Efficient Synthesis of Zwitterionic Sulfobetaine Group Functional Polyurethanes via "Click" Reaction

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ABSTRACT: A novel polyurethane material containing zwitterionic sulfobetaine groups has been synthesized using the copper-catalyzed 1,3-dipolar cycloaddition (azide-alkyne click chemistry). A standard two-step polyaddition method was used to produce the well-defined polyurethane based on polycarbonatediol (PCDL) with alkyne groups. These polyurethanes containing alkyne units were then efficiently clicked using 3-((2-azidoethyl)dimethylammonio)propane-1-sulfonate (DMPS-N_3). The novel PU material was characterized by ^{1}H NMR, Fourier transform infrared (FTIR) spectrometer, gel permeation chromatography (GPC), elemental analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). This facile "click" reaction provides a useful tool for the development of novel functional polyurethanes for biomedical applications. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1251–1257, 2011

Key words: polyurethane; synthesis; "click"; reaction; zwitterionic sulfobetaine; thermal properties

INTRODUCTION

The interest in biocompatible polymers for medical applications is continuously increasing. Among these different classes of polymers, polyurethane has been widely used in various biomedical applications, such as artificial hearts, vascular grafts, and pacemaker leads, due to their outstanding mechanical and chemical properties, and moderately good biocompatibility.

Over the past few years, several approaches have been used to enhance the biocompatibility of PU, including self-assembled monolayers (SAMs),[1] polymer blends,[2–4] graft polymerization,[5,6] and interpenetrating polymer networks (IPNs).[7–10] Merlin and coworkers[7] synthesized semi-interpenetrating polymer networks (semi-IPNs) using biocompatible polyurethane and acrylamide monomer. The obtained polymer networks showed good thermal stability and compatibility. Besides the change of methods, some appropriate functional groups have also been incorporated into PU to improve the blood compatibility of PU material, such as poly(ethylene glycol) (PEG),[11,12] heparin,[13–15] phospholipid polymer,[16–18] zwitterionic sulfobetaine monomer,[19–25] and so on. In the above functional groups, sulfobetaines with side groups [$-N^+(CH_2)_nSO_3^-$, $n = 3, 4$] have received increasing attention in zwitterionic materials due to their biocompatibility and facile handling and synthesis. For example, Lin and his coworkers have developed many PU films of good blood compatible by grafting the sulfobetaine onto the surface.[19–25] However, these methods usually involve multiple reaction steps. The reactivity and the grafting rate are moderate. Compared with above methods, click reaction, defined by Sharpless and coworkers,[26] offers a powerful method for the controlled manipulation of macromolecular architecture and polymer synthesis because of its quantitative yields, mild reaction condition, and tolerance of a wide range of functional groups.[27–36] Recent works by Du Prez have shown that "click" chemistry is a promising tool for side-chain functionalization of polyurethanes.[37,38]

We are interested in synthesizing blood compatible polyurethane containing zwitterionic sulfobetaine groups as potential candidate for short-term blood-contacting applications. To fulfill this purpose, alkyne-containing polyurethane based on polycarbonatediol (PCDL) and hexamethylene diisocyanate (HDI) were first prepared. Then the 3-((2-azidoethyl)dimethylammonio)propane-1-sulfonate(DMPS-N_3) monomer was grafted into the polymer via click reaction. The side-chain functional PU was characterized by ^{1}H NMR, Fourier transform infrared spectrometer (FTIR), gel permeation chromatography (GPC), and elemental analysis, thermogravimetric

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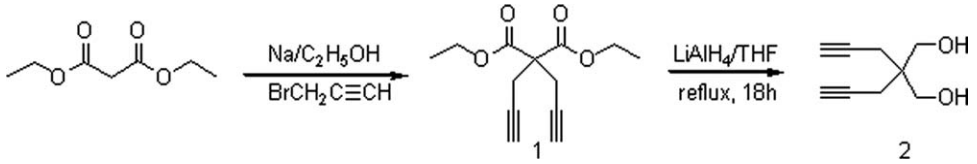


Scheme 1 Synthesis of 2,2-di(prop-2-ynyl)propane-1,3-diol (DPPD).

analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

Sodium azide, 1, 3-propane sultone, HDI, lithium aluminum hydride were purchased from Aldrich. PCDL with molecular weight 1000 Da was dried under vacuum at 60°C for 8 h to remove any absorbed water. Diethyl methylmalonate, 3-bromoprop-1-yne, sodium, and dimethylaminoethyl chloride hydrochloride were purchased from Aladdin Reagent and were used without further purified.

