Polymer Bulletin 31, 75–82 (1993)

Polymer Bulletin

Study of deblocking and crosslinking reactions of a blocked isocyanurate cationomer

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Summary

A cationic adduct of a partly blocked hexamethylene isocyanurate and N-methyldiethanolamine was prepared and applied as a crosslinker in one-pack water-borne polyurethane system. The deblocking and crosslinking reactions were followed by FTIR, TGA and DSC techniques. Deblocking started at about 100°C, while at higher temperatures urethane, allophanate, and urea linkages were formed. The efficiency of the cationic crosslinker was evaluated by determining the insoluble part of the crosslinked polyurethane ionomer films. Films of a good solvent resistance were obtained using 15 wt% of the cationic crosslinker and 0.05 wt% of a catalyst at 130°C.

Introduction

In the last years, for environmental reasons, solvent borne polyurethane (PU) coatings and adhesives have been gradually replaced by water-borne systems (1-4). The solubility and/or dispersibility of hydrophobic polyurethanes in water can be achieved by introducing ionic centres into the polymer backbone. Usually, PU ionomers give stable water dispersions and films with good mechanical properties (5). Water and organic solvent resistance as well as mechanical properties of these films can be improved by crosslinking.

The so called one-pack or one-component systems may consist of a mixture of hydroxy terminated PU of low molar mass and blocked isocyanate crosslinker (6-8). The one-pack systems are non-reactive at room temperature and can be therefore stored for a longer period of time. They become reactive at elevated temperatures, when the relatively weak bonds of the blocked isocyanate moieties thermally dissociate (Eq. 1). Subsequently, the released NCO groups react with a nucleophile to give stronger bonds (Eq. 2) and to enable the crosslinking :

$$\text{R-NH-COR}' \text{ -----> } \text{R-NCO} + \text{R}'\text{H} \qquad 1$$

$$\text{R-NCO} + \text{R}''\text{-XH} \text{ -----> } \text{R-NH-CO-X-R}'' \quad \text{X} = \text{N, O, S} \qquad 2$$

This work is a continuation of our previous studies on ionomeric blocked crosslinkers and on the curing of one-pack PU water-borne dispersions (9). In this paper, the deblocking and crosslinking reactions of a cationic crosslinker on the basis of hexamethylene isocyanurate (DDA) partly blocked by butanonoxime, and of the triblocked DDA reference compound, was studied by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TGA,) and differential scanning calorimetry (DSC). The courses of the reactions in the presence or without a catalyst

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were followed by FTIR thermal analysis. The molar mass distribution of the prepared compounds was determined by size exclusion chromatography (SEC). The efficiency of the ionomeric crosslinker in a water-borne cationic PU system was estimated by determining the insoluble part of the crosslinked films.

Experimental

Materials

1,3,5-Tris(isocyanatohexamethylene)isocyanurate, Desmodur DA (DDA, Bayer), toluene diisocyanate (TDI, 80% of 2,4 and 20% of 2,6 isomers, Soda So), 2-butanonoxime (BOX, Fluka), dibutiltin dilaurat (DBTDL with 18% tin content, Acima) and hydrochloric acid (HCl, Kemika) were used as received. Polycaprolacton (CAPA, M_n = 2000 from Solvay) was dried under vacuum by heating at 120°C for 1h, while trimethylol propane (TMP Perstorp Polymer) at 50°C for 8h. N-methyldiethanolamine (NMDEA, Merck) and tetrahydrofuran (THF, Merck) were dried over molecular sieves 4Å.

Synthesis

The cationic crosslinker was synthesized in the following way: in the first step, a part of NCO groups of DDA was blocked by a dropwise addition of BOX in THF solution at room temperature. In the next step, the remained free NCO groups reacted with NMDEA. The molar ratio of DDA:BOX:NMDEA was 2:4:1. The ionic centres in the crosslinker were formed by quaternization with an equivalent quantity of HCl.

As a reference a triblocked DDA was prepared in a THF solution, as well.

The cationic polyurethane (PU) ionomer was synthesized by a standard prepolymer process (10). The prepolymer was prepared from CAPA and TDI and was chain extended by NMDEA and by TMP in a THF solution. After quaternization with HCl, the PU ionomer was dispersed in water, and THF vacuum distilled. The concentration of the ionic groups was 0.35 mmol g^{-1} while the concentration of OH groups was 0.10 mmol g^{-1}. The PU ionomers were crosslinked by 15 or 20 wt% of the ionomeric crosslinker calculated on the solid content of dispersions. The films were prepared by drying the mixtures in thin layers for two days at room temperature and for 24 hours at 50°C. They were crosslinked by heating in a drying oven at different temperatures over 100°C. In some cases DBTDL was used as a catalyst.

