

Synthesis and simultaneous self-assembly of novel antibacterial polyurethanes

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Abstract. Novel physically crosslinked polyurethane (PUII) based on isophorone diisocyanates (IPDI) was prepared by a conventional two step method. The chemical structures of the PUII were characterized by fourier transform infrared (FTIR), proton nuclear magnetic resonance (¹H-NMR), gel permeation chromatography (GPC) and scanning electron microscopy (SEM). The PUII hydrogels were subjected to solvent-induced self-assembly in THF + water to construct a variety of morphologies. The self-assembly morphology of the PUII was observed by scanning electron microscopy (SEM). Different amounts (0.2%, 0.4%, 0.6%, 0.8%, 1.0%) of 1,3,5-Tris(2-hydroxyethyl)hexahydro-1,3,5-triazine (TNO) was added as antibacterial agent to the polyurethane prepolymers. The inhibiting capacity of the antibacterial films to the Escherichia coli, Staphylococcus aureus, Bacillus subtilis and Gray mold has been studied. The inhibiting capacity of films for each strain effect became obvious with the increase of content of antibacterial agent and the sensitive degree to all kind of bacterial species was different.

1. Introduction

Polyurethanes (PUs) are one of the crucial classes of polymers with wide applications and properties, because their properties can easily be tailored by varying the components from which they are constructed [1]. Polyurethanes offer excellent versatility in terms of their mechanical properties and are widely applied in many fields. In general, the synthesis of polyurethanes is carried out in two stages. The first stage is the synthesis of a prepolymer containing free isocyanate groups and in the second stage there are reactions of chain extension or crosslinking of the polymer chains. PUs are composed of hard segments and soft segments. In the hard segment of polyurethane, ethyl urethane forms hydrogen bond, which is a kind of chemical bond. Hard segment structure determines the mechanical properties of polyurethane materials. However, the morphology and mechanical properties of polyurethane materials depend largely on the structure of the soft segment [2]. Self-assembled polyurethanes (PUs) are a special class of biodegradable and biocompatible materials which are currently used in tissue engineering and drug delivery applications [3, 4]. Because of the structural characteristics of polyurethane, it can be applied to many fields: for instance, coatings, adhesives, elastomers, sealants and plastics [5].

Traditionally, PUs are compound of diisocyanate monomers such as 4, 4-diphenylmethane diisocyanate (MDI) and polyatomic alcohol such as Polytetramethylene oxide (PTMG) [6-8]. The polyurethanes obtained with these diisocyanates are easily oxidized and this causes the color change of the products. Under ultraviolet light, a urethane bond is easily damaged and ethyleniminoquinone



generates, so we always find that the color of PUs made by MDI turns yellow [9]. Compare with MDI, isophorone diisocyanates (IPDI) has excellent light stability and chemical resistance [10]. It is generally used in the manufacture of high-grade polyurethane resin.

Copolymer self-assembly behavior has been a hot research topic in recent years. By the structure or properties of different chain segments through chemical bond connected and block copolymers, microphase separation phenomenon will happen at certain conditions, and the formation of the various dimensions of nanometer or submicron structure will form. Self-assembly process and the formation of structure can be controlled by the chain segment of the chemical structure[11-13], chain length, the regulation of the connecting way [14,15], the category and function of the external force field[16,17]. In this study, a novel physically crosslinked polyurethane (PUII) by utilizing Isophorone diisocyanates was synthesized. In order to suppress interference of other substance, we synthesize PUII without dissolvent. The final products are characterized by FTIR, ¹H NMR and SEM. Finally, the assembly behavior of PUII was investigated by SEM. The biocidal activity was examined by using the inhibition zone method.

2. Experimental

2.1. Materials

IPDI (Aladdin, Shanghai) was used without further purification. Polytetramethylene oxide (PTMG, Mw2000) (Aladdin, Shanghai) was dried at 90°C in vacuum for 48 h. 1,4-Dihydroxybutane (BDO) (Chemicals, Tianjin, China) and tetrahydrofuran (THF) were used as received. 1,3,5-Tris(2-hydroxyethyl)hexahydro-1,3,5-triazine (TNO) was dewatered before use. All other reagents and solvents were used as received without further purification.

