

Synthesis and Characterization of Polyurethaneurea–Vinyl Polymer (PUU–VP) Uniform Hybrid Microspheres by SPG Emulsification Technique and Subsequent Suspension Polymerization

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Received 6 March 2002; accepted 20 September 2002

ABSTRACT: Uniform polyurethaneurea–vinyl polymer (PUU–VP) hybrid microspheres of about 20 μm were prepared by a Shirasu porous glass (SPG) membrane emulsification technique and a subsequent radical suspension polymerization process, that is, a mixture of a 40 wt % urethane prepolymer (UP) solution of xylene and a vinyl monomer (VP) containing an initiator was permeated through the uniform pores of the SPG membrane into a continuous phase containing a stabilizer to form uniform droplets. Then, the droplets were allowed to stand for chain extension at room temperature with di- or triamines for 2 h in the absence or presence of ethyl acetate (EA), followed by suspension polymerization at 70°C for 24 h. The effect of the type and the amount of the monomer composition,

crosslinker, and chain extender on the monomer conversion, particle morphology, and stability of the dispersion was investigated. A strong relationship was found between the compatibility of PUU with VP and the stability of the dispersion. The monomer conversion increased and the stability of the dispersion was improved as the amount of the crosslinker was increased. Solid and spherical PUU–VA hybrid particles with a smooth surface and a higher destructive strength were obtained when a trifunctional crosslinker and a chain extender were used together. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 163–178, 2003

Key words: polyurethanes; composites; interpenetrating networks (IPN)

INTRODUCTION

Polyurethane (PU) is a popular material, since it has intermediate characteristics between rubber and plastics. A well-known example of its application is PU foams, which have been used as cushions and structural materials. The applications of PU have been extended to various elastomer formulations, paints, adhesives for polymers and glass, and artificial leather as well as to biomedical and cosmetic fields. In recent years, PU was treated as an environment-friendly material, because the urethane bond resembles the amide bond, which implies possible biodegradability, promoting PU as one of the ecology-conscious materials.

Compared with nonaqueous dispersions of PU, PU aqueous dispersions (emulsions) have attracted more attention and have been extensively studied because they are easily handled and transported and are

friendly to the environment. The emulsions have been applied in waterborne adhesives, screen printing, wood lacquers, leather and textile finishes, and glass fiber sizing, because of the characteristic elasticity and adhesiveness of the emulsions.¹ There are two types of general preparative methods of PU emulsions: forced and spontaneous types. For the latter case, diisocyanates and diols are synthesized separately in the organic phase to yield an urethane prepolymer (UP) with —NCO groups remaining on both chain ends. Stoichiometric ratios between the —NCO and OH groups are strictly maintained in the formulation. Dibutyltin dilaurate is added as a catalyst. An inverse emulsification technique is normally employed to obtain fine emulsions, that is, water is gradually added to the prepolymer solution, inducing a phase inversion. Usually, submicron-size PU spheres are formed by the chain-extension reactions between the —NCO ends and diamines or diols. Dihydroxycarboxylic acids [e.g., dimethylol propionic acid,^{2–9} (DMPA)] or dihydroxytertiary amines (e.g., *N*-methyl diethanolamine)^{10,11} are added in the first stage, neutralized with base (tertiary amines) or acid, respectively, and induce spontaneous emulsion in the aqueous phase.

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Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 20125616.

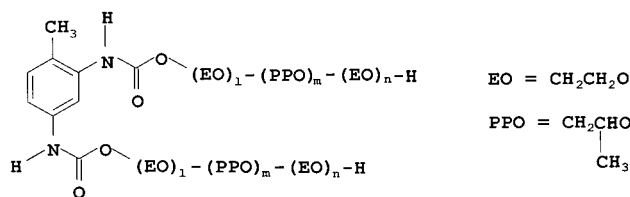
PU shows many excellent properties in applications such as a good film-formation ability, abrasion and scratch resistance, as well as flexibility and toughness. However, it also has some disadvantages, such as high cost, low pH stability, and limited outdoor durability. On the other hand, vinyl polymers (VPs) such as polyacrylate and polystyrene can compensate for these disadvantages. Therefore, hybrid microspheres containing PU and VP became attractive to many researchers in recent years. A direct and popular strategy is to physically mix preformed PU and VP.¹² Although some benefits have been obtained from this approach, the properties of the resulting material do not correspond to the expected values as predicted by the simple "rule of mixtures," because of the limited compatibility between the VP and PU. An alternative approach is to form hybrid particles, which consist of intimately entangled or crosslinked VP and PU chains. Differently from physical blends, which have distinct VP and polyurethaneurea (PUU) domains, the intimately entangled or crosslinked hybrid particle forms an interpenetrating network (IPN) of VP and PUU chains at the molecular level or nanoscale level. This is accomplished by *in situ* polymerization of the vinyl monomers and chain extension of UPs, which have been previously mixed.¹³

The properties of hybrids are usually better than the value predicted by the "rule of mixtures." El-Aasser et al. studied the preparation of hybrid PU–polyacrylate particles by their miniemulsion polymerization technique.¹⁴ First, they synthesized PU end-capped with isocyanate groups from propylene glycol diol (PPG-diol) and methylene diphenyldiisocyanate (MDI) or isophorone diisocyanate (IPDI) in the presence of 2-hydroxyethyl methacrylate (HEMA), which was used for inducing a double bond on the PU chain. After PU was mixed with *n*-butyl methacrylate (BMA) and hexadecane (HD) homogeneously, the mixture was emulsified into an aqueous phase containing sodium lauryl sulfate (SLS) by sonification to form a miniemulsion. Then, the polymerization of BMA was carried out by elevating the temperature. In their study, HD was used as a costabilizer to retard the Ostwald ripening of the miniemulsion droplets, and HEMA was used for crosslinking between PU and PBMA. They found that the hybrid particle showed a core–shell morphology with PMBA as the core and PU as the shell. Hirose et al.¹⁵ synthesized core–shell-type hybrid PU–polyacrylate (A) emulsions by soap-free seeded emulsion polymerization. Three kinds of morphologies, A/PU, PU/A, and A/PU-*graft*-A, were obtained by changing the combination of monomers and compositions and the period and mode of the monomer addition. Kim et al. incorporated HEMA into a PU emulsion and modified it with copolymerizations of glycidyl methacrylate/acrylonitrile and methyl methacrylate/tetramethylene glycol dimethacrylate.^{16,17}

Commercial interests in PU emulsion are still high, and, recently, new PU emulsions hybridized with conventional vinyl monomers by emulsion,^{18,19} soap-free,²⁰ or dispersion polymerizations^{21,22} have been marketed. One of the disadvantages of these emulsions is the polydispersity of the particles, because a vigorous agitation system is required for the forced-emulsion type and wide distributions of the chain length and internal emulsifier concentration exist for the spontaneous emulsions. As the sizes of PU and hybridized PU particles are limited to the submicron range, no practical method has been established to obtain uniform PU spheres of micrometer scale. Larger and uniform particles can be applied as spacers for liquid crystal displays (LCDs), packing materials for column chromatography, protein carriers, and so on.

We have been working with a particular Shirasu porous glass (SPG) membrane emulsification technique. The SPG membrane is a special porous glass membrane with very uniform pores. By applying adequate pressure, an oil phase containing a monomer, an initiator, and other additives permeates through the uniform pores of the membrane into the aqueous phase to form uniform droplets (O/W emulsion). The stabilizer and surfactant dissolved in the aqueous phase are adsorbed on the surface of the droplets to stabilize them. Then, by elevating the temperature to above the decomposition temperature of the initiator, the suspension polymerization proceeds to form uniform particles. During the polymerization, the monodispersity is maintained if the emulsification and polymerization conditions are adequate. With this method, we have successfully prepared monodispersed polystyrene (PSt),²³ poly(styrene-*co*-methyl methacrylate),²⁴ PSt–polyimide,²⁵ poly(styrene-*co*-2-hydroxyethyl methacrylate),²⁶ and poly(styrene-*co*-*N,N*-dimethylaminoethyl methacrylate)²⁷ microspheres. The coefficient of variation (CV) value, which indicates the size distribution of the particles, was about 10%. Furthermore, we also applied the SPG technique to preparations of special particles and microcapsules using an organic solution of a preformed polymer as the oil phase. After the uniform droplets were prepared, the organic solvent was evaporated. With this modified technique, we successfully prepared a polyacide²⁸ biodegradable particle, a PSt/poly(methyl methacrylate) composite particle,^{29,30} and polymer microcapsules containing magnetite³¹ or TiO₂.³²

In a previous study, we successfully prepared a PUU microsphere³³ by emulsifying a UP/xylene solution using the SPG emulsification technique and a subsequent chain-extending reaction of the prepolymer. By studying the effect of the stabilizer, hard segment, and soft segment of the UP and the condition of the chain-extending reaction, the optimum condition for the preparation of PUU microspheres was established, that is, using MST-1 (Scheme 1), an adduct of 2,4-toluene diisocyanate and poly(ethylene ox-



Scheme 1 Chemical formula of stabilizer MST-1.

ide-*b*-propylene oxide-*b*-propylene), as a stabilizer together with a small amount of sodium lauryl sulfate (SLS) to obtain uniform droplets of UP/xylene. —NCO groups completely disappeared within 4.5 h by adding a chain extender, a piperazine (Pz) aqueous solution, followed by the feeding of ethyl acetate (EA). Using the UP-146 prepolymer, a product of 2 mol of norbornane diisocyanatomethyl (NDIM) reacting with 1 mol of a polyester derived from 1,6-hexane diol and adipic acid, both ends of the chain being stopped with 1,6-hexane diol (Scheme 2), can provide dry spherical particles without them adhering to each other.

