been detected by Benson et al.[26] on the basis of a new resonance in the ^{13}C NMR spectra. How far the presence of such head-to-head sequences influences the crystalline areas is unknown. The fact that the extended conformation in the gel reverts to the familiar 3(2.216) helical structure upon heating rules out the possibility of a significant proportion of head-to-head/tail-to-tail sequences in the polymer.

The crystalline conformation of isotactic PMMA is still a matter of debate.[18,27] The virtual bond analysis shows that the isolated 5(2.08) helix is of higher energy than the 10(2.08) helix. It is likely that the conformational transition at 43° which Liquori and co-workers[18] detected on the basis of ultraviolet spectra of PMMA corresponds to a transition between the 5(2.08) and the 10(2.08) helices. The former occurs close to a new minimum at (ϕ_i,ϕ_{i+1}) = (-5,-75°), generated by suitable adjustment of side group positions. In both cases, the rotations of the side groups are important variables in the choice of the preferred conformation and in assessing the relative positions of these helical structures in the overall (ϕ_i,ϕ_{i+1}) domain of the polymer.

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Stopped-Flow Study of the Cationic Polymerization of Styrene Derivatives. 4.[1,2] Polymerization of p-Methoxystyrene by Superacid Initiators

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ABSTRACT: Stopped-flow/rapid-scanning spectroscopy was applied to the cationic polymerization of p-methoxystyrene by superacid initiators (CF_3SO_3H and CH_3COClO_4) to afford absorption spectra of the propagating species centered at ca. 380 nm in $(CH_2Cl)_2$ at 30 °C. The absorbance at 380 nm rapidly increased, reached a maximum within 20–40 ms, and decayed gradually. Correspondingly, the monomer ($[M]_0 = 5.0 \times 10^{-3}$ M) was consumed in a millisecond time scale. From these data, rate constants of propagation (k_p) and initiation (k_i) were determined. The k_p values, ranging from 5.4×10^4 to 1.3×10^5 M^{-1} s^{-1}, clearly exceeded those for other cationic initiators (I_2, $BF_3O(C_2H_5)_2$, etc.). The k_i values and initiation efficiency were much more dependent on initiators and in the order: $CH_3COClO_4 \gtrsim CF_3SO_3H \gg SnCl_4 \sim BF_3O(C_2H_5)_2 \gg CH_3SO_3H > I_2$. Thus, an important characteristic of the superacid initiators is to generate reactive propagating species very rapidly and efficiently. Polymerizations in $(CH_2Cl)_2/CCl_4$ mixtures or in $(CH_2Cl)_2$ containing a common ion salt also gave absorption spectra with the 380-nm peak but resulted in an unexpected increase in k_p based on this band. Involvement of an "invisible" propagating species that participates in monomer consumption without showing any absorption at $\lambda > 300$ nm was proposed and discussed.

The previous papers[1,3,4] of this series deal with application of stopped-flow spectroscopy to the cationic polymerization of p-methoxystyrene by a variety of initiators. We have shown that the propagating species exhibits a distinct absorption centered at ca. 380 nm in 1,2-dichloroethane ($(CH_2Cl)_2$)[3] and have successfully determined rate constants of propagation (k_p)[3] and initiation (k_i)[1] as well as the lifetime of the intermediate.[1] In spite of a minor dependence of the k_p values on initiators (counterions), there were marked differences in k_i and initiation efficiency between metal halides ($SnCl_4$ and $BF_3O(C_2H_5)_2$) and nonmetal halide initiators (I_2 and CH_3SO_3H);[5] the former generated the propagating species more rapidly and efficiently than the latter.

The *p*-methoxystyrene polymerizations in less polar solvents ($(CH_2Cl)_2/CCl_4$ mixtures) were somewhat complicated, indicating the presence of another propagating species that shows no UV-vis absorption but can participate in monomer consumption.[4] It is important that only the nonmetal halides can form this "invisible" species together with the intermediate with the 380-nm absorption. The polymerizations by metal halides apparently proceed simply via the latter propagating species independent of solvent polarity.

