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Preliminary Study of Cationic Copolymerization of α -Methylstyrene and Isobutyl Vinyl Ether. II

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ABSTRACT

α -Methylstyrene (α -MS) and isobutyl vinyl ether (IBVE) were copolymerized by using the $H_2O/EtAlCl_2$ initiator system and CH_2Cl_2 and CH_3Cl solvent in the temperature range from -30 to $-90^\circ C$. As compared to homopolymerization of α -MS, both yields and molecular weights are reduced upon addition of small amounts of IBVE to the feed. The reactivity ratios were calculated by the method of Kelen and Tüdös as well as the Fineman and Ross method, and the combined effect of change of solvent and temperature on reactivity ratios was determined. Effects of feed composition and temperature on the copolymer yield, composition, and number-average molecular weight \bar{M}_n were studied in detail. \bar{M}_n showed a novel exponential dependence on the IBVE concentration in the feed. The overall activation energies of molecular weight were determined from the Arrhenius plots for both homo- and copolymerization systems. Based on these and the yield data, a speculation is made regarding reaction mechanism for molecular weight control. NMR and DTA data are reported, which establish the random nature of the copolymers.

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INTRODUCTION

In cationic polymerization, with the use of chemical initiators, the reactivity of IBVE is generally so large, compared to that of styrene, that any copolymerization between these monomers is almost impossible [1]. The copolymer, however, can be obtained by using more reactive styrene derivatives containing electron-donating groups such as α - and p-methyl-, p-methoxystyrenes on one hand, and less reactive vinyl ether derivatives containing electron-withdrawing groups such as 2-chloroethyl vinyl ether (CEVE). Thus, Dunphy and Marvel [2, 3] studied copolymerization of α -methylstyrene (α -MS) or p-substituted α -methylstyrene with CEVE. Brown and Pepper [4] reported copolymerization of styrene or α -MS with CEVE. In a series of publications Masuda and Higashimura [5-7] reported copolymerization of styrene derivatives with CEVE using a variety of initiator systems and solvents. More recently, Yamamoto and Higashimura [8] published a study of copolymerization of phenyl vinyl ether or cis-phenyl propenyl ether with α - or p-methylstyrene or p-methoxystyrene. These studies indicated that, in general, the copolymerization was possible and was facilitated by using a strong Lewis acid initiator system and a polar solvent.

Ueno, Hayashi, and Okamura [9] seem to be the first to copolymerize isobutyl vinyl ether (IBVE) and styrene. The copolymerization was carried out in bulk by using γ -ray initiation, and reactivity ratios were determined at 0 and 40°C. The feasibility of copolymerization by radiation initiation was explained as due to the presence of free ions in the system. The study with chemical initiators [5-7] had shown an increase in styrene incorporation in copolymer with an increase in the polarity of the medium or with the use of stronger Lewis acids, i. e., on increasing the charge separation. These results suggest that the use of a very weakly nucleophilic counteranion can in principle lead to satisfactory copolymerization between alkyl vinyl ether and styrene or its derivatives, or any cationically polymerizable olefin. Indeed, Heublein and co-workers [10, 11] have reported copolymerization of IBVE with isobutylene and styrene by using strong Lewis acids such as AlCl_3 , though their claims regarding copolymerization are not fully accepted as yet [12].

To test the above hypothesis, α -MS and IBVE were copolymerized by using the $\text{H}_2\text{O}/\text{EtAlCl}_2$ initiator system and CH_2Cl_2 or CH_2Cl_2 solvent in the range from -30 to -90°C. The counteranion EtAlCl_2OH obtained by using the $\text{H}_2\text{O}/\text{EtAlCl}_2$ system, i. e., an ubiquitous impurity, most probably water and EtAlCl_2 , is known to be a weak nucleophile in isobutylene polymerization [13, 14].

EXPERIMENTAL

α -MS, IBVE, and CH_2Cl_2 were freshly distilled over CaH_2 and also stored over it at low temperatures. CH_2Cl_2 was distilled prior

to use through a column packed with CaO (Fischer Scientific Co.) and Molecular Sieves, Type 4A (Linde Div.). EtAlCl_2 (Ethyl Corp.) was used as received. Hexane was distilled over sodium dispersion and stored over Molecular Sieves, type 3A (Linde Div.).