In this study, PUU microspheres hybridized with a VP (polyacrylate or PSt) were prepared, based on the previous study, that is, the UP/xylene mixture dissolved in the monomer (sometimes containing a crosslinker) was emulsified into an aqueous phase by the SPG emulsification technique. Then, the prepolymer was chain-extended by adding a chain-extender solution in the aqueous phase. After 2 h of the chain-extending reaction, the polymerization of the vinyl monomer was carried out by radical polymerization. The effects of the type and amount of the chain extender, monomer, and crosslinker on the particle size, monomer conversion, morphology, and destructive strength of the particle were investigated. It was found that hybrid particles of an IPN structure, with a uniform size, smooth surface, and high destructive strength, can be obtained by adding a trifunctional crosslinker for the vinyl monomer and a trifunctional chain extender for the UP to the system.

EXPERIMENTAL

Materials

UP

The chemical formula of the UP used in this study, UP-146, is shown in Scheme 2 with a brief route of the synthesis. UP-146 is a product of 2 mol of NDIM [2,5(and 6)-bis(isocyanato-methyl)bicyclo[2.2.1]heptane] reacting with 1 mol of a polyester derived from 1,6-hexane diol and adipic acid, both ends of the chain being stopped with 1,6-hexane diol. The prepolymer was synthesized and characterized at Nippon NSC Ltd. and served as a 40 wt % xylene solution. The container of the prepolymer was flushed with nitrogen after the content was withdrawn and stored in a refrigerator.

Solvents

Xylene was reagent grade and used as received. EA was a commercial grade and distilled before use. Methanol was a commercial grade and used as received. All the solvents are purchased from the Kishida Chemical Co. Ltd. (Osaka, Japan).

Chain extenders for UP

The bifunctional chain-extender Pz was reagent grade (provided by Nippon NSC Ltd.). The trifunctional chain-extender, diethylenetriamine (DETA; Kanto Chemical Co.) was reagent grade, 2,2',2''-nitrotriethanol (NTE; Kanto Chemical Co., Tokyo, Japan) was commercial grade, and all the chain extenders were used as received.

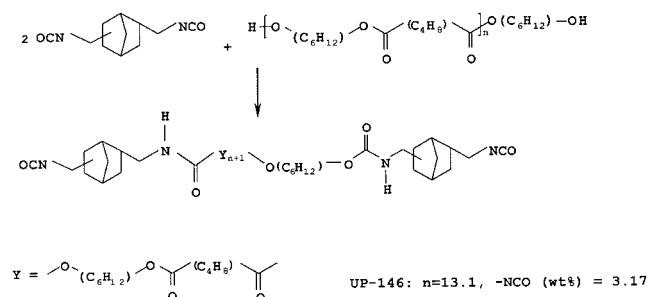
Stabilizers

The MST-1 stabilizer was provided by Nippon NSC Ltd.; a simplified formula, an adduct of 2,4-toluene diisocyanate and poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide), is shown in Scheme 1. It was used with a small amount of SLS (biochemistry grade, Merck, Darmstadt, Germany) to stabilize the emulsion. In a previous study, this stabilizer was found to be more suitable for the preparation of PUU microspheres than were the general stabilizers poly(*N*-vinylpyrrolidone) (PVP) and poly(vinyl alcohol) (PVA). Therefore, it was used in this study.

Monomers

Styrene (St) and methyl methacrylate (MMA) were commercial grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan). Methyl acrylate (MA) and cyclohexyl acrylate (cycloHA) were commercial grade (Kishida Chemical Co.). 2-Ethylhexyl acrylate (2-EHA) and 2-ethylhexyl methacrylate (2-EHMA) were reagent grade (Wako Pure Chemical Industries, Ltd.). All the above monomers were distilled under a vacuum to remove the inhibitor.

A bifunctional crosslinker, ethylene glycol dimethacrylate (EGDMA), was commercial grade (Tokyo Chem-



Scheme 2 Chemical formula and synthesized route of urethane of prepolymer UP-146.

ical Industries, Co., Ltd., Tokyo, Japan) and was distilled under a vacuum. A trifunctional crosslinker, trimethylol propane trimethacrylate (TMPTMA, M-709), was provided by the TOAGOSEI Co., Ltd.) and was used as received.

Initiator

2,2'-Azobis(2,4-dimethylvaleronitrile) (V-65, ADVN; Wako Pure Chemical Industries, Ltd.) was commercial grade and was used as received.

Other chemicals

Sodium nitrite (NaNO_2) was reagent grade (Kishida Chemical Co.) and was used as a water-soluble inhibitor to prevent secondary nucleation in the aqueous phase. The Na_2SO_4 electrolyte was reagent grade (Wako Pure Chemical Industries, Ltd.) and was used to adjust the electrolyte concentration of the aqueous phase. All were used as received. Water was purified by distillation followed by deionization using ion-exchange resins.

Apparatus

A miniature kit for emulsification with an MPG module (microporous glass, a brand name of SPG) installed was purchased from the Ise Chemical Co. A schematic diagram of this kit and the detailed emulsification process were shown in a previous article.²⁸ A membrane with a pore size of 5.2 μm was used in this study. Usually, the droplet size prepared is about six times as large as the pore size of the membrane.²³

Preparation of uniform hybrid microspheres

Emulsification, chain extension, and polymerization

A standard recipe of SPG emulsification conditions is shown in Table I. A 40% xylene solution of the UP (UP-146) was mixed with the monomer and fed into a pressure-tight oil tank. An aqueous phase solution of MST-1 and SLS was fed into a beaker and was stirred gently with a magnet tip. The oil tank was pressurized with nitrogen to a desired level and controlled carefully until a steady release of the droplets in the aqueous phase was established. After the emulsification, the chain-extender aqueous solution was added to the emulsion to perform the chain extension of the UP; sometimes, EA was also added to the emulsion to promote the chain extender to diffuse into the inside of the droplet easily. After the emulsion was allowed to stand at room temperature for 1 h under stirring at 300 rpm, it was transferred to a four-neck glass separator flask equipped with a semicircular anchor-type blade, a condenser, and a nitrogen inlet nozzle. After the emulsion was bubbled with nitrogen gas for an-

TABLE I
Standard Recipe for Preparation
of PUU Hybrid Microspheres

Ingredients	Weight (g)
Disperse phase	
PU prepolymer	4, 6
VP	6, 4
ADV N initiator	0.3, 0.4
Continuous phase	
Water	150–200
SLS	0.15–0.20
NaNO_2	0.015
Na_2SO_4	0.15
MST-1	2, 3
Chain extender/water	(0.1–0.5)/20
EA	5

other 1 h, the nozzle was lifted above the surface of the emulsion and the temperature was elevated to 70°C gradually for the polymerization. The polymerization was carried out for 24 h under a nitrogen atmosphere while it was stirred at a speed of 150 rpm. Actually, therefore, the chain-extending reaction had proceeded for total 2 h before the polymerization started. In a previous study, it was clarified that 4.5 h was needed to complete the chain extension by Pz in the presence of EA. Therefore, the remaining chain-extending reaction of the UP occurred simultaneously when polymerization proceeded.

Analyses

Microscopic observation

The size distribution of droplets before polymerization was observed with an optical microscope (OM; Olympus BH-2 with a digital camera). The size, size distribution, and surface features of the hybrid microspheres after polymerization were observed by a JSM-5300 (JEOL) scanning electron microscope (SEM). The specimens were prepared as follows: The final emulsion after polymerization was diluted with water, dropped onto an aluminum plate attached to the sample stage, dried in a desiccator, and stored in a refrigerator overnight before being exposed to gold sputtering under a vacuum (JFC-1200 Fine Coater, JEOL).