Characterization

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. ^{13}C NMR spectra are obtained as proton-decoupled spectra. Chemical shifts (δ) are expressed in ppm downfield to TMS at $\delta = 0$ ppm and coupling constants (J) are expressed in Hz. High resolution mass spectrometry (HRMS) data were acquired with an APEX III Fourier transform ion cyclotron resonance (FTICR) mass spectrometry.

Infrared spectra were obtained on a BRUKER TENSOR 27 spectrometer with an ATR cell. Each spectrum was an average of 32 scans recorded at a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}.

Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC using DMF as solvent and $NaNO_3$ (5.5 g/L) with a flow rare fixed as 1 mL/min and a temperature of 35°C. PMMA standards having narrow molecular weight distribution were used for calibration.

The weight percentages of C, H, N, and S of the polymers were determined using a Vario EL III elemental analyzer.

TGA experiments were carried out on powders with a TG 209F1 (NETZSCH) analyzer. The samples were heated to 700°C under nitrogen atmosphere at the heating rate of 10°C/min.

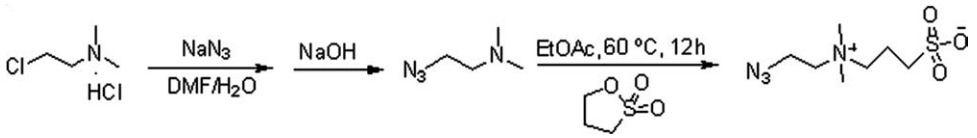
DSC thermograms from −100 to 200°C were obtained with a DSC 204F1 (NETZSCH) analyzer at a heating rate of 5°C/min under a dry nitrogen purge.

The DMA properties in tensile mode were evaluated using a DAM 242C (NETZSCH) analyzer, at a frequency of 1 Hz and a heating rate of 5°C/min. The storage (E') and loss moduli (E'') were determined as a function of temperature (from −100 up to 100°C) for rectangular films.

Synthesis of 2,2-di(prop-2-ynyl)propane-1,3-diol (DPPD) 2

DPPD was prepared according to the modified literature procedures (Scheme 1).[39,40] Diethyl malonate (54 g) was added to dry ethanol (300 mL) containing sodium ethoxide (from sodium 15.6 g). After 30 min, 3-bromoprop-1-yne (84 g) was slowly added to the suspension, and the mixture was heated under reflux for 1 h. After cooling to room temperature, the solvent was removed and H_2O was added. The crude reaction mixture was extracted with dichloromethane (3 × 50 mL). The combined organic phases were washed with 100 mL of H_2O and then dried over anhydrous $MgSO_4$. After removal of the solvent, 60 g of 2, 2-di(prop-2-ynyl)malonate(**1**) was obtained as a yellow solid. Yield: 82%. m. p.: 43°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.22 (q, 4H, CH_3CH_2O, $J = 7.6$ Hz), 2.98 (d, 4H, $CH_2C{\equiv}CH$, $J = 2.4$ Hz), 2.03 (t, 2H, $CH_2C{\equiv}CH$, $J = 2.4$ Hz), 1.26 (t'6H, CH_3CH_2O, $J = 7.6$ Hz).

To a slurry of $LiAlH_4$ (17.4 g, 0.46 mol) in tetrahydrofuran (THF; 600 mL) within a flame-dried, three-neck 1 L round-bottom flask was dropwise added **1** (29 g, 0.123 mol) as a solution in THF (150 mL) via an addition funnel. The reaction mixture was then allowed to stir under reflux for 18 h. A saturated aqueous solution of NH_4OH was added until no more H_2 gas evolved, and then dilute hydrochloric acid was added until the pH reached 7. The reaction mixture was filtered, the filter cake was washed with THF, and the filtrate was concentrated by rotary evaporation. Then, the obtained residue was dissolved in 200 mL EtOAc. The solution was washed twice with 100 mL of water and dried with anhydrous $MgSO_4$. After removal of the solvent, the solid residue was recrystallized from EtOAc. Isolated yield 13.4 g (72%). m. p.:79–80°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.74 (d, 4H, CH_2OH, $J = 4.8$ Hz), 2.44 (t, 2H, CH_2OH, $J = 4.8$ Hz), 2.37 (d, 4H, $CH_2C{\equiv}CH$, $J = 2.4$ Hz), 2.06 (t, 1H, $CH_2C{\equiv}CH$, $J = 2.4$ Hz). ^{13}C NMR (100 MHz,



