

Decomposition of Polyurethane Foams by Alkanolamines

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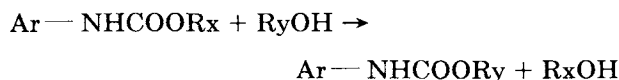
SYNOPSIS

Methylene diphenyl isocyanate (MDI)-based polyurethane flexible foams were decomposed by alkanolamines without a catalyst at 150°C. The decomposition products were completely separated into two layers. The upper liquid layer was a polyether polyol, and the lower liquid layer was methylene diphenyl amine (MDA) and alkanolamine derivatives. These layers were analyzed using gel permeation chromatography (GPC) and ¹³C-NMR. The upper layer was obtained as a relatively pure polyether. The lower layer was observed to be MDA and 2-hydroxyethyl carbamic acid ester prepared from alcoholysis products during the decomposition reaction. It was thought that the decomposition process of polyurethane foam by alkanolamines was not aminolysis but alcoholysis. © 1994 John Wiley & Sons, Inc.

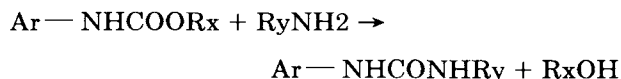
INTRODUCTION

Chemical recycling is timely when the usual material recycling processes are not applicable as in the case of polyurethane foams. Hydrolysis,¹ glycolysis,²⁻⁴ and aminolysis are well-known chemical processes for the decomposition of polyurethane to low molecular products.

The chemistry of glycolysis (alcoholysis) involved in the breakdown of the urethane bonds has been disclosed in a previous work,⁵ where the transesterification of the urethane group has been pointed out to be specific for the polymer degradation:



Aminolysis of polyurethane is assumed to form disubstituted ureas by the exchange reaction of the urethane group:



Alkanolamine has both a hydroxyl group and an amino group in the molecule. It is interesting to ex-

amine alkanolamines as decomposition agents for the breakdown of the urethane group and to learn which group of the alkanolamine decomposes the urethane group.

EXPERIMENTAL

Materials

The methylene diphenyl isocyanate (MDI)-based polyurethane foam has been chosen for the decomposition. The formulation is given in Table I.

The foam is first chopped into pieces suitable for feeding into the glass laboratory apparatus. 4,4'-MDI used for the reaction of MDI and excess monoethanolamine was a commercial product of Nippon Polyurethane Industry Co., Millionate, MT. The other chemicals used were reagent grade.

Instrumentation

Polyether layers of the decomposition products were characterized using gel permeation chromatography (GPC). The GPC system was based on TOSOH HLC8020, TOSOH G2000HXL/G3000HXL columns, a differential refraction detector (RI), and an ultraviolet detector (UV). MDI adducts and the other MDI derivatives were characterized using ¹³C-NMR spectroscopy. The spectra were recorded

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Table I Formulation of MDI-based Urethane Foam

Components of the Foam	Parts by Weight
FA-921 ^a	100
Water	2.5
TEDA-L33 ^b	0.6
TOYOCAT-ET ^b	0.05
SZ-1306 ^c	1.0
Polymeric MDI ^d (NCO Index 100)	41

^a Polyether polyol, $M_w = 6000$, Sanyo Chemical Industries.

^b Amine catalyst, TOSOH Corp.

^c Surfactant, Nippon Unicar Co.

^d 2,4MDI-rich polymeric MDI, NCO content 31%, Nippon Polyurethane Industry Co.

with a Varian UNITY 500 at 500 MHz in CDC13 30% w/v.

RESULTS AND DISCUSSION

Decomposition of MDI-MEA Adducts

MDI-MEA adducts were synthesized from 4,4' MDI with excess monoethanolamine (2-aminoethanol, MEA). MDI, 15 g, was added step by step into 150 g MEA in a glass flask at 25°C. The mixture was heated at 90°C for 1 h. The NMR spectrum of the

MDI-MEA adducts in excess MEA is shown in Figure 1.

