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Thermal deblocking of masked low molecular isocyanates
I. Aliphatic isocyanates

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Abstract

The thermal deblocking of masked isocyanate model substances was investigated by means of simultaneous thermal analysis and quadrupole mass spectrometry system (STA/QMS). The results were compared with additional measurements carried out by differential scanning calorimetry (DSC) and temperature dependent Fourier transform infrared spectroscopy (FTIR). The measured values which were determined as the deblocking temperature depend on the method of investigation. Thermogravimetric and mass spectrometric data depend on the volatility of the components and could differ from those observed by DSC and/or FTIR. Furthermore, the mechanism of deblocking is very complex. Secondary reactions obviously play an important role. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Masked aliphatic isocyanates; Temperature dependent FTIR; Differential scanning calorimetry; Simultaneous thermal analysis; Mass spectrometry

1. Introduction

Polyurethane powder coatings are known for their superior flow characteristics and gloss [1]. Additionally, polyisocyanates on the basis of aliphatic isocyanates show weathering resistance and lightfastness in coatings [2].

Polyurethane powder coatings can be produced based on internally (uretdione) or externally masked isocyanate prepolymers as crosslinkers for hydroxy functional polymer binders, such as acrylates, polyesters and polyethers. Such systems are already too reactive at room temperature to permit formation of one-package coatings. For that reason reversibly blocked isocyanate groups are required in any case [3]. In that way, reactions between NCO- and OH-groups in extrusion processes can be prevented and the resulting powders show good storage stability. However, in both commercial systems curing temperatures of at least 150°C (for ε-caprolactam blocked aliphatic isocyanates 170°C) and higher (up to 220°C for uretdiones) are necessary for curing reactions. The deblocking reaction is the main condition for the start of the curing reaction. This process is followed by the formation of an undesirable volatile blocking agent (in most commercial products ε-caprolactam [4]) in the case of externally blocked polyisocyanates. In connection with stricter laws in the environment legislation the emission of the masking agent must be prevented in future.

The aim of our work was to decrease the deblocking temperature by the use of various blocking agents for

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externally blocked isocyanates and to find mechanisms for the complete incorporation of blocking agents into the polymer network. In the first step, the thermal deblocking of various masked isocyanate model substances was investigated. Such compounds were used which are able to react as blocking agents directly or which exist as end groups in oligomers. This paper deals with aliphatic isocyanates and a following one with aromatic isocyanates.

2. Experimental

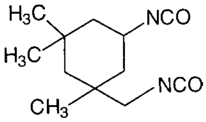
2.1. Preparation of model substances

2.1.1. Isocyanates used for synthesis

Hexamethylenediisocyanate (HDI)

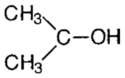
$OCN{-}(CH_2)_6{-}NCO$

Isophorondiisocyanate (IPDI)

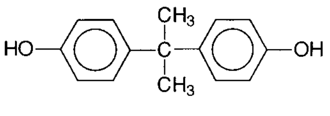


2.1.2. Masking agents used for synthesis

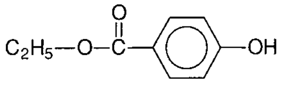
Isopropanol (IP)



Bisphenol A (BPA)



4-Hydroxybenzoic acid ethyl ester (HBEE)



2.1.3. General synthesis in solution

A solution of isocyanate in acetone (dried and distilled under N_2) was put into a four-necked flask, equipped with a glass stirrer, nitrogen inlet, reflux condenser and a dropping funnel. The solution of blocking agent (only aromatic) in acetone or the pure blocking agent (IP) were added dropwise to the isocyanate. Then the solution was stirred and refluxed for 2 up to 24 h in dependence on the blocking agent. The reaction end was controlled by Fourier transform infrared spectroscopy (FTIR) using the isocyanate absorption band (ν (N=C=O)) at 2276 cm^{-1} for HDI and at 2260 cm^{-1} for IPDI.

After cooling, the solution was precipitated with intense stirring in ice–water. In most cases the solid product could be filtered after some hours, washed with water, dried in vacuo, recrystallized in acetone and again dried in vacuo at 40°C.

For the product IPDI/BPA only an oil layer could be separated after precipitation in ice–water. The product was solidified in vacuo at 40°C and recrystallized.

