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Spiro Orthocarbonate Undertaking Radical and Cationic Polymerization

Takeshi Endo,* Shigenobu Maruoka, and Tsutomu Yokozawa

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan. *Received January 16, 1987*

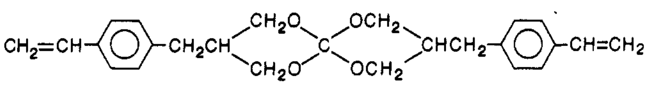
ABSTRACT: For the synthesis and design of materials which expand upon polymerization or curing, a spiro orthocarbonate containing radically polymerizable groups, 3,9-diallyl-1,5,7,11-tetraoxaspiro[5.5]undecane (2), was prepared, and radical polymerization and cationic polymerization of 2 were investigated, respectively. In the radical polymerization of 2, soluble polymer 4 bearing the spiro orthocarbonate moieties was obtained by the selective vinyl polymerization of one double bond with 9.9% shrinkage in volume. The soluble poly(ether carbonate) 5 bearing the diallyl moieties was obtained by the cationic ring-opening reaction of the spiro orthocarbonate moieties of 2 with 4.7% expansion. Further, soluble polymer 4 when treated with a cationic initiator afforded cross-linked polymer 6 with 1.8% expansion. On the other hand, when soluble polymer 5 was treated with a radical initiator, cross-linked polymer 7 with 12.8% shrinkage was obtained.

Introduction

Commercially available monomers such as styrene or methyl methacrylate and thermosetting resins such as epoxy or phenol resins are known to undergo a pronounced shrinkage when they polymerize or cure, and therefore this phenomenon causes serious fabrication problems. Thus, we reported that spiro orthocarbonates are cationically polymerized with expansion during polymerization to give poly(ether carbonate).[1-5]

For a potential use of spiro orthocarbonates in the area of industrial materials, we wish to propose a spiro orthocarbonate containing a radically polymerizable group that can introduce the spiro orthocarbonate moieties to commercially available polymers after radical copolymerization with vinyl monomers and that can be expected to undergo curing with expansion by the cationic ring-opening transfer reaction of the spiro orthocarbonate moieties.

In our previous paper,[6] we reported the synthesis and polymerization of a spiro orthocarbonate containing distyryl units, 3,9-bis(4-vinylbenzyl)-1,5,7,11-tetraoxaspiro[5.5]undecane (1), that gave cross-linked polymers by either radical or cationic polymerization. Herein we wish to report the synthesis and polymerization of diallyl spiro orthocarbonate, 3,9-diallyl-1,5,7,11-tetraoxaspiro[5.5]undecane (2), which can give soluble polymers by either radical or cationic polymerization. These soluble polymers can give cross-linked polymers by cationic or radical initiation, respectively. Further, the present paper describes the evaluation of volume changes of 2 and soluble polymers during polymerization and cross-linking, respectively.



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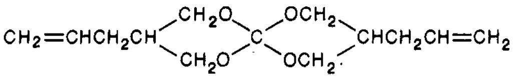

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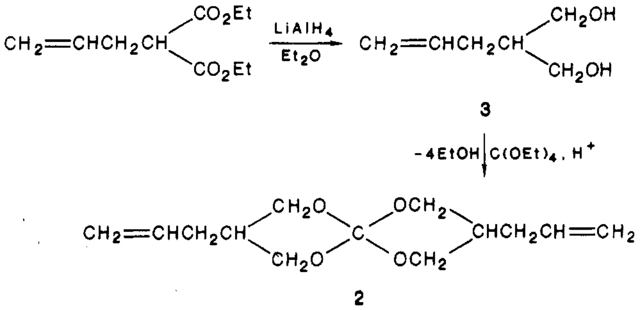
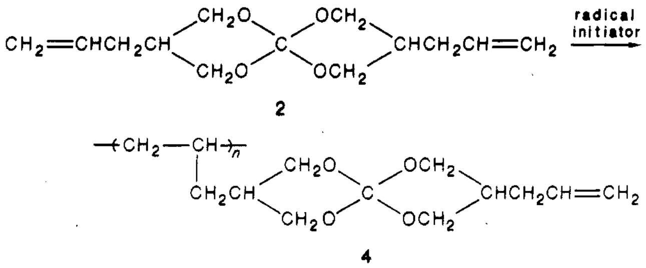
Results and Discussion

