

Infrared Dichroism Study of Segmented Polyurethaneurea with Triblock Polyether Soft Segments

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ABSTRACT: Infrared (IR) dichroism study of segmented polyurethaneurea (SEUU) with ABA type triblock copolymer as a soft segment was carried out, where A stands for poly(oxyethylene) (PEO) and B stands for poly(oxytetramethylene) (PTMO). IR dichroism analysis of SEUU films under elongation suggested that the introduction of PEO units to the ends of PTMO brought about more aggregation of the hard segments, *i.e.*, the better microphase separation in SEUU than segmented polyurethaneurea (SPUU) prepared from PTMO. Under uniaxial extension, the crystalline hard segment domain oriented transverse to the stretch direction at early stage, the degree of orientation being larger with the increase of PEO content. The larger was the PEO content, the better the microphase separation in SEUU.

KEY WORDS Segmented Polyurethaneurea / Infrared Dichroism / Microphase Separation / Triblock Copolyether / Poly(oxyethylene) / Poly(oxytetramethylene)

The relationship between structure and properties in block copolymers has been much focused in recent years with the increasing importance of thermoplastic elastomers.^{1,2} They include styrenic block copolymers (triblock copolymers) and segmented polyurethanes (multiblock copolymers). In order to understand their properties, it is necessary to elucidate their higher order structures, and the structural change according to elongation, because elastomers have a very large extensibility.

“Segmented” polyurethaneureas are multiblock copolymers that possess a general structure $(A-B)_n$, where A is a hard segment and B is a soft segment.³ The soft segment is usually a polyether or a polyester chain with molecular weight between several hundreds and a few thousand; the hard segment is formed from diisocyanate and diamine. The hard segments aggregate to form glassy or semi-

crystalline domains in the soft segment matrix. Namely, the multiblock polymer undergoes microphase separation due to the chemical incompatibility between the polyether or polyester segment and the hard segment containing urethane or urea blocks.^{3,4} At service temperature, the soft segment matrix is in a rubbery state, whereas the hard segment domain serves not only as a thermally reversible crosslink to give rubber elasticity and but also as a reinforcing filler to afford mechanical strength. The dependence of the properties of segmented polyurethaneurea on the chemical composition is now well recognized.⁵ Recently, there has been a growing appreciation that the physical properties are determined not only by the chemical structure but also by the extent of the phase separation between the soft and the hard segments.³ These two factors are closely related and a change in the chemical structure may alter the degree of phase

separation.

Infrared (IR) spectroscopy is the principal method to characterize hydrogen bonding and is of use to investigate phase separated structures in polyurethaneurea.^{6,7} Hydrogen bonding may be formed between NH and C=O groups and between NH and C–O–C groups. Both the frequency shifts and the intensity changes are caused by hydrogen bond formation. The intensity of each hydrogen bonded vibration can potentially yield the degree of phase separation in the polyurethaneurea. Orientation study by transmission IR dichroism has been recognized as a powerful technique to probe morphology and nonlinear viscoelastic behavior of segmented polyurethaneurea, as it is sensitive to changes in the microenvironments of the hard and the soft segments.⁸ Orientation of the soft segment can usually be followed using the asymmetric CH₂ stretch vibration, the group residing primarily in the soft segment.⁸ Hard segment orientation can be characterized by the carbonyl group of the urea linkage and NH group located entirely in the hard segment. These bands split into free and hydrogen bonded components.⁹ By IR dichroism measurement, we can take advantage for the quantitative evaluation of orientation behavior of each segment separately.

Novel hydrophilic segmented polyurethaneureas (SEUU) were prepared from ABA type copolyether, *i.e.*, poly(oxyethylene)-*b*-poly(oxytetramethylene)-*b*-poly(oxyethylene),¹⁰

which showed a good blood compatibility as well as excellent mechanical properties.^{11–15} The introduction of poly(oxyethylene) (PEO) unit to the ends of poly(oxytetramethylene) (PTMO) was found to result in the better microphase separation in SEUU.¹⁶ This morphological effect improved not only the antithrombogenicity but also the mechanical properties of SEUU.¹⁶

In this report, the morphology and the orientation behavior in SEUU are investigated by IR dichroism. The IR dichroism measurement will give important information on the change of the microphase separated structure with elongation, and will also be useful for consideration of the effect of morphology on blood compatibility.

