

Design Strategy for Waterborne Polyurethane with Sodium Sulfonate Groups on the Soft Segments

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ABSTRACT: The field of waterborne polyurethane (WPU) is gaining a great deal of momentum from both a commercial and academic sense because of increasing environmental and sustainable awareness. For polyurethane (PU) to be dispersible in water, the hydrophilic groups are very important in the design of the polymer chains. Herein, we present a design strategy for WPU having hydrophilic groups on the soft segments through the reaction of as-synthesized OH-terminated poly(ϵ -caprolactone) diols containing a sodium sulfonate group with diisocyanate. A stable aqueous dispersion was then obtained, and this was followed by a subsequent chain extension reaction and emulsification. We found that the PU dispersion particles were a core-shell structure with a good particle size distribution, and the obtained films exhibited a low tensile strength and a high elongation at break. This approach provided valuable information for fundamental research in the production, modification, property enhancement, and new applications of these materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39657.

KEYWORDS: applications; crystallization; mechanical properties; polyurethanes; structure; property relations

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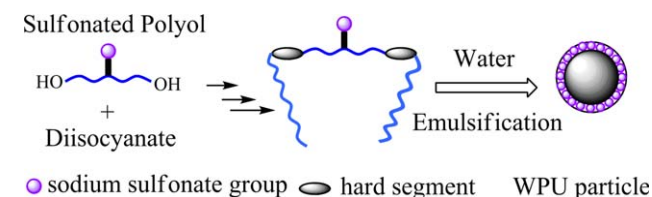
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INTRODUCTION

Polyurethanes (PUs), with tunable and versatile properties, are one of the most important polymeric materials. Because of their simple preparation and promising applications, much attention has paid to the development and design of materials consisting of both linear and crosslinked PUs.^{1–3} As their properties vary from the species of polyol and diisocyanate, the variation of soft- or hard-segment concentration, the nature and ratios of the chain extenders, and the density of chemical crosslinks, they could be easily designed with a wide variety of chemical and mechanical properties for engineering applications.^{4–29} However, conventional PUs, containing a significant amount of volatile organic solvents, are insoluble and/or undispersible in aqueous media. The increased demands for minimized volatile organic components and hazardous air pollutant levels have motivated research on the development of environmentally friendly products by both industrial and academic organizations. Waterborne technology is an effective process for meeting concerns about environmental pollution and health and safety risks, and the driving force for future development in this environmentally friendly technology have become evident. For PU to be dispersible in water, hydrophilic groups were designed to incorporate to the polymer chains to obtain dispersion followed by emulsification. The challenge within the industry is to maintain or improve properties at an excellent dispersion in water and also to meet the need for a rea-

sonable shelf life. Economic competitiveness and environmental concerns have also driven scientists and technologists to constantly explore newer chemistries and approaches for improving the efficiency of waterborne polyurethanes (WPUs) with minimum volatile organic components.

WPU can be prepared from ionic and/or nonionic hydrophilic PU.³⁰ As the hydrophilic group is of primary importance to the synthesis of WPU, many strategies have been developed to incorporate hydrophilic groups into the PU chains for the preparation of WPU. They can be mainly divided into two avenues. The first is the introduction of hydrophilic groups into the hard segment of PU chains. In this approach, hydrophilic groups, such as salt carboxylate groups and/or salt sulfonate groups,³¹ are usually introduced into WPU through chain extenders. Dimethylolpropionic acid (DMPA),^{32–35} one of the most commonly used hydrophilic compounds, can be introduced into the PU chain for the reaction between its two OH groups and the —NCO of diisocyanate. Subsequent neutralization by tertiary amines can electrostatically stabilize the DMPA-based aqueous polyurethane dispersions (PUDs). Sulfonated PU, with hydrophilic groups on the hard segment of the PU chains, can also be prepared by the reaction of PU with NaH to remove the urethane hydrogen^{36,37} followed by the reaction with alkyl sulfone to yield a polymer with anionic sulfonate groups. The other strategy is the introduction of hydrophilic groups into the soft segment of PU chains, in



Scheme 1. Strategy for the incorporation of sodium sulfonate groups into polymer chains. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which poly(ethylene glycol) has commonly been used as a non-ionic hydrophilic group.³⁸ Another alternative sulfonated polyol is based on dimethyl 5-sulfoisophthalate sodium salt.^{39–42} In this method, the ionic or nonionic hydrophilic polyols, as raw material species, are reacted with the —NCO groups of diisocyanate to obtain PU ionomers with hydrophilic groups on the soft segment.

