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Elucidating the Mechanism of Carbocationic Polymerization of α-Methylstyrene

The Effect of Temperature and Proton Trap on Molecular Weights

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Summary

The polymerization of α-methylstyrene (αMeSt) using the "H_2O"/$SnCl_4$ initiating system and ethyl chloride solvent has been investigated over the temperature range from -40° to -122°C in the presence and absence of the proton trap 2,6-di-tert-butylpyridine (DtBP). Arrhenius (ln $\overline{M}_n$ versus 1/T) plots obtained with poly(αmethylstyrene) (PαMeSt) samples prepared in the absence of DtBP reveal the existence of two sharply defined temperature regimes (see Figure 1): at higher temperatures from -40 to ∿-86°C, the slope of the Arrhenius plot yields $\Delta H_{\overline{M}_n} = -4.90 \pm 0.25$ kcal/mole whereas at lower temperatures, from ∿-86° to -122°C, $\Delta H_{\overline{M}_n} = -0.3$ kcal/mole. With PαMeSt samples prepared in the presence of DtBP the $\Delta H_{\overline{M}_n}$ obtained for the higher temperature regime increases to -1.67 ± 0.20 kcal/mole whereas the $\Delta H_{\overline{M}_n}$ reflecting the lower temperatures remains the same as that obtained in the absence of DtBP. These observations are readily explained by postulating a change in mechanism at ∿-86°C: Evidently the $\overline{M}_n$ of PαMeSt is determined over the higher temperature regime by chain transfer to monomer which is frozen out at lower temperatures where termination becomes $\overline{M}_n$ determinant. In the absence of DtBP chain transfer to monomer is operative which leads to the higher Arrhenius slope over the higher temperature regime; however, over the lower temperature regime where chain transfer is absent and termination is $\overline{M}_n$ controlling, the Arrhenius slope remains unchanged. Evidence obtained from a Mayo plot (negligible intercept in the $1/\overline{M}_n$ versus $1/[\alpha MeSt]_o$ plot, Figure 2) with samples prepared at -92°C, corroborates this postulate. Molecular weight dispersities ($\overline{M}_w/\overline{M}_n$) as a function of temperature have been determined in the presence and absence of DtBP (Figure 3). The proton trap affects $\overline{M}_w/\overline{M}_n$ only over the higher temperature regime which also suggests that chain transfer to monomer is frozen out at ∿-86°C and that the polymerization becomes termination dominated at low temperatures.

Introduction

Analysis of the temperature profile of molecular weights yielded most important clues as to the polymerization mechanism in isobutylene systems (KENNEDY and TRIVEDI, 1978). Briefly it has been found that the slope of the $\ln\overline{M}_n$ versus 1/T (Arrhenius) plot changes sharply from a higher value ($\Delta H_{\overline{M}_n} = -6.6 \pm 1.0$ kcal/mole) at higher temperatures to a lower value ($\Delta H_{\overline{M}_n} = -1.8 \pm 1.0$ kcal/mole) at lower temperatures. The phenomenon was general in nature and appeared with a great variety of initiator and solvent systems. The effect of temperature on $\overline{M}_n$ has been explained by a sharp change in the mechanism. At relatively higher temperatures $\overline{M}_n$ is determined by chain transfer to monomer which is frozen out by cooling and termination becomes $\overline{M}_n$ controlling at relatively lower temperatures. The regime over which the main $\overline{M}_n$ determining event is chain transfer to monomer has been termed "transfer-dominated", that over which termination is $\overline{M}_n$ determining "termination dominated".

While the effect of temperature on PαMeSt molecular weights has been investigated by several groups of workers (DAINTON, et al. 1953; HUANG, et al. 1975; SIGWALT, et al. 1977 and TRIVEDI, 1980) evidence for a phenomenon similar to that found with isobutylene has not yet been published, probably because the temperature ranges used by the previous workers did not extend to sufficiently low levels.

We started our investigations by determining the effect of temperature on the $\overline{M}_n$ of PαMeSt obtained with the "H_2O"/$SnCl_4$ initiating system in the range from -40° to -122°C. Arrhenius plots were constructed which revealed the anticipated sharp change in the mechanism. The phenomenon was identical to those found with isobutylene (see above). In view of this phenomenological similarity between these systems we postulated that in the αMeSt system too, chain transfer to monomer is $\overline{M}_n$ determining at higher temperatures which is effectively frozen out and termination becomes $\overline{M}_n$, determining over the lower range.

