Macromolecules 1988, *21*, 2339–2346

(5) Eliel, E. L.; Hartman, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807.

(6) Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem.* **1976**, *98*, 567.

(7) Tien, C. F.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1976**, *98*, 7109. Mathis, C.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1982**, *104*, 634.

(8) Huang, S. S.; Mathis, C.; Hogen-Esch, T. E. *Macromolecules* **1976**, *14*, 1802.

(9) (a) Vancea, L.; Bywater, S. *Macromolecules* **1981**, *14*, 1776. (b) Tien, C. F.; Hogen-Esch, T. E., unpublished results.

(10) Buese, M. A.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1985**, *107*, 4509.

(11) Configurations at chiral sulfur are shown by a subscripted S; *pro-R* or *-S* refer to the Cahn–Ingold–Prelog configuration of the chiral center formed upon cation-side (syn) reaction.

(12) Bywater, S. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1986**, *27*(1), 149.

(13) The *pro-R* and *pro-S* positions of the cation in the carbanion center (Scheme I) refer to the (*R*) and (*S*) asymmetric centers $P-CH_2-C^*(R)(CXY)-CH_2C(R)(CXY)^-$, M^+ formed upon subsequent cation-side monomer addition. The Cahn–Ingold–Prelog relative priorities of the groups attached to the asymmetric center formed upon monomer addition is defined as $CXY > PCH_2 > CH_2C(R)CXY > R$.

(14) Soum, A.; Hogen-Esch, T. E. *Macromolecules* **1985**, *18*, 690.

Kinetics of Methyl, Ethyl, and Isopropyl Vinyl Ether Polymerizations Initiated by Trityl Salts

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ABSTRACT: Kinetics of methyl, ethyl, and isopropyl vinyl ether (MVE, EVE, IPVE) polymerizations initiated by $Ph_3C^+SbCl_6^-$ in CH_2Cl_2 were examined between −40 and 0 °C by using adiabatic calorimetry and spectrophotometry as previously applied to isobutyl vinyl ether (IBVE) polymerization. Behavior of these polymerizations is close to that of IBVE, and a similar kinetic scheme is proposed. Again, initiation is slow (duration comparable to that of propagation), and significant transfer and termination processes are observed. Values of rate constants for initiation (k_i = 0.6–15 L mol^{-1} s^{-1} at 0 °C) and for propagation (k_p = 260–11 200 L mol^{-1} s^{-1} at 0 °C) reflect the same order of overall reactivity: MVE < EVE < IBVE < IPVE. Nevertheless, this increase is less pronounced for propagation than for initiation, particularly from EVE to IPVE, which in fact might suggest a fall in reactivity of the growing cations with increasing bulkiness of the side group. As a conductimetric study on polymerization and postpolymerization media (EVE) has shown that propagation takes place essentially on free ions, this would agree with differences in solvation states of the propagating species. A detailed comparison of the kinetic parameters (k_p, E_p, $\Delta S^{\ddagger}{}_p$) of these chemically initiated polymerizations with data reported for radiation-induced processes led to a good agreement between the two systems (EVE apart) and supports the existence of equilibria between dissociated ions of different reactivities—bare, chain solvated, and solvent solvated—depending on the size of monomer side group. It appears thus that solvation of the growing cations by CH_2Cl_2, recently proposed by Stannett et al., may be considered in cationic polymerization.

Introduction

We previously reported a reexamination of the kinetics of the cationic polymerization of isobutyl vinyl ether (IBVE) initiated by triphenylmethyl hexachloroantimonate ($Ph_3C^+SbCl_6^-$) in methylene dichloride.[1] We observed a relatively slow initiation with respect to propagation (incomplete initiator consumption at temperatures equal to or lower than 0 °C) and significant transfer and termination processes. This showed that the system was not the simple model of cationic polymerization presented in earlier studies,[2,3] even if we agree with a predominant contribution of free ions in the propagation process.

Investigation of bulk radiation induced polymerization of the same monomer[4,5] led to much larger rate constants. The factor of ~6 observed at 0 °C between the k_p of the radiochemical and chemical system is not necessarily incoherent since, independently of any solvation process, the change in reactivities of the two bare free cations might be explained by the difference in dielectric constants in the bulk ($D \sim 3$) and in CH_2Cl_2 solution ($D \sim 9$). Later studies performed on other alkyl vinyl ethers[6-8] by both radiation and chemical initiation techniques showed that such differences in k_p were not limited to isobutyl vinyl ether, and they focused our interest upon the kinetic aspects of methyl (MVE), ethyl (EVE), and isopropyl (IPVE) vinyl ethers polymerization initiated by $Ph_3C^+SbCl_6^-$ in CH_2Cl_2 solution. Preliminary results were communicated elsewhere,[9] and this paper deals with a more complete discussion of the relative reactivities of the different ethers together with a comparison with the rate constants reported for radiochemical initiation in solution.[10-13]

Experimental Section

All reagents were thoroughly purified and handled by using high-vacuum techniques as previously described.[1] Instantaneous monomer and initiator concentrations were obtained from coupled adiabatic calorimetry and spectrophotometry as before. The adjunction of a conductivity cell (platinum plates 10 × 30 mm, cell constant 0.051 cm^{-1}) in the reactor allowed measurement of the instantaneous values of conductivity.

The conductimetric study was also performed on the reaction medium after the polymerization by adding successively, in vacuo and at the requisite temperatures, known volumes of solvent contained in suitable ampules.

Number-average molecular weights were measured by using either vapor-pressure osmometry (Hewlett-Packard 300) or membrane osmometry (Mechrolab).

Results

Kinetic Study. All rate constants were computed by using the kinetic scheme already applied for IBVE polymerization (see ref 1):

1. initiation

$$I + M \xrightarrow{k_i} P_1^+$$

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2. propagation

$$P_n^+ + M \xrightarrow{k_p} P_{n+1}^+$$

3. transfer to monomer

$$P_n^+ + M \xrightarrow{k_{trm}} P_n + P_1^+$$

4. unimolecular termination (assumed)

$$P_n^+ \xrightarrow{k_t} P_n$$

Internal initiation rate constants k_i are computed from the plots of R_i versus the experimental [M][I] product. The following linear relationship allows the determination of internal ($k_p + k_{trm}$) and k_t constants:

$$-\frac{1}{\ln (M_0/M)} \frac{d \ln M}{dt} = (k_p + k_{trm}) \frac{I_0 - I}{\ln (M_0/M)} - k_t$$

The ratio k_p/k_{trm} is calculated from

$$\frac{k_p}{k_{trm}} = \frac{(M_c/I_c)\mathrm{DP}_n}{(M_c/I_c) - \mathrm{DP}_n}$$

where

$$M_c = M_0 - M \qquad I_c = I_0 - I$$

and together with the ($k_p + k_{trm}$) value leads to both k_p and k_{trm} values.

