Hydrogen Bonding and Morphological Structure of Segmented Polyurethanes Based on Hydroquinone—Bis(β -hydroxyethy)ether as a Chain Extender

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ABSTRACT: Two series of polyether polyurethanes based on hydroquinone bis(β -hydroxyethy) ether (HQEE) or 1,4-butanediol (BDO) as a chain extender were prepared by a one-step bulk polymerization process. Their hydrogen bonding and morphological structure were studied by means of Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). Compared with BDO-based polyurethanes, HQEE-based polyurethanes showed better phase segregation and higher extent of ordering in the hard domain. Besides shortrange hydrogen bonds, a considerable amount of long-range hydrogen bonds existed in amorphous phase of the hard domain. The soft segment was easier to crystallize, and the melting temperature of the hard domain was elevated in HQEE-based polyurethanes. Its hard domain displayed a banded structure, rather than spherulitic structure in BDO-based polyurethanes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2895–2902, 1999

Key words: hydroquinone—bis(β -hydroxyethy)ether; polyurethane; chain extender; hydrogen bond; morphology; hard domain structure

INTRODUCTION

Segmented polyurethane elastomers are block copolymers consisting of alternating hard and soft segments which, due to thermodynamic incompatibility, separate into two phases. Hard-segment-rich hard domains play the role of physical crosslinks and act as higher modulus fillers in soft-segment-rich soft matrix. When the molecular weight of polyurethane is high enough, its mechanical properties and high-temperature behavior are determined mainly by hard domains. The enhancement of the hard domain cohesion due to crystallization and hydrogen bonding be-

tween hard segments may result in a significant increase of these properties.^{2,3}

The urethane hard segment is often made of a diisocyanate and a diol as chain extender. The polyurethane elastomers based on aliphatic diols, such as ethylene glycol (EDO), butanediol (BDO), and hexanediol (HDO), have been investigated in detail, and a considerable number of valuable results have been obtained,²⁻⁷ while very few studies on the polyurethane elastomers based on aromatic diols have been made, especially on their morphological structure and hydrogen bonding behavior. Hydroquinone-bis(β -hydroxyethy) ether (HQEE) is a typical representative of the diols. The polyurethane elastomers based on HQEE as chain extender provide excellent physical properties, 8,9 such as high strength and resilience, low permanent set, reduced hysteresis loss, and good heat resistance, especially

Samplea	Chain Extender	Mole Ratio PTMO– Extender–MDI	Hard Segment Content (wt %)	[η] (mL/g)
PU1000B1	BDO	1:1:2	39.2	86.1
PU1000B2	BDO	1:2:3	50.3	94.2
PU1000H1	HQEE	1:1:2	43.7	89.9
PU1000H2	m HQEE	1:2:3	56.0	78.6
PU2000B1	BDO	1:1:2	23.2	70.3
PU2000B2	BDO	1:2:3	32.2	69.6
PU2000B3	BDO	1:3:4	39.2	62.3
PU2000H1	HQEE	1:1:2	26.2	78.9
PU2000H2	$ m H ilde{Q}EE$	1:2:3	37.0	76.2
PU2000H3	HQEE	1:3:4	44.9	79.7

^a PU1000 series use PTMO ($M_n = 1000$) as the soft segment; PU2000 series use PTMO ($M_n = 2000$) as the soft segment.

the remaining higher strength and resilience at elevated temperature. It is most likely that these properties are due to the role that the hard domains composed of HQEE reacted with a diisocyanate play in the polyurethane elastomer. Quantitative differential scanning calorimetry (DSC) evaluation has shown that the degree of phase segregation of polyurethanes based on HQEE is higher than that based on BDO.¹⁰

In this report, two series of poly(ether-urethane) block copolymers with hard segments derived from diphenyl methane diisocyanate (MDI) reacted with HQEE or BDO were prepared by a one-step bulk polymerization process. Their hydrogen bonding behavior, phase segregation, and morphological structure were investigated.

