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Stereochemistry of Anionic Vinyl Polymerization. Effects of Ion Pair Prochirality on Chain Statistics

A. H. E. Mueller

Institut für Physikalische Chemie, Universität Mainz, D-6500 Mainz, FRG

T. E. Hogen-Esch*

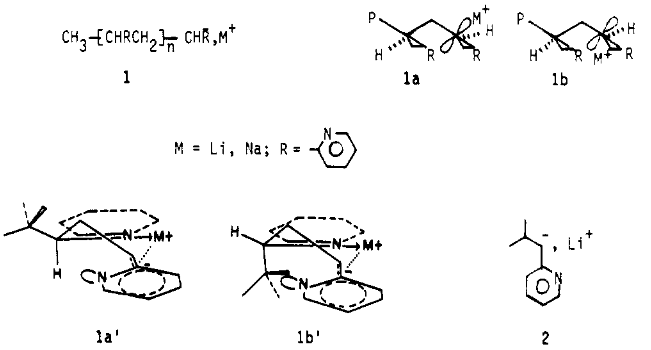
Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611. Received September 1, 1987

ABSTRACT: A model for the stereochemistry of anionic vinyl polymerization has been formulated in which enantiomeric chiral ion pairs (PCH_2CHR^-, M^+) are intermediates. Vinyl monomer attack on the chain end is postulated to occur on the cation side, and enantiomeric chiral ion pairs are produced depending on the mode of monomer presentation to the chain end (*pro-R* or *pro-S*). If the rate of ion pair inversion is slow compared to monomer addition, this model is shown to lead in general to first-order Markoff chains provided that the monomer concentration is constant. If the rate of ion pair inversion is fast with respect to monomer addition, Bernoullian statistics are obtained. Non-Markoff statistics are obtained when the rates of ion pair inversion and monomer addition are comparable.

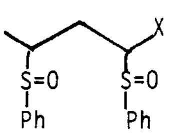
Introduction

The occurrence of chiral ion pairs of carbanions as intermediates in organic reactions has been recognized and studied by several workers.[1-6] This concept has also been addressed in anionic vinyl polymerizations. For instance, the remarkably high stereoselectivity of methylation of anions 1 (Chart I) has been attributed to a greater stability of ion pair diastereomer **1a** compared to **1b**.[7,8] This preference may be explained by intramolecular coordination of Li or Na by the penultimate pyridine nitrogen. The resulting structure, **1a′**, is preferred over the diastereoisomeric **1b′** on account of butane-gauche and other nonbonded interactions in the latter. Although this interpretation is supported by several other studies, direct evidence for the existence of distinct ion pair diastereoisomers has been lacking. This is not surprising since spectroscopic differences between them would be expected to be small and because the rate of their interconversion is probably very high. Thus ^1H NMR studies of ion pair 2 at −78 °C in THF show only a single methyl doublet for the diastereotopic methyl groups of the Li salt of 2-isobutylpyridine.[9]

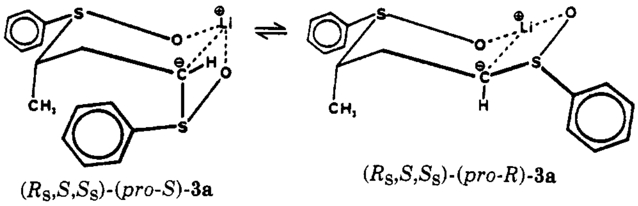
Chart I



However, more recent studies[10] on the stereochemistry of methylation of (R_S,S,S_S)-1-lithio-1,3-bis(phenylsulfinyl)butane (**3a**) in THF strongly suggest the configurational stability of diastereomeric ion pairs (R_S,S,S_S)-*pro-S* and (R_S,S,S_S)-*pro-R*.[11] Thus in THF at −78 °C (R_S,S,S_S)-(*pro-S*)-**3a** formed under kinetic control is methylated with syn (cation side) electrophilic attack to form (R_S,S,S,S_S)-**3b**. However, warming of an identical solution of **3a** in THF to 0 °C followed by recooling to −78 °C and methylation at that temperature results in the formation of *meso*-(R_S,S,R,S_S)-**3b**. This curious dependence of stereochemistry on the prior time–temperature profile of the reaction is most readily explained by thermodynamic control at 0 °C resulting in the formation of the more stable (R_S,S,S_S)-(*pro-R*)-**3a** and an interconversion between the two ion pair diastereoisomers being slow on the reaction time scale at −78 °C. Analogous observations on the interconversion of (R_S,S,R_S)-(*pro-R*)-**3a** and (R_S,S,R_S)-(*pro-S*)-**3a** also tend to support this interpretation.[10]



