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Lifetime of the Propagating Species in the Cationic Polymerization of p-Methoxystyrene[1]

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ABSTRACT. Lifetime of the propagating species and initiation rate constants (k_i) were evaluated for the cationic polymerization of p-methoxystyrene initiated by I_2, CH_3SO_3H, $BF_3O(C_2H_5)_2$, and $SnCl_4$. The lifetime was found to be fairly long, ranging from 0.2 to several seconds in 1,2-dichloroethane at 30°C; that for the intermediate generated by iodine (2-6 s) much exceeded the others. The k_i value increased in the order: $I_2 < CH_3SO_3H \ll BF_3O(C_2H_5)_2 \sim SnCl_4$.

The key intermediate in cationic vinyl polymerization is the propagating species (carbocation) which controls the reaction rate and the structure of product polymers. Until quite recently, however, quantitative description of its chemistry has met with difficulty because of its short lifetime relative to the available time-resolution in measurements. Recent application of stopped-flow spectroscopy to cationic polymerization has overcome this difficulty to afford electronic spectra, instantaneous concentration, and propagation rate constants of the intermediates for several systems, as reported by SORGO et al. (1973), LORIMER and PEPPER (1976), PEPPER (1976), KUNITAKE and TAKARABE (1976, 1978), and by us (SAWAMOTO and HIGASHIMURA (1978a, b)). In this paper we wish to discuss the formation and decay (lifetime) of the propagating species in the cationic polymerization of p-methoxystyrene on the basis of our stopped-flow measurements.

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[1] Stopped-Flow Study of the Cationic Polymerization of Styrene Derivatives. Part 3.

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RESULTS and DISCUSSION

Initiation Rate Constant. In the p-methoxystyrene polymerization by a wide variety of cationic initiators, the propagating species exhibits a strong absorption centered at 380 nm (SAWAMOTO and HIGASHIMURA, 1978a, b). Its instantaneous concentration ($[P^*]$), followed by observing the absorbance at 380 nm by the stopped-flow method, increases with time, reaches a maximum, and decreases gradually. Since the spectra consisted of only the 380-nm band even at the very early stage of the reaction, the initiation rate (R_i) was determined from the initial slope of $[P^*]$ vs. time plots. The R_i value then gave the initiation rate constant (k_i) with the assumption of a bimolecular initiation reaction between an initiator and the monomer:

$$R_i = \frac{d[P^*]}{dt}(t \rightarrow 0) = k_i [C]_o [M]_o \qquad (1)$$

where $[C]_o$ and $[M]_o$ represent the initial concentrations of the initiator and monomer, respectively. Experiments in this work were done in the same way as described elsewhere (SAWAMOTO and HIGASHIMURA, 1978a).

Table I lists the R_i and k_i values for the polymerization in 1,2-dichloroethane at 30°C with four initiators (I_2, CH_3SO_3H, $BF_3O(C_2H_5)_2$, and $SnCl_4$). For the respective initiators practically constant k_i values were obtained independent of $[C]_o$; therefore, the initiation must proceed through a simple addition of an initiator to a monomer molecule, as assumed in Eq. 1. The k_i value increased in the following order: $I_2 < CH_3SO_3H << BF_3O(C_2H_5)_2 \sim SnCl_4$. It is of interest that this order agrees with the empirical activity order of cationic initiators, while the corresponding propagation rate constants (k_p) hardly depended on the initiators ($4 \times 10^3 - 2 \times 10^4$ $M^{-1}s^{-1}$ in 1,2-dichloroethane at 30°C) (SAWAMOTO and HIGASHIMURA, 1978a).

Lifetime of the Propagating Species. As $[P^*]$ maintained its maximal value ($[P^*]_{max}$) for a certain period (from a few to several tens seconds, depending on the initiators) before its gradual decay, we considered $[P^*]_{max}$ as the stationary concentration of the propagating species. This led to estimation of its mean lifetime (τ) according to Eq. 2:

$$\tau = [P^*]_{max}/R_i \qquad (2)$$

The values for the four initiators are given in Table

I. It should be noted that Eq. 2 yields a minimum estimate of τ, because the initiation rate when $[P^*]$ = $[P^*]_{max}$ must be smaller than its initial value.

