

Capillary flow properties and dissolved state of segmented poly(urethane-urea)/*N,N*-dimethylacetamide solution as a function of temperature

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Capillary flow properties of a concentrated *N,N*-dimethylacetamide (DMAc) solution of segmented poly(urethane-urea) (PUR) prepared from 4,4'-diphenylmethanediisocyanate (MDI), polytetramethyleneoxide (PTMO), and ethylenediamine (EDA) (polymer concentration, 30.0 wt%; hereafter referred to as 'PUR-solution') as well as the dissolved state was investigated as functions of solution temperature (T_{sol}) and shear rate ($\dot{\gamma}$): non-Newtonian index n in the equation $\eta_s = k\dot{\gamma}^{-n}$ decreased remarkably with increase in T_{sol} in the range more than about 90°C. The logarithmic shear viscosity ($\log \eta_s$) of the PUR-solution as a function of $1/T_{\text{sol}}$ gave two linear regions below and above 90°C, suggesting that the activation energy of flow of the PUR-solution estimated in the T_{sol} range from 90 to 130°C (ΔE_h) was higher than that (ΔE_l) in the T_{sol} range of 40–80°C. The $\Delta E_h - \Delta E_l$ value was proved to become somewhat smaller as $\dot{\gamma}$ increased, indicating that the shear stress might control the dissolved state of PUR to some extent but this contribution is much smaller than that by T_{sol} . ^1H and ^{13}C n.m.r. analysis on the dissolved states of PUR in the solution revealed existence of some hydrogen bondings mainly between N–H and C=O of urea groups, and suggested that the sudden decrease in η_s of the PUR-solution at more than about 90°C is associated with a steep decrease in the average strength of the hydrogen bondings. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(urethane-urea); capillary flow property; concentrated solution)

INTRODUCTION

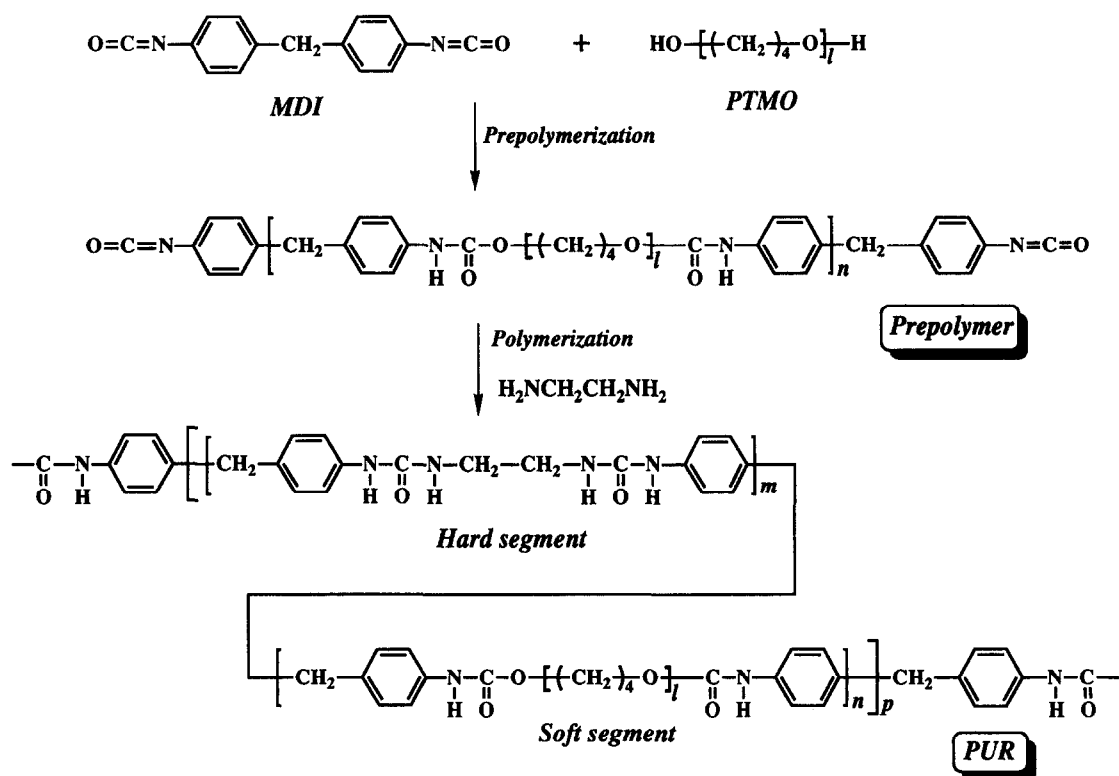
Segmented poly(urethane-urea)s (PURs) are a kind of block copolymers composed of soft and hard segments. In general, they are made in a two-stage process^{1–3}: (1) formation of NCO-terminated prepolymers and (2) the reaction of the prepolymer with diamine, giving PUR (Scheme 1). The soft segment usually consists of aliphatic polyether or polyester urethane block and the hard segment is a polyurea block. It is known that there are several kinds of hydrogen bondings between the hard and hard segments, and the hard and soft segments in the solid state, where most of the hydrogen bondings are formed by the N–H and C=O groups. The strong hydrogen bondings are formed in the hard segment domains which are regarded as physical crosslinking points and play an important role in the elastic properties of PUR materials^{4–9}. Kaji and Murano¹⁰ demonstrated the schematic illustration of phase-separated heterogeneous structure composed of the hard domains and soft domains in a stretched and heat set PUR sample. PURs are widely applicable to a number of industrial products as functional plastics due to their outstanding elastic properties; elastomers, foams, adhesives, paints, etc. In

particular, they are in great demand for functional fibres with excellent stretching properties, and hence numerous investigators have studied the morphology, rheological properties, and many industrial applications of PUR fibres.

However, the PUR fibres are mainly produced by wet spinning and dry spinning methods which inevitably require the following two processes: the extrusion of spinning solution through a spinneret under some definite temperature conditions and the removal of solvent to give fibres¹¹. Therefore, the extrusion conditions in relation to the dissolved state of PUR might be one of important determinants of final yarn structures and properties, as is the case with other many polymer melts during their melt spinning. Concerning the dissolved state of PUR, Itoh *et al.*¹² have recently revealed by the static light scattering technique that the mean square radius of gyration ($\langle S^2 \rangle$) of PUR becomes progressively larger with time in concentrated DMAc solutions but unfortunately the view points mentioned above have been ignored there.

