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Cocatalysis in Cationic Polymerization*

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ABSTRACT

Problems concerned with the principles of cocatalysis and coinitiation as a part of cationic polymerization are discussed. When the established concept of different reactive particles, i.e., contact and separated ion-pairs or free ions, is applied to cationic initiation and propagation centers, then common features for one general process can be drawn even in so diverse cases as "pseudocationic" polymerization, solvent "cocatalysis," polymerization during condensation and induced by co-monomer addition. A special case of activation by solvent is "cocatalysis" by water.
The model for these cases was found during the interpretation of waves observed on styrene polymerization curves. The formation of ion-pairs proceeds spontaneously. The activation and deactivation of these ion-pairs is effected via coordination of suitable molecules with the former, i.e., by equilibrium shifts

contact (peripheral solvated) ion-pairs $\rightleftharpoons$

$\rightleftharpoons$ separated ion-pairs $\rightleftharpoons$ free ions

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*Part of this work was presented at the International Symposium on Cationic Polymerization held in Rouen, France, September 1973.

INTRODUCTION

In the course of last few years only two detailed papers [1, 2] summarizing the problems of cocatalysis (coinitiation) have been published. There are, however, many problems open to discussion, e.g., those about the principles of cocatalysis, polymerization induced by comonomer addition [3], polymerization during condensation [4], and pseudocationic polymerization [5]. In this work a contribution to the current discussion about the basic principles of "cocatalytic" effects is made by taking into account the solvation of initiating ion-pairs and ions. The coordination of molecules present with these species is also considered. We have already reported [6, 8] on the strong influence of the solvation of active centers upon the rate of cationic polymerization.

In 1958 Colclough and Dainton [7] published their observation concerned with curious effects accompanying the $SnCl_4$ catalyzed polymerization of styrene in CCl_4 which proceeds through a series of jumps. In our studies of this monomer [8] we confirmed the experimental observation of these authors. The onset of polymerization of styrene is seen after a long "inhibition" period, and the conversion curve contains waves. This observation was made in other nonpolar solvents and when $[H_2O] \leq [SnCl_4]$. Since the original explanation about the origin of these waves is no longer plausible, we attempted to find another interpretation. It was found that the waves are a good model for most effects encountered during the study of cocatalysis. The polymerization of styrene under given conditions demonstrates the retardation and even inhibition by water, and on the other hand a pronounced acceleration by the latter. This happens spontaneously and it is repeated several times during one polymerization process.

We believe that this model is very useful in our attempts to explain processes so far generally denoted as cocatalysis (coinitiation).

EXPERIMENTAL

Information about the origin, purification, and manipulation with chemicals as well as polymerization and isolation of polymers including experimental techniques, have been described [8]. The method of determination of water in the polymerizing medium has also been published [9].

Chlorine in polystyrene was determined by a modified Schöniger method [10]. The Cl content was determined potentiometrically by $AgNO_3$.

Tin was determined both spectroscopically and polarographically. For qualitative determination the sample was ignited in a cavity of a graphite rod, while emission spectrum was taken on a PGS 2 Zeiss instrument. The quantitative determination was carried out polarographically after previous kjeldahlization. The polarograms were recorded within the range of potentials of 0.4 to 0.8 V vs SCE. The concentration of Sn was then calculated using a calibration curve.

RESULTS

In Fig. 1 there are several contraction curves obtained during styrene polymerization initiated by $SnCl_4$ in the presence of water. The contraction is directly proportional to conversion.

The data on Cl and Sn content in polystyrene obtained under different conditions are summarized in Table 1.