EXPERIMENTAL

Materials

The materials used in this study were a series of segmented polyurethaneureas (SPUU and SEUU) prepared by the prepolymer method as described in the previous paper.¹⁰ The polyether segments were PTMO for SPUU and PEO-*b*-PTMO-*b*-PEO for SEUU. The hard segment was formed by the reaction of isocyanate group from 4,4'-diphenylmethane diisocyanate (MDI) and amino group from ethylenediamine (ED). The chemical structures of segmented polyurethaneureas and their starting materials are shown in Figure 1. The characteristics of these polymers are given in Table I together

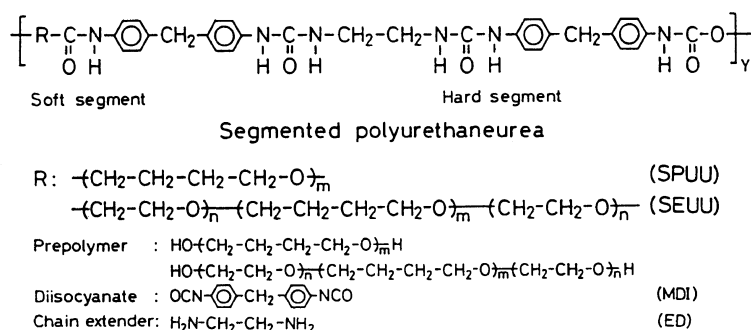


Figure 1. Chemical structures of segmented polyurethaneureas and their starting materials.

with some molecular properties of the prepolymers. The number-average molecular weight (M_n) of PTMO for SPUU and the PEO unit content for SEUU varied, while the hard block length was held constant. The larger the PEO unit content, the larger the soft segment length.

Preparation of Thin Film

N,N'-Dimethylacetamide (DMAc) solution of a polymer (4 wt%) was casted onto a Petri type glass dish followed by gradual solvent evaporation at 50°C under a reduced pressure (<5 mmHg). The resulted film was dried in a vacuum oven at 50°C for several days to constant weight. The dried films were kept in a vacuum desiccator at room temperature until just before the experiment. The thickness of the films was *ca.* 10 μm , which was measured by a microscope.

Infrared Measurement

IR absorption spectra were recorded on an IR spectrophotometer DS-403G (Japan Spectroscopic Co., Ltd.) with a resolution of 10 cm^{-1} . Elongational strain was applied by a stretching device, and IR measurements were

carried out using a silver chloride (AgCl) polarizer inserted between the sample and the detector at 20°C and at *ca.* 65% relative humidity.

RESULTS AND DISCUSSION

Infrared Analysis

IR spectra of SPUUs and SEUUs are illustrated in Figure 2. The designation of several important bands is shown in the spectrum of SEUU-2, where "B" and "F" mean hydrogen bonded and free (not hydrogen bonded), respectively, and "UT" and "UA"

Table I. Properties^a of segmented polyurethaneurea

Sample code	Prepolymer		PEO content ^d mol%	Hard segment content ^e wt%	CTI ^f
	M_n^b	M_w/M_n^b			
SPUU-2	1830	1.5	0	23.4	3.6
SPUU-3	2840	1.6	0	16.5	2.8
SEUU-1	2090	1.4	12	21.1	4.2
SEUU-2	2180	1.5	22	20.4	4.6
SEUU-3	2430	1.5	33	18.7	4.9

^a Taken from Ref 10.

^b Measured by vapor pressure osmometer.

^c Measured by gel permeation chromatography.

^d Measured by ^1H NMR.

^e Calculated from the ratio of feed reagents.

^f Clotting time index measured by Lee-White method.