At this point we reasoned that if our conception of proton trapping by sterically hindered amines is correct (KENNEDY and CHOU, 1979) and these proton-specific bases, e.g., DtBP, are able specifically to abort chain transfer to monomer (KENNEDY and GUHANIYOGI, 1981) then they should affect $\overline{M}_n$ only over the transfer-dominated higher temperature regime but not over the termination-dominated lower temperature regime. Accordingly we decided to carry out a series of αMeSt polymerizations in the presence and absence of DtBP but otherwise under identical conditions and to analyze the $\overline{M}_n$'s of PαMeSt's obtained over the -40° to -122°C range.

Experimental

$SnCl_4$ was purified by repeated distillation under vacuum from anhydrous P_2O_5. αMeSt was washed free of initiator, dried over $CaCl_2$, distilled under vacuum and finally dried over sodium films. DtBP (Ega-Chemie 97%) was dried over anhydrous BaO, distilled under vacuum and reacted with dry BCl_3. Pure and dry DtBP was then distilled into a break-seal. Ethyl chloride (Linde, Pure Grade) was dried over CaO before use.

Polymerizations were carried out under a dry nitrogen atmosphere in a stainless steel enclosure in capped pyrex tubes. The reactants were equilibrated for 30 mins in a pentane bath prior to charging "H_2O"/$SnCl_4$ solutions. The time of polymerization was varied from 1 to 15 mins. so as to obtain conversions less than 15%. Polymerizations were terminated by the addition of chilled methanol. Yields of PαMeSt were calculated after drying the polymers in a vacuum oven at 60°C for several days.

Molecular weights were determined using a Waters High Pressure GPC using a series of 500, 10^3, 10^4, 10^5 and 10^6 Å Styragel columns. The instrument was calibrated with polystyrene standards.

Results and Discussion

I. Arrhenius and Mayo Plots

First orienting experiments have been run to work out convenient polymerization conditions and to obtain reproducible results. With a little experience yields could be controlled not to exceed 15%. Yields were higher in the absence than in the presence of DtBP at higher temperatures; e.g., 28%, 37% and 30% at -40°, -51° and -61°C, respectively.

Figure 1 shows the results of two sets of experiments in the form of ln $\bar{M}_n$ versus 1/T (Arrhenius)plots, one carried out in the absence of DtBP (circles) the other in the presence of this proton trap (triangles). The plot obtained with PαMeSt samples prepared in the absence of DtBP exhibits a relatively high least square slope in the -40° to -86°C range, $\Delta H_{\bar{M}_n} = -4.90 \pm 0.25$ kcal/mole, and a much lower slope in the -86° to -122°C range $\Delta H_{\bar{M}_n} \simeq -0.3$ kcal/mole.

In contrast, the $\bar{M}_n$'s obtained in the presence of DtBP are much higher over the higher temperature range than those harvested in the absence of this pyridine, whereas the $\bar{M}_n$'s obtained over the lower temperature range are the same in the presence or absence of DtBP. $\Delta H_{\bar{M}_n}$ (disregarding the two data points at -40°C) = -1.67 ± 0.20 kcal;/mole for the higher temperature range and -0.30 kcal/mole for the lower range.

These observations can be explained along the following lines: The break in the Arrhenius line is

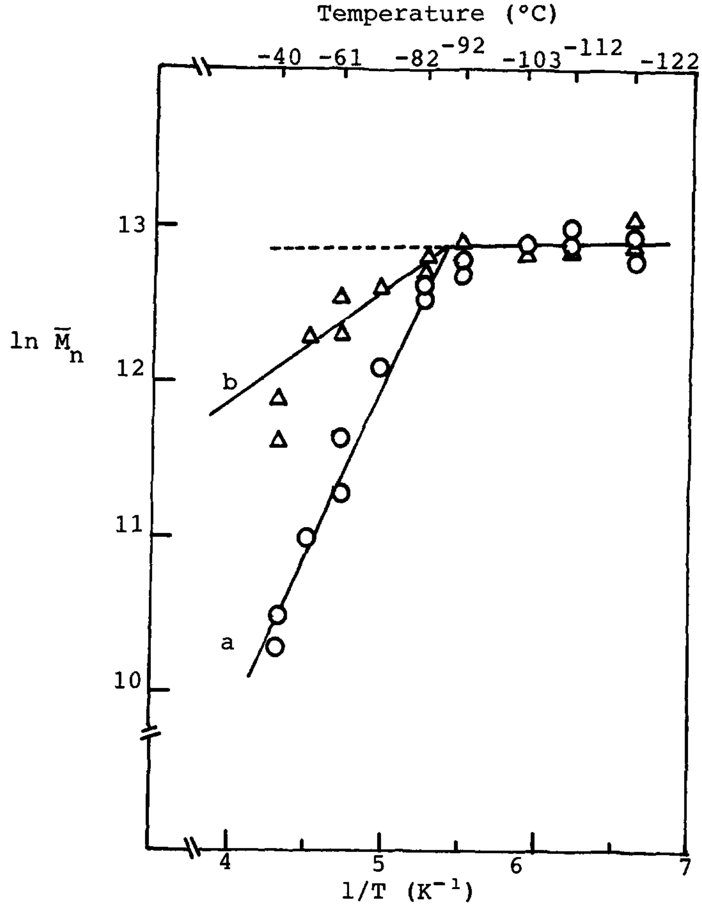
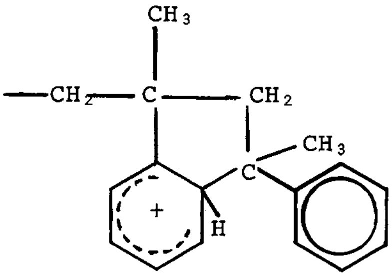


