

Cationic Polymerization of Styrene by $\text{CF}_3\text{SO}_3\text{H}$. An Investigation by Stopped-Flow/Rapid-Scan Spectrophotometry and Rapid Quenching*

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ABSTRACT: The polymerization of styrene with $\text{CF}_3\text{SO}_3\text{H}$ was studied at 30°C in dichloroethane using a stopped-flow/rapid-scan spectrophotometer. The reaction was rather simple in the early stage (up to 1 sec), the only observable absorption being that of the polystyryl cation (340 nm). The rate of the cation formation was approximately first order in styrene and acid concentrations. The polymer was characterized by gel-permeation chromatography of the rapid quenching product. The average degree of polymerization was 5-20 for $[\text{CF}_3\text{SO}_3\text{H}]$, 3-10 mM and $[\text{styrene}]$, 0.01-0.4M. The amount of the polystyryl cation formed was 1-4% of the total acid and the rate constant of propagation was estimated to be $(2-4) \times 10^5 \text{M}^{-1} \text{sec}^{-1}$.

KEY WORDS Cationic Polymerization / Styrene / Propagating Species / Stopped-Flow Technique /

The kinetic analysis of the elementary processes of the cationic polymerization of vinyl monomers has been generally unsuccessful, because direct observation of the short-lived propagating species is rather difficult.

Recently, De Sorgo, *et al.*,¹ observed a transient absorption at 340 nm upon mixing of styrene and perchloric acid at -80°C, which they assigned to the polystyryl cation. Subsequently, kinetic analyses were carried out for the complex polymerization process of this system.² More recently, we showed that short-lived propagating cations can be detected quite readily by using a stopped-flow/rapid-scan spectrophotometer.³ In this paper we describe a kinetic analysis of the cationic polymerization of styrene initiated by $\text{CF}_3\text{SO}_3\text{H}$.

EXPERIMENTAL

Materials

Commercial styrene was washed and distilled from CaH_2 under nitrogen. $\text{CF}_3\text{SO}_3\text{H}$ (Wako Pure Chem. Ind.) was used without further purification. Dichloroethane was washed, dried

over CaCl_2 , and distilled from P_2O_5 . In some cases, the purified solvent was further distilled from CaH_2 . The solvent was stored over molecular sieve (4 Å).

Procedures

The reaction was followed by a stopped-flow/rapid-scan spectrophotometer (Union Giken Co. Model RA1300). The mixing chamber was covered by a polyethylene bag filled with dry nitrogen. The reservoir and the photocell were washed thoroughly with dry dichloroethane, evacuated, and filled with dry nitrogen. The initiator and monomer solutions were prepared by the syringe technique or in a dry box under dry nitrogen, and were injected into the reservoirs of the rapid mixing apparatus through serum caps. The water content of these solutions, as determined by a coulometric Karl-Fischer apparatus (Hiranuma Sangyo Co., Aquacounter AQ-1), was always less than 1 mM. The reaction rate was not affected by the water content if it was maintained at a value below 1 mM.

The rapid-quenching apparatus was built by connecting three jacketed reservoirs (for solutions of initiator, monomer, and quencher) using

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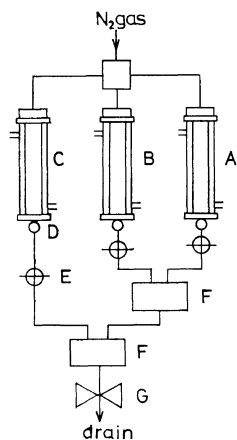


Figure 1. Rapid-quenching system: A, reservoir for monomer solution; B, reservoir for initiator solution; C, reservoir for quenching solution; D, needle valve; E, stop-cock; F, jet mixer; G, magnetic valve.

two Teflon four-jet mixers and a magnetic valve (see Figure 1). By applying nitrogen pressure, the initiator and monomer solutions were mixed and then the quenching solution (0.2-M CH_3ONa in methanol) was introduced using the second mixer. The quenching time was controlled by changing the nitrogen pressure and the length of the Diflon tube which connected the two mixers. The quenched product was washed with water, dried, diluted with tetrahydrofuran, and subjected to gel-permeation chromatography: solvent, tetrahydrofuran; instrument, Hitachi 635; columns; Shodex 802 A, 803 A, and 804 A. A part of the quenched product was diluted with dichloroethane after the work-up, and the unreacted monomer was determined by UV spectroscopy.

