(4) Ilavsky, M.; Prins, W. *Macromolecules* **1970**, *3*, 415–425 et seq.
(5) Ratner, B. D.; Miller, I. F. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2425–2445.
(6) Lee, H. B.; Jhen, M. S.; Andrade, J. D. *J. Colloid Interface Sci.* **1975**, *51*, 225–231.
(7) Collett, J. H.; Spillane, D. E. M.; Pywell, E. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (1), 141–142.
(8) Janáček, J.; Kolařík, J. *Collect. Czech. Chem. Commun.* **1964**, *29*, 492–499.
(9) Janáček, J.; Kolařík, J. *Collect. Czech. Chem. Commun.* **1965**, *30*, 1597–1603.
(10) Kolařík, J.; Janáček, J. *Collect. Czech. Chem. Commun.* **1967**, *32*, 4224–4231.
(11) Shen, M. C.; Strong, J. D. *J. Appl. Phys.* **1967**, *38*, 4197–4202.
(12) Barešová, V. *Collect. Czech. Chem. Commun.* **1969**, *34*, 545–552.
(13) Murayama, T. *Dynamic Mechanical Analysis of Polymeric Materials*; Elsevier Scientific: New York, 1978.
(14) Wilson, T. W. Ph.D. Thesis, North Carolina State University, Raleigh, NC, 1986.
(15) Wilson, T. W.; Turner, D. T. *J. Dental Res.* **1987**, *66* (5), 1032–1035.
(16) Turner, D. T.; Crenshaw, M. A.; Haque, Z. U.; Wilson, T. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (1), 295–296.
(17) Rasmussen, D. H.; MacKenzie, A. P. *J. Phys. Chem.* **1971**, *75*, 967–973.
(18) Angell, C. A. In *Water*; Franks, F., Ed.; Plenum: New York, 1982; Vol. 7, Chapter 1.
(19) Franks, F. *Cryobiology* **1983**, *20*, 335–345.
(20) Derbyshire, W. In *Water*; Franks, F., Ed.; Plenum: New York, 1982; Vol. 7, Chapter 4.
(21) Ubbelohde, A. R. *Melting and Crystal Structure*; Clarendon: Oxford, 1965; Chapter 15.
(22) Morozov, V. N.; Gevorkian, S. G. *Biopolymers* **1985**, *24*, 1785–1799.

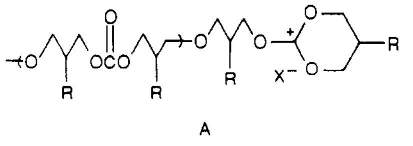
T. W. Wilson and D. T. Turner*

Dental Research Center and Department of
Operative Dentistry, University of North Carolina
Chapel Hill, North Carolina 27599-7455

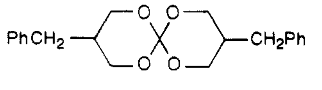
Received June 8, 1987

Polymerization and Block Copolymerization Initiated by Unusually Stable Living Propagating Species Formed in the Cationic Polymerization of Spiro Ortho Carbonate[1]

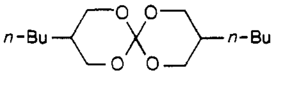
Current interest in the area of polymer synthesis has been directed to the living polymerization based on the stable propagating end species. This offers the crucial synthetic method for polymers of controlled molecular weights. Living cationic,[2] anionic,[3] coordination,[4] radical,[5] and group-transfer[6] polymerizations are of recent advances in this field. Meanwhile, the cationic polymerization of spiro ortho carbonate (SOC) forming a polyether–carbonate alternative copolymer is believed to proceed via trialkoxycarbenium ion (A) as a possible propagating species.[7] Since this type of carbenium ion is well-known to be quite stable as reported by Olah et al.,[8] this growing end (A) should still remain living after the completion of the polymerization. We have confirmed the special stability of the end species and now disclose the preliminary results on it.



A



SOC 1



SOC 2

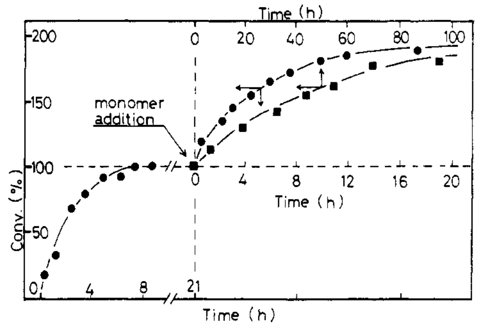


Figure 1. Time–conversion curves of the cationic polymerization of SOC 1 with Ph$_3$C$^+$BF$_4^-$ in chlorobenzene at room temperature.[10] At the first stage (0–21 h) SOC 1 was polymerized completely within 9 h (●). At the second stage, fresh SOC 1 dissolved in the solvent (in the same concentration) added to the poly(SOC 1) solution was consumed within ca. 30 h (●), while it took ca. 120 h to consume fresh SOC 1 added to the poly(SOC 1) solution after heating at 120 °C for 2 h (■).

