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ORIGINAL CONTRIBUTION

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Polyurethane acrylate microgel synthesized by emulsion polymerization using unsaturated self-emulsified polymer

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Abstract Polyurethane (PU) acrylate microgels were obtained by emulsion polymerization of self-emulsified PU acrylate terminated by 2-hydroxyethyl methacrylate without any extra emulsifier and crosslinker. Moreover, the PU acrylate was also used as stabilizer and crosslinker to synthesize poly (methyl methacrylate) (PMMA)–PU composite microgels via emulsion polymerization, which provided a new method to synthesize PU microgels and their composite microgels. The kinetics of microgel synthesis was studied by gel permeation chromatography. The dynamic rheological behaviors indicated that a crosslinked structure was formed. The frequency dependency of the loss tangent and complex viscosities showed strong relationships with the microgel structure. Those microgels with rigid PMMA core showed higher ability to slide than the soft PU acrylate microgel, which had influence on the changing of loss tangent with frequency. All the microgels swollen in tetrahydrofuran exhibited high viscosities and strong shear-thinning behaviors. As a sort of flexible microgel, the PU microgel was able to form a coherent film at room temperature, which was distinct from hard microgels.

Keywords Polyurethane microgel · Self-emulsified polymer · Dynamic rheology · Emulsion polymerization

Introduction

Microgels are defined as intramolecularly crosslinked macromolecules. They have particles of colloidal dimensions (i.e., 1~1,000 nm) and a three-dimensional structure [1]. Microgels can swell in good solvents and collapse in poor solvents [2]. Due to their finite swelling ratio limited by the degree of crosslinking, microgels are strictly insoluble but can form a colloidal dispersion. The properties of microgels, including the swelling ratio, are varied with the crosslink density, constituents, and the dispersing medium [3–7]. Because of their special structure and properties, microgels were applied in the coating industry to control rheological behavior [8–12]. They can also be used as matrices for catalysts [13], metal salts [14, 15], and biological substances [16].

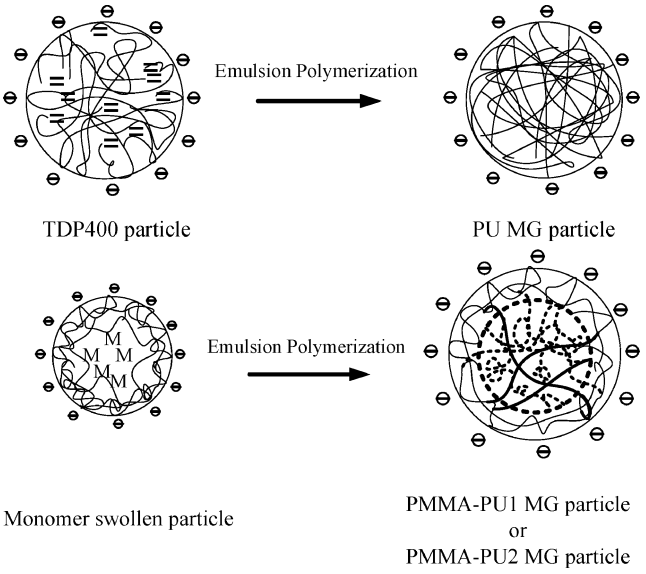
The number of microgel systems reported to date is rather limited. The majority of the work relates to poly-*N*-isopropylacrylamide (polyNIPAM), polystyrene (PS), and poly(methyl methacrylate) (PMMA) systems. PolyNIPAM microgels are the most actively studied microgel system, which can swell in water below the lower critical solution temperature [16, 17]. The overwhelming majority of nonaqueous microgels are PS and PMMA systems [3, 5, 18]. They can swell in some organic solvents. Obviously, the above-mentioned microgels are all made of hard polymer systems. Microgels using flexible polymer systems are seldom found in the literature.

Polyurethane (PU) microgels are a sort of flexible microgel systems. Moreover, PU is an important biocompatible material [19]. It is believed that PU microgels have the potential applications in pharmaceutical uptake, release systems, and biological areas. Graham and Mao [20] and Li et al. [21] have synthesized PU microgels in organic solvents. Because there is a critical concentration above which macrogelation occurred, the concentration of solu-

tion polymerization must be lower than the critical concentration to prevent the intermolecular reaction.

Microgels can also be prepared in emulsion. Emulsion polymerization is efficient in avoiding macroscopic network formation. The radical polymerization was carried out in a restricted volume.

