Heterogeneous Cross-Linking of Polymer Latexes

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The preparation of a porous material by cross-linking of latex particles is described. The particles were obtained by the concentrated emulsion procedure. A concentrated emulsion of methyl methacrylate with an internal phase ratio of 0.91 was prepared first, by using an aqueous solution of sodium dodecyl sulfate as the continuous phase. When the polymer conversion reached about 20%, the concentrated emulsion was dispersed in a dilute aqueous solution of hexamethylenediamine. The latexes flocculated in the presence of diamine, upon heating at 40 °C. However, the flocculated solid became insoluble in benzene only after subsequent heating at 150 °C. IR, HPLC, and swelling studies suggest that cross-linking, produced by the diamine, is responsible for insolubilization. The materials thus obtained exhibit higher equilibrium swelling and faster swelling than the bulk cross-linked materials.

Introduction

Conventionally, cross-linking is performed homogeneously by dissolving a cross-linking agent in the monomer or polymer. A novel type of cross-linking, which we call heterogeneous, because it involves the cross-linking on the surface of and between latexes, is suggested in this paper.

Latex particles were prepared by the concentrated emulsion technique. This method has been successfully employed in this laboratory to prepare various polymer latexes such as polystyrene,[1] polyacrylamide,[2] and copolymer of styrene and methacrylic acid.[3] Some distinctive features of this method are (1) the utilization of a small volume fraction of continuous phase (typically less than 10%) and (2) the persistence of the dispersed phase structure throughout polymerization. The concentrated emulsion method was employed because the latex concentration can be easily controlled by the addition of various amounts of aqueous solution.

When the concentrated emulsion of methyl methacrylate in water was about 20% polymerized, upon heating at 40 °C, it was dispersed in a dilute aqueous solution of hexamethylenediamine (HMDA). The polymer conversion was limited to 20% because it was difficult to disperse the latexes of higher conversions. Upon further heating at 40 °C, the polymer latexes were found to flocculate and to form a rigid and porous material. However, only after subsequent heating at 150 °C, the flocculated solid became insoluble in benzene. This is a result of the cross-linking produced by the aminolysis between HMDA and poly(methyl methacrylate) on the surface of, between, as well as inside the particles. The cross-linked material, thus prepared,had higher equilibrium swelling and faster swelling than the conventional homogeneous cross-linked material.

Experimental Section

Materials. Methyl methacrylate (MMA, Aldrich) was distilled before polymerization. Azobisisobutyronitrile (AIBN, Alfa), which was used as initiator, was recrystallized from methanol. Sodium dodecyl sulfate (SDS, Aldrich) and hexamethylenediamine (HMDA, Aldrich) were used as received. The water was deionized and distilled.

Polymerization and Synthesis. The concentrated emulsion of MMA was prepared at room temperature by dropwise addition of the monomer (30 mL) containing AIBN (0.3 g) to a small amount of stirred water (3 mL) containing SDS (0.3 g). Details regarding the preparation of the concentrated emulsion were provided in a previous paper.[1] A mild centrifugation was employed to pack the concentrated emulsion into a tube (15-mL capacity). Polymerization was carried out subsequently, upon heating at 40 °C in the presence of air. When the polymer conversion reached about 20% (after about 4 h), the concentrated emulsion was dispersed in a dilute aqueous solution of HMDA (one-third of the emulsion by weight). The colloidal dispersion thus obtained was further heated at 40 °C for 18 h, and during this time, the latexes aggregated into an opaque solid. Further, the obtained solid was washed with fresh water and dried at 50 °C for 24 h. The dried solids were cut in the form of disks (11-12-mm diameter × 1-mm thickness) and then heated in a sand bath at 150 °C under a nitrogen stream to achieve cross-linking.

