Macrocyclic Formals. 7. The Nature of the Growing Species in the Cationic Polymerization of 1,3,6,9-Tetraoxacycloundecane

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ABSTRACT: The polymerization of 1,3,6,9-tetraoxacycloundecane initiated with the triethyloxonium tetrafluoroborate and boron trifluoride ether complex was studied. The reaction proceeded in two stages, in the first cyclic oligomers were formed via oxonium ion mechanism and in the second high polymers were mainly formed via carbocationic mechanism, and then the reaction system reached an equilibrium consisting of cyclic oligomers and high polymers. The support for the above mechanism comes from the copolymerization study of styrene with the monomer, which suggested the carbocationic nature of the growing species during high polymer formation stage.

The polymerization of 1,3-dioxolane seems to be very complex, and several research groups have proposed different reaction mechanisms.[1-4] As a part of the studies on the polymerization of cyclic acetals, we have been studying the polymerization of macrocyclic formals.[5-10] It was found that the polymerization of macrocyclic formals of polyethylene glycols, such as 1,3,6,9-tetraoxacycloundecane, initiated with boron trifluoride ether complex proceeded in two stages.[6,9] In the first stage, only cyclic oligomers were formed. Contrary to this, high polymers were mainly formed in the second stage, and the whole reaction system reached an equilibrium after a long enough reaction time.[10] This was also true in the reaction with triethyloxonium tetrafluoroborate as initiator, presumably because the same active species having BF_4^- as counterion was formed from both initiator systems. No apparent differences were expected, nor were they observed between the two initiator systems. This is probably because only a part of the initiator is converted into active species having BF_4^- counterion.

It would be very interesting to study the nature of the growing species in each stage in order to obtain a detailed knowledge of the reaction mechanism of the polymerization of macrocyclic formals. This might be helpful in understanding the reaction mechanism of the polymerization of 1,3-dioxolane.

Experimental Section

Reagents. Boron fluoride ether complex (BF_3) was purified by fractional distillation. Triethyloxonium tetrafluoroborate (TEFB) was prepared according to Meerwein,[11] and its concentration was determined by measuring spectroscopically the concentration of phenyl ethyl ether formed after the reaction with sodium phenoxide.[12] Triethylamine was purified by distillation over calcium hydride. Dichloromethane and 1,2-dichloroethane were washed with sulfuric acid and distilled over phosphorus pentoxide after refluxing for 5 h. 1,3,6,9-Tetraoxacycloundecane (TOCU) was synthesized from triethylene glycol and paraformaldehyde and purified by fractional distillation over lithium aluminum hydride.[9,13] Styrene (St) was purified by fractional distillation over calcium hydride. Methanol was distilled over magnesium methoxide.

Procedure. The polymer of TOCU was synthesized with 1 mol % of BF_3 as an initiator, purified by reprecipitation from benzene into *n*-hexane, and freeze-dried. Isolation and identification of cyclic oligomers have been previously reported.[6,9]

The reactions were carried out under nitrogen atmosphere. The reaction was initiated by adding predetermined amounts of BF_3 or TEFB into a dichloromethane solution of TOCU, cyclic dimer of TOCU, or preformed polymer in a one-necked flask fitted with a three-way stopcock capped with a serum cap in a thermostated bath. The copolymerization procedure between TOCU and St was similarly carried out. The reaction was terminated with excess triethylamine. The conversion of monomers TOCU and St was determined by gas chromatography on the sample taken out from the reaction system with a syringe through the serum cap. The depolymerization of preformed polymer and polymerization of cyclic dimer were monitored by GPC by determining the concentration of cyclic oligomers by a Toyo Soda high-speed liquid chromatograph connected with 4 ft of TSK gel G 2000 H8 (exclusion limit 2.5×10^2 Å, TP/F 8000) eluted with 1 mL/min tetrahydrofuran or with 2 ft of G 2000 H8 and 2 ft of G 4000 H8 (exclusion limit 1×10^4 Å, TP/F 8000) eluted with 1 mL/min chloroform. The higher count number indicates the lower molecular weight. One elution count on the chromatograph approximately corresponds to 1.2 mL of elution volume for tetrahydrofuran and 0.67 mL for chloroform. The sensitivity of each cyclic oligomer was assumed to be proportional to its concentration in unit moles (ratio of the weight of polymer in grams to the molecular weight of the monomer). The effects of methanol were studied by adding it at three different stages, initially to the monomer solution, during the first oligomer formation stage, and finally during the second, i.e., polymer, formation stage.

