Notes

Photoinitiated Cationic Cross-Linking of 4-Methylene-2-phenyl-1,3-dioxolane with 2,2′-(1,4-Phenylene)bis(4-methylene-1,3-dioxolane)

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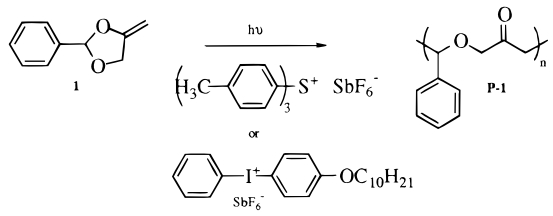
Introduction

Substantial efforts have been directed at finding systems that undergo little or no volume changes upon polymerization, due, in large part, to the requirements in many important technologies, such as strain-free composites, stereolithography, dental materials, and many imaging applications.[1,2] The ring-opening polymerization of heterocyclic monomers has been reported to occur with small volume decreases (shrinkage) or, in a limited number of examples volume increases (expansion).[2−4] Of these, 1,3-dioxolane derivatives have been the object of considerable attention. The free radical and cationic polymerization of 1,3-dioxolane derivatives possessing an exocyclic methylene functional group has been found to undergo two modes of polymerization, 1,2-addition and ring-opening.[5] Polymerization via 1,2-addition typically results in large volume decreases in converting monomer to polymer, generally over 20%. However, ring-opening polymerization of dioxolane monomers occurs with much smaller shrinkages, reportedly less than 10%.[5,6]

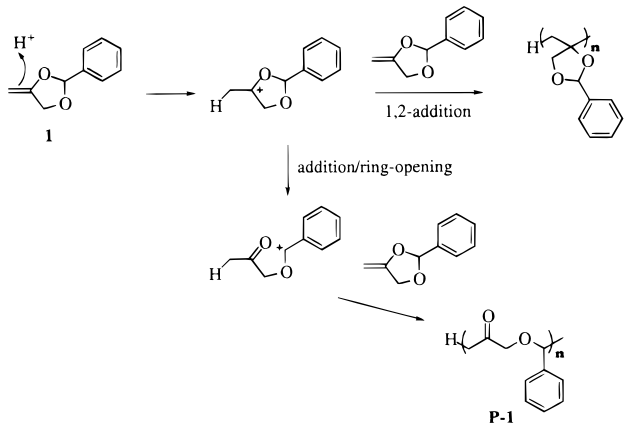
Photoinitiated free radical polymerization has been utilized in a host of important applications, ranging from photoresist technologies to coatings and dental composites. As prevalent as photoinitiated free radical polymerization has become, serious limitations for this type of process exists, primarily due to oxygen inhibition. In the last decade, increased efforts have focused on the study of photoinitiated cationic polymerization of a variety of vinyl ether and heterocyclic monomers and photoinitiators.[2−4] Since the landmark work of Crivello *et al.*,[7,8] onium salts, in particular aromatic sulfonium and iodonium, have proven remarkably useful as cationic photoinitiators.

4-Methylene-1,3-dioxolane and its 2-alkyl derivatives afforded mixtures of 1,2-addition and addition/ring-opened polymer products under cationic conditions,[9−14] while copolymerization with maleic anhydride yielded predominantly 1,2-addition polymerization.[15] The cationic polymerization of 2-isopropenyl-4-methylene-1,3-dioxolane, initiated with methanesulfonic acid at −78 °C or with benzyl(4-hydroxyphenyl)methylsulfonium hexafluoroantimonate at room temperature, underwent isomerization polymerization, resulting in a poly(keto−ether).[16−19] Meanwhile, the use of a stronger catalyst generated a cross-linked polymer. 2-Ethenyl-4-methylene-1,3-dioxolane was also found to be susceptible to ring-opening cationic polymerization. Cross-linked polymers were obtained when BF_3OEt_2 or CF_3SO_3H were used, while soluble polymers resulted upon initiation with CH_3SO_3H.[19]

