Olefin Polymerizations and Copolymerizations with Aluminum Alkyl-Cocatalyst Systems. IV. The Polymerization of Styrene

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SUMMARY

The mechanism of cationic styrene polymerization with the $AlEt_2Cl/RCl$ (R = alkyl or aryl) catalyst-cocatalyst system has been investigated. Polymerization initiation, i.e., cocatalyst efficiency, is apparently determined by the relative stability and/or concentration of the initiating carbonium ions provided by the cocatalyst RCl. Whereas n-butyl, isopropyl, and sec-butyl chlorides exhibit low cocatalyst efficiencies because of low ion concentrations, triphenyl methyl chloride is a poor cocatalyst because the stability of the derivative triphenyl methyl ion is much higher than that of the propagating styryl ion. Alkyl halides that give ions of intermediate stability are efficient cocatalysts. Isobutyl chloride and benzyl chloride seem to be exceptions and the reasons for this are discussed. A general simple scheme of the polymerization mechanism is proposed.

The $AlEt_2Cl$/t-butyl chloride and $AlEt_2Cl$/3-chloro-1-butene initiator systems, which give rise to flash polymerizations, are examined in some detail. With these initiators in polar solvents, polymerization rates (conversions) increase with decreasing temperatures. To explain this effect, a termination mechanism which involves the gegen-ion is proposed. The relatively high rate of termination in nonpolar solvents is attributed to the presence of growing contact ion pairs in these diluents.

INTRODUCTION

Although the literature concerning the cationic polymerization of styrene is quite voluminous [1], it appears that the AlR_2Cl/RX catalyst system has

not yet been used to study the details of the mechanism of the polymerization. These systems were found to be efficient, highly active initiators for the polymerization of cationically active monomers (e.g., styrene, isobutylene, etc.) in general [2-5]. The polymerization of isobutylene and the copolymerization of isobutylene-isoprene mixtures with AlR_2Cl and/or AlR_3 catalysts in conjunction of Brønsted acid and alkyl halide cocatalysts has been discussed in detail [2, 3]. The present paper deals with the mechanism of styrene polymerization initiated by the AlR_2Cl/RX system.

EXPERIMENTAL

The experimental technique, materials used, and their purity were the same as described previously in this series of publications [2, 3].

RESULTS AND DISCUSSION

Styrene Polymerizations with the AlEt$_2$Cl/RX Initiator System

Styrene can be efficiently polymerized with $AlEt_2Cl/RX$ (where R is H or an alkyl group, and X is halogen) initiator systems [2, 3]. As discussed previously in detail in connection with isobutylene [3], the extent of polymerization obtained with this initiator is determined by a balance between the stability and availability of carbonium ions generated by the following reaction:

$$AlEt_2Cl \ + \ RX \ \rightleftharpoons \ R^{\oplus} \ [AlEt_2ClX]^{\ominus}$$
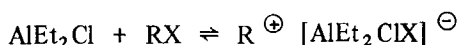
This general concept was found to be true for the polymerization initiation of styrene also. Experimentally small amounts of alkyl halides were introduced to quiescent styrene-$AlEt_2Cl$ mixtures stirred in methyl chloride diluent at $-50°C$. Polymerizations started immediately (flash polymerization). After 5 min the reaction was terminated by introducing cold methanol, and the polymer was recovered by evaporating the liquid components and drying in vacuo. Results are shown in Table 1. The first column in the table shows the alkyl halides (RX) used; the second column indicates the structure of the initiating carbonium ions, generated by the above equation. The carbonium ions are arranged by increasing ion stabilities. The other important columns in the table are columns 4 and 7 which give the catalyst-cocatalyst mole ratio ($[AlEt_2Cl]/[RCl]$) employed and

cocatalyst efficiency (g PSt/[RCl]), i.e., the amount of polystyrene obtained per mole of alkyl halide added, respectively.

Just a glance at the last column in Table 1 reveals an enormous spectrum in cocatalyst efficiencies. In particular, lowest cocatalyst efficiencies (0-25) were obtained with n-butyl, isopropyl, sec-butyl, allyl, and methallyl chlorides, whereas highest cocatalyst efficiencies ($> 10^6$) were produced by 3-chloro-1-butene, crotyl chloride, t-butyl chloride, 1-chloro ethylbenzene, and diphenyl chloromethane.

Some of the cocatalyst efficiencies listed in column 7 are minimum values and are indicated by the $>$ sign. In these experiments monomer conversions were in excess of 85% so that the catalyst efficiencies were probably limited by the availability of unconverted monomer ("catalyst starvation").

The catalytic efficiency of these various agents can be explained by the same hypothesis as that used in connection with isobutylene [3]. Polymerization initiation is determined by carbonium ion stability and/or carbonium ion availability. Ionization according to $RCl + AlEt_2Cl \rightleftharpoons R^{\oplus} [AlEt_2Cl_2]^{\ominus}$ will be facilitated by low bond dissociation energies of the alkyl halide and low ionization potentials of the alkyl group, and importantly, by solvation of the ions. Evidently, the forward reaction does not occur, or occurs only to an insignificant degree, with alkyl chlorides yielding primary or secondary carbonium ions (except isobutyl chloride, discussed later). If these very reactive ions could form, they would immediately initiate the polymerization of styrene, which propagates by the relatively more stable styryl ion

$$R-CH_2-\overset{\oplus}{C}H-C_6H_5$$
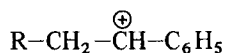
By augmenting the stability (concentration) of the initiating cations, initiation is facilitated, which explains why ions derived from 3-chloro-1-butene, crotyl chloride, etc., are excellent cocatalysts. In these cases the overall stability of the initiating ion and that of the propagating styryl ion are similar. However, if the stability of the initiating ion is increased further, e.g., to the trityl cation, initiation cannot occur because the stability of this ion far exceeds that of the propagating carbonium ion and there is no driving force for the initial electrophilic attack.