RESULTS AND DISCUSSION

Spectroscopic Observations

Typical rapid scan spectra for the reaction of styrene and $\text{CF}_3\text{SO}_3\text{H}$ are shown in Figure 2.

A new peak appeared at 340 nm immediately after mixing. This peak is most probably attributed to the polystyryl cation, as already discussed by Pepper² and by us.³ The peak intensity became maximal at 40–60 msec; its life time was 200–300 msec. No other spectral changes were observed during this period.

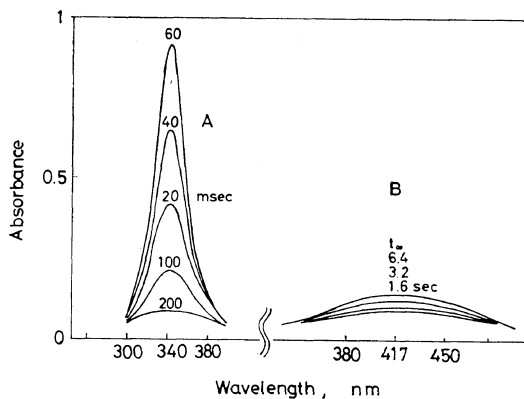


Figure 2. Rapid-scan spectra: 30°C, dichloroethane solvent; A, [styrene], 0.276M; [$\text{CF}_3\text{SO}_3\text{H}$], 11 mM; B, [styrene], 0.112M; [$\text{CF}_3\text{SO}_3\text{H}$], 17 mM.

Therefore, the reaction seems to consist only of initiation, propagation, and, probably, chain transfer and termination. However, another peak appeared at 417 nm after 1 sec, and its intensity slowly increased with time. This absorption is fairly stable in the reaction mixture, but is instantaneously quenched by methanol or water.

The formation of the phenylindane end group has been known for a long time in the cationic polymerization of styrene monomers.⁴ Bertoli and Plesch⁵ showed that the 3-methyl-1-phenylindanyl cation possessed absorption maxima at 304 nm (ϵ , 12,000 $\text{l mol}^{-1} \text{cm}^{-1}$) and at 415 nm (ϵ , 35,000 $\text{l mol}^{-1} \text{cm}^{-1}$). Therefore, the new peak observed at 417 nm is assigned to the phenylindanyl cation slowly formed at the chain end. Recently, Chmelir, *et al.*, also observed the formation of the phenylindanyl cation at 415 nm.⁶

Initiation Kinetics

The initiation kinetics were studied on the basis of the stopped-flow spectrum. Figure 3 is a typical example of the spectrum. A sharp rise of the 340-nm absorption is observed after a certain dead time (usually *ca.* 18 msec). Therefore, the point for the sharp rise was taken as $t=0$. The absorption usually decreased to the level of $t=0$ after 200–300 msec. The base line for determination of the absorbance was obtained as shown in Figure 3.

The rate of formation of the styryl cation was determined from the initial slope of the absorbance increase at 340 nm.

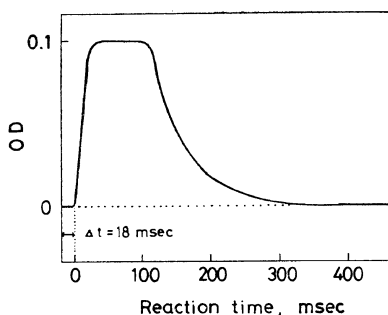
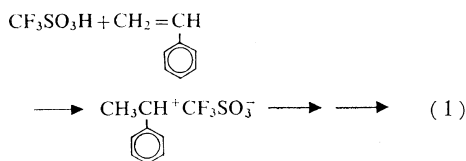


Figure 3. Stopped-flow spectrum: 30°C, dichloroethane solvent; [styrene], 0.40M; [CF₃SO₃H], 5.7 mM.