Scheme 1



Scheme 2



Predominant addition/ring-opening polymerization of 4-methylene-2-phenyl-1,3-dioxolane (**1**) was recently reported using WCl_6 or BF_3 as initiators, though molecular weights were relatively low (M_w ca. 5000).[20,21] Prior to our earlier communication,[5] there was only one account of the photoinitiated cationic polymerization of **1**. η^5-2,4-Cyclopentadiene-1-yl([1,2,3,4,5,6-η]-1-methylethylbenzene)iron(I) hexafluorophosphine resulted in ring-opening polymerization of **1** upon exposure to UV light.[6] Interestingly, prior to our earlier work,[5,22,23] no investigations of the photoinitiated cationic polymerization of methylene dioxolane monomers using sulfonium or iodonium salts were reported nor were the thermal properties of polymers derived from the addition/ring-opening of **1**, despite the increased use of onium salt photoinitiators (Scheme 1).

We found that **1** underwent exclusive photoinitiated addition/ring-opening, using either tris(4-methylphenyl)sulfonium hexafluoroantimonate or 4-(decyloxyphenyl)phenyliodonium hexafluoroantimonate, to form a poly(alkylene ether ketone) with glass transition temperatures (T_gs) in the range 26−35 °C, depending on molecular weight.[5,23] Clean addition/ring-opening polymerization was observed, likely due to the stability of the postulated benzylic carbocation formed as a propagating species (Scheme 2).[6] Dioxolane monomer **1** was also found to undergo photoinitiated cationic copolymerization with acyclic vinyl ether, cyclic vinyl ether, and spiroorthoester monomers.[23]

In order to investigate the potential usefulness of **1** for structural composite applications, efforts were re-

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quired to generate polymers with higher T_gs. We found copolymerization of **1** with cyclic vinyl ethers, 2,3-dihydrofuran or 2,3-dihydropyran, led to copolymers with T_gs substantially higher than the ring-opening homopolymer of **1**.[23] Although there have been two reports of the difunctional dioxolane 2,2′-(1,4-phenylene)bis(4-methylene-1,3-dioxolane) (**3**),[10,24] there have been no reports of its cationic, particularly photoinitiated, polymerization, and details of its synthesis and characterization are sparse. Herein, we wish to report the preparation, characterization, and photoinitiated cationic homo- and copolymerization of **3**, a potentially important cross-linking agent for cationic polymerizations.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. THF and toluene were refluxed over Na and then distilled prior to use. 2,3-Dihydrofuran (DHF) was distilled before use. 4-Methylene-2-phenyl-1,3-dioxolane (**1**),[6,10] tris(4-methylphenyl)sulfonium hexafluoroantimonate,[7] and 4-(decyloxyphenyl)phenyliodonium hexafluoroantimonate[8] were synthesized according to existing procedures. All other reagents were used as received from commercial suppliers.

^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer ($CDCl_3$ or benzene-d_6 solution, referenced to TMS at δ 0.00 ppm). DSC analyses were secured using a DuPont Model 2100 DSC instrument using a scan rate of 10 °C/min (under N_2), T_gs were recorded from the scan after which no appreciable change occurred. UV−visible spectroscopic measurements were using a Hewlett-Packard diode array spectrophotometer (Model 8452A). FT-IR spectra were recorded on Nicolet Impact 400 or Perkin-Elmer Spectrum 2000 spectrometers. High- and low-resolution EI mass spectra were obtained using JEOL Model SX102A and Hewlett-Packard GC/MS (Model 5972A MSD) mass spectrometers, respectively. Photolyses were conducted at room temperature with a 450-W Hanovia medium pressure Hg arc lamp, housed in a water-cooled quartz immersion well, with or without a Pyrex filter, as indicated. For unfiltered photolysis, samples were contained in quartz tubes. For Pyrex-filtered photolysis, a Pyrex filter was placed between the UV lamp and water-cooled jacket to absorb most of the emitted IR radiation, with samples contained in glass vials.

