Colloid Polym Sci 277:1205–1209 (1999)

SHORT COMMUNICATION

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Monodisperse micron-sized crosslinked polystyrene particles. IV. Effect of network structure on polymerization procedure

Received: 1 April 1999
Accepted in revised form: 29 June 1999

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Abstract Monodisperse micron-sized polystyrene particles crosslinked using urethane acrylate were produced by dispersion polymerization in ethanol solution and the effect of the crosslinked network structure on the polymerization procedure was studied. The influences of the concentrations of the initiator and urethane acrylate on the particle diameter (D_n), the particle number density (N_p), and the polymerization rate (R_p) were found to obey the approximate relationships $D_n \propto [\text{initiator}]^{0.43} [\text{urethane acrylate}]^{0.05}$, $N_p \propto [\text{initiator}]^{-1.30} [\text{urethane acrylate}]^{0.19}$, and $R_p \propto [\text{initiator}]^{0.24 \pm 0.02}$. The power-law dependence of D_n and N_p on the initiator concentration showed a similar trend to that of linear polystyrene reported in the literature. Especially, it was found that urethane acrylate does not have a serious effect on D_n and N_p of the particles produced. The dependence of R_p on the initiator concentration was observed to be higher than that of linear polystyrene, suggesting that there is still competition between heterogeneous polymerization and solution polymerization because of the crosslinked network structure of the primary particle.

Key words Monodisperse micron-sized polystyrene particles · Urethane acrylate · Particle diameter · Particle number density · Polymerization rate

Introduction

Recently, there has been considerable interest in the production of polymer particles by dispersion polymerization, due mainly to their spherical shape and highly monodisperse size distribution [1–3]. One of the characteristics of this dispersion polymerization is that once the primary particles form, particle growth continues through the diffusion of the monomers in the medium into the primary particles [3, 4]. This is the main contribution of the extremely high monodispersity of the final polymer particles. However, in the dispersion polymerization of crosslinked polymer particles using divinyl monomers, particle growth is achieved by the precipitation of the nucleated oligomers or particles onto the surface of the primary particles, because of the nonswellability of the crosslinked primary particles [5, 6]. This different polymerization procedure enhances the possibility to generate second nucleation during the particle growth stage, which eventually leads to the polydisperse size distribution.

In our previous work [7, 8], we successfully produced highly monodisperse micron-sized crosslinked polystyrene particles. As a useful monomer-swellable crosslinker, a urethane acrylate was designed with a flexible tetramethylene oxide in the middle and two vinyl groups at both ends enabling a crosslinked network to be formed [8, 9]. Owing to the flexible molecular structure of the urethane acrylate, the styrene monomers in the ethanol medium seemed to readily diffuse into the primary particles during particle growth.

The aim of this study is to understand the polymerization procedure for the polystyrene particles crosslinked with urethane acrylate. The influences of the concentrations of initiator and urethane acrylate on the particle diameter, the particle number density, and the polymerization rate were examined.

Experimental

Materials

Toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry Co.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w = 1.0 \times 10^3$ g mol^{-1}, Hyosung BASF), polyvinylpyrrolidone (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 inhibitor in 2-hydroxyethyl methacrylate (HEMA, Aldrich) and styrene (Aldrich) was removed using a removing column (Aldrich). 2,2′-azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) was recrystallized from methanol.

Synthesis of urethane acrylate crosslinker [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 let in 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 so that 2 mol TDI reacted with 1 mol PTMG, resulting in molecular structures having flexible poly(tetramethylene oxide) 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 in the reactor, 2 mol HEMA was reacted with the residual isocyanates at 45 °C for 12 h, capping the molecular ends with the reactive vinyl groups. The reaction end point was determined by the disappearance of the NCO stretching peak (2270 cm^{-1}) using IR spectroscopy. The reaction procedure and molecular structure are presented in Scheme 1.