The diameters of about 300 particles were counted to calculate the average diameters. The size distribution was expressed by a CV value, which is defined as

$$CV(\%) = [\sum(d_i - \bar{d})^2 / N]^{1/2} / \bar{d} \quad (1)$$

where d_i is the diameter of the i th particle; \bar{d} , the average diameter; and N , the total number of particles counted.

The morphology inside the hybrid microspheres was observed with an H-700 (Hitachi) transmission electron microscope (TEM). TEM specimens were pre-

pared by cutting ultrathin films (ca. 100 nm thickness) from particles embedded in the epoxy resin with an RMC MT-7000 ultramicrotome (ATOM TECH Ltd., England) and setting them on the copper meshes. The PUU domain was stained with the vapor of an OsO₄ aqueous solution for 1 day in a sealed bottle at room temperature.

FTIR measurement

The conversion of the —NCO group was estimated from a Fourier transform infrared (FTIR; Avatar 360, Nicolet) spectrum. The UP was smeared directly onto a polyethylene card (Sumitomo 3M), which served for the IR measurement. After it was dried in a desiccator for several 10's of minutes, IR measurement was carried out. A peak at 2260 cm⁻¹, specific for the stretching oscillation of —NCO, was monitored. For the measurement of the samples after chain extension and polymerization, the powder of the purified particles was used to prepare a thin film with KBr.

Measurement of destructive strength

The destructive strength of a hybrid particle was measured by a Shimadzu PCT-200 powder compression analyzer. By applying a pressure head of the size of 500 μm (or 50 μm) onto a particle, the particle was pressed continuously by an increasing load from 1 to 200 kgf (1 kgf = 9.8 × 10⁻³ N). The strain of the particle was monitored with a precision of 0.01 μm by a differential transformer. The stress when the strain was 10% was referred to as the destructive strength, which was calculated from following equation:

$$Sb(S10) = (2.8 \times P)/(\pi \times d^2), \quad (2)$$

where *Sb* is the destructive strength (kgf/mm²); *S10*, the stress at 10% strain of the particle (kgf/mm²); *P*,

the applied load (kgf); and *d*, the diameter of the particle (mm).

Measurement of monomer conversion

The conversion of the vinyl monomer was determined gravimetrically. The polymer was precipitated by methyl alcohol from the serum, separated by centrifugation, dried in a vacuum, and weighed. The conversion of the vinyl monomer was estimated by abstracting the PUU weight from the total conversion, assuming that the conversion of PUU was 100%. It has been clarified that the conversion of —NCO of the UP was attained at 100% after reaction with Pz in the presence of EA.³³

RESULTS AND DISCUSSION

In this study, various VPs were used to prepare hybrid microspheres with a UP. In a previous study to prepare PUU microspheres, it was found that the chain-extending reaction needed about 4.5 h when a Pz aqueous solution was added followed by EA.³³ When EA was not added, about 40% of —NCO group remained unreacted even after 6 h, because Pz was not able to diffuse into the inside of the droplet completely after the chain extension on the particle surface was finished in the absence of EA. This is ascribed to the hydrophilicity of Pz and the barrier of the chain-extended PUU polymer on the surface. It was also found in the previous study that the —NCO group reacted with water slowly in the absence of Pz; only 40% of —NCO reacted even after 6 h. This is because the polymer film that formed on the surface of the particle after the —NCO on the surface had reacted with water: Water could not enter into the droplet any more to react with the —NCO. Therefore, it was concluded that a small part of the chain extension was ascribed to

TABLE II
Recipe and Results of Noncrosslinking PUU/Acrylic Polymer Hybrid System

Ingredients/results	Run no.		
	6920	6921	6923
Disperse phase (g)			
PU prepolymer	4.00	6.00	6.00
MMA	6.00	4.50	4.50 (MA)
2-EHMA	2.00	1.50	1.50 (2-EHA)
ADVN	0.40	0.40	0.40
Continuous phase (g)			
Water: 150.0, SLS: 0.20, NaNO ₂ : 0.015			
MST-1	2.00	2.00	3.00
Pz/water	0.3/20	0.5/20	0.5/20
Results			
Monomer conversion (%)	58.3	44.6	23.1
Diameter (μm)	15.80	15.09	19.84
CV (%)	10.10	9.18	17.53

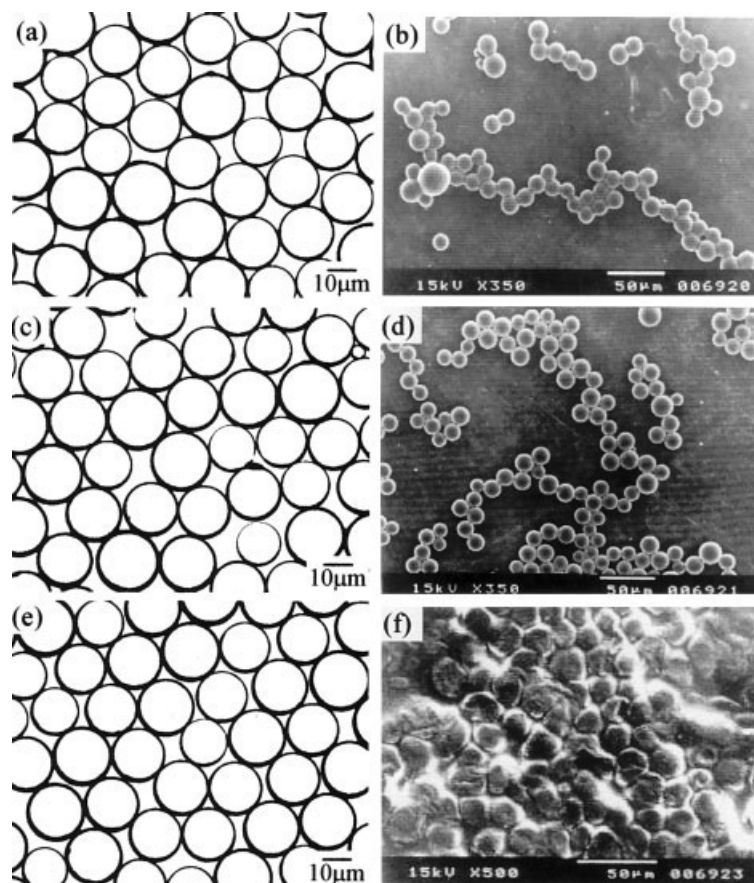


Figure 1 OM micrographs of droplets before polymerization and SEM micrographs after polymerization for PUU-Pz/acrylic polymer hybrid system. (a,c,e)OM; (b,d,f)SEM. PUU/(MMA) + 2-EHMA) (g/g): (a,b)1/2; (c,d)1/1. PUU/(MA + 2-HMA) (g/g): (e,f) 1/1.

the reaction of —NCO with water and that most of the chain extension was due to that of —NCO with Pz. In this study, the uniform droplets containing the UP, the vinyl monomer, and the initiator were prepared first; then, the polymerization of the vinyl monomer was

initiated after the chain-extending reaction had proceeded for 2 h in the absence or presence of EA. Therefore, the morphology and internal structure of the hybrid particles were controlled both thermodynamically and kinetically, that is, not only were they

TABLE III
Recipe and Results of Noncrosslinking PUU/(Acrylic + St) Polymer Hybrid System

Ingredients/results	Run no.		
	6932	6933	6934
Disperse Phase (g)			
PU prepolymer		6.00	
St		3.00	
2-EHA	3.00	—	—
CycloHA	—	3.00	—
MA	—	—	3.00
ADV N		0.30	
Continuous phase (g)			
Water: 175.0, SLS: 0.15, NaNO_2 : 0.015, Na_2SO_4 : 0.15, MST-1: 3.00			
Pz/water (g/g)		0.5/20	
EA		5.0	
Results			
Monomer conversion (%)	97.0	76.0	54.6
Diameter (μm)	20.53	18.46	16.99
CV (%)	10.52	9.60	12.61

controlled by the hydrophilicity of the two components, but they also depended on the chain-extending rate of the UP and the polymerization rate of the vinyl monomer. The higher polymerization rate and the crosslinking of the polymer chain would prevent the polymer from realizing a thermodynamically equilibrium morphology. A detailed discussion follows.

