Effect of the structure of chain extenders on the dynamic mechanical behaviour of polyurethane

J. Y. BAE, D. J. CHUNG, J. H. AN*
Department of Polymer Science and Engineering, SungKyunKwan University, Chunchun-dong 300, Changan-gu, Suwon, 440-746, Korea
E-mail: jhahn@yurim.skku.ac.kr

D. H. SHIN
Cheil Synthetic Textiles Co. Ltd., #14, Nongseo-ri, Kiheung-eub, Yongin-gun, Kyunggi-do, Korea

The dynamic mechanical behaviors of polyurethanes with different types of non-linear chain extenders are compared with those of corresponding linear chain extender. The T_g of the soft segment matrix showed much variation depending on the type of the chain extenders. The use of non-linear chain extender results in at least 30 °C shift toward the higher temperature compared with the sample with 1,4-butanediol. The softening temperature of the hard segment domains is dependent on the detailed structure of the chain extender. Cyclic chain extender and some chain extenders with pendent groups showed a quite significant increase in the softening temperature and well-developed rubbery plateau regions. In tan δ peaks, the peak representing the soft segment matrix becomes much sharper and larger when non-linear chain extenders are employed.
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1. Introduction

Polyurethanes are known to be very attractive material for sound and vibration damping application, since it is possible to change its range (narrow or broad) as well as the position of glass transition by controlling the chemical structure. This is certainly due to the varieties of morphology that polyurethane can provide. Thermoplastic elastomers based on polyurethanes are block copolymers composed of hard and soft blocks. Since the soft and hard segments are chemically dissimilar, they are phase separated. Depending on the incompatibility level between the soft and hard segment as well as the degree of interaction among the same segments, the hard segments may form discrete domains or be dispersed in a soft segment matrix. In the former case, two separate glass transitions could be observed and either one or both of soft segments and hard segment phase could be crystallized [1–3].

In this report, dynamic mechanical spectroscopy has been employed as a major tool for the investigation of polyurethane. The dynamic mechanical spectroscopy has been used in the study of many block copolymer systems such as polystyrene-diene based one [4–7]. However, there exists a major difference between polystyrene based block copolymer and segmented polyurethane. The styrene based block copolymers are amorphous material with only a few relatively high molecular weight blocks. In many cases, the domain size is large enough to allow the direct observation

by Transmission Electron Microscopy. Therefore, the interpretation of the dynamic mechanical spectra is relatively straight forward. On the other hand, in the case of the segmented polyurethane, the length of each blocks is very short and the domain composed of the hard segment is too small for the direct observation. The possibility of crystallization and hydrogen bonding makes the interpretation of the dynamic mechanical spectra more complicated.

In this study, the dynamic mechanical spectra of the polyurethane containing several different types of chain extender are compared while the types and molecular weight of the soft segment as well as diisocyanate are fixed. By introducing the chain extender with different bulkiness as well as rigidity, it may provide the change in the degree of phase mixing, hard domain structure and hydrogen bonding.

2. Experimental
2.1. Materials
As a polyol, poly(tetramethylene ether) glycol [PTMG M.W. = 1000; Aldrich] is used after vacuum dried and 4,4′-diphenylmethane diisocyanate [MDI, Tokyo Kasei] is used as received. The chain extenders used in this study are summarized in Table I.

2.2. Preparation of specimen
Preparation of the polyurethane was carried out by the two-step method [8]. Prepolymer was obtained by the

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* Author to whom all correspondence should be addressed.

TABLE I Chain extenders for polyurethanes

Diols	Structures
1,3-Propanediol	$HO-CH_2-CH_2-CH_2-OH$
1,4-Butanediol	$HO-CH_2-CH_2-CH_2-CH_2-OH$
1,5-Pentanediol	$HO-CH_2-CH_2-CH_2-CH_2-CH_2-OH$
1,4-Pentanediol	$HO-CH_2-CH_2-CH_2-CH-OH$ $\quad\quad\quad\quad\quad\quad CH_3$
2,5-Hexanediol	$HO-CH-CH_2-CH_2-CH-OH$ $\quad\quad CH_3 \quad\quad\quad\quad CH_3$
2,5-Dimethyl-2,5-hexanediol	$\quad\quad CH_3 \quad\quad\quad CH_3$ $HO-C-CH_2-CH_2-C-OH$ $\quad\quad CH_3 \quad\quad\quad CH_3$
1,4-Cyclohexanediol	$HO-\langle\hexagon\rangle-OH$
1,4-Cyclohexanedimethanol	$HO-H_2C-\langle\hexagon\rangle-CH_2-OH$

Figure 1 The tan δ of polyurethanes containing linear chain extenders with different length.