Synthesis of Diallyl Spiro Orthocarbonate 2. Diallyl spiro orthocarbonate 2 was prepared from commercially available diethyl allylmalonate in two steps. The reduction of diethyl allylmalonate with lithium aluminum hydride ($LiAlH_4$) in ether afforded diol 3 in 80% yield. Diol 3 was then reacted with tetraethyl orthocarbonate in the presence of *p*-toluenesulfonic acid to afford diallyl spiro orthocarbonate 2 (Table I). The reaction was first carried out in dibutyl phthalate (DBP) according to the procedure reported previously.[7] However, 2 could not be separated from DBP by distillation because the boiling point of 2 was close to that of DBP. When the reaction was carried out in diglyme, 2 was obtained in 74% yield. When 3 was allowed to react with tetraethyl orthocarbonate in bulk in the presence of an acid catalyst, 2 was formed in 95% yield.



Radical Polymerization of 2. Radical polymerization of 2 was carried out with azobis(isobutyronitrile) (AIBN) or di-*tert*-butyl peroxide (DTBP) as radical initiators (Table II). In bulk polymerization, 2 was hardly converted to polymer with AIBN at 60 °C, whereas cross-linked polymer was obtained with DTBP at 120 °C. However, soluble polymer 4 was formed by solution polymerization in benzene with DTBP at 120 °C.



The IR spectrum of polymer 4 showed the characteristic absorptions of a spiro orthocarbonate at 1205 and 1005 cm^{-1}, and an absorption attributable to an allyl group (C=C) at 1640 cm^{-1} was also observed. In the ^1H NMR spectrum of polymer 4, the signals corresponding to the spiro protons were not changed, while the intensity of the signals corresponding to the allyl protons was reduced to one-half the initial intensity. Further, the signal assignable to the methylene and methine protons of the repeating polymerized allyl (C=C) units appeared at δ 0.8-2.9. These facts clearly indicate that polymer 4 consisted of a chain structure obtained by the selective polymerization of one of the double bonds in 2.

Cationic Polymerization of 2. Cationic polymerization of 2 was carried out with BF_3OEt_2, $SnCl_4$, $GeCl_4$, and a

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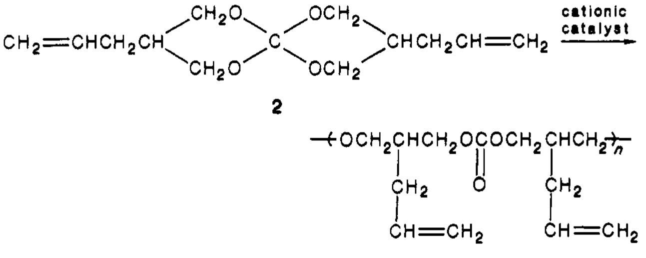
Table I
Preparation of Diallyl Spiro Orthocarbonate 2

entry	solvent	temp, °C	time, h	yield, %
1	DBP[a]	110	9	b
2	diglyme	110	9	74
3		110	9	95

[a] Dibutyl phthalate. [b] 2 could not be separated from the solvent.

benzylsulfonium salt[8] as cationic catalysts. The results are summarized in Table III. BF_3OEt_2, $SnCl_4$, and the benzylsulfonium salt were effective for polymerization of 2 at 120 °C, whereas $GeCl_4$ and the benzylsulfonium salt used at 100 °C were not as effective. High molecular weight polymer of 5 was obtained with BF_3OEt_2, while the benzylsulfonium salt gave a low molecular weight polymer of 5 although the yield was high.



