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SAXS and dynamic viscoelastic studies on segmented polyurethaneurea solutions

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The microstructure and dynamic mechanical properties of segmented polyurethaneurea (SPUU) in concentrated dimethyl acetamide (DMAc) solutions have been investigated by means of small-angle X-ray scattering (SAXS) and viscoelastic measurements, respectively. Kratky plots of SAXS intensity functions indicated the following: (1) Formation of hard segment domains introduced mainly by hydrogen bondings is promoted with increasing ratio of isocyanate to hydroxyl groups ([NCO]/[OH]) and polymer concentration, C_p. (2) The degree of completion of the hard segment domains increases with temperature up to 55°C and then gradually decreases by further increase of temperature. An analogy was found between [NCO]/[OH] dependence of the dynamic storage $G'(\omega)$ and loss shear moduli $G''(\omega)$ for SPUU in DMAc and time dependence of those for a chemically gelling system. $G'(\omega)$ and $G''(\omega)$ indicated that the properties of SPUU solutions change from sol-like to gel-like with increasing [NCO]/[OH]. By varying [NCO]/[OH], a relationship of $G'(\omega) \approx G''(\omega) \approx \omega^k$ was observed around $[\mathrm{NCO}]/[\mathrm{OH}] = 1.6$. The exponent k is evaluated to be 0.67, which was similar to the literature value obtained at the gelation point. This corresponds to the 'gelation threshold' of the chemical gelation process. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: dynamic mechanical properties; SAXS; segmented polyurethaneurea solution; hydrogen bond; chemical gelation)

INTRODUCTION

Segmented polyurethaneurea (SPUU) is a multi-block copolymer which consists of rigid hard segments and flexible soft segments, and has a microphase separated structure due to thermodynamic incompatibility between these segments. Owing to their good mechanical properties, such as high elasticity, durability, and antithrombogenicity[1], SPUUs are extensively used in medical and/or industrial fields, including artificial heart blood vessels, shock absorbents, textiles, paints, adhesives, and soil conditioners[2,3]. Because the mechanical properties of SPUU depend greatly on the degree of completion of microphase separation and formation of hydrogen bonding, a large number of studies on the mechanical and thermal properties of SPUU have been carried out using various methods, such as differential scanning calorimetry (d.s.c.), small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (*FT*i.r.)[4–27]. In order to study the degree of completion of hard segment domains, *FT*i.r. is commonly employed, which provides some information on hydrogen bonding between N–H and C=O groups in the hard and/or soft segments[28–37].

Fibres made of SPUU are regarded as one of the most important materials having high elasticity, e.g. Spandex. However, the mechanical properties of SPUU fibres are significantly depressed if spun from a spinning solution containing gelled SPUU. Since gelation is related to aggregation of hard segment domains, it is worthwhile to investigate the solution properties and structure as a function of the hard segment content. Although several papers on the properties of polyurethane (PU) solutions have been reviewed by Petrovic and Ferguson[4], the mechanism of the domain formation in PU and SPUU has not been well elucidated. It is obvious that the degree of hydrogen bonding depends on temperature, polymer concentration, and the fraction of the hard segment.

In this paper, we discuss the structure and viscoelastic properties of a series of SPUU concentrated solutions. The ratio of isocyanate to hydroxyl groups (= [NCO]/[OH]) has been chosen as a parameter indicating the relative content of the hard segment. In the literature, only a few papers describe the effects of [NCO]/[OH] on thermal and mechanical properties of segmented polyurethane. For example, Spathis *et al.*[21] studied the [NCO]/[OH] dependence of morphology in segmented polyurethane elastomers, by means of *FT*i.r., d.s.c., and the thermally stimulated depolarization current method (TSDC), while keeping the total hard segment content constant. Nierzwicki and Wysocka[22] studied the change of the glass transition temperature, T_g, by varying [NCO]/[OH] and suggested that T_g was determined by the competition of microphase separation and cross-linking. If the microphase separation is a dominant contributor to T_g, the T_g maximum should appear at [NCO]/[OH] = 1. However, in reality, the cross-linking effect has to be taken into account. Since cross-links reduce the mobility of hard segments, these

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lead to an increase of the transition temperature, i.e. a shift of the maximum in T_g toward the side of $[NCO]/[OH] > 1$.

