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Structure−Mechanical Property Relationships for Poly(carbonate urethane) Elastomers with Novel Soft Segments

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ABSTRACT: A series of eight aliphatic polycarbonate (PC) glycols with various methylene numbers ($HO-[(CH_2)_mOC(=O)O]_n-(CH_2)_m-OH$, m = 3, 4, 5, 6, 7, 8, 9, and 10) were employed as a soft segment for a synthesis of polyurethane elastomers (PUEs). First of all, viscosity, glass transition temperature, melting point, and crystalline structure of these new PC-glycols were investigated. The PC-glycol-based PUEs were synthesized using the PC-glycols, 4,4′-diphenylmethane diisocyanate, and 1,4-butanediol by a one-shot method. Differential scanning calorimetry and small-angle X-ray scattering measurements revealed that the degree of microphase separation of the PC-glycol-based PUEs became first weaker and then stronger with increasing number of methylene groups of PC-glycols. The threshold carbon number for the degree of microphase separation was six. In the tensile testing, Young's modulus of the PUEs decreased and increased with an increase in the methylene number, which can be explained by the degree of microphase separation. Tensile strength and elongation at break of the PC-glycol-based PUEs increased and decreased with increasing the number of methylene groups. These results are associated with the ease of packing of the PC-glycol chains.

Introduction

Polyurethanes (PUs) can be classified as a polar polymer because the urethane linkage possesses strong polar groups. This property assists the PUs for their use in a variety of industrial applications.[1−7] The fact that the PUs can be derived from a wide variety of starting materials is well recognized. These starting materials are employed properly depending on the purposes.

Generally, the polyurethane elastomers (PUEs) possess a segmented structure, which is composed of the hard and soft segments. The soft segment chains incorporated in the PUEs are generally formed with a polymer glycol with a molecular weight of 1000−3000.[7−15] These polymer glycols can often be classified into polyester-, polyether-, and polycarbonate-glycols. The carbonate polymer glycol, which is a relatively new one, have a high resistance to heat, hydrolysis, and ultraviolet light in comparison with conventional ester- and ether-based PUEs.[16−22] There are some examples of the polycarbonate (PC)-glycol-based PUEs reported in the literature. Casetta et al. reported the effect of side methyl groups on the mechanical properties of the PUEs. Incorporation of side methyl groups made the polymer glycol maintain its liquid state at room temperature, and the PUEs obtained showed slightly lower Young's modulus and tensile strength than usual.[16] Earlier, we reported the PUEs synthesized based on poly(tetramethylene-*co*-hexamethylene) carbonate glycol. As the results, it was revealed that the crystallization behavior and mechanical properties of the resultant PUEs can be controlled by a molar fraction of the copolymerized monomer.[17] Further, there are some another reports on the PUEs based on PC-glycol with different numbers of methylene groups in the literature.[18,19] Thus, the number of methylenes of the PC-glycols is thought to be an important factor on the properties of the PUEs incorporating them as well as their own properties. However, there is no report on such a systematic and basic study, even if the PC-glycol has become quite popular recently. Therefore, a study on the relation between the microphase-separated structure and mechanical property of the PC-glycol-based PUEs is desired.

In this study, we employed PC-glycols with different numbers of methylene groups (C3−C10) as a soft segment for a synthesis of the PUEs. The microphase-separated structure and mechanical properties of these eight PC-glycol-based PUEs were first investigated using wide-angle X-ray diffraction, differential scanning calorimetry (DSC), and tensile testing, and then the influence of the number of methylene groups was discussed.

Experimental Section

Materials. The PC-glycols with various methylene numbers in the repeating unit ($HO-[(CH_2)_mOC(=O)O]_n-(CH_2)_m-OH$, m = 3, 4, 5, 6, 7, 8, 9, and 10, M_n = 2000) were kindly supplied from Asahi Kasei Chemicals, Co., Ltd. The nomenclature *Cm*-2 denotes the number of methylene groups and a thousand digit of a molecular weight of polycarbonate glycols. Functionality and purity of all the PC-glycols were greater than 1.98 and 99.2%, respectively. These magnitudes were provided by the company.

