



The effects of the molecular weight and structure of polycarbonatediols on the properties of waterborne polyurethanes



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ABSTRACT

A series of waterborne polyurethanes (WPU) were synthesized by a pre-polymer process from isophorone diisocyanate, 1,6-hexamethylene diisocyanate and polycarbonatediol with varying molecular weight (1000–2000 Da) and molecular structure (copolycarbonate and homopolycarbonate). The effect of polycarbonatediols on the performance of the emulsion was studied by means of apparent viscosity, particle size distribution and Zeta potential analysis. Fourier transform infrared spectroscopy, thermal gravimetric analysis, differential scanning calorimetry, X-ray diffraction, dynamic mechanical analysis, physical and mechanical measurements and water droplet contact angle tests were employed to characterize the thermal stability, crystallinity, low temperature flexibility, physical and mechanical properties and wettability of the films derived from the emulsions. The results indicated that WPU dispersions with mean particle size in the range of 50–70 nm and Zeta potential value about –50 mV displayed excellent storage stability. It was found that the mean particle size, thermal stability, crystallinity, low temperature flexibility, mechanical properties and hydrophobicity increased and the particle distribution decreased with the increase of molecular weight of the polycarbonatediols. Moreover, copolycarbonate-based WPUs showed higher crystallinity of hard segments, thermal stability and wettability than the homopolycarbonate-based ones.

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1. Introduction

Polyurethanes are widely used in different applications such as coatings and adhesives due to their superior properties like gloss, toughness, flexibility at low temperature, abrasion resistance, excellent mechanical and physical properties and film formation ability [1–3]. The traditional solvent-based polyurethanes have been at a discount on account of the utilization of considerable toxic volatile organic compounds (VOCs). Hence, waterborne polyurethanes (WPUs) have received increasing attention of researchers because of the low level of VOCs emissions and reduced manufacturing cost.

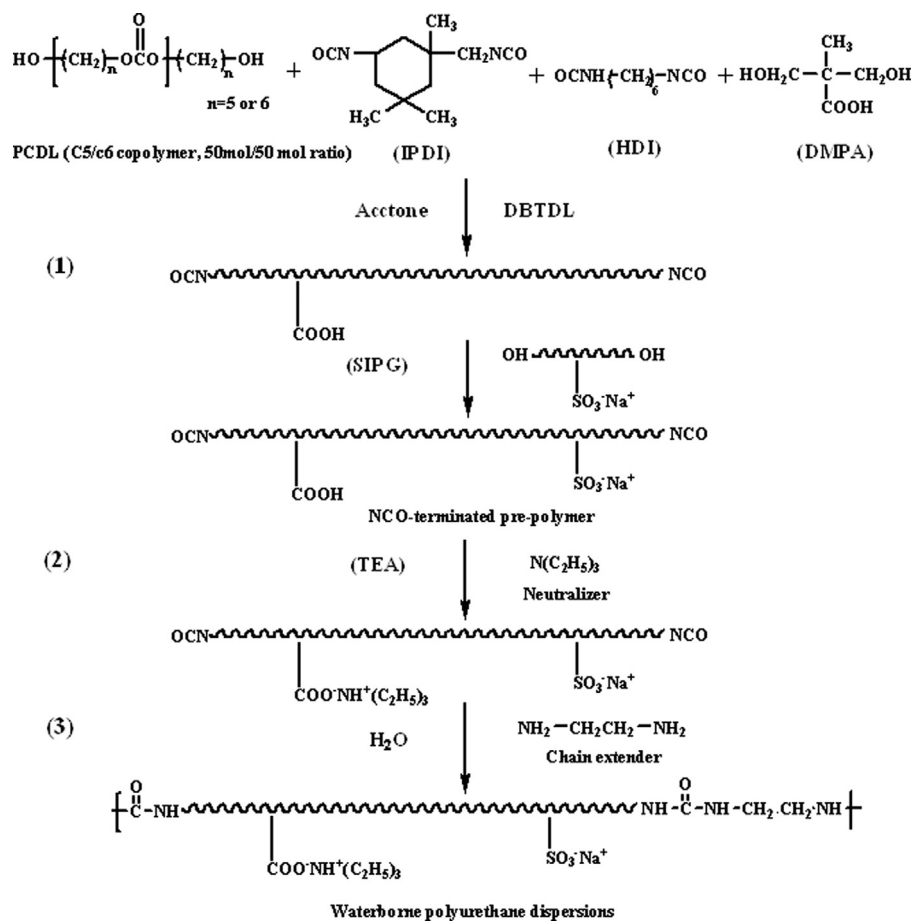
The polyurethanes are generally composed of polyol (soft segment), diisocyanate (hard segment) and low-molecular-weight diol component (chain extender, hard segment). Several excellent review articles have described the chemistries and processes used to manufacture WPUs [4–7]. The effects of various factors such

