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A Contribution to the Kinetics of the Polymerization of Styrene with CF_3SO_3H as Catalyst

Nieves Cardona-Sütterlin

Institut für Physikalische Chemie, Universität Mainz, 6500 Mainz, Federal Republic of Germany

Summary

The time dependence of the cationic polymerization of styrene in CH_2Cl_2 with CF_3SO_3H as catalyst can be formally described as being first-order with respect to monomer concentration $[M]_0$. The reaction rate shows a third-order dependence in catalyst concentration $[C]_0$. A high polymer and a low polymer polystyrene fraction are found at $[M]_0 > 0.2$ mole · l^{-1}. The reaction rate of the high polymer fraction is proportional to $[C]_0^3$, that of the low polymer fraction probably proportional to $[C]_0^2$. The polymerization active species may thus be triple ions in the first and ion pairs in the second case.

Introduction

Various efforts have been made to describe the cationic polymerization of styrene with protonic acids. But up to now there is no satisfactory explanation for either the mechanism (1) or identity of the growing species (2,3,4). The attempt to increase the concentration of the growing species (5) by using trifluormethansulfonic acid as catalyst has not led to the desired results. The few contributions hitherto made to the cationic polymerization of styrene in dichloromethane with CF_3SO_3H as catalyst express different opinions, (6,7,8). Higashimura et al (8) attribute the experimentally found complex relation between reaction rate and monomer concentration to the change in the dielectric constants of the polymerization system, whereas Chmelir et al (6,7) explain it as a result of the formation of a little reactive monomer/catalyst complex. In the present contribution both conceptions shall be considered in the light of new experimental results.

Experimental

Dichloromethane was dried simultaneously with P_2O_5 and CaH_2 (9). The specific conductivity was between

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$2.5 \cdot 10^{-9}$ and $3 \cdot 10^{-9}\,\Omega^{-1}\mathrm{cm}^{-1}$ in all experiments. The conductivity messurements and the purification of the other substances are described in a previous paper (7). At monomer concentrations ≤ 0.2 mol $\cdot$ l^{-1} polymerization was carried out in an adiabatic glass calorimeter (7), the time conversion curves resulting from the recorded heat of polymerization. At monomer concentrations > 0.2 mol $\cdot$ l^{-1} the experiments were performed in a thermostated glass reactor equipped with a three-way valve for introduction of the different components in dry nitrogen atmosphere. Solvent, monomer and catalyst solution were fed into the reaction vessel in this order. In this case the determined polymerization rates are not dependent on wether CH_2Cl_2 has been dried with P_2O_5 and CaH_2 or with P_2O_5 only. The polymerization was stopped by addition of a 10 % aqueous methanol solution and the conversion analized gravimetrically. The share of the high and low molecular polymer fractions were determined from GPC-curves.

Results

For monomer concentrations ≤ 0.2 mol$\cdot l^{-1}$ the experimental results at -15 °C up to about 70 % conversion are fairly well described by the usual first-order plot (Fig.1).

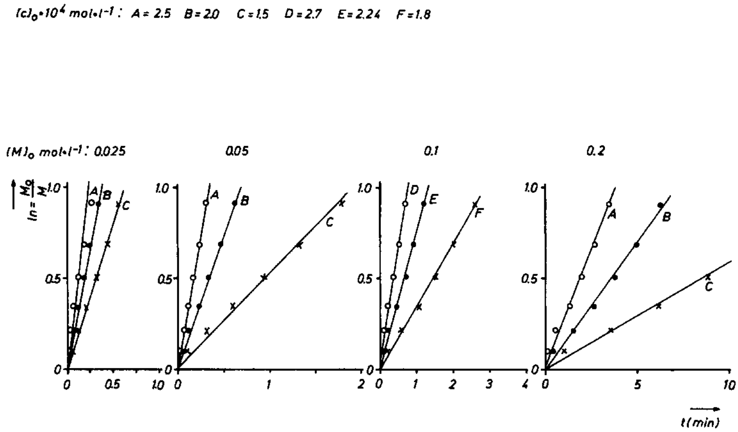

Fig.1: First-order plot for $[M]_0 \leq 0.2$ mol$\cdot l^{-1}$ at -15 °C.

