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Formation of linear and crosslinked polyurethane nanoparticles that self-assemble differently in acetone and in water

Magdalena Serkis-Rodzeń[a,*], Milena Špírková[a,*], Pavel Matějíček[b], Miroslav Štěpánek[b]

[a] Nanostructured Polymers and Composites Department, Institute of Macromolecular Chemistry AS CR, Prague, Czechia
[b] Department of Physical and Macromolecular Chemistry, Charles University in Prague, Czechia

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ABSTRACT

For the first time, stable water-borne polyurethane dispersions (PUDs) leading to mechanically strong polyurethane (PU) coatings were prepared without any chain extender. Elimination of this step and using of water-crosslinking gives promising applications of PUDs as biomaterials and production on an industrial scale. The PU system consists of polycarbonate macrodiol (PCD), (2,2-bis(hydroxymethyl)) propionic acid (DMPA), 1,6-diisocyanatohexane (HDI) and *N*,*N*-diethylethanamine (TEA). Fourier transform infrared spectroscopy (FTIR), dynamic mechanical thermal analysis (DMTA), static light scattering (SLS), dynamic light scattering (DLS) and atomic force microscopy (AFM) enabled the study of the assembly of the PU chains/nanoparticles into supramolecular structures in acetone and in water. In acetone, the self-assembly of isocyanate-terminated pre-polymer chains occurs in the form of either PU solutions (linear PUs) or PU dispersions (crosslinked PUs). Due to a phase inversion, spherical linear or water-crosslinked PU dispersions are formed after water addition. The isocyanate-to-total hydroxyl ratio is very important; a slight isocyanate (NCO) excess of 1.05 leads to linear rod-like nanoparticles in acetone followed by a core-shell structure after water addition. An isocyanate excess of 1.5 leads to compact sphere or micro-gel particles initially crosslinked by moisture in acetone, and the final crosslinking and phase inversion occurs after water addition. The chain lengths of the linear PUs and the mesh sizes in PU networks increase with the PCD:DMPA ratio. Thus, the design of PU nanoparticles with desired sizes, shapes and crosslink densities is possible. Unlike the substantially different shapes, sizes and compactness of PUs in acetone, all PUDs in water are spherical nanoparticles with an average diameter from 21 to 72 nm, a zeta potential from −40 to −65 mV and a size-dispersity index from 0.05 to 0.22.

1. Introduction

In recent years, polyurethane water dispersions (PUDs) have been extensively used to replace conventional polyurethanes (PUs) to eliminate the emission of organic solvents to the atmosphere. PUDs have found application as environmentally friendly coatings and adhesives in industrial and biomedical applications due to their excellent mechanical and chemical properties and good biocompatibility [1–4].

Different polyols can be used to prepare PUDs. Among them, polycarbonate diols (PCDs) represent a relatively new class. In comparison to polyester- or polyether-based PUDs, they are biocompatible biomaterials with better hydrolytic, thermal and mechanical resistance [1,5,6].

In addition to PCDs, which build so-called soft segments, other components are used in the synthesis of PUDs. The so-called hard segments are composed of isocyanate and low-molecular-weight chain extenders and enhances mechanical properties of the final PUs. Moreover, the incorporation of dihydroxylic acids provides dispersity of PU chains in water due to the presence of ionic groups. The most widely used is 2,2-bis(hydroxymethyl)propionic acid (DMPA), which acts not only as an internal emulsifier but also as a chain extender[6–8].

Among PUDs based on PCDs, mostly diamines and diols are used as chain extenders. García-Pacios et al. applied diethyleneglycol as a short diol and monohydrated hydrazine as a chain extender [1,2,5,7], while Cakić et al. [3,6], Liu et al. [9] and Lee et al. [10,11] used ethylene diamine. The disadvantages of amines are their unpleasant odors and toxicity. To minimize the toxic influence of the chain extenders, butane-1,4-diol (BD) was used in our

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* Corresponding authors.
E-mail addresses: serkis@imc.cas.cz (M. Serkis-Rodzeń), spirkova@imc.cas.cz (M. Špírková).

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previous work [12–14] and by Fang et al. [15] Even though BD is safer than amines, it has a pronounced effect on the central nervous system [16].

To expand the application of PUDs as medical biomaterials, such as scaffolds for skin regrowth [17], in this work, we fully eliminated the chain extension step (see, e.g., Fig. 1, line 3, in Ref. [12]). This approach enabled the acquisition of materials with reduced toxicity, manufacturing cost and energy consumption. To the best of our knowledge, this is the first study describing novel stable PUDs based on PCDs without using any chain extender based on a short diamine or diol.

Due to incompatibility between the hard and soft segments in PUs, phase separation occurs and leads to various morphologies [18,19]. Therefore, PUDs can self-assemble and create different microstructures. Understanding the process of nanoparticle formation would be helpful for modification of the dispersions and improvement of their properties [20,21]. Although several studies describe the assembly of PUDs, they are mostly focused on already-reacted particles dispersed in water [20,22] or PU film formations [23]. There is only one publication that reports the self-organization of PU nanoparticles in the pre-polymerization stage [21]. However, despite the PUs being prepared without a chain extender, the paper reports an SCF simulation study describing nanoparticles already dispersed in water.

This article describes experimental research focused on the formation of PU nanoparticles in the initial pre-polymerization stage in acetone followed by the dispersion step (phase inversion) in water. The course of the two-step polymerization was monitored by infrared spectroscopy. We report on the self-assembly behavior of PU nanoparticles using AFM and light scattering methods. Here, we also compare the effect of water-crosslinking and the molar ratio of the reagents on the particle morphology and properties.