Our present work is devoted to synthesize a new kind of PU microgels by emulsion polymerization. The self-emulsified PU acrylate terminated by 2-hydroxyethyl methacrylate (HEMA), which was synthesized by us, have a special structure with both unsaturated C=C bonds and hydrophilic groups in the polymer [22]. The hydrophilic groups can make the polymer stabilized in water without extra emulsifier. With the unsaturated bonds at the ends of the polymer chain, the PU can act as polyfunctional compounds, which would lead to the formation of a gel structure. With such a peculiar structure, we think that the PU acrylate should be able to self-polymerize to form microgels in emulsion without any extra emulsifier and crosslinker. Moreover, the PU acrylate can act as stabilizer and crosslinker for synthesizing composite microgels. Methyl methacrylate (MMA) monomer participated in the copolymerization of microgel. The PMMA–PU composite microgels were successfully synthesized by emulsion polymerization.



Scheme 2 Schematic representation of the microgel synthesis

Experimental

Materials and synthesis of unsaturated self-emulsified PU acrylate

2,4-Tolylene diisocyanate (TDI) was vacuum distilled before use. Dimethylolpropionic acid (DMPA, >99%), polypropyleneoxide glycol (PPG, Mn=400) were maintained in vacuum at 80 °C for 2 h to remove the moisture. HEMA (>98%), acetone (analytically pure), and triethylamine (TEA, analytically pure) were dried by molecular sieves. Dibutyltin dilaurate (analytical pure) was used as catalyst to synthesize the precursor. MMA (>98%) was vacuum distilled before use. MMA and ethylene glycol dimethacrylate (EGDMA, >98%) were used as monomers preparing the composite microgels. Ammonium persulfate (APS) was used as the initiator for emulsion polymerization.

The basic precursor used in the experiments was self-emulsified PU acrylate named TDP400, which was synthesized in our laboratory. The molecular weight of the synthesized precursor was set to 4,000 g/mol and the carboxyl amount was set to 0.5 mmol/g. TDP400 was synthesized in acetone solution under N_2 purge. PPG and TDI were reacted at 40 °C for 2 h. DMPA neutralized by a stoichiometric amount of TEA was dissolved in acetone. Then this solution of DMPA was added to extend the polymer chain and incorporate the carboxyl as a hydrophilic group. In the end, HEMA was poured into the reactor to react with the residual —NCO and incorporate unsaturated C=C group into the polymer (as shown in Scheme 1). The weight ratio of PPG:DMPA:TDI:HEMA was 767:100:528:97. The molecular weight and carboxyl amount of TDP400 were controlled by the ratio of the reactants.

Preparation of microgels

Three kinds of microgels with different structures were prepared. The schematic representation of the microgel polymerization is shown in Scheme 2. Table 1 lists the sample code and the formulation used in the study. For PMMA–PU1 MG and PMMA–PU2 MG system, the TDP400 polymer was vacuum distilled to remove the acetone solvent and dissolved in MMA and EGDMA monomers. The deionized water was dropped into the TDP400 acetone solution or TDP400 monomer solution to form an aqueous emulsion by phase inversion method. After adding water, the dispersion of TDP400 was distilled with a rotary vacuum evaporator to remove the acetone solvent.

The dispersions were poured into a glass reactor with a stirrer, a reflux condenser, and a thermometer. The dispersions were stirred and heated to 65 °C under N_2 purge. A certain amount of APS was added into the reactor and initiated the polymerization. The reaction lasted about 5 h.

Scheme 1 The structure scheme of TDP400 precursor

Table 1 Formulation of microgel synthesis

Sample code	TDP400 (g)	MMA (g)	EGDMA (g)	APS (g)	Water (g)	Crosslink density (mol/g)
PU MG	25	0	0	0.125	75	2.5×10^{-4}
PMMA-PU1 MG	12.5	12.5	0	0.125	75	1.25×10^{-4}
PMMA-PU2 MG	12.5	10.6	1.9	0.5%	75	5.04×10^{-4}

The resulting latex concentration was approximately 25% by weight. The crosslink density was defined as:

$$Cross\ link\ density = \frac{the\ amount\ of\ the\ crosslinker}{the\ total\ weight\ of\ the\ microgel}$$

Measurement and characterization

Molecular weight

Molecular weights and molecular weight distributions during the synthesis process of PU MG were measured by gel permeation chromatography (GPC). Tetrahydrofuran (THF) was used as the eluant at a flow rate of 1.0 ml/min. The experiment was performed on three Waters Styragel Columns (HR 6, HR 4, and HR 3) held at 30 °C. The system was calibrated with PS standards.

Particle size

Quasielastic light scattering (Zetasizer 3000HSA from Malvern Instrument) was used to investigate the particle size in water and THF. The microgel emulsion was diluted to about 0.3% by the pure water or THF solvent for testing.

Rheological behavior

The microgel emulsions was concentrated to nearly solid by heating and dissolved in THF for rheological behavior tests.

