Cationic Polymerization of Epoxide by Fluorenylphosphonium Salts as Thermally Latent Initiators. Substituent Effect on the Initiator Activity

Tatsuya Toneri, Fumio Sanda, and Takeshi Endo*

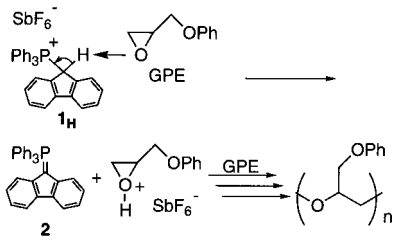
Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

Received May 2, 2000
Revised Manuscript Received December 28, 2000

Introduction

It is an issue of great interest and importance to control the initiation step of polymerization and curing of thermosetting and photocuring resins. "Latent catalysts" function as initiators solely by external stimulations such as heating and photoirradiation, which have been utilized for fillers, adhesives, packings, and paints. These initiators must be inert under ambient conditions but transformed into active species to initiate a reaction by appropriate external stimulations. Pappas et al. have reported pioneering works on onium salt-based thermal initiators.[1] Crivello et al.,[2] Abu-Abdoun et al.,[3] and Yagci et al.[4] have developed a variety of onium salt-based cationic photoinitiators, which are applicable to photo resist and curing systems. We have also developed benzylsulfonium,[5] benzylpyridinium,[6] benzylammonium,[7] and phosphonium[8] salts with less nucleophilic counteranions like hexafluoroantimonate and hexafluorophosphonate as thermal- and photolatent cationic initiators for the polymerization of styrene and epoxides. Among these latent initiators, only benzylphosphonium salts release a proton as an active species, which is different from the other benzylonium salts releasing a benzyl cation as the active species, probably because phosphonium salts easily form the corresponding stable ylides by releasing a proton. Phosphonium salts have been widely utilized as useful intermediates in organic synthesis,[9] which show more variety of reactivities compared with the corresponding pyridinium and ammonium salts due to the participation of the d-orbital. We extended the idea of latent initiators to a fluorenylated quaternary phosphonium salt, 9-fluorenyltriphenylphosphonium hexafluoroantimonate (**1$_H$**), to find that it served as a highly active thermally latent cationic initiator in the polymerization of epoxide.[10] The fluorenyl methine proton was confirmed as the initiating species which would be formed via a nucleophilic attack of glycidyl phenyl ether (GPE) at **1$_H$** by an S_N2 mechanism to eventually give an oxonium cation (Scheme 1). We examined the effect of counteranion to find that the salt with a less nucleophilic counteranion showed a higher activity. We have also reported that **1$_H$** serves as an effective photoinitiator in the polymerization of cyclohexene oxide, whose active species is also a proton.[11] The high activity of **1$_H$** may ascribe to the delocalization effect of the negative charge on the fluorene ring.[12] The stability of fluorenyltriphenylphosphonium ylide (**2**) may be also effective to suppress the termination reaction resulting in the high activity of **1$_H$**. Significant features of the phosphonium salts involve the possibility of activity control by substituents on the fluorenyl ring and phosphine as well as easy handling owing to their chemical stability and less hygroscopic nature. This paper describes the synthesis of several fluorenyltriphenylphosphonium salts and the effect of substituents (R) at the fluorene ring and phosphine on the initiator activity in the polymerization of epoxides.

Scheme 1



Experimental Section

Materials. GPE, cyclohexene oxide (CHO), and nitromethane were distilled over calcium hydride. Benzene was distilled over sodium. Triphenylphosphine was recrystallized from *n*-hexane. *N*-Bromosuccinimide, benzoyl peroxide, 2-nitro-, 2-bromo-, 2-hydroxy-, and 9-bromofluorenes, dimethyl sulfoxide, dimethyl sulfate, $KSbF_6$, ether, ethanol, acetonitrile, and tri-*n*-butylphosphine were used without purification. Fluorenyltriphenylphosphonium hexafluoroantimonate (**1$_H$**) was synthesized according to the reported method.[10]

Measurements. ^1H and ^{13}C NMR spectra were recorded with JEOL JNM-EX-90 and JNM-EX-400 spectrometers using tetramethylsilane as an internal standard in acetone-d_6. IR spectra were measured with a JEOL JIR-5300 spectrophotometer. Number and weight-average molecular weights (M_n and M_w) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC HLC-8020 system, equipped with three consecutive polystyrene gel columns (TSKgels G5000HXL, G4000HXL, G2500HXL), using LiBr solution in DMF (5.8 mM) as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and refractive index and ultraviolet detectors. Elemental analysis was carried out with Yanaco Type MT-5 CHN and SX-Elements microanalyzer YS-10.

