Syntheses and Reactions of Urethanes of Cellobiose and Cellulose-Containing Uretdione Groups

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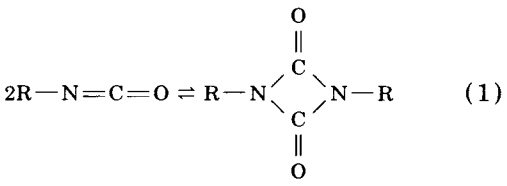
SYNOPSIS

Urethanes of cellobiose and cellulose-containing uretdione groups are synthesized by the reaction of aliphatic and aromatic diisocyanate uretdiones with the saccharides. The syntheses are performed as a heterogeneous reaction in dimethyl acetamide using dibutyl tin dilaurate as a catalyst, as well as a homogeneous reaction in dimethyl acetamide–lithium chloride. Thus, semisynthetic prepolymers are formed that offer the reactivity of (blocked) isocyanate groups. To demonstrate their reactivity, ring opening of the uretdiones is performed by the addition of a secondary amine to yield the corresponding ureas.

INTRODUCTION

The discussion about using biopolymers as a (renewable) carbon resource for the chemical industry is still going on. According to that, polysaccharides like cellulose receive continuous attention.

One of the concepts using cellulose, and its basic unit cellobiose, for polymer syntheses deals with the addition of diisocyanates to form urethanes. A number of such compounds have been described in the literature.[1-5] Beyond that it is known that polyurethane syntheses can be modified by the application of blocked isocyanates. For example, the reversible dimerization of isocyanates yielding uretdiones [Eq. (1)] represents an elegant capping method because no side products due to the removal of the protecting groups have to be separated.[6]



$$2R{-}N{=}C{=}O \rightleftharpoons R{-}N\begin{array}{l}\diagup C(=O)\diagdown \\ \diagdown C(=O)\diagup\end{array}N{-}R \qquad (1)$$

Uretdione urethanes of saccharides have not been reported yet to the best of our knowledge. The idea to synthesize such uretdione prepolymers is to combine the variety of NCO reactions with the potential of saccharide resources opening a new field of semisynthetic polyurethanes–ureas.

EXPERIMENTAL

Materials

The cellulosic material used in this work is a desized and bleached linen fabric donated by Windel Textil (Bielefeld, F.R.G.). The dimers of hexamethylene diisocyanate and 2,4-toluylene diisocyanate are gifts of Bayer AG, Leverkusen. D-Cellobiose was purchased from Aldrich, lithium chloride from Riedel-de Haen AG, Seelze, and all other reagents and solvents from E. Merck, Darmstadt. The chemicals are of laboratory reagent grade and used without further purification.

Syntheses

All steps are carried out in a nitrogen atmosphere avoiding any moisture.

Uretdione Urethanes of Cellobiose

As an example, D-cellobiose, 0.2 g (4.7 mmol OH), is dispersed in 4 mL of *N,N*-dimethyl acetamide (DMAC) after stirring at room temperature for 10 min. In a nitrogen stream 182.2 μL (1.15 mmol of

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unblocked NCO) of hexamethylene diisocyanate uretdione (HMDIU), and 18.3 μL (0.03 mmol) of dibutyl tin dilaurate are added. The mixture is stirred at 45°C for 1 h. After centrifugation the separated product is washed well with acetone and ether. Finally it is dried at room temperature *in vacuo*. An analogous procedure is carried out with 0.2 g of D-cellobiose, 203 mg (1.16 mmol of unblocked NCO) of 2,4-toluylene diisocyanate uretdione (TDIU), and 18.3 μL of dibutyl tin dilaurate at 40°C for 30 min.

The solution of DMAC–lithium chloride is prepared according to Ref. 7 with a salt content of 7.5%. As an example, 0.5 g (11.75 mmol OH) of D-cellobiose is dissolved in 5 mL of DMAC–LiCl at 120°C. After adding 460 μL (2.9 mmol NCO) of HMDIU, the mixture is stirred at 120°C for 30 min and then poured into water to precipitate the polyurethane. The precipitate is collected on a Büchner funnel and washed well with water, methanol, and acetone. Finally the product is dried *in vacuo*. The stoichiometric ratio of the reagents and the concentration of cellobiose depend on the intended degree of crosslinking.