The molar extinction coefficient of the styryl cation was assumed to be $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, according to De Sorgo, *et al.*¹ This assumption is reasonable, since the extinction coefficient of the dimethylphenylcarbenium ion (λ_{max} , 326 nm) was reported to be $11,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ by Olah and coworkers.⁷

Figure 4 shows the dependence of the rate of initiation at $t=0$ on the monomer concentration at a constant concentration of CF₃SO₃H. The rate of the cation formation is curved downward. The reaction order estimated from the double logarithmic plot was 0.7–1.0. On the other hand, the rate was fairly proportional to the acid concentration, as shown in Figure 5. Thus, the following equation is obtained for the initiation reaction under the present conditions

$$v_i = \left(\frac{d[\text{P}^+]}{dt} \right)_{t=0} = k_i [\text{styrene}]^n [\text{CF}_3\text{SO}_3\text{H}]^m \quad (2)$$

where $n=0.7-1.0$ and $m \cong 1.0$.

The nonlinear dependence of the polymerization rate on the styrene concentration in a similar system was suggested by Sawamoto, *et al.*,⁸ to be due to the polarity change of the medium.

Chmelir^{6,9} carried out a kinetic study on a similar system (styrene—CF₃SO₃H—CH₂Cl₂) and

suggested the rapid formation of an inactive monomer—initiator complex and the initiation by species formed from two or three molecules of the acid. Thus, the polymerization rate as determined calorimetrically was 2.6–3.0 th order in CF₃SO₃H. These results are quite different from our observations. In this study, the formation of the styryl cation was approximately first order both in initiator and in monomer. Chmelir discussed the polymerization kinetics on the basis of the monomer consumption (calorimetry) rather than the amount of the propagating species. The formation of the polymerizing species over a long period such as they used could show much more complex kinetics than those observed by us in the early stage of the reaction. In fact, according to Chmelir,

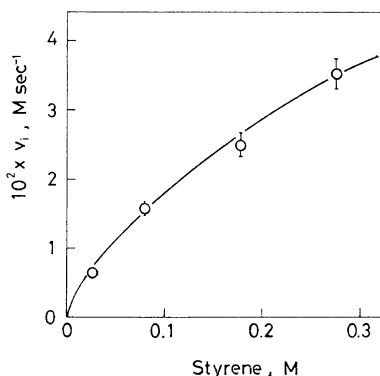


Figure 4. Initiation rate at $t=0$ vs. monomer concentration: [CF₃SO₃H], 14mM, 30°C, dichloroethane.

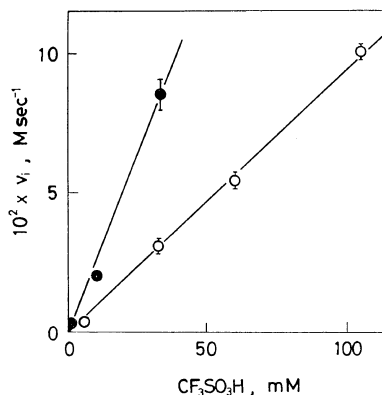


Figure 5. Initiation rate at $t=0$ vs. acid concentration: ●, [styrene], 0.276M; ○, [styrene], 0.027M.

the conductivity of the polymerization mixture gave a maximum with respect to the monomer concentration.

The initiation rate constant k_i was calculated from eq 2 to be in the range of $15\text{--}30M^{-1}\text{sec}^{-1}$. This value is much greater than that estimated for the initiation by $\text{Ph}_3\text{C}^+\text{SnCl}_5^-$ ($k_i=8.8 \times 10^{-4}M^{-1}\text{sec}^{-1}$).¹⁰ On the other hand, the protonation of 1,1-diphenylethylene is much faster ($k_i=3000\text{--}4000M^{-1}\text{sec}^{-1}$) under the same condition.¹

Propagation Process

In the presence of equimolar or excess initiator ($[\text{CF}_3\text{SO}_3\text{H}] \geq [\text{styrene}]$), the absorbance at 340 nm decreased rapidly after having reached a maximum value. The quenching product obtained under this condition contains unreacted monomer and styrene oligomers, as can be seen from its gel-permeation chromatogram (Figure 6A). The oligomer peaks for up to the octamer are clearly separated, except for those for the pentamer and heptamer. The assignment was carried out based on a calibration curve which was

obtained using benzene, styrene, and monodisperse oligostyrenes ($M_w=900, 2030, 4080$, etc.). The average degree of polymerization ($\text{DP} \geq 2$) was calculated from the weight fraction of each peak (for separated peaks of up to hexamer), and using eq 3 for higher oligomers.