The assignment of the absorption bands is evident from the structural formulae in the figure. The two bands designated as "l" and "m" in the spectrum correspond to the carbon of the urethane group and the carbon of the urea group, respectively. It was interesting that the MDI-MEA adducts were synthesized as a mixture of the MDI-MEA urethane adduct and the MDI-MEA urea adduct. These urethane and urea adducts may be formed in similar molar quantities, as indicated by the integrated intensities of the NMR spectrum.

The MDI-MEA adducts were decomposed in the presence of excess MEA at various temperatures (120, 130, and 140°C) for 3 h. The decomposed products were characterized by ¹³C-NMR during the decomposition reaction.

The time dependencies of ¹³C-NMR spectra at 120, 130, and 140°C are shown in Figure 2. It is observed that the MDI-MEA adducts react with excess MEA to form methylene diphenyl amine (MDA). It is known that the absorption band at 114 ppm is the typical band of the benzene ring of MDA, and also 156 and 164 ppm are, respectively, the urethane carbonyl band and the urea carbonyl band. As shown in Figure 2, the intensity of the 114 ppm band increases with decomposition time and increasing temperature. At the same time, the 156 ppm band of the urethane carbonyl decreases in in-

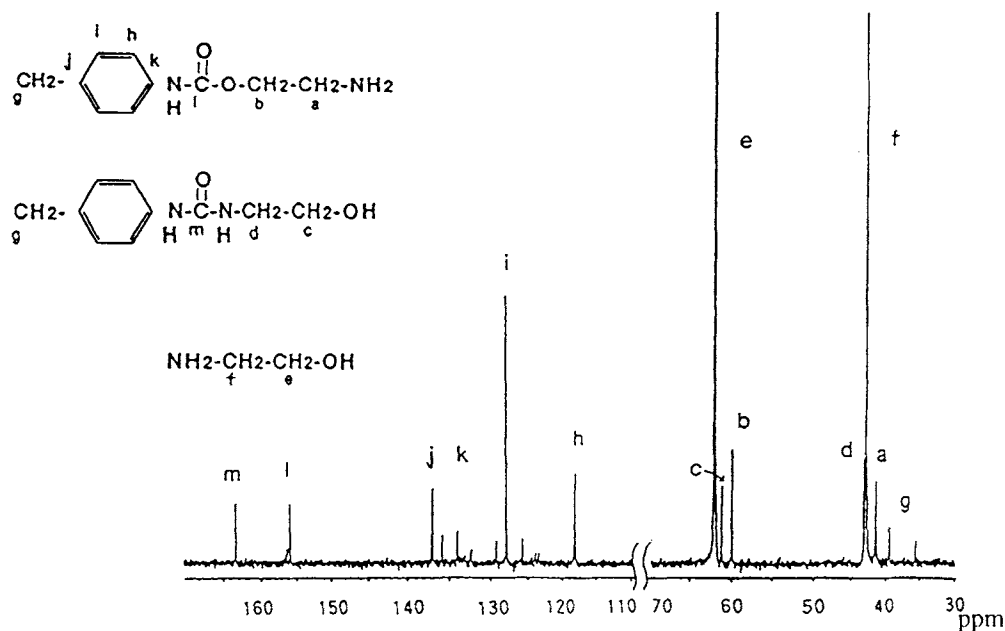


Figure 1 500 MHz ¹³C-NMR spectrum of MDI-MEA adducts.

