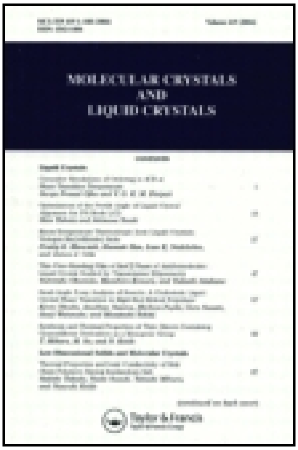

Molecular Crystals and Liquid Crystals

Synthesis of High-performance Polyurethane Elastomers with Ultra-low Monol Content Poly(oxy propylene)

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SYNTHESIS OF HIGH-PERFORMANCE POLYURETHANE ELASTOMERS WITH ULTRA-LOW MONOL CONTENT POLY(OXY PROPYLENE)

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For a fundamental understanding of the unsaturation (monol) content effect in propylene oxide based polyether polyols (PPG) on the properties of 4,4′-methylene diisocyanate/1,4-butanediol cured polyurethane (PU) elastomers, a series of PPG samples with different monol content from 0.035 to 0.005 meq/ were synthesized by using both KOH and double metal cyanide catalysts. The monol content contained in PPG is demonstrated to be a key factor to achieve high-performance PU elastomer. The mechanical properties of low monol PPG derived PU approached to those of poly(tetramethylene ether glycol) derived PU. The narrow MWD of PPG together with low monol content results in a reduction of viscosities of both PPG and resulting PU prepolymer.

Keywords: double metal cyanide catalyst; mechanical property; polyether polyols (PPG); polyurethane; unsaturation (monol)

INTRODUCTION

Propylene oxide based polyether polyols (PPG) are used in a wide range of polyurethane applications. These polyoxypropylene polyols are produced commercially through the base catalyzed (using an alkali metal salt such as KOH) propoxylation of so-called starters (or initiators), which have two or more hydroxyl groups. It is well known that base catalyzes not only the addition of propylene oxide to the growing polymer molecule, but also a side reaction in which propylene oxide isomerizes to allyl alcohol [1,2]. Allyl alcohol acts as a monofunctional

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*Corresponding author. Tel.: +82-51-510-2466, Fax: +82-51-513-7720, E-mail: ilkim@pnu.edu starter resulting in the production of the propoxylated allyl alcohol, often referred to as monol.

Double metal cyanide (DMC) complexes are also well-known catalyst for the polymerization of epoxides and the synthesis of PPG [3]. The DMC catalyst, originally discovered by General Tire Inc. [4], was revisited starting in the middle of 1980's, with improvements made by some companies – including ARCO [5], Shell [6,7], and Asahi Glass [8]. The DMC catalysts produce PPG with reduced levels of unsaturation (typically 0.015 to 0.002 meq/g) relative to conventional KOH catalyzed PPG (typical unsaturation of 0.03 to 0.10 meq/g) [5]. The mechanical properties and processing characteristics of polyurethane (PU) elastomers derived from PPG with high monol content are inferior to those prepared from high performance polyols like poly(tetramethylene ether glycol) (PTMEG) [1]. The relatively low molecular weight propoxylated allyl alcohol (monol) acts as a chain terminator, disrupting the chain reaction required to build a high molecular weight polymer. Thus, as the monol content increases, the functionality of the polyol decreases and thus the ultimate molecular weight of any segmented elastomer formed from the macroglycol is diminished. Accordingly, KOH catalyzed PPG cannot be utilized for the applications requiring high-performance elastomers. The DMC catalyzed PPGs have much lower monol contents and might be utilized for the high-performance applications.

It is the purpose of this report to investigate the effect of monol content (PPG functionality) on the mechanical properties of PUs. We also compare KOH- and DMC-catalyzed PPG to PTMEG. The elastomers produced with low monol PPGs expected to have enhanced properties in contrast to those based on conventional base-catalyzed PPG. However, there have been no detailed reports investigating the effect of monol content on the properties of resulting elastomers.

