Suspension Polymerization and Characterization of Transparent Poly(methyl methacrylate-co-isobornyl methacrylate)

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Abstract: A methacrylate copolymer based on isobornyl methacrylate (IBMA) and methyl methacrylate (MMA) was synthesized in an aqueous suspension via free-radical polymerization. The potential of this copolymer as a heat-resistant optical polymer is also discussed. 1,1,3,3-tetramethylbutyl peroxy-2-ethyl hexanoate and n-octyl mercaptan were used as the initiator and chain transfer agents, respectively. The effect of IBMA on the properties of the copolymer was investigated. The composition of the copolymer was analyzed using ^{1}H-NMR, and the heat resistance by measuring the glass transition temperature, which exhibited a linear dependency on the IBMA content in the copolymer. Variation of the chain transfer content used in the synthesis step was effective for the optimization of the copolymer for practical use.

Keywords: polymer synthesis, suspension polymerization, heat resistant, transparent copolymer, isobornyl methacrylate.

Introduction

Poly(methyl methacrylate) (PMMA) has been highly attractive as a transparent polymer due to its excellent transparency, weather resistance and low birefringence.[1,2] It has been already commercially deployed as a light guiding plate in liquid crystal display (LCD) and also widely investigated for other possible optical applications.[3-7]

However, conventional PMMA has relatively low glass transition temperature (T_g) which significantly restricts its possible applications as an optical material when heat resistance is required such as optical lenses and diffusing sheet for LCD TV backlight.[8,9] Thus, it is crucial to improve heat resistance of PMMA without damaging its own advantages. One of the most effective ways to achieve this goal is to copolymerize MMA with other monomer such as N-substituted maleimide which has been extensively studied as a comonomer to increase T_g.[10-13] Enhancement of heat resistance of the copolymers synthesized by MMA and N-substituted maleimide was mostly attributed to their rigid and bulky substituents in the structure. However, residual N-substituted maleimide after reaction brought coloration of the copolymer at high temperature which is highly undesirable.[12]

After the recent success of commercialization of the high pure grade PMMA via suspension polymerization (HP02, LG MMA Corp.), isobornyl methacrylate (IBMA) has been considered to be a potential candidate as a comonomer for heat-resistant polymer using conventional polymerization system. IBMA has hydrophobic bulky bicyclic isobornyl groups which can improve thermal property when copolymerized. Moreover, its refractive index is similar to that of MMA and it prevents from lowering transparency due to optical inhomogeneity.[14] In spite of expected advantages, few studies are reported on the copolymerization of MMA with IBMA employing suspension polymerization for a heat-resistant transparent polymer. In this paper, we report the result for suspension copolymerization of MMA and IBMA.

Experimental

Materials. MMA (LG MMA Corp., reagent grade) and IBMA (Aldrich) containing 150 ppm of p-methoxyphenol (MEHQ) were used as received. 1,1,3,3-tetramethylbutyl peroxy-2-ethyl hexanoate (TMPO, purity 70%, Akzo Nobel) was used as an initiator and n-octyl mercaptan (NOM, Aldrich) as chain transfer agent as purchased. Suspension stabilizer was sodium salt of methacrylic acid-methacrylic ester copolymer (0.02 wt%) and pH of the aqueous medium was set to 7.4 by the buffer salts.

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Copolymerization Procedure. Copolymer of MMA and IBMA was prepared by suspension polymerization in four-necked, round bottom flask equipped with a reflux condenser, a nitrogen gas inlet, and a thermometer. Weight ratio of the continuous aqueous phase to the dispersed organic phase was fixed to 2:1 in this experiment. In monomer phase, initiator and chain transfer agent were dissolved. After the introduction of the aqueous medium and monomer phase, the assembly was placed in a thermostatted water bath (80 °C), followed by stirring with a mechanical stirrer (600 rpm). The reaction was carried out for 2.5 h followed by cooling down to room temperature. The copolymer beads were isolated by filtration, washed with double distilled water and dried at 40 °C for 24 h.

In order to characterize the properties of the beads, 10 g of beads were dissolved in THF and precipitated into the excess of methanol. Final product was fully dried in vacuum for 48 h.

Characterization. Molecular weight and polydispersity of poly(MMA-co-IBMA) were measured by GPC (Waters 600) with a Millenium 2010 chromatography manager equipped with four Waters Styragel columns of HR 1, HR 2, HR 4, and HR 5. The eluent (THF) was used with a flow rate of 1.0 mL/min. PMMA standards with narrow molar mass distribution were used for calibration.