Figure 1. Arrhenius plots for $\bar{M}_n$ of PαMeSt ([αMeSt] = 0.77M, [SnCl$_4$] = 3.40 x 10^{-3}M, C_2H_5Cl solvent)
a) [DtBP] = 0
b) [DtBP] = 1.00 x 10^{-3}M

due to a change in the mechanism. At higher temperatures chain transfer to monomer is $\bar{M}_n$ controlling which is frozen out at ∿-86° and at lower temperatures termination becomes $\bar{M}_n$ controlling. The phenomenon is the same as that analyzed with isobutylene polymerizations by KENNEDY and TRIVEDI (1978). As to the effect of DtBP, it affects the $\bar{M}_n$'s only over the transfer-dominated higher temperature regime. We theorize that an interaction (complexation?) must exist between the propagating carbenium ion and DtBP and that due to the existence of this $\sim CH_2-\overset{+}{C}(CH_3)C_6H_5 \cdot DtBP \cdot SnCl_4OH^-$ complex the rate of chain transfer to monomer decreases more than that of propagation. The slope of the Arrhenius line in this regime leads to $\Delta H_{\bar{M}_n} = -1.67 \pm 0.20$ kcal/mole which may reflect the activation enthalpy difference between proton abstraction and propagation in the presence of DtBP. While we could speculate, the detailed mechanism of how DtBP facilitates proton abstraction which ultimately leads to chain transfer to monomer remains obscure. Termination in αMeSt polymerization initiated by "H_2O"/$SnCl_4$ below $\sim$-86°C may conceivably involve intramolecular cyclization leading to a relatively stable (dormant) substituted indane carbenium ion:



This carbocation intermediate also forms above $\sim$-86°C, however, at the higher temperatures sufficient energy is available for rapid proton loss either to monomer or DtBP.

The fact that transfer is essentially absent over the lower temperature regime has been established independently by direct experiment. Thus the negligible least square intercept ($k_{tr,M}/k_p \sim 2.5 \times 10^{-5}$) obtained in the Mayo plot constructed with PαMeSt samples prepared at -92°C, shown in Figure 2, indicates the virtual absence of chain transfer to monomer in the low temperature region.

