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SHORT COMMUNICATION

Convenient synthesis of novel fluorinated polyurethane hybrid latexes and core-shell structures via emulsion polymerization process with self-emulsification of polyurethane

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Abstract Novel fluorinated polyurethane hybrid latexes in the size range of 40–50 nm, fluoroalkyl acrylate as fluorinated monomers, with various fluorine content (*F*%=9~26 wt%) were successfully prepared via emulsion polymerization process without traditional emulsifier. The waterborne polyurethane, which was synthesized by using isophronediisocyanate, dimethylol propionic acid, polyethylene glycols, etc., served not only as copolymerizable macromonomer but also as polymeric high molecular weight emulsifier. The structures of polyurethane macromonomer and fluorinated polyurethane were characterized by Fourier transform infrared and H^1-NMR. Particle size, zeta potential, micromorphology of the latex par.ticles, and surface properties were investigated by dynamic light scattering, potential particle size analyzer, transmission electron microscopy, and contact angle measurement, respectively. Results illustrated that the advantage of this process is that the size of fluorinated polyurethane hybrid particle is less sensitive to the composition. Furthermore, it was showed that fluorinated polyurethane latex particles had core-shell structures, especially when the content of fluorine was 26.08 wt%. Moreover, there was an obvious migration of fluorinated groups to the surface during the formation of fluorinated polymer films, although fluorinated groups were covered by polyurethane in latex particles.

Keywords Fluorinated polyurethane latex · Core-shell · Emulsion polymerization

Introduction

It is well known that fluorinated polyurethanes (PUs) possess a whole range of very interesting bulk and surface properties, such as excellent environmental stability, water and oil repellency, biocompatibility, excellent thermal stability, and chemical resistance [1–5]. Waterborne fluorinated polyurethanes have attracted more and more attention because they are nontoxic, nonflammable, and noncontaminative, and they have excellent properties above.

At present, waterborne fluorinated polyurethane are generally prepared by direct water dispersion method, which is that fluorinated polyurethanes are first prepared in organic solvent and then are dispersed into water to get waterborne fluorinated polyurethane dispersion. For instance, Chul Hwan Lim et al. [6] first synthesized fluorinated polyurethane by using fluorine-modified diisocyanate as hard segment and then dropped water with emulsifiers to prepare waterborne anionic fluorinated polyurethane dispersion. Hyelin Lim et al. [7] prepared fluorine-containing polyurethane with perfluoroalkyl groups and dispersed it into water to get aqueous fluorine-containing polyurethane. Turri et al. [8, 9] utilized a fluorocarbon-containing diol as chain extender to synthesize fluorinated polyurethane–urea anionic aqueous dispersions by direct water dispersion method. The direct water dispersion method general needs some emulsifiers and always leads large particle size.

Polyurethanes are an interesting class to design polymeric emulsifiers. Hydrophilic segment of polyurethane

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may usually act as an internal emulsifier, which endows polyurethane with self-emulsification. In this article, we are interesting in preparing novel fluorinated polyurethane hybrid latexes via emulsion polymerization process by designing a kind of copolymerizable polyurethane macromonomer and utilizing its self-emulsification instead of traditional surfactant. It is well known that conventional emulsion polymerization is stabilized with traditional low molecular weight surfactants. Low molecular weight surfactants are able to migrate to the polymer surface, where delamination and corrosion can be a consequence [10]. Polymeric surfactants have only a limited possibility to migrate because of their much lower diffusion rate. If copolymerizable surfactants are used there is no migration possible. Obviously, compared with conventional method, this convenient method utilized copolymerizable polyurethane macromonomer instead of low molecular weight surfactants and avoids the migration problem of surfactants. As far as we know, there are no other reports describing the preparation of fluorinated polyurethane hybrid latexes via emulsion polymerization process by the use of polyurethane macromonomer. In this way, partly double bond-end capped and having self-emulsification polyurethane macromonomer was first built and synthesized. Secondly, a series of novel fluorinated polyurethane hybrid latexes containing various fluorine contents were successfully synthesized by emulsion polymerization process emulsified by polyurethane macromonomer. Last, particle size, Zeta potential, micromorphology of the latex particles and surface free energies of fluorinated polyurethane latex (FPUL) films were investigated by dynamic light scattering (DLC), potential particle size analyzer, transmission electron microscopy (TEM) and contact angle measurement, respectively.