2.2. Preparation of PUII

PUII was prepared by a two-step addition polymerization. A 250 mL glass reactor equipped with a heating element, a mechanical stirrer, a charging and sampling port, and a nitrogen inlet and outlet was charged with polytetramethylene oxide 2000 (15 g, 0.0075 mol) and isophorone diisocyanates (4 g, 0.018 mol). The reaction temperature was 60-70°C, and the reaction was continuous for 3 hours at this temperature. Then small amount of 1,4-Dihydroxybutane (BDO) as chain extender were added and allowed to react for 60 min. During the experiment, the characteristic peaks of the prepolymer were observed by using FTIR analyses until the peak (2265 cm⁻¹) disappeared. The PUII was injected with water methanol mixture precipitation (v/v 1:3) and dried in a vacuum oven at 30 °C. Molecular weight: 7.9×10⁴ g/mol (Mn). IR (figure 1): 3328 cm⁻¹ (–NH), 2939 cm⁻¹ (–CH), 1707 cm⁻¹ (C=O), 1546 cm⁻¹ (–CN), 1239 cm⁻¹ (C–O–C, PUII), 1108 cm⁻¹ (C–O–C, PTMG). ¹H NMR (The spectrum was taken in CDCl₃, figure 2): δ=0.96-0.98 ppm (d, e, f, CH₃, IPDI), 1.62-1.63 ppm (b, CH₂, PTMG), 3.06 ppm (g, CH₂, IPDI), 3.40-3.41 ppm (c, CH₂O, PTMG), 4.06-4.07 ppm (a, OCH₂, PTMG), 7.29 ppm (h, NH, PUII).

2.3. Preparation of PUII with antibacterial agent

Different amounts(0.2%, 0.4%, 0.6%, 0.8%, 1.0%) of 1,3,5-Tris(2-hydroxyethyl)hexahydro-1,3,5-triazine (TNO) was added as antibacterial agent to the polyurethane prepolymers after BDO was superinduced and allowed to react for 60 min.

2.4. Characterization

IR spectra were recorded with a BRUKER-VECTOR22 FT-IR spectrophotometer using KBr disks. Nuclear magnetic resonance (¹H NMR) spectra were recorded in CDCl₃ on a Bruker AVANCE III 400 MHz apparatus. By gel permeation chromatography (GPC) method for the determination of molecular weight and its distribution of polymer using water 515 pump and the 2410 type showed differential refractometer polystyrene gel column HT2, HT3, and 4 are connected in a serial way. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards with dispersity of 1.08-1.12

obtained from water were employed to calibrate the instrument. Scanning electron microscopy (SEM) measurements were done on a JEOL JSM-5600 LV SEM. The samples were fabricated by dropping one blob of the mixed solution of PUII, THF and water onto a glass patch, and then evaporated for 48 h under ambient temperature. Finally, the samples were coated with gold and observed by SEM.

3. Results and discussion

3.1. Synthesis of PUII

Novel physically crosslinked polyurethane (PUII) based on isophorone diisocyanates was prepared by a conventional two step method. The chemical structure of the final polymer (PUII) was characterized with FTIR in KBr matrices. The FT-IR spectra of PUII are shown in figure 1. As shown in figure 1, the peaks at 3328 cm^{-1} ($-\text{NH}$), 2939 cm^{-1} ($-\text{CH}$), 1707 cm^{-1} ($\text{C}=\text{O}$), 1546 cm^{-1} ($-\text{CN}$), 1239 cm^{-1} ($\text{C}-\text{O}-\text{C}$, PUII), 1108 cm^{-1} ($\text{C}-\text{O}-\text{C}$, PTMG) are observed, which demonstrate the synthesis is successful.

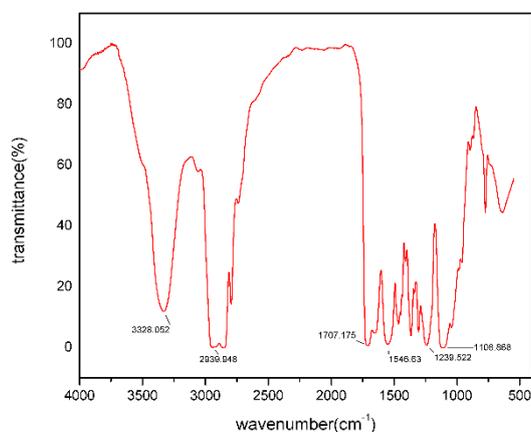


Figure 1. FTIR spectrum of the PUII.

^1H NMR spectrum of the PUII was shown in figure 2. In the ^1H NMR spectrum of PUII (figure 2), peak corresponding to the OCH_2 (a) of the PTMG, was observed at 4.06-4.07 ppm. The peak related to the CH_2 (b) of PTMG appeared between 1.62 and 1.63 ppm. Other peaks were listed as follows: 3.40-3.41 ppm (c, CH_2O , PTMG), 0.96-0.98 ppm (d, e, f, CH_3 , IPDI), 3.06 ppm (g, CH_2 , IPDI), 7.29 ppm (h, NH , PUII). This confirms the successful incorporation of IPDI to the polyurethane backbone.

