

Scheme 2.

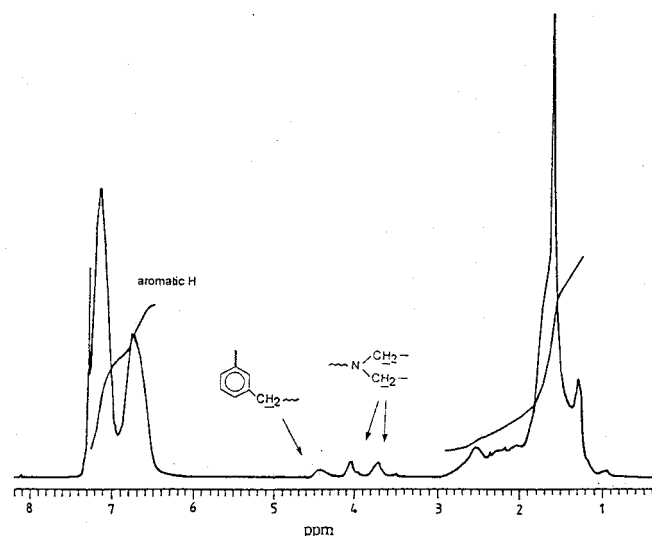


Figure 1. Proton NMR spectrum of styrene copolymer.

Copolymerization of styrene with *m*-chloromethylstyrene was carried out at first using azobisisobutyronitrile (AIBN) in toluene at 70 °C, followed by the reaction with sodium *N,N*-diethylthiocarbamate dissolved in acetone for 10 hr at room temperature.⁴ The resulting polymer was then isolated by precipitation into methanol. It was found that the chloride group was converted into the dithiocarbamate group quantitatively by proton NMR analysis. As shown in Figure 1, the chemical shifts at 4.4 and 3.9 ppm correspond to resonances of $-\text{Ph}-\text{CH}_2-$ and $-\text{S}-\text{C}(=\text{S})-\text{N}(\text{CH}_2\text{CH}_3)_2$, respectively, with integral ratio of 1:2. Peak splitting at about 3.9 ppm arises from hindered rotation around the C-N bond.

From the integration of the NMR peaks content of the dithiocarbamate group was determined. This determination method, on the other hand, have not been used extensively. Instead, many researchers relied on elemental sulfur analysis⁵ or UV spectroscopy.⁶ The NMR characterization method in this study was sensitive enough to determine the functionalities of polystyrene prepared by various methods. Telechelic polystyrene prepared by thermal homolysis of tetraethylthiuram disulfide showed functionality of almost 2.0 as predicted^{3,7} when the number average molecular weight was 18,100 determined by gel permeation chromatography. When polystyrene was prepared by initiation of AIBN in the presence of diethylthiuram disulfide,^{7,8} functionality was ranged from

1.0 to 2.0.

Because the second step gives quantitative conversion easily, this one-pot synthesis has a couple of advantages. Omitted preparation step of the dithiocarbamate containing monomer eliminate a rather tedious purification step,⁹ and this makes the synthesis more convenient and less time consuming. One can avoid chain transfer reactions between dithiocarbamate groups and free radical species during copolymerization. Besides, it is easy to predict copolymer composition because the reactivity ratio of chloromethyl styrene is quite well documented compared to that of **1**. Because used substitution reaction condition is very mild, this synthetic scheme is applicable to many copolymer systems containing other than styrene.

Acknowledgment. This work was supported by Korea Science and Engineering Foundation (951-1101-034-2).