2. Experimental section

2.1. Materials

Commercial aliphatic PCD, trademark T4672, with a molecular weight M_w ~2770 g mol^{-1} (detected by GPC) was kindly provided by Asahi Kasei Chemical Corporation, Tokyo, Japan. DMPA, 1,6-diisocyanatohexane (HDI) and *N*,*N*-diethylethanamine (TEA) were received from Sigma-Aldrich. Dried acetone (max. 0.0075 wt% H_2O) was obtained from Merck KGaA, Darmstadt, Germany. Dibutyltin dilaurate (DBTDL, Sigma-Aldrich), 10 wt% solution in Marcol oil, was used as the catalyst.

2.2. Preparation procedure

PUDs were prepared via an acetone process without the chain extension step using varying PCD:DMPA molar ratios to control the amount of the soft and hard segments. The ratio $[NCO]:[OH]_{total}$ ($[OH]_{total} = [OH]_{PCD} + [OH]_{DMPA}$) was set either at 1.05 to obtain linear PUs or at 1.5 for water crosslinked PUs. The sample codes describe the type and molar ratio of the used components and are marked as PUx/y:z for nanoparticles dissolved/dispersed in acetone and PUDx/y:z for the polyurethane water dispersions. In these names, x indicates the ratio $[NCO]:[OH]_{total}$, whereas y:z is the PCD:DMPA molar ratio. For example, the sample PU1.5/1:2 is the acetone dispersion of nanoparticles containing a 1.5-fold excess of NCO groups with a PCD:DMPA ratio equal to 1:2, and PUD1.5/1:2 is the sample of identical composition dispersed in water. The preparation procedure of the PUDs and the possibility of water-crosslinking are given in Fig. 1, and the wt% of the components used for all samples is summarized in Table S1.

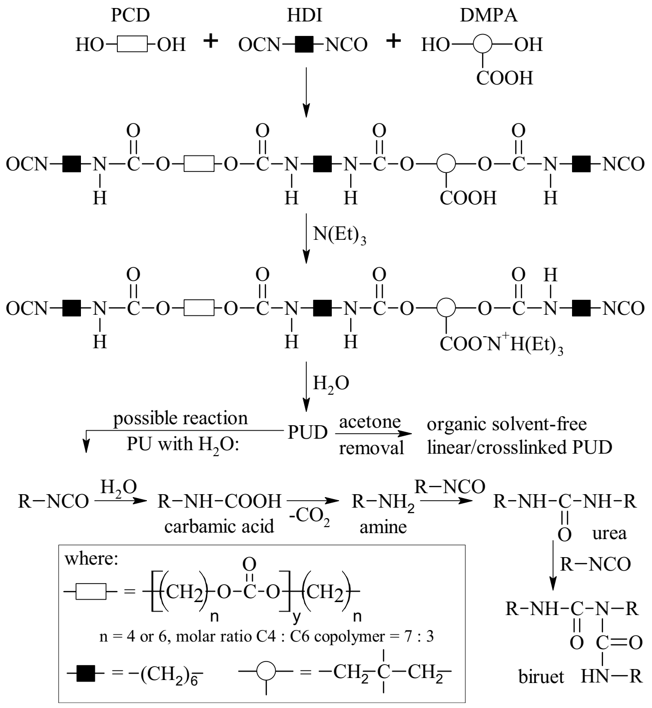

Fig. 1. Synthesis scheme of PUDs and possible reaction of PU with H_2O.

PCD, DMPA, HDI, the catalyst (0.05 mol of DBTDL per mol of NCO groups) and acetone were placed into a round bottom flask and mixed at a rate of 700 rpm at 60 °C for 4 h until a constant NCO content was reached. Then, TEA was added to fully neutralize the carboxylic groups and mixed for 30 min at 55 °C followed by the gradual addition of water. The latter step involves not only the phase inversion but also the reaction of water with unreacted NCO groups, if present. Organic solvent-free PUDs were obtained after acetone removal using a rotavap under reduced pressure.

2.3. Characterization techniques

Fourier transform infrared spectroscopy (FTIR) was used to monitor the isocyanate, urethane, urea and biuret bond formations in the PU nanoparticles. The FTIR spectra were obtained using a PerkinElmer Spectrum 100 spectrometer equipped with a universal ATR accessory with a diamond crystal.

Light scattering measurements of acetone solutions at the reaction step before water addition were carried out using an ALV instrument (ALV, Langen, Germany) consisting of a 633 nm He-Ne laser source, an ALV CGS/8F goniometer, an ALV High QE APD detector and an ALV 5000/EPP multibit, multitau autocorrelator. The refractive index increments, d n/d c, were measured using an Optilab T-rEX refractive index detector (Wyatt Technology Corporation) connected to a Cole-Parmer syringe pump at 0.123 for PU dispersions in acetone. Static light scattering (SLS) results were treated by the Berry method. Dynamic light scattering (DLS) data were evaluated by fitting the obtained normalized autocorrelation functions of the scattered light intensity to the second-order cumulant expansion and treated as dynamic Zimm plots. Details of the LS data analysis are given in the Supplementary results (equation S1).

Electrophoretic light scattering (ELS) measurements were used to determine the ζ-potentials of water PUDs from their electrophoretic mobilities using the Smoluchowski approximation. For this purpose, a Nano-ZS zetasizer (Malvern Instruments, UK) was