

Synthesis and Properties of Polyurethane–Polystyrene-Grafted Interpenetrating Polymer Networks Using a Microgel Process

HUI CHEN* and JIANN-MING CHEN

Department of Chemical Engineering, National Central University, Chung-Li, 320, Taiwan, Republic of China

SYNOPSIS

Polyurethane–polystyrene-grafted interpenetrating polymer networks (IPNs) were prepared in the presence of a soluble microgel. The objective was to understand the effect of the microgel on the physical and mechanical properties of the IPN systems. Three types of microgels were prepared by the condensation reaction of various amounts of tolylene diisocyanate (TDI) with linear polystyrene containing hydroxyl groups. The structure of the microgel was determined by gel permeation chromatography and intrinsic viscosity measurement. Increasing the amount of TDI resulted in a microgel having a more compact structure. The dynamic mechanical behavior, mechanical properties, densities, and swelling ratios of the IPNs were determined. Only one broad T_g was observed in each of the dynamic mechanical spectra of the IPNs, whether the IPNs were prepared from microgel or not. This is because of increased compatibility of the two networks by the grafting reaction. Using a microgel to prepare IPNs could further improve the degree of network interpenetration. In addition, higher tensile strength and elongation at break were obtained for the IPNs, when the proper structure of the microgel was used. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are materials containing two network polymers, at least one of the constituents being polymerized or cross-linked in the immediate presence of the others.^{1–3} In the limiting case of high compatibility, the two polymers can be visualized as being interpenetrating on a molecular scale and are continuous throughout the macroscopic sample. This is the reason why IPNs can improve mechanical properties, lower moisture adsorption, give high impact strength, and retain their properties at high temperatures. However, phase separation can occur during polymerization due to the differences in the respective compatibilities of the constituent polymers, the rate of network formation, and the rate of phase separation.⁴

In earlier studies,^{5,6} the soluble intramolecularly cross-linked *n*-butyl acrylate microgel was introduced to prepare IPNs and the two-component IPNs of poly(*n*-butyl acrylate)–poly(methyl methacrylate) could be prepared by the simultaneous polymerization process. The compatibility of the two constituent networks can be improved in the presence of a microgel, because the monomeric precursors of the second polymers were easy to interpenetrate in a soluble microgel. However, due to the great difference in the reactivity between the monomer and cross-linking agent used in the preparation of a soluble microgel,⁷ the radical copolymerization had a low conversion. Furthermore, the heterogeneous structure formed made the monomer difficult to interpenetrate into the center of the microgel.

In addition, the solubility parameters between polyurethane (PU) and polystyrene (PS) are so different that obvious phase-separation occurs in their IPNs. To solve this problem, several approaches have been reported in the literature. These include introducing opposite charge groups in the polymeric components,^{8–11} synthesizing IPNs under high

* To whom correspondence should be addressed.

pressure,^{4,12-14} or adding hydroxyethyl methacrylate.^{15,16} In this study, a soluble reactive microgel having homogeneous structure and high conversion was used to synthesize PU-PS IPNs in an effort to promote the interpenetration. The homogeneous structure of the microgel was obtained by reacting various amounts of tolylene diisocyanate (TDI) with hydroxyl groups in the polystyrene backbone.¹⁷ This microgel was then used to react with poly(propylene glycol) (PPG), TDI, and trimethylolpropane (TMP) to form a series of grafted IPNs. This article presents the use of a reactive microgel in the preparation of IPNs and its influences on the dynamic mechanical and physical properties of the IPNs prepared.

EXPERIMENTAL

Materials

Styrene (S), 2-hydroxyethyl methacrylate (HEMA), and toluene were dried over anhydrous sodium sulfate and distilled under vacuum. Polypropylene glycol (PPG) and trimethylolpropane (TMP) were dried at 80°C for 10 h under a vacuum of 0.1 mmHg. All other materials were used without further purification.

Preparation of S/HEMA Copolymer

S, HEMA, tetrabromomethane (chain transfer agent), and α,α' -azobisisobutyronitrile (initiator) were charged into a 1 L three-necked flask. The copolymerization was carried out at 70°C under nitrogen atmosphere and terminated at about 33 wt % yield. The solution was poured into a large excess of methanol, and the solids precipitated were filtered and dried.

Preparation of Reactive Microgel

Various types of reactive microgels were prepared by reacting the S/HEMA copolymer prepared above with various amounts of TDI at 60°C in toluene under nitrogen atmosphere.

