

Preparation of High Molecular Weight Poly(methyl methacrylate) with High Yield by Room Temperature Suspension Polymerization of Methyl Methacrylate

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Abstract: To obtain high molecular weight (HMW) poly(methyl methacrylate) (PMMA) with high conversion, methyl methacrylate (MMA) was polymerized in suspension using a room temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN), and the effects of polymerization conditions on the polymerization behavior of MMA and the molecular parameters of PMMA were investigated. On the whole, the experimental results well corresponded to the theoretically predicted tendencies. These effects could be explained by a kinetic order of ADMVN concentration calculated by an initial rate method and an activation energy difference of polymerization obtained from the Arrhenius plot. Suspension polymerization at 25 °C by adopting ADMVN proved to be successful in obtaining PMMA of HMW (number-average degree of polymerization (P_n): 30,900-36,100) and of high yield (ultimate conversion of MMA into PMMA: 83-93 %) with diminishing heat generated during polymerization. The P_n and lightness were higher and polydispersity index was lower with PMMA polymerized at lower temperatures.

Keywords: HMW PMMA, High conversion, MMA, Suspension polymerization, ADMVN

Introduction

Poly(methyl methacrylate) (PMMA) has very interesting features, such as outstanding water-clear color, stability of properties upon severe conditions, high surface resistivity, and resistance to weathering and moisture. Due to these superior characteristics, PMMA has been widely used as sizer, additive, coating and polishing agents, binder, sealer, transparent neutron stopper, optical fiber, high voltage application, and outdoor electrical application [1,2]. To enhance these properties, it is essential to achieve high molecular weight (HMW) and superior molecular structure, namely minimum quantity of branches. In particular, to increase the molecular weight which is fundamental factor affecting physical properties, improvement of polymerization methods of methyl methacrylate (MMA) is necessary. Furthermore, it has been reported that bulk polymerization of MMA leads to rapid acceleration in the rate and the formation of a network polymer even at low conversion. The formation of a network polymer is considered to occur by a chain transfer mechanism. Thus HMW PMMA of structural superiority has been prepared only by special polymerization methods.

In general, four polymerization methods of MMA (bulk, solution, emulsion, and suspension) have been known. In bulk polymerization [3], HMW PMMA can be obtained but the increased polymerization rate arising from the higher

polymerization heat results in a side reaction and it is difficult to control the viscosity of the reaction mixture. Thus, HMW PMMA with high yield is hardly prepared. To reduce the polymerization heat and the viscosity of the medium, solution polymerization of MMA was tried. However, branch formation caused by frequent chain transfer reactions to monomer makes it unfavorable to obtain HMW PMMA with the conversion over 40-50 % owing to the high viscosity of the reaction solution.

Radical polymerization shows more tolerance to water, compared with the ionic counterparts. Therefore, suspension, emulsion, and dispersion processes in aqueous or alcoholic media are widely employed in radical polymerization [4]. It was known that molecular weight and polymerization rate were increased simultaneously by emulsion polymerization of MMA. However, it is difficult to rule out side chain formation reaction. Until now, in these polymerization methods described above, HMW PMMA can be prepared only by the use of special initiation system or ultraviolet ray radiation methods accompanied by a complicated polymerization apparatus.

The mechanism of suspension polymerization in the droplet is basically identical to that of bulk polymerization and water used as a reaction medium minimizes exotherm and viscosity enhancement generated during polymerization [4]. Owing to these advantages, suspension polymerizations of MMA has a possibility of producing HMW PMMA with high conversion. There have been many researches on the

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suspension and nonaqueous dispersion polymerization methods [5-17]. Especially, suspension polymerization of MMA yields PMMA in the form of tiny beads, which are primarily used as molding powders and ion-exchange resins. The water in suspension polymerization serves as both the dispersion medium and a heat-transfer agent. Until now, suitable protective colloids for the preparation of acrylic suspension polymers include cellulose derivatives, polyacrylate salts, starch, poly(vinyl alcohol), gelatin, talc, clay, and clay derivatives. These materials are added to prevent the monomer droplets from coalescing during polymerization [5,6].