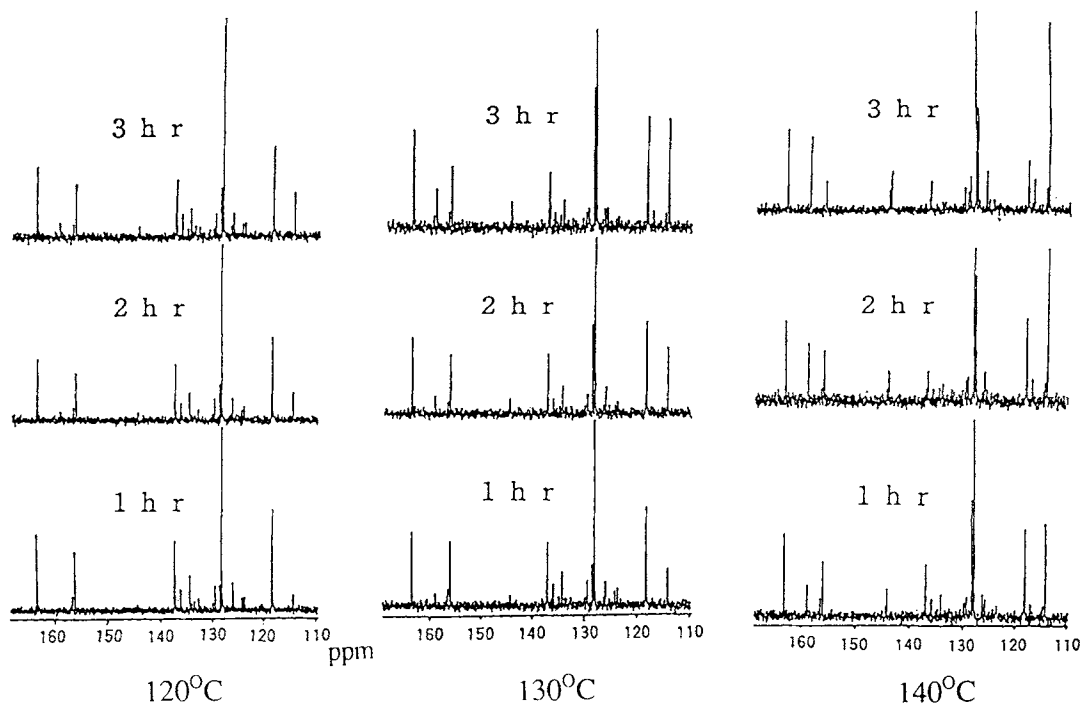


Figure 2 Time dependencies of ^{13}C -NMR spectra in MDI-MEA decomposition at various temperatures.

tensity, and the 164 ppm band of the urea carbonyl shows no change, whereas, the 159 ppm band is newly generated at 120°C , 2 h, and increases in significant intensity at 140°C , 3 h.

In a previous work,⁶ the possibility of forming 2-oxazolidone has been shown in the decomposition reaction of the MDI-MEA urea adduct and MEA. In the present work, we noted the formation of 2-oxazolidone but could not detect its presence by NMR spectra. The 159 ppm band seemed to be the carbonyl band of the aliphatic urethane group. Thus, 2-hydroxyethylcarbamic acid 2-aminoethylester (HECE) may be formed in the decomposition of MDI-MEA adducts by excess MEA.

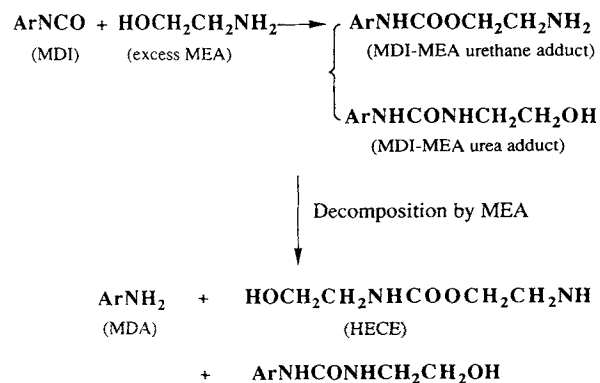
The reaction of MDI and MEA and the decomposition of MDI-MEA adducts is shown in Scheme 1. The new product HECE was readily hydrolyzed by adding water at 80°C , 1 h. The 159 ppm band disappeared completely after the hydrolysis. The hydrolysates were monoethanolamine and carbon dioxide.