Synthesis of Difunctional Dioxolane Precursor 2.[10] 3-Chloro-1,2-propanediol (8.69 g, 0.0789 mol), 5.01 g terephthaldehyde (0.0374 mol) and 4.3 mg of *p*-toluenesulfonic acid monohydrate (0.0226 mmol, 0.019 mol%) were combined in 100 mL toluene, and the mixture was heated to reflux until 1.3 mL of water (equivalent to 97% conversion) was collected in a Dean-Stark trap. The reaction mixture was allowed to cool to room temperature and was washed with 5% NaOH solution, and the aqueous phase was extracted with Et_2O. The organic phase was dried over anhydrous K_2CO_3. Solvents were removed under reduced pressure, resulting in 11.54 g of liquid (97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (s, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 5.97 (s, 1H, benzyl-H), 5.75 (s, 1H, benzyl-H), 4.42 (s, 2H, O−CH_2), 4.20 (s, 1H, O−CHRR′), 4.09 (s, 2H, O−CH_2), 3.89 (s, 1H, O−CHRR′), 3.58 (m, 4H, CH_2Cl).

Synthesis of 2,2′-(1,4-phenylene)bis(4-methylene-1,3-dioxolane) (3). To a stirred solution of 14.51 g potassium *tert*-butoxide (0.129 mol) in 50 mL THF was added 11.54 g of **2** (0.036 mol) at room temperature under N_2. After completion of the addition, the reaction was stirred at 70 °C for 20 h. The reaction mixture was allowed to cool to room temperature, and the precipitate was removed by suction filtration. Subsequently, the solvent was removed under reduced pressure and the filtrate was washed with saturated $NaHCO_3$. The aqueous phase was extracted with Et_2O. The organic phase was dried over anhydrous K_2CO_3 and stored over anhydrous K_2CO_3. The solvents were removed under reduced pressure, affording 7.32 g of solid (82% yield), with a mp of 64 °C. ^{1}H NMR (300 MHz, benzene-d_6): δ 7.42 (s, 2H, Ar−H), 7.13 (s, 2H, Ar−H), 5.83 (s, 2H, benzyl-H), 4.48 (q, 2s, O−CH_2), 4.25, 4.20, 4.10, 4.03 (4 q, 4H, =CH_2), 3.70 (q, 2s, O−CH_2). GC/MS (70 eV, EI): *m/z* 85.05 (29.7%), 89.00 (21.7%), 91.00 (46.9%), 103.00 (15.9%), 105.05 (18.2%), 131.00 (19.0%), 133.00 (23.5%), 175.00 (28.1%), 246.00 (M^+, 100%), 247.00 (M + 1, 17.8%). High-resolution MS: calcd M^+, 246.0892; observed accurate M^+, 246.0882. UV−vis (THF): λ_{max} = 238 nm.

Photoinitiated Polymerization of 3 with Tris(4-methylphenyl)sulfonium Hexafluoroantimonate. In a sealed quartz tube, a mixture of 103.3 mg of **3** (0.42 mmol) and 0.8 mg of tris(4-methylphenyl)sulfonium hexafluoroantimonate (0.0015 mmol, 35.7 mol%) was irradiated with an UV lamp at 45 °C for 20 min. The resulting cross-linked homopolymer was washed with THF and filtered. The brittle solid was dried in vacuo, affording 15.5 mg (15%) of polymer; T_g = 67 °C.

Photoinitiated Copolymerization of 4-Methylene-2-phenyl-1,3-dioxolane (1) and 3. Three copolymers were synthesized following the same procedure but varying the mole ratios of comonomers.

