

Preparation of Polyurethaneurea (PUU) Uniform Spheres by SPG Membrane Emulsification Technique

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Received 28 May 1999; accepted 10 September 1999

ABSTRACT: Uniform polyurethaneurea (PUU) spheres were prepared from 20–40 wt % urethane prepolymer (UP) solution of xylene. Uniform droplets were formed with the Shirasu porous glass (SPG) membranes of 1.42, 5.25, and 9.5 μm pore size, dispersed in an aqueous phase with dissolved stabilizers, and allowed to stand for the chain extension at the room temperature with diamines that were added after the emulsification. The reaction progressed rapidly by an addition of ethyl acetate to the aqueous phase, promoting the diffusion of diamines into the droplets. The reaction of —NCO groups with water did not hamper the emulsification process, which normally occurred in 1 to 2 h, yielding stable droplets with the coefficient of variation around 10%. No instability or coagulation occurred, while standing for the chain extension, and solid, spherical PUU particles of 5–20 μm were obtained after removal of the solvent. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2237–2245, 2000

Key words: polyurethaneurea; urethane prepolymer; emulsion; Shirasu porous glass (SPG) membrane; polymer particles

INTRODUCTION

Polyurethane (PU) has been gaining in popularity among industries requiring intermediate characteristics between rubber and plastics; in particular, its foams have been used as cushions and structural materials. Application fields are extending to various elastomer formulations, paints, adhesives for polymers and glass, artificial leather, and biomedical polymers. As for environmental concerns, the urethane bond resembles the amide bond, which implies possible biodegradability, promoting polyurethane as one of the ecology conscious materials. Polyurethane emulsions, either forced or spontaneous types, have been extensively studied because of the

characteristic elasticity and adhesiveness of the emulsions.¹ These emulsions have been applied for waterborne adhesives, screen printing, wood lacquers, leather and textile finishes, and glass fiber sizing. In routine procedures to prepare the spontaneous PU emulsions, diisocyanates and diols are step polymerized in organic phase to yield urethane prepolymer (UP), with NCO groups remaining on both chain ends. Stoichiometric ratios between NCO and OH groups are strictly maintained in the formulation. Dibutyltin dilaurate is added as a catalyst. Inverse emulsification technique is normally employed to obtain fine emulsions. Water is gradually added to the prepolymer solution, inducing a phase inversion, and submicron-size PU spheres are formed by the chain extension reactions between NCO ends and diamines or diols. Dihydroxy carboxylic acids (e.g., dimethylol propionic acid,^{2–9} DMPA) or dihydroxy tertiary amines (e.g., *N*-methyl diethanol

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Journal of Applied Polymer Science, Vol. 77, 2237–2245 (2000)
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amine)^{10,11} are added in the first stage, neutralized with base (tertiary amines) or acids, respectively, and induce spontaneous emulsion in the aqueous phase. Satguru et al.² investigated the colloidal aspects of PU emulsion, stabilized with anionic ionomers and nonionic stabilizers, and reported that, unlike the acrylate emulsions obtained by conventional emulsion polymerizations, the PU spheres showed a rather wide size distribution with the average diameter around 50–60 nm. Their morphological study revealed that the PU spheres were in an open/swollen state with the domains rich in water. Kim et al.^{3–10} also investigated the effects of ionomers and nonionic stabilizing moieties in PU on the particle size and its distribution, and the mechanical properties of films. They employed various types of diisocyanates (isophoron DI, diphenylmethane DI, dicyclohexylmethane DI, and hexamethylene DI) and soft segments (polyesters, polyethers, polyols and the mixture of these) in their series of articles.

