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PREPARATION AND CHARACTERIZATION OF WATER-SWELLABLE POLYURETHANE UREA GELS

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ABSTRACT

The properties of a series of water-swellaible polyurethane urea gels are described. The materials were prepared from polyethylene glycol as soft blocks and 4,4'-diphenylmethane-diisocyanate and ethylenediamine as hard blocks. The length of the hard and soft blocks was determined by using ^1H NMR. The thermal transitions of the multiblock copolymer were determined by using DSC. The water uptake of the gels was measured together with the mechanical properties in both dry and wet conditions. It was possible to produce thermoreversible polyurethane urea gels which were highly hydrophilic. The mechanical properties of the gels improved, both in dry and wet conditions, by increasing the length of the hard blocks, which also changed the water uptake of the gels.

INTRODUCTION

Polyurethane urea (PUR urea) is a multiblock copolymer, of the type $-(\text{AB})_n-$, which consists of soft A-blocks and hard B-blocks. The A and B-blocks are thermodynamically incompatible and undergo phase separation. By careful selection of the soft and hard blocks, and the distribution between them, it is possible to tailor-make the final properties of the polymer.

If the network can be swollen in water or biological fluids, the PUR urea gels may become potential candidates for the replacement of soft tissue, as carriers for bioactive macromolecules, or for the release of drugs. The biocompatibility of gels and hydrogels is attributed to their ability to simulate natural tissue due to their high water content [1].

The PUR urea gels in this study were made of difunctional monomers which make the polymer chains linear. The network was formed by physical crosslinks. The soft A-blocks in this study were made of polyethylene glycol (PEG). The hydrophilicity of the gels was varied by using different lengths of the soft A-blocks. The hard B-blocks were made of 4,4'-diphenylmethanediisocyanate (MDI) and ethylenediamine (EDA). Thus, the hard blocks consisted of urethane as well as urea groups.

Structure-property relationships of PUR urea have been extensively studied. Studies have been made in order to relate property changes to different kinds of soft blocks [2] as well as to the length of the soft block [2, 3]. Other studies have related property changes to hard block content and the length of the hard block [4-8]. The length of the hard block also has a strong effect on the ability of the polymer to phase separate [9]. High resolution NMR spectroscopy has proved useful for the analysis of linear polyurethane urea [10-12]. In the literature, data has been presented on the ^{13}C NMR and ^1H NMR of the prepolymer formed by the reaction of PEG with MDI and its subsequent chain extension with EDA.

The purpose of our research was to synthesize and characterize hydrophilic gels based on polyurethane urea. The gels should have good mechanical properties in dry and wet conditions, and these properties were studied. The water uptake of the gels was determined, and DSC was used to determine the thermal transitions of the multiblock copolymer.

The determination of the length of soft and hard blocks of a series of polyurethane ureas using ^1H NMR is also presented.

EXPERIMENTAL

Materials

The number-average molecular-weight of the polyethylene glycols was 400, 1500, and 4000 g/mol as given by the manufacturer (Berol Nobel AB) and their melting points were 3, 48, and 62°C, respectively. A catalyst residue in PEG was deactivated by treating PEG with HCl. PEG was then dehydrated under vacuum at 100°C for at least 12 h. MDI (Bayer

AB) with a melting point of 44°C and DMSO (Merck AB contains less than 0.03% water) were used without further purification. EDA (Fluka AB) was dried by treatment with powdered Al_2O_3 .

Polymer Preparation

A four-necked kettle, equipped with stirrer, nitrogen inlet and outlet, and a thermometer, was charged with MDI. After melting the MDI, PEG was slowly added while stirring. The NCO:OH ratio was 2 : 1. The reaction was carried out under nitrogen purge at 70–80°C for 150 min. The prepolymer was dissolved in DMSO and chain-extended with EDA. The chain-extension reaction was carried out under nitrogen purge at room temperature for 10 min. The NCO : NH_2 ratio was set to 0.98 : 1. To increase the length of the hard blocks, additional MDI was added in the chain-extension reaction. The reactions are summarized in Fig. 1.

The NCO content of the prepolymers was determined by using an ASTM procedure (D 1638-74).

Preparation of Films

The polymer solution (30 wt%) produced in the chain-extension reaction was cast on dry glass-plates. The gel was obtained in dry condition by evaporating the solvent.