References

- Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127.
- Otsu, T.; Yamashita, K.; Tsuda, K. *Macromolecules* **1986**, *19*, 287.
- Reghunadhan Nair, C. P.; Clonet, G. J. *Macromol. Sci., Review* **1991**, *C31*, 311.
- Monomer content in feed was 46 wt% and AIBN concentration was 0.34 mol% to the monomer. Polymer yield was 64% after 24 hr. Mole fraction of comonomer in feed was 3.9 mol%, and that in polymer was 4.1 mol%. Number average molecular weight of the obtained polymer was 39,000 with polydispersity of 1.98.
- Yamashita, K.; Ito, K.; Tsuboi, H.; Takahama, S.; Tsuda, K. *J. Appl. Polym. Sci.* **1990**, *40*, 1445.
- Otsu, T.; Matsunaga, T.; Kuriyama, A.; Yoshioka, M. *Eur. Polym. J.* **1989**, *25*, 643.
- Van Kerckhoven, C.; Vanden Broeck, H.; Smets, G.; Huybrechts, J. *Makromol. Chem.* **1991**, *192*, 101.
- Shefer, A.; Grodzinsky, A. J.; Prime, K. L.; Busnell, J. P. *Macromolecules* **1993**, *26*, 2240.
- Vinylbenzyl dithiocarbamate is purified by recrystallization from methanol with 80% yield (ref. 2). Reported mp of the para derivative is 57 °C.

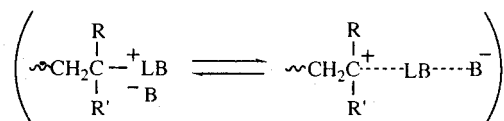
Enhancement of Initiator Efficiency in Cationic Polymerization of Isobutyl Vinyl Ether

Chang Gi Cho

Department of Textile Engineering,
Hanyang University,
Seoul 133-791, Korea

Received April 29, 1996

It has been reported that an added Lewis base (or election



monomer \longrightarrow propagation

R = H, CH₃ LB = Lewis base
R' = alkoxy, CH₃ B⁻ = counter ion

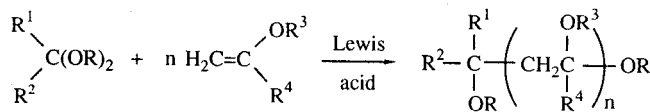
Scheme 1.

donor) promotes livingness of the cationic polymerization systems by regulating the reactivity of carbocationic propagating species. Alkyl sulfides,¹ ethers,² esters,³ amines,⁴ dimethyl sulfoxide,⁵ and dimethyl acetamide⁶ were used in the living polymerizations of vinyl ethers and isobutylene, and they slow down the propagation reactions considerably in the polymerizations. The slow rate of propagation, on the other hand, gives an additional advantage when one uses an initiation system which has a low initiator efficiency under ordinary conditions. The better chance of initiator participation in the polymerization increases the initiation efficiency, and this makes the scope of cationic initiators wider, and makes the development of a new initiation system easier (Scheme 1).

Acetals and orthoesters undergo electrophilic addition reactions to vinyl ethers to generate adducts or oligomers in the presence of Lewis acids,⁷⁻⁹ and the reported reactivity sequence increases in the order; saturated acetals < methyl orthoformate < benzaldehyde acetals < α,β -unsaturated acetals.¹⁰ Applications, however, have been limited to the synthesis of low molecular weight oligomers (Scheme 2).

Among them aldehydes have been used in many C-C bond-forming reactions in the presence of Lewis acid.¹¹⁻¹² A few examples are as initiators in Aldol-type group transfer polymerization¹³ or as a coinitiator with trimethylsilyl trifluoromethanesulfonate.¹⁴

In this study acetals, orthoesters, and aldehydes as possi-



Scheme 2.

ble initiators in cationic polymerization of isobutyl vinyl ether (IBVE) were examined in the presence of a Lewis base. Dimethyl sulfide was used as the Lewis base because it can accommodate various types of initiation systems without any side reaction. Also the effect of excess Lewis acid on the initiation reaction was examined.