Results and Discussion

Two-Stage Nature of the Polymerization. The two-stage nature of the polymerization of macrocyclic formals including TOCU and 1,3-dioxolane with BF_3 as an initiator has already been reported.[6,8,9] Typical time–conversion relationships in the polymerization of TOCU with BF_3 and TEFB as initiators determined by gas chromatography by measuring the disappearance of monomer are shown in Figure 1. The reaction proceeded in two stages in the sense of monomer consumption. Corresponding to this, in the typical gel chromatogram shown in Figure 2, the cyclic oligomers were formed in the first slower stage and high polymers were formed during the second faster stage. A, B, C, and D in the chromatogram are cyclic dimer, trimer, tetramer, and pentamer, respectively. In the first stage, the amounts of cyclic oligomers increased with reaction time and seemed to reach certain values. The values in unit moles, calculated from the conversion of monomer at the points where the curves of monomer consumption passed inflection points, are 0.105, 0.099, and 0.103 M, respectively, for the three curves (a), (b), and (c) in Figure 1 at 0 °C. These values are almost constant irrespective of initial concentration of monomer (when higher than 0.2 M) or the kind of initiator. This, together with the fact that there were almost no changes in the concentration of cyclic oligomers in the second stage, seemed to suggest that the concentration of each cyclic oligomer had reached equilibrium concentration at the end of the first stage, irrespective of the kind of initiator or the initial concentration of monomer (when higher than 0.2 M). In the second stage, there was almost

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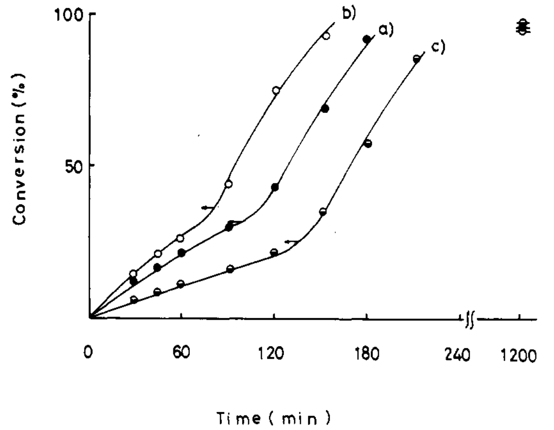


Figure 1. Time–conversion relationship of the polymerization of TOCU by BF_3 (a) or TEFB (b and c) in dichloromethane at 0 °C: (a) $[TOCU]_0 = 3.25 \times 10^{-1}$ M, $[BF_3]_0 = 1.38 \times 10^{-2}$ M; (b) $[TOCU]_0 = 2.76 \times 10^{-1}$ M, $[TEFB]_0 = 5.50 \times 10^{-2}$ M; (c) $[TOCU]_0 = 4.67 \times 10^{-1}$ M, $[TEFB]_0 = 2.00 \times 10^{-2}$ M.

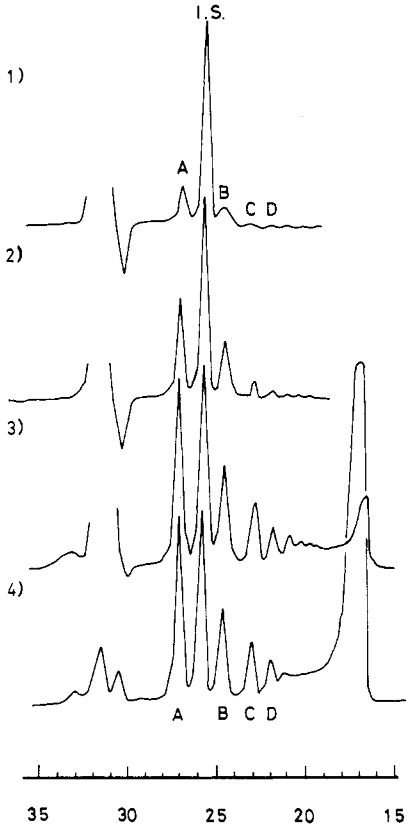


Figure 2. Change in GPC in the course of polymerization at 0 °C in dichloromethane ($[TOCU]_0 = 3.25 \times 10^{-1}$ M, $[BF_3]_0 = 1.38 \times 10^{-2}$ M): (1) 5 min (3% conversion); (2) 60 min (21% conversion); (3) 120 min (42% conversion); (4) 200 min (96% conversion) of reaction time. THF—4 ft of G 2000 H8 were used.

