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Olefin Polymerizations and Copolymerizations with Aluminum Alkyl-Cocatalyst Systems. V. The Molecular Weight and Molecular Weight Distribution of Polystyrene

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SUMMARY

The polymerization of styrene with the cationic initiator system AlR_2Cl/RCl was investigated further. Earlier conclusions [1] were corroborated and expanded by an analysis of the number and weight average molecular weights. Alkyl halides with low (high) R–Cl bond dissociation energies are efficient (poor) coinitiators for the polymerization of styrene. In the presence of efficient RCl coinitiators, the molecular weights strongly decrease and the molecular weight distributions strongly increase with increasing conversions (Fig. 1). With poor coinitiators, only low conversions are obtained even in the presence of large amounts of $AlEt_2Cl$. The data are discussed in terms of a previously proposed mechanism [1].

INTRODUCTION

Aspects of our research concerning the polymerization-initiation of styrene with the cationic initiator system $AlEt_2Cl$/RCl have been published [1]. In that work styrene was polymerized by the introduction of various alkyl halides to a quiescent monomer-$AlEt_2Cl$-solvent mixture in the temperature range of +20 to -78°C, and the requirements for successful polymerization were elucidated. The present paper discusses parameters which control conversion, molecular weights ($\bar{M}_n$ and $\bar{M}_w$), and molecular weight distribution (MWD) of polystyrenes produced by the above-mentioned catalyst system.

EXPERIMENTAL AND RESULTS

The preparation of the particular polymers studied in this paper has already been described in detail [1]. In fact, Table 1, which summarizes our results, contains some published data (Table 1 in Ref. [1]) and, therefore, should be viewed as an addendum to the earlier compilation. Figure 1 is a representation of the data in Table 1 by plotting conversion, $\bar{M}_n$, $\bar{M}_w$, and MWD against the (logarithm of) number of moles of various alkyl halide (RCl) coinitiators used in conjunction with 7.0×10^{-5} mole (or 4.12×10^{-3} mole/liter of $AlEt_2Cl$. The molecular weights were determined by gel permeation chromatography with a Waters Assoc. instrument. The data show a considerable amount of scatter, which is understandable in view of the large number of experiments performed with about a dozen different alkyl halides. The merit of this pictorial representation is that it shows unmistakable and clear trends, which are discussed in this paper.

The Effect of RCl Concentration on Conversion

The bottom part of Fig. 1 shows the effect of alkyl halide concentration on styrene conversions attained after 5 min of polymerization at -50°C. The conversion data can be grouped into three distinct classes. The first group of conversions are the very low values (< 10%) obtained with the largest amounts of alkyl halides (10^{-5} -10^{-3} mole RCl) employed. The alkyl halides in this group are n-butyl chloride, isopropyl chloride, sec-butyl chloride, allyl chloride, and methallyl chloride. The straight, almost horizontal line drawn through these groups of points indicates that in this RCl concentration range conversions are practically unaffected and remain low even in the presence of relatively large amounts of alkyl halides. The alkyl halides in this group have the largest R—Cl bond dissociation energies and consequently should have considerable difficulty in producing the initiating carbonium ion [1, 2]. Thus, in these systems the carbonium ion concentration is low and only a small amount of polymer can form.

The second group of conversions were obtained with 3-chloro-1-butene, crotyl chloride, t-butyl chloride, 1-chloro-ethylbenzene, and diphenyl chloromethane, i.e., alkyl halides which readily produce quite stable carbonium ions (relatively low R–Cl bond strength) under mild conditions. Evidently, very small quantities of these alkyl halides are able to produce a sufficient concentration of carbonium ions for efficient initiation and ~10^{-6} mole RCl suffices to polymerize the charges completely. The ascending part of the conversion/RCl curve in the range from ~10^{-7} to ~10^{-6} mole RCl might also be due to a "cleaning-up" period, a period during which a small number of growing chains are consumed by adventitious impurities in the charge.