Uretdione Urethanes of Cellulose

The linen fabric is pulverized in a fiber mill. To increase the accessibility of the cellulose molecules, and to remove the crystal water, the following procedure is followed: After soaking the material in water for some days, a solvent exchange (water → methanol → DMAC) is carried out according to Ref. 7, and the fibres are suspended in DMAC or dissolved in DMAC–LiCl.

As an example, a heterogeneous mixture is achieved with 0.1 g (1.85 mmol OH) of pretreated cellulose, 173.2 μL (1.14 mmol NCO) HMDIU, and 9.2 μL dibutyl tin dilaurate. The reaction is carried out at 40°C for 4 h as described earlier. If HMDIU is replaced by 161 mg (0.93 mmol NCO) of TDIU, the synthesis requires 8 h at 2°C.

For homogeneous reactions the pretreated cellulose is dissolved in DMAC–LiCl to yield a concentration of 1% (w/v). Depending on the intended degree of substitution (DS), the solution can be diluted by adding DMAC to lower the viscosity. For example, a DS of 1.5 is obtained when a mixture of 10 mL of DMAC–LiCl containing 0.1 g (1.85 mmol OH) of cellulose, 140 μL (0.92 mmol NCO) of HMDIU, and 10 mL of DMAC is heated to 80°C for 360 min. The isolation of the product is achieved by pouring the mixture into water as described earlier. If HMDIU is replaced by 107 mg (0.62 mmol NCO) of TDIU, the reaction requires 20 min at 50°C (concentration of cellulose 0.75%) to yield a DS of 1.

Ring Opening of the Immobilized Uretdiones

A 50-mg sample is suspended in 1 mL of DMAC adding 1 mL of dibutylamine and 10 μL of dibutyl tin dilaurate. The mixture is stirred at 100°C (TDIU compound) or at 130°C (HMDIU compound) for 1 h. Afterward it is cooled to room temperature and 2 mL of methanol are added. Back titration is achieved with hydrochloric acid using bromophenol blue as an indicator. The blank experiments are carried out in the same way taking cellulose for the immobilized uretdiones.

Analyses

FTIR analyses are performed with a Nicolet 60SX Fourier transform infrared spectrometer by transmission and photoacoustic (MTEC model 20c) technique. The transmission spectra are taken by 250 scans with a resolution of 4 cm^{-1} using a TGS detector, and the photoacoustic spectra were obtained by 150 scans, a mirror velocity of 20, and a resolution of 8 cm^{-1}. ^{13}C-NMR analyses are carried out with a Bruker EXP-2000 spectrometer (50.3 MHz) by 40,000 scans and 50°C with DMSO-d_6 as an external standard. Differential scanning calorimetry is performed with a Perkin-Elmer DSC-7 under nitrogen flow. The sample weight is about 10 mg and the heating rate 10 K/min. The nitrogen content of the urethane uretdiones is determined by elemental analysis using a Carlo Erba EA-1106 analyzator.

RESULTS AND DISCUSSION

In this work the dimers of hexamethylene (HMDIU) and 2,4-toluylene diisocyanate (TDIU) are used as representatives of aliphatic and aromatic uretdiones. The corresponding urethanes of cellobiose and cellulose are prepared via two different routes:

1. A heterogeneous reaction in the presence of dimethyl acetamide (DMAC) as a polar swelling medium, and dibutyl tin dilaurate as a catalyst.
2. A homogeneous reaction carried out in DMAC–lithium chloride as a solvent.