The aims of this paper are (1) to quantify the degree of completion of hard segment domains by SAXS as a function of temperature and polymer concentration, (2) to analyse [NCO]/[OH] dependence of their viscoelastic properties, and (3) to elucidate the structure–property relationship of SPUU in concentrated solutions.

EXPERIMENTAL

Samples

A series of segmented polyurethaneureas (SPUU) with different [NCO]/[OH]'s (1.4, 1.5, 1.6, 1.7, 1.8), in 35 wt% dimethyl acetamide (DMAc) solutions, were supplied by Asahi Chemical Industry Co. Ltd (Japan). The SPUUs consist of soft segment [(poly(tetramethylene glycol)-4,4'-diphenylmethane diisocyanate (PTMG-MDI)] and hard segment [ethylenediamine/diethylamine-MDI (EDA-MDI)] as shown in *Figure 1*. Diethylamine (DEA) was used to adjust the molecular weight of the SPUU. Because it has only one functional group, DEA is located at the end of a SPUU chain. The number-average molecular weight, M_n, of PTMG was about 1800. *Table 1* denotes the chemical compositions of the SPUUs. [NCO]/[OH] shows the ratio of isocyanate to hydroxyl groups. The larger the [NCO]/[OH] becomes, the higher the fraction of hard segments in the SPUU polymer. The SPUU solutions were diluted to 20, 25, and 30 wt% by mixing with DMAc solvent at 60°C, where hydrogen bondings are expected to degrade. Then these samples were used for SAXS and viscoelastic measurements without any further treatments.

SAXS

Small-angle X-ray scattering (SAXS) was carried out at the Photon Factory of the National Laboratory for High Energy Physics, Tsukuba, Japan. A brilliant X-ray beam (wavelength, $\lambda = 1.488$ Å) from synchrotron orbital radiation (SOR) was used as the incident beam. The sample was sealed in a stainless steel cell with thin mica windows. The sample thickness was about 1 mm. The sample cell was placed in a temperature-controlled sample holder. The scattered X-ray was detected with a one-dimensional position sensitive proportional counter, placed at 1.9 m apart from the sample position. Each sampling time was 300 s. The observed scattered intensity was corrected for open beam, cell scattering, solvent scattering at each temperature, and transmittance. The sampling temperatures were 25, 45, 55, 65 and 85°C. Each sample was kept at the given temperature for 90 min in order to obtain the equilibrium state before a SAXS measurement was performed.

Viscoelasticity

Viscoelastic measurement was conducted with a MR-300 soliquidmeter, Rheology Co. Ltd. A sample was placed between two parallel plates of 18 mm diameter. The sample thickness was 1.0 mm. A periodic shear strain was loaded to the sample. The parallel plates with the sample were placed in the sealed chamber to prevent solvent evaporation. The frequency (ω) was varied from 0.06 to 40 Hz. The strain angle was fixed to be 2.0 deg. Three temperatures, 25, 55 and 85°C were chosen for the experiment. The maximum strain amplitude given to the samples was about 0.3 in shear units (s.u.). Therefore, we assume that the sample deformation is in the context of linear viscoelasticity.

RESULTS AND DISCUSSION

Composition dependence of SAXS

Figure 2 shows the Kratky plots ($q^2I(q)$ vs q) of SAXS intensity functions for samples with polymer concentration, C_p, of 35 wt%. q is the magnitude of the scattering vector. Although there is no peak in $q^2I(q)$ for $[NCO]/[OH] = 1.4$, a scattering maximum appears in $q^2I(q)$ for SPUU solutions with $[NCO]/[OH] \geq 1.6$ at around $q = 0.05$ Å^{-1}. This peak increases with [NCO]/[OH], which indicates that microphase separation consisting of hard and soft segment domains is progressively formed in solution with increasing [NCO]/[OH]. The long period of this microstructure, $L (\equiv 2\pi/q_{max})$, is estimated to be about 125 Å, where q_{max} is the peak position in the scattering curves. Since q_{max} has little dependence on [NCO]/[OH], it is obvious that the contrast between the hard and soft segment domains increases with [NCO]/[OH], while keeping a constant

