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Cationic Polymerization of Cyclic Sulfides

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ABSTRACT

The mechanism of the cationic polymerization of several thietanes and of propylene sulfide under the influence of triethyloxonium tetrafluoroborate in methylene chloride is described.

The thietane polymerizations stop at limited conversions because of a termination reaction occurring between the reactive chain ends (cyclic sulfonium salts) and the sulfur atoms of the polymer chain. The maximum conversions obtained under identical conditions differ markedly for the different monomers. Ratios of rate constants of propagation (k_p) to rate constants of termination (k_t) have been calculated. The differences in k_p/k_t values for the different monomers are explained in terms of differences in basicity and differences in steric hindrance of the monomers compared to the corresponding polymers.

In the case of propylene sulfide it is proposed that the main termination reaction is the formation of 12-membered ring sulfonium salts by an intramolecular reaction of the third sulfur of the growing polymer chain with the reactive chain

end (three-membered ring sulfonium salt). This terminated polymer is able to reinitiate the polymerization, for example, by reaction of a monomer molecule at the exocyclic carbon atom of the sulfonium salt function. The cyclic tetramer of propylene sulfide is formed in this reaction. After complete polymerization, formation of cyclic tetramer continues, probably via a backbiting mechanism.
In methylene chloride as solvent, the absolute value of the rate constant of propagation for 3,3-dimethylthietane changes with changing concentration of initiator and by adding different amounts of indifferent electrolyte to the reaction mixture. From these changes, and assuming that the value of the dissociation constant of the growing chain-ends is close to values of dissociation constants of low molecular weight sulfonium salts, separate rate constants for propagation via free ions and ion-pairs were calculated.
The propagation constant of free ions is about 70 times higher than that of ion pairs in methylene chloride at 20°C. Free ions and ion pairs are nearly equally reactive in nitrobenzene.

INTRODUCTION

The polymerization of three- and four-membered ring sulfides under the influence of a variety of initiators has been described in a great number of publications [1]. For the cationic polymerization of these substances it is generally accepted that the growing chain ends are cyclic sulfonium ions and that propagation occurs by a nucleophilic attack of monomer at the reactive chain end. However, the natures of initiation, termination, and eventually of other reactions are not exactly known. The purpose of this study was to come to a better understanding of these reactions, to measure rate constants where possible, and to find a correlation between the structure and properties of different monomers and their polymerization behavior. Up to now a series of thietanes and one thiirane—propylene sulfide— have been studied. The present paper presents a survey of the obtained results. Part of these have been published in detail elsewhere and will be discussed only briefly here.

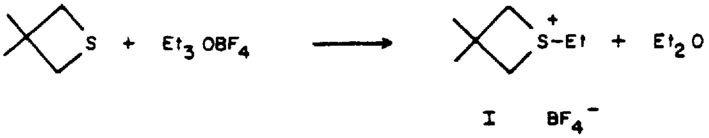
RESULTS AND DISCUSSION

Mechanism of Polymerization

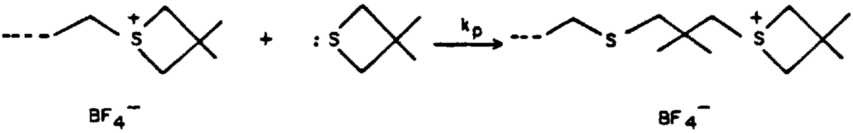
Two monomers have been used to study the mechanism of polymerization: 3,3-dimethylthietane (DMT) and propylene sulfide (PS).

The polymerizations were carried out in methylene chloride as solvent.

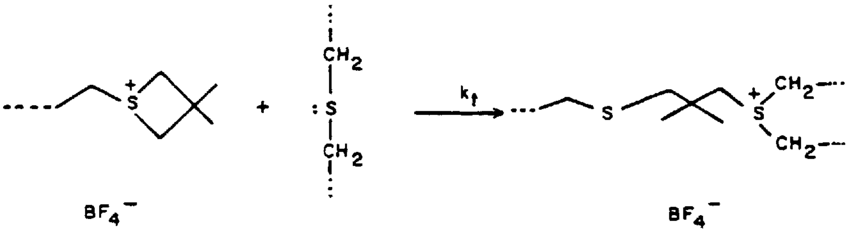
DMT is polymerized under the influence of different kinds of cationic initiators such as strong mineral acids, Lewis acids, and strong alkylating agents. After a series of preliminary experiments it was found that the polymerization initiated by triethyloxonium tetrafluoroborate (TEFB) gave rather simple kinetics because the initiation reaction with this initiator is immediate and quantitative. This was shown by conductometry [2], by NMR spectroscopy [2], and especially by the finding that time-conversion curves obtained with TEFB are identical to those obtained with S-ethyl-3,3-dimethyltrimethylene sulfonium tetrafluoroborate (I) [3]. This substance was prepared from DMT and TEFB.