Steady rheological behaviors were measured by Haake VT550 Viscometer. Dynamic rheological behaviors were tested by Advanced Rheology Expansion System. A parallel plate was used with a diameter of 25 mm. Strain sweep was performed before frequency sweep at a fixed frequency (10 rad/s) to obtain the linear viscoelastic region where the storage modulus (G′) and the loss modulus (G″) are independent of applied strain at any frequency. According to the strain sweep curves, a strain of 0.5% ensured the operation in the linear elastic region. Frequency dependencies of the shear G′ and G″ moduli were measured within the frequency range of 0.1–100 rad/s at 20 °C. The concentrates of all the microgel/THF solutions were adjusted to 11% by weight.

Film formation and the coating properties

The iron board was coated with the microgel emulsion and dried with infrared lamps to get rid of the water. The film of the microgel emulsion was stripped off the iron board. The gel content was measured by Soxhlet extraction method using THF as solvent. The extraction was carried out for 48 h.

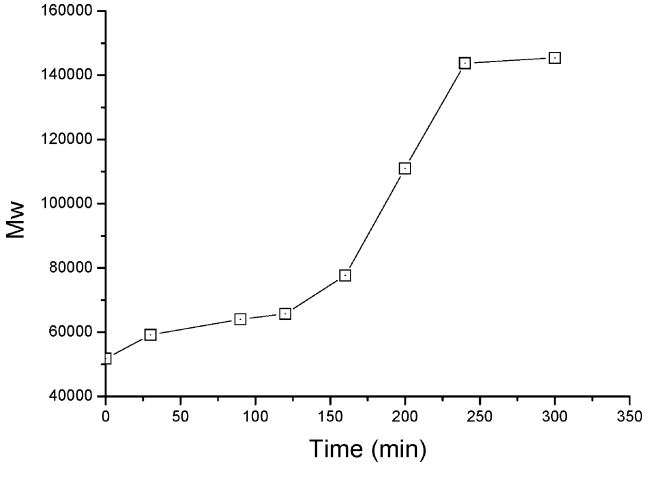


Fig. 1 Weight average Mw of PU MG microgel during the reaction in emulsion

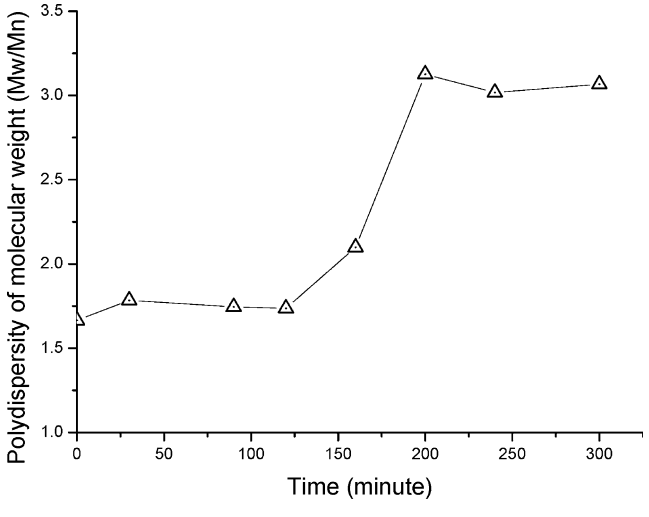
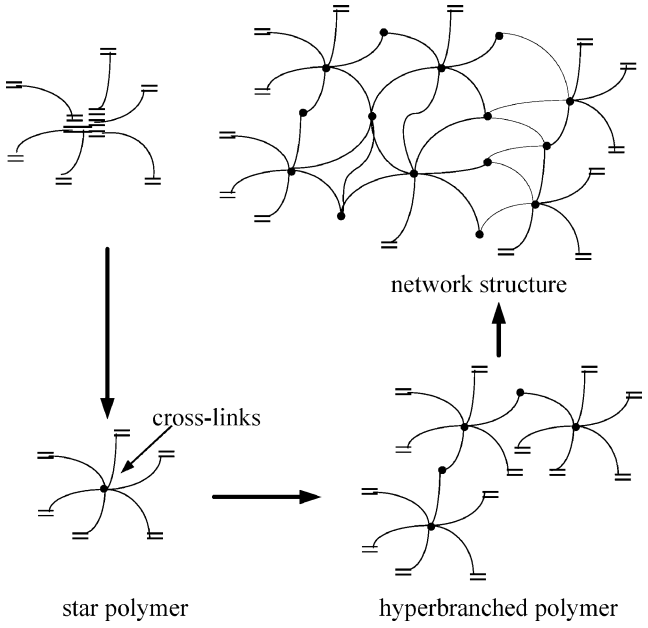


Fig. 2 The changing of the polydispersity (Mw/Mn) during the reaction process of the PU MG microgel



Scheme 3 Schematic representation of the growing process of the network structure

The test of pencil hardness, crosshatch adhesion (/25), impact strength, and absorbability of water for the coatings followed GB/T 6739-1996, GB 9286-88, GB/T 1732-93, and GB/T 1738-1979, respectively.

