Synthesis and Properties of Thermally Resistant Poly(amide-imide)s

Kang-Ching CHAN and Teh-Chou CHANG[†]

Department of Chemical Engineering, Chung Yuan Christian University, Chung Li, Taiwan 32023, Republic of China

(Received February 23, 1998)

ABSTRACT: A series of poly(amide-imide)s has been synthesized by the direct polycondensation of biphenyl imide containing diacids with aromatic diamines using triphenylphosphite (TPP) as the condensation agent in a *N*-methyl-2-pyrrolidone (NMP)-pyridine solution containing 3.5 wt% LiCl. The direct polycondensation was markedly facilitated to give high-molecular-weight $(0.24 < \eta_{inh} < 2.38)$ of poly(amide-imide)s in quantitative yield. The thermal properties of the obtained poly(amide-imide)s were examined by DSC and TGA. The synthesized poly(amide-imide)s possessed glass transition temperature in the range of 285—337°C. The poly(amide-imide)s exhibited excellent thermal stabilities and had 10% weight loss at the temperature in the range of 475—597°C under nitrogen atmosphere. With the exception of polymer BP-2 series, the poly(amide-imide)s showed good solubility in NMP, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

KEY WORDS Poly(amide-imide)s / Biphenyl Imide / Direct Polycondensation / Thermal Stability /

Aromatic polyimides were one of the most thermostable polymers. Owing to the rigidity of the imide ring, most of the polyimides possessed high thermal resistance (the decomposition > 500° C), high tensile strength, and high modulus. However, the applications of the majority of polyimides are limited because of their infusibility and insolubility. Thus, for the processing of polyimides and many copolyimides, such as poly(amide-ester-imide)s,¹ poly(amide-imide)s,² poly(imide-carbonate)s,³ and poly-(ester-imide)s⁴ have been prepared. The solubilities of the polyimides were improved by the copolymerization, but the thermostabilities were depressed. In order to increase the solubility without significantly descreasing the thermostability, the synthesis of poly(amide-imide)s seems more important than the other copolyimides.

Various synthetic methods for the preparation of poly(amide-imide)s have been disclosed in many reports, such as (1) by the solution polymerization of an amide containing diamine with a dianhydride,⁵ (2) by the solution polymerization of a diamine with an acylchloride phenylanhydride, 6,7 (3) by the solution polymerization of a diisocyanate with trimellitic anhydride,⁸ (4) by the solution polymerization of N, N'-bis(trimethylsilyl)substituted aromatic diamines with 4-chloroformylphthalic anhydride,⁹ (5) by the direct polycondensation of a diamine with an imide containing diacid.¹⁰ Among these methods, the direct polycondensation was the most convenient approach for synthesizing high molecular weight poly(amide-imide)s on a laboratory scale. The direct polycondensation using triphenylphosphite (TPP) as the condensation agent for the synthesis of polyamides has been developed by Yamazaki¹¹ in 1974. Recently, Russo has applied this method for the preparation of polyamides (Kevlar) with a high inherent viscosity of $9.0 \,\mathrm{dl}\,\mathrm{g}^{-1}.^{12}$

In this study, a series of fully aromatic poly(amideimide)s with high molecular weights were synthesized by the direct polycondensation of the biphenyl imide containing diacids with aromatic diamines using TPP as the condensation agent in a *N*-methyl-2-pyrrolidone (NMP)-pyridine solution containing LiCl. The effects of the amounts of LiCl and TPP and the temperature on the yield and molecular weight of the synthesized poly(amide-imide)s were investgated. In addition, the effects of biphenylene and naphthylene structures in poly(amide-imide)s on the thermal properties and solubilities were also investigated.

EXPERIMENTAL

Materials and Measurements

Trimellitic anhydride (TMA) (Merck Co.), 4-aminobenzoic acid (Merck Co.), 3-aminobenzoic acid (Tokyo Kasei Co.), 4-(aminomethyl)benzoic acid (Merek Co.), 4,4'-biphthalic anhydride (Tokyo Kasei Co.), 1,5diaminonaphthalene (Tokyo Kasei Co.), 4,4'-diaminodiphenylmethane (Merck Co.), 4,4'-diaminodiphenyl ether (Merck Co.), 1,4'-bis(p-aminophenoxy)benzene (Tokyo Kasei Co.), 4,4'-diamino-3,3'-dimethyldiphenylmethane (Tokyo Kasei Co.), 4,4'-diaminodiphenylsulfone (Merck Co.), 4,4'-(hexafluoroisopropylidene)dianiline (Aldrich Co.), 1,4-phenylenediamine (Merck Co.), and triphenyl phosphite (RDH Co.) were used without further purification. LiCl (RDH Co.) was dried under vacuum at 130°C for 4 h and at 160°C for 8 h. Pyridine and NMP were purified by distillation over KOH and P_2O_5 . respectively, prior to use.