Preparation of PS Microgel-PU or S/HEMA Copolymer-PU IPNs

The IPNs were prepared by the following procedure: The microgel or S/HEMA copolymer prepared previously, PPG, and TMP (the equivalent ratio of PPG : TMP was 5 : 1) were dissolved in toluene to form a 20 wt % solution. The solution was reacted with TDI at 60°C for 0.5 h before reaching the gel

point. This was cast into a glass plate mold and the resulting film was dried at 30°C for 20 h, then cured at 90°C for 3 h and at 110°C for 2 h. The IPNs were obtained by drying the films in vacuum until the weight of the films were unchanged.

Characterization

The intrinsic viscosity of the copolymer and microgels were carried out in toluene at 25°C. The concentration of the hydroxyl group in the microgel or copolymer were determined by the acetic anhydride titration method.¹⁸ The molecular weight distribution of the copolymer and microgels were measured by GPC, using a Waters Model 410 type, at 40°C with a flow rate of 1.0 mL/min. The dynamic viscoelastic properties of the IPNs were measured by using a "Rheovibron" DDV-II-C type (Toyo Measuring Instruments Co., Tokyo) at a frequency of 110 Hz. The measurements were taken over a temperature range from -80 to 160°C and a heating rate of 1.0°C/min. The tensile strength and elongation at break were measured on an Instron 1320 at room temperature with a crosshead speed of 15 mm/min (ASTM testing method D882-79). The densities of the samples were determined by the ASTM D297-15 procedure by measuring the apparent weight of the specimens in air and in water on an analytical balance with a precision within 0.1 mg. The swelling ratios of the samples were measured by the following procedure: The dried sample W_d g was swollen in toluene for 7 days. The excess toluene was removed by wiping with a filter paper, then the sample was weight W_s g. The swelling ratio was calculated by using the following equation:

$$\text{Swelling ratio} = (W_s - W_d) / W_d$$

RESULTS AND DISCUSSION

Preparation of S/HEMA Copolymer and Microgels

S/HEMA copolymer, in which the PS backbone contains hydroxyl groups, was prepared by the copolymerization of S with HEMA in toluene. The reaction conditions and characteristics are shown in Table I.

There is essentially no difference in the value of the reactivity ratio ($r_{\text{HEMA}} = 0.65$, $r_{\text{S}} = 0.57$)¹⁹ between HEMA and S. Thus, the yield of copolymer can be 33% without changing the composition of the copolymer. In other words, the overall average composition of HEMA in the resulting copolymer

Table I Reaction Conditions and Characteristics of S/HEMA Copolymer^a

[HEMA] [S] (%)	Conversion (Wt %)	$M_n^b \times 10^{-4}$	$\frac{d[\text{HEMA}]^c}{d[S]}$ (%)	$[\eta]^d$ (mL/g)
5.00	33.1	1.54	6.83	10.3

^a Other conditions: [AIBN] = 3.1×10^{-2} mol/L; [CB_{r4}] = 8.65×10^{-2} mol/L, at 60°C.

^b Determined by GPC.

^c Composition in copolymer, by acetic anhydride titration.

^d Intrinsic viscosity, in toluene at 25°C.

(6.82 mol %) is about the same as that in the initial reaction mixture (5.00 mol %). Consequently, the copolymer with uniform composition can be expected. The number-average molecular weight of the copolymer is 1.5×10^4 . Therefore, there are about nine hydroxyl groups in each PS backbone. These reactive functional groups in the PS backbone are adequate in number to react with TDI to form cross-linked structures in the microgels and IPNs. As shown in Table II, three types of microgels can be obtained by adding different amounts of TDI in the microgel solution.

In general, by increasing the amount of TDI in the microgel solution, the intermolecular reaction of microgels are increased and the intrinsic viscosity of the microgel is also increased. However, the results of this study show that there was little difference in the intrinsic viscosity among various microgels obtained and these values are the same as that of the original copolymer. This can be explained by their GPC profiles shown in Figure 1.