These clear differences between the two classes of initiators have prompted us to investigate the *p*-methoxystyrene polymerization by superacid initiators, trifluoromethanesulfonic acid (CF_3SO_3H) and acetyl perchlorate (CH_3COClO_4), because they belong to the nonmetal halide initiators[6] but are similar to metal halides in that they can effectively initiate polymerizations proceeding without frequent termination.[6,7] CH_3COClO_4 will act as initiator in the same way as perchloric acid, a superacid; both will yield the same counterion ClO_4^-. In this work emphasis was placed on differences and similarities between polymerizations by superacids and other initiators. Rapid-scanning spectroscopy, coupled with the stopped-flow technique, was newly introduced to conveniently obtain absorption spectra of rapidly forming intermediates. We wish to report that the superacid initiators are characterized by their ability to induce polymerizations very rapidly with a high initiation efficiency, while inheriting the nature of the nonmetal halides that can form an "invisible" propagating species.

Experimental Section

Materials. The synthesis of *p*-methoxystyrene and solvent purification methods were described previously.[3] CF_3SO_3H (Sumitomo 3M Co., purity ≥98%) was obtained commercially and used as reported.[7] CH_3COClO_4 was prepared from acetyl chloride and silver perchlorate.[8] Tetra-*n*-butylammonium trifluoromethanesulfonate (n-$Bu_4NSO_3CF_3$) was synthesized by the reaction of the corresponding ammonium hydroxide with CF_3SO_3H.[9] Tetra-*n*-butylammonium perchlorate (n-Bu_4NClO_4) was a commercial product (Nakarai Chemicals, polarographic grade) and was used as received. These common ion salts were dried overnight in vacuo before use.

Procedures. Details of stopped-flow experiments were given in our previous paper.[3] Polymerizations (monomer concentration, $[M]_0$ = 5.0 mM) were done at 30 °C under dry nitrogen with 0.7–0.9 mM of water as impurity. Rapid-scan absorption spectra of the polymerization solution were obtained on a stopped-flow apparatus equipped with a multichannel photodiode detector and a high-speed data processor (RA-401 and RA-450, Union Giken, Japan). The detector consisted of 256 photodiodes which cover ca. 100 nm for simultaneous absorbance measurement at each wavelength. The detection system was capable of recording ten time-resolved spectra in each run at desired time intervals after mixing; the shortest observation time was 10 ms. They were usually displayed automatically as difference spectra relative to that of the corresponding monomer solution.

Results and Discussion

Polymerization in $(CH_2Cl)_2$. On mixing *p*-methoxystyrene and CF_3SO_3H or CH_3COClO_4 in $(CH_2Cl)_2$ at 30 °C, rapid-scan spectra of the polymerization solution exhibited a strong absorption centered at ca. 380 nm. Figures 1 and 2 show examples of these spectra for CF_3SO_3H and CH_3COClO_4 initiators, respectively. The intense absorptions were identical with those observed for the propagating species with the other cationic initiators examined previously (I_2, CH_3SO_3H, $SnCl_4$, and $BF_3O(C_2H_5)_2$).[3] We therefore assigned the 380-nm peak to the propagating species of *p*-methoxystyrene, the λ_{max} of which does not depend on initiators.

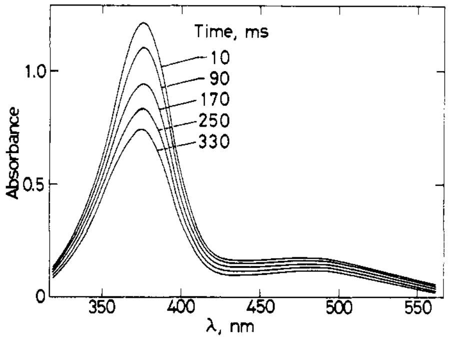

Figure 1. Rapid-scan absorption spectra of the *p*-methoxystyrene/CF_3SO_3H system in 1,2-dichloroethane at 30 °C: $[M]_0$ = 5.0 mM; $[C]_0$ = 0.10 mM.