At higher monomer concentrations (Fig.2), however, increasing deviations are found at ever lower conversions.

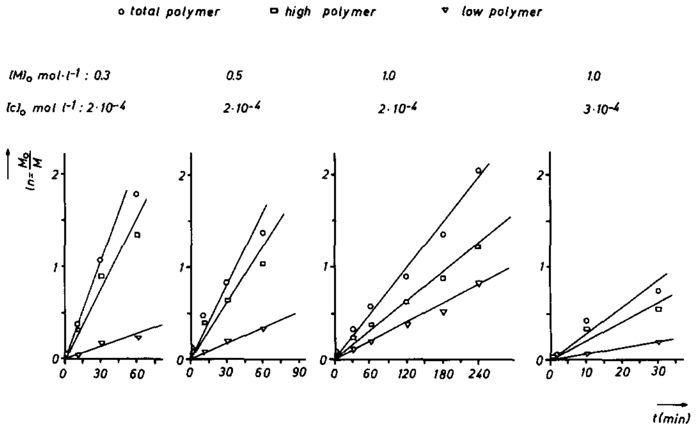

Fig.2: First-order plot for $[M]_0 > 0.2$ mol·l^{-1} at -15°C.

From the bimodal molecular weight distributions in GPC resulting at $[M]_0 > 0.2$ mol·l^{-1} one can estimate the quantities of a low polymer and a high polymer fraction. The results are given in Tab.1 and plotted in Fig.2 together with those of the total polymer.

Table 1

$[M]_0$ (mol·l^{-1})	$[c]_0 \cdot 10^4$ (mol·l^{-1})	Conversion (%)	Time (min)	Low Polymer Fraction	High Polymer Fraction
0.3	2	8	1	0.11	0.89
		32	10	0.16	0.84
		66	30	0.16	0.84
		79	60	0.14	0.86
0.5	2	12	1	0.16	0.84
		38	10	0.17	0.83
		57	30	0.23	0.77
		75	60	0.24	0.76
1.0	2	8	3	0.22	0.78
		30	30	0.32	0.68
		44	60	0.33	0.67
		64	120	0.39	0.61
		78	180	0.41	0.57
		87	240	0.40	0.60
1.0	3	7	1	0.13	0.87
		35	10	0.19	0.81
		53	30	0.26	0.74

The apparent rate constants k' calculated from Fig.1 and Fig.2 are collected in Tab.2. k' is dependent on the monomer concentration.

Table 2

$[c]_0$ (mol·l⁻¹) → $[M]_0$ (mol·l⁻¹) ↓	$2.7\cdot10^{-4}$ $k'\cdot10^2$ (s⁻¹)	$2.5\cdot10^{-4}$ $k'\cdot10^2$ (s⁻¹)	$2.2\cdot10^{-4}$ $k'\cdot10^2$ (s⁻¹)	$2.0\cdot10^{-4}$ $k'\cdot10^2$ (s⁻¹)	$1.8\cdot10^{-4}$ $k'\cdot10^2$ (s⁻¹)	$1.5\cdot10^{-4}$ $k'\cdot10^2$ (s⁻¹)
0.025		7.5		4.1		2.5
0.05		5.0		2.5		0.92
0.1	2.2		1.3		0.55	
0.2		0.43		0.23		0.13
0.3				0.06		
0.5				0.05		
1.0				0.02		

Fig.3 shows the plot according to our(7) earlier proposed complex hypothesis in the form

$$f(M) = \ln \frac{M_0}{M} + 2\,Km(M_0-M) + \frac{Km^2}{2}(M_0^2-M^2) = k'_K t$$

for $[M]_0 \leq 0.2$ mol·l⁻¹. The complex hypothesis plot does not agree as well with the experimental results as the first-order plot in Fig.1. On the one hand we obtain ordinate interceps which are not readily understood on the other hand the deviations are more pronounced and set in at lower conversions and monomer concentrations. Therefore we do not give the corresponding plot for $[M]_0 > 0.2$ mol·l⁻¹.