no change in the amounts of cyclic oligomers, and the average molecular weight of the polymer did not change much, either. Only the amounts of polymer increased with the consumption of monomer in the second stage. These facts will imply that the polymerization reactions are fast with fast termination or transfer in the second stage but that the propagation in the first stage is rather slow compared with the fast formation of cyclic oligomers.

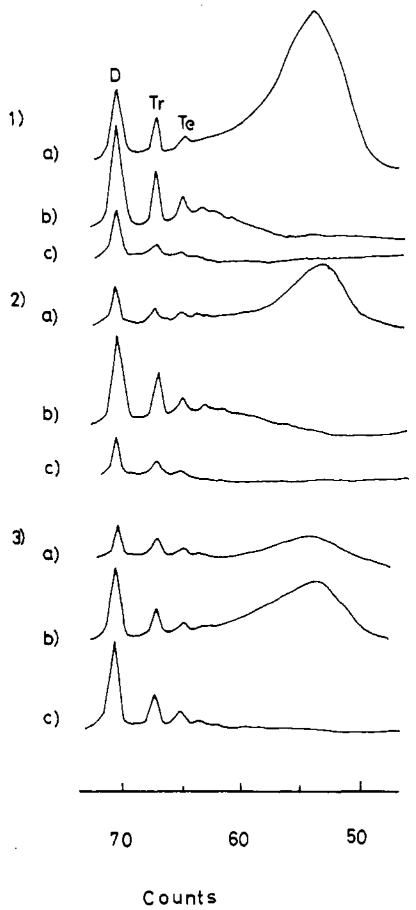
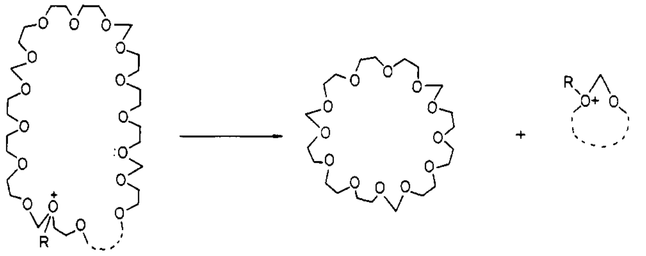


Figure 3. Equilibration of the reaction system by BF_3 starting from (1) monomer, (2) polymer, and (3) cyclic dimer at 0 °C in dichloromethane. Reaction time 180 min: (1) (a) 0.40 M, (b) 0.075 M, (c) 0.050 M; (2) (a) 0.448 unit moles, (b) 0.067 unit moles, (c) 0.050 unit moles; (3) (a) 0.30 unit moles, (b) 0.25 unit moles, (c) 0.04 unit moles. $CHCl_3$—2 ft of G 2000 H8 and 2 ft of G 4000 H8 were used for GPC. D, Tr, and Te indicate the cyclic dimer, trimer, and tetramer, respectively.

Cyclic Oligomer Formation. In order to understand the cyclic oligomer formation process a little more clearly, depolymerization of preformed polymer and polymerization of cyclic dimer of TOCU were carried out. The product distributions are shown in Figure 3. The product distributions, started from the same concentration (corresponding to unit moles) of the polymer, dimer, and monomer, are quite similar after 180 min of reaction indicating that the reaction systems reached an equilibrium after 180 min. By changing the initial concentrations, the systems were proved to be in equilibrium. If the initial concentration (in unit moles) of the polymer was low enough, the polymer was completely depolymerized to cyclic oligomers. At the concentration of 0.05 M (in unit moles), only cyclic dimer and trimer can be seen in the chromatograms of the reaction mixtures started from monomer or polymer. As mentioned before, the amounts of cyclic oligomers did not change so much in the second stage when the initial concentration of monomer was higher than 0.2 M. This means that the cyclic oligomers are in equilibrium with each other soon after the first stage. The equilibrium concentration of the cyclic dimer was the highest, 1.60×10^{-2} M, with the concentration of higher cyclic oligomers decreasing with increasing molecular weight.[15] The detailed data on the equilibrium ring concentrations will be published elsewhere.[16] The results of the polymerization of cyclic dimer gave interesting information. If the cyclic oligomers were formed only through a "ring-expansion" reaction, the oligomers formed from the cyclic dimer of TOCU (22-membered ring) should be even-membered rings, for instance, cyclic tetramer