MVE Polymerization. This monomer is gaseous at room temperature (bp = 8 °C (760 mmHg)). Moreover, polymerization rate at −40 °C was too slow to be measurable by calorimetric techniques. Thus our experiments were performed within the −20 to 0 °C temperature range.

The polymerization enthalpy, computed from temperature rise and recovered polymer, was found to be $\overline{\Delta H_p}$ = −16 kcal mol^{-1}. As we previously observed for IBVE, initiation of MVE polymerization by Ph_3C^+ was not instantaneous, and internal first orders with respect to monomer and initiator were also observed (Figure 1).

This is opposite to what was reported by Ledwith et al.[7] for the initiation reaction of MVE by tropylium cation, and this behavior might be related to the differences in the geometries of the two initiator cations. Although we observed a slightly sigmoidal shape of the R_i plot at the highest temperature (0 °C), the initiation rate constants were measured at −20, −10, and 0 °C. Activation energies for initiation and propagation were found to be respectively 8.7 and 11.1 kcal mol^{-1} (Table I and Figure 2). This monomer leads to the most stable active species as indicated by the values of k_t and by the variation of [P$^+$] during the polymerization (Figure 4).

For each step of the polymerization, values of the rate constants are considerably lower than for the other ethers (Table I), and this large difference in reactivity places MVE apart. It must be noted that all attempts at radiochemical polymerization of this monomer were unsuccessful, but this was however interpreted by chain terminator effect of byproducts resulting from monomer radiolysis.[14]

EVE Polymerization. Even if the values of k_t express a stability of EVE growing cations comparable to that observed with MVE, kinetic curves show significant termination processes, even at −25 °C, and this does not agree with Ledwith's and Stannett's conclusions concerning experiments with successive monomer additions. They reported, either with IBVE[2] or with EVE,[6] that a new addition of monomer (same concentration) at the end of a polymerization (yield 90%) restarts the reaction with a similar rate, and thus they assumed that no termination had occurred.

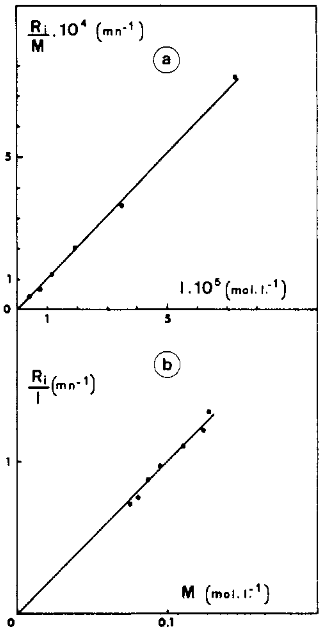


Figure 1. MVE polymerization at −20 °C in CH_2Cl_2. First internal orders with respect to initiator (a) and monomer (b): $[M]_0$ = 0.128 mol L^{-1}; $[I]_0$ = 7.3 × 10^{-5} mol L^{-1}.

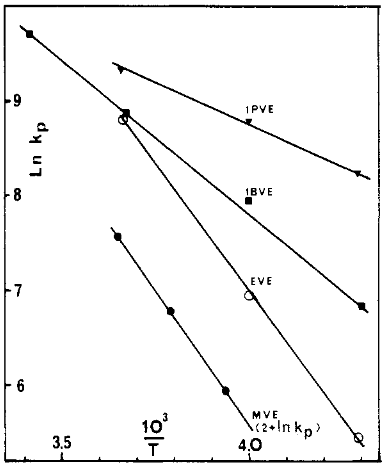


Figure 2. Arrhenius plots for the propagation rate constant for MVE, EVE, IBVE, and IPVE.

We carried out a similar experiment at −25 °C (see Figure 3). The complete kinetic treatment, taking into account the values of the rate constants (Table I), led to the active center concentrations given in Table II and Figure 3a. It should be noted that when the second charge of monomer is added, (1) there remains 20% of initiator and (2) active center concentration is only 71% of the consumed initiator, which shows that termination cannot be neglected. The second addition of monomer accelerates the consumption rate of the remaining initiator and leads to new active centers. Thus polymerization rate increases since [M] and [P*] both increase (Figure 3b). Concentrations of eventually remaining initiator were not reported from Ledwith's and Stannett's experiments, but it seems likely that in these two cases initiation by the remaining salt might roughly compensate for the destruction of previously formed active centers and thus explain the comparable rates observed when adding a new charge of monomer.

IPVE Polymerization. This polymerization proceeds more rapidly ($t_{1/2}$ ~ a few seconds) than for EVE, and initial monomer concentrations were lowered to maintain

Table I
Initiation, Propagation, Transfer, and Termination Rate Constants for MVE, EVE, and IPVE Polymerizations Initiated by $Ph_3C^+SbCl_6^-$ in CH_2Cl_2 at Different Temperatures

monomer	T, °C	k_i, L mol^{-1} s^{-1}	E_i, kcal mol^{-1}	k_p, L mol^{-1} s^{-1}	E_p, kcal mol^{-1}	k_{trm}, L mol^{-1} s^{-1}	E_{trm}, kcal mol^{-1}	k_t, s^{-1}
MVE	0	0.6		260		3.5		0.017
	-10	0.31	8.7	120	11.1	1.5	15	0.01
	-20	0.17		52		0.4		0.003
EVE	0	2.3		7000		74		0.02
	-25	0.8	6.7	1020	10.8	7.9	13	0.01
	-40	0.27		230		1.2		
IBVE[a]	20	16		15400		570		0.8
	0	5.4		6800		180		0.2
	-25	0.75	9.3	2800	5.5	27	9.8	0.03
	-40	0.3		920		8		0.01
IPVE	0	15		11200		135		2.3
	-25	6	5.6	6500	3.5	46	5.8	0.4
	-40	2.5		3700		22		0.1

[a] Results previously reported.[1] Concentration ranges: $[M]_0 = 2\text{–}15 \times 10^{-2}$ M; $[Ph_3C^+]_0 = 5.5\text{–}8 \times 10^{-5}$ M.

Table II
Successive Polymerizations of EVE at -25 °C

	$[I]_0$,[a] mol L^{-1}	$[M]_0$,[a] mol L^{-1}	$[P^*]_{max}$[b]
first run	6.4×10^{-5}	5.8×10^{-2}	3.7×10^{-5}
new addn of monomer	1.2×10^{-5}	7.4×10^{-2}	4.8×10^{-5}

[a] Initiator and monomer concentrations at the beginning of each run. [b] $[P^*]_{max} = [R_p/M]_{max}/(k_p + k_{trm})$.

