Cationic Oligomerization of Methylstyrenes: Effects of the Methyl Group and Catalysts on Product Distributions

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ABSTRACT: In the cationic oligomerization of *o*-, *m*-, and *p*-methylstyrenes, effects of reaction conditions and of the position of the methyl group on the molecular weight distribution and the structure of the products were elucidated. In the oligomerization with oxo acids in C_6H_6, dimer was the main product, whereas higher oligomers were formed in $(CH_2Cl)_2$. On the other hand, metal halides yielded higher oligomers in both solvents, and the molecular weight distribution hardly depended on solvent polarity. Only the unsaturated dimer was formed by oxo acids in C_6H_6, whereas that produced by oxo acids in $(CH_2Cl)_2$ and metal halides in both solvents yielded cyclic as well as unsaturated end groups. In general, the methylstyrenes gave higher oligomers than styrene.

The cationic oligomerization of vinyl compounds is always accompanied by transfer and termination reactions at room temperature because the intermediate carbocation is usually unstable; therefore it is useful for production of oligomers especially at higher temperature. We have recently found that the molecular weight distribution (MWD) of oligostyrenes could be controlled by the proper choice of catalysts, solvents, and reaction temperature.[1] For instance, linear dimers,[2] trimers, or tetramers[1] were produced in high yield under suitable conditions. The MWD depended greatly on the nature of catalysts, and this was explained in terms of the interaction[3] between the growing carbocation and the counterion derived from the catalysts.

The related studies reported so far only deal with the conversion of linear dimers of styrene,[4,5] α-methylstyrene,[5] and 1,1-diphenylethylene[6] in the presence of an acid. For the oligomerization of methylstyrenes, however, there are no studies concerned with controlling the MWD and structure of products, except for our preliminary account that oxo acids or their derivatives [acetyl perchlorate ($AcClO_4$) and trifluoromethanesulfonic acid (CF_3SO_3H), etc.] formed oligomers with high dimer content.[7] It is expected that introduction of a methyl group at different positions in the monomers would affect the MWD and end-group structure.

In the present work, therefore, we studied extensively the possibility of controlling the MWD and structure of products in the cationic oligomerization of *o*-, *m*-, and *p*-methylstyrenes. The effects of catalysts, solvent polarity, and temperature were examined with special attention to catalytic differences between oxo acids and metal halides.

Experimental Section

Materials. *p*-Methylstyrene (*p*-MeSt) was obtained by standard methods.[8,9] After the solution was washed and distilled, a monomer having a purity higher than 99% (by gas chromatography) was obtained. Commercial *o*-methylstyrene (*o*-MeSt) and *m*-methylstyrene (*m*-MeSt) (purity >99%; by gas chromatography) were distilled twice over CaH_2 under reduced pressure just before use. Solvents (benzene (C_6H_6) and 1,2-dichloroethane $(CH_2Cl)_2$) were used as reported.[1] $AcClO_4$ was synthesized as described elsewhere.[10] Commercial BF_3OEt_2, $EtAlCl_2$, $SnCl_4$, and bromobenzene were used after distillation under reduced or atmospheric pressure. *p*-Toluenesulfonic acid (p-$CH_3C_6H_4SO_3H$) and CF_3SO_3H (both guaranteed reagents) were used without further purification.

Procedure. Reactions were carried out as in our previous work.[1] Good reproducibilities were observed for the reaction rate as well as for the MWD and structure of products, if the water concentration in the reaction mixture was kept constant.

Table I
Dimer Fractions in Methylstyrene Oligomers Formed by Oxo Acids at 70 °C ($[M]_0$ = 0.10 M)

		dimer fraction, wt %		
catalyst	solvent	*p*-MeSt	*m*-MeSt	*o*-MeSt
p-$CH_3C_6H_4SO_3H$	C_6H_6	90.0		
CF_3SO_3H	C_6H_6	80.1		
$AcClO_4$	C_6H_6	85.3	87.4	97.4
$AcClO_4$	$(CH_2Cl)_2$	18.5	36.9	47.3

MWD of the products was measured by liquid chromatography (LC) in chloroform on a JASCO-FLC-A 700 chromatograph with a refractive index detector at room temperature. When necessary, the dimer fraction was separated from a product by using the same apparatus. The analytic (7.2 mm i.d. × 500 mm) and preparative columns (21.5 mm i.d. × 500 mm) were packed with JSP-101 polystyrene gel. ^1H NMR spectra (100 MHz) were recorded on a Varian HA-100 spectrometer at room temperature in CCl_4.