Instrumentation. The relative molecular size distribution of the polymer was determined by gel permeation chromatography with 500-, 10^4-, and 10^6-Å pore size columns (Waters, Ultrastyragel). Methylene chloride with a flow rate of 1 mL/min was used as the mobile phase, and the wavelength of the detector was 245 nm. The concentrations of MMA and HMDA in the separated liquid phase were determined by HPLC with a μ-Bondapak C_{18} column using CH_3CN/H_2O (50/50 by volume) as the mobile phase. The retention volumes for MMA and HMDA were 5.8 and 13 mL, respectively. IR spectra were recorded with a Perkin-Elmer 727B infrared spectrophotometer, and scanning electron microscopy (SEM) was carried out with an Amray 100A instrument. The latex samples for SEM were prepared by placing a drop of dilute latex solution on a clean cover glass and evaporating at room temperature. Micrographs of the solid samples were taken on their fractured surfaces. A layer of gold was deposited prior to observation.

Swelling Measurements. After the disks were heated at 150 °C for cross-linking, they were immersed in benzene (15 mL) at room temperature, and the amount of benzene absorbed was determined gravimetrically. The excess of benzene present on the sample surface was removed by evaporation at room temperature for a short time prior to weighing. The equilibrium extent of swelling, S, was calculated from the expression

$$S = (W_s - W_0)/W_0$$

where W_0 is the weight measured before immersion and W_s is the weight measured after no change with immersion time was detected.

Results and Discussion

Figure 1 is a scanning electron micrograph of the PMMA latexes produced by the concentrated emulsion polymerization method. It shows that polymerization leads to the formation of spherical particles whose diameters range from submicrons to microns. This partially polymerized system was subsequently dispersed in an aqueous HMDA solution. Upon heating at 40 °C, the latexes flocculated into an opaque solid, leaving an aqueous solution and a small amount of bulk polymer. The compositions of the

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[2] Kim, K. J.; Ruckenstein, E. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 285.

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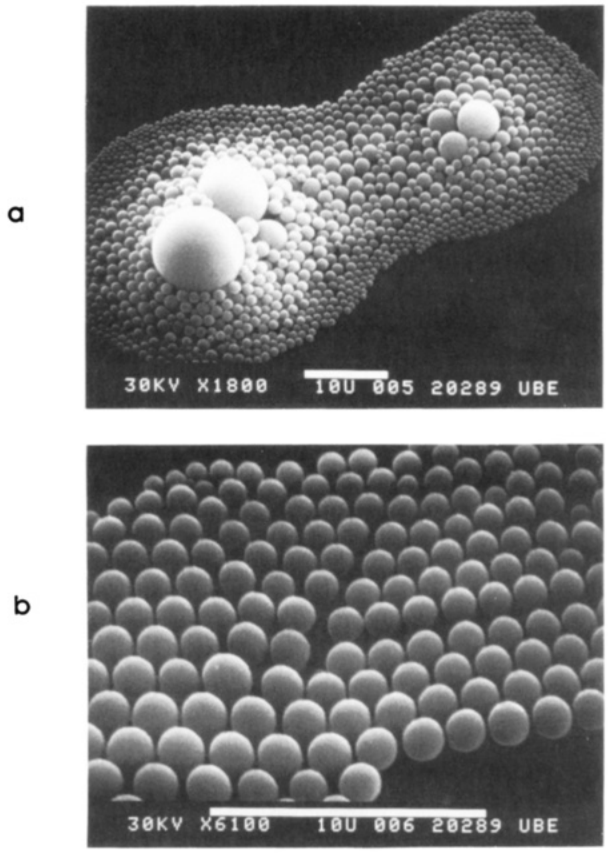

Figure 1. Scanning electron micrographs at two different magnifications of PMMA latexes obtained by the concentrated emulsion polymerization.

Table I. Weight Percent in the Separated Phases after Heating at 40 °C for 18 h

mole ratio (HMDA/ MMA × 10^2)	bulk polymer,[a] wt % with respect to total monomer	MMA in water, wt % with respect to total monomer	HMDA in water, wt % with respect to total HMDA employed
1.3	0.2	0.2	0.9
2.6	0.1	0.1	negligible

[a] Obtained by the precipitation of the entire separated phase in methanol.

separated phases are listed in Table I. The fact that only small amounts of monomer and bulk polymer were separated from the main solid phase indicates that the coalescence of the dispersed phase of the concentrated emulsion (which is responsible for the formation of a bulk monomer phase and hence for some bulk polymerization[1]) is insignificant during the heating process. It is also interesting to note that the separated aqueous phase contains a negligible amount of HMDA. This proves that most of the HMDA is efficiently incorporated into the solid phase by adsorption on the large surface of the latex particles as well as by dissolution in the particles.