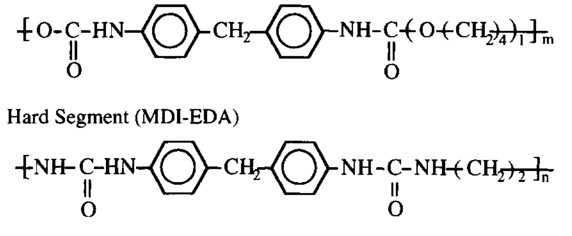

Figure 1 Chemical structures of the hard and soft segments

Table 1 Chemical composition of SPUU

[NCO]/[OH]	PTMG/MDI/EDA + DEA
1.4	1/1.4/0.4
1.5	1/1.5/0.5
1.6	1/1.6/0.6
1.7	1/1.7/0.7
1.8	1/1.8/0.8

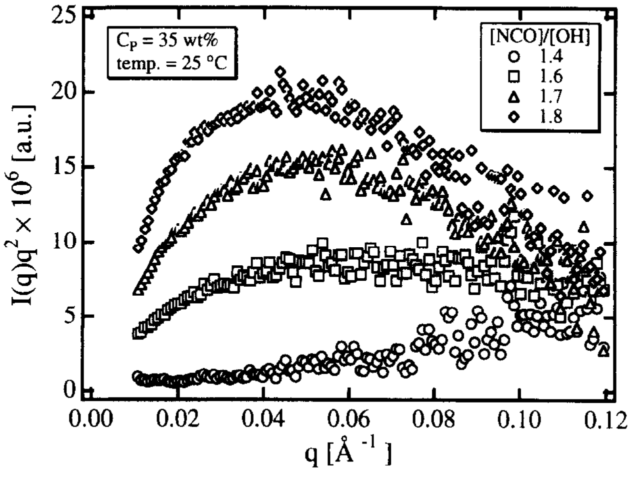

Figure 2 Kratky plots of SAXS intensity functions for 35 wt% SPUU solutions having different [NCO]/[OH]'s at 25°C

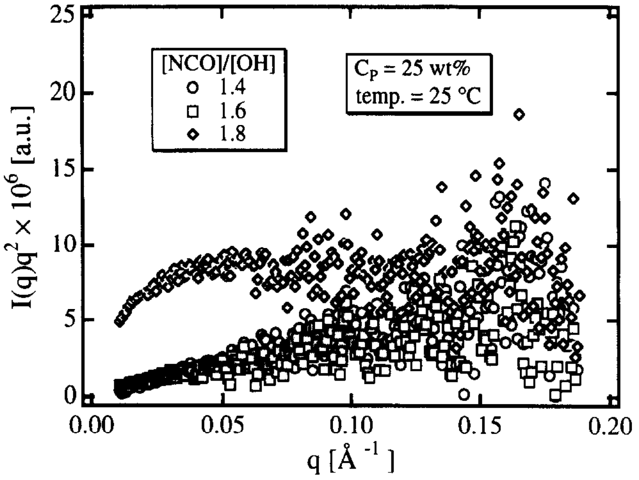

Figure 3 Kratky plots of SAXS intensity functions for 25 wt% SPUU solutions having different [NCO]/[OH]'s at 25°C

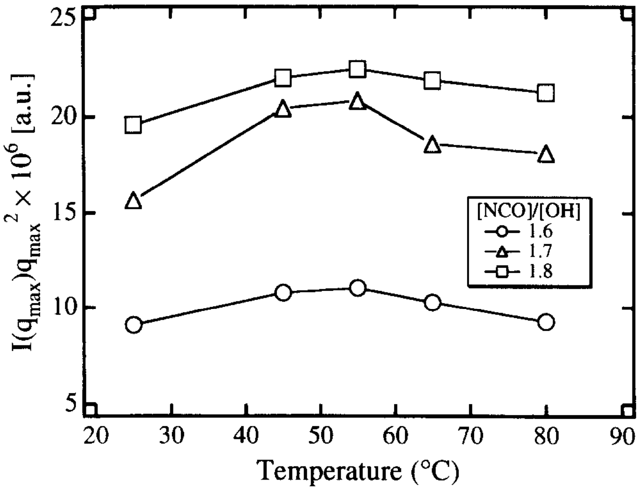

Figure 5 Temperature dependence of $I(q_{\max})q_{\max}^2$

value of L. A similar tendency was observed for 25 and 30 wt% solutions. In the case of $C_P = 25$ wt%, however, no peak appeared except $[NCO]/[OH] = 1.8$ as shown in *Figure 3*. This is simply due to a decrease of the degree of completion of the domain structure by dilution. For C_P's lower than 10 wt%, no peak was detected even for SPUU solution with $[NCO]/[OH] = 1.8$. It is also reported that L is about 85 Å, i.e. $q_{\max} \approx 0.075\,\text{Å}^{-1}$ for bulk films with the same [NCO]/[OH]'s[38]. By assuming an isotropic deswelling of microdomain structure, one can easily estimate $L(C_P)$ as a function of C_P. For example, L_{bulk}, (L for the bulk) is given by,

