Polymerization of Methyl Acrylate in the Presence of 2-Mercaptobenzothiazole

U. N. DWIVEDI and B. C. MITRA, *Department of Plastics Technology, Harcourt Butler Technological Institute, Kanpur 209002, India*

Synopsis

Azobisisobutylronitrile-initiated polymerization of methyl acrylate was carried out in a dilatometer at 60°C for 180 min in the presence of 2-mercaptobenzothiazole. The 2-mercaptobenzothiazole acts as a retarder. The values of various kinetic parameters such as rate of polymerization, average degree of polymerization, inhibition constant, and Schulz's constant have been calculated for the present system.

INTRODUCTION

Kar[1] studied the effect of Methylene Blue on the polymerization of acrylic monomer. Foord[2] and later Schulz[3] reported the effect of nitrocompounds on the polymerization of styrene. Srivastava[4,5] has reported the effect of Methylene Blue and Crystal Violet on the kinetics of polymerization of styrene and methyl methacrylate, respectively. The interest in the present investigation is to find additives which will control the rate of polymerization and the molecular weight of the polymer in the bulk polymerization of methyl acrylate, where autoacceleration from the start of the polymerization creates heat transfer problems because of a sudden virulent increase in the rate and degree of polymerization.

EXPERIMENTAL

The monomer was washed by the standard method. The initiator azobisisobutyronitrile (AIBN) was recrystallized twice with ethanol. The 2-mercaptobenzothiazole (BDH grade) was used as such. The reaction was carried out for 180 min at 60°C using a dilatometer, which was degassed by a successive freezing–thawing cycle and sealed under vacuum of about 10^{-4} mm Hg. The polymer was precipitated and dried to a constant weight. The rate of polymerization (R_p) was calculated with the help of the following formula:[4]

$$R_p = \frac{1000SM}{60V_s} \tag{1}$$

where S is the slope of volume contraction versus time plot, M refers to the mole of monomer polymerized per centimeter contraction, and V_s is the volume of solution.

A plot of $1/R_p$ versus polymerization time was linear. The slope and intercept of the plot were used to calculate the rate of initiation (R_i) using the following formula:[5]

Journal of Applied Polymer Science, Vol. 29, 4199–4201 (1984)
 CCC 0021-8995/84/124199-03$04.00

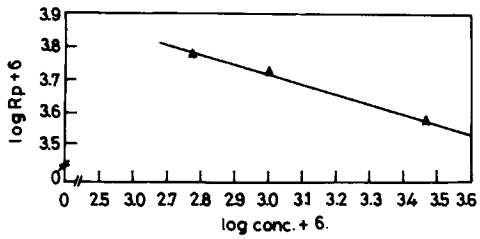

Fig. 1. Relationship between rate of polymerization and concentration of 2-mercaptobenzothiazole. MA = 10.93 mol/L, AIBN = 1.08 × 10 mol/L, time = 180 min, T = 60°C.

$$\frac{\text{slope}}{\text{intercept}} = \frac{R_i}{\text{retarder}} \tag{2}$$

The viscosity of the polymer was determined by using the Ubbelohde viscometer with benzene solvent at 30°C. The average degree of polymerization ($\bar{p}_n$) was calculated with the help of the following formula:[6]

$$\eta_{\text{int}} = 12.8 \times 10^{-3}\, \bar{p}_n^{0.71} \tag{3}$$

The value of the inhibition constant (K_z) was calculated by determining the value of K_z/K_p using the method given by Melville[7] since the value[8] of K_p was taken as 2090 mol/s. The value of Schulz's constant was calculated with the help of the following equation:[9]

$$Q_r = \frac{\text{retarded rate of polymerization}}{\text{unretarded rate of polymerization}} \tag{4}$$

RESULTS AND DISCUSSION

The effect of 2-mercaptobenzothiazole (Mz) on polymerization of methyl acrylate was studied by varying its concentration from 5.91 × 10^{-4} to 29.55 × 10^{-4} mol L^{-1} keeping the concentrations of methyl acrylate and AIBN constant. The R_p was found to be 14.2 × 10^{-3} mol L^{-1} s^{-1} in the absence of Mz. However, when 5.91 × 10^{-4} mol L^{-1} of Mz was added, no polymerization occurred up to 90 min. The R_p was found to be 1.15 × 10^{-4} after 100 min and, finally, 6.05 × 10^{-4} after 180 min. This shows that Mz acts as a retarder. When the concentration of Mz was increased further by two and five times, the R_p further reduced to 5.42 × 10^{-4} and 3.86 × 10^{-4} mol L^{-1} s^{-1}.