All experiments were carried out under nitrogen in a dry box equipped with a cold bath. The moisture content was below 30 ppm. To a cooled mixture of monomers and solvent in a three-necked flask, EtAlCl_2 solution in hexane (1.5 M) was added dropwise. The exotherm was noted, and the reaction was quenched after 15 min by adding cold MeOH. The copolymer was precipitated in excess MeOH, filtered, and dried in a vacuum oven at 60°C overnight.

Solubility tests using hexane were carried out in a Soxhlet apparatus for 24 hr. The NMR spectra were recorded in CDCl_3 solvent at room temperature by using a JEOL FX60Q, Model (60 MHz). Gel-permeation chromatography was carried out in THF solvent at 25°C by using a Waters Associates' Model 200 instrument. Four columns of pore sizes 10^3 , 10^4 , 10^5 , and 10^6 Å were used. Since calibration curves for the two homopolymers as well as copolymers were not available, universal calibration curve was utilized. Mark-Houwink constants for P α -MS and PIBVE used were, respectively, $[\eta] = 2.49 \times 10^{-4} \bar{M}_w^{0.647}$ (in benzene at 30°C) [15] and $[\eta] = 7.55 \times 10^{-5} \bar{M}_w^{0.75}$ (in benzene at 30°C) [16].

Molecular weights obtained for copolymers using these equations were within 15% and generally within 10% of each other. Hence, the values obtained using only the first equation (for P α -MS) are reported here.

Differential thermal analysis (DTA) was carried out by using a DuPont Model 900 instrument at a heating rate of 20°C/min in a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out by using DuPont Model 950 instrument with a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of Poly(α -MS-co-IBVE)

The synthesis of homo- as well as copolymers of α -MS and IBVE was carried out by using the $\text{H}_2\text{O}/\text{EtAlCl}_2$ initiator system and CH_2Cl_2 or CH_3Cl solvent. The effect of monomer feed composition on the yield, composition, and molecular weight of the copolymer prepared in CH_2Cl_2 at -50°C and in CH_3Cl at -70°C is given in Table 1. The trends obtained for both systems were similar. Thus, the coiniciator efficiency, i. e., weight of copolymer obtained per mole EtAlCl_2 concentration in M, for the CH_2Cl_2 system decreased significantly at first from $> 10,000$ to 2500 as IBVE concentration in the feed was increased from 0 to 10 mole %. Thereafter, it increased with the

TABLE 1. Effect of Monomer Feed Composition on the Yield, Composition, and Molecular Weight of Poly(α -MS-co-IBVE) Copolymers^a

α -MS (mole %)	CH ₂ Cl ₂ (-50°C)			CH ₃ Cl (-70°C)		
	Yield (g)	α -MS in copolymer (mole %)	\bar{M}_n $\times 10^{-3}$ (g/mole)	Yield (g)	α -MS in copolymer (mole %)	\bar{M}_n $\times 10^{-3}$ (g/mole)
100	61	100	30.2	26	100	73.7
93	5	68	13.2	—	—	—
90	27	79	11.0	1	64	32.3
80	—	—	—	10	27	—
75	13	30	15.6	6	19	58.9
65	—	—	—	5	12	77.0
50	11	9	37.0	9	8	109.0
25	—	—	—	15	0	241.0
10	7	1	180.0	—	—	—
0	11	0	204.0	22	0	258.0

^aConditions: CH₂Cl₂ or CH₃Cl = 300 ml; EtAlCl₂ = 1.5×10^{-3} M; α -MS + IBVE = 100 ml.

IBVE concentration, reaching nearly 6300 for the IBVE homopolymerization. Similarly, using CH₃Cl, the coinitiator efficiency decreased from > 16,000 to 200 and subsequently increased up to 7300 as IBVE concentration in the feed increased from 0 to 10 to 100 mole %. The coinitiator efficiency for homopolymerization of α -MS shown here is for incomplete conversions obtained by stopping the polymerization with MeOH addition. The actual efficiency, therefore, is very high, since nearly complete conversion of α -MS can be obtained. Importantly, small amounts of IBVE in the feed have a severe detrimental effect on the copolymer yield. This suggests that IBVE acts as an inhibitor in addition to being a comonomer, though the mechanism of inhibition is not known.