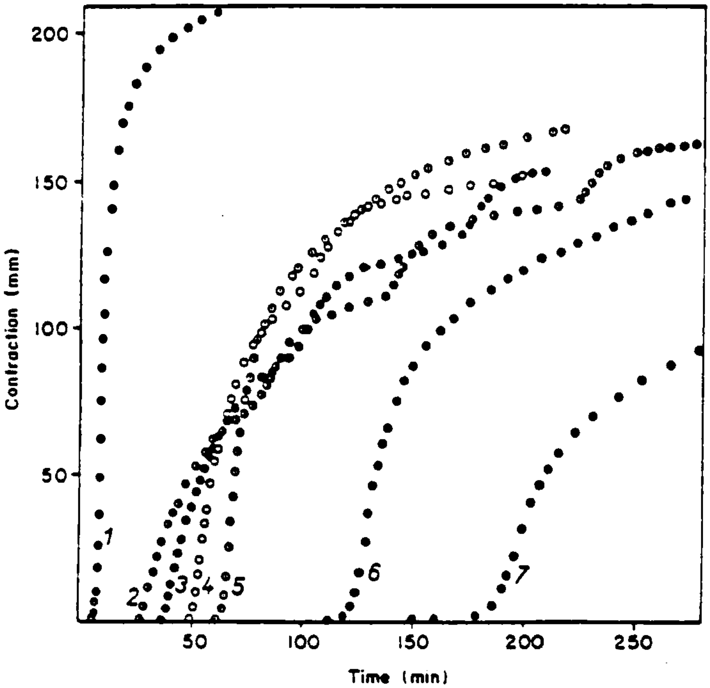


FIG. 1. Contraction curves for styrene polymerization. Styrene concentration, 3.0 moles/kg; temperature, 35°; $SnCl_4$ concentration, 6.6 mmoles/kg. (1) Polymerization in 1,1,2,2-tetrachloroethane; $[H_2O]$ = 2.0 mmoles/kg. Other polymerizations carried out in toluene with water concentrations of (2) 0.3, (3) 0.5, (4) 3.5, (5) 8.8, (6) 15.0, and (7) 20.0 mmoles/kg.

TABLE 1. The Influence of Solvent and Amount of Initiator on the Cl and Sn Contents in Polystyrene

						Sn			Cl	
Solvent	No.	[M] (moles/kg)	$10^3 \times [SnCl_4]$ (moles/kg)	$10^3 \times [H_2O]$ (moles/kg)	MW 10^{-3}	a	b	c	d	e
TCE[f]	1	0.9	6.6	1.2	10.2	-			0.84	179
Toluene	1	4.9	6.6	4.5	7.2	+	265	17.4	0.11	60
	2	4.9	6.6	8.0	7.5	+	284	19.2	0.14	76

[a] Spectral determination (- absent, + present).
[b] Polarographic determination (μg of Sn/1 g of polymer).
[c] % Sn with regard to $SnCl_4$ used.
[d] % Cl w/w.
[e] % Cl with regard to the amount used (in the form of $SnCl_4$).
[f] TCE = 1,1,2,2-tetrachloroethane.

INTERPRETATION OF RESULTS

The polymerization of styrene is, under given conditions, unambiguously a cationic process. Contact and/or solvent separated ion-pairs are formed from $SnCl_4$. The existence of free ions is very unlikely in the nonpolar styrene-toluene mixture. In spite of the fact that all components capable of producing active centers are present in the system, long inhibition periods were observed. Since both ionization and dissociation processes are very fast, it seems plausible to admit that contact ion-pairs are not able to initiate polymerization.

Let us assume that spontaneous termination (by counterions) leads both to unreactive polymer and an unreactive form of $SnCl_4$ (hydrate, see further). Thus the following reaction scheme can be written:

$$SnCl_4 + H_2O \rightleftharpoons SnCl_4 . H_2O \qquad (1)$$

$$SnCl_4 . H_2O + H_2O \rightleftharpoons SnCl_4 . 2H_2O \qquad (2)$$

$$SnCl_4 . 2H_2O + H_2O \rightleftharpoons SnCl_4 . 3H_2O \qquad (3)$$

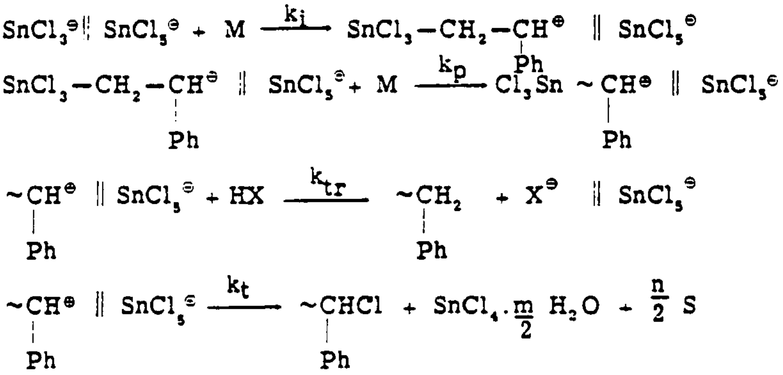
$$2SnCl_4 \rightleftharpoons Sn_2Cl_8\ (SnCl_3{}^{\oplus}\ SnCl_5{}^{\ominus}) \qquad (4)$$

$$Sn_2Cl_8 + mH_2O \rightleftharpoons Sn_2Cl_8 . (H_2O)_m \qquad (5a)$$

$$Sn_2Cl_8 + nS \rightleftharpoons Sn_2Cl_8 . (S)_n \qquad (5b)$$

$$Sn_2Cl_8(S)_n + Sn_2Cl_8(H_2O)_m \rightleftharpoons 2SnCl_3{}^{\ominus} \parallel SnCl_5{}^{\ominus} \qquad (6)$$

$$SnCl_3{}^{\ominus} \parallel SnCl_5{}^{\ominus} + H_2O \rightleftharpoons Sn_2Cl_8(S)_{\frac{n}{2}}(H_2O)_{\frac{m}{2}+1} \qquad (7)$$
$$= \tfrac{1}{2}Sn_2Cl_8(S)_n + \tfrac{1}{2}Sn_2Cl_8(H_2O)_m + H_2O$$