Experimental section

Materials and methods

Isophronediisocyanate (IPDI) was purchased from Hüls. Dimethylol propionic acid (DMPA), stannous caprylate (SC) and polyethylene glycols (PEG) with molecular weight of 1,000 g/mol were used as received. Hydroxyethyl methacrylate (HEMA) was purchased from Tokyo Kasei Kogyo. Hexafluorobutly acrylate (HFBA) was purchased from XEOGIA Fluorine-silicon Chemical Co. *N*-methyl-2-pyrrolidone (NMP, chemistry purity (CP) grade) and 2-phenoxyethanol (CP grade) were used. Triethylamine (CP grade) was used as neutralization agent. Potassium persulfate ($K_2S_2O_8$, 99+%) was used as a water-soluble initiator.

Synthesis of polymerizable and surfactant PU dispersion

Partly acrylate-endcapped polyurethane macromonomers in this study were prepared based on IPDI, DMPA, HEMA, TEM, and methanol and PEG. First, in a three-necked flask, IPDI, DMPA, PEG, SC, and NMP were added in turn, and the mixture was heated to 110 °C for 3 h. Second, after cooling the prepolymer, HEMA, 2-phenoxyethanol (HEMA/2-phenoxyethanol=1:1) were added and reacted for 6 h. Reactive completion was monitored by the absence of infrared (IR) absorption of the free NCO group at 2,270 cm^{-1}. Lastly, the polyurethane macromonomer was allowed to disperse into deionized water with vigorous stirring. The solid content of polyurethane macromonomer is 40 wt%. PU macromonomer is $\overline{\mathrm{M}}\mathrm{n} = 7.4143 \times 10^3$, $\overline{\mathrm{M}}\mathrm{w} = 1.1523 \times 10^4$ and polydispersity index (PDI)=1.55.

Synthesis of fluorinated polyurethane latexes

The general recipe used for the preparation of FPUL is listed in Table 1. A reactor vessel with four necks, equipped with a reflux condenser, a mechanical stirrer, a thermometer, and a nitrogen gas inlet was charged with PU dispersion and an amount of deionized water, which has a pH level of 8. After stirring for 30 min, HFBA was allowed to disperse into the mixture solution with vigorous stirring for 30 min followed by an increase in the temperature up to 80 °C. Then, the solution of $K_2S_2O_8$ in water with $K_2S_2O_8$ mass concentration of 0.5 wt% was dropped in system in 2 h, and heating was continued for another 4 h to form FPULs.

Characterization and sample preparation

The gel permeation chromatography (GPC) experiments were carried out by passing a 1.0 g/l tetrahydrofuran (Tedia)

Table 1 Characteristics of fluorinated polyurethane latex

Sample	PU/ HFBA (w/w)	The content of PU in water %(w/w)	*F* (wt%)[a]	Solid content (%)	Particle size (Dv, nm)	ζ/mV
FPUL1	1:4	16.00	9.66	16.31	115	−54.2
FPUL2	3:8	14.55	13.17	16.35	117	−54.0
FPUL3	1:2	13.33	16.10	16.46	108	−53.8
FPUL4	3:4	11.42	20.70	16.14	110	−52.7
FPUL5	4.6:5.4	10.22	26.08	16.23	116	−50.0

[a] The theoretical weight fraction of fluorine in the monomer mixture

solution of the polymers through Agilent 1100 high-pressure chromatograph. A GPC calibration curve was obtained using polystyrene standards.

Fourier transform infrared (FTIR) data were obtained with infrared spectroscopy (MX-1E, FTIR, USA). Each sample for infrared analysis was prepared by casting a film on KBr window.

H^1-NMR spectra data were obtained with a BRUCK AC-P (300 MHz). Deuterodimethyl sulfoxide was used as deuterated solvent.

Surface tensions were measured with BYZ-1 interface tension instrument. Samples for surface tension measurement were the polymer solutions in water with different polyurethane content. These reported values are an average of three measurements.

The particle sizes (the volume-average partial size, Dv) were measured using (DLC, SHIMAD2U SALD-2001). Zeta potential (ζ) of the latexes was measured with Zetasizer Nano ZS surface potential particle size analyzer.

A TEM (JEM-100CX) was employed to study the morphology of FPULs particles. TEM specimens were prepared by aspirating and aqueous sample onto to a copper EM grid. A few minutes after the deposition, the aqueous solution was blotted away with a strip of filter paper, stained with a 2-wt% aqueous solution of phosphotungstic acid and dried in air of for few hours.