The profile of microgel I is broader than that of the copolymer due to the intermolecular cross-linking reaction that occurred between TDI and the copolymer, which have almost the same intrinsic viscosity. This suggests that the structure of microgel I is more compact than that of the copolymer due to the remarkable intramolecular reaction that occurred in the microgel as described above. The same

result was also obtained in microgel II. It is clear that the structure of microgel II is more compact than that of microgel I. However, the GPC profile of microgel III is intermediate between microgels I and II. This means that greater intramolecular reaction occurred during the preparation of microgel III and, so, the more compact structure of the microgel is obtained. From these results, it can be concluded that microgels can be prepared by the reaction of TDI and hydroxyl groups of the copolymer and the structure of the resulting microgels can be controlled by the amount of TDI used in the reaction system.

Dynamic Mechanical Behavior

The IPN compositions are coded as listed in Table III for the convenience of presentation. The letters denote the polymer type (U for polyurethane, MI

Table II Reaction Conditions and Characteristics of Microgel

Run No.	TDI		$[\eta]$ (mL/g)
	Copolymer (Wt %)		
Microgel I	0.644		9.31
Microgel II	0.913		10.90
Microgel III	1.180		10.70

Other conditions: at 60°C for 4 h in toluene (25 wt %).

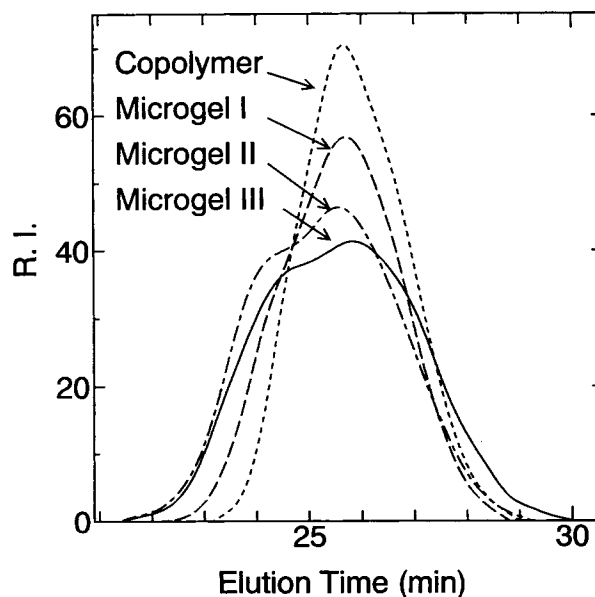
**Figure 1** GPC profiles of S/HEMA copolymer and microgels.

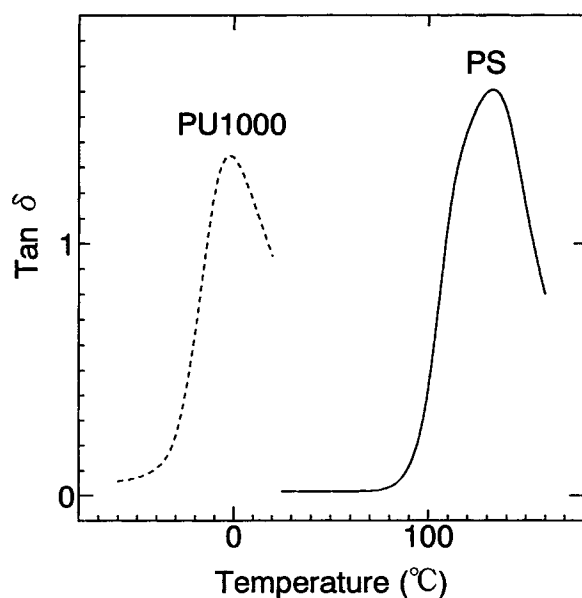
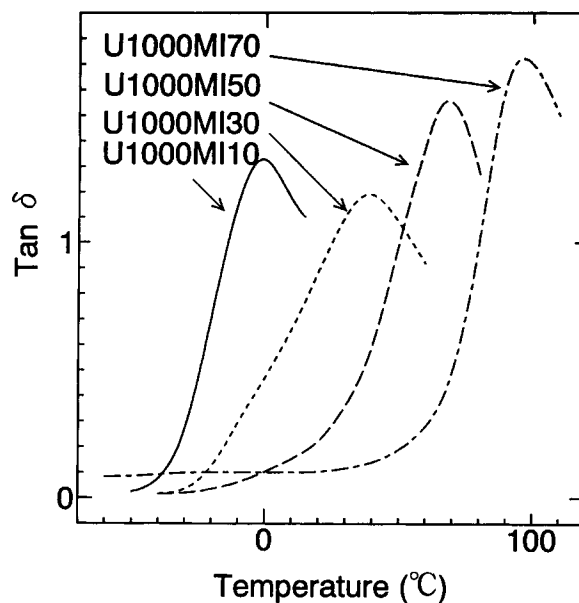
Table III Composition of Samples