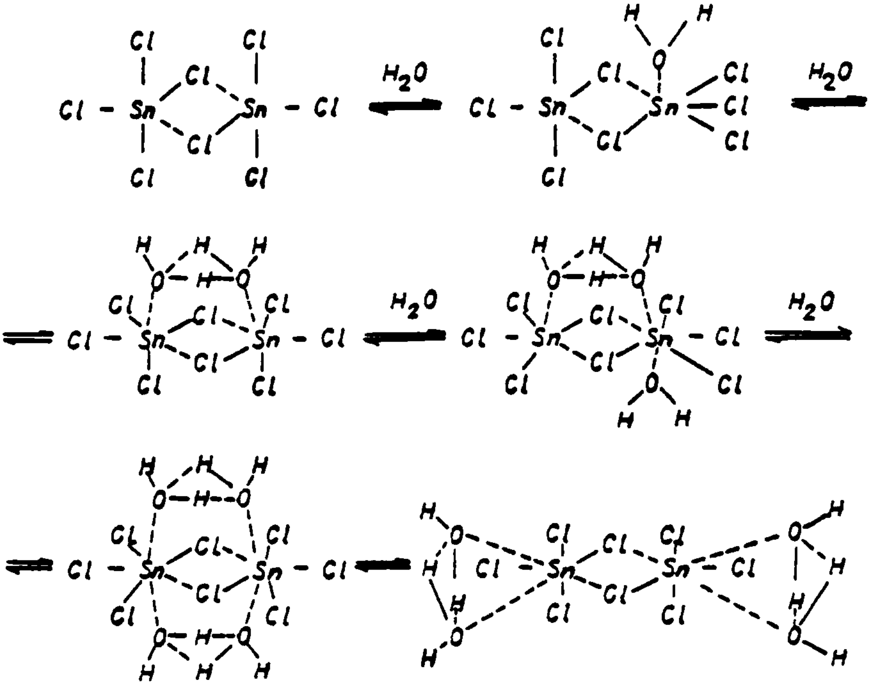
$$SnCl_3{}^{\ominus} \parallel SnCl_5{}^{\ominus} + M \xrightarrow{k_i} SnCl_3{-}CH_2{-}\underset{\displaystyle Ph}{\underset{|}{CH}}{}^{\oplus} \parallel SnCl_5{}^{\ominus} \qquad (8)$$

$$SnCl_3{-}CH_2{-}\underset{\displaystyle Ph}{\underset{|}{CH}}{}^{\ominus} \parallel SnCl_5{}^{\ominus} + M \xrightarrow{k_p} Cl_3Sn \sim \underset{\displaystyle Ph}{\underset{|}{CH}}{}^{\oplus} \parallel SnCl_5{}^{\ominus} \qquad (9)$$

$$\sim\underset{\displaystyle Ph}{\underset{|}{CH}}{}^{\oplus} \parallel SnCl_5{}^{\ominus} + HX \xrightarrow{k_{tr}} \sim\underset{\displaystyle Ph}{\underset{|}{CH_2}} + X^{\ominus} \parallel SnCl_5{}^{\ominus} \qquad (10)$$

$$\sim\underset{\displaystyle Ph}{\underset{|}{CH}}{}^{\oplus} \parallel SnCl_5{}^{\ominus} \xrightarrow{k_t} \sim\underset{\displaystyle Ph}{\underset{|}{CHCl}} + SnCl_4 . \frac{m}{2}\ H_2O + \frac{n}{2}\ S \qquad (11)$$

There are several reactions in the reaction scheme whose existence was not directly proven. They are, however, included because of strong circumstancial evidence. These are mainly Reactions (4), (6), and (11). According to the first one, the dimer Sn_2Cl_3 formation is assumed. Its existence or the existence of its autoionic form (ion-pair) is, however, necessary for the Sn—C bond to be formed (Sn found in the polymer). Peripheral solvated dimers (ion-pairs) are formed from the dimer in the presence of water and solvent, respectively, as described in Eq. (5). Reaction (5a) is thought plausible on the basis of the observation of the lengthening of the inhibition period with an increasing concentration of water. The reaction can be visualized as consecutive solvation of dimer with water:



The stabilization of a growing center by four molecules of styrene in the case of pseudocationic polymerization [11] can be regarded as an analog of Reaction (5b). The $SnCl_3^{\oplus}SnCl_5^{\ominus}$ externally solvated by monomer (solvent) is not, unlike $\sim C^{\oplus}ClO_4^{\ominus}$, active in polymerization.

