The Amine Degradation of Network Polyurethanes

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SYNOPSIS

Amine degradation was studied for the network polyurethanes (PPG–TDI–BD) and model compounds of allophanate, urethane, and urea linkages (1,3-diphenyl methylallophanate, 4-methyl-*m*-phenylenedicarbamate, and 1,3-diphenylurea) in DMSO at a low temperature below 70°C. Among the model compounds, only the allophanate reacted with an equimolar amount of aliphatic primary amine to give urea and urethane. However, the other compounds did not react. It was found that the concentration of allophanate groups is determined by using H_2SO_4–MeOH solution and bromphenol blue.

By this method crosslinking densities of the network polyurethanes were determined and compared with those estimated from stoichiometric calculation and from rubber elasticity. The crosslinking densities determined by the amine degradation of polyurethanes cured under air atmosphere were 22~48% of those estimated stoichiometrically. In contrast, both values of polyurethane cured under nitrogen atmosphere were in good agreement.

INTRODUCTION

Relation between structure and physical properties of polyurethanes were described in many publications[1,2]. In those publications, physical properties are correlated to structural factors such as structure of crosslinked site, crosslinking density, molecular weight of polymer glycols as starting materials, the structure and concentration of polar groups, and so on. These structural factors are usually calculated from the stoichiometry of the relative amount of starting materials with the consideration of chemical kinetics. In the course of the reaction of polyurethane formation, a number of side reactions are conceivable. Therefore it seems natural that absolute values of these structural factors are not estimated correctly.

Though NMR and IR are used for studies of structure, absolute values of these structural factors are not determined by these methods with satisfactory accuracy.

The object of this paper is to establish a method of determination of crosslinking density of polyurethanes by degradation method.

There have been many studies concerning thermal degradation[3,4] and hydrolysis[5,6,7] of polyurethanes. In both treatments, urethane, urea, allophanate, and biuret linkages in polyurethanes are decomposed and polymer glycols, amines, and linear polyurethanes are formed. Though these methods are useful for composition analyses and recovery of starting materials, both methods are not available for determining the structural factors because the

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thermal and hydrolytic reactions have not a specific selectivity of degradation to the linkages.

Reactions between model compounds of polar linkages in polyurethanes and amine have been also reported. For the reactions of amines with disubstituted ureas at 120 and 180°C, it was shown that aromatic amines hardly reacted with aliphatic ureas but aliphatic amines easily react with aromatic ureas with the liberation of aromatic amines[8]. Mukaiyama et al[9] showed that carbamates dissociate in the presence of an amine at above 120°C and produce urea derivatives. F. B. Daivns et al[10] reported that methylenediurethane and phenylmethylenediurethane did not react with aniline at 160~230°C. Kogon[11] showed that an equilibrium exists between urethane and allophanate with considerable dissociation constant at 106°C and above. Reaction temperature in the referred studies has been limited to a high temperature abovt 100°C. The reactions at a low temperature below 70°C are not described. The results of these studies suggested that certain amine may have a specific selectivity of degradation to the polar linkages.

Reactions of polyurethane with amine were also reported. Sandrige et al[12] demonstrated that polyurethane foams, which were prepared by using 120% of theoretical isocyanate requirement, were attacked by aniline at 140°C. Arnold[13] reported that the allophanate and the biuret linkages are broken by hot aniline at much faster rate than the urethane and urea linkages. Side reactions may occur, because the reaction temperature was too high in these experiments. The quantitative treatments were not discussed for the degradation of allophanate and biuret linkages. Okuto[14] showed that polyurethane was made soluble into DMSO, and DMA etc. by degrading the allophanate and biuret linkages with aliphatic primary amine, and that NMR investigation

of degradation products gave the quantitative informations about crosslinkages. Though relative concentrations of crosslinkages in polyurethanes are determined at 10~20% of accuracy, absolute concentrations are not determined.

In this study model compounds were treated with several amines in polar solvent for the purpose to see whether amines have a specific selectivity of degradation to the polar linkages at low temperatures. Next, the polyurethanes were degraded by amine degradation and the crosslinking densities of the polyurethanes were determined by a back-titration of amine.
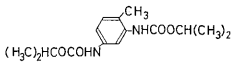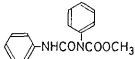
EXPERIMENTAL

1. Preparation of model compounds

Diisopropyl-4-methyl-*m*-phenylenedicarbamate was prepared by the reaction of 2,4-tolylene diisocyanate (TDI) with isopropyl alcohol at 80°C. 1,3-diphenyl methylallophanate was prepared from phenylisocyanate and methanol according to the direction of Kogon[15]. Diphenylurea was prepared by the reaction of phenylisocyanate with aniline.