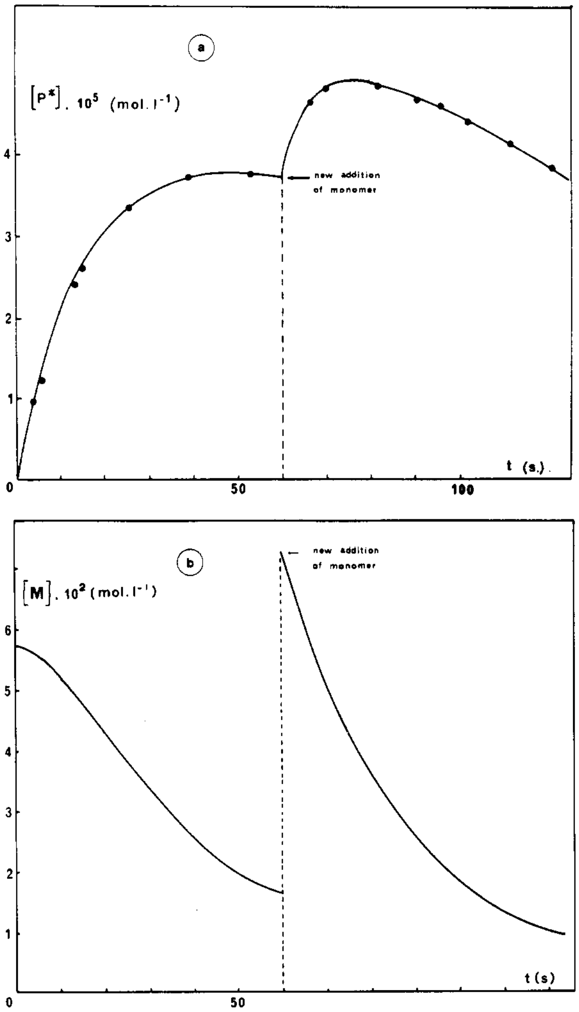


Figure 3. Successive additions of EVE at −25 °C (see Table II): (a) variation of active centers concentration; (b) monomer consumption.

the rates in a range compatible with the calorimetric technique. For both initiation and propagation IPVE appears to be the most reactive of the vinyl ethers we studied (Table I). Here again, active centers cannot be considered as stable at any temperature; even at −25 °C, their concentration goes clearly through a maximum as shown in Figure 4.

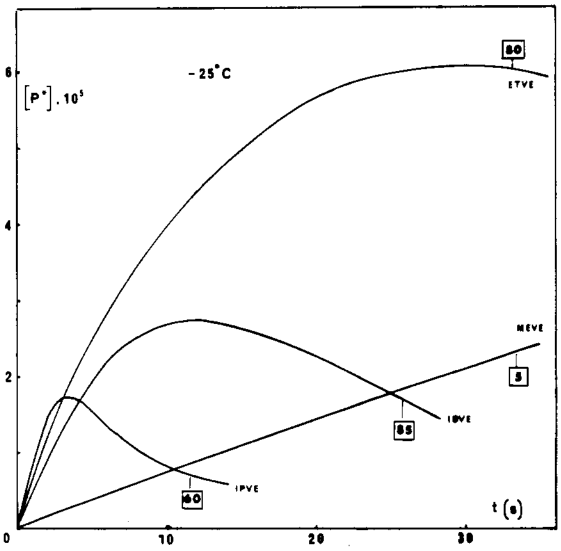
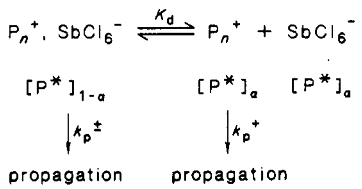


Figure 4. Comparative variation of active centers concentrations at −25 °C. Numbers in squares refer to monomer conversion (percent) at different times: MVE $[M]_0 = 0.129$ mol L^{-1}, $[I]_0 = 7.3 \times 10^{-5}$ mol L^{-1}; EVE $[M]_0 = 0.125$ mol L^{-1}, $[I]_0 = 8.7 \times 10^{-5}$ mol L^{-1}; IPVE $[M]_0 = 0.06$ mol L^{-1}, $[I]_0 = 5.9 \times 10^{-5}$ mol L^{-1}; IBVE $[M]_0 = 0.035$ mol L^{-1}, $[I]_0 = 5.9 \times 10^{-5}$ mol L^{-1}.

Conductimetric Study. The propagation rate constants obtained from the kinetic study are overall values that do not take into account an eventual equilibrium between different active species such as, for instance, in the simplest case of ion pairs and free ions:



$$\begin{array}{ccc} P_n^+, SbCl_6^- & \xrightleftharpoons{K_d} & P_n^+ \; + \; SbCl_6^- \\ [P^*]_{1-\alpha} & & [P^*]_\alpha \quad [P^*]_\alpha \\ \downarrow k_p^{\pm} & & \downarrow k_p^{+} \\ \text{propagation} & & \text{propagation} \end{array}$$

$$k_p(\text{measured}) = (1 - \alpha)k_p + \alpha k_p^{+}$$

$$K_d = \frac{[P^*]\alpha^2}{1 - \alpha} \qquad \text{with} \quad [P^*] = [P_n^+] + [P_n^{\pm}]$$

The $[P^*]$ value may be computed from $[P^*] = (R_p/[M])/(k_p + k_{trm})$, but K_d determination is severely complicated by the instability of active centers, the variation of their concentration, the contribution of remaining initiator to overall conductivity, and the common-ion effect

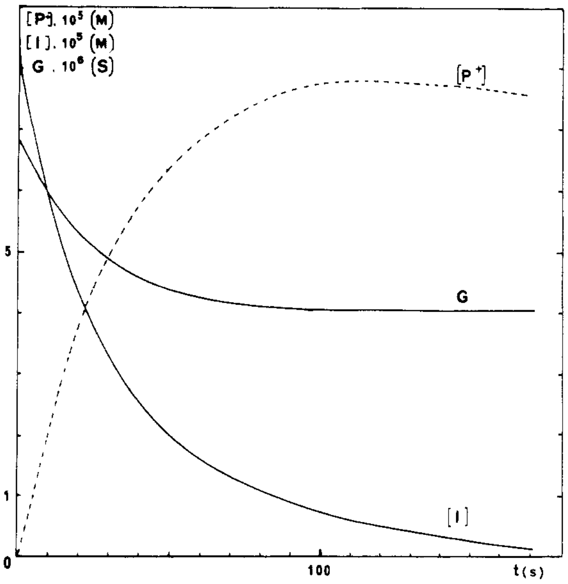


Figure 5. Polymerization of EVE at −40 °C: simultaneous variation of [P^+] active centers concentration, [I] initiator concentration, and G overall conductivity.

