

Synthesis and Structure–Property Relationships of UV-Curable Urethane Prepolymers with Hard–Soft–Hard Blocks

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SYNOPSIS

UV-curable urethane prepolymers derived from diisocyanates, rigid diols, and polypropylene glycols of different molecular weights and end-capped with 2-hydroxyethyl methacrylate were prepared by stepwise addition reactions. These prepolymers have the common structure, HEMA-hard segment-soft segment-hard segment-HEMA. As the weight ratio of soft segment to hard segment and thus the rigidity varied, the cured films from these prepolymers exhibited a wide range of mechanical and other key properties such as oxygen permeability.

INTRODUCTION

Polyurethanes are a unique class of polymers which have a wide range of applications because their properties can be readily tailored by the variation of their components. Polyurethanes are used extensively as foams, coatings, adhesives, elastomers, and fibers.¹ Many other applications have been explored.

Urethanes have also been prepared as radiation-curable prepolymers which may contain more than one polymerizable group such as acrylate and methacrylate units. They have been found in many demanding applications such as moisture-curing varnishes, coatings, and sealants.² These well-studied prepolymers were prepared by reacting polyols of diverse composition with excess diisocyanates and end capping with hydroxyalkyl acrylate or methacrylate. Unlike thermoplastic polyurethane elastomers, these prepolymers contained no well-defined hard segments and thus did not exhibit mechanical properties typical of thermoplastic elastomers.¹

When hard segments are built into the urethane prepolymer structure, it is expected that these prepolymers would preserve the excellent mechanical properties of the thermoplastic elastomers while remaining radiation curable. For example, prepolymers derived from aromatic diisocyanates, hydrogenated bisphenol-A, a polyetherdiol, and end

capped with 2-hydroxyethyl methacrylate (HEMA) have been claimed to have superior mechanical properties suitable for use as adhesives, sealants and coatings.³

In this paper, urethane prepolymers with well-defined hard–soft–hard segments were systematically studied and the structure–property relationships were obtained.

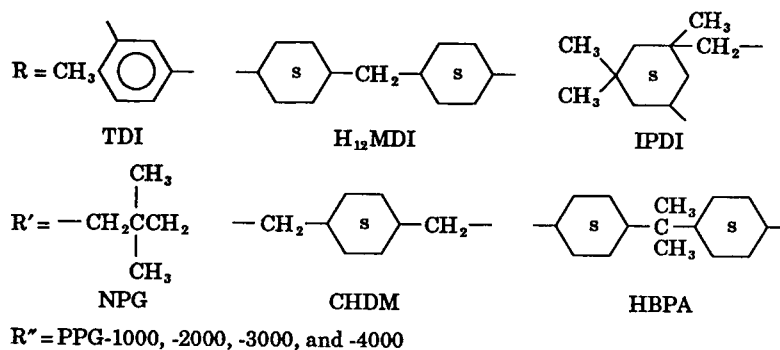
EXPERIMENTAL

Reagents/Monomers/Catalysts/Solvents

Toluene-1,4-diisocyanate (TDI, from Kodak), dicyclohexyl methane-4,4'-diisocyanates (H_{12} MDI, from Mobay), isophorone diisocyanate (IPDI, from Huls), and cyclohexane-1,4-dimethanol (CHDM, from Aldrich) were purified by distillation under reduced pressure before use. Polypropylene glycols (PPGs, from Olin) and hydrogenated bisphenol-A (HBPA, from American Tokyo Kasei) were dried under vacuum (60°C) before use. 2,2-Dimethyl-1,3-propanediol [or neopentyl glycol (NPG) from Aldrich] was purified by sublimation. HEMA was purified by distillation under reduced pressure.

The catalysts, 1,4-diazabicyclo[2,2,2]octane (Dabco, from Aldrich) and dibutyltin dilaurate (DBTDL, from Aldrich), were used as received. Benzoin methyl ether (BME) was recrystallized from methanol. Methylene chloride and toluene were dried over 4A molecular sieves.