Figure 2 Storage modulus of polyurethanes containing linear chain extenders with different length.

reaction of PTMG and MDI. Diisocyanate was added in excess, then the mixture was stirred continuously for half hour at 55–60 °C. The prepolymer was then reacted with the chain extenders. The mixture was stirred continuously for 15 min. The mix was degassed after becoming viscous and was poured into mold. The contents in the mold were cured in oven at 100 °C for 16 h. The molar ratio of PTMG : MDI : chain extender is 1 : 3 : 2 in all synthesis.

2.3. Characterization

The dynamic mechanical spectrum is recorded with Dynamic Mechanical Thermal Analyzer (Polymer Laboratory Inc.) at 1 Hz with a heating rate of 3 °C/min. Samples are band shape ($3.8 \times 10 \times 5$ mm) and are measured in a single cantilever mode.

Differential scanning calorimetry has been employed to check the crystallinity of each sample and glass transitions with Perkin Elmer Model DSC 7 using 10 °C/min of heating rate.

3. Results and discussion
3.1. Polyurethane chain extended with linear chain extender

Figs 1 and 2 compare the tan δ and storage modulus of polyurethanes containing three different types of linear chain extender, 1,3-propanediol, 1,4-butanediol and 1,5-pentanediol. In Fig. 1, the decrease in the glass transition representing the soft segment phase with increasing methylene groups in the chain extender is observed, even though it is marginal (4–5 °C). The decrease in T_g could be attributed to the decrease in polarity and additional flexibility by the increasing number of methylene sequence in the chain extender. The similar trend has been observed in other works [9] by DSC characterization using a homologue series of diols. When the storage moduli shown in Fig. 2 are compared, the modulus of 1,4-butanediol chain extended samples shows slightly higher value compared with the other two. This is probably due to the difference in the hard segment structure depending on whether the chain extender has an even or odd number of methylene groups as pointed out in Blackwell's work [10].
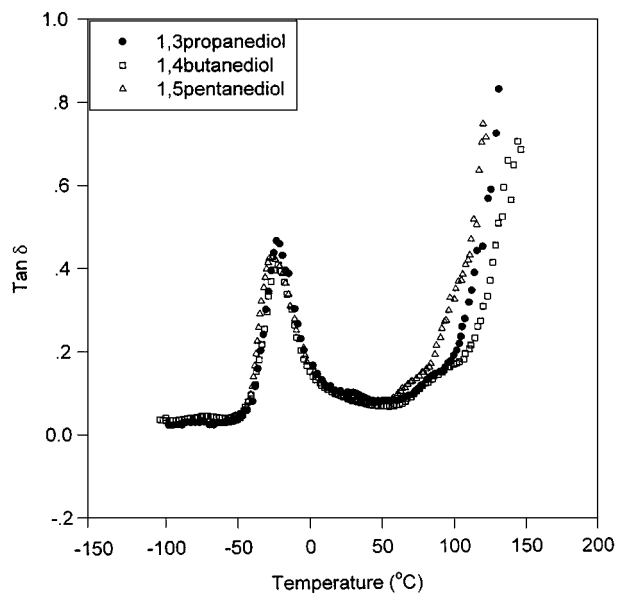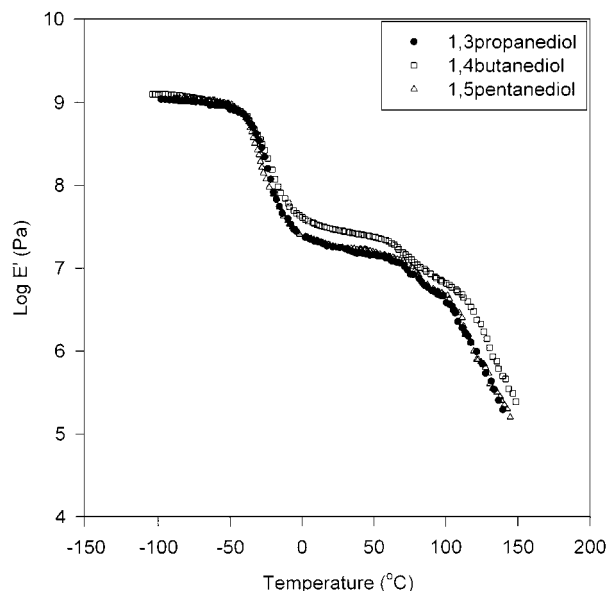
The even diol adopts the lowest energy fully extended conformation that allows for hydrogen bonding in both directions perpendicular to the main axis, which is not possible in odd diol. If compared among even diol or among odd diols separately, the polyurethane with higher number of methylene units in the chain extender is expected to have lower modulus as exemplified in Camberlin et al.'s work [11], in which the polyurethane with 1,10-decanediol showed lower modulus in rubbery plateau region compared with 1,4-butanediol. However, almost similar modulus values are observed in both 1,3-propanediol and 1,5-pentanediol in our case. All of the samples show the decrease in modulus around 70 °C as a result of hard segment softening.
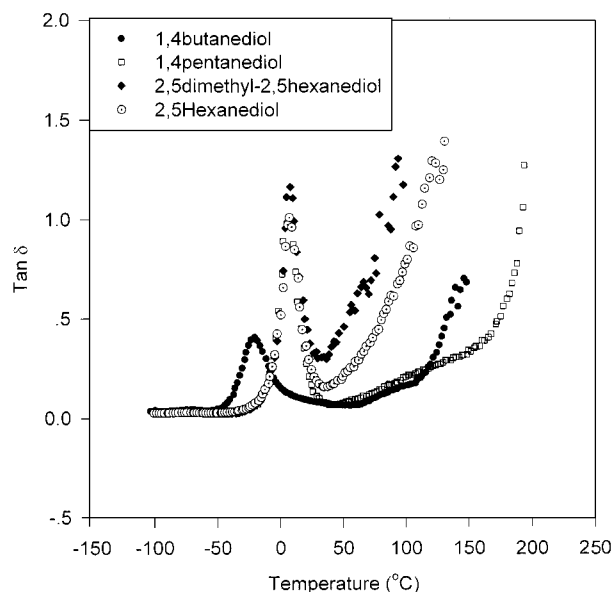
Figure 3 Effect of pendent groups in the chain extender on the tan δ behaviour of polyurethanes.