In this article, the capillary flow properties of a concentrated *N,N*-dimethylacetamide (DMAc) solution of PUR (30.0 wt%) prepared from 4,4'-diphenylmethanediisocyanate (MDI), polytetramethyleneoxide (PTMO), and ethylenediamine (EDA) were

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Scheme 1 Typical route of synthesis of segmented poly(urethane-urea) (PUR)

investigated, as functions of solution temperature (T_{sol}) and shear rate ($\dot{\gamma}$), in relation to the dissolved state of PUR.

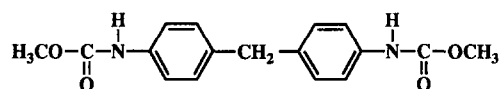
EXPERIMENTAL

Materials

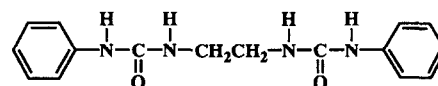
MDI manufactured by Nippon Polyurethane Industry Co. Ltd. (Tokyo) was freshly distilled at 185°C/3 Toll (1 Toll = 133.322 Pa). The purity of MDI thus prepared was higher than 99.9% as determined by the conventional titration method¹³. PTMO manufactured by Asahi Chemical Industry Co. Ltd. (Tokyo) was heated before use at 90°C/3 Toll for 4 h to reduce the moisture content to 15 ppm as measured by a moisture meter, Model CA-03 produced by Mitsubishi Chemical Industry Co. Ltd. (Tokyo). The number-average molecular weight (M_n) of PTMO was 2020 as determined by the end group analysis¹⁴. Reagent grade DMAc, supplied by Mitsubishi Gas Chemical Co. Ltd. (Tokyo), was dried over molecular sieves (4A) and distilled before use with small amounts of phosphorus pentoxide to keep moisture contents below 30 ppm. Special grade EDA, methanol, and phenylisocyanate, purchased from Wako Pure Chemical Industries Ltd. (Osaka), were used without further purification. Special grade lithium chloride (LiCl) was also commercially available from Wako Pure Chemical Industries Ltd.

Preparation of model compounds

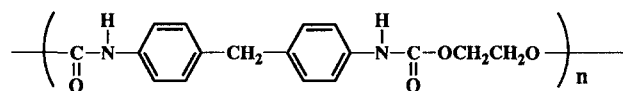
Dimethyl 4,4'-diphenylmethane dicarbamate (M-Ut) was synthesized by the reaction of MDI (114.8 mmol) with methanol (459.4 mmol) in DMAc at 20°C for 2 h. On the other hand, phenylisocyanate (35.3 mmol) was allowed to react with EDA (17.1 mmol) to give 1,2-bis(*N'*-phenylureido)ethane (M-Ur) in DMAc at 0°C



M-Ut



M-Ur



M-PU

Scheme 2 Model compounds

for 2 h. These two model compounds were recrystallized from methanol before use, and their chemical structures were confirmed by ¹H n.m.r. measurements. A polyurethane (M-PU) as a model compound was prepared by the reaction between MDI and ethyleneglycol ([NCO]/[OH] = 1.23 molar ratio) in DMAc at 50°C for 3 h, followed by pouring the reaction mixture into a large amount of methanol¹⁵. The chemical formula of these model compounds are shown in Scheme 2.

Preparation of the 'PUR-solution'

The concentrated DMAc solution of PUR (30.0 wt%) (hereafter referred to as 'PUR-solution'), was prepared in the following two processes using PTMO, MDI, EDA, and DMAc; a 1000 ml reaction flask equipped with stirrer, dropping funnel, and two two-way cocks was used for the polymerization. MDI and PTMO were dissolved in DMAc in the flask ($[\text{NCO}]/[\text{OH}] = 1.60$ molar ratio), after which the mixture was stirred slowly at 15°C for 2.5 h under nitrogen to give a 35 wt% of NCO-terminated prepolymer solution (*Prepolymerization*). After titrating the residual NCO groups in the prepolymer solution using di-*n*-butylamine, a DMAc solution of the chain extender EDA equivalent to the NCO groups was quickly added with vigorous stirring to obtain the 'PUR-solution' (*Polymerization*).

The viscosity-average molecular weight (\overline{M}_v) of the PUR estimated by the following Mark-Houwink-Sakurada equation (1) reported by Kamide *et al.*¹⁶ was 6.5×10^4 .

$$[\eta] = 0.101 \overline{M}_v^{0.159} \quad (\text{DMAc, } 25^\circ\text{C}) \quad (1)$$

The calculated hard segment content in the PUR was 8 wt%, and the PUR-solution kept the original capillary flow properties for several months without gelation at low temperature (e.g. $< \sim 5^\circ\text{C}$).

Preparation of the PUR-solution containing 0.6 wt% of LiCl

LiCl (1.81 g) was added to the PUR-solution (300 g), and the mixture was stirred slowly at 70°C for 7 h under nitrogen to give the PUR-solution containing 0.600 wt% of LiCl.

Measurement of shear viscosity (η_s) of the PUR-solution

A capillary rheometer (Toyo Seiki Capirograph 1B) was used for the measurements of shear viscosities (η_s) of the PUR-solution under the solution temperature (T_{sol}) ranging from 40 to 130°C and the shear rate ($\dot{\gamma}$) ranging from 48.64 to $4.864 \times 10^4 \text{ s}^{-1}$. A capillary having diameter (D) of 0.50 mm and length (L) to diameter ratio (L/D) of 4.0 was used. From the Arrhenius plot [$\eta_s = A \exp(\Delta E/RT)$] and the power-law relationship ($\eta_s = k \dot{\gamma}^{-n}$) the apparent activation energy of flow (ΔE) and the $\dot{\gamma}$ dependence of η_s were evaluated.

N.m.r. measurements

N.m.r. spectra were recorded on a Jeol GSX-400 spectrometer (^1H frequency of 399.78 MHz or ^{13}C frequency of 100.54 MHz). ^1H n.m.r. spectra were measured for a sample as 20.0 wt% solution of PUR prepared by dilution of the PUR-solution with deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) in range 30 to 140°C under the following operating conditions: pulse width, 8.0 ms (45° pulse); pulse delay time, 2.635 s; acquisition time, 1.365 s; number of pulses, 16; data point, 16 K; tetramethylsilane (TMS) as internal standard (0 ppm).

The measurements of ^{13}C spin-lattice relaxation times (T_1) of C=O groups in PUR were carried out using inversion recovery (IR) method for the PUR-solution placed in a rounded glass cell inserted into the sample tube (10 mm ϕ) containing $\text{DMSO-}d_6$ and a small amount of TMS. The operating conditions are as

follows: pulse sequence, $180^\circ-t-90^\circ$; acquisition time, 0.655 s; number of pulses, more than 300; data point, 8 K.

