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Preparation of uniform and porous polyurea microspheres of large size through interfacial polymerization of toluene diisocyanate in water solution of ethylene diamine

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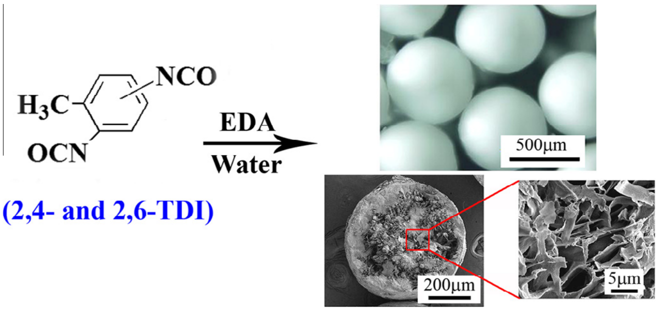
HIGHLIGHTS

- Highly uniform polyurea (PU) microspheres of size from 400 μm to 750 μm are prepared.
- The process is done by adding toluene diisocyanate (TDI) to a diamine H_2O solution.
- The uniformity is achieved with pore size ⩾210 μm of the needle for TDI addition.
- The PU microspheres consist of a coarse shell and a core with macroporous structure.

GRAPHICAL ABSTRACT

Large, macroporous and highly monodisperse polyurea microspheres of size about 750 μm are prepared through interfacial polymerization by drop-wise addition of toluene diisocyanate into aqueous solution of ethylene diamine.



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ABSTRACT

Uniform and porous polyurea (PU) microspheres of large size, with the diameter between 400 μm and 750 μm, are prepared through interface polymerization by drop-wise addition of toluene diisocyanate (TDI) to an aqueous solution of ethylene diamine (EDA). TDI addition is done through a needle with pore size of 60 μm or larger at constant rate associated with the needle pore size. Effects of the needle pore size for TDI addition, EDA concentration in water and polymerization temperature on the formation of the PU spheres are studied. Results indicate that PU spheres are obtained with varied needle pore size. However, highly uniform PU spheres are achieved only with the needle pore size of 180 μm or larger. In order to get uniform microspheres, polymerization should be carried out at 60–65 °C with EDA/TDI molar ratio kept at 2/21–4/21. Out of these limits, the uniformity of the polymer spheres is deteriorated. Morphology of the microspheres is examined under scanning electron microscope, which shows that the microspheres are consisting of a coarse shell and a core with macroporous structure. The mechanism of the polymerization and PU sphere formation are discussed.

1. Introduction

Uniform polymer microspheres have been widely used in a number of advanced technology fields such as crystal display, enzymes immobilization, photonic crystals [1], colloidosomes

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fabrication [2,3], drug delivery etc [4–6]. Conventional methods for their preparation include suspension, dispersion and emulsion polymerizations as well as Shirasu porous glass membrane emulsification with a post polymerization [7]. A common problem in these processes is the need for surfactants or stabilizers, which are unpleasant in many applications, particularly in biological and medical fields. Precipitation polymerization provided an alternative [8–12]. Through step-polymerization of diisocyanate with the in-situ produced amines by its reaction with water, significant advancement has been made, where highly uniform polyurea (PU) microspheres were fabricated with high yields [10,11].

Up to date, the size of the uniform microspheres produced through precipitation polymerization of diisocyanates has been limited to a dozen of microns [10–15]. In this paper, a novel process, based on the same reactions of diisocyanate, is presented, which is involved with an interface polymerization of toluene diisocyanate droplets in an aqueous solution of ethylene diamine. Highly uniform PU microspheres of very large diameter (from 400 μm to 750 μm) are obtained through this process without need for any surfactant and protective agents. In addition, the microspheres are rich of amine groups and also possess porous structure, which may be useful for different applications, such as enzyme immobilization, catalysis reactor, adsorption and removal of dyes and metal ions.

2. Experimental

2.1. Materials

All chemicals are China domestic products. Toluene diisocyanate (TDI, a mixture of 2,6- (20%) and 2,4-isomers, industrial grade), was from Beijing Keju Chemicals Ltd. Acetone (AP grade) was purchased from Laiyang Fine Chemicals, Shandong. Ethylene diamine (EDA, AP grade) was from Fuyu Fine Chemicals, Tianjin. Potassium bromide (KBr, AP grade) was from Kemiou Chemical Reagent Co., Tianjin. All water used was double-distilled. Deuterated dimethyl sulfoxide (DMSO-d_6, 99.9%) was from Sigma-Aldrich.