Scheme I



(44-membered ring), hexamer (66-membered ring), and so on. The actual products are shown by GPC of the reaction systems, Figure 3(3), to be the same as obtained from monomer. The formation of odd-membered rings and their concentrations can be well explained by equilibrium between cyclic oligomers through a "back-biting" reaction, though a "ring-expansion" mechanism is not necessarily excluded. The back-biting or ring contraction reaction can be written, for example, as in Scheme I.

The ring-contraction reaction may correspond to the "back-biting" reaction in the linear growing chain. At present, we have not concluded which one is the real mechanism. Our experimental results strongly indicated that in either linear growing chain or macrocyclic oxonium ion mechanism, a back-biting type reaction could be responsible for the formation of cyclic oligomers in the first stage.

In order to obtain a little more quantitative information on cyclic oligomer formation, the polymerizations of TOCU and the cyclic dimer and the depolymerization of preformed polymer by TEFB, which has a definite counterion, were kinetically studied. Assuming first-order kinetics for the initiator and the monomer or the dimer in the respective polymerization reactions, and assuming first-order kinetics for the growing end in the depolymerization reaction, the following equations were derived: for the polymerization of monomer

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\mathrm{P},1}f_1[\mathrm{I}]_0\{[\mathrm{M}] - [\mathrm{M}]_\mathrm{e}\} \quad (1)$$

for the polymerization of dimer

$$-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k_{\mathrm{P},2}f_2[\mathrm{I}]_0\{[\mathrm{D}] - [\mathrm{D}]_\mathrm{e}\} \quad (2)$$

and for the appearance of the dimer in degradation

$$\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = f_\mathrm{P}d_{\mathrm{d},2}[\mathrm{I}]_0 - k_{\mathrm{P},2}f_2[\mathrm{D}][\mathrm{I}]_0 \quad (3)$$

where, $k_{\mathrm{p},i}$ and $k_{\mathrm{d},i}$ are rate constants of polymerization of or depolymerization to cyclic i-mer, respectively; [M], [D], and [I] are concentrations of monomer, dimer, and initiator, respectively; and f_1, f_2, and f_P are initiator efficiencies for each reaction, which are assumed to be the same, f. Here we consider the equilibrium through back-biting.

$$\mathrm{P}_n{}^* \underset{k_{\mathrm{P},i}}{\overset{k_{\mathrm{d},i}}{\rightleftarrows}} \mathrm{P}_{n-i}{}^* + \text{c-M}_i$$

$$\text{for } i \geq 2,\ n >> 1$$

$$K_i = k_{\mathrm{d},i}/k_{\mathrm{P},i} \quad (4)$$

On integration of eq 1 and 2 with the initial condition [M] = $[\mathrm{M}]_0$, [D] = $[\mathrm{D}]_0$ at $t = 0$,

$$\ln \frac{[\mathrm{M}]_0 - [\mathrm{M}]^\mathrm{e}}{[\mathrm{M}] - [\mathrm{M}]_\mathrm{e}} = k_{\mathrm{P},1}f[\mathrm{I}_0]t \quad (5)$$

$$\ln \frac{[\mathrm{D}]_0 - [\mathrm{D}]_\mathrm{e}}{[\mathrm{D}] - [\mathrm{D}]_\mathrm{e}} = k_{\mathrm{P},2}f[\mathrm{I}_0]t \quad (6)$$

