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Crystallinity and hydrogen bonding of hard segments in segmented poly(urethane urea) copolymers*

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Polyurea hard segment model compounds and a series of segmented poly(urethane urea) (SPUU) copolymers, with hard segment content ranging from 18.8–91.0%, were synthesized based on 4,4′-diphenylmethane diisocyanate (MDI), 3,5-diethyltoluenediamine (DETDA), and ethylene-oxide-capped poly(propylene oxide) polyether diol (PPO). By analysis of model compounds, crystallization of DETDA–MDI hard segments was confirmed and relationships between urea hydrogen bonding with morphological changes were suggested. The crystallization, however, was not complete in the copolymers even when the hard segment content was high. New spectral evidence for phase inversion is presented. Fourier transform infra-red analysis suggested that the equilibrium of urea hydrogen bonding between crystalline region and amorphous regions was affected mainly by morphological changes (phase inversion) and was almost independent of chemical composition of the SPUU copolymers under certain morphological conditions both before and after phase inversion. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(urethane urea); hydrogen bonding; crystallite)

INTRODUCTION

Segmented poly(urethane urea) (SPUU) copolymers consist of incompatible hard and soft segments that demix on a molecular level to form a microphase separated structure. The hard segments are typically polyurea blocks formed by reacting 4, 4′-diphenylmethane diisocyanate (MDI) with low molecular weight diamine, and the soft segments are typically polyether blocks.

It is generally accepted that the factors determining the final properties of the copolymers are hard segment content and crystallinity, hydrogen bonding properties, degree of microphase separation, and copolymer molar mass[1–17]. Several model studies have been made on linear SPUU[6–8] or polyurea copolymers[9,10] based on 3,5-diethyltoluenediamine (DETDA), and these studies emphasize the improved thermal properties of materials containing polyurea hard segments, compared with those of conventional polyurethane copolymers. Such studies are in general agreement with published studies of SPUU copolymers[11–15]. The improvement in SPUU properties arises from the higher driving force to microphase separation[8,14] and stronger hydrogen bonding properties[7–8, 12–18] in the urea-containing systems. The hydrogen bonding properties of the copolymers have been studied by some researchers[1–6, 16–18]. Some complex properties of urea hydrogen bonding and its possible effects on morphology have been shown.

There are different statements about the crystallization of hard segments in SPUU copolymers. Willkomm *et al.*[9] and Chen *et al.*[10] reported that MDI–DETDA hard segments were amorphous in the SPUU copolymers prepared by reaction injection molding (RIM) process or by two-step solution polymerization. Ryan *et al.*[13] indicated that no evidence of crystallinity was found by using thermal methods and wide angle X-ray diffraction (WAXD) for SPUU copolymers formed by RIM process. The SPUU copolymers that Ryan *et al.* studied were based on a system of ethylene oxide-capped poly(propylene oxide) polyether triol, MDI and DETDA, which is a typical RIM chemical system. However, Xiu[7] declared that well-formed spherulites of DETDA–MDI hard segments in SPUU copolymers were observed by polarized light microscopy when the hard segment content was high. The chemical system that Xiu studied was analogous to that studied by Ryan, but the polyether was a polyether diol and the copolymers were prepared by a two-step solution polymerization. In addition to the polymerization technique and the structure of polyethers, we noted that the materials described in references 9–14 were based on DETDA and liquefied MDI and were non-crystalline, whereas the materials described in reference 7 were based on DETDA and pure 4,4′-MDI but are spherulites.

The present study focuses on the crystallization and hydrogen bonding properties of a series of linear SPUU copolymers. Effects of hard segment content on

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morphological changes of the copolymers are also included. The chemical system of the copolymers is analogous to that Xiu studied[7], but the formulations were designed to cover a broader range of hard segment content from 18.8% to 91.0%. Two model compounds of DETDA-MDI hard segments were also synthesized.

EXPERIMENTAL

Raw materials

Ethylene oxide capped poly(propylene oxide) diol (PPO, ZS-2185^R, content of ethylene oxide = 15%, $\bar{M}_n = 2000$, Jinling Petrochemical Industry Corp.) was dehydrated at 40°C under vacuum for more than 24 h prior to use. MDI (purity > 99.6%, freezing point > 38.1°C, Yantai Synthetic Leather General Factory) was heated at 60°C for 2 h and filtered through a heated filter. The NCO content of the purified MDI was 33.18%. Phenyl isocyanate (PhNCO, M = 119.3, purity > 98%, $d = 1.090$–1.096 g cm^{-3}, $n_D = 1.535$–1.537) was commercially available. Diethyltoluenediamine (DETDA, 2, 4-/2, 6-isomer = 20/80, Ethyl Corp). was dehydrated at 40°C under vacuum before use. Dibutyltin dilaurate (DBTDL, Kosmos 19, Goldsmidt A.G.) was used as a catalyst. *N,N*-dimethylformamide (DMF) was stored over a 4Å molecular sieve for 1 week and distilled immediately before use.