Nonaqueous dispersion polymerizations of MMA have been conducted by several researchers using various diluent systems, including aliphatic hydrocarbon, hexane, and methanol [7-10]. Hsiao *et al.* [11,12] and Lepilleur and Beckman [13] prepared PMMAs of number-average molecular weights (M_n)s of 23,000-339,000 and 52,000-400,000, respectively, by adopting dispersion polymerization of MMA in supercritical carbon dioxide at 65 °C using polymeric stabilizers. Srinivasan *et al.* [14] obtained PMMA of M_n of 13,000-157,000 using dispersion polymerization in hexane at 70 °C. Yildiz and Hazer [15] conducted dispersion copolymerization of MMA and styrene at 50-80 °C using macromonomeric azoinitiator.

Recently, several researchers have been reconsidering suspension polymerization of MMA with an industrial viewpoint. Nishikawa *et al.* [16] conducted living radical suspension polymerization of MMA with ruthenium complex as an initiator. They could prepare PMMA of M_n of about 100,000. Polacco *et al.* [17] have also performed the study on the suspension polymerization of MMA with agarose as suspending agent at 70 °C and measured the particle-size distribution. These polymerizations, however, were conducted at polymerization temperature of over 50 °C. In these cases, molecular weight reduction in PMMA is accelerated inevitably.

In this study, a room-temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN), which can lower the polymerization temperature down to room temperature [18-22] was selected in suspension polymerization of MMA to obtain HMW PMMA with high yield. The effects of polymerization conditions on the polymerization behavior of MMA and molecular parameters of PMMA were investigated.

Experimental

Materials

MMA (Acros Organics, 99 %) was washed with 40 % aqueous solution of sodium bisulfite and water and distilled at reduced pressure. The initiator ADMVN (Wako Co., 99 %) was recrystallized twice from absolute methanol before use. Poly(vinyl alcohol) (PVA) with M_n of 127,000 and degree of saponification of 88 % (Aldrich Co.) was used as a suspending agent. Other extra-pure grade reagents were used without further purification. Water used for total procedures was deionized.

Table 1. Suspension polymerization conditions of MMA

Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration	0.00005 mol/mol of MMA
	0.0001 mol/mol of MMA
	0.0003 mol/mol of MMA
Suspending agent concentration	1 g/dl of water
	2 g/dl of water
	3 g/dl of water
	5 g/dl of water
	7 g/dl of water
MMA/water	0.25 l/l
	0.50 l/l
	0.75 l/l
	1.00 l/l
Rpm	100, 300, 500, 1 000
Temperature	25 °C, 35 °C, 45 °C

Suspension Polymerization of MMA

In a typical reaction, suspending agent was dissolved in water under nitrogen atmosphere and constant stirring in a 250 ml reactor fitted with a condenser. After degassing, MMA monomer along with the ADMVN was added all at once at a fixed polymerization temperature. Completing the polymerization, the reaction mixture was cooled and kept for 1 day to obtain spherical PMMA particles. To eliminate residual MMA and suspending agent, polymerized PMMA was filtered and washed with warm water. Conversions were averages of five determinations. The detailed polymerization conditions are listed in Table 1.

Characterization

The molecular weight of PMMA was calculated by using equation (1) [23].

$$[\eta] = 5.5 \times 10^{-5} [M_n]^{0.76} \text{ (in benzene at 25 °C)} \quad (1)$$

where $[\eta]$ is intrinsic viscosity. Number-average degree of polymerization (P_n) of PMMA was calculated from M_n .

The molecular weight distribution and polydispersity index (weight-average molecular weight (M_w/M_n)) were obtained by gel permeation chromatography (GPC). Waters GPC Model 515 equipped with a band of four Styragel columns using tetrahydrofuran (THF) as an eluent against polystyrene standards. The calculations were based on a calibration curve obtained with 14 polystyrene standards. The calculations were range of 2,500-8,500,000 ($M_w = 2,500; 4,000; 20,000; 35,000; 50,000; 90,000; 200,000; 400,000; 600,000; 1,920,000; 2,000,000; 4,300,000; 8,500,000$) purchased from Aldrich. The molecular weight of the sample is the polystyrene equivalent molecular weight.

Homogeneous 1.0 g/dl solutions PMMAs in THF which

were obtained at polymerization temperatures of 25, 35, and 45 °C were poured onto stainless steel tray and dried at room temperature to produce films. The lightness of the PMMA film was measured by Color eye (I.D.I., model C).