The structures of these model compounds were confirmed by elementary analyses, IR spectra, and melting points. (Table 1)

Table 1. Model Compounds.

Name	Structure	m.p. (°C)
1,3-diphenylurea	⬡-NHCONH-⬡	236.0
Diisopropyl 4-methyl-*m*-phenylene-dicarbamate	(H₃C)₂HCOCOHN / ⬡-NHCOOCH(CH₃)₂ with CH₃	134.0
1,3-diphenyl methyl allophanate	⬡-NHCONCOOCH₃ with ⬡	123.0

2. Preparation of polyurethanes

Polyurethanes were prepared from polypropylene glycol (PPG) and TDI by prepolymer technique. The crosslinking agent was 1,4-butanediol (BD). PPG was supplied by courtesy of Sanyo Kasei Company. The number-average molecular weight, $\overline{M}n$, of PPG was determined to be 1897 by vapor pressure osmosis method.

TDI was of commercial origin and purified by fractional distillation under reduced pressure (b.p. 89.8°C/3mmHg). The purity was checked by amine-eqivalent method[1,17]. BD was obtained commercially and purified by fractional distillation under reduced pressure (b.p. 91.5°C/3mmHg).

The details of the preparation of polyurethanes are as follows. PPG, which was previously dried by passing dry air at 80°C, was weighed into a three-necked separable flask equipped with a nitrogen inlet and outlet connected to drying tube, thermometer, and vacuum stirrer.

The flask was heated to 80°C in an oil bath, and was then evacuated to degas PPG. Double molar equivalent isocyanate ($K=NCO/OH=2$) was weighed accurately into the flask. The reaction mixture was stirred vigorously under nitrogen atmosphere. Small amount of the reaction mixture was titrated at regular time intervals by amine-equivalent method in order to check the extent of reaction.

When the reaction was completed, a required molar equivalent of BD was added and the mixture was stirred vigorously. After the agent was thoroughly dispersed, the flask was evacuated to eliminate the bubbles.

The resultant viscous liquid was then poured into a mold coated with sillicone vanishes. Next, the reaction mixture was heated to 120°C for 50~60 hrs. in an air bath to complete the crosslinking reaction. In some cases atmosphere was substituted by inert gas.

The content of allophanate linkage can be controlled by selecting the molar ratio of BD to NCO in prepolymer ($M=$mole of BD/mole of NCO groups in prepolymer).

The composition of the samples prepared from PPG and TDI are shown in Table 2. No. 4 sample is the one cured under nitrogen atmosphere.

3. Gel fraction and swelling measurement

Gel fraction and swelling ratio were measured. A small piece of polyurethane (about 0.3g) was immersed in benzene. The specimen was weighed repeatedly until swelling equilibrium was attained. The gel fraction and swelling ratio were then calculated by eqs. (1) ~(3).

$$g = W_b / W \qquad (1)$$

$$Q = \frac{(W_a - W_b)/d_s}{W_b/d_p} \qquad (2)$$

$$q = 1 + Q \qquad (3)$$

where g denotes gel fraction, Q the volume ratio of solvent in the swollen state to gel in the unswollen state, q the swelling ratio, W the weight of specimen, W_a the weight of swollen specimen, W_b the weight of gel, and d_s and d_p are the density of solvent and polymer, respectively.

4. Density measurement

A specimen was weighed in atmosphere and in water. The density of polymer was calculated by eq. (4).

$$d_p = W \ d_w/(W - W_c) \qquad (4)$$

where d_p denotes the density of polymer W_c is the weight of specimen in water, and d_w the density of water at the temperature of the measurement.