Synthesis of PUEs. The PUEs were prepared from a PC-glycol, 4,4′-diphenylmethane diisocyanate (MDI: Nippon Polyurethane Industry, Co., Ltd., Japan), and 1,4-butanediol (BD: Wako Chemical, Co., Ltd., Japan) by a one-shot method. The polymer glycols were dried with dried nitrogen gas under reduced pressure at 100 °C for 1 h, and then, BD was added into the dried PC-glycol. The mixture of the PC-glycol and BD was mixed well with MDI with a ratio of NCO INDEX = [NCO]/[OH] = 1.03−1.05 at 80 °C for 5 min, where [NCO] and [OH] are the concentration of NCO groups of MDI and total OH groups of the PC-glycol and BD. The viscous mixture was poured into the centrifugal mold and reacted at 110 °C for 12 h. After removing from the centrifugal mold, the sample was postcured at 100 °C for 24 h.

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Table 1. Basic Properties of PC-Glycols Used in This Study

sample	$\overline{M_n}^a$	no. of carbonate groups/molecule	state (27 °C)	viscosity (Pa·s) (80 °C)	T_g/°C	T_m/°C
C10-2	1997	10	solid	1.31		58.3
C9-2	1951	10	solid	1.36		53.0
C8-2	1961	11	solid	1.39		51.5
C7-2	1972	12	solid	1.59	−62.4	48.7
C6-2	1958	13	solid	2.39	−55.6	36.5
C5-2	1945	14	solid	3.77	−49.0	41.1
C4-2	1952	16	solid	3.96	−46.1	59.2
C3-2	1892	18	liquid	4.05	−31.5	

[a] M_n was determined by an end group equivalent method.

Viscosity. The melt viscosity value of PC-glycols was measured with a rotational viscosity meter (Tokyo Keiki Co., Ltd., Japan). The sample with a volume of 1.5 mL was placed on the stage and measured with a conical rotator at 60 °C and the shear rate of 0.524 rad s^{-1}.

Chain and Microphase-Separated Structures. Molecular arrangement of the PUEs was evaluated using wide-angle X-ray diffraction (WAXD). WAXD profiles were obtained at 25 °C with a 2θ scan mode using a RINT2200 (Rigaku, Co., Ltd. Japan) diffractometer. A voltage and current of X-ray source were set to be 30 kV and 16 mA, respectively.

In order to investigate the microphase-separated state of the PUEs, a small-angle X-ray scattering (SAXS) measurement was carried out. A rotating anode generator (Rigaku, Ltd. Co., Japan) was used as an X-ray source. The wavelength of the incident X-ray was 0.154 nm, and the camera length was 1717 mm.

Thermal Properties. Thermal properties were analyzed based on DSC measurement. The thermograms were obtained with a DSC (Rigaku DSC 8230, Rigaku Denki Co. Ltd. Japan) from −130 to 250 °C with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. As-prepared samples were simply cooled down to around −140 °C, and then measurements were started.

Dynamic Viscoelastic Properties. The dynamic viscoelastic properties were measured with a DMS 6100 (Seiko Instruments, Co., Ltd., Japan) between −150 and 250 °C with a heating rate of 2 °C min^{-1} under a nitrogen atmosphere. The size of samples used was 5.0 mm × 25.0 mm × 0.5 mm. Imposed strain and frequency were 0.2% and 10 Hz, respectively.

Mechanical Properties. Tensile tests were performed with an Instron type tensile tester (Shimadzu Autograph AGS-100A, Japan) at various temperatures, which are 50 °C above the glass transition temperatures of the soft segment in the PUEs. The dimension of samples were 5.0 mm × 100.0 mm × 0.5 mm. An initial length and elongation rate were set to be 30 mm and 10 mm min^{-1}, respectively.

Results and Discussion

Characterization of PC-Glycols. Table 1 shows the basic properties of the PC-glycols used in this study. Figure 1 shows the number of methylene groups dependence of the viscosity value, the glass transition temperature (T_g), and melting point (T_m) of the PC glycols. C3-2 was only in the liquid state at room temperature. The viscosity value and the T_g decreased with an increase in the number of methylene groups. This behavior arises because the flexible methylene chain and rigid carbonate groups increased and decreased, respectively. For C8-2, C9-2, and C10-2, the T_g was not detected, even though the samples were quenched from above the T_m of each PC-glycol. This is simply due to quite fast crystallization of the PC-glycol like polyethylene. Discussion on the T_m will be stated later. The viscosity value of the PC-glycol steeply decreased at the methylene number of six. There are two factors which may affect the viscosity value. These are a monomeric friction and chain stiffness. The monomeric friction force is thought to decrease with increasing methylene number because an increase the number of methylene groups, which are nonpolar parts, causes decreasing intermolecular interaction. On the contrary, the chain stiffness decreases with an increasing number of methylene groups. Thus, these two factors led to a decreasing viscosity value with increasing methylene number. This property will be accompanied as the soft segment chains, when the PC-glycols are incorporated in the PUEs.