Figure 2 presents micrographs of the surface of two solids after heating the dispersed system at 40 °C for 18 h and subsequent drying. It should be noted that the solid material is composed of small particles whose sizes are quite consistent with those of the spherical latexes of Figure 1. This suggests that the polymer latexes flocculate in the presence of HMDA to form a solid without drastic changes in the size and shape of individual particles. For comparison, the partially polymerized system was also dispersed in the same amount of water free of HMDA and then heated at 40 °C. As opposed to the case in which the diamine was present and rigid solids were obtained, fairly loose and brittle solids were formed in the absence of HMDA. This indicates that HMDA facilitates the latex flocculation leading to a more rigid solid. Nevertheless,

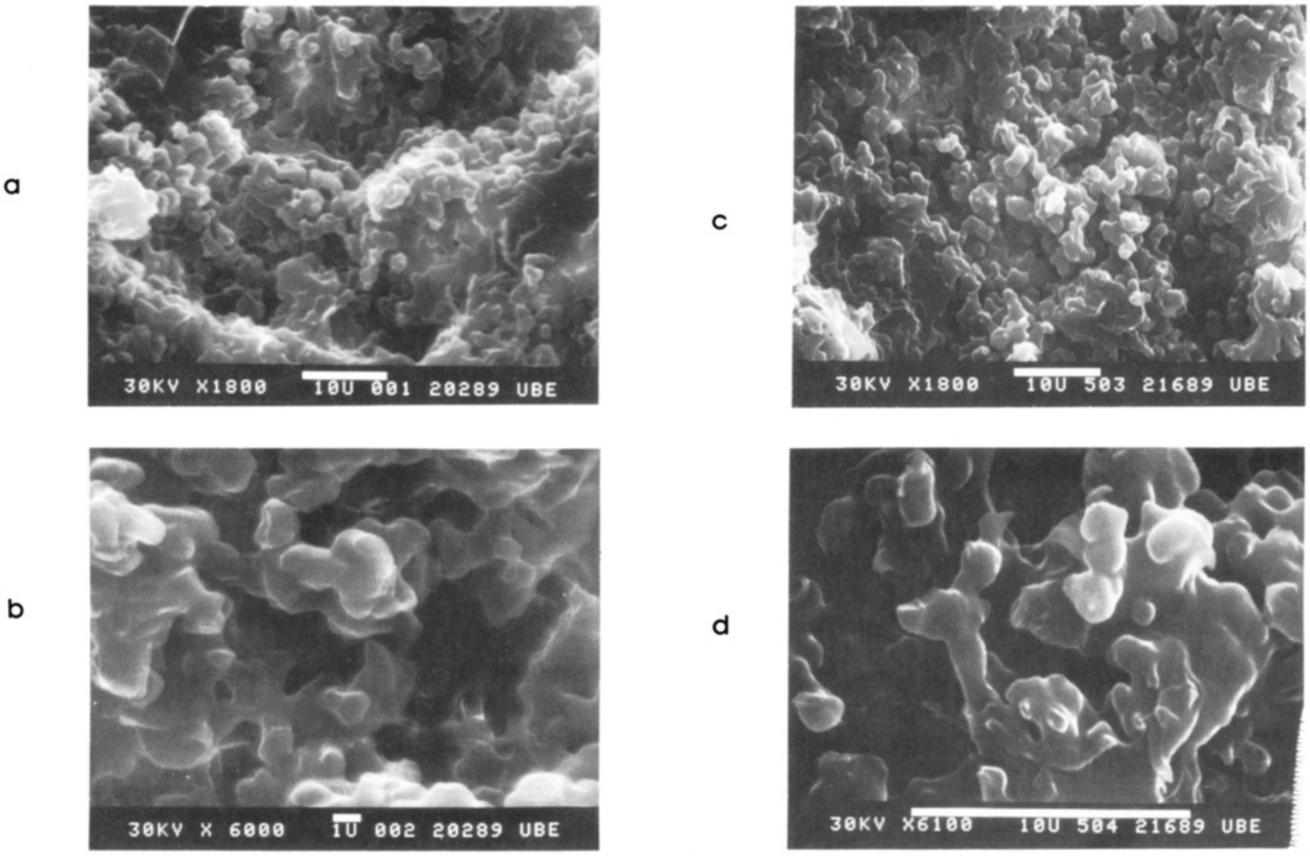

Figure 2. Scanning electron micrographs of the surface of the solids before heating at 150 °C (before cross-linking): a and b 6.5×10^{-3} mole ratio of HMDA/MMA; c and d 2.6×10^{-2} mole ratio of HMDA/MMA.

