

Reaction Study of Water-Borne Polyurethanes Based on Isophorone Diisocyanate, Dimethylol Propionic Acid, and Poly(hexane neopentyl adipate glycol)

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Received 29 May 2003; accepted 17 September 2003

ABSTRACT: The reaction of isophorone diisocyanate (IPDI) with poly(hexane neopentyl adipate glycol) (HNA) and dimethylol propionic acid (DMPA) was researched through an analysis of the contents of the NCO groups of the prepolymers through which water-borne polyurethanes (PUs) could be formed. The reaction activity of DMPA with IPDI was studied and compared to that of HNA on the basis of an investigation into the effects of the temperature and catalyst on the prepolymerization and the viscosity of the prepolymers. The results showed that the reaction of IPDI with DMPA was much slower than the reaction of HNA,

and so DMPA was concluded to be a relatively inert nucleophilic reagent for attacking IPDI. A temperature of 80°C was suitable, with dibutyl tin dilaurate as a catalyst, for producing prepolymers from IPDI and mixtures of HNA and DMPA, whereas 60°C without catalysis was enough to complete the reaction of IPDI with HNA. This study may be helpful in understanding the prepolymerization of water-borne PUs and in manufacturing them. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 161–164, 2004

Key words: polyurethanes; ionomers; viscosity

INTRODUCTION

Water-borne polyurethanes (PUs) represent a major trend of PU development because of increasing concern about environmental pollution and health and safety risks.¹ Water-borne PUs are PU ionomers consisting of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized or quaternized, respectively, to form salts, and water-borne PU dispersions can be defined as binary colloidal systems in which PU particles are dispersed in continuous aqueous media.² In contrast to solvent-borne PUs, in which PUs form solutions in solvents, water-borne PUs exist as aqueous dispersions, and they have found applications in the automobile, construction, furniture, adhesive, and textile industries. The increasing acceptance of water-borne PUs has been motivated by more stringent environmental requirements.^{3,4} Besides environmental regulations, the superior quality of water-borne PUs over solvent-borne systems is also a cause for this substitution.^{5,6}

Water-borne PUs represent a well-established area of polymer science, and their versatility and tailor-made properties have resulted in much research into their reactions.⁷ Dimethylol propionic acid (DMPA) is

commonly incorporated into PU backbones because it is very effective for water dispersion in the subsequent neutralization reaction with triethylamine.^{8,9} However, the reaction of DMPA with isophorone diisocyanate (IPDI) has not been thoroughly researched before. In this article, we examine the reaction of IPDI with poly(hexane neopentyl adipate glycol) (HNA) and DMPA through an analysis of the contents of NCO groups of the prepolymers. Surprisingly, DMPA is a relatively inert nucleophilic reagent for attacking NCO groups in comparison with HPA.

EXPERIMENTAL

Materials

IPDI (Degussa Corp.) was used as received. DMPA (Bayer) was dried at 105°C. HNA (molecular weight = 2000) was dehydrated at 120°C *in vacuo* before use. *N*-Methyl pyrrolidone (NMP) was dried over 4-Å sieves before use. All percentages are by weight unless otherwise indicated.

Preparation of the prepolymers

HNA was dehydrated in a reaction kettle, equipped with a thermometer, a stirrer, an inlet and outlet for dry nitrogen, and a heating jacket, at 120°C *in vacuo* for 2 h. IPDI and DMPA, dissolved in NMP, were placed in the kettle with stirring. The reaction was carried out under the protection of a dry nitrogen atmosphere in

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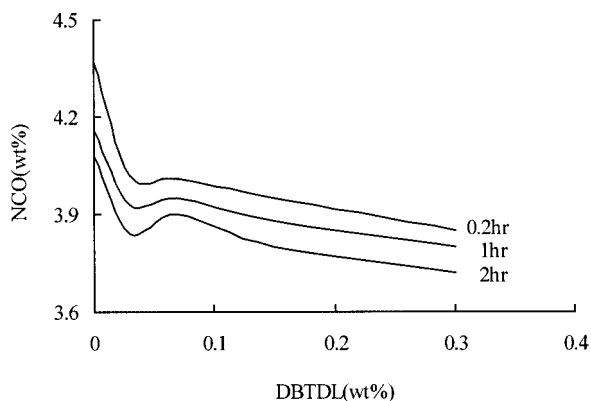


Figure 1 Effect of the catalyst on the prepolymerization.

a constant-temperature oil bath. A series of prepolymers were prepared with different amounts of dibutyl tin dilaurate (DBTDL) as the catalyst from 40 to 80°C. The NCO group content by weight was measured by titration with dibutylamine.