Contact angle were measured with an OCA20 (Data Physics) contact angle goniometer. The samples for contact angle measure were prepared by casting the polymer latexes onto clean glass wafers. The glass wafers were kept in an oven at 40 °C for 24 h, 50 °C for24 h, and 100 °C for 12 h. Contact angles were measured on 1 ul of water and diiodo-methane at 12 °C and the results reported are the mean values of three replicates.

Results and discussion

Identification of the PU macromonomer and FPUL structure

Polyurethane macromonomer, as copolymerizable emulsifier in emulsion polymerization process, was designed and synthesized by incorporating PEG and DMPA into the polyurethane backbone chain and capping the isocyanate groups with a mixture of HEMA and 2-phenoxyethanol. Figure 1 shows the structure of the PU macromonomer. The structures of polyurethane and fluorinated polyurethane were characterized by FTIR and H^1-NMR.

PU macromonomer

Fourier transform infrared The N–H stretching and bending vibrations of polyurethane appear at about 3,342 and 1,544.7 cm^{-1}. Carbonyl peak (C=O) and C–O–C peak are observed at 1,715.5 and 1,111.8 cm^{-1}. The spectrum shows no NCO peak at 2,270 cm^{-1}.

H^1-NMR The peaks at 5.48–6.03 ppm correspond to characteristic peak of double bonds. The peak at 3.6 ppm corresponds to $-CH_2CH_2O-$ group.

Fluorinated polyurethane latex

Fourier transform infrared The peaks at 1,154.4 and 1,189.8 cm^{-1} correspond to the characteristic absorption of CF2 and CF3 groups. The absorption at 1,753.8 cm^{-1} is related to the C=O bond of the poly (HFBA). It is clear that it is possible to synthesize FPULs by using copolymerizable polyurethane macromonomer and HFBA via emulsion polymerization process.

Surface tension of polyurethane macromonomer in water

The target of this work is to use polyurethane macromonomer as copolymerizable emulsifier in emulsion polymerization process to prepare novel fluorinated polyurethane hybrid latexes. It is necessary to check whether it behaves similarly to low molecular weight emulsifier in terms of surface activity. The plot of the surface tension versus concentration of the polyurethane macromonomer is showed in Fig. 2. As we expected, the surface tension decreased with increasing concentration of

