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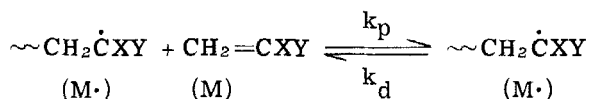
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ABSTRACT

A procedure for determining the ceiling temperature in radical polymerization was proposed. By means of this procedure, the ceiling temperature in radical polymerization of 2,6-dimethylphenyl methacrylate was determined. It was noted that the introduction of the methyl groups in the 2- and 6-positions of phenyl methacrylate lowered remarkably the ceiling temperature as the results of steric hindrance. This polymer was consistently found to undergo easily thermal decomposition into the monomer. These results were explained by increased steric requirement between α -, 2-, and 6-methyl groups in the polymer.

INTRODUCTION

The concept of a ceiling temperature (T_c) has been applied to actual polymerization systems as summarized by Ivin [1] and other workers [2, 3]. According to this concept, the propagation reaction is expressed by introducing the depropagation reaction into the kinetic scheme:



where k_p and k_d are rate constants for propagation and depropagation reactions, respectively.

At ordinary temperatures, $k_p[\text{M}\cdot][\text{M}] \gg k_d[\text{M}\cdot]$, and hence the rate of polymerization (R_p) is expressed simply as $R_p = k_p[\text{M}\cdot][\text{M}]$. However, at higher temperatures, $k_d[\text{M}\cdot]$ becomes important, and at T_c , $k_p[\text{M}\cdot][\text{M}] = k_d[\text{M}\cdot]$, i.e., $R_p = 0$. Although the polymer-monomer equilibria are affected by some polymerization conditions, T_c , which is closely related to the polymerization ability of the monomer in a thermodynamic sense, is one of the important factors in a consideration of the reactivity of vinyl monomers. When the polymerization proceeds via a radical chain mechanism, the lifetime of the growing radical is too short to attain polymer-monomer equilibrium. Therefore, as we have already reported [4], T_c is usually determined by extrapolation of the plot of R_p against the polymerization temperature to $R_p = 0$. In this paper the determination of T_c by an improved procedure is described.

In a previous paper [6] the absolute rate constants k_p and k_t (termination) in the radical polymerization of 2,6-dimethylphenyl methacrylate (DMPM) were determined, and it was found that the observed k_p value was much smaller than that of phenyl and methyl methacrylates (see later). This finding seemed to suggest that the T_c of this monomer was lower than that of the other methacrylate monomers. Therefore, the present paper also describes the result of T_c determination of this monomer.

EXPERIMENTAL

Polymerizations were carried out in sealed tubes. For polymerization at temperatures close to T_c , solutions of the monomer and the initiator were heated to the polymerization temperature separately by using H-shaped sealed tubes in order to avoid polymerization before attaining thermal equilibrium. Depending on the polymerization temperature, three kinds of initiators were used in order to measure R_p over the temperature range from 40 to 135°C: 2,2-azobisisobutyronitrile, 1,1'-azobis-1-cyclohexanecarbonitrile, and tert-butyl peroxide were employed for the polymerizations from 40 to 75°C, from 80 to

95°C, and from 100 to 135°C, respectively. The efficiency of initiation (f) for the azo initiators was assumed to be 0.5, and that for tert-butyl peroxide was assumed to be 1.0. *p*-Xylene was chosen as the solvent. To minimize the effect of changing the initiator concentration, polymerization time did not exceed one-third of the half life of the initiator. Less than 20% of the initial amount of initiator may decompose during this period.