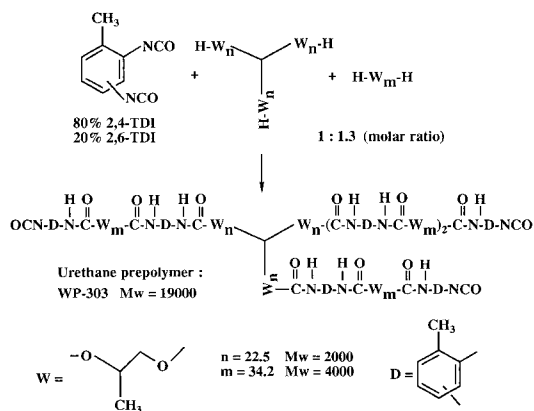
Hybrid PU emulsions have been successfully prepared by employing a two-stage process. In the first stage, polyurethane prepolymer, normally incorporating ionomer, is formed in organic media. After the addition of monomers, the oil phase is dispersed in water, neutralized with tertiary amines or acids, and polymerized. Vanderhoff et al.¹² applied their miniemulsion polymerization process and successfully obtained stable hybrid PU–polyacrylate emulsions without using conventional ionomers. They used acrylic monomers (butyl acrylates) as the solvent for the urethane prepolymer synthesis, and incorporated pendant double bonds in the prepolymer chains by adding small amounts of allyl alcohol and hydroxyalkyl methacrylates.

The stability of emulsions in the second stage polymerization was maintained by the mixed stabilizers, sodium lauryl sulfate, and water-insoluble hexadecane. Hirose et al.¹³ synthesized core/shell-type hybrid PU–polyacrylate (A) emulsions by soap-free seed emulsion polymerization. Three kinds of morphologies, A/PU, PU/A, and A/PU-graft-A, were obtained by changing the combination of monomers, compositions, and the period and mode of the addition. DMPA was incorporated as an anionic ionomer. Kim et al.,^{14–15} as in the patent by Vanderhoff et al., incorporated 2-hydroxyethyl acrylate (HEMA) in PU emulsion and modified them with the copolymerizations of glycidyl methacrylate/acrylonitrile, and methylmethacrylate/tetra-methyleneglycol dimethacrylate.

Commercial interests in PU emulsions are still high, and recently new PU emulsions hybridized with conventional vinyl monomers by emulsion,^{16–17} soap-free,¹⁸ or dispersion polymerizations^{19,20} have been marketed.

One of the disadvantages of these emulsions is polydispersity of the particles because a vigorous agitation system is required for the forced emulsion type, and wide distributions of 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 μm scale (desirably, up to several tens of a μm). Larger PU particles, if they are reasonably uniform, can be applied as spacers, packing materials for column chromatography, protein (enzyme) carriers, and so on.

We have been working with a particular membrane emulsification technique. Subsequent suspension polymerization yielded fairly uniform polymeric microspheres.^{21,22} Shirasu porous glass (SPG) membranes made of hydrophilic Al_2O_3 – SiO_2 has a uniform pore size distribution with a nominal size ranging from 0.1 to 18 μm .²³ For an emulsification of oil-in-water (O/W) type, the oil phase is allowed to permeate through the pores of the membrane pushed by a carefully controlled pressure, and the droplets adsorb stabilizer molecules dissolved in water and are stabilized. Addition of water-insoluble substances to the oil phase, and the uniform size of the droplets, provide additional stability, and the polymerization normally proceeds without any break-up or coagulation of the droplets. The SPG emulsification can also be applied to the preparation of polymer particles from a polymer solution or microencapsulation of fine solid particles suspended in a polymer solution. In the former case, natural polymers, or those synthesized from polymerizations other than the radical mechanism, can be readily emulsified by dissolving in volatile solvents such as methylene chloride and chloroform. These solvents are easily removed. Preparation of uniform polylactide particles,²⁴ and composite polystyrene (PST) and polymethyl methacrylate (PMMA) particles,²⁵ were done by this solvent evaporation process. The morphology development between PST and PMMA was investigated in the presence of a solubilizer, lauryl alcohol. The same principle is applied for the preparation of uniform polyurethane urea (PUU) spheres in this article. Xylene solution of PU prepolymer was