The third group of conversions consists of only two alkyl halides: isobutyl chloride and benzyl chloride. The peculiar position of these two compounds has already been discussed in our earlier report [1]. The point was made that isobutyl chloride probably initiates by the t-butyl cation which arises from the initial primary isobutyl cation via hydride shift ($(CH_3)_2CHCH_2\oplus \longrightarrow (CH_3)_3C^{\oplus}$). This mechanism is applicable to this discussion as well: Evidently, the production of the primary isobutyl ion is slow, and larger than stoichiometric amounts of $AlEt_2Cl$ are necessary to generate a sufficient amount of the more stable t-butyl ion, the true initiating species (discussed later). The isobutyl chloride data could also have been caused by ~0.1% of -butyl chloride in isobutyl chloride. Since gas chromatography showed a maximum of only 0.4% t-butyl chloride impurities in isobutyl chloride, this alkyl halide can be regarded as a true coinitiator. Benzyl chloride, the second exception, produces only a small amount of initiating benzyl ions, probably because most of the benzyl cations are prevented from initiation by self-alkylation and polybenzyl formation [1], a process which occurs with the greatest of ease even at much lower temperatures than -50°C [3].

The mechanism proposed in our earlier paper [1] explains these observations. The gist of this mechanism (disregarding chain transfer steps) can be summarized by Eqs. (1), (2), and (3).

In the first set of equations the RCl cocatalyst and $AlEt_2Cl$ catalyst interact to produce the carbonium ion $R^{\oplus}$ and the corresponding gegen-ion $AlEt_2Cl_2^{\ominus}$. At this point $R^{\oplus}$ can either initiate the polymerization of styrene (St) or can extract the ethyl group of the gegen-ion to produce a saturated hydrocarbon, REt. In the absence of styrene monomer only the latter reaction will take place. This has been demonstrated by independent experiments to be discussed elsewhere. The polymerization of styrene may terminate at any degree of polymerization (at any

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

Alkyl halide coinitiator added	Conc. of alkyl halide, moles	Initiator ratio, $AlEt_2Cl/RCl$	Yield, g	Conv., %	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1. n-Butyl-Cl	9.5×10^{-4}	0.08	0.024	1.0	567.9	311.0	1.8
	3.7×10^{-5}	2.0	0	0	–	–	–
2. Isopropyl-Cl	1.1×10^{-3}	0.07	0.015	0.65	593.3	265.0	2.0
	3.7×10^{-5}	2.0	0	0	–	–	–
3. Sec-butyl-Cl	9.5×10^{-4}	0.08	0.024	1.0	572.3	282.5	2.0
	3.7×10^{-5}	2.0	0	0	–	–	–
4. Allyl-Cl	1.03×10^{-3}	0.073	0.018	0.79	–	–	–
	4.9×10^{-4}	0.15	0.165	7.3	570.8	282.1	2.0
	2.5×10^{-4}	0.30	0.099	4.4	551.0	307.8	1.8
	2.5×10^{-5}	3.0	0.072	3.1	–	–	–
5. Methallyl-Cl	1.03×10^{-3}	0.073	0.006	0.26	461.7	175.1	2.6
	4.1×10^{-4}	0.18	0.022	0.95	335.2	149.1	2.2
	2.04×10^{-4}	0.37	0.018	0.82	412.0	197.0	2.1
	2.04×10^{-5}	3.7	0.046	2.00	454.1	218.3	2.1
6. 3-Chloro-1-butene	1.66×10^{-6}	45	2.076	91.3	386.0	53.7	7.2
	1.66×10^{-6}	45	2.108	93.1	373.6	57.9	6.4
	9.3×10^{-7}	80	1.973	87.0	–	–	–
	7.7×10^{-7}	96	1.957	86.2	520.3	159.0	3.3
	7.7×10^{-7}	96	1.774	78.2	540.1	186.0	2.9
	6.5×10^{-7}	114	1.507	66.3	479.4	152.3	3.1
	3.3×10^{-7}	214	0.570	25.1	604.0	244.5	2.5