PROCEDURE FOR T_c DETERMINATION

As with other chain reactions, radical polymerization consists of initiation, propagation, and termination reactions. Although we have to know the temperature dependency of k_p in order to determine T_c , knowing the absolute values of k_p is not an easy task. Fortunately, the temperature dependency of k_t is very small and the ratio of rate constants $k_p'/k_t^{0.5}$ instead of k_p can be used for T_c determination. Knowledge of the rate of initiation expressed by $2fk_i[I]$ allows evaluation of the ratio $k_p'/k_t^{0.5}$ at different temperatures according to the following equations;

$$\begin{aligned} -d[M]/dt &= k_p[M][M\cdot] - k_d[M\cdot] = (k_p - k_d/[M])[M][M\cdot] \\ &= k_p'[M][M\cdot] \end{aligned}$$

$$k_p'/k_t^{0.5} = (\ln [M]_0/[M])/2fk_i[I]^{0.5}t$$

where $[M]_0$ is the initial concentration of the monomer, k_t denotes the rate constant for the termination reaction, k_i denotes the rate constant for the decomposition of the initiator, $[I]$ is the concentration of the initiator, and t is the polymerization time. Calculation of k_i at individual temperatures was done by using the Arrhenius equation from the literature [5].

When $\log k_p'/k_t^{0.5}$ is plotted against the reciprocal of the polymerization temperature instead of against the temperature, the plot gives a curve whose slope approaches infinity at T_c :

$$\frac{d(\log k_p'/k_t^{0.5})}{d(1/T)} = \frac{k_d E_d/R[M] - k_p E_p/R}{(k_p - k_d/[M])/k_t^{0.5}}$$

where R is the gas constant, E_p is the activation energy of the propagation reaction, and E_d is the activation energy of the depropagation reaction.

Since $k_p = k_d/[M]$ at $T = T_c$,

$$\lim_{T \rightarrow T_c} \frac{d(\log k_p'/k_t^{0.5})}{d(1/T)} = \infty$$

RESULTS AND DISCUSSION

The experiments reported in this paper were directed toward testing how the steric hindrance of the methyl groups in the 2- and 6-positions of the benzene ring of DMPM affect T_c . There are indications that the methyl groups in the 2- and 6-positions locate conformationally close to the reacting carbon-carbon double bond of the monomer or the carbon-carrying unpaired electron of the polymer radical. On the basis of the absolute rate constants of elementary reactions in radical polymerization and copolymerization, we have shown that DMPM monomer and poly(DMPM) radical are less reactive than phenyl methacrylate (PMA) monomer and poly(PMA) radical, respectively [6]. The effect of the methyl group on the reactivities was accounted for by steric hindrance as expected from the molecular model shown in Fig. 1.

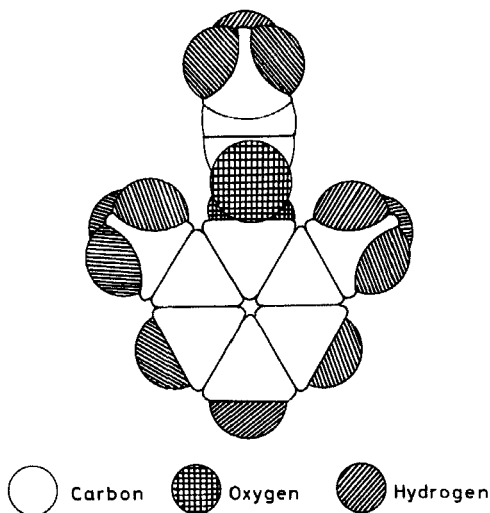


FIG. 1. Space filling molecular model of DMPM.