Figure 4 Effect of pendent groups in the chain extender on the storage modulus behaviour of polyurethanes.

3.2. Polyurethane chain extended with non-linear chain extender

In Fig. 3, the tan δ behaviors of polyurethane with three different types of non-linear chain extenders are compared with that of 1,4-butanediol. The all of the non-linear chain extenders, 1,4-pentanediol, 2,5-hexanediol, and 2,5-dimethyl-2,5-hexanediol have the same numbers of carbons in the main chain as 1,4-butanediol has, while introducing different numbers or shape of pendant groups. The tan δ behavior can be separated into two groups, the sample with 1,4-butanediol showed tan δ peak representing the soft segment matrix at much lower temperature (around 30 °C lower) as well as with much smaller height compared with the other three samples with non-linear chain extenders. The increase in the soft segment T_g could be explained based on two different points of views. It can be either due to the presence of hard segments in the soft-segment matrix or due to the restrictions introduced by the hard-segment domains where the chain ends of the soft segment were anchored. It is not probable that the chain end restriction results in such substantial increase in the soft segment T_g, since Camberlin and Pascault [12] has shown that the chain end restriction could raise only about 4 °C when the chain extender is varied from 1,4-butanediol to 4,4′-methylene bis(2-chloroaniline). Therefore, such a large increase in the T_g suggests that the soft segments phase contains a substantial amount of hard segments. In fact, if we take the reported values of the glass transition temperature of PTMG and the hard segment composed of 1,4-butanediol and MDI, which are −48 °C [13] and 110 °C [14], respectively, the glass transition temperature of the soft segment matrix containing non-linear chain extender is near to the value calculated from equations assuming completely miscible state such as Fox equation.