7. Crotyl-Cl	2.5×10^{-5}	3.6	2.234	98.5	360.1	45.5	7.9
	6.2×10^{-7}	123	1.945	85.8	502.8	95.7	5.3
	3.2×10^{-7}	234	2.006	88.3	482.9	136.5	3.5
	1.3×10^{-7}	725	0.228	10.0	576.4	287.2	2.0
8. t-Butyl-Cl	7.4×10^{-7}	100	1.948	85.8	566.0	169.0	3.3
	7.4×10^{-7}	100	1.935	85.3	551.2	163.0	3.4
	5.8×10^{-7}	129	0.209	9.2	549.8	270.2	2.0
	2.8×10^{-7}	268	0.118	5.2	–	–	–
	1.0×10^{-7}	750	0.036	1.6	576.1	266.1	2.2
9. Isobutyl-Cl	9.5×10^{-4}	0.08	2.153	95.0	501.4	96.0	5.2
	3.2×10^{-4}	0.23	0.978	43.0	604.7	314.0	1.9
	1.6×10^{-4}	0.47	0.286	12.6	602.2	242.8	2.5
	3.7×10^{-5}	2.0	0.025	1.12	–	–	–
	1.8×10^{-5}	4.1	0.010	0.45	568.1	336.2	1.69
	8.0×10^{-7}	94.0	0	0	–	–	–
	8.0×10^{-7}	94.0	0	0	–	–	–
10. Benzyl-Cl	1.7×10^{-5}	4.4	0.213	9.4	586.9	310.5	1.89

Table 1. (continued)

Alkyl halide coinitiator added	Conc. of alkyl halide, moles	Initiator ratio, $AlEt_2Cl/RCl$	Yield, g	Conv., %	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
11. 1-Chloro-ethylbenzene	1.8×10^{-5}	4.1	2.27	100	–	–	–
	5.5×10^{-7}	136	1.676	74.0	516	190.1	2.7
	2.7×10^{-7}	278	0.794	34.9	626.3	288.5	2.2
12. Diphenylchloro-methane	1.1×10^{-5}	6.8	2.27	100	368.0	52.6	7.0
	3.4×10^{-7}	220	1.410	62.3	599.3	229.1	2.6
	1.7×10^{-7}	440	0.631	27.8	531.2	230.3	2.3
13. Triphenylchloro-methane	6.9×10^{-6}	11	0	0			

