Popcorn Polymerization
7. Study on Popcorn Polymerization of Methyl Methacrylate by Differential Scanning Calorimeter

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Summary
        The popcorn polymerization of methyl methacrylate (MMA) by
use of the styrene popcorn polymer as a seed material was carri-
ed out by differential scanning calorimetry (DSC), and the
possibility of the kinetic study was investigated. As the result,
this process may be represented by the following equation:

$$\frac{[P\cdot] d[P\cdot]}{d\,x} = k[\text{Seed}]$$

where $[P\cdot]$ is the concentration of radicals, x is the fractional
conversion of MMA, k is a constant, and [Seed] is the amount of
seed.
        The proof for this equation was confirmed from measurements
of both ESR and DSC.

Introduction
        Styrene popcorn polymer is obtained by adding a very small
amount of divinylbenzene to the polymerization system of styrene
in the absence of the catalyst (radical or ionic initiator).
This styrene popcorn polymer is insoluble in almost organic sol-
vent, and has low swelling capacity. It differs from the usual
glassy polymer-gels (IMMERGUT 1953). A small amount of obtained
popcorn polymer has the activity of the seed and the ability of
popcorn polymer-formation of other vinyl monomer, e.g., MMA.
        Recently, we have reported the popcorn polymerization of
MMA initiated with styrene-divinylbenzene system popcorn polymer
(TATSUMI et al. 1982). The popcorn polymerization is a heteroge-
neous process in which polymer forms discrete particles insolu-
ble in the monomer. Because of the high rate of the polymeriza-
tion and a sudden acceleration in the rate, it is difficult to
follow the kinetic behaviors for the popcorn polymerization.
        In this paper, the popcorn polymerization of MMA by using
styrene popcorn polymer as the seed material was carried out by
DSC, and the possibility of the kinetic study was investigated.

Experimental
        Material   Styrene popcorn polymer was prepared by the spon-
taneous polymerization of styrene with 0.23 mol% divinylbenzene
at 55°C. The product was obtained in an almost 100% yield. Sty-
rene popcorn polymer without any treatment showed weak ESR sig-
nal, but after thorough washing with methanol, the signal dis-
appeared. Styrene popcorn polymer used in this reaction was what
showed no ESR signal.

MMA and 2,2´-azobisisobutyronitrile (AIBN) were purified by conventional method.

Procedure   MMA was popcorn polymerized with styrene popcorn polymer and 0.01 mol/l of AIBN in bulk polymerization at 80°C. The apparatus used was a differential scanning calorimeter DSC-30 (Shimadzu, Japan). The popcorn polymerization of MMA was carried out in a sealed aluminium pan. The areas between the curve and the baseline in DSC thermograms were measured planimetrically. From these areas, the heat of polymerization was calculated. To the heat, the heat of polymerization corresponding to that of the residual monomer was added, the sum was regarded as the total heat of reaction. The residual monomer content was determined calorimetrically at rising temperature scanning. After each isothermal polymerization the sample was heated from 50 to 180°C at a heating rate of 10°C/min. The rate of polymerization was calculated from DSC thermograms by using the data of the heat of polymerization of MMA (54.8 KJ) (HORI et al. 1968). The popcorn polymerization of MMA in an ampoules was also examined independently.
      ESR measurements were made by use of a JOEL JES, FE-1X spectrometer with an x-band microwave bridge with 100 KHz field modulation.

Results and Discussion
      In an ampoule, 5 ml MMA in the presence of 0.2 g styrene popcorn polymer seed was almost converted into its popcorn polymer without any added initiator after 24 h at 40°C. In a pan used for DSC measurement, MMA popcorn polymer was not obtained in the presence of the seed, though heating at 80°C, but it was obtained by the further addition of AIBN more than 10^{-3} mol/l to this system.
      So the popcorn polymerization of MMA was carried out isothermally at 80°C with styrene popcorn polymer and 0.01 mol/l of AIBN. DSC curves obtained in this polymerization are shown in Fig. 1. The conversion shown in Fig. 1 was calculated as a fraction of the heat of polymerization at the isothermal run to the sum of heats at the isothermal and rising temperature runs. A
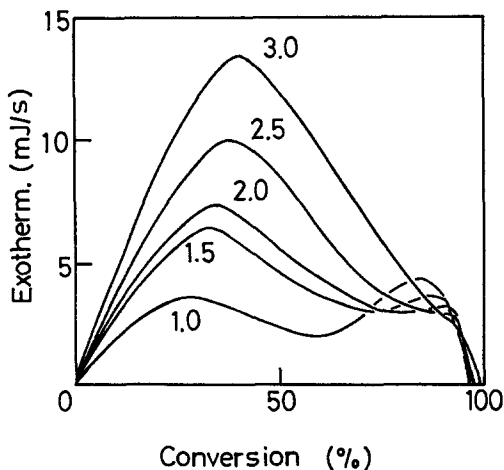

Fig. 1. DSC curves for the popcorn polymerization of MMA by using styrene popcorn polymer seed at 80°C: MMA 10 mg, AIBN 0.01 mol/l. Amounts of seed (mg) are indicated beside the curves.