Decomposition of Polyurethane Foam

The decomposition was carried out by heating the foam in the presence of MEA at 130 and 150°C . In the 1000 mL glass flask, the chopped foams (150 g) were fed into the heated MEA (150 g). The reaction

time indicates the period from when the mixture becomes a homogeneous solution to the sampling time. The samples were cooled in a small glass tube, and the separated lower layer (MDI derivative) was characterized using ^{13}C -NMR spectroscopy. The time dependencies of ^{13}C -NMR spectra of the decomposition products at 130°C are shown in Figure 3.

It seems that on decomposition by MEA the urethane bonds of the foam are broken down by the hydroxyl group of MEA, and MDI-MEA urethane adducts, carbamic ester (HECE), and MDA are formed. In Figure 3, it is observed that the 156 ppm



Scheme 1

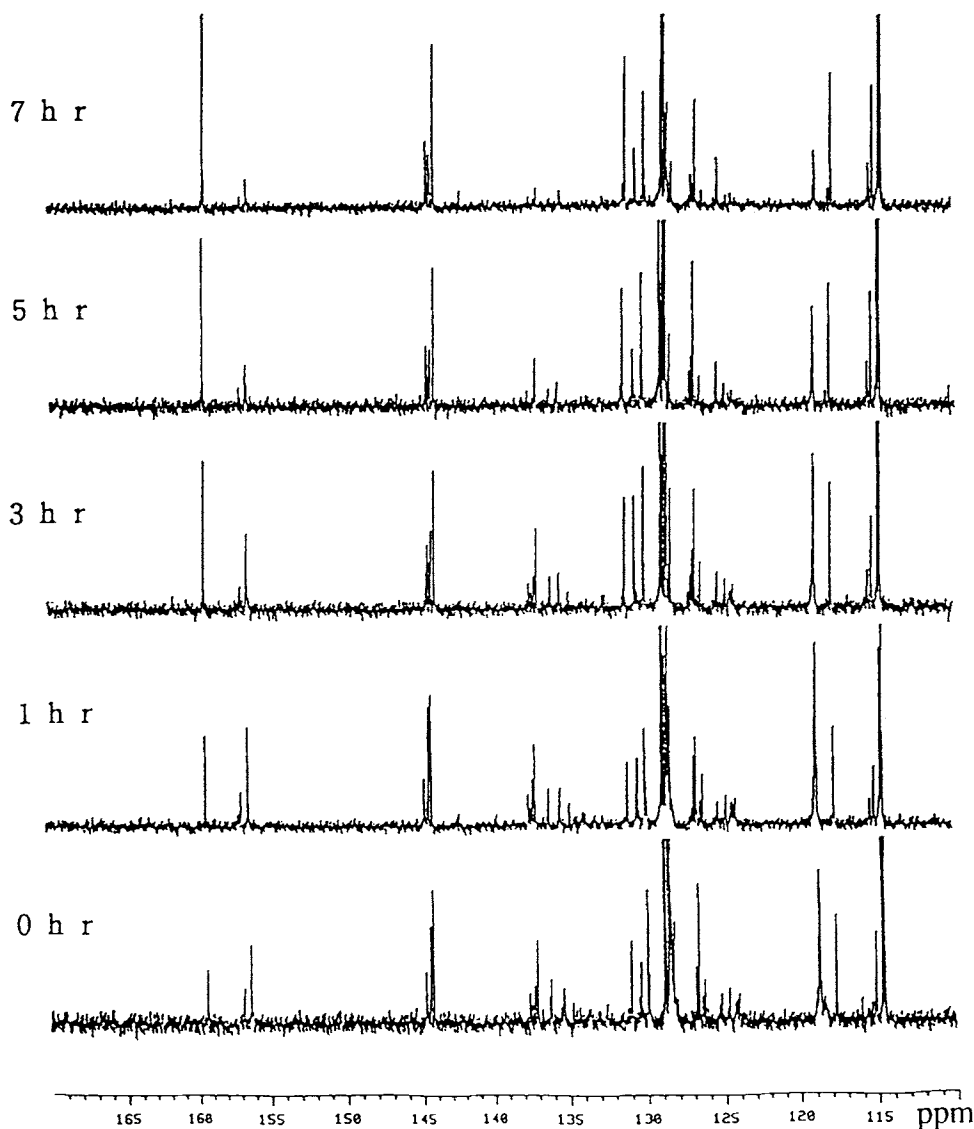


Figure 3 Time dependencies of ^{13}C -NMR spectra of decomposition products at 130°C .

band increases early in the reaction and after 1 h decreases gradually. The 114 ppm band of MDA and the 159 ppm band of HECE increase in intensity, and the 164 ppm band of the MDI-MEA urea adduct is not generated.