Two exceptions are noted. Isobutyl chloride probably initiates via the t-butyl carbonium ion which arises from the initial isobutyl carbonium ion by hydride shift. Since n-butyl, isopropyl, and sec-butyl chlorides do not initiate styrene polymerizations at $[AlEt_2Cl]/[RCl]$ ratios > 1, it may be safely assumed that no primary or secondary carbonium ions are generated

Table 1. Polymerization of Styrene with the $AlEt_2Cl/RX$ Initiator System[a]

Alkyl halide cocatalyst added	Structure of presumed initiating carbonium ion	Conc. of alkyl halide, moles	Catalyst ratio, $AlEt_2Cl/RCl$	Polystyrene yield		Cocatalyst efficiency, gPSt/[RCl]
				g	%	
n-Butyl-Cl	C–C–C–C$^\oplus$ or $^\oplus$C–C–C–C	9.5×10^{-4}	0.08	0.024	1.0	25
		3.7×10^{-5}	2.0	0	0	0
Isopropyl-Cl	C, C, C$^\oplus$	1.1×10^{-3}	0.07	0.015	0.65	13
		3.7×10^{-5}	2.0	0	0	0
sec-Butyl-Cl	C–C$^\oplus$, C, C	9.5×10^{-4}	0.08	0.024	1.0	25
		3.7×10^{-5}	2.0	0	0	0

Compound	Structure					
Allyl-Cl	$C^{\oplus}$—C=C	1.03×10^{-3}	0.073	0.018	0.79	17
		4.9×10^{-4}	0.15	0.165	7.3	340
		2.5×10^{-4}	0.30	0.099	4.4	400
		2.5×10^{-5}	3.0	0.072	3.1	2,860
Methallyl-Cl	$C^{\oplus}$, C—C=C	1.03×10^{-3}	0.073	0.006	0.26	6
		4.1×10^{-4}	0.18	0.022	0.95	52
		2.04×10^{-4}	0.37	0.018	0.82	93
		2.04×10^{-5}	3.7	0.046	2.00	2,300
3-Chloro-1-Butene	C—$C^{\oplus}$—C=C	1.66×10^{-6}	45	2.076	91.3	>1,250,000
		1.66×10^{-6}	45	2.108	93.1	>1,270,000
		9.3×10^{-7}	80	1.973	87.0	>2,120,000
		7.7×10^{-7}	96	1.957	86.2	>2,540,000
		7.7×10^{-7}	96	1.774	78.2	2,300,000
		6.5×10^{-7}	114	1.507	66.3	2,320,000
		3.3×10^{-7}	214	0.570	25.1	1,730,000
Crotyl-Cl	$C^{\oplus}$—C=C—C	2.5×10^{-5}	3.6	2.234	98.5	>10,900
		6.2×10^{-7}	123	1.945	85.8	>3,140,000
		3.2×10^{-7}	234	2.006	88.3	>6,200,000
		1.3×10^{-7}	725	0.228	10.0	2,220,000

Table 1. (Continued)

Alkyl halide cocatalyst added	Structure of presumed initiating carbonium ion	Conc. of alkyl halide, moles	Catalyst ratio, $AlEt_2Cl/RCl$	Polystyrene yield		Cocatalyst efficiency, gPSt/[RCl]
				g	%	
t-Butyl-Cl	$\begin{array}{c}C\\|\\C-C\oplus\\|\\C\end{array}$	7.4×10^{-7}	100	1.948	85.8	>2,600,000
		7.4×10^{-7}	100	1.935	85.3	>2,600,000
		5.8×10^{-7}	129	0.209	9.2	360,000
		2.8×10^{-7}	268	0.118	5.2	420,000
		1.0×10^{-7}	750	0.036	1.6	375,000
Isobutyl-Cl	$\begin{array}{c}C-C-C\oplus\\|\\C\end{array}$ or $\begin{array}{c}\oplus\\C-C-C\\|\\C\end{array}$	9.5×10^{-4}	0.08	2.153	95.0	>2,270
		3.2×10^{-4}	0.23	0.978	43.0	3,050
		1.6×10^{-4}	0.47	0.286	12.6	1,840
		3.7×10^{-5}	2.0	0.025	1.12	690
		1.8×10^{-5}	4.1	0.010	0.45	560
		8.0×10^{-7}	94.0	0	0	0
		8.0×10^{-7}	94.0	0	0	0

Benzyl-Cl	$C^{\oplus}$—C_6H_5	1.7×10^{-5}	4.4	0.213	9.4	12,500
1-Chloro-ethylbenzene	C—$C^{\oplus}$—C_6H_5	1.8×10^{-5}	4.1	2.27	100	>126,000
		5.5×10^{-7}	136	1.676	74.0	3,050,000
		2.7×10^{-7}	278	0.794	34.9	2,930,000
Diphenylchloro-methane	C_6H_5—$C^{\oplus}$—C_6H_5	1.1×10^{-5}	6.8	2.27	100	>208,000
		3.4×10^{-7}	220	1.410	62.3	4,150,000
		1.7×10^{-7}	440	0.631	27.8	3,700,000
Triphenylchloro-methane	$(C_6H_5)_3C^{\oplus}$	6.9×10^{-6}	11	0	0	0

aConditions: Each charge consisted of 2.5 ml (0.021 mole) of styrene, 0.095 ml (7×10^{-5} mole) of $AlEt_2Cl$ in 15 ml of methyl chloride; the mixture was stirred at −50°C and the dilute cocatalyst in methyl chloride solution was introduced gradually.
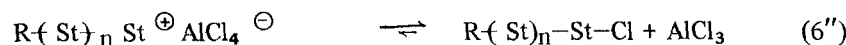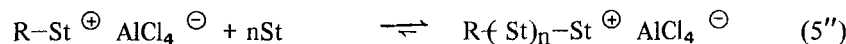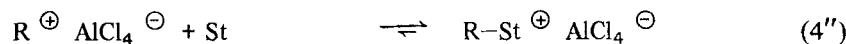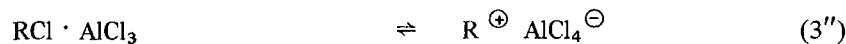
under these conditions. However, isobutyl chloride, which by chloride ion extraction would also yield a primary cation, does cocatalyze the polymerization of styrene. Evidently, in this case ionization is facilitated by the two electron-releasing methyl groups. Moreover, it is possible that concertedly with ionization (rate-determining step) hydride shift to the more stable tertiary ion occurs so that the t-butyl carbonium ion is the true initiating species:

$$C{-}C{-}C{-}Cl + AlEt_2Cl \longrightarrow C{-}C{-}\overset{\oplus}{C}\,AlEt_2Cl_2\overset{\ominus}{} \longrightarrow C{-}\overset{\oplus}{C}{-}C\ \ AlEt_2Cl_2\overset{\ominus}{}$$
$$\underset{\displaystyle C}{|} \qquad\qquad\qquad \underset{\displaystyle C}{|} \qquad\qquad\qquad \underset{\displaystyle C}{|}$$
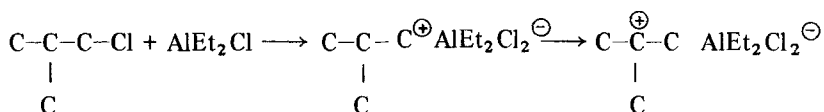
   The second exception is the behavior of benzyl chloride, whose cocatalyst efficiency is unusually low. This is explained by the self-alkylation of the benzyl ion to yield polybenzyl. Due to this side reaction, the effective concentration of benzyl cations available for initiation in the system must be strongly reduced. The polyalkylation of benzyl chloride to polybenzyl is an extremely rapid process and proceeds with great rapidity even at very low temperatures (below $-100°C$) [6].

   A quantitative examination of the effect of $[AlEt_2Cl]/[RCl]$ ratios on cocatalyst efficiencies is revealing. According to the data in Table 1 the catalyst-cocatalyst ratio strongly influences cocatalyst efficiencies. The first three halides in Table 1 give polymer only when the catalyst-cocatalyst ratio is $\ll 1$ but not when the ratio is > 1. Allyl and methallyl chlorides give rise to primary allylic carbonium ions whose stability is greater than that of the ions derived from the first three halides in Table 1; by increasing the catalyst-cocatalyst ratio from 0.007 to 3 or 4 with these allylic halides, the cocatalyst efficiency increases by about three orders of magnitude. Finally, the cocatalyst efficiency increases to $> 10^6$ with halides yielding branched allyl cations, the t-butyl cation, and cations stabilized by the phenyl group (except the trityl ion).

   According to the equilibrium proposed earlier ($RCl + AlEt_2Cl \rightleftharpoons R^{\oplus}AlEt_2Cl_2^{\ominus}$), [3] ionization and consequently the rate of initiation should increase by augmenting the concentration of either of the two reagents on the left. Evidently this simple concept does not explain the observations with n-butyl, isopropyl, and sec-butyl chlorides. To explain all the data, the original concept is expanded by proposing the following set of simplified processes (simplified by disregarding the effect of solvation and the fact that all the alumino-organic species might exist, in reality, as dimers):

$$RCl + AlEt_2Cl \rightleftharpoons RCl \cdot AlEt_2Cl \tag{1}$$

$$RCl \cdot AlEt_2Cl \rightleftharpoons REt + AlEtCl_2 \tag{2}$$

$$RCl \cdot AlEt_2Cl \rightleftharpoons R^{\oplus} AlEt_2Cl_2^{\ominus} \tag{3}$$

$$R^{\oplus} AlEt_2Cl_2^{\ominus} + St \rightleftharpoons R-St^{\oplus} AlEt_2Cl_2^{\ominus} \tag{4}$$

$$R-St^{\oplus} AlEt_2Cl_2^{\ominus} + nSt \rightleftharpoons R(St)_n St^{\oplus} AlEt_2Cl_2^{\ominus} \tag{5}$$

$$R(St)_n-St^{\oplus} AlEt_2Cl_2^{\ominus} \rightleftharpoons R(St)_n-St-Et + AlEtCl_2 \tag{6}$$

$$RCl + AlEtCl_2 \rightleftharpoons RCl \cdot AlEtCl_2 \tag{1'}$$

$$RCl \cdot AlEtCl_2 \rightleftharpoons REt + AlCl_3 \tag{2'}$$

$$RCl \cdot AlEtCl_2 \rightleftharpoons R^{\oplus} AlEtCl_3^{\ominus} \tag{3'}$$

$$R^{\oplus} AlEtCl_3^{\oplus} + St \rightleftharpoons R-St^{\oplus} AlEtCl_3^{\ominus} \tag{4'}$$

$$R-St^{\oplus} AlEtCl_3^{\ominus} + nSt \rightleftharpoons R(St)_n-St^{\oplus} AlEtCl_3^{\ominus} \tag{5'}$$

$$R(St)_n St^{\oplus} AlEtCl_3^{\ominus} \rightleftharpoons R(St)_n-St-Et + AlCl_3 \tag{6'}$$

$$RCl + AlCl_3 \rightleftharpoons RCl \cdot AlCl_3 \tag{1''}$$

$$RCl \cdot AlCl_3 \rightleftharpoons R^{\oplus} AlCl_4^{\ominus} \tag{3''}$$

$$R^{\oplus} AlCl_4^{\ominus} + St \rightleftharpoons R-St^{\oplus} AlCl_4^{\ominus} \tag{4''}$$

$$R-St^{\oplus} AlCl_4^{\ominus} + nSt \rightleftharpoons R(St)_n-St^{\oplus} AlCl_4^{\ominus} \tag{5''}$$

$$R(St)_n St^{\oplus} AlCl_4^{\ominus} \rightleftharpoons R(St)_n-St-Cl + AlCl_3 \tag{6''}$$

where (1), (1'), and (1'') are processes for the complexation of the alkyl halide with the various aluminum catalysts, respectively; (2) and (2'') are processes leading to the destruction of the initial alumino-organic compound with the simultaneous in situ formation of a new aluminum compound, respectively; (3), (3'), and (3'') show the ionization of the hypothetical molecular complexes obtained in the first three processes,