^{1}H-NMR spectra of copolymers were obtained by using 600 MHz NMR spectrometer (DMX-600, Bruker) which was dissolved in about 8 wt% solutions of CDCl$_3$. The internal reference standard of the measurement was tetramethylsiloxane (TMS).

Differential scanning calorimetry (DSC) was carried out to determine T_g of samples with a Perkin Elmer Pyris 6 DSC instrument. Samples were loaded in hermetically sealed cells. Differential calorimetric data were collected in a temperature range of 20 to 180 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Decomposition temperature (T_d) was determined by thermogravimetric analyzer (TGA). The analysis was conducted with Perkin Elmer Pyris 6 TGA at a heating rate of 20 °C/min from 30 to 500 °C. T_d was estimated by the first derivatives of weight loss with temperature.

Size of the particles was measured by a Malvern Mastersizer 2000 apparatus and their image was observed by an optical microscope (DMR, Leica).

Processability of copolymer was evaluated by a melt flow index (MFI) using melt indexer F-B01 (Toyoseiki). Total weight (g) of the molten polymer flowed for ten minute under the external shear force of 3.8 kg at 230 °C was measured.

Results and Discussion

Synthesis of MMA/IBMA Copolymers. To investigate the effects of copolymer composition and reaction conditions on polymer properties for corresponding applications, copolymerizations were performed. The reaction conditions and characterization of the resulting copolymers are summarized in Table I.

Temperature profile of the reaction media was observed during the reaction. About 90 min from the beginning of the reaction, peak evolution due to the abrupt increase of the reaction temperature was detected (Figure 1). Since viscosity of the dispersed monomer droplets increases with polymerization of monomers, the accumulated heat at certain conversion level due to the increased viscosity accelerated the reaction where conversion reached almost completion. Dispersed organic phase changed to hard bead and it was free from coagulation at the end of peak evolution in the temperature profile.[15,16] However, terpolymer designated M-I-S (MMA 60 wt%, IBMA 20 wt%, styrene 20 wt%) showed longer reaction time to reach peak evolution than that of M-I series. This phenomena seems to indicate slow copolymer-

Table I. Feed Ratio and Characterization of Poly(MMA-co-IBMA)^a

Polymer code^b	f_M/f_I^c	F_M/F_I^d	$10^{-3} M_n$	M_w/M_n	T_g (°C)	T_d (°C)^e
M-I05	97.7/2.3	97.9/2.1	97	1.69	120.5	307.1
M-I15	92.6/7.4	93.0/7.0	108	1.50	124.9	304.4
M-I25	87.0/13.0	86.9/13.1	99	1.65	128.4	298.7
M-I40	76.9/23.1	77.8/22.2	115	1.68	131.9	285.8
M-I-S^f	68.0/10.2/21.8	61.3/11.9/26.8	118	1.76	119.0	346.0
M-IC2	87.0/13.0	87.3/12.7	127	1.71	128.2	303.7
M-IC4	87.0/13.0	87.0/13.0	73	1.60	127.6	303.3
M-IC5	87.0/13.0	87.1/12.9	62	1.51	127.3	303.0
M-M	100.0/0	100.0/0	103	1.59	119.3	333.9