Synthesis of 2-Nitro-9-bromofluorene. A solution of 2-nitrofluorene (9.72 g, 46 mmol), *N*-bromosuccinimide (8.11 g, 46 mmol), and benzoyl peroxide (0.11 g, 0.5 mmol) in 70 mL of dry benzene was refluxed for 43 h. A precipitate of succinimide formed during this process was removed by filtration. The filtrate was concentrated by rotary evaporation to obtain solid 2-nitro-9-bromofluorene. Yield: 90%. ^1H NMR ($CDCl_3$): $\delta = 8.51-7.27$ (m, 7H, Flu), 6.05 (s, 1H, CHBr) ppm.

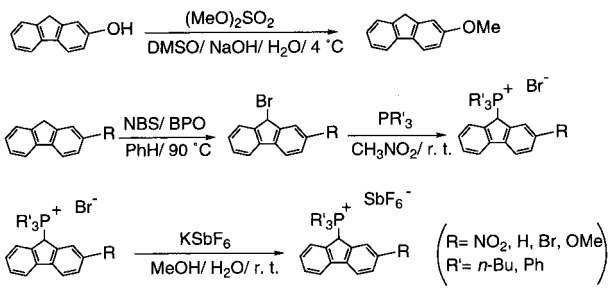
Synthesis of 2,9-Dibromofluorene. The title compound was synthesized by the reaction of 2-bromofluorene with *N*-bromosuccinimide and benzoyl peroxide in a manner similar to that used for 2-nitro-9-bromofluorene. Yield: 90%. ^1H NMR ($CDCl_3$): $\delta = 7.79-7.27$ (m, 7H, Flu), 5.95 (s, 1H, CHBr) ppm.

Synthesis of 2-Methoxy-9-bromofluorene. To a solution of 2-hydroxyfluorene (0.1 g, 0.6 mmol) in 2.7 mL of dimethyl sulfoxide were added a solution of NaOH (0.04 g) in H_2O (1.0 mL) and dimethyl sulfate (0.16 mL) at 4 °C. After the mixture was stirred at 4 °C for 15 min, it was poured into H_2O to isolate 2-methoxyfluorene by filtration in 64% yield. The title compound was synthesized by bromination of 2-methoxyfluorene with *N*-bromosuccinimide and benzoyl peroxide in the similar manner with 2-methoxy-9-bromofluorene. Yield: 28% ^1H NMR

* To whom all correspondence should be addressed. Present address: Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan. E-mail: tendo@poly.yz.yamagata-u.ac.jp.

10.1021/ma000759v CCC: $20.00
Published on Web 02/02/2001

Scheme 2



($CDCl_3$): δ = 8.08−7.14 (m, 7H, Flu), 5.86 (s, 1H, CHBr), 3.76 (t, 3H, OMe) ppm.