Results and Discussion

Suspension Polymerization Behavior of MMA

In a free radical polymerization, the rate of polymerization (R_p) may be expressed by equation (2) [4].

$$R_p = k_p[M][I]^{0.5}(fk_d/k_t)^{0.5} \quad (2)$$

where f is the initiator efficiency, $[M]$ and $[I]$ are the concentrations of monomer and initiator, and k_d , k_p , and k_t are reaction rate constants of initiator decomposition, propagation and termination, respectively. This expression predicts that the rate of polymerization is increased as the efficiency and concentration of initiator are increased. Figure 1 presents the initial conversion rate measured within 15% conversion in the suspension polymerization of MMA at 25 °C using ADMVN. It was shown that the higher the initiator concentration, the higher the polymerization rate. This tendency agrees with the theoretical prediction in equation (2).

The dependence of polymerization rate on initiator concentration can be determined by the initial-rate method [24]. For small changes in initiator concentration, the polymerization rate can be approximated to the corresponding ratio of increments. If a measurement is made at two different initiator concentrations of one component with the other held constant, the order with respect to that component can

be simply determined by using equations (3)-(9).

$$-(d[M]_1/dt) = (R_p)_1 = k[M]_1^{n_1}[I]_1^{n_2} \quad (3)$$

$$-(d[M]_2/dt) = (R_p)_2 = k[M]_2^{n_1}[I]_2^{n_2} \quad (4)$$

$$-(d[M]_3/dt) = (R_p)_3 = k[M]_3^{n_1}[I]_3^{n_2} \quad (5)$$

$$(R_p)_1/(R_p)_2 = ([I]_1/[I]_2)^{n_{2a}} \quad (6)$$

$$(R_p)_2/(R_p)_3 = ([I]_2/[I]_3)^{n_{2b}} \quad (7)$$

$$(R_p)_3/(R_p)_1 = ([I]_3/[I]_1)^{n_{2c}} \quad (8)$$

$$n_2 = (n_{2a} + n_{2b} + n_{2c})/3 \quad (9)$$

This procedure can be used to determine all exponents like n_1 , n_2 , n_3 . From the calculation, it was found that the suspension polymerization rate of MMA was proportional to the exponent 0.81 of ADMVN concentrations. Some discrepancy appeared between theoretical (0.5) and experimental (0.81) values. This anomaly with respect to normal kinetic behavior is generally accounted for by assuming that the precipitation of the growing polymers severely restrains bimolecular chain termination and hence that the radicals do not reach a stationary concentration.

Figure 2 illustrates conversion-time histories of suspension polymerization for temperature levels of 25, 35, and 45 °C. The rate of conversion was increased with increasing polymerization temperature. Increase of conversion with time was

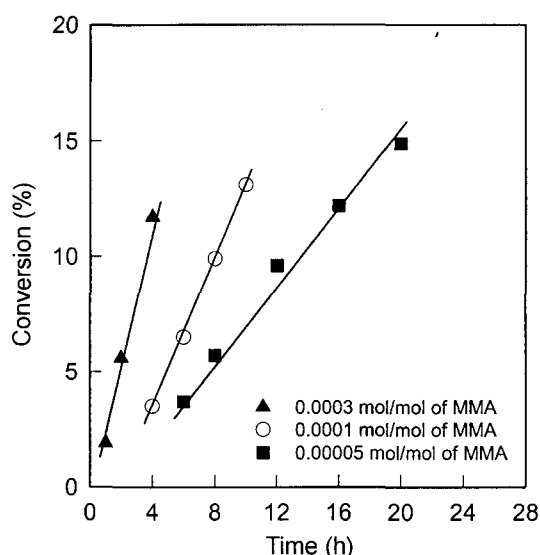


Figure 1. Initial conversion of MMA into PMMA suspension polymerized at 25 °C using suspending agent concentration of 2 g/dl of water, MMA/water of 0.5 l/l, and agitation speed of 300 rpm with polymerization time.