Elemental analysis of synthesized monomers were measured by a Perkin-Elmer 2400-CHN Elemental Analyzer. IR spetra ranging from 400 cm⁻¹ to 4600 cm⁻¹ of the synthesized polymers which were cast on NaCl discs were obtained on a JASCO FT-IR-7000 instrument. Wide angle X-ray diffraction powder patterns were measured by a Rigaku D/MAX III, V XRD Xray diffractometer at room temperature with Cu- K_{α} radiation using a Ni-filter.

Visual observation of phase transitions was made by using a Leitz Ortholux 2 POL BK polarizing microscope equipped with a Linkam THMS 600 heating stage. Thermal transition properties were characterized using a Du Pont 2000 DSC at a heating rate of 20° C min⁻¹ under a nitrogen atmosphere. The thermal stability of

[†] To whom all correspondence should be addressed.



Scheme 1. The general synthetic routes and structures of imide-diacid monomers

the poly(amide-imide)s were measured by thermogravimetry on a Perkin Elmer TGA 7 at a heating rate of 20°C min⁻¹ under a nitrogen atmosphere. Tensile properties of poly(amide-imide) films were performed on a Micro-Computer Universal Testing Machines (Hung Ta Instrument Co.) at a constant testing rate of 60 $mm min^{-1}$.

Monomer Synthesis

N,N'-Bis(3-carboxyphenyl)-1,1'-biphthalimide (BP-1). 4.4'-Biphthalic anhydride (0.04 mol) and 3-aminobenzoic acid (0.08 mol) in 250 ml of NMP were stirred in a 500 ml flask at room temperature for 2h and then the temperature was raised to 140°C for another 2h. Acetic anhydride (0.1 mol) was added into the reactor and reacted at reflux temperature for 2h. The resulting mixture was poured into water and filtered. The crude product was extracted with hot ethanol and dried overnight at 85°C under vacuum. The final product was obtained in 61.1% yield as a yellow powder with a melting point of 409-411°C.

IR (KBr): $1777, 1723, \text{ and } 731 \text{ cm}^{-1}$ for imide group. $3600-2400 \text{ cm}^{-1}$ for -COOH group.

Other monomers, N,N'-bis(4-carboxyphenyl)-1,1'-biphthalimide (BP-2), N,N'-bis(4-carboxylphenylmethyl)-1,1'-biphthalimide (BP-3), 1,5-di(4-carboxyphthalimido)naphthalene (NAI), N-(4-carboxyphenyl)trimellitimide (M1), and 4,4'-bis(4-carboxyphthalimido)diphenylmethane (MAI) were prepared by a similar procedure. Monomers NAI, M1, and MAI were recrystallized from N,N-dimethylacetamide (DMAc) or N,N-dimethylformamide (DMF). The yields and elemental analyses of the monomers were listed in Table I.

Polymer Synthesis

Polymer P1-M. A solution of TPP (11 mmol) in pyridine (4 ml) was added dropwise to a solution of monomer BP-1 (2.5 mmol) and LiCl (0.5 g) in NMP (7 ml). The mixture was stirred at room temperature



Scheme 2. The general synthetic routes and structures of polymers.

for 30 min then at 95°C for 10 min, 4,4'-diaminodiphenyl methane (MDA) (2.5 mmol) in NMP (2 ml) was then added dropwise to this mixture over a period of 30 min. The resulting mixture was reacted at 95°C for another 3 h. More NMP was added during the polymerization in order to keep the reaction mixture at an exceptable viscosity, and thus stirrable. After the polymeization the whole mixture was poured into methanol. The precipitated polymer was filtered and washed with methanol and dried at 85°C under vacuum for 12h. Other polymers in this study were prepared by the similar procedure. The yields, solubilities and thermal properties of all polymers synthesized were listed in Tables III-V.