^{a}Initiator concentration is set to 0.3 part based on the total monomer weight as 100 part. ^{b}M-IX: M-I represents poly(MMA-co-IBMA), X is feed wt% of IBMA. M-ICx: C stands for chain transfer agent with 0.x part. ^{c}Mol% ratio of the feed composition where M is MMA and I is IBMA respectively. ^{d}Mol% ratio of MMA and IBMA in the copolymer calculated from the ^{1}H-NMR spectrum. ^{e}Degradation temperature measured by peak temperature of the first derivative of the mass loss with the temperature on the TGA thermogram. ^{f}Feed ratio of the reactant is MMA (60 wt%), IBMA (40 wt%), and styrene (20 wt%).
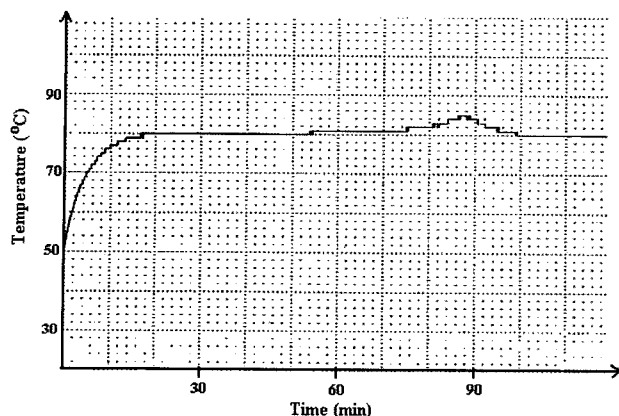
Figure 1. Temperature profile of the reaction media with the reaction time.
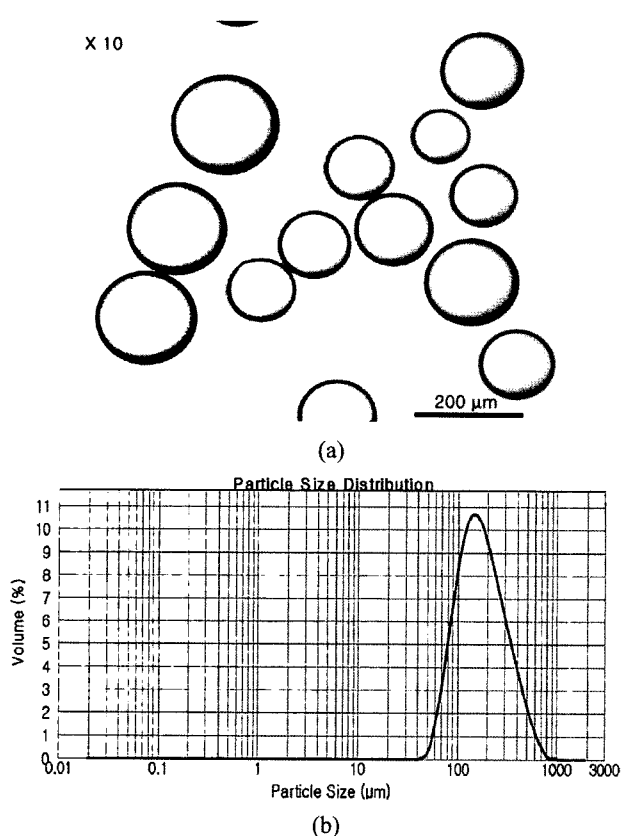

Figure 2. Optical microscope image of the copolymer (M-I25) beads and its size distribution.

Figure 3. NMR spectra of poly(MMA-*co*-IBMA).

ization reaction by styrene incorporation.[17]

The size and image of copolymer beads were obtained after the reaction and the representative image and unimodal distribution of particle size are illustrated in Figure 2 (M-I25). Synthesized transparent polymer particles showed smooth surface and sphere shape, which imply that suspension polymerization has been successfully conducted with the present experimental conditions. Average diameter of
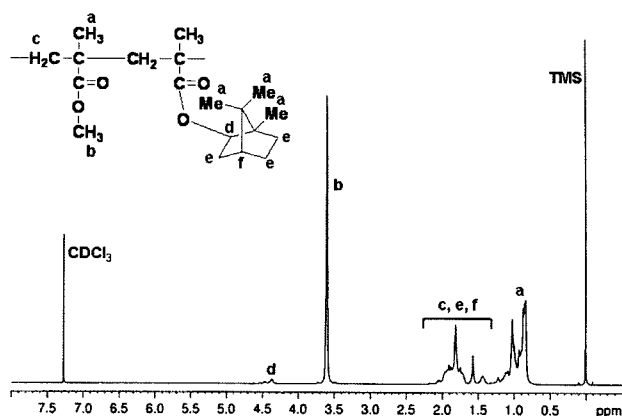
the beads was in the range of 150-200 μm for all series prepared in this experiment. Since the particle size and distributions are affected by various conditions such as, type of impeller, dimensions of the reactor, concentration of suspending agent and so forth, it is hard to draw conclusion from the result of particle size measurement only with the variation of composition and CTA concentration. However, it should be noted that stable synthesis condition was obtained and maintained for all prepared polymers from the observation of clean surface of beads and unimodal distribution.

The prepared copolymers were characterized and the results are summarized in Table I. Poly(MMA-*co*-IBMA)s showed unimodal molecular weight distributions and the polydispersity exhibited narrow distribution in the range of 1.50-1.76. Contents of MMA and IBMA in the synthesized copolymer (mol%) was calculated from the quantitative peak analysis of the corresponding ^{1}H-NMR spectrum of poly(MMA-*co*-IBMA) (Figure 3).[18] Mole fraction of IBMA in the poly(MMA-*co*-IBMA) was estimated by the proton peak area of methine on the isobornyl group attached to the COO side group (δ=4.33 ppm) and proton peak of the methoxy group of MMA (δ=3.56 ppm) (eq. (1)).

$$\text{Mole \% of IBMA in Copolymer} = \frac{I_{4.33}}{I_{4.33}+1/3I_{3.56}} \times 100(\%)$$

(1)

where, I_x represents proton peak area of corresponding peak x.