RESULTS AND DISCUSSION

Effect of the catalyst on the prepolymerization

To maintain the low viscosity of the prepolymers, we kept the molar ratio of NCO groups to OH groups in the prepolymerization at 2:1. The effect of the catalyst on the prepolymerization is displayed in Figure 1: HNA was reacted with IPDI at 80°C by catalysis with DBTDL for reaction times of 0.2, 1, and 2 h. A small amount of DBTDL could obviously accelerate this reaction, as shown in Figure 1, but with the further addition of DBTDL to the reaction mixture, the reaction rate changed only a little. This indicates that DBTDL hardly catalyzed side reactions; therefore, DBTDL was a very good catalyst for catalyzing the reaction between OH groups and NCO groups.¹⁰

The effect of DBTDL on the viscosity of the prepolymers was researched, as shown in Figure 2. The vis-

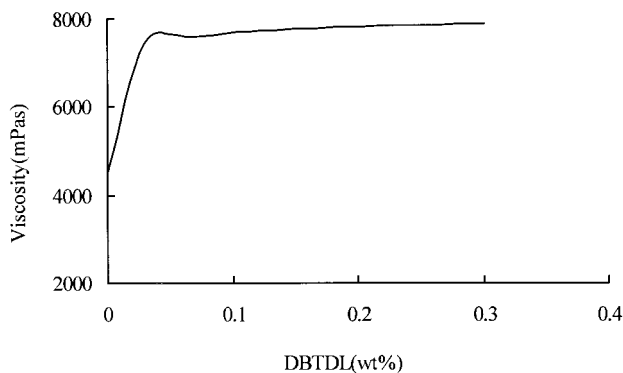


Figure 2 Effect of the catalyst on the viscosity of the prepolymers.

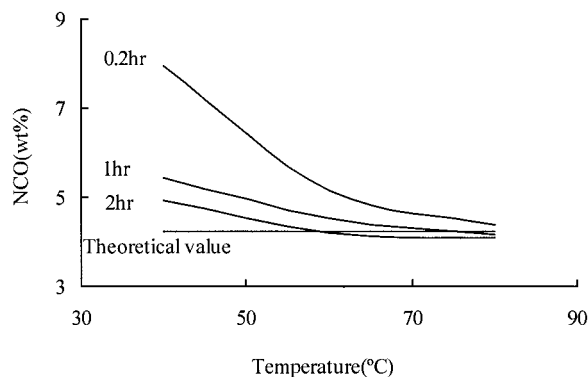


Figure 3 Effect of the temperature on the prepolymerization.

cosity of the prepolymers increased with the addition of DBTDL but was unchanged when the amount of DBTDL exceeded 0.05%. The activity of the two NCO groups (one attached to a six-member ring and one to CH_2) of IPDI is known to be different; the one attached to the six-member ring is more active.¹¹ Without the addition of DBTDL, most of the OH groups reacted with NCO groups attached to six-member rings, so the average molecular weight of the prepolymers was kept very low, and the viscosity was also low. As DBTDL was consumed, more NCO groups attached to CH_2 could react with OH groups, and this increased the possibility of producing high-molecular-weight prepolymers and also caused an increase in the viscosity. Although the concentration of DBTDL was kept between 0.05 and 0.3%, the activity of the NCO group connected to CH_2 did not change much, and so the viscosity of the prepolymers remained unchanged within the range of DBTDL.