Synthesis of 2-Nitrofluorenyltriphenylphosphonium Hexafluoroantimonate ($\mathbf{1_{NO_2}}$), 2-Bromofluorenyltriphenylphosphonium Hexafluoroantimonate ($\mathbf{1_{Br}}$), 2-Methoxyfluorenyltriphenylphosphonium Hexafluoroantimonate ($\mathbf{1_{OMe}}$), and Fluorenyltri-*n*-butylphosphonium Hexafluoroantimonate ($\mathbf{1_{P}}_{n-\mathbf{Bu}}$). The title compounds were synthesized from the corresponding 9-bromofluorenes according to the reported method.[10] $\mathbf{1_{NO_2}}$: yield 7%, mp 274.0−275.0 °C. ^{1}H NMR (acetone-d_6, 0.1 M): δ = 8.39−7.40 (m, 22H, Ph, Flu), 7.19 (d, J = 16.4 Hz, 1H, CH) ppm. ^{13}C NMR (acetone-d_6, 0.1 M): δ = 149.29, 147.95, 141.26, 138.00, 137.14, 136.43, 134.73, 131.25, 130.78, 127.72, 126.43, 123.57, 122.80, 122.42, 118.21, 117.37, 42.43 ppm. IR (KBr): 3094, 1615, 1588, 1530, 1439, 1343, 1109, 997, 911, 849, 820, 803, 749, 708, 691, 660, 534 cm^{-1}. Anal. Calcd for $C_{31}H_{23}NO_2PSbF_6$: H, 3.27; C, 52.57; N, 1.98. Found: H, 3.23; C, 53.01; N, 2.00. $\mathbf{1_{Br}}$: yield 41%, mp 272.0−273.0 °C. ^{1}H NMR (acetone-d_6, 0.1 M): δ = 7.96−7.27 (m, 22H, Ph, Flu), 7.00 (d, J = 16.4 Hz, 1H, CH) ppm. ^{13}C NMR (acetone-d_6, 0.1 M): δ = 142.28, 138.17, 136.28, 135.97, 134.66, 133.72, 131.13, 130.85, 130.52, 129.22, 127.43, 123.41, 122.13, 121.54, 118.42, 117.57, 42.14 ppm. IR (KBr): 3067, 1588, 1566, 1441, 1406, 1339, 1321, 1144, 1109, 1069, 997, 880, 833, 801, 747, 723, 710, 691, 660, 540, 525, 511 cm^{-1}. Anal. Calcd for $C_{31}H_{23}PBrSbF_6$: H, 3.12; C, 50.17. Found: H, 2.98; C, 49.85. $\mathbf{1_{OMe}}$: yield 4%, mp 267.0−268.0 °C. ^{1}H NMR (acetone-d_6, 0.1 M): δ = 7.96−7.05 (m, 22H, Ph, Flu), 6.90 (d, J = 16.0 Hz, 1H, CH), 3.54 (s, 3H, CH_3) ppm. ^{13}C NMR (acetone-d_6, 0.1 M): δ = 160.62, 143.40, 141.13, 137.49, 136.08, 135.50, 134.69, 131.02, 130.61, 127.29, 122.77, 121.03, 118.78, 117.94, 117.17, 112.82, 55.83, 41.90 ppm. IR (KBr): 3015, 2905, 1607, 1497, 1462, 1439, 1271, 1221, 1140, 1109, 1036, 997, 932, 853, 804, 783, 752, 723, 693, 660, 540, 513 cm^{-1}. Anal. Calcd for $C_{32}H_{26}POSbF_6$: H, 3.78; C, 55.44; F, 16.44. Found: H, 3.60; C, 54.93; F, 16.15. $\mathbf{1_{P}}_{n-\mathbf{Bu}}$: yield 7%, mp 236.0−237.0 °C. ^{1}H NMR (acetone-d_6, 0.1 M): δ = 8.11−7.51 (m, 8H, Flu), 5.55 (d, J = 17.2 Hz, 1H, CH), 2.31 (m, 6H, CH_2), 1.40 (m, 12H, CH_2CH_2), 0.86 (m, 9H, CH_3) ppm. ^{13}C NMR (acetone-d_6, 0.1 M): δ = 142.87, 137.33, 130.65, 129.13, 127.16, 122.20, 41.06, 24.23, 18.07, 13.44 ppm. IR (KBr): 3065, 2965, 2936, 2876, 1451, 1414, 1383, 1314, 1237, 1154, 1100, 911, 822, 741, 660, 633, 505 cm^{-1}. Anal. Calcd for $C_{25}H_{18}PSbF_6$: H, 6.01; C, 49.77; F, 18.19. Found: H, 6.01; C, 49.50; F, 18.11.

Polymerization. Typical procedure: GPE (333 mg, 2.21 mmol) and an initiator (0.02 mmol) were placed in a polymerization ampule containing a small magnetic stirrertip. The ampule was cooled, evacuated, and sealed off. The ampule was heated at a desired temperature for a set time. After that, it was cooled immediately with liquid nitrogen. The monomer conversion was estimated by ^{1}H NMR of the crude polymerization mixture after warming to room temperature.

Results and Discussion

Synthesis of Initiators. All the fluorenylphosphonium salts were synthesized by the reaction of the corresponding 9-bromo-fluorenes with triphenylphosphine or tri-*n*-butylphosphine, followed by the counteranion exchange with $KSbF_6$ in MeOH/H_2O according to the literature as shown in Scheme 2.[10] Their structures were determined by NMR and IR spectroscopy besides elemental analysis.