Synthesis of hard segment model compounds

Two hard segment model compounds, labelled M_1 and M_2 were synthesized by reacting PhNCO or PhNCO and MDI with DETDA. For compound M_1, a solution of PhNCO (5.045 g, 0.0423 mol) in DMF (100 ml) was added dropwise into a solution of DETDA (3.762 g, 0.0211 mol) in DMF (100 ml). After stirring for 3 h at 40°C, the solution was evaporated under a reduced pressure to give a solid residue. The residue was washed with benzene and then maintained in a vacuum oven at 60°C for 1 week to remove traces of DMF. Found: C, 72.30%; H, 6.60%; N, 13.54%. Calculated for $C_{25}H_{28}N_4O_2$: C, 72.12%; H, 6.73%; N, 13.46%. Annealing was performed at 160°C for 1 h and at 60°C for 1 week. Before being subjected to characterization, the solid was milled in a ball mill. Infra-red (i.r.) (KBr) showed peaks at 3289, 2980, 2950, 2890, 1645, 1600, 1563, 1510, 1450, 1311, 1240, 1090, 1059, 1030, 892, 875, 752, 692 cm^{-1}.

For compound M_2, a solution of PhNCO and MDI in DMF was added dropwise into a solution of DETDA in DMF. Other procedures were the same as described above. Found: C, 72.29%; H, 6.81%; N, 13.47%. Calculated for $C_{51}H_{56}N_8O_4$: C, 72.49%; H, 6.68%; N, 13.26%. I.r. (KBr) peaks were at 3289, 2980, 2950, 1645, 1600, 1563, 1450, 1311, 1240, 1105, 1059, 1030, 875, 752, 692 cm^{-1}.

Synthesis of SPUU copolymers

SPUU copolymers were prepared from MDI, DETDA, and PPO by a one-step solution polymerization. In a stirred vessel, MDI was dissolved in DMF and maintained at 60°C. Stoichiometrical quantities of DETDA and PPO were mixed in DMF. DBTDL (1.0×10^{-3} g g^{-1} of PPO) was added to the mixture, which was then injected into the MDI/DMF solution by a surgical syringe. Reaction was carried out at 60°C for 4 h. The chemical compositions and hard segment contents of the copolymers are listed in *Table 1*.

Fourier transform infra-red spectroscopy

Fourier transform infra-red (*FT*i.r.) spectra were recorded by a Nicolet 5DXC *FT*i.r. spectrometer. Two hundred scans at 4 cm^{-1} resolution were signal-averaged and stored as data files for further analysis. The SPUU samples were prepared by solution casting 5% SPUU copolymer in DMF directly onto a piece of KBr plate. A thin film of the SPUU sample was formed after rapid evaporation of the DMF under vacuum, and the SPUU film specimen was then maintained in a vacuum oven at 60°C for 1 week to remove traces of DMF. Spectra showed no evidence of residual solvent.

In the infra-red analyses, integrated intensities of the absorption bands were corrected for sample thickness differences using the CH_3 stretching band near 2980 cm^{-1} as normalizing factor. A curve-resolving technique based on a nonlinear least-squares optimization was used for fitting the band outlines in the carbonyl region with a combination of Lorentzian and Gaussian curve shapes.

Wide-angle X-ray diffraction studies

Wide-angle X-ray diffraction (WAXD) measurements were performed on a D/MAX-IIIA X-ray diffractometer employing nickel-filtered CuKα radiation (1.5418 Å) at an operational voltage of 40 kV. The SPUU specimens were prepared by precipitation in water and dried in a vacuum oven at 80°C for 1 week. Crystallinity was calculated by a curve-resolving technique based on the same computer program described in the *FT* i.r. section.