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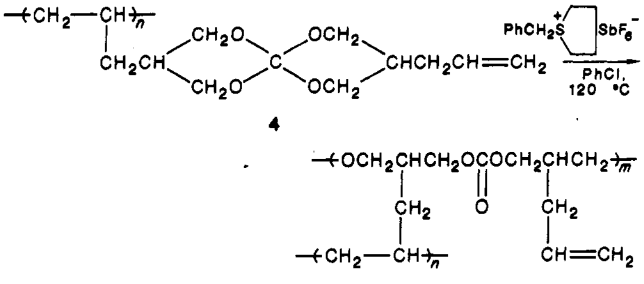
5

The IR spectra of polymer 5 showed the characteristic absorptions of a linear carbonate at 1745 and 1255 cm^{-1} and an absorption attributable to an allyl group (C=C) at 1640 cm^{-1}. In the ^1H NMR spectra of polymer 5, the signals corresponding to the allyl protons were not changed. Further, the signal assignable to the methylene protons on a carbon atom adjacent to an oxycarbonyloxy moiety at δ 4.0–4.3 and the signal assignable to the methylene protons on a carbon atom of an ether linkage at δ 3.3–3.6 were observed. From these spectral data, polymer 5 consisted of a poly(ether carbonate) structure bearing the diallyl moieties, which was formed by the selective cationic ring-opening polymerization of the spiro orthocarbonate moiety, similar to that of unsubstituted spiro orthocarbonates.[1-4]

Cross-Linking of Polymers 4 and 5. To demonstrate the utility of monomer 2 as functionalized materials which expand upon polymerization or curing, we attempted the cross-linking of polymers 4 and 5. Polymer 4 was treated with a benzylsulfonium salt as a latent thermal cationic catalyst in chlorobenzene at 120 °C for 18 h to afford cross-linked polymer 6 in 88% yield by ring-opening polymerization of the spiro orthocarbonate function. In the IR spectrum of 6, two characteristic absorptions of a spiro orthocarbonate moiety of polymer 4 at 1205 and 1005 cm^{-1} disappeared almost completely, whereas absorptions attributable to a linear carbonate at 1745 and 1250 cm^{-1} were observed. These facts indicate that substantially all the spiro orthocarbonate moieties of polymer 4 underwent the ring-opening reaction to give cross-linked polymer 6 containing the carbonate and ether groups.



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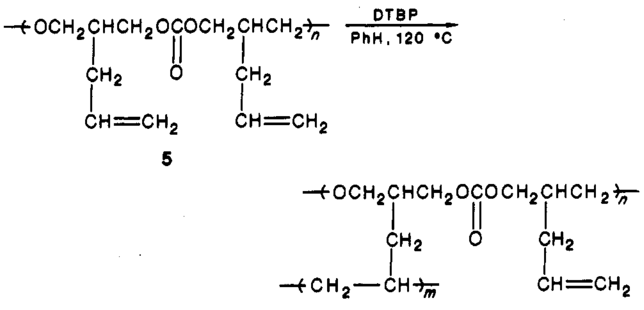
cross-linked polymer 6



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cross-linked polymer 7

Further, polymer 5 was heated in benzene in the presence of DTBP as radical initiator at 120 °C for 18 h to give cross-linked polymer 7 in 78% yield, which was presumably formed by the polymerization of some of the allyl moieties of 5.

Evaluation of the Volume Change during Polymerization and Cross-Linking. The volume change on formation of 2 and soluble polymers 4 and 5 during polymerization and their cross-linking should be noted on the basis of the measured densities of 2 and polymers 4–7, respectively (Scheme I). As indicated in Scheme I, spiro orthocarbonate 2 affords soluble polymer 4 by radical

Table II
Radical Polymerization of 2

entry	initiator (mol %)	solvent	temp, °C	time, h	yield, %[a]	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
1	AIBN (3)	bulk	60	48	3[c]		
2	DTBP (3)	bulk	120	24	24[c,d]		
3	DTBP (3)	benzene[e]	120	48	34[c]	9980	2.36