Designation	Sample Composition
PPG1000	PPG with $M_n = 1000$
PS	Polystyrene networks with copolymer
PU	Polyurethane networks
PU1000	PU based on PPG1000
M	Microgel
U1000MI	IPNs (PU1000/microgel I)
U1000MI50	IPNs (PU1000/microgel I; 50/50)
U1000S50	IPNs (PU1000/PS; 50/50)

for microgel I, S for polystyrene); the first number denotes polyurethane prepared with various molecular weights of PPG (e.g., U1000 for $M_n = 1000$); the second number denotes the weight percentage of networks II (e.g., MI 50 for microgel I with 50 wt %).

The dynamic mechanical properties (the loss tangent, $\tan \delta$) of the PU1000 and PS are shown in Figure 2. The PS and PU1000 have sharp α -relaxations at 131 and -5°C , respectively. However, changing the cross-linking density of PU by using U400 or U2000 shifted the α -relaxations to the temperatures of 26 and -31°C , respectively.

The extent of phase mixing of the PU and microgel (or PS) is reflected, at least qualitatively, in the dynamic mechanical properties of the IPN material. Phase-separated materials exhibit two glass transitions, one for each phase. Shifting and broad-

**Figure 2** Temperature dependence of $\tan \delta$ of PU and PS networks.**Figure 3** Temperature dependence of $\tan \delta$ of U1000MI series IPNs.

ening are indicative of molecular mixing. Figure 3 shows the $\tan \delta$ curve of U1000MI IPNs with various compositions.

In that temperature range studied, only one transition is observed for each IPN and these peaks are located between the peaks of PU and PS. Similarly, only one transition peak is observed for the low cross-linking density of network I, U2000MI series. This is shown in Figure 4.

However, Kim et al.²⁰ reported that the conventional PU-PS IPNs exhibit two distinct glass transition temperatures, corresponding to the respective component networks. This indicates that the compatibility is more prominent in the IPNs prepared by the present microgel process, compared to the conventional-method-prepared IPNs. The same results are also obtained in IPNs with different types of microgels. The $\tan \delta$ curves of the U1000MI50 series and U1000S50, having a fixed composition of 50 wt % PU/50 wt % microgel or PS, are shown in Figure 5.

As the structure of the microgel becomes more compact (microgels II and III), the transition peaks are shifted to higher temperature. That means that the IPNs prepared with microgels II and III have a higher effective cross-linking density, although the initial cross-linker concentration used to prepare IPNs are the same. Thus, the improvement of the effective cross-linking density is due to a greater degree of interpenetration between networks. The microgel in the IPNs' synthesis plays two roles: One

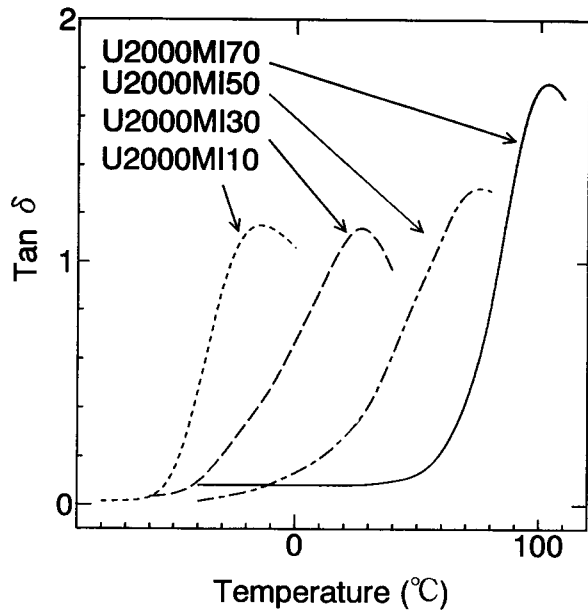


Figure 4 Temperature dependence of $\tan \delta$ of U2000MI series IPNs.

is to enhance the compatibility of the polymerizing mixture by the grafting reaction between two phases. The other is that the urethane component readily interpenetrates into the microgel to promote entanglement between them.