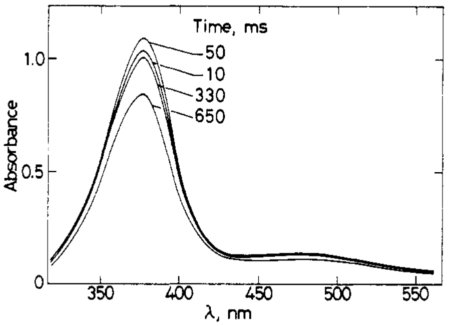

Figure 2. Rapid-scan absorption spectra of the *p*-methoxystyrene/CH_3COClO_4 system in 1,2-dichloroethane at 30 °C: $[M]_0$ = 5.0 mM; $[C]_0$ = 0.030 mM.

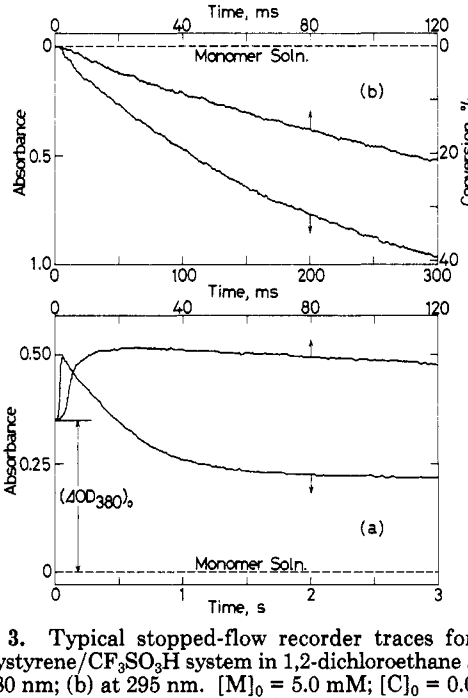

Figure 3. Typical stopped-flow recorder traces for the *p*-methoxystyrene/CF_3SO_3H system in 1,2-dichloroethane at 30 °C: (a) at 380 nm; (b) at 295 nm. $[M]_0$ = 5.0 mM; $[C]_0$ = 0.050 mM. The dashed lines indicate the absorbances of the corresponding monomer solution recorded under the same detector conditions.

The absorbance at 380 nm rapidly increased, reached a maximum within 20–40 ms, and decayed gradually, as exemplified in Figure 3a. Corresponding to this, the monomer (monitored at 295 nm)[3] disappeared quickly in a millisecond time scale (Figure 3b); for example, a 50%

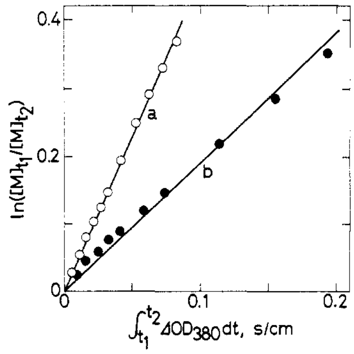

Figure 4. Plots of eq 1 for the *p*-methoxystyrene polymerizations in 1,2-dichloroethane at 30 °C: t_1 = 10 ms; $[M]_0$ = 5.0 mM. Initiator: (a) CF_3SO_3H, 0.10 mM; (b) CH_3COClO_4, 0.030 mM.

conversion was obtained at $t \sim 500$ ms under the conditions given in Figure 3. Polymerizations by the other initiators proceed much more slowly with time scales of seconds.[3] It should be noted in Figure 3a that the absorbance at 380 nm when the flow stopped ($t = 0$) clearly exceeds that of the corresponding monomer solution. The difference is represented as $(\Delta OD_{380})_0$ in Figure 3a. The large $(\Delta OD_{380})_0$ indicates that a considerable amount of the propagating species is formed within the dead time (t_d) of the stopped-flow apparatus. $(\Delta OD_{380})_0$ for the other initiators was negligibly small,[3] suggesting much faster initiation by the superacid initiators (see below). Therefore, the absorbance change at 380 nm due to the propagating species (ΔOD_{380}) was determined with the monomer solution as reference.