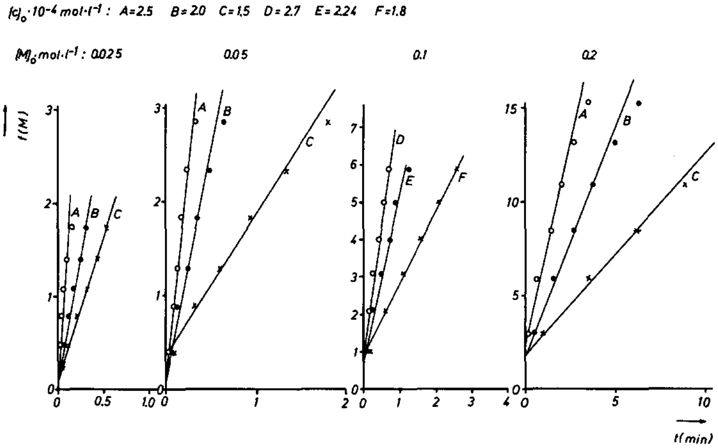

Fig.3: Complex hypothesis plot for $[M]_0 \leq 0.2$ mol·l⁻¹ at -15°C.

The constants k'_K calculated from Fig.3 are collected in Tab.3. k'_K is also dependent on the monomer concentration although the drift is something lower than for k' in a comparable range.

Table 3

$[C]_0 (mol \cdot l^{-1}) \rightarrow$	$2.7 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
$[M]_0 (mol \cdot l^{-1}) \downarrow$	$k'_K \cdot 10^2 (s^{-1})$	$k'_K \cdot 10^2 (s^{-1})$	$k'_K \cdot 10^2 (s^{-1})$	$k'_K \cdot 10^2 (s^{-1})$	$k'_K \cdot 10^2 (s^{-1})$	$k'_K \cdot 10^2 (s^{-1})$
0.025		24		9.5		6.3
0.05		16		8.6		3.5
0.1	14		9.1		4.2	
0.2		9.1		5.0		2.4

In Fig.4 the apparent rate constants k' calculated from Fig.1 are plotted against the catalyst concentration. It is evident that the plot does not agree with relationship $k' = k[C]_0$ but very well with $k' = k[C]_0^3$.

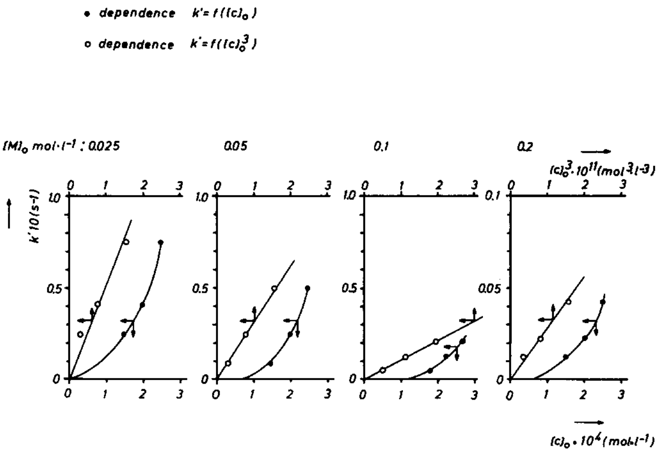

Fig.4: k' dependence on catalyst concentration for $[M]_0 < 0.2$ mol·l⁻¹ at -15 °C.

The analogous plot for k' from Fig.2 is given in Fig.5. The high polymer fraction obeys a third-order dependence on the catalyst concentration whereas the low polymer fraction is probably better described by a second-order dependence. This suggestion is based on few messurements and should be confirmed experimentally.