Noncrosslinking system

PUU-Pz/acrylic polymer hybrid microspheres

First, the MMA and 2-EHMA monomers were used together to prepare a PUU hybrid microsphere; the detailed recipe is shown in Table II. The MMA/2-EHMA ratio was fixed at 3/1 (g/g), and the ratio of the UP/vinyl monomer was changed from 1/2 and 1/1 (g/g). The added amount of Pz was increased correspondingly, according to the contents of the UP. EA was not added after the Pz aqueous solution was fed, considering that the high polymerization temperature can promote Pz to diffuse into the inside of the droplet even in the absence of EA. The OM micrographs of the droplets before polymerization and the SEM micrographs of hybrid particles after polymerization are shown in Figure 1(a–d). For each sample, monodisperse droplets and fairly uniform particles were obtained. However, it was found that the surface was not as smooth when the magnification of the SEM was higher (the SEM is not shown here), irrespective of the prepolymer/monomer ratio. The slight rough surface of the hybrid microspheres resulted from the phase separation between PUU and the acrylic polymer. It is suggested that PUU and the acrylic polymer were not blended homogeneously. Furthermore, a small amount of aggregation was observed when the emulsion was transferred to the polymerization reactor after a chain extension of 1 h, that is, the emulsion was not very stable during the chain-extending reaction. This result suggested that Pz did not diffuse into the inside of the droplets effectively and that the chain-extending reaction (crosslinking) between the droplets occurred, leading to coagulation between the droplets.

From Table II, it is known that the monomer conversion was relatively low, below 60%. One reason for a low monomer conversion was the aggregation formed due to the chain-extending reaction between the droplets as described above. Another reason was ascribed to the relative hydrophilicity of MMA. A part of MMA diffused into the aqueous phase, and then its polymerization in the aqueous phase was inhibited by the water-soluble inhibitor NaNO_2 , leading to a lower monomer conversion.

To decrease the phase separation between PUU and the VP and to obtain a hybrid particle with a smooth surface and well-blended morphology, MA and 2-EHA were used instead of MMA and 2-EHMA (run

6923), respectively, considering that the incompatibility between two components possibly was ascribed to the steric hindrance of the $-\text{CH}_3$ connected to the main chain; the recipe and the results are also shown in Table II, and the corresponding OM and SEM micrographs are shown in Figure 1(e,f). Although uniform droplets were obtained after emulsification, it

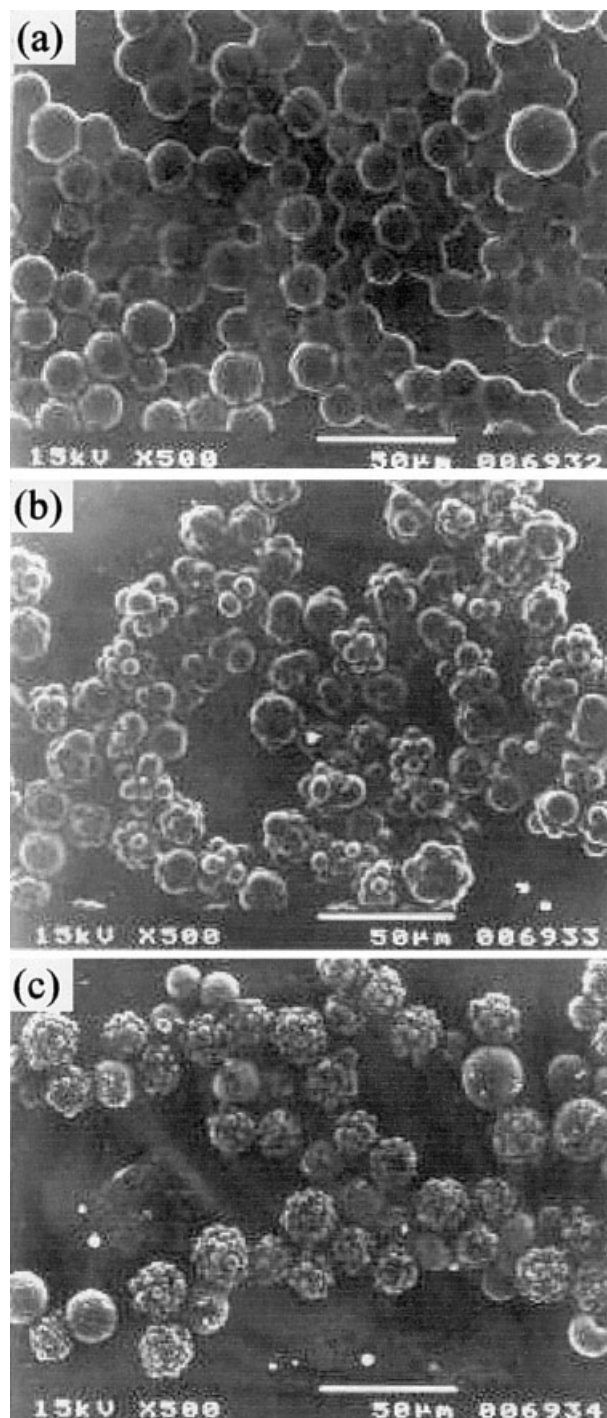


Figure 2 SEM micrographs for PUU-Pz/(acrylic + St) polymer hybrid microspheres. PUU/monomer (g/g): 1/1; St/acrylic monomer (g/g): 1/1. (a) St/2-EHA; (b) St/cycloHA; (c) St/MA.

was known from the SEM micrographs that the particles adhered to each other. The monomer conversion was very low, only 23%. This was because 2-EHA and MA are more hydrophilic, respectively, than are 2-EHMA and MMA. The monomer diffused into the aqueous phase more quickly, leading a low monomer conversion. Because a large part of the monomer remained, the particles easily adhered to each other when they were dried from the emulsion. Furthermore, with a polymerized hydrophilic acrylic polymer located preferentially on the surface, it was more difficult for Pz to diffuse into the inside of the particle; as a result, the chain-extending reaction was retarded. Therefore, the particle was soft due to the low molecular weight of PUU, resulting in easy adhesion between the particles. Therefore, EA was added to the emulsion after the feeding of the Pz aqueous phase in the following experiment, to promote the diffusion of Pz into the inside of the particles.

As described above, the hydrophilic acrylic monomer resulted in a relatively low monomer conversion, although the phase separation between PUU and the acrylic polymer was not so apparent. To enhance the monomer conversion, a relatively hydrophobic monomer, St, was added into the polymerization system in the next experiment.

PUU-Pz/(acrylic + St) polymer hybrid microspheres

To investigate the effect of the vinyl monomer type on the characteristics of the hybrid particles, St was added into the polymerization system with various acrylic monomers. There are two purposes for adding St into the system: (1) for limiting the polymerization locus in the inside of the droplet, therefore increasing the monomer conversion, and (2) for increasing the monodispersity of the droplets. Because the SPG membrane is composed of hydrophilic material, the higher the oil phase is, the easier it is to obtain a uniform droplet.²⁶ The St was copolymerized with

three kinds of acrylic monomers, 2-EHA, cycloHA, and MA. The order of their hydrophobicity is 2-EHA > cycloHA > MA. The recipe and corresponding results are shown in Table III, and SEM micrographs of the hybrid particles are shown in Figure 2. It was clear that more apparent phase separation occurred on the particle surface, especially when St was copolymerized with cycloHA and MA, which are more hydrophilic than is 2-EHA. This phenomenon resulted from the higher interfacial tension between PUU and the vinyl copolymer, that is, the compatibility of the two polymer components was poor. From Table III, it is known that the monomer conversion decreased as the hydrophilicity of the monomer increased. When St was copolymerized with 2-EHA and cycloHA, the monomer conversion was higher than with the MMA/2-EHMA system. However, when the St/MA mixture was used, the monomer conversion was close to that of the MMA/2-EHMA system. The same reason for the case of the MMA/2-EHMA system can be applied. As the hydrophilicity of the oil phase increased, more monomer diffused into the aqueous phase and then was inhibited by the water-soluble inhibitor. Furthermore, it was observed that more aggregates formed with increase of the hydrophilicity of the monomer. This result also was similar to the MMA/2-EHMA system. Because of the hydrophilic polymer located on the surface of the hybrid particle, the diffusion of Pz into the droplets was retarded, resulting a chain-extending reaction between the particles.