Propagation occurs by a nucleophilic attack of the monomer on the α-carbon of the cyclic sulfonium ion:



Termination occurs when, instead of monomer, a sulfur atom of the already formed polymer reacts with the cyclic sulfonium ion. This reaction forms a nonstrained sulfonium ion which cannot reinitiate polymerization.



Because sulfonium salts are stable compounds, they remain unchanged after isolation of the polymers. The formation of branched structures is reflected by an increase of the molecular weight of the polymers [2].

This mechanism of termination was confirmed by kinetic measurements [2]. At 20°, values for k_p and k_t were found to be 6.5×10^{-3} and 3.3×10^{-4} mole^{-1} sec^{-1}, respectively. As a consequence of this termination reaction, the polymerization of DMT (and of other thietanes) stops before all monomer is consumed (Fig. 1).

By studying the kinetics of polymerization of DMT at different temperatures the enthalpy of activation $\Delta H^{\ddagger}$ and the entropy of activation $\Delta S^{\ddagger}$ for propagation and termination reactions were determined. The following values were obtained:

Propagation: $\Delta H_p^{\ddagger} = 12.5$ kcal/mole

$\Delta S_p^{\ddagger} = -26$ cal deg^{-1} mole^{-1}

Termination: $\Delta H_t^{\ddagger} = 7.4$ kcal/mole

$\Delta S_t^{\ddagger} = -49$ cal deg^{-1} mole^{-1}

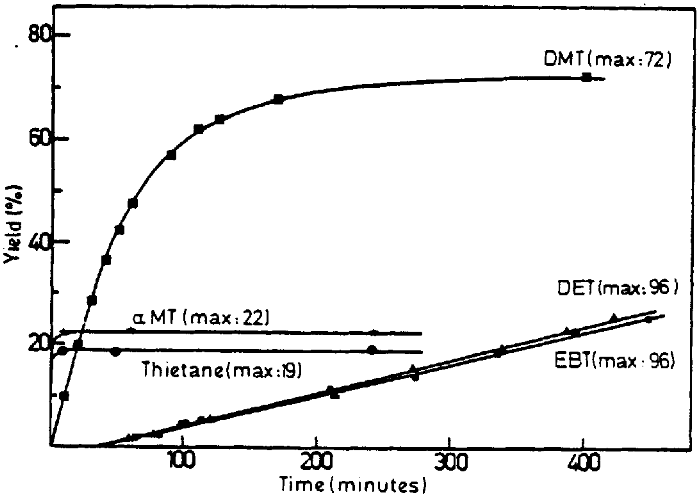


FIG. 1. Time-conversion curves of the polymerization of thietane, α-methylthietane, 3,3-dimethylthietane, 3,3-diethylthietane, and 3-ethyl-3-butylthietane in CH_2Cl_2 at 20°C. Monomer concentration: 2.0 mole/liter. TEFB concentration: 0.035 mole/liter.

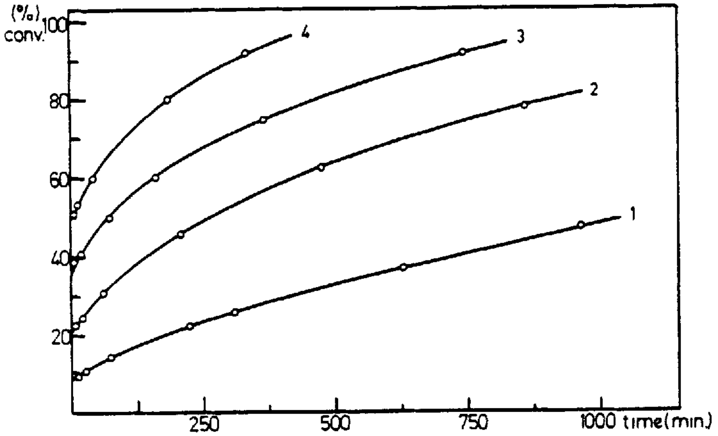


FIG. 2. Time-conversion curves of the polymerization of PS in CH_2Cl_2 at 0°C. Monomer concentration: 2.77 moles/liter. TEFB concentration: (1) 0.0082; (2) 0.025; (3) 0.045; and (4) 0.060 mole/liter.