Scheme 2 Procedure for the synthesis of 3-((2-azidoethyl)dimethylammonio)propane-1-sulfonate.

$CDCl_3$, ppm): δ 80.2,77.1, 66.2, 41.9, 21.6. FTIR (ATR): υ(C≡C) = 2120 cm^{-1}, υ(C≡C*H*) = 3284 cm^{-1}, υ(OH) = 3325 cm^{-1}.

Synthesis of 3-((2-azidoethyl)dimethylammonio)-propane-1-sulfonate (DMPS-N_3) 3

As shown in Scheme 2, the compound **3** was synthesized according to the following procedure: A solution of dimethylaminoethyl chloride hydrochloride (14.4 g, 100 mmol) in DMF/water (v/v: 7:3, 100 mL) was added sodium azide (10.0 g, 154 mmol) and a catalytic amount of NaI, followed by heating the mixture at 80°C for 2 days. After cooling to room temperature, the mixture was neutralized with solid Na_2CO_3. Then NaOH (pellet) was added to the above solution until pH = 11. The mixture solution was extracted with ethyl acetate (50 mL) and diethyl ether (3 × 50 mL). The combined organic phase was dried with $MgSO_4$, filtered, and the solvent was partially evaporated, slowly and carefully, under vacuum at room temperature. The residual ethyl acetate solution was added 1,3-propane sultone (24.4 g, 200 mmol) directly. And the reaction was heated overnight at 70°C. The obtained white solid was collected, washed with EtOAc and diethyl ether yield, and finally dried under vacuum to yield azide **3** as a white solid (12.2 g, 52%). ^{1}H NMR (400 MHz, D_2O, ppm): δ 3.87 (br, 2H, N_3CH_2), 3.50 (m, 4H, $CH_2N^+(CH_3)_2CH_2$), 3.09 (s, 6H, $N^+(CH_3)_2$), 2.91 (t, 2H, $CH_2CH_2SO_3^-$, *J* = 6.8 Hz),2.16 (m, 2H, $CH_2CH_2SO_3^-$). ^{13}C NMR 100 MHz, D_2O, ppm): δ 63.2, 62.1, 51.2, 47.3, 44.6, 18.2. HRMS (ESI, *m/z*) Calcd for $C_7H_{16}N_4SO_3Na$: 259.0841 $(M + Na)^+$. Found 259.0835. FTIR (ATR): υ(N_3) = 2114 cm^{-1}, υ(SO_3^-) = 1041 cm^{-1}.

Synthesis of alkyne-containing polyurethane

Alkyne-containing PU was synthesized by a standard two-step polyaddition method with molar ratios of PCDL: diisocyanate: chain extender (DPPD) of 1:2:1 (Scheme 3). In the first step, diisocyanate terminated prepolymers were made by reacting HDI with 1000 Da (molecular weight) PCDL. This reaction was run for 2 h at 80°C in a nitrogen environment. Subsequently, DPPD was added to the reaction mixture. The chain extension reaction was carried out at 70°C for an additional 12 h. The resulting polymer was precipitated in methanol. Then the polymer was filtered and washed with methanol. The polymer was dried under vacuum before characterizations.