Results and discussion

Kinetics of microgel synthesis and the network structure

Microgel (sample PU MG) synthesis was monitored by GPC. The weight average molecular weight (Mw) was calibrated as standard PS. Although it is not accurate, the comparatively GPC data can provide some information about the process of synthesis. Mw increases with the increasing reaction time (as shown in Fig. 1). Before 150 min, the increasing rate of Mw is slow. At around 180 min, the slope of Mw curve becomes larger. After 250 min, Mw does not markedly increase and the slope is almost zero. Because the reaction was restricted within a small emulsion droplet, Mw did not grow further after the reaction was terminated in a droplet. It is shown in Fig. 2 that the initial polydispersity is comparatively low. But at around 180 min, both Mw and the polydispersity increase sharply. It is indicated that more and more TDP400 precursor was reacted and macromolecule with large molecular weight was produced.

Because the probability of the difunctional precursor reacted with itself is small, the free radical polymerization

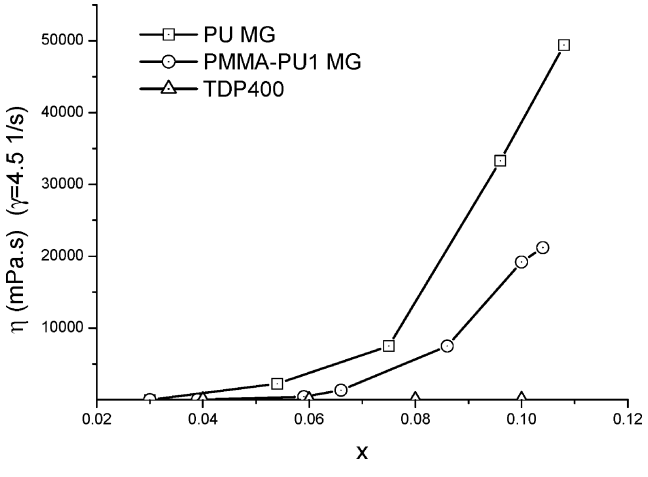


Fig. 3 Viscosity as a function of concentration for different THF solution. The temperature is 25 °C and the solvent is THF

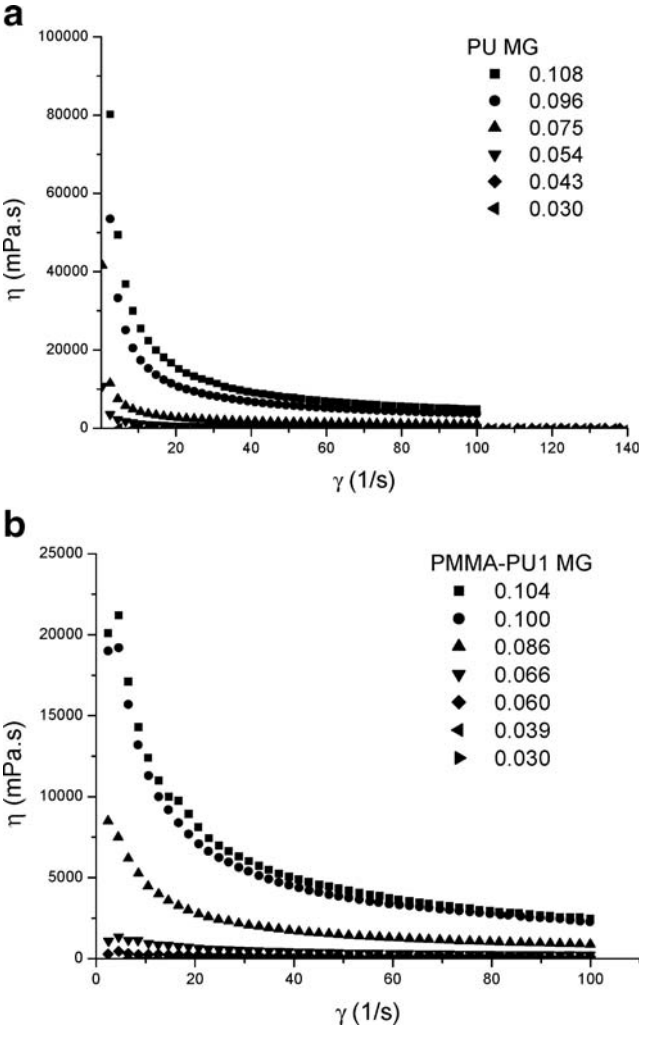


Fig. 4 Viscosity as a function of shear rate at different concentrations for the microgels and linear polymer solution. The temperature is 25 °C and the solvent is THF

