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Monodisperse micron-sized polymethylmethacrylate particles having a crosslinked network structure. V

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Highly monodisperse micron-sized polymethylmethacrylate (PMMA) particles crosslinked with carboxylic group-containing urethane acrylates (CUA) were produced by simple dispersion polymerization in methanol. In proper condition, CUA employed as a crosslinker had an excellent ability to achieve the monodisperse PMMA particles to the concentration of about 10 wt%. This arose from the fact that CUA formed monomer-swellable primary particles due to its structurally long tetramethylene oxide groups in the molecule. The influence of the concentrations of the initiator and CUA on the particle diameter (D_n), particle number density (N_p), and polymerization rate (R_p) was found to obey the following approximate relationship, $D_n \propto [\text{initiator}]^{0.41}[\text{CUA}]^{-0.06}$, $N_p \propto [\text{initiator}]^{-1.22}\,[\text{CUA}]^{0.21}$, and $R_p \propto [\text{initiator}]^{0.34\pm0.03}$, respectively. The power law dependence of D_n and N_p on the initiator concentration coincided well with that of linear polymers in the literature. Especially, in this study, it was found that CUA did not have a serious influence on the nucleation. However, the dependence of R_p on the initiator concentration was observed to be higher than that of linear polymers, suggesting that uniquely, the solution polymerization process competed with the heterogeneous polymerization during polymerization, because of the crosslinked network structure of the primary particles.

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1. Introduction

Micron-sized polymer particles produced by dispersion polymerization have found a wide variety of applications in coatings, inks, dry toners, instrument calibration, chromatography, biomedical treatment, biomedical analysis, and microelectronics [1–4].

One of the features in this dispersion polymerization procedure is that after the stable particles (primary particles) are formed, particles grow until they reach their final size by capturing monomers, nuclei and/or oligomeric radicals from the medium. Therefore, under favorable conditions, where neither new nucleation nor coagulation is present, highly monodisperse polymer particles can be obtained [5–13].

Relative to the production of the crosslinked polymer particles in the field of dispersion polymerization, however, only a few researches have been performed [12, 14–16]. A second nucleation during particle growth stage, rough surfaces of the final particles, and coagulation were commonly observed [12, 14]. Therefore, in dispersion polymerization for crosslinked polymer particles, some different polymerization mechanism has been proposed [15, 16]. That is, the particle growth goes on through the precipitation of nucleated oligomers and/or newly formed particles onto the surface of the primary particles, because of the nonswellability of the highly crosslinked primary particles. They also stressed the importance of preparing monomer-swellable primary particles.

Based on the abovementioned concept, in our previous works [17–19], we successfully produced highly monodisperse micron-sized crosslinked polystyrene and PMMA particles, respectively. As a useful monomer-swellable crosslinker, a urethane acrylate was designed with flexible tetramethylene oxide in the middle and two vinyl groups on both molecular ends. Especially, in the case of PMMA dispersion polymerization, it was found that the matching of the solubility of the urethane acrylate and MMA monomer was a prerequisite for the monodispersity of the crosslinked PMMA particles [19]. To achieve this purpose, we employed a carboxylic group-containing urethane acrylate (CUA) as a crosslinker. When forming primary particles, this CUA seemed to help the monomer diffusion from the medium into the primary particles. Furthermore, only when the molecular weight of the CUA was sufficiently high, monodisperse PMMA particles could be obtained to about 10 wt% CUA concentration, based on total monomer weight. In lower molecular weight of CUA, the MMA monomer diffusion was restricted, resulting in favorable second nucleation.

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In this study, we produced highly monodisperse micron-sized crosslinked PMMA particles over the molecular weight range of CUA. The effect of the polymerization temperature, CUA concentration, and CUA molecular weight on the particle sizes, size distributions, and polymerization kinetics was studied, and the particle formation procedure was considered.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, Tokyo Chemical Industry Co., Ltd.) was vacuum distilled before use. Poly(tetramethylene glycol) (PTMG, $M_w = 1.0 \times 10^3$, 1.4×10^3, and 2.0×10^3 g·mol^{-1}, Hyosung BASF), polyvinylpyrrolidone (PVP K-30, $M_w = 4.0 \times 10^4$ g·mol^{-1}, Aldrich Chemical Co.), di-2 ethylhexyl ester of sodium sulfosuccinic acid (Aerosol-OT, American Cyanamid), and dimethylolpropionic acid (DMPA, Aldrich Chemical Co.) were used as received. Inhibitor in hydroxyethyl methacrylate (HEMA, Aldrich Chemical Co.) and methylmethacrylate (MMA, Junsei Chemical Co.) was removed through a removing column (Aldrich Chemical Co.). Methanol (J. T. Baker) was used without further purification. 2,2-azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) was recrystallized from methanol.