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Scheme 1 (Continued)

The first step is the formation of the hard segment. The second step is the formation of the triblock polymer of the hard segment endblocks with the soft segment midblock, and the third step is the end-capping reaction. Prepolymers with longer hard segments or multiblocks were possible because they were prepared by stepwise addition reactions.

In order to study the structure–property relationships of acceptable optical quality cured films, a selected number of diisocyanates, short chain diols, and long chain flexible polyols were used to construct the prepolymers with different weight ratios of hard to soft segment. Thus films of a wide range of stiffness were obtained. The diisocyanates utilized were toluene-2,4-diisocyanate (TDI), dicyclohexyl methane 4,4'-diisocyanate (H₁₂MDI), and isophorone diisocyanate (IPDI). The rigid diols studied were neopentyl glycol (NPG), cyclohexane-1,4-dimethanol (CHDM), and hydrogenated bisphenol-A (HBPA). They offer hard segments of different stiffness because they contain 0, 1, and 2 rings, respectively. It should be noted that the CHDM used is a mixture of cis and trans isomers. Among the flexible polyols, PPGs of molecular weight 1000, 2000, 3000, and 4000 were used.

Because of high reactivities of diisocyanates,¹ particularly the aromatic diisocyanates, it is desirable to control the reaction conditions carefully to avoid side reactions, such as dimerization, trimerization, self-polymerization, allophanate, and urea formation. The reaction should be carried out in an inert atmosphere. The reaction temperatures were 45–80°C for the first and second steps and 45°C or below for the third step.

When TDI was used, there was no need to use a catalyst for the first step. In other cases either Dabco or DBTDL (0.1–0.5%) was used to promote the reaction. In order to favor the desired structure, the

diols were added in succession and the isocyanate content after each step of reaction was checked. The isocyanate content should be 50 and 25% of the original amount, respectively, after the first and second steps of the reaction sequence. The reaction were deemed complete when the isocyanate content was within 2% of the appropriate value.

When CHDM was used as the short chain diol, it was found that the hard segments derived were so crystalline (particularly when TDI was used) that precipitation could occur unless more solvent was used.

The Curing of Urethane Prepolymers

Because these urethane prepolymers were end-capped with methacrylate groups, they were readily polymerized with an initiator such as BME with UV. Because of the viscous nature of these prepolymers, it was preferred to cure them in solution to form films for characterization.

In general the cured films were transparent except those derived from H₁₂MDI. The solvent extractables were 5% or less, indicating the successful functionalization of the prepolymers and the efficiency of curing.

Structure–Property Relationships

The dried, cured urethane prepolymer films were characterized for their key physical properties. In the following, the oxygen permeabilities, contact angles, and important mechanical properties were described. These properties are important in possible applications such as biomedical devices.

Figure 1 shows the relationships of oxygen per-

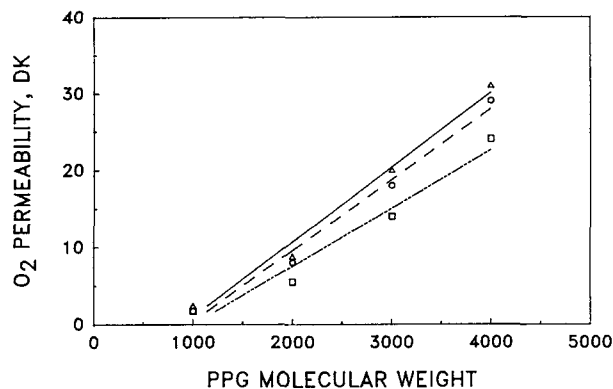


Figure 1 Oxygen permeability vs. PPG molecular weight in cured prepolymers TDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