In this study, we designed a strategy for WPU with sodium sulfonate groups on the soft segments, as illustrated in Scheme 1. The sodium sulfonate group is a salt of a strong acid and a strong base and is freely dissociated in water; this, in turn, enhanced the dissociation degree and efficiency for stabilizing PUD. In this process, OH-terminated poly(ϵ -caprolactone) diols containing a sodium sulfonate group ($\text{PCL—SO}_3\text{Na}$) was synthesized to react with diisocyanate. The chain extension reaction proceeded subsequently by the addition of ethylenediamines to form a PU ionomer. An aqueous dispersion of the PU ionomer was then obtained. An understanding of this approach would provide valuable information for applications in WPU industries because of its simple, inexpensive, and nontoxic process.

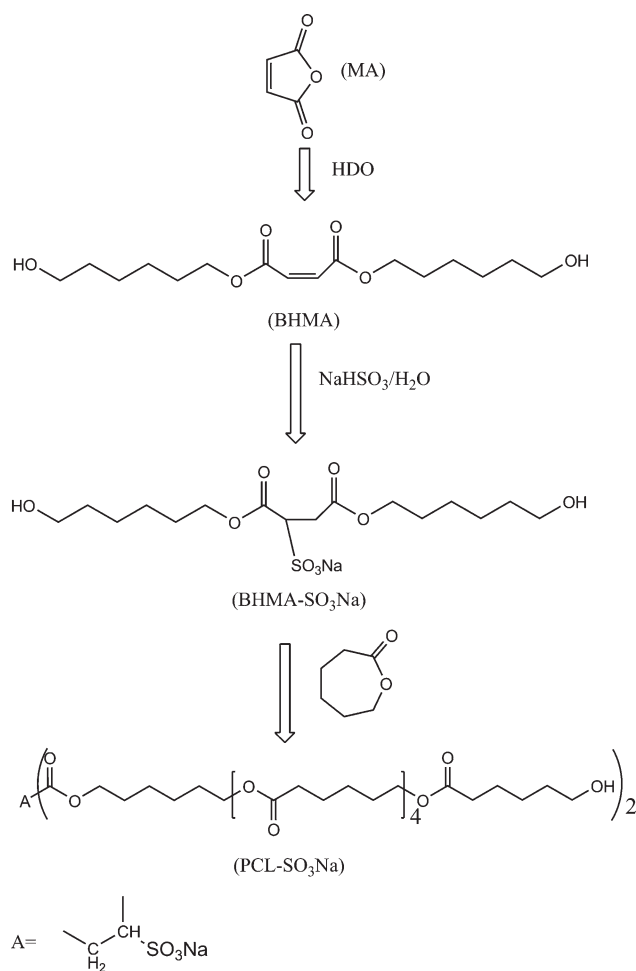
EXPERIMENTAL

Materials

Maleic anhydride (MA), 1,6-hexanediol (HDO), NaHSO_3 , acetone, dibutyltin dilaurate (DBTDL), stannous octoate catalyst, and anhydrous ethylenediamine, obtained from Sinopharm Chemical Reagent Co, Ltd., were analytically pure and were used without further purification. ϵ -Caprolactone (CL) was dried over CaH_2 for 48 h at room temperature and distilled under reduced pressure before use. Isophorone diisocyanate (IPDI) and poly(*n*-butylene adipate glycol) (PBA) 2000 [number-average molecular weight (M_n) = 2000] were purchased from Bayer Chemical.