The polymerization mechanism of PS is somewhat different from that proposed for DMT. Inspection of typical time-conversion curves obtained at 0°C (Fig. 2) shows that the reaction can be divided in two parts: an initial very fast stage which is clearly nonstationary (A-stage), and a subsequent stage which is very much slower, apparently stationary, and which leads to quantitative yields (B-stage). The yield at which the A-stage stops and the initial rate of the B-stage depend on the initiator concentration.

It is believed that the reactions which occur during the A-stage of the polymerization are similar to those proposed for the mechanism of DMT polymerization. However, the termination reaction in the case of DMT was a second-order reaction whereas in the case of PS it is a first-order reaction as demonstrated by the following. The rate of polymerization R_p is given by

$$R_p = -dm/dt = k_p m[P_n^+] \tag{1}$$

where m = monomer concentration and $[P_n^+]$ = concentration of growing chains. If termination is a monomolecular reaction, the rate (R_t) is given by

$$R_t = -d[P_n^+]/dt = k_t[P_n^+] \tag{2}$$

Dividing Eq. (1) by Eq. (2) gives

$$\frac{dm}{d[P_n^+]} = \frac{k_p}{k_t} m \qquad (3)$$

If it is accepted that initiation is immediate and quantitative, $[P_n^+]$ at t = 0 is equal to C_0, the initiator concentration. Integration of Eq. (3) between the limits $[P_n^+] = C_0$ and $[P_n^+] = 0$ (end of A-stage) leads to

$$\ln \frac{m_0}{m_f} = \frac{k_p}{k_t} C_0 \qquad (4)$$

where m_0 is initial monomer concentration and m_f is the concentration of monomer when the A-stage of the polymerization has stopped.

Figure 3 shows that Eq. (4) is in agreement with the experimental facts. From the slope of the straight line it was found that $k_p/k_t = 9.1$ liters/mole. This value is correct only if initiation with TEFB is quantitative and immediate as in the case of DMT.

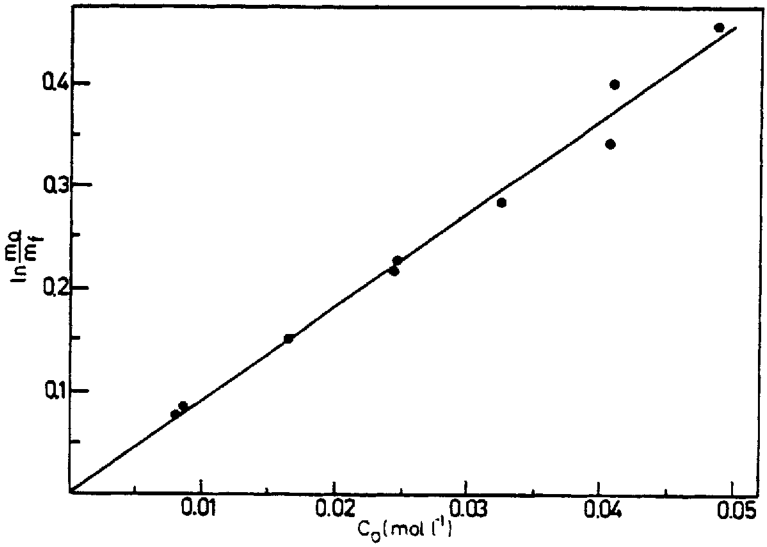
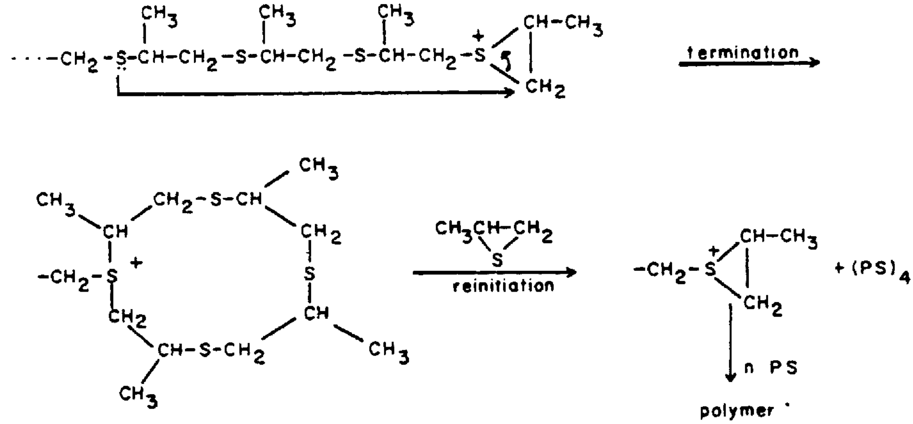