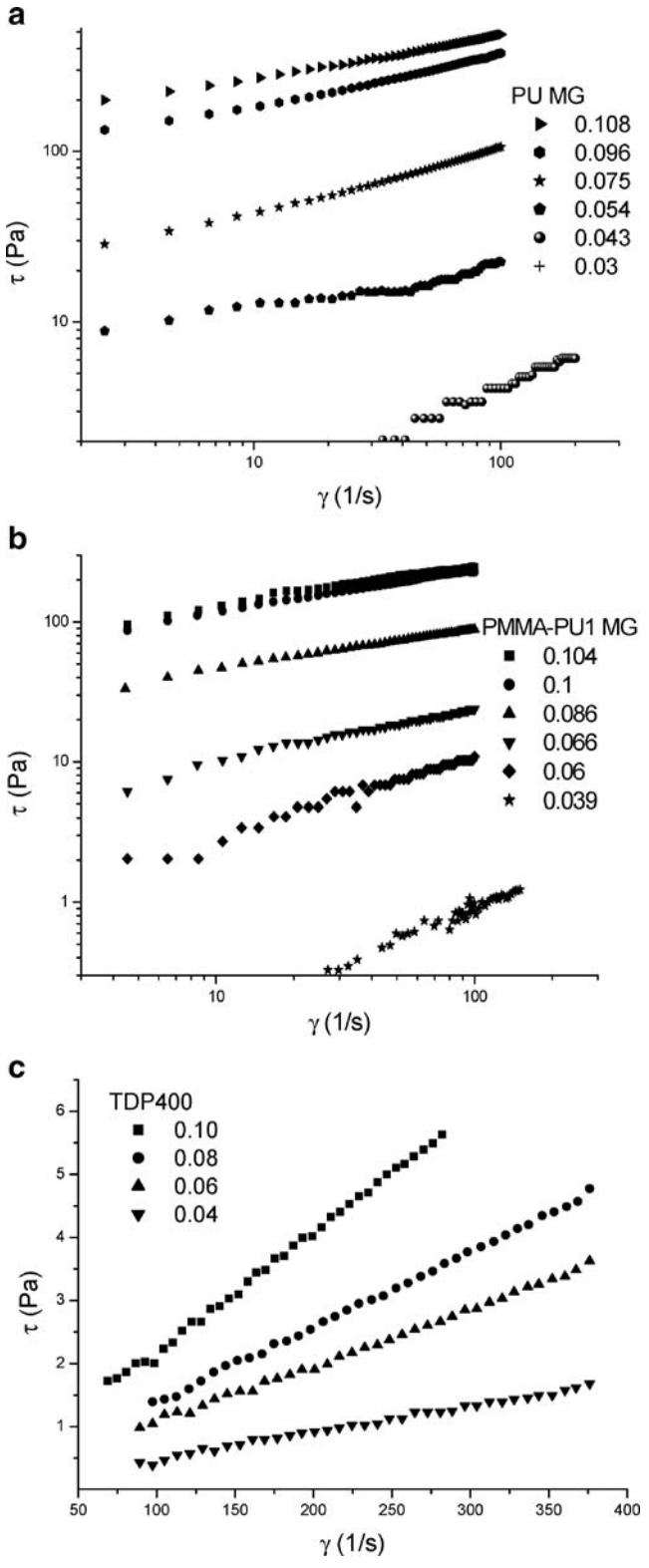


Fig. 5 Shear stress as a function of shear rate at different concentrations for the microgels and linear precursor solution. The temperature is 25 °C and the solvent is THF

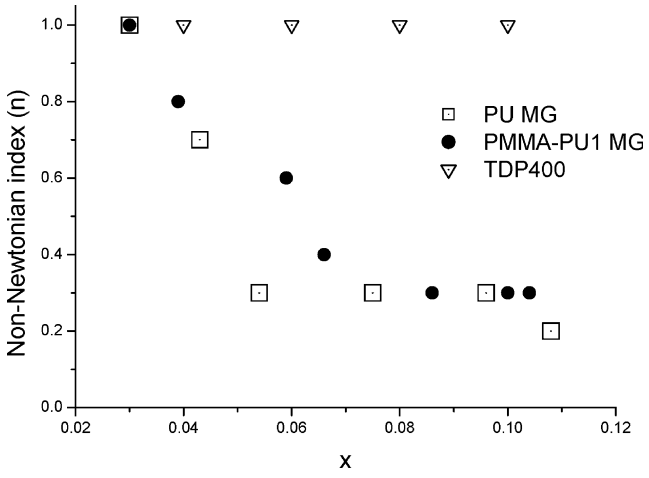


Fig. 6 Variation of non-Newtonian index (*n*) with the concentration of different microgels and linear polymer solutions. The temperature is 25 °C and the solvent is THF

of the difunctional precursor can form a polyfunctional star polymer (as shown in Scheme 3). This is because the degree of the polymerization was low due to the low double bond density, which can also be estimated from the GPC data. Besides, the carbon bond is much shorter compared with the chain length of the precursor. So we can neglect the length of the carbon chain, which unite the precursors and regard the macromolecular as a star-shaped polymer. Every vinyl group at the end of the star polymer can grow a new star polymer. A hyperbranched structure is formed during the reaction. When one star polymer meets another star polymer, the crosslinked structure is formed. The formation of the crosslinked structure may be the cause of the sudden increase of Mw and the polydispersity.