EXPERIMENTAL

Materials

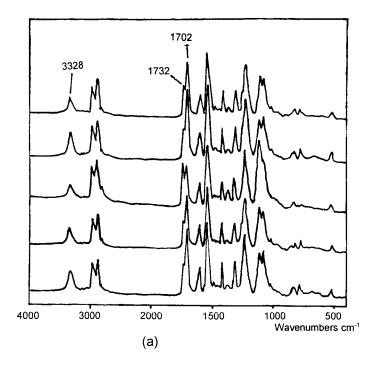
Poly(tetramethylene oxide) (PTMO) (Henan Hongyi Chemical Co.) has an OH number of 56.3 or 112.4 mg KOH/g, corresponding to the molecular weight of 2000 or 1000, respectively. They were dehydrated under reduced pressure at 70–80°C for 12 h. 4,4′-Diphenylene methane diisocyanate (MDI) (Yantai synthetic leather plant) and 1,4-butanediol (BDO) (Shanghai Chemical Reagent No. 2 Plant) were distilled under reduced pressure just before use. Hydroquinone-bis(β -hydroxyethy) ether (HQEE), from Eastman Chemical Co., was purified by recrystallization in hot water.

Preparation of Polyurethanes

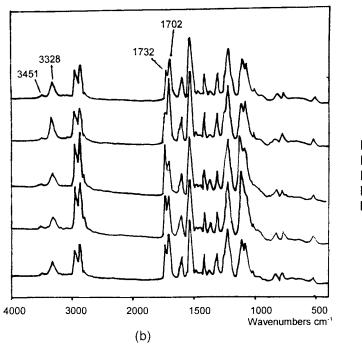
Polyurethanes were synthesized by one-step bulk polymerization process. PTMO and BDO or melted HQEE were premixed, and MDI was added into the mixture and stirred until the viscosity and temperature started to rapidly increase. The resulting mass was then poured into a polytetrafluoroethylene (TFE) mold at 110°C and cured for 6 h at 120°C. The samples were taken out from the mold and kept in desiccator for at least 1 month before measurement. Their chemical composition are listed in Table I.

Measurement

The intrinsic viscosity were measured in dimethylformamide (DMF) at 30°C. Infrared (IR) spectra were recorded on a Nicolet MAGN Fourier transform infrared (FTIR) spectrophotometer. The spectra were recorded at 4 cm⁻¹ resolution, and 32 scans were collected for a good signal averaging to obtain a signal-to-noise ratio. Thin films were cast from DMF solution. In order to have a constant thermal history for each of samples, the samples were heated to 100°C and cooled to room temperature before recording any spectrum. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer DSC-4. Samples on the order of 5-15 mg were sealed in standard aluminum pans. The DSC head was purged with nitrogen, and the data were collected at 10°C/min from -80 to 280°C. A JEM-100SX analytical transmission electron microscope was used to obtain micrographs with 100,000× magnification. The specimens were osmicated with 2% osmic acid



PU1000H1 PU1000H2 PU2000H1 PU2000H2 PU2000H3



PU1000B1 PU1000B2 PU2000B1 PU2000B2 PU2000B3

Figure 1 FTIR spectra recorded at room temperature of (a) HQEE-based polyure-thanes and (b) BDO-based polyure-thanes.

and then sectioned with a Ultracut-E ultramicrotome having a low-temperature attachment and a diamond knife. The sections of approximately 800 Å thickness were obtained and placed on 200-mesh copper grids.