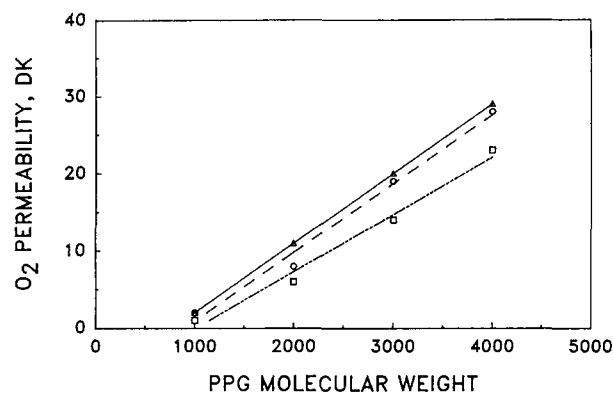


Figure 3 Oxygen permeability vs. PPG molecular weight in cured prepolymers H₁₂-MDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

meability of the cured films versus the molecular weight of PPG used for TDI-based prepolymers. As expected, the higher the molecular weight of PPG, the higher the oxygen permeability for each short chain diol, NPG, CHDM, and HBPA, used. For the same molecular weight of PPG used, among the three different diols used, NPG-based prepolymer gave the highest oxygen permeability and HBPA-based prepolymer gave the lowest oxygen permeability. Figures 2 and 3 illustrate the same relationships for IPDI- and H₁₂MDI-based prepolymers respectively and the same trends were observed. In general, the longer the soft segments, the shorter the hard segments and, thus, the higher the flexibility of the cured prepolymers, the higher the oxygen permeability of the cured polyurethane films. *Dk*'s as high as 33 were obtained when PPG-4000 was used.

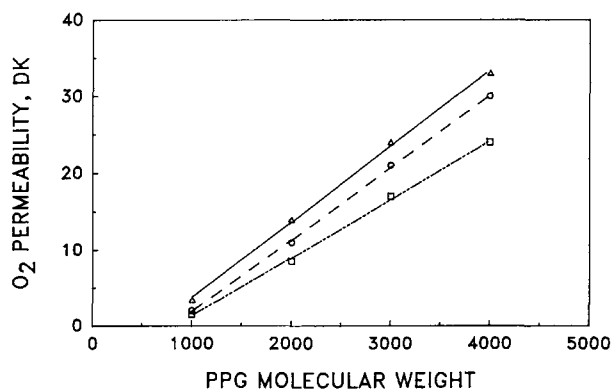


Figure 2 Oxygen permeability vs. PPG molecular weight in cured prepolymers IPDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

Figure 4 shows the relationship of oxygen permeability versus wt % PPG in the prepolymer. It was found that for the same wt % PPG, the TDI series gave lower *Dk* value than the IPDI and H₁₂MDI series. This indicates that the tight packing of the hard segment had an adverse effect on oxygen permeability. The two aliphatic diisocyanate series (IPDI and H₁₂MDI) had roughly the same degree of rigidity of the hard segments and have identical *Dk* values.

The contact angle is often a measure of surface wettability. This property of a polymer is important if it is to be used as a medical device. The contact angles of the cured urethane prepolymers were all in the range of 30–40°, indicating that they are wettable.

All cured polyurethane films were elastic in nature. Figure 5 shows the relationship of tensile mod-

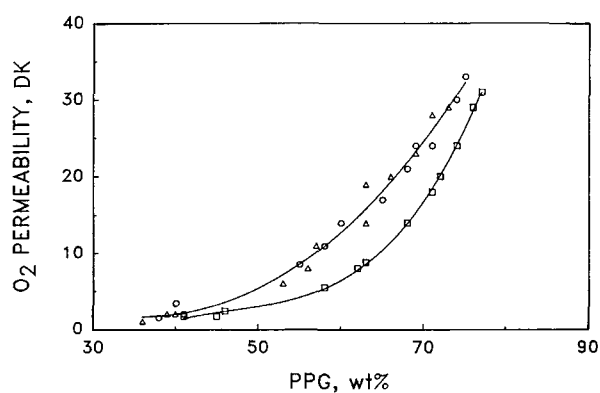


Figure 4 Oxygen permeability vs. PPG weight fraction in cured urethane prepolymers: (\square) TDI series; (\circ) IPDI series; (Δ) H₁₂MDI series.