Photoinitiated Copolymerization of 1 with 3 in a 10:1 Mole Ratio. In a sealed quartz tube, a mixture of 176.1 mg of **1** (1.09 mmol), 27.1 mg of **3** (0.1 mmol), and 1.1 mg of tris-(4-methylphenyl)sulfonium hexafluoroantimonate (0.002 mmol, 0.17 mol %) was irradiated with an UV lamp at room temperature for 40 min. The resulting cross-linked polymer was washed with CH_2Cl_2 and filtered. The brittle, solid material was dried in vacuo, affording 134.9 mg (66%) of polymer; T_g = 52 °C. FT-IR (cm^{-1}): 3031, 2922, (H−C−H), 1728 (ν(C=O)), 1612, 1502 ($\nu_{aromatic}$(C=C)), 1114, 1025 (ν(C−O)); T_g = 35 °C.

Photoinitiated Copolymerization of 1 with 3 in a 5:1 Mole Ratio. A mixture of 204.0 mg of **1** (1.26 mmol), 60.0 mg of **3** (0.24 mmol), and 1.1 mg of tris(4-methylphenyl)-sulfonium hexafluoroantimonate (0.002 mmol, 0.14 mol%) was irradiated for 40 min. The polymerization afforded 146 mg (55%) of solid; T_g = 66 °C.

Photoinitiated Copolymerization of 1 with 3 in a 2:1 Mole Ratio. A mixture of 201.0 mg of **1** (1.24 mmol), 152.0 mg of **3** (0.62 mmol), and 0.18 mg of tris(4-methylphenyl)-sulfonium hexafluoroantimonate (0.0033 mmol, 0.18 mol%) was irradiated for 40 min. The polymerization afforded 216.3 mg (61%) of solid polymer; T_g = 67 °C.

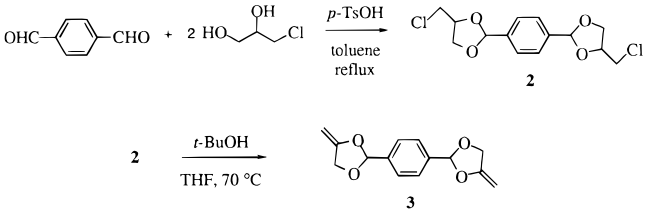
Photoinitiated Copolymerization of 1 with 3 in a 10:1 Mole Ratio Using (4-decyloxyphenyl)phenyliodonium Hexafluoroantimonate as Initiator. In a sealed quartz tube, a mixture of 164 mg of **1** (1.01 mmol), 25.0 mg of **3** (0.10 mmol), and 1.4 mg of (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate (0.0032 mmol, 0.29 mol%) was irradiated with an UV lamp, filtered through Pyrex, and held at room temperature for 20 min. The resulting cross-linked polymer was washed with THF and filtered. The brittle solid material was dried in vacuo, affording 182.4 mg (96 %) of polymer; T_g = 53 °C.

Photoinitiated Copolymerization of 1 with 2,3-Dihydrofuran and 3 in a 5:1:1 Mole Ratio. In a sealed quartz tube, a mixture of 203.3 mg of **1** (1.25 mmol), 19.0 mg of DHF (0.27 mmol), 59 mg of **3** (0.24 mmol), and 1.5 mg of tris(4-methylphenyl)sulfonium hexafluoroantimonate (0.0028 mmol, 0.16 mol %) was irradiated with an UV lamp at room temperature for 40 min. The resulting cross-linked polymer was washed with THF and filtered. The solid was dried in vacuo, affording 235.3 mg (84%) of polymer; T_g = 59 °C.