Table 1 Chemical compositions, designation codes and hard segment contents of SPUU samples

Codes	PPO/DETDA/MDI Molar ratio	Hard segment content W_h (%)	Urea group % [UA]/([UA] + [UT])
SPUU-18.8	1.00/0.67/1.67	18.8	40.0
SPUU-27.8	1.00/1.49/2.49	27.8	59.9
SPUU-36.8	1.00/2.58/3.58	36.8	72.0
SPUU-45.8	1.00/4.00/5.00	45.8	80.0
SPUU-54.9	1.00/6.01/7.01	54.9	85.7
SPUU-63.9	1.00/9.01/10.01	63.9	90.0
SPUU-72.9	1.00/14.01/15.01	72.9	93.3
SPUU-81.9	1.00/24.01/25.01	81.9	96.0
SPUU-91.0	1.00/54.07/55.07	91.0	98.2

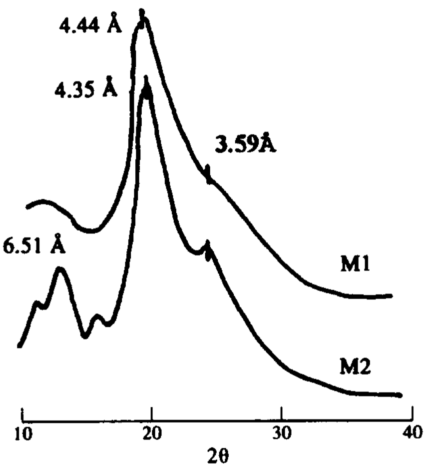


Figure 1 WAXD spectra of model compounds M_1 and M_2

Differential scanning calorimetry

The differential scanning calorimetry (d.s.c.) experiments were conducted using a Du Pont 1090A calorimeter with samples in a nitrogen atmosphere. D.s.c. scans were carried out starting from ambient temperature at a heating rate of 20°C min^{-1}. The sample size was approximately 10 mg.

RESULTS AND DISCUSSION

Crystallization characteristics

WAXD patterns (*Figure 1*) revealed the crystallization of the two hard segment model compounds. According to Ishihara[1,19] and Born and Hespe[20] the reflection with a lattice spacing of 4.44 Å or 4.35 Å corresponds to the plane that formed by hydrogen bonding of urea groups. The reflection with a lattice spacing of 6.51 Å does not appear in the WAXD spectrum of M_1. This reflection was considered to be related to the structure of diphenylmethane unit in M_2.

The crystal structures of the model compounds M_1 and M_2 are described in *Figure 2*. The data for bond lengths and bond angles, which were used in calculation of the patterns, were cited from the literature[20]. The molecular distance (d_{UA}) was considered to correspond to the lattice space of 4.44 Å or 4.35 Å, the same as for Ishihara *et al.*[19] and Born and Hespe[20].

D.s.c. curves (*Figure 3*) of the two model compounds provided further evidence for crystallization of DETDA–MDI hard segments. *Figure 3* reveals that melting points of the crystallites were 308°C and 346°C for M_1 and M_2 respectively. High melting temperature (370°C) was also reported by Ishihara *et al.*[19] for a crystalline polyurea prepared from MDI and 4,4′-diphenylmethane diamine.