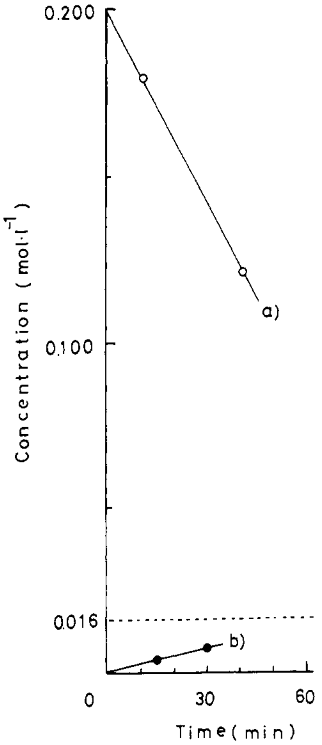


Figure 4. Change in the concentration of cyclic dimer of TOCU (a) in polymerization and (b) in depolymerization of preformed polymer at 0 °C in dichloromethane by TEFB: (a) $[\text{dimer}]_0$ = 0.20 M (0.40 unit moles), $[\mathrm{TEFB}]_0$ = 0.03 M; (b) [polymer] = 0.28 unit moles, $[\mathrm{TEFB}]_0$ = 0.05 M (0.16 M is the equilibrium concentration of dimer).

and integration of eq 3 with the initial condition [D] = 0 at $t = 0$ gives

$$\ln \frac{K_2}{K_2 - [\mathrm{D}]} = k_{\mathrm{P},2}f[\mathrm{I}]_0t \quad (7)$$

The changes in concentration of cyclic dimer determined by GPC in the polymerization of cyclic dimer and depolymerization of polymer are shown in Figure 4.

At 0 °C, $[\mathrm{M}]_\mathrm{e}$ and $[\mathrm{D}]_\mathrm{e} = K_2$ were determined to be 1.39×10^{-2} and 1.30×10^{-2} M, respectively. Applying eq 4 and 5 to the initial stage of the polymerization of TOCU in Figure 1 and the dimer in Figure 4, $fk_{\mathrm{p},1} = 1.70 \times 10^{-3}$ M^{-1} s^{-1} and $fk_{\mathrm{P},2} = 6.94 \times 10^{-3}$ M^{-1} s^{-1} were obtained, and applying eq 7 for the initial stage of the depolymerization in Figure 4, $fk_{\mathrm{P},2} = 6.64 \times 10^{-3}$ M^{-1} s^{-1} was obtained. Using $K_2 = 1.6 \times 10^{-2}$ M, $fk_{\mathrm{d},2}$ was calculated to be 1.06×10^{-4} s^{-1}.

Let us compare roughly the rates of propagation of monomer and dimer and the rate of formation of cyclic dimer at 60 min of reaction time of the curve (c) of Figure 1. $[\mathrm{M}]_0$ was 0.467 M, $[\mathrm{I}]_0$ was 0.05 M, and the conversion was 10.0%. At the point [D] being 0.010 M, the rates were calculated as follows: rate of polymerization of monomer = 1.70×10^{-3} M^{-1} s^{-1} × (0.467 × 0.90) M × 0.05 M = 3.57×10^{-5} M s^{-1}; rate of polymerization of dimer = 6.64×10^{-3} M^{-1} s^{-1} × 0.010 M × 0.05 M = 3.32×10^{-6} M s^{-1}; and rate of the formation of dimer = 1.06×10^{-4} s^{-1} × 0.05 M = 5.30×10^{-6} M s^{-1}. Because 1 mol of the dimer corresponds to 2 unit moles of monomer, the ratio of polymerization to formation of dimer in the polymer chain is 35.7/(5.30 × 2) = 3.37.

This value indicates that the polymerization rate of monomer is very slow if we consider all kinds of cyclic oligomer formation even at 10% conversion. Thus, the

