Dyes and Pigments 142 (2017) 371–378

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Iridescent structural colors from self-assembled polymer opal of polythiourethane microspheres

Feihu Li, Bingtao Tang*, Shufen Zhang

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116024, PR China

ARTICLE INFO

Article history:
Received 8 February 2017
Received in revised form
21 March 2017
Accepted 28 March 2017
Available online 31 March 2017

Keywords:
Structural colors
Artificial opal
Polythiourethane
Phase separation
Polymer microspheres

ABSTRACT

Artificial structural color materials from self-assembled colloidal spheres, which are similar to natural opals, are currently a subject of extensive investigation. However, the shortage of available colloidal spheres, especially polymer spheres for building artificial opals is still a major restriction for their practical application. Herein, a new kind of artificial opals with iridescent structural colors were prepared from the self-assembly of novel polythiourethane microspheres (PTUMS). The PTUMS with narrow size distribution were prepared through a simple phase separation process. Particle sizes can be easily adjusted from 175 nm to 304 nm, which is important for the construction of tunable structural colors. Sufficient surface charges were obtained from the reaction between the terminal isocyanate groups and water. Thus, PTUMS can arranged into periodic opal structures through self-assembly process and generate iridescent structural colors. The present study provided an effective and convenient approach to prepare artificial structural color materials from new kind of polymer microspheres. This was very important for the practical application of artificial opals in coating and paints.

1. Introduction

Natural opal has long been sought due to its pure and intense color, which is often referred as structural color [1–5]. The structural colors are generated from the interaction of visible light with periodic micro/nanostructures in opals [5–8]. Owing to their unique characteristics, such as eye-catching, non-photobleachable and energy-saving [9,10], the artificial opals with iridescent structural colors have long been extensively studied and proposed as active component of full color displays, anti-counterfeiting and imaging technology, printing and painting, textile industry, and photonic devices [11–21].

The artificial colloidal crystal films [22,23] are generally fabricated through vertical deposition method [24–27], "lifting" method [28–30], and spin coating [23,31,32]. As another important kind of colloidal crystal structure, spherical colloidal crystals were generated by solvent evaporation-induced crystallization, in situ polymerization of ordered crystallization arrays, template replication and microfluidics technology [33–35]. The key factor of colloidal assembly for constructing artificial structural color opals is to prepare colloidal spheres with good morphology regularity, high zeta potential (sufficient surface charge) and considerable monodispersity. However, to date, only several kinds of microspheres, such as polystyrene (PS) [36–38], polymethylmethacrylate (PMMA) [39,40], resorcinol/formaldehyde (RF) [41], and SiO_2 [42] can meet the above requirements and are used to construct structural color opals. The shortage of available colloidal spheres, especially polymer spheres for building artificial opals is still a major restriction for their practical application. Thus, it is urgently necessary to synthesis new colloidal spheres with unique properties for the construction of artificial opals.

Polythiourethane (PTU), which is an important class of the polyurethane (PU) family, possesses good biocompatibility and excellent optical and mechanical properties [43,44]. For example, the incorporation of sulfur into the PTU polymer chain can remarkably improve optical properties, flexibility, and crystallinity than conventional PU materials [44,45]. Thus, PTU is an ideal candidate material for the preparation of polymer microspheres. The design and synthesis of PTU colloidal spheres with specific properties through phase separation process would open new opportunities for the preparation of artificial opals with desired structural colors.

In the present study, we demonstrated the preparation of novel polythiourethane microspheres (PTUMS) through a simple phase

* Corresponding author.
E-mail address: tangbt@dlut.edu.cn (B. Tang).

http://dx.doi.org/10.1016/j.dyepig.2017.03.059
0143-7208/

separation process for the construction of artificial opals. Raw PTU was synthesized from the polycondensation reaction between 4,4′-thiobisbenzenethiol and toluene-2,4-diisocyanate (TDI). PTUMS presented regular spherical morphology, narrow size distribution, and controllable particle size derived from the accurate control of phase separation condition. Furthermore, sufficient negative surface charge (zeta potential of approximately −35.6 mV) was achieved because the terminal isocyanate groups could readily reacted with water to form carboxyl groups on the particle surface. After thermal-assisted self-assembly of the PTUMS, novel PTU opals with iridescent and tunable structural colors were easily achieved.