Scheme 1. Polymerization Mechanism of Styrene with the $AlEt_2Cl/RCl$ System

$$RCl + AlEt_2Cl \rightleftharpoons RCl \cdot AlEt_2Cl \rightleftharpoons R^{\oplus}\ AlEt_2Cl_2^{\ominus} \xrightarrow{St} R\text{-}St^{\oplus}\ AlEt_2Cl_2^{\ominus} \underset{\text{---}}{\overset{St}{\rightleftharpoons}}\text{-}RSt_n^{\oplus}\ AlEt_2Cl_2^{\ominus} \xrightarrow{\rightleftharpoons} RSt_nEt + AlEtCl_2$$

$$REt + AlEtCl_2 \rightleftharpoons RCl \cdot AlEtCl_2 \rightleftharpoons R^{\oplus}\ AlEtCl_3^{\ominus} \xrightarrow{St} RSt^{\oplus}\ AlEtCl_3^{\ominus} \underset{\text{---}}{\overset{St}{\rightleftharpoons}}\text{-}RStn^{\oplus}\ AlEtCl_3^{\ominus} \xrightarrow{\rightleftharpoons} RSt_nEt + AlCl_3$$

$$REt + AlCl_3 \rightleftharpoons RCl \cdot AlCl_3 \rightleftharpoons R^{\oplus}AlCl_4^{\ominus} \xrightarrow{St} RSt^{\oplus}\ AlCl_4^{\ominus} \underset{\text{---}}{\overset{St}{\rightleftharpoons}}\text{-}RStn^{\oplus}\ AlCl_4^{\ominus} \xrightarrow{\rightleftharpoons} RStnCl + AlCl_3$$
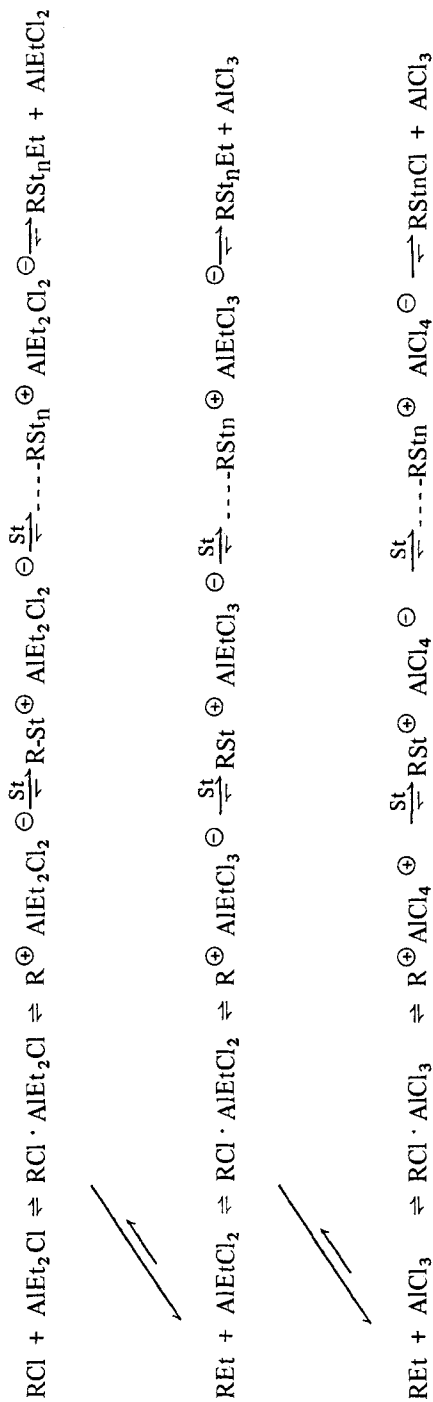
respectively; and the rest of the processes indicated by (4), (4'), (4''), (5), (5'), (5''), (6), (6'), and (6'') are the initiation, propagation, and termination of styrene polymerizations by the various catalytic species, respectively.

The combination of these events leads to the mechanism shown in Scheme 1. According to this mechanism the catalyst and cocatalyst first give a molecular complex $RCl \cdot AlEt_2 Cl$ (or $RCl \cdot Al_2 Et_4 Cl_2$) which can either ionize to $R^{\oplus} AlEt_2 Cl^{\ominus}$ (or $R^{\oplus} Al_2 Et_4 Cl_3^{\ominus}$) or decompose to yield $AlEtCl_2$. Only the ionized species can initiate polymerization. With n-butyl, isopropyl, or sec-butyl chlorides, the concentration of the ionized species is vanishingly small because of the low stability of the primary or secondary ions. Consequently, the competing reaction to $AlEtCl_2$, in conjunction with the excess RCl present, will provide the initiating ionic species $R^{\oplus} AlEtCl_3^{\ominus}$. Since $AlEtCl_2$ is more acidic than $AlEt_2Cl$ (i.e., the $AlEtCl_3^{\ominus}$ gegen-ion is more stable than the $AlEt_2 Cl_2^{\ominus}$), $R^{\oplus} AlEtCl_3^{\ominus}$ ionizes to a larger extent than $R^{\oplus} AlEt_2 Cl_2^{\ominus}$ and thus is able to initiate the polymerization. In other words, with n-butyl, isopropyl, and sec-butyl chlorides, the true catalyst is the $AlEtCl_2$ formed in situ. This explains why polymerization initiation occurs only when the $AlEt_2 Cl/RCl$ concentration is $\ll 1$ but not when the ratio is > 1. With allyl, methallyl, etc. chlorides, ions of intermediate and high stability are obtained and initiation occurs also when the $AlEt_2 Cl/RCl$ ratio is > 1. Evidently in these systems, due to higher ion stabilities, the $R^{\oplus} AlEt_2 Cl_2^{\ominus}$ species dissociates to a higher degree and is able to provide a sufficiently large ion concentration of ions of suitable intermediate stability for initiation. With trityl chloride the ion concentration is certainly high enough; however, initiation cannot occur because of the relatively high stability of the carbonium ion.

Independent experiments substantiate the proposed mechanism. In an experiment 6 aliquots of a t-butyl chloride solution were added consecutively to a continuously stirred styrene-$AlEt_2 Cl$-methyl cyclohexane charge. Figure 1 shows the increase in conversions as a function of t-butyl chloride cocatalyst introduction. (Conversions were determined with a series of 10-ml samples withdrawn during the run.) Several molecular weights have also been determined and they are also indicated in the figure with the corresponding samples. The inset in Fig. 1 is a plot of moles/liter styrene converted calculated from the final plateau of conversions on each aliquot cocatalyst introduction as a function of amount of cocatalyst added.