Scheme 1

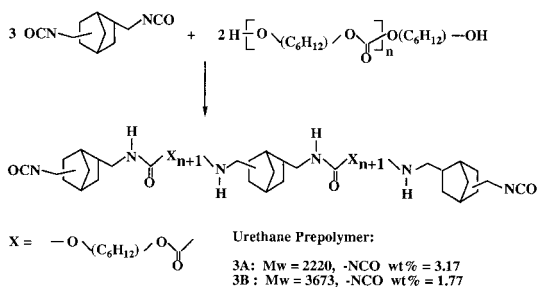
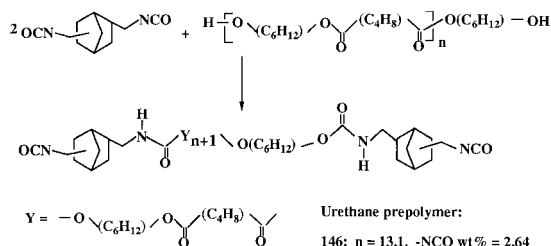
emulsified with SPG membranes of different pore sizes, the chain extension reaction followed with an addition of piperazine in the aqueous phase. An addition of amphiphathic ethyl acetate promoted the reaction. After the removal of xylene, the dried particles were smooth, and did not adhere with each other. In the following sections, detailed descriptions about the emulsification, chain extension, and the final products will be given.

EXPERIMENTAL

Materials

Urethane Prepolymer

The chemical formulae of urethane prepolymers mostly used in our experiments are shown in Schemes 1, 2, and 3 with brief routes of the synthesis. Dibutyltin dilaurate was used as a catalyst at 343 K. WP-303 is composed of amorphous soft segments, 4 mol of two-functional polypropylene glycol (PPG, $MW = 2000$) and 1 mol of trifunctional PPG ($MW = 4000$), which are connected


Scheme 2

Scheme 3

with toluenediisocyanates (TDI, a mixture of 80% 2,4- and 20% 2,6-derivatives). Its average molecular weight was 19,000 from the GPC measurement based on polystyrene standards. The remaining $-\text{NCO}$ group was calculated as 2.84 wt. %. UP-3A and UP-3B possess crystalline soft segments and bulky hard segments; 3 mol of norbornane diisocyanatomethyl (NDIM) {2,5(and 6)-bis(isocyanato-methyl)bicyclo[2.2.1]heptane} react with 2 mol of polyhexyl carbonate, the molecular weight of which are 2000 for UP-3B, and 1000 for UP-3A, respectively. UP-146 is a product of 2 mol of NDIM reacting with 1 mol of polyester derived from 1,6-hexane diol and adipic acid, both ends of the chain being stopped with 1,6-hexane diol. These prepolymers were all synthesized and characterized at Nippon NSC Ltd, and served as the 40 wt % xylene solution. All the containers of the prepolymers were flushed with nitrogen after the content was withdrawn, and stored in a refrigerator.

Solvents

Xylene was reagent grade and used as received. Ethyl acetate was a commercial grade, and distilled before use. Methanol was a commercial grade, and used as received. All the solvents and chemicals were purchased from Kishida Chemical Co. Ltd. unless otherwise stated.

Stabilizers

Polyvinyl pyrrolidone (PVP, average $MW = 40,000$, Nakarai Chemical Co. Ltd.) was a commercial grade. Polyvinyl alcohol (PVA, average degree of polymerization = 1700, and 88% hydrolyzed, Kurarey) was commercial grade. A simplified formula of MST-1, an adduct of 2,4-toluene diisocyanate and poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) is shown below (Nippon NSC Ltd.). These stabilizers were used with a small amount of sodium lauryl sulfate

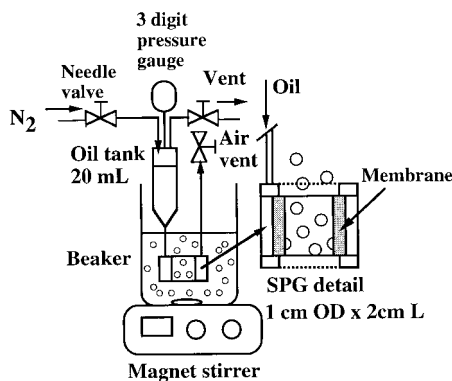
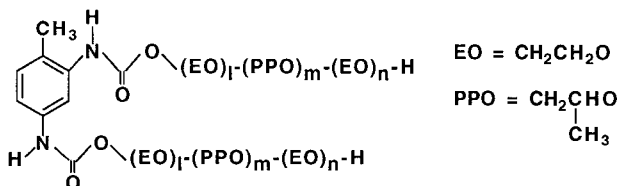


Figure 1 Schematic diagram of SPG emulsification kit.