Dispersion polymerization of styrene and urethane acrylate

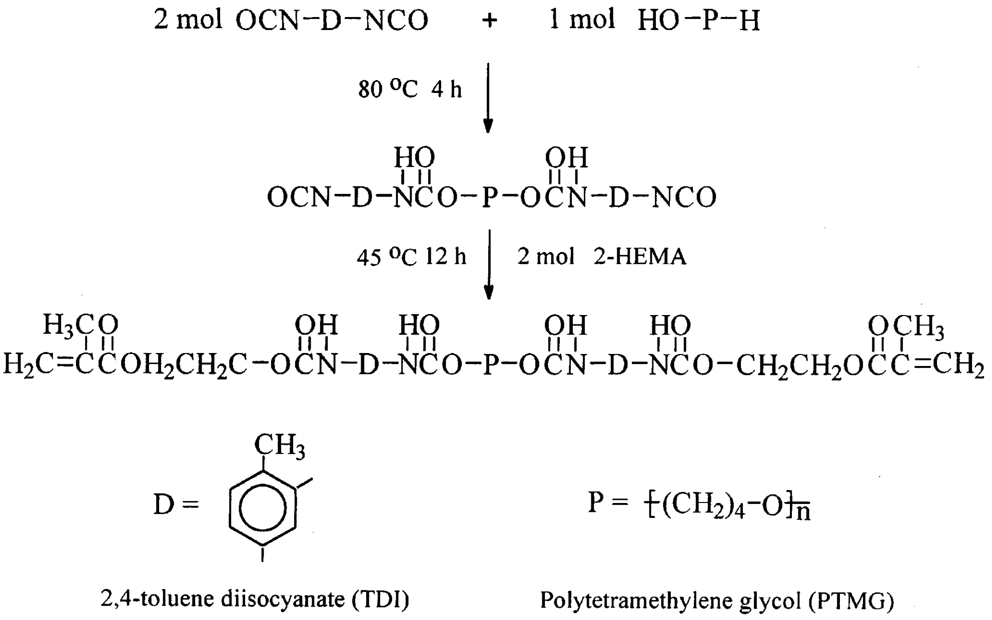
A general dispersion polymerization procedure was followed [3–5, 7, 8]; AIBN, PVP, Aerosol-OT, styrene, urethane acrylate, and ethanol were weighed into 50-ml glass vials. For the polymerization kinetics study, the amounts of AIBN and urethane acrylate added were varied. After sealing in a nitrogen atmosphere, 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 used are summarized in Table 1.

Measurements

Molecular weights were measured at 25 °C using a model 410 gel permeation chromatograph equipped with Styragel HR 1–4 columns from Waters Associates. The average molecular weights of urethane acrylate calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards were $M_n = 1.8 \times 10^3$ g mol^{-1} and $M_w = 2.5 \times 10^3$ g mol^{-1}. Particle diameters were measured using a scanning electron microscope (SEM, JSM-6300, JEOL). Diameters of about 200 individual particles were measured from SEM photographs and the average was taken. Conversions were determined by a gravimetric method. The vials containing 10 g total ingredients were extracted from the thermostated water bath at different 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 fractional conversion was calculated as follow [11]

$$C = \frac{M_2 - M_1 \times (W_2 + W_3)}{M_1 \times W_1} \quad , \qquad (1)$$

where C is the calculated fractional conversion, M_1 is the weight of the sample before drying, M_2 is the weight of the sample after



Scheme 1 Reaction procedure and schematic molecular structure of urethane acrylate (*UA*)

Table 1 The standard recipe for the dispersion polymerization of styrene and urethane acrylate (*UA*)[a]

Ingredient	Weight (g)
Styrene	0.970
UA (3 wt%)	$0.030^{\mathrm{variable}}$
Polyvinylpyrrolidone	0.179
Aerosol-OT	0.045
2,2′-azobis(isobutyronitrile)[b]	$0.010^{\mathrm{variable}}$
Ethanol	8.777

[a] 70 °C; 24 h; 10 wt% of monomer concentration based on total weight
[b] The weight percentage was varied against the total monomer weight (1 wt% in this simple)

drying, w_1 is the weight percentage of the monomers (styrene monomer and urethane acrylate) w_2 is the weight percentage of the stabilizer, and w_3 is the weight percentage of initiator.