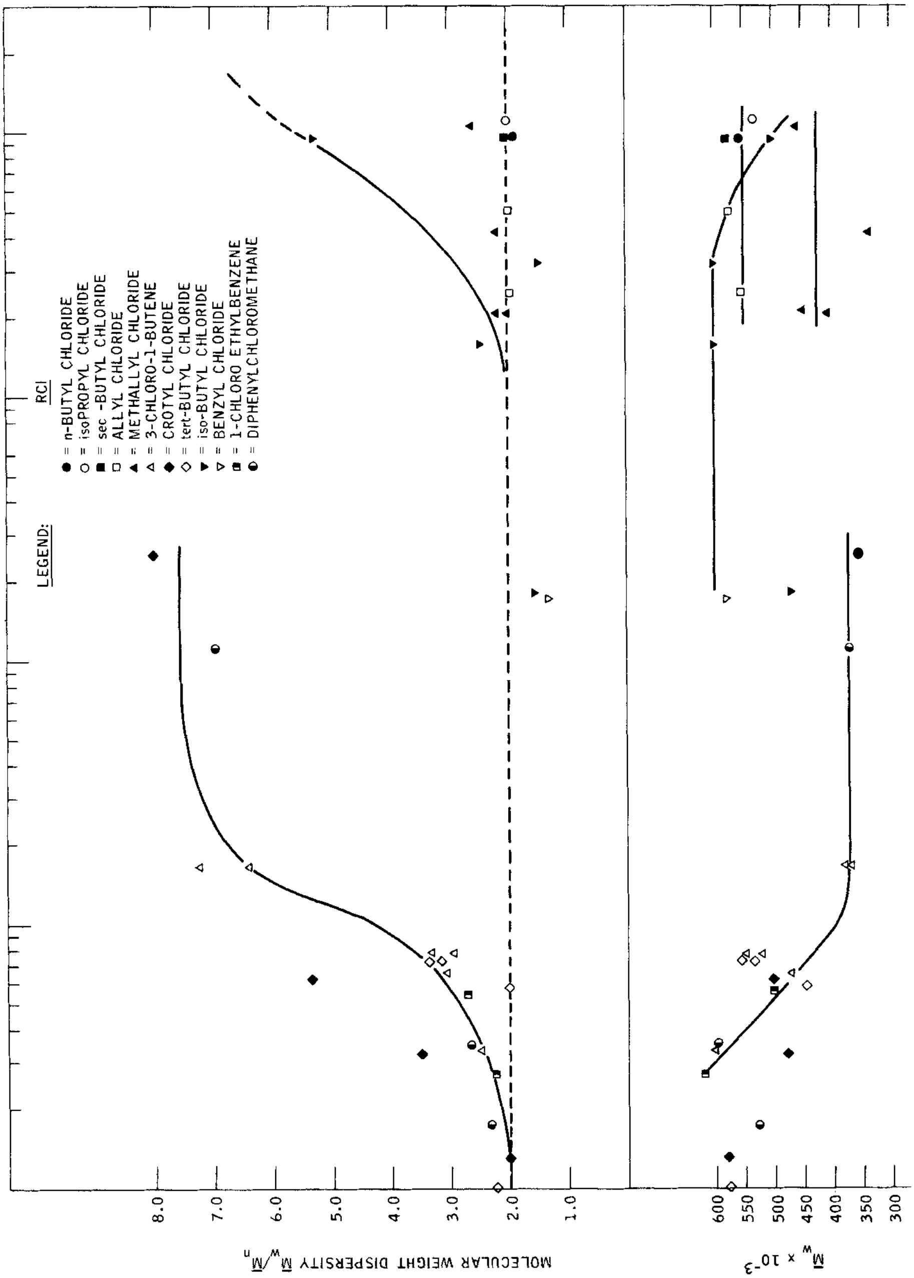
[a] Conditions: Each charge consisted of 2.5 ml (0.021 mole or 0.833 mole/liter) of styrene, 0.095 ml (7×10^{-5} mole or 4.12×10^{-3} mole/liter) of $AlEt_2Cl$ in 15 ml of methyl chloride; the mixture was stirred at -50°C and the dilute cocatalyst in methyl chloride solution was introduced gradually. After 5 min the polymerization was terminated with cold methanol and the polymer recovered by evaporating the volatile components and drying in vacuo at 50°C.