Results

Effect of the Methyl Group on the MWD of Oligomer. Oligomerization by Oxo Acids. Figure 1 shows MWD of *o*-, *m*-, and *p*-MeSt oligomers obtained in polar ($(CH_2Cl)_2$) and nonpolar (C_6H_6) solvents with the $AcClO_4$ catalyst at a low temperature (5 °C). In this figure, some of the LC curves were depicted under magnification to show the MWD more clearly. A striking difference was found between the MWD for both solvents. The main fraction was dimer in C_6H_6, whereas it was higher oligomers in $(CH_2Cl)_2$. *p*-MeSt oligomers were of higher molecular weights than *m*-MeSt oligomers, irrespective of solvent polarity. *o*-MeSt gave lower oligomers than *m*-MeSt in C_6H_6 but led to higher oligomers than *m*-MeSt in $(CH_2Cl)_2$.

Figure 2 illustrates LC traces for *o*-, *m*-, and *p*-MeSt oligomers produced by $AcClO_4$ at a high temperature (70 °C). The molecular weights of products were lowered by elevating the temperature from 5 to 70 °C (cf. Figure 1), and this effect was remarkable in $(CH_2Cl)_2$.

Other oxo acids (CF_3SO_3H and p-$CH_3C_6H_4SO_3H$) gave similar results under the same conditions. Table I shows the dimer content of the oligomers obtained with the oxo acid catalysts at 70 °C. Dimers were obtained in very high yield in C_6H_6. In spite of their difference in acid strength and structure, all three catalysts formed linear unsaturated dimers predominantly (vide infra). It is noteworthy that *o*-MeSt in conjunction with $AcClO_4$ achieved the almost perfect selectivity for its linear dimer in C_6H_6.

Oligomerization by Metal Halides. Figure 3 shows LC traces for the *o*-, *m*-, and *p*-MeSt oligomers produced by BF_3OEt_2 as a metal halide catalyst. The molecular

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Table II
Composition (wt %) of Methylstyrene Oligomers Formed by Metal Halides at 70 °C ($[M]_0$ = 0.10 M)

		p-MeSt			*m*-MeSt			*o*-MeSt		
catalyst	solvent	dimer	trimer	tetramer	dimer	trimer	tetramer	dimer	trimer	tetramer
$SnCl_4$	C_6H_6	6.1	8.7	13.8						
$EtAlCl_2$	C_6H_6	22.3	13.0	16.2						
BF_3OEt_2	C_6H_6	5.4	15.4	13.0	25.0	34.3	18.2	32.5	22.0	16.3
BF_3OEt_2	C_6H_6[a]	10.3	20.7	15.9	37.0	37.4	15.6	55.8	21.0	12.2
BF_3OEt_2	$(CH_2Cl)_2$[a]	6.6	11.5	18.1	40.7	32.6	17.2	28.9	20.8	14.2

[a] At 80 °C.

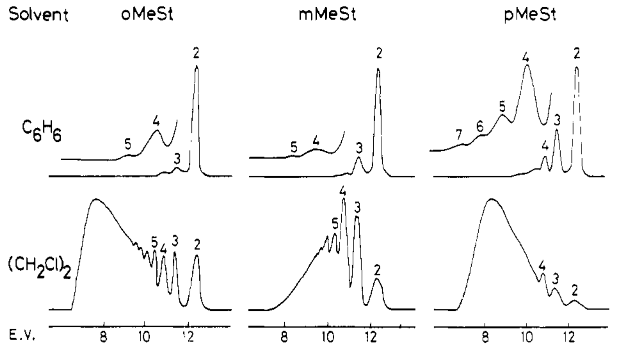


Figure 1. Effect of solvent on MWD in the oligomerization of methylstyrenes by $AcClO_4$ at 5 °C: $[M]_0$ = 0.10 M; [C] = 0.50 (in $(CH_2Cl)_2$) and 1.0 mM (in C_6H_6); conversion >61%. The numbers indicate the degree of polymerization.