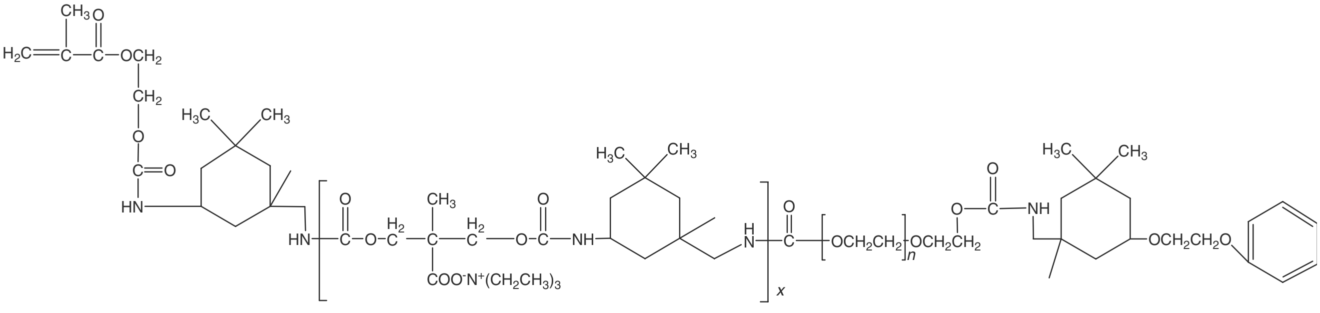


Fig. 1 Structure of the polyurethane macromonomer

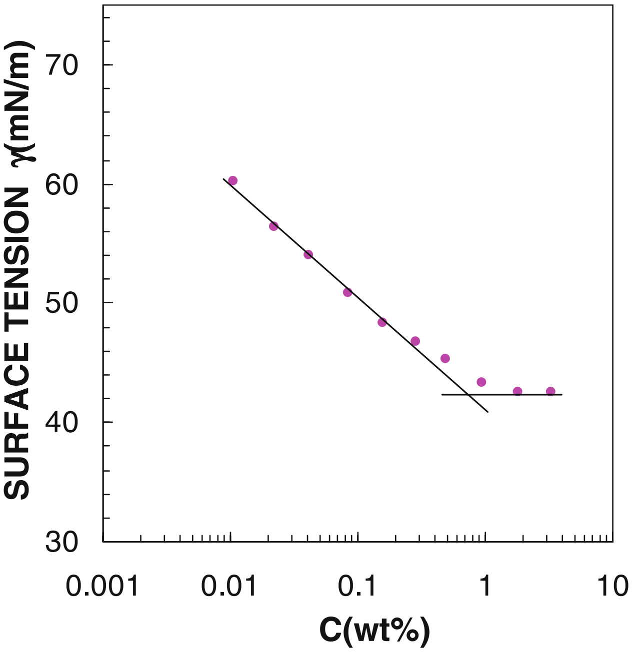


Fig. 2 Surface tension versus polyurethane water solution with different content

the polyurethane macromonomer. There was inflection point in the curve as known for typical surfactants. The polyurethane macromonomer could reduce the surface tension of water to 42.55 mN/m when the content of polyurethane is only 0.95% (w/w), which is the critical micelle concentration. It confirmed the copolymerizable polyurethane macromonomer with $\overline{M}w = 7.4143 \times 10^3$ and PDI=1.55 behaved similarly to low molecular weight emulsifiers and was polymeric high molecular weight emulsifier.

Synthesis and characterization of latex particles

Fluorinated polyurethane hybrid latexes with various compositions were successfully prepared by $K_2S_2O_8$-initiated emulsion polymerization process, which testified the emulsification of the PU macromonomer was excellent. Basic characteristics of the resulting latex particles were summarized in Table 1. Five variables were investigated: (1) the ratio of polyurethane to HFBA, (2) the content of PU in water, (3) the solid contents of FPUL, (4) the particle size of FPUL, (5) Zeta potential of FPUL. In all cases, the solid contents of FPUL were close to anticipated value of 16.67%. The volume-average particle size (Dv) had range from 110 to 117 nm. The results indicated that the latex particles size (Dv) was less sensitive to the content of fluorine via emulsion polymerization process in our reactive system, which was different from the reports of other aqueous fluorinated polyurethane prepared by direct water dispersion process. For example, Hyejin Lim et al. [7] found that diameters of waterborne fluorinated polyurethane particles, prepared by direct water dispersion process, had a range from 200 to 1,100 nm and increased according to the contents of F-diols. Similar results were also reported by Chul Hwan Lim et al. [6]. The results demonstrated that

