A Novel Synthetic Strategy to Aromatic-Diisocyanate-Based Waterborne Polyurethanes

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ABSTRACT: Based on aromatic diisocyanate [e.g., 2,4-tolylene diisocyanate (TDI)], a novel synthetic strategy to waterborne polyurethanes was introduced. Ionized polyoxyethylated amine (NPEO) played an important role in the preparation process as both a polyether soft segment and an internal emulsifier. First, a segmented surfactant prepolymer was synthesized. Second, the prepolymer was charged to a water dispersion of a hydrophobic polyol [e.g., polytetrahydrofuran (PTMO)] directly to obtain a stable emulsion. Third, a chain-extension procedure was performed directly in water with PTMO to achieve a stable aqueous polyurethane dispersion. Neither aliphatic diisocyanate nor excess isocyanate group fraction was added. An extra end-capping reaction or external emulsifier was also unnecessary. Films cast from emulsions exhibited reasonable mechanical properties. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1621–1626, 1998

Key words: aromatic-diisocyanate-based waterborne polyurethane; polyoxyethylated amine; surfactant prepolymer; internal emulsification; freeze-thaw stability

INTRODUCTION

Polyurethane block copolymers define an important class of thermoplastic elastomers. Their unusual mechanical properties should be attributed to the specific microphase-separated morphology, which consists of hard-segment-rich and soft-segment-rich domains.¹ Since ions could be introduced into in both hard and soft segments, and many exciting properties could be entrusted to polyurethane matrix with the ionization process,^{1,2} great attention has also been drawn to polyurethane ionomers. There has been a wide range of work done in the field of synthesis and characterization of various kinds of polyurethanes and polyurethane ionomers.^{3–5} However, as preparation methods are concerned, most of them should still be classified as the conventional organic-solvent-based two-step or one-shot procedure, 3 which is also being widely employed in industry.

Due to the stronger calls for low-pollution chemical industry, aqueous polyurethanes have been forcing their way into the marketplace. Furthermore, waterborne polyurethanes possess their unique price advantage, for the costly organic solvents could be replaced by the aqueous medium. In the past 50 years, much literature and thousands of patents were issued, which kept steady improvement of the production technology and the quality of waterborne polyurethanes. The work of Dr. D. Dieterich and his colleagues of Bayer A. G. should be noted,^{6,7} which pioneered and inspired much of the work in this area. Today, waterborne polyurethanes have begun to penetrate into application areas previously serviced only by their solventborne analogs, especially as coatings for various fibers, adhesives for

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alternative substrates, primers for metals, caulking materials for sewer sealants, emulsion polymerization media for different monomers, paint additives, defoamers, associative thickeners, pigment pastes, and textile dyes.^{8–18}

However, some problems are still remained unsettled, especially the synthetic methods, which will influence faster development in this field. As current preparation processes are concerned, most of them could be classified as 1 of the following 5 procedures: acetone process,^{19,20} melt dispersion process,²¹ prepolymer mixing process,²²⁻²⁵ ketimine (and ketazine) process,^{26,27} and other processes using "capped" prepolymers.^{28,29} Because of the high reactivity of isocyanate groups with water, complicated techniques are often involved in these processes. Generally speaking, urea segment formation, or a large amount of organic solvent consumption, or extra end-capping reactions, or excess isocyanate group fraction, or special requirements for reagents (e.g., aliphatic diisocvanates, or ionic chain-extenders as internal emulsifiers) can't be completely avoided in these processes, which result in poor manageability. Consequently, the improved complexity of the techniques has become the major hindrance for further development and application of waterborne polyurethanes. Therefore, new processes with better manageability are crucial for further development in this field. Discoverv of new processes has not only theoretical significance but also practical importance as well.

Various polyoxyethylated amines (NPEO) have been well exploited with their original main usage as cationic surfactants.³⁰ Since tertiary amine supplies an ideal ionization site and could be conveniently converted to different types of cationomers, anionomers, and zwitterionomers,² recently, synthesis and characterization of NPEObased polyurethane ionomers have been studied in this lab, and some interesting properties have been observed.² In this work, ionized NPEO reacted with 2.4-tolylene diisocyanate (TDI) to form a prepolymer with a specific structure characteristic of coexistence of hydrophilic central segments and hydrophobic end groups. When added to a water dispersion of the hydrophobic polytetrahydrofuran (PTMO), isocyanate groups could be inserted into the surface of PTMO droplets and chain-extended with PTMO to accomplish the high-molecular-weight buildup step. Neither aliphatic diisocyanate nor excess isocyanate group fraction was required. An extra end-capping reaction or external emulsifier was also unnecessary.