The effect of feed composition on the copolymer composition was very marked, and small increases in IBVE concentration in the feed significantly increased its concentration in the copolymer. Apparently, this effect was greater when CH₃Cl was used than with CH₂Cl₂. From the data reported in Table 1, reactivity ratios were calculated after Kelen and Tüdös with [17] or without [12] using conversion data. For the CH₂Cl₂ system, r_1 and r_2 were, respectively, 11.60 and 0.17

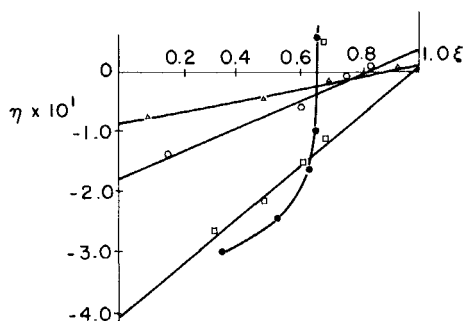


FIG. 1. Kelen-Tüdös plot for determining reactivity ratios in the copolymerization of α -MS and IBVE: (\circ) CH_2Cl_2 (-50°C), without using conversions; (Δ) CH_2Cl_2 (-50°C) using conversions; (\bullet) CH_3Cl (-70°C) without using conversions; (\square) CH_3Cl (-70°C), using conversions.

when the conversions were included in the calculation (α -MS is M_2). When conversions were not included, r_1 and r_2 were 11.83 and 0.46, respectively (Fig. 1). Interestingly, r_2 is more sensitive to conversion than r_1 . This was further corroborated by the fact that r_1 and r_2 obtained by using a Fineman-Ross plot were 12.6 and 0.49. Since conversions are below 30%, the similarity in these r_1 and r_2 values with previous ones when conversions are neglected is not surprising.

The inclusion of conversion data is even more important for the CH_3Cl system, where both Fineman-Ross and Kelen-Tüdös plots were nonlinear when conversions were neglected. However, a good linear plot was obtained for the α -MS feed concentration range from 50 to 80 mole %, when conversions were included in the calculation (Fig. 1). The r_1 and r_2 values were, respectively, 12.54 and 0.03. Such a large difference in reactivity ratios explains why IBVE incorporation in the copolymers is greater than that of α -MS. The difference in reactivity ratios is probably even greater with the use of a nonpolar solvent or a weak Lewis acid (strongly nucleophilic counteranion), making the copolymerization extremely difficult. The reason for the sensitivity of only r_2 to the conversion is not clear.

A change in solvent and temperature from CH_2Cl_2 at -50°C to CH_3Cl at -70°C increased r_1 slightly and reduced r_2 significantly. Masuda and Higashimura [5] have also determined changes in the reactivity ratios for the system α -MS and CEVE. Using $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}$ initiator, CH_2Cl_2 and toluene solvents, at 23° and -78°C in their study, r_1 was found to decrease and r_2 to increase when solvent was changed from toluene to the more polar CH_2Cl_2 . In their subsequent publication [6], they reported relative reactivity of CEVE against α -MS when toluene, CH_2Cl_2 , and $\text{C}_2\text{H}_5\text{NO}_2$ were solvents and AlBr_3 , $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}$,

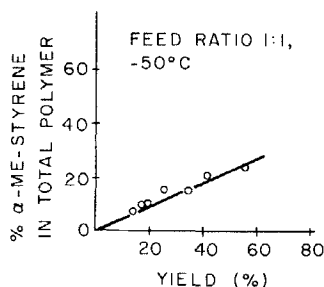


FIG. 2. Effect of monomer conversion on the α -MS content of copolymer. Feed ratio 1:1, -50°C .

and $\text{BF}_3 \cdot \text{OEt}_2$ were catalysts. They showed that the relative reactivity of CEVE decreased in changing solvent from toluene to CH_2Cl_2 but increased again in $\text{C}_2\text{H}_5\text{NO}_2$. Though the reactivity ratios are not reported, their findings suggest that probably r_1 decreases and/or r_2 increases with solvent change from toluene to CH_2Cl_2 . Subsequently, r_1 increases and r_2 decreases with the use of $\text{C}_2\text{H}_5\text{NO}_2$ ($\alpha\text{-MS} = \text{M}_2$). The results of this study concur closely with those of Higashimura, in that the reactivity of vinyl ether increases with a change of solvent to CH_3Cl , a more polar solvent than CH_2Cl_2 . The increase in r_1 and decrease in r_2 with the use of CH_3Cl at -70°C as compared to use of CH_2Cl_2 at -50°C can be explained on the basis of higher solvating power of the former system. The growing carbenium ions are thus expected to be less reactive and hence more selective in CH_3Cl than CH_2Cl_2 . The higher selectivity in CH_3Cl results in an increase in r_1 , since vinyl ether cation now prefers to add to more reactive IBVE than $\alpha\text{-MS}$, thus increasing k_{11} and decreasing k_{12} . Similarly, the $\alpha\text{-MS}$ cation prefers to add to more reactive IBVE, thus bringing about an increase in k_{21} but a decrease in k_{22} . This results in a decrease in r_2 . From these data, however, it is not possible to separate the effects of solvent and temperature.

