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Conductance Stopped-Flow Study of Cationic Polymerizations of p-Methoxystyrene and Styrene

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SUMMARY: Conductance stopped-flow analysis on the initial phase of cationic polymerizations of p-methoxystyrene and styrene revealed rapid changes in conductance (within 20-50 ms) that were related to the initiation process. Initiation rate constants were obtained for CF_3SO_3H, CH_3COClO_4, and $BF_3O(C_2H_5)_2$ initiators in 1,2-dichloroethane at 30°C. They agreed closely with those determined by stopped-flow spectroscopy, and decreased with increasing monomer concentration.

INTRODUCTION

Conductometric analysis in the cationic polymerization of vinyl compounds can give insight into the electrochemical and kinetic nature of the propagating species (carbocation), because it is an unstable weak electrolyte that leads to changes in the conductance of the polymerization solution on its formation (initiation) and subsequent propagation or termination. In view of its short lifetime (HIGASHIMURA and SAWAMOTO, 1978) these changes must occur too fast to be completely analyzed by conventional conductance measurements as done in previous studies (GANDINI and PLESCH, 1964, 1968; DUNN et al., 1976; CHMELIR et al., 1977).

The recent development of the conductance stopped-flow (κ-SF) technique has now enabled us to follow a fast reaction conductometrically with a millisecond time resolution (OKUBO et al., 1979). By this method we have investigated the initial processes in cationic polymerizations of p-methoxystyrene and styrene. This report describes preliminary κ-SF data which are related to the initiation process by comparison with our results by stopped-flow spectroscopy (UV-SF) (HIGASHIMURA and SAWAMOTO, 1978; SAWAMOTO and HIGASHIMURA, 1979). Brief κ-SF studies with an apparatus having a relatively long dead time (∿100 ms) have recently been reported for the styrene polymerization by perchloric acid (PEPPER, 1974, 1976; LORIMER and PEPPER, 1976).

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EXPERIMENTAL

κ-SF measurements were performed under dry nitrogen at 30°C on an apparatus described in detail elsewhere (OKUBO et al., 1979; dead time ∿1 ms). The conductometric cell was of an inside dimension 2 mm x 2 mm x 10 mm with two platinum plates fixed on the opposite inside walls. A three-way cock was attached to each reservoir so that monomer and initiator solutions could be supplied against a continuous nitrogen stream. The water concentration in the cell was estimated to be below 1 mM. Procedures for UV-SF spectroscopy and handling of materials were reported (SAWAMOTO and HIGASHIMURA, 1978, 1979).

RESULTS and DISCUSSION

Polymerization of p-Methoxystyrene. The reactions of p-methoxystyrene with three cationic initiators (CF_3SO_3H, CH_3COClO_4, and $BF_3O(C_2H_5)_2$) were followed by the κ-SF method in 1,2-dichloroethane at 30°C. Figure 1 illustrates typical recorder traces for the CH_3COClO_4 initiated polymerization.

The conductance of the reaction mixture exhibited distinct two relaxations: an initial fast increase ($t < 20$ ms, curve a) followed by a much slower decrease (40 ms $< t < 2$ s, curve b), each of which was asymptotic to an equilibrium value. Both processes gave linear log(Δκ)-time plots (Δκ: the deviation of the conductance from the equilibrium value) to yield pseudo-first-order rate constants. The monomer conversions at the equilibrium stages were 18% (∿10 ms) and 80% (∿1.0 s). Similar results were obtained with the other initiators.

The initial increase in conductance (Fig. 1a) most likely resulted from the initiation reaction. If this is the case, its pseudo-first-order rate constant, k, will be related to the initiation rate constant, $k_i(\kappa)$, by Eq. 1 because the monomer was in large excess over an initiator ($[M]_0 >> [C]_0$):

$$k = k_i(\kappa)\,[M]_0 \qquad (1)$$

Table I lists the $k_i(\kappa)$ values in 1,2-dichloroethane for the three initiators.

Under the same conditions as in the κ-SF measurements the initiation rate constant, $k_i(UV)$, was separately determined spectroscopically by the UV-SF method on the basis of Eq. 2 (HIGASHIMURA and SAWAMOTO, 1978):