Results and discussion

For the polystyrene particles crosslinked with urethane acrylate, we tried to understand the polymerization procedure further. A SEM photograph and a particle size histogram for the polystyrene particles crosslinked with 3 wt% urethane acrylate are shown in Fig. 1. As shown, the particles obtained had high monodispersity and clear surfaces. Particle diameters obtained for a series of compositions are listed in Table 2. These results are regarded as being closely related to the unique polymerization procedure, when crosslinking with urethane acrylate occurred.

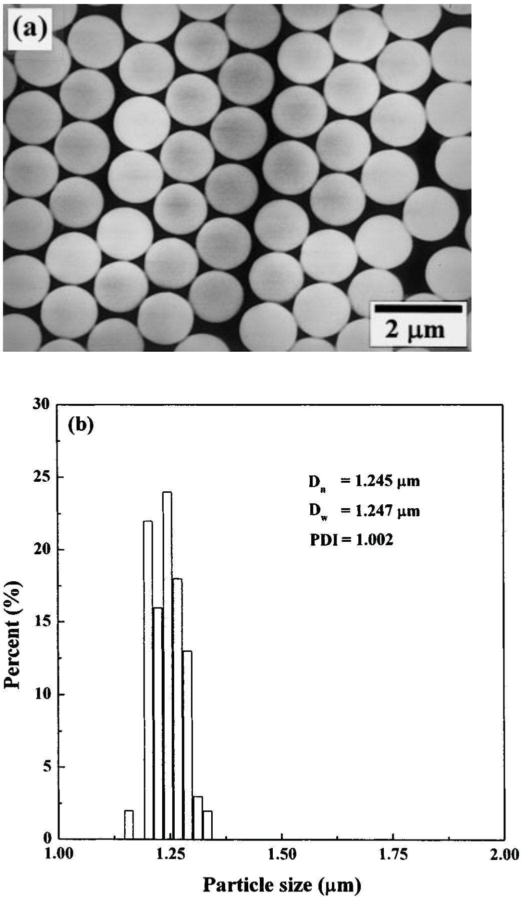


Fig. 1 **a** Scanning electron microscope photograph and **b** particle size histogram of polystyrene particles crosslinked with 3 wt% UA

Table 2 The particle sizes of the crosslinked polystyrene particles[a]

UA[b]	Particle size (*μ*m)		Polydispersity index	C
	D_n	D_w	(D_w/D_n)	
UA-0.5-3	1.060	1.072	1.011	0.92
UA-1-3	1.245	1.247	1.002	0.94
UA-2-3	1.960	1.970	1.005	0.95
UA-2.5-3	2.010	2.020	1.005	0.95
UA-1-0.5	1.340	1.341	1.001	0.93
UA-1-1	1.291	1.292	1.001	0.95
UA-1-5	1.185	1.248	1.053	0.96

[a] 70 °C; 24 h; 10 wt% of monomer concentration based on total weight
[b] UA-α-β; α and β correspond to the concentrations (weight percentage based on the total monomer weight) of 2,2′-azobis (isobutyronitrile) and UA, respectively