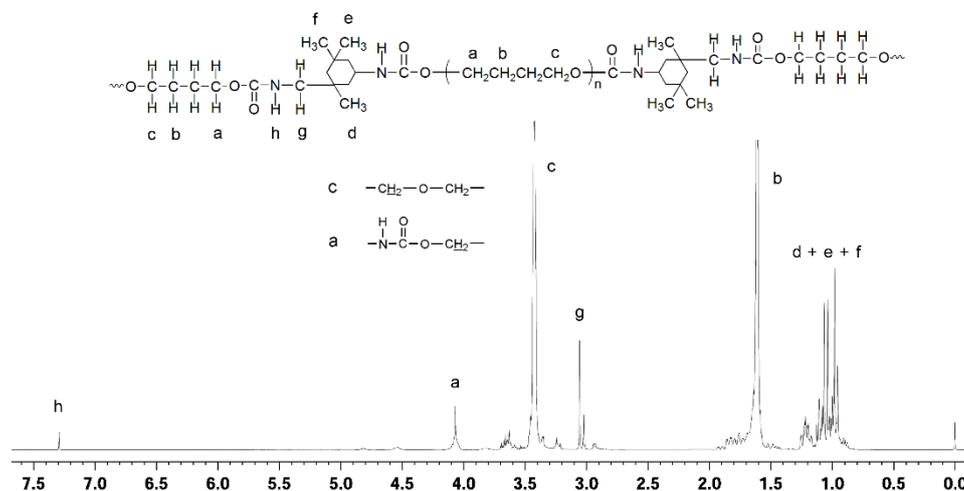


Figure 2. ^1H NMR spectrum of the PUII.

GPC results indicate that the materials do not contain oligomers, and the PUII has molecular weight distributions (weight-average molecular weight of 72,000-79,000 and polydispersity of 1-2).

3.2. Self-assembly behavior of PUII

The self-assembly behavior of PUII was investigated by dissolving in the mixed solution of THF and water. Six samples (THF: water=90: 10/ 80: 20/ 70: 30/ 60: 40/ 50: 50/ 40: 60, v/v, corresponding serial number: 1-6) were prepared for SEM measurement. The samples were fabricated by dropping one blob of the mixed solution of PUII, THF and water onto a glass patch, and then evaporated for 48 h under ambient temperature. Finally, the samples were coated with gold and observed by SEM.

As shown in figure 3, (a)-(d), the SEM images of samples demonstrate that the polymer creates irregular globular morphologies. The average particle diameter was calculated by SEM images and the sizes range from 1 μ m to 7 μ m. The samples of number 6 and 1 (THF: water= 40: 60/ 90: 10) are correspondingly shown in figure 3(a) and figure 3(c). Figure 3(b) and figure 3(d) respectively reveal particulars of number 6 and 1. The space between irregular globular morphologies is gradually diminished when the quantity of water increases. So water quantity plays an important role in the self-assembly behavior. In this study, number 5 (THF: water= 50: 50) is critical value. When the ratio of THF/water is over this point, the aggregation becomes uncontrollable. By using scanning electron microscope techniques confirmed the good reproducibility of the microscopic material with solvent induced in the assembly process.

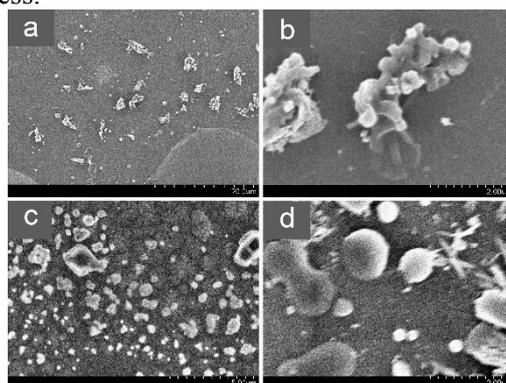


Figure 3. SEM images of PUII self-assembly behavior.

3.3. Antimicrobial properties

The inhibition zone method was employed. The PUII films with different amounts (0.2%, 0.4%, 0.6%, 0.8%, 1.0%) of 1,3,5-Tris (2-hydroxyethyl) hexahydro-1,3,5-triazine (TNO) were challenged with *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* and Gray mold. As shown in Table 1. The results showed that when a small amount of antibacterial agent were added, the antibacterial effect of films on Gray mold was more obvious. When more antibacterial agent was added, the films showed better inhibitory effect on *Staphylococcus aureus* and *Escherichia coli*. In addition, the inhibitory effect on the *Bacillus subtilis* was not effective.

Table 1. The antibacterial circle diameter of different samples.

The content of antibacterial agent /%	The antibacterial circle diameter /mm			
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	Gray mold
0	0	0	0	0
0.2	14.1	10.2	10.3	17.8
0.4	18.1	11.7	11.9	18.5
0.6	19.3	18.3	13.8	19.1
0.8	20.9	21.9	15.5	19.9
1.0	23.2	22.1	17.1	22.2

4. Conclusions

In this work, a novel polyurethane (PUII) based on isophorone diisocyanates was synthesized with no dissolvent and characterized by FTIR, ¹H NMR, GPC and SEM.

The self-assembly behavior of PUII also has been tested, and the results showed that the micron materials created irregular globular morphologies.

Antimicrobial property of the films contained antibacterial agent against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* and Gray mold was examined and showed different antibacterial properties.

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