5. Procedure of amine degradation and analysis

A small piece of polyurethane (or model

Table 2. Synthesized Polyurethanes

Sample No.	formulation		properties		
	K	M	g(%)	q	d(g/cm³)
1	2.056	0.318	——	——	1.105
2	2.136	0.319	93.1	4.71	1.103
3	1.998	0.338	92.3	8.50	1.067
4*	1.995	0.335	91.0	8.89	1.061
5	2.022	0.263	69.5	11.80	1.116
6	2.016	0.348	86.3	8.71	1.124
7	2.394	0.289	98.1	4.83	1.074

*Cured under nitrogen atmosphere.

compound) was weighed into a 30 ml reaction tube with a cork stopper covered with aluminum foil. Three to five ml of primary amine-dimethylsulfoxide solution (ca. 0.1 mmole amine/1 g DMSO) was pipetted into the reaction tube and weighed. The tube was placed in a thermostat. At appropriate time intervals, the tubes were removed from the thermostat. The residual amount of the amine was determined by titration with 0.1N H_2SO_4 –methanol solution, a microburet and bromphenol blue as indicator being used. The endpoint was determined as the point where the disappearence of a blue color and the appearance of a yellow color persist for at least 15 sec. A blank was carried along simultaneously with the samples.

Molar concentration of linkage that consumed amine per unit weight of sample, A_{obs}, was calculated by eq. (5).

$$A_{obs} = (B-S)N/1000w \qquad (5)$$

where B=milliliters of H_2SO_4 required for
the titration of the blank
S=milliliters of H_2SO_4 required for
the titration of the sample
N=normality of the H_2SO_4 solution
W=grams of sample used

The residual polyurethane was filtered, washed with methanol, dried under reduced pressure, and weighed. The extent of reaction was calculated as a ratio of the weight decreases to the weight of undecomposed polyurethane.

6. Measurement of modulus of polyurethane

A strip cut from the polyurethane sheet was used. The thickness of specimen was measured by a thickness gage. Then the stress-strain relationship was measured by Shimadzu Autograph (an Instron-type automatic tensile tester with a constant temperature bath). All measurements were carried out at constant temperature.

RESULTS AND DISCUSSION

1. Amine degradation of Model Compounds

Previous investigations of the reactions of urethane and urea with amine have dealt almost exclusively with the reactions at high temperatures. Mukaiyama and Hoshino[10] reported that the dissociation of urethanes proceeded to essentially 100% completion of the presence of 10 molar excess of an amine at above 120°C.

$$RNHCOOR \rightleftarrows RNCO + HO\text{-}R$$
$$RNCO + HNRR \rightarrow RNHCONRR$$
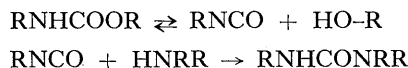
In the present study, reactions of diisopropyl-4-methyl-m-phenylenedicarbamate, diphenyl-urea, and 1,3-diphenyl methylallophanate were treated with butylamine in DMSO solution at low temperatures of 30, 50, and 70°C. The results are shown in Fig. 1. In order to study
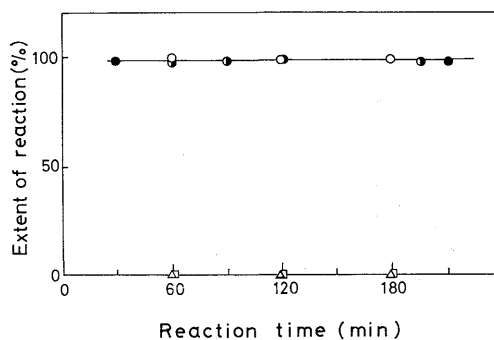
Fig. 1. Time dependence of reaction between
model compound and butylamine.
    ○ allophanate 70°C
    ◑ allophanate 50°C
    ● allophanate 30°C
    △ urea 70°C
    □ urethane 70°C

the effect of amines on the dissociation of these compounds, propylamine, hexylamine, and aniline were used at 30, 50, and 70°C. The results of these amine degradation were similar to that of butylamine except the case of aniline which could not decompose the model compounds. In Table 3 are shown melting points and values of elementary analy-

Table 3. Reactions between model compound and hexylamine at 70°C.

Model compound	Starting material				Reaction product			
	m. p. (°C)	C (%)	H (%)	N (%)	m. p. (°C)	C (%)	H (%)	N (%)
1,3-diphenylurea	236.0	73.65	5.71	13.27	235.5	73.23	5.70	12.99
Diisopropyl 4-methyl-m-phenylenedicarbamate	134.0	61.04	7.38	9.39	135.0	60.82	7.46	9.99
1,3-diphenyl methylallophanate	123.0	66.86	5.13	10.17	65.0	70.74	8.99	12.59

ses of starting materials and products obtained from the reaction with hexylamine at 70°C. For urethane and urea, m. p. and values of elementary analyses of the products are in good agreement with those of starting materials. IR spectra of products and starting

product becomes stronger compared with that of allophanate.

