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SHORT COMMUNICATION

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Monodisperse micron-sized cross-linked polystyrene particles. VI. Understanding of nucleated particle formation and particle growth

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Abstract The procedure of nucleated particle formation and particle growth in dispersion polymerization was studied with the intention of understanding the production of monodisperse polystyrene particles cross-linked with urethane acrylate (UA). The time required for the formation of primary particles was determined exactly from the turbidity measurement of the reaction mixture with the polymerization time. It could be found that differing from conventional divinyl cross-linkers, such as divinylbenzene, UA had a boundary concentration where the association and coagulation of preformed nuclei with other oligomers and/or nuclei effectively took place until the primary particle formed. Similarly to linear polystyrene particles, the particle number density of the primary particles cross-linked with UA remained constant to the final particles. This observation verifies the suggestion that the primary particles cross-linked with UA readily absorbed the monomers from the medium during the stage of particle growth.

Key words Nucleated particle formation · Urethane acrylate · Turbidity measurement · Boundary concentration · Stage of particle growth

Introduction

Micron-sized polymer particles having extreme monodispersity have been produced by dispersion polymerization in polar media [1, 2]. They had spherical shapes and clear surfaces. The main contribution of these characteristics could be found in that once the primary particles formed they grew by the diffusion of the monomers in the medium [3, 4]. However, in case of cross-linking, a somewhat different polymerization mechanism was proposed [5, 6]; because the primary particles are also cross-linked, they grow by the precipitation of oligomers and/or small particles generated in the medium. Therefore, the resulting particles commonly have a polydisperse size distribution, a rough surface, and even coagulum.

Previously, we produced monodisperse micron-sized polymer particles having a cross-linked network structure by simple dispersion polymerization [7–9]. From the studies, we could find that the monomer swellability of the primary particles played a crucial role in determining the monodispersity and shape of the final particles. Moreover, the urethane acrylate (UA) used as a cross-linker exhibited an excellent ability in absorbing monomers in the medium during the stage of particle growth. One interesting observation is that the presence of UA did not have a serious influence on the particle formation [10]. To understand this result, the procedure of nucleated particle formation and continued particle growth should be elucidated more systemically.

The aim of this study is to deduce the particle formation procedure for polystyrene particles cross-linked with UA. The critical time (T_c) required for the formation of primary particles was determined accurately by turbidity measurements. Then, the effect of cross-linker concentration on the T_c values was examined.

Experimental

Materials

Toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry Co.) was vacuum distilled before use. Poly(tetramethylene glycol) (PTMG, $M_w = 1.0 \times 10^3$ g mol^{-1}, Hyosung BASF), poly(vinylpyrrolidone) (PVP K-30, $M_w = 4.0 \times 10^4$ g mol^{-1}, Aldrich), and di-2-ethylhexyl ester of sodium sulfosuccinic acid (Aerosol-OT, American Cyanamid) were used as received. The inhibitors in 2-hydroxyethylmethacrylate (HEMA, Aldrich), styrene (Aldrich), and divinylbenzene (DVB, Aldrich, purity 55% isomer) were removed using a removing column (Aldrich). 2,2-Azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) was recrystallized from methanol.

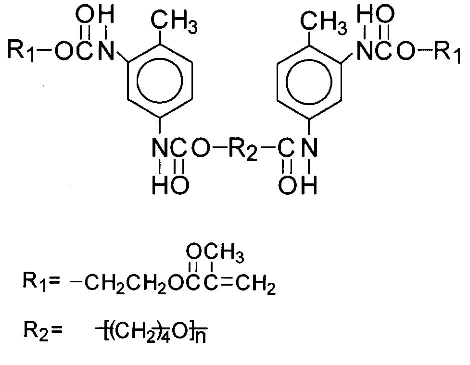
Synthesis of UA cross-linker [7–10]

All reactions were carried out in a four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. TDI (2 mol) was poured into the glass reactor and nitrogen gas was inlet for 10 min to eliminate the residual moisture. Then, 1 mol PTMG was added slowly into the reactor. The reaction temperature was raised to 80 °C, resulting in the molecular structures having flexible poly(tetramethylene oxides) in the middle and isocyanates at the ends. The required NCO value during the reaction was determined using the dibutylamine back-titration method. After dissolving 1 wt% dibutyltindilaurate into the reactor, 2 mol HEMA was continuously reacted with the residual isocyanates at 45 °C for 12 h, resulting in the molecular ends being capped with the reactive vinyl groups. Other detailed reaction conditions were described in our previous studies. Average molecular weights measured by gel permeation chromatography were $M_n = 1.8 \times 10^3$ g mol^{-1} and $M_w = 2.5 \times 10^3$ g mol^{-1} [7]. The molecular structure of UA is presented in Scheme 1.