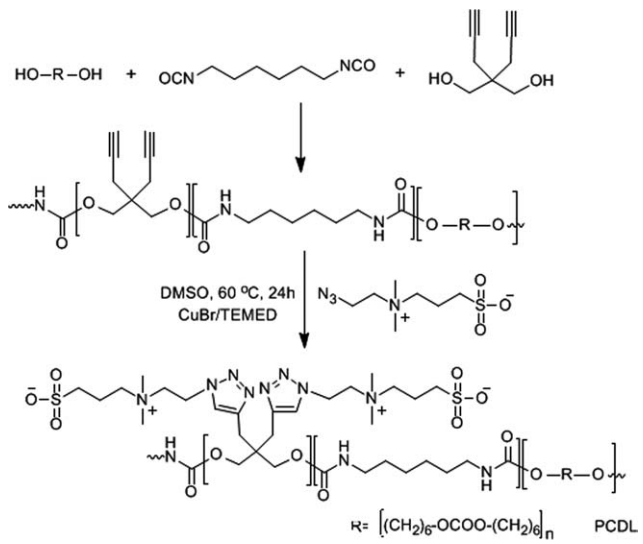
Huisgen 1, 3-dipolar cycloaddition onto polyurethane

The azide functional zwitterionic monomer, DMPS-N_3, was coupled to the alkyne groups by a copper-catalyzed azide/alkyne "click" reaction (Scheme 3). In a schlenk tube, alkyne-functionalized PU and azide compound (DMPS-N_3) were dissolved in dimethylsulfoxide (DMSO), and the copper catalyst based on CuBr/TEMED was added to this solution. The reaction was performed for 24 h under nitrogen atmosphere at 60°C. The resulting polymer was precipitated in dilute ammonia water. The obtained solid was filtered off, extensively washed with dilute ammonia water and distilled water, and finally dried under vacuum overnight before further characterizations.

RESULTS AND DISCUSSION

Synthesis of the azide compound (DMPS-N_3)

The azide compound was synthesized from the commercially available dimethylaminoethyl chloride hydrochloride. This was easily realized by nucleophilic substitution reaction using an excess of sodium azide. Then the obtained 2-azido-N,*N*-



Scheme 3 Synthesis of PU via "click" reaction.

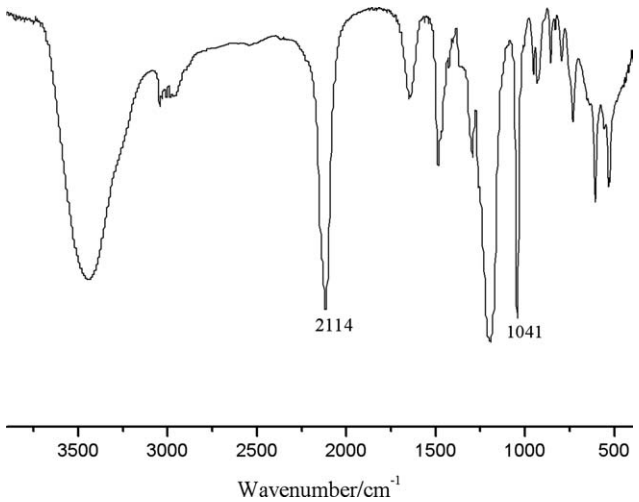


Figure 1 FTIR spectrum of DMSP-N_3.

dimethylethanamine was directly reacted with the 1,3-propane sultone in view of the explosivity of azide compound. The obtained white solid was fully characterized by NMR, FTIR, and HRMS. The FTIR spectrum of DMPS-N_3 (Fig. 1) shows the appearance of a new intense band at 2114 cm^{-1} and 1041 cm^{-1}, typical of the azide and SO_3^- group, respectively. The chemical shift at 3.09 ppm in ^1H NMR spectrum of DMPS-N_3 (Fig. 2) is assigned to the methyl proton signal of $N^+(CH_3)_2$ from the zwitterionic sulfobetaine group. The ^{13}C NMR spectrum is shown in Figure 3. These results proved that the azide compound has been prepared successfully.