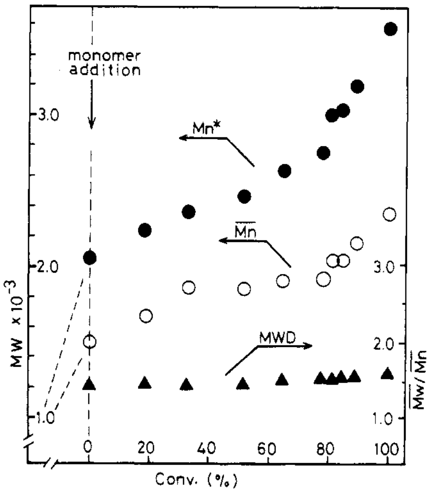


Figure 2. Molecular weight $\overline{M}_n$ (○), M^* (●), value of peak top in GPC), and MWD (▲) of the poly(SOC 1) at the second stage, obtained with Ph$_3$C$^+$BF$_4^-$ in chlorobenzene at room temperature, as a function of monomer conversion.

Cationic polymerization of SOC 1 with Ph$_3$C$^+$BF$_4^-$ or BF$_3$OEt$_2$ was found to proceed at room temperature (RT).[9] Time–conversion of the polymerization was obtained by ^{1}H NMR work (Figure 1).[10] To our surprise, after the complete consumption of SOC 1, the polymerization clearly took place again when the same amount of fresh SOC 1 was introduced to the reaction system (Figure 1). The added monomer was consumed thoroughly in 30 h in the second stage. Furthermore, fresh SOC 1 added to the living poly(SOC 1) solution, which was obtained by heating at 120 °C for 2 h after the complete polymerization at the first stage, was consumed similarly, though the rate decreased (Figure 1). This supports strongly the presence of a stable and long-lived propagating end of the poly(SOC 1).

As shown in Figure 2,[11] $\overline{M}_n$ and M^* (peak top value) of the sample withdrawn from the polymerization solution of the second stage undoubtedly increased roughly in proportion to the monomer conversion. MWD ($\overline{M}_w/\overline{M}_n$) was not narrow but approximately constant (1.45–1.61) during the polymerization.

On the other hand, block copolymerization was carried out with another SOC 2, which was added after the complete consumption of SOC 1.[12] The initial poly(SOC 1)

0024-9297/88/2221-1186$01.50/0

($\overline{M}_n$ 4600, MWD 1.95) was changed to block copolymer poly(SOC 1)$_x$-*block*-(SOC 2)$_y$ ($\overline{M}_n$ 10600, MWD 1.66, x:y = 62:38). The block copolymer was soluble in n-hexane but insoluble in MeOH (yield 69%), while the initial poly(SOC 1) was insoluble in n-hexane (yield 87%). This change of solubility as well as the change of $\overline{M}_n$ confirms unambiguously the occurrence of the block copolymerization.

By the similar manner, the block copolymerization of the living poly(SOC 1) with n-BVE (n-butyl vinyl ether) was attempted to give block copolymer poly(SOC 1)$_x$-*block*-(n-BVE)$_y$ with complete consumption of n-BVE without any homopolymer.[12,13] Monodispersed GPC peaks of the crude polymers both before and after the copolymerization, either of which showed the same shape by both UV and RI detection, indicated an obvious shift of $\overline{M}_n$ to the high molecular weight region.[14] As expected, most of the block copolymer (80–90%) became soluble in n-hexane. This solubility change was consistent with the segment ratio (x:y = 37:63 by NMR).

The similar block copolymerization with n-BVE occurred with use of the heated poly(SOC 1) (for 2 h at 120 °C) as the initiator as mentioned above. However, the blocking efficiency was low and a homopolymer of n-BVE was produced according to the results of GPC. Moreover, poly[(SOC 1)(SOC 1)] formed by two-step polymerization was still living and could initiate the polymerization of n-BVE[12] to afford the block copolymer poly[(SOC 1)(SOC 1)]-*block*-(n-BVE) along with a small amount of poly(n-BVE).

Similar results were obtained with poly(SOC 1) formed in the polymerization with a thermally latent catalyst $PhCH_2\overline{S^+CH_2CH_2CH_2CH_2}SbF_6^-$ at 120 °C for 3 h. Fresh SOC 1 fed to the poly(SOC 1), which was kept at 120 °C for more than 10 h, was consumed very slowly. Meanwhile, n-BVE added to the polymer solution was polymerized at less than RT.[12] The polymer obtained as the n-hexane-insoluble part was also the block copolymer poly(SOC 1)$_x$-*block*-(n-BVE)$_y$ (20% yield, x:y = 80:20, $\overline{M}_n$ 5400, MWD 1.40; poly(SOC 1), $\overline{M}_n$ 4900, MWD 1.42). Thus, the poly(SOC 1) was still living even at such a high temperature, although its activity dropped obviously.