Figure 4 shows the time changes of the ^{13}C -NMR spectra during the decomposition of the foam by MEA at 150°C . Compared with 130°C , the rate of decomposition at 150°C was much faster. At higher temperature, the decomposition of the foam will proceed at a significant rate when the mixture of the foam and MEA become homogeneous. The 156 ppm band of the MDI-MEA urethane adduct is ex-

tinguished at 150°C 2 h. The 159 ppm band of HECE maintains its intensity even after 3 h, and the 164 ppm band of the MDI-MEA urea adduct is not generated.

To confirm the formation of the MDI-MEA urethane adduct and HECE, we decomposed the urethane foam using diethanol amine (DEA) instead of MEA. Figure 5 shows the time dependencies of ^{13}C -NMR spectra during the decomposition of foam by DEA at 150°C .

As shown in Figure 5, the 156 ppm carbonyl band of the MDI-MEA urethane adduct shifts to 158 ppm in the case of the MDI-DEA urethane adduct. The

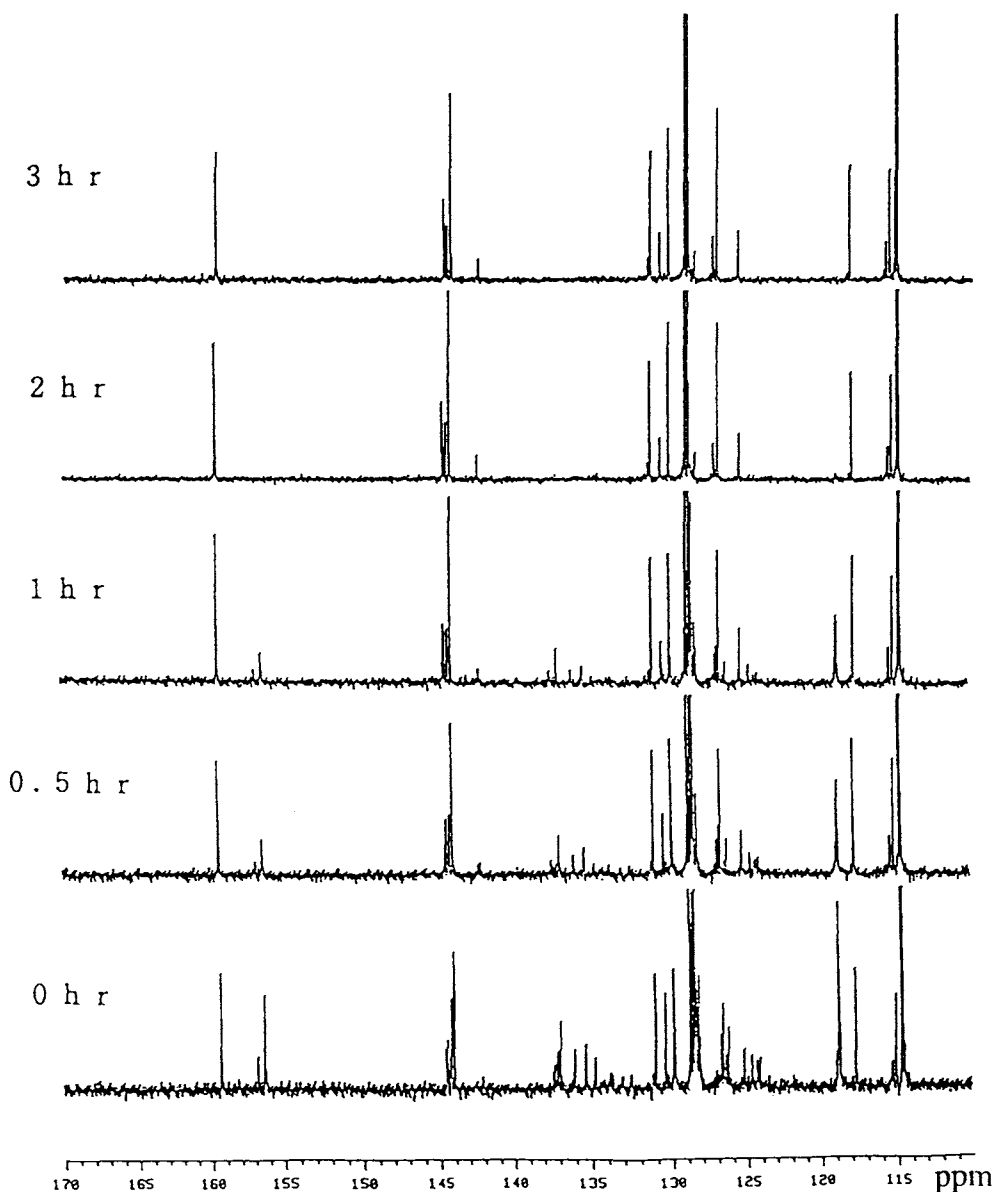


Figure 4 Time dependencies of ^{13}C -NMR spectra of decomposition products at 150°C .

159 ppm band of HECE is not shifted. In contrast to the reaction with MEA, the decomposition by DEA permits formation of the MDI-DEA urea adduct. The 164 ppm urea band is slightly generated at 150°C , 3 h. The 158 ppm urethane band and the 159 ppm HECE band are observed at relatively high intensity.

Recovery of Polyethers from Polyurethane Foams

When the decomposition by alkanolamines was carried out by heating the foam, the decomposition

products were separated into two layers on standing at room temperature. The upper layer was polyether, and the lower layer was MDI derivatives as described above. The polyether layer was characterized using GPC. The degree of the polyether recovery was determined from the purity of the polyether. The purity was evaluated by measuring the content of MDI derivatives in the polyethers. The content was determined from the GPC peak area ratio of two GPC peaks measured using an ultraviolet (UV) detector and a differential refraction (RI) detector. The peak