TABLE I
Effect of 2-Mercaptobenzothiazole on Rate of Polymerization[a]

Concn. × 10^4	$R_p \times 10^3$ (mol L^{-1} s^{-1})				
	100 min	120 min	140 min	160 min	180 min
5.91	1.15	2.288	3.52	4.57	6.05
11.82	—	1.15	2.46	3.60	5.42
29.55	—	—	1.14	2.37	3.86

[a] Temperature = 60°C, MA = 10.93 mol/L, AIBN = 1.08 × 10^{-2} mol/L.

TABLE II
Various Constants of Polymerization of Methyl Acrylate in Presence of 2-Mercaptobenzothiazole[a]

k_z/K_p	$K_z \times 10^4$	$R_i \times 10^4$	$Q_r \times 10^5$	$\bar{p}_n \times {}^{-4}$
0.753	3.12	0.018	3.89	17.25
0.601	2.51	0.016	3.49	14.06
0.386	1.59	0.011	2.41	12.70

[a] Temperature = 60°C, time = 180 min, $R_{p0} = 14.2 \times 10^{-3}$ mol L^{-1} s^{-1}.

A graph (Fig. 1) of log R_p versus log [Mz] is linear, the slope of which gave the following quantitative relationship:

$$1/R_p \partial \text{Mz}^{0.30}$$

An examination of Table I also shows that R_p increases with time. This is because of consumption of retarder with time.

The retarding effect of Mz may be due to either a decrease of the rate of initiation (R_i) or an increase of the rate of termination (R_t). The effect of Mz on R_t was studied by plotting a graph between R_p/R_{p0} (where R_p and R_{p0} are the rate of polymerization in the presence and absence of Mz, respectively) and $\sqrt{\eta}_{\text{int}}/\sqrt{\eta}_{0,\text{int}}$ (where, η_{int} and $\eta_{0,\text{int}}$ are the intrinsic viscosity of the polymer prepared in the presence and absence of Mz, respectively) when no straight line was observed. This shows that R_t is independent of Mz. A study of Table II shows that Mz decreases R_i. When concentration of Mz is increased from 5.91×10^{-4} to 29.55×10^{-4} mol L^{-1} the R_i decreased from 0.018×10^{-4} to 0.01×10^{-4} mol L^{-1} s^{-1}. Thus, it can be concluded that the retarding effect of Mz is due to the decrease of R_i. An examination of Table II also reveals that inhibition constant (K_z), Schulz's constant (Q_r), as well as the degree of polymerization ($\bar{p}_n$), also decrease with an increase of the concentration of Mz. The effect of Mz on $\bar{p}_n$ may be attributed to chain transfer reaction. The present study, therefore, reveals that Mz acts as a retarder for this system and on increasing the amount of this retarder the R_p value decreases. The effect is due to the decrease of R_i and not the increase of R_t. On the other hand, this retarder could not affect the autoacceleration.

References

1. I. Kar, B. M. Mandal, and S. R. Palit, *Makromol. Chem.*, **127**, 195 (1969).
2. S. G. Foord, *J. Chem. Soc.*, 48, (1940).
3. G. V. Schulz and H. Karmerer, *Chem. Ber.*, **80**, 237 (1947).
4. A. K. Srivastava, P. K. Misra, and G. N. Mathur, *Indian J. Chem. A*, **21**, 303 (1982).
5. A. K. Srivastava, J. S. P. Rai, and G. N. Mathur, *Curr. Sci.*, **51**(7), 352 (1982).
6. M. S. Matheson, E. E. Aver, E. B. Belvilaaqua, and R. J. Hart, *J. Am. Chem. Soc.*, **71**, 2610 (1949).
7. H. W. Melville and W. F. Watson, *Trans. Faraday Soc.*, **44**, 886 (1948).
8. N. Fahrman and R. B. Mesrobian, *J. Am. Chem. Soc.* **76**, 3281 (1954).
9. *Encyclopedia of Polymer Science and Technology*, Interscience New York, 1967, Vol. 7, p. 646.

Received October 14, 1982
Accepted March 6, 1984
Corrected proofs received November 5, 1984