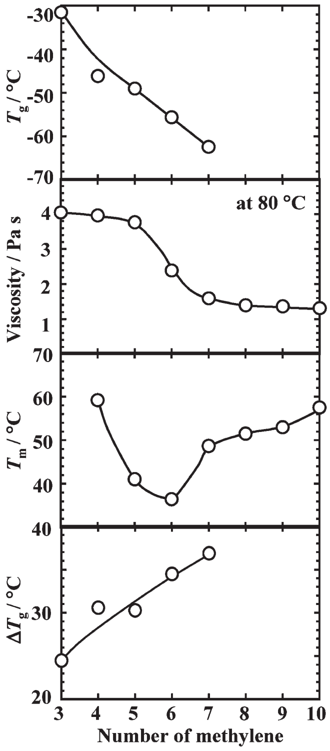

Figure 1. Number of methylene dependence of viscosity, glass transition temperature (T_g), melting point (T_m) of the PC-glycols, and ΔT_g. ΔT_g is subtraction between the T_g in the PUEs and the T_g of original PC-glycol.

In order to evaluate the crystalline state and structures, WAXD measurement was carried out for eight PC-glycols at 25 °C. Figure 2 shows WAXD profiles for PC-glycols. The WAXD profiles for the PC-glycols except C3-2 exhibited two crystalline peaks at the temperature. Thus, C3-2 with a molecular weight of 2000 is amorphous. In the literature, high molecular weight poly(trimethylene carbonate) is in the crystalline state, and the molecular chains are packed in the orthorhombic unit cell.[23] Since the effect of end groups is remarkable for the low molecular weight of C3-2 used in this study, this effect prevents crystallization of whole chains. In the WAXD profiles of the crystalline PC-glycols, C4-2

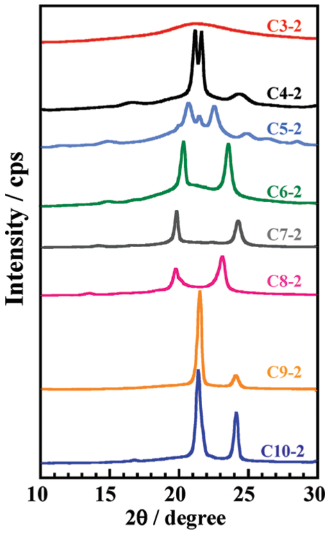

Figure 2. WAXD profiles for the PC-glycols with various numbers of methylene chains measured at 25 °C.

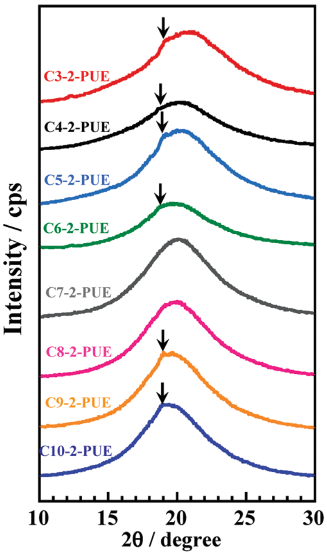

Figure 3. WAXD profiles of the PC-glycol-based PUEs measured at 25 °C.