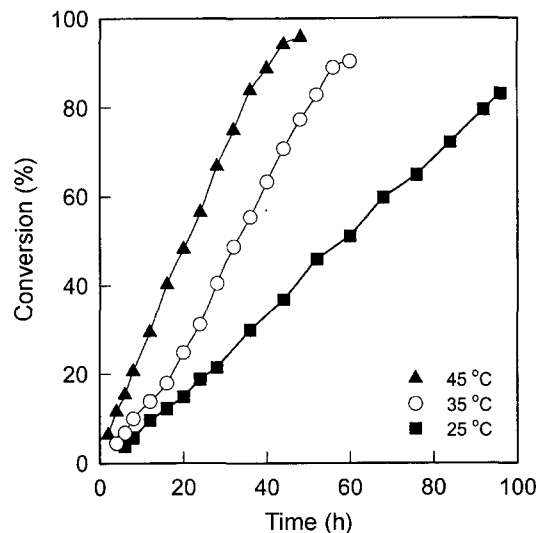


Figure 2. Ultimate conversion of MMA into PMMA suspension polymerized using ADMVN concentration of 0.00005 mol/mol of MMA, suspending agent concentration of 2 g/dl of water, MMA/water of 0.5 l/l, and agitation speed of 300 rpm with polymerization time.

abruptly diminished during polymerization, probably due to the inefficient transfer and diffusion of heat because of the MMA formed at the early stage of polymerization. These features were clearly observed in benzoyl peroxide (BPO)- or azobisisobutyronitrile (AIBN)-initiated free-radical polymerization of MMA above 50 °C. It might be thought that the acceleration in rate is a consequence of diffusion controlled termination reactions in these polymerizations. In contrast, at 25 °C, the conversion was linearly increased without any abrupt changes in the slope. This might be explained by diminishing heat generated during polymerization at lower polymerization temperature by ADMVN. The ultimate conversion of suspension polymerization, the conversions at 25 °C increased linearly up to 83 % in spite of very low ADMVN concentration of 0.00005 mol/mol of MMA, which was absolutely impossible at bulk polymerization. This can be explained by an advantage of precipitation (suspension) polymerization of MMA. Furthermore, autoacceleration described above seems not to be so noticeable in the suspension polymerization of MMA at 25 °C using ADMVN, as shown in Figure 2. This is an indicative of suppression of chain transfer reaction during polymerization. Below ADMVN concentration of 0.00005 mol/mol of MMA, effective suspension polymerization could not occur.

The rate of conversion is increased with an increase in the initiator concentration as depicted by equation (10) [4].

$$P_{eq} = 1 - \exp(-2k_p(f[I]/k_t k_i)^{1/2}) \quad (10)$$

where P_{eq} and k_i are conversion at the equilibrium of polymerization and reaction rate constants of initiation, respectively. Effect of initiator concentration on the conversion of MMA in suspension polymerization at 25 °C is shown in

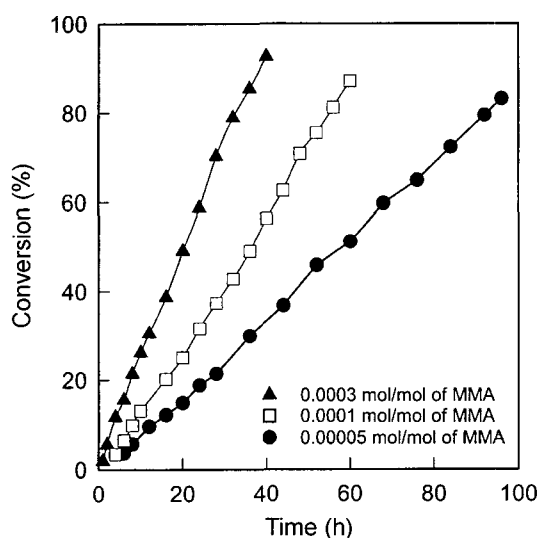


Figure 3. Ultimate conversion of MMA into PMMA suspension polymerized at 25 °C using suspending agent concentration of 2 g/dl of water, MMA/water of 0.5 l/l, and agitation speed of 300 rpm with polymerization time.

Figure 3. The conversion rate was increased as the ADMVN concentration was increased, which were well coincident with the theoretical predictions in equation (10). This is because the extent of retarding polymerization is lower at higher ADMVN concentrations. High ultimate conversions (83-93 %) were obtained at all ADMVN concentrations. This explains the fact that suspension polymerization of 25 °C by ADMVN is a useful one for producing PMMA with high yield.