The assignment of ^1H and ^{13}C n.m.r. spectra of the PUR-solution was carried out using the model compounds (M-Ut and M-Ur) and the literature data¹⁷.

RESULTS AND DISCUSSION

Capillary flow properties of the PUR-solution

Figure 1 shows the plots of the shear viscosity (η_s) vs the shear rate ($\dot{\gamma}$) of the PUR-solution at typical solution temperatures (T_{sol}) of 40, 85, 100, and 120°C in the $\dot{\gamma}$ region of 7.30×10^2 – $4.86 \times 10^4 \text{ s}^{-1}$. In the $\dot{\gamma}$ region examined, the experimental data gave linear plots. The estimated n values in the equation $\eta_s = k \dot{\gamma}^{-n}$, i.e. non-Newtonian index, are plotted against T_{sol} as shown in Figure 2. There were observed distinctly two linear regions and the n value decreased remarkably with increase in T_{sol} at more than about 90°C. This result indicates that the capillary flow property of the PUR-solution changes drastically below and above 90°C

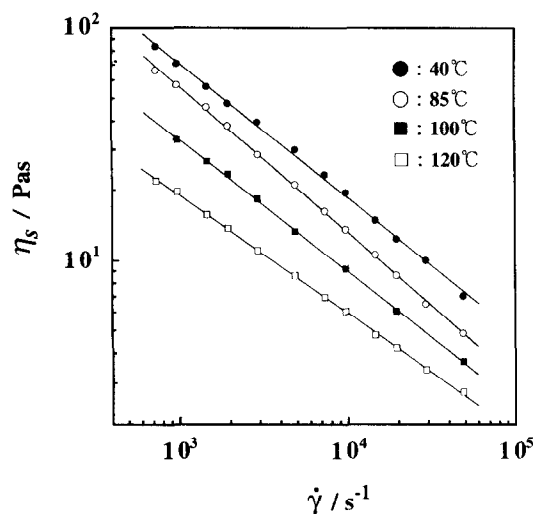


Figure 1 Plots of the shear viscosity (η_s) of the PUR-solution against the shear rate ($\dot{\gamma}$) in the region of 7.30×10^2 – $4.86 \times 10^4 \text{ s}^{-1}$ at the solution temperature of 40 (●), 85 (○), 100 (■), and 120°C (□)

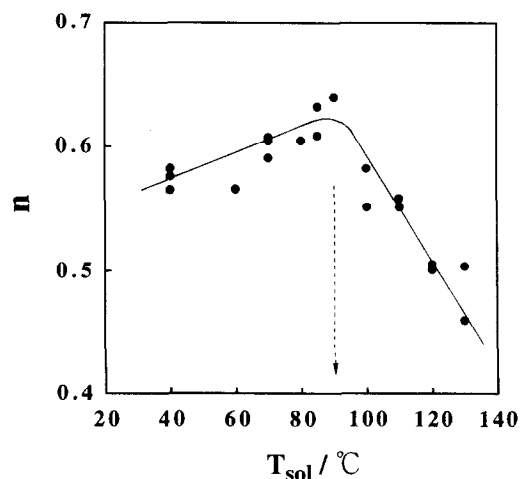


Figure 2 Solution temperature (T_{sol}) dependence of n values estimated in the equation $\eta_s = k \dot{\gamma}^{-n}$ for the PUR-solution

(40–90 and 90–130°C), and the non-Newtonian behaviour becomes weaker with raising T_{sol} in the higher temperature region. As will be discussed in detail later, the PUR chains dissolved in the concentrated DMAc solution is assumed to keep an appreciable interaction with each other in the lower temperature region, but the average strength of the interaction might decrease abruptly when T_{sol} rises beyond about 90°C.

Figure 3 shows the $1/T_{\text{sol}}$ dependence of the $\log \eta_s$ of the PUR-solution in the $\dot{\gamma}$ region of 7.30×10^2 – $4.86 \times 10^4 \text{ s}^{-1}$. In all cases examined, two linear regions were detected and an abrupt decrease in η_s of the PUR-solution in the T_{sol} range from 90 to 130°C was observed. The η_s of the PUR-solution measured at 120°C ($\dot{\gamma} = 7.30 \times 10^2 \text{ s}^{-1}$) was 18.6 Pas, which was 13.0 Pas lower than the value estimated by extrapolation of the linear plot of $\log \eta_s$ vs $1/T_{\text{sol}}$ in the temperature region of 40–80°C to 120°C. In contrast, the lowering of η_s by heating the PUR-solution at 120°C for 1.0 h was only 1.25 Pas and no new peak was observed in the ^1H n.m.r. spectra even after the measurements of the PUR-solution containing DMSO- d_6 (DMAc/DMSO- $d_6 = 1.3$ weight ratio; the concentration of PUR is 20.0 wt%) in the temperature region of 30–140°C. This clearly suggests that the abrupt decreases in η_s above around 90°C shown in Figure 3 were not attributable to some side reactions such as thermal decomposition of urethane groups in the PUR chains.

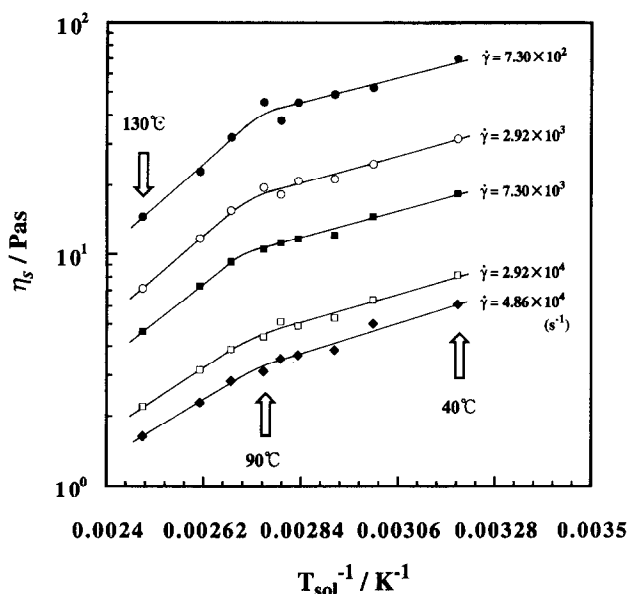


Figure 3 Solution temperature (T_{sol}) dependence of the shear viscosity (η_s) of the PUR-solution in the shear rate ($\dot{\gamma}$) region of 7.30×10^2 – $4.86 \times 10^4 \text{ s}^{-1}$