2.2. Synthesis of carboxylic group-containing urethane acrylates (CUA) [17–22]

The reaction procedure and schematic molecular structure of CUAs designed are presented in Scheme 1. Here, we named CUA 1, 2, and 3 for the urethane acrylates synthesized. Serial numbers, 1, 2, and 3 correspond to the molecular weight of PTMG, 1.0×10^3, 1.4×10^3, and 2.0×10^3 g·mol^{-1}, respectively.

All reactions were carried out in a 4-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. In the first step, 2 mole of IPDI was poured into the glass reactor and nitrogen gas was inlet for 10 min to eliminate the residual moisture. After dissolving 1 wt% of dibutyltindilaurate (DBTDL), 1 mole of DMPA dissolved in DMAc was dropped into the reactor slowly at room temperature. The reaction was carried out at 80°C for 4 h, resulting in the molecular structure having a carboxylic acid group in the middle and isocyanates on both ends. The change of NCO value during reaction was determined using dibutylamine back titration method to find out the end point of reaction [23].

In the second step, 0.5 mole of PTMG was added slowly into the reactor to incorporate a polytetramethylene oxide group into the molecular backbone with the same method of the first step. In the last step, after dissolving 1 wt% DBTDL into the reactor again, 2 mole of HEMA was reacted to the residual NCO groups at 45°C for 12 h, capping the molecular ends with reactive vinyl groups. The reaction end point was determined by the disappearance of the NCO stretching peak (2270 cm^{-1}) through IR spectroscopy.

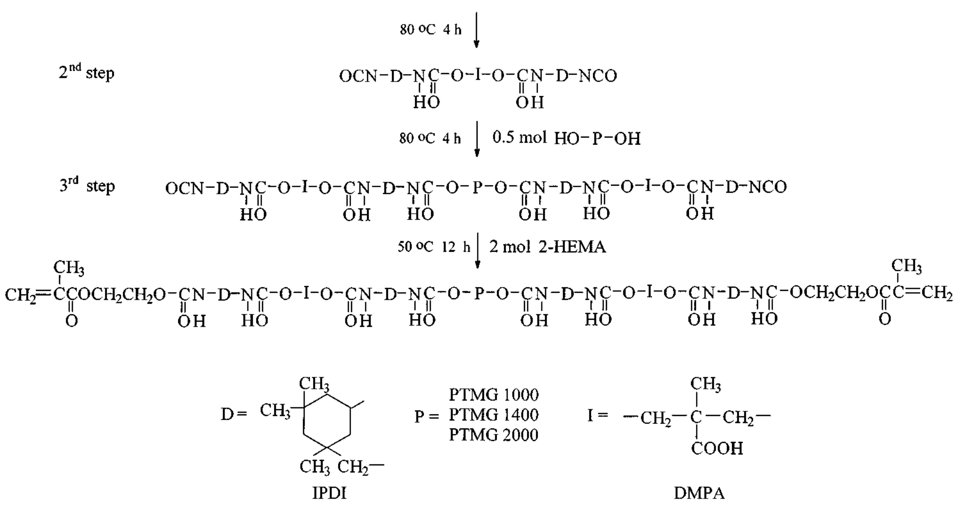
To purify DMAc, unreacted HEMA, and DMPA, the reaction mixture was precipitated from water and filtered several times and dried *in vacuo*.

2.3. Dispersion polymerization of MMA and CUA

General dispersion polymerization procedure was followed [12, 15–19]; AIBN, PVP, Aerosol-OT, MMA, CUA, and methanol were weighed into 50ml glass vials. After sealing in nitrogen atmosphere, the vials were submerged in a thermostated water bath and tumbled with the rotation speed of 40 rpm. The polymerization was carried out for 24 h at 54°C, 58°C, and 62°C, respectively. The obtained spheres were centrifuged for 10 min at 8,000 rpm. The supernatant was then decanted and the remaining precipitate was repeatedly washed in the distilled water by six centrifugations, and dried *in vacuo* at ambient temperature overnight. A standard recipe is summarized in Table I.

2.4. Measurements

Molecular weight distributions for CUAs synthesized were measured by a model 410 GPC equipped with



Scheme 1 Reaction procedure and schematic molecular structure of the carboxylic group-containing urethane acrylates (CUA).

TABLE I The standard recipe for the dispersion polymerization[a]

Ingredient	Weight (g)
MMA	0.950
CUA[b]	0.050$^{\text{variable}}$
PVP K-30[c]	0.400
Aerosol-OT	0.045
AIBN[d]	0.010$^{\text{variable}}$
Methanol	8.545

[a] 58°C; 24 h; 10 wt% of monomer concentration based on total weight.
[b] wt% of CUA was varied against MMA (5 wt% in this example).
[c] 4 wt% of PVP K-30 ($M_w = 4.0 \times 10^4$ g·mol^{-1}) based on total weight was added.
[d] wt% of 2,2′-azobis(isobutyronitrile) was varied against total monomer weight (1 wt% in this sample).