Dispersion polymerization of styrene and UA

The general dispersion polymerization procedure was followed [3–5, 7]. AIBN, PVP, Aerosol-OT, styrene, UA, and ethanol were weighed into 50-ml glass vials. After sealing in a nitrogen atmosphere, the vials were submerged in a thermostated water bath and tumbled with a rotation speed of 40 rpm. The polymerization was carried out at 70 ± 0.1 °C. All ingredients are summarized in Table 1.

Turbidity measurement



Scheme 1 Molecular structure of the urethane acrylate synthesized

Table 1 Standard recipe of dispersion polymerization: 70 °C; 24 h; 10 wt% of monomer concentration based on total weight

Ingredients	Weight (g)
Styrene	1.000
Cross-linker[a]	Variable
Poly(vinylpyrolidone)	0.178
Aerosol-OT	0.045
2,2-azobis(isobutyronitrile)	0.010
Ethanol	8.777

[a] Urethane acrylate and divinylbenzene were added with varying concentration

The turbidity change of the reaction mixtures was measured with a thermooptical analyzer (Mettler FP90). The reaction mixture was sealed in a glass tube of 1-mm inner diameter. Then, the light intensity was detected every 10 s at 70 °C. The turbidity was calculated from following equation [11, 12]:

$$\tau = \frac{1}{l}\ln\frac{L_0}{L} , \qquad (1)$$

where, l is the light path length, L_0 is the incident light intensity, and L is the light intensity after passing through the path.

Particle size analysis

Vials containing all the ingredients listed in Table 1 were submerged in the thermostated water bath at 70 ± 0.1 °C. To adjust the polymerization conditions to the turbidity measurement, the polymerization was carried out at the stationary state. Right after the extraction of the vial, a drop of 1% hydroquinone solution was added and quenched in ice water. Then, the particle diameters were measured with a Zetasizer (Malvern Instruments). The diameters of the final particles were measured with a scanning electron microscope (Jeol, JSM-6300) [7–10].

Results and discussion

In dispersion polymerization of linear polymers, the particle formation procedure is usually described as follows [3, 13]. At the beginning of the polymerization, the system is homogeneous. Then, unstable nuclei appear suddenly and quickly aggregate with each other. Lastly, primary particles are formed. These primary particles grow until all monomers in the medium are consumed. However, for the cross-linked system, it is difficult to understand clearly the procedure of nucleation and primary particle formation. This is attributed to the cross-linked network structure of the primary particles. Here, we tried to understand the particle formation procedure in the cross-linked system by employing turbidity measurements.

The turbidity change of the reaction mixture containing different cross-linkers with the polymerization time is shown in Fig. 1. At the initial stage, the turbidities of the reaction mixtures were near zero; however, after a certain polymerization time, the turbidity started to increase. One interesting thing is that the time (we named this the critical time, T_c) when the turbidity increased suddenly was very accurate and

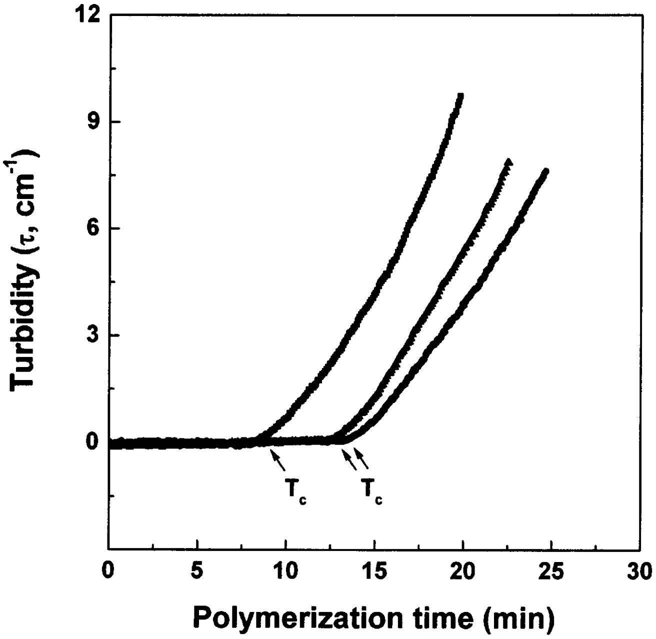


Fig. 1 Turbidity change with polymerization time at the stationary state: linear polystyrene (*PS*) (-■-), PS cross-linked with 3 wt% urethane acrylate (*UA*) (-●-), and PS cross-linked with 0.5 wt% divinyl benzene (DVB) (-▲-). Each cross-linker concentration was selected considering the difference in molecular weight and cross-linking density: 3 wt% UA = 0.5 wt% DVB = 0.002 mol%