Table III
Conductimetric Parameters Observed on the Reaction Medium at the End of EVE Polymerization[a]

T, °C	-50	-40	-30	-20
$10^4\Lambda_0$, m^2 S mol^{-1}	43.5	50.7	59.1	68.8
$10^4\Lambda_0\eta$, m^2 S mol^{-1} P	0.46	0.47	0.48	0.49
K_D, mol L^{-1}	4.6×10^{-5}	4.3×10^{-5}	4.1×10^{-5}	3.9×10^{-5}
interionic dist a, Å	5.38	5.39	5.41	5.43

[a] [P^*] at the end of polymerization = 3.7×10^{-5} M.

of this remaining initiator upon the active species dissociation equilibrium.

However, it is observed that in all cases the overall conductivity value of the medium decreases as the initiator is consumed and then remains at a constant level as soon as the active centers maximum concentration is reached (Figure 5). The plateau value of the conductivity remains constant even at the temperatures for which termination reactions occur. This might mean that active centers are transformed into inactive ionic species presenting similar conductimetric behavior in solution. This may be understood since conductivity is carried out essentially by the more mobile counterion. Thus, if termination gives rise to ionic species having the same counterion and if its dissociation is similar—as seems to be implied by conductivity values—a conductimetric study at the end of polymerization could lead to an approximate value of K_d.

EVE polymerization, at low temperature for which conductivity of the reaction medium remains stable for hours, allows thus the successive dilutions needed for the determination of a K_d. According to Fuoss's method, the value of this dissociation constant varies from 3.9×10^{-5} M at −20 °C to 4.6×10^{-5} M at −50 °C (Table III), and the dissociation enthalpy, determined from ln K_D versus $1/T$ (four temperatures from −50 to −20 °C), was found to be $\Delta H_d = -0.6 \pm 0.1$ kcal mol^{-1} (Figure 6).

Discussion

Initiation. Whatever the monomer, initiation is relatively slower than propagation, and active centers cannot be considered as stable in the conditions reported. The maximum active center concentration is noticeably lower than initiator concentration, especially at lower temperatures. Thus in no case may a "living" scheme be applied.

The initiation rate constant k_i is obtained from R_i versus [M][I] plots, but these plots show a slightly sigmoidal shape (Figure 7), which indicates that the rate of initiator consumption during the polymerization deviates from the linearity that would be expected from the initiation process alone, if only one type of initiating species was involved. This phenomenon might be related to the dissociation equilibrium of the initiator, taking into account the eventual difference in reactivities of trityl ion pairs and dissociated ions. As $K_D \sim 1.94 \times 10^{-4}$ mol L^{-1} at −25 °C,[15] the dissociation coefficient of the salt was calculated to be at least 0.9, within the range of initiator concentrations we used. This would lead to an almost negligible deviation from linearity, even when considering the ion pairs as unreactive (Figure 7). A more probable explanation might involve a secondary reaction consuming $Ph_3C^+SbCl_6^-$ independently from the initiation process, such as, for example, a reaction with the unsaturated ends of terminated chains. In this case the deviation from linearity of the R_i plot would be dependent on active centers concentration, which we indeed observed.

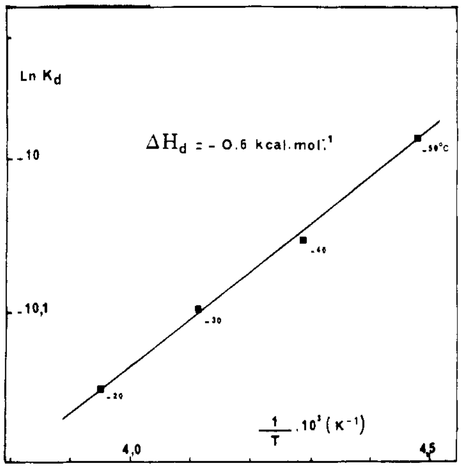


Figure 6. Conductivity of the reaction medium at the end of EVE polymerization: temperature dependence of the dissociation constant.

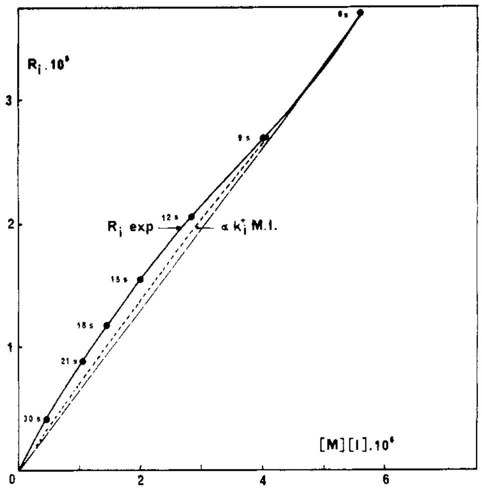


Figure 7. Plot of R_i versus [M][I] for polymerization of EVE-initiated by Ph_3C^+ in CH_2Cl_2. The dotted curve represents the theoretical plot when considering ion pairs as unreactive (see text).

But, whatever this side reaction may be, the deviation is limited and does not modify significantly the value of k_i, which may be obtained from the mean slope with an accuracy of ±10%.

These k_i values express the intrinsic reactivities of the various vinyl ethers toward the same cation (Ph_3C^+) and are in the following order:

$$\text{MVE} < \text{EVE} < \text{IBVE} < \text{IPVE}$$

Table IV
Kinetic Parameters of Radiochemically and Chemically Induced Polymerizations of Vinyl Ethers at 0 °C (Literature Data and This Work)

	radiation initiated[a]				chemically initiated[b]				
monomer	$10^{-3}k_p$, $M^{-1}\ s^{-1}$	$(E_p)_{app}$, kcal mol^{-1}	$\Delta S^{\ddagger}{}_p$,[d] cal $mol^{-1}\ K^{-1}$	ref	$10^{-3}k_p$, $M^{-1}\ s^{-1}$	$(E_p)_{app}$, kcal mol^{-1}	$\Delta S^{\ddagger}{}_p$, cal $mol^{-1}\ K^{-1}$	$\Delta S^{\ddagger}{}_i$, cal $mol^{-1}\ K^{-1}$	ref
MVE	no polymerization			14	0.26	11.1 ± 0.5	−9	−30	this work
					0.14 (av)	14.1			7
EVE	8.3 (bulk)	10.8		34	7.0	10.8 ± 0.5	−3	−34	this work
	5.7[c] (bulk)	13	+3	10	1.5 (av)	10.0			7
	0.88[c] (CH_2Cl_2)	7	−21	11	5.1 (av)	9.9			3
IBVE	38 (bulk)	7.6		5	6.8	5.5 ± 0.5	−23	−24	this work
	38 (bulk)	9.6		4	4.0 and 6.8 (av)	6.0			2
					9.2	7.1			3
IPVE	900 (bulk)	1.8		5	11.2	3.5 ± 0.5	−29	−35	this work
	500[c] (bulk)	5.3	−15	13					
	8.6[c] (CH_2Cl_2)	4.9	−25	13	16.0[e]	~4			8

[a] $[M]_0$ from 2 M to bulk. [b] $[M]_0$: 2×10^{-2} to 2×10^{-1} M; solvent CH_2Cl_2; initiator Ph_3C^+ or $C_7H_7^+$. [c] Extrapolated to 0 °C. [d] Values computed from frequency factors or kinetic data reported in the corresponding references. [e] Value observed for $[I]_0$ comparable to the initiator concentrations we used in this work ($(5-8) \times 10^{-5}$ M).

