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Polymerization of Styrene

Comment on the Papers A Contribution to the Kinetics of the Polymerization of Styrene with CF_3SO_3H as Catalyst **and** Measurements on the Temperature Dependence of the Cationic Polymerization of Styrene in CH_2Cl_2 with CF_3SO_3H as Catalyst **by N. Cardona-Sütterlin, Polymer Bulletin 1, 149 (1978) and 1, 307 (1979)**

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CARDONA-SÜTTERLIN (1978) has recently published kinetic data for the polymerization of styrene catalyzed by triflic acid and she concludes that the polymerization rate obeys the first-order dependence on the monomer concentration. The work she describes was performed in the Sonderforschungsbereich 41, Chemie und Physik der Makromoleküle, Sektion Mainz, with the cooperation of the present autors.

The dependence of the polymerization rate on the monomer concentration $[M]_0$ is evidently not linear because the value of the reaction rate constant k shown in Table 2 depends on the initial monomer concentration. Also the dependence of the conversion on the time (Fig. 1 and 2) may be only approximately denoted as a first-order reaction because the points show a systematic deviation from a straight line. Correct lines plotted through the points in Fig. 1 and in Fig. 2 give ordinate intercepts and furthermore such lines describe the course of polymerization only to the conversion of about 70%. The conclusion derived from Fig. 5 (a second- and a third-order dependence in respect to the catalyst concentration) is not verified enough experimentally - each line in Fig. 5 is given only by two points.

In the view of the previously known observations (i.e., s-shaped conversion curves, decrease of the polymerization rate with increasing monomer concentration, etc.), it was understood that the polymerization of styrene catalyzed by strong protic acids (HAMANN et al. 1972, PEPPER 1974, CHMELIR 1973, 1975) must be more complicated as a reaction with a simple first order in respect to the monomer concentration.

The foregoing observations lead us to assume a new reaction mechanism (CHMELIR et al. 1975, 1977) for the polymerization of styrene catalyzed

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by triflic acid with a practically inactive catalyst-monomer-complex which is in equilibrium with other active propagating species. Thus, the formation of the initiating species becomes a relative slow process which depends on the concentration of the inactive catalyst-monomer-complex and therefore depends also on the change of monomer concentration during polymerization. Under assumption that the concentration of undissociated catalyst molecules and the concentration of the catalyst-monomer-complex are much greater than the concentration of the ionic species (free ions and triple ions), the following dependences describe the rate of polymerization

$$-\frac{dM}{dt} = \frac{[M]}{(1 + K_m M)^2} (k_p K_1 HA_o^2 + k_p'' K_1^{3/2} K_2^{1/2} K_3 [HA]_o^3), \qquad (1)$$

and the integrated form is given by

$$f[M] = \ln \frac{M_o}{M_t} + 2 K_m (M_o - M_t) + \frac{K_m^2}{2} (M_o^2 - M_t^2) \qquad (2)$$

$$f[M] = (k_p K_1 [HA]_o^2 + k_p'' K_1^{3/2} K_2^{1/2} K_3 [HA]_o^3) t$$

where K_m denotes the monomer complexation constant, K_1, K_2 and K_3 the equilibrium constants, k_p and k_p'' the propagation rate constants, $[HA]_o$ the initial catalyst concentration, $[M]_o$ the initial monomer concentration and $[M]_t$ the concentration of monomer at the time t.

We have also shown previously that linear curves are obtained by the use of eq. 2 for plotting of the dependence of $f[M]$ versus time (CHMELIR et al. 1977, Fig. 11). CARDONA-SOTTERLIN (1978) found also linear curves by the use of eq. 2 as demonstrated in Fig. 3 in her paper. The intercepts of the straight lines with the $f[M]$ - axis correspond to the conversion of the fast non-equilibrium stage of polymerization and this effect was discussed previously.