From the result of NMR spectra, composition of copolymer was almost identical to the feed ratio. The reactivity ratios for the copolymerization were also calculated for better understanding of the random copolymerization of MMA and IBMA. Assuming terminal model of copolymerization,[19] comonomer composition can be expressed as eq. (2).

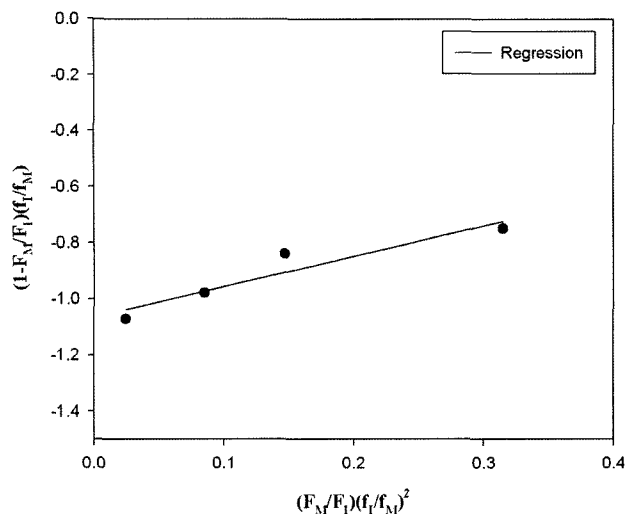$$\frac{F_M}{F_I} = \frac{f_M}{f_I} \cdot \frac{(f_M \cdot r_M + f_I)}{(f_M + r_I \cdot f_I)}$$

(2)

Figure 4. Plot (eq. (3)) of the copolymer with different composition for reactive ratio determination.

Figure 5. Propagation kinetic constant rate of copolymerization with the change of IBMA mole fraction.

where M and I represent MMA and IBMA, respectively. F_M/F_I is the molar ratio of the two monomer units in the copolymer. f_M and f_I are the relative mole fractions in the feed. The parameters r_M and r_I are the reactivity ratios of two monomers, respectively. Eq. (2) can be rewritten to obtain monomer reactive ratio as:

$$\left(1-\frac{F_M}{F_I}\right)\cdot\left(\frac{f_I}{f_M}\right)=\left(\frac{F_M}{F_I}\right)\cdot\left(\frac{f_I}{f_M}\right)^2\cdot r_I\cdot r_M \qquad (3)$$

Since the sampling of copolymers at low conversion ratio (>10 wt%) was unsatisfactory for the suspension polymerization, F_M and F_I were obtained from the bulk copolymerization of MMA and IBMA at low conversion ratio (5-8 wt%). However, there was no significant difference of the F_M and F_I values compared with those of final copolymer (over 96% conversion) by suspension polymerization.

Figure 4 shows the extrapolation results of the calculated values using eq. (3) varying compositions of the copolymers. The reactivity ratio, r_I and r_M, can be obtained from the slope and interception of the extrapolated line. The reactivity ratio was obtained from Figure 4 as 1.07 for r_M and 1.08 for r_I, respectively. This suggests that the copolymerization of MMA and IBMA would show almost Bernoullian behavior where $r_I=r_2=1$.

Recently, propagation rate coefficients (k_p) was measured by the combination of pulsed-laser-initiated polymerization (PLP) and polymer analysis using size-exclusion chromatography (SEC).[20] Using the k_p data obtained by PLP-SEC method, the propagation constants for the copolymer can be calculated using eq. (4).