Both routes are suitable to achieve the intended derivatization of the saccharides. In principle, a selec-

Table I Conditions of Typical Reactions of Cellobiose with Different Uretdiones[a]

Medium	HMDIU	TDIU
DMAC, dibutyl tin dilaurate	OH–HCO = 4 : 1, c_{cellob} = 5%, 45°C, 60 min	OH–NCO = 4 : 1, c_{cellob} = 5%, 40°C, 30 min
DMAC–LiCl	OH/NCO = 4 : 1, c_{cellob} = 10%, 120°C, 30 min	OH/NCO = 4 : 1, c_{cellob} = 5%, 50°C, 20 min

[a] (OH–NCO means the molar ratio of saccharide hydroxyl groups to unblocked isocyanate groups, and c_{cellob} the concentration (w/v) of cellobiose.

tive NCO addition to the primary hydroxyl groups of the saccharide residues would be expected, because they are much more reactive than the secondary ones.[1-3] But in the presence of catalysts or complexing solvents a complete loss of selectivity is observed as concluded from gelation that occurs due to crosslinking also in the case of cellobiose.

Because of its aromatic isocyanate groups, TDIU is considerably more reactive than the aliphatic HMDIU. As a consequence, the uretdione ring of TDIU exhibits a limited stability in polar organic media like DMAC, which is the only kind of solvent compatible with TDIU to some extent. Fortunately, the derivatization of the unblocked isocyanate groups enhances the stability of the uretdione ring.[8]

Syntheses of the Uretdione Urethanes of Cellobiose

The parameters of some typical reactions of HMDIU and TDIU with cellobiose are summarized in Table I. The conversion of isocyanate is controlled by infrared spectroscopy.

Figure 1 gives the FTIR spectra of the uretdione urethanes obtained. Both spectra exhibit a broad, strong peak due to the C–O stretching vibrations of the pyranose component in the region around 1050 cm^{-1}. Furthermore there are characteristic carbonyl stretching bands at frequencies of 1770 cm^{-1} (uretdione) and 1710 cm^{-1} (urethane). The peak owing to the N–H deformation vibration of the urethane occurs at 1540 cm^{-1}. Characteristic bands in the spectrum of the TDIU compound [Fig. 1(a)] are at 1600 cm^{-1} and 1500 cm^{-1} owing to aromatic skeletal vibrations. In both spectra a medium intensity absorption band occurs around 1630 cm^{-1} due to adsorbed water, which cannot be removed quantitatively because of the hydrophilic saccharide hydroxyl groups.[9] The IR spectra of the products synthesized via heterogeneous or homogeneous reaction are virtually identical.

The obtained polyurethane uretdiones of cellobiose are insoluble in nearly all common solvents; a poor solubility is observed in solvents of the amide type. The reason for that fact is the partial crosslinking indicated by gelation during synthesis. Although the homogeneous reaction carried out in DMAC–LiCl yields soluble products, only a slight solubility in DMAC is observed after precipitating the polymer in water. The concentration of the DMAC solution is proved to be much too low to allow ^{13}C-NMR analysis. For that purpose it is necessary to use an aliquot of the DMAC–LiCl preparation without isolating the product.

Figure 2 shows the ^{13}C-NMR spectra of the HMDIU cellobiose polyurethane [Fig. 2(a)] and of HMDIU [Fig. 2(b)]. Both samples are dissolved in DMAC–LiCl. It is evident that the peak at 129 ppm due to the unblocked NCO groups disappears since

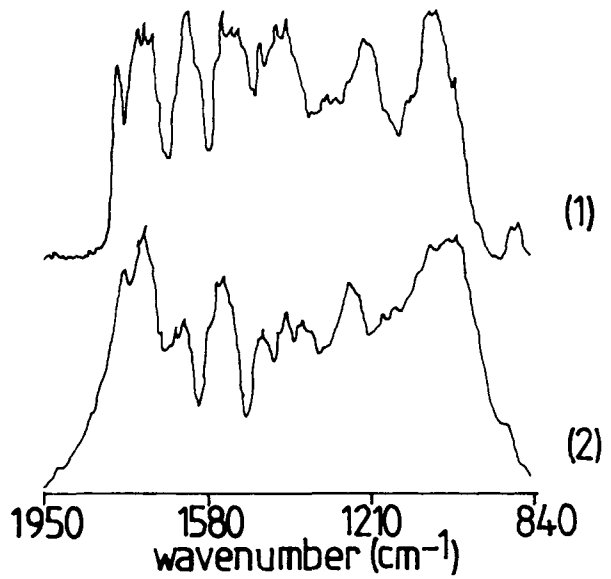


Figure 1 FTIR spectra of uretdione urethanes of cellobiose: (a) TDIU compound, photo acoustic, and (a) HMDIU compound, KBr tablet.