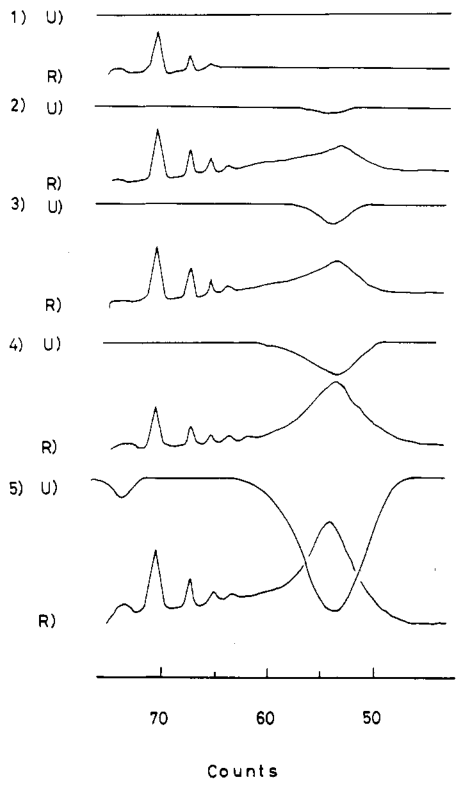


Figure 5. Change in GPC in the course of polymerization of TOCU with St by BF_3 at 0 °C in dichloromethane detected by (U) UV and (R) ($[TOCU]_0 = 3.81 \times 10^{-1}$ M, $[St]_0 = 3.70 \times 10^{-1}$ M, $[BF_3]_0 = 1.16 \times 10^{-2}$ M): (1) 40 min, 9.6%; (2) 90 min, 26%; (3) 150 min, 66%; (4) 180 min, 93%; (5) 240 min, 97% conversion of TOCU.

consumed monomer would be converted into cyclic oligomers. It will take roughly 0.016 M/($5.30 \times 10^{-6} - 3.32 \times 10^{-6}$) M s^{-1} = 135 min for the cyclic dimer to reach equilibrium. This time coincides with the actual time very well. Thus, the system was considered to be in equilibrium just before the second stage of the polymerization.

The Nature of the Growing Species. It was reported that 1,3-dioxolane could be copolymerized with styrene.[17] This was attributed to the carbocationic nature of the propagating species of the polymerization. In order to obtain an idea about the active species in the polymerization of TOCU, copolymerization of TOCU with styrene was carried out. The reaction was monitored by gas chromatography and GPC equipped with ultraviolet spectrophotometer and differential refractometer as detectors. By using the RI and UV detectors simultaneously, one can detect the formation of cyclic oligomers of TOCU (sensitive to only RI detector) and the formation of co-oligomers or copolymers (sensitive to both RI and UV detectors) in the same chromatogram. The changes in GPC chromatogram in the course of reaction are shown in Figure 5 for the system of TOCU with St by BF_3. The change was also quite similar for the system using TEFB as an initiator. The quantitative changes of monomers in the reaction are shown in Figures 6 and 7 for the systems with BF_3 and TEFB as initiators.

The following facts were noticed: (1) Even in copolymerization with styrene, TOCU was consumed quite similarly compared with the consumption of TOCU in homopolymerization. (2) Styrene was not consumed during the first stage of the consumption of TOCU. Accordingly, there was no incorporation of styrene into cyclic oligomers during the first oligomer formation stage. (3) Styrene was consumed only with the formation of high polymers and was incorporated into the copolymer.

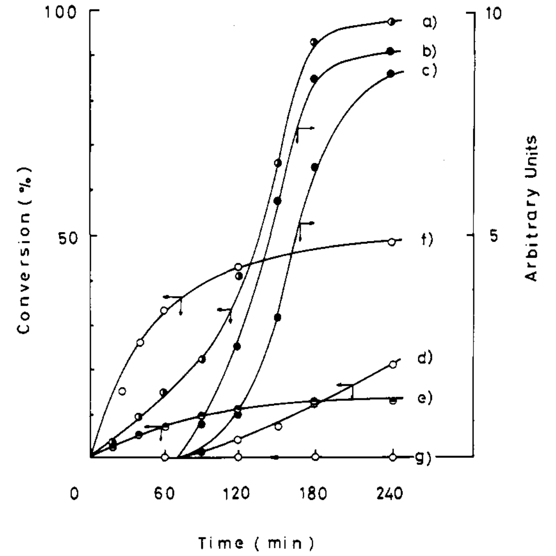


Figure 6. Change in the quantities of TOCU and St in the course of copolymerization at 0 °C in dichloromethane ($[TOCU]_0 = 3.81 \times 10^{-1}$ M, $[St]_0 = 3.90 \times 10^{-1}$ M, $[BF_3]_0 = 1.16 \times 10^{-2}$ M): (a) TOCU; (b) formed polymer; (c) UV absorption of polymer; (d) St; (e) cyclic dimer of TOCU; (f) St in homopolymerization with the same concentration of BF_3; (g) St in oligomer.