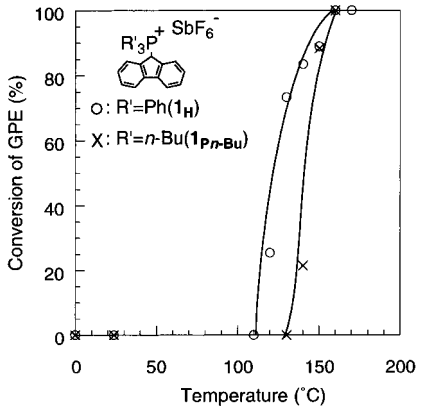


Figure 1. Temperature−conversion relationships in the bulk polymerization of GPE with 1 mol % of $\mathbf{1_H}$, and $\mathbf{1_{P}}_{n-\mathbf{Bu}}$ for 1 h.

Polymerization. The activities of the fluorenyltriphenylphosphonium salts ($\mathbf{1_H}$, $\mathbf{1_{NO_2}}$, $\mathbf{1_{Br}}$, $\mathbf{1_{OMe}}$, and $\mathbf{1_{P}}_{n-\mathbf{Bu}}$) were evaluated in the bulk polymerization of GPE, because all the initiators were soluble in GPE at room temperature. The polymerization proceeded homogeneously. The substituents at the fluorene ring or phosphine and polymerization temperature slightly affected the molecular weight of the obtained polymer. Figure 1 shows the temperature−conversion relationships in the polymerization of GPE with triphenyl and tri-*n*-butylphosphonium salts $\mathbf{1_H}$ and $\mathbf{1_{P}}_{n-\mathbf{Bu}}$ at the temperatures ranging from 0 to 170 °C. Neither salt initiated the polymerization below 110 °C, whereas the polymerization rapidly proceeded above 120 and 140 °C. The both salts served as thermally latent initiators in the polymerization of GPE. The triphenylphosphonium salt $\mathbf{1_H}$ showed activity larger than the tri-*n*-butylphosphonium salt $\mathbf{1_{P}}_{n-\mathbf{Bu}}$. The M_ns of the obtained polymers ranged from 2300 to 4100. The M_n increased with the GPE conversion (Table 1).

The higher activity of $\mathbf{1_H}$ may be ascribed to the higher acidity, which is attributable to the larger resonance delocalization effect by the phenyl group on the phosphine resulting in a stable ylide. The extent of a 2p−3d orbital resonance of the C−P bond is observed; i.e., the contribution of ylene structure may be larger in the case of $\mathbf{1_H}$ than $\mathbf{1_{P}}_{n-\mathbf{Bu}}$ (Scheme 3). In fact, Meriwether and Fiene have reported that the d-orbital resonance of PPh_3 is larger than that of PBu_3 by IR spectroscopic studies on nickeldicarbonyldiphosphines.[13] Phenyl group would increase the positive charge on phosphorus due to the −I effect and therefore permit a larger contribution of ylene form to the resonance hybrid.[14] On the other hand, alkyl substituents would decrease the contribution of ylene form due to the +I effect. Consequently, the ylide formed from $\mathbf{1_H}$ would be less nucleophilic than that from $\mathbf{1_{P}}_{n-\mathbf{Bu}}$, resulting in the higher activity of the former.

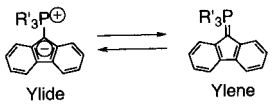
Figure 2 depicts the temperature−conversion relationships in the polymerization of GPE with a series of triphenylphosphonium salts, whose activity order is as follows: $\mathbf{1_H}$ > $\mathbf{1_{NO_2}}$ > $\mathbf{1_{Br}}$ > $\mathbf{1_{OMe}}$, which may indicate that the introduction of an electron-withdrawing subsituent on the fluorene ring accelerate the polymerization of GPE except for $\mathbf{1_H}$. This is in good accordance with the order of acidities of 2-substituted fluorenes, i.e., pK_a values in aqueous dimethyl sulfoxide containing tetramethylammonium hydroxide (Table 2).[15] This ten-