(1) x TDI + y BD + z Neutralized NPEO
$$\xrightarrow{50 \sim 70^{\circ}C}$$
 Prepolymer

(2) Prepolymer + (x-y-z) PTMO $\frac{25 \,^{\circ}\text{C}}{\text{in water}}$ Emulsion

(3) Emulsion $\xrightarrow{80 \sim 90 \degree C}$ Waterborne Polyurethane

Scheme 1 Synthetic route to waterborne polyure-thanes.

Films cast from emulsions exhibited reasonable mechanical properties. Since neutralized NPEO could act as an internal emulsifier of both ionic and nonionic types, the resultant emulsions demonstrated satisfactory freeze-thaw stability.

EXPERIMENTAL

Materials

2,4-Tolylene diisocyanate (TDI) (80%, with 2,6-tolylene diisocyanate as the remainder) was degassed and purified by vacuum distillation. Polyethylene oxide (PEO) ($M_n = 600, 1000$), polytetrahydrofuran (PTMO) ($M_n = 650, 1000$), 1,4-butanediol (BD) (99%), stannous octoate catalyst, and hydrochloric acid were used as received.

Polyoxyethylated *n*-butylamines (NPEO) ($M_n = 573, 1246$) were prepared as reported in the literature.² Their number-average molecular weights were determined by means of terminal group analysis and reaffirmed by vapor phase osmometry (VPO), also according to the literature.² Synthesized NPEOs could be directly used without after-treatment.

Sample Preparation

A series of waterborne polyurethanes were synthesized as follows, which is outlined in Scheme 1.

First, NPEO was neutralized by hydrochloric acid stoichiometrically. After vacuum distillation to remove water and residual hydrogen ions, it was mixed with BD. Then TDI was added at 50- 70° C, and the reaction continued for 1 h at 70° C. After cooling to room temperature, the isocyanate-terminated prepolymer was directly transferred to a water dispersion of PTMO with vigorous stirring to make a homogeneous emulsion. Finally, the temperature was raised to $80-90^{\circ}$ C, and the chain-extension reaction could be accomplished after 2–3 h of reaction. The compositions and designations of the synthesized samples are

Sample Designation	TDI	BD	PTMO650	PTMO1000	NPEO573	NPEO1246
WBPU573-30/70	1.76	0.76	0.3		0.7	
WBPU573–50/50	1.76	0.76	0.5		0.5	
WBPU1246-50/50	2.94	1.94		0.5		0.5
WBPU1246-70/30	2.94	1.94		0.7		0.3

Table I The Synthesized Waterborne Polyurethanes

listed in Table I. All the samples possess similar hard segment concentrations (HSC $\approx 38\%$).

Films were cast from emulsions on a Teflon plate at 60°C, then stored at room temperature in a vacuum desiccator before further testing.

Characterization

Freeze-thaw stability of the emulsions was measured as follows. First, 2 mL of emulsion was sealed in a weighing bottle and placed in an air oven at 90°C for 5 h. Then it was immediately transferred to a refrigerator at 0°C for 5 h, which concludes a typical testing cycle. At least 10 testing cycles were performed at each sample to observe whether any system heterogeneity (for example, phase separation or precipitation) could be detected in response to temperature mutations.

Uniaxial stress-strain testing was performed at room temperature using a Instron material testing system, with a crosshead speed of 50 mm/ min. Three dumbbell-shaped samples were cut from the films, and the typical film thickness is about 0.5 mm. The reported values of Young's modulus and elongation at break are averaged testing results.

RESULTS AND DISCUSSION

Reaction Mechanism

Due to the high reactivity of aromatic isocyanate groups with water, generally speaking, common aromatic diisocyanates could not be directly applied in water to synthesize waterborne polyurethanes without end-capping reactions or excess diisocyanate usage.