$$L_{\text{bulk}} \cong \left(\frac{C_P}{100}\right)^{1/3} L(C_P)$$

For $C_p = 35$ wt%, $L_{\text{bulk}} = 88.1$ Å, which is very close to the observed value. Therefore, it can be deduced that a microdomain structure is formed in a solution with $C_p \leq 35$ wt% and a bulk SPUU consists of a microdomain structure created by isotropic deswelling of the solution during solidification process.

Temperature dependence of SAXS

Figure 4 shows the temperature dependence of SAXS intensity profile (in Kratky plot) for the sample with $[NCO]/[OH] = 1.7$ and $C_p = 35$ wt%. We expected a decrease in the peak intensity with increasing temperature because of dissociation of hydrogen bonding between hard segments. Note that hydrogen bondings are formed not only between hard segments but also between hard or soft segments and the solvent. However, only the hydrogen bondings between hard segments contribute to formation of microphase separation[39]. Because of this, we are concerned only with the hydrogen bonds between hard segments in a solution. As shown in the figure, the peak intensity increased with temperature until 55°C and then decreased again, while the scattering curves kept an almost constant $q_{\max}$.

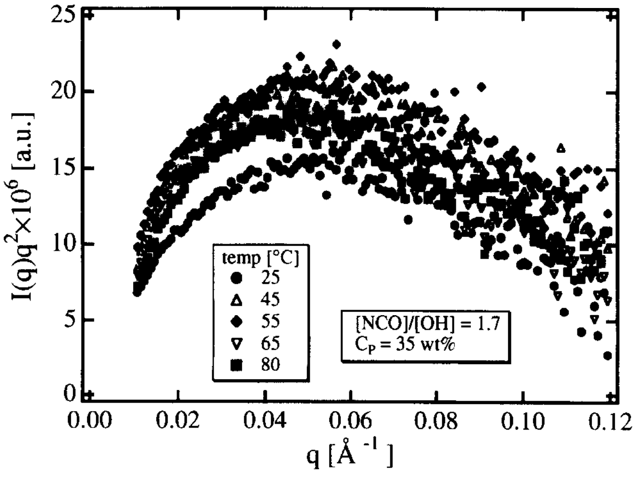

Figure 4 Kratky plots of SAXS intensity functions for 35 wt% SPUU solutions with $[NCO]/[OH] = 1.7$ at different temperatures

Figure 5 shows the temperature dependence of the peak intensities at $I(q_{\max})q_{\max}^2$ for SPUU's with $[NCO]/[OH] = 1.6$, 1.7 and 1.8. This indicates that the degree of completion of the hard segment domain increases gradually up to 55°C (regime I) and then decreases with further increasing temperature (regime II). Regime I is explained as an increase of mobility of polymer chains with temperature. Regime II, on the other hand, is due to scission of hydrogen bonds. This behaviour is analogous to the degree of crystallization vs temperature plot for semicrystalline polymers undergoing cold crystallization. Quenched crystalline polymers start to crystallize with increasing temperature before melting, and the degree of crystallization has a maximum at the cold crystallization temperature.