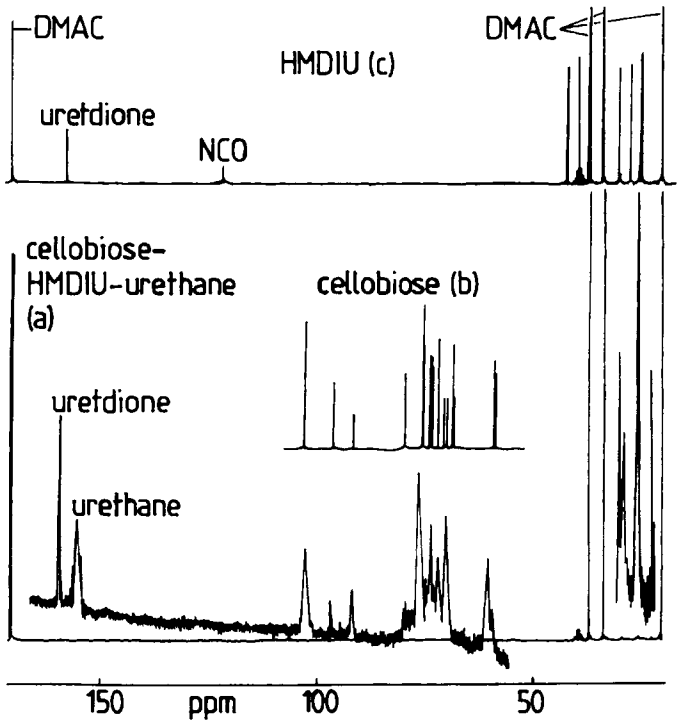


Figure 2 ^{13}C-NMR spectra of (a) HMDIU polyurethane of cellobiose, of (b) cellobiose, and of (c) HMDIU. The samples are dissolved in DMAC–LiCl.

the isocyanate is converted into urethane, resulting in a new signal at 154 ppm. The peak at 159 ppm owing to the uretdione ring does not change. The peaks in the region 60–102 ppm are due to cellobiose carbones.[10] Figure 3 gives the ^{13}C-NMR spectra of the TDIU cellobiose polyurethane [Fig. 3(a)] and TDIU [Fig. 3(b)]. Both samples are dissolved in DMAC–LiCl. Since solvents like DMAC weakly catalyze the ring opening of TDIU, the prolonged time needed for NMR analysis causes the complete destruction of the uretdione ring, and, as a consequence, the corresponding signal cannot be found in spectrum 3b. The signal at 125 ppm is due to the unblocked isocyanate groups. The spectrum of the TDIU cellobiose polyurethane is characterized by a resonance at 153 ppm owing to the urethane linkage, and a signal at 161 ppm due to the uretdione ring, which is now stabilized upon the derivatization of TDIU. It is evident from the spectrum that no unblocked NCO groups remain (disappearing of the peak at 125 ppm).

Some attempts were made to achieve the synthesis of cellobiose polyurethanes in the absence of any catalyst or complexing solvent. Under these conditions the uretdione ring should remain completely unaffected and crosslinking should be avoided. The uretdione and cellobiose (OH–NCO molar ratio 4 : 1) were suspended in DMAC and stirred overnight at room temperature. IR investigations show that in case of HMDIU no reaction takes place. On the other hand gelation is observed when using TDIU.

As is evident from the ^{13}C-NMR and FTIR analyses, polyurethanes of cellobiose-containing uretdione groups can be obtained by the polyaddition of diisocyanate uretdiones to cellobiose. As mentioned earlier the disaccharide is used as a model system representing cellulose. Nevertheless, the presented compounds of cellobiose may be interesting polymers themselves.