FIG. 3. Determination of k_p/k_t for the polymerization of PS according to Eq. (4).

The proposed mechanism of monomolecular termination is the formation of (mainly) 12-membered ring sulfonium ions. Evidence for this kind of reaction was found in the fact that a cyclic tetramer of PS could be isolated from the polymerizing mixture [4].

The formation of this tetramer and reinitiation of the polymerization (B-stage) are possibly the consequences of the same reaction: attack at the exocyclic carbon atom of the large cyclic sulfonium ion by monomer.



The mechanism of the reinitiation reaction is now under investigation.

Formation of tetramer continues when polymerization has stopped; that is, when all monomer is consumed. Apparently the backbiting reaction occurs not only at growing chain ends but also at polymers ending with a tetrameric sulfonium salt. After several days at room temperature, the polymer is degraded to a mixture of low molecular weight polymer and cyclic tetramer.

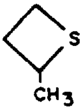
Influence of Basicity and Steric Hindrance on Polymerization Behavior

Except for initiation, all reactions occurring during the polymerization of cyclic sulfides are reactions between sulfides and sulfonium ions, and the course of polymerization is dictated by the rate differences of the different reaction steps. Reactions carried out with low molecular weight model compounds [5] have shown that the rate of a reaction between a sulfide and a sulfonium salt depends on two factors: 1) the difference in basicity of the reacting sulfide and that of the formed sulfide, and 2) steric hindrance.

The very different maximum conversions obtained with different thietanes, which are governed by the values of k_p/k_t, can be explained in terms of differences in basicity and steric hindrance between monomer and formed polymer. Basicities of monomers and of model compounds for the corresponding polymers have been measured by measuring the difference of absorption maximum ($\Delta\nu_{OH}$) of the OH-function of phenol and the phenol-sulfide complex formed by hydrogen bonding [6]. Table 1 lists $\Delta\nu_{OH}$ values for monomers and for model compounds of the corresponding polymers, the difference of $\Delta\nu_{OH}$ between monomer and polymer-model compounds ($\Delta\Delta\nu_{OH}$), and the observed values of k_p/k_t.

According to the $\Delta\nu_{OH}$ values, the sulfur atoms in the polymer chain always have a higher basicity than the corresponding monomers. However, the difference in basicity increases in the order DET < DMT < α-MT < thietane. The value of k_p/k_t decreases in the same order.

TABLE 1. Correlation between Relative Basicity and Values of k_p/k_t for Different Thietanes

Monomer	$\Delta\nu_{OH}$ of monomer (cm^{-1})	$\Delta\nu_{OH}$ of model compound for polymer (cm^{-1})	$\Delta\Delta\nu_{OH}$ (cm^{-1})	k_p/k_t
	241	252	11	1.1
 (α-MT)	252	261	9	2.4
 (DMT)	248	255	7	28
 (DET)	250	255	5	450

Inspection of molecular models clearly shows that the steric hindrance around a sulfur atom is more important in the polymers than in the monomers because of the ring structure of the latter. Steric hindrance increases in the series polythietane < poly-α-MT < poly-DMT < poly-DET. Therefore termination should be relatively less important and k_p/k_t increases in the same order. These conclusions are in agreement with the values of the thermodynamic constants obtained for the polymerization of DMT (see Mechanism of Polymerization Section). Because of the higher basicity of the polymeric sulfide function compared to monomer, the activation enthalpy for termination $\Delta H_t^‡$ is lower than the activation enthalpy for propagation $\Delta H_p^‡$ (7.4 kcal/mole compared to 12.5). Because of the higher steric hindrance, $\Delta S_t^‡$ is much more negative than $\Delta S_p^‡$ (-49 cal deg^{-1} $mole^{-1}$ compared to -26). The importance of basicity and steric hindrance is also well illustrated by experiments in which a small amount of a low molecular weight sulfide is added to the polymerizing reaction mixture. As shown in Table 2, lower yields of polymer are obtained only if the added sulfide has a higher basicity than the monomer. However, if the added sulfide carries bulky groups (for example, di-tert-butyl sulfide), its presence has little or no effect.