Such large differences in reactivity ratios can bring about heterogeneity in copolymer composition, if polymerization is allowed to proceed to higher conversions. This was indeed found for the 1:1 feed ratio using CH_2Cl_2 at -50°C (Fig. 2). Thus, $\alpha\text{-MS}$ content increased from 7 mole % to 23 mole % as the conversion increased from 15% to 55% by addition of more EtAlCl_2 . Thus, incremental addition of IBVE and EtAlCl_2 became necessary to obtain both reasonably homogeneous composition and high conversion. Table 2 shows data obtained at different temperatures by using this technique. Both yield and $\alpha\text{-MS}$ content of the copolymer seem to decrease below -70°C . While the decrease in yield is probably due to inefficient initiation at lower temperatures, a decrease in $\alpha\text{-MS}$ content signifies a change in reactivity ratios, as discussed above, making IBVE more reactive at lower temperatures.

TABLE 2. Effect of Temperature on the Yield, Composition and Molecular Weight of α -MS-co-IBVE Copolymers^a

Temp. (°C)	CH ₂ Cl ₂ ^b			CH ₃ Cl ^c			CH ₃ Cl ^d		
	Yield (g)	α -MS (mole %)	$\bar{M}_n \times 10^{-3}$ (g/mole)	Yield (g)	α -MS (mole %)	$\bar{M}_n \times 10^{-3}$ (g/mole)	Yield (g)	α -MS (mole %)	$\bar{M}_n \times 10^{-3}$ (g/mole)
-30	34	78	5.5	16	54	6.3	11	71	6.0
-50	48	74	—	15	45	10.9	18	76	9.5
-70	35	79	17.0	11	42	17.9	9	66	24.6
-85	17	65	62.0	—	—	—	—	—	—
-90	—	—	—	4	37	127.8	5	67	77.7
-93	5	66	94.0	—	—	—	—	—	—

^a IBVE and EtAlCl₂ solutions added in three equal batches.

^b 95 ml α -MS, 15 ml IBVE, 2.4 ml EtAlCl₂ solution.

^c 95 ml α -MS, 15 ml IBVE, 1.2 ml EtAlCl₂ solution.

^d 97 ml α -MS, 9 ml IBVE, 1.2 ml EtAlCl₂ solution.

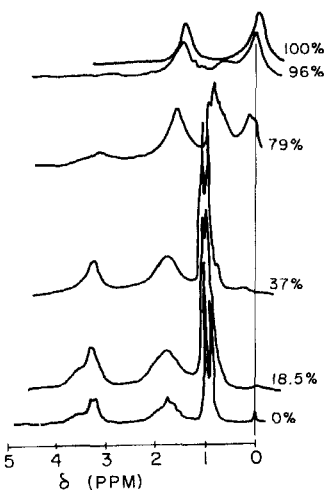


FIG. 3. NMR spectra of $P(\alpha\text{-MS-co-IBVE})$ as a function of $\alpha\text{-MS}$ content of the copolymers.

Characterization of Poly($\alpha\text{-MS-co-IBVE}$)

Solubility Study. An extraction study of selected samples showed that a copolymer containing as high as ~ 70 mole % $\alpha\text{-MS}$ was soluble in hot hexane. However, the copolymer having 80 mole % $\alpha\text{-MS}$ remained insoluble.