RESULTS AND DISCUSSION

Polymer Synthesis

A series of imide-diacid monomers was prepared from corresponding biphenyl dianhydride and trimellitic anhydride with diamines and aminoacids, respectively, as listed in Table I. The imidization of all the synthesized monomers was completed by using acetic anhydride, and monomers obtained were in a high yield. These monomers showed poor solubility in common organic solvent at room temperature. However, they were partially soluble in NMP at 95°C at the beginning of the polymerization, and the reaction mixture became

Table I. The properties of imide-diacid monomers

Monomer	Yield/%	mp °C	Formula (MW)	Elemental analyses/%			
					С	Н	N
BP-1	61.1	409-410	C ₃₀ H ₆₀ N ₂ O ₈	Calcd	67.67	3.03	5.26
			(532.47)	Found	67.81	3.19	5.25
BP-2	87.9	428-432	$C_{30}H_{16}N_{2}O_{8}$	Calcd	67.67	3.03	5.26
			(532.47)	Found	67.66	3.13	5.27
BP-3	70.8	390-392	$C_{32}H_{20}N_{2}O_{8}$	Calcd	68.57	3.60	5.00
			(560.52)	Found	68.54	3.78	5.10
NAI	85.0	>450	$C_{28}H_{14}N_{2}O_{8}$	Calcd	66.41	2.79	5.53
			(506.43)	Found	61.13	3.01	5.84



Figure 1. The concentration of LiCl on the inherent viscosity of the Poly(amide-imide)s. M1 = MDA = 5 mmol, TPP = 11 mmol, NMP = 2 ml, pyridine = 8 ml, and temperature = 95°C.

homogeneous while these monomers reacted with diamines to form poly(amide-imide)s.

The inherent viscosity of the synthesized polymers by the direct polycondensation is dependent upon several factors, such as: the type and the amounts of the condensation agents and metal halides, the concentrations and the reactivities of the monomers, the reaction temperature, and the solubilities of the monomers and polymers. In this study, the effects of the various amount of the LiCl and TPP, and various temperatures on the inherent viscosities of the synthesized poly(amide-imide)s were investigated.

The effect of the concentrations of LiCl on the inherent viscosities of the poly(amide-imide)s was shown in Figure 1. As reported by Higashi,¹³ the addition of LiCl was effective in lowering the electronic density of *N*phosphonium salts and preventing formation of the byproduct, phenylester compound. A maximum viscosity of 1.35 dl g^{-1} was obtained at the concentration of 3.5 wt% of LiCl. Further increase of the LiCl caused a sharp decrease of the inherent viscosity of the resulting poly(amide-imide).

A higher reaction temperature would destroy the stability of *N*-phosphonium salt and a lower temperature would depress the reactivity of the monomers. The effect of reaction temperature on the inherent viscosity of the poly(amide-imide)s was shown in Figure 2. The highest viscosity was obtained at the reaction temperature of



Figure 2. The effect of reaction temperature on the inherent viscosity of the poly(amide-imide)s. MAI = MDA = 5 mmol, TPP = 11 mmol, NMP = 20 ml, pyridine = 8 ml, and LiCl = 3.5 wt%.

Table II. The effect of the amount of TPP on the inherent viscosity of the poly(amide-imide)s^a

TPP	Excess	$\eta_{\rm inb}/{ m dl}{ m g}^{-1}$ b		
mmol	%	95°C	100°C	
10	0	0.52	0.32	
11	10	1.35	0.66	
12	20	0.53	0.49	
13	30	0.39	0.24	

^a M1 = MDA = 5 mmol; LiCl = 1.0 g (3.5 wt%); NMP = 20 ml and pyridine = 8 ml. ^b Measured at a concentration of 0.5 g dl^{-1} in NMP at 30° C.

95°C.

The effect of the amount of TPP on the inherent viscosity of the poly(amide-imide)s was shown in Table II. The highest inherent viscosity of 1.35 dl g^{-1} was obtained, when an excess amount of LiCl (10 mol%) was used at 95°C. All of the poly(amide-imide)s synthesized at 95°C had a higher inherent viscosity than those of the polymers prepared at 100°C. Therefore, in this study, the best reaction condition was achieved at 20 ml NMP, 8 ml pyridine, and 3.5 wt% LiCl in the presence of 11 mmol of TPP at 95°C.