RESULTS AND DISCUSSION

Hydrogen Bonding Structure

The hard segment units derived from MDI reacted with HQEE and BDO are as follows, respectively:

In both cases, the N—H group of the urethane serves as the proton donor, while the acceptors may include the carbonyl oxygen and alkyl oxygen atom in the urethane group. In the HQEE-MDI hard segment, the alkyl aryl ether oxygen atom is likely to be proton acceptor. It is generally

accepted that the alkyl oxygen in urethane group is not inclined to form a hydrogen bond with NH.¹¹ As for the alkyl aryl ether oxygen, it is proved by examining the model compound consisting of HQEE and phenyl isocyanate by FTIR that it is not inclined to form a hydrogen bond with NH either. 12 This fact is thought to be due to p- π -conjugation of the oxygen atom with the benzene ring and lowering its electronegativity. Therefore, in the interior of two types of hard domains, only the carbonyl oxygen atom can form a hydrogen bond with NH group. If polyether is a soft segment of the polyurethanes, the hydrogen bonding may exist between the NH group of hard segment dispersed in the soft segment phase and ether (COC) oxygen of the soft segment. Hydrogen bonding significantly affects the morphology and properties of polyurethanes and is one of their typical structural features; investigation of the hydrogen bonding structure is of importance in understanding the relation between its structure and properties.

FTIR is the most useful method to investigate the hydrogen bonding structure of polyurethanes; there is a significant number of previously published in-depth studies about this. 13-18 Several spectral regions are involved in the hydrogen bonding, as follows: N—H stretching, C=O stretching, and C—O—C stretching vibration. It is generally agreed that the C=O stretching re-

Table II Weight Fraction of Hard Segment Mixed with Soft Segment Calculated from the Infrared Data

Sample ^a	Hard Segment Content f (wt %)	Fraction of Hydrogen Bonded C=O X_b (mol %) ^b	Fraction of Hard Segment in Soft Matrix W_2 (wt %) $^{\rm c}$	Fraction of Hard Segment Mixed with Soft Segment (wt %) ^d
PU1000B1	39.2	58.4	21.2	54.1
PU1000B2	50.3	73.3	21.3	42.4
PU1000H1	43.7	65.3	21.2	48.5
PU1000H2	56.0	81.2	19.3	34.5
PU2000B1	23.2	35.2	16.4	70.7
PU2000B2	32.2	49.8	19.3	60.0
PU2000B3	39.2	61.3	20.0	51.0
PU2000H1	26.2	46.3	16.0	61.1
PU2000H2	37.0	64.7	17.2	46.5
PU2000H3	44.9	73.2	17.9	39.8

^a See Table I.

Fraction of hydrogen-bonded C=O, X_b (mol %) = A1702/(A1702 + A1732) × 100. The fraction of the hard segment in the soft matrix, $X_b = (1 - X_b) f/[(1 - X_b) f + (1 - f)]$. Fraction of hard segment mixed with soft segment (wt %) = W_2/f .

gion is favorable for the analysis of hydrogen bonding in polyurethane, qualitatively or quantitatively. The IR spectra of two series of polyurethanes, recorded at room temperature, are shown in Figure 1. As can be observed, unlike BDObased polyurethanes, the absorption band at 3451 cm⁻¹ associated with the free NH group seems to be absent in HQEE-based polyurethanes. This indicates that approximately 100% N—H groups in HQEE-based polyurethanes are hydrogenbonded. It is also noted that the carbonyl peak of urethanes splits into the following two peaks: the one at about 1702 cm⁻¹ results from self-association of NH with C=O in the interior of the hard domain; another at 1732 cm⁻¹ is related to the free carbonyl group present in the mixed soft segment phase. Because the extinction's coefficients of free and bonded carbonyl groups are almost the same, ¹⁹ the fraction of carbonyl groups bonded to NH in the hard segment domain and the weight fraction of the hard segment mixed with soft segment phase can be calculated based on the area of these two peaks in Figure 1. In interpreting the calculations, we have assumed that the hydrogenbonded carbonyls exist only in the hard segment domain. Table II shows the results of the calculation. It can be noted that at the same molar composition the fraction of hard segment mixed with soft segment phase in HQEE-based polyurethanes is obviously lower than that in BDO-based polyurethanes. This denotes that HQEE-based polyurethanes exhibit a higher degree of phase segregation than BDO-based polyurethanes. With the increase of hard segment content or soft segment length, the degree of phase segregation for both HQEE- and BDO-based polyurethanes is elevated. This is consistent with the results reported previously. 11,20 Comparing the HQEE-MDI hard segment with the BDO-MDI hard segment, it can be noted that the —O—(O)—O linkage contained in the HQEE-MDI hard segment enhances its stiffness and cohesion of the hard domains, resulting in a greater incompatibility between the hard and soft segment. Therefore, it is not hard to explain why HQEE-based polyurethanes are more phase-separated than BDO-based polyurethanes.