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remarked autoacceleration effect was observed as two peaks in the course of polymerization. In order to examine the autoacceleration effect of the first peak, the ratio of the heat of polymerization of this peak to the total heat of polymerization of MMA was calculated from the area of DSC curve shown in Fig. 1. Relationship between the percentages of the heat of polymerization of the first peak and the amounts of the seed is shown in Fig. 2. The heat of polymerization of the first peak is dependent on the amount of seed regardless of the concentration of AIBN. But the autoacceleration effect seems to be essentially different from that of the second peak. The autoacceleration effect of the second peak is due to the gel effect in bulk polymerization of MMA.
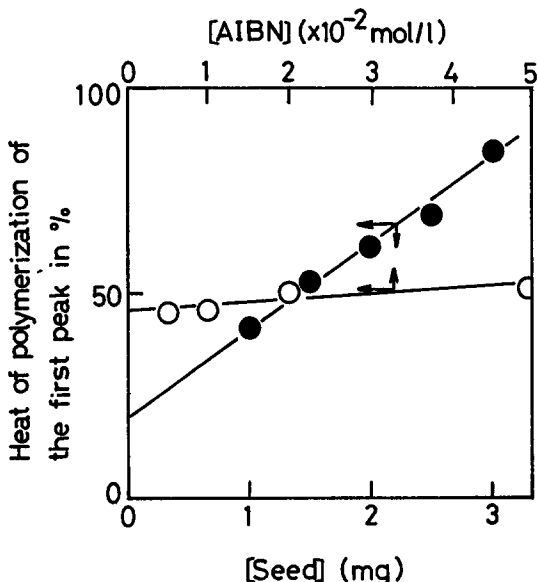

Fig. 2. Relationship between the percentages of the heat of polymerization of the first peak as shown in Fig. 1 and both amounts of seed and concentration of AIBN.

The ESR spectra of popcorn polymerization of MMA under the same conditions as those of experiment by DSC were observed. The ESR signal obtained from the growing seed was a spectrum consisting of 5+4 lines spread over a region of 100 gauss. This spectrum was identical with ESR spectrum obtained from the copolymer of MMA with 40% glycol dimethacrylate (ATHERTON et al. 1959). Consequently, the signal observed in the growing popcorn polymer is thought to be propagation chain radical of MMA. The magnitude of change in the ESR signal was dependent on the rate of popcorn polymerization obtained from the experiment by DSC. The propagation radical chain trapped inside of popcorn seed is difficult to termination, and propagates itself indefinitely. If it will be assumed that these lead to the autoaccelerating effect of the first peak in the course of polymerization, the following expression may be enabled. Let the number of trapped radicals per unit weight of the seed increase in proportion to the conversion of formed MMA popcorn polymer as a first approximation.
Then,

$$\frac{[P\cdot]d[P\cdot]}{d\,x} = k_1[Seed] \tag{1}$$

where $[P\cdot]$ is the concentration of radicals trapped in the seed, x is the fractional conversion of MMA, k_1 is a constant, and [Seed] is the amount of seed.

In the initial stage of polymerization, integration of eq. (1) leads to

$$\left(\frac{[P\cdot]}{[P\cdot]_0}\right)^2 - 1 = 2k_1\frac{[Seed]}{[P\cdot]_0^2}x \tag{2}$$

where $[P\cdot]_0$ is the concentration of radical initiated by AIBN in monomer, and approximately satisfies $[P\cdot]_0 = (R_i/k_t)^{1/2}$ where R_i is the rate of initiation, and k_t is the rate constant of termination.

It may be fully considered that monomer concentration is constant in the vicinity of the radicals, and the polymerization rate is proportion to $[P\cdot]$. Then eq. (2) can be rewritten by

$$\left(\frac{R_x}{R_0}\right)^2 - 1 = k_2x \tag{3}$$

where R_x is the rate at conversion x, and R_0 is the initial rate of polymerization. Further, k_2 is a constant containing the amount of seed and the concentration of AIBN as parameter in the following eq. (4):

$$k_2 = k_1\frac{k_t}{k_d}\frac{[Seed]}{[AIBN]} \tag{4}$$

where k_d is the rate constant of the thermal decomposition of AIBN.

It is possible to determine k_2 from experiment as follows. From eq. (3), the plot of $(R_x/R_0)^2$ over the first peak of the DSC curve can be seen to be linear. The all experimental results satisfy this relationship for the popcorn polymerization of MMA. These data are recorded in Fig. 3 and 4. The values of k_2 are obtained from the slops in the these figures. The value of k_2 against [Seed] and $[AIBN]^{-1}$, respectively, should give linear plots as long as eq. (4) hold. As shown in Fig. 5, straight
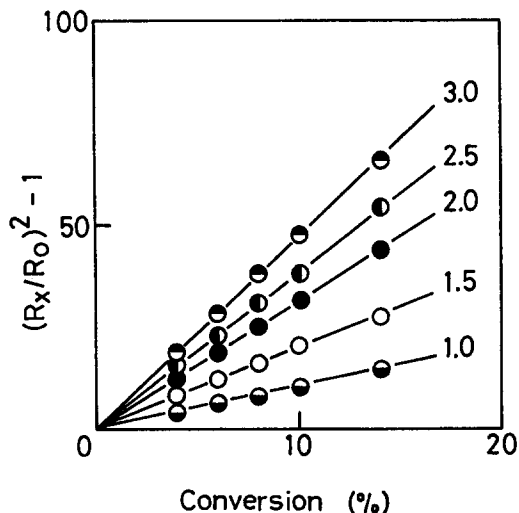