Synthesis of alkyne-containing polyurethane

As seen in Scheme 3, the PU was obtained from oligomeric diol and alkyne diol monomers via a two-step polyaddition method. Figure 4(a) shows ^1H NMR spectrum of PU containing alkyne. The typical resonance of the alkyne proton appearing at 2.83 ppm proves that the alkyne diol has been incorporated in the polymer. It is evident that the peak appears at 6.96 ppm, which is assigned to the protons of —OCON*H*—.[41] The peak at 4.03 ppm is assigned to the protons of DPPD and PCDL adjacent to oxygen atom. The peaks at 1.31 and 1.56 ppm corresponding to the —$CH_2C\boldsymbol{H}_2CH_2$— protons of PCDL and HDI, the peaks at 3.34 ppm dealing with —$C\boldsymbol{H}_2O$— protons of PCDL and urethane are also observed in Figure 4(a). The alkyne-containing PU was also characterized by FTIR spectroscopy to further confirm the incorporation of the alkyne diol in the polymers. In the spectrum [Fig. 5(b)], the strong peak around 3350 cm^{-1} is ascribed to the stretching vibration of *N*—H bond in the urethane segments. The appearance of intense bands around 1700 cm^{-1} is from the carbonyl group in urethane groups. The band at 3284 cm^{-1} (C≡C—H) and the small signal at 2120 cm^{-1} (C≡C) are related to the terminal alkyne, which further proved the alkyne functional units have been incorporated into the polymer successfully during the polymerization process.

"Click" reaction onto alkyne-containing polyurethane

The initial "click" reaction of alkyne-containing PU with 3-((2-azidoethyl)dimethylammonio)propane-1-sulfonate was carried out in DMSO to maintain the solubility of PU and the zwitterionic sulfobetaine group. Figure 4 shows the overlay of the ^1H NMR spectrum of the original polymer PU and the final polymer obtained after the "click" reaction with

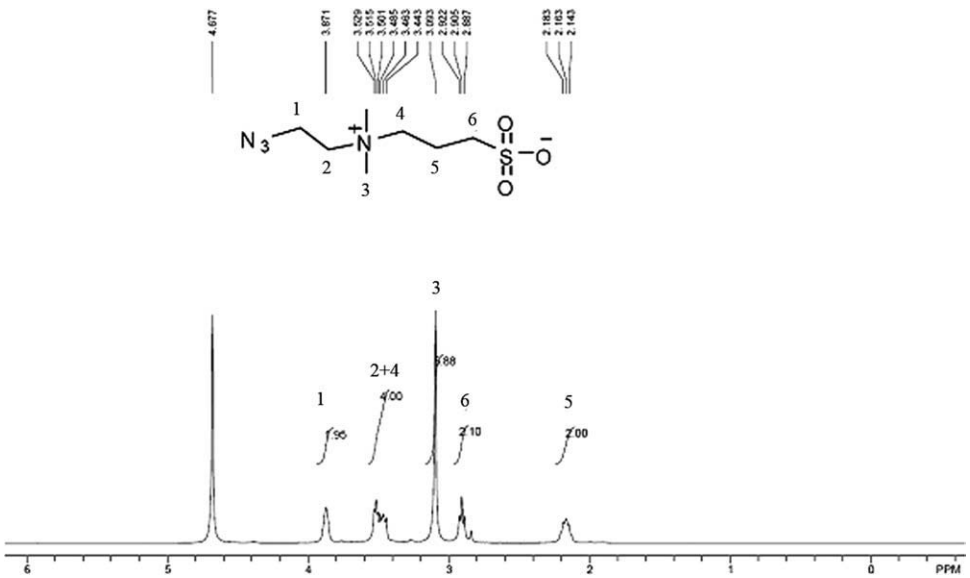


Figure 2 ^1H NMR spectrum of DMSP-N_3 in D_2O.