Methods

IR spectra were taken on a Perkin Elmer FTIR 1725X spectrometer. The measurements at elevated temperatures were performed on a Spectra Tech high temperature cell. Samples were prepared by casting the THF solutions of the dried compounds onto NaCl plates. In some cases, the samples were gradually heated to higher temperatures (temperature was progressively increased in 5°C increments and held for two minutes at each level); in other cases, the samples were heated to selected temperatures, and spectra taken in regular time intervals. The deblocking and crosslinking reactions were followed by monitoring the change of NCO groups absorbance at 2270 cm^{-1} as a function of temperature and of time relative to the absorbance at 766 cm^{-1} (internal standard). The IR spectra of the triblocked DDA and of the cationic crosslinker samples heated up to 300°C in DSC apparatus, prepared as KBr pellets, were also taken.

The molar mass distribution was determined by size exclusion chromatography. A modular Perkin Elmer liquid chromatograph equipped with a differential refractometer LC-30 as a detector, PLgel columns with pore diameters of 1 and 5 x

10^{-8}m, and THF as eluent with a flow rate of 1 ml /min was used. Molar masses were calculated relative to polystyrene reference materials.

Thermogravimetric measurements were performed on a TA 2000 instrument using a 951 Thermogravimetric Analyzer (TA Inst. Inc. USA). The samples were heated up to 600°C with a rate of 10°C/min. The instrument was purged by helium at a flow rate of 50 ml/min.

Differential scanning calorimetry measurements were made on a Perkin Elmer DSC-7. The dried samples were heated in the temperature interval from 25 to 270°C with a rate of 5°C/min. Holes were made in the lids of the pans to permit the volatile substances to escape.

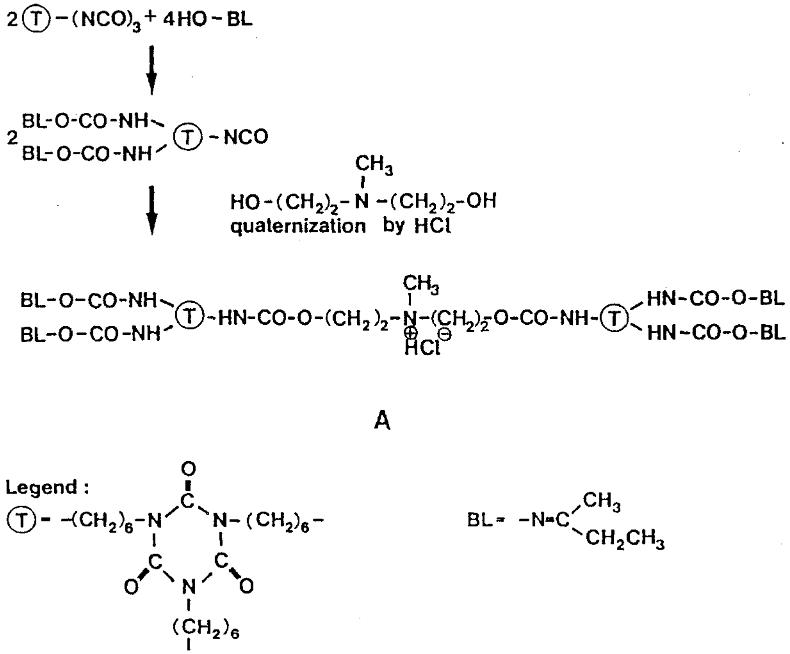
The insoluble part (the gel fraction) of the crosslinked PU films was determined by THF extraction in a Soxhlet apparatus for 6 hours.

Results and discussion

Characterization of the cationic crosslinker

According to the molar ratio of raw materials and to literature data for the corresponding anionic crosslinker (11) the reactions presented in Scheme 1 can run. However, our previous findings indicated a poor selectivity of the blocking reaction (9).

The SEC analysis of the blocked cationic crosslinker (Figure 1) shows a mixture of oligomeric compounds. It is obvious that besides the compound A (Scheme 1), some other compounds are formed. Some possible structures are presented in Scheme 2.



Scheme 1:
Synthesis of ionomeric blocked polyisocyanate.