Effect of Polymerization Conditions on Molecular Parameters

In a free radical polymerization process, the kinetic chain length, ν , is expressed by equation (11) [4].

$$\nu = k_p[M]/2(fk_d k_t [I])^{1/2} \quad (11)$$

Referring to equation (11), the degree of polymerization may be decreased as the efficiency and concentration of initiator are increased. (P_n)s of PMMA polymerized in suspension are shown in Figures 4 and 5. Figure 4 shows temperature effect and Figure 5 shows initiator concentration effect, respectively. In accordance with the predictions by equation (11), P_n of PMMA was increased as initiator concentration was decreased. HMW (PMMA)s having various (P_n)s of 8,000-36,000 could be prepared. It should be noted that PMMA with P_n of up to 36,000 could be prepared from suspension polymerization at 25 °C at conversion of ca. 83 % using minimum ADMVN concentration of 0.00005 mol/mol of MMA. Therefore, it can be concluded that the suspension polymerization of MMA at room temperature using low temperature initiator ADMVN is an effective

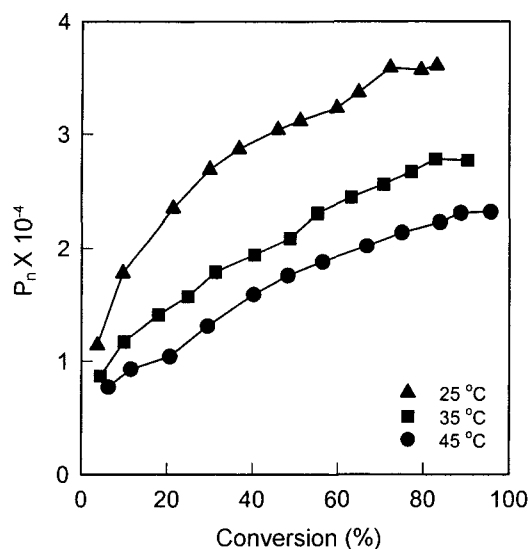


Figure 4. P_n of PMMA obtained by the suspension polymerization using ADMVN concentration of 0.00005 mol/mol of MMA, suspending agent concentration of 2 g/dl of water, MMA/water of 0.5 l/l, and agitation speed of 300 rpm with conversion.

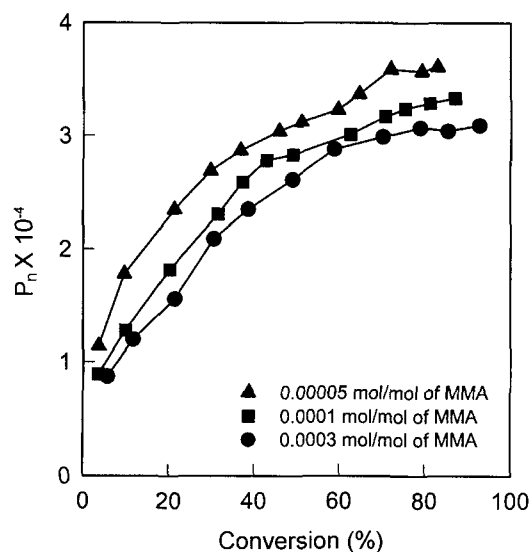


Figure 5. P_n of PMMA obtained by the suspension polymerization at 25 °C using suspending agent concentration of 2 g/dl of water, MMA/water of 0.5 l/l, and agitation speed of 300 rpm with conversion.

method to increase both yield and molecular weight at the same time.

As is well known, molecular weight of polymer prepared by the suspension polymerization method is controlled by the type and amount of initiation and suspending agent, the polymerization temperature, the monomer-to-water ration, and the agitation speed. So, we checked effects of these factors on the molecular weight of PMMA. Figure 6 presents effect of suspension polymerization conditions such as ADMVN concentration, suspending agent concentration, MMA/water ratio, and agitation speed on the molecular weights of PMMA, respectively. PMMA was sampled at similar conversions of about 30 and 60 %, respectively, to precisely clarify effect of polymerization conditions. Figure 6(a) shows effect of concentration of suspending agent. At concentration of 2 g/dl of water, maximum (P_n)s of PMMA (26,900 at 30 % and 32,300 at 60 %) were obtained and this tendency was nearly same irrespective of ADMVN concentration. Below this concentration, suspending agent could not make stable dispersion required for effective suspension polymerization owing to a insufficient concentration. In contrast, at higher concentration of 7 g/dl of water, significant increase of viscosity of polymerization medium made it difficult to agitate the system. From these results, it was found that optimum concentration of suspending agent is about 2 g/dl of water in this polymerization of MMA at 25 °C. Figure 6(b) is plots of P_n of PMMA vs. MMA/water ratio, which show that the lower the value, the higher the molecular weight: maximum (P_n)s of PMMA were 27,500 at 30 % and 32,900 at 60 %. This might be explained by the fact that the lower polymerization, termination, and chain transfer rates by water, which effectively diminishes the high