Such a sequence agrees with the Ledwith et al. hypothesis about stronger steric interference to resonance and its effect on reactivity of alkyl vinyl ethers toward electrophiles when the size of the substituent increases.[16,17] This order is also supported by the copolymerization experiments performed by Yuki et al.[18] from the ratio of the initial rates of monomers consumption in CH_2Cl_2 solution and more recently by Deffieux et al.[19] from the composition of copolymers obtained by radiation in bulk with equimolar amounts of monomers. The value observed by Deffieux (reactivity of IPVE/reactivity of EVE ~ 5 at +1 °C) agrees roughly with the ratio of ~6.5 between the initiation constants we obtained for these monomers at the same temperature. Nevertheless, if we consider the relative overall reactivities in homopolymerization, any discussion about the steric effects of the alkoxy group would be valid only if the cationic species resulting from each monomer are in comparable dissociation and solvation states, which is not necessarily the case as considered later in this paper.

Nature of Propagating Species. The k_p values are overall values representing the sum of the contributions of several species in equilibrium (ion pairs or free ions, solvated or not).

The dissociation coefficient α can be calculated from the dissociation constant K_d, but the only direct conductimetric measurements available for cationic active centers concern the more stable oxonium cations, which gave K_d of the order of 3×10^{-5} M at 0 °C in CH_2Cl_2 solution for SbF_6^- counterion (poly(THF),[20] polyoxepane[21]). A more satisfactory reference might be the model salt of EVE propagating species ($C_2H_5-O-{}^+CH-CH_3$, $SbCl_6^-$), the K_d of which was reported to be in the range $1.0-1.4 \times 10^{-5}$ M at −6 °C, depending upon the interpretations of the authors.[22,23]

Our conductimetric study was performed on solutions for which the final conducting species were found to present a similar conductimetric behavior as that of the propagating ions |poly(EVE^+, $SbCl_6^-$|. On the basis of our data, the K_d value we obtained (3.6×10^{-5} extrapolated at 0 °C) is compatible with the above results for such a cation associated to the $SbCl_6^-$ counterion. Its order of magnitude is probably the same for carbocationic species resulting from the various vinyl ethers. This means that, for the active center concentrations observed in our experiments ($[P^*] \sim 1-4 \times 10^{-5}$ M), the dissociation coefficient is at least in the range 0.6–0.8 and that the free ions contribution largely predominates even at the beginning of the polymerization when the common-ion effect of unconsumed initiator may be effective.

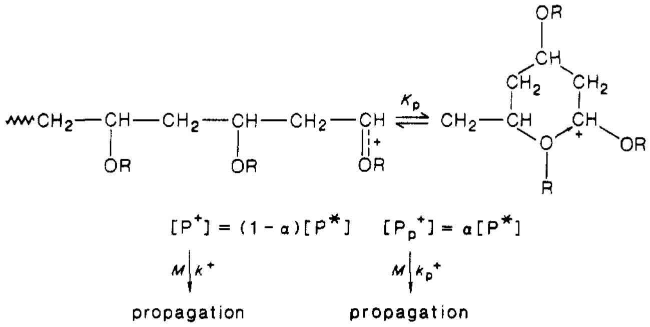
Nevertheless, the contribution of ion pairs may be neglected only if the $k_p^+/k_p^{\pm}$ ratio is large enough. Few papers deal with the relative reactivities of free ions and ion pairs in cationic polymerization, but the values reported for the $k_p^+/k_p^{\pm}$ ratio range between ~4 and 12 for vinyl monomers (*N*-vinylcarbazole,[24] *p*-methoxystyrene,[15,25] styrene[26,27]). If we assume similar values in the case of vinyl ethers, it appears obvious that the free-ion contribution controls the propagating kinetics.

General Behavior of Chemically Initiated Polymerization. Table IV compares our kinetic results with literature data from chemical initiation and with those from radiation polymerization as measured or extrapolated to 0 °C.

In the case of chemically initiated polymerizations a correct agreement between our values of k_p and literature data is observed at 0 °C. At this temperature, initiation is rapid enough with respect to propagation, and the simple kinetic treatment used by Ledwith[2,7] and Stannett,[3,8] assuming instantaneous and complete initiation, may lead to more reliable values than at lower temperatures. An accurate comparison is obviously difficult because these values are apparent k_p and the determination of absolute constants k_p^+ ($\sim k_p/\alpha$) implies the knowledge of the true active centers concentrations and then of α. It should be noted that most of literature values for k_p are averaged on a large range of initiator concentrations, generally from 1 to about 10 times higher than the concentrations we used. Thus, if we assume the same K_d for all ethers (say $K_d \sim 3 \times 10^{-5}$ M at 0 °C), the corresponding α may be as low as 0.2, leading to proportionally lower k_p. This appears to be verified in all related papers[2,3,7,8] as the k_p values vary significantly with initiator concentration.

Let us examine first the order of reactivities of the different ethers (Tables I and IV, Figure 2). In the case of chemical initiation in CH_2Cl_2 solution, this order should be best reflected by the initiation rate constants k_i, corresponding to reactions with the same carbocation. These constants increase by a factor of 25 (at 0 °C) with the steric hindrance around the oxygen atom (from MVE to IPVE). The reactivities for homopropagation also increase roughly in the same direction (at least for $T < 0$ °C) but with very little variation from EVE to IPVE. As previously considered by Ledwith et al.,[16,17] this increase might result from a restricted conjugation of the oxygen atom, leading thus to a lower stabilization of the monomer. This cannot be the only factor since the fall in reactivity from IPVE to EVE depends upon the type of polymerization and appears drastic in the case of bulk radiochemical systems.

