

Recycling of Polyurethanes. Degradation of Microporous and Flexible Polyurethanes by Phosphonic Acid Diesters

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The primary aim of these studies is to develop a new method for converting polyurethane waste materials and used polyurethanes into reusable products which can be used in the preparation of polymers with reduced flammability. Microporous polyurethane elastomer based on diphenylmethane diisocyanate (MDI) and polyester polyol and flexible polyurethane foam based on toluene diisocyanate and polyester polyol have been degraded and have been converted into liquid by phosphonic acid diesters. The structure of degraded products has been studied by ^1H , ^{13}C and ^{31}P NMR spectroscopy. The likely reaction mechanism of the chemical degradation of polyurethanes is presented.

Introduction

Recycling of polymer waste materials and used polymers is one way to conserve the natural resources and reduce environmental stress. The chemical degradation of polyurethanes (rigid, flexible or polyurethane elastomers) involves well-known methods of hydrolysis [1], glycolysis [2-4] and aminolysis [5,6]. The degradation of microporous polyurethane elastomers has been accomplished by treatment with mono-, di-, and triethanolamine [7] and ethylene glycol [8], as well as by catalytic glycolysis with 1,4-butanediol [9].

We have developed a new method for converting polyurethane waste materials and used polyurethanes into reusable products [10-13] which can be used in the preparation of polymers including polyurethanes with reduced flammability. Herein we report on the chemical degradation of microporous polyurethane elastomer and flexible polyurethane foam by phosphonic acid diesters.

Materials and methods

Microporous polyurethane elastomer, based on MDI and polyester polyol and flexible polyurethane foam based on toluene diisocyanate and polyester polyol were chosen for degradation. Dimethyl phosphonate $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$ and diethyl phosphonate $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{H}$, Fluka, commercially available.

Method for a chemical degradation of polyurethanes

Into a three necked flask equipped with a stirrer, thermometer and reflux condenser polyurethane cut into small pieces 3-5 mm large and phosphonic acid diesters at the weight ratio 1: 3 were placed. The degradation were performed at 150°C for polyurethane elastomer with heating for 30, 60, 90 and 120 min and at 160°C for flexible polyurethane foam with heating for 1, 2 and 3 hours. The temperature was decreased to 60°C and the non reacted phosphonic acid diester was removed under

vacuum and reused for degradation. Degraded products represent liquids.

Results and Discussion

Degradation of Microporous Polyurethane Elastomer by Dimethyl phosphonate

It has been found that when heating microporous polyurethane elastomer based on MDI and polyester polyol Bayflex 2003E with demethyl phosphonate at 142°C the polyurethane elastomer degrades. A homogeneous liquid product is obtained after 45 min heating at 142°C and after 30 min at 150°C. The ^1H , ^{13}C and ^{31}P NMR studies showed that the degraded products represent phosphorus containing oligourethanes (Table 1).

Table 1. Phosphorus-Containing Products from the Chemical Degradation of Microporous Polyurethane Elastomer by Dimethyl Phosphonate

N	Structure	^{31}P NMR, δ , ppm, J, Hz	Content, %
1		7.28, dq 3J(P,H) = 11.4 1J(P,H) = 651.5	64.0
2		5.97, d 1J(P,H) = 656.6	6.8
3		11.09, dsex 3J(P,H) = 11.2 1J(P,H) = 708.1	12.0
4		10.66, dqintets 3J(P,H) = 9.78 1J(P,H) = 708.0	17.2

Degradation of Flexible Polyurethane Foam by Diethyl phosphonate

Flexible polyester polyurethane foam was converted into liquid after treatment by diethyl phosphonate. The data from the NMR studies confirm the formation of the same structures (Table 2) as in the case of demethyl phosphonate.

Mechanism of the Degradation of Polyurethanes by Phosphonic Acid Diesters

The formation of products 1, 2 and 6 results from the alkylation of the urethane group by phosphonic acid diesters (Scheme 1). Products 3, 4 and 5 are formed as a result of the exchange reactions between the urethane group and the alkoxy groups of phosphonic acid diesters (Scheme 1). The experimental results show that increasing the duration of the degradation process lowers viscosity of the final product whilst the contents of phosphorus increases.