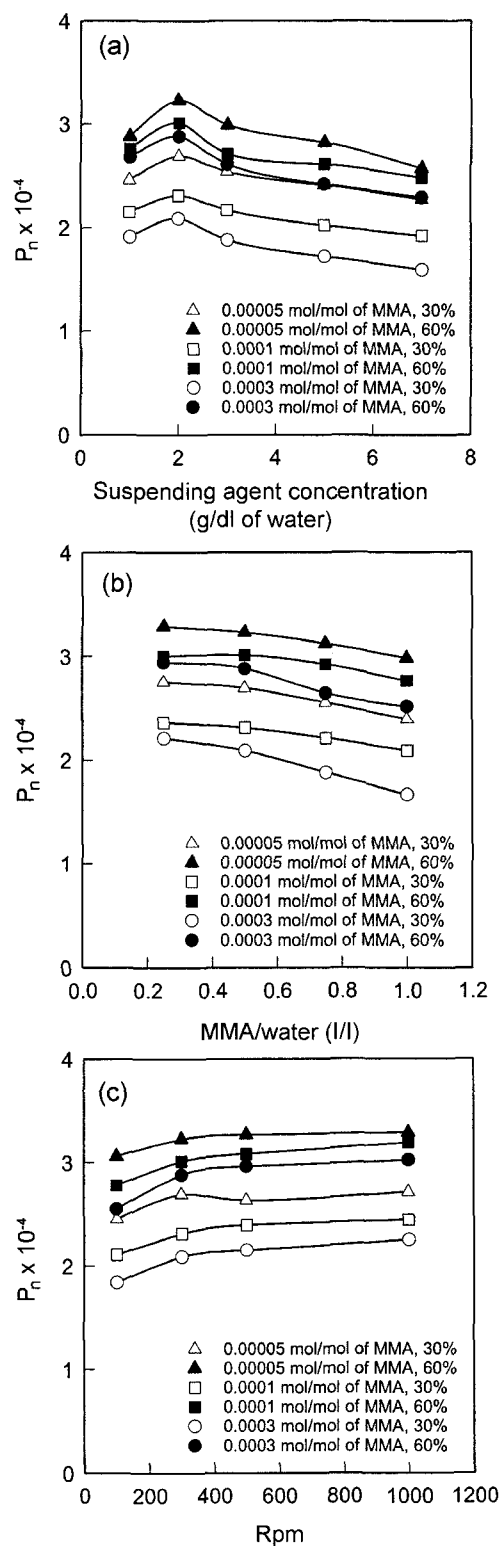


Figure 6. Suspending agent concentration (a), MMA/water (b), and agitation speed (c) dependencies on the P_n of PMMA: a, MMA/water = 0.5 l/l and 300 rpm; b, suspending agent concentration = 2 g/dl of water and 300 rpm; c, suspending agent concentration = 2 g/dl of water and MMA/water = 0.5 l/l.

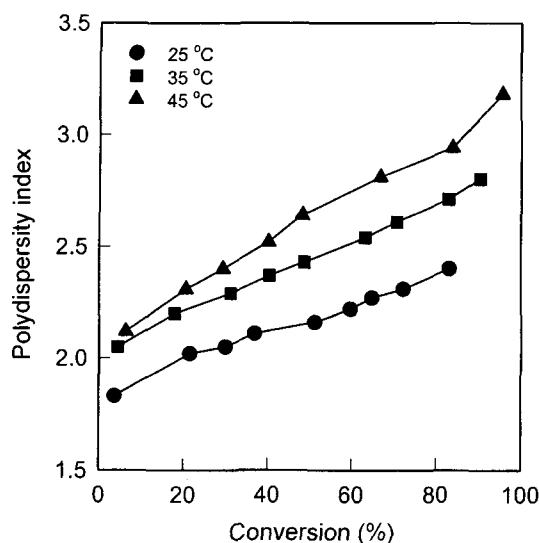


Figure 7. Polydispersity index of PMMA obtained by the suspension polymerization using ADMVN concentration of 0.00005 mol/mol of MMA, suspending agent concentration of 2 g/dl of water, MMA/water of 0.5 l/l, and agitation speed of 300 rpm with conversion.

exotherm of MMA generated during polymerization, increased the linearity and the molecular weight of PMMA. The effect of agitation speed is shown in Figure 6(c). Molecular weight of PMMA increased with the agitation speed. But, over 500 rpm there was no difference in molecular weight.