Interaction between SPUU and water

It should be pointed out here that contamination of water to SPUU leads to a dramatic effect on the microstructure of the SPUU/DMAc solution. An SPUU/DMAc solution becomes opaque by exposing the solution in air. The effect of water contamination is demonstrated clearly in *Figure 6*, which shows a dramatic increase in the SAXS intensity with a distinct peak. As shown in the figure, the peak position is very close to that without water contamination, i.e. $q \approx 0.05\,\text{Å}^{-1}$. This indicates that growth of hard segment domains takes place due to the change of solvent nature from good to poor by water contamination, which is mainly ascribed to the high affinity of the urea groups in the hard segment with water molecules by hydrogen bonding. It is clear that water contamination results in macrophase separation as evidenced by clouding of the

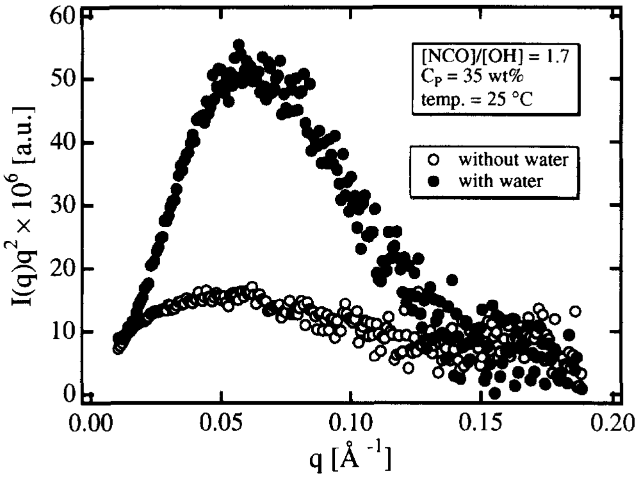

Figure 6 Kratky plots of SAXS intensity functions for 35 wt% SPUU solutions ([NCO]/[OH] = 1.7) with (closed symbols) and without water contamination (open symbols)

solution. However, the presence of the peak suggests that the microphase separated structure still remains in the system.

Frequency dependence of viscoelasticity

Figure 7 shows the frequency dependence of dynamic storage and loss shear moduli, $G'(\omega)$ (open symbols) and $G''(\omega)$ (closed symbols), for 35 wt% SPUU solutions observed with different [NCO]/[OH]'s at 25 and 85°C. The curves were shifted horizontally by factor A to avoid overlap. At 25°C (upper figure), both $G'(\omega)$ and $G''(\omega)$ increase monotonically with ω and the frequency dependence becomes smaller as [NCO]/[OH] increases. $G''(\omega)$ is always larger than $G'(\omega)$ at low [NCO]/[OH]'s i.e. 1.4 and 1.5. At [NCO]/[OH] = 1.6, $G'(\omega)$ and $G''(\omega)$ curves approach each other and become collinear. For [NCO]/[OH] = 1.7 and 1.8, $G'(\omega)$ has a slope smaller than $G''(\omega)$ and also $G'(\omega)$ becomes larger than $G''(\omega)$. A similar behaviour in viscoelasticity was observed in a gelation process of dimethylsiloxane in a reactor batch by Winter and coworkers[40] and in the cross-linking reaction of telechelic polyoxypropylene by Takahashi *et al.*[41]. Both of them observed a cross-over of $G'(\omega)$ and $G''(\omega)$ during the cross-linking process. The gelation threshold is defined as the point that $G'(\omega)$ exceeds $G''(\omega)$, i.e. $G'(\omega) = G''(\omega)$. Similarly, we regard the curves at [NCO]/[OH] = 1.6 as the gelation point in this paper.