Four series of novel high molecular weight poly(amideimide)s were synthesized by the direct polycondensation from imide-diacids with various aromatic diamines in

Polymer	Mor	nomer	Additional NMP/ml	$\frac{\eta_{\rm inh}^{\rm b}}{\rm dlg^{-1}}$	Yield	Film°
	Diimide-diacid	Diamine			%	
NAI series			1 1 10 10 10 10 10 10 10 10 10 10 10 10			
PN-M	NAI	MDA	0	0.40	99	_
PN-O	NAI	ODA	0	0.50	99	Brittle
PN-2O	NAI	20DA	0	0.43	99	Brittle
PN-S	NAI	SO2-DA	0	0.25	99	_
PN-DM	NAI	DMDA	0	0.30	99	
PN-6F	NAI	6F-DA	0	0.24	87	
BP-1 series						
P1-M	BP-1	DMA	15	1.63	99	Flexible
P1-O	BP-1	ODA	20	2.04	99	Flexible
P1-S	BP-1	20DA	30	1.41	99	Flexible
P1-2O	BP-1	SO2-DA	10	0.45	99	Brittle
P1-DM	BP-1	DMDA	20	2.38	99	Flexible
P1-6F	PB-1	6F-DA	10	0.82	99	Flexible
BP-2 series						
P2-M	BP-2	DMA	35	1.99 ^d	96	_
P2-O	BP-2	ODA	35	1.76 ^d	99	
P2-S	BP-2	20DA	10	1.13 ^d	97	
P2-2O	BP-2	SO2-DA	10	0.57	99	_
P2-DM	BP-2	DMDA	30	0.95	99	Flexible
P2-6F	PB-2	6F-DA	25	2.14	99	Flexible
BP-3 series						
P3-M	BP-3	DMA	10		90	
P3-O	BP-3	ODA	15	1.03	99	Flexible
P3-S	BP-3	20DA	10	0.65	99	Flexible
P3-2O	BP-3	SO2-DA	10	0.35	99	Brittle
P3-DM	BP-3	DMDA	10	0.60	99	Flexible
P3-6F	PB-3	6F-DA	10	0.46	99	Flexible

Table III. Viscosity and film properties of poly(amide-imide)s^a

^a Polymerization was carried out with 5 mmol monomer, 11 mmol TPP, 8 ml pyridine, and 0.5 g LiCl in 20 ml NMP at 95°C for 3 h under a nitrogen atmosphere. ^b Measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C. ^cCasted on a glass plate at 150°C for 12 h. ^d Measured at a concentration of 0.5 g dl^{-1} in NMR containing 2 wt% of LiCl at 30°C.



NMP, containing pyridine, TPP, and LiCl, according to the recipe described above. In order to reduce the viscosity of the reaction mixture, further amount of NMP was added during the polymerization. All poly(amideimide)s were isolated as yellowish materials in quantitative yields. As shown in Table III, it might be owing to the steplike and rigid structure of 1,5-naphthylene unit, the inherent viscosities of polymers NAI series were lower than those of the other series. The poly(amide-imide)s derived from 4,4'-diaminodiphenylsulfone (SO₂-DA) showed lower inherent viscosity than those derived from other diamines. This result was due to the sulfone group, an electron-withdrawing group, which decreases the nucleophilic basicity of the amino group. The inherent viscosities of synthesized poly(amide-imide)s were in the range of 0.24— 2.38 dl g^{-1} in NMP at 30°C.

The structures of the resulting poly(amide-imide)s were characterized by FT-IR spectroscopy. As shown in Figure 3, the typical FT-IR spectrum of polymer P3-M showed the characteristic absorption bands of -NH- of the amide group at 3358 cm⁻¹, the carbonyl group of the imide ring at 1775, 1721, and 731 cm⁻¹, the carbonyl group of the amide at 1671 cm⁻¹, the phenylene group at 1591 and 1518 cm⁻¹, and C–N of the imide ring at 1373 cm⁻¹.

Properties of the Poly(amide-imide)s

With the exception of polymers series BP-2, the synthesized poly(amide-imide)s showed good solubilities in aprotic solvents, such as DMF, N,N-dimethylacetamide (DMAc), and NMP as listed in Table IV. Owing to the para-substituted structure and high rigidity, poly-(amide-imide)s BP-2 series possessed poor solubility in most of the solvent listed in Table IV. However, they were soluble in a solution NMP containing 2 wt% of LiCl or H_2SO_4 . Poly(amide-imide)s derived from 4,4'-(hexafluoroisopropylidene)dianiline (6F-DA) had a better solubility than other poly(amide-imide)s in this study. It may be due to the presence of the hexafluoroisopropylidene units, the packing of macromolecular chains in tight structures through hydrogen bonding between amide groups is probably disturbed and, consequently, the solvent molecules can penetrate easily to solubilize the chains.¹⁴ In general, the solubilities of the poly-