Propagation Rate Constants. Correlation of ΔOD_{380} with monomer consumption was examined according to the following equation:[3]

$$\ln \frac{[M]_{t_1}}{[M]_{t_2}} = \frac{k_p}{\epsilon_{380}} \int_{t_1}^{t_2} \Delta OD_{380}\, dt \qquad (1)$$

where $[M]_{t_1}$ is the monomer concentration at time t_1 and ϵ_{380} represents the molar absorption coefficient of the propagating species (2.8×10^4 M^{-1} cm^{-1}).[3] Because we could not follow the very early stage of the reaction even by the stopped-flow method, t_1 was usually taken as 10–20 ms instead of zero. Both CF_3SO_3H and CH_3COClO_4 gave linear plots of eq 1 passing through the origin at all the initiator concentrations ($[C]_0$) employed (e.g., Figure 4), which supported the validity of our spectral assignment. Table I summarizes k_p values determined from the slope of these plots together with those reported previously.[3] They were virtually invariant in the ranges of $[C]_0$ examined. Table I also lists initiation efficiencies ($[P^*]_{max}/[C]_0$) where $[P^*]_{max}$ is the maximal concentration of the propagating species based on ΔOD_{380}.

The k_p values for the two superacid initiators are in the range of (5.6–13) × 10^4 M^{-1} s^{-1} and up to 20 times larger than those for the other initiators. Furthermore, the oxo acids and their derivative (CF_3SO_3H, CH_3SO_3H, and CH_3COClO_4), regardless of their acid strengths, yielded more reactive propagating species than the metal halides ($SnCl_4$, etc.). These dependences of k_p on initiators should be indications that the reactivity of the propagating species is under the influence of counterions even in $(CH_2Cl)_2$, a polar solvent, and may require re-examination of our previous suggestion for predominance of a free ionic propagation in this solvent.[3] It is of interest that the counterions derived from oxo acids that carry a few oxygen atoms enhanced the reactivity of propagating carbocations more effectively than the presumably bulkier counterions from metal halides.

Table I
Rate Constants for *p*-Methoxystyrene Polymerization in $(CH_2Cl)_2$ at 30 °C ($[M]_0$ = 5.0 mM)

initiator	$[C]_0$, mM	$k_p \times 10^{-4}$,[a] M^{-1} s^{-1}	k_i,[b] M^{-1} s^{-1}	$[P^*]_{max}/[C]_0$,[a] %
CH_3COClO_4	0.030	5.4	120 000	~100
		5.7	120 000	~100
	0.050	7.7	120 000	~100
	0.10	11	81 000	63
		11	87 000	68
CF_3SO_3H	0.050	10	50 000	36
		13	62 000	42
	0.075	13	52 000	39
	0.10	13	49 000	38
$SnCl_4$[c]	0.050	1.1[e]	33[f]	27[e]
$BF_3O(C_2H_5)_2$[c]	0.50	0.60[e]	14[f]	4.2[e]
$Ph_3C^+SbCl_6^-$[d]	0.086	1.6	0.89	
CH_3SO_3H	5.0	2.3[e]	0.64[f]	0.090[e]
I_2	5.0	0.47[e]	0.037[f]	0.11[e]

[a] $\epsilon_{380} = 2.8 \times 10^4$ M^{-1} cm^{-1}. [b] $R_i(t \to 0) = k_i[M]_0[C]_0$; see text. [c] $[H_2O]$ = 0.7–0.9 mM.[3] [d] CH_2Cl_2, 25 °C, $[M]_0$ = 40 mM; ref 12. [e] Reference 3. [f] Reference 4.