Scheme 1

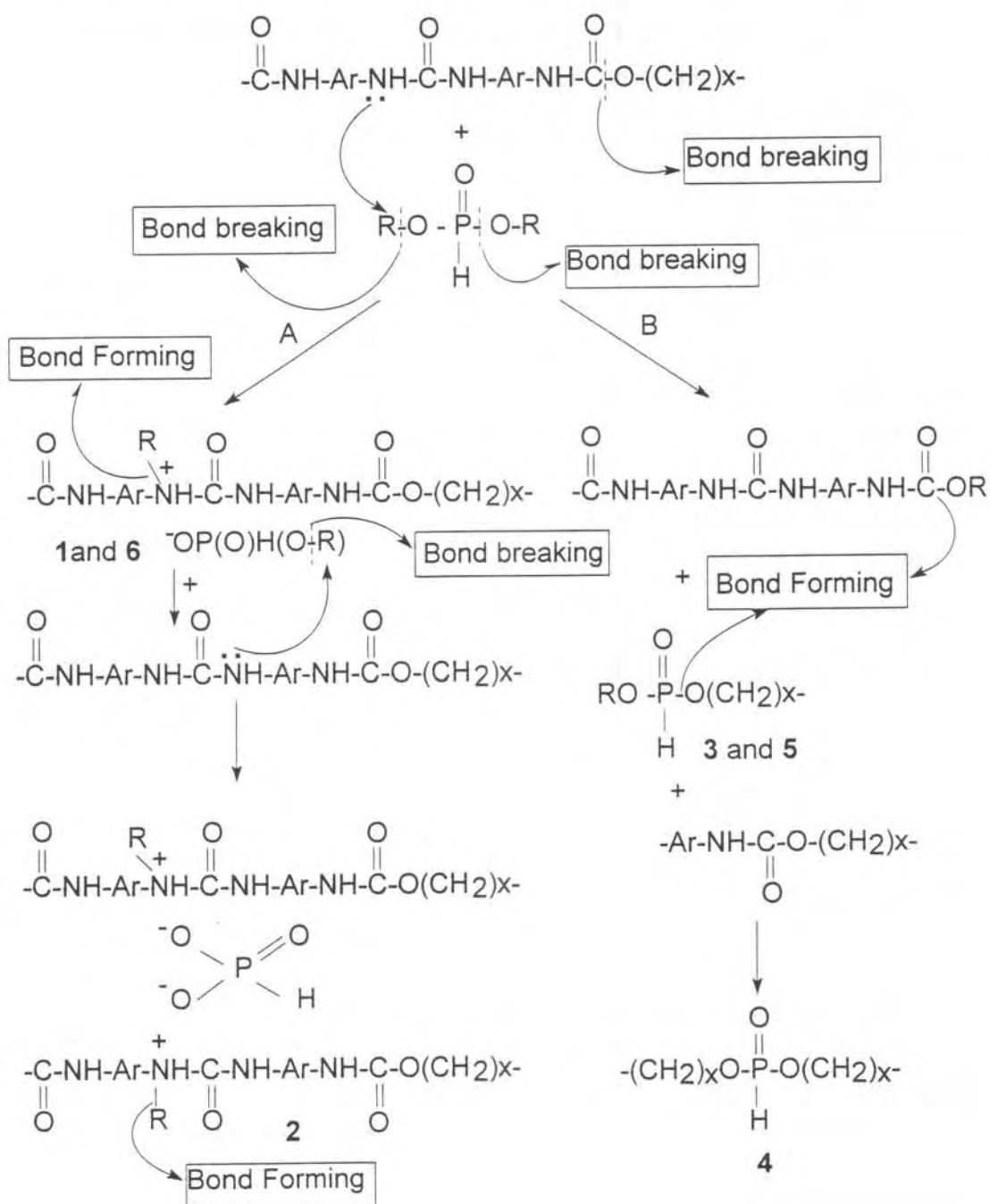


Table 2. Phosphorus-Containing Products from the Chemical Degradation of Flexible Polyester Polyurethane Foam by Diethyl Phosphonate

N	Structure	^{31}P NMR, δ , ppm, J, Hz	Content, %
5	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{O}(\text{CH}_2)_x- \\ \\ \text{H} \end{array}$	8.68, dqintets $3J(\text{P}, \text{H}) = 9.24$ $1J(\text{P}, \text{H}) = 692.2$	45.0
6	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2 \\ \\ \text{NHCNH} \\ \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2 \\ \\ \text{NHCNH} \\ \\ \text{CH}_3 \end{array}$ $\text{OP(O)H(OCH}_2\text{CH}_3)$	5.50, d $3J(\text{P}, \text{H}) = 8.32$ $1J(\text{P}, \text{H}) = 655.2$	10.0

Conclusions

We have found that phosphonic acid diesters can be used as a degrading agent for polyurethanes. The results obtained demonstrate that the chemical degradation proceeds without any catalysts. The degradation products are phosphorus containing oligourethanes with phosphonate end groups.

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