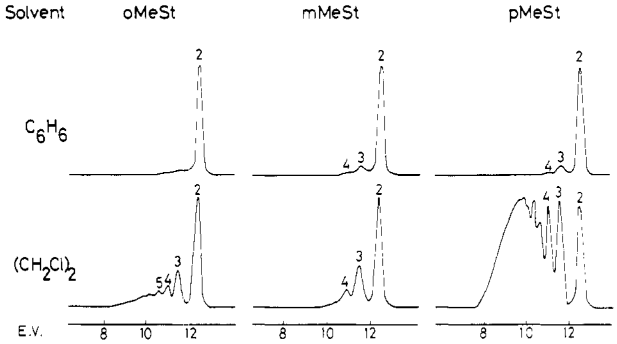


Figure 2. Effect of solvent on MWD in the oligomerization of methylstyrenes by $AcClO_4$ at 70 °C: $[M]_0$ = 0.10 M; [C] = 0.01 (in $(CH_2Cl)_2$) and 1.0 mM (in C_6H_6); conversion >68%. The numbers indicate the degree of polymerization.

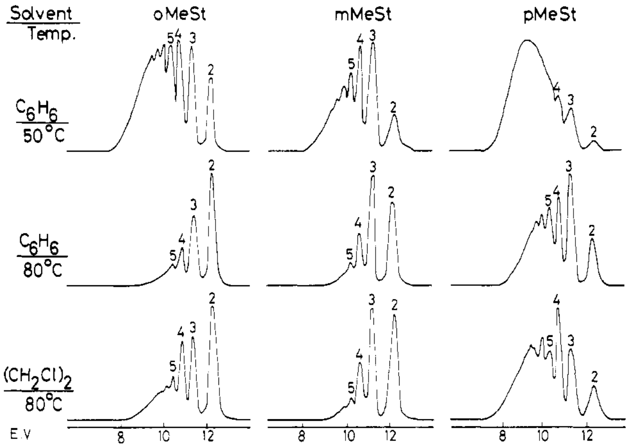


Figure 3. Effect of temperature and solvent on MWD in the oligomerization of methylstyrenes by BF_3OEt_2: $[M]_0$ = 0.10 M; [C] = 5.0 mM; conversion >54%. The numbers indicate the degree of polymerization.

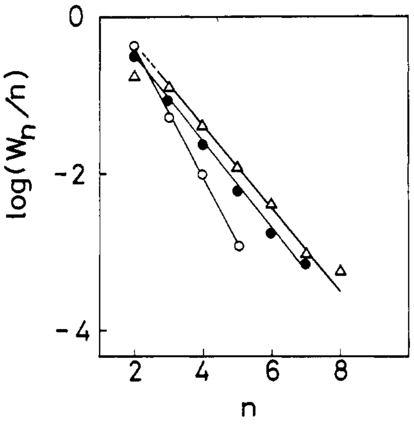


Figure 4. Plots of log (W_n/n) against *n* for the products formed by various catalysts ($[M]_0$ = 0.10 M): (●) from *m*-MeSt by $AcClO_4$ in $(CH_2Cl)_2$ at 70 °C; (○) from *p*-MeSt by CF_3SO_3H in C_6H_6 at 70 °C; (△) from *m*-MeSt by BF_3OEt_2 in C_6H_6 at 80 °C.

weight of these oligomers was always higher than that of the corresponding products formed by $AcClO_4$. In contrast to those in the oligomerization by $AcClO_4$, the MWD was almost independent of solvent polarity, as shown in Figure 3. *p*-MeSt yielded higher oligomers than *m*-MeSt irrespective of reaction conditions, as in the $AcClO_4$-catalyzed oligomerizations.