These results lead a conclusion as follows: 1) Disubstituted urea and urethane linkages are not decomposed at 70°C with the primary amine–DMSO solution. 2) The rate of degra-
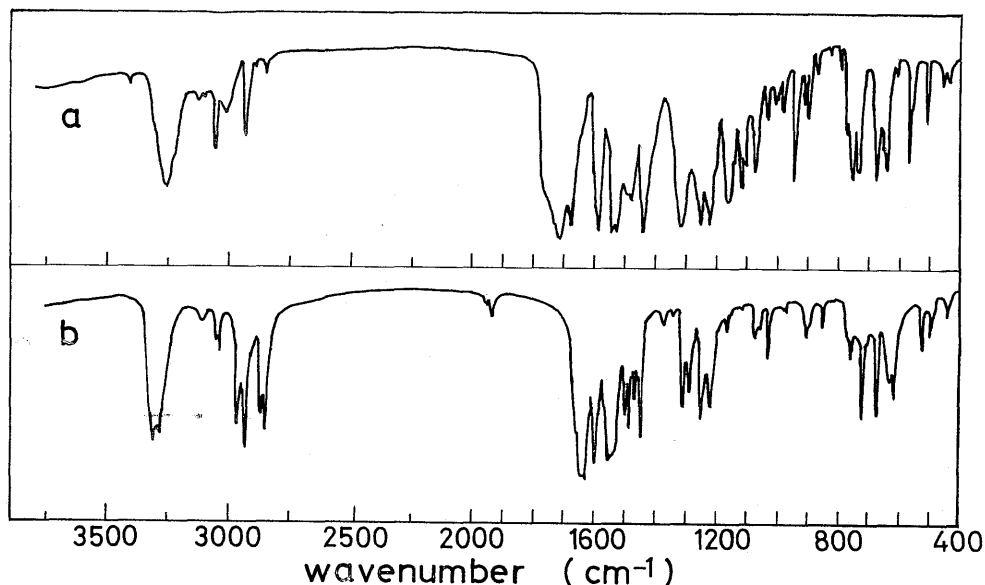
Fig. 2. Infrared Spectra of 1,3-diphenyl methylallophanate (a) and the degradation product (b).

materials are also in good agreement. In contrast, allophanate gave a product which is different from the starting material. IR spectra of allophanate and its product are shown in Fig. 2. The allophanate exhibits absorption band for the C=O stretching vibration at 1725 and 1693 cm^{-1}, and for NH stretching vibration at 3250cm^{-1}. The degradation product exhibits absorptions for C=O at 1630 cm^{-1} and for NH at 3330 cm^{-1}. Relative intensity of CH stretching vibration of the

dation of allophanate with amine increases as the basicity of reactant amine increases. 3) Allophanate linkage reacts quantitatively with aliphatic primary amine as shown below.
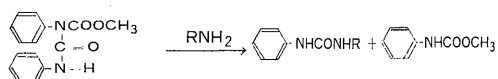
2. Amine degradation of Network Polyurethanes

Amine degradation of polyurethanes were attempted at 30, 50, and 70°C, according to

the informations obtained from the degradations of model compounds.