Polymer Characterization

Molecular-Weight Determination. SEC (size exclusion chromatography) analysis was used. The samples were dissolved at room temperature in dimethylformamide (DMF) with a concentration of 7.5 g/L. The samples were analyzed by means of a Perkin-Elmer Liquid Chromatograph (Series 2) with a refractive index (RI) detector and two Styragel columns (Polymer Laboratories) at a flow rate of 1 mL/min. The elution volume of the polymers was compared with the elution volumes of polystyrene standards.

Stress-Strain Measurement. Uniaxial stress-strain experiments were carried out on film samples (56 mm long and 6 mm wide) with a J J Instrument T 30K at room temperature at a crosshead speed of 50 mm/

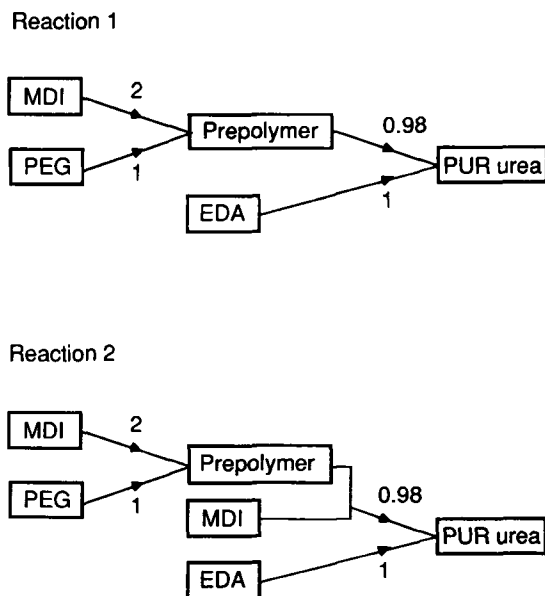


FIG. 1. Reactions 1 and 2: Prepolymer and chain extension reactions.

min. The thickness of each specimen was measured with a film thickness gauge.

Water-Absorption Tests. Samples (1.5×1.5 cm) were cut from the films, thoroughly dried in vacuum, weighed, and were then soaked in deionized water at room temperature for 2 days. They were weighed again after removing the water on the surface of the specimen with filter paper.

Nuclear Magnetic Resonance (NMR). The determination of the chemical composition was carried out by means of $^1\text{H-NMR}$ spectroscopy by using a Varian XL-200 NMR instrument at 70°C ($\text{DMSO-}d_6$).

Differential Scanning Calorimeter (DSC). The thermal transitions of the multiblock copolymer were detected by using a Perkin-Elmer DSC-7. The experiments were carried out by dynamic scanning using two heating rates ($10^\circ/\text{min}$ and $40^\circ/\text{min}$) under constant flow of helium in the range of -120 to 360°C .

RESULTS

Monomer Stoichiometry

The PUR ureas were made by the two-step reactions described in Fig. 1. A series of PUR ureas, which differ in the length of the soft blocks, were made by using Reaction 1 (Fig. 1). The polymers thus obtained were denoted PUR urea 400, 1500, and 4000 according to the molecular weight of the PEG used.

Three series of PUR ureas, which differ in the length of the hard blocks, were made by using Reaction 2 (Fig. 1). The length of the hard blocks was varied by adding extra MDI and EDA to the chain-extension reaction. The extra MDI was dissolved in the prepolymer solution, and EDA was added in a stoichiometric ratio. The polymers thus obtained were denoted according to the molecular weight of the PEG used and the mole % of added NCO in the chain-extension reaction. The different PUR ureas are summarized in Table 1.

SEC Analysis

PUR urea 400, 1500, and 4000 had $\bar{M}_n^s = 100,000\text{--}130,000$ g/mol ($\bar{M}_n^s = \bar{M}_n$ for PUR urea obtained by using a polystyrene calibration curve). The molecular weight distribution was also similar for the differ-