TABLE 2. Influence of Sulfides on the Maximum Yield in the Polymerization of DMT[a]

Sulfide	Basicity ($\Delta\nu_{OH}$, cm^{-1})	Max yield (%)
-	-	55
ϕ_2S	174	55
$(\phi CH_2)_2S$	222	55
Et_2S	262	35
$(i\text{-}Pr)_2S$	269	51
	270	18
$(t\text{-}Bu)_2S$	280	56

[a] m_0 = 1.1 moles/liter, [TEFB] = 0.02 mole/liter, [sulfide] = 0.055 mole/liter; sulfide added 2 min after initiation.

Nature of the Propagating Species

In the polymerization of DMT under the influence of TEFB, the initial rate of propagation R_0 is given by

$$R_0 = km_0C_0 \tag{5}$$

A plot of R_0 against C_0 should give a straight line going through the origin for different polymerizations with equal monomer concentration. As shown in Fig. 4, this is not the case with methylene chloride or benzene as solvent. This is attributed to a difference in rate constants for the propagations via free ions and via ion pairs.

The reactive chain-ends in this polymerization are sulfonium salts, and the following equilibrium will exist

$$P_n^+A^- \text{ (solv)} \underset{}{\overset{K_d}{\rightleftharpoons}} P_n^+ \text{ (solv)} + A^- \text{ (solv)}$$

If α is the degree of dissociation of the growing chains, and k' and k" are the propagation constants for free ion and ion pair propagation, respectively, the following equation can be derived [7]:

$$R_0/m_0C_0 = k'' + \alpha(k' - k'') \tag{6}$$

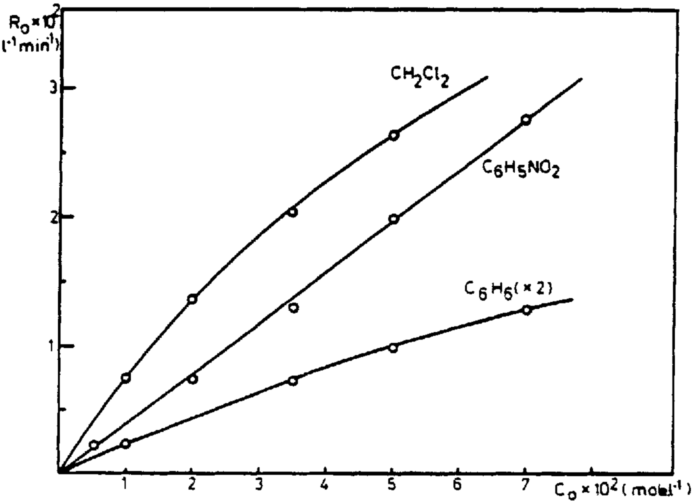
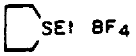


FIG. 4. Dependence of initial rate of polymerization of DMT on TEFB concentration in methylene chloride, nitrobenzene, and benzene. Temperature: 20°C. m_0: 2.0 moles/liter.

TABLE 3. Dissociation Constants (in liters/mole) of Sulfonium Salts in Different Solvents at 20°C

	Solvent	
Sulfonium salt	CH_2Cl_2	$C_6H_5NO_2$
$Et_3S\ BF_4$	1.3×10^{-5}	2.2×10^{-2}
	4.5×10^{-5}	2.0×10^{-2}
		1.5×10^{-2}

The degree of dissociation of an electrolyte depends on the dissociation constant K_d and its concentration C according to

$$\alpha^2 C + \alpha K_d - K_d = 0$$

It was not possible to measure the dissociation constant of the growing cyclic sulfonium salt during the polymerization of DMT because of the occurrence of the termination reaction. The dissociation constant of different sulfonium tetrafluoroborates have been measured in methylene chloride and in nitrobenzene by means of conductivity measurements and by using the Fuoss equation [8]. Table 3 gives a survey of the values obtained. The dissociation constants in benzene could not be determined because no conductivity could be detected.

Assuming that the dissociation constant of the growing chain in the polymerization of DMT has a value close to those of the sulfonium salts mentioned in Table 3 and using the average values of Table 3, the degrees of dissociation α, corresponding to different concentrations of growing chains, have been calculated.