(SLS, Merck, biochemistry grade) to stabilize the emulsion.



Other Chemicals

Piperazine (Pz), a chain extender for urethane prepolymer, was reagent grade, and used as received. Ethyl acetate was used as a promoter for piperazine diffusing into the hydrophobic droplets, and undergo the reaction with the remaining —NCO group.

Apparatus

SPG membrane emulsification was done by using a 2 cm (length) × 1 cm (outer diameter) SPG tube installed in a tiny kit (Kiyomoto Co., Ltd.).^{24,25} The detail of the apparatus can be seen in Figure 1, and the references given above.

Procedure

A schematic diagram of the SPG emulsification system is shown in Figure 1. Forty to fifty wt % xylene solution of polyurethane prepolymer was diluted with xylene to a desired concentration, and fed in the pressure-tight oil tank. An aqueous solution of MST-1 and SLS was fed in 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 the steady release of the droplets in the aqueous phase was

established. Normally the emulsification took 100 to 120 min. In some experiments, the applied pressure was slightly increased to maintain the flow rate of the oil phase, normally 1 mL/5 min. The gradual decrease of flow rate was probably due to the fouling of the membrane, as the reaction of UP with water was not completely ruled out when the droplets were released from the pores. After the emulsification, ethyl acetate was added in the emulsion followed by an aqueous solution of piperazine. The emulsion was allowed to stand at room temperature for 24 h (maximum) with occasional samplings for the measurements of droplet size and the conversion of —NCO.

Analyses

An optical microscope (OM, Olympus) was used for observation of the droplet size and distribution. Emulsion droplets immediately after the SPG membrane emulsification and in the final period were measured. The final emulsions after the chain-extending reaction were diluted with water or methanol, dropped on to an aluminum plate attached to the sample stage of a SEM (JSC-5100, JEOL), dried in a desiccator, and stored in the freezer of a refrigerator overnight before being exposed to gold sputtering under vacuum (JFC-1200 Fine Coater, JEOL). Solvent-free PUU particles were observed with the SEM. Some of the emulsions were directly freeze dried, and observed with the SEM.

The conversion of —NCO was estimated from FTIR (Avatar 360, Nicolet) spectra. The emulsion sample was diluted with toluene, and centrifuged. The separated oil phase was smeared on a polyethylene card (Sumitomo 3M), which served for the IR measurement. A peak at 2260 cm⁻¹, specific for the stretching oscillation of —NCO, was monitored, and normalized with a peak at 2900 cm⁻¹ corresponding to the stretching of —CH— in aliphatic hydrocarbons and polyethylene. The reliability of this method was confirmed by the back titration method: remaining —NCO was treated with an excess amount of 1,4-diaminobutane, and the extra amino groups were titrated with hydrochloric acid.

RESULTS AND DISCUSSION

Selection of Stabilizer

The selection of the stabilizers, in order to maintain stable emulsions during the SPG emulsifica-