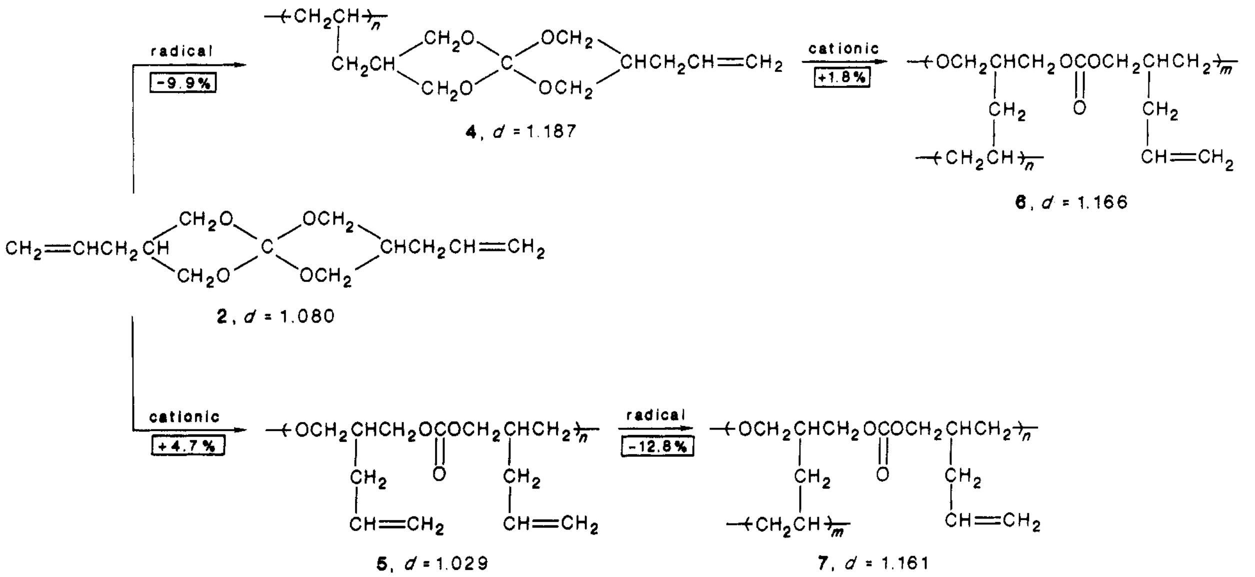
[a] Insoluble in n-hexane. [b] By GPC calibrated with standard polystyrene. [c] Monomer was recovered from the part soluble in n-hexane. [d] Cross-linked polymer. [e] [monomer] = 50 wt %.

Table III
Cationic Polymerization of 2[a]

entry	initiator	(mol %)	temp, °C	time, h	yield, %[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	BF_3OEt_2	(3)	120	24	42[d]	15400	3.49
2	$SnCl_4$	(3)	120	24	38[d]	4900	3.37
3	$GeCl_4$	(3)	120	24	3[e]		
4	f	(2)	120	24	58[d]	3530	3.46
5	BF_3OEt_2	(2)	60	24	29[e]	5670	1.72
6	f	(2)	100	24	4[d]		

[a] Bulk polymerization. [b] Insoluble in n-hexane. [c] By GPC calibrated with standard polystyrene. [d] Oligomer was obtained from the part soluble in n-hexane. [e] Monomer was recovered from the part soluble in n-hexane. [f] S-Benzyltetrahydrothiophenonium hexafluoroantimonate.

Scheme I



polymerization with 9.9% shrinkage and soluble polymer **5** by cationic polymerization with 4.7% expansion, respectively. In the cross-linking process, soluble polymer **4** affords cross-linked polymer **6** by cationic initiation with 1.8% expansion, and soluble polymer **5** gives cross-linked polymer **7** with 12.8% shrinkage. It is demonstrated, in this way, that the spiro orthocarbonate functionality undergoes expansion not only on polymerization but also on cross-linking and, further, monomer **2** can control volume change in the polymerization and cross-linking by the initiation methods.