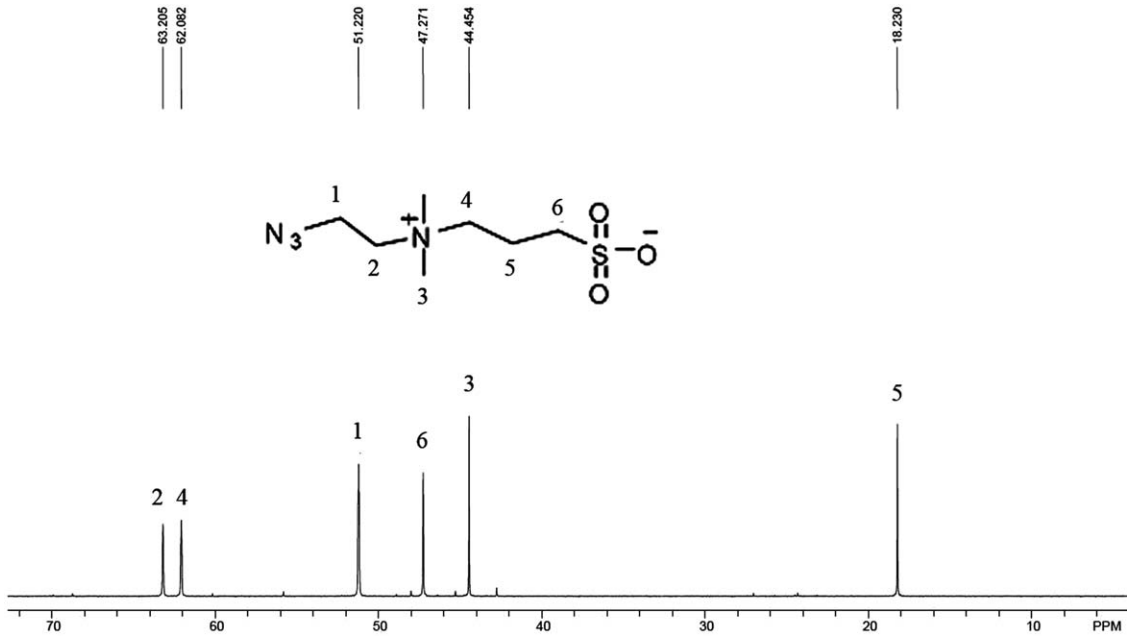


Figure 3 Proton-decoupled ^{13}C NMR spectrum of DMSP-N_3 in D_2O.

DMPS-N_3. The success of the click reaction was confirmed by the complete disappearance of the alkyne signal at 2.83 ppm [2, Fig. 4(a)] and the appearance of the proton linked to the formed triazole ring at 8.13 ppm [2′, Fig. 4(b)]. The complete disappearance of the alkyne proton at 2.83 ppm reveals that the "click" reaction was quantitative. Particularly important, a new and strong proton signal at 3.08 ppm [3, Fig. 4(b)] came from the 3-((2-azidoethyl)dimethylammonio)propane-1-sulfonate group can be seen, which means that the novel PU material containing zwitterionic sulfobetaine monomer has been successfully synthesized.

It can also be seen from Table I that the higher number-average and weight-average molecular weights were obtained after "click" reaction.