NMR Study of Copolymer Composition. The NMR spectra of the copolymers are complicated as compared to those of the homopolymers. However, a direct comparison of phenyl peak ($\delta \sim 7.0$) with the methyl peak ($\delta \sim 0$) of $\alpha\text{-MS}$ leaves no doubt that the peak at $\delta \sim 0$ does not account for all the methyl groups present in $P \alpha\text{-MS}$ (Fig. 3). Similarly, a comparison between the peak at $\delta \sim 3.1$ and that $\delta \sim 1.0$ arising from PIBVE shows that there are more methyl groups than that can be accounted for on the basis of IBVE. Apparently, a closer study reveals that possibly, depending on the triad distribution of the $\alpha\text{-MS}$ unit, the Me- peak may possibly be at $\delta \sim 0$ or $\delta \sim 0.9\text{-}1.0$. That is, for M-M-M triad, the center Me- unit has a peak at $\delta \sim 0$. However, for I-M-M or M-M-I as well as I-M-I triads, the Me- absorption shifts to higher fields, possibly due to lower steric strains in these triads and is observed at $\delta \sim 0.9$. Though a detailed analysis of sequence distribution is not carried out, the NMR spectra do provide a direct proof that random copolymers rather than a mixture of homopolymers, are present. Unfortunately, complications arising probably because of stereoregularity of the IBVE as well as $\alpha\text{-MS}$ units do not allow further analysis of the spectra. These spectra,

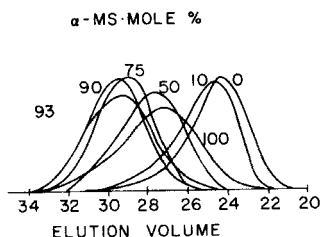


FIG. 4. GPC curves of P(α -MS-co-IBVE) prepared with $\text{H}_2\text{O}/\text{EtAlCl}_2/\text{CH}_2\text{Cl}_2$ at -50°C as a function of α -MS content in the feed.

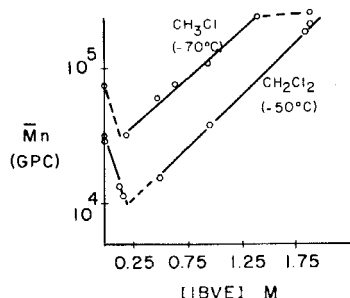


FIG. 5. Effect of IBVE concentration in the feed on the number-average molecular weight of poly(α -MS-co-IBVE).

nevertheless, provide an accurate measure of composition of copolymers and so have been used in this study.

Molecular Weight Study. The effect of monomer feed composition on the number-average molecular weight (\bar{M}_n) as determined by using GPC is shown in Table 1 and Fig. 5. The GPC curves obtained for copolymers prepared using CH_2Cl_2 at -50°C are shown in Fig. 4. These data show that small concentrations of IBVE in the feed significantly lower the molecular weights of copolymers as compared to homo P α -MS. The \bar{M}_n subsequently increases with an increase in IBVE concentration, and fairly high molecular weight PIBVE can be obtained. Interestingly, the molecular weights are higher for the $\text{CH}_2\text{Cl}_2/-70^\circ\text{C}$ system than for $\text{CH}_2\text{Cl}_2/-50^\circ\text{C}$ system. Apparently the chain-breaking reactions are retarded on using more polar solvent and/or lower temperature. The GPC curves shown in Fig. 4 are fairly monomodal, indicating homogeneous copolymer compositions and absence of any homopolymers.

Figure 5 gives a plot of $\log \bar{M}_n$ versus IBVE concentration for both

the systems studied. Interestingly, a linear relationship was observed. Generally, in cationic copolymerization such plots are U-shaped, and it is believed that this is probably the first time such a linear dependence has been detected. The plots can be represented by the equation,

$$\bar{M}_n = A e^{\pm B(M)}$$

where A seems to depend on the solvent and temperature and B on the overall activation energy of chain breaking reactions. The positive slope of two curves equals 0.64 ± 0.1 . Such an exponential relation between the molecular weight and monomer concentration, to the best of our knowledge, has not yet been found in cationic copolymerization. Additionally, it probably signifies the overall greater importance of IBVE in the molecular weight controlling reaction as compared to α -MS. Unfortunately, the system is complicated because an increase in IBVE concentration in the feed also increases the polarity of medium. What effect this will have remains a matter of speculation.