Complexes with relatively strongly bonded ligands are likely to be formed from Sn_2Cl_8 and water. On the other hand, less precisely defined solvates will be formed in the presence of less polar molecules of styrene or toluene. The principal reaction in the scheme is Reaction (6) which describes the formation of active centers from peripheral hydrated (solvated) dimers. The reaction is justified by the fact that styrene does not polymerize in nonaqueous medium or in the presence of an excess of water (i.e., if only one of the products of Reaction 5 is present). When both components are present in a reasonable proportion, then the time necessary for formation of polymerization-active particles (induction period) is very short. Free water deactivates active centers (Reaction 7). The spontaneous formation of ion-pairs separated from each other by water and monomer (solvent) can thus be expected only when practically all free water had been removed.

The existence of Reaction (11) was corroborated by finding Cl in the polymer. An inactive hydrate is formed from $SnCl_4$ and water which previously separated both ions. It follows from the relationship between the reaction rate and initial concentration of water in the system that $m > 2/3 - 4$.

Let us follow the scheme (1)-(11) step by step. The equilibria (1)-(3) will be established promptly. A dimer formed (4) is successively peripherally solvated by the hydrocarbon S, though the hydration by m molecules of water will predominate. The equilibrium (5a) will be reached slowly and it will be appreciably shifted to the right. This upsets equilibria (1)-(3), and the water present will be transferred into hydrate shells of dimers. As none of these species is capable of initiation, no polymerization occurs.

Mutual interaction of peripheral solvated dimers (Reaction 6) leads to the formation of separated ion-pairs (active centers). These centers are deactivated while peripheral solvate is regenerated as long as free water is present. The active ion-pairs separated by water and monomer (solvent) will be formed only after the disappearance of the inhibiting water. The greater the value of $[H_2O]_0$, the later this happens (the inhibition period). The amount of hydrated component necessary for formation of separated ion-pairs will also be greater, thus rendering faster polymerization. The reaction rate will, of course, decrease again in the presence of an excessive amount of water. Part of the $SnCl_4$ will be bonded with water in an inactive species.

At low concentration of water ($[H_2O]_0 \leq [SnCl_4]_0$) the formation of separated ion-pairs will be an avalanche-like process, the initiation will proceed, and the macromolecules will propagate. Sooner or later the termination (11) will occur and polymerization will cease. The inactive forms of $SnCl_4$ (hydrates) will accumulate and in order to start the next polymerization initiated by the second generation of active ion-pairs, a regenerating process will have to take place via equilibria (1)-(6). The whole process can be repeated several times. Each following wave is, however, initiated by a lower concentration of $SnCl_4$ since part of Sn remains bonded in the polymer formed by the previous generation of active centers. The formation of waves is determined by a certain relation between the period of active centers formation (induction period) and the mean lifetime of the centers. The induction period increases with an increase in the initial amount of water. When $[H_2O]_0 > [SnCl_4]_0$ Reactions (1)-(11) proceed more or less simultaneously after the onset of the first wave. This creates unfavorable conditions for the formation of waves.

Another reaction leads to the formation of ion-pairs in relatively polar 1,1,2,2-tetrachloroethane. No Sn was found to be present in the polymer, though a considerable amount of Cl was detected. Ion-pairs are probably formed through a reaction analogous to Reaction (14) (see below). The solvent is, however, able to activate ion-pairs by separating them. Thus in 1,1,2,2-tetrachloroethane the waves are not formed and the "inhibition" periods are short [8, 12].

DISCUSSION

The author believes that dividing the initiation process into three steps may be of use:

1. Formation of ion-pairs (free ions).
2. Activation of primarily formed species (the influence of medium upon ion-pairs).
3. The initiation itself (interaction of ions or ion-pairs with the monomer).