2.1.4. General synthesis in melt

Isocyanate and blocking agent were dried at 50°C for 4 h under vacuum. The two substances were homogenized in a mortar using a pistill. Then the mixture was put in a three-necked flask equipped with stirrer and nitrogen inlet. The reaction was carried out using an oil bath at a temperature of 100°C. The end of the reaction was detected by FTIR.

All products were analyzed by ^{1}H NMR. The differences in synthesis conditions are shown in Table 1.

2.2. Thermoanalytical measurements

DSC experiments were performed on a Perkin-Elmer DSC-7 at a heating rate of 10 K min^{-1} in nitrogen atmosphere. The temperature range was varied depending on the thermogravimetrical results of the system investigated.

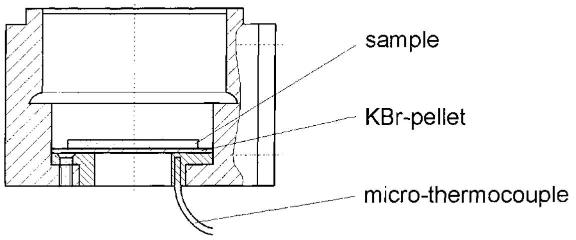
The TG/DSC/MS investigations were carried out using a Simultaneous Thermal Analyzer STA 409/249 coupled with a Quadrupole Mass Spectrometer QMS 403 Skimmer System (Netzsch) in the temperature range between 10–500°C in helium atmosphere at a heating rate of 10 K min^{-1}. The gas flow rate at the inlet was 125 cm^3 min^{-1}. The DSC/TG sample holder and aluminium pans were used. The atomic mass units (amu) were recorded every 20 K in the range between 10 and 195 amu. For the comparison of the experiments all measured intensities of interesting mass numbers were normalized to the sample mass, which was (5±1) mg.

Table 1
Synthesis conditions and ^{1}H NMR analysis of the samples

Isocyanate/ masking agent	Synthesis	Molar ratio	Reaction time (h)	^{1}H NMR investigation δ (ppm)
HDI/HBEE	Solution	1:2	2	δ NH 7.88
IPDI/HBEE	Solution	0.9:4	4	δ NH–CH 7.95; δ NH–CH_2 7.86 unreacted HBEE
HDI/BPA	Melt	0.9:2	3.5	δ NH 7.66 oligomer content
IPDI/BPA	Solution	0.9:4	24	δ NH–CH 7.62; δ NH–CH_2 7.73 unreacted BPA; oligomers
HDI/IP	Solution	1:2	6	δ NH 6.92
IPDI/IP	Solution	1:2	8	δ NH–CH 6.84; δ NH–CH_2 6.96

2.3. Temperature dependent FTIR measurements

Temperature dependent FTIR measurements were carried out on KBr-pellets (1 mg substance in 400 mg KBr) with a Bruker IFS 66 spectrometer in a variable temperature cell (P/N 21.500 by Specac). This cell with the pellet in it was evacuated before starting the measurement. In this manner, disturbing air components, like CO_2 and vapor, and absorbed water on the surface of the pellet were removed. The cell kept evacuated during the measurement. Volatile constituents which were evolved during the deblocking process could only evaporate if they were released on the surface of the pellet. The heating rate of the temperature cell was 10 K min^{-1}. The start temperature was 25°C and the maximum program temperature was 250°C. It was necessary to carry out a calibration to determine the start temperature of the deblocking process, because the heating rate of the temperature cell was non-linear above 200°C. We monitored the temperature of the cell by using a supplementary special micro-thermocouple which was installed near the sample (see Scheme 1). In this way the temperature of the sample is detectable with a precision of ±1°C [5]. The maximum real temperature reached was 233°C.



Scheme 1. Schamatic drawing of variable temperature cell.

All pellets were heated for 1 h. The annealing temperature was reached after about 35 min. IR-spectra were recorded every minute. Then a spectrum of the final state at 25°C was recorded after cooling the pellet in the temperature cell for at least 3 h.

2.4. ^{1}H NMR investigations

^{1}H NMR analysis of synthesized urethanes was performed on a Bruker DRX 500 spectrometer operating at 500.13 MHz. DMSO-d_6 was used as a solvent, lock and internal standard (δ (^{1}H)=2.50 ppm).

