INFLUENCE OF WATER UPON THE RATE
OF CATIONIC POLYMERIZATION OF STYRENE. I.

POLYMERIZATION INITIATED BY $\sim Si^+HSO_4^-$

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The polymerization of styrene initiated by $\sim Si^+HSO_4^-$ has been studied. The rate of reaction is a function of components concentration and of the quality of solvent. Water participates in the polymerization process as a cocatalyst. The shape of curve expressing the dependence of polymerization rate upon water concentration is determined by the polarity of the reaction medium; in non-polar media the rate increases with the increasing water concentration whereas an opposite effect is seen if polar media are used. In the mixture of polar and non-polar solvents this dependence proceeds through a maximum.

Although numerous authors of cationic polymerization studies have specifically pointed out the effects that were tentatively ascribed to solvation[1,2], the solvation as a process involved in determining the activity of an initiating active center has, with several exceptions[3], been paid a little attention. Szwarc[4] emphasized the importance of solvation of ion pairs in the process of anionic polymerization. It is still generally believed that it is possible to consider either direct initiation[5] or that the presence of cocatalyst possessing acidic proton or ability to form a suitable complex[6-8] is necessary . Formal shape of a cocatalytic curve (the dependence of polymerization rate upon water concentration), observed in the case of styrene polymerization[1,9,10] or other monomers[11-17] is identical with that described by us when examining the polymerization of heterocycles[18,19]. Of course, some deviations were also observed[20,21]. During our studies concerned with the heterocycles polymerization we came to the conclusion that it is solvation which transforms an inactive or little active ion pair of the initiator into the active center[16]. It is of no significance whether this activation through solvation involves compound with acidic proton or without this proton; all the components of the system participate in solvation according their solvation ability. This ability is determined by concentration, basicity and probably by other properties[18,19]. If this is really so, then it is difficult to define the cocatalyst as a compound possessing acidic proton. From this viewpoint, the cocatalyst could be any compound able to activate an inactive ion pair. And since this activation proceeds *via* the solvation process any compound capable of native ion pair solvation will act as a cocatalyst.

Complications of ionic polymerization caused by cocatalysis are demonstrated by a very interesting observation indicating that the ratio of catalyst to cocatalyst concentration may sometimes determine the principal course of the reaction *i.e.* if the reaction is cationic or anionic[22].

By examining the influence of water on the cationic polymerization of styrene we hope to contribute to the formation of comprehensive theory of cocatalysis which, to our knowledge, does not exist to date although some authors[23] are referring to it.

EXPERIMENTAL

Chemicals and Procedure. Styrene stabilised by *p*-tert-butylpyrocatechol was washed with 5% NaOH, water, dried over calcium chloride and then vacuum distilled under a dry nitrogen atmosphere. Toluene (analytical grade) was rectified prior to use, 1,1,2,2-tetrachloroethane was washed with distilled water till the neutral reaction and then twice vacuum distilled. The initiator was prepared by the polymerization of octamethylcyclotetrasiloxane in the presence of concentrated sulphuric acid (analytical grade); a storage solution was prepared by dissolving the polymer in toluene[24] (5 mol/l).

The water concentration in the storage solution of the monomer in toluene — 1,1,2,2-tetrachloroethane mixture was determined[18,19,25] and the water content was adjusted to a required value (drying over the molecular sieve or adding water). Firstly, a known amount of the initiator was transferred into dried glass dilatometer[19], tempered at 35°C ± 0·05°C in a thermostated bath. Then the corresponding amount of monomer was added while stirring. After about two minutes of contact of first drops of monomer with the initiator, the position of a meniscus was recorded ($t = 0$). The difference in mm, occurring between the meniscus position at $t = 0$ and that at $t > 0$ was measured during the polymerization. It was confirmed experimentally that the concentration is strictly proportional to the conversion of monomer to polymer (at 35°C and 15% vol. of styrene in toluene, the proportionallity constant equals to 0·50 mm^{-1}); the rate of polymerization was thus determined from the contraction curve (mm/min) by graphical derivation at the inflexion point. The same monomer and solvents used under the same conditions gave identical curves, deviations were less than ±5%; the results were used as a standard when changing over to a new batch of monomer and solvents, resp. In certain exceptional cases when anomalies
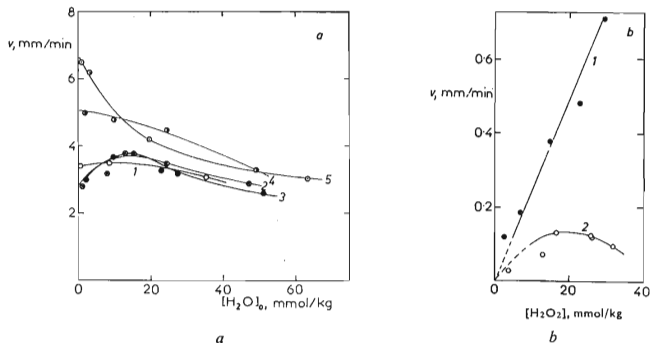
The Dependence of the Polymerization Rate of Styrene in Solution (*a*) and in Bulk (*b*) upon the Initial Concentration of Water at 35°C

a Concentration of monomer 15% vol., concentration of initiator 78 mmol/kg; concentration of toluene in a mixed solvent toluene–1,1,2,2-tetrachloroethane (% vol.): *1* (100), *2* (75), *3* (50), *4* (25), *5* (0). *b* Concentration of initiator (mmol/kg): *1* (101·6); *2* (50·9).

appeared during the change from one series to another, the materials were discarded. Some polymer samples were isolated for molecular weight determination. For this purpose the dilatometer contents were poured into the excess of methanol. The polymer was washed with methanol and dried to constant weight.