TABLE 1. Chemical Structure of PUR Ureas

Polymer denoted as	Mol % added NCO	Soft block used	%HB
PUR urea 400	0	PEG 400	58.2
PUR urea 400, 4	4	PEG 400	58.7
PUR urea 400, 13	13	PEG 400	59.7
PUR urea 1500	0	PEG 1500	27.1
PUR urea 1500, 11	11	PEG 1500	28.3
PUR urea 1500, 17	17	PEG 1500	28.9
PUR urea 1500, 29	29	PEG 1500	30.1
PUR urea 4000	0	PEG 4000	12.4
PUR urea 4000, 8	8	PEG 4000	12.9
PUR urea 4000, 16	16	PEG 4000	13.4
PUR urea 4000, 22	22	PEG 4000	13.8

ent polymers, $2.5 \leq \bar{M}_w/\bar{M}_n \leq 3.5$. It should be noted, however, that PUR urea 400 was not completely soluble in DMF. All solutions for SEC analysis were filtered before injection, and for PUR urea 400, about half of the sample was retained by the filter. The SEC analysis for the PUR ureas made by using Reaction 2 indicate a slight shift toward lower elution volumes for PUR ureas 1500 and 4000. The solubility of these polymers in DMF became poorer as more MDI was added to the chain-extension reaction. For PUR ureas in the 1500 series, the molecular weight distribution became bimodal as shown in Fig. 2 when 11 mol% NCO or more was added. For PUR ureas in the 4000 series, as much as 22 mol% NCO could be added before the molecular weight distribution became slightly bimodal.

PUR urea 400 gelled completely in DMSO after adding 4 mol% NCO, and it was impossible to dissolve or melt. The chain-extension reactions for PUR ureas 400 were then performed in a more dilute solution, i.e., 9% (w/w) prepolymer in DMSO. Thus, the viscosity varied from fluid to

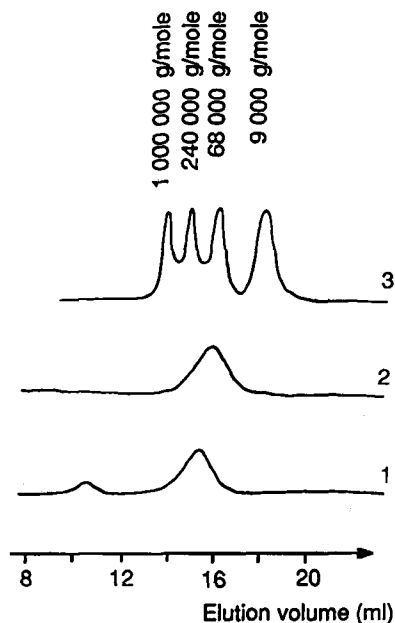


FIG. 2. Size exclusion chromatograms for PUR ureas 1500. 1: PUR urea 1500, 11 mol% extra NCO added. 2: PUR urea 1500, no extra NCO added. 3: Polystyrene standards.

solid gel depending on how much NCO was added. However, these solid gels melted easily.

NMR Analysis

The ^1H -NMR spectrum for PUR urea 1500 is shown in Fig. 3. The assignment of all peaks of interest was made by using literature data [10–12].

The average length of the hard blocks was determined as the molar ratio of MDI molecules to urethane groups. The hard blocks, regardless of their structure, are terminated by two urethane groups formed during the prepolymer reaction. During the chain-extension reaction, no new urethane groups could be formed, but the length of the hard blocks increased by adding MDI and EDA molecules between the urethane groups. The MDI : urethane ratio was determined by comparing the resonances of the aromatic protons from MDI at 7.0–7.5 ppm with the proton of the urethane groups at 9.6 ppm. The results are shown in Figs. 4–6, in which the ratios determined by using ^1H NMR are compared with the theoretical values calculated from the stoichiometry of the polymerization reactions.

The average length of the soft blocks was determined by comparing

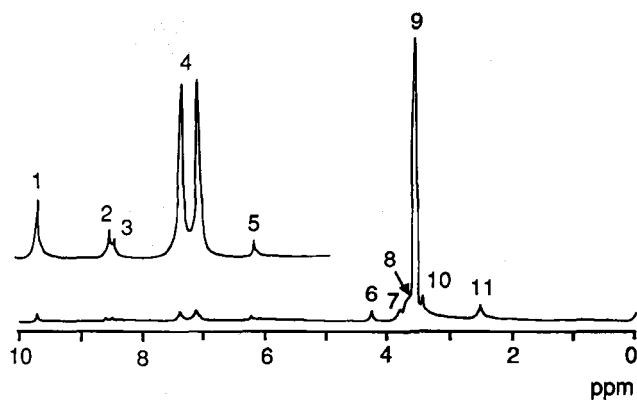


FIG. 3. ^1H -NMR spectrum for PUR ureas 1500. Peaks denoted as: (1) proton in urethane groups; (2), (3), and (5) protons in urea groups; (4) aromatic protons in MDI; (6) and (8) protons in PEG end groups adjacent to urethane groups; (7) protons from methylene group in MDI; (9) protons from PEG sequences; (10) protons from water in DMSO; and (11) residual protons in DMSO.