This experiment indicates that no polymerization occurs on $AlEt_2 Cl$ introduction but polymerization commences immediately on t-butyl chloride addition. The presence of some unidentified impurities in the
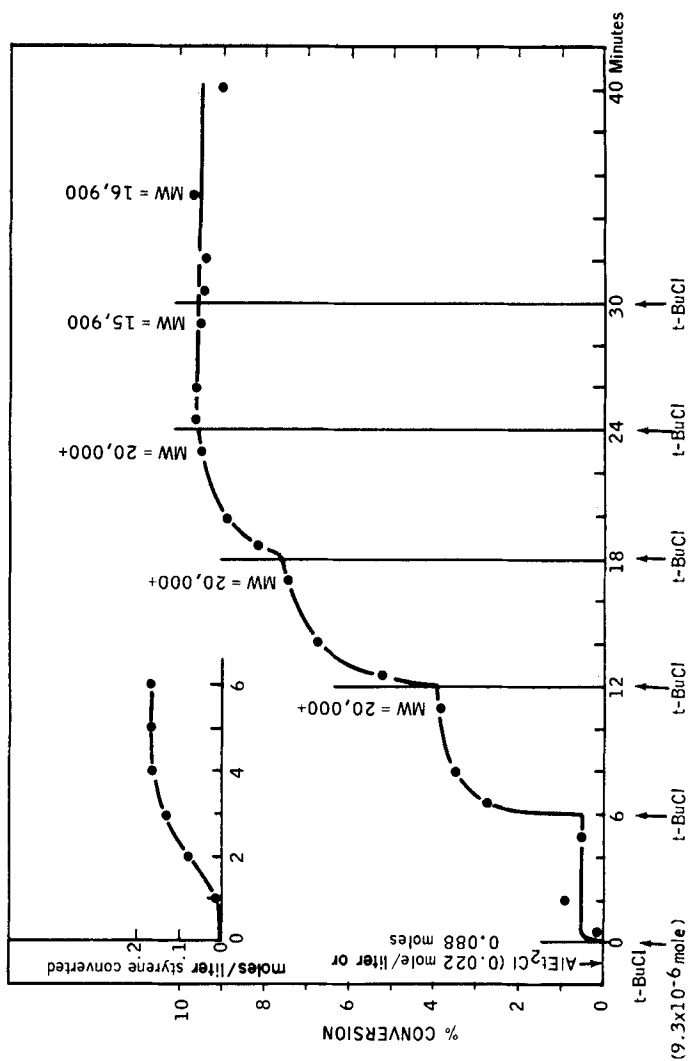
Fig. 1. The effect of consecutive additions of t-BuCl cocatalyst on the polymerization of styrene at 20°C.

system is indicated by the fact that the first t-butyl chloride addition yields only a very small amount of conversion ($\sim$ 0.5%). Evidently this impurity in the charge is scavenged by the growing polymer. After this impurity is removed, conversions become proportional to the amount of cocatalyst introduced, (i.e., second and third t-butyl chloride additions). Monomer consumption declines after the fourth cocatalyst addition, and polymerization stops for all practical purposes after the fifth cocatalyst introduction at rather low conversions. Significantly, at this point a total of (4 $\times$ 9.3 $\times$ 10^{-6} =)3.7 $\times$ 10^{-5} moles t-butyl chloride were added to the system, which initially contained 8.8 $\times$ 10^{-2} moles $AlEt_2Cl$; i.e., a large amount of excess $AlEt_2Cl$ did not initiate polymerization. These findings indicate that concurrently with initiation, a competing catalyst-destroying side reaction also occurs.

In another similar experiment, $AlEt_2Cl$ was added twice to the charge, first at the beginning of the run and then in an equal amount (8.8 $\times$ 10^{-2} mole) between the third and fourth consecutive t-butyl chloride additions. No polymerization occurred on the second $AlEt_2Cl$ introduction. These results indicate that no "free" cocatalyst is available in the system.

Kinetic Studies with the $AlEt_2Cl$/t-Butyl Chloride and $AlEt_2Cl$/3-Chloro-1-Butene Initiator Systems

After having established that the polymerization of styrene can be initiated by a variety of $AlEt_2Cl$/RX catalyst-cocatalyst combinations [2, 3], the details of this reaction were investigated with the efficient $AlEt_2Cl$/t-butyl chloride and $AlEt_2Cl$/3-chloro-1-butene initiator systems.

The polymerization of styrene with the $AlEt_2Cl$/t-BuCl or $AlEt_2Cl$/3-chloro-1-butene initiator system is a flash reaction. Upon cocatalyst introduction into the quiescent styrene-$AlEt_2Cl$ mixture, polymerization starts instantaneously and propagates very rapidly to a certain conversion and molecular weight level. The polymerization stops before complete monomer consumption. This is similar to the phenomenon found in the styrene-$AlCl_3$ system investigated by Jordan and Mathieson [7, 8]. Evidently the catalyst is somehow consumed before all the monomer is converted. The conversion level and molecular weights are affected by reaction variables, i.e., reagent concentration, polarity of the medium, and temperature. Some representative conversion versus time curves are shown in Fig. 2. As indicated by this figure, final conversions are reached very rapidly (within seconds in most cases) after initiation (i.e., cocatalyst addition) so that final conversion levels can be obtained readily by horizontal back-extrapolation to the ordinate. Figure 2 also shows two curves
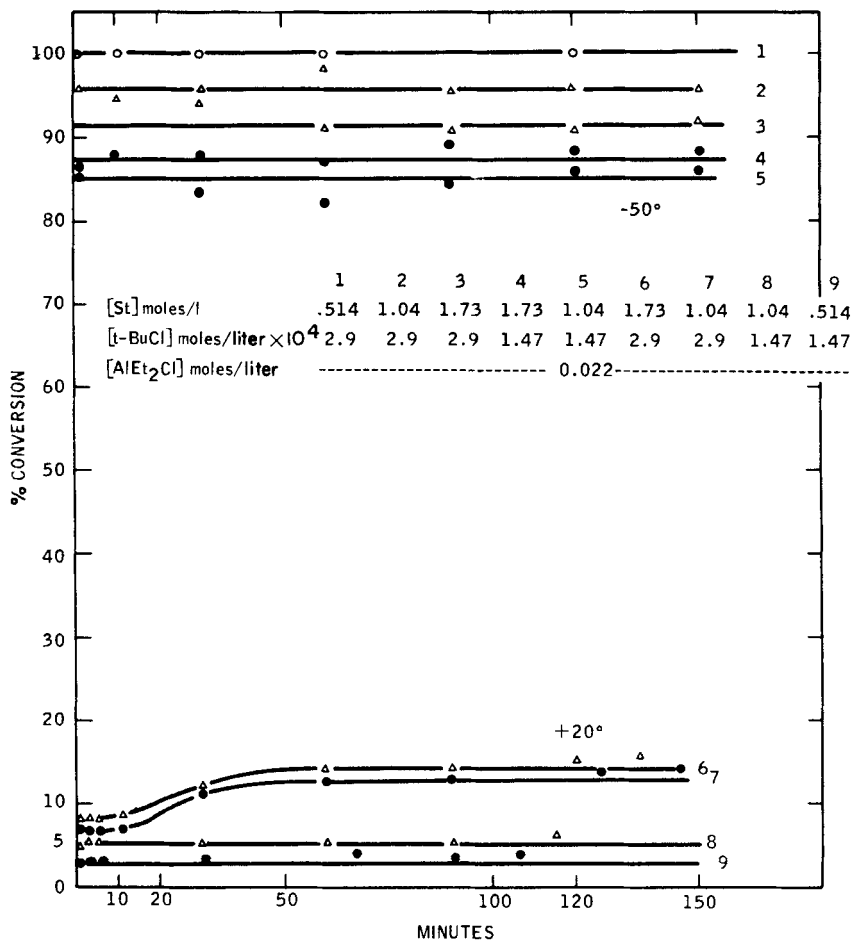
	1	2	3	4	5	6	7	8	9
[St] moles/l	.514	1.04	1.73	1.73	1.04	1.73	1.04	1.04	.514
[t-BuCl] moles/liter $\times 10^4$	2.9	2.9	2.9	1.47	1.47	2.9	2.9	1.47	1.47
[AlEt$_2$Cl] moles/liter					0.022				