Syntheses of Uretdione Urethanes of Cellulose

The cellulosic material used in this work is linen, a bast fiber containing 65–89% of cellulose. Thus, it is intended to demonstrate the variety of renewable resources suitable for polymer synthesis.

Since native cellulose is characterized by a complex supramolecular structure, an effective pretreatment of the fiber is necessary to improve its accessibility. Furthermore the content of crystal water (about 10%) has to be reduced to avoid hydrolysis of the isocyanate. For that purpose a successive solvent exchange (water → methanol →

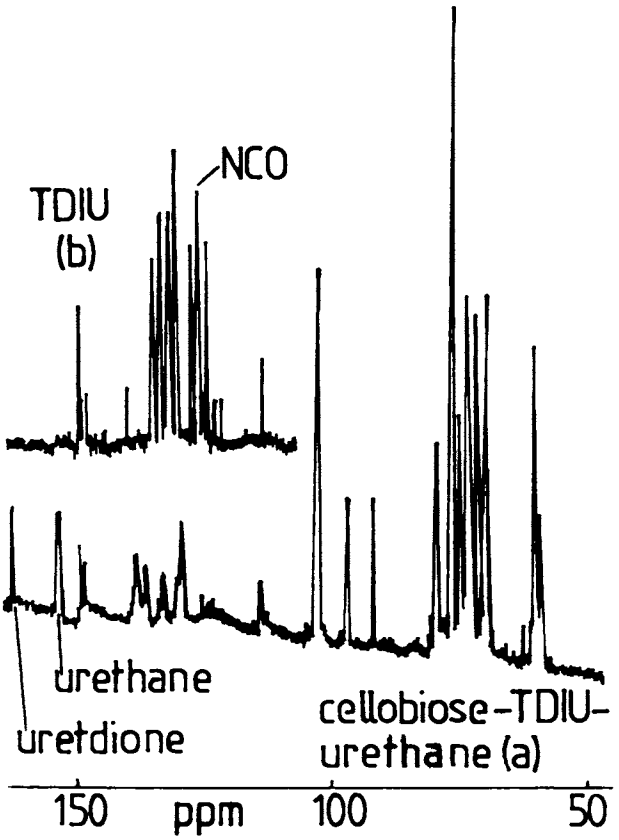
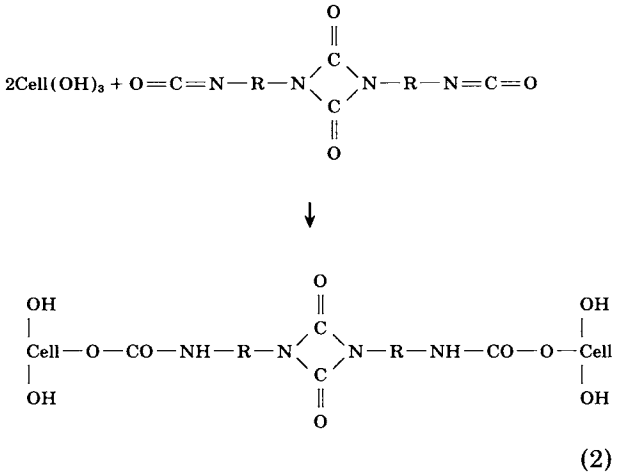


Figure 3 ^{13}C-NMR spectra of (a) TDIU polyurethane of cellobiose and of (b) TDIU. The samples are dissolved in DMAC–LiCl.

DMAC) is necessary. In a subsequent step the cellulose can be dispersed in DMAC or dissolved in DMAC–LiCl.

In analogy to cellobiose, both a heterogeneous system (DMAC, dibutyl tin dilaurate) and a homogeneous system (DMAC–LiCl) is used to synthesize the uretdione urethanes of cellulose. Because of its high molecular weight (ca. 486,000) the concentration of the linen cellulose dissolved in DMAC–LiCl is limited to 1%. The optimum concentration depends on the intended degree of substitution (DS).



The parameters of some typical reactions of HMDIU and TDIU with cellulose are summarized in Table II. The conversion of isocyanate is again controlled by infrared spectroscopy.

