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Measurements on the Temperature Dependence of the Cationic Polymerization of Styrene in CH_2Cl_2 with CF_3SO_3H as Catalyst

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Summary

The cationic polymerization of styrene in CH_2Cl_2 with CF_3SO_3H as catalyst and at low monomer concentrations shows, at -15 °C, -45 °C and -60 °C, the same formal dependence on monomer concentration. The dependence on the catalyst concentration is approximately but not exactly of a third order.

The unimodal molecular weight distributions at $[M]_0 < 0.2$ mol·l^{-1} become broader with decreasing polymerization temperature and increasing monomer concentration and change to bimodal or trimodal distributions at $[M]_0 > 0.2$ mol·l^{-1}. The addition of $(Bu)_4N^+CF_3SO_3^-$ to the polymerization system shows that the two higher molecular peaks are produced by free ions. The activation energy of the total reaction is found to be 3.5 kcal·mol^{-1}.

Introduction

As reported in a previous paper (1) the kinetics of the cationic polymerization of styrene in CH_2Cl_2 with CF_3SO_3H as catalyst at -15 °C are not yet fully understood as far as the rate dependence on monomer concentration is concerned. First order kinetics (2) and a complex hypothesis (3) are two conceivable models.

The increasing conductivity of the polymerizing systems from the beginning up to the end of the polymerization (1, 3, 4) suggest that the active species are mostly ions in a complicated equilibrium. This equilibrium is influenced by the monomer concentration. As a result, unimodal and bimodal molecular weight distributions are found for $[M]_0 < 0.2$ mol·l^{-1} and $[M]_0 > 0.2$ mol·l^{-1} respectively.

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In the case of the unimodal distributions there is every indication that the active species are mostly triple ions because the reaction rate is found to depend rather well on the third power of the catalyst concentration. For the same reason triple ions should be responsible for the formation of the high polymer fraction in the bimodal distributions. Since there is some indication of a second order dependence with respect to catalyst concentration, the low polymer fraction is probably formed by ion pairs.

In the present contribution the investigation of the above-mentioned polymerization system is extended to several temperatures.

Experimental

The polymerization procedure and the purification of the components used were carried out as described on an earlier occasion(1). The polymerization temperatures were -15°C, -45°C and -60°C.

The salt tetrabutyl ammonium trifluoromethane sulfonate, $(Bu)_4N^+CF_3SO_3^-$, was prepared by dropwise addition of an aqueous solution of approx. 10^{-2} mol·l^{-1} CF_3SO_3H to a 10% aqueous tetrabutyl ammonium solution at room temperature. The purification of the salt was effected by repeated recrystallization from a solution in ethyl acetate with hexane as precipitant. The melting point of the product used was about 114-115°C. The number- and weight-average molecular weights of the polymers were calculated from GPC curves by a special computer program(5).

Results

Fig. 1 shows the usual first-order plot for low monomer concentrations at Polymerization temperatures of -15°C, -45°C and -60°C. The -15°C values have been published in a previous paper(1) but in this context a few are quoted for comparison. It should be noted that a similar complex hypothesis plot(3) would also be possible.

Fig.2 gives the dependence $k' = k[C]_0^3$ for the low monomer concentrations at the above-mentioned temperatures.

In Fig.3 the unimodal GPC curves for the monomer concentrations $[M]_0 = 0.05$ mol·l^{-1} and $[M]_0 = 0.1$ mol·l^{-1} and two different catalyst concentrations are shown for three polymerization temperatures. The dotted distribution curve results at a temperature of $-15\,^{\circ}C$ upon addition of $1\cdot10^{-5}$ $mol\cdot l^{-1}$ $(Bu)_4N^+CF_3SO_3^-$.

The results from Fig.3 are collected in Table 1 $U = \frac{Mw}{Mn} - 1$ is a measure of the broadness of the molecular weight distribution. The polymers belong to a conversion of 90%.