3. Results and discussion

The deblocking reaction which results in free isocyanate groups is an equilibrium reaction (see Eq. (1)):

$$R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}B \rightleftharpoons R{-}N{=}C{=}O + HB \qquad (1)$$

To reach a complete reversion of isocyanate groups an excess of blocking agents was used for the synthesis of some model substances (see Table 1), especially for reactions with the lower reactive IPDI isocyanate. Furthermore the reaction between bifunctional isocyanates and bifunctional blocking agents results in oligomers. In this case an excess of blocking agent was necessary. The remained free blocking agent could not be separated completely by recrystallization in every sample and made it difficult to determine the deblocking especially by TG and DSC.

The rate and extent of elimination reaction depend on several variables: the structure of R and HB including substituents [3,6,7], solvents [8], the presence of catalysts [9] and temperature. In order to obtain distinct differences for the deblocking temperature, no catalyst was used for the deblocking reaction. For that reason, it was necessary to avoid the use of any catalyst even during synthesis of model substances.

It was recognized early that thermal dissociation of urethanes generally takes place in the following order [3,10]:

Alkyl–NHCOO–Alkyl	250°C
Aryl–NHCOO–Alkyl	200°C
Alkyl–NHCOO–Aryl	180°C
Aryl–NHCOO–Aryl	120°C

In addition, the deblocking temperature decreases with increasing acidity of isocyanate and blocking agent [3].

The determination of deblocking temperatures depends on the volatility of the adduct components and the method of investigation. Since the blocking agent is volatile during deblocking, the temperature of starting weight loss by means of thermogravimetrical measurements was used as an indication. In case of thermal stability of the components (isocyanate and the blocking agent) at the deblocking temperature it was not possible to get reasonable TG results.

The deblocking reaction shows an endothermic effect in the DSC curves, and the observed deviation from the baseline was determined as the deblocking temperature.

However, the total vaporization of the blocking agent in many cases leads to pollution of the measuring system, followed by a baseline shift and a deterioration of the signal/noise ratio. Therefore, the DSC-7 was only used to determine transitions (glass or melting transition) of the model compounds, which take place at lower temperatures and to determine the

Table 2
Deblocking temperatures of urethane model substances consisting of aliphatic isocyanates with aliphatic or aromatic masking agents

Isocyanate/masking agent	Start of deblocking T_S (°C)			Maximum of deblocking T_{max} (°C)	
	DSC-7[f]	FTIR	STA–QMS	FTIR	STA–QMS
HDI/HBEE	130	118	TG/DTG: 150 DSC: 170[a] MS: 155	163	DTG: 119/211 DSC: 213 MS: 215
IPDI/HBEE	170	177	TG/DTG: 85 DSC: 130–140[a] MS: 100[c] MS: 140[d]	>233[b]	DTG: 185/324 DSC: 195 MS: 195
HDI/BPA	170	162	TG/DTG: 180 DSC: 225–235[a] MS: 200	230	DTG: 291 DSC: 287 MS: 290
IPDI/BPA	175	183	TG/DTG: 180 DSC: 200–210[a] MS: 180	>233[b]	DTG: 275 DSC: 273 MS: 275
HDI/IP	185	183[e]	TG/DTG: 150 DSC: 190[a] MS: 150	>233[b]	DTG: 231 DSC: 233 MS: 230
IPDI/IP	180	177	TG/DTG: 150 DSC: 205[a] MS: 150	>233[b]	DTG: 249 DSC: 250 MS: 250

[a] Extrapolated onset-temperature.

[b] The maximum temperature of the FTIR cell was 233°C.

[c] Masking agent.

[d] Isocyanate.

[e] Value calculated using absorption band at 2336 cm^{-1}.

[f] Estimated value.

start of the deblocking reaction to minimize the disruptive effect on the baseline.

Using the STA–MS system besides TG and DSC mass spectrometric data are available.

Using FTIR measurements, the formation of the antisymmetric isocyanate C–N stretching absorption band of the different isocyanate monomers at 2276 cm^{-1} for HDI and 2260 cm^{-1} for IPDI was monitored for deblocking. All data determined by DSC-7, FTIR and STA–MS are summarized in Table 2.

Fig. 1 shows the comparison of the different signals obtained by STA–MS of the system HDI/HBEE. It can be seen in the DSC curve that the endothermic reaction due to the deblocking starts directly after the melting (peak maxima of melting at 117 and 133°C for HDI/HBEE). The first deviation in the DTG curve and the first signs of mass numbers were found at about 150°C. This value is higher than the value determined by DSC or FTIR because the volatility of the components is not given at the start of deblocking reaction.