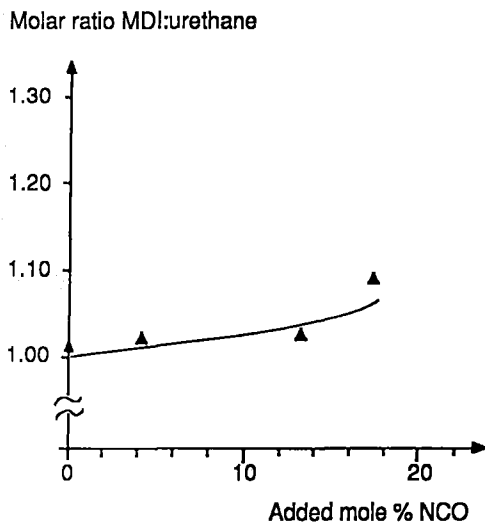


FIG. 4. Average length of hard blocks as determined by ^1H NMR for PUR ureas 400. (—) Theoretical values, \bar{M}_n for PEG 400 g/mol. (\blacktriangle) NMR values.

the resonances from the $-(\text{CH}_2\text{CH}_2\text{O})_n-$ protons at 3.5 ppm with the protons from the $-\text{CH}_2\text{CH}_2\text{O}-$ end groups adjacent to urethane groups at 4.2 ppm. The results are given in Table 2.

DSC Analysis

By using DSC, the glass transition temperatures (T_g^{soft}) and heat capacity changes for the soft segments of PUR ureas in the 400 and 4000 series could not be detected at any heating rate. For all PUR ureas in the 1500 series, a distinct T_g^{soft} was detected at -44°C ($\pm 2^\circ\text{C}$).

The thermal transitions associated with the melting of the soft blocks were found well below 100°C (Fig. 7) in the DSC thermograms for all the PUR ureas. The enthalpy of melting for the soft blocks differed between different samples for the PUR ureas 400 as seen in Table 3. For all the PUR ureas in the 1500 series, the enthalpy of melting for the soft blocks was a constant 29 J/g. The enthalpy of melting for PUR ureas in the 4000 series varied slightly between 15 and 30 J/g.

The transition associated with the hard blocks was located above

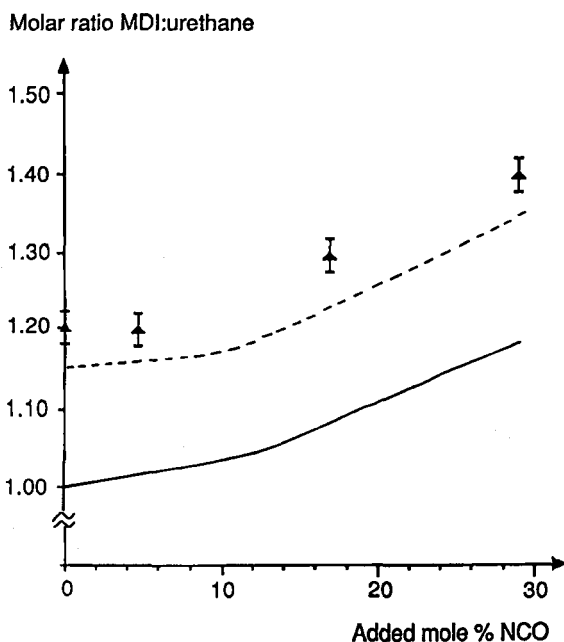


FIG. 5. Average length of hard blocks as determined by ^1H NMR for PUR ureas 1500. (—) Theoretical values, \bar{M}_n for PEG 1500 g/mol. (- -) Theoretical values, \bar{M}_n for PEG 1720 g/mol. (\blacktriangle) NMR values.

290°C , at which point the hard blocks melted and the polymer degraded. No glass transition temperature of the hard blocks could be detected for any PUR urea.