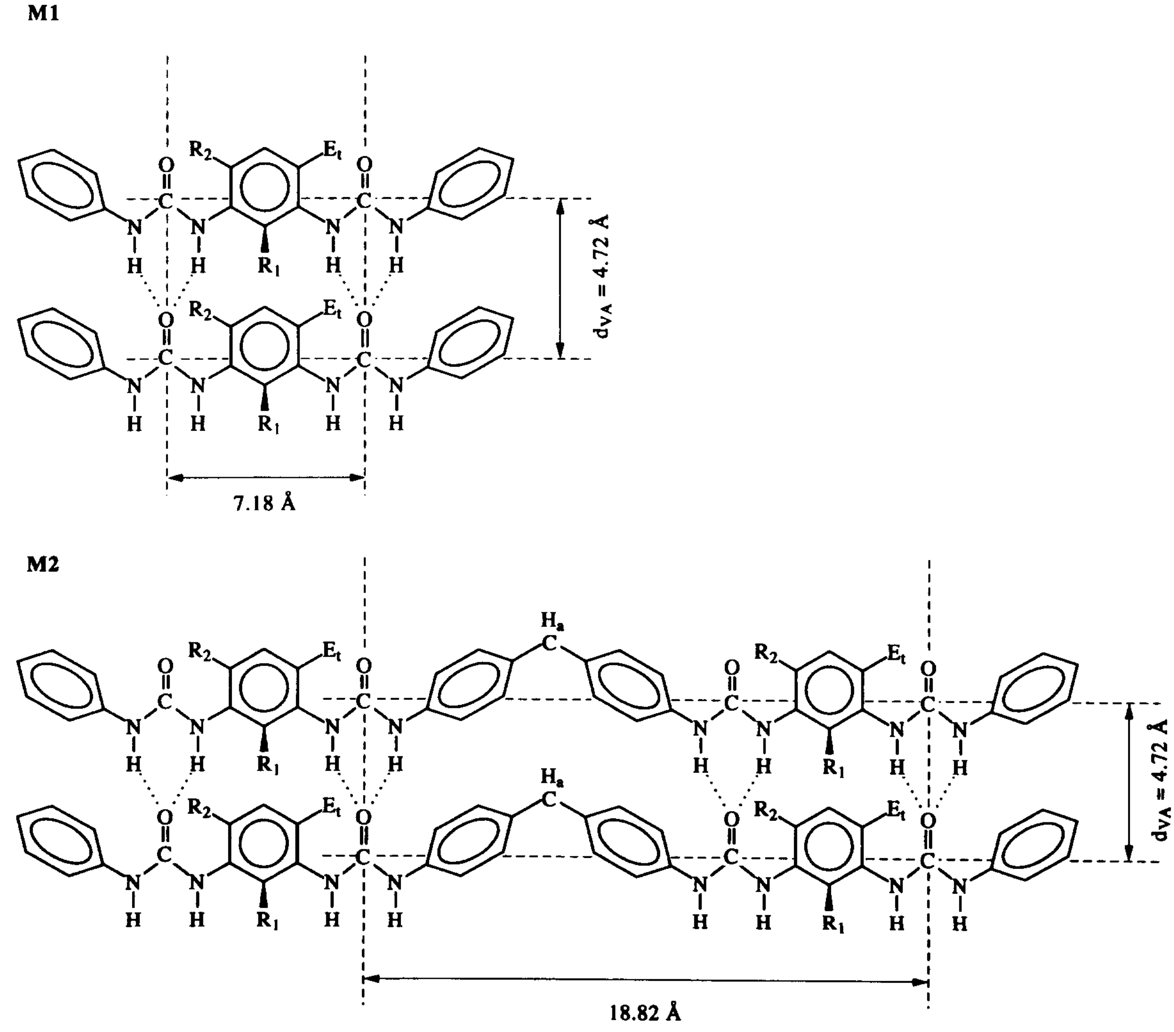


Figure 2 Crystallite pattern of hard segment model compounds

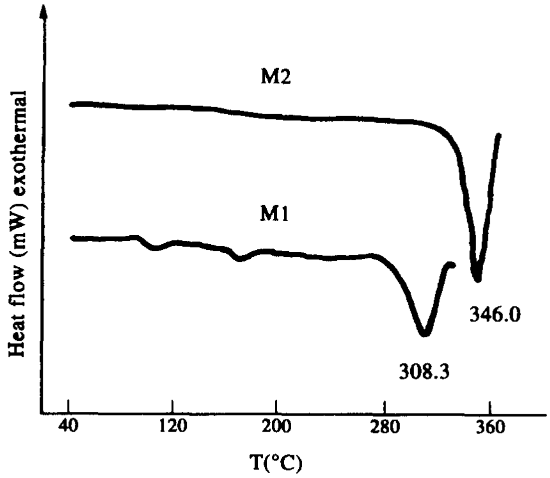


Figure 3 D.s.c. curves of the hard segment model compounds

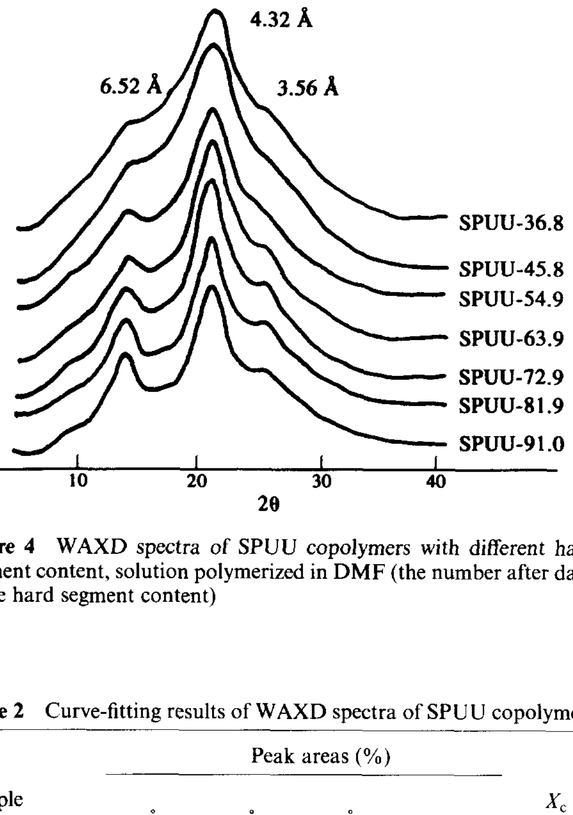


Figure 4 WAXD spectra of SPUU copolymers with different hard segment content, solution polymerized in DMF (the number after dash is the hard segment content)

Table 2 Curve-fitting results of WAXD spectra of SPUU copolymers

Sample number	Peak areas (%) 6.52 Å	4.32 Å	3.56 Å	amorphous	X_c (%)
SPUU-36.8	8.59	8.44	11.80	71.17	28.83
SPUU-45.8	19.70	11.33	5.56	63.40	36.60
SPUU-54.9	19.80	15.01	10.77	45.49	54.51
SPUU-63.9	18.92	17.51	15.97	47.60	52.40
SPUU-72.9	21.64	19.29	13.90	45.16	54.84
SPUU-81.9	15.31	21.72	21.40	41.56	58.44
SPUU-91.0	17.68	23.60	20.84	37.89	62.11