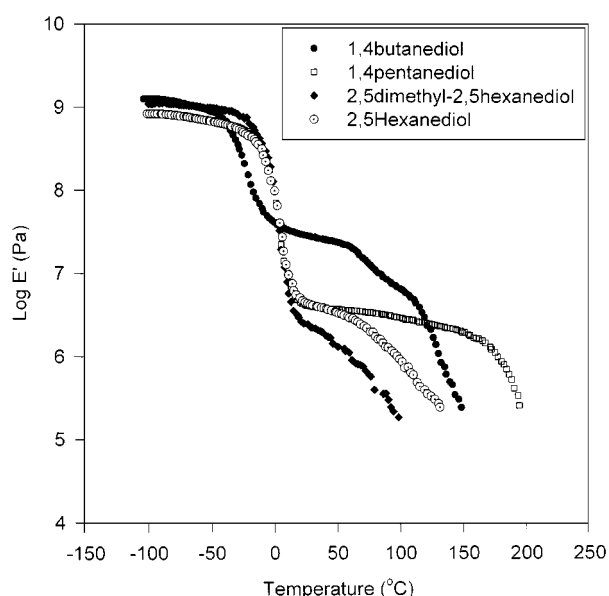The height of tan δ peak is clearly dependent on the choice of the chain extenders. Also, the area under the

tan δ of the samples with non-linear chain extenders becomes larger compared to 1,4-butanediol. Since this peak is representing the soft segment phase, such difference might be caused by different degree of phase mixing or chain end restriction by the hard segments. The peak area is known to have some dependence on the phase volume [15, 16]. Therefore, in the case of non-linear chain extender, the substantial amount of hard segments included in the soft segment matrix may cause the increase in the volume of the soft segment matrix, then result in the increase in the peak area. However, since there exists no known theory that can provide a quantitative relation between the peak height or area and the structural information of the system, we can not make a judgment on the detailed cause of such variation.

The storage modulus behavior in Fig. 4 shows two characteristic features. First, all of the non-linear chain extenders result in higher soft segment glass transition temperatures compared with linear 1,4-butanediol, while almost same glass transition temperatures are observed among non-linear chain extenders. Secondly, the softening temperature of the hard segments shows the dependence on the detailed structure of non-linear chain extender. As the structure of non-linear chain extender becomes simpler, the softening temperature is shifting from 10 °C for 2,5-dimethyl-2,5-hexanediol to 170 °C for 1,4-pentanediol. Also when the modulus in the plateau region is compared, that of 1,4-butanediol is higher than those composed of other non-linear chain extenders, suggesting that the hard segment based on 1,4-butanediol has well-ordered structure, such as crystal. It can be confirmed from DSC characterization shown in Figs 5–7. In Fig. 5, the polyurethane based on 1,4-butanediol is annealed at various temperatures. The endotherm peak which is believed to be the melting of hard segments composed of MDI and 1,4-butanediol, appeared around 60 °C. With increasing annealing temperature, it is shifted to the higher temperature. On
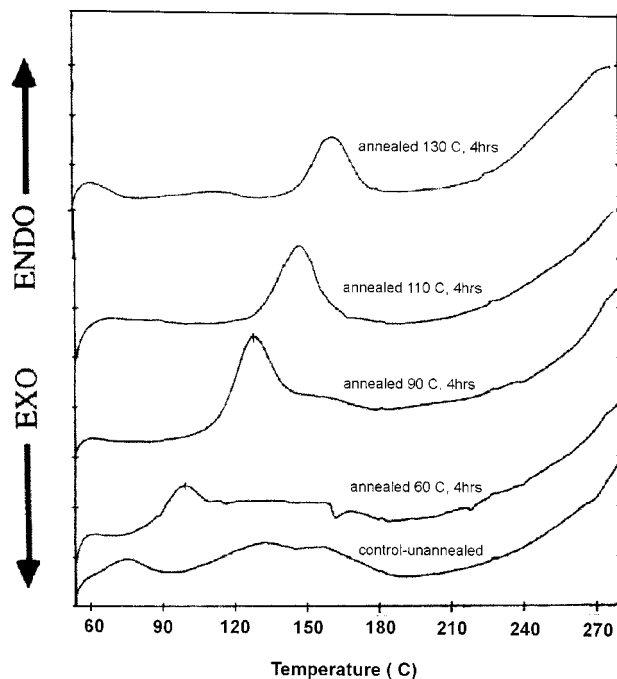
Figure 5 DSC thermogram of the polyurethane chain extended with 1,4-butanediol under different annealing condition.
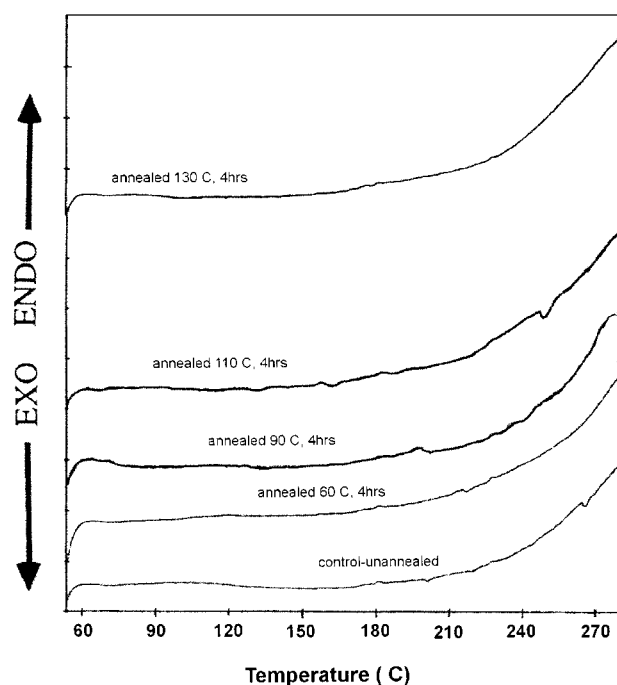