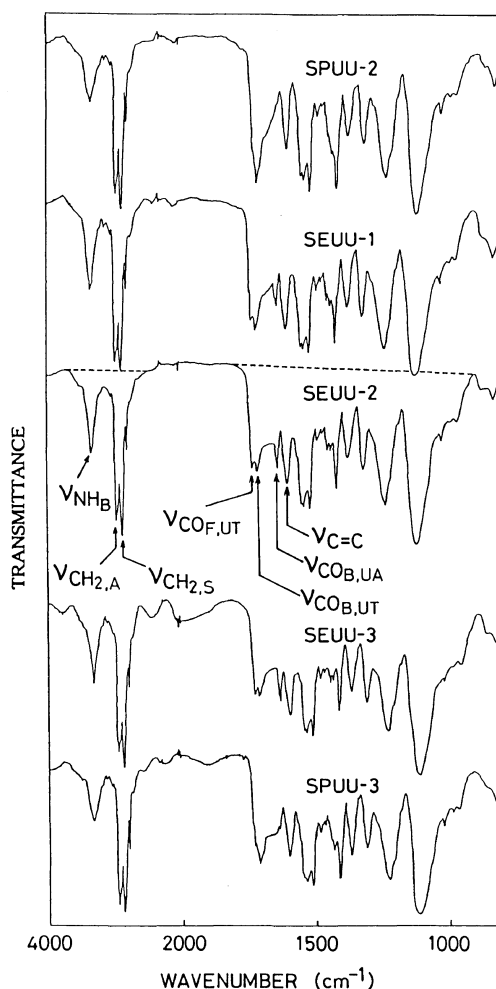


Figure 2. IR spectra of segmented polyurethaneureas.

are abbreviations for urethane and urea, respectively. The absorption of the asymmetric CH_2 stretching vibration ($\text{CH}_{2,A}$) and the symmetric CH_2 stretching vibration ($\text{CH}_{2,S}$) appeared at 2960 cm^{-1} and 2870 cm^{-1} , respectively. The NH absorption peak located at 3330 cm^{-1} (NH_B) indicates that most of the NH groups are hydrogen bonded, while the free NH absorption peak at 3445 cm^{-1} is negligible. In the region between 1620 cm^{-1} and 1750 cm^{-1} , the absorption peak at 1730 cm^{-1} is due to the free urethane carbonyl group ($\text{C}=\text{O}_{F,UT}$), the peak at 1710 cm^{-1} to the hydrogen bonded urethane carbonyl group ($\text{C}=\text{O}_{B,UT}$), and the peak located at 1635 cm^{-1} is due to the hydrogen bonded urea carbonyl group ($\text{C}=\text{O}_{B,UA}$). The absorption of free urea carbonyl group was reported to appear at 1695 cm^{-1} ,¹⁷ but it was not clearly detected in every sample. In the spectra of SPUU-2 and SPUU-3, the peaks of $\text{C}=\text{O}_{F,UT}$ and $\text{C}=\text{O}_{B,UA}$ were not clearly observed, and several shoulders appeared between 1635 cm^{-1} and 1695 cm^{-1} . These results suggest the segregation of the two segments in SPUU is not enough to differentiate all the peaks.

The relative absorbances of the bonded and the free carbonyl groups give the fraction of the hydrogen bonded urethane groups (H_{UT}) which is defined as,

$$H_{UT} = A(1710)/(A(1710) + A(1730)) \quad (1)$$

where $A(1710)$ and $A(1730)$ are the absorbances of the bonded and the free urethane carbonyl absorption peaks at 1710 cm^{-1} and 1730 cm^{-1} , respectively.¹⁸⁻²⁰ On the other hand, the ratio of the relative absorbance of the hydrogen bonded urea carbonyl absorption peak to that of the $\text{C}=\text{C}$ stretching absorption peak of the benzene ring at 1600 cm^{-1} is used as an index of the degree of the hydrogen bond of the urea carbonyl groups in the hard segments. That is to say, the ratio that can be used as an index of the cohesive force of the hard segments (C_h) is given by^{19,20}

Table II. Results of IR and DSC measurements

Sample code	IR		DSC ^c
	H_{UT} ^a	C_h ^b	ΔQ ^d mjmg ⁻¹
SPUU-2	0.623	0.546	4.23
SPUU-3	0.573	0.731	6.38
SEUU-1	0.544	0.698	9.23
SEUU-2	0.512	0.789	11.43
SEUU-3	0.505	0.806	15.35

^a The fraction of the hydrogen bond in urethane groups. See eq 1.