The SPUU samples crystallized, as the WAXD spectra indicate (see *Figure 4*). The reflection at 4.32 Å in *Figure 3* may belong to the planar reflection caused by hydrogen bonding of urea groups in hard segments, while the peak at 6.52 Å should be assigned to the planar diffraction related to the diphenylmethane units.

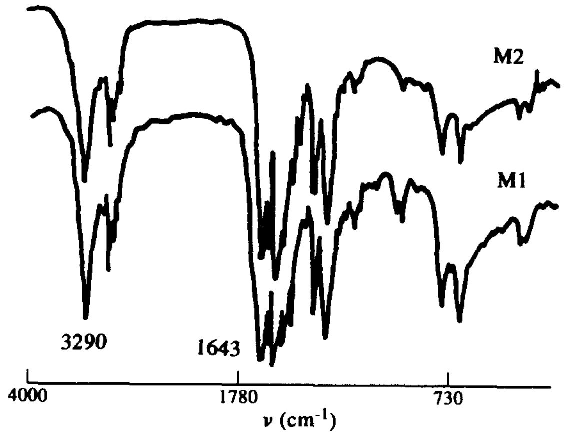


Figure 5 *FT*i.r. spectra of hard segment model compounds M_1 and M_2

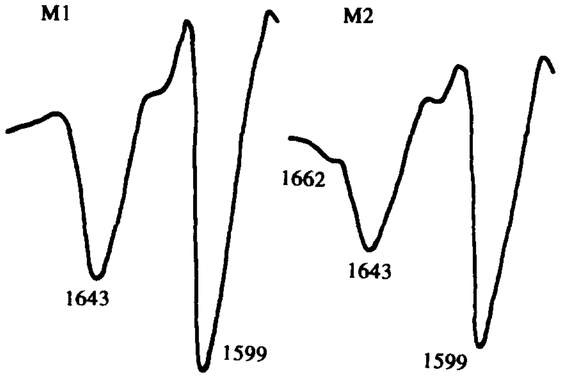


Figure 6 Second order derivative spectra of *Figure 3* in C=O region

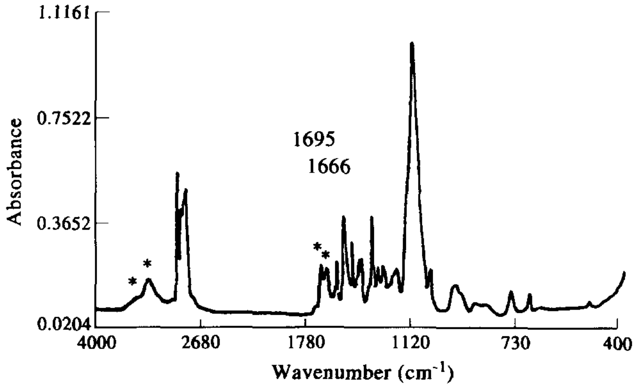


Figure 7 *FT* i.r. spectrum of liquid polyurea compound based on PPO and PhNCO

Table 2 shows results curve-fitting results obtained by the WAXD spectra. The crystallinity of the SPUU specimens in *Table 2* was defined as

$$X_c = \frac{Area\ (6.52) + Area\ (4.32) + Area\ (3.56)}{Area\ (6.52) + Area\ (4.32) + Area\ (3.56) + Area(amorphous)}$$