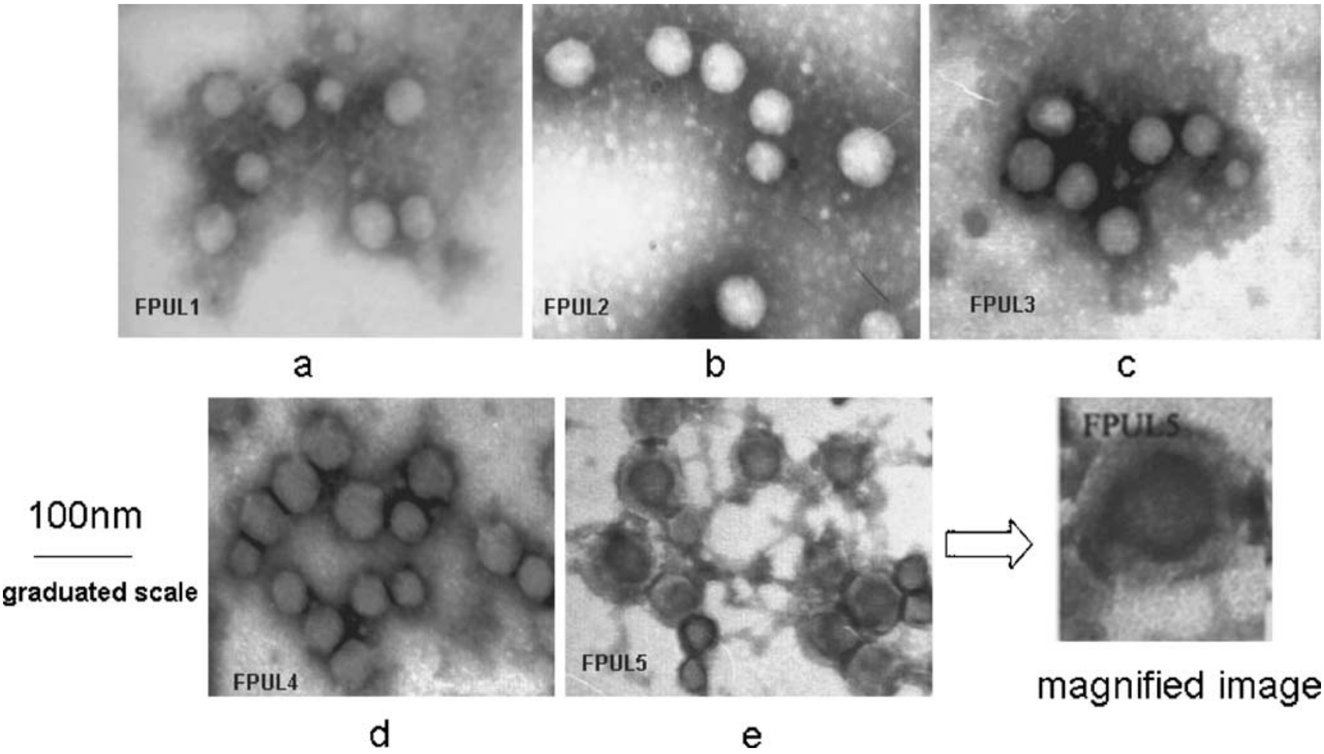
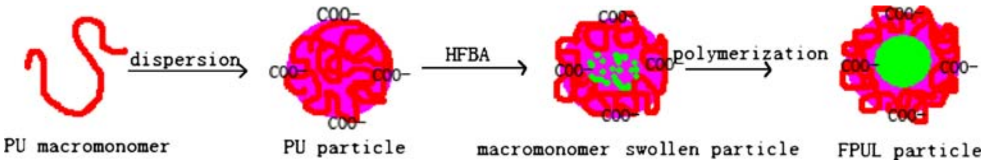


Fig. 3 TEM micrographs of fluorinated polyurethane latex particles

Fig. 4 Schematic illustration of the formation of novel fluorinated polyurethane particle



emulsion polymerization process differs from direct water dispersion process and is a very effectual method to prepare fluorinated polyurethane hybrid latexes. At the same time, compared with the preparation of fluorine polymer particles by the conventional emulsion polymerization [11–13], this convenient method can synthesize high fluorine-containing fluorinated polymer particles without traditional emulsifier and is a straightforward and simple approach to synthesize FPULs. Moreover, because of the anionic polyurethane macromonomer used and the sulfated end groups [R–OSO_3]$^-$ generated by the radical initiator system, the hybrid particles had a strong negative surface charge confirmed by zeta potential. The values of the surface charge density of novel fluorinated polyurethane hybrid particles were less than −50 mV. It exhibited that the fluorinated polyurethane hybrid latexes had good mechanical stability. The results indicated that the HFBA content had little effect on the particle surface charge.

Figure 3 shows TEM pictures of FPUL1, FPUL2, FPUL3, FPUL4, and FPUL5. The TEM images also confirmed that the FPUL particles remained appreciatively unchanged, with an average diameter of 40~50 nm. Obviously, FPUL particles presented obviously core-shell structures when the content of fluorine was 26.08 wt% (Fig. 3e). According to prior literature [14], the polyurethane/styrene hybrids had particle with a polyurethane shell, an intermediate layer and a polystyrene core because the polymer particles had structured morphology (microphase separation). Moreover, in this work, polyurethane macromonomer is not completely homogenous with HFBA. In addition, our published results suggested there was a microphase separation in the bulk of the fluorinated polyurethane [15]. Therefore, we deemed that the reason that an FPUL hybrid particle had core-shell morphology was mainly due to the inside-migration of a hydrophobic monomer (HFBA) and the higher incompatibility between fluorinated side chains and polyurethane segment because of large differences in chemical structure. With the increasing fluorine content, especially when the content of fluorine was 26.08 wt%, the core-shell structure with hydrophilic polyurethane shell and hydrophobic poly (HFBA) core tended to be outstanding, as displayed in Fig. 3e. Hirose et al. [16] and Dong et al. [17] observed an analogous trend of particle size change at lower Acrylic (AC)/PU ratios and the AC/PU core/shell structure. They explained that at lower AC/PU ratios, the hydrophobic AC can easily diffuse into PU particles where the free radical chain-growth polymerization takes part and a core/shell structure can be formed. The probabilities of coalescence of particles are little because the ionic density on the PU particle surface is high. The particle size of hybrid emulsion is almost the same as that of polyurethane dispersion. Because of the same trend in particles growth, it may be assumed that the mechanism of particles growth at lower HFBA/PU ratios (5.4:4.6) in the present work is similar to the one proposed by Hirose et al. [16] and Dong et al. [17]. In addition, we found that a lot of polymers deposited during the polymerization period, and it was difficult to form a latex when HFBA/PU ratio is less than 5.4:4.6 because of the strong hydrophobility of HFBA. Accordingly, the model of the polymerization mechanism at lower HFBA/PU (5.4:4.6) ratios we presumed is shown in Fig. 4. The hydrophobic monomer (HFBA) first migrates inside the polyurethane macromonomer particles. Secondly, polymerization in the particles is initiated by radical initiators. Lastly, as the free radical chain-growth polymerization took part, the core-shell structure fluorinated polyurethane hybrid latexes particles were formed.