TABLE II The molecular weights of the carboxylic group-containing urethane acrylates

Symbol	M_w (g·mol^{-1})	M_n (g·mol^{-1})	PI[a]	DMPA[b] (wt%)
CUA1	8.3×10^3	6.3×10^3	1.32	10.23
CUA2	1.1×10^4	6.5×10^3	1.69	8.88
CUA3	1.4×10^4	7.1×10^3	1.91	7.41

[a] PI $= M_w/M_n$.
[b] The content of DMPA calculated from the total urethane acrylate weight.

Styragel HR 1–4 columns from Waters Associates at 25°C. The flow rate of the carrier solvent, THF, was 0.5×10^{-6} m^3 min^{-1}. The average molecular weights of the CUAs calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards are listed in Table II.

The particle diameter was measured with a field-emission scanning electron microscope (FE-SEM, JMS-6340F, JEOL). Specimens were prepared by diluting the recovered particles with distilled water and placing a drop on a cover glass. The drop was dried at room temperature and then coated under vacuum with a thin layer of gold. Diameters of about 200 individual particles were measured from SEM photographs and the average was taken. The polydispersity index (PDI) was determined as follows,

$$D_n = \frac{\sum_{i=0}^{n} d_i}{N} \tag{1}$$

$$D_w = \frac{\sum_{i=0}^{n} d_i^4}{\sum_{i=0}^{n} d_i^3} \tag{2}$$

$$\text{PDI} = \frac{D_w}{D_n} \tag{3}$$

where, D_n is number average diameter, D_w is weight average diameter, N is the total number counted, and d_i is the diameter of particle i.

Fractional conversions were determined with conventional gravimetric method. The vials containing 10 g of the total ingredients (1 g of MMA and CUA) in Table I were extracted from the thermostated water bath at chosen time-intervals. Promptly, a drop of 1% hydroquinone solution was added into the vial and quenched in ice water. Each sample was then dried under vacuum at ambient temperature, until the weight change was less than 0.001 g. The conversion was calculated as follow [24],

$$Cv = \frac{M_2 - M_1 \times (W_2 + W_3)}{M_1 \times W_1} \tag{4}$$

where, Cv is the calculated fractional conversion, M_1 is the weight of the sample before drying, M_2 is the weight of the sample after drying, w_1 is the wt% of the monomer, w_2 is the wt% of the stabilizer, and w_3 is the wt% of the initiator.

3. Results and discussion

3.1. Effect of CUA concentration

Crosslinked PMMA particles were produced with varying the CUA concentration in methanol at 58°C for 24 h. Fig. 1 shows SEM photographs at a given CUA2 concentration based on total monomer weight: 0 wt% (a), 2 wt% (b), 5 wt% (c), and 10 wt% (d). In overall CUA concentration, stable particles could be obtained without any coagulum. In these SEM photographs, it was notable that not only the particle sizes were highly monodisperse but also the particles were spherical and very clear, even in the crosslinked state.

It has been accepted that conventional crosslinkers form a hard and glassy surface of the primary particles, which makes it difficult to swell the primary particles by vinyl monomers in the medium [15, 16]. Therefore, the consequent polymer particles displayed broad size distributions and rough surfaces upon adding a small amount of crosslinkers (more than 0.5 wt%). However, unlike general observations, in the case of using CUA as a crosslinker, highly monodisperse PMMA particles could be produced even in the moderate CUA concentration. This can be elucidated by considering the surface characteristics of the primary particles crosslinked by CUA [17–19]. The primary particles crosslinked by CUA can be readily swollen by the MMA monomers in the media during particle growth, because of the peculiar molecular structure of the CUA; long tetramethylene oxide groups in the molecular backbone. However, at 10 wt% of CUA concentration, although the spherical particles were observed, the surface was considerably rough, as shown in Fig. 1d. This was believed to be due to the high CUA concentration, which produced the primary particles of high crosslinking density, alternatively, leading to the favorable precipitation of the new primary particles and/or oligomer radicals onto the initial particles [15–19].

To examine the effect of the molecular weight of CUAs on the crosslinked PMMA, particles were produced with changing the molecular weight of CUAs. Fig. 2 shows the SEM photographs of the PMMA particles crosslinked with 5 wt% CUAs; CUA1 (a) and CUA3 (b). The PMMA particles crosslinked with 5 wt% CUA1 displayed widely polydisperse size distributions instead of the monodispersity. Moreover, rough surfaces and multiplet particles were observed. The main reason for these results was likely to be the low molecular weight of the CUA, as listed in Table II. The