In all cases, the apparent activation energy for propagation increases significantly when decreasing the hindrance around the oxygen (and simultaneously the apparent reactivity), and this may agree with a solvation equilibrium depending upon the access to the solvating atom. Such a solvation by the polymer, involving the basic oxygens of the side groups, may most probably be intramolecular and was early proposed by Bawn and Ledwith[28] and suggested again by Stannett[10] and by ourselves[9,29]:



as $\alpha = K_p/(1 + K_p)$, then $k_{app} = k^+/(K_p + 1) + K_p k_p^+/(K_p + 1)$. If the bare cations are reasonably assumed to be much more reactive, i.e., $k^+ \gg K_p k_p^+$, it follows that $k_{app} = k^+(1/(K_p + 1))$, from which it is possible to deduce

$$E^{\ddagger}_{app} \cong E^{\ddagger}_{(+)} - \Delta H_p K_p/(K_p + 1)$$

where $E^{\ddagger}_{(+)}$ is the activation energy for propagation on the bare free cation and ΔH_p the solvation enthalpy. Then it appears that if $K_p \gg 1$, then

$$E_{app} \sim E^{\ddagger}_{(+)} - \Delta H_p$$

if $K_p \ll 1$, then

$$E_{app} \sim E^{\ddagger}_{(+)} - \Delta H_p K_p \sim E^{\ddagger}_{(+)}$$

Since ΔH_p is negative, it appears that the higher the K_p, the higher will be the apparent activation energy. This is in agreement with a polymer solvation process increasing from IPVE to MVE and particularly important for the MVE and EVE propagating cations.

In the case of polymerizations chemically initiated in CH_2Cl_2 solution (Table IV), examination of activation entropy differences leads to a similar conclusion: even if the values of about −35 eu may be a bit too low (errors up to 10 eu are possible), activation entropies for initiation $\Delta S^{\ddagger}_i$ are close for the four ethers and correspond roughly to the $\Delta S^{\ddagger}_{imm}$ for the immobilization of a monomer upon a bare free end.[30] The activation energies $E^{\ddagger}_i$ (Table I) do not vary too much, with a tendency to decrease for more bulky substituents (except in the case of IBVE). These $\Delta S^{\ddagger}_i$ and $E^{\ddagger}_i$ values are apparently compatible with an absence of a marked desolvation effect of the initiating cation in the transition state. This confirms that initiation takes place either on an unsolvated trityl cation or without solvation change during the process. On the other hand, large differences appear between the activation entropies for propagation (Table IV). The values of $\Delta S^{\ddagger}_p$ we observe for IPVE and IBVE are close to those of $\Delta S^{\ddagger}_i$, showing that monomer immobilization is the largely predominant contribution to the activation entropy of the propagation step. This is no more true for the less hindered ethers, EVE and MVE, for which the noticeably higher values of $\Delta S^{\ddagger}_p$ might imply the supplementary contribution of a positive desolvation term $\Delta S^{\ddagger}_{desolv}$.

Thus a simple intramolecular solvation equilibrium of the propagating cation, depending upon the size of the side alkyl group and on the accessibility of the oxygen atom, may coherently account for the activation parameters we obtained in the case of the chemically initiated polymerization in CH_2Cl_2.

Nevertheless, two remarks should be made:

(1) The entropic contribution resulting from desolvation ($\sim$+20 to +30 cal mol^{-1} K^{-1}) would appear somewhat too positive with respect to the gain of freedom when passing from the cyclic complex to the open chain in the transition state and would probably correspond better to the liberation of a small molecule.

(2) The differences observed between the "chemical" k_p values are surprisingly small ($k_{p,EVE} \cong k_{p,IBVE} \cong 0.6k_{p,IPVE}$), and if we take into account the enhancement by a factor of 7 in monomer reactivity as observed from initiation rates and due to conformational effects, this would in fact reflect a decrease in propagating center reactivity from the more (EVE, MVE) to the less (IPVE) intrasolvated cations.

This might mean that intrasolvation is not the only—and even not the prevalent—factor governing the kinetics of these "chemically" initiated polymerizations in CH_2Cl_2.

Comparison between Chemical- and Radiation-Induced Polymerizations. The first point that must be emphasized is correlated with the above remark: a factor of about 100 is obtained between the reactivities of EVE and IPVE when polymerization occurs by radiation in bulk, whereas we observed similar reactivities by chemical initiation in CH_2Cl_2 (Table IV).

The second point concerns the large differences observed between bulk radiation constants and those measured in CH_2Cl_2 solution with either radiation or chemical initiation. This shows obviously an important role of the solvent, and the considerable reduction of k_p has been discussed by Stannett and co-workers, who reexamined in their recent series of papers[10–13] the radiation polymerization of EVE and IPVE in the presence of methylene dichloride, benzene, and other solvents.

Let us compare in more detail the "radiation" (bulk and solution) and "chemical" (solution) kinetic parameters. For IPVE, a correct agreement is observed in CH_2Cl_2 solution between the k_p, E_p, and $\Delta S^{\ddagger}_p$ for the two types of initiation. Radiation polymerization in bulk led to a k_p value about 60 times higher and to a less negative $\Delta S^{\ddagger}_p$. A first explanation for this higher rate could be the dielectric constant effect as radiation experiments performed by Stannett et al.[13] in media of increasing polarity (from bulk, $D = 3$, to monomer–nitromethane mixture, $D = 19.5$ at 30 °C) follow roughly the Laidler–Eyring linear relation between $\ln k_p$ and D^{-1} (see Table II in ref 13). Values of $\Delta S^{\ddagger}_p$ observed in CH_2Cl_2 solution for IPVE (−25 cal mol^{-1} K^{-1}, radiation; −29 cal mol^{-1} K^{-1}, chemical) show that in both cases the main contribution results from immobilization of monomer on an unsolvated end and that the equilibrium between bare and intrasolvated cations is shifted toward the former. The value observed in bulk (−15 cal mol^{-1} K^{-1}) is higher but still negative, and this might indicate that in low polarity medium a partial autosolvation cannot be neglected even in the case of the more bulky IPVE cations.