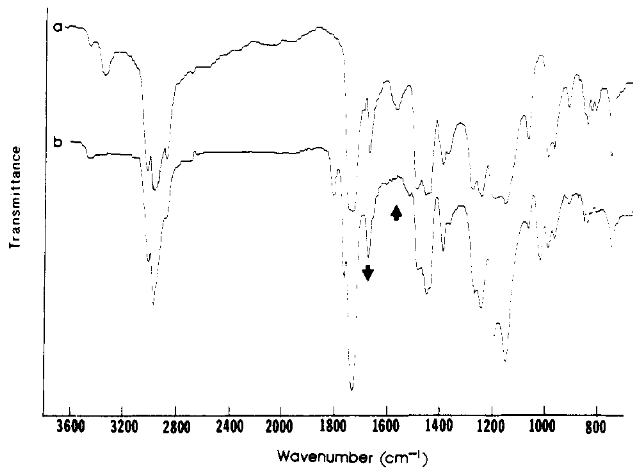

Figure 3. IR spectra of HMDA (23 wt %) embedded in PMMA: (a) before heating; (b) after heating (150 °C, 20 h).

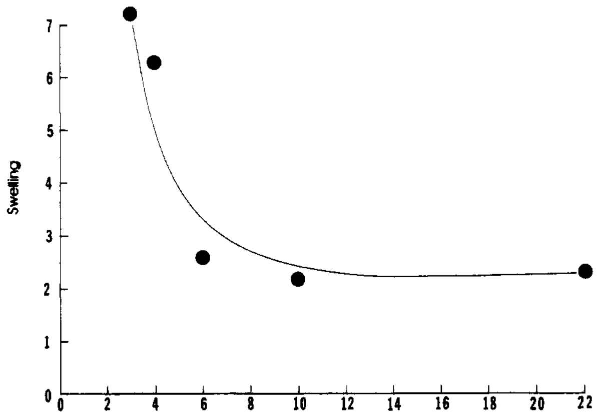

Figure 4. Extent of swelling as a function of heating time at 150 °C (3.3×10^{-2} mole ratio of HMDA/MMA).

the morphologies of the porous solids obtained do not show any appreciable differences at low and high HMDA concentrations (compare Figure 2a with 2c and Figure 2b with 2d). Even additional heating at 150 °C for 22 h has not produced morphological changes.

Because of the small amount of diamine employed, the occurrence of the aminolysis reaction in the solid prepared here could not be demonstrated by direct observation of IR changes. To test the aminolysis reaction in the solid state, IR studies have been carried out by embedding HMDA (23% by weight) in PMMA. Figure 3 contains the IR spectra obtained before and after heating at 150 °C for 20 h under nitrogen. The band at 1700 cm^{-1}, which was observed before heating, can be assigned to the carbonyl group of PMMA which is hydrogen bonded to the amine group, because this band disappeared when HMDA was removed by soaking the sample in hot water (50 °C) for 18 h. The diamine band at 1600 cm^{-1} disappeared after heating, whereas the band at 1700 cm^{-1} persisted after heating because of the formation of a new carbonyl linkage. In addition, after heating at 150 °C, the sample was no longer soluble in benzene, which is a good solvent for PMMA. One may, therefore, conclude that cross-linking due to the aminolysis between HMDA and PMMA does indeed take place in the solid state at 150 °C.