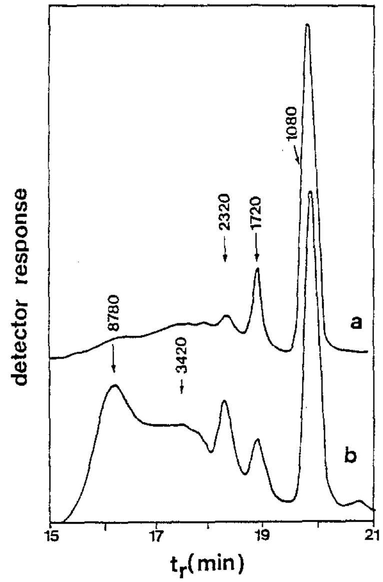
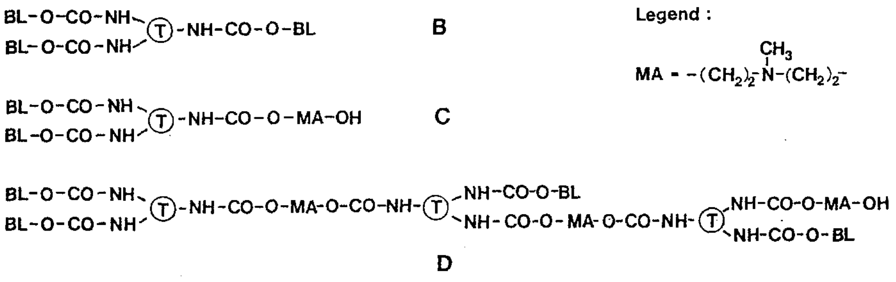


Figure 1:
SEC curves of triblocked DDA (a) and of cationic crosslinker (b).

An information about the composition of the cationic crosslinker was obtained by comparing its SEC curve with the SEC curve of the triblocked DDA compound (Figure 1). It was assumed that the strongest signal (M_{peak} = 1080) belonged to the triblocked DDA (B) and/or to the compound C with a partly reacted NMDEA. Their signals might overlap because of approximately the same molar masses. As regards the higher oligomers, a great number of compounds and small differences between their molar masses made a good SEC separation difficult.



$$\begin{matrix}\text{BL-O-CO-NH}\searrow\\ \text{BL-O-CO-NH}\nearrow\end{matrix}\textcircled{T}\text{-NH-CO-O-BL} \qquad \mathbf{B}$$

$$\begin{matrix}\text{BL-O-CO-NH}\searrow\\ \text{BL-O-CO-NH}\nearrow\end{matrix}\textcircled{T}\text{-NH-CO-O-MA-OH} \qquad \mathbf{C}$$

$$\begin{matrix}\text{BL-O-CO-NH}\searrow\\ \text{BL-O-CO-NH}\nearrow\end{matrix}\textcircled{T}\text{-NH-CO-O-MA-O-CO-NH-}\textcircled{T}\begin{matrix}\nearrow\text{NH-CO-O-BL}\\ \searrow\text{NH-CO-O-MA-O-CO-NH-}\end{matrix}\textcircled{T}\begin{matrix}\nearrow\text{NH-CO-O-MA-OH}\\ \searrow\text{NH-CO-O-BL}\end{matrix}$$

$$\mathbf{D}$$

Legend :

$$\text{MA} = -(\text{CH}_2)_2\text{-}\overset{\text{CH}_3}{\overset{|}{\text{N}}}\text{-}(\text{CH}_2)_2\text{-}$$

Scheme 2:
Triblocked DDA (B) and two possible structures of the cationic crosslinker.

Deblocking and crosslinking reactions of the blocked compounds

TGA analysis

The differential thermogravimetric (DTG) curves of the cationic crosslinker and of the triblocked DDA compound were compared to the DTG curve of DDA (Figure 2). It can be seen that the DTG curves of the blocked compounds have a strong peak between 150 and 230°C whilst the DTG curve of DDA has the first maximum at around 280°C. Therefore, the peak with the maximum at around 200°C was ascribed to the weight change caused by the deblocking of BOX. The degradation of isocyanurate ring took place at over 400°C (12).

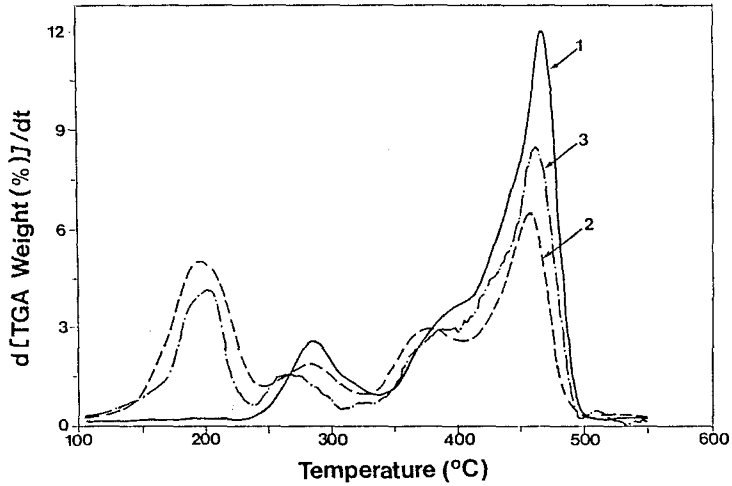


Figure 2:
DTG curves of DDA (1), triblocked DDA (2) and cationic crosslinker (3).