Experimental Section

Solvents. Diethyl ether, dibutyl phthalate (DBP), diglyme, benzene, and chlorobenzene were purified by distillation. Commercially available *p*-toluenesulfonic acid monohydrate was dehydrated by heating at 100 °C for 6 h in vacuo. Tetraethyl orthocarbonate was prepared from chloropicrin and sodium ethoxide according to the reported procedure.[9] *S*-Benzyltetrahydrothiophenonium hexafluoroantimonate was prepared according to the previously reported method.[10]

^{1}H NMR spectra were obtained on a JEOL PMX-60. FTIR spectra were recorded on a JASCO FT/IR-3. Elemental analysis was performed on a Yanaco CHNcorder MT-2. The average molecular weight and the molecular weight distribution of polymers were measured with a Waters 6000-A GPC unit using μ-Styregel columns, and the eluent was tetrahydrofuran. The densities of monomer **2** and polymer **5** were measured with a 5 ϕ-in.-diameter glass tube calibrated with the density of water. The densities of polymers **4**, **6**, and **7** were measured with a density measurement apparatus by ASTM Based Density Gradient method (Shibayama Scientific Co., Ltd.).

Synthesis of Diallyl Spiro Orthocarbonate 2. To a suspension of $LiAlH_4$ (11.89 g, 313.3 mmol) in absolute ether (300 mL), a solution of diethyl allylmalonate (24.88 g, 124.3 mmol) in absolute ether (10 mL) was added dropwise at room temperature. After the addition, the mixture was refluxed for 1 h and stirred overnight at room temperature. A saturated sodium sulfate solution was slowly added to the reaction mixture. A white mass was filtered and the filtrate was evaporated. The residue was fractionally distilled to obtain diol **3** (11.51 g, 80% yield, bp 90–93 °C/1 torr). Diol **3** (13.68 g, 117.8 mmol) and tetraethyl orthocarbonate (11.33 g, 58.9 mmol) were heated at 110 °C for 9 h in the presence of anhydrous *p*-toluenesulfonic acid (0.12 g); the theoretical amount of ethanol was collected in a trap. Triethylamine (0.24 mL) was added, and the solution was allowed to stand at room temperature overnight. The reaction mixture was fractionally distilled to obtain diallyl spiro orthocarbonate **2** (13.45 g, 95% yield): bp 128–131 °C/0.10 torr; IR (neat) 1640, 1205, 1005 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83–2.23 (m, 2 H), 2.03 (d, J = 5.6 Hz, 4 H), 3.48–4.22 (m, 8 H), 4.87–5.18 (m, 4 H), 5.44–6.09 (m, 2 H). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98%; H, 8.39%. Found: C, 65.15%; H, 8.53%.

Radical Polymerization of 2. The following general procedure is described using entry 3 in Table II as a typical example. Polymerization of **2** was carried out in a sealed tube. Monomer **2** (0.50 g, 2.08 mmol) was polymerized in benzene (0.50 g) using DTBP (6.0 mg, 2 mol %) as initiator at 120 °C for 48 h. The polymer was purified by dissolution in methylene chloride, followed by reprecipitation with *n*-hexane to give polymer **4** (0.16 g, 34% yield): IR (KBr) 1640, 1205, 1005 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.9 (br, 3 H), 1.1–1.6 (br, 2 H), 1.8–2.4 (br, 4 H), 3.5–4.3 (br, 8 H), 4.8–5.4 (br, 2 H), 5.4–6.2 (br, 1 H). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98%; H, 8.39%. Found: C, 64.08%; H, 8.48%.