To investigate the effects of the microgel on the properties of IPNs, the IPNs prepared without microgels, U1000S50, are also synthesized and char-

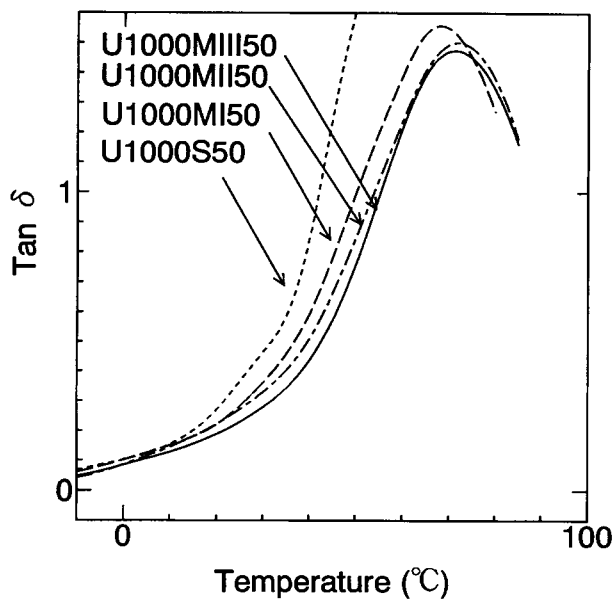


Figure 5 Temperature dependence of $\tan \delta$ of U1000M50 series and U1000S50 IPNs.

acterized. Whether or not they were prepared in the presence or absence of a microgel, both kinds of IPNs are grafted. As shown in Figure 5, the peak of IPNs prepared without a microgel (U1000S50) shifts to a lower temperature and increases in magnitude. Loss modulus vs. temperature plots (Fig. 6) confirm that two distinct glass transition temperatures are observed only in the IPNs prepared without a microgel system, such as U1000S50. This behavior suggests that the homogeneous structure of microgel present in IPNs improves the compatibility of two phases due to their ease of interpenetration.

For the compatibility of IPNs, Frisch and co-workers²¹ developed an equation to describe the relationship between glass transition temperature and degree of interpenetration in IPNs:

$$\frac{T_g - \langle T_g \rangle_{av}}{\langle T_g \rangle_{av}} = \frac{X'_c}{1 - X'_c} \quad (1)$$

where T_g is the T_g of an IPN; X'_c , the entanglement mole fraction; and $\langle T_g \rangle_{av}$, the average T_g calculated from eq. (2) or (3):

$$\langle T_g \rangle_{av1} = w_1 T_{g1} + w_2 T_{g2} \quad (2)$$

$$\frac{1}{\langle T_g \rangle_{av2}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (3)$$

where T_{g1} is the T_g of network I; T_{g2} , the T_g of net-

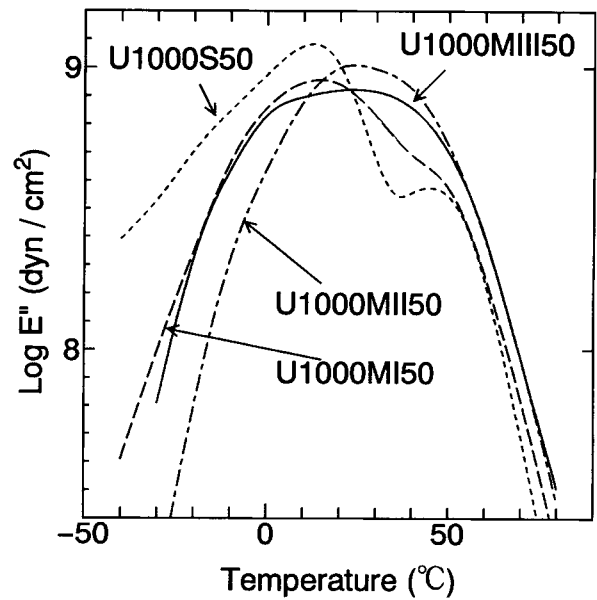


Figure 6 Temperature dependence of loss modulus (E'') of U1000M50 series and U1000S50 IPNs.