^b The cohesive index of the hard segments. See eq 2.

^c Calculated from the DSC curves of Ref 10.

^d The heat of fusion of the hard segment domains.

$$C_h = A(1640)/A(1600) \quad (2)$$

where $A(1640)$ and $A(1600)$ are the absorbances at 1640 cm^{-1} and at 1600 cm^{-1} , respectively. H_{UT} and C_h were calculated and listed in Table II.

C_h of SEUU was larger than that of SPUU, and the order of C_h is SEUU-3 > SEUU-2 > SEUU-1 > SPUU-3 > SPUU-2. This order suggests that the aggregation of the hard segments is more promoted in SEUU than SPUU, and the degree of their aggregation increases with the increase of PEO contents. In a study on segmented polyurethaneureas with polyether soft segments, the microphase separated structure was found to become more distinct with the increase of molecular weight of polyether in the soft segment.²¹ In SEUU, as the increase of PEO content is accompanied by the increase of M_n , both factors contributed to the microphase separation. However, C_h 's of SEUUs were larger than that of SPUU-3 with PTMO segments whose M_n is 2840. This result apparently suggests the effect of PEO units on morphology. On the contrary to C_h , H_{UT} decreased in the opposite order of C_h , *i.e.*, SEUU-3 < SEUU-2 < SEUU-1 < SPUU-3 < SPUU-2. Generally, it has been known that the better the microphase separation, the larger

the C_h , and the smaller the H_{UT} .²⁰ Therefore, the IR analysis suggests that the presence of PEO units brought about more aggregation of the hard segments, *i.e.*, better microphase separation in SEUU.

Infrared Dichroism Analysis

Analytical procedure for segmented polyurethaneurea The use of IR dichroism involves orienting a sample and measuring the absorbances of selected bands with radiations polarized perpendicular and parallel to the orientation direction. If the transition moment vector of a particular vibration has been preferentially aligned, the two absorbances (A_{\perp} and A_{\parallel}) will not be equal and the dichroic ratio (D) may be calculated with the following eq 3.

$$D = A_{\perp} / A_{\parallel} \quad (3)$$

A_{\perp} and A_{\parallel} are the absorbances measured with radiation polarized perpendicular and parallel to the stretching direction, respectively. The dichroic ratio can be related to an orientation function (F^D).²¹

$$F^D = (1 - D) / (1 + 2D) \quad (4)$$

Several functional groups were used to conduct segmental orientation analysis in the soft and the hard segment domains of the segmented polyurethaneurea in this study. They include (1) the asymmetric CH_2 stretching band at 2940 cm^{-1} , which is a measure of soft segment orientation, (2) the $C=O$ stretching band at 1640 cm^{-1} , a measure of the orientation of urea linkages within the hard segment domains, and (3) the NH band at 3317 cm^{-1} , which characterizes the average hard segment orientation. The transition moment vectors of asymmetric vibration of CH_2 , $C=O$ and NH stretching bands are reported to be oriented by about 90° , 78° , and 90° , respectively, with respect to the segment (or the chain) axes.^{8,19} According to the above definition, the positive F^D means the negative (transverse) orientation of the corresponding

segments axis and the transition moments for the perpendicular dichroism. For the simplicity in data manipulation, straight base lines were

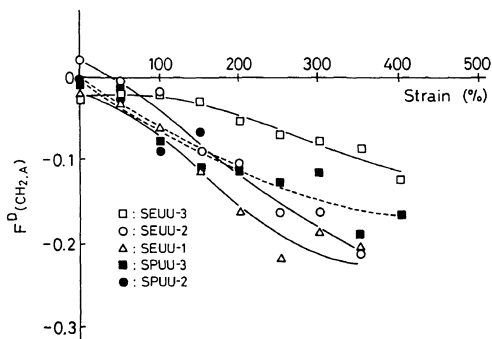


Figure 3. Elongation dependence of the orientation function of asymmetric CH_2 for segmented polyurethaneureas.

