

Eugenol-based non-isocyanate polyurethane and polythiourethane

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Abstract Global resource crisis and severe environmental problems have compelled world scientists to develop sustainable and green chemical materials. In this work, eugenol, a cheap and renewable phenol derivative found in cloves, is successfully utilized to prepare hydroxyl non-isocyanate polyurethanes (HNIPU), with number-average molecular weights (M_n) from several to dozens of kilodaltons. First, a diepoxide intermediate is synthesized through three steps in 43.9% total yield. Second, this diepoxide reacts with CO₂ at atmospheric pressure to form an intermediate possessing two cyclic carbonate groups in moderate yield. Third, the cyclic carbonate-containing intermediate further reacts, with compounds such as 4,4'-diaminodiphenyl methane, 1,6-hexanediamine and *p*-xylene diamine by nucleophilic ring-opening to obtain the desired HNIPUs. Furthermore, the diepoxide intermediate and CS₂ undergo addition reaction to form cyclic dithiocarbonate intermediate that further reacts with 4,4'-diaminodiphenyl methane to afford polythiourethane (PTU). The resulting PTU contains mercapto groups in its each unit. Number-average molecular weight of PTU is M_n 2800 Da. Finally, crosslinking reactions occur between the mercapto groups of PTU and crosslinkers (1,6-hexanediol acrylate and/or cardanol) by thiol-ene reactions under UV ($\lambda = 365$ nm) irradiation conditions, leading to their corresponding crosslinked polymers. The optimized conditions for preparing crosslinked polymers include: PTU/cardanol/1,6-hexanediol acrylate = 1:1:0.05 (mass ratio), and UV irradiation time for 30 min. This work

is expected to expand applications of eugenol and to provide a new route to NIPUs and PTUs using various diamines.

Keywords Eugenol · Non-isocyanate polyurethane (NIPU) · Polythiourethane (PTU) · Renewable resource · UV-curing

Introduction

Polyurethanes (PUs) are one of the most important polymers due to their outstanding properties such as good chemical resistance, high elasticity, and strong abrasive performance. Thus, PUs have found versatile applications in coatings, paints, adhesives, foams, elastomers, and so on [1–3]. Consequently, global PUs output is expected to reach 18 million tons in 2016 [4]. For example, PUs show the best comprehensive properties in organic coatings in comparison with methacrylate resins, epoxy resins, polyesters, etc. But carbamate groups in PUs are conventionally formed by reactions between diols/polyols and diisocyanates/polyisocyanates. The use of highly toxic isocyanates in PUs manufacturing processes may inevitably affect the health of production workers and limit their wider scale applications in high-safety-required medical or bio-materials. To solve this problem, non-isocyanate polyurethanes (NIPU) are desired and have been studied by chemists and chemical engineers [5–7]. There are mainly three approaches for preparation of NIPU: ring-opening reactions between five-membered cyclic carbonates and di/multi-amines, leading to hydroxyl-containing non-isocyanate polyurethanes (HNIPU) [8]; the other is self-polymerization of monomers containing hydroxyl and in situ-forming isocyanate groups [9]; the third is the exchange reactions between carbamates [10, 11]. Among

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