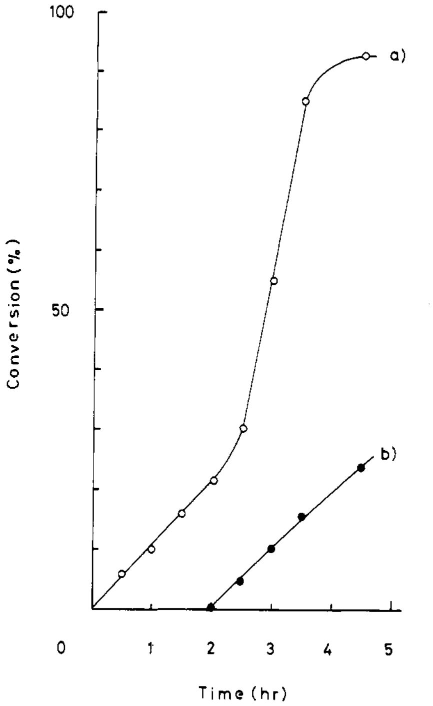


Figure 7. Time–conversion relationships of TOCU and St in copolymerization by TEFB in dichloromethane at 0 °C ($[TOCU]_0 = 4.67 \times 10^{-1}$ M, $[St]_0 = 5.82 \times 10^{-1}$ M, $[TEFB]_0 = 2.0 \times 10^{-2}$ M): (a) TOCU; (b) St.

The fact that styrene reacted only in the second stage, and not in the first stage, to give copolymer suggested that there were two different active species in the polymerization and that the species which produced high polymers in the second stage of the polymerization had a carbocationic character and copolymerized styrene with TOCU, although Plesch proposed the ring-expansion mechanism by secondary oxonium ion for the incorporation of styrene into cyclic oligomers.[18] Recently, Yokoyama[2d] reported the direct observation of a carbocation in the equimolar reaction of 1,3-dioxolane with TEFB by NMR spectroscopy. Consequently, at present, the active species in the second stage is considered to have carbocationic nature.

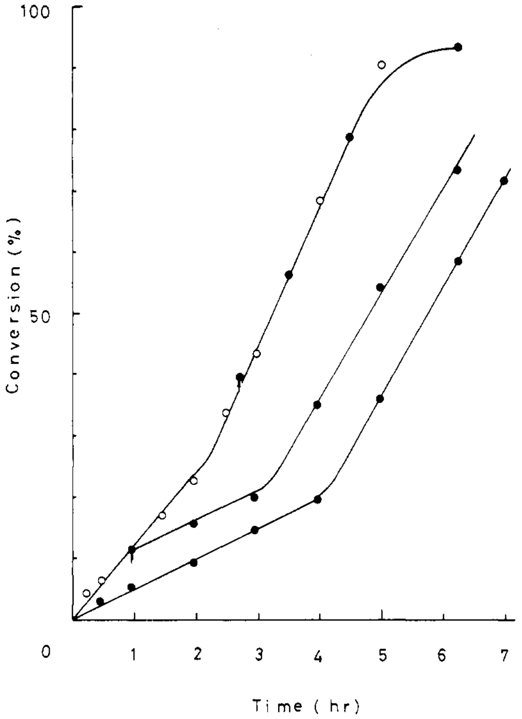


Figure 8. Influence of adding methanol to the polymerization system in dichloromethane at 0 °C ($[TOCU]_0 = 3.50 \times 10^{-1}$ M, $[BF_3] = 1.02 \times 10^{-2}$ M, [methanol] = 0.51×10^{-2} M). The time of addition was indicated by an arrow: (○) conversion without methanol; (●) conversion with methanol.

Although the nature of the active species in the first oligomer formation stage was not clear, it was considered that it had an oxonium ionic character because there was no sign of co-oligomer formation with styrene nor the consumption of styrene in the first stage. The effects of solvent on reaction rates reported[7] were also consistent with the oxonium ionic character of the species in the first stage. In ether solvents the reactions were very slow.

The effects of adding methanol into the system were rather interesting. The effects on reaction rate are shown in Figure 8. The effect of adding methanol to the reaction system was significant in the cases of initial addition and the addition during the oligomer formation stage. The comsumption of TOCU and the formation of cyclic oligomers were slowed down but were not completely stopped. The amounts of total oligomers reached a certain amount before the polymer was formed even in the presence of methanol. From these significant retarding effects by methanol and ether solvents on the first oligomer formation stage, it was considered that the active species in the first stage had an oxonium ionic character and that the reaction was retarded by competitive coordination of methanol or ether solvents. Contrary to this, the apparent effect was not significant when methanol was added during the second polymer formation stage (curve b), probably because the propagation reaction in the second stage was much faster than the reaction with methanol, or the methanol was acting only as a rapid chain transfer agent.