$$\bar{M}_n = \frac{\sum H_i}{\sum H_i/M_i} \quad (3)$$

Here H_i is the height of the fraction of molecular weight M_i . When a higher monomer concentration ($[\text{styrene}] \gg [\text{CF}_3\text{SO}_3\text{H}]$, ordinary polymerization condition) was employed, the molecular weight was higher, as shown in Figure 6B.

The presence of a shoulder is noticed in the dimer peak of Figure 6A. Therefore, the dimer fraction may contain isomeric products. Otherwise, each oligomer peak is seemingly simple. This fact suggests that the polymerization process consists of simple additions even in the oligomeric range.

The elucidation of the oligomer structure would be particularly interesting in connection with the initiation mechanism. A study is under way in these laboratories to attempt to separate oligomers and to determine their structures.

A bimodal distribution such as observed by Sawamoto, *et al.*, was not detected in this system.⁸

As shown in Figure 2, the formation of polystyryl cation showed a maximum at 40–60 msec. This maximal period changes with initiator and monomer concentrations. Figure 7 gives the time course for the formation of the styryl

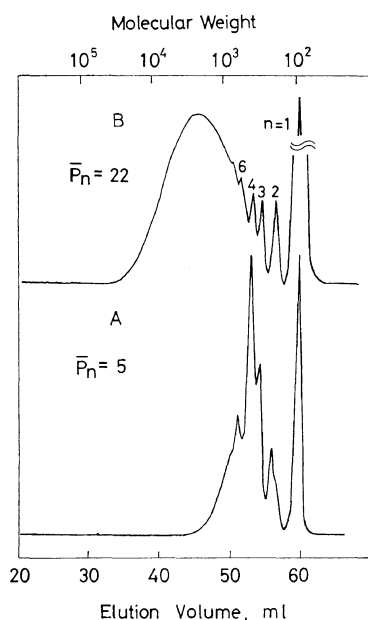


Figure 6. Gel-permeation chromatogram of polystyrene: A, $[\text{CF}_3\text{SO}_3\text{H}]$, 15 mM; $[\text{styrene}]$, 14.5 mM; quenching time, 45 msec; B, $[\text{CF}_3\text{SO}_3\text{H}]$, 2.9 mM; $[\text{styrene}]$, 0.40M; quenching time, 23 msec. n denotes the number of the monomer units in the oligomer.

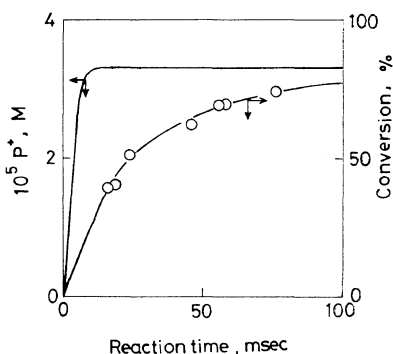


Figure 7. Formation of styryl cation and monomer consumption: $[\text{CF}_3\text{SO}_3\text{H}]$, 2.9 mM; $[\text{styrene}]$, 0.40M.

Cationic Polymerization of Styrene

 Table I. Formation of styryl cation (P^+)

CF_3SO_3H , mM	Styrene, M	$10^4 [P^+]_{max}$, M	t_1^a , msec	t_2^b , msec	$\frac{[P^+]_{max}}{[CF_3SO_3H]_0} \times 100$
17.2	0.112	5.6—6.3	30—35	0	3.2—3.7
15.8	0.0645	4.6—4.7	48—62	2—20	2.9—3.0
6.6	0.204	1.7—1.8	48—52	20—40	2.6—2.8
2.9	0.399	0.33—0.44	10—14	40—80	1.1—1.6
5.3	0.397	0.64—0.66	26—30	60—70	1.2—1.3

^a t_1 , time required for attaining $[P^+]_{max}$.