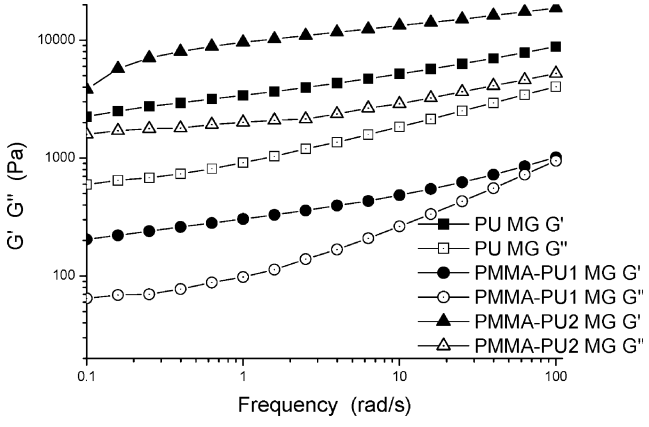


Fig. 7 Frequency dependence of the storage modulus (G′, *filled symbol*) and loss modulus (G″, *open symbol*) where the microgels' concentration is 11wt%, the temperature is 20 °C, and the strain is 0.5%

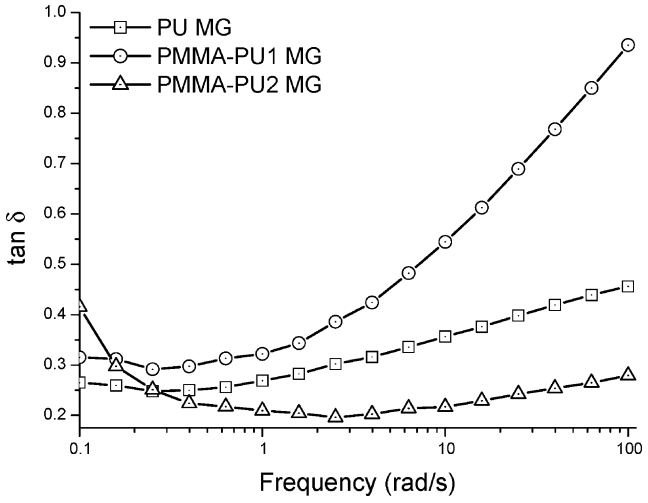


Fig. 8 Frequency dependence of tan (δ) at fixed strain of 0.5% where the microgels' concentration is 11 wt% and the temperature is 20 °C

Rheological behaviors

Flow properties

All rheological investigations were carried out using THF as the solvent for linear TDP400 precursor and the microgels. The viscosity increases sharply with increasing concentration. PU MG system has higher viscosity than the PMMA–PU1 MG system in the concentration range of 4 to 10wt% as shown in Fig. 3.

Figure 4a,b displays flow curves of PU MG and PMMA–PU1 MG samples. The curves of the microgel solutions are coincided with power law $(\tau = K\gamma^n)$ as shown in Fig. 5a,b.

When the concentrations are above 4wt%, both of the microgel samples begin to show shear-thinning behaviors.

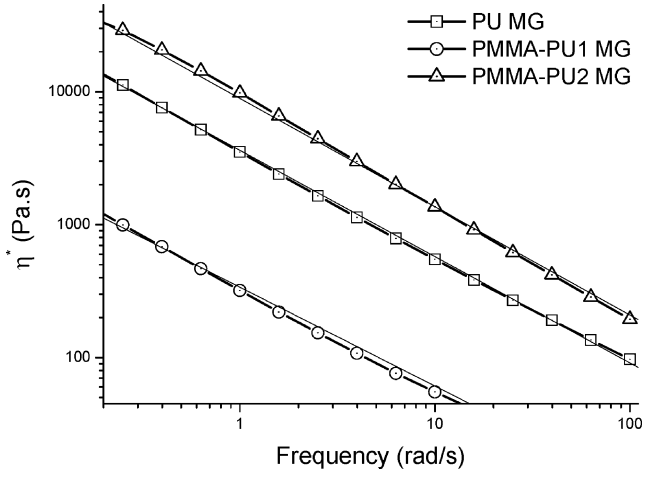


Fig. 9 Frequency dependence of the complex viscosity for the microgels

As the concentration continuously increases, both of the microgels exhibit highly shear-thinning behaviors and the value of non-Newtonian index becomes lower and lower. As shown in Fig. 6, the PU MG system always has the lower value of n than the PMMA–PU1 MG system in the concentration range of 4 to 10wt%.

The PU MG microgel, which is polymerized by TDP400, is found to have distinct rheological behaviors from TDP400 (as shown in Fig. 5c). The THF solutions of the TDP400 are Newtonian flows below the concentration of 10wt% and their viscosities are very low compared with those of the PU MG microgel.