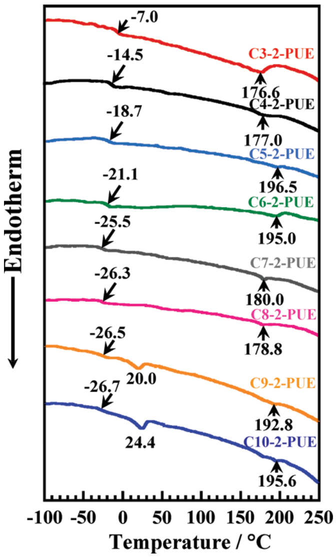

Figure 4. DSC thermograms of the PC-glycol-based PUEs.

and C5-2 were quite different from others. Since C4-2 and C5-2 have the larger number of carbonate groups, these polar and stiff groups can strongly affect the crystal structure. On the basis of earlier our computer simulation study for the crystal structure, the molecular chains of C4-2 and C5-2 possess not only a zigzag structure but a helix structure.[20] On the contrary, the PC-glycol with a larger methylene number (C6-2−C10-2) exhibited sharper crystalline peaks at different peak positions in comparison with C4-2 and C5-2. Because the PC-glycols with a larger methylene number do not bear many carbonate groups, the packing structure is mainly governed by the properties of the methylene chain, resulting in the formation of a zigzag structure. On the basis of our earlier studies, the crystal systems of all the PC-glycols with larger methylene number were estimated to be orthorhombic.[20] Especially, C9-2 and C10-2 exhibited a quite similar crystal structure with polyethylene, indicating that the existence of carbonate groups no longer affect the crystal structure.

Here, the T_ms of the PC-glycols are discussed combining with the WAXD results. As shown in Figure 1, the T_m first decreased up to the methylene number of six and then gradually increased with increasing methylene number. In other words, the T_m of C6-2 was the lowest of the eight PC-glycols studied. Let us regard C6-2 as a datum. With decreasing methylene number from six, the crystal structure is close to a helix structure as clarified by WAXD. This leads to increasing intramolecular interaction, resulting in an increasing T_m. On the other hand, with increasing methylene number from six, the number of carbonyl group decreases; the property is close to that for paraffin with the T_m of 90 °C.

Microphase-Separated Structure and Mechanical Properties of PC-Glycol-Based PUEs. Figure 3 shows the WAXD profiles for the PC-glycol-based PUEs at 25 °C. First, the crystalline peaks observed for original PC-glycols shown in Figure 2 totally disappeared. This can be easily explained that the incorporation of the hard segment chains restricts the crystallization of the soft segment chains in the PUEs. As a result, these specific PUEs obtained exhibited an excellent elastic property. Second, the WAXD profiles for the PC-glycol-based PUEs except C7-2-PUE and C8-2-one exhibited a weak crystalline peak at 18.9°. The peak positions of these small peaks observed correspond well to that for (101) plane of -(MDI-BD)$_n$- crystal.[24−26] Therefore, the hard segment chains in these six PUEs were crystallized well compared with other two PUEs.

Figure 4 shows DSC thermograms of the PC-glycol-based PUEs. The T_gs assigned to the soft segment chains were observed from −26.7 to −7.0 °C. To discuss the degree of microphase separation of the PUEs, ΔT_g (subtraction between the T_g in the PUEs and the T_g of original PC-glycol) was calculated for all the PUEs. Figure 1 shows the methylene number dependence of the ΔT_g for the PC-glycol-based PUEs. First of all, we shall discuss the microphase-separated structure of C3-2-, C4-2-, C5-2-, and C6-2-PUEs. In the range of three to six of the methylene number, ΔT_g increased with increasing number of methylene groups. Because the ΔT_g increases with increasing interaction between two different components (the hard segment and soft segment for this case), it is reasonable to consider that the increasing ΔT_g corresponds to, and also promotes, increasing solubilization of the hard segment chains into a soft segment phase, that is, decreasing degree of microphase separation. Also, the normalized melting peak area (heat of fusion) of the crystallized hard segment domains decreased with increasing number of

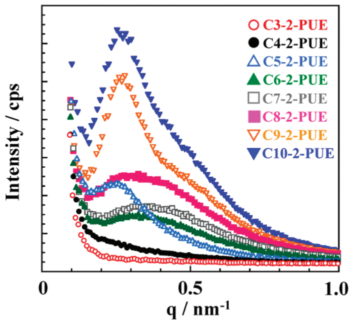

Figure 5. SAXS profiles of the PC-glycol-based PUEs measured at 25 °C.