EXPERIMENTAL

Material

1.4-Buthanediol (Aldrich) was distilled and stored over Linde type 4 A molecular sieves. Dimethylformamide (DMF, Aldrich) was dried by stirring with $MgSO_4$. 4,4′-Methylene diisocyanate (MDI) purchased from Aldrich were used as received. Polymerization grade of propylene oxide (PO) and polytetramethylene ether glycol (molecular weight = 1800; PTMEG) were donated by SKC Company (Korea) and BASF Korea Ltd., respectively. PPGs containing different amount of monol were synthesized by using KOH catalyst (**PPG-1**) or DMC catalyst (**PPG-2** and **PPG-3**) according

TABLE 1 Characterization of PPGs and PTMEG used in this Study

			^{13}C NMR (mol%)			GPC	
Sample	Cat. Used	Unsaturation (meq/g)	*mm*	*mr*	*rr*	M_n(g/mol)	MWD
PPG-1	KOH	0.035	27.2	38.8	34.0	3590	1.11
PPG-2	DMC	0.013	24.2	27.3	48.5	4180	1.04
PPG-3	DMC	0.005	18.0	32.2	49.8	4290	1.04
PTMEG	–	0.0	–	–	–	1800	2.21

to the reported procedures [1]. The characterization result of the polymers are summarized in Table 1.

Synthesis of PU Elastomer

The PU elastomer of its functionality of 2 was prepared according to a conventional method [1,4,5] using 1,4-butanediol as a chain extender and controlling hard segment (HS) from 34 wt% to 19 wt%. The PU prepolymer mixture was blended uniformly and poured into the molds (100 × 10 × 0.7 mm) and cured at 100°C for 24 h in an air-circulating dry oven.

Characterization

Infrared (IR) spectra of the polyurethane film were obtained in transmission mode using a React IR (Asi Applied system). ^{1}H and ^{13}C NMR spectra of the polyols were performed on a Varian Gemini 2000 with $CDCl_3$ as a solvent. The total degree of unsaturation of polyols was measured by titration method according to ASTM D2847. Molecular weight distribution (MWD) was measured using a Waters 150 instrument operated at 25°C, with a set at 10^4, 10^3, and 500 angstroms columns. Polystyrene standard with low polydispersities were used to generate a calibration curve.

The tensile strength tests of PU elastomers (100 × 10 × 1 mm in size) were carried on an Instron 4466 according to the specification of ASTM D882. The crosshead speed was set at 500 mm/min. For each data point, three samples were tested and the average value was taken and reported. Thermal property of PU elastomers were assessed by DSC with a Seiko model 220 differential scanning calorimeter (DSC). In all cases, samples were cooled to about –100°C and heated to 100°C at a rate of 10°C/min, cooled again to –100°C, and heated again to 100°C at a rate of 10°C/min, employing a nitrogen purge. Result of the second heating run were normalized on a weight basis.

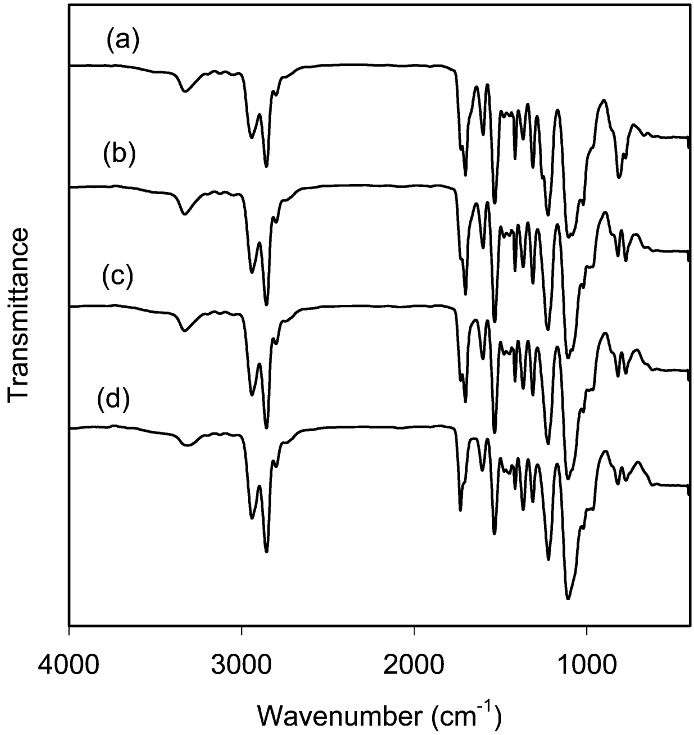

FIGURE 1 Infrared spectra of **PPG-3** based PU elastomer films of different hard segment: (a) 34, (b) 29, (c) 24, and (d) 19 wt%.

RESULTS AND DISCUSSION

PPG samples showing different monol content (from 0.035 to 0.005 meq/g) were synthesized by using both KOH and DMC catalysts as shown in Table 1. Even if they have somewhat different molecular weight, polydispersity, and microstructure, it may be assumed that the differences have little influence on the physical properties of resulting polyurethanes. As a result the physical properties of PU elastomers synthesized by the same procedure is assumed to be mainly influenced by the monol content of polyol. Analysis of the PPGs using ^{13}C NMR spectroscopy showed that they have a random distribution of the configurational sequences and head-to-tail regiosequence, even if the amount of [*rr*] triad of PPF produced by DMC catalyst was larger than that of POP by conventional KOH catalyst.