From the results mentioned thus far, the polymerization of SOC is not the ideal living polymerization but has a few of the characteristics of living polymerization.[15] Most interesting is the great stability of the growing end species. This living end is regarded as one of the most stable species,[2] as assumed from its structure. Recent ^{1}H, ^{13}C, and ^{19}F NMR studies on its structure suggest the trialkoxycarbenium ion as expected.[16] In addition, the formation of poly(SOC)-*block*-(n-BVE) would attract attention as a unique block copolymer between cyclic ether and vinyl monomers. We believe that this study should provide a new polymerization process involving stable propagating species as well as an attractive entry to synthesize a wide variety of new block copolymers of considerably controlled molecular weights.

Acknowledgment. We thank Drs. M. Sawamoto of Kyoto University and M. Hiza of Yokohama Rubber Co. for helpful discussions.

Registry No. SOC 1, 107711-17-1; PSOC 1, 107711-20-6; (SOC 1)(SOC 2) (block copolymer), 113180-82-8; (SOC 1)(n-BVE) (block copolymer), 113180-83-9.

Supplementary Material Available: Experimental procedures and a figure of GPC change (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part of this work has been presented: Endo, T.; Sato, H.; Takata, T. 8th International Symposium on Cationic Polymerization and Related Processes, Munchen, 1987; Abstract p 57.

(2) (a) Sawamoto, M.; Higashimura, T. *Makromol. Chem., Macromol. Symp.* **1986**, *3*, 83. (b) Higashimura, T.; Sawamoto, M. *Adv. Polym. Sci.* **1984**, *62*, 49. (c) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265, 2228. (d) Kennedy, J. P.; Kelen, T.; Tudos, F. *J. Makromol. Sci.-Chem.* **1982**, *A18* (9), 1189. (e) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *16*, 317. (f) Zsuga, M.; Kelen, T. *Ibid.* **1986**, *16*, 285.

(3) (a) Takeda, N.; Inoue, S. *Macromolecules* **1981**, *14*, 1162. (b) Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. *Makromol. Chem.* **1981**, *182*, 1073. (c) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358. (d) Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148. (e) Inoue, S.; Aida, T. In *Ring-Opening Polymerization*; Ivin, K. J.; Saegusa, T., Eds.; Elsevier: London, 1983; Vol. 1, Chapter 4.

(4) (a) Doi, Y.; Ueki, K.; Keii, T. *Macromolecules* **1979**, *12*, 814. (b) Doi, Y.; Keii, T. *Adv. Polym. Sci.* **1986**, *73/74*, 201. (c) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holms, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (d) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 874. (e) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985**, *97*, 507.

(5) Otsu, T.; Yoshida, M.; Kuriyama, A. *Polym. Bull.* **1982**, *7*, 45.

(6) (a) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Harnham, W. B.; RajanBau, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. (b) Sogah, D. Y.; Webster, O. W. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 927.

(7) (a) Endo, T.; Bailey, W. J. *J. Polym. Sci., Polym. Symp.* **1978**, *64*, 17. (b) Endo, T.; Bailey, W. J. *Makromol. Chem.* **1975**, *76*, 2897. (c) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1735. (d) Endo, T.; Katsuki, H.; Bailey, W. J. *Makromol. Chem.* **1976**, *177*, 3231. (e) Endo, T.; Arita, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 137.

(8) Olah, G. A.; Olah, J. A.; Svoboda, J. J. *Synthesis* **1973**, 490.

(9) Recently, we have reported synthesis and polymerization (120 °C) of SOC 1 as a moisture-resistant SOC: Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416.

(10) Materials: SOC 1 (140 mg, 4 × 10^{-4} mol); $Ph_3C^+BF_4^-$ (6.8 mg, 5 mol %); chlorobenzene (417 mg, 3.7 × 10^{-3} mol).

(11) We believe that the deviation from the ideal behavior is due to (i) incomplete correspondence to the calibration based on standard polystyrene in GPC and (ii) small time lag in the initiation step because of lower solubility of $Ph_3C^+BF_4^-$ in chlorobenzene. Disappearance of the yellow color of the catalyst took several minutes.

(12) Experimental details are given in the Supplementary Material.

(13) Poly(SOC 1); $\overline{M}_n$ 2100 (M* 3000), MWD 1.51. Poly(SOC 1)$_x$-*block*-(n-BVE)$_y$; $\overline{M}_n$ 5900 (M* 6800), MWD 1.34, x:y = 59:41 (insoluble in n-hexane) and $\overline{M}_n$ 2700 (M* 5700), MWD 2.12 (soluble in n-hexane).

(14) Figure of GPC change appears in Supplementary Material.

(15) Back-biting may be one of the factors which induce deviation from ideal behavior.

(16) In the experiments using CF_3SO_3H, $CF_3SO_3SiMe_3$, and CF_3SO_3Me, trialkoxycarbenium ion with counter anion $CF_3SO_3^-$ was detected by the NMRs: this work is under intensive investigation.

Takeshi Endo,* Hiroyuki Sato, and Toshikazu Takata

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Received November 24, 1987

New Organometallic Polymers Containing Tungsten Carbene Complexes[1]

Inorganic and organometallic polymers containing transition metals, lanthanides, or main-group elements (P, Si, Sn, Li, or Pb) are a very intriguing group of materials and are currently receiving considerable attention.[2] These polymers have many useful applications as chemically