Semi-IPN system

PUU-Pz/(2-EHA-EGDMA) polymer hybrid microspheres

A system where one component was crosslinked and another component remained uncrosslinked was named a semi-IPN. As described above, adding the hydrophobic St monomer into the polymerization system increased the monomer conversion; however, a

TABLE IV
Recipe and Results of PUU/Acrylic Polymer Semi-IPN System

Ingredients/results	Run no.				
	6931	6928	6927	6929	6930
Disperse phase (g)					
PU prepolymer			6.00		
2-EHA	6.00	4.00	3.00	2.00	—
EGDMA	—	2.00	3.00	4.00	6.00
ADVN			0.30		
Continuous phase (g)					
Water: 170.0, SLS: 0.20, NaNO ₂ : 0.015, Na ₂ SO ₄ : 0.15, MST-1: 3.00					
Pz/water: 0.5/20, EA: 5.0					
Results					
Monomer conversion (%)	76.0	91.2	86.2	88.0	95.9
Diameter (μm)	18.28	20.28	18.57	23.21	24.46
CV (%)	12.18	15.77	9.73	12.24	17.05

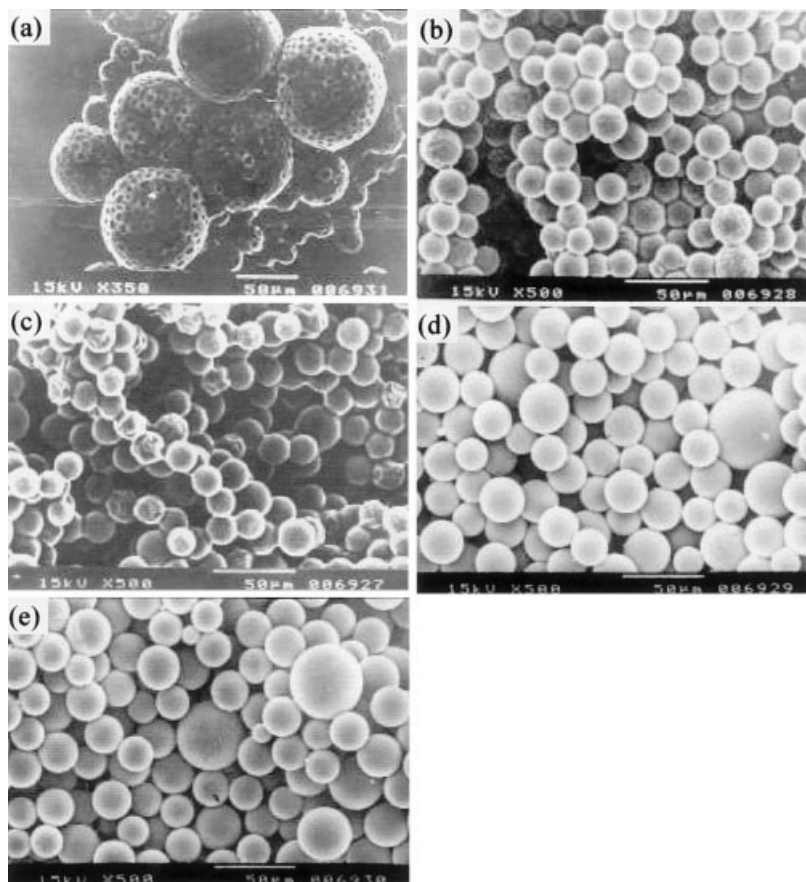


Figure 3 SEM micrographs for PUU-Pz/(acrylic-EGDMA) polymer hybrid microspheres. PUU/monomer (g/g): 1/1. EGDMA/2-EHA monomer (g/g): (a) 0/1; (b) 1/2; (c) 1/1; (d) 2/1; (e) 1/0.

more apparent phase separation occurred than with the acrylic polymer system. This will affect the mechanical strength of the hybrid particles. Therefore, to improve the compatibility between PUU and VP, a bifunctional crosslinker, EGDMA, was added to the polymerization system instead of MMA (or MA) for the acrylic polymer system, because it was considered that the crosslinking in the polymerization could re-

strict the phase separation between the two polymer components. Furthermore, adding a crosslinker into the monomer phase can increase the polymerization rate. Since the polymerization of the monomer inside the droplet and monomer diffusion into the aqueous phase competed against each other, increasing the polymerization rate of the monomer inside the droplet would retard the monomer diffusion into the aqueous

TABLE V
Recipe and Results of PUU/PS_t Semi-IPN System

Ingredients/results	Run no.				
	6939	6937	6936	6938	6930
Disperse phase (g)					
PU prepolymer			6.00		
St	6.00	4.50	3.00	1.50	—
EGDMA	—	1.50	3.00	4.50	6.00
ADV _N			0.30		
Continuous phase (g)					
Water: 175.0, SLS: 0.15, NaNO ₂ : 0.015, Na ₂ SO ₄ : 0.15, MST-1: 3.00					
Pz/water: 0.5/20, EA: 5.0					
Results					
Monomer conversion (%)	84.9	84.2	87.5	92.7	95.9
Diameter (μm)	—	18.37	16.38	18.88	24.46
CV (%)	—	10.65	10.60	13.68	17.05

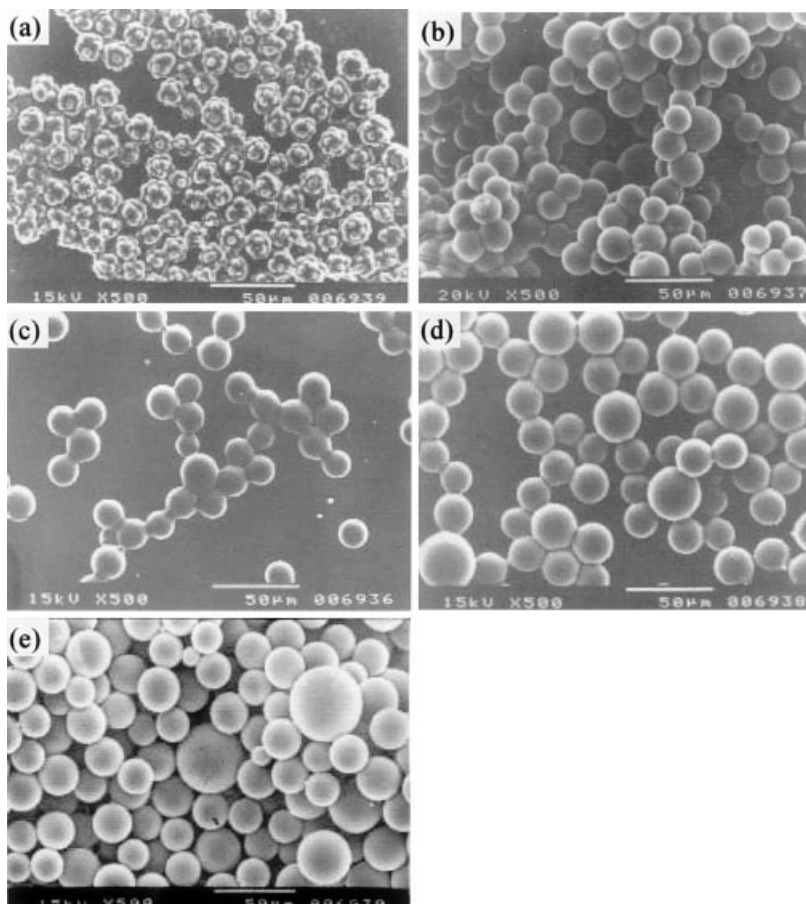


Figure 4 SEM micrographs for PUU-Pz/(St-EGDMA) polymer hybrid microspheres. PUU/monomer (g/g): 1/1. EGDMA/St monomer (g/g): (a) 0/1; (b) 1/3; (c) 1/1; (d) 3/1; (e) 1/0.

phase, resulting in a higher monomer conversion. The results are shown in Table IV and the corresponding SEM micrographs are shown in Figure 3. From Figure 3, it is observed that there were many small holes on the particle surface when 2-EHA was used solely, while the surface was relatively smooth when it was used together with EGDMA. This was because the phase separation between PUU and the acrylic poly-

mer occurred when 2-EHA was used solely. As a result, the phase separation between the acrylic polymer domain and xylene also occurred. After the sample was dried, the holes resulted from the xylene formed. On the other hand, the phase separation between PUU and the acrylic polymer was suppressed kinetically by EGDMA, because the crosslinking restricted the migration of the polymer.