Table I Performance of Stabilizer on the Monodispersity of Droplets

| Stabilizer | Run No. | Prepolymer (g) | Content (wt %) | Stabilizer (g) | Stability of Droplets |
|------------|---------|----------------|----------------|----------------|---|
| PVP | 9629 | 1.23 | 10.0 | 0.51 | Wide size distribution in the later stage of emulsification |
| PVP | 9632 | 2.42 | 20.0 | 1.00 | same as 9629 |
| PVP | 9633 | 3.62 | 30.0 | 1.51 | same as 9629 |
| PVP | 9634 | 4.90 | 40.0 | 2.00 | same as 9629 |
| PVP | 9635 | 4.81 | 40.0 | 4.00 | Stable, uniform size distribution |
| PVP | 9637 | 4.81 | 40.0 | 8.00 | Stable, uniform size distribution |
| PVA | 9619 | 4.01 | 40.0 | 0.352 | Wide size distribution |
| PVA | 9618 | 4.04 | 40.0 | 0.501 | Wide size distribution |
| PVA | 9617 | 4.01 | 40.0 | 1.00 | Wide size distribution |
| MST-1 | 9646 | 4.00 | 40.0 | 0.50 | Stable, uniform size distribution |
| MST-1 | 9647 | 4.00 | 40.0 | 2.00 | Stable, uniform size distribution |
| MST-1 | 9650 | 5.00 | 50.0 | 2.00 | Stable, uniform size distribution |

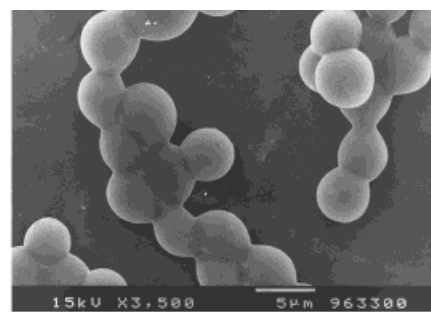
Continuous phase—water 150 g, SLS 0.05 g plus stabilizer appeared in the first column. Dispersion phase—total weight 10 g, solvent: xylene/hexadecane 9:1. Urethane prepolymer—WP-303.

tion and the subsequent chain-extending reaction period, was done for three stabilizers by using WP-303 as a prepolymer. The result is shown in Table I. When PVP and PVA were used, uniform droplets were formed initially and up to the middle stage of the emulsification. However, larger droplets gradually appeared in the later stage, creating a noticeable amount of coagulum after the chain-extension reaction. Unrealistically high concentrations of PVP (run 9635 and 9637), compared to the weight of WP-303, yielded stable emulsions. PVA was selected with the consideration that its pendant hydroxyl groups may preferentially react with —NCO groups, and anchor on the surface of the droplets. Contrary to this expectation, the amount of coagulum increased at the end of the chain-extending reaction. MST-1, which has a hydrophobic toluene as an anchor linked with two EO-*b*-PPO-*b*-EO chains (water-soluble moieties), provided good stability of the emulsion and maintained the narrow size distribution of the droplets. MST-1 was selected as the sole stabilizer in the later experiments. In this series of experiments, hexadecane was used as a water-insoluble additive to enhance the stability of the droplets based upon our previous reports.^{20,21} However, it became clear that the UP-xylene droplet was sufficiently stable without the

addition of HD, and HD was omitted from the formulation in the later experiments.

Comparison between Urethane Prepolymers to Prepare Spherical PUU Particles

WP-303, having a branched soft segment in the chain, was employed at first to obtain solid and spherical PUU particles. As shown in Figure 2, a dent was observed on the surface of the dried PUU particles, and they easily adhered with each other after the normal drying of the emulsion at



UP = WP-303, $\bar{d}_p = 7.06 \mu\text{m}$, CV = 27.2 %

Figure 2 SEM photograph of PUU spheres prepared from WP-303.

Table II Effect of Prepolymer Structure on the Feature of Dried PUU Particles

| Prepolymer | Hard Segment | Soft Segment (mol wt) | wt % in Xylene | PUU Particles after Drying |
|------------|---------------|--------------------------|----------------|-------------------------------|
| WP-303 | 2,4-(2,6-)TDI | PPG (4000/2000) | max 50 | dent, stick together |
| UP-3A | NDIM | PC (1000) | 10-20 | dent |
| UP-3B | NDIM | PC (2000) | 10-20 | spherical, separate |
| UP-146 | NDIM | PE (ca. 3000) | 20 | spherical, separate |