According to Eq. (6), a plot of R_0/m_0C_0 against the corresponding value of α allows the calculation of k' and k" (Method A in Table 4). Another method (Method B in Table 4) consisted in measuring initial rates of polymerization in the presence of various amounts of an indifferent electrolyte with known dissociation constant (in this case triethyl sulfonium tetrafluoroborate). The presence of the electrolyte influences the degree of dissociation and again Eq. (6) allows the calculation of k' and k".

The results obtained for the polymerization in methylene chloride are shown in Figs. 5 and 6. When nitrobenzene is the solvent, k' - k" is practically zero so that a straight line parallel to the abscissa was

TABLE 4. Rate Constants of Propagation via Free Ions (k') and via Ion Pairs (k") for the Polymerization of DMT with TEFB as Catalyst at 20°C

Solvent and used value of K_d	k' (liters $mole^{-1}$ min^{-1})		k" (liter $mole^{-1}$ min^{-1})	
	Method A	Method B	Method A	Method B
CH_2Cl_2 $K_d = 2.9 \times 10^{-6}$	5.4	5.2	0.07	0.07
$C_6H_5NO_2$ $K_d = 1.9 \times 10^{-2}$	0.19	0.23	0.20	0.22

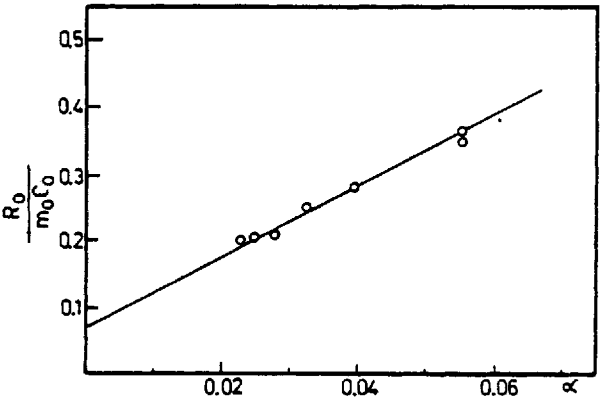


FIG. 5. Determination of k' and k" according to Eq. (9) for polymerization of DMT in methylene chloride (Method A).

obtained. In order to get a better evaluation of k' and k", Eq. (6) was changed into

$$\frac{R_0}{m_0 C_0 \alpha} = k' + k'' \frac{1 - \alpha}{\alpha} \tag{7}$$

A plot of $R_0/m_0C_0\alpha$ against $(1 - \alpha)/\alpha$ now gives a straight line with a slope equal to k" and an intercept with the ordinate equal to k'. Figures 7 and 8 show the results.

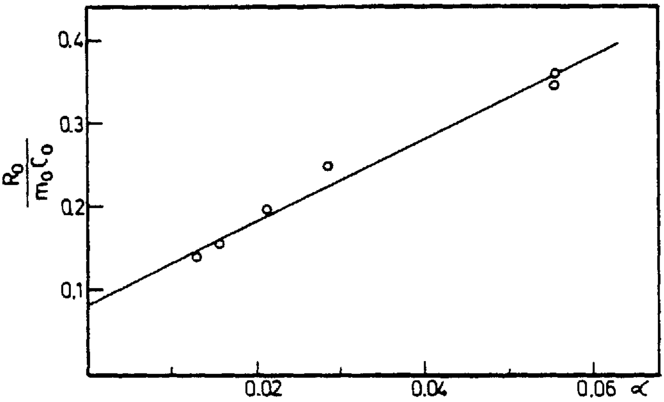


FIG. 6. Determination of k' and k" according to Eq. (6) for polymerization of DMT in methylene chloride (Method B).

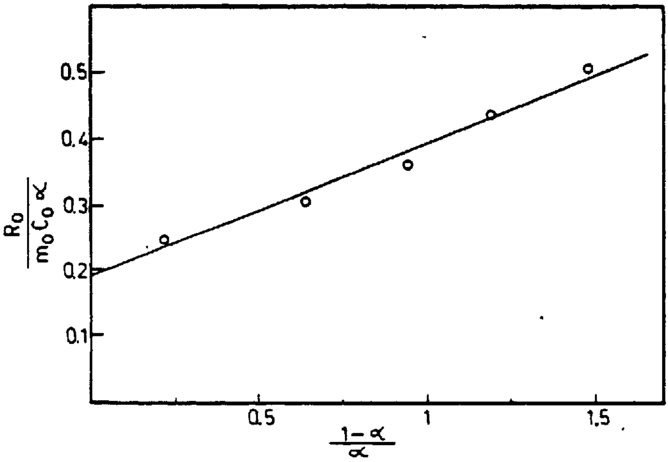


FIG. 7. Determination of k' and k" according to Eq. (7) for polymerization of DMT in nitrobenzene (Method A).