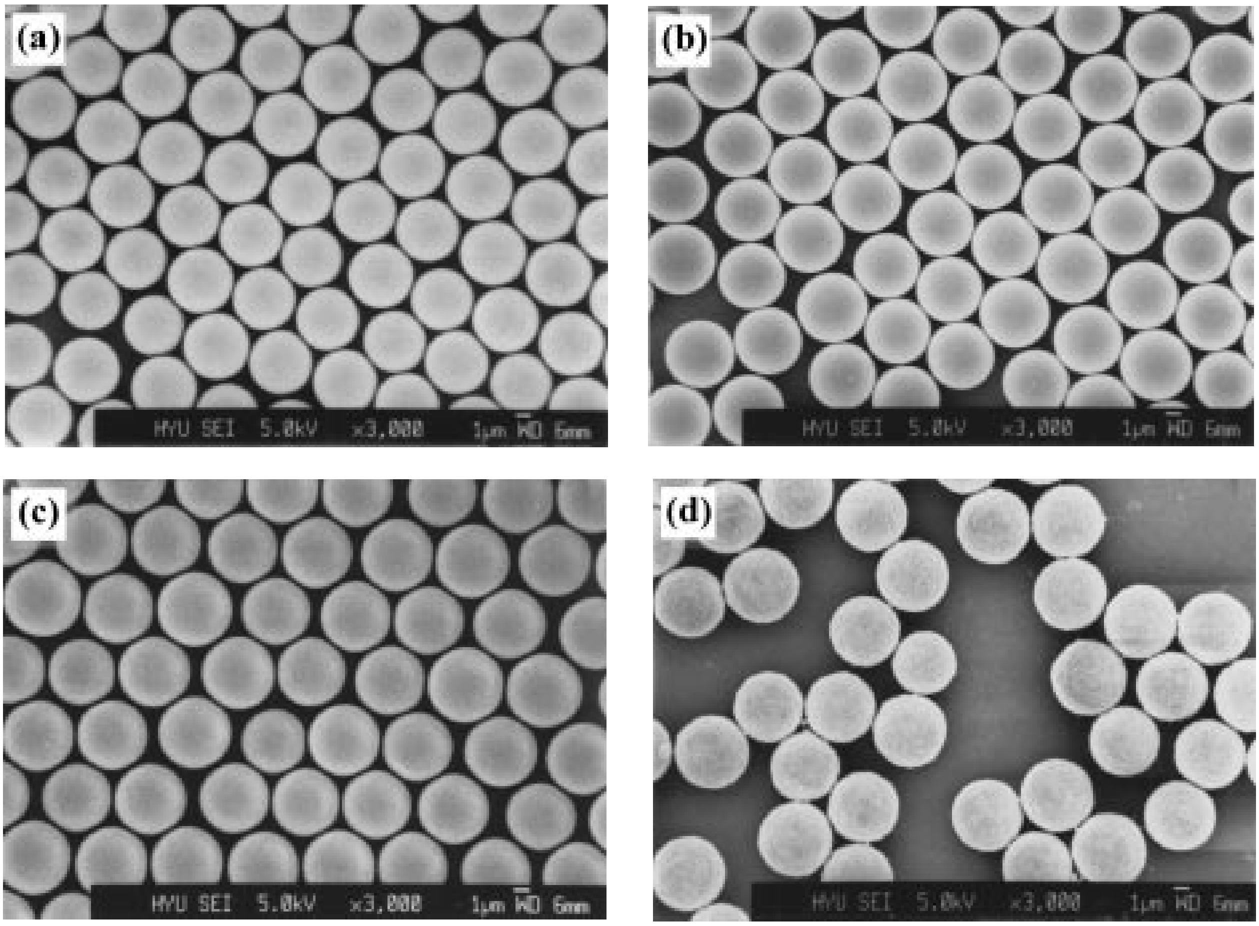


Figure 1 SEM photographs of PMMA particles produced with the CUA concentration (CUA2): 0 wt% (a), 2 wt% (b), 5 wt% (c), and 10 wt% (d) at 58°C for 24 h in methanol.

low molecular weight of CUA1 caused the crosslinking density of the primary particles to increase. Therefore, the particle growth was achieved by the precipitation of the oligomer radicals and/or polymers generated in the continuous phase, resulting in favorable formation of the secondary particles.

In Table III, the average particle sizes and size distributions for PMMA particles with the concentration of CUAs are summarized. The final size of the crosslinked PMMA particles had a tendency toward increasing with the increase of the CUA concentration. However, only slight size increase was observed. Related to this result, the carboxylic groups in the molecular backbone of the CUA were considered to have an ability to enhance the solubility of the monomer mixture [19] and stabilize the primary particles together with PVP and Aerosol-OT [12]. When the molecular weight of CUAs was lowered, larger PMMA particles could be obtained. This can be explained by considering the content of carboxylic groups in the CUA molecules. As listed in Table II, CUA1 has the highest DMPA content, resulting in the highest solubility of the monomer mixture in the medium. So, better solvency of the monomer mixture in the medium led to longer chain lengths of oligomers before precipitation [12, 17, 18].