Synthesis of $\text{PCL—SO}_3\text{Na}$

The reaction was performed in a four-necked, cylindrical flask equipped with a thermometer, a mechanical stirrer, a nitrogen



Scheme 2. Schematic synthesis of $\text{PCL—SO}_3\text{Na}$.

inlet, and a water-cooled distillation condenser. A 2:1 molar ratio of HDO to MA and stannous octoate as a catalyst were used. The reactions were carried out under a nitrogen flow by gradual heating to 205°C for a period of 2 h and held at about 205°C over 30 min, and then bis(6-hydroxyhexyl) maleate (BHMA) was obtained. After the product was cooled to 98°C, a clear solution of 27 wt % NaHSO_3 (1 mol/mol of MA) was added to the reaction vessel. The nitrogen flow was discontinued, and the mixture was reacted at 74–84°C for 21 h. The water was distilled *in vacuo* for a period of 1 h, and the temperature was gradually increased to 162°C. Then, sodium 1,4-bis(6-hydroxyhexyloxy)–1,4-dioxobutane-2-sulfonate ($\text{BHMA—SO}_3\text{Na}$) was synthesized. The CL was added to the previous vessel, and the $\text{PCL—SO}_3\text{Na}$ was obtained

Table I. Formulations of the Samples, Contents of $\text{—SO}_3\text{Na}$ Hydrophilic Groups in the PU Films, GPC M_n Values, and PDIs of the PU Films

Sample	Sample composition				$\text{—SO}_3\text{Na}$ ($\times 10^4$ mol/g)	M_n (Da)	M_w (Da)	PDI
	$\text{PCL—SO}_3\text{Na}$ (mol)	PBA (mol)	IPDI (mol)	Ethylenediamine (mol)				
PUDA	0.007	0.01	0.02	0.004	1.96	38,053	86,031	2.26
PUSB	0.006	0.01	0.02	0.005	1.75	40,869	97,904	2.40
PUDC	0.0055	0.01	0.02	0.0055	1.6	49,872	119,404	2.39

M_w , weight-average molecular weight.

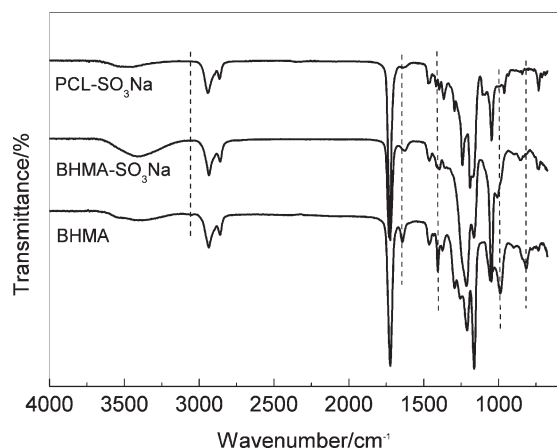


Figure 1. FTIR spectra of PCL-SO₃Na, BHMA-SO₃Na, and BHMA.

after the mixture was reacted at 120–130°C for 76 h with a nitrogen flow. The overall synthesis reaction of PCL-SO₃Na is schematically shown in Scheme 2.

Synthesis of PUDs Based on PCL-SO₃Na

PBA 2000 and PCL-SO₃Na were added to a 250-mL, three-necked, round-bottomed flask fitted with a mechanical stirrer, a thermometer, and a nitrogen inlet/outlet. The mixture was carried out at 110°C for 1 h at reduced pressure to remove the water. After it was cooled to 75°C, IPDI and DBTDL were poured into the flask to react at 80°C for 3 h under a dry nitrogen flow. Then, acetone was slowly added to obtain a homogeneous mixture, and the prepolymer was extended by the addition of ethylenediamine and allowed to react at 50°C for 2 h. The dispersion was accomplished by the slow addition of water under vigorous stirring. After the acetone was removed under reduced pressure, the PUDs based on PCL-SO₃Na with about 40 wt % solid content were obtained. Scheme 3 shows a typical synthesis route of PUDs based on PCL-SO₃Na. By changing the formulation of the samples and repeating the preparation procedure, we obtained the samples PUDA, PUDB, and PUDC. The formulation of samples, the content of -SO₃Na hydrophilic groups in the PU films, the gel permeation chromatography (GPC) M_n values, and the polydispersity index (PDI) values of the PU films are summarized in Table I.

