those of the reported DOPO-containing poly(ester–amide–imide)s [11]. The relatively good thermal stability of the poly(ester–amide–imide)s might be due to their low DOPO content and imide structure. On the other hand, IPDTs for the DOPO decomposition were found to be 422–427 °C, to tell that the DOPO decomposition was independent of the decomposition of the polymer main chains. It is noteworthy that all of the DOPO-incorporated polyamides showed high IPDT of 928–1086 °C. The high IPDT reveals the high thermal stability of the DOPO-polyamides, and should come from the attached DOPO groups. For the DOPO-PA, DOPO groups decomposed at low temperature region (exhibiting an IDT of 310 °C and an IPDT of 422 °C) to form a phosphorus-rich char with relatively high thermal stability. The thermally stable char retard the decomposition of the polymers, since the $T_{\max2}$ was shifted to high temperatures and the $R_{\max2}$ value was reduced (Table 2). Incorporating DOPO into polyamides, therefore, retarded the polymers' thermal degradation rates and enhanced the residuals' thermal stability. The properties were expected to be potentially useful for some heat insulating materials.

From stress–strain tests, the polymer films based on the prepared DOPO-containing polyamides showed acceptable tensile strength of 42.0–52.8 MPa with the elongation at break of 3.12–4.31%. Incorporation of DOPO groups into the polyamides significantly increases the polyamides' tensile strength and the brittleness. For PA-1 to PA-6, the Young's modulus was 506–555 MPa. An especially high modulus of 869 MPa was found for PA-7.

4. Conclusion

The aromatic polyamides' solubility in organo-solvents was significantly improved with incorporation of bulk, non-coplanar, and polar DOPO groups into the polymers as pendent groups. The resulted polyamides exhibited comparable glass transition temperatures and mechanical properties to the ordinary aromatic polyamide, which was insoluble in organic solvents. Thermal stability at high temperature region and flame retardation property of the polyamides were also improved with the incorporation of the phosphorus-containing DOPO groups.

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References

[1] Cassidy PE. Thermally stable polymers. New York: Marcel Dekker; 1980.

[2] Jeong HJ, Oishi Y, Kakimoto MA, Imai Y. J Polym Sci, Part A: Polym Chem 1990;28:3193.

[3] Spiliopoulos IK, Kikroyannidis JA. Macromolecules 1998;31:1236.

[4] Spiliopoulos IK, Kikroyannidis JA, Tsivgoulis GM. Macromolecules 1998;31:522.

[5] Liaw DJ, Liaw BY, Tsai MY. Polym J 1997;29:474.

[6] Liaw DJ, Liaw BY, Su KL. J Polym Sci, Part A: Polym Chem 1999; 37:1997.

[7] Negi YS, Suzuki YI, Kawamur I, Kakimoto MA, Imai Y. J Polym Sci, Part A: Polym Chem 1996;34:1663.

[8] Delaviz Y, Gungor A, MaGrath JE. Polymer 1993;34:210.

[9] Wan IY, Kashiwagi T, McGrath JE. Polym Prepr 1994;35(1):233.

[10] Srinivasan R, McGrath JE. Polym Prepr 1992;33(1):503.

[11] Liou GS, Hsiao SH. J Polym Sci, Part A: Polym Chem 2001;39:1786.

[12] Jeong KU, Kim JJ, Yoon TH. Polymer 2001;42:6019.

[13] Lee YJ, Gungor A, Yoon TH, McGrath JE. J Adhes 1995;55:165.

[14] Wu CS, Liu YL, Chiu YS. Polymer 2002;43:1773.

[15] Wang CS, Lin CH. Polymer 1999;40:4387.

[16] Wang CS, Lin CH, Chen CY. J Polym Sci, Part A: Polym Chem 1998; 36:3051.

[17] Liu YL. J Polym Sci, Part A: Polym Chem 2002;40:359.

[18] Liaw DJ, Liaw BY, Yang CM, Hsu PN, Hwang CY. J Polym Sci, Part A: Polym Chem 2001;39:1156.

[19] Liaw DJ, Hsu PN, Chen JJ, Liaw BY, Hwang CY. J Polym Sci, Part A: Polym Chem 2001;39:1557.

[20] Liaw DJ, Liaw BY, Yang CM. Macromolecules 1999;32:7248.

[21] Doyle CD. Anal Chem 1961;33:77.

[22] Park SJ, Kim HC, Lee HI, Suh DH. Macromolecules 2001;34:7573.

[23] Park SJ, Cho MS. J Mater Sci 2000;35:3525.