

INFLUENCE OF WATER UPON THE RATE
OF CATIONIC POLYMERIZATION OF STYRENE. II.*
POLYMERIZATION INITIATED BY SnCl_4

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The dependence of the rate of styrene polymerization upon the water concentration in different media of varying polarity was measured at various temperatures and concentrations of monomer and initiator respectively. The dependence of the overall polymerization rate upon the concentration of water exhibits a maximum whose position changes with the polarity of reaction medium and it is also dependent on other reaction conditions. The cocatalytic interactions between the initiator and water or other components of polymerizing system are based on the solvation leading to the activation of the initiator.

Many relatively inconsistent data appear in the literature describing cocatalytic effects during cationic polymerization of styrene: Okamura and Higashimura¹ observed a maximum polymerization rate in benzene at the ratio $[\text{H}_2\text{O}]/[\text{SnCl}_4] = 1$ whereas Colclough and Dainton² found the same ratio being equal to 2 for the polymerization in 1,2-dichloroethane. Overberger, Ehrig and Marcus³ pointed out that the maximum polymerization rate could be observed at various $[\text{H}_2\text{O}] : [\text{SnCl}_4]$ ratios depending on the character of the solvent used. They explained this observation on the basis of selective solvation by nitrobenzene. Another studies in which various initiators, solvents and monomers were used, contributed significantly to the collection of facts about cationic polymerization, namely about its cocatalysis. These materials have, however, not been used for plausible explanation of the effect of cocatalysis⁴.

In our paper⁵ we examined the polymerization of styrene initiated by $\sim\text{Si}^{(+)}$. $\text{HSO}_4^{(-)}$. The experiments with another initiator described in the present paper are to extend the previous observation. To be able to compare our results with those already published^{2,3} we selected stannic chloride as a catalyst. Such a comparison is a very valuable one, especially in the case of cationic polymerization — the reaction with generally poor reproducibility. We believe that this advantage will, at least in certain cases, compensate for disadvantages caused by the complexity of possible reactions of stannic chloride.

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EXPERIMENTAL

Materials, their purification, instruments and the working procedure were described in previous communication. Commercial stannic chloride, pure, was used in form of toluene or 1,1,2,2-tetrachloroethane solution. In some cases the initiator was distilled in the presence of phosphorus pentoxide prior to use. No difference between the polymerization rates was observed when purified chloride and commercial product was used resp. To follow the influence of ultrasonic waves on the polymerization course a 70 W ultrasonic soldering iron (Kovopodnik, Brno) was employed. The tip of the soldering iron was fixed resiliently to the dilatometer bulb which was immersed into a constant temperature bath; blank experiments have shown that no overheating of the dilatometer contents occurred.

RESULTS AND DISCUSSION

Contrary to the polymerization initiated by $\sim\text{Si}^{(+)}\text{HSO}_4^{(-)}$ the polymerization of styrene in the presence of SnCl_4 starts after an inhibition period whose length depends on water, monomer and initiator concentration, on temperature and the way of adding the components. The maximum rate is a function of solvent polarity, concentration of styrene and water (Fig. 1), initiator concentration (Fig. 2a) and temperature (Fig. 2b). The order of reaction with regard to the initiator varies at 35°C from 1 to 3.5 depending on polarity of the reaction medium, concentration of water and monomer, resp. The external order with regard to monomer increases from 1 to 4 in medium whose dielectric constant is 2.4. In the medium where the dielectric constant is 4.9 and 7.0 resp. it decreases from 4 to 1 when the water concentration increases. The internal order with regard to monomer (calculated from conversion curves) is approximately constant and its value strongly depends on the polarity of the reaction medium. When the polymerization is carried out in non polar solvents containing low concentration of water (lower than that corresponding to the maximum rate) then the appearance of "waves" on contraction curves is seen (Fig. 3); similar phenomenon observed during the polymerization of styrene in CCl_4 has already been reported by Colclough². The apparent activation energy of polymerization is not constant within the region of temperatures used.

The abscissa of the maximum reaction rate is shifting towards lower concentrations of water when increasing the polarity of the reaction medium. In an extreme case – at low concentration of styrene in 1,1,2,2-tetrachloroethane solution – the ascending part of the cocatalytic curve (rate vs $[\text{H}_2\text{O}]$) is already missing; water in this case acts as a typical catalytic poison. The above described effect is entirely identical with that observed during the styrene polymerization in dichloromethane⁶ using boron fluoride as a catalyst. The amount of water in the system required for attaining the maximum polymerization rate increases with decreasing polarity of the reaction medium. It appears again⁵ that toluene and styrene are not equivalent as to the properties determining the final concentration or reactivity of centres. Such properties could be the ability to solvate the initiator, ability to form a bond with other compounds that are capable of solvating ion pairs (solubility of e.g. water.)