The initiation efficiencies ($[P^*]_{max}/[C]_0$) of the superacid initiators also definitely exceeded those of the metal halides. In particular, CH_3COClO_4 led to a 100% efficiency at lower $[C]_0$. The significant conclusions drawn from this quantitative initiation are that in the CH_3COClO_4-initiated polymerization we can determine *all* the propagating species involved by monitoring the absorbance change at 380 nm and that the k_p values thus obtained are reliable if the assumed ϵ_{380} is correct. Therefore, the observed large k_p values for CH_3COClO_4 do not result from imperfect detection of the propagating species, or underestimation of its concentration. It may be safe to extend this to the closely related polymerization by CF_3SO_3H where initiation is not quantitative but much more effective than in those by $SnCl_4$ and $BF_3O(C_2H_5)_2$.

Initiation Rate Constants. We previously noted a great dependence of k_i on initiators.[1] In that work, k_i values were determined from the initial polymerization rate, $R_i(t \to 0)$, on the basis of a bimolecular initiation:

$$R_i(t \to 0) = \frac{d[P^*]}{dt}(t \to 0) = k_i[M]_0[C]_0 \qquad (2)$$

where $[P^*]$ is the concentration of the propagating species. However, with CF_3SO_3H and CH_3COClO_4 the following equation was employed to estimate k_i, because the very fast polymerization by the superacid initiators prevented direct determination of $R_i(t \to 0)$ from a ΔOD_{380} vs. time plot (cf. Figure 3a):

$$R_i(t \to 0) = \frac{1}{t_d} \frac{(\Delta OD_{380})_0}{\epsilon_{380}} = k_i[M]_0[C]_0 \qquad (3)$$

The dead time t_d was taken as 1 ms.[10,11] It must be kept in mind that this method implicitly underestimates $R_i(t \to 0)$ and hence k_i because it assumes a linear increase of ΔOD_{380} within the dead time. The k_i values thus obtained were compared in Table I with those previously reported.[1,12]

The initiation rate, in sharp contrast to the k_p values, changed with initiators very greatly (by factors of up to 3×10^6) to give the order: $CH_3COClO_4 \gtrsim CF_3SO_3H \gg SnCl_4 \sim BF_3O(C_2H_5)_2 \gg Ph_3C^+SbCl_6^- \sim CH_3SO_3H > I_2$. The superacid initiators yielded very large k_i values ranging from 4.9×10^4 to 1.2×10^5 M^{-1} s^{-1} in spite of the underestimation of $R_i(t \to 0)$. The initiation efficiency also depended clearly on initiators and showed a close correlation with the change in k_i. These facts indicate that the

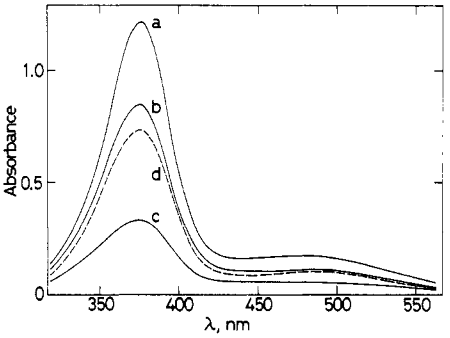

Figure 5. Effects of solvent and a common ion salt (n-$Bu_4NSO_3CF_3$) on the absorption spectra of the p-methoxystyrene/CF_3SO_3H systems at 30 °C: t = 10 ms; $[M]_0$ = 5.0 mM; $[C]_0$ = 0.10 mM. Solvent: (a) $(CH_2Cl)_2$; (b) $(CH_2Cl)_2/CCl_4$ (80/20 v/v); (c) $(CH_2Cl)_2/CCl_4$ (60/40 v/v); (d) $(CH_2Cl)_2$ containing n-$Bu_4NSO_3CF_3$ (0.050 mM).

initiation step is a bimolecular reaction between the monomer and an initiator,[1] in which k_i reflects directly the activity of initiators to result in its great dependence. It can be emphasized that the above stopped-flow approach provides a quantitative and direct measure for the activity of a wide variety of initiators including metal halides.