It can be noticed, judging by the reviews [1, 2] and other relevant papers, that the authors working in the field of cationic polymerization have focused their attention predominantly to Points 1 and 3; Point 2 remains, barring a few exceptions [6, 8], neglected. In the case of anionic polymerization, the situation is quite different. The information available in this field is more detailed, mostly due to the interest in "living" polymers by Szwarc [13] and his school and by other workers. Coinitiation is not mentioned in connection with anionic polymerization. This is probably due to the fact that the mechanism of formation of initiating ion-pairs or free ions is satisfactorily explained. Also, the general principles governing the changes of reactivity are well established. The observation of principal importance is that contact ion-pairs are practically unreactive in comparison with free ions or with those ion-pairs separated by solvent molecules [14, 15]. There is no reason not to believe that the same relationships are valid in the case of cationic polymerization. Those authors trying to explain only the formation of ion-pairs or free ions are tackling only a part of the problem of initiation in cationic polymerization. Unless only contact ion-pairs are formed, and unless their separation or dissociation will occur, no polymerization takes place, and if it does occur, it will be very slow.

1. To explain the formation of ion-pairs or free ions (depending

upon the polarity of medium) from Brønsted acids is not difficult:

$$HClO_4 \rightleftharpoons H^{\oplus} + ClO_4^{\ominus} \qquad (12)$$

The formation of the latter from Lewis acids is much more complicated. According to present knowledge, it is possible to postulate reactions leading to the formation of ion-pairs or free ions by the following equations (Friedel-Crafts catalysts were employed as an example of Lewis acids; A denotes metal atom, X halogen, and M monomer):

$$AX_n + M \rightleftharpoons {}^{\oplus}M{-}AX_n^{\ominus} \qquad \text{(e.g., Refs. 16-18)} \qquad (13)$$

$$AX_n + RX \rightleftharpoons R^{\oplus}AX_{n+1}^{\ominus} \rightleftharpoons R^{\oplus} + AX_{n+1}^{\ominus} \qquad \text{(e.g., Ref. 19)} \qquad (14)$$

$$2AX_n \rightleftharpoons AX_{n-1}^{\oplus}AX_{n+1}^{\ominus} \rightleftharpoons AX_{n-1}^{\oplus} + AX_{n+1}^{\ominus} \qquad \text{(e.g., Refs. 20 and 21)} \qquad (15)$$

$$AX_n + H_2O \rightleftharpoons H^{\oplus}AX_nOH^{\ominus} \rightleftharpoons H^{\oplus} + AX_nOH^{\ominus} \qquad \text{(e.g., Ref. 22)} \qquad (16)$$

$$AX_n + M^{\oplus} \rightleftharpoons M^{\oplus}\,AX_nH^{\ominus} \rightleftharpoons M^{\oplus} + AX_nH^{\ominus} \qquad \text{(e.g., Ref. 2)} \qquad (17)$$

This set of reactions is certainly not complete. There is, however, a definite number of them. To pinpoint particular reaction for a particular system should not, however, represent unsurmountable difficulties. This problem has not yet been solved. The author believes that this is due to the great number of possibilities in the further step — the activation. The character of the medium surrounding the primarily formed species determines, together with physical factors (mainly temperature), the reactivity of the initiating and growth-determining species. As most of solvents and impurities in systems for cationic polymerization are of nucleophilic character, the cation solvates first. In this way the active center becomes "contaminated."

2. Let us now assume that contact ion-pairs are formed in a relatively nonpolar environment via one or several reactions, (12)-(17). Let us examine the conditions under which these contact ion-pairs are transformed into solvent separated ion-pairs and free ions, respectively:

$$Ac^{\oplus}B^{\ominus} \overset{S}{\rightleftharpoons} Ac^{\oplus} \parallel B^{\ominus} \overset{S}{\rightleftharpoons} Ac^{\oplus} + B^{\ominus} \qquad \text{(e.g., Ref. 14)} \qquad (18)$$

It will depend upon the character of the salt and solvent, whether the contact and solvent separated ion-pairs will be thermodynamically distinguishable particles, whether they will be present together with free ions in solution, and whether the existence of some kind of species will be, under given conditions, unlikely [23, 24]. In most cases, equilibrium (18) will be shifted to the right with decreasing temperature. The shift is very important. Hogen-Esch and Smid reported [25] that at 25° in tetrahydrofurane, fluorenyl$^{\ominus}$ Na$^{\oplus}$ is almost exclusively in form of contact ion-pairs (95%) whereas at -80° it is completely solvent separated. They also presented evidence about the dependence of the fraction of solvent separated ion-pairs upon the solvent and the kind of counterion [24]. The addition of a small amount of strongly solvating agent influences the position of equilibrium (18). Fluorenyllithium forms contact ion-pairs in dioxane. A small amount of dimethylsulfoxide can convert the latter into solvent separated ion-pairs [25]. There is not much information about the rate of equilibrium establishment (18); in general the process is very fast. There are, however, reasons to believe that the conversion of solvent separated ion-pairs into contact ones might be retarded by desolvation, which is the process possessing a certain activation energy [26].