The dependence of the particle diameter (D_n) and the particle number density (N_p) for polystyrene particles crosslinked with 3 wt% urethane acrylate on the initiator concentration is shown in Fig. 2. It was found that D_n and N_p followed power laws with exponents of 0.43 and −1.30, respectively. This power-law dependence coincided well with the earlier work of Tseng et al. [3], Lu et al. [4], and Paine et al. [12]. They obtained exponents of 0.39–0.4 for the particle size dependence and an exponent of −1.2 for the particle number density dependence. At the present stage, it is difficult to deduce an exact polymerization procedure from the power-law dependence; however, the above result implies that the polymerization procedure was fairly similar to that of linear polystyrene, even in the crosslinked state. That is, irrespective of the presence of urethane acrylate, the rate of association of the oligomers and/or the coagulation rate of the unstable nuclei to form larger primary particles had a tendency towards increasing with an increase in initiator concentration [3]. One possible explanation for this result lies in the monomer-swellable molecular structure of urethane acrylate, as described previously [7, 8]. Then, it is necessary to examine the effect of the concentration of urethane acrylate on the particle formation. The dependence of D_n and N_p for the crosslinked polystyrene particles on the concentration of urethane acrylate is shown in Fig. 2b. The powers of D_n and N_p were −0.05 and 0.19, respectively, which reveals

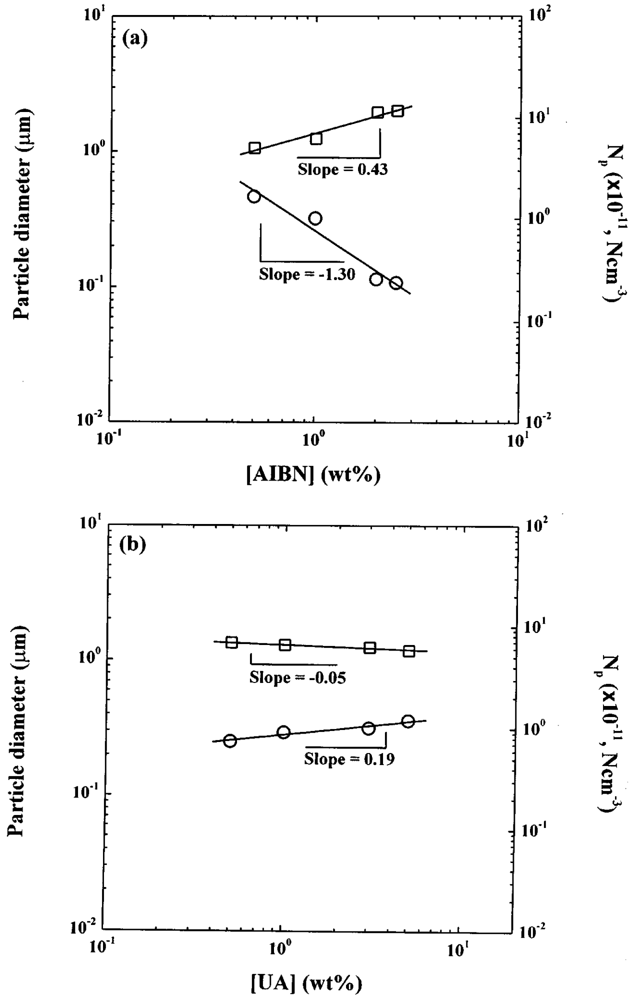


Fig. 2 Dependence of particle diameter (□) and particle number density (○) of polystyrene particles crosslinked with UA on concentrations of **a** 2,2′-azobis(isobutyronitile) (*AIBN*) (3 wt% UA) and **b** UA (1 wt% AIBN)