Mechanical Properties

The stress-strain measurements for PUR ureas synthesized via Reaction 1 are given in Fig. 8. The mechanical properties decreased in wet conditions. The most hydrophilic gels had no mechanical strength at all in wet conditions. As the length of the hard blocks increased, mechanical properties such as tensile strength at break, extensibility, and modulus were improved as shown in Fig. 9. The improvement was most pronounced in dry conditions.

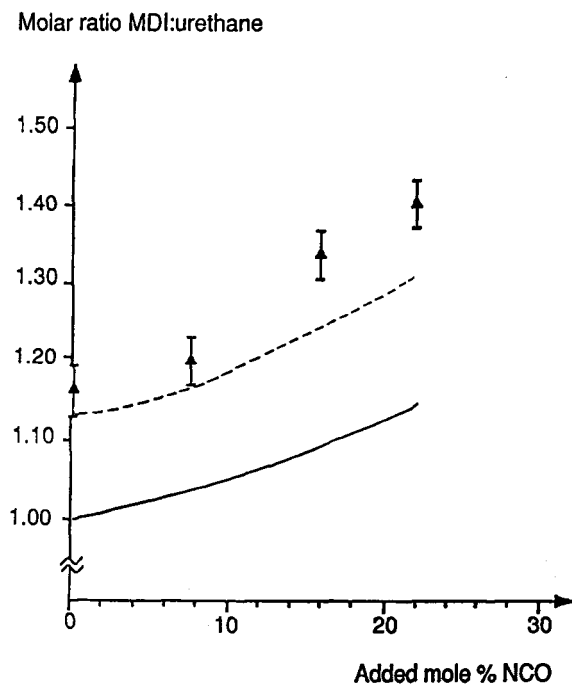


FIG. 6. Average length of hard blocks as determined by ^1H NMR for PUR ureas 4000. (—) Theoretical values, \bar{M}_n for PEG 4000 g/mol. (- -) Theoretical values, \bar{M}_n for PEG 4500 g/mol. (\blacktriangle) NMR values.

TABLE 2. Average Length of Soft Blocks as Determined by ^1H NMR

PUR urea	n from $-(\text{CH}_2\text{CH}_2\text{O})_n-$
400	7
1500	37
4000	100

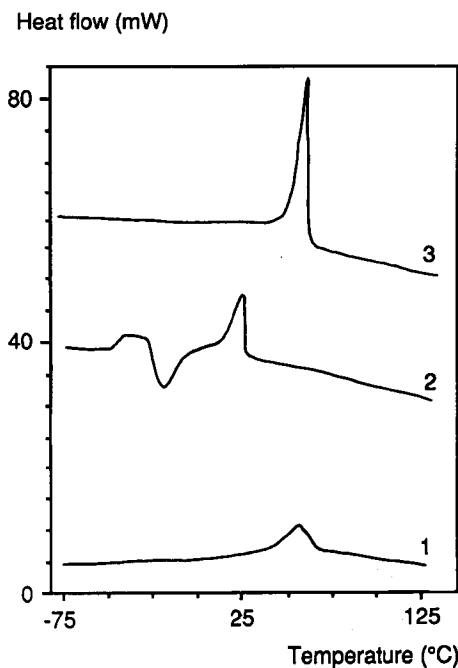


FIG. 7. DSC thermograms for PUR ureas. Soft block melting endotherms. 1: PUR urea 400. 2: PUR urea 1500. 3: PUR urea 4000.

Water Uptake Tests

As expected, water uptake increased as the length of the soft block increased. However, for PUR urea gels synthesized via Reaction 2, unexpected results were obtained. For PUR urea gels from the 400 and 1500 series, water uptake increased as the length of the hard block increased.