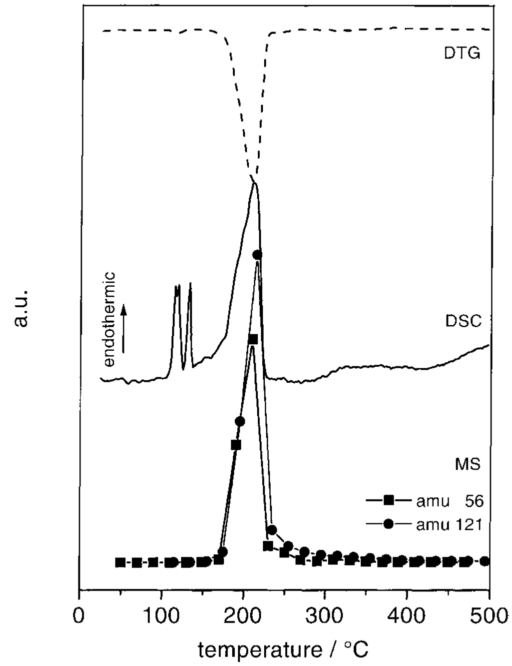


Fig. 1. Comparison of the signals obtained by STA–MS of the system HDI/HBEE: (—) DSC; (- - - -) DTG; (— ■ —)56 amu; (— ● —) 121 amu.

Fig. 2 shows the isocyanate range in the FTIR-spectra of the sample HDI/HBEE at different temperatures. All spectra were baseline corrected. Nearly with the beginning of deblocking besides the new isocyanate absorption band at 2276 cm^{-1} two new bands at 2336 and 2369 cm^{-1} were found. Our interpretation is that the band is caused by carbon dioxide, which is evolved by a secondary reaction. The band increases parallel with the isocyanate band during heating. After cooling at the final state, the isocyanate band is almost not detectable but the two new CO_2-

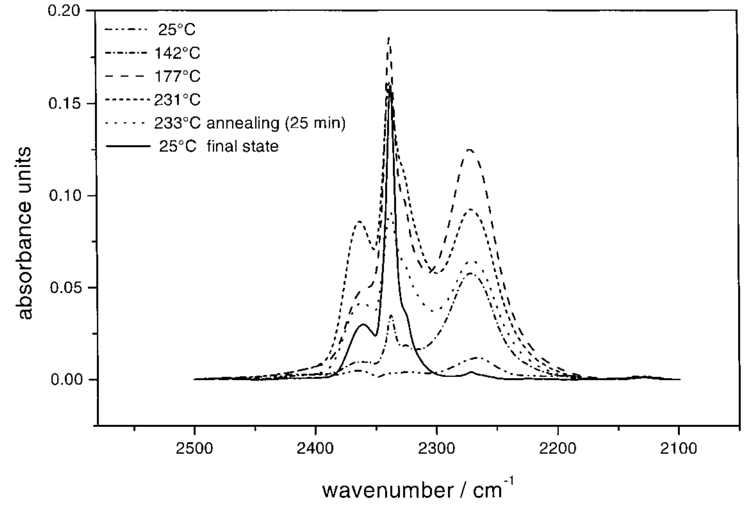
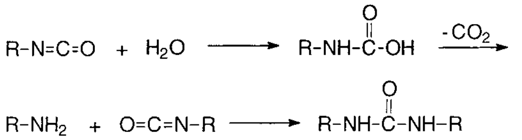


Fig. 2. Temperature dependent FTIR spectra of the deblocking reaction of the urethane model compound HDI/HBEE in the range between 2500 and 2100 cm^{-1}.

bands remain. We assume that the intensity relation of the two CO_2-absorbtion bands and the NCO-band are dependent on each other. For that reason in cases where no isocyanate band was obtained the deblocking temperatures were calculated using the absorption band at 2336 cm^{-1}. Two secondary reactions are possible which could cause the formation of carbon dioxide (see Eqs. (2) and (3)):



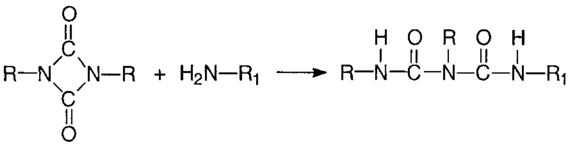
$$R\text{-}N{=}C{=}O + H_2O \longrightarrow R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \xrightarrow{-CO_2}$$

$$R\text{-}NH_2 + O{=}C{=}N\text{-}R \longrightarrow R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R \qquad (2)$$

$$R{-}N{=}C{=}O + O{=}C{=}N{-}R \xrightarrow{-CO_2} R{-}N{=}C{=}N{-}R \qquad (3)$$

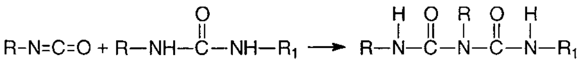
Carbodiimide, amine and urea were not detected by FTIR during the reaction.