Other metal halides ($SnCl_4$ and $EtAlCl_2$) gave products similar to those formed by BF_3OEt_2. Table II shows the composition of the methylstyrene oligomers produced by the metal halides in C_6H_6 at 70 or 80 °C. The reactions by the metal halides were characterized by the lower yields of dimers and the higher yields of trimers and tetramers than in those by the oxo acids. These features were also found in the oligomerization of styrene.[1]

Calculation of Transfer Constants. Our previous paper[1] has provided a method for calculation of the transfer constant (k_{tr}/k_p) from the MWD of oligomers, where k_{tr} and k_p indicate the rate constants of transfer and propagation, respectively. On the assumption that elementary processes are composed of initiation, propagation, and transfer, that is, a chain-breaking reaction which is of zero order with respect to monomer, the following relationship holds between the degree of polymerization *n* and the weight fraction W_n of the *n*-mer:[1]

$$\log (W_n/n) = n \log \alpha + \text{constant} \qquad (1)$$

where

$$\alpha = \frac{k_p[M]}{k_p[M] + k_{tr}} = \frac{1}{1 + k_{tr}/(k_p[M])} \qquad (2)$$

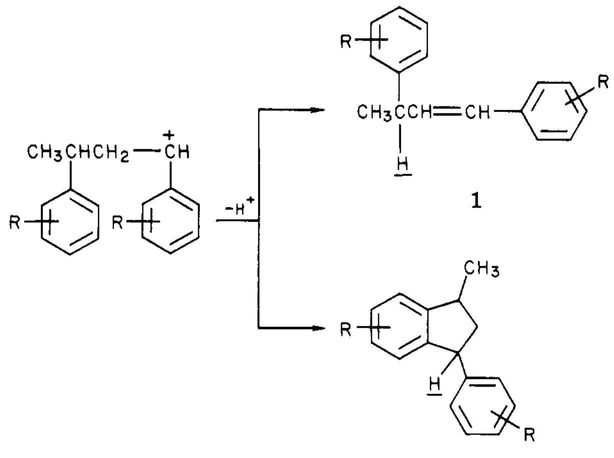
If plotting $\log(W_n/n)$ against *n* gives a straight line, the transfer constant k_{tr}/k_p can be calculated from its slope ($\log \alpha$) on the basis of eq 2. In this calculation, [M] in eq 2 was taken as the mean of the initial and final monomer concentrations in each run.[1] The oxo acids always gave linear plots of eq 1, as shown in Figure 4. In clear contrast, plots for metal halides showed deviations from linearity in the range of low degrees of polymerization. These de-

Table III
Transfer Constants (k_{tr}/k_p) for the Oligomerizations of Styrene and Methylstyrenes at 70 °C ($[M]_0$ = 0.10 M)[g]

catalyst	solvent	(k_{tr}/k_p) × 10^2,[a] mol/L			
		St[e]	*p*-MeSt	*m*-MeSt	*o*-MeSt
p-$CH_3C_6H_4SO_3H$	C_6H_6	144	59		
CF_3SO_3H	C_6H_6	22	34		
$AcClO_4$	C_6H_6	74.9	44.2	81.8	402
$AcClO_4$	$(CH_2Cl)_2$	6.8	2.4	15.1	4.2[b]
$SnCl_4$	C_6H_6	11[d]	4[c]		
$EtAlCl_2$	C_6H_6	6.9[d]	5.0[c]		
BF_3OEt_2	C_6H_6	8.3[c]	2[b]	12.4[b]	8.3
BF_3OEt_2	$(CH_2Cl)_2$[f]	8.1[d]	4[c]	11.3[b]	4.1[b]

[a] Plots of eq 1 were linear over the whole range of n unless otherwise stated. [b] With $n \geqslant 3$. [c] With $n \geqslant 4$. [d] With $\geqslant 5$. [e] From ref 1. [f] At 80 °C. [g] The products were obtained at a conversion >50% (see Figures 1-3).

Scheme I



2

R = CH_3 or H

viations can be attributed to a weak interaction between the growing carbocation and the counterion, as in the styrene oligomerization with metal halides.[1] Table III lists the k_{tr}/k_p values determined from linear portions of the plots. The corresponding values for styrene presented in the previous paper[1] are also shown for comparison. The oxo acids in C_6H_6 gave very large transfer constants, an order of magnitude larger than others.

End-Group Structure. The unstable growing chain of styrene or its derivatives is liable to undergo transfer reactions including β-proton elimination to give a dimer (oligomer) with a terminal double bond (**1**) and intramolecular cyclization leading to its cyclic isomer (**2**) (Scheme I), where, for simplicity, only the formation of dimers was shown and counterions were omitted. Because of the difficulty in determining quantitatively the end-group structure of higher oligomers, the dimer fraction was separated from the product by preparative LC, and subsequently its structure was determined by ^{1}H NMR on the basis of relative amounts of the protons underscored in Scheme I (**1**, δ 3.5 (m, ArCH)[11]; **2**, δ 4.3 (t, Ar_2CH)[4]).