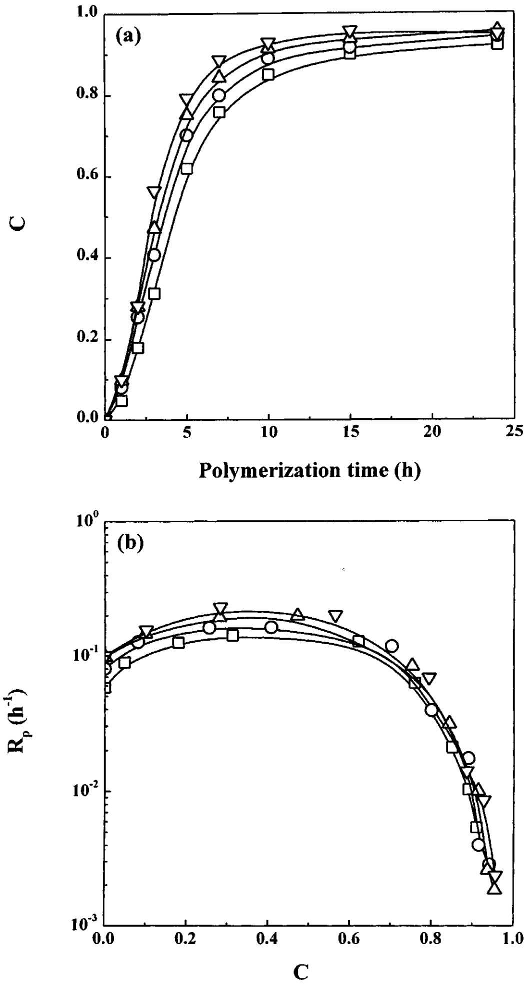


Fig. 3 a Fractional conversion–polymerization time curves and **b** polymerization rate–fractional conversion curves for polystyrene particles crosslinked with 3 wt% UA with changing AIBN concentration 0.5 wt% (□), 1 wt% (○), 2 wt% (△), 2.5 wt% (▽)

that the influence of urethane acrylate on particle formation was negligible. The slight deviation in D_n and N_p might be due to a trace of the crosslinked network structure.

The conversion–polymerization time curves and the polymerization rate (R_p)–conversion curves for the polystyrene particles crosslinked with 3 wt% urethane acrylate with changing initiator concentration are shown in Fig. 3. In the low conversion region, R_p increases with an increase in initiator concentration. In contrast in the high conversion region (beyond 0.4), R_p is independent of the initiator concentration. This suggests that there is competition between solution polymerization and heterogeneous polymerization [6]. In order to evaluate the polymerization process, R_p in Fig. 3b was replotted double-logarithmically against the initiator concentration at various fractional conversions and this plot is shown in Fig. 4. For selected conversions, R_p was observed to follow the dependence of the 0.24 ± 0.02 power on the initiator concentration, which is a relatively high value compared with the linear polystyrene dependence of the 0.1 power [4]. In the dispersion polymerization for the linear polystyrene, R_p was nearly independent of the initiator concentration. This observation suggests that heterogeneous polymerization predominates throughout the polymerization process [4, 5]; however, for our polymerization system, it can be said that heterogeneous polymerization could not dominate the whole polymerization process. 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, and this also made the solution polymerization process favorable.

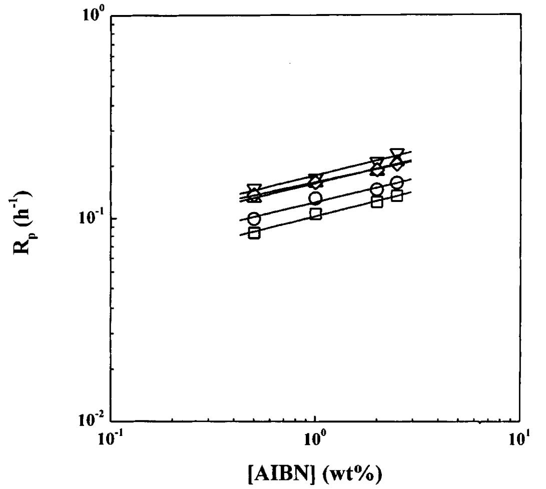


Fig. 4 Dependence of polymerization rate of polystyrene particles crosslinked with 3 wt% UA on AIBN concentration at selected fractional conversion: 0.05 (□), 0.1 (○), 0.2 (△), 0.4 (▽), 0.5 (◇)

From the above results, it is deduced that although urethane acrylate imparted crosslinked network structure to the polystyrene particles it only had a slight influence on the polymerization procedure by means of its monomer-swellable characteristics. Uniquely, the urethane acrylate crosslinked polystyrene particles followed the solution polymerization process together with heterogeneous polymerization.

Acknowledgement The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1999 (98-017-D00010).

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