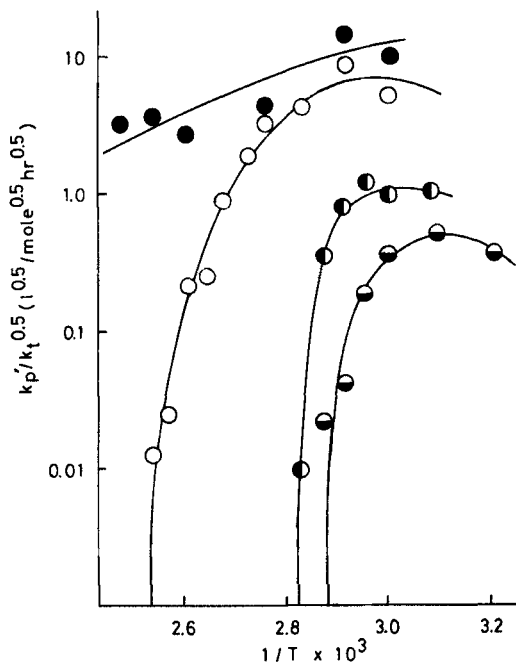


FIG. 2. Plots of $\log k_p'/k_t^{0.5}$ against $1/T$ for DMPM polymerization at $[M] = 3.19$ mole/L (\circ), 1.00 mole/L (\bullet), and 0.64 mole/L (\odot), and for PMA polymerization at $[M] = 0.64$ mole/L (\bullet).

Figure 2 shows the results of polymerization at different temperatures, and $\log k_p'/k_t^{0.5}$ is plotted against $1/T$. At each concentration of the monomer, $\log k_p'/k_t^{0.5}$ increases with an increase in temperature over a certain temperature range, and at a higher temperature $\log k_p'/k_t^{0.5}$ decreases abruptly from $1/50$ to $1/500$ of that at the lower temperature range, depending on monomer concentration.

Extrapolating the curves, we determined T_c at different monomer concentrations. The T_c of DMPM at $[M] = 3.19$, 1.00 , and 0.64 mole/L were determined to be 122 , 81 , and 73°C , respectively.

When the monomer solution was heated in ordinary sealed tubes in the presence of the initiator, $k_p'/k_t^{0.5}$ indicated that polymerization could occur even above T_c . However, when the monomer solution and the initiator solution were mixed at the polymerization temperature, no polymer formation was observed. We concluded that the

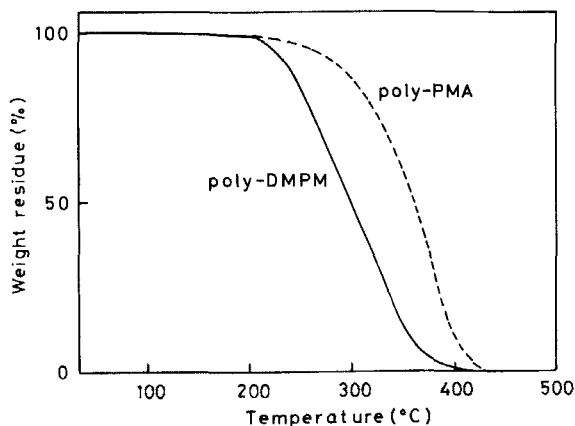


FIG. 3. Thermogravimetric curves of poly(DMPM) (—) and poly(PMA) (- - -).

apparent polymer formation above T_c was due to polymerization proceeding before thermal equilibrium was attained.

The results of PMA polymerization are also shown in Fig. 2 for comparison. The plot for PMA does not show any break over the temperature range examined at $[M] = 0.64$ mole/L. Under the same conditions, the T_c of methyl methacrylate (MMA) determined was 140°C . This is comparable to 145°C at $[M] = 0.64$ mole/L calculated from the graph given by Schulz et al. [7].

Apparently the introduction of methyl groups as the ortho-substituent caused a remarkable lowering of T_c , probably due to steric hindrance in the propagation reaction. Generally, the T_c of a monomer is critically dependent on the bulkiness of the substituent bound directly to the carbon-carbon double bond. However, the steric effect of a substituent so remote from the double bond as the methyl groups was observed to be in accordance with the conformation given in Fig. 1.

In connection to this low ceiling temperature, it was also found by thermogravimetric analysis that poly(DMPM) degraded to DMPM monomer with greater facility than poly(PMA) to PMA or poly(MMA) to MMA monomer. Thermogravimetric curves are shown in Fig. 3. These findings seem to be due to steric crowding of the methyl groups between adjacent DMPM monomer units along the main polymer chain.

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