TABLE VI
Recipe and Results of PUU/PSt IPN System

Ingredients/results	Run no.			
	6943	6942	6940	6944
Disperse phase (g)				
PU prepolymer		6.00		
St	6.00	4.50	3.00	0
EGDMA	0	1.50	3.00	6.00
ADVN		0.30		
Continuous phase (g)				
Water: 200.0, SLS: 0.15, NaNO ₂ : 0.015, Na ₂ SO ₄ : 0.15, MST-1: 3.00				
DETA/water: 0.5/20, EA: 5.0				
Results				
Monomer conversion (%)	—	98.0	96.3	100.0
Diameter (μm)	—	15.69	16.47	21.62
CV (%)	—	10.41	18.33	9.34

Therefore, the domain size of the phase-separated acrylic polymer decreased. As a result, the phase separation between xylene and the acrylic polymer was not apparent. Furthermore, monomer conversion and the particles showed an increasing trend as the EGDMA content was increased. When EGDMA was added, the monomer conversion attained was above 86%, while it was only 76% in the absence of EGDMA. This was because the polymerization rate increased and polymerization was restricted in the inside the droplet due to the bifunctionality of EGDMA, as expected.

On the other hand, the particles tended to adhere to each other as evidenced by SEM observation after they were dried when the EGDMA/monomer ratio was lower than 1/1 (g/g), due to the softness of the polymer particle, which resulted from the low T_g of poly(2-EHA). When the EGDMA/monomer ratio was higher, the hybrid particles were distributed separately after being dried. However, the size distribution of the particles became broader. This was because EGDMA was relatively hydrophilic: It wetted the pore wall of the SPG membrane,²⁶ leading to nonuniform droplets. Therefore, it is necessary to incorporate a hydrophobic monomer other than 2-EHA into the polymerization system, for example, the St monomer.

PUU-Pz/(St-EGDMA) polymer hybrid microspheres

To overcome the above disadvantages, to obtain uniform, well-blended, and well-separated hybrid particles, a semi-IPN structure was prepared by crosslinking PSt with EGDMA. The EGDMA/monomer ratio was increased from 0/1 to 1/0 (g/g). The recipe and the corresponding results are shown in Table V and the SEM micrographs of the hybrid particles are shown in Figure 4. As with the case of the acrylic polymer system, the surface became smoother and the monomer conversion became higher as the EGDMA contents increased. When only St was used without the addition of EGDMA, an apparent phase separation occurred and many particles coagulated into a large aggregate. When a small amount of EGDMA was added [EGDMA/St = 1/3 (g/g)], there was no phase separation observed on the surface; however, the particles adhered and aggregated to each other as evidenced by SEM observation [Fig. 4(b)]. On the other hand, when only EGDMA was used, the size distribution of the particles became broader although the monomer conversion was the highest among all the samples, because of the high hydrophilicity of EGDMA. Therefore, the recipe of EGDMA/St = 1/1 (g/g) was the most adequate, taking the monomer conversion, monodispersity of the particle, and smoothness of the particle surface into the consideration.

The above result confirmed again that the crosslinking of a VP restricted the mobility of the polymer, thus suppressing the phase separation between the two com-

ponents, increasing the compatibility, and forming hybrid particles with smooth surfaces. Furthermore, as the compatibility between the two components increased by adding a crosslinker, the emulsion became stable and the formation of aggregates decreased.

IPN system

PUU-DETA/(St-EGDMA) polymer hybrid microspheres

A system where two components are both crosslinked and the two networks formed by two polymer com-

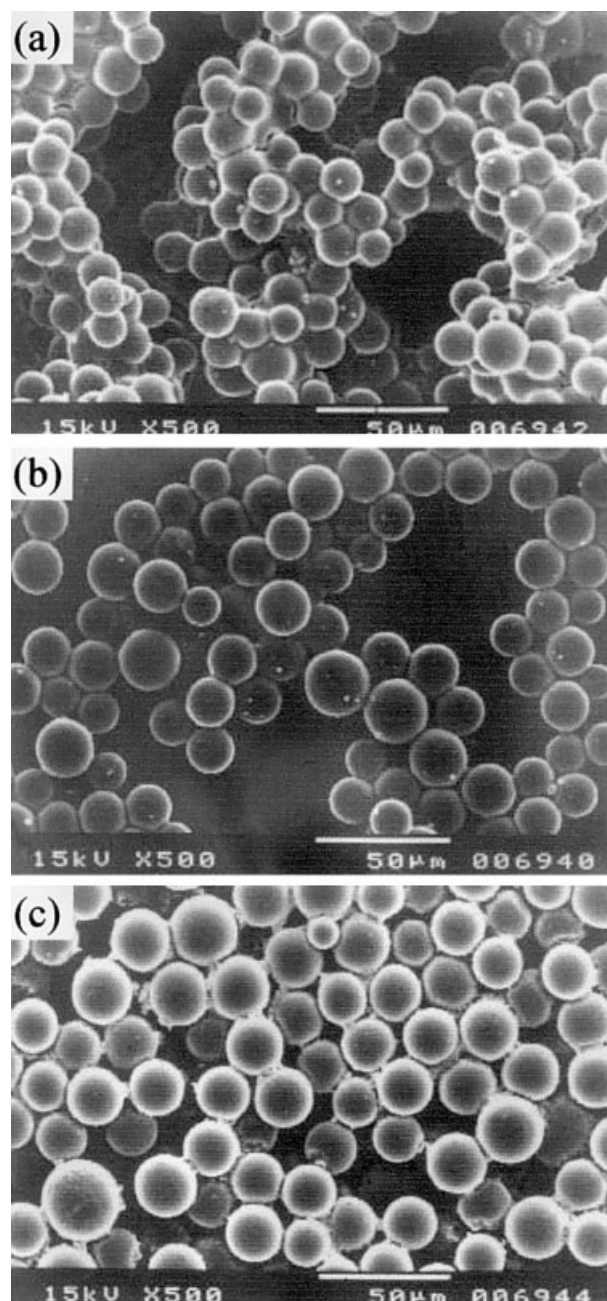


Figure 5 SEM micrographs for PUU-DETA/(St-EGDMA) polymer hybrid microspheres. PUU/monomer (g/g): 1/1. EGDMA/St monomer (g/g): (a) 1/3; (b) 1/1; (c) 1/0.

TABLE VII
Effect of DETA Amount on of PUU/PSt IPN Hybrid Particles

Ingredients/results	Run no.					
	6946	6947	6940	6936	6948	6945
Disperse phase (g)						
PU prepolymer				6.00		
St				3.00		
EGDMA				3.00		
ADVN				0.30		
Continuous phase (g)						
Water: 200.0, SLS: 0.15, NaNO ₂ : 0.015, Na ₂ SO ₄ : 0.15, MST-1: 3.00						
DETA/water	0.1/20	0.3/20	0.5/20	0.5/20 (Pz)	0.1/20 (NTE)	0.5/20 (NTE)
EA				5.0		
Results						
Monomer conversion (%)	100.0	100.0	96.3	87.5	68.0	70.1
Diameter (μm)	17.72	16.66	16.47	16.38	—	—
CV (%)	10.6	11.59	18.33	10.60	—	—
Destructive strength (kgf/mm^2)	17.75	24.09	26.26	20.93	—	—

ponents, respectively, interpenetrate each other, is named an IPN. Here, a trifunctional chain extender, DETA, was used instead of Pz to constitute a three-dimensional network of PUU. It was considered that the

crosslinking of PUU simultaneously with the crosslinking of VP would restrict the migration of both PUU and the VP, thus suppressing the phase separation and further improving the compatibility of the two components.