TABLE III The effect of CUA concentrations on the crosslinked PMMA particles[a]

CUA[b]	Particle size (μm) D_n	D_w	PDI (D_w/D_n)	Remarks
CUA1-0	4.176	4.180	1.001	Monodisperse
CUA1-2	4.500	4.950	1.100	Monodisperse
CUA1-5	4.860	6.318	1.300	Multiplet, rough surface
CUA1-10	—	—	—	Coagulation
CUA2-0	4.176	4.180	1.001	Monodisperse
CUA2-2	4.400	4.409	1.002	Monodisperse
CUA2-5	4.600	4.614	1.003	Monodisperse
CUA2-10	4.810	4.902	1.020	Rough surface
CUA3-0	4.176	4.180	1.001	Monodisperse
CUA3-2	4.190	4.194	1.001	Monodisperse
CUA3-5	4.235	4.239	1.001	Monodisperse
CUA3-10	4.511	4.520	1.002	Monodisperse

[a] 58°C; 24 h; 10 wt% of monomer concentration based on total weight.
[b] CUAα-β; α corresponds to the molecular weight of CUA, and β to the concentration of CUA based on total monomer weight.

3.2. Effect of the polymerization temperature

Fig. 3 shows the SEM photographs of the PMMA particles crosslinked with 5 wt% CUA2 at different temperatures: 54°C (a), 58°C (b), and 62°C (c). In our study, it was found that in the case of using CUA as a crosslinker, the polymerization temperature played a crucial role in obtaining the monodisperse crosslinked PMMA particles. When the PMMA particles were produced at low temperature, small particles were by-produced [19]. However, at elevated temperature, highly monodisperse PMMA particles could be obtained successfully. This indicates that under proper

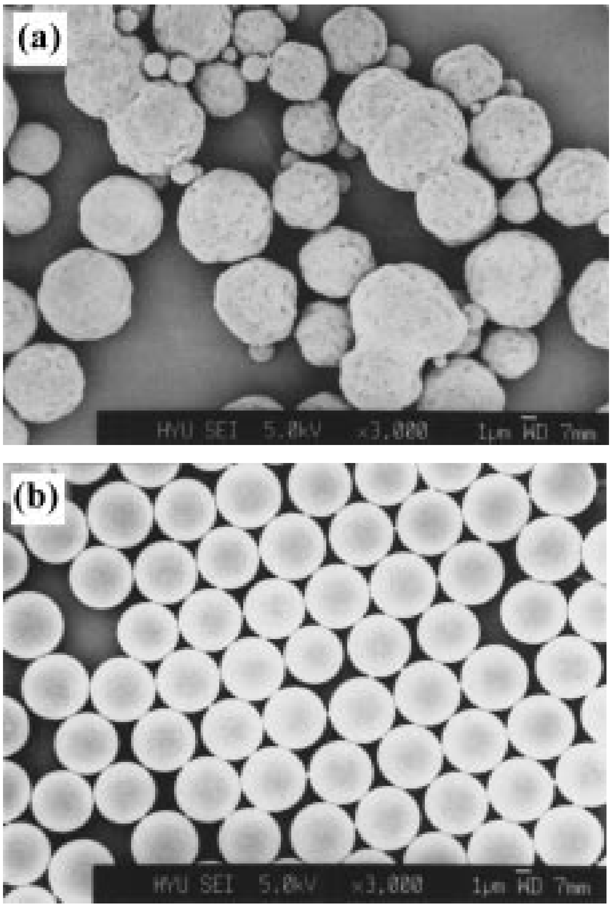


Figure 2 SEM photographs of PMMA particles produced with the molecular weight of CUAs: CUA1 (a) and CUA3 (b) at 58°C for 24 h in methanol. 5 wt% CUA was added based on total monomer weight.

temperature conditions, nucleation during the particle growth was suppressed by diffusion. Moreover, in this study, when the polymerization temperature was enhanced, the MMA monomers in the medium seemed to be readily captured by the crosslinked primary particles, which eventually resulted in the restriction of the new generation of the primary particles.

The average particle sizes and the size distributions obtained are illustrated in Table IV. The particle size was found to increase with the increase of the polymerization temperature. As is well known, the growing polymer chains precipitate and form the primary particles during the nucleation period. At higher temperature, however, the growing polymer chains are readily terminated before reaching a critical polymer chain length for the precipitation, resulting in fewer primary particles [25, 26]. Finally, the particles produced are of a larger diameter, as shown in Fig. 3.

3.3. Particle nucleation and polymerization process

For the crosslinked PMMA particles produced using CUA, in this study, we tried to understand the nucleation stage and polymerization procedure. Fig. 4 shows the dependence of the particle diameter (D_n) and particle number density (N_p) for the PMMA particles crosslinked with 5 wt% CUA2 on the initiator concentration. It was found that D_n and N_p followed the power law with index 0.41 and −1.22, respectively.