In order to solve this problem, a brand-new synthetic route was designed in this article. It was originated from the specific reaction mechanism detailed as follows, which was tightly related with the chemical structure of the prepolymer, as shown in Scheme 2(a). Neutralized NPEO segments were located in the middle of the prepolymer, possessing hydrophilic properties. Meanwhile, urethane hard segments were situated in both ends of the prepolymer, characteristic of hydrophobic properties. Consequently, the resultant prepolymer could act as an internal emulsifier of both ionic type and nonionic type. When the prepolymer was charged to the water dispersion of PTMO, the hydrophobic hard segments tended to insert into the hydrophobic PTMO droplets. As the remaining isocyanate groups were attached on urethane hard segments, they could be brought in during this process and protected against the attack of water. At the same time, since the neutralized NPEO segments could be dissolved in water, the dispersed PTMO droplets could therefore be stabilized due to both of the effects of "diffuse electrical double layer"³¹ and "entropic repulsion"³¹ contributed by the neutralized NPEOs. When heated to appropriate temperatures, the isocyanate groups contained in PTMO would continue to react with PTMO to accomplish the chain-extension procedure. The whole process was expressed in Scheme 2(b). As a result, common aromatic diisocyanate could be directly applied to prepare aqueous polyurethanes stoichiometrically without other requirements.

In brief, it should be noted that both the tailormade structure of the surfactant prepolymer and the emulsification step were very crucial for realizing the proposed reaction mechanism, which will be further discussed in detail in the following sections.

Prepolymer Preparation

As mentioned above, preparation of prepolymers with a specific structure comprises one of the decisive factors for successful achievement of aqueous polyurethanes, according to the proposed reaction mechanism.

Because polyoxyethylated amines were used to synthesize prepolymer and the tertiary amine usually supplied a strong catalyst for the reaction



Scheme 2 (a) Chemical structure of the surfactant prepolymer. (b) Emulsification and reaction process.

between urethane and isocyanate groups, it should be noted that crosslinking allophanate structure formation should be carefully avoided in this step.² According to our previous work, adoption of a one-shot procedure could guarantee no existence of excess isocyanate groups, thus effectively excluding the possibility of the reaction between urethane and isocyanate groups and avoiding the allophanate structure formation.² However, since a stepwise synthetic route was applied in this work instead of the one-shot procedure, the NPEOs had to be thoroughly neutralized before prepolymerization in order to deprive their catalytic capabilities completely. As a result, neither gel formation nor much-enhanced viscosity was encountered during prepolymerization, meaning that crosslinking structures were successfully avoided.

However, satisfactory control of the reaction is still not enough, for the chemical structure of the resultant prepolymer is much more important. As mentioned above, the nature of the prepolymer should be characteristic of a surfactant structure, which possesses both hydrophilic segments and hydrophobic segments in the same molecular chain.

As hydrophobic segments are concerned, they are composed of segmented urethane hard segments. It has been well known that without lowmolecular-weight chain extenders, segmented polyurethane with appropriate phase separation morphology could not be achieved.³ In fact, if the prepolymer was derived from TDI and NPEOs, the synthesized prepolymer could not exhibit sufficient hydrophobic properties, mainly due to its homogeneous morphology. When the prepolymer was added to the water, the isocyanate groups attached on the end of the molecular chain could not be protected by the hydrophobic PTMO droplets, which should be ascribed to the hydrophilic properties of the whole molecular chain. As a result, because of the high reactivity of isocyanate groups with water, gel formation or even precipitation always occurred. As a contrast, when suitable amount of low-molecular-weight chain extender (e.g., BD) was used to prepare the prepolymer, a segmented structure with an appropriate phase separation morphology could be achieved. When the prepolymer was charged to water, isocyanate groups could be inserted into the surface of PTMO droplets and protected against the attack of water. Meanwhile, since the hydrophilic neutralized NPEO segments would be dissolved in water, the dispersed PTMO droplets were stabilized, and the emulsification process could be accomplished.