$$\begin{tikzcd}
\mathrm{RCl} + \mathrm{AlEt_2Cl} \arrow[r, shift left=1] & \mathrm{R^{\oplus}AlEt_2Cl_2^{\ominus}} \arrow[l, shift left=1] \arrow[rr, shift left=1, "\mathrm{nSt}"] \arrow[dr, "\mathrm{-\,REt}"'] & & \mathrm{RSt_n^{\oplus}AlEt_2Cl_2^{\ominus}} \arrow[ll, shift left=1] \arrow[dl, "\substack{\mathrm{-\,RSt_nEt} \\ \text{(polymer)}}"] & & \\
& & \mathrm{AlEtCl_2} \arrow[dll, dashed] & & & (1) \\
\mathrm{RCl} + \mathrm{AlEtCl_2} \arrow[r, shift left=1] & \mathrm{R^{\oplus}AlEtCl_3^{\ominus}} \arrow[l, shift left=1] \arrow[rr, shift left=1, "\mathrm{nSt}"] \arrow[dr, "\mathrm{-\,REt}"'] & & \mathrm{RSt_n^{\oplus}AlEtCl_3^{\ominus}} \arrow[ll, shift left=1] \arrow[dl, "\substack{\mathrm{-\,RSt_nEt} \\ \text{(polymer)}}"] & & \\
& & \mathrm{AlCl_3} \arrow[dll, dashed] & & & (2) \\
\mathrm{RCl} + \mathrm{AlCl_3} \arrow[r, shift left=1] & \mathrm{R^{\oplus}AlCl_4^{\ominus}} \arrow[l, shift left=1] \arrow[rr, shift left=1, "\mathrm{nSt}"] & & \mathrm{RSt_n^{\oplus}\,AlCl_4^{\ominus}} \arrow[ll, shift left=1] \arrow[r, shift left=1] & \mathrm{RSt_nCl} + \mathrm{AlCl_3} \arrow[l, shift left=1] & (?)\ (3)
\end{tikzcd}$$

value of n in $\mathrm{RSt_n^{\oplus}}$) by an analogous reaction giving rise to $\mathrm{RSt_nEt}$. In either case, along with the ethylated hydrocarbon, $\mathrm{AlEtCl_2}$ is also formed. This Lewis acid is a very efficient cationic initiator in its own right and, particularly in the presence of RCl, can readily initiate the polymerization of further styrene molecules. The process may then continue along the lines indicated by the second (and eventually along the third) set of equations in the overall mechanism.

The alkyl halides with relatively low R–Cl bond dissociation energies (e.g., tertiary halides, substituted allylic halides, benzylic halides, etc.) most likely initiate styrene polymerization according to the first set of equations. In conjunction with these halides, the relatively weakly acidic $\mathrm{AlEt_2Cl}$ is still a sufficiently strong chlorine-acceptor to break the R–Cl bond. With n-butyl chloride, allyl chloride, etc. (i.e., primary, secondary, and unsubstituted allylic halides), $\mathrm{AlEt_2Cl}$ is not acidic enough to accept the halogen and to dissociate the R–Cl bond. Therefore, with the latter alkyl halides the more acidic $\mathrm{AlEtCl_2}$ (or $\mathrm{AlCl_3}$) has to be produced in situ to produce carbonium ions. However, even with strong Lewis acid the ion concentrations produced from these alkyl halides remain low, and only low styrene conversions are obtained.

Isobutyl chloride is an interesting exception. According to our hypothesis the primary ions do not form, or are formed with great difficulty, in the presence of $\mathrm{AlEt_2Cl}$. Thus, isobutyl chloride is expected to be, at best, a quite inactive cocatalyst in conjunction with $\mathrm{AlEt_2Cl}$. However, according to the data, isobutyl chloride is quite an efficient coinitiator in the presence of larger than molar amounts of $\mathrm{AlEt_2Cl}$. The explanation for this is presumably that under these conditions $\mathrm{AlEtCl_2}$ (or $\mathrm{AlCl_3}$), which


LEGEND:
RCl
● = n-BUTYL CHLORIDE
○ = isoPROPYL CHLORIDE
■ = sec-BUTYL CHLORIDE
□ = ALLYL CHLORIDE
▲ = METHALLYL CHLORIDE
△ = 3-CHLORO-1-BUTENE
◆ = CROTYL CHLORIDE
◇ = tert-BUTYL CHLORIDE
▼ = iso-BUTYL CHLORIDE
▽ = BENZYL CHLORIDE
⊟ = 1-CHLORO ETHYLBENZENE
⊖ = DIPHENYLCHLOROMETHANE
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
MOLECULAR WEIGHT DISPERSITY $\bar{M}_w/\bar{M}_n$
600
550
500
450
400
350
300
$\bar{M}_w \times 10^{-3}$