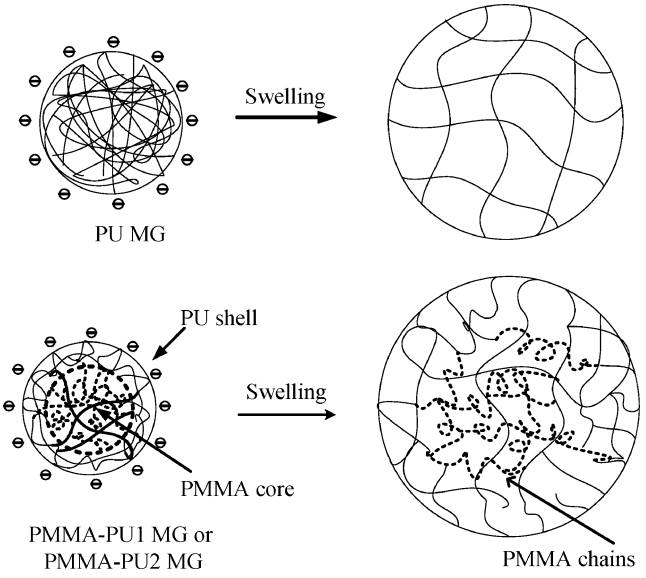
This indicated that the polymerization of TDP400 was accomplished in emulsion and obviously a new structure polymer totally different from TDP400 was produced after emulsion polymerization.

Viscoelastic behavior

Figure 7 displays the results obtained from the dynamic rheological experiments for the three kinds of microgel samples. At the concentration of 11wt%, the G′ is larger than the G″ for all of the microgel samples. The samples reveal a dominant elastic behavior. This indicates that the crosslinked structures are formed.

In our experiments, higher crosslinked microgel showed higher G′. The G′ increases as the crosslink density increases. Microgels with higher crosslink density show higher elastic behaviors.

Figure 8 shows the frequency dependency of the loss tangent tan (δ). The tan (δ) of all the samples decreases in the low frequency range and increases as frequency becomes larger. Such variation of tan (δ) relates to the crosslinked structure of microgels. When the frequency is



Scheme 4 Schematic representation of swelling of the microgels

Table 2 Particle size and the swelling ratio of the microgels

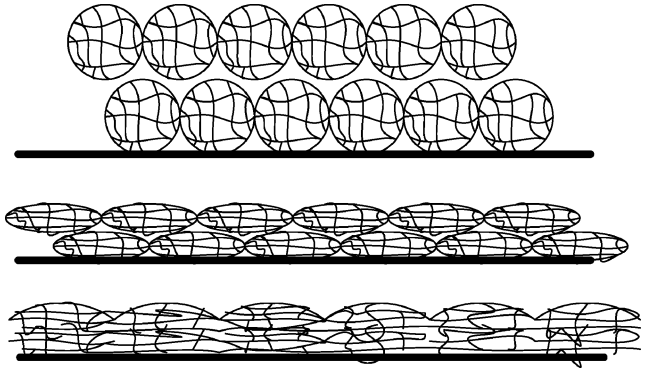
Sample code	Monomer particle		Microgel in water		Microgel in THF		(R_{THF}/R_{H2O})
	R_V (nm)	PI	R_V (nm)	PI	R_V (nm)	PI	
PU MG	21	1.5	44	1.57	139	1.03	32
PMMA–PU1 MG	41.2	1.44	84.6	1.96	226	1.18	19
PMMA–PU2 MG	40.4	1.57	63.2	1.52	121.4	1.38	7

R_V Radius of volume average particle, *PI* polydispersity index, and R_{THF}/R_{H2O} radius of volume average particle/radius of number average particle

sufficiently low, the microgel particles can follow the slow oscillation and slide with each other. The sliding between the crosslinked particles is the main cause of the internal friction. As the frequency increases, $\tan(\delta)$ decreases. This is because the individual swollen microgel cannot move with a high frequency and the friction caused by the segmental movement gradually becomes the main influential factor of the $\tan(\delta)$. In the high frequency range, the slope is positive. This is because the segment movement cannot follow the oscillation in high frequency and the internal friction increases as the frequency increases.

The PMMA-PU2 MG sample has a wider frequency range (0.1~2 rad/s) than that of the other samples (0.1~0.2 rad/s) in which the slope is negative It is attributed to its hard PMMA core and higher crosslink density, which can help form a more compact particle and tend to slide in a higher frequency. It seems that the PMMA–PU2 MG particles have a higher ability to slide. Moreover, in the low frequency range (<0.2 rad/s), $\tan(\delta)_{PMMA-PU2} > \tan(\delta)_{PMMA-PU1} > \tan(\delta)_{PU}$. This is indicated that the internal friction in low frequency is contributed mainly by the sliding of the microgels; thus, the microgels with higher ability to slide also have the higher internal friction in low frequency. Compared with PMMA–PU2 MG and PMMA–PU1 MG microgels, PU MG particles are softer and have no hard core. Its sliding ability is weaker than the others, so its internal friction is lower.