Effect of the temperature on the prepolymerization

The reactions between HNA and IPDI with respect to the temperature are shown in Figure 3, which indicates an increase in the temperature increased the

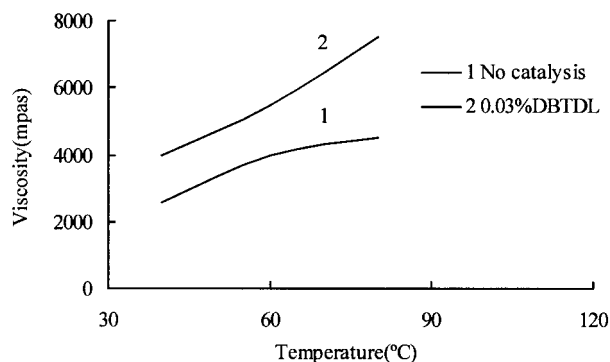


Figure 4 Effect of the temperature on the viscosity of the prepolymers.

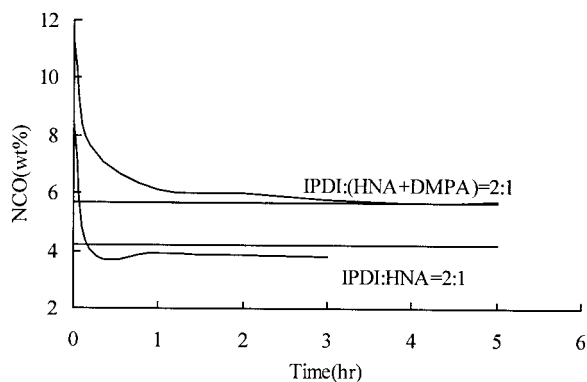


Figure 5 Comparison of the polymerization reactions with and without the addition of DMPA.

reaction rate. Figure 3 also reveals that at 60°C, this reaction was complete in 2 h, and it was complete at 80°C in 1 h without the catalysis of DBTDL. The effect of the temperature on the viscosity of the prepolymers was also investigated, as shown in Figure 4, from which we can see that the viscosity of the prepolymers increased as the temperature increased, with or without the catalysis of DBTDL. The viscosity of the prepolymers with the catalysis of DBTDL was higher than that without DBTDL. This agreed with the previous results. As the temperature rose, the activity of the NCO group connected to CH₂ increased, causing the formation of some large molecules, and side reactions also easily occurred, forming some three-dimensional structures; both factors increased the viscosity of the prepolymers.

Activity comparison of DMPA with HNA

DMPA is commonly used in the production of water-borne PUs.¹² However, its activity is rarely studied. We compared the reactions between IPDI and HNA with and without the addition of DMPA. The results in Figure 5 show that under the catalysis of DBTDL,

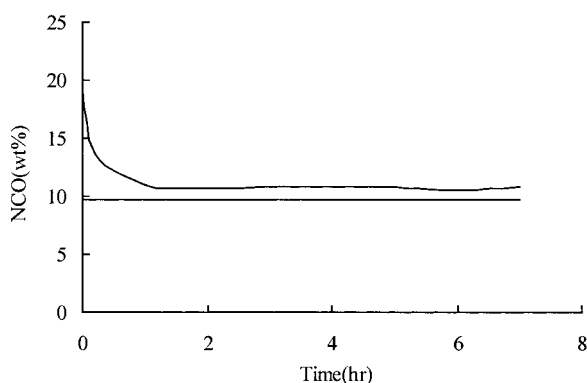


Figure 6 Prepolymerization process between DMPA and IPDI.

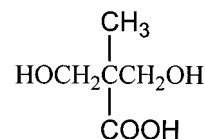


Figure 7 Structure of DMPA.

the completion of the reaction with the addition of DMPA was delayed to 3 h; only about 20 min was needed without DMPA. DMPA made the reaction slow down very dramatically, so we could infer that the activity of DMPA was much lower than that of HNA.

To confirm the results and arguments of this discussion, we reacted only DMPA with IPDI at 80°C under the catalysis of DBTDL. Figure 6 shows that the reaction was very difficult to complete under these conditions. Compared with HNA (see Fig. 5), DMPA was a very inert nucleophilic reagent. The inertness of DMPA originated in its structure, as shown in Figure 7.