Table 1. Polymerization of GPE with Fluorenyltriphenylphosphonium Salts (1_H, 1_{Pn-Bu}, 1_{NO_2}, 1_{Br}, and 1_{OMe}) for 1 h[a]

init	temp (°C)	conv[b] (%)	M_n (M_w/M_n)[c]
1_H	24	0	
	110	0	
	120	26	2300 (1.2)
	130	73	3700 (1.4)
	140	84	4100 (1.4)
	150	89	4100 (1.4)
	160	100	4100 (1.4)
1_{Pn-Bu}	24	0	
	140	22	2500 (1.1)
	150	88	3800 (1.3)
	160	100	4000 (1.3)
1_{NO_2}	24	0	
	130	4	
	140	19	3200 (1.4)
	150	47	3600 (1.4)
	160	72	4900 (1.8)
	170	100	4600 (1.7)
1_{Br}	24	0	
	120	0	
	130	1	
	140	1	
	150	27	3100 (1.3)
	160	36	3100 (1.3)
	170	52	3300 (1.4)
	180	84	3900 (1.5)
	190	100	3800 (1.6)
1_{OMe}	24	0	
	160	0	
	170	9	
	180	12	3000 (1.3)
	190	56	3200 (1.4)
	200	100	4800 (1.7)

[a] Conditions: initiator: 1.0 mol % vs GPE for 1 h. [b] Determined by ^{1}H NMR. [c] Estimated by GPC based on polystyrene standards.

Scheme 3



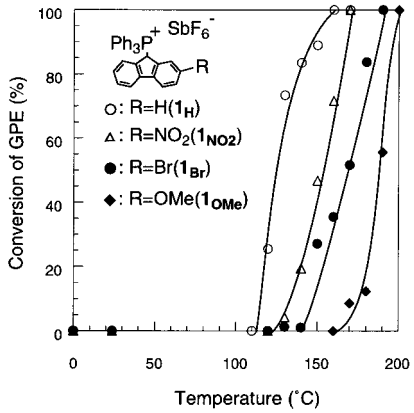


Figure 2. Temperature−conversion relationships in the bulk polymerization of GPE with 1 mol % of 1_{NO_2}, 1_{Br}, 1_{OMe}, and 1_H for 1 h.

dency is also supported by the ^{1}H NMR chemical shift of the fluorenylmethine proton of the phosphonium salts as summarized in Table 2. The unexpectedly high activity of 1_H may indicate that the activities of the fluorenylphosphonium salts depend on the bulkiness of the substituents on the fluorene ring as well as the electronic factors.

As we have reported the crystal structure,[10] the fluorenylmethine proton is sterically hindered from a nucleophilic attack by an epoxide molecule. Themoinitiated polymerization of CHO with 1_H 1_{NO_2}, and 1_{Br} was carried out in CH_2Cl_2 at 60 °C to elucidate the monomer steric effect on the activity order of the fluorenylphosphonium salts (Scheme 4). The salts could polymerize CHO at 60 °C, although it required 6 h to achieve significant difference in CHO conversion (1_{NO_2} > 1_{Br} > 1_H) as summarized in Table 3. CHO commonly shows cationic polymerizability higher than GPE, because of the contribution of stable cyclohexyl cation and higher nucleophilicity based on the restricted conformation of the epoxide moiety.[16] Consequently, the order of the initiator activity would agree with that expected from electronic factor in CHO polymerization, which was different from GPE polymerization probably involving a steric factor as well.

Table 2. pK_a of 2-Substituted Fluorenes and ^{1}H NMR Chemical Shift of Fluorenylmethine Proton of Phosphonium Salts (1_X)

	substituent (X)			
	NO_2	Br	H	OMe
pK_a of 2-substituted fluorene[a]	17.96	20.56	22.10	22.36
^{1}H NMR chem shift of 1_X[b] (δ, ppm)	7.19	7.00	7.00	6.90

[a] Data from ref 10. [b] Measured in acetone-d_6 with 0.02 M reagent concentration.