TDI = toluenediisocyanate, NDIM = norbornanediisocyanatomethyl, PPG = polypropylene glycol, PC = polycarbonate, PE = polyester.

room temperature. To provide crystallinity to the soft segment, polyester and polycarbonates were incorporated in UP-146, and UP-3A and -3B, respectively. The hard segment was also replaced with a bulky NDIM. The highest UP concentrations in xylene were limited to 20 wt %; however,

UP-3B and UP-146 yielded well-separated PUU spheres without any faults on the surface. In UP-3A, with the molecular weight of PC being 1000, phase separation between xylene and PUU was observed after the addition of chain extenders, leading to the formation of dents on the surface. The low molecular weight PC inserted between NDIM hard segments was probably too rigid to swell in the solvent as the chain extension progressed. Lee et al.²⁶ concluded that the shorter chain length of the soft segment (poly(tetramethylene adipate)glycol, PTAd) favored achieving better compatibility with the hard segment (isophoron diisocyanate, IPDI). They observed the melting point of PTAd as the chain length of PTAd became longer. This different tendency was probably due to the different chemical structures and rigidity of the soft (PC to PTAd) and hard (NDIM to IPDI) segments, and also the presence of xylene in our system. UP-146 yielded solid PUU spheres with an excess amount of the chain extender, Pz. A simple comparison is given in Table II with the conformational difference of prepolymers. More detailed results and discussions will

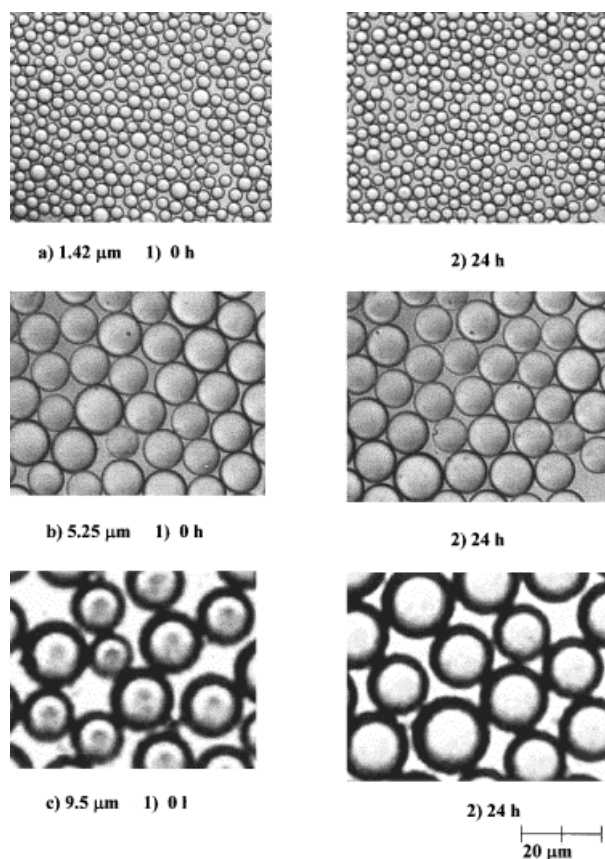


Figure 3 OM photographs of emulsion droplets obtained from 20 wt % PUP-146B in xylene. Droplets obtained from the pore size of (a) 1.4, (b) 5.25, and (c) 9.5 μm , and photographs taken immediately after the emulsification and 24 h elapsed after the chain extension.

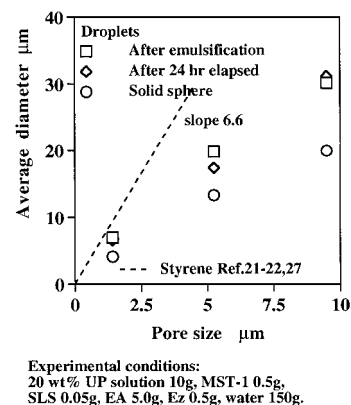


Figure 4 Relationship between average droplet size and pore size of the membrane.