The results show that the crystallinity X_c increased with increasing hard segment content. The extent of crystallinity was always lower than the hard segment content. It is suggested reasonably that the crystallization was not complete so that a considerable number of hard segments remained in the amorphous phase. No evidence

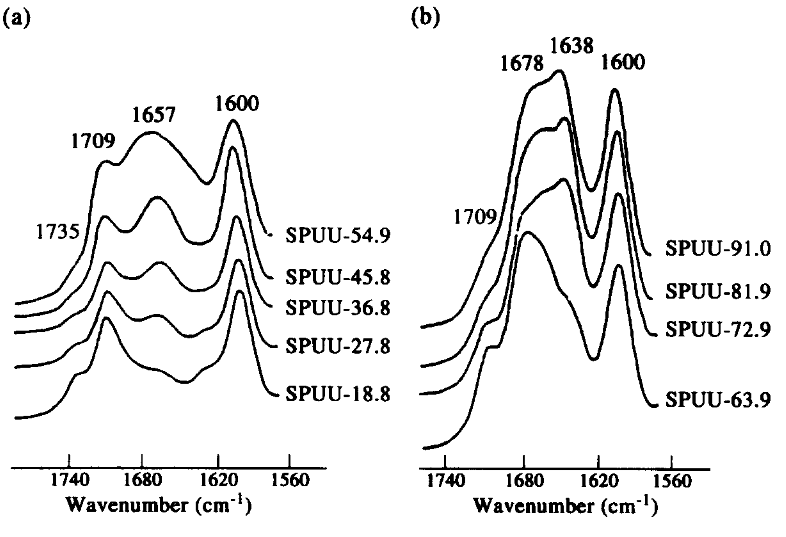


Figure 8 *FT* i.r. spectra of SPUU samples polymerized in DMF (the number after dash is the percentage content of hard segment)

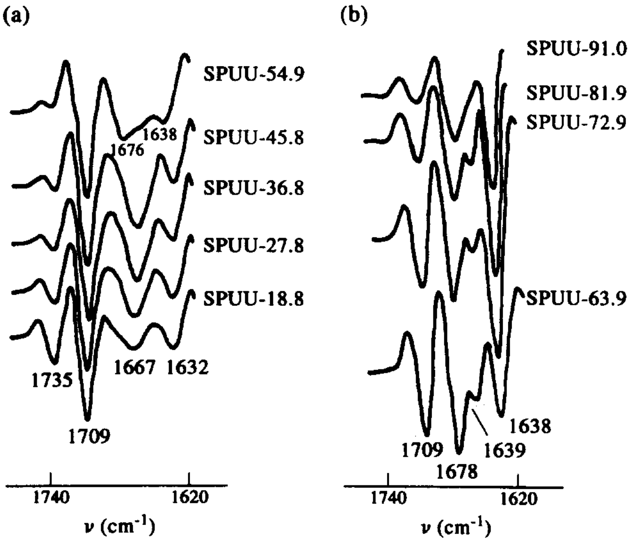


Figure 9 Second order derivative spectra of *Figure 8*

of spherulites was found in the copolymers by polarized light microscopy even when the hard segment content was high. This led us to believe that the crystallinity of the copolymers was not well-organized, and that the size of the crystallinites was less than 0.2 μm, i.e. below the resolution of light[21].

Hydrogen bonding properties

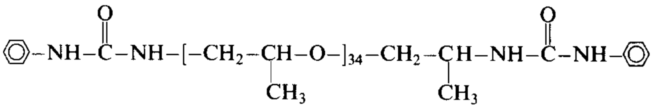
In order to understand the hydrogen bonding properties of SPUU copolymers, i.r. stretching bands must be correlated to morphological changes. We were interested in the carbonyl stretching bands because the quantitative results based on N–H bands are questionable. The N–H absorption coefficients in the region are strongly frequency dependent, as indicated by Coleman *et al.*[22].