PTMEG has higher reactivity primary hydroxyl groups and can therefore be used in both one-shot and prepolymer processing. However, PPG, with

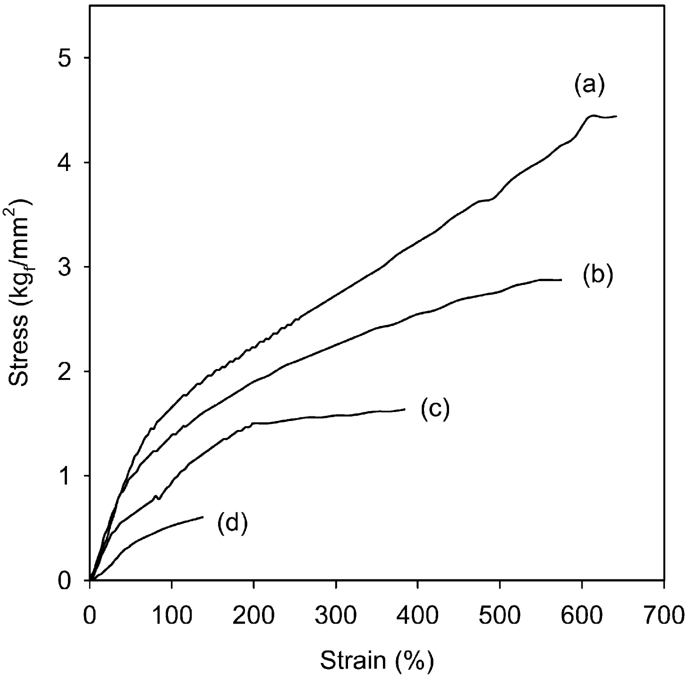

FIGURE 2 PU elastomer (HS = 29 wt%) stress/strain curves derived from various PPG of (a) **PTMEG**, (b) **PPG-3**, (c) **PPG-2**, and (d) **PPG-1**.

their secondary hydroxyl groups, need to be prepared with diisocyanate to form a prepolymer. Excess MDI was added to the PPG and reacted at 80°C in an inert atmosphere until all hydroxyl group reacted. After preparing the prepolymer, the next step was that of chain extension with a 1,4-butanediol to make the final polyurethane elastomers. The hard segment contents were controlled on the basis of urethane content, as described by Flory (Eq. (1)):

$$\%HS = \frac{100(R-1)(M_{di}+M_{do})}{(M_g+R(M_{di})+(R-1)(M_{do}))} \tag{1}$$

where M is number average molecular weight, R is the mole ratio of isocyanate to PPG and subscripts g, di, and do refer to PPG, MDI, and 1,4-butanediol (mole average molecular weight), respectively.

Figure 2 shows IR spectra of PU films using **PPG-3** (monol content = 0.005 meq/g) by controlling the hard segment 19, 24, 29, and 34 wt%. Films were cast from the polymer-DMF solutions on glass plates using a doctor blade to achieve final post-drying film thickness ranging

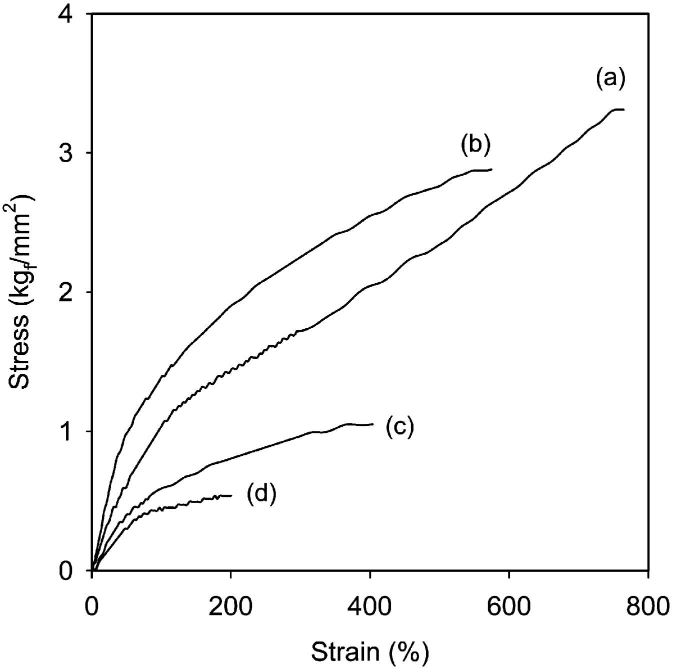

FIGURE 3 PU elastomer (HS = 19 wt%) stress/strain curves derived from various PPG of (a) **PTMEG**, (b) **PPG-3**, (c) **PPG-2**, and (d) **PPG-1**.