Table 1 Apparent activation energies of flow of the PUR-solution estimated in the regions of 40–80°C (ΔE_l) and 90–130°C (ΔE_h) at each shear rates ($\dot{\gamma}$)

$\dot{\gamma}$ (s^{-1})	Activation energy, ΔE (kJ mol^{-1})		$\Delta E_h - \Delta E_l$ (kJ mol^{-1})
	ΔE_l (40–80°C)	ΔE_h (90–130°C)	
2.92×10^2	1.3	37.8	36.5
9.73×10^2	2.8	32.3	29.5
1.95×10^3	3.0	27.4	24.4
4.86×10^3	3.8	24.0	20.2
1.95×10^4	7.0	17.5	10.5

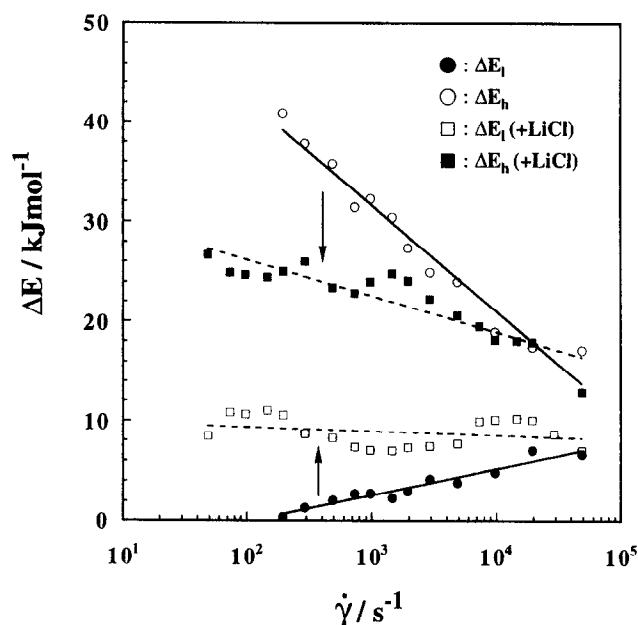


Figure 4 Plots of the apparent activation energies of flow estimated in the solution temperature (T_{sol}) regions of 40–80°C (ΔE_l) and 90–130°C (ΔE_h) against shear rate ($\dot{\gamma}$). ● and ○, data for the PUR-solution; □ and ■, data for the PUR-solution containing 0.600 wt% of LiCl

The apparent activation energies of flow in the two regions of 40–80°C (ΔE_l) and 90–130°C (ΔE_h) were evaluated as a function of $\dot{\gamma}$ and are shown in Table 1, and more detailed $\dot{\gamma}$ dependence is demonstrated in Figure 4. Evidently, ΔE_l (●) increases with increase in $\dot{\gamma}$ but the reverse is true for ΔE_h (○), resulting in the lowering of the $\Delta E_h - \Delta E_l$ value with increase in $\dot{\gamma}$ and $\Delta E_h - \Delta E_l$ can be expressed by

$$\Delta E_h - \Delta E_l = -14.1 \log \dot{\gamma} + 71.5 \quad (2)$$

The lowering of the $\Delta E_h - \Delta E_l$ value is considered to be attained by forced orientation of the PUR chains in the solution at higher $\dot{\gamma}$. In the $\dot{\gamma}$ region from 48.6 to $4.86 \times 10^4 \text{ s}^{-1}$, however, the abrupt decrease in η_s of the PUR-solution always appeared at 80–90°C as shown in Figure 3. These results indicate that the shear stress might control the capillary flow properties but this contribution is much smaller than that by T_{sol} . From Figure 4, ΔE_l and ΔE_h are about 5 and 22 kJ mol^{-1} at $\dot{\gamma} = 7.8 \times 10^3 \text{ s}^{-1}$, respectively. On the other hand, Tomokiyo *et al.*¹⁸ reported using the same capillary rheometer that the apparent activation energy of melt flow of nylon-66 was about 46 kJ mol^{-1} at $\dot{\gamma} = 7.8 \times 10^3 \text{ s}^{-1}$. The value for melt flow (46 kJ mol^{-1}) was apparently closer to the ΔE_h of 22 kJ mol^{-1} rather than that of 5 kJ mol^{-1} estimated in the region of 40–80°C. The average strength of hydrogen bondings among PUR chains, if the strong interactions exist at lower T_{sol} , is assumed to decrease with raising T_{sol} . Accordingly, the production of higher energy barriers to flow of the PUR-solution in the region of 90–130°C may be based on the cleavage of the hydrogen bondings concerning N–H and C=O groups of the PUR chains. All the above results point to more or less the difference of the dissolved state of PUR below and above 90°C.

Dissolved state of the PUR-solution

It is well known that the solid state microstructures in PUR fibres have a lot of domains of interchain interaction (i.e. hydrogen bonding) between N-H and C=O groups in the hard segments, which form networks

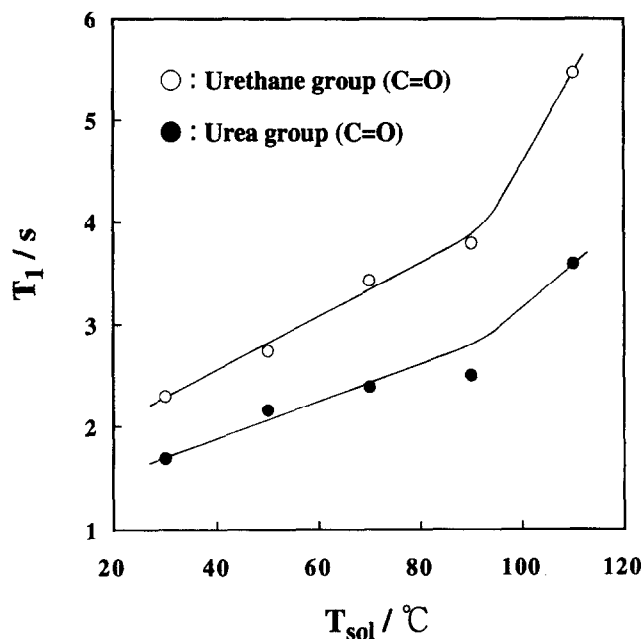


Figure 5 Solution temperature (T_{sol}) dependence of the average ^{13}C spin-lattice relaxation times (T_1) of C=O in ureas (\bullet) and urethane (\circ) groups of PUR in the PUR-solution

in the microstructure. These hard segment domains disturb the plastic flow in the PUR fibre, capable of recovering from the deformation⁴⁻¹⁰.