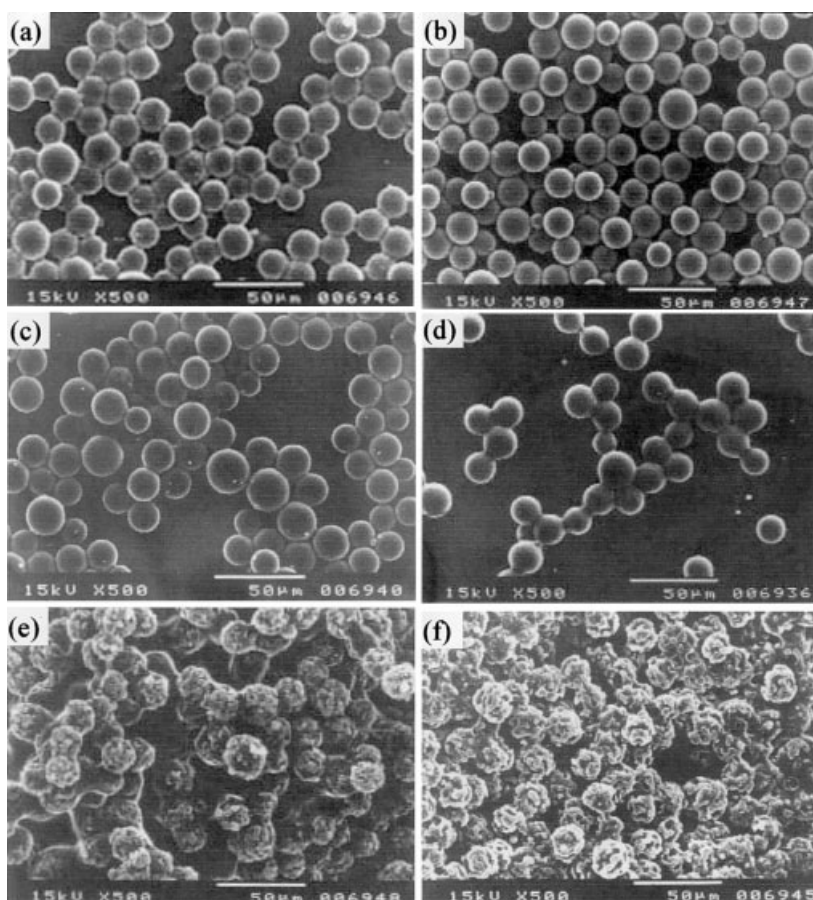


Figure 6 SEM micrographs for PUU/(St-EGDMA) polymer hybrid microspheres showing the effect of the amount and type of chain-extender. PUU/monomer (g/g): 1/1; EGDMA/St monomer (g/g): 1/1; amount of chain-extender (g): (a) DETA 0.1; (b) DETA 0.3; (c) DETA 0.5; (d) Pz 0.5; (e) NTE 0.1; (f) NTE 0.5.

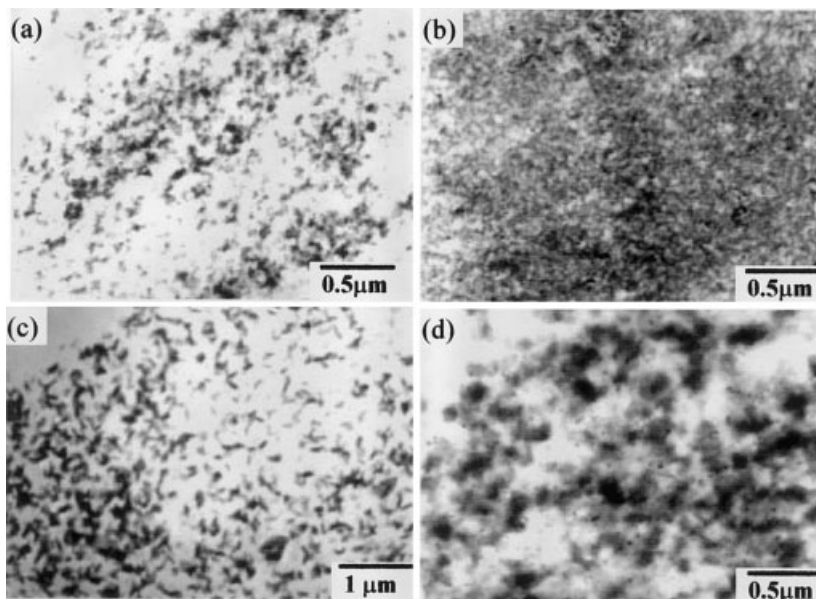


Figure 7 TEM micrographs for PUU/(St-EGDMA) polymer hybrid microspheres showing the effect of the amount and type of chain-extender. PUU/monomer (g/g): 1/1; EGDMA/St monomer (g/g): 1/1; amount of chain extender (g): (a) DETA 0.1; (b) DETA 0.3; (c) DETA 0.5; (d) Pz 0.5.

For the chain-extending reaction, DETA/water [0.5/20 (g/g)] was added followed by the addition of 5 g of EA in the emulsion as above. For the crosslinking of the VP component, EGDMA was used again, and the EGDMA/St ratio was varied from 0/1 to 1/0 (g/g). The results are shown in Table VI and SEM micrographs of the hybrid particles are shown in Figure 5.

A similar trend was observed with the increase of EGDMA, as with the case of Pz. When EGDMA was not added, the droplets coagulated to a larger bulk; an SEM micrograph is not available. When the EGDMA amount was lower [EGDMA/St = 1/3 (g/g)], the particles adhered to each other and aggregates were observed on the SEM micrographs, although the particle surface became smoother. When the EGDMA/St

ratio was higher than 1/1 (g/g), particles with smooth surfaces were obtained, being free from aggregation.

Next, the amount of DETA was varied from 0.1 to 0.5 g; St/EGDMA was fixed at 1/1 (g/g). The results are shown in Table VII, with the results of Pz and the SEM micrographs of the hybrid particles shown in Figure 6. From the SEM micrographs, it was evident that the particle surface became smoother with the increase of DETA. The micrographs of the ultrathin film are shown in Figure 7(a–c), with that chain-extended with Pz [Fig. 7(d)]. The sample was stained with OsO₄ vapor; the black domain represents the PUU domain. When the bifunctional chain-extender Pz was used, the PUU domain size was larger and the distribution of the PUU domain in the particle was not

TABLE VIII
Recipe and Results of PUU–PSt IPN System Using Trifunctional Crosslinker TMPTMA

Ingredients/results	Run no.				
	6943	6950	6949	6951	6952
Disperse phase (g)					
PU prepolymer			6.00		
St	6.00	4.50	3.00	1.50	—
TMPTMA	—	1.50	3.00	4.50	6.00
ADVN			0.30		
Continuous phase (g)					
Water: 200.0, SLS: 0.15, NaNO ₂ : 0.015, Na ₂ SO ₄ : 0.15, MST-1: 3.00,					
DETA/water: 0.5/20: EA: 5.0.					
Results					
Monomer conversion (%)	—	100.0	100.0	81.5	89.5
Diameter (μm)	—	17.58	19.97	21.46	21.55
CV (%)	—	11.64	9.64	10.67	10.05
Destructive strength (kgf/mm ²)		226	172	280	221

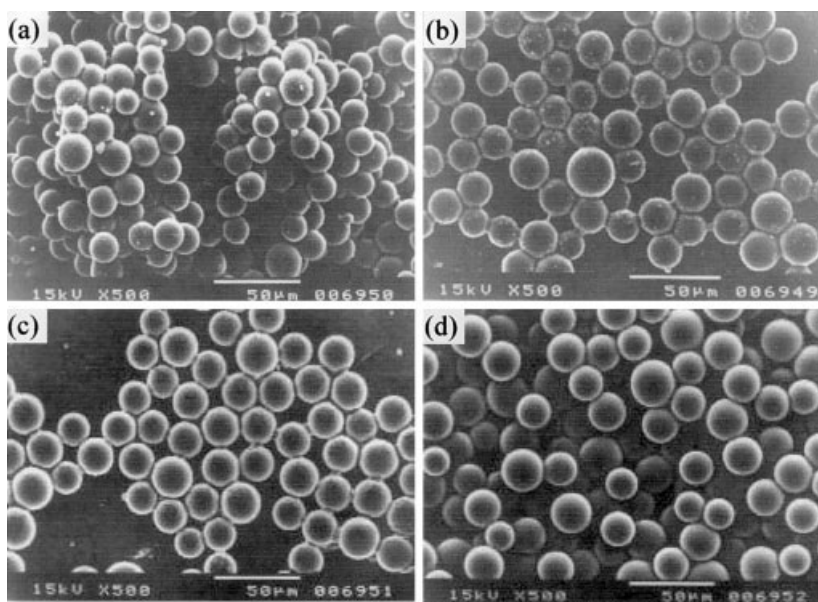


Figure 8 SEM micrographs for PUU-DETA/(St-TMPTMA) polymer hybrid microspheres. PUU/monomer (g/g): 1/1. TMPTMA/St monomer (g/g): (a) 1/3; (b) 1/1; (c) 3/1; (d) 1/0.

uniform. As the amount of the trifunctional chain-extender DETA was increased, the PUU domain size became smaller and the PUU domains were connected to each other uniformly, that is, a more “real” IPN structure was formed. The destructive strength was measured and is also shown in Table VII. From Table VII, it is known that the destructive strength increased as the DETA amount increased, due to the IPN structure formation. In comparing the cases where the same amount of DETA and Pz were used, the destructive strength of the former was higher than that of the

latter, that is, the destructive strength of the IPN structure was higher than that of the semi-IPN structure.