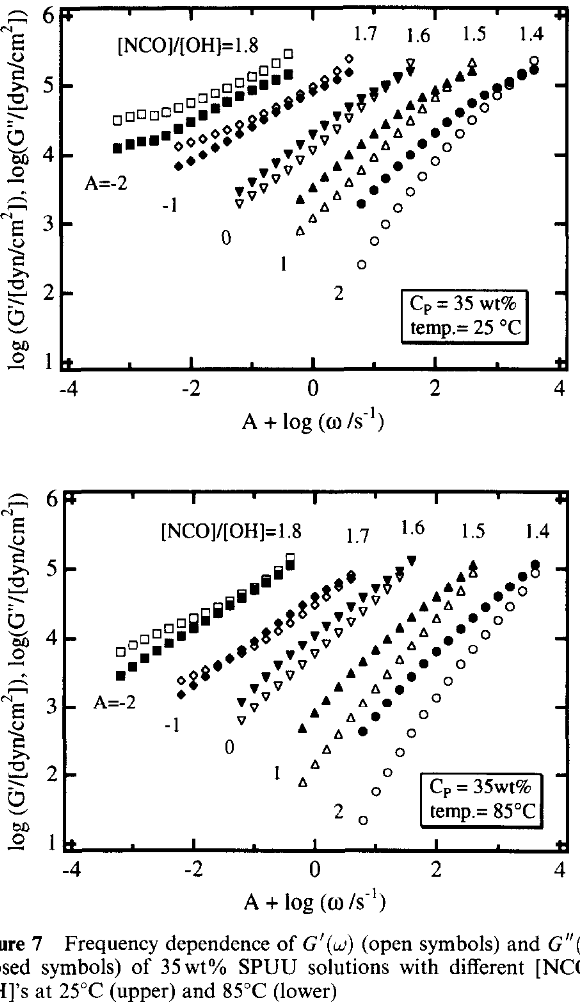

Figure 7 Frequency dependence of $G'(\omega)$ (open symbols) and $G''(\omega)$ (closed symbols) of 35 wt% SPUU solutions with different [NCO]/[OH]'s at 25°C (upper) and 85°C (lower)

Regarding ω dependence, it is known that a power law relationship of $G'(\omega) \approx G''(\omega) \approx \omega^k$ is observed at the gelation point[42]. k is related to the space and fractal dimensions, d and d_f as follows,

$$k = \frac{d}{d_f + 2} \tag{4}$$

The fractal dimension, d_f, at the gelation point is estimated to be 2.5 by percolation theories[42]. Using the value $d_f = 2.5$ for $d = 3$ for the space dimension, $k = 0.67$ is calculated. Actually, Takahashi *et al.* found $k = 0.67$–0.68 at the gelation point for a silyl terminated polyoxypropylene gel[41]. In our SPUU with [NCO]/[OH] = 1.6, $k = 0.69$ is observed, which indicates that SPUU solutions for [NCO]/[OH] $\geq$ 1.6 show a gel-like behaviour. This is because hard segment domains formed in solution behave as physically cross-linking points. At [NCO]/[OH] = 1.8 a slope of $G'(\omega)$ approaches zero, which means that the three-dimensional network is formed in the system. At 85°C (lower figure), $G'(\omega)$ and $G''(\omega)$ becomes lower than those at 25°C. This is probably because of the degradation of hydrogen bondings between hard segments with increasing temperature.

$G'(\omega)$ and $G''(\omega)$ for 30 wt% solutions at 25 and 85°C are shown in *Figure 8*. From this figure, it is also easy to understand that $G'(\omega)$ and $G''(\omega)$ for each [NCO]/[OH] decrease with increasing temperature. Furthermore, by comparing with *Figure 7*, it is also found that $G'(\omega)$ and $G''(\omega)$ for each [NCO]/[OH] decrease with decreasing C_p. This indicates that the SPUU solutions lose structural heterogeneity by dilution. This conclusion is supported by the results of SAXS measurement.

An interesting result was obtained by investigating the C_p dependence of viscoelasticity. *Figure 9* shows the C_p dependence of $G'(\omega)$ at 0.6 Hz and 25°C. At $C_p = 25$ wt%, $G'(\omega)$ decreases with [NCO]/[OH] up to 1.6 and then increases by further increase of [NCO]/[OH]. Similarly, at $C_p = 30$ wt%, $G'(\omega)$ at [NCO]/[OH] = 1.6 is the smallest of all. At $C_p = 35$ wt%, $G'(\omega)$ increases with [NCO]/[OH], which was what we expected. By assuming that $G'(\omega)$ increases with the degree of completion of the hard segment domain structure, the upturn at [NCO]/[OH] = 1.6 indicates that an increase of the fraction of hard segments does not necessarily give rise to increase in