Figures 5 and *6* show *FT* i.r. spectra and the corresponding second order derivative spectra in the C=O region of M_1 and M_2. For compound M_1; a single absorption band was found at 1643 cm^{-1} (see *Figure 6*). We considered that this band was related directly to the urea groups hydrogen-bonded in the crystal region with a lattice spacing of 4.44 Å (see *Figure 1*). Accordingly, the 1643 cm^{-1} band is assigned to ordered urea carbonyl groups.

Table 3 Assignment of absorption band in C=O region of i.r. spectrum of SPUU coploymers[1–3,5,7,15–18,20]

Wave number (cm^{-1})		Assignment
1735	$\nu^{UT}_{C=O,\text{ free}}$	free urethane carbonyl
1709	$\nu^{UT}_{C=O,\text{ bonded}}$	hydrogen-bonded urethane carbonyl
1691	$\nu^{UT}_{C=O,\text{ free}}$	free urea carbonyl
1678–1659	$\nu^{UA}_{C=O,\text{ disorder}}$	hydrogen-bonded, disorder urea carbonyl
1643–1632	$\nu^{UA}_{C=O,\text{ bonded}}$	hydrogen-bonded, ordered urea carbonyl

In addition to the absorption band at 1643 cm^{-1}, the model compound M_2 showed another weak band at 1662 cm^{-1} in its second order derivative spectrum (*Figure 6*). The origin of the 1662 cm^{-1} band was judged by reference to the spectrum of a liquid polyurea model compound:



$$\text{Ph}-NH-\overset{\overset{O}{\|}}{C}-NH-[-CH_2-\underset{\underset{CH_3}{|}}{C}H-O-]_{34}-CH_2-\underset{\underset{CH_3}{|}}{C}H-NH-\overset{\overset{O}{\|}}{C}-NH-\text{Ph}$$

which was characterized in detail in our previous work[18]. In its i.r. spectrum (*Figure 7*), the 1662 cm^{-1} band can be observed clearly. It is obvious that the band has nothing to do with crystallization because the spectrum is based on a liquid compound in which only short range or disordered structure is allowed. As a result, the 1662 cm^{-1} band is attributed to disordered urea carbonyl groups. According to this result, we can emphasize that the materials based on pure 4,4′-MDI and DETDA can be crystalline but may exist in the form of non crystalline in the copolymers based on the materials as hard segments.

Figures 8 and *9* show the *FT* i.r. spectra and corresponding second order derivative spectra in the C=O region for the SPUU copolymers containing 18.8–91.0% hard segments. In these spectra multiple bands were clearly observed. The assignments of these absorption bands are listed in *Table 3*. Curve-fitting results for the *FT* i.r. spectra are listed in *Tables 4a* and *4b*.

Table 4a Least-square curve fitting for C=O region of *FT*i.r. spectra of SPUU copolymers

		Peak areas (%)							
Sample[a] number	[UA] (%)	1735 (cm^{-1})	1709 (cm^{-1})	1691 (cm^{-1})	1667 (cm^{-1})	1632 (cm^{-1})	$X_{b,UT}$ (%)	$X_{b,UA}$ (%)	$X_{o,UA}$ (%)
SPUU-18.8	40.0	13.7	26.5	14.0	25.8	20.0	65.9	76.6	43.7
SPUU-27.8	59.9	9.3	25.1	14.6	28.2	22.7	72.9	77.7	44.6
SPUU-36.8	72.0	4.1	21.9	16.4	32.2	25.3	84.2	77.8	44.0
SPUU-45.8	80.0	2.8	15.4	18.2	35.4	28.2	84.6	77.8	44.3

[a] The number after dash: hard segment content

Table 4b Least-square curve-fitting for C=O region of *FT*i.r. spectra of SPUU copolymers

		Peak areas (%)							
Sample[a] number	[UA] (%)	1735 (cm^{-1})	1709 (cm^{-1})	1678 (cm^{-1})	1659 (cm^{-1})	1638 (cm^{-1})	$X_{b,UT}$ (%)	$X_{b,UA}$ (%)	$X_{o,UA}$ (%)
SPUU-54.9	85.7	2.5	15.0	29.2	20.2	32.6	85.7	100	39.8
SPUU-63.9	90.0	0	14.3	25.6	24.8	35.4	100	100	41.3
SPUU-72.9	93.3	0	8.3	24.8	25.5	41.4	100	100	45.1
SPUU-81.9	96.0	0	7.6	22.9	26.6	42.9	100	100	46.4
SPUU-91.0	98.2	0	5.8	15.4	29.5	49.3	100	100	52.3