Table IV summerizes the effect of reaction conditions on the fraction of **2**. Under these conditions, the end-group structure was influenced little by conversions ranging from 60 to 90%, and the unsaturated dimers were not converted into the cyclic ones during the reactions. The dimers produced by the oxo acids in C_6H_6 were only unsaturated ones, whereas those formed by the oxo acids in $(CH_2Cl)_2$ and the metal halides in both solvents had not only unsaturated but also cyclic end groups. Particularly, the end-group structure was almost completely cyclic (>90%) in the BF_3OEt_2 catalysis in $(CH_2Cl)_2$. It should be noted that the content of cyclic end groups varied greatly from 18 to 95% according to reaction conditions, showing a sharp contrast to the constant predominance of unsaturated end groups in styrene dimers.

Table IV
Structure of Dimers of Styrene and Methylstyrenes at 70 °C (Conversion 60-90%)

catalyst	solvent	cyclic dimer (**2**), %			
		St	*p*-MeSt	*m*-MeSt	*o*-MeSt
p-$CH_3C_6H_4$-SO_3H	C_6H_6	0	0		
CF_3SO_3H	C_6H_6	0	0		
$AcClO_4$	C_6H_6	0	0	0	0
$AcClO_4$	$(CH_2Cl)_2$	0	18	26	29
$SnCl_4$	C_6H_6		58		
$EtAlCl_2$	C_6H_6		71		
BF_3OEt_2	C_6H_6	5	56		
BF_3OEt_2	C_6H_6[a]		31	64	45
BF_3OEt_2	$(CH_2Cl)_2$[a]		92	94	95

[a] At 80 °C.

Discussion

Effect of Reaction Conditions (Catalysts and Solvents). In contrast to the small solvent effects on the MWD of oligomers formed by the metal halides (Figure 3), the oxo acids yielded products, the distributions of which differed considerably in polar and nonpolar solvents (Figures 1 and 2). The products in a nonpolar solvent were of low molecular weight (Figures 1 and 2), gave large transfer constants (Table III), and had only unsaturated end groups (Table IV). All of these characteristics indicate the promoted β-hydrogen transfer from the growing end, which should be induced by strong interaction of the oxygen atoms in the counterion that associates close to the cationic site.[2]

In the reactions by the metal halides, on the other hand, the products were of high molecular weight even in a nonpolar solvent to give smaller k_{tr}/k_p values (Figure 3 and Table III), and both the MWD and the transfer constants depended little on solvent polarity. The counterions derived from the metal halides should be reluctant to interact with the growing end even in a nondissociated state because of their bulkiness and lack of nucleophilic oxygen atoms. Therefore the transfer constants are always small, and the effect of solvent was hardly observed.

The fact that larger k_{tr}/k_p values were obtained with a weaker oxo acid suggests that a more nucleophilic counterion derived from it accelerates transfer reactions through the strong interaction with the growing carbocation. Although a clear difference could not be detected between the transfer constants for the metal halides, $EtAlCl_2$, a stronger Lewis acid, resulted in more cyclized end groups than BF_3OEt_2 and $SnCl_4$, as shown in Table

IV. A similar trend has been reported for some styrene derivatives.[12]

The facility in cyclization leading to the cyclic structure decreased in the order (Table IV):

(metal halide in polar solvent) >
(metal halide in nonpolar solvent) >
(oxo acid in polar solvent) ≫
(oxo acid in nonpolar solvent)

This is quite the reverse of that for the transfer constant (Table III). The strength of the interaction between the growing end and the counterion should also follow the above order, and thus it can be concluded that intramolecular cyclization predominates over β-proton elimination when the cation–anion interaction is weakened (vide infra).

Effect of the Methyl Group. *o*-MeSt and *p*-MeSt are more reactive than styrene,[13,14] and they gave higher oligomers except for *o*-MeSt in C_6H_6. Another effect of the methyl group is the promotion of cyclization that led to more cyclic end groups than in the styrene oligomerizations (Table IV). The electron-donating methyl group not only weakens the interaction between the growing carbocation and the counterion, but also increases the electron density of the penultimate phenyl group in the cation. Thus, the intramolecular cyclization preceded the β-proton elimination that might need the assistance of the counterion. In *m*-MeSt oligomerizations, the cyclization will be further facilitated by the increased electron density of positions ortho to the methyl group.