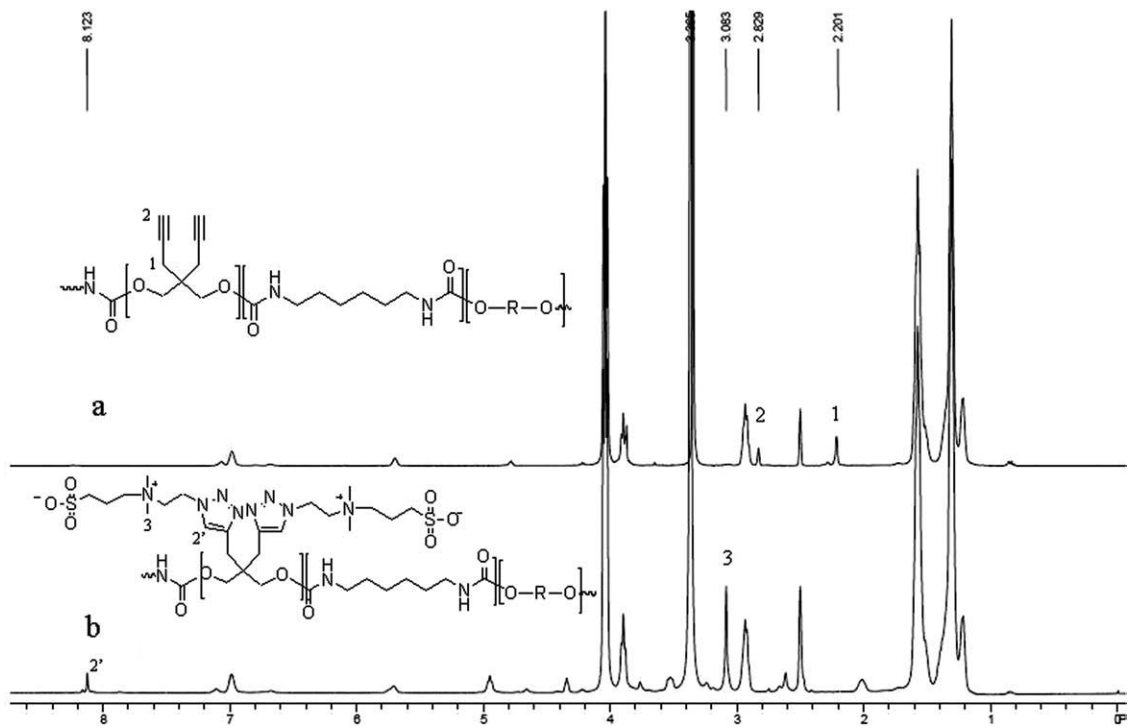


Figure 4 ^1H NMR spectra of PU containing alkyne (a) and PU containing zwitterionic sulfobetaine groups (b).

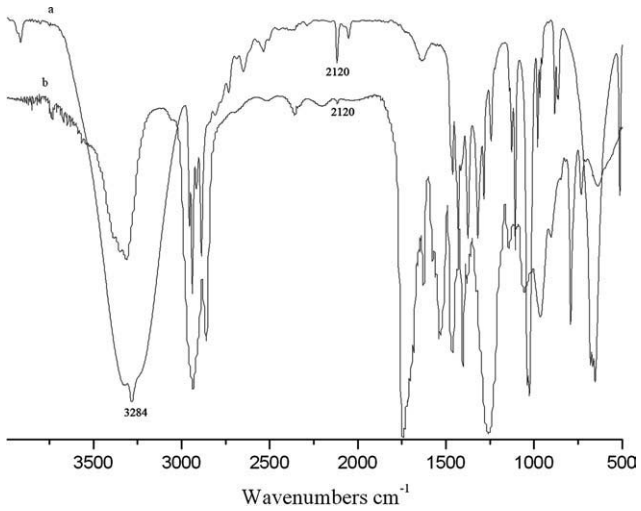


Figure 5 FTIR spectra of the alkyne diol DPPD (a) and PU containing alkyne (b).

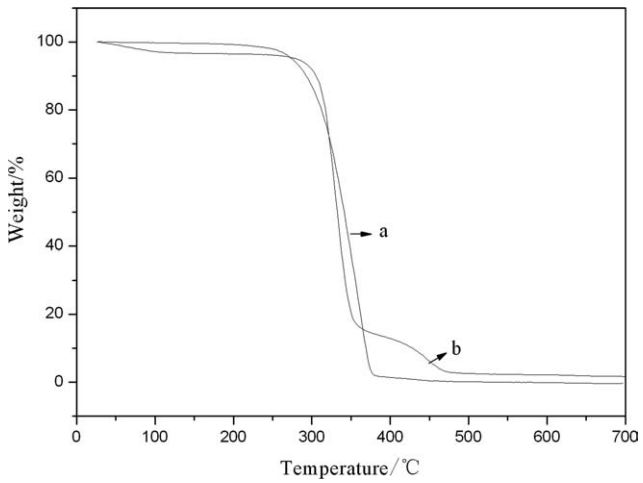


Figure 6 TG curves of the PU before (a) and after (b) "click" reaction with DMSP-N_3.

The bulk elemental analysis for PU before and after "click" reaction is given in Table II. Compositions of C, H, N, and S were obtained from elemental analysis, and O% was calculated as O% = 100% − C% − H% − N% − S%. The increasing amounts of S indicated that the zwitterionic sulfobetaine was incorporated into the backbones of the polymers.

Thermal properties

The thermal stability of PU before and after "click" reaction was examined by TG under nitrogen atmosphere. The thermogravimetric curves of PUs are shown in Figure 6. From Figure 6(a), we can observe that the degradation thermogram of PU before "click" reaction is only one degradation stage. TG analysis revealed that the PU before "click" reaction is stable up to 270°C and the maximum decomposition rate is at 345°C. Nevertheless, without further weight loss was observed when the temperature above 380°C. As shown in Figure 6(b), the curve consists of two stages. The first stage, from 275 to 372°C, is caused by the degradation of backbone of PU. The second stage, from 372 to 470°C can be responsible for the decomposition of the triazole ring in the side chain of PU.[40]