Obviously, under the special conditions in the KBr-pellet, other secondary reactions of deblocked isocyanate could not be excluded. We suggest, therefore, the mechanism of formation of biuret or allophanate structures. These enclose further reactions of two NCO-groups yielding uretdione. Then the evolved primary amine (resulting from the first step of reaction in Eq. (2)) reacts immediately with uretdione resulting in a biuret structure (Eq. (4)).



(4)

Another reaction resulting in biuret reaction products is given in Eq. (5) with the reaction of urea (also reaction in Eq. (2)) and deblocked isocyanate.



$$R\text{-}N{=}C{=}O + R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R_1 \longrightarrow R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R_1 \qquad (5)$$

In Fig. 3 the integral absorbances of isocyanate and carbon dioxide absorption bands of HDI/HBEE were calculated by integration of the band areas. The start of deblocking could be determined after 12 min at 118°C. The maximum integral absorbance of isocyanate was reached after 18 min at 163°C. At higher temperatures, a fast decrease was observed up to the end of the heating cycle. During annealing at 233°C, the rate of isocyanate decreases slowly. The integral absorbance of the carbon dioxide band has nearly the same time-variation. These absorbances are shifted to

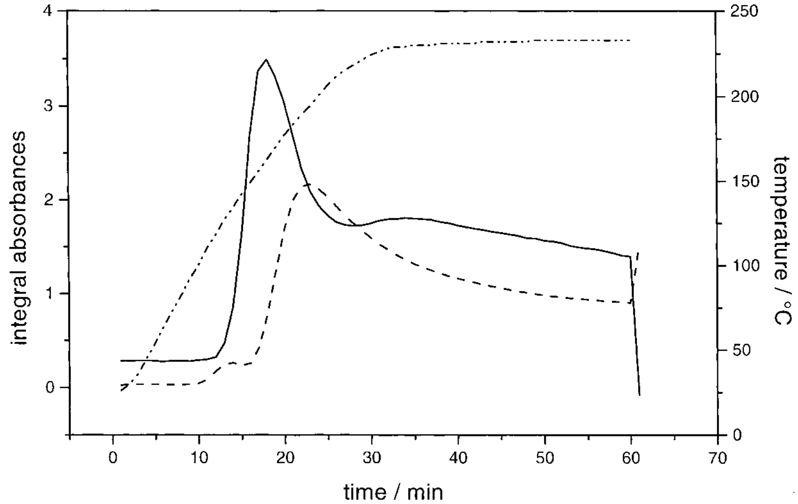
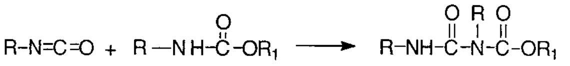


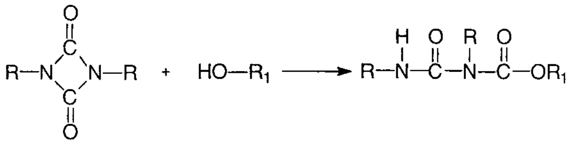
Fig. 3. Integral absorbances of isocyanate and carbon dioxide vibration during the deblocking reaction of the urethane model compound HDI/HBEE studied by FTIR in dependence on time during the non-linear heating: (—) NCO (2303–2200 cm^{-1}); (- - - -) CO_2 (2349–2307 cm^{-1}); (—··—··) temperature.

higher temperatures. The decrease of the NCO-band, especially during cooling, could be partly explained by the formation of allophanate structures. Generally, allophanate structures will be formed resulting from the reaction of a urethane with isocyanate (Eq. (6)) or from the reaction of uretdione with alcohol (Eq. (7)).



$$R{-}N{=}C{=}O + R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OR_1 \longrightarrow R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OR_1$$

(6)



(7)

This fact was concluded from the following analytical evidences (see Fig. 4):

δ NH (urethan) at 1536 cm^{-1} is absent at temperatures above 224°C and did not arise again during cooling. It could be concluded that all NH groups of the starting material are absent in the final state. A new δ NH absorption band at 1558 cm^{-1} nascented with low intensity during heating and further increased during cooling. However, the intensity of the NH absorption band at 1558 cm^{-1} after cooling is lower than the detected intensity of the NH absorption band of the initial urethane.