methyelene as shown in Figure 4. Therefore, it is conceivable that the degree of microphase separation of the PC glycol-based-PUEs became weaker with increasing number of methylene groups of the PC-glycols less than six. Since the PC-glycol molecules with a smaller number of methylene groups are very stiff and a specific structure, for example a helical one, might be formed, the frequency of the formation of hydrogen bond between the oxygen atom of carbonate groups and hydrogen atoms of NH groups of the hard segment chains is low for the PC-glycols with many carbonate groups. This is thought to be the reason that the degree of microphase separation becoming weaker with increasing number of methylenes. Greater than seven methylene groups, the ΔT_g was not obtained because the T_g of the original PC-glycol could not be determined due to the rapid crystallization rates. The T_g of the soft segment in the PC-glycol-based PUEs were almost comparable, but the T_ms of the hard segment of the C9-2-PUE and C10-2-one were 15 °C higher than for C7-2-PUE and C8-2-one. Furthermore, another endothermic peak was observed at around 20 °C for the C9-2-PUE and C10-2-one. This endothermic peak can be assigned to the melting of the crystallized soft segment chains. This crystallization of the soft segment chains may have also assisted the segregation of the hard and soft segments. As the result, it is inferred that even the amorphous soft segment phase of the C9-2-PUE and C10-2-one forms a quite rich phase. Therefore, the degrees of microphase separation of the C9-2-PUE and C10-2-one are stronger in comparison with the C7-2-PUE and C8-2-one due to both polarity difference between two segments and crystallization behavior of the soft segment.

Summarizing these results mentioned above, the degree of microphase separation of the PC-glycol-based PUEs became first weaker and then stronger with increasing number of methylene groups within the PC-glycols. Also, for the C9-2-PUE and C10-2-one, the soft segment partially crystallized in the soft segment phase.

Figure 5 shows SAXS profiles of the PC-glycol-based PUEs. Scattering peaks, which are assignable to the interdomain spacing of the hard segment domains, were observed for the C5-2−C10-2-PUEs but not for C3-2- and C4-2-PUEs. The reason that the obvious peaks were not observed for the C3-2- and C4-2-PUEs might be due to similar electron density between the soft and hard segments. The electron densities were calculated for the PC glycol and the hard segment chains based on the literature,[20,24−26] when they are assumed to be in the crystalline state. The electron density ratios of the PC-glycols to the hard segment chains were ca. 0.80 for C5-2−C10-2-PUEs and ca. 0.95 for C4-2- and C3-2-PUEs. Hence, although the degrees of microphase separation of the C4-2- and C3-2-PUEs are strong, no distinct peak was observed. Since the electron density fluctuates with changing number of methylene groups of PC-glycol in this study, peak intensity will not be discussed. For the C5-2-, C6-2-, C7-2-, and C8-2-PUEs, one broad peak was observed in their SAXS profiles at around 0.26−0.35 nm^{-1}. The spacings calculated from these peaks were 9.0−12.0 nm. This scattering is thought to be the interdomain spacing of the hard segment. On the contrary, both a strong peak and shoulder were observed at ca. 0.26 and 0.53 nm^{-1} for the C9-2- and C10-2-PUEs, respectively. The spacings calculated from the peak and shoulder were 12.0 and 5.9 nm, respectively. Thus, the shoulder is believed to arise from the second-order interference based on the difference in electron density between the soft and hard segment regions. The interdomain spacing for the C7-2−C10-2-PUEs increased from 8.7 to 12 nm with increasing number of methylene groups. As discussed above, the degree of microphase separation became stronger with the number from seven to ten of the methylene number. Thus, the increase in the interdomain spacing is associated with the formation of pure phases and also the decrease of solubilized believed to be hard segment chains into the soft segment phase.

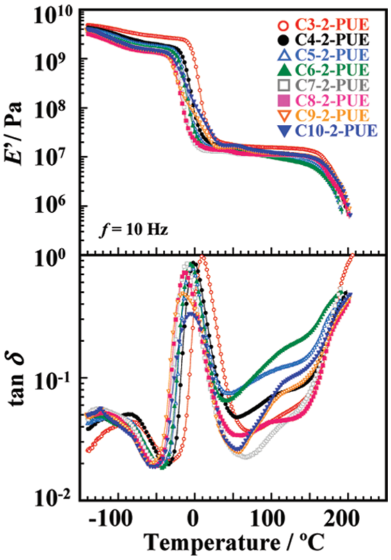

Figure 6. Temperature dependence of storage modulus (E') and loss tangent (tan δ) of the PC-glycol-based PUEs.