PU Film Preparation

We obtained the PU films by placing an aqueous PUD in a polytetrafluoroethylene mold (120 × 120 mm²) and allowing it to dry at room temperature for a week followed by heating at 60°C for a day.

Measurement

¹H-NMR was recorded on a 400-MHz Bruker NMR spectrometer (Avance III) in CDCl₃ or D₂O with tetramethylsilane (TMS) as the internal standard.

The molecular weight and PDI values of the samples were determined by a Waters GPC instrument (Waters Corp.) equipped linearly with two Styragel columns [Styragel HR 4 tetrahydrofuran (THF) 7.8 × 300-mm column, Styragel HR 5 THF 7.8 × 300-mm column] with a guard column, a Waters 1515 isocratic high performance liquid chromatography (HPLC)

pump, and a Waters 2414 refractive-index detector at 40°C. THF was used as the eluent at a flow rate of 1.0 mL/min, and the samples (5 mg) were dissolved in 5 mL of THF. Monodisperse polystyrene was used as the standard for calibration.

Fourier transform infrared (FTIR) spectra were obtained by the attenuated total reflectance (ATR) method on a Nicolet 5700 FTIR spectrometer. The spectra were collected at 32 scans with

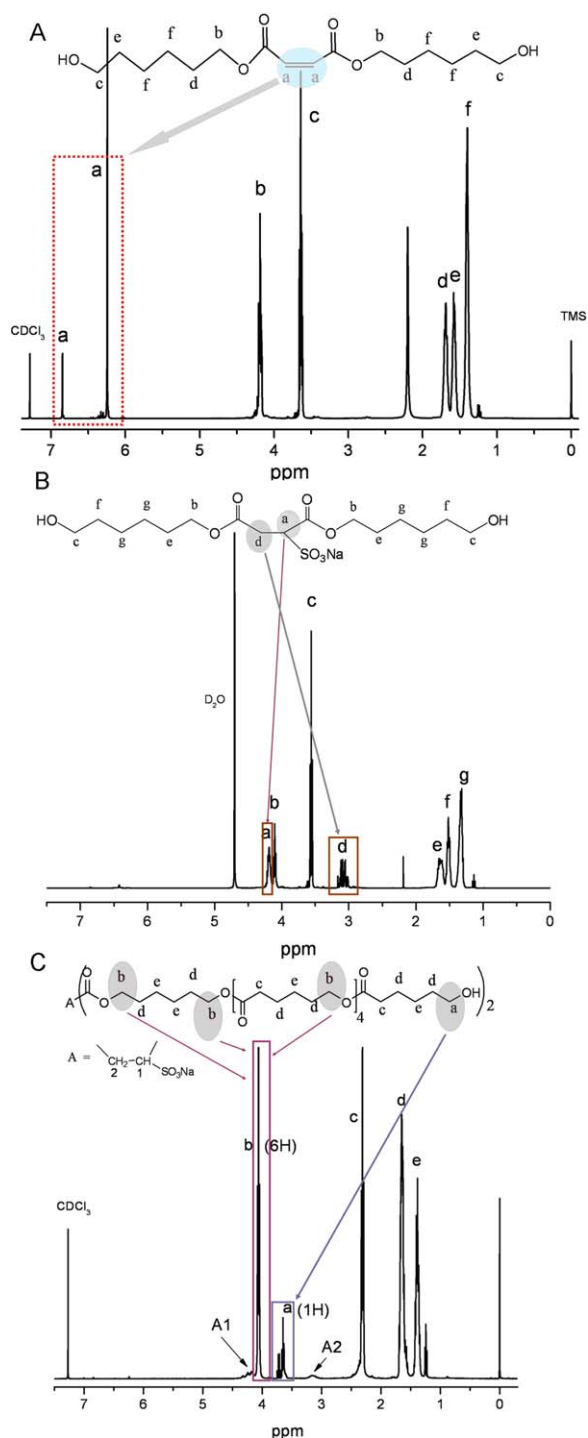


Figure 2. ¹H-NMR spectra of (A) BHMA, (B) BHMA-SO₃Na, and (C) PCL-SO₃Na. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