TABLE 3. Enthalpy of Melting of Soft Blocks for PUR Ureas 400

Mol % added NCO	Enthalpy of melting, J/g
0	97
4	60
13	125
17	100

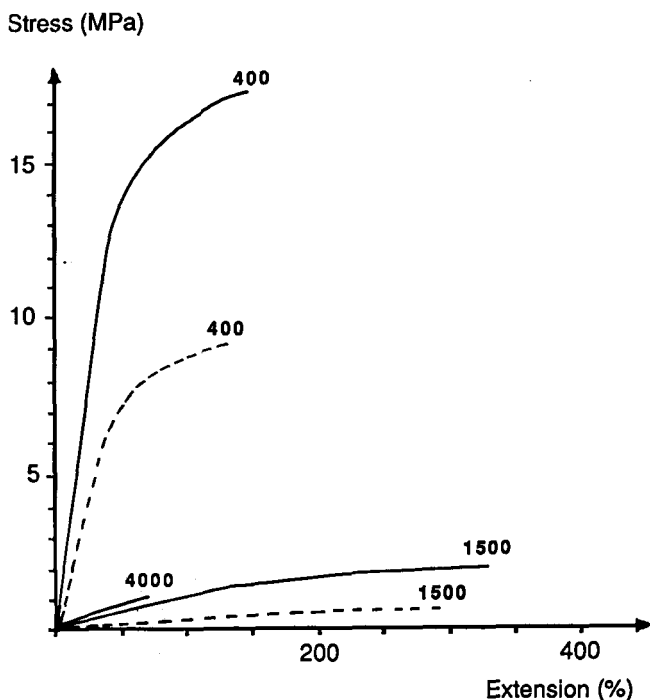


FIG. 8. Stress-extension curves for PUR ureas 400, 1500, and 4000. (—) Dry condition. (---) Wet condition.

The increase was especially obvious for PUR urea 400. The water uptake changed from 60% when no extra NCO was added to 460% when 13 mol% was added.

DISCUSSION

Chemical Structure

The properties of the multiblock PUR ureas depend on the nature and lengths of the soft and hard blocks. In order to make hydrophilic polymers with gel-forming ability in the presence of water, PEG was used for the soft blocks. It was intended to regulate the water uptake of the gels by varying the length of the PEG blocks.

MDI and EDA were chosen as constituents of the hard blocks, since they are known to yield polymers with high degrees of phase separation

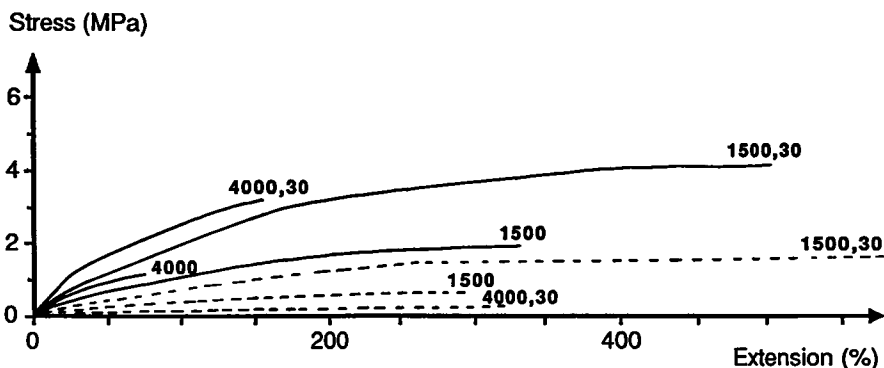


FIG. 9. Stress-extension curves for PUR ureas 1500 and 4000; PUR ureas 1500, 30 mol % NCO added; and 4000, 30 mol % NCO added. (—) Dry condition. (- -) Wet condition.

[8, 13, 14]. The length of the hard blocks was varied by changing the stoichiometry in the chain-extension reaction by the addition of extra MDI and the corresponding amount of EDA. Longer hard blocks yielded gels with better mechanical properties but also decreased solubility in DMSO. Since films were made from solutions, the solubility criterion put an upper limit to the length and number per molecule of the hard segments at a specific polymer concentration. As will be seen below, an increase in hard segment length was not always accompanied by a decrease in water uptake of the polymer.

SEC Analysis

SEC analysis of DMF solutions of all PUR urea preparations gave number-average molecular weights in the range 100,000–130,000 g/mol using polystyrene standards. Cooper et al. found for similar systems that molecular weights using polystyrene standards can be 30% too high [15]. However, even if the molecular weights were lower by 30%, they were high enough to validate the conclusion that the copolymers were multiblock with at least 10–50 blocks of each type.

The solubility of the PUR ureas became poorer in DMF as the length of the hard blocks increased. At the same time, the molecular weight distribution shifted toward a bimodal distribution. A second peak increased as the hard block length increased, corresponding to molecular

weights of several millions, which is probably due to aggregation of polymer molecules.