Additionally, we can not observe free OH groups of the blocking agent at 1050 cm^{-1}.

A new carbonyl absorption band at 1690 cm^{-1} (allophanate) was formed during heating. This band reached the highest intensity in the final spectrum at room temperature.

Fig. 5 shows analogously to the system HDI/HBEE the curves obtained for IPDI/HBEE. At first sight it seems that the deblocking of this system starts at lower temperatures than of HDI/HBEE. It can be seen in the DSC curve obtained by STA–MS that the endothermic reaction due to the deblocking starts at lower temperatures immediately after the melting (peak maxima of melting at 88 and 109°C for IPDI/HBEE). However, T_S values which were measured by DSC-7 as well as FTIR are clearly higher compared with HDI/HBEE. The detection of mass number 121 (HBEE) at lower temperatures than of 110 (IPDI) and also the shift of maximum temperature to lower values indicate that this system contains unreacted HBEE resulting from the HBEE excess during synthesis which could not be removed completely after synthesis as proved by ^{1}H NMR investigation of the sample.

Deblocking of BPA masked samples starts between 170–180°C. The differences of T_S values determined

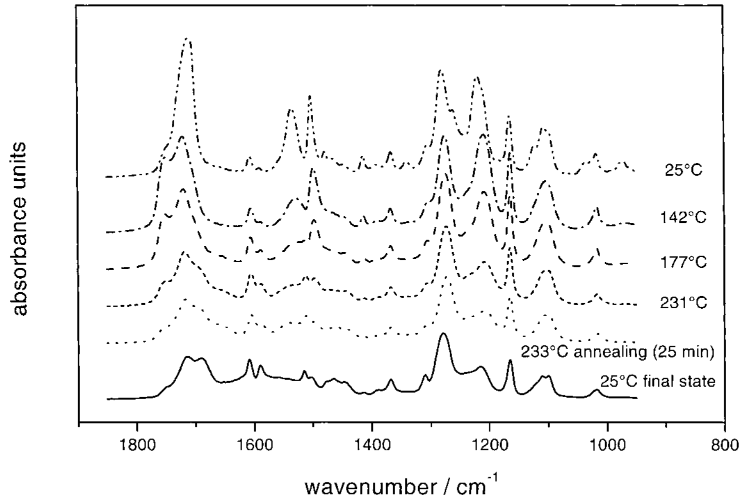


Fig. 4. Temperature dependent FTIR spectra of the deblocking reaction of the urethane model compound HDI/HBEE in the range between 1850 and 950 cm^{-1}.

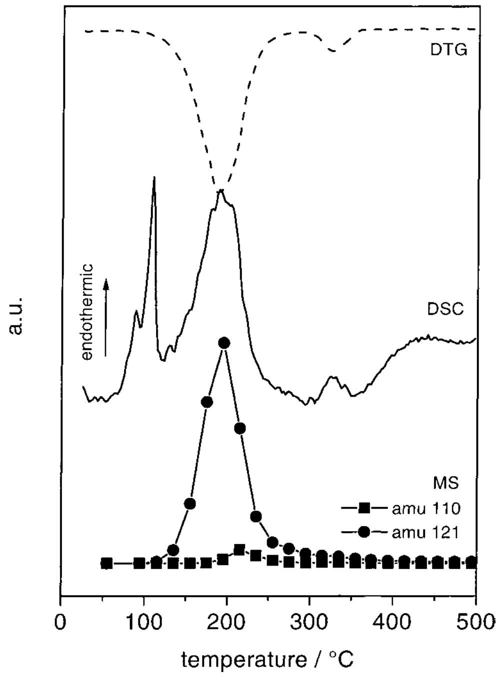


Fig. 5. Comparison of the signals obtained by STA–MS of the system IPDI/HBEE: (—) DSC; (- - - -) DTG; (— ■ —) 110 amu; (— ● —) 121 amu.

between HDI and IPDI blocked with BPA are something lower compared with HBEE-blocked samples. Furthermore, T_S values in samples with BPA as the blocking agent are less dependent on the isocyanate used (Fig. 6). In contrast to IPDI/HBEE, the HDI/HBEE model substance deblocks at lower temperatures.