2.2. Preparation of large and uniform microspheres

For a typical process, 400 g of water was first added into a three-necked glass reactor with flat bottom, followed by addition of 0.3 g (4.99 mmol) of EDA. The content was rapidly heated to 65 °C, and 6.10 mL (35.02 mmol) of TDI was added drop-wise at a rate of 130 mL/h through a needle with pore size of 260 μm with help of a pump. Special care was taken with TDI addition that the tip of the needle must be placed underneath of the surface of the EDA aqueous solution, to assure that TDI droplets do not lash on the aqueous surface, so that to keep them in spherical shape. At the same time, the glass reactor was installed onto a mobile plate-rotor which allows the glass reactor to horizontally rotate to avoid TDI droplets stacking up and to protect them from eventual aggregation. The reaction was allowed for a supplementary 5 h up completion of TDI addition. The sample microspheres were then separated, rinsed 3 times using acetone, and dried up in a vacuum oven at 70 °C to constant weight (about 6 h). Similar runs were also carried out by varying the pore size of the needle, the rate for TDI addition and the temperature of polymerization etc.

2.3. Determination of TDI amount converted to polyurea

The reaction in this process seems very simple: TDI reacts with EDA to form polyurea (PU). Or it reacts with water to yield toluene diamine in a first step with release of carbon dioxide, the in-situ formed toluene diamine reacts with TDI to form PU as depicted in Fig. 1.

However, to determine the exact conversion of TDI from the PU yield is quite difficult because the relative amount of TDI reacted with EDA to that reacted with water is unknown, and the compositions of the PUs formed are also different. To have an estimate for TDI converted to PU, wet product at end of the polymerization (which contained PU, unreacted TDI and adsorbed water) was weighed (m_1) after careful separation. This wet sample was dried up to constant weight (m_2) at 120 °C under vacuum (4 h). The weight loss ($m_1 - m_2$) was obtained, which was considered as the total weight of unreacted TDI and absorbed water in the wet sample. The dried sample (m_2) was immersed in water at the same temperature for a same time period as for the polymerization to get the dried sample with full water absorbed as that prior to drying up, and the sample after this water absorption was weighed again (m_3). Water amount absorbed in the wet sample was therefore obtained as ($m_3 - m_2$); and unreacted TDI was deducted as ($m_1 - m_3$). Taking TDI amount charged (M), its reacted amount, i.e. equivalent to TDI conversion though not the same as conventionally defined, was obtained:

$$\text{Reacted TDI} = \frac{M - (m_1 - m_3)}{M} \times 100\%$$

Alternatively, a parallel polymerization was carried out, in which exactly the same amounts of water and EDA as in the microsphere preparation were mixed up to make a solution, and the same amount of TDI was pumped in under vigorous stirring to avoid formation of any PU particles. The system was allowed to polymerize at 65 °C for 6 h to assure all TDI and EDA being fully reacted at end of the process. Solid polymer was collected by filtration at end of the polymerization and dried up to constant weight (denoted as m_a) at 120 °C under vacuum. This dry product was taken as the PU yield (100%) with all TDI fully reacted. In each run for microsphere preparation, the samples were collected and processed the same way, with the finally dried polymer denoted as m_i. Compared with the PU amount obtained in the parallel polymerization (100% converted, m_a), the percentage of PU thus obtained for each run (m_i/m_a) was considered as the amount of

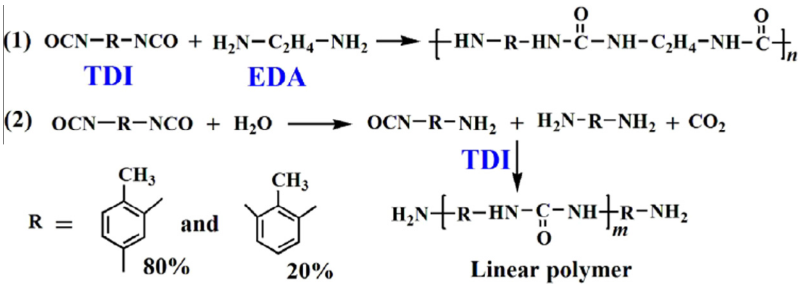

Fig. 1. Chemical reactions in the polymerization of toluene diisocyanate (TDI) in aqueous solution of ethylene diamine (EDA).