Table 1 shows the summary of the polymerization results with different pairs of initiator aldehyde-Lewis acid. The amount of Lewis acid was always excess to the initiator. Polymerization was started by injecting a Lewis acid into a monomer-initiator-dimethyl sulfide solution by a dry syringe. The observed \bar{M}_n (by GPC) was usually lower than the calculated one, probably due to the presence of adventitious impurities such as water.¹⁶ In some cases higher \bar{M}_n s were observed due to the lower initiation efficiency. \bar{M}_n values measured by GPC matched very closely with the \bar{M}_n s measured by vapor phase osmometry.

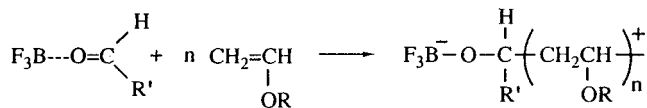
Benzaldehyde dimethyl acetal-Lewis acids gave polymers with narrow polydispersity. But SbCl₅ gave a polymer with slightly broad polydispersity, probably due to the ability of self-initiation of the acid.¹⁷ The acetal generates α -alkoxy carbenium ion in the presence of a Lewis acid as in the Scheme 2. Orthoesters are believed to follow the similar initiation route. With aldehydes, higher \bar{M}_n s were observed than calculated one except Entry 7. The NMR spectra of polymers obtained with cinnamaldehyde initiator showed the presence of double bonds, and \bar{M}_n by GPC of Entry 10 was very close to \bar{M}_n calculated from the integral ratio of the NMR spectrum.

It is generally accepted that the Lewis acid activates the carbonyl compound by forming an adduct prior to C-C bond formation. Upon complexation, the positive charge density at the carbonyl atom is increased.¹⁸ Therefore the polymeri-

Table 1. Polymerization of IBVE by Cationogen-Lewis acid^a

Entry	Initiator (I)	Lewis acid (LA)	[LA]/[I]	[Me ₂ S]/[I]	\bar{M}_w/\bar{M}_n	\bar{M}_n	
						GPC ^b	Calcd ^c
1	PhCH(OMe) ₂	BF ₃ OEt ₂	2.4	30	1.12	6490	9000
2	PhCH(OMe) ₂	BF ₃ SMe ₂	2.8	42	1.01	10100	12600
3	PhCH(OMe) ₂	EtAlCl ₂	4.8	60	1.03	10800	18500
4	PhCH(OMe) ₂	TiCl ₄	4.8	60	1.17	9400	18500
5	PhCH(OMe) ₂	SbCl ₅	4.8	60	1.35	4480	18500
6	PhCHO	BF ₃ OEt ₂	5	30	1.03	13400	9000
7 ^d	PhCHO	EtAlCl ₂	3.7	d	1.10	4990	9000
8	HC(OMe) ₃	BF ₃ OEt ₂	5	30	1.09	7010	9000
9	PhC(OMe) ₃	BF ₃ OEt ₂	5	30	1.10	15000	9000
10	PhCH=CHCHO	BF ₃ OEt ₂	1.5	13	1.41	2940	2000
11	PhCH=CHCHO	BF ₃ OEt ₂	1.5	33	1.04	7210	4900
12	PhCH=CHCHO	EtAlCl ₂	1.5	13	1.05	3870	2000

^a [IBVE]₀ = 0.76 M; temp., -30 °C; solvent, CH₂Cl₂; quantitative conversion resulted. ^b Eluent was THF. ^c Calculated from mol. wt. of IBVE (101.16) × 0.76/[I]₀. ^d Solvent, Me₂S; temp., 0 °C.

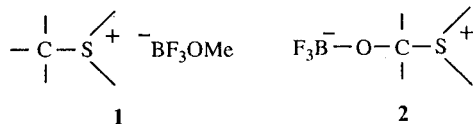


Scheme 3.

zation may undergo via zwitterionic propagating species, though it is not clear whether the excess BF_3 can react further with the negatively charged chain end or not (Scheme 3).