Cationic Polymerization of 2. A typical polymerization (entry 1 in Table III) was performed as follows. Monomer **2** (0.68 g, 2.84 mmol) was polymerized in bulk in the presence of BF_3OEt_2 (12 mmg, 3 mol %) at 120 °C for 24 h in a sealed tube. The polymer was purified by dissolution in dichloromethane, followed by reprecipitation with *n*-hexane to give polymer **5** insoluble in *n*-hexane (0.31 g, 46% yield). The *n*-hexane layer was concentrated under reduced pressure, yielding oligomer soluble in *n*-hexane (0.34 g, 49% yield). Insoluble polymer: IR (neat) 1745, 1640, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.7–2.4 (br, 6 H), 3.3–3.6 (br, 4 H), 4.0–4.3 (br, 4 H), 4.9–5.2 (br, 4 H), 5.5–6.2 (br, 2 H). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98%; H, 8.39%. Found: C, 64.26%; H, 8.50%.

Cross-Linking of Polymer 4. Cross-linking of **4** (0.20 g) was carried out in chlorobenzene (1.00 g) in the presence of benzyltetrahydrothiophenonium hexafluoroantimonate (7.0 mmg, 2 mol % based on the spiro orthocarbonate) at 120 °C for 18 h in a sealed tube. The reaction mixture was poured into agitated methanol. The washed polymer was dried under reduced pressure to afford cross-linked polymer **6** (0.18 g, 83% yield): IR (KBr) 1745, 1640, 1250 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98%, H, 8.39%. Found: C, 63.63%, H, 8.40%.

Cross-Linking of Polymer 5. Cross-linking of **5** (0.20 g) was carried out in benzene (1.02 g) in the presence of DTBP (4.0 mg, 1.6 mol % based on the allyl groups) at 120 °C for 18 h in a sealed tube. Cross-linked polymer **7** was isolated by pouring the reaction mixture into agitated methanol, followed by drying under reduced pressure (0.16 g, 78% yield): IR (KBr) 1745, 1640, 1255 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98%; H, 8.39%. Found: C, 63.39%; H, 8.36%.

Registry No. **2**, 110374-62-4; **2** (homopolymer), 110374-63-5; **3**, 42201-43-4; $H_2C{=}CHCH_2CH(CO_2Et)_2$, 2049-80-1; $C(OEt)_4$, 78-09-1; $C(OET)_4$, 78-09-1.

References and Notes

(1) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1735.
(2) Endo, T.; Bailey, W. J. *Makromol. Chem.* **1975**, *176*, 2897.

(3) Endo, T.; Bailey, W. J. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2525.
(4) Endo, T.; Katsuki, H.; Bailey, W. J. *Makromol. Chem.* **1976**, *177*, 3231.
(5) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416.
(6) Endo, T.; Maruoka, S.; Yokozawa, T. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(7) Endo, T.; Okawara, M. *Synthesis* **1984**, 837.
(8) Endo, T.; Arita, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 137.
(9) Rabjohn, N. *Organic Syntheses*; Wiley: New York **1963**, *Coll. Vol. 4*, 457.
(10) Endo, T.; Uno, H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 359.

Hydrogen Iodide/Zinc Iodide: A New Initiating System for Living Cationic Polymerization of Vinyl Ethers at Room Temperature[1]

Mitsuo Sawamoto, Chihiro Okamoto, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received April 30, 1987*

ABSTRACT: Zinc iodide in conjunction with hydrogen iodide (HI/ZnI_2) as an initiating system led to living cationic polymerization of isobutyl vinyl ether in toluene in a wide temperature range from −40 °C to above room temperature (+40 °C) or in methylene chloride below 0 °C. The HI/ZnI_2 system also induced living polymerization of an ester-functionalized vinyl ether (2-acetoxyethyl vinyl ether) in methylene chloride at −15 °C. In all cases, the number-average molecular weight of the polymers increased in direct proportion to monomer conversion and further increased on addition of a fresh feed of monomer at the end of the first-stage polymerization. The molecular weight distribution of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$) throughout the reaction. The polymer molecular weights at the same conversion were inversely proportional to the initial concentration of hydrogen iodide, whereas they were independent of the initial ZnI_2 concentration. The overall polymerization rate, however, progressively increased with increasing concentration of the zinc salt. It was proposed that ZnI_2, as a weak Lewis acid, electrophilically activates the hydrogen iodide derived CH–I terminal of the growing polymer and thereby induces living propagation, as iodine does in the living polymerization initiated by the hydrogen iodide/iodine system.