Among the superacid initiators, CH_3COClO_4 gave larger k_i and $[P^*]_{max}/[C]_0$ than CF_3SO_3H, but an opposite order was observed for the k_p values. A possible explanation for the former may be that CF_3SO_3H, a free protonic acid, associates (or dimerizes) in $(CH_2Cl)_2$ to render it less reactive and less efficient in initiation than CH_3COClO_4 which is a mixed anhydride and cannot dimerize. On the other hand, the counterion $CF_3SO_3^-$ will be less nucleophilic than ClO_4^- to give a more reactive propagating species with a larger k_p, because CF_3SO_3H is a stronger protonic acid than $HClO_4$.

Thus, an important characteristic of the superacid initiators is to form reactive propagating species (large k_p) very rapidly (large k_i) and efficiently (large $[P^*]_{max}/[C]_0$). It is noteworthy that they are much more reactive in initiation than the metal halides which have been regarded as having large activities.[13]

Solvent Effects. p-Methoxystyrene polymerizations by the two superacid initiators were also carried out in less polar media, namely in $(CH_2Cl)_2/CCl_4$ solvent mixtures with dielectric constants 5–10, so that insight could be obtained into the effect of solvent polarity on the nature of the propagating species, especially on possible formation of an "invisible" species[4] characteristic of the nonmetal halide initiators. Figure 5 shows rapid-scan spectra of the polymerization solutions with CF_3SO_3H initiator in three solvents (t = 10 ms). CH_3COClO_4 gave similar profiles. In all solvents absorptions appeared at ca. 380 nm, which agreed in both position and shape very closely with those observed in $(CH_2Cl)_2$. However, $[P^*]_{max}$ decreased steadily with decreasing solvent polarity. This is clearly shown in Figure 6 where $[P^*]_{max}$ values for CF_3SO_3H and CH_3COClO_4 are plotted as functions of solvent dielectric constant.

In all the solvents examined, ΔOD_{380} changed with time in the same way as in $(CH_2Cl)_2$ and monomer consumption proceeded in millisecond time scales (see Figure 3). Plots of eq 1 for the two initiators gave straight lines through the origin irrespective of solvent polarity, from the slope of which rate constant k_p was obtained. Figure 7 depicts dependences of the k_p values on solvent dielectric constant. They increased monotonically with decreasing solvent polarity, showing a close correlation with the sharp decrease in $[P^*]_{max}$ seen in Figure 6. These trends are just the same as those observed with I_2 and CH_3SO_3H (nonmetal halides).[4]

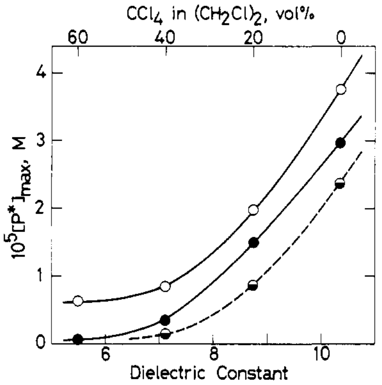

Figure 6. Dependence of the maximal concentration of the propagating species ($[P^*]_{max}$) on solvent dielectric constant at 30 °C: $[M]_0$ = 5.0 mM. Initiator: (○) CF_3SO_3H, 0.10 mM; (●) CH_3COClO_4, 0.030 mM; (◒) CH_3COClO_4, 0.030 mM, with n-Bu_4NClO_4, 0.15 mM.