Because there are discrepancies between the values of the "first-order reaction rate constant" k (Table 2) and of the rate constant derived according to eq. 2 (Table 3) reported by CARDONA-SOTTERLIN (1978) and those calculated by us direct from the experimental data, the recalculated values for both rate constants are collected in the following Table.

TABLE 1

Dependence of the "first-order rate constant" k and of the rate constant f[M]/t according to eq. 2 on the initial monomer concentration $[M]_0$.

Styrene [M]	Triflic Acid [M] . 10^4	"First-order Reaction Rate Constant" k k . 10^3 (sec^{-1})	Rate Constant According to eq. 2 f[M]/t 10^2 . f[M]/t (sec^{-1})
0.025	2.0	47.33	7.0
0.05	2.0	24.16	6.3
0.10	2.2	12.0$^{+)}$	6.6$^{+)}$
0.10	1.8	5.5$^{+)}$	3.3$^{+)}$
0.20	2.0	2.27	3.5
0.30	2.0	0.60	3.2
0.50	2.0	0.45	4.0
1.00	2.0	0.13	5.8

$^{+)}$Most experiments were carried out with a catalyst concentration 2.0 . 10^{-4} mol/l and only two experiments reported here were carried with a little higher (2.2 . 20^{-4} mol/l) and a little smaller (1.8 . 10^{-4} mol/l) catalyst concentration which must be taken in account by comparation of the different rate constants.

Table 1 clearly demonstrates that there are no systematic deviations in the rate constant according to eq. 2 (f[M]/t-value) and the differences between them are in the limit of the experimental errors. On the other hand "the first-order reaction rate constant" k changes its value systematically from 47.3 . 10^{-3} to 0.13 . 10^{-3} sec^{-1} when the initial monomer concentration is changed from 0.025 to 1.00 mol/l. Therefore it is clearly shown that the polymerization reaction does not obey the first-order dependence on the monomer concentration.

The polymerization of styrene at lower temperatures reported by CARDONA-SÜTTERLIN (1979) does not show the same formal dependence on the monomer concentration at higher initial monomer concentration (above 0.2 mol/l). The dependence of the polymerization rate on the monomer concentration $[M]_0$ is also here evidently not linear because the values of the reaction rate constant (slopes in Fig. 1 and in Fig. 2) depend on the initial monomer concentration. Furthermore only low conversions were obtained if the polymerization took place at very low temperatures. For example at -60°C and a monomer concentration of 0.5 mol/l was obtained a conversion of about 8% and further polymerization did not take place. These observations confirm the idea that the polymerization must be more complex as a first-order reaction in respect to the monomer too.

Similarly as shown for the anionic polymerization of styrene (BÖHM et al. 1972), also the activation energy of cationic polymerization of styrene is a complex quantity which includes activation energies of all propagating species: Contact and solvent separated ion-pairs, free ions and triple ions. This all must be taken into account because the activation energy can achieve positive as well as negative values and therefore the reported conclusions (CARDONA-SÜTTERLIN 1979) in relation to the rate constant are not correct.

In conclusion, it seems adequate to say that the catalyst-monomer-complex theory is able to describe the observed phenomena to a certain extent. The small deviations of the f[M]/t values at low monomer concentration (Tab. 1) and the deviations at the beginning of polymerization (a very fast polymerization was observed immediately after the mixing of the monomer with the catalyst solution - the conversion corresponding to this fact non-equilibrium stage of polymerization is given by the intercepts of the straight lines with the f[M]-axis (CARDONA-SÜTTERLIN 1978, Fig. 3, CHMELIR et al. 1977, Fig. 9 and 11)) are caused probably by a relatively slow establishment (in relation to the rate of polymerization) of different equilibria between the propagating species. The bimodale molecular weight distribution seems also to confirm the proposed complex reaction mechanism with different propagation species.

On the other hand it is clearly shown (Tab. 1) that the polymerization rate does not obey the first-order dependence on the monomer concentration.

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