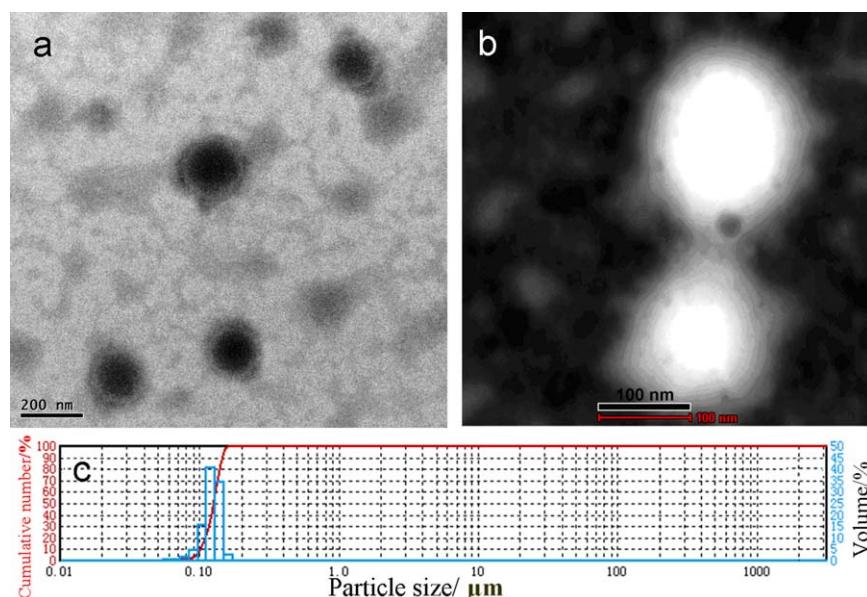


Figure 3. (a) TEM micrograph, (b) dark-field image, and (c) particle size distribution of PUDA PUDs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a spectral resolution of 2 cm^{-1} in the frequency range $600\text{--}4000\text{ cm}^{-1}$.

Differential scanning calorimetry (DSC) analysis was carried out with a Mettler DSC822e differential scanning calorimeter under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ in the range -50 to 200°C . First, the samples were heated to 200°C and maintained there for 5 min to erase all previous thermal history. Then, the samples were cooled to -50°C at a rate of $10^\circ\text{C}/\text{min}$. Finally, the samples were heated to 200°C at a rate of $10^\circ\text{C}/\text{min}$. The melting curves were recorded in the heating process. The weights of all specimens were approximately 6.0 mg.

The morphology of the particles in the dispersion was observed on a field emission transmission electron microscope (FEI Tecnai G2 F20) with a field emission gun operating at 200 kV. The dispersions were diluted to about 1 wt % and deposited onto a carbon film grid. Then, the grids were dipped into a 2 wt % aqueous phosphotungstic acid solution. After drying, the samples were characterized. Particle size analysis in the aqueous

PUD was carried out via laser particle size analysis with a Winner2308A particle sizer. The measurement was done at room temperature. A small amount of aqueous PUD was added to a deionized water tank. The instrument also had an ultrasonic probe that was used to enhance the dispersion of the sample in the detection cell. D90 was reported here to describe to volume distribution of PUD. The D90 describes the diameter where ninety percent of the distribution has a smaller particle size and ten percent has a larger particle size. The tensile properties were tested on a universal testing machine (Lloyd, United Kingdom) at a speed of $10\text{ cm}/\text{min}$, and the film samples were $70 \times 20\text{ mm}^2$ with a thickness of 1 mm.

RESULTS AND DISCUSSION

PCL- SO_3Na was prepared via the ring-opening polymerization of CL with BHMA- SO_3Na as an initiator according to ref. 43. The ϵ -caprolactone monomer was initiated in bulk by the hydroxyl

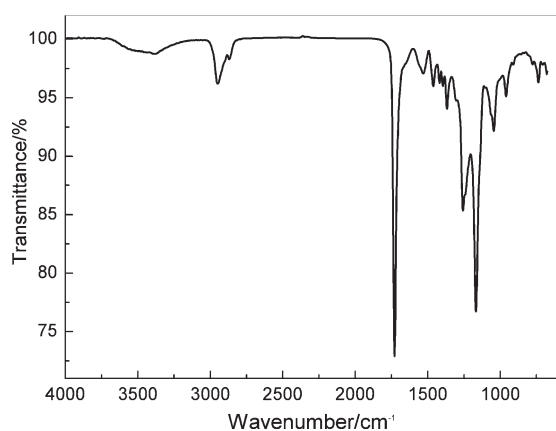


Figure 4. ATR-IR spectrum of the PUDA film.