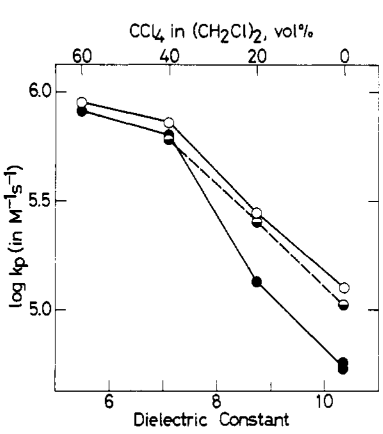

Figure 7. Dependence of propagation rate constant (k_p) on solvent dielectric constant at 30 °C: $[M]_0$ = 5.0 mM. Initiator: (○) CF_3SO_3H, 0.10 mM; (●) CH_3COClO_4, 0.030 mM; (◒) CH_3COClO_4, 0.030 mM, with n-Bu_4NClO_4, 0.15 mM.

The unexpected increase of k_p in less polar solvents strongly suggests, in line with our previous proposal,[4] involvement of a new propagating species that can contribute to monomer consumption without showing any UV-vis absorption. If this "invisible" (spectroscopically inactive) propagating species predominates in less polar media, $[P^*]$ will be underestimated when determined from only ΔOD_{380}, resulting in overestimation of k_p as observed. Importantly, CH_3COClO_4, which formed the propagating species with the 380-nm band almost quantitatively in $(CH_2Cl)_2$ (Table I), also generated the "invisible" species in $(CH_2Cl)_2/CCl_4$ mixtures. We therefore concluded that the formation of the "invisible" propagating species in less polar solvents is a common characteristic of the polymerizations by nonmetal halide initiators (I_2, CH_3SO_3H, and superacids) in spite of their large differences in activity (k_i).

Common Ion Salt Effects. The nature of the "invisible" species attracts our interest. Its predominance in nonpolar solvents suggests that a common ion salt in a polar solvent may also lead to its formation by suppressing free-ionic propagating species. Thus polymerizations by CF_3SO_3H and CH_3COClO_4 were performed in $(CH_2Cl)_2$ containing the corresponding ammonium salt, n-$Bu_4NSO_3CF_3$ or n-Bu_4NClO_4.[14] Although addition of an excess of common ion salt induced no change in the position and shape of absorption spectra of the polymerization solution (with the 380-nm peak only), the peak

Table II
Common Ion Salt Effects on *p*-Methoxystyrene Polymerization in $(CH_2Cl)_2$ at 30 °C ($[M]_0$ = 5.0 mM)

initiator[a]	[salt],[b] mM	[salt]/$[C]_0$	$k_p \times 10^{-4}$,[c,d] $M^{-1}\,s^{-1}$	$[P^*]_{max}/[C]_0$,[d] %
CH_3COClO_4	0	0	5.6[e]	~100[e]
	0.015	0.50	5.5	~100
	0.15	5.0	11	79
	0.60	20	15	45
CF_3SO_3H	0	0	13	38
	0.050	0.50	15	21
	0.10	1.0	36	5.9

[a] $[C]_0$: CH_3COClO_4, 0.030 mM; CF_3SO_3H, 0.10 mM. [b] Salt: *n*-Bu_4NClO_4 for CH_3COClO_4; *n*-$Bu_4NSO_3CF_3$ for CF_3SO_3H. [c] k_p as defined by eq 1. [d] $\epsilon_{380} = 2.8 \times 10^4$ $M^{-1}\,cm^{-1}$. [e] Average of two experiments.

intensity clearly decreased in comparison to that in a salt-free $(CH_2Cl)_2$ at the same $[C]_0$. Figure 5d shows an example of such spectral change in the presence of *n*-$Bu_4NSO_3CF_3$.