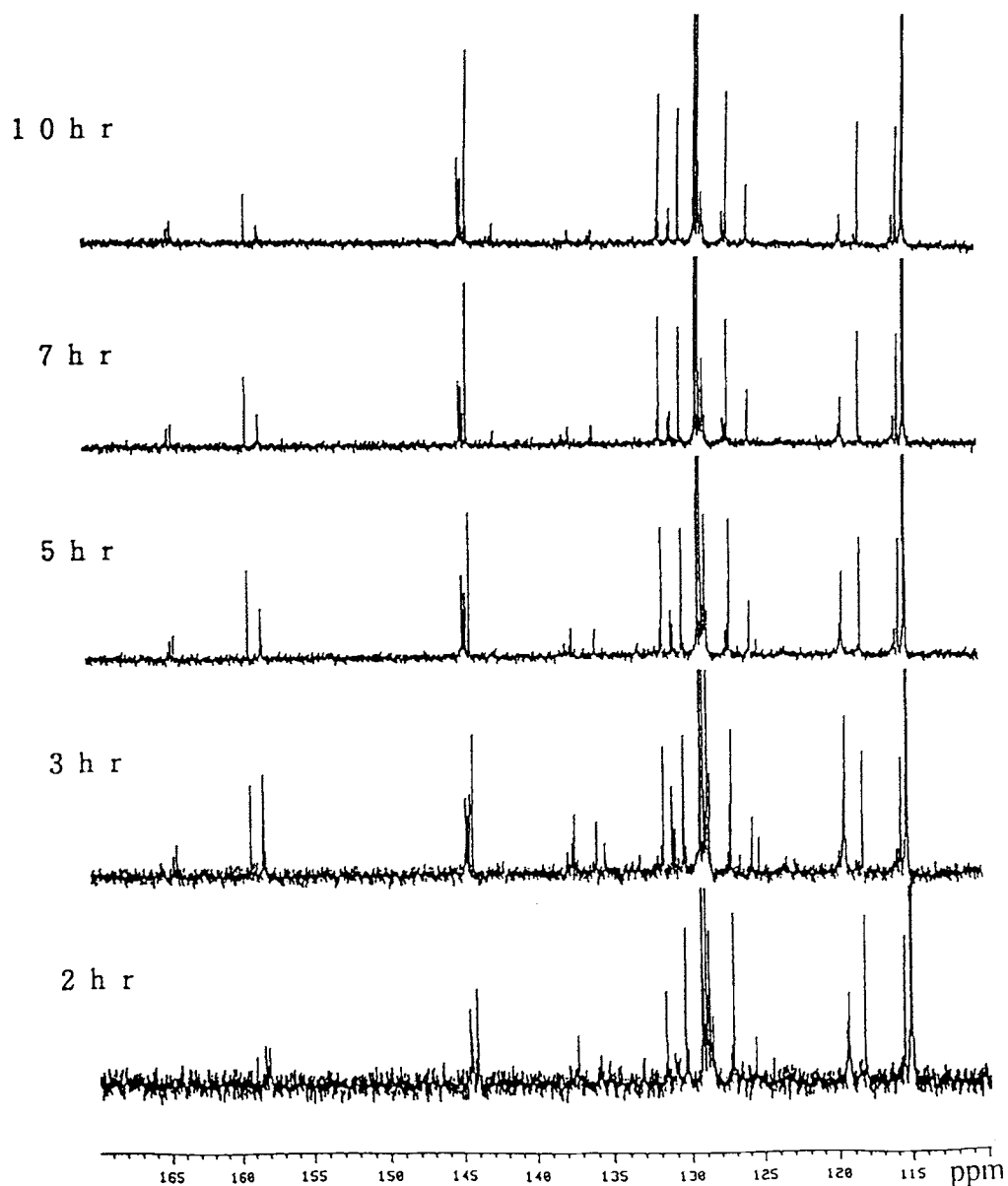


Figure 5 Time dependencies of ^{13}C -NMR spectra of decomposition products by DEA at 150°C .

area by the UV detector gives the content of MDI derivative in polyethers. The MDI content in the undecomposed foam was evaluated by the GPC peak area ratio of the polyether-MDI prepolymer that had a known content of MDI.

Figure 6 shows the influence of alkanolamines on the polyether recovery from polyurethane foam decomposition at 150°C . The decomposition by MEA requires 2–3 h essentially to complete reaction. On the other hand, DEA require 10 h or more.

Decomposition Mechanism of Polyurethane by MEA

In this work, it is shown that the decomposition process of MDI-MEA urethane adducts by MEA is alcoholysis by the hydroxyl group of MEA in preference to aminolysis by the amino group, and also the decomposition of urethane foam by MEA is not aminolysis but alcoholysis. The amino group of MEA is more basic than is the hydroxyl group.

Therefore, it was expected that aminolysis would take precedence over alcoholysis. To explain the reason, we propose the decomposition mechanism in Figure 7.

The urethane group has strong intermolecular hydrogen bonding because of the presence of the carbonyl group. In the decomposition process, the amino group of MEA will associate with the carbonyl group in the urethane foam and then form a strong hydrogen bond between the amino group and the carbonyl group. Also, a hydrogen bond between the ether of the urethane group and the hydrogen of the hydroxyl group in MEA will form as shown in Figure 7. On heating, the C—O bond of the urethane group will be broken. The resulting MDI-MEA urethane adduct and polyether are prepared. The reason underlying alcoholysis by MEA seems to be the protection of the amino group by the carbonyl group of urethane.