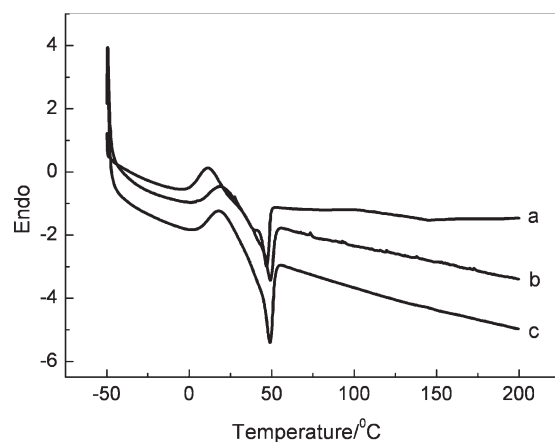


Figure 5. DSC curves of PU films with different contents of hydrophilic groups: (a) PUDA, (b) PUDB, and (c) PUDC.

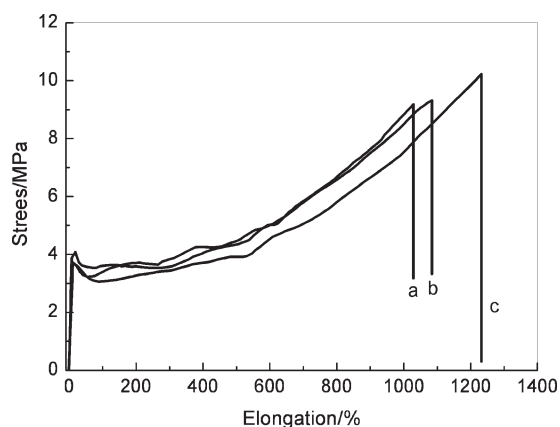


Figure 6. Stress–strain curves of PU films with different contents of hydrophilic groups: (a) PUDA, (b) PUDb, and (c) PUDc.

group of BHMA–SO₃Na, and this resulted in a bihydroxyl-terminated PCL–SO₃Na with a sodium sulfonate group.

The molecular structures of PCL–SO₃Na, BHMA–SO₃Na, and BHMA were characterized by FTIR spectroscopy, and the spectra are shown in Figure 1. Several peaks at 3056, 1650, 1410, 992, and 810 cm⁻¹, assigned to the vibrations of the –C=C– bonds of BHMA, showed great changes and disappeared in the curves of PCL–SO₃Na and BHMA–SO₃Na; this indicated that the –C=C– bonds were sulfonated. Several peaks at 1200–1000 cm⁻¹ changed greatly because of the incorporation of sodium sulfonate group. The molecular structures of PCL–SO₃Na, BHMA–SO₃Na, and BHMA were further characterized by ¹H-NMR, as shown in Figure 2. The resonance signals at 6.24 and 6.84 ppm were due to carbon–carbon double bonds (cis–trans units of MA),⁴⁴ and the presence of two multiple bands at 4.20 and 3.63 ppm in Figure 2(A) indicated the formation of diester maleate.⁴⁵ The signals of carbon–carbon double bonds disappeared in Figure 2(B), which demonstrated that the carbon–carbon double bonds were completely sulfonated. *M_n* of PCL–SO₃Na was found to be 1560 g/mol through calculation with the following equation:⁴⁶

$$DP_{CL} = 2(I_b/I_a - 2 + 1)$$

$$M_n = 114DP_{CL} + 420$$

where *I_a* and *I_b* are the intensities of the chemical shifts at a and b, respectively, in Figure 2(C); DP_{CL} is the number-average degree of polymerization of the poly(*ε*-caprolactone) blocks; 114 is the molar mass of a CL repeat unit, and 420 is the total molar mass of BHMA–SO₃Na.