Table II shows the effects of common ion salts on k_p and initiation efficiency. The former was determined on the basis of eq 1; corresponding plots of eq 1 were linear at all salt concentrations. Common ion salts in $(CH_2Cl)_2$ gave rise to increases in k_p and decreases in $[P^*]_{max}$. For instance, *n*-$Bu_4NSO_3CF_3$ in amounts equimolar with CF_3SO_3H increased k_p by a factor of 2.8 and reduced $[P^*]_{max}$ to 16% of its original value. Lorimer and Pepper[15] have recently found a similar phenomenon in their stopped-flow study on the styrene polymerization by perchloric acid. These facts indicate that salt addition in a polar solvent and decreasing solvent polarity have very similar effects upon k_p and $[P^*]$; both promote formation of the "invisible" propagating species.

In less polar solvents, common ion salt effects similar to the above also operated (see Figures 6 and 7 for $[P^*]_{max}$ and k_p, respectively), but gradually to lesser extent with decreasing solvent polarity. Virtually no effect was observed in a sufficiently nonpolar solvent containing 40% CCl_4. This decrease of salt effects is consistent with increasing contribution of the salt-insensitive "invisible" propagating species in less polar media as discussed above.

Therefore, the "invisible" species seems to prevail under conditions where the ionic dissociation of the propagating species is suppressed by common ion salts and nonpolar solvents. This, together with its spectroscopic inactivity, implies that its nature differs greatly from that of a free carbocationic species.[16] Further study is necessary for a definite conclusion on this subject, although a proposal has been made recently.[15]

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References and Notes

(1) Part 3 of this series: T. Higashimura and M. Sawamoto, *Polym. Bull.*, 1, 11 (1978).

(2) This work was presented in part at the 27th Symposium of the Society of Polymer Science, Japan, November 1978.

(3) M. Sawamoto and T. Higashimura, *Macromolecules*, 11, 328 (1978).

(4) M. Sawamoto and T. Higashimura, *Macromolecules*, 11, 501 (1978).

(5) "Nonmetal halide" initiators (or simply, "nonmetal halides") mean cationic initiators other than metal halides and may include molecular halogens, protonic acids, and their derivatives.[6]

(6) T. Higashimura, T. Masuda, and M. Sawamoto, "Preprints Polymer Colloquium", Kyoto, September 1977, p 26.

(7) T. Masuda, M. Sawamoto, and T. Higashimura, *Makromol. Chem.*, 177, 2981 (1976).

(8) T. Masuda and T. Higashimura, *J. Macromol. Sci., Chem.*, **5**, 547 (1971).

(9) M. Sawamoto, T. Masuda, and T. Higashimura, *Makromol. Chem.*, 177, 2995 (1976).

(10) The dead time of a stopped-flow apparatus similar to ours has been determined to be 1.0–3.0 ms when water is the solvent.[11] The use of less viscous organic solvents such as $(CH_2Cl)_2$ may reduce the dead time to some extent.

(11) S. Kunugi and N. Ise, *Z. Phys. Chem. (Frankfurt am Main)*, 91, 69 (1974); S. Kunugi, Thesis, Kyoto University, 1978, p 4.

(12) R. Cotrel, G. Sauvet, J. P. Vairon, and P. Sigwalt, *Macromolecules*, 9, 931 (1976).

(13) G. A. Olah in "Friedel-Crafts and Related Reactions", Vol. I, G. A. Olah, Ed., Interscience, New York, 1963, p 879; G. A. Olah, "Friedel-Crafts Chemistry", Wiley, New York, 1973, p 419.

(14) Separate experiments showed that these salts alone cannot initiate *p*-methoxystyrene polymerization under our experimental conditions.

(15) J. P. Lorimer and D. C. Pepper, *Proc. R. Soc. London, Ser. A*, 351, 551 (1976).

(16) A referee has suggested the possibility that in less polar solvents a part of the propagating species may be ion pairs with the same 380-nm absorption but with a higher reactivity that causes the observed increase in k_p. However, according to our data (Figure 7), this leads to unreasonably large k_p values of about 10^6 $M^{-1}\,s^{-1}$ and thus seems less likely to us.