Figure 6 shows the temperature dependence of the storage modulus (E') and loss tangent (tan δ) for the PC-glycol-based PUEs measured at a frequency of 10 Hz. First of all, the gradual decreasing E' value and the peak of tan δ were observed at around −100 °C. These decreases were distinct with increasing methylene number. This transition was assigned to the well-known relaxation of methylene chains, which is called as crankshaft and kink motions.[27] In the range of −40 to −10 °C, the E' value and tan δ steeply decreased and increased, which is assignable to the α-relaxation of the soft segments. The temperature shifted to the lower temperature side with increasing number of methylene groups. For the C7-2-, C8-2-, C9-2-, and C10-2-PUEs, a slight decrease of the E' value was observed at 50−60 °C, which can be attributed to the melting of the crystallized soft segment chains. These trends correspond well to the T_gs and T_ms of the soft segment chains obtained by DSC shown in Figure 4. Furthermore, the peak height of the α-relaxation in the tan δ curve decreased with increasing methylene number. The transition width of the C9-2- and C10-2-PUEs were quite broad in comparison with other ones. Since the soft segment chains in the C9-2- and C10-2-PUEs are partially

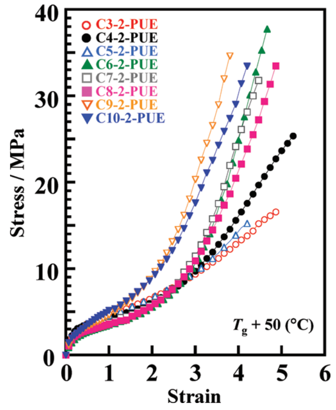

Figure 7. Stress–strain curves of the PC-glycol-based PUEs measured at $T_g + 50$ °C.

Table 2. Young's Modulus of PC-Based PUEs Measured at $T_g + 50$ °C

sample	Young's modulus/MPa	tensile strength/MPa	elongation at break
C3-2-PUE	26.0	16.6	4.9
C4-2-PUE	24.3	25.4	5.3
C5-2-PUE	21.6	15.2	4.2
C6-2-PUE	16.4	37.7	4.7
C7-2-PUE	16.2	31.8	4.5
C8-2-PUE	16.5	33.5	4.9
C9-2-PUE	19.8	34.6	3.8
C10-2-PUE	21.9	33.5	4.2

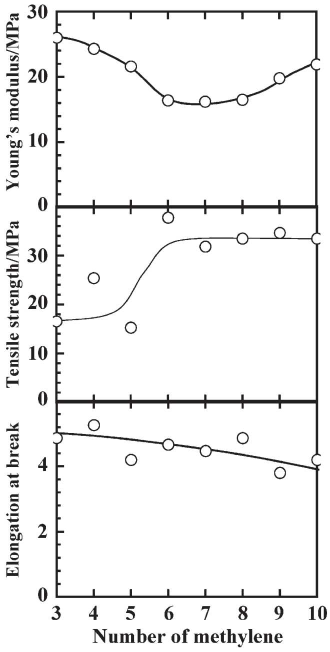

Figure 8. Number of methylene dependence of Young's modulus, tensile strength, and elongation at break of the PC-glycol-based PUEs.

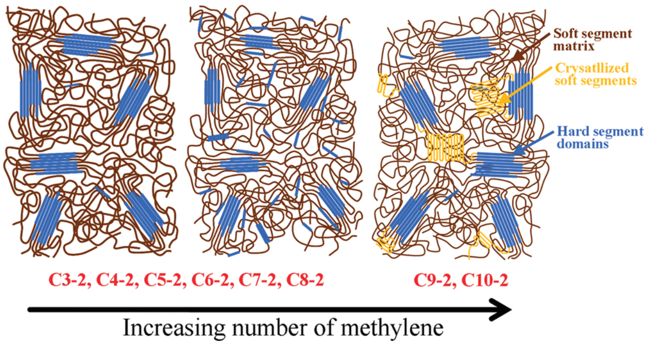

Figure 9. Schematic illustration of the microphase-separated state of the PC-glycol-based PUEs. The degree of microphase separation of the PC-glycol-based PUEs became first weaker and then stronger with increasing number of methylene of the PC-glycols. For the C9-2-PUE and C10-2-one, the soft segment partially crystallized in the soft segment phase.