Figure 6 DSC thermogram of the polyurethane chain extended with 1,4-pentanediol under different annealing condition.

the other hand, when the polyurethane is chain extended with either non-linear chain extender (Fig. 6) or cyclic chain extender (Fig. 7), any significant endotherm peaks can not be found with various annealing conditions.

When the modulus is compared among non-linear chain extenders, 1,4-pentanediol that has the simplest structure among tested, shows well-extended plateau region while this plateau region becomes shortened as the chain extenders are getting bulkier, indicating that the bulkiness of the chain extender is preventing the
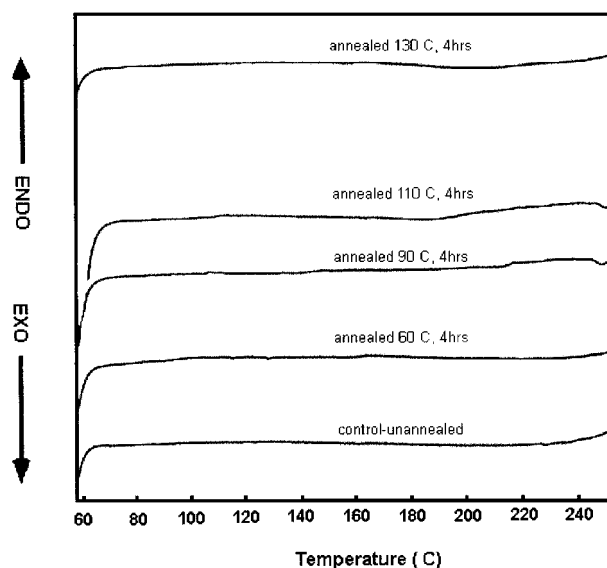

Figure 7 DSC thermogram of the polyurethane chain extended with 1,4-cyclohexanediol under different annealing condition.

hard segment domain formation. Also, the decrease in the hydrogen bonding and the facilitated phase mixing due to the presence of the pendant groups might be the cause of the softening temperature variation. It is worth while to note the behavior of 1,4-pentanediol, which has the behavior of typically phase separated system, such as well-developed rubbery plateau region. However, since this system shows more phase mixing compared to 1,4-butanediol if judged based on the shift of soft segment T_g, they seem to contradict each other.

Therefore, the polyurethane containing non-linear chain extender seems to have quite different overall morphology compared with that of 1,4-butadiol. In the case of 1,4-butanediol, the hard segments will form well-ordered association and crystals due to the effective hydrogen bonding, resulting in microcrystalline hard segment domains dispersed in the soft segment matrix. On the other hand, when the non-linear chain extenders are used, the hard segments are difficult to have ordered structure due to the bulkiness of the chain extenders even though a certain degree of hydrogen bonding is possible. Then, the polyurethane with non-linear chain extender might have non-crystalline hard segment domains with less degree of order.