Conclusion

The polymerization of TOCU with BF_3 or TEFB proceeded in two stages. The active species in oligomer formation and high-polymer-formation stages were considered to be oxonium ionic and carbocationic. The polymerization reaction proceeded with fast propagation, with fast termination or transfer resulting in the formation of almost constant, but rather low, molecular weight polymer (molecular weight about 20 000).[5]

References and Notes

(1) (a) V. Jaacks; W. Kern *Makromol. Chem.* **1963**, *62*, 1. (b) V. Jaacks; K. Boehlke; E. Eberius *ibid.* **1968** *118*, 354.

(2) (a) M. Okada; Y. Yamashita; Y. Ishii *Makromol. Chem.* **1964**, *80*, 196. (b) E. A. Bergmen; E. B. Ludvig; V. A. Ponomarenko; S. S. Medvedev *Vysokomol. Soedin., Ser. A* **1969**, *11*, 200. (c) Y. Yokoyama, M. Okada; H. Sumitomo *Makromol. Chem.* **1975**, *176*, 795. (d) Y. Yokoyama; M. Okada; H. Sumitomo *ibid.* **1978**, *179*, 1393.

(3) (a) P. H. Plesch; P. H. Westermann *J. Polym. Sci., Part C* **1968**, *16*, 3837. (b) Y. Firat; F. R. Jones; P. H. Plesch; P. H. Westermann *Makromol. Chem., Suppl. 1* **1975**, 203. (c) P. H. Plesch *Pure Appl. Chem* **1976**, *48*, 287. (d) P. E. Black; D. J. Worsfold, *J. Macromol. Sci., Chem.* **1975**, *9*, 1523.

(4) (a) S. Penczek *Makromol. Chem.* **1970**, *134*, 299. (b) S. Penczek **1974**, *175*, 1217. (c) A. Stolarczyk; P. Kubisa; S. Penczek *J. Macromol. Sci., Chem.* **1977**, *11*, 2047. (d) P. Kubisa *J. Macromol. Sci., Chem.* **1977**, *11*, 2247. (e) P. Kubisa; S. Penczek *Macromolecules* **1977**, *10*, 1216. (f) P. Kubisa; S. Penczek *Makromol. Chem.* **1978**, *179*, 445.

(5) M. Okada; S. Kozawa; Y. Yamashita *Makromol. Chem.* **1969**, *127*, 66.

(6) Y. Yamashita; Y. Kawakami; K. Kitano *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 213.

(7) Y. Kawakami; Y. Yamashita *Polym. J.* **1977**, *9*, 227.

(8) Y. Kawakami; Y. Yamashita *Macromolecules* **1977**, *10*, 837.

(9) Y. Kawakami; J. Suzuki; Y. Yamashita *Polym. J.* **1977**, *9*, 519.

(10) Y. Yamashita; J. Mayumi; Y. Kawakami; K. Ito *Kobunshi Ronbunshu* **1978**, *35*, 615.

(11) H. Meerwein "Organic Synthesis", Collect. Vol. V; Wiley: New York, 1973; p 1080.

(12) T. Saegusa; S-I. Matsumoto *J. Polym. Sci., Part A-1* **1968**, *6*, 1559.

(13) M. J. Astle; J. A. Zaslowsky; D. G. Lufyatis *Ind. Eng. Chem.* **1954**, *46*, 787.

(14) J. M. Andrews; J. A. Semlyen *Polymer* **1972**, *13*, 142.

(15) (a) P. J. Glory; J. A. Semlyen *J. Am. Chem. Soc.* **1966**, *88*, 329. (b) H. Jacobson; W. H. Stockmayer *J. Chem. Phys.* **1950**, *18*, 1600.

(16) Y. Yamashita; J. Mayumi; Y. Kawakami; K. Ito, in preparation. See also: C. Rentsch; R. C. Schulz *Makromol. Chem.* **1978**, *179*, 1403.

(17) Y. Yamashita; M. Okada; M. Hirota *Makromol. Chem.* **1969**, *122*, 284.

(18) J. Cooper; P. H. Plesch *J. Chem. Soc., Chem. Commun.* **1974**, 1017.