$$\langle k_p \rangle = \frac{(r_M\cdot f_M^2 + 2f_M\cdot f_I + r_I\cdot f_I^2)}{\left(f_M\cdot\dfrac{r_M}{k_{p,M}} + f_I\cdot\dfrac{r_I}{k_{p,I}}\right)} \qquad (4)$$
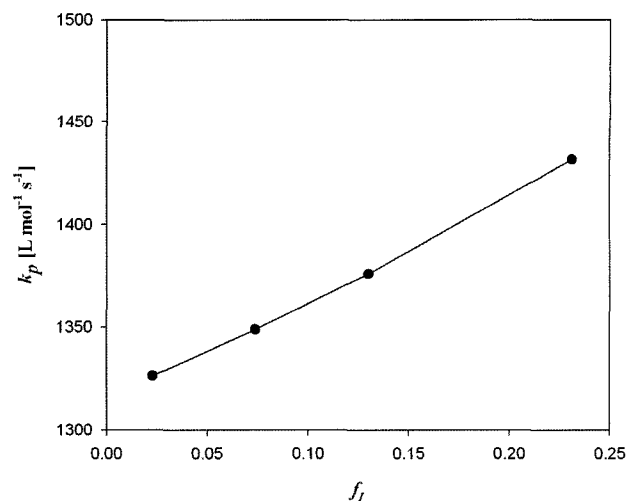
The k_p values of MMA and IBMA at 80 °C was adopted from the PLP-SEC results.[21-23] The calculated results of k_p for copolymerization were drawn in Figure 5. It shows that the propagation rate slightly increases with the increase of IBMA mole fraction. It is important to obtain kinetic constants of copolymerization since it provides feasibility of the system application to the scaled-up plant. From the result, copolymerization of MMA and IBMA can be performed in the PMMA production line without severe change of reaction conditions.

Effects of IBMA Content on Copolymer Property. T_g of the copolymer was used as a criteria of the heat resis-
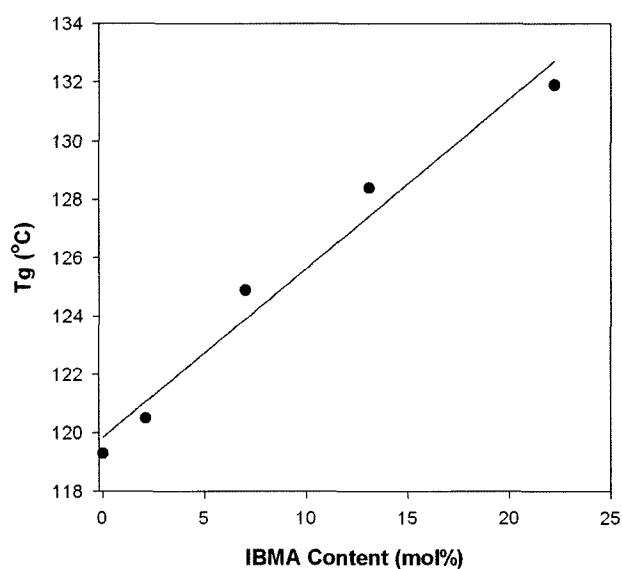

Figure 6. Glass transition temperature of the copolymer with the variation of IBMA content.

tance improvement. Figure 6 illustrates the change of T_g with the variation of IBMA in the copolymer and its linear regression result. It shows that the T_g correspondingly increased with the increase of IBMA feed content. It can be attributed to the increase of bulky side group from IBMA. Linear regression treatment of data by statistical software MINITAB (Ver 13.1) resulted following linear correlation of IBMA feed content and T_g of the poly(MMA-*co*-IBMA).

T_g of the copolymer (°C)=120.0+0.580×[IBMA]

where, [IBMA] is the mole percent of IBMA in copolymer.

An addition of the feed amount of IBMA in copolymer by 1 mol% increased the T_g of the copolymer by 0.58 °C.

Thermal degradation of the poly(MMA-*co*-IBMA) was also investigated and it was observed that T_d decreased with the increase of IBMA feed content. It is expected that IBMA would provide favorable sites for unzipping process of the copolymer. Generally, for the polymerization of PMMA, comonomers such as methyl acrylate, ethyl acrylate, styrene and so forth are applied to suppress depolymerization. These comonomers commonly possess α-substituted carbon at the double bond which shows higher enthalpy change for propagation compared to double bond with α,α'-substituted carbon.[24] Thus terpolymer (M-I-S) composed of MMA, IBMA, and styrene exhibited high T_d due to the styrene effect on the prevention of decreasing T_d.