Surface properties of the fluorinated polyurethane latexes films

Table 2 shows the contact angles and surface energies of the films of FPUL1, FPUL3, and FPUL5 respectively. The wetting liquids used for the contact-angle measurements were water and diiodo-methane, the surface tensions of which were suggested by Owens and Wendt [18]. The total surface energies and their polar and dispersion components were calculated by Fowkes' equation as follows:

$$r_{\mathrm{LV}}(1+\cos\theta) = 2\left[\left(r_S^d\right)^{1/2}\left(r_{\mathrm{LV}}^d\right)^{1/2} + \left(r_S^p\right)^{1/2}\left(r_{\mathrm{LV}}^p\right)^{1/2}\right]$$

where p and d are the polar and dispersion components of each surface energy, θ is the contact angle, r_{LV} is the interfacial tension at the liquid vapor, and r_{S} is the sum of

Table 2 Contact angle and surface tension results of fluorinated polyurethane latexes

Sample	Content angle (degrees)		Surface (dyn/cm)		Tension
	H_2O	CH_2I_2	r^d	r^p	r
PU	41	46.6	26.96	30.78	57.75
FPUL1	104.8	88.5	11.93	2.37	14.31
FPUL3	106.7	92.5	10.26	2.37	12.63
FPUL5	103.2	90.4	10.85	3.16	14.01

the surface tension components $\left(r_{\mathrm{S}}^{d}+r_{\mathrm{S}}^{p}\right)$. By measurement of the contact angles on a solid surface with two wetting liquids, the polar and dispersion components of the surface tensions are known. Consequently, the total surface energy of a solid and its components can be calculated. The low critical surface tension reflects a higher concentration of CF_3 on the surface [19]. The pure polyurethane showed a high surface energy of 57.75 dyn/cm due to the present of hydrophilic properties, such as the carboxyl group on the surface of the film. With introducing fluorinated groups into polyurethane, the surface energy of FPUL films tended to decrease sharply. For FPUL1, FPUL3, and FPUL5, surface tension of 14.31, 12.63, and 14.01 was obtained, respectively. The surface free energies of the films decrease by more than 75.47%. It was clear that the low surface energies of FPUL films came mainly from the chemical structure of HFBA, which had strong hydrophobic fluorinated groups. The results indicated the surfaces of films had obvious water and oil repellency and amount of CF3 groups had migrated onto the outmost surface during the formation of film although they were covered by polyurethane. However, the surface energy of FPUL5 was similar to FPUL1. It seemed that increasing fluorine inside polyurethane did not always reduce the surface energy of the FPULs film when the content of fluorine was high.

Conclusions

This work demonstrates that emulsion polymerization process is a very powerful method to prepare fluorinated polyurethane hybrid latexes (40~50 nm in diameter). PU macromonomer behaved not only as copolymerizable macromonomer but also as an excellent polymeric emulsifier. Especially, it was found the advantage of this method was that the final particle size was less sensitive to the composition confirmed by particle size analysis and TEM. FPUL particles had obviously core-shell structures, especially when the content of fluorine was 26.08 wt%. Furthermore, the hydrophobic character and oil repulsion of the fluorinated polymer was not affected by polyurethane as emulsifier and −CF3 groups had migrated onto the outmost surface during the formation of film.

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