-50°

+20°

% CONVERSION — MINUTES

Fig. 2. Conversion versus time plots in the styrene-AlEt$_2$Cl/t-BuCl system using chlorobenzene solvent at -50 and +20°C.

with a short induction period ($\sim$ 10 min). The explanation for this discrepancy remains obscure. Conversions were obtained in these two cases by back-extrapolation to the ordinate from the final horizontal plateau.

From the conversions obtained in curves such as those in Fig. 2 it was possible to compute the number of moles of styrene converted and to plot these numbers versus initial styrene concentrations. Figures 3 and 4 show these results. Significantly, we obtained a family of fairly well-defined
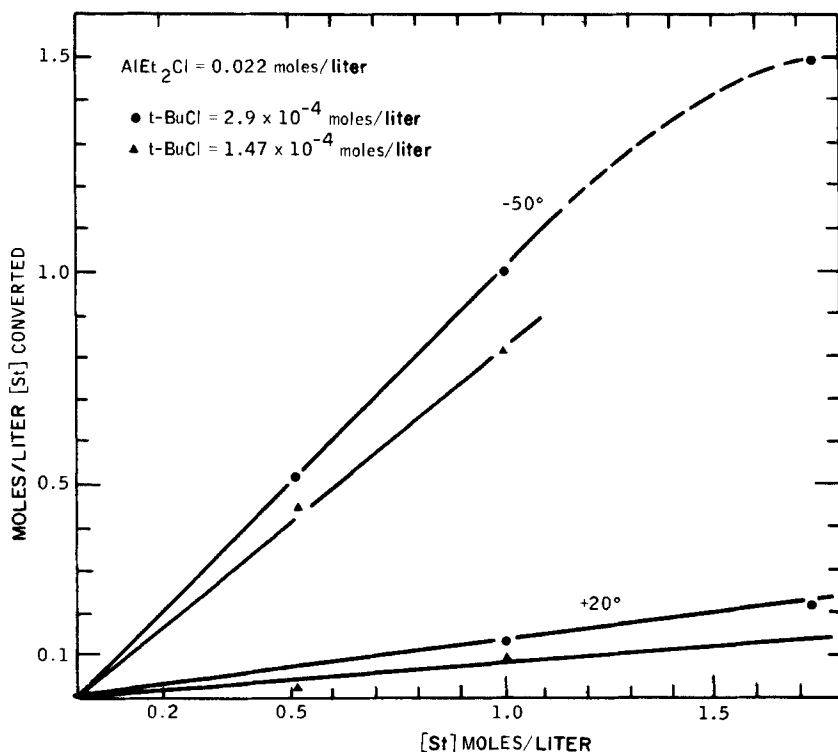
Fig. 3. The effect of initial styrene concentration on the amount of poly-sytrene formed in chlorobenzene at –50 and +20°C.

straight lines going through the origin. In particular, Fig. 3 represents data obtained with the $AlEt_2Cl$/t-butyl chloride initiator in chlorobenzene solvent at 20 and –50°C using two catalyst-cocatalyst ratios. Figure 4 shows our findings with the $AlEt_2Cl$/3-chloro-1-butene initiator system in chloroben-zene, methylcyclohexane, and n-heptane solvents at 20 and –50°C.

    Evidently there is not much difference in the overall rates of styrene polymerizations with t-butyl chloride or 3-chloro-1-butene cocatalysts under similar conditions (cf. Figs. 3 and 4). This is expected because of the similar reactivities of the tertiary and substituted allylic chlorines in these molecules.