Effects of CTA Amount on the Properties of Poly(MMA-*co*-IBMA). Chain transfer method is normally used to control molecular weight, structure, and functionality in free radical polymerization.[25] It can be achieved by the introduction of chain transfer agent. When transparent polymers are
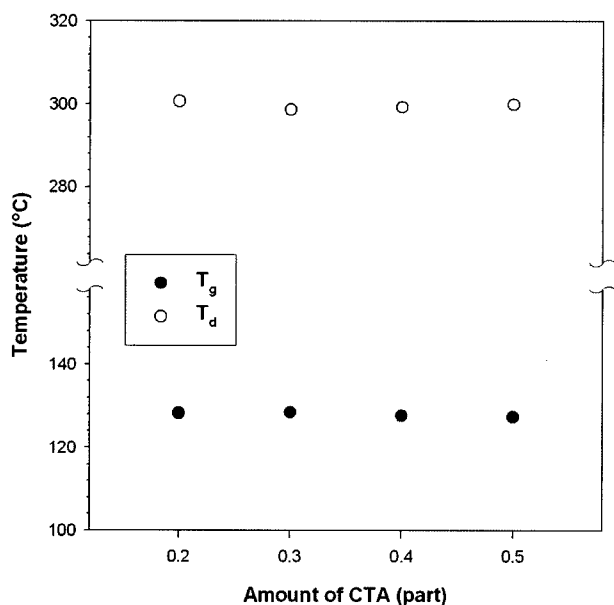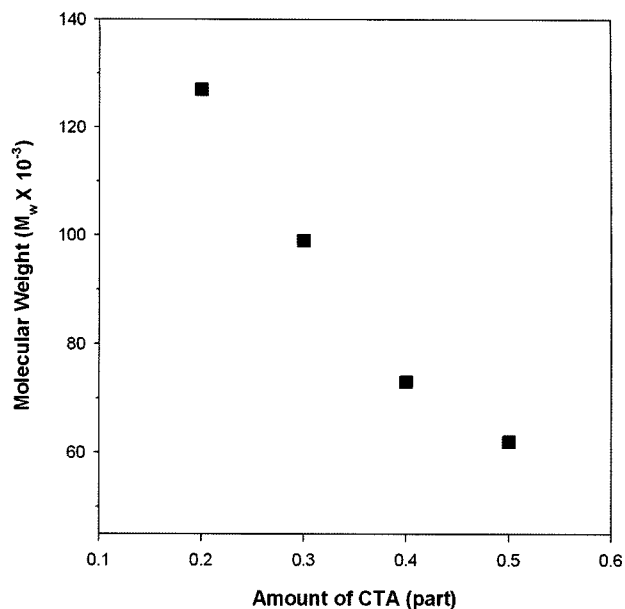
Figure 8. Molecular weight of the copolymer with the variation of CTA content in the feed.

applied to the optical purposes, they require various forming processes such as injection molding, extrusion and so on. Thus it is inevitable to consider molecular weight together with its melt flow index (MFI) in the sense of practical application.

Figure 7 shows T_g and T_d of the copolymers with the variation of CTA amount. There was no significant change with the change of CTA amount used. However, the molecular weight of copolymer decreased with the increase of *n*-octylmercaptan (Figure 8). Based on the results, it can be concluded that CTA, *n*-octylmercaptan, plays important role only on the molecular weight without significant degradation of thermal properties. Also from the ^{1}H-NMR analysis, there was little effects of NOM on the composition of MMA and IBMA in poly(MMA-*co*-IBMA).

Processing feasibility of the samples for various optical devices was evaluated by MFI. Since conventional PMMA has MFI ranging from 1 to 10 for the extrusion and injection molding, it is appropriate for the new copolymer's MFI should be placed within the range. MFI results shown in Table II presents the amount of NOM should be lower than 0.4 for practical use when synthesized with the reaction

Figure 7. T_g and T_d with the variation of CTA content in the feed.

Table II. Melt Index Change with the CTA Content[a]

	M-IC2	M-I25	M-IC4	M-IC5
CTA Content (Part)	0.2	0.3	0.4	0.5
Melt Index (g/10 min)	2.7	8.9	22.4	24.4

[a]Amount of polymer flow through orifice under 230 °C, 3.8 kg load for 10 min.

conditions suggested in this report.

Conclusions

Suspension copolymerization of MMA and IBMA was successfully performed and the resulting copolymers can be applied to a heat resistant transparent polymer. Copolymerization kinetic showed that MMA and IBMA goes almost ideal copolymerization. The effect of IBMA and CTA contents on the properties of the copolymer was investigated. The measured thermal properties clearly showed that heat resistance was improved by the IBMA content. Additionally, copolymer prepared using NOM lower than 0.4 parts had appropriate MFI which showed processibility for the optical purposes. IBMA affords a heat resistance to the PMMA resin by copolymerization without damaging the characteristics of transparent resins. Optical properties of the poly(MMA-co-IBMA) need to be examined and are currently underway.

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