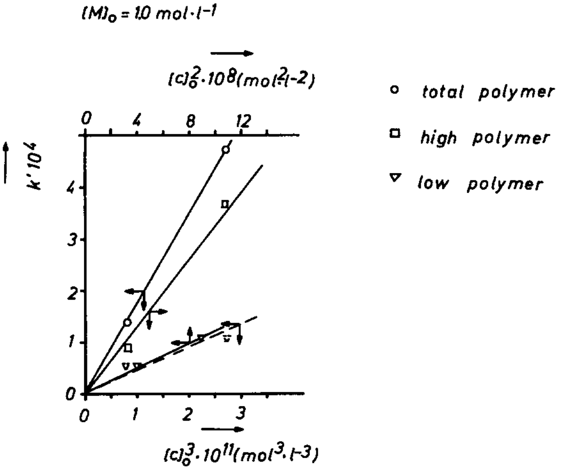

Fig.5: k' dependence on catalyst concentration for $[M]_0 > 0.2$ mol l^{-1} at -15°C.

In Fig.6 the change of the specific conductivity of the system during polymerization is plottet as a function of monomer concentration for different conversions. $\varkappa$ passes through a maximum with increasing monomer concentration and becomes higher with increasing conversion.

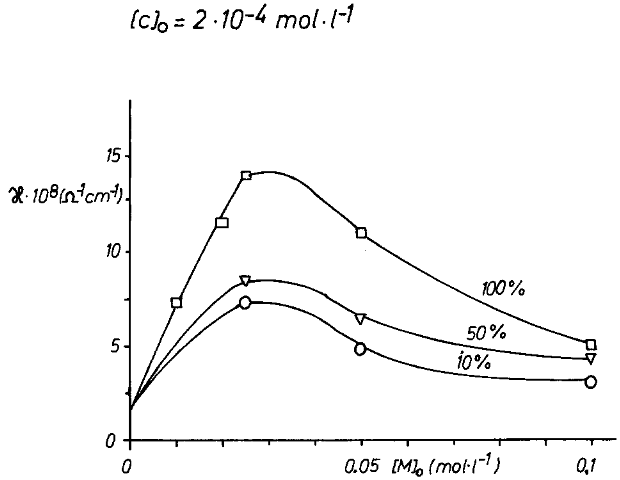

Fig.6: Specific conductivity as a function of $[M]_0$ for different conversions.

Discussion

The cationic polymerization of styrene in the system CH_2Cl_2/CF_3SO_3H at -15 °C may be described first order as a function of time up to relativly high conversions. This initially formal first order dependence applies both to the total reaction rate and to the reaction rate of the individual species. The drift of k' with the monomer concentration shows, however, that there is no simple first order mechanism but additional effects which influence the kinetics. If it were only the formation of the active species by dissoziation of a little reactive monomer/catalyst complex which determines the reaction as proposed earlier by us(7), the constants k'_K collected in Tab.3 should be the same for all monomer concentrations. But k'_K changes with the monomer concentration although less markedly than k'. The fact that the specific conductivity increases from the beginning to the end of the polymerization (Fig.6) is only difficult to explain on the assumption of a monomer catalyst complex. On the other hand, it is not yet absolutely clear whether the observed complex reaction rate dependence of the monomer concentration can be explained quantitatively as the sole consequence of the changed dielectric constant, as proposed by Higashimura et al(8). k' and the dielectric constant vary monotonously with $[M]_0$ (Tab.2) whereas the specific conductivity, mainly caused by polystyryl ions (7), passes through a maximum (Fig.6). The obtained results can neither confirm nor rule out the attempted interpretation via the complex hypothesis nor the attempted explanation via the dielectric constant. However, the latter approach offers some possibilities of interpretation which are not as easily provided by the complex hypothesis.

According to the present results there is no doubt that the reaction rate depends about third-order on the catalyst concentration, at least for lower monomer concentrations. The first-order dependence in $[C]_0$ found by Higashimura et al(8) probably is only a result of the few experimental points. This means that it is mainly triple ions which function as active species. Triple ions would thus also be responsible for the formation of the high polymer fraction at $[M]_0 > 0.2\ mol\cdot l^{-1}$ whereas the still somewhat uncertain second-order in catalyst concentration in the case of the low polymer fraction might be indicative of the intervention of ion pairs as another active species in the reaction run.

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