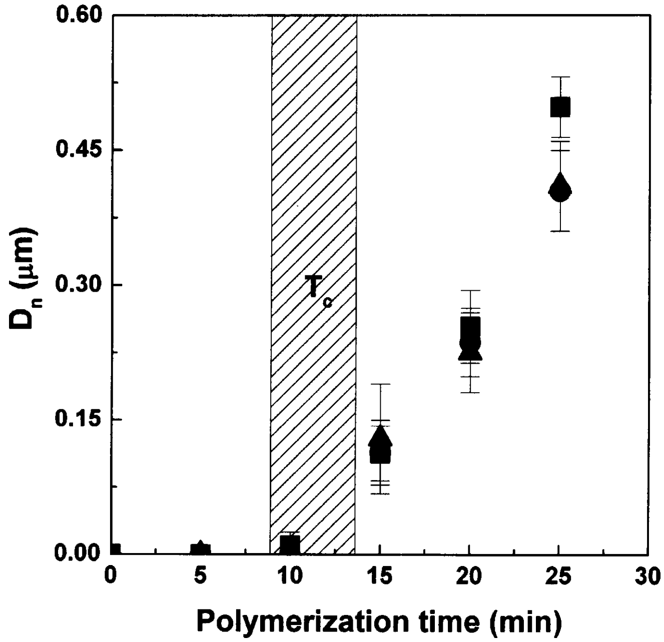


Fig. 2 Average particle diameter with polymerization time at the stationary state: linear PS (-■-), PS cross-linked with 3 wt% UA (-●-), and PS cross-linked with 0.5 wt% DVB (-▲-)

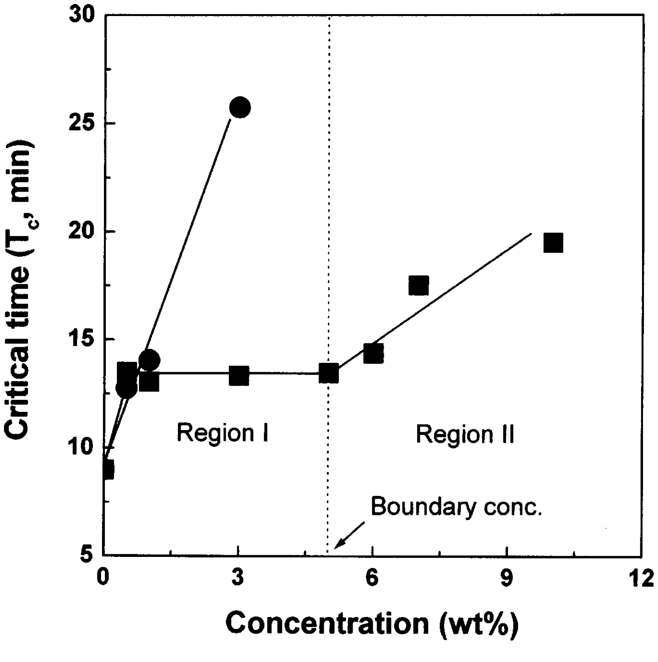


Fig. 3 Critical time with the concentration of the cross-linkers UA (-■-) and DVB (-●-)

reproducible. Considering that the uncertainties in the measured turbidities contribute to the majority of the measured error for the particle size at low turbidities, the particle sizes detected at T_{c} are located in the hundreds-of-nanometer range [12]. On the basis of this, we regarded this T_{c} as the time when the primary particles formed. To validate the T_{c} values determined by turbidity measurements, the particle size analysis was carried out under the same polymerization conditions as for the turbidity measurements and the results are shown in Fig. 2. From the data, it is difficult to obtain an exact trend of the variation in particle size with the polymerization time during the primary particle formation. This is because nucleation and coagulation took place simultaneously within a few minutes [13]. However, it turns out that even though there was a somewhat large error deviation in the particle sizes, the time when the particles were detected was in good accord with the T_{c} values determined by the turbidity measurements.