As the solubility of water in styrene is somewhat higher than that in toluene, the equilibrium $[\text{H}_2\text{O}]_S \rightleftharpoons [\text{H}_2\text{O}]_F$ (where S denotes water bonded in solvating envelopes, subscript F stands for free water) will be shifted to the left in the mixtures containing higher concentrations of toluene, other conditions being unchanged. The abscissa intersecting the maximum is a function of the equilibrium position. A shift of this abscissa was indeed observed as follows from Figs 1 and 2. The same effect should, however, be operative—this time in reversed direction—when 1,1,2,2-tetrachloroethane is used instead of styrene. The abscissa corresponding to the maximum is, in this case, smaller. The result is thus just opposite to that expected according to the hypothesis about the reactivity of centers being determined only by the affinity of solvent and monomer towards water. The only plausible explanation as to this inversion is

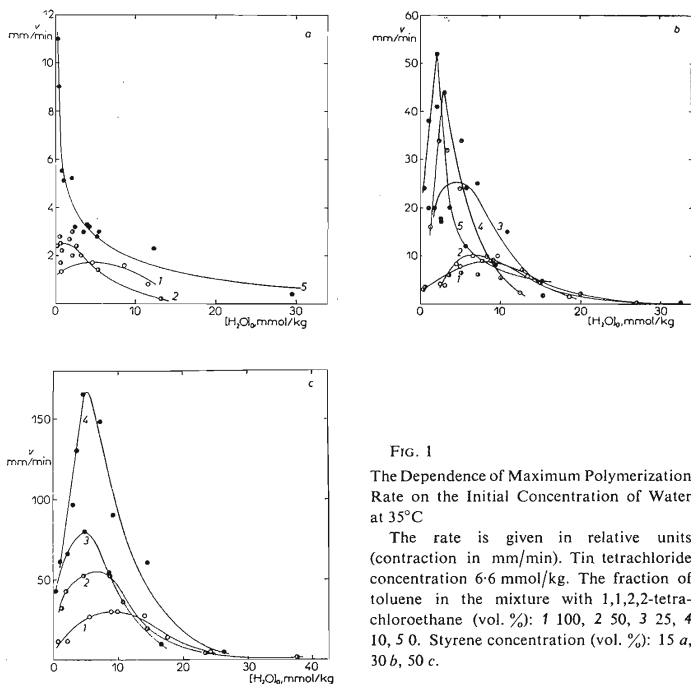


FIG. 1

The Dependence of Maximum Polymerization Rate on the Initial Concentration of Water at 35°C

The rate is given in relative units (contraction in mm/min). Tin tetrachloride concentration 6.6 mmol/kg. The fraction of toluene in the mixture with 1,1,2,2-tetrachloroethane (vol. %): 1 100, 2 50, 3 25, 4 10, 5 0. Styrene concentration (vol. %): 15 *a*, 30 *b*, 50 *c*.

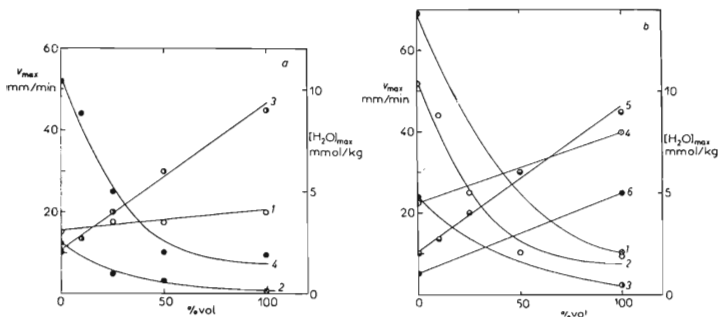


FIG. 2

The Shift of a Maximum with Changing Polarity of the Reaction Mixture (Different Toluene Concentrations in 1,1,2,2-Tetrachloroethane)

Initial styrene concentration 30% vol. Curves: *a* 1 $[H_2O]_{max}$ and 2 v_{max} at $[SnCl_4]_0 = 2.3$ mmol/kg, 3 $[H_2O]_{max}$ and 4 v_{max} at $[SnCl_4]_0 = 6.6$ mmol/kg at temperature 35°C; *b* temperature (°C) for v_{max} : 1 50, 2 35, 3 20; $[H_2O]_{max}$: 4 50, 5 35, 6 20; $[SnCl_4]_0 = 6.6$ mmol/kg.