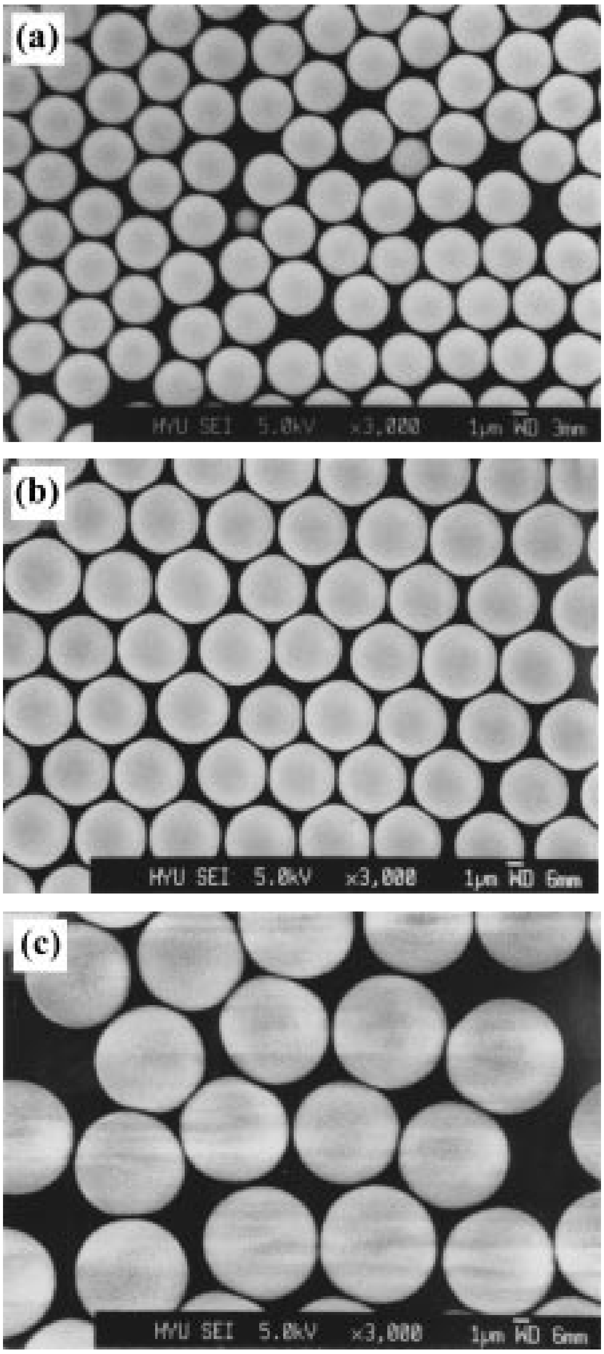


Figure 3 SEM photographs of PMMA particles produced with the polymerization temperature: 54°C (a), 58°C (b), and 62°C (c) for 24 h in methanol. 5 wt% CUA2 was added based on total monomer weight.

This power law dependence showed good agreement with earlier works in the literature [5, 12, 27]. They obtained the 0.39–0.4 power for particle size dependence and the −1.2 power for particle number density dependence, respectively. From the above result, it can be possibly revealed that the nucleation procedure of the crosslinked PMMA particles was fairly similar to that of linear polymers. That is, irrelative to the presence of CUA, the rate of association of the oligomers and/or the coagulation rate of the unstable nuclei to form larger primary particles had a similar trend [12]. Then, it is necessary to examine the effect of the concentration of CUA on the particle nucleation. Fig. 5 shows the dependence of D_n and N_p for the crosslinked PMMA particles on the CUA2 concentration. The powers of

TABLE IV The effect of polymerization temperature on the crosslinked PMMA particles[a]

Reaction temp.	CUA[b]	Particle size (μm) D_n	D_w	PDI (D_w/D_n)	Remarks
54 °C	CUA2-0	3.020	3.050	1.010	Monodisperse
	CUA2-2	3.220	3.252	1.010	Monodisperse
	CUA2-5	3.308	3.440	1.040	Relatively monodisperse
	CUA2-10	4.100	4.551	1.110	Bimodal
62 °C	CUA2-0	6.715	6.764	1.002	Monodisperse
	CUA2-2	6.910	6.931	1.003	Monodisperse
	CUA2-5	7.200	7.272	1.010	Monodisperse
	CUA2-10	—	—	—	Coagulation

[a] 24 h; 10 wt% of monomer concentration based on total weight.

[b] CUAα-β; α corresponds to the molecular weight of CUA (in this case, CUA2, 1.4×10^3 g·mol^{-1}), and β to the concentration of CUA based on total monomer weight.