crystallized, the crystallite can play the role of cross-linking points. Thus, the number of relaxation modes was increased, resulting in more gradual decreasing E' and broadening of tan δ peak. Furthermore, there is a possibility in which the recrystallization of the C9-2 and C10-2 chains slightly occurred as well. The order of the E' value at the rubbery plateau region was as follows: C3-2-PUE > C10-2-PUE > C9-2-PUE > C4-2-PUE > C5-2-PUE > C6-2-PUE = C7-2-PUE = C8-2-PUE. This trend will be discussed with Young's modulus obtained from tensile testing. At 150–200 °C, decreasing E', which corresponds to the melting of the crystallized hard segment domains, was observed. The starting temperatures were consistent with T_ms of the hard segment domains obtained by DSC.

Figure 7 shows stress–strain curves for the PC-glycol-based PUEs measured at $T_g + 50$ °C. Table 2 and Figure 8 summarize Young's modulus, tensile strength, and elongation at break of the PC-glycol-based PUEs obtained from Figure 7. Young's modulus of the PUEs first decreased and then increased with an increase in the methylene number. This trend corresponds well to the E' value at the rubbery plateau region. As stated above, the degree of microphase separation of the PUEs decreased and increased with increasing methylene number. Thus, in the PUEs with well-microphase-separated state, the hard segment domains work as physical cross-linking points. This causes the increasing Young's modulus for the C3-2-PUE and C4-2-one. For the C9-2- and C10-2-PUEs, the degree of microphase separation is strong and also the soft segment chains are crystallizable as well. Therefore, these elastomers showed higher Young's moduli.

In the larger strain region, the stress value for the C3-2-, C4-2-, and C5-2-PUEs gradually increased, whereas the C6-2–C10-2-PUEs exhibited steep increasing stress. This can be explained by the ease of packing of the soft segment. That is, C3-2 is amorphous and C4-2 and C5-2 are not so crystallizable in comparison with the PC-glycols with the larger number of methylenes. As the result, the low packing ability of the soft segment chains caused the gradual increasing stress. On the contrary, the tensile strength of the C3-2-, C4-2-, and C5-2-PUEs exhibited the low value compared with other PUEs. This result also can be explained by the crystallizability of the soft segments. In contrast, for the C6-2–C10-2-PUEs, packing of the soft segment chains occur easily under elongation, resulting in a decrease and increase in elongation at break and tensile strength, respectively.

Figure 9 shows the schematic illustration of the microphase-separated state of the PC-glycol-based PUEs. The C3-2-, C4-2-, C9-2-, and C10-2-PUEs possess stronger microphase separation compared with other four PUEs. This trend is originated from the property of the soft segment chains, such as chain stiffness, cohesion force, and crystallizability.

Conclusions

The number of methylene groups of the PC-glycols greatly affects many properties of the PUEs incorporating them as well as their own properties. C3-2 was in the amorphous state at room temperature, whereas others were in the crystalline state. Not only a crystal system but crystallinity of the crystalline PC-glycols was dependent on the number of methylene groups. As increasing the number of methylene groups, crystallinity increased and was closed to the property of polyethylene. These properties of the PC-glycol were obviously detected even for the PUEs consisting of these PC-glycols, MDI, and BD. DSC and SAXS measurements revealed that the degree of microphase separation of the PC-glycol-based PUEs became first weaker and then stronger with increasing number of methylene groups of PC-glycols. The threshold methylene number was six. Dynamic viscoelastic properties exhibited similar temperature trend with DSC results. And the E' value at the rubbery plateau region corresponded well to Young's modulus obtained from tensile testing. The order C3-2-PUE > C10-2-PUE > C9-2-PUE > C4-2-PUE > C5-2-PUE > C6-2-PUE = C7-2-PUE = C8-2-PUE was associated with the degree of microphase separation. Elongation at break and tensile strength of the C3-2-, C4-2-, and C5-2-PUEs were larger and smaller than for other PUEs due to difficulty of packing of the soft segment chains. The insights obtained in this study are quite useful for the molecular design of the PUEs with various applications.

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