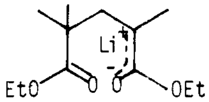
3a, X = Li
3b, X = CH_3



(R_S,S,S_S)-(*pro-S*)-**3a**

(R_S,S,S_S)-(*pro-R*)-**3a**

NMR experiments by Bywater on the Li salt of living dimer 4 of ethyl methacrylate in toluene[12] show a sharp absorption due to a pair of methyl groups at 15 °C which splits into two equal but broad signals at −55 °C separated by ~120 Hz and possibly attributable to ion pair inversion with respect to the C–C–O plane.



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The above results would appear to indicate the feasibility of such intermediates in polymerization reactions of ion pairs having an asymmetric center in close proximity to the ionic intermediate. This would be especially appropriate if the asymmetric center is brought into close proximity of the ion pair, for instance, through coordination of one of the ions with the asymmetric center as in the case of 1 or 3. This situation may prevail in the anionic polymerization of monomers $CH_2{=}CR{-}C(X)Y$, where R = H or alkyl, X = O or N, and Y = O, N, or C. Typical examples of such monomers are alkyl acrylates, alkyl methacrylates, vinyl ketones, acrylamides, 2-vinylpyridine, etc. In such a case the metal ion may be coordinated with

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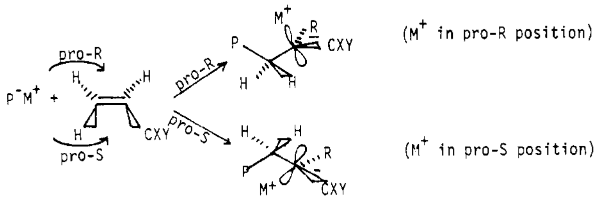
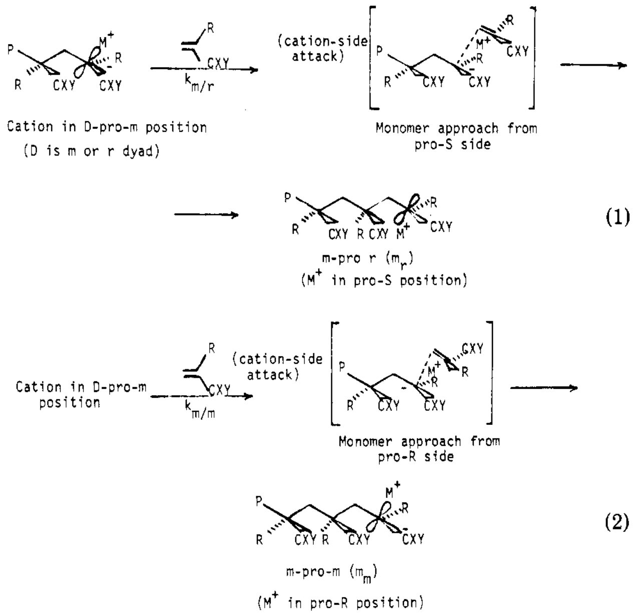
Scheme I



Scheme II



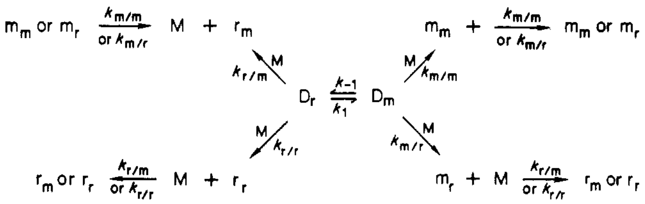
the X atom of the penultimate group, especially in media of low polarity. In this article we will discuss the polymerization stereochemistry of such a model and the resulting chain statistics of polymerization. The results of the calculations on such a model show that Bernoullian, first-order Markoff, or more complex statistics are obtained depending on the rate of interconversion of the chiral ion pairs and the rate of propagation.

Discussion

The monomer $CH_2{=}C(R)C(Y){=}X$ may approach the polymer carbanion (P^-M^+) with one of its (*pro-R* or *pro-S*) prochiral faces, and this would then tend to place the counterion in the corresponding *R* or *S* prochiral positions (Scheme I).[13] These positions will be termed *pro*-m or *pro*-r respectively depending on the type of diad formed after subsequent cation-side reaction with a new monomer and is written as a subscript on the preceding diad (Scheme II). Thus m_r upon reaction will yield a mr_r or mr_m heterotactic triad with the cation at the corresponding *pro*-r or *pro*-m positions, and the corresponding rate constants are designated as $k_{r/r}$ and $k_{r/m}$. The reaction rates are thus assumed to depend only on the direction of monomer attack on the carbanion (*pro*-m or *pro*-r) and its mode of monomer presentation (*pro*-R or *pro*-S) and not on the stereochemistry of the last two permanent asymmetric centers. Examples of such reactions are given in Scheme II. It should be stressed that this description of the reacting system is very general and would be consistent with other modes of reaction.