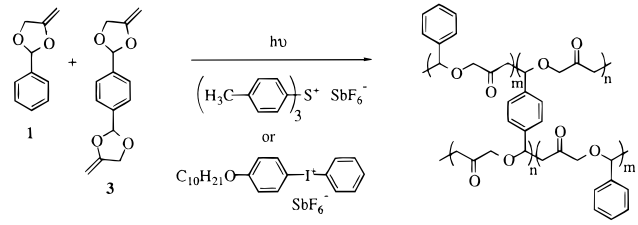
Results and Discussion

A strategy involving cross-linking was pursued in order to increase the T_g of polymers derived from the cationic ring-opening polymerization of dioxolane **1**. Difunctional dioxolane **3** was synthesized as a cross-linking agent. Though this compound had been previously reported, synthetic details are sparse and only a boiling point was given.[10,24] The synthesis of **3** was accomplished via a two-step synthesis, illustrated in Scheme 3. The ^{1}H NMR spectrum of **3** is shown in Figure 1. Exocyclic methylene resonances were observed as quartets at 4.25, 4.20, 4.10, and 4.03 ppm,

Scheme 3



Scheme 4



benzylic protons were observed as a singlet at 5.83 ppm, and the methylene absorptions appeared as quartets at 4.48 and 3.70 ppm. Dioxolane **3** was found to melt sharply at 64 °C.

To confirm formation of **3**, the molecular ion for **3** was recorded by GC/MS at *m/z* 246.00 (M^+, 100% relative abundance), while the observed accurate mass of 246.0882 (M^+) was secured by high resolution MS (calcd $M^+ = 246.0892$). Dioxolane **3** had $\lambda_{max} = 238$ nm. Thus, the difunctional dioxolane cross-linker **3** was expeditiously obtained from commercially available starting materials in just two steps. Dioxolane **3** can easily be recrystallized and is stable upon storage at low temperature in the dark. It should be noted, however, that both **1** and **3** readily undergo polymerization and isomerization, presumably a 1,3-hydrogen shift, upon exposure to acid. Thus, glassware was soaked in NH_4OH before use. Even the residual DCl in $CDCl_3$ caused significant isomerization, necessitating the use of benzene-d_6 as NMR solvent.

Previous results from this laboratory on photoinitiated cationic homo- and copolymerizations of dioxolane **1** revealed exclusive addition/ring-opening polymerization occurred, providing soluble poly(ether ketone)s with T_gs in the range of 26−35 °C, illustrated in Scheme 1.[23] ^{1}H NMR analysis of **P-1** indicated an absence of olefinic methylene hydrogens, demonstrating no olefinic ($=CH_2$) moieties were present in the polymer, lending credence to an addition/ring-opening process.[23] In a similar manner, the homopolymerization of **3** was carried out photochemically, using tris(4-methylphenyl)sulfonium hexafluoroantimonate as initiator, in the bulk with the sample heated to 45 °C in a silicon oil bath. As expected, a cross-linked material was obtained that was not soluble in common organic solvents, having a T_g of 67 °C. Due to the predominance of addition/ring-opening of **1**, under photoinitiated cationic conditions, difunctional dioxolane **3** likely undergoes the same process, a feature verified by the virtually identical IR spectra of **P-1** and the polymer of **3**. A clear increase in T_g was indeed realized through the use of the dioxolane cross-linker relative to the homopolymer of **1** (**P-1**).

Copolymerizations of dioxolane **1** with dioxolane cross-linker **3** were conducted with 10:1, 5:1, and 2:1 mole ratios of **1** and the difunctional dioxolane **3**, respectively, using tris(4-methylphenyl)sulfonium hexafluoroantimonate as initiator and 40 min photolysis times (Scheme 4). The cross-linked polymers were characterized by DSC and had T_gs ranging from 52 to