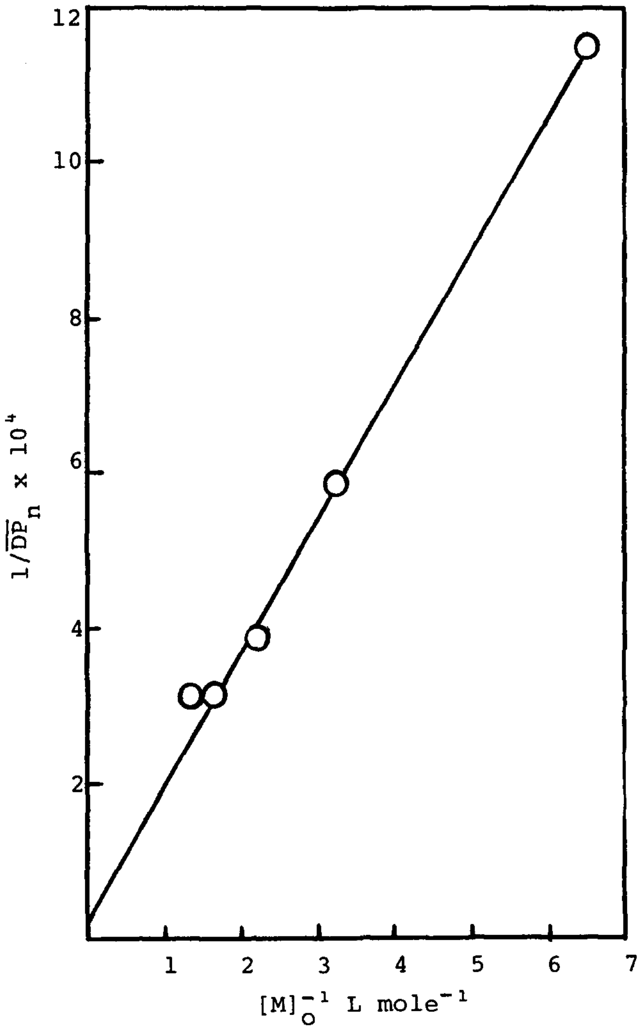


Figure 2. Mayo Plot of PαMeSt([αMeSt] = 0.154M to 0.77M. [$SnCl_4$] = 3.42 x 10^{-3}M; 90% C_2H_5Cl by volume, rest αMeSt + pentane, -92°C)

II. Molecular Weight Dispersities

Molecular weight dispersities (MWD) of PαMeSt's obtained over the -40° to -122°C range in the absence and presence of proton trap have been determined. Figure 3 shows the data. The $\overline{M}_w/\overline{M}_n$ versus T plots are undistinguishable over low temperatures in the absence

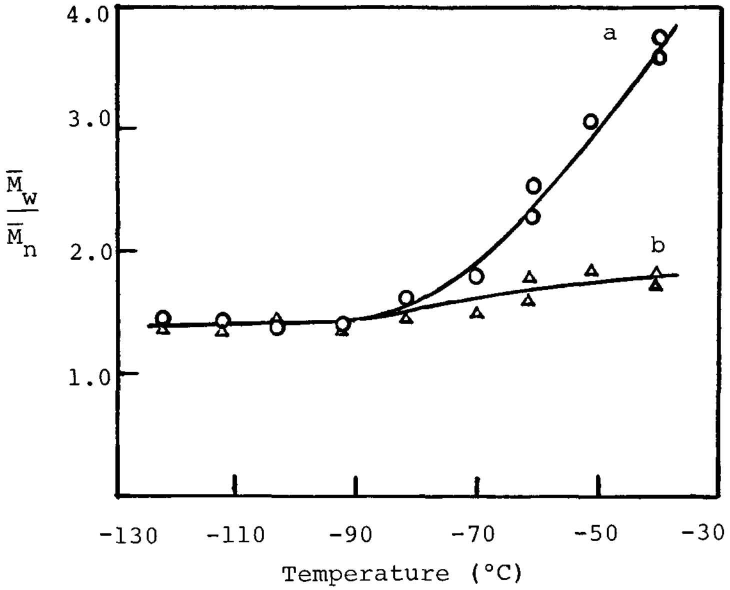


Figure 3. Molecular weight dispersity versus temperature plots for PαMeSt ([αMeSt] = 0.77M; [$SnCl_4$] = 3.42 x 10^{-3}M in C_2H_5Cl solvent)
a) [DtBP] = 0
b) [DtBP] = 1.00 x 10^{-3}M

or presence of DtBP. Both plots are essentially parallel to the horizontal axis, $\bar{M}_w/\bar{M}_n$ = 1.4-1.5 in the -122° to -86°C range, indicating that DtBP does not affect the mechanism over this regime. In contrast, DtBP strongly affects the result above ∿-86°C: While the plot obtained with samples prepared in the absence of DtBP increases strongly with increasing temperatures ($\bar{M}_w/\bar{M}_n \simeq$ 3.8 at -40°), that reflecting PαMeSt's prepared in the presence of proton trap exhibits a much smaller effect, indeed $\bar{M}_w/\bar{M}_n$ does not even reach 2.0 at -40°C.

The analysis developed to explain the results presented in the form of Arrhenius and Mayo plots above is also in concord with the MWD data and repetition is unnecessary. It is of particular interest that in the presence of DtBP $\bar{M}_w/\bar{M}_n \simeq$ 1.5 over the whole temperature range investigated. This phenomenon together with an analysis of the effect of DtBP on molecular weights and MWD is being discussed in detail in a series of manuscripts now in preparation. However, a satisfactory explanation has not yet been developed.

Acknowledgement

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