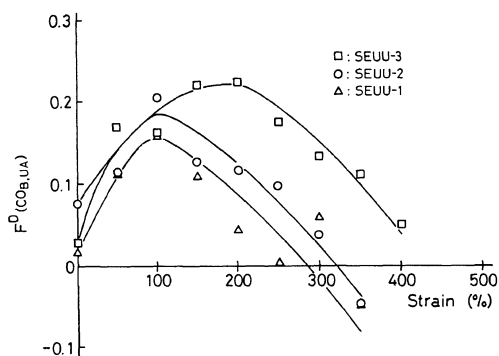


Figure 4. Elongation dependence of the orientation function of hydrogen bonded $C=O$ urea for segmented polyurethaneureas.

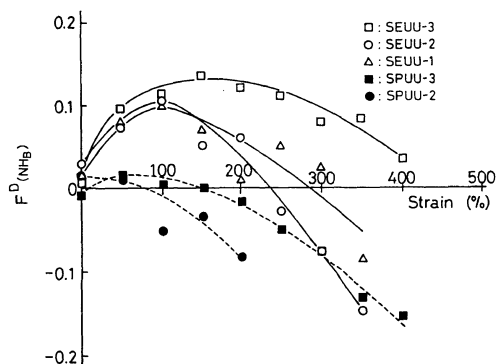


Figure 5. Elongation dependence of the orientation function of hydrogen bonded NH for segmented polyurethaneureas.

assumed at range of $3700\sim 2450\text{ cm}^{-1}$ for the NH and the asymmetric CH_2 band, and of $1800\sim 900\text{ cm}^{-1}$ for the $\text{C}=\text{O}$ stretching band.

Figures 3, 4, and 5 show the elongation dependence of the orientations of $\text{CH}_{2,\text{A}}$, $\text{C}=\text{O}_{\text{B,UA}}$ and NH_{B} , respectively. In Figure 4, $F^D(\text{C}=\text{O}_{\text{B,UA}})$ curves of SPUU-2 and SPUU-3 were not displayed because the peaks of their $\text{C}=\text{O}_{\text{B,UA}}$ did not appear clearly as shown in Figure 2.

Soft Segment Orientation Figure 3 shows the soft segment orientation behavior plotted against elongation for SEUUs and SPUUs. The positive orientation to the direction of stretch was observed in every sample. The changes of the orientation factors are less compared with those of hard segments. In SEUU series, the larger $F^D(\text{CH}_{2,\text{A}})$ was observed with the formation of the rigid hard segment domain. This observation suggests that the soft segment orientation of SEUU-3 was much affected by the hard segment domains, which may be explained by assuming that the microphase separation in SEUU-3 was the most complete one, and its hard segment domain was most rigid among the segmented polyurethaneureas used in this study.

Hard Segment Orientation Studies The orientation behavior of $\text{C}=\text{O}_{\text{B,UA}}$ and NH_{B} gave important information on the change of the hard segment domains under uniaxial extension. Both in Figures 4 and 5 the hard segment domains were found to initially orient transverse to the stretch direction, and after reaching the maximal orientations their crystalline regions gradually broke up with increasing strain. Then, they became to orient positively with further elongation after passing the maximum of the negative orientation. It is also apparent that the larger the PEO content, the more negative the orientation functions of $\text{C}=\text{O}_{\text{B,UA}}$ and NH_{B} among the samples of 12 to 33 mol% PEO content. In addition, the elongation at the maximum of the negative orientation became larger with the increase of PEO content. On the contrary the transverse

orientation of SPUU-3 was very small and that of SPUU-2 was not clearly detected as shown in Figure 5. Generally the microphase separation of segmented poly(ether urethaneurea) was known to be promoted by the increase of the molecular weight of soft segment.²² Therefore, from the transverse orientation of SPUU-3 and SEUUs, the effect of the molecular weight on SEUU is concluded to be smaller than that of the presence of PEO units at the ends of PTMO.