Values for T_S and T_{max} using FTIR measurements for sample HDI/BPA were detected using the absorption band at 2272 cm^{-1}. Simultaneously an absorption band at 2336 cm^{-1} was observed during the measurement (Fig. 7). The two absorption bands increased up to 230°C and show a slow decrease during annealing at 233°C. After cooling the NCO absorption band was not detected but the absorption band at 2236 cm^{-1} showed the highest intensity during the masurement. Here we postulate the same secondary reactions like in the system HDI/HBEE. In addition, two increasing absorption bands of carbodiimide at 2170 and 2158 cm^{-1} were found at temperatures above 190°C. But the intensity of these bands is much weaker.

Deblocking in combination with aliphatic isopropyl alcohol as blocking agent starts at 150°C which can be

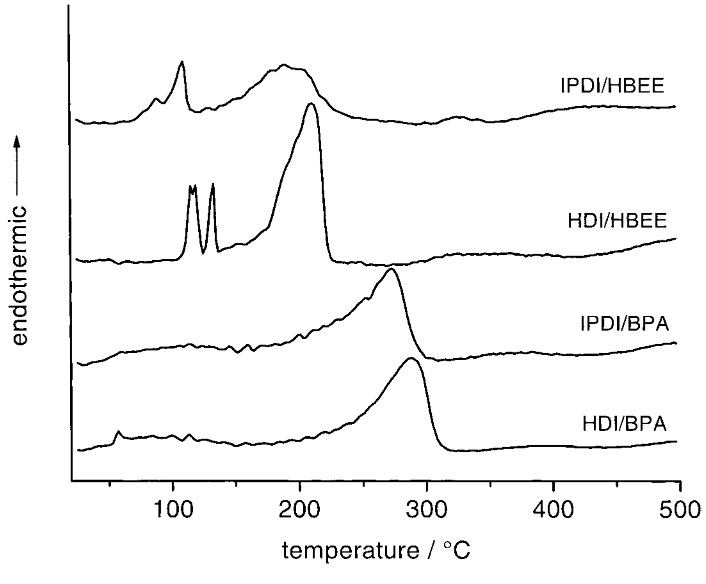


Fig. 6. Comparison of DSC curves obtained by STA–MS of HDI and IPDI masked with HBEE and BPA.

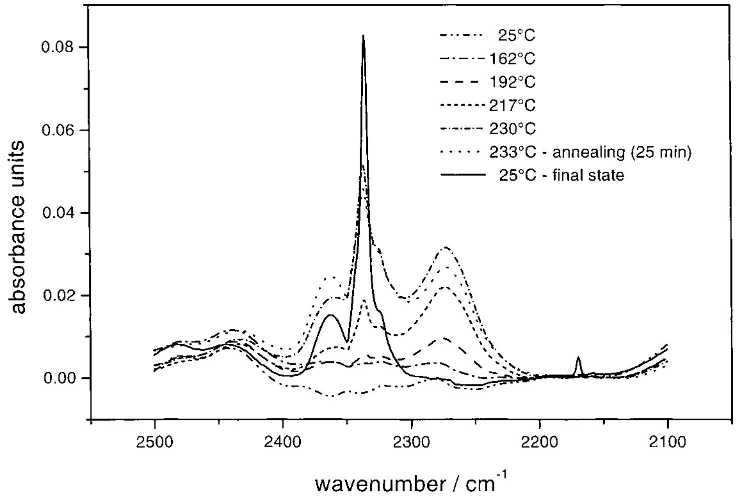


Fig. 7. Temperature dependent FTIR spectra of the deblocking reaction of the urethane model compound HDI/BPA in the range between 2500 cm^{-1} and 2100 cm^{-1}.

observed by the detection of mass number 45 as stable fragment of the alcohol used and the deviation in the DTG curve of the samples.

Fig. 8 shows the isocyanate range from FTIR-spectra of sample IPDI/IP at different temperatures. Compared to the sample HDI/HBEE the same absorption bands were observed in the range between 2100 and 2500 cm^{-1}.