In Fig. 3, time dependence of the extent of reaction which were determined by the gravi-
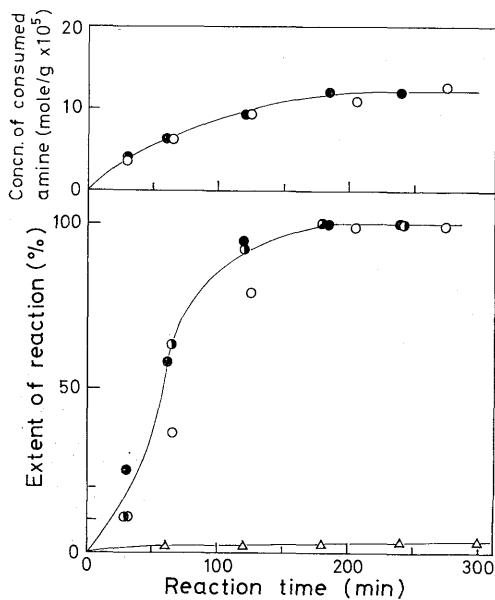
Fig. 3.   Time dependence of the extent of reaction
of amine degradations of network
polyurethane (at 50°C, Sample 1).
◐ propylamine,   ○ butylamine,
● hexylamine,   △ aniline,
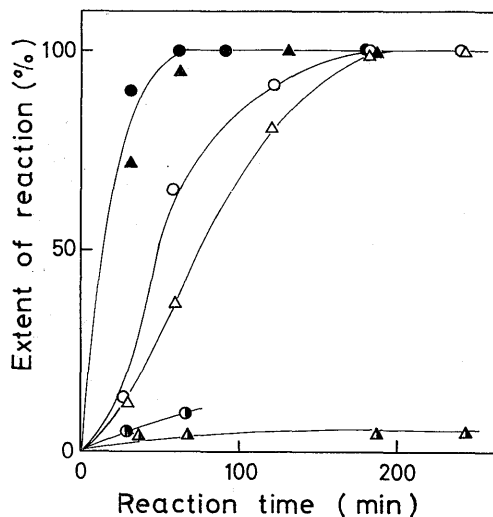
Fig. 4.   Temperature dependence of the extent of
reaction (sample 1).

	butylamine	hexylamine
30°C	▲	◐
50°C	△	○
70°C	▲	●

metric and titration methods are shown for the four different amines. In Fig. 4, temperature dependences of the extent of reaction which were determined by gravimetric method are shown. It is apparent that the rate of the amine degradation of polyurethanes increased as the basicity of amine increased and reaction temperature elevated. These results agree with that of thermal decomposition of the urethanes.

The rate of reaction determined by gravimetric method was greater than that determined by the other method. A mechanism of amine degradation of the polyurethane can be suggested from these observations. Allophanate linkages in network polyurethanes are decomposed at random to give linear polyurethanes which have branching due to the residual allophanate linkages. The branching polyurethanes are further decomposed to straight chains.

The levelling off of the extent of reaction and the concentration of consumed amine in Fig. 3 give the evidence of the completion of the degradation. Amine degradation of the polyurethanes was completed in 3~4 hrs. at 70°C and in 24 hrs. at 30°C, and homogeneous solution was obtained. All of allophanate linkages in the polyurethane were decomposed.

It is concluded that aliphatic primary amine-DMSO solution is a suitable reagent for the degradation of allophanate linkage in the network polyurethanes and that the concentration of allophanate groups is determined from the amount of the consumed amine by using the back-titration.

3. Determination of crosslinking density

In the use of diol as curing agent, chain-lengthening reaction of NCO-terminated prepolymer with diol occur and the residual isocyanate groups react with urethane groups to form the network structure through the branching reaction (allophanate formation). Since the allophanate linkages formed in

network polyurethanes act as crosslinked sites,

$$\sim\!\!\sim NHCOO \sim\!\!\sim + OCN\!\!\sim\!\!\sim\!\!\rightarrow\!\!\sim\!\!NCOO\!\!\sim\!\!\sim$$
$$\begin{array}{c} | \\ C=O \\ | \\ N-H \\ \wr \\ \wr \end{array}$$

the concentration of allophanate groups per unit volume of polymer equals the crosslinking density. Therefore, the amine degradation of polyurethanes is very useful to the determination of crosslinking density.

Crosslinking density of the network polyurethanes was estimated from the three diffrent methods.

1) Calculation from the stoichiometry of starting materials (Method 1)

In the couse of crosslinking reaction of polymer diisocyanate with butanediol, chain lengthening reaction through urethane formation and branching reaction through allophanate formation proceeds simultaneously. However, the rate of the latter reaction is much slower than that of the former. Therefore, it may be assumed that the excess of isocyanate groups over hydroxyl groups of BD lead to crosslinking, and that the number of isocyanate groups in excess is equal to that of crosslinking. Crosslinking density, [I], is expressed by eq. (6).

$$[I] = \frac{(K-1)(1-2M)[NCO]_0}{KW} \qquad (6)$$

where K is the molar ratio of NCO groups of diisocyanate to OH groups of polyol, M the molar ratio of curing agent to NCO groups in prepolymer, $[NCO]_0$ the molar quantity of isocyanate groups, W the total weight of starting materials.