Then in order to elucidate the abrupt decrease in the shear viscosity of the PUR-solution at more than about 90°C , the dissolved state of PUR in the PUR-solution was investigated using ^{13}C and ^1H n.m.r. measurements at first. Figure 5 shows the T_{sol} dependence of average ^{13}C spin-lattice relaxation times (T_1) of C=O in the urea (\bullet) and urethane (\circ) groups of PUR chains in the PUR-solution. The ^{13}C n.m.r. spectrum of the PUR-solution gave a C=O peak of urethane groups at around 154 ppm and a urea C=O peak was observed at about 156 ppm. The T_1 values in the urethane groups were longer than those in the urea groups at the same T_{sol} , suggesting that the urea C=O segmental motions were on the whole suppressed in comparison with those of urethane groups in the PUR-solution. Interestingly, the T_1 values of urethane (\circ) groups drastically increased above about 90°C , indicating that segmental motion of urethane groups is much restricted in the dissolved state of PUR in the lower T_{sol} region.

Figure 6 demonstrates a fraction of structural formula of PUR and ^1H n.m.r. spectrum of the PUR-solution containing DMSO- d_6 as an n.m.r. lock solvent (DMAc/DMSO- $d_6 = 1.3$ weight ratio) measured at 30°C . Three single peaks were observed at the magnetic field near 9.5, 8.5, and 6.2 ppm, assigned to H^a (urethane), H^b (urea), and H^c (urea) of N-H groups in the structural formula, respectively. The full lines in Figure 7 show the T_{sol} dependence of half-height linewidth of the H^a peak [$\Delta\nu_{1/2}(H^a)$; \diamond], H^b peak

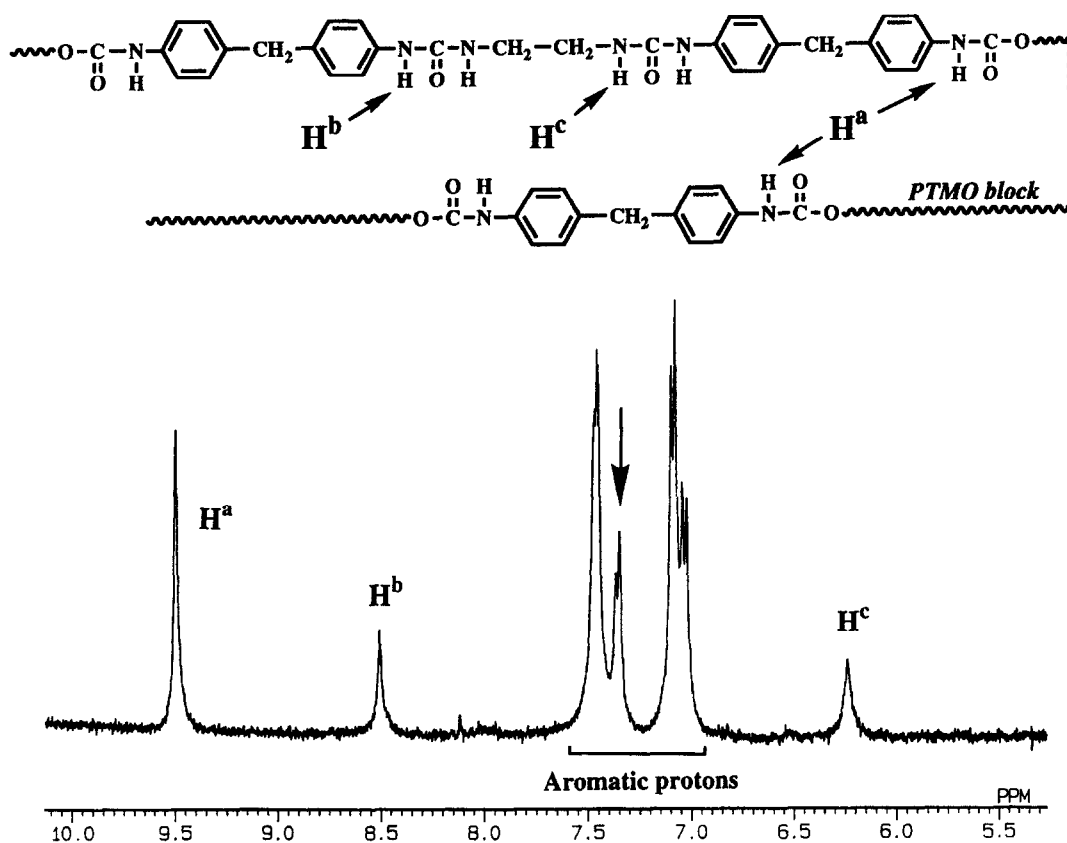


Figure 6 A fraction of structural formula of PUR and ^1H n.m.r. spectrum of the PUR-solution containing DMSO- d_6 (DMAc/DMSO- $d_6 = 1.3$ weight ratio) measured at 30°C (TMS = 0 ppm)

$[\Delta\nu_{1/2}(H^b); \circ]$, and H^c peak $[\Delta\nu_{1/2}(H^c); \square]$. Evidently, the $\Delta\nu_{1/2}(H^c)$ values were larger than those of $\Delta\nu_{1/2}(H^a)$ and $\Delta\nu_{1/2}(H^b)$. This ^1H n.m.r. analysis suggests that the partial motion of N-H groups in the urethane and urea groups in the PUR-solution were on the whole restricted in the following order: $H^c \gg H^b > H^a$.

Saotome *et al.*¹⁹ examined the melting points of various polyurethane and polyurea compounds, and reported that polyurea compounds had about 70–100°C higher melting points than those of the corresponding polyurethane. They suggested consequently that the intermolecular cohesion energy of urea groups was larger than that of urethane groups. Then we investigated the solubilities of the model compounds (M-Ut and M-Ur) in 100 g of DMAc at 40°C, and the solubility of M-Ur was found to be only 1.6 g although that of

M-Ut was as high as 53.4 g. This shows the existence of relatively strong interactions among urea groups even in the DMAc solution, and supposes the inter- and intramolecular interactions in the hard segments in the PUR-solution.