When the initial ratio of Lewis acid to initiator increased, \bar{M}_n decreased and better \bar{M}_w/\bar{M}_n was obtained. But larger than 5 fold excess BF_3SMe_2 did not influence the result of the polymerization. A very similar result was obtained with $\text{PhCHOBF}_3\text{SMe}_2$. These results, therefore, indicate that a Lewis acid makes a preinitiation equilibrium with the initiator as reported by many workers.^{7,19} And the Lewis acid facilitates the quantitative formation of carbocationic species.

Dimethyl sulfide, on the other hand, may involve in the preinitiation equilibrium. The sulfide is possible to facilitate the formation of carbocation by shifting the equilibrium through the formation of sulfonium ion (1 or 2). Also it may deter the reaction by shifting the equilibrium of Lewis acid-sulfide complexation, by reducing the rate of dissociation of Lewis acid-sulfide complex to free acid which is more reactive in the reaction. Therefore the sulfide has compensational effect by itself on the preequilibrium reaction.



In the polymerization, the \bar{M}_n of the polymer was controlled by the initiator concentration, and good polydispersity was obtained by applying excess Lewis acid. With a benzaldehyde acetal, a plot of initiator concentration versus $1/\bar{M}_n$ of obtained polymer showed linear relationship. A similar result was obtained with benzaldehyde. The intercept value shows the $1/\bar{M}_n$ when no initiator was used. In this case the \bar{M}_n is controlled by cationogens which are present as impurities in the system. Major component is thought to be water and this can be eliminated by careful purification of the reagents and using a proton trap.

References

1. Cho, C. G.; Feit, B. A.; Webster, O. W. *Macromolecules*

- 1990, 23, 1918.
2. Higashimura, T.; Kishimoto, Y.; Aoshima, S. *Polym. Bull.* **1987**, 18, 111.
 3. Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, 22, 1009.
 4. Higashimura, T.; Aoshima, S.; Sawamoto, M. *Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, 29(2), 1.
 5. Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, J. P. *Polym. Bull.* **1988**, 20, 413.
 6. Zsuga, M.; Kennedy, J. P. *Polym. Bull.* **1989**, 21, 5.
 7. Hoaglin, R. I.; Hirsh, D. H. *J. Amer. Chem. Soc.* **1949**, 71, 3468.
 8. Hatada, K.; Hasegawa, T.; Kitayama, T.; Yuki, H. *J. Polym. Sci., Polymer Letters Ed.* **1976**, 14, 395.
 9. Povarov, L. S. *Russ. Chem. Rev. (Engl. Transl.)* **1965**, 34, 639.
 10. Brueggen, U.; Lammers, R.; Mayr, H. *J. Org. Chem.* **1988**, 53, 2920.
 11. Snider, B. B. *Acc. Chem. Res.* **1980**, 13, 426.
 12. Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, 54, 1481.
 13. Sogah, D. Y.; Webster, O. W. *Macromolecules* **1986**, 19, 1775.
 14. Cho, C. G.; Feit, B. A.; Webster, O. W. *Macromolecules* **1992**, 25, 2081.
 15. Cho, C. G.; McGrath, J. E. *J. Macromol. Sci.-Chem.* **1988**, A25, 499.
 16. In order to reduce adventitious water, sulfuric acid treated methylene chloride was distilled successively over phosphorus pentoxide and calcium hydride under dry argon. Monomer was distilled over Na-K alloy. Dimethyl sulfide was distilled over 9-borabicyclo[3.3.1]nonane. Polymerization was run in a single neck flask equipped with a 3-way stopcock.
 17. Ledwith, A.; Sherrington, D. C. In *Reactivity, Mechanism and Structure in Polymer Chemistry*; Jenkins, A. D.; Ledwith, A., Eds.; John Wiley & Sons.: London, 1974; Chapter 9.
 18. Reetz, M. T.; Huellmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, 108, 2405.
 19. Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991; Chapter 5.