The combination of the negative orientation of the hard segments and the positive orientation of the soft segment at low elongation has been widely observed,^{9,17,18} and a few mechanisms to explain this orientation behavior have been proposed.^{18,23,24} However, the essence of the mechanisms is not much different from each other. Namely, at relatively small elongation, the crystalline lamellae or glassy domains would be taken as orientation units floating in a matrix of the soft segments. In these units, the lamellar axis should be the principal orientation axis which gives its positive orientation. Because the principal axis of urethane or urethaneurea linkage is perpendicular to the axis of lamellae or glassy domains, the initial lamellar orientation results in the negative orientation of hard segments. At relatively large elongations, on the other hand, the oriented lamellae would disintegrate into small fragments. Then, the hard segment axis turns out to be the principal orientation axis giving its positive orientation.

To support the observations on SPUU and SEUU, it is useful to compare the heat of fusions (ΔQ_{h}) of the hard segment domain in segmented polyurethaneurea which was obtained from DSC measurements reported.¹⁰ The value of ΔQ_{h} shows the degree of the hard segment crystallinity, *i.e.*, the larger the ΔQ_{h} , the more rigid hard segment was formed. The values of ΔQ_{h} for the present polyurethaneureas listed in Table II. ΔQ_{h} of SPUU-2 was smaller than that of SPUU-3. This result

suggested the aggregation of the hard segment in SPUU-3 was better than that of SPUU-2, which is in accord with the results of IR and IR dichroism studies. ΔQ_h 's of SEUUs (M_n of soft segment = 2090 ~ 2430) were larger than that of SPUU-3 whose M_n of soft segment is 2830, and ΔQ_h also became larger with the increase of PEO content. Table II suggests that SEUU-3 had the most crystalline domain, *i.e.*, the most rigid hard segment domain among SEUUs. These results suggest that the aggregation of the hard segments was most promoted in SEUU-3 whose oxyethylene unit content was the highest among SEUUs.

In order to explain this effect of oxyethylene units in the ends of PTMO segment, it is assumed that oxyethylene (C–C–O) units have a larger mobility than oxytetramethylene (C–C–C–C–O) units in the DMAc solution. This assumption is based on that the rotations along C–O–C bonds are easier than C–C–C bonds, because the presence of ether oxygen stabilizes *gauche* conformation.²⁵ Additionally, the fraction of C–O–C bonds is larger in PEO than PTMO. In the preparation of polymer film by solution casting in this study, it is considered that the higher the mobility of polymer segment in DMAc solution, and the larger the time until the mobility of polymer chain was frozen, the more the microphase separation was pronounced. The difference of solubility might also affect the mobility of the segments in the solution. Namely, solubility parameter (δ) of DMAc is 10.8²⁶ and is nearer to that of PEO units (δ ; 9.8²⁷) than that of PTMO units (δ ; 9.2²⁶). These factors explain the reasons why the microphase separation of SEUUs was more pronounced by the introduction of PEO units compared with that of SPUU.

CONCLUSION

The IR analyses suggests that the introduction of PEO units has promoted the microphase separation in SEUU, which was in agreement

with the results of DSC, dynamic mechanical measurement and SAXS. The orientation behavior of the soft and the hard segments was measured under uniaxial extension by IR dichroism. Initially, the crystalline hard segment domains oriented transverse (negative) to the stretch direction. The crystalline regions gradually broke up with increasing strain, and they began to positively orient to the stretch direction. The larger the PEO content, the more negative orientation continued to the higher elongation, which is explained by assuming that the introduction of PEO units to the ends of PTMO chain resulted in the more aggregation of hard segments to form the crystalline regions in SEUU. The soft segment orientation was positive to stretch direction in every sample.

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