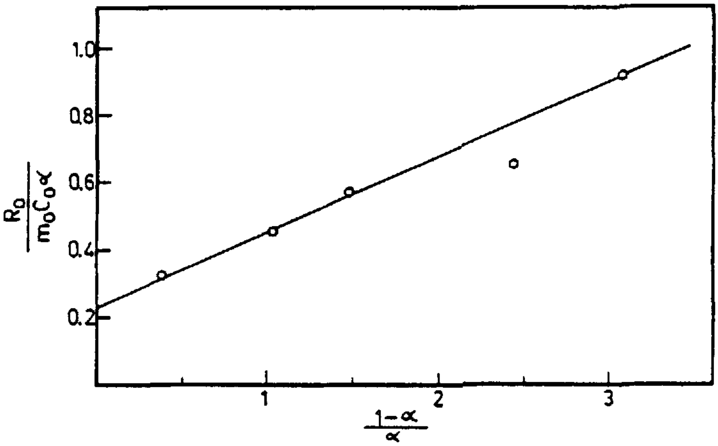


FIG. 8. Determination of k' and k" according to Eq. (7) for polymerization of DMT in nitrobenzene (Method B).

Table 4 gives a survey of the values of k' and k'' for the polymerization of DMT in methylene chloride and in nitrobenzene. From this table it follows that propagation via free ions is about 70 times faster than via ion pairs in methylene chloride.

This difference in rate constants is much smaller than in the case of anionic vinyl polymerization where propagation via free ions is about 10^3 times faster than propagation via ion pairs [9]. The same difference has been found in the anionic polymerization of propylene sulfide [10]. A possible reason for the smaller difference in the cationic polymerization of DMT is that in this case the growing chain is attacked in the α-position of the electrically charged atom whereas in anionic polymerizations the reaction occurs at the charged atom itself.

In nitrobenzene the reactivity of the free ions is about 20 times less than in methylene chloride. This can be ascribed to two factors. First, in the transition state of the propagating step the positive charge is spread out over three atoms, and this is unfavorable in a solvent of high dielectric constant. Second, the free ions are probably more solvated in nitrobenzene and therefore less available for nucleophilic attack by monomer. Free ions and ion pairs are approximately equally reactive in nitrobenzene.

EXPERIMENTAL

Synthesis and purification of DMT, solvents, and TEFB have been described in previous papers [2, 3].

Time-conversion curves of PS polymerizations were obtained by gravimetry. The polymerizations were carried out in a reaction tube constructed in such a way that it was possible to take samples at regular intervals under a stream of dry nitrogen. The samples were precipitated in a 10-fold volume of methanol and the obtained suspension was evaporated in vacuo at a temperature below 30°C until a constant weight was obtained. The synthesis of substituted thietanes and of model compounds for the corresponding polymers will be described in a separate paper. Triethyl sulfonium tetrafluoroborate was prepared by reaction of TEFB with diethyl sulfide as described by Meerwein [11]. Ethyl tetramethylenesulfonium tetrafluoroborate and ethyl pentamethylenesulfonium tetrafluoroborate were made in situ by adding TEFB to a slight excess of tetrahydrothiophene or pentamethylenesulfide in methylene chloride. NMR spectroscopy showed that all oxonium salt had reacted within a few seconds. Conductivities for the determination of dissociation constants were measured at 20 ± 0.02°C in a tube provided with a nitrogen inlet and two platinum electrodes which were connected with a Wayne and Kerr B641 apparatus. The experiments were conducted in such a manner that the solution was always under an atmosphere of dry nitrogen. The concentration ranges were 5×10^{-4} to 5×10^{-5} mole/liter for methylene chloride solutions and 10^{-2} to 10^{-3} mole/liter for nitrobenzene solutions. The values of dissociation constants reported here are somewhat different from values published earlier because the Fuoss equation was used instead of the simple Ostwald dilution law.

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