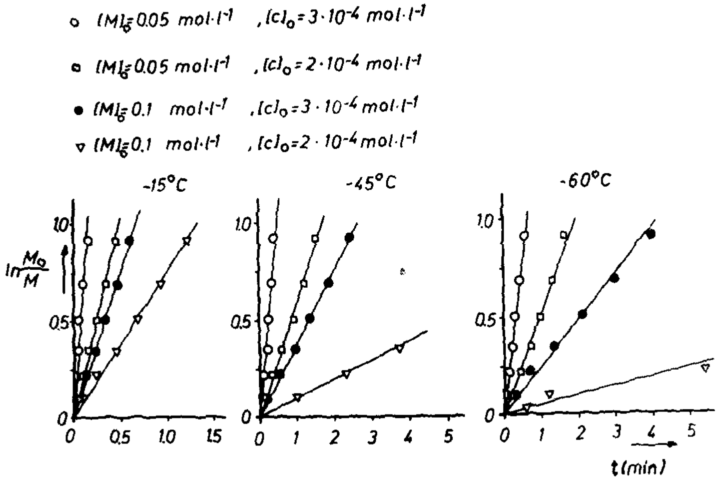

Fig.1: First-order plot for $[M]_0 < 0.2\ mol\cdot l^{-1}$ at different polymerization temperatures.

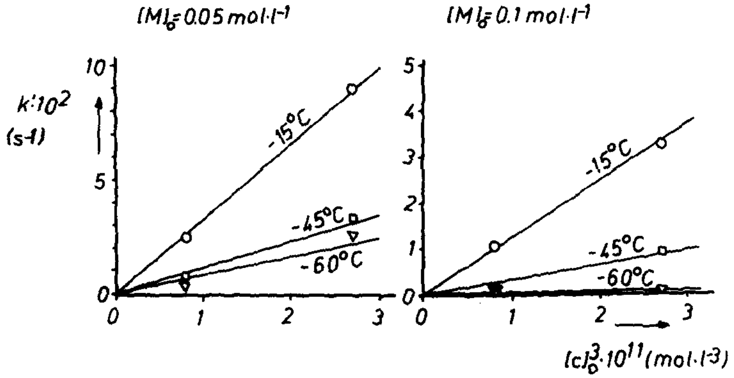

Fig.2: k' dependence on catalyst concentration for $[M]_0 < 0.2$ mol l^{-1} at different polymerization temperatures.

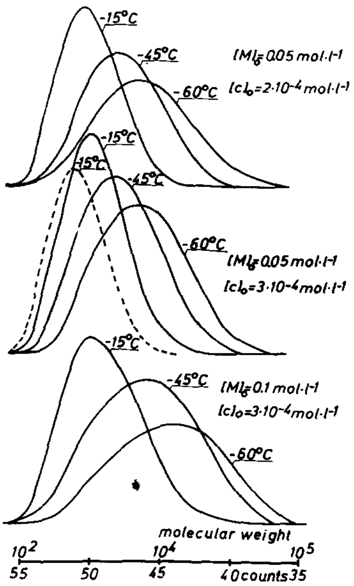

Fig.3: GPC curves for $[M]_0 = 0.05$ and 0.1 $mol \cdot l^{-1}$ and two different catalyst concentrations at three different polymerization temperatures. Dotted distribution results after addition of salt.

Table 1

$[M]_0$ (mol·l-1)	$[c]_0$ (mol·l-1)	[salt] (mol·l-1)	T (°C)	M_w	M_n	U
0.05	$2 \cdot 10^{-4}$	0	-15	2810	1250	1.25
		0	-45	7070	2910	1.43
		0	-60	17780	6550	1.71
0.05	$3 \cdot 10^{-4}$	0	-15	3220	1460	1.21
		$1 \cdot 10^{-5}$	-15	2080	1040	1.0
		0	-45	6760	2910	1.32
		0	-60	16800	6330	1.65
0.1	$3 \cdot 10^{-4}$	0	-15	4780	1870	1.56
		0	-45	13100	4580	1.86
		0	-60	25620	8400	2.05

The catalyst concentration is almost without influence on the molecular weight, but the latter increases noticeably with increasing monomer concentration. The distributions in particular become broader with increasing monomer concentration and decreasing temperature.