It is clear then that four types of monomer addition are envisioned, corresponding to rate constatns $k_{m/m}$, $k_{m/r}$, $k_{r/m}$, and $k_{r/r}$. The rates of ion pair inversion of the cation from the *pro*-r to the *pro*-m face of the carbanion and vice versa are termed k_1 and k_{-1}, respectively, and are also assumed to be independent of the preceding permanent diad.

Scheme III



The resulting reaction diagram is given in Scheme III, where D is an m or d diad and M is monomer.

Application of steady-state conditions for each of the four ionic species produces the following equations:

$$d[r_r]/dt = -[r_r](k_{r/m} + k_1) + [m_r]k_{r/r} + [r_m]k_{-1} = 0 \tag{3a}$$

$$d[m_m]/dt = -[m_m](k_{m/r} + k_{-1}) + [r_m]k_{m/m} + [m_r]k_1 = 0 \tag{3b}$$

$$d[r_m]/dt = -[r_m](k_{m/m} + k_{m/r} + k_{-1}) + ([r_r] + [m_r])k_{r/m} + [r_r]k_1 = 0 \tag{3c}$$

$$d[m_r]/dt = -[m_r](k_{r/m} + k_{r/r} + k_1) + ([r_m] + [m_m])k_{m/r} + [m_m]k_{-1} = 0 \tag{3d}$$

in which $[r_r]$, $[m_m]$, $[r_m]$, and $[m_r]$ are the concentrations of the four ionic species. If the monomer concentration is kept constant during the polymerization, then we can define $k_{r/r}$, $k_{m/m}$, $k_{r/m}$, and $k_{m/r}$ as the pseudo-first-order rate constants of reaction given by $k_{r/r} = k'_{r/r}[M]$, $k_{m/m} = k'_{m/m}[M]$, etc., where $k'_{r/r}$, $k'_{m/m}$, etc., are the corresponding second-order rate constants.

Replacing concentrations of the ionic species in eq 3b by fractions (r_r, m_r, etc.) and solving by using eq 3a–d and the required relationship

$$r_r + m_m + r_m + m_r = 1 \tag{4}$$

lead to

$$r_r = \frac{(k_{m/r} + k_{-1})(k_{r/r}k_m + k_{-1}k_r)}{k_y k_z}; \qquad r_m = \frac{k_r(k_{r/m} + k_1)(k_{m/r} + k_{-1})}{k_y k_z}$$

$$m_r = \frac{k_m(k_{r/m} + k_1)(k_{m/r} + k_{-1})}{k_y k_z}; \qquad m_m = \frac{(k_{r/m} + k_1)(k_r k_{m/m} + k_1 k_m)}{k_y k_z} \tag{5}$$

where

$$k_m = k_{m/m} + k_{m/r}; \quad k_r = k_{r/m} + k_{r/r}$$
$$k_y = k_{r/m} + k_{m/r} + k_1 + k_{-1}; \quad k_z = k_r k_m + k_{-1}k_r + k_1 k_m \tag{5a}$$

The fraction of chain diads may be calculated by setting

$$m = (r_m + m_m)k_m/k_p; \quad r = (r_r + m_r)k_r/k_p \tag{6}$$

where k_p, the overall pseudo-first-order rate constant of polymerization, is given by

$$k_p = (r_m + m_m)k_m + (r_r + m_r)k_r = [k_m(k_{r/m} + k_1) + k_r(k_{m/r} + k_{-1})]/k_y \tag{6a}$$

Substitution of eq 5 into eq 6 gives the fractions of diads:

$$m = \frac{(k_{r/m} + k_1)k_m}{k_m(k_{r/m} + k_1) + k_r(k_{m/r} + k_{-1})}$$
$$r = \frac{(k_{m/r} + k_{-1})k_r}{k_m(k_{r/m} + k_1) + k_r(k_{m/r} + k_{-1})} \tag{7}$$