Table III Mole of Piperazine to the Final Conversion of —NCO Group

| Prepolymer | Droplet Size μm | Moles of —NCO in Oil Phase 10^{-4} mol | Moles of Piperazine Added in Continuous Phase/ 10^{-4} mol | Ethyl Acetate Fraction in Continuous Phase ^a | Final Conversion (%) |
|------------|----------------------------|--|--|---|----------------------|
| UP-3A | 19.0 | 1.50 | 0 | 0.017 | 34.7 |
| UP-3A | 19.0 | 1.50 | 5.07 | 0.017 | 60.7 |
| UP-3A | 18.9 | 1.52 | 0 | 0.017 | 28.4 |
| UP-3A | 18.9 | 1.52 | 10.15 | 0.017 | 71.4 |
| UP-3B | 18.8 | 0.835 | 0 | 0.017 | 40.4 |
| UP-3B | 18.8 | 0.835 | 5.27 | 0.017 | 89.4 |
| UP-146 | 19.1 | 12.8 | 0 | 0.029 | 70.0 |
| UP-146 | 19.8 | 12.8 | 58.1 | 0.029 | ca. 100 |

SPG pore size = 5.25 μm .

^a EA/(EA + water) (w/w).

follow for the spheres prepared from UP-3B and UP-146.

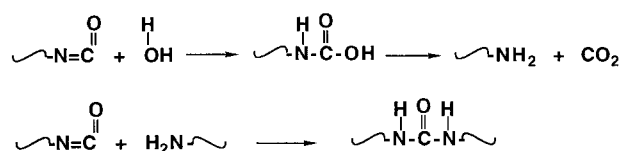
Droplet Size and Distribution

Optical microscope (OM) photographs of the emulsion droplets, 20 wt % of UP-146 in xylene, are shown in Figure 3. The average pore sizes of the SPG membranes were 1.4, 5.25, and 9.5 μm , respectively. As time elapsed after emulsification, the emulsions remained stable, retaining the initial uniformity after 24 h. A slight shrinking of the droplets, due to the evaporation of xylene, was noticeable in the photos after 24 h had elapsed. The coefficient of variation (CV) was around 10% or even less, indicating excellent monodispersity.

The relationship between the average droplet size and the pore size is shown in Figure 4. A linear relationship was obtained as in the previous correlations with hydrophobic styrene monomer,^{21,22,27} however, the slope was much smaller than the other plot, down from 6.6 to 3.4. This difference is mainly due to the increase of viscosity of the oil phase present, and also to the difference in interfacial tension between the aqueous phase and oil phase.

Reaction of —NCO Groups with Water and Piperazine

After the UP droplets were released to the aqueous phase, —NCO groups located at the surface of the droplets are susceptible to react with water molecules, eventually converting to amine, which reacts with other —NCO groups as follows:



Scheme 4

A cyclic diamine, piperazine (Pz), was added to complete the chain extension of UP chains. Amphiphilic solvent, ethyl acetate, was added to promote the diffusion of Pz from the aqueous phase to the droplets. The conversion of —NCO group with and without the chain extender is shown in Table III for different UPs. It is clear that the reaction with water is not effective in converting all —NCO groups present in the droplets because the reaction progressed from the surface to the inside, expanding the diffusion barrier for water molecules. UP-146 yielded a higher conversion compared to those with UP-3A and -3B, probably because of the presence of longer, more flexible soft segments (polyester) in the chains. In the experiments of UP-3A and -3B, when the low excess concentration of Pz (barely a few times the stoichiometrically required amount) to the —NCO group was used, the final conversion never attained completion. Because Pz was partitioned between the aqueous phase and the droplets (oil phase), the concentration of Pz in the droplets was too low. An adequate amount of Pz, enough to convert all —NCO groups, was investigated, and the result is shown in Figure 5. When 0.5 g [$5.81(10^{-3})$ mol] of Pz was added against 2.0 g of UP-146 [equivalent to $1.07(10^{-3})$ mol —NCO], the specific peak of 2260 cm^{-1} in the FTIR spectrum, resulting from the stretching os-