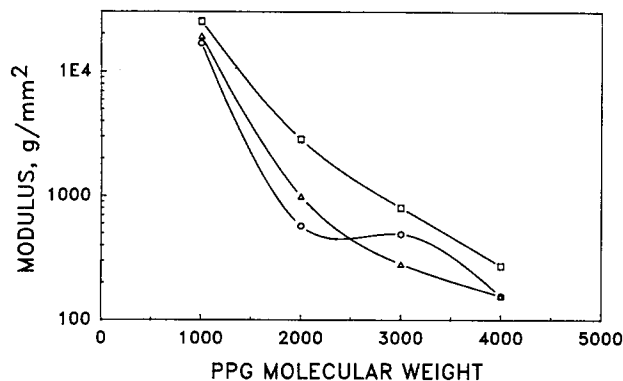


Figure 5 Modulus vs. PPG molecular weight in cured prepolymers TDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

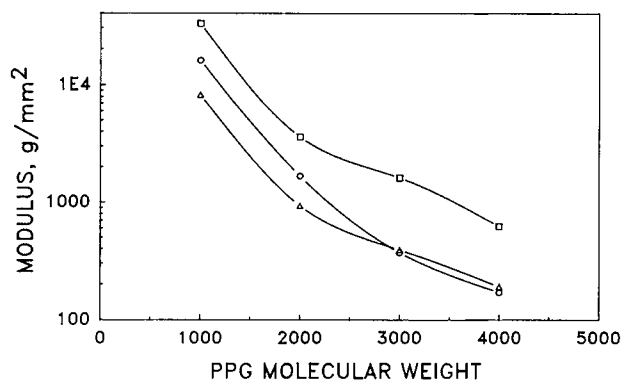


Figure 7 Modulus vs. PPG molecular weight in cured prepolymers H_{12} MDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

ulus of the cured films with the molecular weight of PPG for the TDI-based urethane prepolymers. The higher the molecular weight of PPG, the lower the modulus. For the same molecular weight PPG used, HBPA-based prepolymers gave the highest modulus, whereas NPG-based prepolymers gave the lowest modulus. This can perhaps be explained by the difference in the ratio of hard to soft segments and crosslinking density. Larger hard to soft segment ratios and higher crosslinking densities gave films with higher modulus. Figures 6 and 7 illustrate the same relationships for the IPDI- and H_{12} MDI-based prepolymers, respectively. The same correlations were found in these two series of prepolymers. In general, CHDM-based prepolymers gave cured films with less predictable characteristics in modulus. This may be due to the high crystalline nature of the hard segments. The modulus of the prepolymers

in this study ranged from 33000 to 100 g/mm^2 , which provides latitude for potential biomedical device applications.

Figure 8 shows the relationships of the tear strength of the cured films with the molecular weight of PPG for the TDI-based urethane prepolymers. The tear strengths of the cured films were too high to be measured for prepolymers derived from PPG of M_n 1000. The tear strength decreased as the molecular weight of PPG increased. In general, HBPA-based prepolymers gave the highest tear strength, while NPG-based prepolymers gave the lowest tear strength. When PPG of molecular weight 4000 was used, all the prepolymers gave the same tear strengths as they approximately had roughly the same hard to soft segment ratio as well as the same crosslinking density. Finally Figures 9 and 10 illustrate the same relationships for the IPDI- and