from 0.6 to 0.7 mm. Immediately on casting, the coated glass plates were placed within a circulating hot air oven heated to 100°C for a period over 2 h. The uniform PU elastomers films could be straightforwardly obtained by employing these procedures as shown in Figure 2, appearing 2600–3000, 930–950, 1100–1110 and 1445–1450 cm^{-1} arising from PPG and 1720–1730 cm^{-1} arising from urethane C=O linkage.

In order to investigate the basic performance of PPGs produced in this study as a raw material for PU elastomers, the stress-strain behavior of PU films fabricated by the same conditions was investigated. Figure 2 shows the stress-strain curves of PU films (HS = 29 wt%) fabricated by using PPGs with different monol content. PTMEG-based PU film was also synthesized for the comparison. The tensile behavior of a strained thermoplastic elastomer generally depends on the size, shape, and concentration of the hard domain, intermolecular bonding within the hard domains, and the ability of the soft segment to crystallize under strain [9,10]. If we assume these factors are not the decisive ones since all samples were prepared by using PPG with similar molecular weight at the same conditions, the unsaturation level of PPG seems to deeply influence elastomer properties. Lower unsaturation content clearly has a positive effect on all elastomer mechanical properties. Dramatic property improvements are seen comparing elastomer based on KOH-catalyzed PPG with that of DMC-based PPG. The stress-strain curves in Figure 2 clearly show that the elastomer based on low monol PPG exhibits much greater modulus build with increasing elongation. Dynamic mechanical thermal analysis (DMTA) showed that the polymers derived from **PPG-3** and **PTMEG** have better defined morphologies, with sharper transitions, indicating better phase separation between hard and soft segment domains. The glass transition temperatures **PPG-1**, **PPG-2**, **PPG-3** and **PTMEG** derived polymers were -37.0, -70.2, -75.1, and 11°C, respectively.

Similar stress-strain behavior of the PU films of different hard segment (HS = 19, 24, and 34 wt%) was observed. Figure 3 shows stress-strain curves of the PU elastomer (HS = 19 wt%). Again it can be seen that there is a clear improvement of mechanical properties by using low monol PPG, approaching to the quality of PTMEG derived PU elastomer. All this improvements indicate that significant changes occur in the polymer as the monol content is reduced. The reduction of monol content means an increase of the PPG functionality. As a result the benefits are attributable to an increase in the PU molecular weight. Slightly raising the functionality from 1.94 (**PPG-1**) to 1.98 (**PPG-3**) by reducing the monol content increases the ultimate PU molecular weight by a factor of three from 84,000 to 280,000 (calculated from the Carothers equation).

The narrow MWD of **PPG-3**, with a secondary hydroxyl group, results in viscosity which is an order of magnitude lower than PTMEG, 165 cP (at 40°C) vs. 1200 cP (at 40°C). The handling requirements for **PPG-3** is minimal since it is noncrystallizing liquids with pour points of about -30°C. In addition PU based on noncrystallizing **PPG-3** will not cold harden like PTMEG. Accordingly the PU prepolymer (HS = 19 wt%) based on **PPG-3** had a viscosity one tenth of the PTMEG prepolymer, 2150 cP (at 40°C) vs. 24800 cP (at 40°C). This lower viscosity seems to be due to the substantially narrower MWD of PPG-3 and to a lesser degree, the higher NCO/OH of the **PPG-3** based prepolymer. Lower viscosity prepolymers offer advantages in processability. This gives the PU manufacturer much more latitude in terms of processing conditions such as temperature and catalyst combinations.

CONCLUSION

A series of PPG samples with different monol content from 0.035 to 0.005 meq/g were synthesized by using both KOH and DMC catalysts.

We showed that the reduction of monol content in PPG is a key factor to achieve high-performance PU elastomer. The reduction of monol results in PU elastomers showing much higher final molecular weight and thus improved mechanical properties, approaching to those of the PTMEG derived PU. The narrow MWD of PPG together with low monol content results in a reduction of viscosities of both PPG and resulting PU prepolymer. A fundamental understanding of the monol effect allows one to obtain the maximum benefits from the low monol PPG and to realize the opportunity for designing new high performance PU products.

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