Polymer	Solvent							
	H ₂ SO ₄	NMP	2 wt% LiCl NMP	DMAc	DMF	DMSO	THF	<i>m</i> -Cresol
PN-M	+	+	+	+	+	+		_
PN-O	+	+	+	+	+	+	_	s
PN-2O	+	+	+	+	+	+		s
PN-S	+	+	+	+	+	+	_	_
PN-DM	+	+	+	+	+	+		+
PN-6F	+	+	+	+	+	+	+	+
P1-M	+	+	+	+	+	h	_	+
P1-O	+	+	+	+	+	+		+
P1-S	+	+	+	+	+	h		+
P1-2O	+	+	+	+	+	+	_	+
P1-DM	+	+	+	+	+	+	_	+
P1-6F	+	+	+	+	+	+	S	+
P2-M	+	_	h	_	_	_	_	-
P2-O	+	_	h		_	_		
P2-S	+		h	_	_	_	_	_
P2-2O	+	+	+	h	_	_		_
P2-DM	+	h	h				_	S
P2-6F	+	+	+	+	+	h	_	+
Р3-М	+		_		_	_	_	_
P3-O	+	+	+	+	h		_	+
P3-S	+	+	+	+	h	_		+
P3-2O	+	+	+	+	+	+	_	+
P3-DM	+	+	+	+	+	+	_	+
P3-6F	+	+	+	+	+	+	s	+

Table IV. Solubility of poly(amide-imide)s^a

 a^{+} , soluble at room temperature; h, soluble on heating; s, swelling on heating; -, insoluble.

(amide-imide)s which were derived from various diamine structures were in the order of:



^a Measured by DSC at a heating rate of 20° C min⁻¹ on the second heating. ^b Thermogravimetric analyses conducted at a heating rate of 20° C min⁻¹ under a nitrogen atmosphere.

CF_3 CF_3 H_3C	○ - CH ₂ - () - CH ₃ > ()	\rightarrow -so ₂ - $\langle \bigcirc \rangle$
6F-DA	DM-DA	SO ₂ -DA
> ()-0-() > (◯o-(◯)-o-(◯)	> ()-CH2-()
ODA	2 O-DA	MDA

The transition temperatures of the synthesized poly-(amide-imide)s were characterized by DSC measurements as shown in Table V. The DSC curves of most poly(amide-imide)s exhibited a step transition corresponding to a glass transition temperature (T_g) . However, no endothermic peak corresponding to the melting transition temperature (T_m) was detected. These results indicated that these poly(amide-imide)s possess an amorphous characteristic, which was confirmed by WAXD measurements in Figure 7. The non-crystallinity may be due to the polymers NAI series with a rigid structure, and thus no glass transition was observed for polymers NAI series. It was important to note that most of the poly(amide-imide)s with biphenyl imide structure possessed notable high glass transitions ($>300^{\circ}$ C). As listed in Table V, it was reasonable that polymer BP-3 series with an aliphatic chain exhibited lower glass transition than those of other series, and polymers BP-2 series with *para*-substituent structure had higher glass transition than those of polymers BP-1 series with metasubstituent structure. Therefore, the glass transition

Table V. Thermal properties of poly(amide-imide)s



Figure 4. The DSC curves of polymers P1-6F, P2-6F, and P3-6F.



Figure 5. The TGA curves for polymers NAI series.

of the synthesized poly(amide-imide)s were in the order of: BP-2 series > BP-1 series > BP-3 series.

In addition, poly(amide-imide)s derived from 6F-DA possessed a higher glass transition than those of other poly(amide-imide)s in the same series. The DSC curves of poly(amide-imide)s with 6F-DA structures were shown in Figure 4. Glass transitions were located at 335°C, 354°C, and 303°C for polymers P1-6F, P2-6F, and P3-6F, respectively.

The thermostabilities of the poly(amide-imide)s were examined by TGA measurements. As shown in Table V,



Figure 6. The TGA curves of polymers BP-1 series.