DSC analysis

By heating the cationic crosslinker and the triblocked DDA compound, exothermic reactions were detected in the temperature range between 130 and 300°C (Figure 3). Because of the relatively weak thermal effect of the blocked isocyanate dissociation (13) the endothermic deblocking reaction could not be distinguished from the stronger exothermic crosslinking reaction. Namely, in the observed temperature range, besides deblocking some simultaneous exothermic reactions are possible. One of them is the formation of allophanate linkages between the released NCO groups and the urethane groups of partly deblocked compounds (14). Reac-

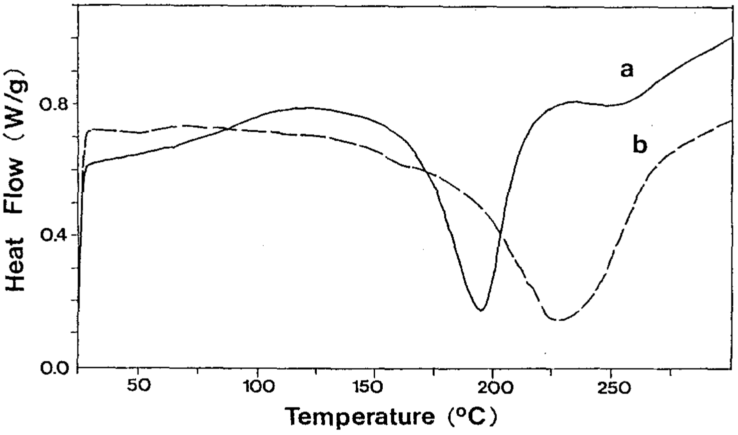


Figure 3:
DSC curves of cationic crosslinker (a) and of triblocked DDA (b).

tion between the released NCO and OH groups of the partly reacted NMDEA (see structures C,D) in the ionomeric adduct can also take place. The presence of the structures with one reacted OH group of NMDEA in the ionomer crosslinker was confirmed by NMR studies (15). The reaction of NCO groups with traces of moisture could be expected as well.

The maximum of the main exothermic reaction for the cationic crosslinker is at a temperature of 192°C which is lower than for the triblocked compound (225°C, Figure 3). This was attributed to the presence of the catalyst in the ionomeric sample.

Kinetics of the overall reactions obtained by heating the ionomeric crosslinker and the triblocked DDA was calculated; the enthalpy of the exothermic reaction was found to be 82 kJ per mol for the blocked NCO groups in the case of ionomeric crosslinker (peak maximum at 192°C) and 107 kJ/mol (peak maximum at 225°C) in the case of triblocked DDA; the activation energy was about 156 and 82 kJ/mol, respectively; the overall reaction in both cases was of first order.

FTIR analysis

FTIR thermal method enables the simultaneous study of the deblocking and crosslinking reactions. The spectra of the samples, gradually heated to different temperatures, indicated that deblocking started at around 100°C; at this temperature, namely, the absorbance of the free NCO groups could be detected.

The course of the deblocking of the cationic crosslinker without or with a catalyst (0.5 wt% of DBTDL) was followed by monitoring the change of the NCO absorbance vs time at 150°C (Figure 4). In the system without catalyst, the NCO absorbance appreciable increased in 20 minutes (curve a). In the presence of DBTDL, the NCO absorbance reached a lower maximum value in a shorter time, obviously because DBTDL accelerated the crosslinking reactions i.e. the consumption of the deblocked NCO groups (curve b).

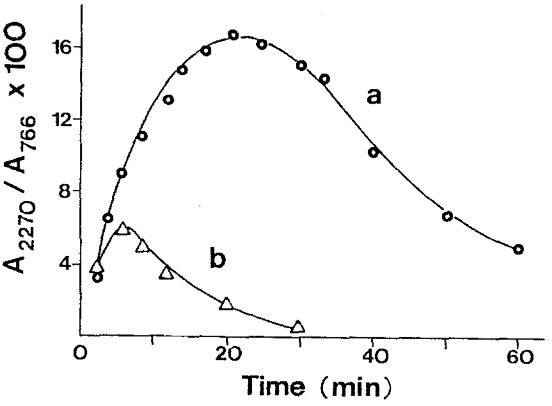


Figure 4: Absorbance of NCO groups vs time at 150°C; without catalyst (a), with catalyst (b).