as the structure and content of diisocyanates, polyols, hydrophilic groups, neutralizing agents and chain extenders on the preparation of polyurethane dispersions and their properties have been studied extensively [8–12]. Besides, thermal properties, phase separation, and physical properties of polyurethanes prepared from different polyols were also studied [13–15]. García-Pacios et al. [16] compared the properties of polycarbonate-based, polyether-based and polyester-based WPUs. Their results showed polycarbonate-based WPUs displayed a lower degree of phase separation between the soft and the hard segment and higher adhesive strength than the regular polyether-based and polyester-based WPUs. In some studies, polycarbonate-based WPUs were also proved possessing excellent hydrolysis resistance and weatherability. In addition, organic solvent resistance is found to be the most outstanding property for the polycarbonate-based WPUs [17,18].

Recent studies [19–22] demonstrated that the ionic group content, the molecular weight of the polyol, the solids content and the hard/soft segment ratio determined the polycarbonate-based WPUs properties. Previous studies [21,23,24] have shown that an increase in the molecular weight of the polycarbonate of 1,6-hexanediol was accompanied by a decrease in the mean particle

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Scheme 1. The preparation process for waterborne polyurethane dispersions.

size and viscosity of the WPUs, elevated micro-phase separation degree, hard domain order and crystallinity of the WPU films. Nevertheless, only a few studies have been devoted to establish the structure–property relationships of polycarbonate-based WPUs. The pioneering work of Foy et al. [25–27] demonstrated that the polyurethane and the thermoplastic elastomer containing units of the novel copolycarbonate as soft segments exhibited remarkably improved flexibility, elastic recovery and resistance to oxidative degradation as compared to those of the conventional polymers. More recently, Lee et al. [28–30] described the effect of the molecular structure of the polycarbonatediols (PCDLs) on the mean particle size of the polyurethane dispersions and tensile strength of the films, which showed no obvious trend.

Although the PCDLs based WPUs have been studied by several groups, the relationship between the performance and the polymer structure is unclear by far. The objective of the present study is to investigate the influence of the molecular weight and structure of PCDLs on the macroscopic properties of WPU dispersions and films. In addition, in order to make commercially useful samples, all of the experiments were run with high solid contents (typically about 40%) and low mean particle diameter. WPUs derived from isophorone diisocyanate (IPDI), 1,6-hexamethylene diisocyanate (HDI), dimethylol-propionic acid (DMPA) and various PCDLs were prepared by a pre-polymer process. PCDLs have almost identical M_n (1000 or 2000), and hydroxyl groups contents in the chain. However, they differ in the chemical constitution and therefore in the regularity of the polymer chain.

2. Experimental

2.1. Materials

Polycarbonatediols with molecular weight of 1000 Da (PCDL 5651, PCDL 6001) and 2000 Da (PCDL 5652, PCDL 6002) were kindly provided by Asahi Kasei Chemical Corporation (Tokyo, Japan). PCDL 5651 and 5652 (C5/C6 copolymer PCDL) were prepared by random copolymerization of 1,5-pentanediol and 1,6-hexanediol. PCDL 6001 and 6002 (C6 homo PCDL) were produced from 1,6-hexanediol by transesterification with ethylene carbonate. The code for the samples is expressed as name XXXX, where first two XX indicate the numbers of methylene units in the copolymer (C5 and C6), the third X is the molar ratio of the pentane units, and the last X denotes the thousand digits the molecular weight of PCDL. For instance, 5651 is the PCDL with M_n of 1000, and molar ratio of C5 pentane to C6 hexane units is 5/5; 6001 with M_n of 1000 is composed of C6 hexane units besides carbonate groups. The PCDLs were dried at 120 °C under 5 mm Hg pressure for 2 h before used.

Isophorone diisocyanate and 1,6-hexamethylene diisocyanate (98 wt% purity) were supplied by Bayer Co. (Germany). Dimethylol propionic acid (DMPA, 98 wt% purity) were supplied by Dongying Saimeike Chemical Co., Ltd. (Dongying, China). The sulfonic acid-based polyester diol (SIPG), made in our laboratory, was used as an internal emulsifier, without further purification. The dibutyltin dilaurate (DBTDL) was supplied by Tianjin Institute of Fine Chemicals Division (Tianjin, China). Ethylenediamine (EDA) (AP, Shijiazhuang Hejia Health Productions Co., Ltd). Triethylamine (TEA) with chemically pure was purchased from Shanghai

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