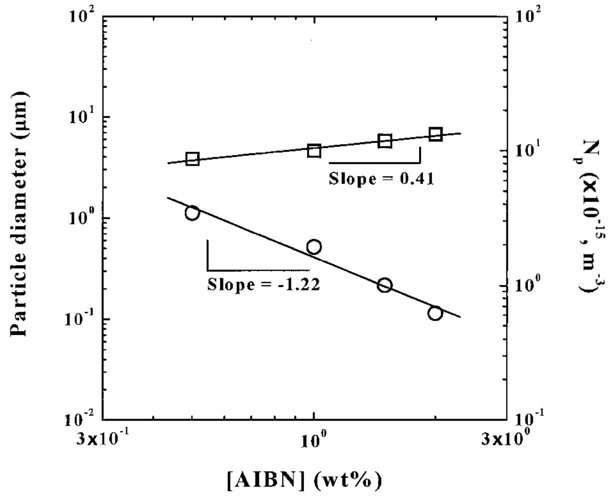


Figure 4 Dependence of particle diameter (-□-) and particle number density (-○-) of PMMA particles crosslinked with 5 wt% CUA2 on AIBN concentration.

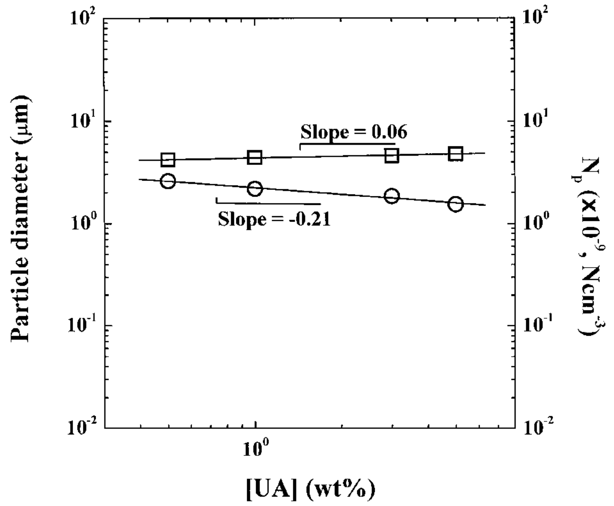


Figure 5 Dependence of particle diameter (-□-) and particle number density (-○-) of PMMA particles initiated with 1 wt% AIBN on CUA concentration.

D_n and N_p were 0.06 and −0.21, respectively. This result well confirms that the CUA concentration had a negligible influence on the particle nucleation.

Fig. 6 shows the conversion-polymerization time curves (a) and the polymerization rate (R_p)-conversion curves (b) for the PMMA particles crosslinked with 5 wt% CUA2 with changing initiator concentration. In the low conversion region, R_p increased with the increase of initiator concentration. On the contrary, in the high conversion region, R_p came to be independent on the initiator concentration. This elucidates that there is competition between solution polymerization and heterogeneous polymerization [27]. In order to confirm the polymerization process in detail, R_p in Fig. 6b was replotted double-logarithmically against the initiator concentration at various fractional conversions and shown in Fig. 7. In selected conversions, R_p was observed to follow a 0.34 ± 0.03 power dependence on the initiator concentration, which is relatively higher value, compared with the linear polymers of 0.1 power [27]. In the dispersion polymerization for the linear polymers, R_p was nearly independent on the initiator concentration, which arises from the dominant heterogeneous polymerization process over the polymerization process [15, 27]. Alternatively, then, for our

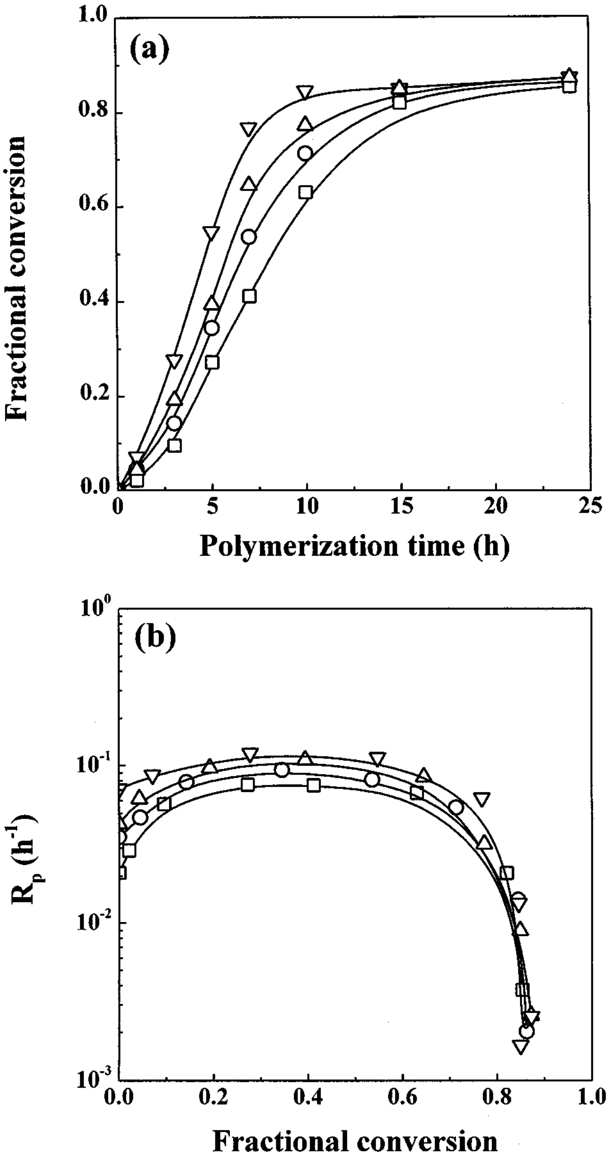


Figure 6 Fractional conversion-polymerization time curves (a) and polymerization rate-fractional conversion curves (b) for PMMA particles crosslinked with 5 wt% CUA2 (based on total monomer weight) with changing AIBN concentration: 0.5 wt% (-□-), 1 wt% (-○-), 1.5 wt% (-△-), and 2 wt% (-▽-) at 58°C in methanol.