The situation is less coherent for EVE, as the kinetic parameters observed for polymerizations chemically initiated in CH_2Cl_2 differ by a factor of $\sim$8 from those obtained by radiation in CH_2Cl_2 solution and are in fact comparable to those obtained from radiation in bulk. Radiation polymerizations of EVE were also performed in media of increasing polarity by Stannett et al. (see again Table II in ref 13). The plot of $\ln k_p$ versus D^{-1} deviates from the Laidler–Eyring relationship, but the average slope of the curve is noticeably smaller than that observed in the case of IPVE. This might indicate that the radius of the propagating cations in the ground state is larger for

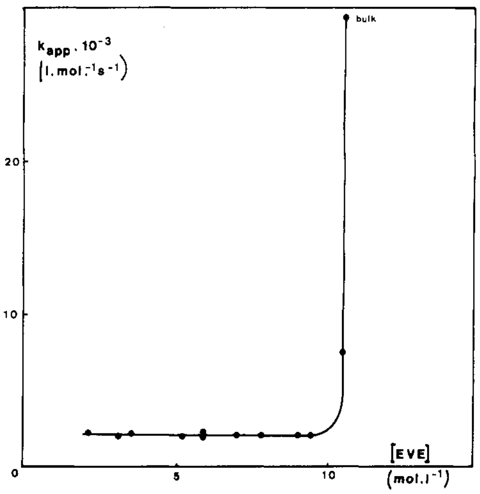
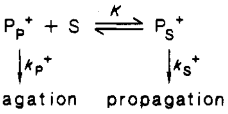


Figure 8. Variation of apparent k_p with monomer concentration for radiation-induced polymerization of EVE in CH_2Cl_2 solution at 22 °C: (●) results from Stannett et al.;[11] (—) theoretical curve computed with $k_P{}^+ = 29\,400$ L mol^{-1} s^{-1}, $k_s{}^+ = 2000$ L mol^{-1} s^{-1}, $K \geqslant 100$ L mol^{-1}.

EVE than for IPVE [$d \ln K/d(1/D) = Z^2e^2/(2RT)(1/r - 1/r^\ddagger)$ for reactions between ions and neutral molecules (Laidler–Eyring;[31] r and $r^\ddagger$ are the radii of the ion respectively in the ground state and the activated complex)] and that most of the active species are solvated in the case of the former monomer. It was also observed by Stannett et al.[11] that a small amount of CH_2Cl_2 in the monomer depressed drastically the rate of radiation polymerization.

The simplest explanation could be a strong termination effect from radiolysis products of the solvent, but further increase in CH_2Cl_2 concentration did not modify the apparent k_p, which is not coherent with this proposal. Stannett interpreted the leveling off of the constant by a local dielectric constant effect and a preferential solvation of the cations by the solvent rather than by the chain. In the case of EVE, if the concentration of unsolvated cations is low enough to consider only the propagation on the polymer and solvent solvated ends

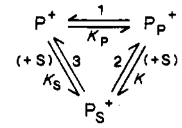


the apparent rate constant is given by

$$k_{app} = \frac{k_P{}^+}{K[S] + 1} + \frac{k_S{}^+K[S]}{K[S] + 1}$$

Using the $k_P{}^+ = 29\,400$ L mol^{-1} s^{-1} observed by radiation in bulk for EVE at 22 °C and the values for the different [M]/[S] ratios that were reported,[11] we adjusted the parameters $k_S{}^+$ and K until the theoretical plot of k_{app} versus [EVE] (or [S]) fits with experimental data (Figure 8). This leads for EVE polymerizations performed by radiation in CH_2Cl_2 solution at 22 °C to values of $k_S{}^+ \sim 2 \times 10^3$ L mol^{-1} s^{-1} and $K \geqslant 100$ L mol^{-1} and would account for the much higher reactivity of the oxygen-solvated species as observed in bulk ($k_P{}^+/k_S{}^+ \sim 15$) and for the strong shift of the above equilibrium toward the CH_2Cl_2-solvated cations. Even if it is unexpected, such a predominent solvation by the solvent might be supported by the high Π^* value (0.8) obtained for CH_2Cl_2 in the [0–1.0] solvatochromic Taft's classification of solvent polarities–polarizabilities[32] as well as by the more recent evaluation of cation- and anion-solvating tendencies made for various solvents from computer analysis of a large number of organic reactions.[33]

Thus a general description of both systems (radiation and chemical initiation) would involve three different propagating species in equilibrium:



In bulk (radiation), only the autosolvation (equilibrium 1) is to be considered, depending on the bulkiness of the monomer side group. It accounts for the large difference in reactivities, $E^\ddagger{}_p$ and $\Delta S^\ddagger{}_p$ observed for EVE and IPVE. In CH_2Cl_2 solution the three species might coexist, but their relative concentrations are still depending on the nature of the monomer. For MVE and EVE the two types of solvation occur, and, neglecting the less probable unsolvated free ions, the propagation kinetics is controlled by equilibrium 2. Even if the solvent-solvated species are less reactive than the autosolvated ones, they predominate as shown by the high $\Delta S^\ddagger{}_p$ value we observed for the chemically initiated system, which better corresponds to the liberation of a small solvent molecule. In the case of radiation polymerizations of EVE, even if the results of Stannett support well a solvation process by CH_2Cl_2, it must be noticed that reverse values of $E^\ddagger{}_p$ and $\Delta S^\ddagger{}_p$ would have been expected between bulk and solution systems.

For the more bulky IPVE, the intramolecular autosolvation process is strongly hindered, but solvation by CH_2Cl_2 is to be considered. thus the propagation kinetics is depending on unsolvated and solvent-solvated free ions (equilibrium 3). The very negative values of $\Delta S^\ddagger{}_p$ that are observed as well for chemical as for radiation polymerization show that the main propagation process does not involve a desolvation step. This supposes that propagation takes place essentially on unsolvated species, even if equilibrium 3 is strongly shifted toward the solvent-solvated cations, as indicated by the rather low values of the apparent k_p in solution (chemical and radiation) with respect to the k_p observed in bulk (radiation) for IPVE.

Such a scheme involving competitive solvation process, i.e., the autosolvation and the solvation by CH_2Cl_2 proposed by Stannett et al. for radiation systems, may also account for our chemically initiated polymerizations and particularly explain the small differences we observed for the k_p from EVE to IPVE and the corresponding apparent decrease in reactivity of the growing cation when the bulkiness of the monomer is increased. Comparison of our results about IPVE polymerizations initiated by Ph_3C^+ with those obtained by radiation (bulk and solution) is fairly coherent (k_p, $E^\ddagger{}_p$, $\Delta S^\ddagger{}_p$) and supports the above interpretation. On the other hand, there is an obvious discrepancy between our results and those observed by radiation in the case of EVE polymerization, and we have no explanation yet.

To conclude, we have shown in this work that the kinetic behavior of the cationic polymerization of methyl, ethyl, and isopropyl vinyl ethers initiated in CH_2Cl_2 solution by $Ph_3C^+SbCl_6^-$ between −40 and 0 °C is similar to that we previously reported for isobutyl vinyl ether. Kinetic parameters were determined for each step of the polymerization, and it was confirmed that these systems cannot be considered as living even if at the lowest temperatures the termination rate is rather low. A conductimetric study performed on polymerization and postpolymerization media (EVE) showed that propagation takes place essentially on free ions. The overall reactivity falls in the order IPVE > IBVE > EVE > MVE, but this fall is much less pronounced for propagation than for initiation, which might be interpreted by a decrease of reactivity of the cationic species when increasing the bulkiness of the side group. A detailed comparison of our chemically initiated reactions with recent data reported about bulk and solution radiation-induced ionic polymerization of vinyl ethers leads to a good agreement (EVE apart) between the two systems and supports the existence of equilibria between free ions of different reactivities—bare, solvent solvated, and chain solvated—depending upon the nature of the side group. It seems thus that the solvation of growing cations by CH_2Cl_2 previously proposed by Stannett et al. may be considered in cationic polymerization.