The transfer constant for the *o*-MeSt/$AcClO_4$ system in C_6H_6 was abnormally larger than the corresponding values for *p*-MeSt and *m*-MeSt (Table IV). This difference may be caused by the steric hindrance of the ortho methyl group that disturbs the approach of monomers toward the cationic site. On the other hand, the peculiarity of *o*-MeSt was not observed in a polar solvent (see Figures 1 and 2 and Table III) or in the reactions by the metal halide catalysts (Figure 3 and Table III). Consequently, it was concluded that the marked steric hindrance of the ortho methyl group operates only when there is a strong interaction between the growing carbocation and the counterion.

In sum, the MWD and structure of the methylstyrene oligomers have revealed clear differences in catalytic behavior between the oxo acids and the metal halides, which can be interpreted consistently in terms of the interaction between the growing carbocation and the counterion.

References and Notes

(1) T. Higashimura, M. Hiza, and H. Hasegawa, *Macromolecules*, **12**, 217 (1979).
(2) T. Higashimura and H. Nishii, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 329 (1977).
(3) T. Higashimura, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20** (1), 161 (1979).
(4) A. R. Taylor, G. W. Keen, and E. J. Eisenbraun, *J. Org. Chem.*, **42**, 3477 (1977).
(5) J. M. Barton and D. C. Pepper, *J. Chem. Soc.*, 1573 (1964).
(6) G. Evans et al., *J. Chem. Soc.*, 2982, 4123 (1959); 3532 (1961).
(7) H. Nishii and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1179 (1977).
(8) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).
(9) C. S. Marvel and G. L. Schertz, *J. Am. Chem. Soc.*, **65**, 2054 (1943).
(10) T. Masuda and T. Higashimura, *J. Macromol. Sci., Chem.*, **5**, 547 (1971).
(11) S. W. Ela and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 5777 (1966).
(12) R. Wolovsky and N. Maoz, *J. Org. Chem.*, **38**, 4040 (1973).
(13) C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor, and T. Alfrey, Jr., *J. Am. Chem. Soc.*, **74**, 4848 (1952).
(14) C. G. Overberger, T. M. Chapman, and T. Wojnarowski, *J. Polym. Sci., Part A*, **3**, 2865 (1965).

Determination of the Rate Constants of the Elementary Steps in the Cationic Polymerization of Styrene by Trifluoromethanesulfonic Acid[1]

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ABSTRACT: The cationic polymerization of styrene initiated by CF_3SO_3H was investigated in 1,2-dichloroethane at −1 to 30 °C by the stopped flow/rapid scan spectroscopy which was combined with the rapid quenching technique. The rate constants of the elementary steps, initiation (k_i), propagation (k_p), spontaneous transfer and termination ($k_{t'}$), and transfer to monomer (k_{tm}), were determined at four temperatures on the basis of the time courses of the cation formation, monomer consumption, and molecular weight of the quenched polymer. The k_p value varied from 5×10^4 to 2×10^5 M^{-1} s^{-1} in the temperature range studied, and $k_{t'}$ was 100–300 s^{-1}. The lifetime of the propagating species ranged from 5 to 100 ms. $(n\text{-Bu})_4N^+CF_3SO_3^-$ was added as a common ion salt, but its influence on the rate constants was small. The activation energy as determined from the Arrhenius plots was 7 and 15 kcal/mol for the k_p and k_{tm} processes, respectively. The transfer constants k_{tm}/k_p and $k_{t'}/k_p$ were close to 0.01 at the 0–30 °C range, in agreement with those reported for the H_2SO_4 initiator.

Fundamental kinetics of the cationic polymerization of vinyl monomers remained unsolved for some time because of the inability to detect the short-lived propagating species. Several years ago, however, De Sorgo et al.[2] 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 performed for the complex polymerization behavior of this system.[3,4] We have similarly observed the absorption of the polystyryl cation, using trifluoromethanesulfonic acid as initiator,[5] and carried out a preliminary kinetic study based on the direct determination of the

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