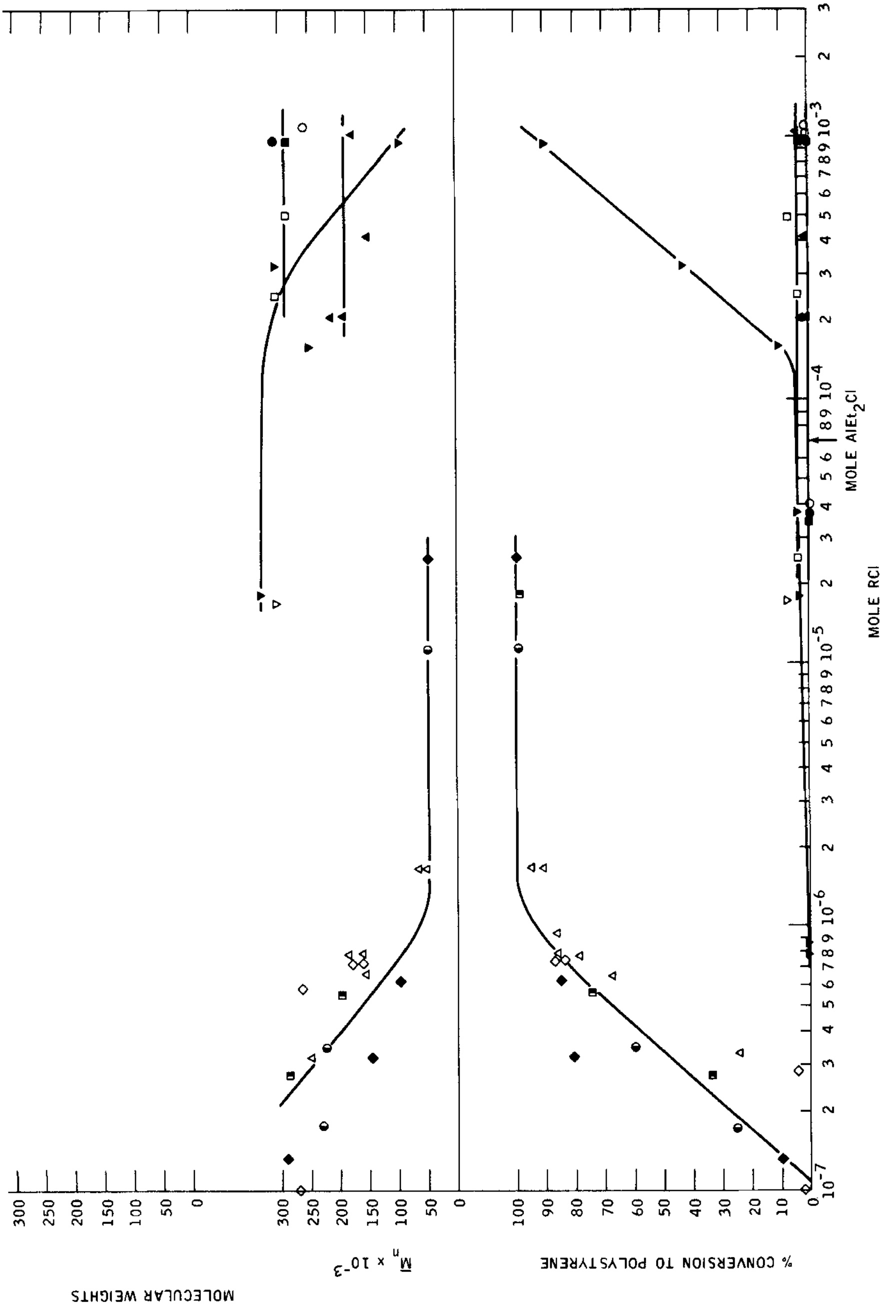


Fig. 1. Polymerization of styrene with AlEt$_2$Cl/RCl initiator system. Dependence of conversion, molecular weights ($\overline{M}_w$ and $\overline{M}_n$), and molecular weight dispersity ($\overline{M}_w/\overline{M}_n$) on coinitiator (RCl) concentration.

is a sufficiently strong Lewis acid to break the isobutyl-Cl bond, may start to be formed; the momentarily formed isobutyl cation then immediately rearranges to the more stable t-butyl ion, a very efficient initiating entity.