Let us compare the above-mentioned conditions with the effects called "cocatalysis."

21. Cocatalysis by water (alcohols, carboxylic acids, etc.). In spite of the opinion that the importance of water as a cocatalyst is probably overestimated [2, 4, 8], water is still considered as being a dominant "cocatalyst." The necessity of water being present in order to effect the polymerization of any monomer has not been proven. It is always possible to find conditions (solvent, temperature, etc.) under which a given monomer (+ initiator) polymerizes in nonaqueous solution. The water can, however, start polymerization [27], accelerate [7] or retard it, or even inhibit it [28]; it can have both effects depending on concentration [6-8] or it can have no influence upon the polymerization at all [5, 29].

Certain observations indicate that the hypothesis about the initiation by ion-pairs or free ions formed in reaction analogous to Eq. (16) (perhaps with the participation of monomer) is oversimplified:

(a) The results of Eastham who found that the isomerization of 2-butenes proceeds only in the presence of "free" BF_3 [30].

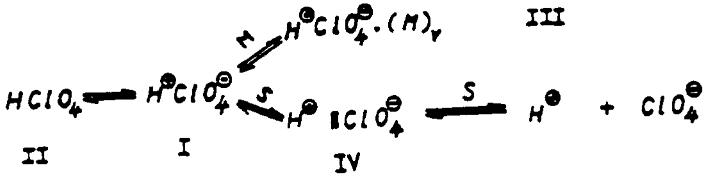
(b) The inhibition periods observed during styrene polymerization [28].

It seems than coordination with initiator is a more typical reaction of water at low concentrations than are hydrolytic reactions [31]. If a stable complex is formed between AX_n and water, e.g., an analog to Reactions (1)-(3), and (5a), then water will have a retarding or even an inhibiting effect both in nonpolar and "polar" environment (e.g., see the behavior of system [28]). If the monomer (solvent) is displaced from solvate shells of separated ion-pairs by water — similarly to Reaction (7) — polymerization will again be decelerated both in nonpolar and "polar" system (polymerization [6-8] at higher concentrations of water). Water may enhance the ion-pair formation in systems where the initiator is present in the form of contact ion-pairs, thus starting [27] or accelerating [7, 8] polymerization. It seems, however, that besides the water, monomer or solvent also participates in the formation of solvent separated ion-pairs: the water alone forms inactive forms, e.g., peripheral hydrated ion-pairs.

It can be expected that in certain cases the interactions between monomer (solvent) molecules solvating peripherally the initiator ion-pairs will be so strong that water will be unable to penetrate to more intimate proximity of the ion-pair, and thus no influence of water upon the polymerization will be seen (see, e.g., Refs. 5 and 29). The fact that $Li^{\oplus}$,$Na^{\oplus}$ salts crystallized from water solutions of 1,4-dioxane contain dioxane in the lattice corroborates this idea. 1,4-Dioxane is a more powerful solvation agent than water [32] in this case.

22. Cocatalysis by solvent (monomer). According to present opinion, only Reaction (14) is considered as coinitiation by solvent. The role of solvent is, however, more complex. RX, with several exceptions, has a pronounced dipole moment and it will thus participate in transformation (18) through dipole-dipole interactions [33]. To separate both functions of RX is, at present, impossible. The initiator concentration is usually low. Thus a small quantity of a suitable solvent will be able to induce sufficient shift of equilibrium (18) toward more active forms. This will be mainly due to the fact that a better solvating compound can be more selectively coordinated [34, 35]. The above-mentioned equilibrium shift may, of course, be caused not only by solvent but also by impurities or by the monomer. Special "kinds" of cationic polymerization can be recognized depending upon the effect of solvating component.

221. Pseudocationic polymerization. Let us consider $HClO_4$ initiator dissolved in the mixture of dichloromethane and styrene. Only active centers are formed from $HClO_4$. Side reactions do not take place to a significant extent [5, 36, 37]. The number of species derived from $HClO_4$ is thus quite restricted (in the case of growing species, H is replaced by ~C):



(19a)

(19b)

The nonionized form II (ester), the peripheral solvated contact ion-pair III, the solvent separated ion-pair IV, or even free ions can be formed from the contact ion-pair I. There is little doubt about the equilibrium according to Eq. (19b) being established fast in the binary system HClO -dichloromethane. The presence of styrene, however, upsets this equilibrium. If we admit the possibility of stabilization of the contact ion-pair I through peripheral solvation by styrene (Eq. 19a), then a complete explanation of behavior during "pseudocationic" polymerization can be given.