DSC thermograms of PU before and after "click" reaction are illustrated in Figure 7. In the DSC curve of the PU before "click" reaction (a), there are three transition temperatures, the fist transition temperature is the glass transition temperature (T_g) of the soft segment, the second and third transition temperatures are the melting temperatures (T_m) of the hard segment. According to the reported work,[42] the multiple hard melting endotherms are due to short-range order of the hard phase. In the DSC curve of the PU after "click" reaction (b), soft segment T_g is rarely changed and hard segment T_m is much broader and spread in a wide temperature range. We also observed that the center of the T_m moved to a higher

TABLE I
The Results of GPC

Simple	M_n	M_w	PDI	% Area
PU	17955	22077	1.23	100.00
PU-DMSP	19377	22606	1.17	100.00

TABLE II
Bulk Elemental Weight Percentages

	Elemental compositions (%)				
Simple	N	H	C	O	S
PU	3.00	7.94	58.89	30.17	–
PU-DMSP	5.48	7.78	55.45	20.90	1.39

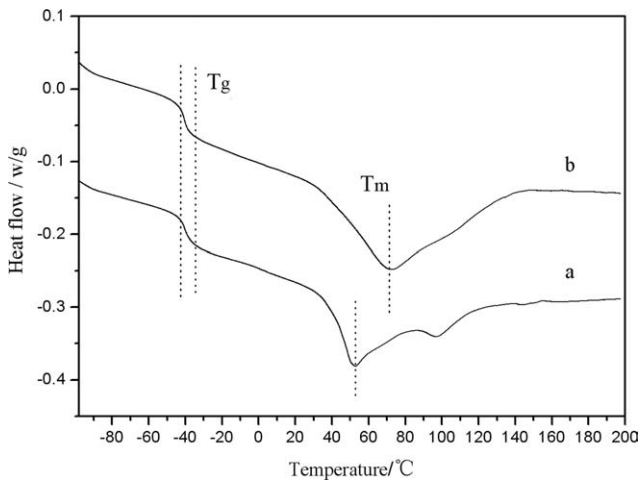


Figure 7 DSC curves of the PU before (a) and after (b) "click" reaction with DMSP-N_3.

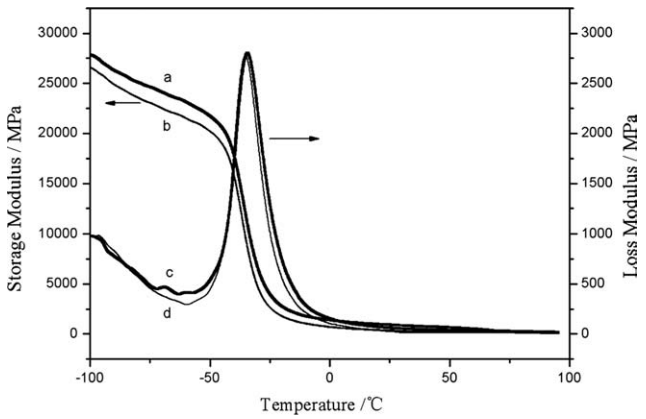


Figure 8 Storage and loss modulus versus temperature for PU before (a,c) and after (b,d) "click" reaction with DMSP-N_3.

temperature after "click" reaction, this may be the influence of the zwitterionic sulfobetaine groups.

Storage and loss modulus for the PU are displayed in Figure 8. It can be seen that the PU before "click" reaction shows higher storage modulus at any given temperature [Fig. 8(a,b)]. As seen in Figure 8(c,d), a transition can be observed in loss modulus spectra. The values of the glass transition temperature (peak points of transition) are almost the same, which are consistent with the DSC results.

CONCLUSIONS

In summary, we have described the synthesis of a new type of PU containing zwitterionic sulfobetaine groups via "click" reaction. The synthesized monomers and the resulted PU have been fully characterized by ^{1}H NMR and FTIR. Moreover, it has been proved by TG measurements that PU before and after "click" reaction shows good thermal stability. Such properties make them promising materials for biomedical applications. DSC shows the glass transition temperature of PU before and after "click" reaction is rarely changed. DMA results indicate that PU before "click" reaction shows higher storage modulus. This simple "click" reaction strategy provides a useful tool for the development of novel functional polyurethanes for biomedical applications. The expansion of this method to the novel functional polyurethanes and the research of the biomedical application on these materials are ongoing in our laboratory.

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