Figure 7. The WAXD of polymers BP-1 series.

polymers NAI series did not possess excellent thermostabilities because of their low molecular weights, but the other synthesized poly(amide-imide)s with biphenyl imide structures possessed moderately high thermal resistance. With the exception of polymers NAI series, most of polymers BP-1, BP-3 series did not show obvious weight loss up to the temperature of approximately 500°C and their 10% weight loss temperature were in the range of 481—597°C under nitrogen atmosphere. The TGA curves of polymers NAI series and BP-1 series were shown in Figures 5 and 6, respectively.

In order to study the crystalline characteristics of the synthesized poly(amide-imide)s, they were subjected to WAXD measurements at room temperature. Most of the poly(amide-imide)s possessed amorphous nature. For examples as shown in Figure 7, polymer BP-1 series are exhibited amorphous characters and the films of polymer BP-1 series shows transparent and flexible



Figure 8. The WAXD of polymers PN-M, P1-M, P2-M, and P3-M.

	Viceosity	Tensile stress			
Polymer		Yield point	Elongation %		
	dlg^{-1}	kg cm ⁻²			
BP-1 series					
P1-M	1.63	591.4	1.56		
P1-O	2.04	562.1	1.04		
P1-2O	1.41	510.6	3.26		
P1-DM	2.38	588.1	2.65		
P1-6F	0.82	633.5	1.48		
BP-3 series					
P3-2O	0.65	433.0	3.42		
P3-DM	0.60	450.3	2.87		

Table VI. Tensile properties of polyamide-imide films

properties. The WAXD of polymers PN-M and P3-M were shown in Figure 8. With the exception of polymer P3-M showing semi-crystalline patterns, all poly(amideimide)s derived from MDA showed amorphous characteristics. However, the semi-crystalline property did not provide a higher initial decomposition temperature.

The tensile properties of some of poly(amide-imide)s have been performed in the form of films at room temperature. The data of tensile properties of poly-(amide-imide)s are shown in Table VI. All of these poly(amide-imide)s possessed good mechanical properties with high tensile strength and low elongation at break. It may be suggested that these poly(amideimide)s can be applied as new materials for engineering plastics.

CONCLUSION

A series of high molecular weight poly(amide-imide)s have been prepared. The best reaction condition was achieved by reacting 5 mmol of monomer at 20 ml NMP, 8 ml pyridine, 3.5 wt% LiCl in presence of 11 mmol of TPP at 95°C. The poly(amide-imide)s with biphenylene structure (P1—P3 series) possessed excellent thermostability (5% weight loss of these poly(amide-imide)s are around 490°C) and good solubilities in common aprotic solvents, such as NMP, DMAc, and DMF. Thus, these poly(amide-imide)s showed the potential application as the new high-performance and thermal resistant material.

Acknowledgment. The authors are indebted to the National Science Council of Republic of China for financial support of this work (NSC-84-2216-E-033-006).

REFERENCES

- C. H. Li, A. Jung, A. L. Liang, and T. C. Chang, J. Appl. Polym. Sci., 56, 1661 (1995).
- 2. C. P. Yang and W. T. Chen, Makromol. Chem., 194, 1595 (1993).
- S. J. Sun and T. C. Chang, J. Polym. Sci., Part A, Polym. Chem., 32, 3039 (1994).
- 4. H. R. Kricheldorf and R. Pakull, Macromolecules, 21, 551 (1988).
- 5. B. M. Culbertson, U.S. Pat, 3453236 (1969).
- Y. Imai and H. Uchiyama, J. Polym. Sci., Part B, Polym. Lett., 8, 559 (1970).
- 7. W. M. Alvino, J. Appl. Polym. Sci., 19, 651 (1975).
- 8. H. E. Sheffer and G. C. Zielinski, U.S. Pat. 3518230 (1970).
- Y. Oishi, M. Kakimoto, and Y. Imai, J. Polym. Sci., Part A, Polym. Chem., 29, 1925 (1991).
- 10. N. Yamazaki, F. Higashi, and M. Niwano, *Tetrahedron*, **30**, 1319 (1974).
- 11. N. Yamazaki and F. Higashi, Tetrahedron, 30, 1323 (1974).
- 12. S. Russo, A. Mariani, V. N. Ignatov, and I. I. Ponomarev, *Macromolecules*, **26**, 4984 (1993).
- 13. N. Yamazaki, M. Matsumoto, and F. Higashi, J. Polym. Sci., Part A, Polym. Chem., 13, 1373 (1975).
- 14. M. Bruma, F. Mercer, J. Fitch, and P. Cassidy, J. Appl. Polym. Sci., 56, 527 (1995).