Equilibrium (19b) is established quickly after the mixing of components: free ions and solvent separated ion-pairs IV initiate polymerization at a certain rate. Equilibrium (19a) is, however, being established at the same time. This leads to the stabilization of contact ion-pairs by monomer. Relatively inactive species are formed (similarly to reaction 5b), which polymerize slowly. The rate of establishment of equilibrium (19a) is lower than the rate of Reaction (19b). Alternatively, the transformation of IV to I is slow (this effect has already been considered [26] — desolvation is a process of non-zero activation energy). Equilibrium (19a) is strongly shifted to the right in the presence of excessive monomer. Depending on conditions, all initiator will, sooner or later, be transformed into III. The time required for transformations of reactive IV's and free ions into III will be lengthened at lower temperature. After the formation of III from the total amount of initiator, a long "stationary" period is observed during which the polymerization rate is relatively low. As soon as the concentration of stabilizing monomer decreases in the course of progressing polymerization, the reactive products of equilibrium (19b) will again influence the process. When the concentration of monomer decreases under a certain critical limit, which is determined by the stoichiometric ratio of initiator to monomer in peripheral solvated III, the stabilizing effect of monomer will cease. The rate of its further consumption will be high; it will depend upon the concentration of solvent separated ion-pairs and free ions.

It was found that in $H^{\oplus}\ ClO_4^{\ominus}\ (M)_v$ (III in "pseudocationic" active center), the value of $v = 4$. The ester structure [5] was assigned to the center. The evidence presented in order to corroborate this assignment is, however, not convincing. The coordination of monomer molecules with ion-pairs and free ions unavoidably will change the value of the effective dissociation constant and the overall dissociation scheme which is considered only in its simplest form [36]. Possible complications are pointed out, e.g., in Ref. 38. The difference between the reactivity of ester and contact ion-pair need not be significant. The mechanism presented above is unchanged, no matter whether the active centers in the "pseudocationic" step consist of esters II or stabilized contact pairs III.

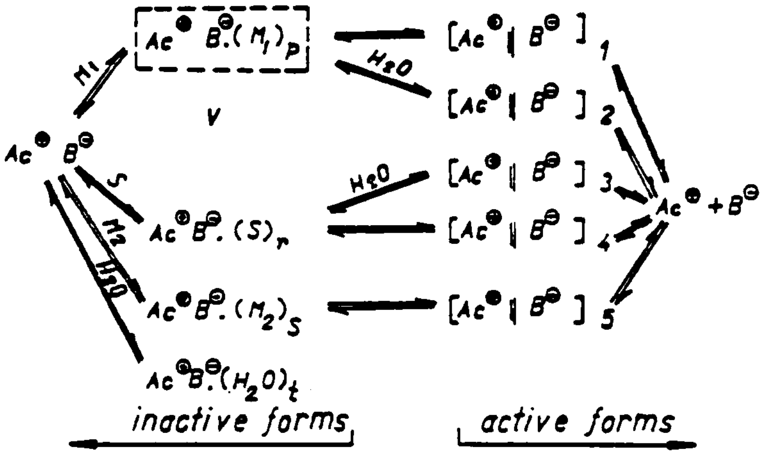
Contact ion-pairs are practically unreactive in most cases of cationic polymerization. It has been observed, however, that if they are formed from very strong acid and if they are surrounded by monomer, they may initiate polymerization. The monomer is bonded very strongly in the solvate shell so that even water cannot penetrate. The accelerating effect of water can also be compensated for by the formation of inactive hydrates (similarly to Reactions 20b and 20e, see below). At stages where separated ion-pairs and free ions exist in the polymerizing system, the influence of water upon the process is identical with that observed in the case of other cationic polymerizations.

All described effects were observed during "pseudocationic" polymerization [36], their sequence being dependent upon the concentration changes of individual initiating and propagating species which are determined by shifts of equilibrium (19).

It seems likely that the above-described conditions can also be created in other system containing initiator-monomer-solvent.