More information concerning the deblocking and crosslinking reactions could be obtained by the subtraction of the spectra at various stages of both reactions. Subtracted (difference) spectra of triblocked DDA heated for 3 and 12 minutes at 150°C are given in Figure 5. In the difference spectrum a, a strong absorption band of the free NCO groups can be seen; the bands at 1735 and 1507 cm^{-1} belong to the dissociated urethane groups. At the same heating conditions but in

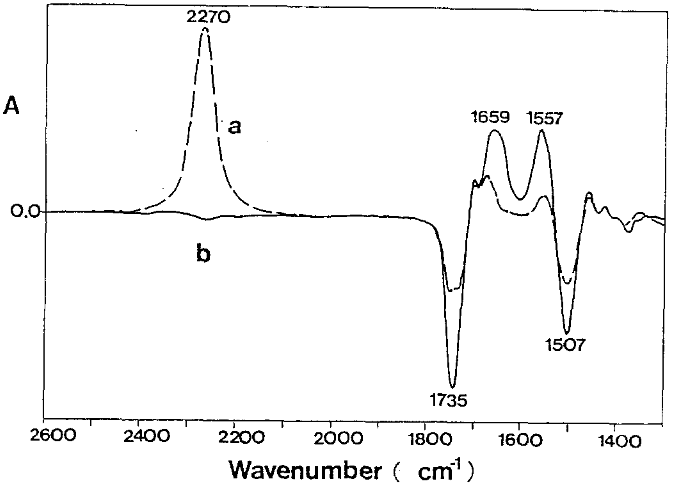


Figure 5:
Difference spectra of the samples heated for 3 and 12 minutes at 150°C; without catalyst (a), with catalyst(b).

the presence of the catalyst (difference spectrum b), no free NCO groups were detected. The new bands in the difference spectra at 1659 and 1557 cm^{-1} were attributed to the allophanate (14) and to the urea groups (16) formed during crosslinking reactions.

In the FTIR spectra of the cationic crosslinker heated up to 200°C, the -N=C=N- band at 2155-2090 cm^{-1} characteristic for the carbodiimide structures (12) was not observed. However, this band was present in the spectra of the samples heated in DSC apparatus up to 300°C.

The application of the ionomeric crosslinker

The efficiency of the ionomeric crosslinker could be estimated by determining the gel fraction of the crosslinked PU films. The films were prepared from the PU dispersions containing different amounts of ionomeric crosslinker and catalyst, and were heated for selected time intervals at 110°, 130° or 150°C. The crosslinked films were extracted with THF and gel fraction was calculated. Some results are presented in Table 1.

It was found that films with 15 wt% of the crosslinker and 0.05 wt% of the catalyst were efficiently crosslinked. Crosslinking reactions proceeded slowly at 110°C, and quickly at 150 °C; the films obtained at 150°C contained small bubbles. The temperature of 130°C was estimated to be the most suitable. At that temperature the reaction time was relatively short and the degree of the film crosslinking was practically the same as at 150°C.

Conclusions

A cationic crosslinker was synthesized from a partly blocked isocyanurate and applied for the preparation of a one-pack water-borne PU system. The crosslinker was a mixture of oligomeric compounds with different structures. The deblocking of the cationic crosslinker and of the triblocked DDA compound started at around

100°C, while at higher temperatures the released NCO groups immediately reacted by forming urethane, allophanate, and urea linkages. Depending on crosslinking conditions (amount of the crosslinker, time and temperature of heating, use of a catalyst), organic solvent resistant PU films were obtained.

Table 1:
The gel fraction of the crosslinked PU films

Sample	Temperature (°C)	Time (min)	Gel fraction (%)
PU resin with 15% of crosslinker	110	60	dissolved
	110	180	40.1
	130	30	56.3
	130	120	62.8
	150	30	73.3
	150	120	74.5
PU resin with 20% of crosslinker	130	30	57.1
	130	120	63.0
	150	30	74.9
PU resin with 15% of crosslinker and 0.05% of catalyst	130	30	77.0
	130	120	84.8
	150	15	84.6
	150	30	86.3
	150	120	86.6

Acknowledgements

The authors are grateful to the Ministry of Science and Technology of the Republic of Slovenia for financial support (Grant C-2539-104).

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Accepted May 19, 1993 C