Figure 4 is a plot of the equilibrium extent of swelling of the flocculated solid against heating time at 150 °C. On heating for less than 3 h, the solid remained completely soluble in benzene. However, the solid became insoluble in benzene upon heating for more than 3 h. The amount of benzene absorbed decreases with the heating time and reaches a saturation value. However, in the absence of HMDA, the sample remained completely soluble in benzene, despite extended heating for 24 h. This confirms that there is a chemical cross-linking due to HMDA. It probably takes place in different degrees between the particles as well as on the surface and inside the particles. Several solids prepared with various amounts of HMDA were heated for a fixed period of time (10 h). As shown in Figure 5, the extent of equilibrium swelling decreases with increasing HMDA concentrations. This provides additional evidence that HMDA directly participates in the chemical reaction that is responsible for insolubilization.

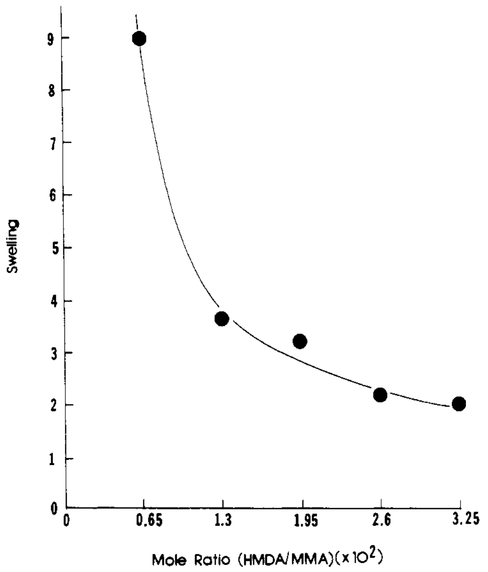

Figure 5. Extent of swelling as a function of the mole ratio HMDA/MMA (heated for 10 h).

Table II. Equilibrium Swelling of Materials[a] Prepared by Heterogeneous and Homogeneous Pathways

mole ratio (HMDA/MMA × 10^2)	heterogeneous	homogeneous
0.65	5.6	2.0
2.6	2.2	1.0

[a] Heated at 150 °C for 22 h.

Table II compares the equilibrium swelling between a heterogeneous cross-linked system and a homogeneous one. It shows that higher swelling is achieved in the heterogeneous system than in the homogeneous one when the same amounts of HMDA are used as the cross-linking agent. This suggests that less cross-linking occurs in the particles than in the homogeneous case and that diamine participates in the cross-linking between particles and on their surface.

The swelling rates in the heterogeneous and homogeneous cross-linkings are compared in Figures 6 and 7 for a similar equilibrium swelling. The swelling of the heterogeneously cross-linked material reaches equilibrium in a time as short as 12 h, while that prepared by homogeneous cross-linking reaches equilibrium in almost 2 weeks.

The possible effect of the GPC traces of the polymer on the swelling rate was also examined. The GPC traces for both heterogeneous and homogeneous systems without cross-linking were determined. As shown in Figure 8, the heterogeneous pathway yields larger molecules. Considering that polymers with smaller molecules, hence with lower molecular weight, are expected to absorb solvent

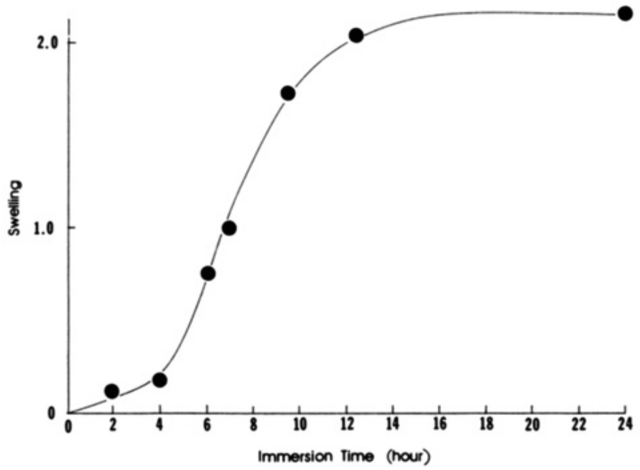

Figure 6. Swelling of the solid obtained by heterogeneous cross-linking as a function of immersion time in benzene at 22 °C. The solid was prepared with 3.3×10^{-2} mole ratio of HMDA/MMA and was heated for 10 h at 150 °C for cross-linking.