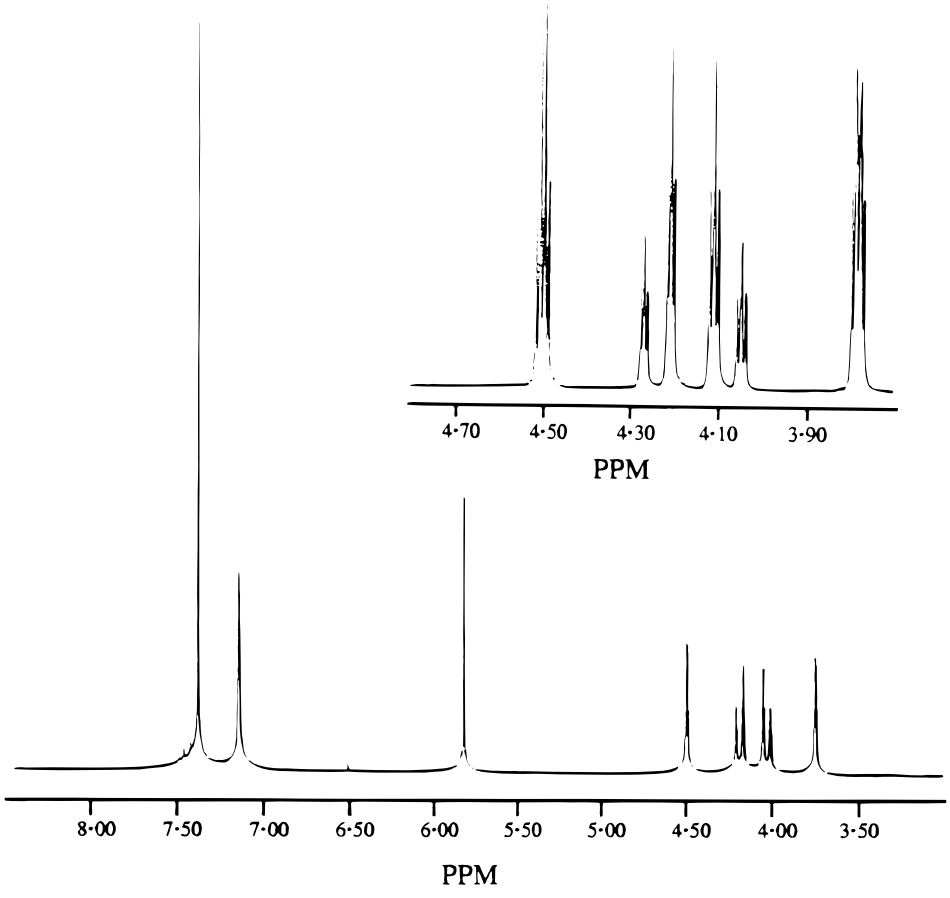


Figure 1. 300 MHz NMR spectrum of **3** in benzene-d_6. The inset is an expansion from 3.68 to 4.80 ppm.

Table 1. Data for the Copolymerization of 1 with 3 Using Tris(4-methylphenyl)sulfonium Hexafluoroantimonate

1/3 (mol ratio)	% yield	T_g (°C)
10:1	66	52
5:1	55	66
2:1	61	67

67 °C (Table 1). As expected, the glass transition temperature for the 10:1 mixture was the lowest, since this contained more of comonomer **1** relative to the other samples (the T_g of homopolymer **P-1** is 25−36 °C, depending on molecular weight). Isolated yields were comparable for all three ratios. FT-IR spectroscopic characterization confirmed formation of a poly(ether ketone) with carbonyl stretching observed at 1728 cm^{-1}, characteristic of a ketone carbonyl. Aromatic C=C stretching occurred at 1612 and 1502 cm^{-1}, while ether C−O stretching/bending was recorded at 1114 and 1025 cm^{-1}. The IR spectrum provided compelling evidence of poly(ether ketone) formation.