The influence of two kinds of alkanolamines on the polyurethane foam decomposition is very strong, as shown in Figure 6. The rate of decomposition by MEA is much faster than that of DEA. In the case of DEA, the steric hindrance at the hydrogen bond may contribute to weakening the association between the amino group of DEA and the carbonyl group of urethane.

The weakness of the association between DEA and carbonyl may partially cause the hydrogen bond between the amino group of DEA and the ether of the urethane group, which bond will produce the MDI-DEA urea adduct in the polyurethane foam decomposition process. In practice, the formation of the MDI-DEA urea adduct is shown in the decomposition process of Figure 5.

In this work, we chose the MDI-based polyure-

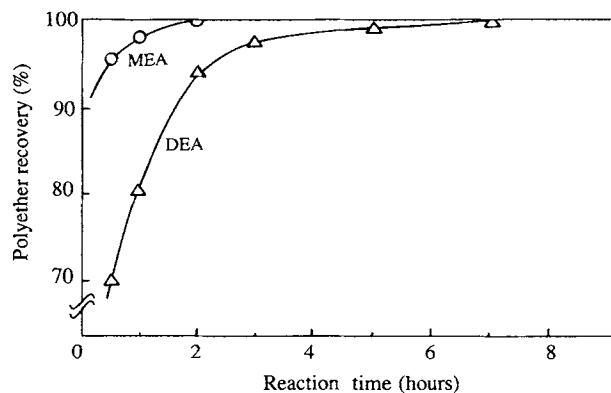


Figure 6 Influence of alkanolamines on the polyether recovery from polyurethane foam decomposition at 150°C.

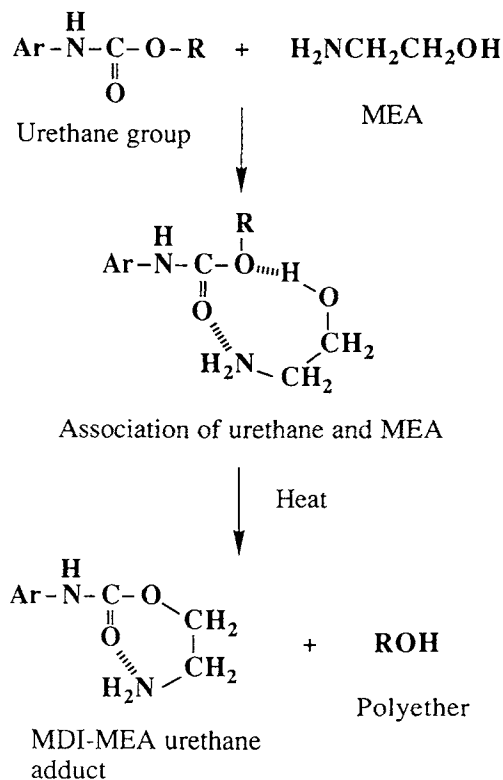


Figure 7 The mechanism of urethane foam decomposition by MEA.

thane flexible foam for the decomposition. It is well known that the practical urethane foams for car seats are more complex with regard to the chemical composition. For example, these foams have been generally manufactured from the mixtures of tolylene diisocyanates (TDI) and MDI as polyisocyanates. Two kinds of polyisocyanates may further complicate the decomposition process. It is necessary to take into account varying polyisocyanates in our next studies.

CONCLUSIONS

MDI-based polyurethane flexible foams were decomposed by MEA and DEA without a catalyst at 150°C. The decomposition products were completely separated into two layers. The upper liquid layer was a poly(ether polyol) and the lower liquid layer was MDA and alkanolamine derivatives. These products were characterized by ^{13}C -NMR and GPC. It was assumed from the chemical structure of the alkanolamine derivatives that the decomposition reaction of urethane foam by MEA was alcoholysis

by the hydroxyl group of MEA. It was proposed that the decomposition reaction began with the association of MEA and the urethane group, followed by the formation of a hydrogen bond between the amino group of MEA and the carbonyl of urethane, then followed by alcoholysis.

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