Table IV Glass Transition Temperature of IPNs

Composition	T_g (K)	$\langle T_g \rangle_{av1}$ (K)	$\langle T_g \rangle_{av2}$ (K)	$X'_{c1} \times 10^2$	$X'_{c2} \times 10^2$
U1000MI30	311.0	308.8	298.1	0.707	4.15
U1000MI50	342.0	336.0	322.2	1.75	5.78
U1000MI70	369.5	363.2	350.6	1.71	5.11
U1000MII30	312.0	308.8	298.1	1.03	4.45
U1000MII50	347.0	336.0	322.2	3.17	7.14
U1000MII70	374.0	363.2	350.6	2.89	6.25
U1000MIII30	317.0	308.8	298.1	2.59	5.96
U1000MIII50	347.0	336.0	322.2	3.17	7.13
U1000MIII70	372.0	363.2	350.6	2.37	5.74
U1000S50	338.0	336.0	322.2	0.592	4.73
PU1000	268.0	—	—	—	—
PS	404.0	—	—	—	—

$\langle T_g \rangle_{av1}$ and X'_{c1} calculated from eqs. (2) and (1), respectively.
 $\langle T_g \rangle_{av2}$, X'_{c2} calculated from eqs. (3) and (1), respectively.

work II; w_1 , the weight fraction of network I; and w_2 , the weight fraction of network II.

Using the above equations, increased cross-linking density due to the interpenetration between networks can be determined from X'_c . As shown in Table IV, the T_g 's of IPNs are higher than those of average values calculated from eqs. (2) and (3). This behavior is independent of how the IPNs were prepared from the different microgels.

The X'_c of IPNs prepared from microgel II or III shows a larger value when compared to those prepared from either microgel I or copolymer. The X'_c of IPNs prepared from the copolymer shows the smallest value. This suggests that the degree of entanglement increases when IPNs are synthesized by the microgel process.

Mechanical Properties

In general, increasing the content of the hard segment (microgels) increases the tensile strength but decreases elongation at break. The IPNs with microgels less than 30 wt % were excluded from comparison of their mechanical properties, because these materials were too soft to determine their thicknesses. The mechanical properties of IPNs are summarized in Table V.

These data show that, at a fixed composition, the IPNs prepared from the proper structure of the microgel, microgels II and III, have higher tensile strength and elongation at break than do the IPNs prepared from microgel I and the copolymer. It is generally believed that the grafting plays a major

role in determining the engineering properties, in addition to the interpenetration effect. The increased physical entanglement due to the use of the microgel process significantly enhanced both the tensile strength (from 70.8 to 87.3 kg/cm²) and elongation at break (from 399 to 455%) of the IPNs systems studied.

Densities and Swelling Ratios

The densities and swelling ratios for IPNs at PU 50 wt % / microgel or copolymer 50 wt % are listed in

Table V Stress-Strain Properties of IPNs

Composition	Tensile Strength (kg/cm ²)	Elongation at Break (%)
U1000MI30	7.15	524.00
U1000MII30	8.07	556.00
U1000MIII30	10.70	540.00
U1000MI50	84.70	354.00
U1000MII50	87.30	455.00
U1000MIII50	76.50	320.00
U1000S50	70.80	399.00
U1000MI70	212.00	8.14
U1000MII70	228.00	7.75
U1000MIII70	216.00	8.02
U1000MI90	225.00	2.77
U1000MII90	247.00	2.88
U1000MIII90	232.00	2.68

Table VI Densities and Swelling Ratios of IPNs

Composition	Density (g/cm ³)	Swelling Ratio
U1000MI50	1.159	2.54
U1000MII50	1.160	2.15
U1000MIII50	1.167	2.30
U1000S50	1.109	2.60

Table VI. The density of IPNs prepared from the copolymer (1.109 g/cm³) is greater than that calculated from the volume additivity of the components (1.080 g/cm³). Furthermore, the great increase in density parallels a similar increase in both T_g and mechanical properties as noted earlier for the IPNs prepared from the microgel. This is attributable to the greater degree of interpenetration resulting from using a microgel to prepare IPNs. The same results are also observed in the swelling behavior.

CONCLUSION

The intrinsic viscosities and GPC profiles of microgels, as well as the dynamic mechanical properties, mechanical properties, density, and swelling ratios of PU/microgel or copolymer based on PS have been studied. Various structures of microgels can be prepared by controlling the amount of TDI, which reacts with the hydroxyl groups in PS. Increasing the amount of TDI results in a more compact structure for the microgel. The IPNs exhibit one glass transition temperature due to the grafting reaction between two networks and the interpenetrating effect. The degree of interpenetration increases when the IPNs are synthesized in the presence of a microgel.

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