[a] The number after dash: hard segment content

In the spectra of the copolymers when hard segment content $\leq$ 54.9%, five peaks, the peaks at 1735, 1709, 1691, 1667, and 1732 cm^{-1}, can be resolved. After hard segment content is larger than 54.9%, four peaks, 1709, 1678, 1659, and 1638 cm^{-1}, were then observed. The band positions and shapes changed remarkably around the hard segment content of 54.9%. Ryan *et al.*[13] observed phase inversion by dynamic mechanical thermal analysis and confirmed a transition at ~55% hard segment content for SPUU copolymers based on DETDA, PPO, and MDI systems by tensile testing. The present results can be explained by phase inversion. When the hard segment content was below 54.9%, hard-segment-rich hard domains were dispersed in a soft-segment-rich matrix. When the hard segment content was above 54.9%, hard segments became the continuous phase. As a result, the fine structures of the urea hydrogen bonding spectra, reflected in the band number of disordered urea carbonyl groups and band positions of both ordered and disordered urea carbonyl groups, were changed.

The degree of hydrogen bonding of urethane groups ($X_{b,UT}$) and urea groups ($X_{b,UA}$), and the percentage of ordered urea–urea hydrogen bonds ($X_{O,UA}$) were defined as follows:

$$X_{b,UT} = \frac{1}{1 + 1.0 \cdot \mathit{Area}\ (1735\,cm^{-1})/\mathit{Area}\ (1709\,cm^{-1})}$$

$$X_{b,UA} = \frac{\sum \mathit{Area}\ (\mathit{bonded})}{\mathit{Area}\ (1691\,cm^{-1}) + \sum \mathit{Area}\ (\mathit{bonded})}$$

$$X_{o,UA} = \frac{\mathit{Area}\ (\mathit{order})}{\mathit{Area}\ (1691\,cm^{-1}) + \sum \mathit{Area}\ (\mathit{bonded})}$$

For the case of hard segment content being less than 54.9%, $\sum$*Area* (*bonded*) = *Area* (1667 cm^{-1}) + *Area* (1632 cm^{-1}), *Area* (*order*) = *Area* (1632 cm^{-1}). For the case of hard segment content being greater than 54.9%, $\sum$*Area* (*bonded*) = *Area* (1678 cm^{-1}) + *Area* (1659 cm^{-1}), *Area* (1638 cm^{-1}), *Area* (*order*) = *Area* (1638 cm^{-1}). From curve-fitting result the three quantities are listed in *Table 4*, where it can be seen that the degree of urethane hydrogen bonding increased with the increase of hard segment content. After phase inversion occurred, the 1735 cm^{-1} band disappeared and therefore the degree of urethane hydrogen bonding reached 100%. This property of the urethane hydrogen bonding results from the increase of the number of urea groups in the copolymers (see *Table 2*), in other words, from the increase in probability of formation of hydrogen bonds.

When the hard segments formed hard domains, hydrogen bonding was not complete but, $X_{b,UA}$ and $X_{O,UA}$ were almost unchanged. Urea groups were hydrogen-bonded completely when hard segments became the continuous phase, but the values of $X_{O,UA}$ were only slightly changed. *FT* i.r. analysis revealed that the distribution of urea hydrogen bonds between crystal region and amorphous regions was affected mainly by morphologic changes (phase inversion). Under certain morphologic condition both before and after phase inversion, the distribution equilibrium was almost independent of chemical composition of the SPUU copolymers.

CONCLUSION

A series of SPUU copolymers based on MDI, DETDA, and PPO were synthesized. Two model compounds for DETDA-MDI polyurea hard segments were prepared. By analysis of model compounds, crystallization of DETDA-MDI hard segments was confirmed and relationships between urea hydrogen bonding with morphologic changes were suggested. Crystallinity of the copolymers increased continuously with the increase of hard segment content.

Hydrogen bonding properties, mainly the band positions and the number of urea carbonyl groups, were sensitive to morphologic changes (phase inversion) of the copolymers. As a result, new spectral evidence for phase inversion was presented in this paper. *FT*i.r. analysis suggested that the equilibrium of urea hydrogen bonding between crystal region and amorphous regions was affected mainly by morphologic changes (phase inversion) and was almost independent of chemical composition of the SPUU copolymers under a certain morphologic condition both before and after phase inversion. Further information is required in order to fully characterize the fine structure of SPUU copolymers.

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