While these observations and those published earlier [1] strongly indicate the decisive role of the balance between carbonium ion stabilities and availabilities for the successful initiation of cationically polymerizable monomers, this thesis has not yet been studied quantitatively. Initiation of, for example, styrene polymerization with a series of suitably substituted 1-chloro ethylbenzenes (i.e., p-OCH_3, m-OCH_3, p-CH_3, m-CH_3, H, p-Cl, and m-Cl) and a correlation of the polymerization rates with $\delta^{\oplus}$ and $\rho^{\oplus}$ could greatly advance our understanding of the mechanism of these polymerizations, and in particular, the relative importance of steric and inductive factors in regard to initiation.

The Effect of RCl Concentration on $\bar{M}_n$, $\bar{M}_w$, and MWD

Figure 1 also shows the effect of alkyl halide concentration on the molecular weights (number average $\bar{M}_n$ and weight average $\bar{M}_w$) and molecular weight distributions expressed by the ratio $\bar{M}_w/\bar{M}_n$. Again, the three classes of above-discussed alkyl halides give three distinct families of molecular weight dependences. Furthermore, relatively high molecular weights are obtained at low conversions, and the molecular weights decrease as the conversions increase. Thus, alkyl halides with high R–Cl bond dissociation energies produce very low conversions and relatively high-molecular-weight polystyrenes. In contrast, alkyl halides with relatively weak R–Cl bonds give rise to high molecular weights when used in low concentrations and produce gradually lower molecular weights by gradually increasing the RCl concentrations. The same holds true also with isobutyl chloride as coinitiator.

These observations indicate a polymerization process involving relatively slow initiation with rapid propagation and termination (or chain transfer).

It should be noted that while the number average molecular weights (particularly with the alkyl halides with weak R–Cl bonds) drop by a factor of 6 (i.e., from ~3×10^5 to ~5×10^4), the weight averages decrease by only a factor of 2 (i.e., from ~6×10^5 to ~3×10^5) over the RCl concentrations studied. This observation is reflected by the corresponding molecular weight distributions, which increase from a $\bar{M}_w/\bar{M}_n$ value of 2 at low RCl concentrations to ~7.5 at the highest RCl concentrations employed. A molecular weight distribution of 2, the most probable MWD, indicates a conventional chain propagation mechanisms with probably one well-defined catalyst species or growing site. This is also the expected value for a conventional (cationic) chain-growth mechanism in which chain transfer is the dominant chain-breaking event. The most probable MWD's obtained at low conversions with RCl with strong R–Cl bonds is also in agreement with this proposition. With increasing conversions the MWD broadens and this again is the expected behavior of a conventional propagation mechanism in which the molecular weights are primarily determined by chain transfer. It is also possible that the unusually large MWD values obtained (~5) at very high conversions are due to branching (by chain transfer to the polymer), as proposed by Endres et al. [4].

REFERENCES

[1] J. P. Kennedy, *J. Macromol. Sci.*, **A3**, 861 (1969).

[2] J. P. Kennedy, in *Polymer Chemistry of Synthetic Elastomers* (J. P. Kennedy and E. Tornqvist, eds.), Wiley (Interscience), New York, 1968, Chap. 5A, Part I, p. 291.

[3] J. P. Kennedy and R. B. Isaacson, *J. Macromol. Chem.*, **1**, 541 (1966).

[4] G. F. Endres, V. G. Kamath, and C. G. Overberger, *J. Am. Chem. Soc.*, **84**, *4813 (1962).*

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