Next, another chain extender, NTE, was used instead of DETA; its amount was varied from 0.1 to 0.5 g. The results are shown in Table VII together with the result of DETA, and SEM micrographs are shown in Figure 6(e,f). Different from the case of DETA, an apparent phase separation between the VP and PUU occurred on the surface, irrespective of the amount of NTE. The reason is not uncertain: Probably because the chain extension occurred too rapidly, it formed a

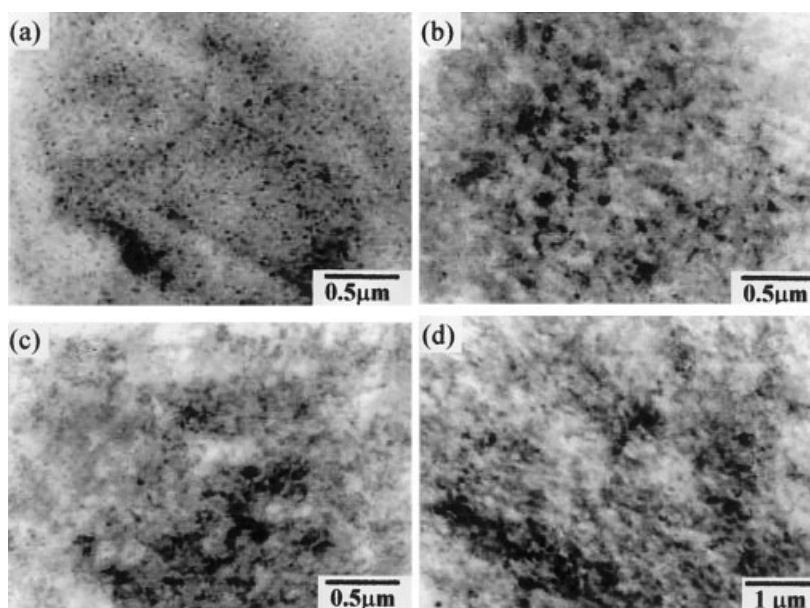


Figure 9 TEM micrographs for PUU-DETA/(St-TMPTMA) polymer hybrid microspheres. PUU/monomer (g/g): 1.1. TMPTMA/St monomer (g/g): (a) 1/3; (b) 1/1; (c) 3/1; (d) 1/0.

dense network before the polymerization of the VP. As a result, the vinyl monomer was driven out of the particle and polymerized on the surface of the particle.

PUU-DETA/(St-TMPTMA) polymer hybrid microspheres

To prepare a hard particle and create an IPN structure with a higher destructive strength, a trifunctional crosslinker, TMPTMA, was used instead of EGDMA. The results are shown in Table VIII and the SEM micrographs are shown in Figure 8. Similar trends were observed with those in the case of EGDMA, that is, when the TMPTMA amount was lower [TMPTMA/St = 1/3 (g/g)], aggregates formed. As the TMPTMA amount increased, the particle surface became smoother and a uniform particle without aggregation was obtained.

The TEM micrographs of the ultrathin film of the hybrid particle are shown in Figure 9. When TMPTMA/St = 1/3 (g/g), the PUU small domain dispersed separately in the PSt continuous phase. However, as the amount of the trifunctional crosslinker (TMPTMA) increased, the PUU domains were connected to each other, that is, a more "real" IPN structure was formed. When TMPTMA was used instead of EGDMA, the polymerization rate of the VP increased further because it has three vinyl groups. Therefore,

the mobility of the PUU polymer was restricted and the IPN structure was fixed.

In comparing the destructive strength when EGDMA and TMPTMA was used, the latter case showed a much higher destructive strength, that is, a fairly hard particle was obtained when the trifunctional crosslinker of the VP was used.

FTIR measurement result

The chain-extending reaction of the UP was confirmed by monitoring the peak of the —NCO group in the FTIR spectrum. It was found that the —NCO group disappeared almost completely when Pz, DETA, or NTE was added followed by EA. A comparison of the IR spectrum before and after the chain-extending reaction is given in Figure 10. Figure 10(a) is an IR spectrum of the prepolymer before the chain-extending reaction and 10(b) is that of the PUU-IPN particle after chain extension. Clearly, the characteristic peak of —NCO in the 2260 cm^{-1} vicinity in Figure 10(a) disappeared completely after chain extension.

In concluding the above results, it is known that adding the crosslinker of VP and the trifunctional chain-extender DETA of UP can improve the compatibility between PUU and VP and can provide the hybrid particles with a smooth surface and IPN structure. Using a trifunctional crosslinker TMPTMA, a

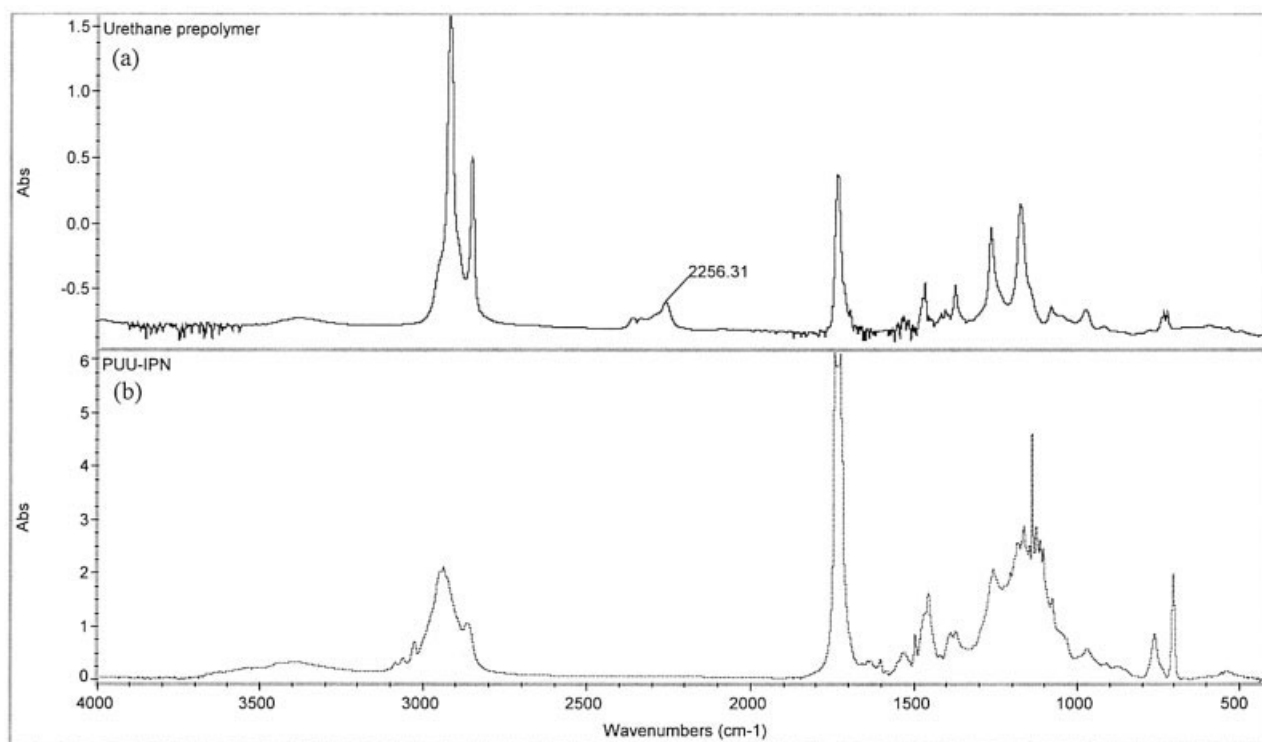


Figure 10 Comparison of IR spectrum before and after chain-extending reaction: (a) urethane prepolymer; (b) PUU hybrid particle after chain-extension.

hybrid particle with a higher destructive strength was obtained. The addition of the crosslinker of a VP has other advantages, that is, the polymerization was limited to the inside of the droplets; as a result, monomer conversion increased, the stability of the dispersion was improved, and the particles did not adhere to each other. The uniform hybrid microspheres with good stability and a higher destructive strength can be used as spacers for LCDs, packing material for chromatography, and carriers of proteins. These applications require hard uniform particles with a high destructive strength.

CONCLUSIONS

Uniform PUU-VP hybrid microspheres with an IPN structure were successfully obtained from a UP and a vinyl monomer by the SPG technique and a subsequent suspension polymerization process. When the crosslinker was not used, the monomer conversion was lower, phase separation between PUU and the VP was apparent, and the dispersion of the particle was not stable. These disadvantages were overcome by adding an adequate amount of the crosslinker and a trifunctional chain extender of the UP. When the trifunctional crosslinker and chain extender were used together, the hybrid particles were solid, did not adhere to each other, and showed a smooth surface and high destructive strength. Various applications of uniform PUU-VP hybrid particles in the electronic and biochemical fields can be considered.

This work was supported by the National Nature Science Foundation of China (Contract No. 20125616).

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