The fractions of triads are given by

$$mm = \frac{m_{\mathrm{m}}k_{\mathrm{m}}}{k_{\mathrm{p}}} = \frac{k_{\mathrm{m}}(k_{\mathrm{r/m}} + k_1)(k_{\mathrm{r}}k_{\mathrm{m/m}} + k_1k_{\mathrm{m}})}{k_{\mathrm{p}}k_{\mathrm{y}}k_{\mathrm{z}}} \quad (8a)$$

$$mr = rm = \frac{m_{\mathrm{r}}k_{\mathrm{r}} + r_{\mathrm{m}}k_{\mathrm{m}}}{k_{\mathrm{p}}} = \frac{2k_{\mathrm{m}}k_{\mathrm{r}}(k_{\mathrm{r/m}} + k_1)(k_{\mathrm{m/r}} + k_{-1})}{k_{\mathrm{p}}k_{\mathrm{y}}k_{\mathrm{z}}} \quad (8b)$$

$$rr = \frac{r_{\mathrm{r}}k_{\mathrm{r}}}{k_{\mathrm{p}}} = \frac{k_{\mathrm{r}}(k_{\mathrm{m/r}} + k_{-1})(k_{\mathrm{m}}k_{\mathrm{r/m}} + k_{-1}k_{\mathrm{r}})}{k_{\mathrm{p}}k_{\mathrm{y}}k_{\mathrm{z}}} \quad (8c)$$

The triads can be shown to correspond to a first-order Markoff process provided [M] is constant. Thus the conditional probabilities P_{mr} and P_{rm} according to a first-order Markoff process are

$$P_{\mathrm{mr}} = 1 - P_{\mathrm{mm}} = \frac{mr}{2m} = \frac{k_{\mathrm{r}}(k_{\mathrm{m/r}} + k_{-1})}{k_{\mathrm{z}}} \quad (9a)$$

$$P_{\mathrm{rm}} = 1 - P_{\mathrm{rr}} = \frac{mr}{2r} = \frac{k_{\mathrm{m}}(k_{\mathrm{r/m}} + k_1)}{k_{\mathrm{z}}} \quad (9b)$$

Likewise the persistence ratio is given by

$$\rho = 2(m\cdot r)/mr = k_{\mathrm{z}}/k_{\mathrm{y}}k_{\mathrm{p}} \quad (10)$$

For a Bernoulli process $P_{\mathrm{mr}} = P_{\mathrm{rr}} = r$, etc., and $\rho = 1.0$. For development of a better understanding of the nature of the Markoff process, it is instructive to discuss the case where the ion pair interconversion is slow compared to propagation:

$$k_{-1}, k_1 \ll k_{\mathrm{p}} \quad (11)$$

In this case the diads and triads reduce to

$$m = \frac{k_{\mathrm{r/m}}k_{\mathrm{m}}}{k_{\mathrm{r/m}}k_{\mathrm{m}} + k_{\mathrm{m/r}}k_{\mathrm{r}}}; \quad r = \frac{k_{\mathrm{m/r}}k_{\mathrm{r}}}{k_{\mathrm{r/m}}k_{\mathrm{m}} + k_{\mathrm{m/r}}k_{\mathrm{r}}} \quad (12a)$$

$$mm = \frac{k_{\mathrm{r/m}}k_{\mathrm{m/m}}}{k_{\mathrm{r/m}}k_{\mathrm{m}} + k_{\mathrm{m/r}}k_{\mathrm{r}}}; \quad mr = \frac{2k_{\mathrm{r/m}}k_{\mathrm{m/r}}}{k_{\mathrm{r/m}}k_{\mathrm{m}} + k_{\mathrm{m/r}}k_{\mathrm{r}}};$$

$$rr = \frac{k_{\mathrm{m/r}}k_{\mathrm{r/r}}}{k_{\mathrm{rm}}k_{\mathrm{m}} + k_{\mathrm{m/r}}k_{\mathrm{r}}} \quad (12b)$$

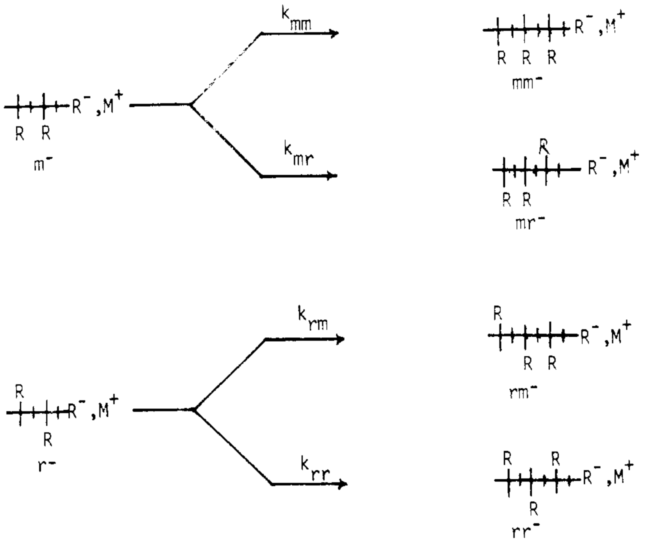
And the Markoff conditional probabilities reduce to