In order to assist in probing the complex hydrogen bonding structure from the IR spectra of these polyurethanes, the technique of Fourier deconvolution is utilized. Their Fourier deconvoluted spectra for carbonyl stretching region are

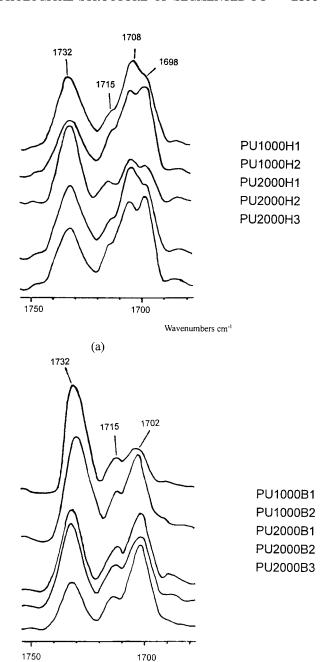


Figure 2 Deconvoluted FTIR spectra in the C=O stretching region of (a) HQEE-based polyurethanes and (b) BDO-based polyurethanes.

(b)

Wavenumbers cm²

shown in Figure 2. As can be seen from the figure, the lowest frequency associated with ordered hydrogen bonded carbonyl in crystallite¹³ for HQEE-based polyurethanes is lower by 4 cm⁻¹ than the one for BDO-based polyurethanes. This indicates the former show a higher extent of or-

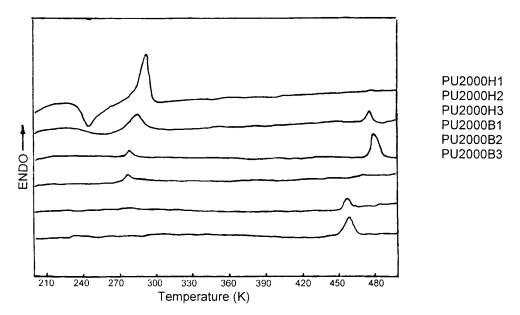


Figure 3 DSC curves of polyurethanes with a 2000-molecular-weight soft segment.

dering and a stronger ordered hydrogen bond. Compared with the BDO-based hard segment, the —O—O— linkage in the HQEE-based hard segment contributes to the ordering due to chain interacting. However, the solubility of the HQEE-MDI hard segment in the polyol is reduced, resulting in a more phase-separated polymer that also can contribute to the order.

Figure 2 shows that two types of disordered hydrogen bonded carbonyls are observed at frequencies intermediate to the free and ordered hydrogen-bonded carbonyls for HQEE-based polyurethanes, but only one for BDO-based polyurethanes. As were assigned previously, ^{13,16} the band at around 1715 cm⁻¹ is associated with the hydrogen bond that is short-range in the amorphous phase of the hard domain or the interfacial phase region, whereas the band at about 1708 cm⁻¹ corresponds to the long-range hydrogen bond in the amorphous phase of the hard domain. With an increase in the hard segment content for HQEE-based polyurethanes, the absorption band at 1732⁻¹ cm associated with free carbonyl diminishes, while the band at 1698 cm⁻¹ increases the most dramatically among hydrogen-bonded carbonyl stretching bands. Qualitatively, the spectra for hydrogen bonded carbonyl is dominated by the band at 1705 cm⁻¹ at a low hard segment content. As the hard segment content is raised, the dominant band is replaced by the component at 1698 cm⁻¹. The contribution from the band near 1715

cm⁻¹ increases little, which means that the fraction of the short-range disordered hydrogenbonded carbonyl decreases. This fact indicates that the hard domain enlarges and the interfacial phase region diminishes with increasing hard segment content.