With increasing length of the hard blocks, the viscosity of the solutions in DMSO, which is a better solvent than DMF, increased. The increase was accompanied by the formation of thermoreversible gels, which was most pronounced for PUR urea 400 polymers.

NMR Analysis

The average length of the hard blocks for PUR ureas 400, 1500, and 4000 as determined by NMR is shown in Figs. 4–6, respectively, and compared with the corresponding theoretical values. The latter were calculated from the stoichiometry of the polymerization reactions by using the following two assumptions:

1. All $-OH$ groups were reacted and formed urethane groups.
2. The amount of water that had reacted with MDI was considered negligible.

Good agreement between molar ratios, determined by proton NMR, and the theoretical ratio was obtained for PUR ureas 400 as seen in Fig. 4. When values for \bar{M}_n of the PEG segments determined by NMR were used for PUR urea 1500 and 4000, better agreement was obtained than when using the manufacturer's values. The calculations were, however, made with the assumption that no water was present. When the water content was considered, better agreement was obtained for all polymers.

It should be mentioned that in all polymerization reactions the stoichiometric calculations were based on the \bar{M}_n value given by the manufacturer. This corresponds to using an excess of MDI in the prepolymer reaction, and thus longer hard blocks were obtained.

PUR Ureas 4000

DSC

A typical DSC thermogram for the 4000 series had a transition around 50°C associated with the melting of the soft blocks. A high temperature transition was located above 290°C . This is in accordance with studies made on PUR ureas composed of poly(tetramethylene oxide), MDI, and EDA [16]. The hard blocks were characterized by a melting endotherm at

290°C immediately before reaching the decomposition temperature. No T_g 's could be detected for either the soft or the hard blocks. The absence of a T_g^{hard} is in agreement with literature data [17]. A possible explanation is that T_g^{hard} escape detection by taking place over a wide range of temperatures. The absence of T_g^{soft} may be due to the fact that crystallization occurs in spite of the fast quenching rate (100°C/min).

Mechanical Analysis

The tensile strength at yield decreased as the length of the soft blocks increased. At the same time, the number of $-(AB)_n-$ blocks in the linear chains decreased and consequently the crosslinking density decreased. Simultaneously, the mechanical strength in wet conditions for the most hydrophilic gels decreased to such a low level as to be difficult to measure for polymers from PEG 4000 made by Reaction 1. By increasing the length of the hard blocks, the mechanical properties were improved considerably in both dry and wet conditions (Fig. 9). However, the modulus of PUR ureas 4000 in dry condition were greater than for the corresponding PUR ureas 1500. This may be due to the fact that PUR ureas 4000 were crystalline at room temperature, while the others were not (Fig. 7). In wet conditions the modulus of PUR ureas 4000 became lower than the modulus of PUR ureas 1500, as the melting point of the crystalline soft blocks in PUR ureas 4000 decreased as water solvated the soft blocks.

Water Uptake

Hydrophilic gels with water uptakes of 650 to 800% were obtained with PEG 4000 as soft blocks; the latter corresponds to 8% added NCO. It is probably an analogous phenomenon to those observed for shorter PEG blocks (see below).

PUR Ureas 1500

DSC

An endothermic transition associated with soft block melting was observed around 20°C in all experiments with polymers having PEG 1500 as soft segments. In some experiments the samples were cooled to -100°C at a rate of 10°C/min and then analyzed at the same heating rate. In these cases only, a single endotherm was observed in the temperature region below 150°C (Fig. 10). A T_g^{soft} transition was found around -44°C .

In other experiments the samples were quenched to -100°C at a cooling rate of $100^{\circ}\text{C}/\text{min}$. When heated to $10^{\circ}\text{C}/\text{min}$, a T_g^{soft} was observed at -44°C ; this was followed by an exotherm at -20°C and an endotherm around 20°C (Fig. 7). The exotherm was due to crystallization of the disordered soft segments which were mobilized above the T_g^{soft} .

All polymers in the PEG 1500 series behaved in a similar manner in quenching experiments. Their T_g^{soft} was -44°C throughout, indicating well-separated soft-phase regions.

Mechanical Analysis

Films made from PEG 1500 polymers had good mechanical properties in both dry and wet conditions. The mechanical properties improved as the length of the hard blocks increased (Fig. 9).