Scheme 4

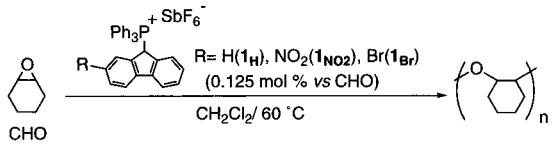


Table 3. Polymerization of CHO with 1_H, 1_{NO_2}, and 1_{Br}[a]

time (h)	init (R)	conv[b] (%)	M_n (M_w/M_n)[c]
1	none	0	
1	NO_2	25	21400 (2.1)
1	Br	0	
1	H	0	
6	none	0	
6	NO_2	80	102000 (2.2)
6	Br	67	145700 (2.2)
6	H	29	76100 (2.2)

[a] Conditions: initiator: 0.125 mol % vs CHO (291 mg) in CH_2Cl_2 (1.0 mL). [b] Determined by ^{1}H NMR. [c] Estimated by GPC based on polystyrene standards.

Summary

We examined the structure−activity relationship of fluorenylphosphonium salts in the polymerization of GPE and CHO. It was suggested that the activity order in GPE polymerization was affected by steric factor as well as electronic factor, while the order in CHO polymerization mainly by electronic factor.

References and Notes

(1) (a) Pappas, S. P.; Hill, L. W. *J. Coat. Technol.* **1981**, *53* (675), 43. (b) Pappas, S. P. *High Solids Coat.* **1983**, *8* (1), 2.
(2) Review: Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4241.
(3) (a) Neckers, D. C.; Abu-Abdoun, I. *Macromolecules* **1984**, *17*, 2468. (b) Abu-Abdoun, I.; Aale-Ali, *Eur. Polym. J.* **1992**, *28*, 73.
(4) (a) Yagci, Y.; Schnabel, W. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 33. (b) Yagci, Y.; Lukac, I.; Schnabel, W. *Polymer* **1993**, *34*, 1130. (c) Yagci, Y.; Endo, T. *Adv. Polym. Sci.* **1996**, *78*, 61. (d) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485. (e) Yagci, Y. *Macromol. Symp.* **1998**, *134*,

177. (f) Onen, A.; Arsu, N.; Yagcl, Y. *Angew. Makromol. Chem.* **1999**, *264*, 56.

(5) (a) Morio, K.; Murase, H.; Tsuchiya, H.; Endo, T. *J. Appl. Polym. Sci.* **1986**, *23*, 5727. (b) Uno, H.; Takata, T.; Endo, T. *Chem. Lett.* **1988**, 935. (c) Endo, T.; Kikkawa, A.; Uno, H.; Sato, H.; Hiza, M.; Takata, T. *J. Polym. Sci., Polym. Lett. Ed.* **1989**, *27*, 73. (d) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1675. (e) Kikkawa, A.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1089. (f) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 203.

(6) (a) Lee, S.-B.; Takata, T.; Endo, T. *Macromolecules* **1990**, *23*, 431. (b) Lee, S.-B.; Takata, T.; Endo, T. *Macromolecules* **1991**, *24*, 2689. (c) Nakano, S.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 475.

(7) (a) Nakano, S.; Endo, T. *Prog. Org. Coat.* **1993**, *22*, 287. (b) Nakano, S.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 505. (c) Nakano, S.; Endo, T. *Prog. Org. Coat.* **1996**, *28*, 143.

(8) (a) Takuma, K.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 862. (b) Takuma, K.; Takata, T.; Endo, T. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 203. (c) Takuma, K.; Takata, T.; Endo, T. *J. Photopolym. Sci. Technol.* **1993**, *6* (1), 67.

(9) Kosolapoff, G. M.; Maier, L. *Organic phosphorus compounds*; Wiley-Interscience: New York, 1972.

(10) (a) Toneri, T.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1957. (b) Toneri, T.; Watanabe, K.; Sanda, F.; Endo, T. *Macromolecules* **1999**, *32*, 1293.

(11) Toneri, T.; Sanda, F.; Endo, T. *J. Photopolym. Sci. Technol.* **1999**, *12*, 159.

(12) (a) Hudson, R. F. *Chem. Br.* **1971**, *7*, 287. (b) Ramirez, F.; Levy, S. *J. Am. Chem. Soc.* **1957**, *79*, 67.

(13) Meriwether, L.; Fiene, M. L. *J. Am. Chem. Soc.* **1959**, *81*, 4200.

(14) Jonson, A. Wm.; LaCount, R. B. *Tetrahedron* **1960**, *9*, 130.

(15) Bowden, K.; Cocheril, A. F. *Chem. Commun.* **1967**, *19*, 989.

(16) Ottar, B. *Acta Chem. Scand.* **1947**, *1*, 283.

MA000759V