2) Calculation based on equilibrium rubber elasticity (Method 2)

According to the theory of rubber elasticity [17], the elastically effective elements in the unit volume, (ν_e/V), are calculated from eq. (7).

$$\left(\frac{\nu_e}{V}\right) = \frac{\tau}{RT\left(\alpha - \dfrac{1}{\alpha^2}\right)} \qquad (7)$$

where τ is the retractive force, α the extension ratio defined by l/l_0 (l is the length under stretched state and l_0 the initial length), R the gas constant, and T the temperature in °K.

Since (ν_e/V) has a relation with (ν_i/V), that is the concentration of internal chain, (ν_i/V) is calculated from the measurement of rubber elasticity. The relation have been derived from the consideration of the network structre of polyurethanes as follows [18],

$$\left(\frac{\nu_i}{V}\right) = \left(\frac{\nu_e}{V}\right)\frac{(K-1)(6M-1)}{2(K-1)(1-2M)}$$
$$M < 1/3 \qquad (8)$$

$$\left(\frac{\nu_i}{V}\right) = \left(\frac{3}{2}\right)\left(\frac{\nu_e}{V}\right) \qquad M \geq 1/3 \qquad (9)$$

The crosslinking density, the number of crosslinkages per unit volume, is $(2/3)(\nu_i/V)$. The number of crosslinkages per unit weight, [II], is $(2/3)(\nu_i/V)(1/d_p)$.

3) Calculation from amine degradation method (Method 3)

The crosslinking density are calculated by eq. (10)

$$[III] = \frac{(B-S)N}{1000W} \qquad (10)$$

The crosslinking densities of sevral polyurethanes calculated by the three different methods are shown in Table 4. The values of crosslinking density determined by method 3 are in fairly good accordance in the order of magnitude with the values determined by other methods. The amine degradation method, therefore, is a useful method for the determination of crosslinking density of polyurethanes.

The values of crosslinking density calculated by amine degradation method of polyurethanes which were cured under air atmosphere are 22~48% of the values estimated stoichiometrically. In contrast, the value by method 3 is

Table 4. Crosslinking Density of polyurethanes calculated by the three different methods.

Sample No.	Crosslinking Density (mole/g×10^4)		
	[I]a)	[II]b)	[III]c)
1	3.340	1.327	1.256
2	3.758	1.600	0.823
3	2.799	0.930	1.342
4d)	2.557	1.228	2.527
5	4.245	—	0.938
6	2.677	—	0.976
7	4.939	—	1.778

a) Calculated from Method 1.
b) Calculated from Method 2.
c) Calculated from Method 3.
d) Cured under nitrogen atmosphere.

in good agreement with the value by method 1 for the polyurethane cured under nitrogen atmosphere. These results lead to the conclusion that side reactions may take place in the course of curing reaction carried out under air atmosphere. Side reactions may have involved the following reactions. Isocyanates of prepolymer and monomeric isocyanates can react with each other to form dimers, trimers, and carbodiimides. The dimer of TDI has been reported to dissociate at 150°C, and not to react with amine under mild conditions. Some of allophanate linkages formed may have dissociated to give linear polymers, because thermal degradation of these network polymers were recognized when these polymer were held at 120°C for 7 days under air atmosphere.

Therefore, discussions of relations between structure and physical propreties by using the structual factors which are calculated stoichiometrically may lead to erroneous results.

The following conclusions may be drawn from the evidence from amine degradation of the polyurethanes in this paper.

1) Disubstituted urea group and urethane group are not decomposed at a low temperature below 70°C with aliphatic primary amine.

2) The allophanate groups react with an equimolar amount of aliphatic primary amine to give urea and urethane.

3) The network polyurethanes (PPG–TDI–BD) are decomposed completely in 3~4 hrs. at 70°C and in 24 hrs. at 30°C

4) The concentration of allophanate groups, that is the crosslinking density of polyurethanes, is determined by back-titration of residual amine with the use of H_2SO_4–MeOH solution and bromphenol blue as indicator.

5) The crosslinking density of the network polyurethanes cured under air atomsphere is smaller than the density estimated stoichiometrically.

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