As already reported[1,2,8] bimodal molecular weight distributions result at -15 °C and higher monomer concentrations. Fig.4 shows the GPC curves for the relatively high monomer concentrations $[M]_0 = 0.5$ $mol \cdot l^{-1}$ and $[M]_0 = 1.0$ $mol \cdot l^{-1}$ at -15 °C and -60 °C. As we see, the trend towards widening distributions with increasing monomer concentration and decreasing temperature, as indicated in Table 1, results in trimodal distributions at -60 °C and high $[M]_0$. As salt is added to the polymerization system in the form of $(Bu)_4N^+CF_3SO_3^-$ the high molecular peak in the bimodal distributions and both higher molecular peaks in the trimodal distributions disappear whereas the low molecular peak remains unchanged.

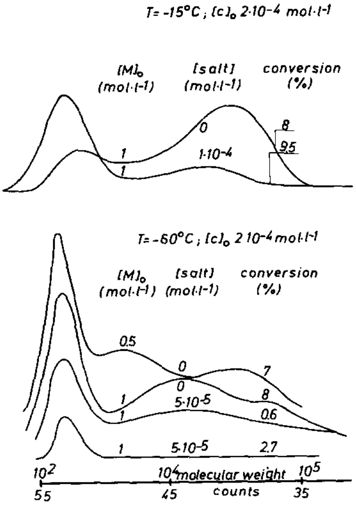

Fig.4: GPC-curves for $[M]_0 = 0.5$ resp. 1.0 $mol \cdot l^{-1}$ at -15 °C and -60 °C.

Fig.5 shows the Arrhenius plot of the rate constants $k = \frac{k'}{[C]_0}$ for $[M]_0 = 0.05$ $mol \cdot l^{-1}$ and 0.1 $mol \cdot l^{-1}$.

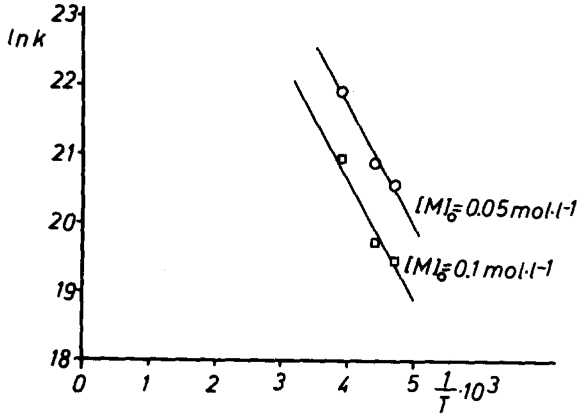

Fig.5: Arrhenius plot.

Discussion

The cationic polymerization of styrene in CH_2Cl_2 with CF_3SO_3H as catalyst and low monomer concentrations shows formally the same dependence on $[M]_0$ at -15°C, -45°C and -60°C. The dependence on $[C]_0$ is approximately but not exactly of a third order. At monomer concentrations $[M]_0 < 0.2$ mol l^{-1} unimodal molecular weight distributions are found over the entire investigated temperature range, which become broader, however, with increasing $[M]_0$ and decreasing temperature. This broadening may suggest that even unimodal distributions involve the action of several species. The influence of the changed dissoziation of the catalyst (1) becomes particularly evident upon the addition of salt. As we see from Table 1 and Fig.3, the molecular weight distribution becomes much narrower as $(Bu)_4N^+CF_3SO_3^-$ is added to the polymerization system. According to Fig.4 bimodal distributions are found by raising $[M]_0$ to > 0.2 mol·l^{-1}. Only the low molecular peak remains when salt is added. As far as its location is concerned this peak is identical with the corresponding peak after salt addition in Fig.3. The established behaviour may be a further indication that the formation of the low molecular peak is attributable to ion pairs. This is also probable because of the rate dependence on catalyst concentration ($k' = k[C]_0^2$) reported in a previous paper (1). A trimodal molecular weight distribution is obtained for the polymerization temperature of -60°C and $[M]_0 > 0.2$ mol·l^{-1}. This points to the fact that the polymerization results from at least 3 species. Two of them are free ions because they disappear upon the addition of salt. The low molecular peak is identical with the peaks mentioned above.

For the activation energy we find from Fig.5 a value of Ea = 3.5 kcal·mol^{-1}. This is a reasonable order of magnitude. Pepper$^{(7)}$ gives a value of Ea = 9 kcal·mol^{-1} for the system styrene/CH_2Cl_2/$HClO_4$. The higher rate constants found in our system styrene/CH_2Cl_2/CF_3SO_3H are indicative of a lower activation energy.

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