The small concentrations of α -MS in the feed lead only to a small decrease in molecular weight. For CH_3Cl system, it seems that as much as 25 mole % α -MS can be used without significantly affecting the molecular weight. Such a mild effect of α -MS is not surprising, in view of the fact that negligible or no incorporation of α -MS in the polymer takes place up to that concentration level of α -MS. Thus, α -MS acts only as an inert diluent in this range. Since decrease in molecular weight is related to the incorporation of α -MS in the copolymer, it can be speculated that the major molecular weight controlling reaction in the copolymerization is the cross-transfer reaction between more reactive α -MS cation and IBVE monomer. This is in the same vein as the report of Kennedy and Chou [18], who hypothesize that the cross-transfer reaction will compete favorably with cross-propagation in the reaction between more reactive cation and monomer.

The effect of temperature on the molecular weights in the homopolymerization and copolymerization of α -MS and IBVE is shown in Fig. 6. The GPC curves obtained in the copolymerization study with the use of CH_2Cl_2 are shown in Fig. 7. While the conversion maintained in the homopolymerizations is low ($\sim 20\%$), that obtained in the copolymerizations is given in Table 2. The activation energy of number-average molecular weight, $\Delta E_{\bar{M}_n}$, was calculated from the slopes of these Arrhenius plots. $\Delta E_{\bar{M}_n}$ is lowest and equals -0.4 ± 0.5 kcal/mole for PIBVE. This was evident in the fact that the increase in molecular weight was small on decreasing the temperature from -30 to -90°C . This low $\Delta E_{\bar{M}_n}$, coupled with the fact that only low conversions were obtained in IBVE homopolymerizations strongly suggests presence of at least one important termination reaction and

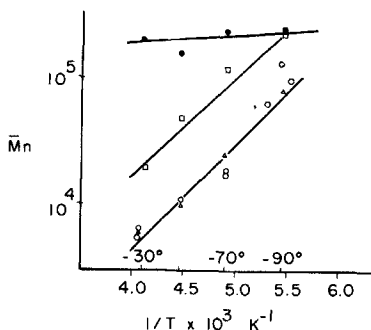


FIG. 6. Effect of temperature on the number-average molecular weight of homopolymers and copolymers of α -MS and IBVE: (●) 100 ml IBVE, 300 ml CH_2Cl_2 , 1.5×10^{-3} M EtAlCl_2 ; (□) 100 ml α -MS, 300 ml CH_2Cl_2 , 1.5×10^{-3} M EtAlCl_2 ; (○) 95 ml α -MS, 15 ml IBVE, 2.4 ml EtAlCl_2 solution, (○) 95 ml α -MS, 15 ml IBVE, 1.2 ml EtAlCl_2 solution; (Δ) 97 ml α -MS, 9 ml IBVE, 1.2 ml EtAlCl_2 solution.

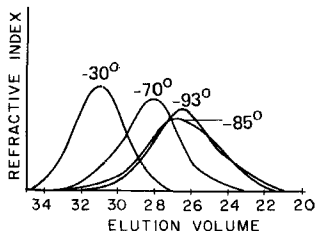


FIG. 7. GPC curves of poly(α -MS-co-IBVE) prepared by using $\text{H}_2\text{O}/\text{EtAlCl}_2/\text{CH}_2\text{Cl}_2$ as a function of temperature. Conditions: 95 ml α -MS, 15 ml IBVE, 2.4 ml EtAlCl_2 solution.

further indicates it to be a major molecular weight-controlling mechanism. Transfer to monomer in such a system is probably negligible or altogether absent.

The $\Delta E_{\overline{M}_v}$ for P α -MS was -3.65 ± 0.5 kcal/mole. The increase in molecular weight of P α -MS was subsequently significant as the temperature was decreased. Such a significant increase in molecular weight with temperature decrease is usually explained on the basis of a decrease in transfer to monomer. Since termination is probably not very important in α -MS polymerization as indicated by the

possibility of getting nearly complete conversions, transfer to monomer may be assumed to be of major importance in the molecular weight control.

For the copolymers, $\Delta E_{\overline{M}_n} = -5.53 \pm 1.0$ kcal/mole, indicating that temperature had highest effect in these systems as compared to the homopolymers. The molecular weight-controlling events in the copolymerization are more difficult to analyze, since the high $\Delta E_{\overline{M}_n}$ indicates transfer to monomer and the low conversions obtained indicate termination. Also, since the value of $\Delta E_{\overline{M}_n}$ for IBVE polymerization under conditions where transfer to monomer becomes the major molecular weight-controlling reaction is not known, further speculation about molecular weight governing mechanisms is not possible.