Based on the above results, the dissolved state of PUR in DMAc was assumed as follows: PUR chains dissolved in DMAc interact appreciably with each other through hydrogen bondings (i.e. C=O ... H-N) between the urea-urea, urea-urethane, and urethane-urethane groups, especially between the urea-urea groups. In particular, the N-H protons adjacent to ethylene groups in hard segments (i.e. H^c) were thought to interact more strongly with C=O groups. The hydrogen bonded state between two hard segments in the PUR-solution might be represented by the equilibrium composed of two possible canonical structure (H^b -O type and H^c -O type), as shown in Scheme 3. The equilibrium state can presumably be considered to lie relatively to the H^c -O type. The existence of the relatively strong hydrogen bondings is expected to affect the capillary flow properties of the PUR-solution.

Relationship between the capillary flow properties and the dissolved state of the PUR-solution

As shown in the full lines in Figure 7, the $\Delta\nu_{1/2}(H^b)$ values (\circ) decreased more rapidly with raising T_{sol} in the region below about 80°C, compared with the temperature region above about 90°C. On the other hand, the minimum $\Delta\nu_{1/2}(H^a)$ value (\diamond) was also obtained at around 80°C. In contrast, the slope of the $\Delta\nu_{1/2}(H^c)$ plots (\square) hardly changed at about 80°C. Figure 8 shows the T_{sol} dependence of the ^1H chemical shift of (a) H^a , (b) H^b , and (c) H^c . All the three N-H peaks shifted to a large extent to higher magnetic fields as a function of T_{sol} . Note that the aromatic proton peaks did not appreciably shift to higher magnetic field with raising T_{sol} , e.g. the aromatic proton peak with arrow mark in the spectrum in Figure 6 shifted slightly from 7.347 ppm (30°C) to 7.298 ppm (140°C). As shown in Figure 8a, the line of the T_{sol} dependence of H^a chemical shift bended at 80–90°C, suggesting an abrupt decrease in the average strength of the hydrogen bondings concerning the H^a protons at the temperature region. In contrast to this, the slope of the line of H^b chemical shift (Figure 8b) changed little at about 90°C, and a bending point was not observed in the H^c line (Figure 8c).

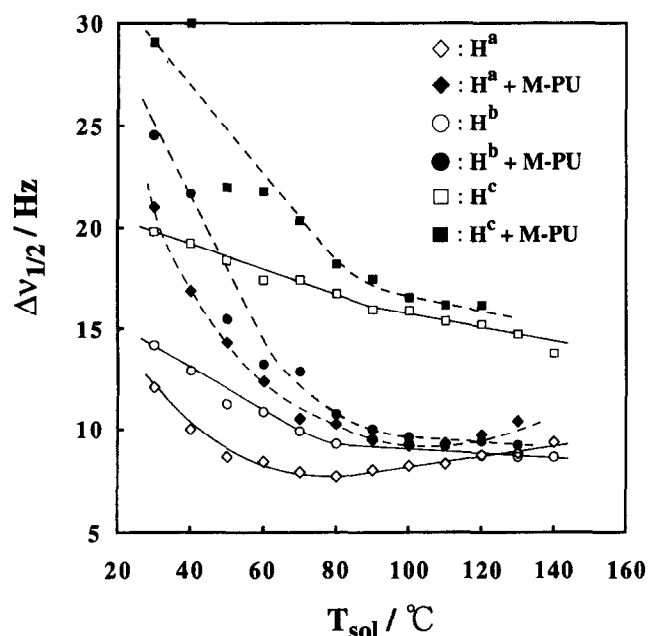
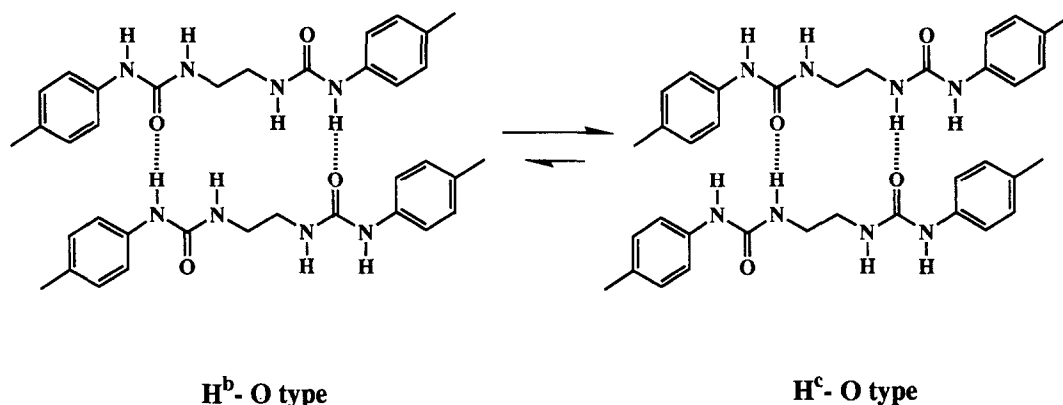


Figure 7 Solution temperature (T_{sol}) dependence of half-height line width of the H^a peak $[\Delta\nu_{1/2}(H^a); \diamond]$, H^b peak $[\Delta\nu_{1/2}(H^b); \circ]$, and H^c $[\Delta\nu_{1/2}(H^c); \square]$ in the ^1H n.m.r. spectrum of the PUR-solution containing $\text{DMSO-}d_6$ ($\text{DMAc}/\text{DMSO-}d_6 = 1.3$ weight ratio). The values of \blacklozenge , \bullet , and \blacksquare were estimated in the ^1H n.m.r. spectrum of the PUR-solution also dissolving a 1.80 wt% polyurethane compound (M-PU)



Scheme 3 Hydrogen bonded state between two hard segments of PUR in the PUR-solution represented by an equilibrium composed of two possible canonical structures (H^b -O type and H^c -O type)