As hydrophilic segments are concerned, neutralized NPEOs are composed of not only ethylene oxide segments as a nonionic emulsifier but ionized tertiary amines as an ionic emulsifier. It should be noted that the neutralized tertiary amine could influence the prepolymer's emulsification capabilities dramatically, for ionic emulsifier is usually considered as more effective than nonionic type. When analogous polyethylene oxides ($M_n = 600, 1000$) were applied instead of the ionic NPEOs, aqueous polyurethane could, by no means, be obtained. It might reaffirm that the neutralized tertiary amine might play a more important role than ethylene oxide segments in the emulsification process.

It should also be suggested that the longer the NPEO molecular chain is, the more effective the emulsification is. When NPEO573 was used. attempts to synthesize waterborne polyurethanes with a molar ratio of PTMO to NPEO higher than 50 : 50 always failed, mainly because of the relatively poorer emulsification capabilities of NPEO573. However, when the NPEO1246 was used instead, a ratio of 70 : 30 could be easily achieved. Why the higher percentage of hydrophobic PTMO could be stabilized by a lower fraction of NPEO might only be attributed to NPEO1246's better emulsification capabilities. Above all, it could be concluded that the higher molecular weight the NPEO is, the more flexible it is and the greater effect of "entropic repulsion" it will contribute to the emulsion.

Emulsification Process

Practical control of the emulsification is a subtle but important process. The charging sequence should be first noted. If the dispersion of PTMO in water was added to the prepolymer, the emulsification would result in a failure, for the emulsification would be too slow for the bulk prepolymer to be dispersed and to let the isocyanate groups be protected in PTMO before its reaction with water to produce precipitation. Actually, it was prepolymer that should be charged dropwise to the water dispersion of PTMO with vigorous stirring.

Temperature control is also quite critical. In this experiment, 2,4-tolylene diisocyanate was employed, the isocyanate groups at 4-position should be fully consumed in prepolymerization due to the obvious reactivity difference between 4-position and 2-position isocyanate groups. As a result, the isocyanate groups at 2-position should remain. Although the remaining isocyanate groups exhibited relatively lower reactivity with water, the emulsification temperature still required careful control. It has been demonstrated by our numerous trials that once the prepolymer has been cooled to room temperature (at about 25° C) before emulsification, the reaction between isocyanate groups and water would be sufficiently inhibited to avoid any precipitation or gel formation, then a stable and homogeneous emulsion could be achieved for a further chain extension reaction.

Preliminary Studies of the Physical Properties

Emulsion Stability

Generally speaking, emulsions resulted from nonionic internal emulsifiers will exhibit enough stability at freezing temperatures but will suffer coagulation at temperature above 70° C.³¹ On the contrary, although ionic internal emulsifiers supply sufficient emulsion stability toward relatively high temperatures, they usually cause the intrinsic unstable property of emulsions on freezing.³¹

Since neutralized polyoxyethylated amines were employed in this article, which acted as an internal emulsifier of both nonionic type and ionic type, the resultant emulsion exhibited satisfactory stability in the whole range of the testing temperatures. This feature might be desirable for their future applications.

Mechanical Properties

As shown in Table II, all the films cast from the emulsions exhibited reasonable mechanical properties. In addition, it has been found that all the films could be promptly dissolved in some organic solvents (e.g., N,N-dimethylformamide, N,N-dimethylacetamide, and dimethyl sulfoxide) again, indicating that linear waterborne polyurethanes were successfully synthesized. All these facts might reaffirm that the proposed reaction mechanism should be correct, and the practical preparation was undergone according to our designed synthetic route.

CONCLUSIONS

A new strategy to synthesize aromatic-diisocyanate-based waterborne polyurethanes was proposed with better manageability. Reaction mechanism was discussed combined with the observed experimental phenomena. Produced emulsions

Sample	Control Sample	WBPU573-30/70	WBPU573–50/50	WBPU1246-50/50	WBPU1246-70/30
Young's modulus (MPa)	2.48	6.10	8.76	10.7	43.4
Elongation at break (%)	1150	567	233	2500	233

 Table II
 Mechanical Properties of Waterborne Polyurethanes

Note that, according to the literature,² the mechanical properties of the solventborne polyurethane ionomer MD-NPEO600-Z were cited as the control sample in this article because an ionized polyoxyethylated amine was also included in this structure as polyether soft segments.

exhibited satisfactory freeze-thaw satiability, and the films cast from the emulsions possessed reasonable mechanical properties.

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