The T_{c} values measured with different concentrations of cross-linkers are shown in Fig. 3. We selected DVB as a conventional divinyl monomer in order to compare it with UA cross-linker. When using DVB, T_{c} increased sharply from low concentrations. This means that when the particles were cross-linked with DVB, it took a long time until the primary particles had fully matured and were detected. There seemed to be a continuous second nucleation. The broad size distribution of the DVB-cross-linked polystyrene particles at high conversion is due to this long nucleation time. The T_{c} values for UA-cross-linked particles showed a different trend. To a certain concentration of UA, the T_{c} values remained

Table 2 Particle characteristics of polystyrene (*PS*) particles cross-linked with urethane acrylate (*UA*) and divinylbenzene (*DVB*)

Symbol[a]	After nucleation[b]		Final particles	
	D_n (μm)	N_p ($\times 10^{-11}$, Ncm^{-3})[c]	D_n (μm)	N_p ($\times 10^{-11}$, Ncm^{-3})
PS	0.497 ± 0.035	0.708	1.516	0.548
PS-UA3	0.405 ± 0.043	1.329	1.245	1.010
PS-DVB0.5	0.410 ± 0.050	1.030	2.077	0.213

[a] PS-$\alpha\beta$: α and β correspond to the selected cross-linker and its concentration based on total monomer weight

[b] The average was taken after five time measurements

[c] Conversions were determined by the gravimetric method [14]. Each sample was dried under vacuum at ambient temperature until the weight change was less than 0.0001 g

constant. Beyond this concentration, the T_c values started to increase. The presence of this boundary concentration suggests that there exist two regions that control the particle formation. That is, before the boundary concentration of UA, the association of oligomers and the coagulation of preformed nuclei with other oligomers and/or nuclei took place effectively until the primary particle formed, irrespective of the presence of UA. Beyond the boundary concentration, however, the continuous second nucleation appeared to be generated just like in the case of DVB. Incidentally, this boundary concentration (about 5 wt%) determined by the T_c values was the maximum concentration where the monodisperse polystyrene particles cross-linked with UA could be produced [8].

In Table 2, the particle number densities, N_p, right after the formation of the primary particles are listed and compared with those of the final particles, allowing the effect of cross-linking on the particle growth to be observed. N_p of UA-cross-linked polystyrene particles displayed a negligible difference between primary particles and final particles just like in the case of linear polystyrene. This result supports our previously proposed polymerization procedure that the primary particles cross-linked with UA grew by monomer diffusion from the medium [7–10]. However, N_p of DVB-cross-linked polystyrene particles was reduced after the formation of the primary particles. This reveals that in conventional cross-linking of divinyl monomers, the primary particles grow by the precipitation of nuclei and/or small particles onto their surface [5, 6].

From these results, we concluded that the monodispersity of the cross-linked polymer particles in dispersion polymerization could be readily achieved by manipulating the time for the formation of the primary particles and by controlling the diffusion characteristics of the monomers in the medium during the stage of particle growth.

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References

1. Barrette KEJ (1975) Dispersion polymerization in organic media. Wiley, New York
2. Ober CK, Lok KP (1987) Macromolecules 20:268
3. Tseng CM, Lu YY, El-Aasser MS, Vanderhoff JW (1986) J Polym Sci Polym Chem Ed 24:2995
4. Lu YY, El-Aasser MS, Vanderhoff JW (1988) J Polym Sci Part B Polym Phys 26:1187
5. Hattori M, Sudol ED, El-Aasser MS (1993) J Appl Polym Sci 50:2027
6. Li K, Stover HDH (1993) J Polym Sci Part A Polym Chem 31:2473
7. Kim JW, Suh KD (1998) Colloid Polym Sci 276:870
8. Kim JW, Suh KD (1999) Colloid Polym Sci 277:210
9. Kim JW, Suh KD (1999) Colloid Polym Sci 277:66
10. Ryu JH, Kim JW, Suh KD (1999) Colloid Polym Sci 277:1205
11. O'Neill ML, Yates MZ, Harrison KL, Johnston KP (1997) Macromolecules 30:5050
12. O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP (1998) Macromolecules 31:2856
13. Shen S, Sudol ED, El-Aasser MS (1994) J Polym Sci Part A Polym Chem 32:1087
14. Ho CH, Chen SA, Amiridis MD, Van Zee JW (1997) J Polym Sci Part A Polym Chem 35:2907