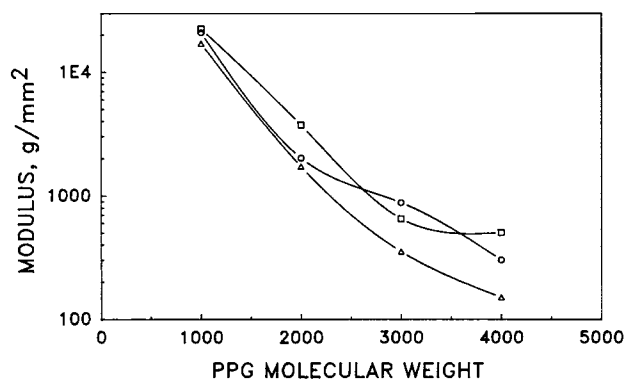


Figure 6 Modulus vs. PPG molecular weight in cured prepolymers IPDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

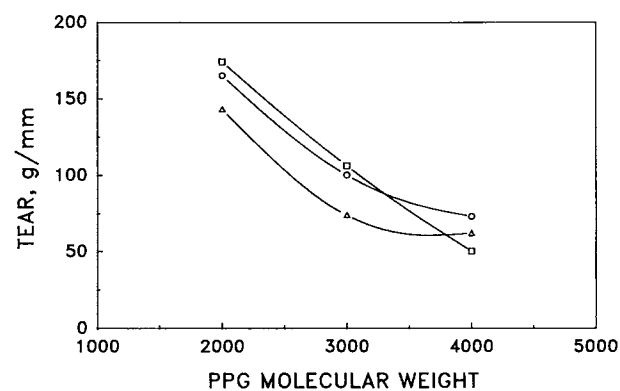


Figure 8 Tear strength vs. PPG molecular weight in cured prepolymers TDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

H₁₂MDI-based prepolymers. The same correlations held, except that the CHDM-based prepolymers had higher tear strengths than those of HBPA-based prepolymers in the H₁₂MDI series. The tear strengths of the cured prepolymers in this study are all higher than 50 g/mm.

These prepolymers, because of their diverse modulus and high tear strengths, provide a wide latitude for various application studies, including their potential for biomedical applications.⁵

CONCLUSION

UV-curable urethane prepolymers with well-defined hard-soft-hard block structures were prepared. The cured materials demonstrated excellent physical properties and provide the foundation for many potential applications.

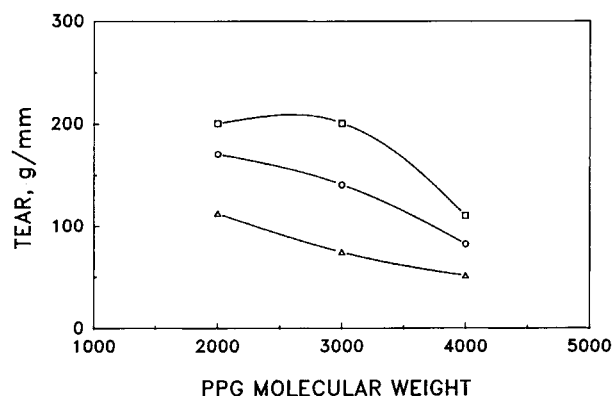


Figure 9 Tear strength vs. PPG molecular weight in cured prepolymers IPDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

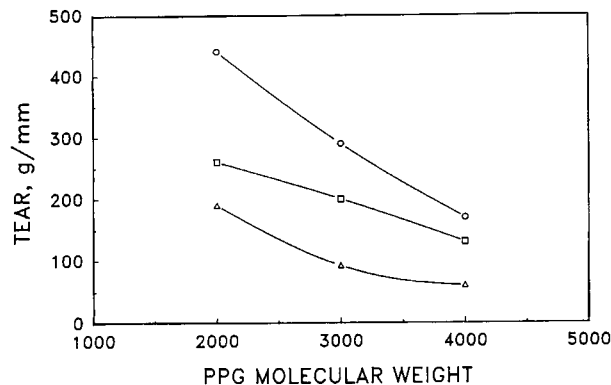


Figure 10 Tear strength vs. PPG molecular weight in cured prepolymers H₁₂MDI series: (Δ) NPG; (\circ) CHDM; (\square) HBPA.

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