2. Results and discussion

2.1. Synthesis and characterization of PTU

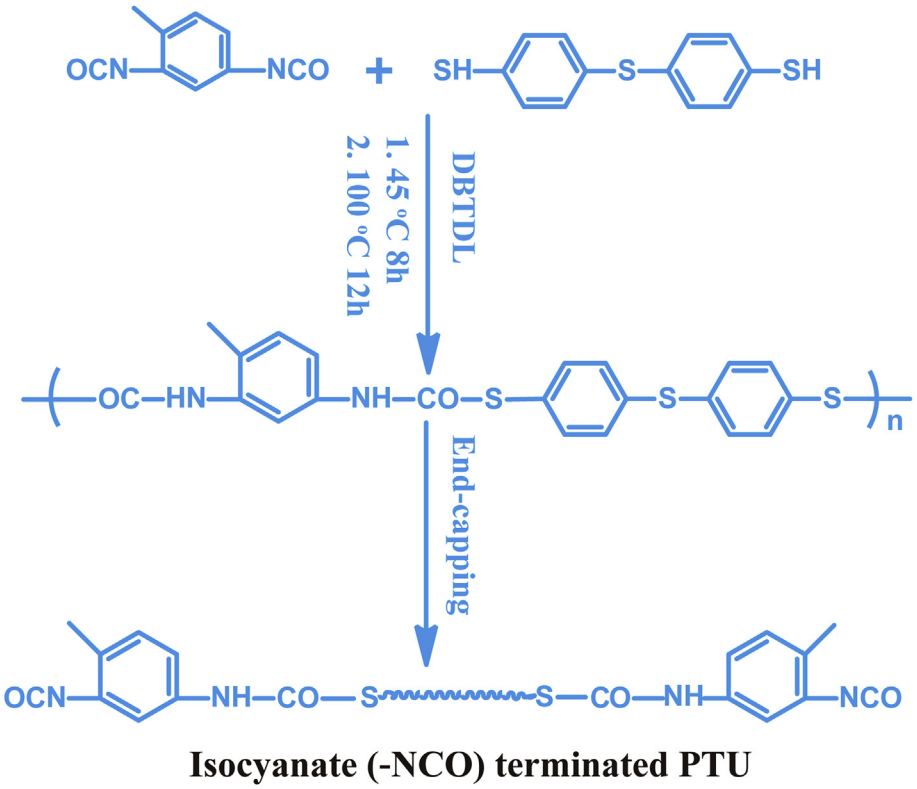
PTU was synthesized through the polycondensation between 4,4′-thiobisbenzenethiol and TDI in the presence of dibutyltin dilaurate as a catalyst in a toluene system (Scheme 1). The chemical structure of the synthesized PTU samples was characterized by FT-IR spectroscopy. Fig. S1a shows the FT-IR spectrum of a representative PTU sample. The strong absorption peak at 2235 cm^{-1} belonged to terminal isocyanate groups (−NCO) vibration, which located at the end of PTU macromolecule chain. The N−H vibration peak at 3268 cm^{-1} and the carbonyl (C═O) vibration peak at 1662 cm^{-1} belonged to the characteristic vibrations for thiourethane linkages and strongly indicated the successful polyaddition of isocyanate and mercapto groups [43].

The refractive index which is an important character of optical materials was also measured. Fig. S2 shows the distribution curve of PTU intrinsic refractive index as a function of wavelength. The intrinsic refractive index was 1.673 when the wavelength was at 589.3 nm (sodium lamp wavelength). The measured results of weight-average and number-average molecular weights were 22914 (Mw) and 20700 (Mn) Daltons, which indicated a molecular weight distribution of 1.107. This result further confirmed the successful polymerization of monomers.

2.2. Preparation of PTUMS through phase separation process

PTUMS were prepared through a modified phase separation method (Scheme 2). The formation mechanism of the phase separation process complies with the nucleation theory and contains several steps, such as particle nucleation, molecular growing, and aggregation, based on the interfacial deposition due to the displacement of the solvent with non-solvent [46,47]. Stable polymer spheres suspensions can be formed under specific conditions, which result in supersaturations of the polymer macromolecules in a ternary polymer/solvent/non-solvent system and transfer it into a metastable region [48–50]. This metastable region is located within the binodal (miscibility limit curve) and spinodal (stability limit curve) of the three component phase diagram based on the hydrophobic solute, the solvent, and the non-solvent [50].

Typically, PTUMS with a hydrodynamic diameter of 196.2 nm were prepared as follows: First, 40 mL of PTU solution (5 mg/mL) was added into a 150 mL beaker. Subsequently, 50 mL of water containing 0.02 wt.% SDBS was added dropwise into the PTU solution under vigorous mechanical stirring (400 r/min, RT). The dropwise addition of the whole aqueous phase was completed in 10 min. The resulting opalescent mixture was stirred sequentially for another 10 min to obtain a balanced emulsion. The mixture was washed three times with water (0.01 wt.% SDBS) in centrifugation/redispersion cycles to remove DMF completely. Finally, the centrifugal sediment was ultrasonically redispersed in water (0.01 wt.% SDBS) and filtered through a nylon filter to obtain PTUMS emulsion for further use.



Scheme 1. Schematic showing the synthesis route of polythiourethane.