The relative intensity of ν (NCO) and ν (CO_2)-absorption bands is shown in Fig. 9. In comparison with the aromatic blocked systems, we observed no maximum during heating or annealing. At the final state, the isocyanate absorption band was still detectable and the intensity only showed a small decrease after cooling. The two bands of carbon dioxide showed a much higher increase compared with the

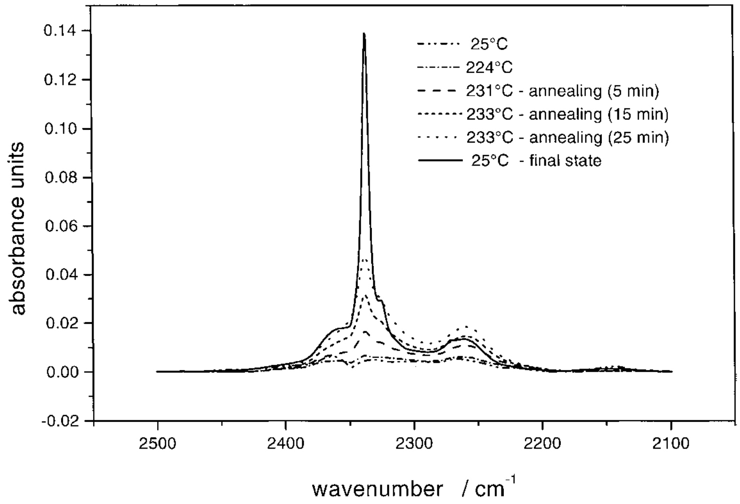


Fig. 8. Temperature dependent FTIR spectra of the deblocking reaction of the urethane model compound IPDI/IP in the range between 2500 and 2100 cm^{-1}.

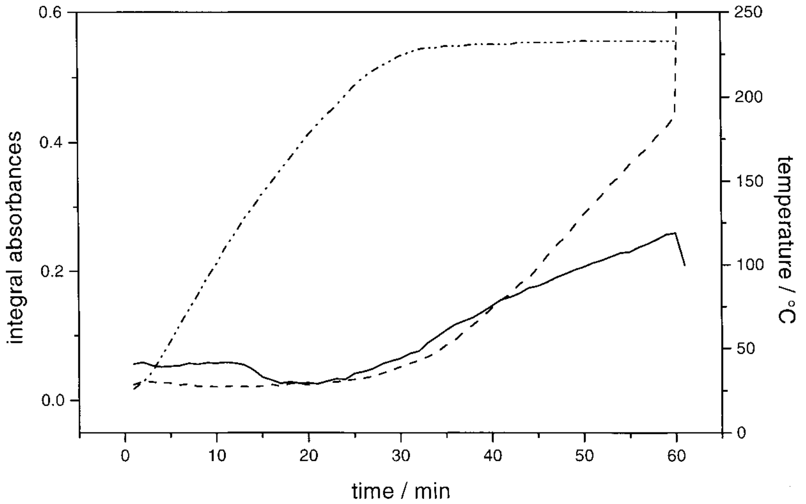


Fig. 9. Integral absorbances of isocyanate and carbon dioxide vibration during the deblocking reaction of the urethane model compound IPDI/IP studied by FTIR in dependence on time: (—) NCO (2283–2230 cm^{-1}); (- - - -) CO_2 (2349–2307 cm^{-1}); (—··—··) temperature.

sample HDI/HBEE. That behavior cannot be explained up to now.

4. Conclusions

It could be concluded as a result of temperature dependent FTIR-measurements that the secondary reactions play an important role for the determination of the deblocking temperature. The secondary reactions result obviously from special conditions in the KBr-pellet. Special conditions means that the receding blocking agent and other nascenting by-products remain in the reaction mixture. An evidence for that is the fact that the urethane HDI/IP did not react with free HDI to allophanates without any catalyst even under reaction conditions in solution and a reaction time of more than 20 h. Therefore, in cases if no isocyanate absorption band was found in the FTIR-spectra, temperature dependent FTIR-measurements should only used for detection of deblocking temperature in combination with other analytical methods.

Finally, it must be concluded that the reaction mechanism in urethane systems, even using these 'simple' blocked isocyanates, is very complex and could not be completely elucidated by FTIR. It was difficult to assign all IR-absorption bands reliably.

A comparison of the determined values (FTIR, DSC) demonstrated for the aromatic blocked aliphatic isocyanates, that HDI has lower deblocking temperatures than IPDI by using of the same blocking agent. The detection of deblocking temperature by STA/MS differ from the FTIR results because of the lower volatilty of both components (isocyanate, blocking agent) at that temperature.

In systems with aliphatic isocyanates and aliphatic blocking agents, the deblocking of IPDI was obtained at lower temperature. The STA/MS measurements in this case seems to be more sensitive compared with FTIR and DSC.

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