222. Polymerization during condensation. Plesch and Sigwalt and co-workers examined low-temperature polymerization of isobutene both in bulk and in dichloromethane solutions. They observed that additions of $TiCl_4$ caused only incomplete polymerization of isobutene. The higher the concentration of water in the system, the higher the rate and yield of polymerization. This effect persisted until a certain "critical" concentration of water was reached. Above this level the rate was no longer dependent upon the amount of water in the system and a complete conversion of monomer could be achieved. During this process, however, the condition was preserved that $[H_2O]_{crit} \ll [TiCl_4]$[39]. After the prepolymerization it was not possible to start the reaction again by adding a solution of $TiCl_4$. Polymerization could be completed when all the contents, or at least the $TiCl_4$, were distilled [3]. When the mixture of $TiCl_4$ with isobutene was maintained for several hours at higher temperature after prepolymerization, partial polymerization occurred upon cooling [40]. It was originally thought that water was the cocatalyst whereas dichloromethane was not [39]. This was objected to [2, 3], but a satisfactory explanation is still lacking.

Let us assume that a certain ion-pair (e.g., $TiCl_3^{\oplus}TiCl_5^{\ominus}$, Reaction 15) is formed in $TiCl_4$ solutions. Another pair is formed from solvating (condensing) $TiCl_4$ (e.g., $ClH_2C^{\oplus}TiCl_5^{\ominus}$, $CH_3(CH_2)_2C^{\oplus}TiCl_4H^{\ominus}$, Reactions 14 and 17). Let us denote the cation in the ion-pair as $Ac^{\oplus}$, the anion as $B^{\ominus}$, M_1 = isobutene, M_2 = indene (α-methylstyrene, styrene, . . .), and S = dichloromethane. The process of activation of the primary ion-pair can be described as follows:



(20a)
(20b)
(20c)
(20d)
(20e)
(20f)

If the ion-pair formed from $TiCl_4$ solution is efficiently stabilized by peripheral solvation by monomer — similarly to "pseudocationic" polymerization — then no solvent (monomer) separated ion-pairs and free ions are formed through Reaction (20a). Practically all initiator is rapidly transformed into species V in the presence of excess of monomer. This contact ion-pair is, unlike $H^{\oplus}ClO_4^{\ominus}(M)_4$, inactive and no polymerization occurs. The solvent separated ion-pairs or free ions can participate in the process only in the presence of water in the system: the water can either decompose V to separated ion-pairs (free ions) or it can inhibit the process of transformation of separated pairs to V. The higher the concentration of water, the greater the amount of separated pairs and ions, and consequently the greater the rate and conversion. Above certain concentration of water, however, the rate increase is compensated for by the formation of inactive hydrates (20f). As soon as the water is used up, so that its activating effect disappears, the polymerization ceases and it is not possible to start it again even by the addition of new $TiCl_4$ in the liquid phase since inactive forms of V are rapidly formed again. Ion-pairs with another counter-ion can be formed from monomolecular $TiCl_4$ and some other component of the system; these will not be stabilized so exclusively by monomer. The equilibrium (20a) can thus be shifted toward active forms (about the influence of counterion on the pair configuration, see, e.g., Ref. 24). Such a system will polymerize no matter whether $TiCl_4$ was evaporated and liquefied alone or with all components of the system [3] or if it was condensed from the vapor phase where it was present after previous heating of the reaction mixture [40].

It follows from the above consideration that: 1) water is not a cocatalyst, 2) water need not always be responsible for "prepolymerization", and 3) the solvent can act as cocatalyst according, e.g., to Ref. 15.

223. Polymerization induced by addition of comonomer. The decomposition of solvate V need not be caused by water. If a component is present whose molecules are, under certain conditions, able to substitute molecules M_1 in V, and if the product can produce solvent separated ion-pairs or free ions (Reaction 20e), then the system will polymerize under these conditions.

This observation has already been made by Sigwalt et al. who added indene (α-methylstyrene) to prepolymerized isobutene in dichloromethane in the presence of $TiCl_4$. They observed only an unimportant increase in conversion. The monomers, however, polymerized completely after cooling [4].

The point 3) remains, at present, open to further discussion.

CONCLUSION

The question of the formation and activation of ion-pairs is an integral part of the problems connected with the initiation of cationic polymerization in a little polar medium. It follows from the concept of activation presented that cocatalysis (coinitiation) as a means for the generation of active centers through the interaction of initiator with a defined cocatalyst does not exist in fact. The characteristic selectivity, as observed in a case such as enzyme-coenzyme, is missing here. Ion-pairs can be formed through several reactions which are mutually interchangable. These primary contact ion-pairs are variously solvated and thus stabilized or, on the other hand, their reactivity is enormously increased by separation and/or dissociation caused by some of the components of the system. The effectiveness of separation is strongly dependent on the dipole moments of both contact ion-pairs and separating molecules and temperature. Although the configuration of solvent separated ion-pairs (free ions) has not been exactly established yet, it seems that the separation of ions by more than one kind of molecules leads to more reactive species than separation caused by only one component.

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