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Registry No. MVE, 107-25-5; EVE, 109-92-2; IPVE, 926-65-8; $Ph_3C^+SbCl_6^-$, 1586-91-0.

References and Notes

(1) Subira, F.; Sauvet, G.; Vairon, J.-P.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 221.

(2) Bawn, C. E. H.; Fitzimmons, C.; Ledwith, A.; Penfold, J.; Sherrington, D. C.; Weightman, J. A. *Polymer* **1971**, *12*, 119.

(3) Chung, Y. J.; Rooney, J. M.; Squire, D. R.; Stannett, V. T. *Polymer* **1975**, *16*, 527.

(4) Hayashi, Ka.; Hayashi, K.; Okamura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 2305.

(5) Goineau, A. M.; Kohler, J.; Stannett, V. T. *J. Macromol. Sci., Chem.* **1977**, *A11*, 99.

(6) Stannett, V. T.; Garreau, H.; Ma, C. C.; Rooney, J. M.; Squire, D. R. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 233.

(7) Ledwith, A.; Lockett, E.; Sherrington, D. C. *Polymer* **1975**, *16*, 31.

(8) Ma, C. C.; Rooney, J. M.; Squire, D. R.; Stannett, V. T. *Polymer* **1979**, *20*, 317.

(9) Subira, F.; Vairon, J.-P.; Sigwalt, P. Proceedings of the 28th IUPAC Symposium on Macromolecules, Amherst, 1982, 151.

(10) Deffieux, A.; Hsieh, W. C.; Squire, D. R.; Stannett, V. T. *Polymer* **1981**, *22*, 1575.

(11) Deffieux, A.; Hsieh, W. C.; Squire, D. R.; Stannett, V. T. *Polymer* **1982**, *23*, 65.

(12) Hsieh, W. C.; Deffieux, A.; Squire, D. R.; Stannett, V. T. *Polymer* **1982**, *23*, 427.

(13) Deffieux, A.; Young, J. A.; Hsieh, W. C.; Squire, D. R.; Stannett, V. T. *Polymer* **1983**, *24*, 573.

(14) Desai, V. R.; Suzuki, Y.; Stannett, V. *J. Macromol. Sci., Chem.* **1977**, *A11*, 133.

(15) Sauvet, G.; Moreau, M.; Sigwalt, P. *Macromol. Chem., Macromol. Symp.* **1986**, *3*, 33–46.

(16) Ledwith, A.; Woods, H. J. *J. Chem. Soc., Part B* **1966**, 753.

(17) Ledwith, A.; Woods, H. J. *J. Chem. Soc., Part B* **1970**, 310.

(18) Yuki, H.; Hatada, K.; Takeshita, M. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 667.

(19) Deffieux, A.; Stannett, V.; Wang, A.; Young, J. A.; Squire, D. R. *Polymer* **1983**, *24*, 1469.

(20) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2413.

(21) Brezinska, K.; Matyjaszewski, K.; Penczek, S. *Makromol. Chem.* **1978**, *179*, 2387.

(22) Ma, C. C.; Garreau, H.; Squire, D. R.; Stannett, V.; Littlejohn, M. A. *J. Macromol. Sci., Chem.* **1977**, *A11*, 1613.

(23) Plesch, P. H.; Stannett, V. T. *J. Macromol. Sci., Chem.* **1982**, *A18*, 425.

(24) Rooney, J. M. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 39.

(25) Goka, A. M.; Sherrington, D. C. *Polymer* **1975**, *16*, 819.

(26) Kunitake, T.; Takarabe, K. *Macromolecules* **1979**, *12*, 1067.

(27) Pepper, D. D. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 29.

(28) Bawn, C. E. H.; Ledwith, A. *Q. Rev., Chem. Soc.* **1962**, *16*, 361.

(29) Subira, F. Thèse de Doctorat es-Sciences, Univ. P. et M. Curie, Paris, 1981.

(30) Sawada, H. In *Thermodynamics of Polymerization*; Dekker: New York, 1976; p 85.

(31) Laidler, K. J.; Eyring, H. *Ann. N.Y. Acad. Sci.* **1940**, *39*, 103.

(32) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(33) Gardner Swain, C.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.

(34) Suzuki, Y.; Chudgar, A.; Rooney, J. M.; Stannett, V. *J. Macromol. Sci., Chem.* **1977**, *A11*, 115.

Adsorption of Sodium Dodecyl Sulfate onto α-Olefin/Maleic Acid Copolymers in Aqueous Solutions

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ABSTRACT: The fluorescence anisotropy of the anthryl group attached to poly(1-decene-*co*-maleic acid), PDMA, poly(1-tetradecene-*co*-maleic acid), PTMA, and poly(1-octadecene-*co*-maleic acid), POMA, has been examined at pH 8 as a function of sodium dodecyl sulfate, SDS, concentration. Adsorption of SDS onto the copolymer occurs at partial ionization of the copolymer resulting in an expansion of the copolymer coil. Expansion of the copolymer is facilitated by SDS destabilization of localized copolymer hydrophobic domains.

Introduction

Fluorescence depolarization or fluorescence anisotropy studies of covalently tagged macromolecules have proven to be an excellent way to probe the dynamics of intramolecular reorientation and of intermolecular interactions in solution.[1-3] The results provide insight into both the local environment and the nature of interactions between macromolecules and solvent systems.

In a previous study[4] we investigated the interaction between SDS and aqueous alkali-soluble α-olefin/maleic acid copolymers using extrinsic fluorescence probes. The fluorescence results gave indirect evidence for SDS interaction with the anionic polyelectrolytes. In this study we investigate the interaction between SDS and aqueous alkali-soluble α-olefin/maleic acid copolymers which are covalently labeled with 9-(hydroxymethyl)anthracene, HMA, as an intrinsic fluorescence probe. The fluorescence anisotropy of the anthryl tag is a function of the freedom of mobility of the tag and has been used to study coil–globule transitions.[5]

α-Olefin/maleic acid copolymers can be considered as polymeric amphiphiles under aqueous alkaline conditions. This leads to the possibility for the formation of polymeric micelles. The micellar structure would depend upon molecular weight, composition, sequential arrangement of repeat units, solution pH, and ionic strength. Interaction of SDS with these copolymers would, in turn, depend upon these properties.

Surfactant/polymer interactions have been studied by using other techniques also such as viscometry, surface

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