DSC Studies of the Structure of Polyurethane

Yves et al. have studied the phase segregation of HQEE- and BDO-based polyurethanes through measuring the variation of heat capacity of their soft segments by DSC. 10 The DSC curves between -80 and 280°C for these polyurethanes with the same kind of soft segment of 2000 molecular weight is examined here. As shown in Figure 3, the crystalline melting peaks of soft segment for HQEE-based polyurethanes occur at about 12°C; and, qualitatively, with the hard segment content increasing, the crystallizing extent decreases; whereas for BDO-based polyurethanes, little crystallization peak of the soft segment is observed, even in low hard segment content. This is because the weight fraction of the hard segment in the soft matrix is higher, as shown in Table II, for BDO-based polyurethanes. As hard segment content increases, melting peaks of hard domains of two types of polyurethanes occur between 160 and 250°C. It is obvious that the melting temperatures for HQEE-based polyurethanes are higher than these for BDO-based polyurethanes. The re-

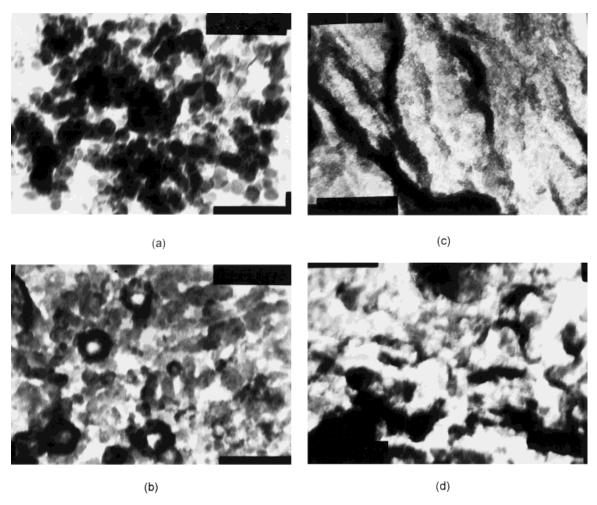


Figure 4 Transmission electron micrographs of polyurethanes (magnification 100,000×): (a) PU1000B2; (b) PU2000B2; (c) PU1000H2; (d) PU2000H2.

sults come from different stiffness of their hard segments and cohesion in their hard domains.

Morphological Structure

Four polyurethane samples with the same chemical composition (i.e., the same average hard segment length) were examined with transmission electron microscopy. Their micrographs are shown in Figure 4, in which the bright region represents soft segment phase, the dark region, and the hard segment domain. It is obvious that the hard segment domains disperse in the continuous soft segment phase, exhibiting the structure of phase segregation. The hard domain of HQEE-based polyurethane displays a banded structure, rather than the spherulitic structure present in the BDO-based polyurethane. This means the in-

terfacial phase region between the hard and soft segment phase of HQEE-based polyurethane is reduced and the degree of phase segregation is elevated, which is consistent with the foregoing results.

CONCLUSION

Compared with the BDO-based hard segment, due to the —O—O— linkage contained in HQEE, the hard segment based on it is more incompatible with polyether soft segment, and the cohesion in the hard domain is enhanced. The polyurethane based on HQEE as a chain extender shows better phase segregation and a higher extent of ordering in the hard domain. Besides

short-range hydrogen bonds, a considerable amount of long-range hydrogen bonds exist in amorphous phase of the hard domains. The soft segment is easier to crystallize and melting temperature of the hard domain is elevated in HQEE-based polyurethane. Its hard domain displays banded structure, rather than spherulitic structure present in BDO-based polyurethane.

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