    Similarly it is not unusual that the overall rates in nonpolar solvents, i.e., methylcyclohexane and n-heptane, are faster at higher temperatures (20°C) than at lower temperatures (–50°C). Also, it is expected that in
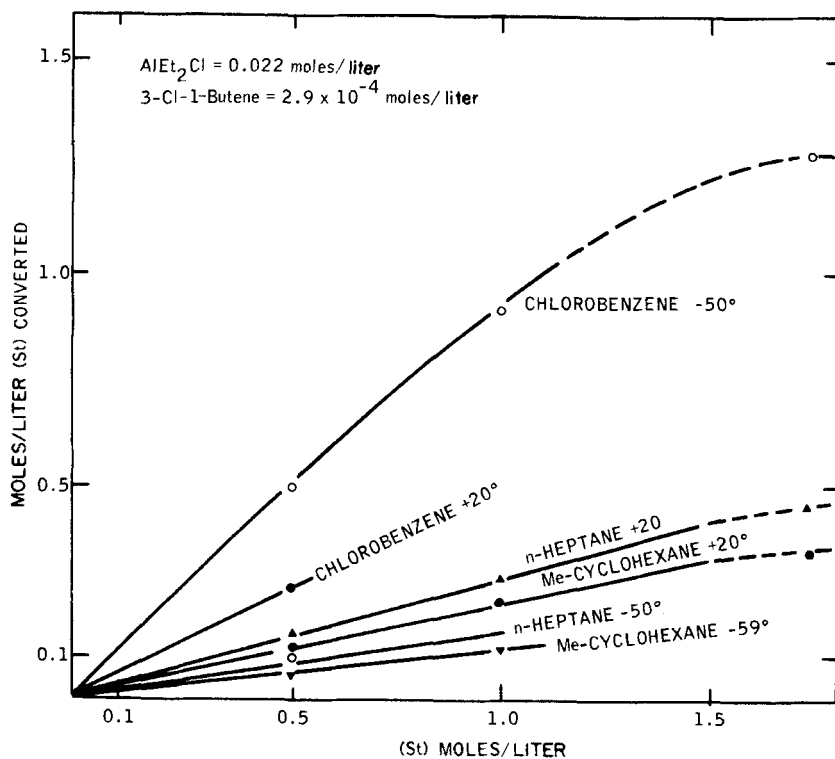
Fig. 4. The effect of initial styrene concentration on the amount of styrene converted using the AlEt$_2$Cl/3-chloro-1-butene catalyst in various solvents at –50 and +20°C.

polar solvent overall rates are faster than in nonpolar solvent (cf. results at 20°C in Fig. 4). However, it is surprising that in polar solvent overall polymerization rates are much higher at –50°C than at 20°C (Figs. 3 and 4). These effects could be explained by assuming that termination is faster in nonpolar medium than in a polar diluent. Slower termination in polar solvent might be due to charge separation by solvation. Solvation of the charged species separates the growing ion from its gegen-ion and consequently retards the alkylation of the growing carbonium ion by the gegen-ion. Since the polarity of the medium increases with decreasing temperatures, termination is increasingly retarded at lower temperatures and polymerization proceeds to high conversions.

At highest monomer concentrations (1.73 moles/liter styrene) the plot

Table 2. Polymerization of Styrene with the AlEt$_2$Cl/t-BuCl Initiator System.
[AlEt$_2$Cl] = 0.022 mole/liter.

[St], moles/liter	[t-BuCl], moles/liter	[St]/[t-BuCl], moles	[St]/[AlEt$_2$Cl], moles	[AlEt$_2$Cl]/[t-BuCl], moles	Conversion, %	Styrene converted, moles/liter	Approx. molecular weight
Chlorobenzene, 20°C							
1.73	2.9 × 10^{-4}	5,900	74	75	12.5	0.216	11,300
1.04	2.9 × 10^{-4}	3,600	46	75	13.5	0.14	10,300
0.514	2.9 × 10^{-4}	1,750	23	75	—	—	9,000
1.73	1.47 × 10^{-4}	11,800	74	150	—	—	9,500
1.04	1.47 × 10^{-4}	7,100	46	150	5.0	0.09	8,700
0.514	1.47 × 10^{-4}	3,500	23	150	2.8	0.015	—
Chlorobenzene, -50°C							
1.73	2.9 × 10^{-4}	5,900	74	75	85.5	1.48	13,500
1.04	2.9 × 10^{-4}	3,600	46	75	96.1	1.00	12,000
0.514	2.9 × 10^{-4}	1,750	23	75	100	0.514	11,000
1.73	1.47 × 10^{-4}	11,800	74	150	—	—	>17,000
1.04	1.47 × 10^{-4}	7,100	46	150	87.0	0.905	>18,000
0.514	1.47 × 10^{-4}	3,500	23	150	91.5	0.47	14,000
Methyl cyclohexane, 20°C							
1.73	2.9 × 10^{-4}	5,900	74	75	24.0	0.41	18,000
1.04	2.9 × 10^{-4}	3,600	46	75	33.5	0.35	15,000
0.514	2.9 × 10^{-4}	1,750	23	75	27.5	0.14	9,500

Table 3. Polymerization of Styrene with the $AlEt_2Cl$/3-Chloro-1-Butene Initiator System. $[AlEt_2Cl] = 0.022$ mole/liter.

[St], moles/liter	[St]/[3ClBu], moles	[St]/[AlEt₂Cl], moles	[AlEt₂Cl]/[3ClBu], moles	Conversion, %	Styrene converted, moles/liter	Approx. molecular weight
Chlorobenzene, 20°C						
1.73	5,900	74	75	—	—	8,000
1.04	3,600	46	75	—	—	7,500
0.514	1,750	23	75	51	0.26	5,000
Methyl cyclohexane, 20°C						
1.73	5,900	74	75	20	0.346	9,500
1.04	3,600	46	75	22	0.229	9,000
0.514	1,750	23	75	24	0.123	6,000
n-Heptane, 20°C						
1.73	5,900	74	75	26	0.450	9,500
1.04	3,600	46	75	27	0.280	8,000
0.514	1,750	23	75	30	0.154	8,000

Chlorobenzene, −50°C						
1.73	5,900	74	75	73	1.27	16,000
1.04	3,600	46	75	88	0.915	16,500
0.514	1,750	23	75	97	0.498	12,500
Methyl cyclohexane, −50°C						
1.73	5,900	74	75	−	−	10,000
1.04	3,600	46	75	12	0.125	6,500
0.514	1,750	23	75	10	0.051	6,000
n-Heptane, −50°C						
1.73	5,900	74	75	−	−	12,500
1.04	3,600	46	75	12	0.12	9,000
0.514	1,750	23	75	20	0.103	7,000

in Figs. 3 and 4 becomes nonlinear. This is explained by premature termina-
tion due to diffusion control at high conversions, i.e., "starvation" of the
propagating site. At low and medium monomer concentrations a straight
relationship describes the system satisfactorily. Whether the system is
homogeneous or heterogeneous has very little, if any, effect on the overall
rates. Thus, the amount of polymer produced in the homogeneous systems
(i.e., in chlorobenzene and methyl cyclohexane) is about the same as that
produced in a heterogeneous system (i.e., n-heptane) under similar experi-
mental conditions. This suggests that propagation is relatively unimpeded
in the swollen phase.