^b t_2 , duration of $[P^+]_{max}$.

Table II. Rate constant of propagation

CF_3SO_3H , mM	Styrene, M	k_p , $M^{-1} sec^{-1}$	
		Steady polymerization ^a	Nonsteady polymerization ^b
2.9	0.40	4×10^5 (40—74) ^c	—
5.3	0.40	2×10^5 (61—77)	2×10^5 (51—61)
6.6	0.20	—	3×10^5 (68—77)

^a k_p was determined according to eq 5.

^b k_p was determined according to eq 4.

^c The number in parentheses indicates the conversion range where k_p was determined.

cation in relation to the conversion at a lower initiator concentration. The amount of the propagating species becomes maximal in ca. 10 msec and then remains constant for about 100 msec. The conversion increased more gradually. The maximal amount of the styryl cation, $[P^+]_{max}$, was $3.4 \times 10^{-5} M$, corresponding to 1.2% of the initiator. It is interesting that only ca. 1% of CF_3SO_3H is used for initiation in the presence of excess monomer, in spite of its very strong acidity. Similar results were reported for the initiation of styrene polymerization by perchloric acid.¹¹ The presence of the steady concentration of P^+ may be explained by either or both of the following factors: (1) only a very small fraction of the acid is effective for initiation and the remaining acid is used for providing favorable microenvironments for proton transfer or is used for stabilizing the propagating ion-pair; (2) the steady concentration of P^+ is maintained because of the balance between the fast initiation and the fast termination.

The amount of P^+ relative to CF_3SO_3H under different conditions is summarized in Table I.

They are in the range of 1—4%. Table I also contains the time required for attaining $[P^+]_{max}$, t_1 , and the duration of the maximum, t_2 . In several cases, t_2 was very short. $[P^+]_{max}$ is attained more quickly and maintained for longer periods, when the ratio of monomer to initiator is high. The rate constant of propagation k_p can be readily determined by obtaining $[P^+]$ and the monomer consumption from either of the following equations.

$$\ln \frac{[M]_0}{[M]_t} = k_p \int_{t_0}^t [P^+] dt \quad (4)$$

$$\ln \frac{[M]_0}{[M]_t} = k_p [P^+] \Delta t \quad (5)$$

Equation 5 was applied to the steady polymerization, where $[P^+]$ is constant. k_p was also estimated graphically from the nonsteady portion, using eq 4. Table II shows k_p values obtained by these two methods. They are $(2\sim 4) \times 10^5 M^{-1} sec^{-1}$. The k_p value estimated for the free-cationic polymerization of bulk styrene (25°C) was $2.4 \times 10^6 M^{-1} sec^{-1,12}$ and k_p for the paired-cation polymerization ($HClO_4$ initiator) was estimated to be $2.6 \times 10^4 M^{-1} sec^{-1}$ at 20° in CH_2Cl_2 .¹¹ Therefore, the propagating species in the present study may be composed of both free and paired styryl cations. The investigation of the common-ion effect would clarify this problem, and will be described in a future publication.

Molecular Weight

Figure 8 gives the time dependence of the molecular weight of the recovered polymer in relation to the conversion change. The molecular weight rapidly decreases with increasing conversion.

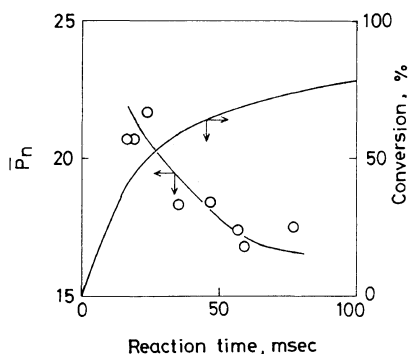


Figure 8. Relation between conversion and molecular weight of the polymer. The reaction condition is the same as that of Figure 6.

This is expected, since spontaneous transfer and termination become favorable due to lowered monomer concentrations at the later stages of polymerization. $[P^+]$ is constant during the reaction time (Figure 7). Therefore, the decrease in \bar{P}_n at the later stages may indicate that spontaneous transfer becomes favorable. The details of the termination mechanism are not yet clear.

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