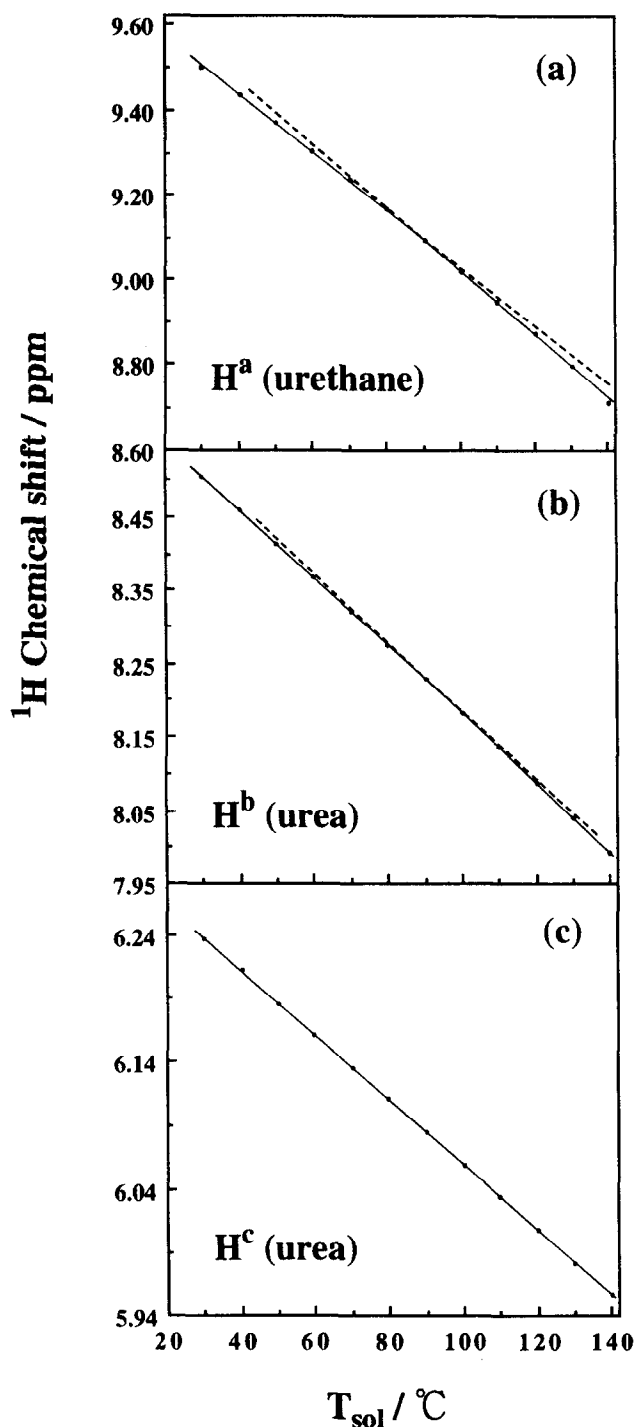


Figure 8 Solution temperature (T_{sol}) dependence of the ^1H chemical shift of (a) H^a , (b) H^b , and (c) H^c of PUR in the PUR-solution containing $\text{DMSO-}d_6$ (DMAc/ $\text{DMSO-}d_6 = 1.3$ weight ratio, TMS = 0 ppm)

It can probably be considered from the above results that the average strength of the hydrogen bondings concerning the H^b and the H^c protons between the urea-urea groups did not appreciably decrease at 80–90°C due to the relatively stable structures illustrated in *Scheme 3*, although the average strength of other kinds of hydrogen bondings (e.g., between the urea-urethane and urethane-urethane groups) decreased abruptly at the temperature region. These assumptions were strongly supported by the results shown in *Figure 5* that the average T_1 of C=O bonds in the urethane groups (○) became longer abruptly above 90°C, compared with that

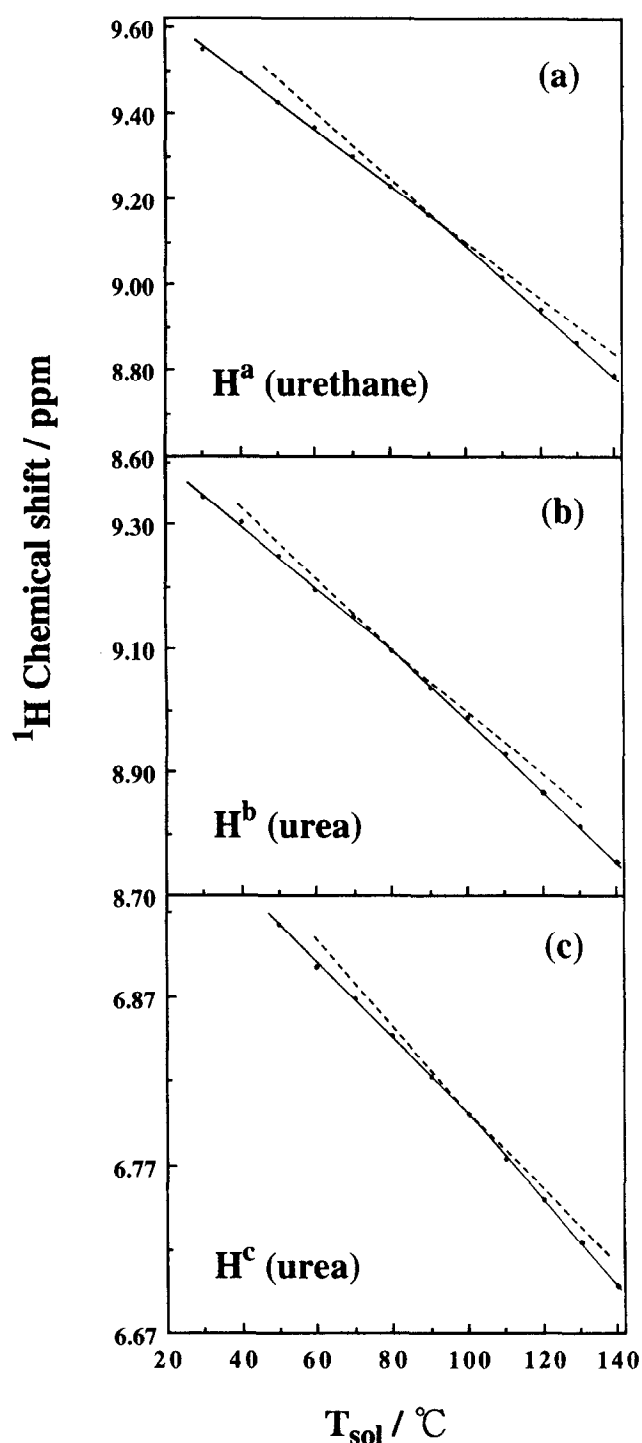


Figure 9 Solution temperature (T_{sol}) dependence of the ^1H chemical shift of (a) H^a , (b) H^b , and (c) H^c of PUR in the PUR-solution containing both $\text{DMSO-}d_6$ (DMAc/ $\text{DMSO-}d_6 = 1.3$ weight ratio) and 0.400 wt% of LiCl (TMS = 0 ppm)

of C=O bonds in the urea groups (●). Furthermore, the $\Delta\nu_{1/2}(H^a)$ (◆), $\Delta\nu_{1/2}(H^b)$ (●), and $\Delta\nu_{1/2}(H^c)$ values (■) increased significantly than the original values in the region below 90°C when a polyurethane compound (M-PU) was dissolved in a concentration of 1.80 wt% in the PUR-solution containing $\text{DMSO-}d_6$ (DMAc/ $\text{DMSO-}d_6 = 1.3$ weight ratio), as illustrated by the broken lines in *Figure 7*. Consequently, the average strength of the hydrogen bondings concerning H^a protons (i.e., between the urea-urethane and urethane-urethane groups) in the PUR-solution was thought to decrease abruptly above