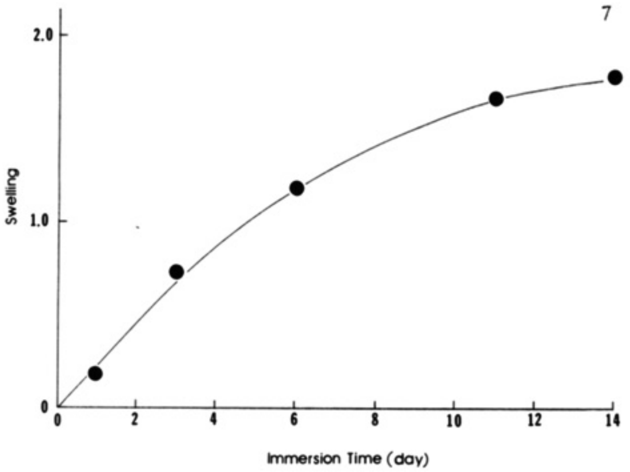

Figure 7. Swelling of the solid obtained by homogeneous cross-linking as a function of immersion time in benzene at 22 °C. The solid was prepared with 6.5×10^{-3} mole ratio of HMDA/MMA and was heated for 22 h at 150 °C.

faster, the molecular weight is unlikely to be a controlling factor in the swelling rate of these systems.

The micrograph of a homogeneously cross-linked system, presented in Figure 9, reveals that its surface is flat and free of voids. This is in sharp contrast with the heterogeneously cross-linked system, which has a rough surface and contains a significant number of voids (Figure 2). Therefore, one can conclude that the large surface area and the easy access of the solvent due to the presence of voids are responsible in part for the rapid swelling of materials prepared by heterogeneous cross-linking.

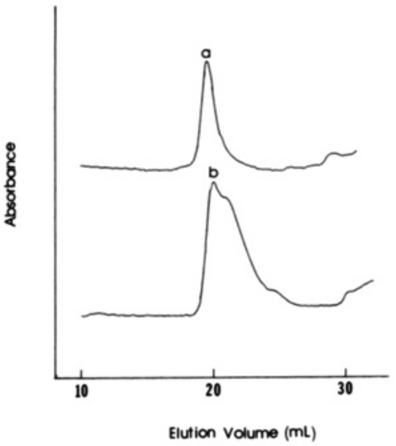

Figure 8. GPC traces of PMMA: (a) the polymerized dispersed phase in the concentrated emulsion before cross-linking; (b) the polymer prepared by bulk polymerization without cross-linking.

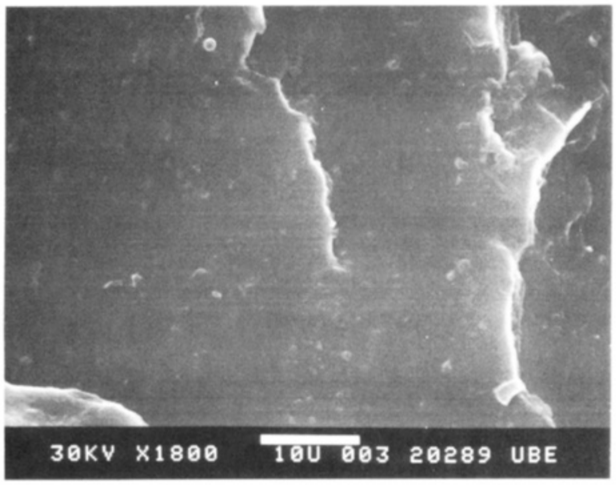

Figure 9. Scanning electron micrograph of the cross-linked polymer prepared by bulk polymerization.

Conclusion

Partially polymerized concentrated emulsions of methyl methacrylate in water were employed to prepare heterogeneously cross-linked solids by dispersing them in dilute aqueous solutions of HMDA. The HMDA-facilitated flocculation of the polymer latexes, which occurs during prolonged heating at 40 °C, leads to a porous material that comprises small particles of micron size. Upon heating at 150 °C, an aminolysis reaction between PMMA and HMDA takes place, leading to what we call heterogeneous cross-linking, since cross-linking between and on the surface of latex particles is very likely involved. Compared to the conventional homogeneous cross-linking, the heterogeneous one developed here has a higher equilibrium swelling as well as faster swelling.