When the copolymerization was carried out on a 10:1 mole ratio of **1** to **3**, for a shorter photolysis time (20 min) using (4-decyloxyphenyl)phenyliodonium hexafluoroantimonate as initiator and filtering the UV radiation through a Pyrex filter, a higher yield was obtained (96%). The sulfonium salt used in this study has an absorption band from 215 to 280 nm while the absorption band for **3** ranges from 200 to 290 nm. On the other hand, the iodonium salt used here has an absorption band that extends out to 340 nm, and is effective as an initiator using longer wavelength UV radiation. Thus, the difunctional dioxolane competes with the sulfonium initiator in absorption of UV light, leading to lower yields, while use of the iodonium salt resulted in a higher yield of polymer since its absorption spectrum extends to longer wavelength.

Photoinitiated copolymerization of **1** with 2,3-dihydrofuran (DHF) and **3** was conducted using 5:1:1 mole ratios, respectively, in bulk at room temperature with tris(4-methylphenyl)sulfonium hexafluoroantimonate. An insoluble copolymer was formed in 84% yield with a T_g of 59 °C. Judicious choice of both comonomers and comonomer/dioxolane ratio should afford control of cross-link density and T_g.

Conclusions

Details of the synthesis and characterization of dioxolane cross-linking agent **3** were presented. A difunctional dioxolane cross-linker, **3**, was synthesized in just two steps from commercially available starting materials. This difunctional dioxolane was successfully copolymerized with the monofunctional analog **1** via photoinitiated cationic polymerization with either a sulfonium or an iodonium salt as the photoinitiator. Polymers with T_gs substantially higher (up to 30 °C higher) than the homopolymer, derived from the cationic ring-opening polymerization of **1**, were obtained. Yields of polymerizations were generally high. Copolymerization of **1** and **3** with a cyclic vinyl ether afforded a cross-linked material with a T_g of 59 °C, demonstrating the versatility of **3**.

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References and Notes

(1) Jacobs, P. F. *Rapid Prototyping and Manufacturing, Fundamentals of Stereolithography*; Society of Manufacturing Engineers: Dearborn, MI, 1992.
(2) Bailey, W. J. *J. Macromol. Sci., Chem.* **1975**, *9*, 849.
(3) Sanda, F.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Educ.* **1994**, *32*, 2517.
(4) Belfield, K. D.; Zhang, G. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1996**, *37* (1), 537.
(5) See, e.g., Belfield, K. D.; Abdelrazzaq, F. B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (1), 539.
(6) Bolln, C.; Frey, H.; Mulhaupt, R. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 587.
(7) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.
(8) Crivello, J. V.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3951.
(9) Fukuda, H.; Hirota, M.; Nakashima, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 171.
(10) Orth, H. *Angew. Chem.* **1952**, *64*, 544.
(11) Goodman, M.; Abe, A. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 3471.
(12) Dietrich, H. J. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2255.
(13) Akkapeddi, M. K.; Reimschuessel, H. K. *Macromolecules* **1979**, *12*, 827.
(14) Bailey, W. J. In *Comprehensive Polymer Science*; Eastmond, G. C.; Ledwith, A.; Russo, S., Sigwalt, P., Eds.; Pergamon: Oxford, England 1989; pp 283−320.
(15) Fukuda, H.; Hirota, M.; Nakashima, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1401.
(16) Park, J.; Kihara, N.; Ikeda, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1083.
(17) Park, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1141.
(18) Park, J.; Kihara, N.; Kobayashi, M.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 199.
(19) Park, J.; Yokozawa, T.; Endo, T. *Makromol. Chem.* **1993**, *194*, 2017.
(20) Kim, T.-M.; Kim, Y.; Gong, M. S. *Macrmol. Chem., Rapid Commun.* **1994**, *15*, 639.
(21) Lee, S.-J.; Park, J.-K.; Gong, M. S. *Bull. Korean Chem. Soc.* **1995**, *16*, 769.
(22) See, e.g.: Belfield, K. D.; Zhang, G. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1995**, *36* (2), 269.
(23) Belfield, K. D.; Abdelrazzaq, F. B. *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 2207.
(24) Reed, B.; Stansbury, J.; Antonucci, J. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1992**, *33* (2), 520.

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