The aqueous PUD was synthesized by the acetone process. The representative transmission electron microscopy (TEM) image of the PUD is shown in Figure 3. We observed that the sizes of the relatively spherical particles were in the range between 80 and 150 nm with a core–shell structure and a good particle size distribution with D₉₀ = 145 nm, where D₉₀ was the volume distribution corresponding to 90 percent of the particle size, means that 90% of particles were less than 145 nm.

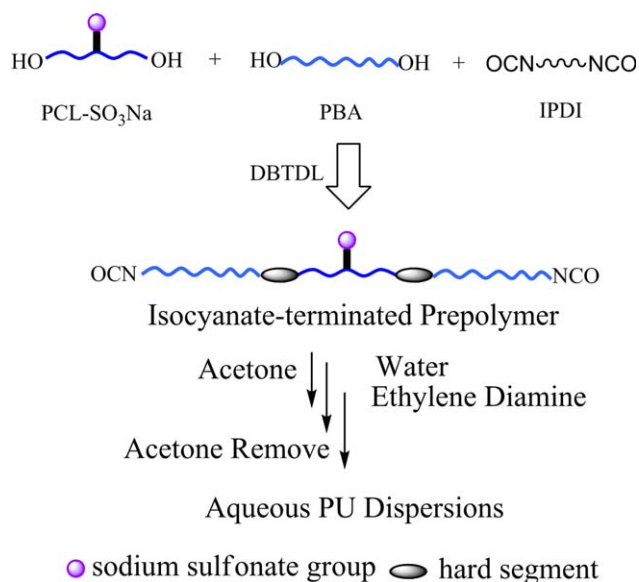
The chemistry of the derived PU films was analyzed by ATR–IR spectroscopy. The ATR–IR spectrum of the PU film is shown in

Figure 4. The most relevant IR bands were as follows: 3384 cm⁻¹ (N–H stretching, indicative of strong interactions via hydrogen bonding), 1531 cm⁻¹ (CN stretching and δNH stretching), 2949 and 2869 cm⁻¹ (alkane C–H stretching vibrations), 1729 cm⁻¹ (C=O stretching due to urethane and ester groups), 1461 cm⁻¹ (CH₂ and CH₃ deformation vibrations), 1394 and 1367 cm⁻¹ (C–N stretching), 1256 cm⁻¹ (ester C–O–C asymmetric stretching vibrations), and 1045 cm⁻¹ (ester C–O–C symmetric stretching vibrations). The sulfur–oxygen bond stretching vibration with single- and double-bond characteristics was evidenced by the bands at 910 and 1167 cm⁻¹, respectively.^{47,48} The results from the IR spectrum proved that there were strong interactions via hydrogen bonding in the PU films, which contributed to crystallization. The melting temperature of the PU films was about 47.6°C (Figure 5).

The typical stress–strain curves for the PU film are shown in Figure 6. As shown in Figure 6, the yield point could be clearly observed; this suggested that hard segments were easy to crystallize in the matrix, as the ions were on the soft segments. The curve showed linear elastic behavior in the low-stress region and plastic deformation in the high-stress region. The initial modulus, tensile strength, and elongation at break were 75.0–87.2 MPa, 9.2–10.3 MPa and 1032.8–1238.5%, respectively. The film behaved more like a rubber, exhibiting a low tensile strength and a high elongation at break.

CONCLUSIONS

We have described a novel synthesis strategy for preparing a PU ionomer with sodium sulfonate groups on the soft segments and for obtaining a stably aqueous PUD derived from this ionomer. First, PCL–SO₃Na was prepared via the ring-opening polymerization of CL with BHMA–SO₃Na as an initiator, and then, this was reacted with diisocyanate to form a PU ionomer. Finally, an aqueous PUD was synthesized by the acetone



Scheme 3. Schematic synthesis of PUD based on PCL–SO₃Na. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

process. Relatively spherical particles, with sizes about 80–150 nm and with a core–shell structure, were observed in the aqueous PUD. The chemistry of the derived PU films was confirmed by FTIR analysis. We also found that the films exhibited a low tensile strength and a high elongation at break.

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