Water Uptake

Water uptake increased as the length of the hard blocks increased up to a maximum at 15% excess NCO. The opposite effect had been expected. The effect cannot be explained in terms of phase separation since the DSC experiments referred to above did not reveal any differences in T_g^{soft} . This is in contrast to earlier observations that the length of the hard blocks has a strong effect on the ability of the polymer to phase separate [9].

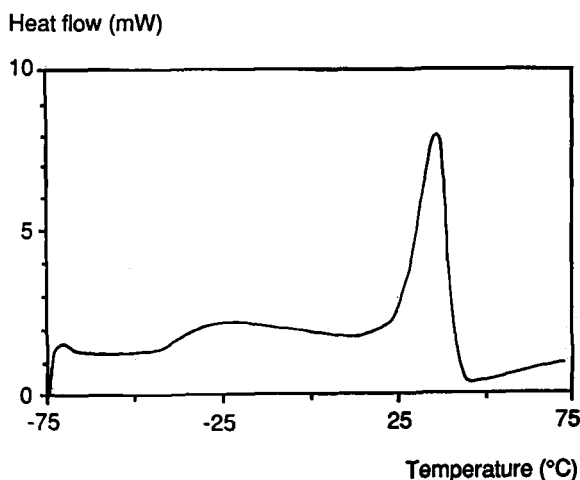


FIG. 10. DSC thermogram for PUR ureas 1500. Slowly cooled.

PUR Ureas 400

DSC

An endothermic transition associated with the melting of the soft blocks was located around 60°C. The transition associated with the hard blocks was located at 290–310°C. No distinct T_g 's were detected. The enthalpy of melting of the soft blocks was much larger than those of PUR ureas 1500 and 4000, which indicates a higher degree of crystallinity.

Mechanical Analysis

In addition to the absence of the T_g^{soft} transition in DSC, preliminary dynamic mechanical analysis (DMA) experiments on PUR urea 400 showed no loss peak corresponding to a T_g^{soft} in the temperature range below the transition associated with the melting of the soft blocks.

Films made from PEG 400 had excellent mechanical properties in both dry and wet conditions, which may be ascribed to the high crosslinking density as compared to other polymers.

Water Uptake

Contrary to what might be expected, the water uptake increased when the length of the hard blocks increased. It was especially obvious for PUR urea 400 where the water uptake changed from 60 to 450%. It was observed that the variation in water uptake was accompanied by an increase of viscosity in the chain-extension solution. When no extra NCO or only 4 mol% extra NCO was added, these solutions had relatively low viscosities. It increased dramatically with the formation of solid gels when 13 mol% or more extra NCO was added. No significant difference in phase separation was found by DSC experiments. However, the endotherm associated with melting of the soft blocks was largest for the gel with the highest water uptake.

A hint to the cause of the difference between the gels with low water uptake and those with high water uptake was given by the way they were formed. The solutions of chain-extended polymers with relatively low viscosities could be cast on dry glass plates at room temperature. As the solvent evaporated, a gel formed gradually which subsequently dried to form a film.

The polymers which formed gels in the chain-extension step had to be melted by heating to 70°C before they could be cast on dry glass plates.

The sols thus gelled upon cooling, with solvent (DMSO) still remaining within the network. Subsequently, the solvent evaporated and the gel formed a film. The formation of a gel at an early stage probably locked the polymer chains in a structure favorable for subsequent swelling in water. The hard blocks underwent phase separation and formed domains which acted as physical crosslinks. The latter were separated by distances determined by the polymer concentration at the moment of gel formation. On the other hand, the polymer solutions from which most of the solvent could be evaporated before gel formation formed denser networks with less ability to swell in water.

CONCLUSIONS

A series of well-characterized water-swelling polyurethane urea gels have been investigated.

The following conclusions can be drawn concerning the nature of the polyurethane urea gels and their characterization:

It was possible to prepare very hydrophilic gels based on polyurethane urea.

It was possible to improve the mechanical strength in both dry and wet conditions by increasing the length of the hard blocks.

^1H NMR could be used for determining the length of the hard and soft blocks.

DSC thermograms indicate well-separated polymer phases. It was, however, not possible to qualitatively determine the degree of phase separation.

By increasing the length of the hard blocks, water uptake was increased for PUR ureas 400 and 1500. This is probably not due to different degrees of phase separation but rather to the fact that different gels were formed by different mechanisms.

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