Both the FTIR spectra of HMDIU and TDIU immobilized on cellulose (Fig. 4) are consistent with the spectra of the corresponding cellobiose compounds (Fig. 1) as to be expected. The coupling to cellulose enhances the stability of the uretdione ring much more than in the case of cellobiose. This effect is represented by the difference in intensity of the peaks due to the carbonyl stretching vibration of uretdione in the FTIR spectra of the TDIU urethanes derived from cellulose [Fig. 4(a)] and cellobiose [Fig. 1(a)]. Compared with the spectra of the corresponding HMDIU compounds [Figs. 4(b) and 1(b)], only a small difference is to be observed because of the enhanced stability of the aliphatic uretdione. The IR spectra of cellulose urethanes synthesized via heterogeneous and homogeneous reaction are virtually identical.

The poor solubility of cellulose in DMAC–LiCl prevents the obtained uretdione urethanes from

Table II Conditions of Typical Reactions of Cellulose with Different Uretdiones[a]

Medium	HMDIU	TDIU
DMAC, dibutyl tin dilaurate	OH–NCO = 2 : 1, c_{cell} = 2.4%, 45°C, 60 min	OH–NCO = 2 : 1, c_{cell} = 2.4%, 2°C, 480 min
DMAC–LiCl	OH/NCO = 3 : 1, c_{cell} = 0.5%, 80°C, 330 min	OH/NCO = 3 : 1, c_{cell} = 0.75%, 50°C, 20 min

[a] OH–NCO means the molar ratio of saccharide hydroxyl groups to unblocked isocyanate groups, and c_{cell} the concentration (w/v) of cellulose.

characterization by ^{13}C-NMR analysis. The degree of substitution (DS) is ascertained by the nitrogen content determined by elemental analysis. The maximum DS is 1.9 in case of the HMDIU urethane and 2.8 in case of the TDIU urethane. Below those values, the DS can be controlled by the stoichiometric ratio of the reagents.

Further characterization of the uretdione urethanes of cellulose is achieved by differential scanning calorimetry (DSC). Both the DSC plots of HMDIU and TDIU immobilized on cellulose (Fig. 5) exhibit a broad exothermic transition around 100°C effected by the desorption of water.[11] At 210°C (HMDIU compound) and 220°C (TDIU compound) exothermic transitions are observed due to pyrolysis of the cellulose component.

To make sure that no degradation of the cellulose component takes place during the synthesis, samples of cellulose dissolved in DMAC–LiCl are heated to different temperatures for one hour. A significant decrease in the viscosity due to depolymerisation is only observed at 100–110°C.

Reactions of the Uretdione Urethanes of Cellulose

The intention to synthesize cellulose derivatives containing uretdione groups is to obtain a bio-prepolymer for various applications using the reactivity of the (blocked) isocyanate groups [see Eq. (3)].

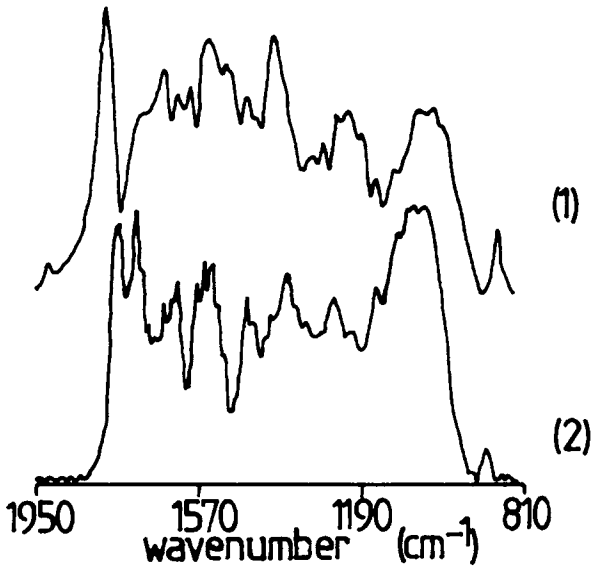


Figure 4 FTIR spectra of uretdione urethanes of cellulose: (a) TDIU compound, KBr tablet, and (b) HMDIU compound, photo acoustic.