RESULTS AND DISCUSSION

The character of the dependence of styrene polymerization rate in solution, initiated by $\sim Si^+HSO_4^-$, upon water concentration is determined by the polarity of reaction medium and it is similar for different styrene concentrations. A typical example is shown in Fig. 1a. The polymerization does not proceed in the absence of solvent (in bulk) and water as a cocatalyst, resp. (Fig. 1b).

At lower initiator concentrations (<30 mmol/kg) the system remains homogeneous up to final conversions of monomer to polymer; these conversions are quite evidently the function of the initial water concentration (Fig. 2). Similar results were observed in the case of non-stationary reaction where the polymerizations resulted in different conversions according the sulphuric acid concentration in the reaction mixture[26]. At higher concentrations of $\sim Si^+HSO_4^-$ (>50 mmol/kg) the maximum conversion is independent of water concentration. Under these conditions the separation of tiny drops was observed in the polymerizing system in the advanced stage of polymerization (microheterogeneity formation). A possible connection between this
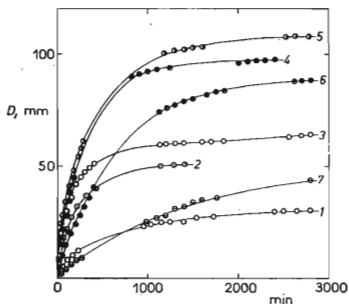

FIG. 2

Contraction Curve for Styrene Polymerization in Toluene (70% vol.) Initiated by $\sim Si^+HSO_4^-$ (23 mmol/kg) at 35°C

Initial water concentration (mmol/kg): *1* 1·0, *2* 5·6, *3* 6·4, *4* 17·0, *5* 21·6, *6* 29·0, *7* 38·9.
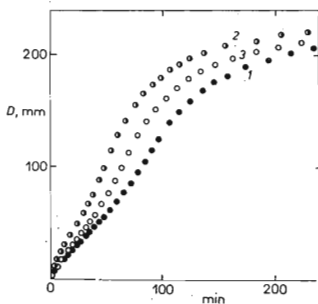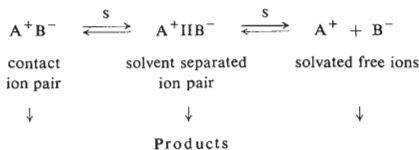
FIG. 3

Waves Observed on Contraction Curves During Styrene Polymerization

Monomer concentration 30% vol., initiator concentration 67 mmol/kg, temperature 35°C, solvent toluene–1,1,2,2-tetrachloroethane 90/10 (vol.); initial water concentration (mmol/kg): *1* (0·9), *2* (1·3), *3* (1·6).

microheterogeneity and a maximum conversion was not examined. When polymerization of styrene is carried out in non-polar medium then the formation of "waves" on contraction curves is observed, the phenomenon reported previously by Colclough and Dainton[10] (Fig. 3).

The reaction mechanism of styrene polymerization initiated by $\sim Si^+HSO_4^-$ is entirely consistent with the hypothesis of activation of originally strongly bonded catalyst ions proceeding *via* solvation, similarly as in the case of trioxane, dioxolane and tetrahydrofurane polymerization[16,18,19], resp. The fact that only a part of the cocatalytic curve can be covered by styrene and its mixtures with solvents, somewhat complicates the situation. Fig. 1 shows that water in non-polar environment accelerates the polymerization whereas in more polar medium (such as 1,1,2,2-tetrachloroethane) it has a decelerating effect. The cocatalytic curve exhibits a maximum when the experiments are carried out in the mixture of styrene–toluene–1,1,2,2-tetrachloroethane. The solvation equilibrium is established in each of the mixtures; the initial point (rate) on a general cocatalytic curve corresponds to this equilibrium. In non-polar solvents, where none of the components is able to solvate the initiator, this initial point lies in the origin. The point is shifted towards higher reaction rates in solvent mixtures where activation of the initiator becomes feasible; the greater the solvation by one or more components of the system, the greater the shift. This effect is observed up to a certain maximum after which the rate decreases, unless the initiator is predominantly solvated by the monomer. If we start an experiment in certain environment than add a strongly solvating agent *e.g.* water, a corresponding part of the cocatalytic curve, from the intial point to the right, is measured. Styrene and toluene — though they have identical dielectric constant — have a different activating (solvating) effects upon the initiator, toluene being more effective. That is why the mixtures with high styrene concentration do not polymerize in the absence of water. In those cases where a part of styrene was substituted by toluene, other conditions being preserved, the system is able to polymerize even in non-aqueous medium. We believe that the interpretation of results is quite consistent with the hypothesis of Winstein–Robinson about the ionic equilibrium[26,27]:

$$A^+B^- \quad \underset{\longleftarrow}{\overset{s}{\longrightarrow}} \quad A^+IIB^- \quad \underset{\longleftarrow}{\overset{s}{\longrightarrow}} \quad A^+ + B^-$$

contact ion pair	solvent separated ion pair	solvated free ions
↓	↓	↓

<div align="center">Products</div>

Strongly bonded ion pairs, solvent separated ion pairs as well as free ions participate in initiation and propagation processes[28] (and possibly in other processes too). Each of these species will, however, act, analogically as in the case of anionic polymerization[28,4], according its reactivity: inactive contact ion pairs, very reactive

solvent separated ion pairs, free ions. The effective reactivity of free ions is, unless they are solvated by the substrate, lower because of steric hindrances caused by the envelope of solvating molecules[16].

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