Differential Thermal Analysis (DTA). Though a large number of samples were subjected to DTA, the analysis of the data was rendered difficult due to multiple peaks present in some of them. This is especially true for samples prepared at high conversions or low IBVE feed concentrations and can be explained in terms of product composition heterogeneity. A close examination of copolymers prepared at lower conversions, however, shows increase in T_g with an increase in α -MS content of the copolymer (Fig. 8). The T_g of PIBVE and $P\alpha$ -MS homopolymers are -19 and $\sim 173^\circ\text{C}$, respectively. An almost linear increase in T_g with α -MS strongly indicates the presence of random copolymers. Thus, products ranging from hard plastic to soft rubber can be obtained by copolymerization of IBVE and α -MS.

Thermogravimetric Analysis (TGA). The TGA curves are shown in Fig. 9 for the two homopolymers as well as copolymers. In the inert nitrogen atmosphere, PIBVE is more resistant to thermal degradation than $P\alpha$ -MS, probably because unzipping is absent in PIBVE. The copolymers show intermediate thermal stability, possibly

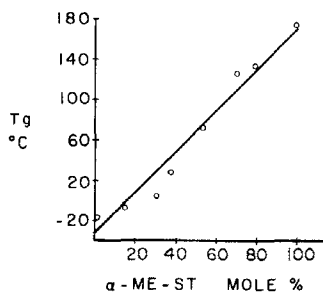


FIG. 8. Effect of α -MS content of poly(α -MS-co-IBVE) on the T_g of the copolymers.

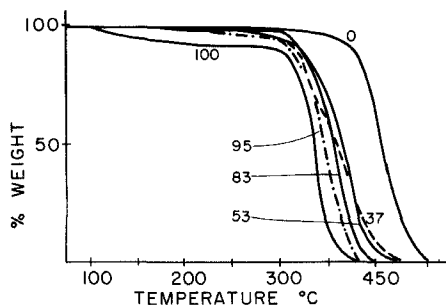


FIG. 9. TGA curves of poly(α -MS-co-IBVE) as a function of α -MS content of copolymers (α -MS in mole %).

indicating the islands of IBVE may inhibit unzipping of P α -MS chains. The weight loss in the region from 100 to 200°C for P α -MS may be due to low molecular weight oligomers of α -MS.

Mechanism of Copolymerization

In spite of a large body of work published on the cationic polymerization of alkyl vinyl ether, the exact mechanism of polymerization is still not well understood. This is especially true when Friedel-Crafts catalysts are used. The earlier postulated mechanisms are summarized by Eley [19] and Lal [20]. The mechanism of polymerization of α -MS by using $\text{H}_2\text{O}/\text{EtAlCl}_2$ in polar medium has not yet been studied. The initiation in both homo- and copolymerizations may be assumed to take place by the addition of a proton to either monomers. The ubiquitous impurity, most likely water, probably serves as a source for protons.

The mechanisms of transfer to monomer and termination in homo- or copolymerization are difficult to elucidate. In the case of IBVE homopolymerization, previous workers have found transfer to monomer to be of greater importance than termination. Thus, Bawn et al. [21] using the $\text{Ph}_3\text{C}^{\oplus}\text{SbCl}_6^{\ominus}/\text{CH}_2\text{Cl}_2$ system in the range from 0 to -25°C concluded that there was no termination but that an efficient chain transfer was present, limiting the molecular weight to about 2000-5000. In a "super dry" system with $\text{Ph}_3\text{CSbCl}_6/\text{CH}_2\text{Cl}_2$ system in the range from 0 to 25°C , Stannett and co-workers [22] similarly concluded that there was negligible termination and efficient monomer transfer was present. Sigwalt et al. [23], using a similar system, concluded that though termination was present, it was much less important than the transfer to monomer. Recalculating Sigwalt's data [23] on the basis of Arrhenius plot, we observed that $\Delta E_{\overline{M}_n} = -3.6 \pm 0.5$ kcal/mole in the temperature range from 20 to -40°C .