3.3. Polyurethane chain extended with cyclic chain extender

When the chain extender is changed to cyclic types such as 1,4-cyclohexanediol and 1,4-cyclohexanedimethanol, the overall trend is very similar to the previous non-linear chain extender case. In Figs 8 and 9, the dynamic mechanical behaviors are summarized. The glass transition temperature of the soft segment phase is decreasing in the order of 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol, and 1,4-butanediol. Also, the polyurethane with 1,4-butanediol has the higher modulus value in the plateau region compared to the other samples with cyclic chain extender. The length of rubbery plateau region in the polyurethane with
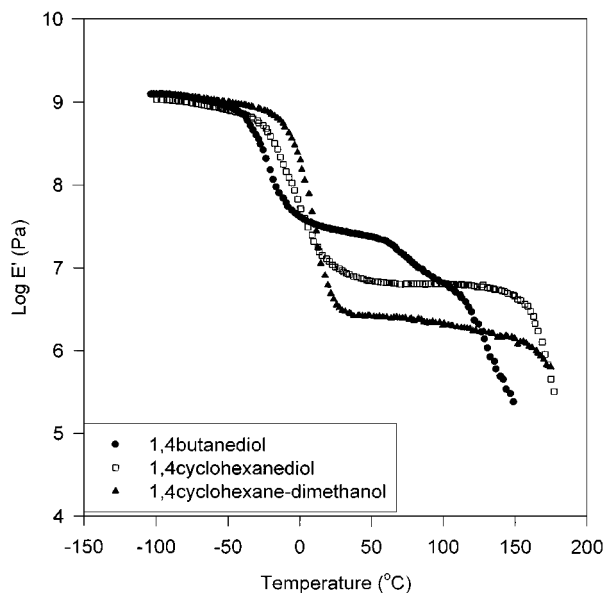
Figure 8 Comparison of storage modulus behaviour between polyurethane with cyclic chain extenders and polyurethane with 1,4-butanediol.
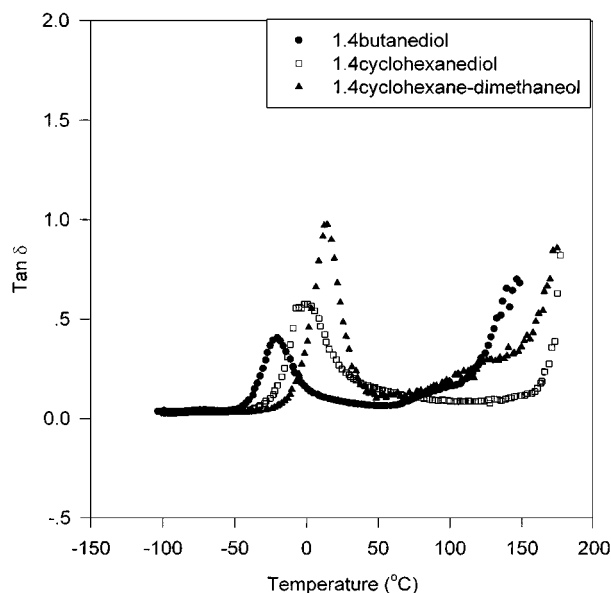

Figure 9 Comparison of tan δ behaviour between polyurethane with cyclic chain extenders and polyurethane with 1,4-butanediol.

cyclic chain extender is comparable to 1,4-pentanediol in Fig. 4 and the softening points of hard segment are around 170 °C, suggesting that the use of the slightly bulky chain extender result in the extended rubbery plateau region. On the other hand, when 1,4-butanediol is employed, the softening of the hard segment begins at much lower temperature.

The tan δ behavior in Fig. 9 indicates that the sample with 1,4-cyclohexane-dimethanol has the highest glass transition temperature as well as the largest peak among three samples. If the structure of 1,4-cyclohexane-dimethanol is compared with 1,4-cyclohexanediol, the presence of additional methylene linkage should provide more flexibility when linked with soft segments. Therefore, the chain end restriction seems to be not the

major reason for the variation in the T_g of the soft segment phase, suggesting that it is due to the difference in the degree of phase mixing.

4. Conclusions

The comparison of the dynamic mechanical behavior between various non-linear chain extender and 1,4-butanediol can be summarized as follows. First, the T_g of soft segment phase is always higher for non-linear chain extender than 1,4-butanediol and the difference is quite substantial (around 30–40 °C), suggesting that quite different type of morphology is expected in the polyurethane with non-linear chain extenders. Secondly, in the case of the modulus level in the rubbery plateau region, the polyurethane with 1,4-butanediol shows the higher value than other non-linear chain extender, which seems to be due to the presence of hard segment crystallinity. Also the use of cyclic chain extender and 1,4-pentanediol which has pendent group results in the shift of hard segment softening temperature well above that of 1,4-butanediol, indicating that the governing factor determining the softening of the hard segment is the structure of chain extenders.

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