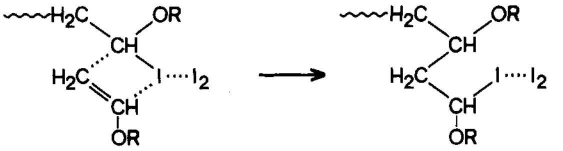
Introduction

A mixture of hydrogen iodide and iodine (HI/I_2) as an initiating system effectively polymerizes vinyl ethers[2] and related vinyl compounds to yield living polymers with a controlled molecular weight and a narrow molecular weight distribution (MWD).[3] Our spectroscopic[4] and kinetic[4,5] studies on the mechanism of these living processes demonstrated that hydrogen iodide generates the growing end, whereas iodine assists its living propagation. Specifically, hydrogen iodide, as an *electrophile*, quantitatively forms a 1:1 adduct [$CH_3CH(OR)$–I; R = alkyl, etc.] with a vinyl ether monomer at the initial stage of polymerization. Although the adduct per se is too stable to initiate vinyl ether polymerization, coexisting iodine electrophilically "activates" (dissociates or polarizes) its carbon–iodine (CH–I) bond and thereby allows the incoming monomer to add into the activated terminal linkage. Repetition of such an activation/addition process leads to living polymers bearing a CH–I terminal [~~~$CH_2CH(OR)$–I] that can in turn be activated by iodine to continue living propagation (eq 1).[5,6] Thus, iodine herein acts as a *Lewis acid* (electron acceptor).

A working hypothesis immediately drawn from this mechanism is that not only the HI/I_2 system but other appropriate combinations of an electrophile and a Lewis acid as well may serve to initiate living cationic polymerization of vinyl monomers. For these binary initiating systems, the electrophile should be such that it forms a stable yet potentially reactive propagating end corresponding to the terminal CH–I unit in the HI/I_2-initiated living polymer; the Lewis acid component should be suitably electrophilic so as to selectively activate the terminal group without inducing cationic polymerization by itself. We recently decided to pursue such binary initiating systems and to establish the scope of *electrophile/Lewis acid* combinations for living cationic polymerization.

In this first study of our series,[1] we selected zinc iodide (ZnI_2) as a Lewis acid to replace iodine in the HI/I_2 initiating system. Among zinc(II) halides, ZnI_2 has been employed least frequently as catalyst or initiator in Friedel–Crafts and related electrophilic reactions including cationic polymerization.[7] No report is thus far available for living cationic polymerization mediated by this iodide. More extensive use is found for zinc chloride and bromide;[7,8] quite recently they were utilized to initiate the group transfer (or "monomer cleavage") polymerization of trialkylsilyl vinyl ethers.[9]

Like iodine, ZnI_2 may interact electrophilically with the growing CH–I terminal, derived from hydrogen iodide, and may thus trigger living polymerization of vinyl ethers and other related monomers. Equations 1 and 2 visualize the expected similarity between the HI/I_2 and HI/ZnI_2 initiating systems. As described in this paper, we found the combination of hydrogen iodide and ZnI_2, as an electrophile/Lewis acid initiating system, to induce living cationic polymerizations of isobutyl vinyl ether (IBVE) and 2-acetoxyethyl vinyl ether (AcOVE; $CH_2{=}CHOCH_2CH_2OCOCH_3$). A particular advantage of the HI/ZnI_2 system over HI/I_2 is that it enables the synthesis



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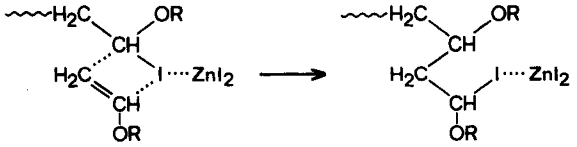

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