The steric effects of the CH₃ and COOH groups in the structure hindered the reaction of DMPA with IPDI, and the electron-withdrawing ability of COOH greatly lowered the nucleophilic activity of OH groups toward NCO groups. We also provide the end structures of HNA for comparison. As either 1,6-hexane diol or neopentane diol could comprise the end groups of HNA, two end structures are presented in Figures 8 and 9. There were neither steric nor electron-withdrawing effects imposed on the hexane diol end groups, the OH groups being more active than those in DMPA. There were steric effects but no electron-withdrawing groups present in the pentyl diol end groups; the end OH groups were not as active as the ones in hexane diol end groups but were perhaps more active than those in DMPA. That explains why DMPA was not as active as HNA for the reaction with IPDI.

Reaction conditions of IPDI and mixed DMPA and HNA

The effect of the catalyst on the prepolymerization of a mixture of DMPA and HNA was examined. The reaction was conducted at 60°C (Fig. 10). Four reactions with no catalyst, 0.03% DBTDL, 0.07% DBTDL, and 0.15% DBTDL were investigated. With a small amount of DBTDL, the reaction proceeded very quickly, in comparison with the reaction with no catalyst, but more of the catalyst had less influence on the

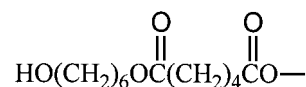


Figure 8 Hexane diol end structure of HNA.

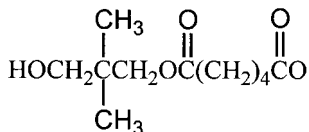


Figure 9 Neopentyl diol end structure of HNA.

reaction. In agreement with Figure 10, 0.1% DBTDL was enough to complete this reaction.

Figure 11 shows that the temperature greatly affected the reaction between IPDI and the mixture of HNA and DMPA. At 60°C, the reaction was completed in 5–6 h; it was completed in 2–3 h at 80°C. The temperature range of 40–60°C was enough for the completion of the reaction of HNA and IPDI, but perhaps 80°C should be used for the reaction between IPDI and a mixture of HNA and DMPA.

CONCLUSIONS

On the basis of this reaction study of IPDI with HNA and DMPA, we can make the following conclusions: (1) DMPA is a much more inert nucleophilic reagent for the reaction with IPDI than HNA, (2) 80°C and

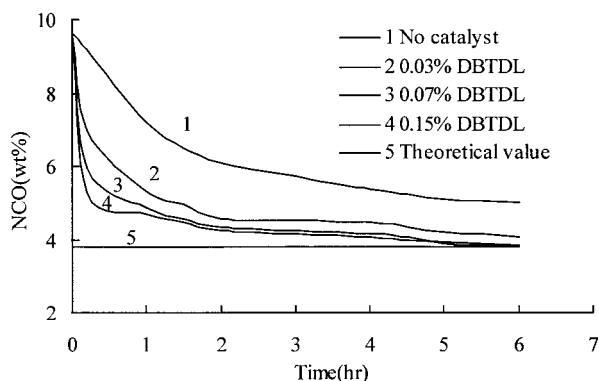


Figure 10 Effect of the catalyst on the prepolymerization of mixtures of HNA and DMPA.

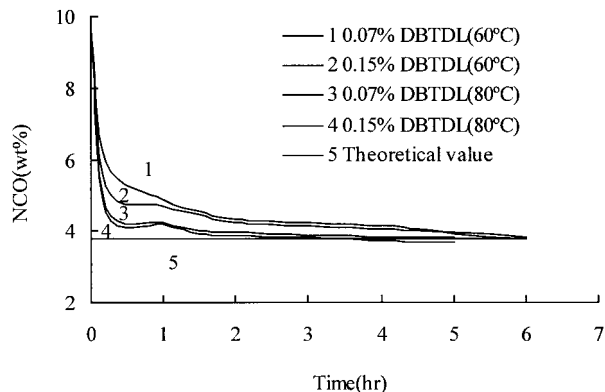


Figure 11 Effect of the temperature on the prepolymerization of mixtures of HNA and DMPA.

0.1% DBTDL are suitable conditions for the reaction between IPDI and a mixture of HNA and DMPA, and (3) the viscosity of prepolymers increases with increasing prepolymerization temperature and the addition of DBTDL.

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