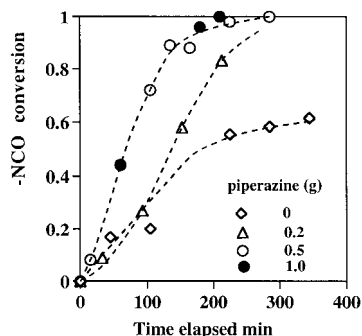


Figure 5 —NCO conversion plotted against time elapsed.

cillation of the —NCO group, completely disappeared after 4.5 h. In the later experiment, 0.5 g of Pz was always added to the emulsions, which contained approximately 2.0 g of UP-146. Also, the amount of amphiphilic ethyl acetate was slightly increased from the weight fraction of 0.017 to 0.025 (based on the weight of the continuous phase) so that the partition of Pz in the droplets was favored, but by no means an overdosage to disturb the stability of the droplets.

Polyurethane-Urea Spheres after the Chain-Extending Reaction

SEM photographs of dried PUU spheres prepared from UP-3B and UP-146 are shown in Figure 6. PUU-3B particles were freeze dried prior to observation, whereas PUU-146 particles were dried at room temperature after being diluted with methanol. Both particles retained a spherical shape, although the surface of UP-3B particles is coarse compared to the smooth surface of PUU-146.

A correlation between the dried particle volume and the predicted one from the droplet volume and composition in the oil phase is shown in Figure 7. The latter, called $V_{calc.}$ in the figure,

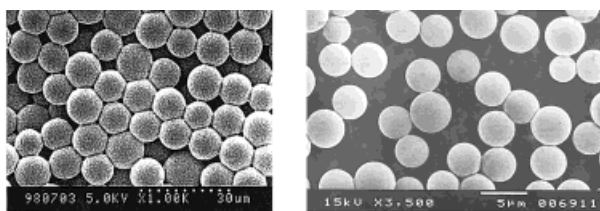
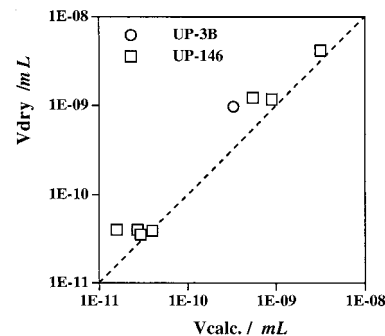


Figure 6 SEM photographs of PUU spheres prepared from (a) UP-3B and (b) UP-146.

a) Run 0703, UP-3B, $\bar{d}_p = 12.3 \mu\text{m}$
CV = 7.65 %

b) Run 6911 UP-146, $\bar{d}_p = 4.05 \mu\text{m}$
CV = 8.44 %



V_{dry} = volume of dried PUU particle
 $V_{calc.}$ = (volume of droplet) \times (UP wt. fraction)

Figure 7 Relationship between observed and calculated volume of PUU spheres after the drying.

can be estimated from the product of droplet volume and the weight fraction of UP in the oil phase. In general, the dried sphere has a larger volume (V_{dry}) than the theoretically predicted value ($V_{calc.}$), implying that the PUU spheres are swollen with xylene, and leave a considerable fraction of voids after drying, as Satguru et al.² observed in their emulsion particles.

CONCLUSION

Fairly uniform polyurethaneurea microspheres were successfully obtained from the urethane prepolymer composed of bulky hard segment (NDIM) and crystalline soft segments, polycarbonate, and polyester. Emulsified in the dilute solutions of xylene, the droplets remained stable during the chain-extending period after the emulsification. When they were dried by freeze drying or after the dilution with methanol, PUU spheres were solid and did not adhere to each other, as was observed when UP with amorphous soft segments (PPO) were used. Various applications of PUU spheres in the field of biochemistry can be considered. For example, protein molecules dissolved in the aqueous phase can be linked on the surface of the droplets through reaction with residual amino groups and —NCO. Our next objective is the preparation of hybridized PUU spheres by the radical polymerization of monomers dissolved in the droplets. An IPN structure can be obtained by adding a crosslinking monomer.

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