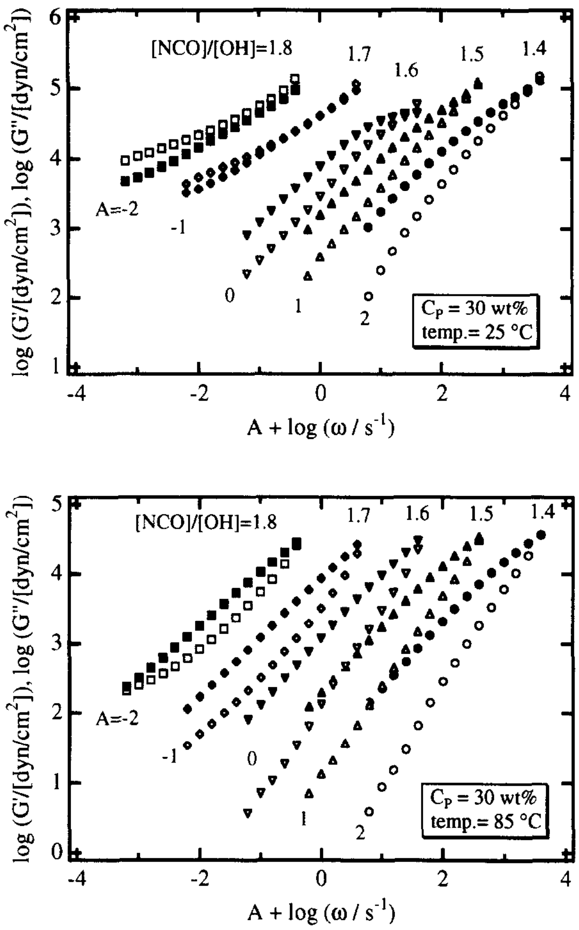

Figure 8 Frequency dependence of $G'(\omega)$ (open symbols) and $G''(\omega)$ (closed symbols) of 30 wt% SPUU solutions with different [NCO]/[OH]'s at 25°C (upper) and 85°C (lower)

the degree of completion of the hard segment domains. This can be explained as follows: At the same C_p as [NCO]/[OH] becomes close to 1, a microphase separation between soft and hard segment domains occurs more readily because of the thermodynamic incompatibility. However, by increasing [NCO]/[OH] (up to 1.6 for the samples with $C_P = 25$ wt% at 25°C), the presence of hard segments in the system reduces the mobility of polymer chains due to the rigidity of hard segments and hampers formation of hard domains. Further increase of [NCO]/[OH] leads an increased chance of coming into contact for hard segments and encourages creation of hard segment domains. Therefore, the degree of completion in the hard segment domains is determined in competition between the mobility and the contact of hard segments. This balance is dependent on C_p as shown in *Figure 9*. This observation, i.e. the presence of an optimum in G' with respect to [NCO]/[OH], corresponds to the result of the T_g shift reported by Nierzwicki and Wysocka[22]. They suggested that the [NCO]/[OH] giving a maximum in T_g is determined by the competition of microphase separation and cross-linking. That is to say, although the rise of [NCO]/[OH] leads to a progress of phase separation and cross-linking formation, the former increases T_g and the latter decreases T_g. This indicates that the rise of the fraction of hard segments does not always lead to the increase of T_g, which also supports our results.