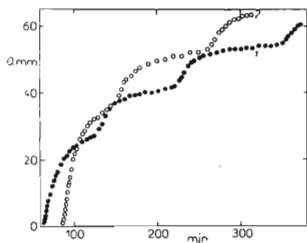


FIG. 3

Waves on the Contraction Curve Observed During Styrene Polymerization in Toluene

Temperature 35°C, styrene concentration 15% vol., $SnCl_4$ concentration 6.6 mmol/kg, initial water concentration [mmol/kg]: 1 0.7, 2 4.6.

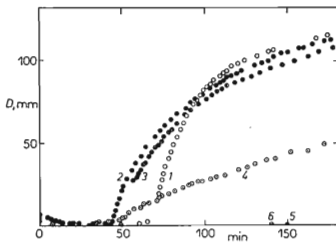


FIG. 4

Polymerization Under the Influence of Ultrasonic Waves

Temperature 35°C, styrene concentration 30% vol. in toluene, $SnCl_4$ concentration 6.8 mmol/kg; initial water concentration mmol/kg: 1, 2 6.9, 3, 4 2.1, 5, 6 42 (even numbered curves correspond to the results obtained in ultrasonic waves field).

following: The solvent itself participates in solvation equilibria^{5,7} thus contributing to the initiator activation.

As the maximum rate is shifting with changing the quality of the reaction medium there is no general ratio catalyst/cocatalyst expressed by an integer at which the polymerization rate has a maximum value. This ratio decreases monotonously from very high values observed in the most polar media, $\lim_{v \rightarrow v_{\max}} ([\text{SnCl}_4]/[\text{H}_2\text{O}]) = \infty$ to c. 0.6 measured in low polarity solvents. It seems that the change in the $[\text{SnCl}_4]/[\text{H}_2\text{O}]$ (generally catalyst/cocatalyst ratio) at which the polymerization rate reaches a maximum with changing the solvent polarity should not be neglected. It follows from the literature data² as well as from our results that this ratio does not have to have a stoichiometric value. The species capable of initiation of the polymerization process need not necessarily have the structure $\text{SnCl}_4 \cdot \text{H}_2\text{O}$ or $\text{SnCl}_4 \cdot 2 \text{H}_2\text{O}$, as it is sometimes believed^{2,3}.

The concentration of water that corresponds to a maximum rate depends on the temperature, the other conditions being unchanged. The shift of the maximum with changing temperature is quite evident; solvation ability of all compounds, including water, decreases with the increasing temperature. Thus more water is necessary for the optimum activation. Also solvation equilibria should be influenced^{5,7} and thus the position of the initial point on the cocatalytic curve⁵. The position of the intercept with the ordinate is also a function of environment. The value of reaction rate extrapolated to zero concentration of water increases with the increasing polarity of the solvent mixture.

The reaction rate at zero concentration of the cocatalyst is a generally accepted criterion of purity of the reaction system. The reaction should not proceed in a "pure" system. This criterion is a rather dubious one from our point of view. The rate will probably always be a function of the position of equilibria^{5,7}. Various solvents can participate on separation and thus on activation of ion pairs by solvation. It is to be expected that the solvation ability of a solvent will increase with its polarity. The determining of zero polymerization rate in the absence of a cocatalyst but in the presence of other solvating agents is thus not justified.

If the change in the polymerization rate with changing polarity of the reaction medium and the concentration of water can be accounted for by a shift of Winstein solvation equilibria⁷ and if our notion about the activation of ion pairs (cocatalysis) is principally correct, then the reaction rate should be influenced not only by "chemical" intervention into solvating envelope enclosing the active centres but also by physical influences. The shift of the maxima was indeed observed when the temperature was changed. This shift is, however, rather small within the temperature range examined. The solvation envelope could perhaps be influenced more selectively, although not without complications, by ultrasonic waves. It is known that ultrasonic waves can effect mechanical dispergation of two immiscible liquids or inversely, they can cause agregation and precipitation of finely dispersed particles^{8,9}. The effect will depend on the frequency of the ultrasonic radiation and on the properties of the environment subjected to it. If these changes are at least partially due to the influence of ultrasonic waves upon the solvation envelope then ultrasonic radiation

might substantially influence the overall polymerization rate. It follows from Fig. 4 that ultrasonic waves have a strong retarding influence on the polymerization of styrene carried out under described conditions.

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