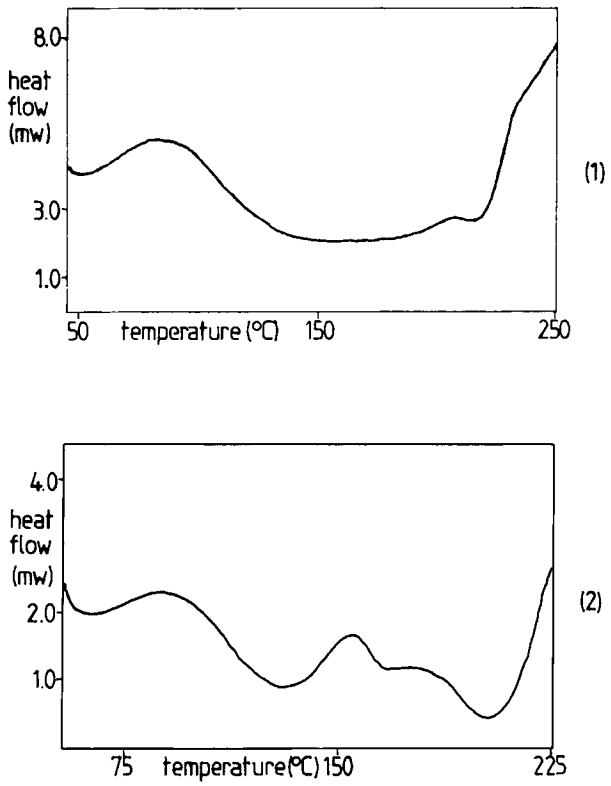
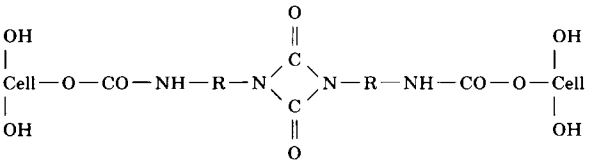


Figure 5 DSC plots of uretdione urethanes of cellulose: (a) TDIU compound and (b) HMDIU compound.



$$\downarrow + 2R'XH$$

$$2\text{Cell}(OH)_2O-CO-NH-R-NH-CO-XR' \quad (3)$$

Therefore all above ring opening reactions of the immobilized uretdiones are investigated. For this purpose nucleophilic reagents like secondary amines are predestined because they are easy to detect. The excess of amine is determined by back titration with hydrochloric acid adjusted by a blank experiment.[12] The reactions are carried out with dibutyl amine, which is suspended in DMAC together with the modified cellulose (NH/NCO molar ratio 30 : 1) and heated for one hour using dibutyl tin dilaurate as a catalyst. It is shown that a reaction of 98% of the uretdione groups with dibutyl amine to yield the corresponding ureas is achieved at 100°C in case of the TDIU compound and at 130°C in case of the

HMDIU compound. The complete conversion of uretdione is proved by IR analysis. The theoretical content of uretdione is calculated from elemental analysis results as described earlier. The temperatures being necessary to perform ring cleavage do not cause a significant degradation of the cellulose component because the polymer is not dissolved but only suspended.

Furthermore the uretdione urethanes of cellulose are dyed with remazol brilliant blue (a reactive dye of the vinyl sulfone type) without damaging the ring as it is proved by IR spectroscopy. This experiment demonstrates that a modification of the prepolymer can also be achieved leaving the uretdione ring unaffected.

CONCLUSIONS

The results presented show that urethanes of cellobiose and cellulose-containing uretdione groups can be obtained by the reaction of aliphatic and aromatic diisocyanate uretdiones with the saccharides. Thus, semisynthetic prepolymers are formed that offer the reactivity of (blocked) isocyanate groups. As a consequence many subsequent reactions like copolymerization, grafting, and immobilization may be achieved. Ring opening of the uretdione is performed at a temperature of 100–130°C in case of amines, which indicates a sufficient stability of the prepolymer before application. On the other hand at this temperature no damage of the cellulosic component takes place.

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