TABLE I

Initiation Rate and Lifetime of the Propagating Species in the p-Methoxystyrene Polymerization in 1,2-Dichloroethane[a]

Initiator	$[C]_o$, 10^{-3}M	$[P^*]_{max}^{b}$, 10^{-6}M	R_i, 10^{-6}Ms^{-1}	k_i, $M^{-1}s^{-1}$	τ, s
I_2	5.0	5.6	0.91	0.037	6.2
	7.5	8.1	1.5	0.040	5.4
	15	21	9.9	0.13	2.1
CH_3SO_3H	3.0	1.9	9.5	0.63	0.20
	5.0	4.5	16	0.64	0.28
$BF_3O(C_2H_5)_2$	0.30	15	21	14	0.71
	0.50	21	35	14	0.60
	1.0	31	66	13	0.46
$SnCl_4$	0.030	7.4	2.8	19	2.6
	0.050	14	8.4	33	1.6
	0.15	41	37	49	1.1

[a] $[M]_o = 5.0 \times 10^{-3}$ M; +30°C.

[b] Data of SAWAMOTO and HIGASHIMURA (1978a).

In spite of this limitation, however, Table I shows that the propagating species derived from p-methoxystyrene has a relatively long lifetime ranging from 0.2 to several seconds. This corresponds to the fact that the polymerization took place in a time scale of seconds. The long lifetime must result from a high stability of the propagating species induced by its electron-donating p-methoxy substituent. Interestingly, the data of KUNITAKE and TAKARABE (1978) suggest a much shorter lifetime of the propagating polystyryl cation (2-30 ms) under similar conditions to ours, although these authors did not explicitly report the lifetime in their original paper.

The τ values in Table I also indicate that iodine can generate, though slowly, a propagating species with a much longer lifetime than the others. This can be related to our recent findings that the iodine-initiated polymerization of p-methoxystyrene under suitable conditions gives "living" polymers that can undergo a block copolymerization with isobutyl vinyl ether (HIGASHIMURA and KISHIRO, 1977; HIGASHIMURA et al.).

TABLE II

Solvent Effect on the Initiation Rate and Lifetime of the Propagating Species in the p-Methoxystyrene Polymerization by $BF_3O(C_2H_5)_2$[a]

Solvent, v/v $(CH_2Cl)_2/CCl_4$	$[P^*]_{max}$[b], $10^{-6}M$	R_i, $10^{-6}Ms^{-1}$	k_i, $M^{-1}s^{-1}$	τ, s
100/ 0	21	35	14	0.60
90/10	13	19	7.5	0.70
80/20	7.3	8.3	3.3	0.87
60/40	2.8	1.9	0.74	1.5

[a] $[M]_o = 5.0 \times 10^{-3}$ M; $[C]_o = 0.50 \times 10^{-3}$ M; +30°C.
[b] Data of SAWAMOTO and HIGASHIMURA (1978b).

From the lifetime data in conjunction with the corresponding k_p values, we can calculate the theoretical degree of polymerization ($DP_{theor.} = k_p[M]_o\tau$). $DP_{theor.}$ for the systems in Table I were 20-150 and agreed well with the observed values (50-100) under similar conditions.

Solvent Effects. Table II summarizes the k_i and τ values for the $BF_3O(C_2H_5)_2$-initiated polymerization in $(CH_2Cl)_2/CCl_4$ solvent mixtures with various dielectric constants (5-10). Eqs. 1 and 2 were applied similarly to obtain these values, because, in the reaction by $BF_3O(C_2H_5)_2$ initiator, [P*] can be properly determined from the absorbance at 380 nm even in nonpolar solvents (SAWAMOTO and HIGASHIMURA, 1978b). The initiation rate decreased with decreasing solvent polarity, in accordance with the expectation that a bimolecular reaction between uncharged molecules (initiator and monomer) forming an ionic intermediate should decelerate in less polar media. The lifetime of the propagating species, on the other hand, showed little dependence on solvent polarity.

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