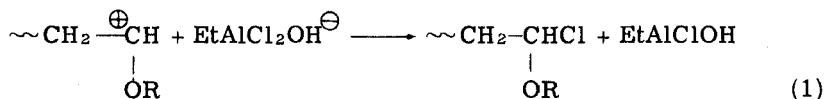
It is important to compare these results with those obtained by using radiation in bulk since the polymerization in both cases is presumed to be by free ions. Thus Hayashi et al. [24] obtained $\Delta E_{\overline{M}_n} = -1.5 \pm 2.5$ kcal/mole, and Stannett et al. [25] found $\Delta E_{\overline{M}_n} = -4.8$ kcal/mole in the temperature range from 0 to 50°C. The difference between the free-ion propagation system and the initiator system used in the present study is obvious. While termination is negligible or absent and $\Delta E_{\overline{M}_n} = -4 \pm 1$ kcal/mole for the free-ion systems, termination is very important, and $\Delta E_{\overline{M}_n} = -0.4 \pm 0.5$ kcal/mole for the H₂O/EtAlCl₂/CH₃Cl system. The very low $\Delta E_{\overline{M}_n}$ and high molecular weights obtained with EtAlCl₂ clearly indicate that transfer to monomer for this system is negligible or even absent [14]. While at least one important termination is suggested by the low conversions obtained. This difference between the radiation or Ph₃C⁺SbCl₆⁻/CH₂Cl₂ systems and H₂O/EtAlCl₂ initiated polymerizations can be explained by the following considerations. Since EtAlCl₂OH counteranion is more nucleophilic than SbCl₆⁻ due to the smaller size and charge delocalization, correspondingly it is expected [14] to be more termination-active and less transfer-active than SbCl₆⁻. Secondly, since the temperature range is distinctly lower (-30 to -90°C) with H₂O/EtAlCl₂ than that (50 to -40°C) with either Ph₃CSbCl₆ or radiation, the higher activation energy-demanding transfer reactions freeze out at lower temperatures. Hence, transfer to monomer in this study seems to be negligible. Bawn et al. [21] suggested that CH₂Cl₂ was an efficient transfer agent. Stannett and co-workers [25] recently showed that though high molecular weights were obtained in the bulk, only low molecular weight PIBVE could be prepared in CH₂Cl₂ by using radiation initiation. However, in this study, PIBVE of 200,000 \overline{M}_n could be easily prepared by using CH₂Cl₂ at -50°C, which showed that CH₂Cl₂ was not an efficient transfer agent, if at all. The reason for the lack of transfer activity of CH₂Cl₂ could be low temperatures and/or the initiator system used. Thus, CH₂Cl₂ may be active as a transfer agent when free ions are involved in the propagation, however, when ion-pairs are responsible for the propagation, it may be inert as a chain transfer agent.

The mechanism of homopolymerization of α -MS is even less studied. Some initial work by Imanishi [16] suggested the presence of both transfer to monomer and termination in α -MS polymerization with BF₃ etherate and CH₂Cl₂ or CH₃Cl. In this study, very high conversions coupled with a relatively high $\Delta E_{\overline{M}_n}$ suggested that probably termination was negligible and transfer to monomer was the major molecular weight-controlling reaction.

In the copolymerization of α -MS and IBVE, we obtained lower conversions and molecular weights as compared to the homopolymerizations.

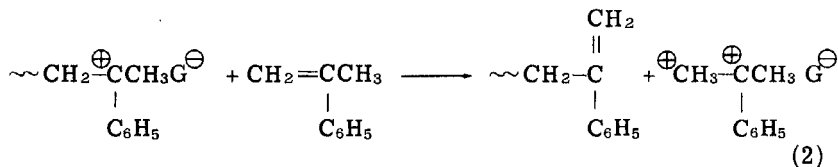
This indicated that important termination and transfer to monomer reactions were taking place. Additionally, the lowering of molecular weights depended on the IBVE concentration suggesting that the rate of transfer and termination were related to it. The above considerations lead to the following tentative proposal of molecular weight control in the copolymerization.

Termination of the vinyl ether cation by chlorination [Eq. (1)] is most likely.

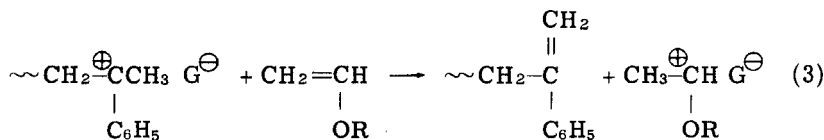


Ethylation or hydridation may also take place.

Chain transfer occurs from P α -MS cation to α -MS [Eq. (2)].



Chain transfer from P α -MS cation to IBVE may be the most important molecular weight limiting reaction [Eq. (3)].



The above mechanism of copolymerization is only speculative, and much work is needed to confirm or improve it.

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