Concurrently with the conversions the number average molecular weights
of select samples were determined (Tables 2 and 3). Usually three molecu-
lar weight determinations were made per run: the first one on a sample
withdrawn as soon as feasible after initiation (usually 0.5 or 1 min after
cocatalyst addition), the second one after about 30 min, and the third one
120 or 150 min after the reaction start.

The VPO method for number average molecular weight determination is
reliable up to about 20,000. However, even below 20,000 molecular
weights the data are only accurate enough to indicate trends. (In these
experiments the runs were terminated by precipitation into methanol and
filtration; consequently, the methanol-soluble, low-molecular-weight poly-
mer fraction was removed from the samples).

In spite of this restriction, it is significant that the molecular weights
remained within what is considered to be experimental scatter during the
course of a particular run and that the final molecular weights were at-
tained already in the first sample, i.e., immediately after cocatalyst addition.

These molecular weight data are in line with the flash reaction model
discussed above. Evidently the polymerization is very rapid and low-
molecular-weight products are obtained.

Under comparable conditions, molecular weights obtained with t-butyl
chloride or with 3-chloro-1-butene cocatalysts seem to be of the same
order of magnitude. This was anticipated; according to our model these
cocatalysts of similar reactivity should give molecular weights of the same
order. Similarly, it was not surprising that molecular weights increase
somewhat with increasing monomer concentrations and that the nature of
the medium (homogeneous versus heterogeneous) had little, if any, effect
on the molecular weights.

Molecular weights appeared to increase somewhat with decreasing tem-
peratures, and this effect is most pronounced in chlorobenzene. This is
the anticipated behavior of molecular weights in a typical cationic

Table 4. The Effect of Temperature and Solvent on the Molecular Weight of Polystyrene Produced with the AlEt$_2$Cl/t-BuCl Initiator System[a]

	n-Heptane			Chlorobenzene			Ethyl chloride		
Temp., °C Range[b]	ΔT	Conv., %	Molecular weight	Temp., °C Range[b]	ΔT	Conv., %	Molecular weight	Temp., °C Range[b]	ΔT
+11 to +25	14	100	5,320	+11 to +15	4	79	3,220	+11 to +14	3
-20 to -17	3	35	8,960	-20 to -10	6	84	6,150	-20 to -8	12
-50 to -47	3	32.5	9,000	-50 to -36	14	93.5	7,350	-50 to -36	14
-78 to -77	1	4.5	9,530	-78 to -62	14	92	14,300	-78 to -60	18

(Ethyl chloride continued) Conv., %: 35, 89.5, 95.2, 96.4; Molecular weight: 4,910, 8,650, 8,980, 22,130

[a]Charge: Styrene: (2.5 ml or 2.26 g or 0.211 mole) or 5.62 moles/liter; AlEt$_2$Cl: (0.035 ml or 0.033 g or 2.7 X 10^{-4} moles) or 7.2 X 10^{-4} moles/liter. Solvent: 35 ml; 0.03 ml of undiluted t-BuCl added to initiate reaction. Reaction time ~ 5 min.

[b]The first temperature is the initial temperature, the second is the highest temperature reached during experiment.

polymerization system. There was not much effect of solvent polarity on molecular weight at 20°C. There might be some measure of a molecular weight-increasing effect due to solvent polarity at low temperatures (cf. Table 3).

Subsequently, a series of comparative experiments were conducted to elucidate the effect of temperature on the molecular weight of polystyrene in various solvents (Table 4). In these runs the charge was styrene (5.62 moles/liter) and $AlEt_2Cl$ (7.2×10^{-3} moles/liter) in 35 ml of solvent (n-heptane, chlorobenzene, or ethyl chloride) at 11, -20, -50, and -78°C. Polymerizations were started by introducing 1 drop (0.03 ml) of pure t-butyl chloride. Under these conditions reactions started immediately, as indicated by the appearance of yellow color in the homogeneous runs (chlorobenzene and ethyl chloride) or haziness in n-heptane, a solvent in which polystyrene is insoluble. In some cases the reactions were quite vigorous and the temperature rose appreciably during the run. Polymerization times were about 5 min after cocatalyst additions at which time the reactions were terminated by the introduction of prechilled methanol. Table 4 shows the conversion and molecular weight data obtained at various temperature ranges in three solvents. The first column in the table shows the range between the inital temperature and the maximum temperature level reached during the run. Since this range is rather broad, in several experiments these polymers formed over a spectrum of temperatures and their distribution is probably quite broad. Also, conversions were high in these runs, which might also influence molecular weights. Consequently, these molecular weights are only useful as approximate indicators of trends. By and large they suggest that the temperature has only a moderate effect on the molecular weights of polystyrene produced under the conditions employed. Similarly, solvent polarity does not seem to affect molecular weights in the 10 to -50°C range. There might be some molecular weight-increasing effect due to solvent polarity at -78°C (cf. values obtained in n-heptane versus those in chlorobenzene and ethyl chloride).

Although these experiments were conducted primarily to study the effect of reaction variables on molecular weights, the data are also of interest from the point of view of rates. In all the experiments shown in Table 4, 0.03 ml of t-butyl chloride was added to identical styrene-$AlEt_2Cl$ charges in various solvents and at various temperatures. Thus, the conversions and temperature effects (ΔT) recorded (in columns 2 and 3, 6 and 7, and 10 and 11 of Table 4) can be regarded as measures for overall rates. In the nonpolar solvent, n-heptane, at 11°C cocatalyst addition results in complete conversion and consequently a large amount of heat evolution ($\Delta T = 14°C$).

As the temperature is gradually lowered to –20°C, etc., the overall rates decrease, less polymer is formed, and less heat is liberated (ΔT = 1-3°C). Conversely, in the polar solvents, chlorobenzene and ethyl chloride, cocatalyst addition at 11°C yields a limited amount of conversion and relatively low amounts of heat (ΔT = 3-4°C). However, as the temperature is increasingly lowered, ultimate conversions and the amount of heat liberated increase considerably. These findings also substantiate our proposed mechanism discussed above.

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