$$P_{\mathrm{mr}} = k_{\mathrm{m/r}}/k_{\mathrm{m}} \qquad P_{\mathrm{rm}} = k_{\mathrm{r/m}}/k_{\mathrm{r}} \quad (13)$$

Note that eq 11–13 are identical with those derived for a kinetic model of a first-order Markoff process with the rate constants for the various additions k_{mm}, k_{mr}, etc., (Scheme IV) replacing $k_{\mathrm{m/m}}$, $k_{\mathrm{m/r}}$, etc.[14] This similarity is of course not accidental but is inherent in the simple model without ion pair interconversion. In this case the monomer addition reaction correlates the configurations of the penultimate chiral carbon, the newly formed chiral carbon (generated from the prochiral ion pair), and the prochiral ion pair (generated from the monomer). Thus a chiral ion pair and a prochiral center corresponding to carbanion and monomer respectively are converted to a covalent chiral carbon and a chiral ion pair that adds a new monomer before it can interconvert to an ion pair of opposite configuration (Scheme I). Thus it is the configurational stability of the ion pair that correlates the last three chiral and prochiral centers of the chain, leading to first-order Markoff statistics.

The model assumes that the stereochemistry of the chain end (*pro*-m or *pro*-r) influences the rate of monomer addition as a given mode of monomer presentation ($k_{\mathrm{m/r}} \neq k_{\mathrm{r/r}}$). This would appear to be reasonable particularly if the Lewis base X of the penultimate asymmetric center coordinates with the metal ion. In such a case chelated six-membered ring structures would be present such as shown in **1a′** and **1b′**, and it is reasonable that the rates of monomer addition to these two structures would differ.

Scheme IV



The case where the ion pair interconversion is fast compared to monomer addition (k_1, $k_{-1} \gg k_{\mathrm{p}}$) is readily obtained by substitution into eq 8 and leads to

$$m = \frac{k_1k_{\mathrm{m}}}{k_1k_{\mathrm{m}} + k_{-1}k_{\mathrm{r}}}; \quad r = \frac{k_{-1}k_{\mathrm{r}}}{k_1k_{\mathrm{m}} + k_{-1}k_{\mathrm{r}}} \quad (14)$$

$$mm = \frac{(k_1k_{\mathrm{m}})^2}{(k_1k_{\mathrm{m}} + k_{-1}k_{\mathrm{r}})^2}; \quad mr = \frac{2k_{\mathrm{m}}k_{\mathrm{r}}k_1k_{-1}}{(k_1k_{\mathrm{m}} + k_{-1}k_{\mathrm{r}})^2};$$

$$rr = \frac{(k_{-1}k_{\mathrm{r}})^2}{(k_1k_{\mathrm{m}} + k_{-1}k_{\mathrm{r}})^2} \quad (15)$$

Clearly the statistics are now Bernoullian with conditional probabilities P_{rm} and P_{mr} equal to m and r, respectively.

Thus the rapid ion pair interconversion decouples the last two chiral centers from the stereochemistry of the newly formed chiral ion pair. However, there still may be a preference for one of the two diastereomeric ion pairs ($k_1 > k_{-1}$ or $k_{-1} > k_1$), and as a result this case may be consistent with the formation of a stereoregular polymer.

In conclusion the concept of ion pair chirality may lead to Bernoullian, first-order Markoff, or more complex statistics depending on the relative rates of ion pair inversion and propagation and on the constancy of monomer concentration. Importantly, first-order Markoff statistics may be generated in the case when there is no effect of the stereochemistry of the last diad on the stereochemistry of monomer addition.

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(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.
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(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 $CXY > PCH_2 > CH_2C(R)CXY > R$.
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Kinetics of Methyl, Ethyl, and Isopropyl Vinyl Ether Polymerizations Initiated by Trityl Salts

F. Subira,* J.-P. Vairon, and P. Sigwalt

Laboratoire de Chimie Macromoléculaire associé au CNRS, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France. *Received July 7, 1987*

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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