$$R_i(t \rightarrow 0) = k_i(UV)\,[M]_0\,[C]_0 \qquad (2)$$

where $R_i(t \rightarrow 0)$ is the initial initiation rate. Except

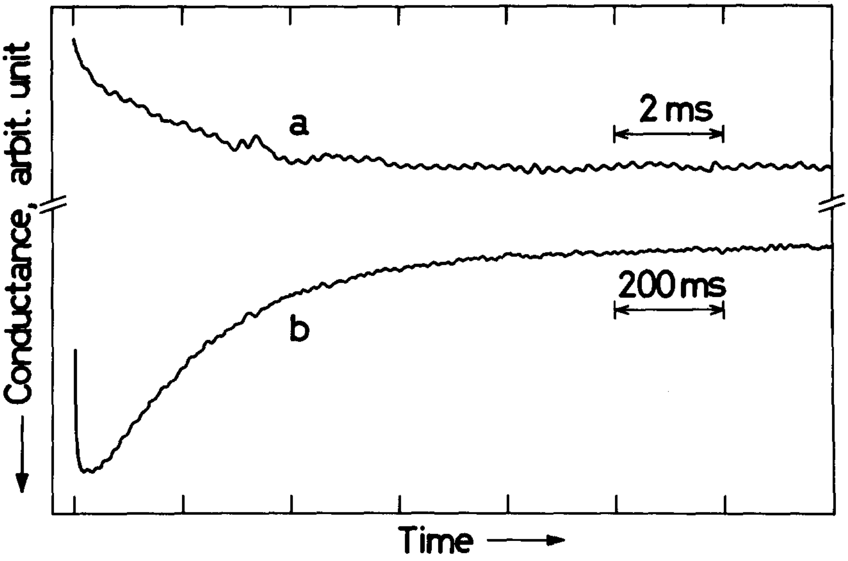

Figure 1. Typical κ-SF recorder traces for the p-methoxystyrene polymerization by CH_3COClO_4 in 1,2-dichloroethane at 30°C: $[M]_0 = 5.0$ mM, $[C]_0 = 0.10$ mM.

TABLE I

Initiation Rate Constants for p-Methoxystyrene Polymerization in 1,2-Dichloroethane at 30°C

Initiator	$[C]_0$, mM	$[M]_0$, mM	$k_i(\kappa) \times 10^{-4}$, $M^{-1}s^{-1}$	$k_i(UV) \times 10^{-4}$, $M^{-1}s^{-1}$
$BF_3O(C_2H_5)_2$	0.50	5.0	0.27	0.0014^a
	1.0	5.0	0.15	0.0013^a
CF_3SO_3H	0.30	5.0	6.8	$4.9^{b,c}$
CH_3COClO_4	0.10	5.0	9.7	8.4^b
	0.20	5.0	8.2	3.6
	0.20	10	3.9	2.3
	0.20	50	0.74	0.82
	0.20	100	0.33	0.41
	0.20	250	0.18	0.21

a) Data of HIGASHIMURA and SAWAMOTO (1978). b) Data of SAWAMOTO and HIGASHIMURA (1979). c) $[C]_0 = 0.10$ mM.

TABLE II

Solvent Effect on Initiation Rate Constants in p-Methoxystyrene Polymerization at 30°C ($[M]_0$= 5.0 mM)

Initiator	$[C]_0$,	$k_i(\kappa) \times 10^{-4}$, $M^{-1}s^{-1}$	
	mM	$(CH_2Cl)_2$	$(CH_2Cl)_2/CCl_4$ [a]
$BF_3O(C_2H_5)_2$	0.50	0.27	0.048
CF_3SO_3H	0.30	6.8	3.0
CH_3COClO_4	0.20	8.2	3.2

a) CCl_4, 60 vol%.

those for $BF_3O(C_2H_5)_2$ $k_i(\kappa)$ and $k_i(UV)$ agreed closely with each other (Table I), which shows clearly that the observed rapid changes in conductance are due to the initiation reaction. Thus, the κ-SF technique was found powerful in the hitherto difficult analysis of the fast initiation processes in cationic polymerizations. It should be noted that the determination of $k_i(\kappa)$ based on Eq. 1 needs only relative changes in conductance, not its absolute values.

The discrepancy between $k_i(\kappa)$ and $k_i(UV)$ for $BF_3O(C_2H_5)_2$ suggests that the initial phase of the polymerization by this metal halide involves complex reactions contributing to conductance changes. The origin of the secondary decrease in conductance (Fig. 1b) is obscure at present, but it may be a decrease of the mobility of the propagating species with increasing chain length.

Effects of Monomer Concentration and Solvent. The data for CH_3COClO_4 in Table I demonstrate a large dependence of $k_i(\kappa)$ on the monomer concentration, $[M]_0$; $k_i(\kappa)$ was inversely proportional to $[M]_0$ ranging from 5.0 to 250 mM. A very similar trend was observed for the $k_i(UV)$ values that were newly obtained at higher $[M]_0$ in this work. Our recent studies also revealed that the propagation rate constants decrease with increasing $[M]_0$ in the cationic polymerization of styrenes (HIGASHIMURA et al., 1979). Such effects of the monomer concentration cannot be explained simply in terms of changes in the medium polarity since $[M]_0$ was relatively small, and they are the subject of our future publications.

Table II summarizes the effect of solvent on $k_i(\kappa)$. Their systematic decrease in a less polar solvent is consistent with the initiation reaction yielding a highly polarized transition state from uncharged reactants.

Similar solvent effects have been found for k_i(UV) (HIGASHIMURA and SAWAMOTO, 1978).

Polymerization of Styrene. κ-SF measurements were also carried out in the polymerization of styrene by CF_3SO_3H in 1,2-dichloroethane at 30°C ($[M]_0$= 20-100 mM, $[C]_0$= 5.0 mM). The k_i(κ) value at $[M]_0$= 20 mM was 180 $M^{-1}s^{-1}$, close to the corresponding k_i(UV) (130 $M^{-1}s^{-1}$). These initiation rate constants were two orders of magnitude smaller than those for p-methoxystyrene (Table I), reflecting the reactivity difference between the two monomers. The rate constant k_i(κ) decreased at higher $[M]_0$ as in the p-methoxystyrene polymerization.

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