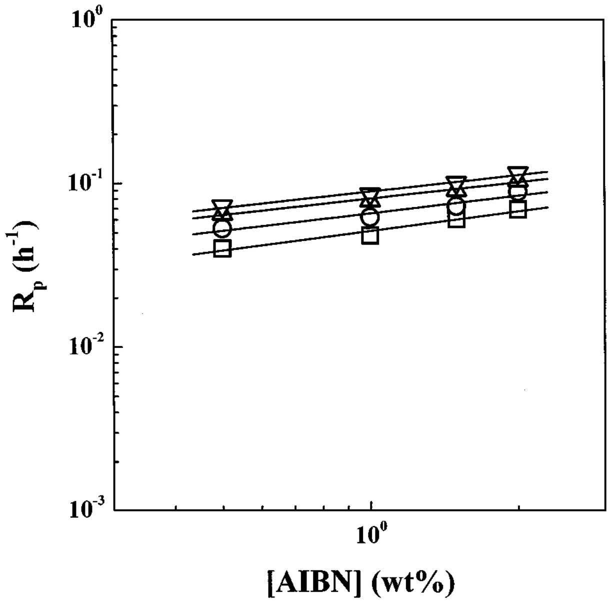


Figure 7 Dependence of polymerization rate for PMMA particles crosslinked with 5 wt% CUA2 on AIBN concentration at various fractional conversions: 0.05 (-□-), 0.1 (-○-), 0.2 (-△-), and 0.4 (-▽-) at 58°C in methanol.

polymerization system, it can be said that the heterogeneous polymerization could not dominate the whole polymerization process. Thus it appeared that, even though the crosslinked primary particles readily absorbed the monomer from the medium, the hindrance caused by their crosslinked network structure still existed, which made the solution polymerization process also favored.

3.4. Particle formation and growth of PMMA particles crosslinked with CUA

Fig. 8 represents a schematic procedure for the particle growth of the PMMA particles crosslinked with CUA, proposed on the basis of this work and published studies in the literature [12, 17–19, 28, 29]. Like conventional dispersion polymerization, MMA, CUA, initiator, stabilizer, and costabilizer are dissolved homogeneously prior to polymerization. As the polymerization is initiated by decomposition of the initiator, so the free radicals react with MMA and CUA. Then, oligomers grow in the dispersion medium until they precipitate to form the primary particles crosslinked with CUA. Concurrently, the stabilizer in combination with the costabilizer and CUA stabilizes the primary particles (Fig. 8a). Then, the crosslinked primary particles grow either by MMA absorption or by oligomer radical adsorption until all monomers are consumed (Fig. 8b). Considering the higher dependence of R_p on the initiator concentration, one important feature is that even though the MMA in the medium can be readily absorbed by the crosslinked primary particles, there may be considerable precipitation of nucleated oligomers and/or polymers onto the crosslinked surface of the primary particles.

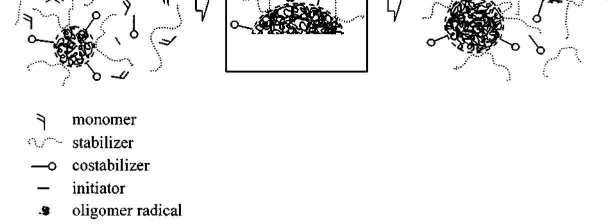


Figure 8 Schematic representation of the particle formation and growth in dispersion polymerization of MMA and CUA.

4. Conclusions

Highly monodisperse micron-sized crosslinked PMMA particles were produced directly by simple dispersion polymerization of MMA and CUA. Highly monodisperse size distribution of the crosslinked particles could be obtained by the monomer-swellable surface of the primary particles, because of the long tetramethylene oxide group in the backbone of the CUA. Carboxylic groups in CUA molecules led to a somewhat smaller number of primary particles by enhancing the solubility of the monomer mixture and stabilizing the primary particles together with PVP and Aerosol-OT. The nucleation followed a similar process to that with linear polymers and the presence of CUA did not have a serious effect on the particle formation. By observing the dependence of the dispersion polymerization rate on the initiator concentration, it was found that the solution polymerization process took place together with the homogeneous polymerization, because of the crosslinked surface of the primary particles.

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