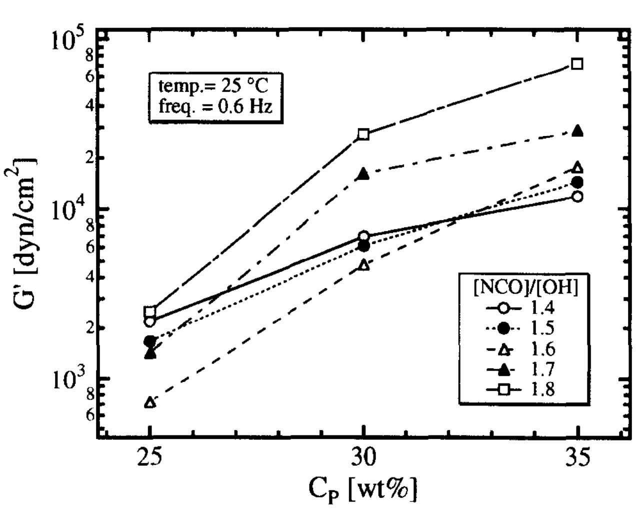

Figure 9 C_p dependence of $G'(\omega)$ at different [NCO]/[OH]'s

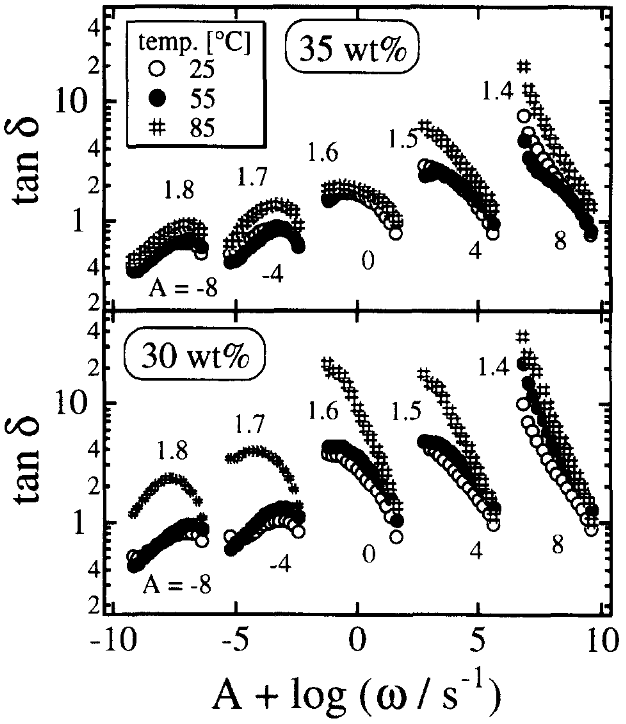

Figure 10 Frequency dependence of tan δ for 30 and 35 wt% SPUU solutions

Figure 10 shows the changes in the loss tangent tan $\delta(\equiv G''(\omega)/G'(\omega))$ with frequency for the samples of 30 and 35 wt% solutions with different [NCO]/[OH]. The curves were also shifted horizontally by factor A to avoid overlap. At [NCO]/[OH] = 1.4 and 1.5 for $C_p = 35$ wt%, tan δ curves have negative slopes because the ω dependence of $G''(\omega)$ is smaller than that of $G'(\omega)$, which is usually observed in polymer solutions having no structural heterogeneity. On the other hand, at [NCO]/[OH] = 1.7 and 1.8, the samples become gel-like and the ω dependence of $G'(\omega)$ is suppressed. Thus, a positive slope appears in the tan δ curve. Apparently, the sample at [NCO]/[OH] = 1.6 has an intermediate property between the two extremes. Therefore, we can distinguish the state of a sample, i.e. either gel-like or sol-like, by examining the sign of slopes of the tan δ curve. At $C_P = 30$ wt% as shown in the figure, the sample at [NCO]/[OH] = 1.6 also has a negative slope, indicating that the sample approaches a sol-like state due to dilution. Furthermore, it is found in *Figure 10* that the decrease of C_p and the increase of temperature leads to annihilation of hard segment domains, monitored as a decrease of $\tan\delta$.

CONCLUSIONS

The microphase separated structure and dynamic mechanical properties of segmented polyurethaneurea (SPUU) in concentrated DMAc solutions were investigated with small-angle X-ray scattering (SAXS) and viscoelastic measurements, respectively, as a function of temperature, polymer concentration (C_p), and [NCO]/[OH]. Kratky plots of the SAXS intensity function, $I(q)$, show a broad peak at $q = 0.05\,\text{Å}^{-1}$, which indicates the presence of the long period (L) being about 125 Å. The peak increased with [NCO]/[OH], indicating that formation of hard segment domains stabilized by hydrogen bondings between hard segments was proceeded by an increase of [NCO]/[OH]. Furthermore, it was found that $I(q)$ increased up to 55°C and then decreased with temperature. This is due to the balance between the increase of mobility of polymer chain and degradation of hydrogen bonds with increasing temperature. On the other hand, the viscoelastic measurement showed that the storage, $G'(\omega)$, and loss moduli, $G''(\omega)$, increased with C_p and with [NCO]/[OH]. This phenomenon was compared with a gelation process of chemically cross-linked gel. At the [NCO]/[OH] corresponding to the gelation point of such a gel, a power law relation of $G'(\omega) \approx G''(\omega) \approx \omega^k$ at $k = 0.67$ was observed, which is very similar to the literature value reported by Takahashi *et al.* Furthermore, it is shown that the state of polymer solutions, either gel or sol, can be discriminated by the slope of the loss tangent ($\tan\delta$) vs ω plot. An interesting tendency was shown by the C_p dependence of $G'(\omega)$. $G'(\omega)$ increased up to $[\text{NCO}]/[\text{OH}] = 1.6$ and then decreased with [NCO]/[OH]. The degree of completion can be explained by a competition between the increase of the mobility of hard segments and the rise of the contact of hard segments.

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