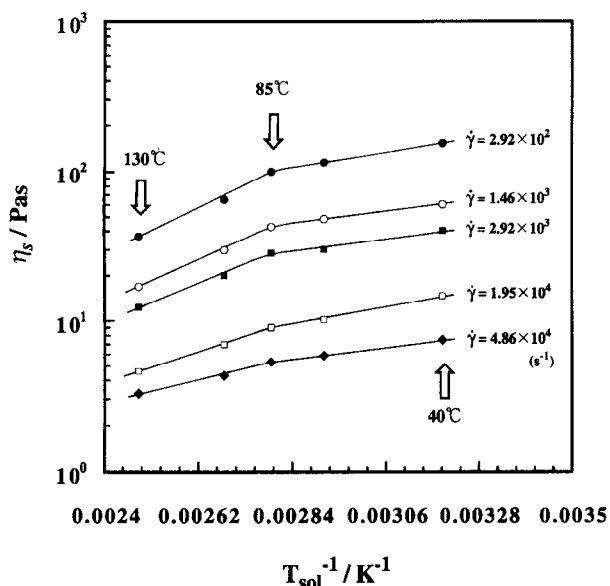


Figure 10 Solution temperature (T_{sol}) dependence of the shear viscosity (η_s) of the PUR-solution containing 0.600 wt% of LiCl in the shear rate ($\dot{\gamma}$) region of 2.92×10^2 – 4.86×10^4 s^{-1}

80–90°C, inevitably accompanying a decrease in the average strength of the interaction of the urea–urea groups. Thus, these changes of the dissolved or association state of PUR in DMAc can be considered to result in the abrupt decrease in the η_s of the PUR-solution over 85°C.

Itoh *et al.*¹² demonstrated by the static light scattering technique that a mean square radius of gyration ($\langle S^2 \rangle$) of PUR chains in DMAc solution of PUR containing LiCl became larger than that in absence of LiCl. Furthermore, Kiguchi *et al.*²⁰ found using ^1H and ^{13}C n.m.r. measurements that the ^{13}C peak of C=O bond and the ^1H peaks of two N–H bonds concerning urea groups of PUR selectively shifted to lower magnetic field by addition of LiCl to a DMAc solution of PUR, although the C=O and N–H peaks of urethane groups hardly changed. These results show a selective interaction between LiCl and urea groups in PUR. It can therefore be expected that the average strength of the hydrogen bondings between the urea–urea groups in the PUR solution was decreased by dissolving LiCl in the solution. Figure 9 shows the T_{sol} dependence of the ^1H chemical shifts of (a) H^a , (b) H^b , and (c) H^c in the PUR-solution containing both DMSO- d_6 (DMAc/DMSO- d_6 = 1.3 weight ratio) and 0.400 wt% of LiCl. As shown in Figure 8c, a completely linear relationship between the H^c chemical shifts and T_{sol} existed in the absence of LiCl. In contrast, a bending point was observed in the presence of LiCl at around 90°C even in the plots of H^c chemical shift against T_{sol} (Figure 9c), indicating a decrease in the average strength of the hydrogen bondings among the urea groups. In other words, this result clarified the existence of the relatively strong interactions through hydrogen bondings described above in the PUR-solution.

Figure 10 shows the $1/T_{\text{sol}}$ dependence of $\log \eta_s$ of the PUR-solution containing 0.600 wt% of LiCl. In addition, the broken lines in Figure 4 indicate both the plots of ΔE_1 (\square) and ΔE_h (\blacksquare) against $\dot{\gamma}$ in the same solution. The plots of $\log \eta_s$ vs $1/T_{\text{sol}}$ in the presence of LiCl also

exhibited the bending points at around 85°C, suggesting that the interactions still remain among PUR chains through hydrogen bondings. However, the $\Delta E_h - \Delta E_1$ values became smaller than those estimated in the absence of LiCl. These experimental results reveal that the $\Delta E_h - \Delta E_1$ value is influenced by the average strength of the hydrogen bondings among PUR chains in the PUR-solution.

From the above discussion, the dissolved state of PUR in the concentrated DMAc solution drastically changed below and above about 90°C. This thermal history imposed on the PUR solution during extrusion through a capillary might be retained and reflect on the structures and tensile properties of the extruded yarns if the history could be effectively quenched by some coagulation procedures. In fact, the tensile properties and the degree of hydrogen bonding of C=O in urea and urethane groups plotted against extrusion temperature were proved to give an inflection point at around 90°C for the extruded yarns coagulated in water. These results will be reported and discussed elsewhere.

CONCLUSION

Capillary flow properties of a concentrated *N,N*-dimethylacetamide (DMAc) solution of segmented poly(urethane-urea) (PUR) prepared from 4,4'-diphenylmethanediisocyanate (MDI), polytetramethyleneoxide (PTMO), and ethylenediamine (EDA) (polymer concentration, 30.0 wt%; hereafter referred to as 'PUR-solution') as well as the dissolved state was investigated as functions of solution temperature (T_{sol}) and shear rate ($\dot{\gamma}$): the logarithmic shear viscosity ($\log \eta_s$) of the PUR-solution as a function of $1/T_{\text{sol}}$ gave two linear regions below and above about 90°C, suggesting that the apparent activation energy of flow of the PUR-solution estimated in T_{sol} range from 90 to 130°C (ΔE_h) was higher than that (ΔE_1) in T_{sol} range of 40–80°C. The $\Delta E_h - \Delta E_1$ value was proved to be somewhat smaller as $\dot{\gamma}$ increased, indicating that the shear stress might control the dissolved state of PUR to some extent but this contribution is much smaller than that by T_{sol} . ^1H and ^{13}C n.m.r. analysis on the dissolved states of PUR revealed the existence of some hydrogen bondings mainly between N–H and C=O bondings of urea groups, and suggested that the sudden decrease in η_s of the PUR-solution over 90°C is associated with a steep decrease in the average strength of the hydrogen bondings.

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