Fig. 3. Relationship between $(R_x/R_0)^2 - 1$ and conversion as a function parameter of amounts of seed (mg) as indicated: MMA 10 mg, AIBN 0.01mol/l.
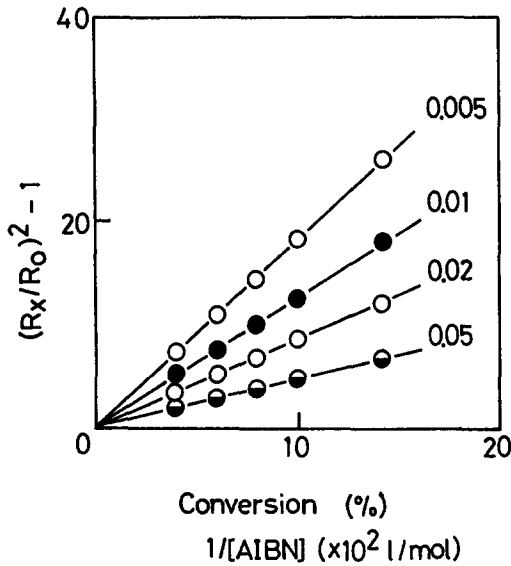
Fig. 4. Relationship between $(R_x/R_0)^2 - 1$ and conversion as a function parameter of concentration of AIBN (mol/l) as indicated: MMA 10 mg, Seed 2 mg.
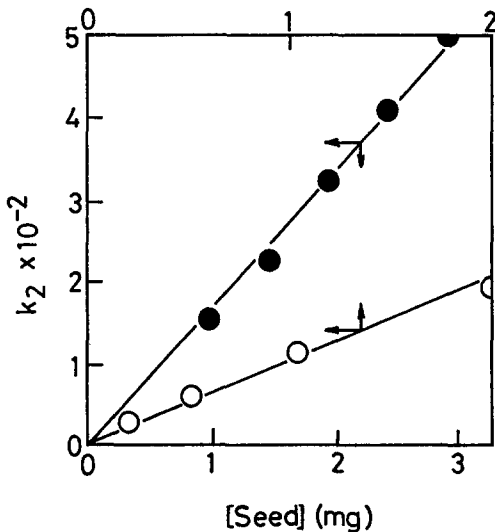

Fig. 5. Relationship between values of k_2 shown in eq. (4) and both amounts of seed and concentration of AIBN.

lines are obtained.

The popcorn polymerization of MMA in DSC was carried out with 2 mg styrene popcorn polymer group obtained by changing divinylbenzene in the range of 0.05 to 0.5 mol% and 0.01 mol/l of AIBN. Consequently, the activity of the seed (k_2-value) in Fig. 6 corresponded to the number of trapped poly(methyl methacrylate) radical in the system.

From the above results, it can be considered that the auto-acceleration effect observed in the initial stage of polymerization is related to the popcorn polymer-formation of MMA in the system as seen from eq. (1). And, it was found that DSC method has enabled the kinetic study of the popcorn polymerization of MMA by use of the popcorn polymer seed.
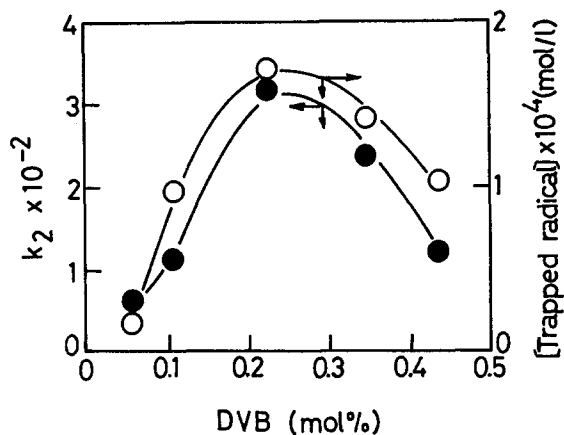
Fig. 6. Values of k_2 obtained from DSC measurments by using styrene popcorn polymer seed prepared by various concentration of divinylbenzene (DVB) and the number of trapped poly(methyl methacrylate) radicals in the system: MMA 10 mg, Seed 2 mg, AIBN 0.01 mol/l.

References

Immergut, E.H.: Makromol. Chem. 10, 193 (1953)
Tatsumi, M. and Yamamoto, S.: J. Chem. Soc. Jpn. 1982, 1386
Hori, K., Mita, I. and Kambe, H.: J. Polym. Sci. A-1 6, 2663 (1968)
Atherton, N.M., Melvlle, D.H. and Whiffen, D.H.: J. Polym. Sci. 34, 199 (1959)

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