In the high frequency range (>0.2 rad/s), $\tan(\delta)_{PMMA-PU1} > \tan(\delta)_{PU} > \tan(\delta)_{PMMA-PU2}$, which is coincident with the decreasing of the crosslink density. The $\tan(\delta)$ is contributed mainly by friction of the segments of the microgel in high frequency. As crosslink density increased, the segments, which can move with the external force became shorter. The shorter segment is believed to have quick response to the external force and have a higher ability to follow the change of the external force. So PMMA–PU2 MG microgel with shorter moving segments have the lowest friction among the three kinds of microgels.



Scheme 5 Schematic presentation of the film-forming process of the PU microgel and PU composite microgels

The frequency dependence of the complex viscosity for the three kinds of microgels are compared in Fig. 9. All of the microgels exhibit shear-thinning behaviors in the whole frequency range. Sample PMMA–PU2 MG with the higher crosslink density shows a higher complex viscosity compared to the other samples. The complex viscosity as a function of the frequency ω can be approximated mathematically by the following equation:

$$\lg|\eta^*| = A + B\lg\omega \quad (1)$$

with A=2.53 and B=−0.744 (PMMA–PU1 MG); A=3.56 and B=−0.800 (PU MG); and A=3.95 and B=−0.815 (PMMA–PU2 MG). Value A increases and value B decreases when the crosslink density increases.

Swelling behavior of microgel particles

The microgel swelling can be controlled not only by crosslink density but also by the solubility properties of the

Table 3 Gel contents and the coating properties of the microgel films

Film sample	Gel content (%)	Pencil hardness	Crosshatch adhesion	Impact strength (50 cm)	
				Front	Back
TDP400	87	4H	1	>50	>50
PU MG	82	3H	1	>50	>50
PMMA–PU1 MG	76	3H	1	>50	>50
PMMA–PU2 MG	69	3H	1	<30	<5

constituent polymers. The swelling behaviors of the PU MG and PMMA–PU1 microgels are shown in Scheme 4.

Although PMMA–PU1 MG had a lower crosslink density than PU MG, its swelling ratio was not higher than PU MG (as shown in Table 2). It is due to the solubility properties of PMMA and PU. THF can form hydrogen bonds with the amido groups of PU chain. The swelling extent of PU is better than that of PMMA in THF. So the microgel composed of PU had a higher swelling extent than those of the composite ones composed of PMMA and PU. After emulsion polymerization, the particle sizes were larger than those before polymerization; it is attributed to coalescence and monomer transportation from water phase to micellar phase. After swelling in THF, all of the polydispersity indexes became smaller than those in water.

Film formation behavior of PU microgels

The PU microgels were found to form a coherent film at room temperature, which is different from those hard microgel systems. Due to the low glass transition temperature of the soft segments, the PU emulsion particles cannot hold their spherical shape at room temperature. After water was evaporated, the particles deformed and coalesced (as shown in Scheme 5). The crosslinked chains interdiffused across the latex particle boundaries and polymer chain entanglements occurred between polymer chains of neighboring latex particles. The cohesive strength was developed by the interdiffusion process and the entanglement of the crosslinked chains. We found that it could form a film and the film could keep more than half of its weight after 48 h in THF.

Table 3 summarizes the properties of the microgel coatings. The coating properties of the films with lower crosslink densities (PU MG and PMMA–PU1 MG) are better than the PMMA–PU2 film with higher crosslink density. It seems that low crosslink density has no evident influence on the coating properties. The interdiffusion and entanglement of the crosslinked chains between neighboring latex particles is greatly hindered by high extent of crosslinking, which results in poor impact strength.

Conclusions

The PU microgels were successfully synthesized by emulsion polymerization using unsaturated self-emulsified PU acrylate. Copolymerization of the PU acrylate with MMA monomer can produce composite microgels. The composite microgel has different properties from the PU microgel.

The tests of dynamic rheological behaviors, steady rheological behaviors, and the swelling behaviors of the microgels indicated that crosslinked structure was formed during the emulsion polymerization. The PU microgel swelling in THF showed a high viscosity and strongly shear-thinning behavior. The frequency dependence of $\tan(\delta)$ revealed that those microgels with rigid core had higher ability to slide than the soft microgel in low frequency. Besides crosslink density, solubility of the constituent polymer also had an influence on the swelling of microgels.

As a sort of flexible microgel system, PU microgels exhibited differences in film-forming ability. We found that it could form a film with a certain extent of mechanical properties and the film could keep half of its weight after 48 h in THF.

The emulsion polymerization of PU acrylate provided a new method to synthesize microgels and composite microgels.

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