In this study, to identify the effects of polymerization temperature and conversion on the molecular weight distribution of the PMMA polymerized, the polydispersity index was obtained through GPC experiments. Figure 7 shows results. From the fact that the polydispersity index were lowest at 25 °C, which are 1.8-2.4, it was concluded that room temperature suspension polymerization of MMA produced linear ultra-HMW PMMA with high yield. P_n and polydispersity index of PMMA polymerized at 25 °C in suspension were 31,200 and 2.16 at 51 % conversion and 36,100 and 2.40 at 83 % conversion, respectively.

Optical transparency of PMMA film is a very important factor for numerous applications of PMMA film to optical devices. The molecular structural defects in PMMA molecule seriously influence the color of the polymer, which are incorporated during polymerization by one of the following reactions: chain transfer, initiation, or termination. Especially, termination by disproportionation is known to increase with an increase in the polymerization temperature. Thus, in this study, optical turbidity of PMMA polymerized was checked. Figure 8 shows effects of conversion and polymerization temperature of MMA on the degree of lightness of resulting PMMA film. The lightness of the PMMA film obtained at lower polymerization temperature and lower conversion was higher than that at higher ones. This may be explained by the

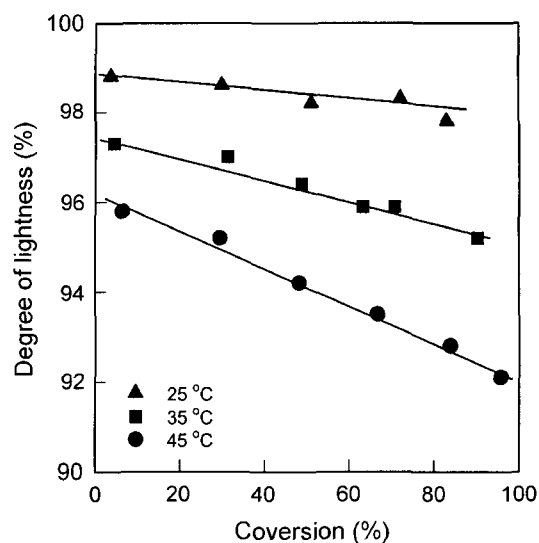


Figure 8. Lightness of the films of PMMA obtained by the suspension polymerization using ADMVN concentration of 0.00005 mol/mol of MMA, suspending agent concentration of 2 g/dl of water, MMA/water of 0.5 l/l, and agitation speed of 300 rpm with conversion.

fact that the amount of side reactions like chain transfer was diminished by the polymerization of MMA at lower temperature, and the polymerization of MMA is largely terminated by recombination rather than by disproportionation at lower temperature.

Conclusions

As is well known, it is not an easy job to obtain HMW PMMA with high conversion and with low polydispersity index by free radical polymerization initiated with AIBN or BPO in bulk because of polymerization exotherm and chain branching during polymerization of MMA. However, a low-temperature initiator, ADMVN seems to be advantageous in suppressing chain transfer reaction because it can lower polymerization temperature down to *ca.* 25 °C. Hence, ADMVN is more effective in preparing HMW PMMA with less branches. Furthermore, suspension polymerization is a powerful method for enhancing conversion.

Through a series of calculation using initial-rate method, it was found that the suspension polymerization rate of MMA at 25 °C was proportional to the exponent 0.81 of ADMVN concentrations.

By suspension polymerization of MMA at 25 °C by ADMVN, HMW PMMA with P_n of 30,900-36,100 and with maximum conversion of MMA into PMMA of 83-93 % was produced. The P_n and lightness were higher and polydispersity index was lower with PMMA polymerized at lower temperatures. Conclusively, this suspension polymerization is expected to be an easy way of producing HMW PMMA with high yield

by simple chemical initiation without using special devices such as irradiation. It is expected that these HMW PMMA microspheres can be used as a spacer material for liquid crystal display. In the near future, we will report on the low-temperature suspension polymerization of MMA using special initiation system for producing HMW stereoregular PMMA with high yield.

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