

# Chemical Degradation of Polyurethanes. II. Degradation of Microporous Polyurethane Elastomer by Phosphoric Acid Esters

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**ABSTRACT:** Microporous polyurethane elastomer, based on 4,4'-diphenylmethane diisocyanate and polyester polyol Bayflex 2003 (Bayer AG), was degraded by phosphoric acid esters  $-(\text{CH}_3\text{CH}_2\text{O})_3\text{P}(\text{O})$  and  $(\text{ClCH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})-$  at 180°C. Structure of degraded products was investigated by means of <sup>1</sup>H-, <sup>13</sup>C-, and <sup>31</sup>P-NMR spectroscopy. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 886–893, 2000

**Key words:** recycling; microporous polyurethane elastomer; chemical degradation; triethyl phosphate; tris(2-chloroethyl) phosphate

## INTRODUCTION

This work continues our investigations on the new method for chemical degradation of polyurethanes by treatment with esters of phosphonic acids.<sup>1</sup> In this paper we report on the chemical degradation of microporous polyurethane elastomer, based on 4,4'-diphenylmethane diisocyanate (MDI) and polyester polyol Bayflex 2003 (Bayer AG), using triethyl phosphate or tris(2-chloroethyl) phosphate as degradation agents.

## EXPERIMENTAL

### Materials and Methods

Microporous polyurethane elastomer based on MDI (Bayer AG) and polyester polyol Bayflex 2003E (Bayer AG) was chosen for degradation. The micro-

porous polyurethane elastomer was cut into small pieces and placed into the glass appliance.

Triethyl phosphate  $(\text{CH}_3\text{CH}_2\text{O})_3\text{P}(\text{O})$  and Tris(2-chloroethyl) phosphate  $(\text{ClCH}_2\text{CH}_2\text{O})_3\text{P}(\text{O})$ , from Aldrich, are commercially available.

### Instruments

Proton (<sup>1</sup>H)-, <sup>13</sup>C-, and <sup>31</sup>P-NMR spectra were recorded on a Bruker apparatus, 500 MHz, in  $\text{CDCl}_3$  solvent. The viscosity was measured on a Brookfield LV viscometer. Phosphorus content was determined on a Specol spectrophotometer, 420 nm wave length.

### Method for Chemical Degradation of Microporous Polyurethane Elastomer

#### By Triethyl Phosphate

Into a three-necked flask equipped with a stirrer, thermometer and reflux condenser was placed 60.1 g of microporous polyurethane elastomer cut into small pieces (3–5 mm in size) and 182.6 g of triethyl phosphate. The degradation proceeds at 180°C. Then the temperature was lowered to

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**Table I** Conditions for Polyurethane Elastomer (PUE) Chemical Degradation by Triethyl Phosphate (TEP) at 180°C

TEP	PUE	Duration of Degradation (h)	Reacted TEP (g)	Yield (g)	Content of Phosphorus (%)
182.6	60.1	5	14.8	73.9	1.96
183.3	60.1	6	15.2	75.3	2.06
185.0	59.9	7	17.3	77.2	2.40
183.0	59.9	8	15.2	75.1	2.06

90°C and the unreacted triethyl phosphate was removed under vacuum (0.1 mmHg). Experiments on the chemical degradation of microporous polyurethane elastomer were performed with heating for 5, 6, 7, and 8 h. The degraded products became liquids. The results from degradation are presented in Table I.

#### By *Tris(2-chloroethyl) Phosphate*

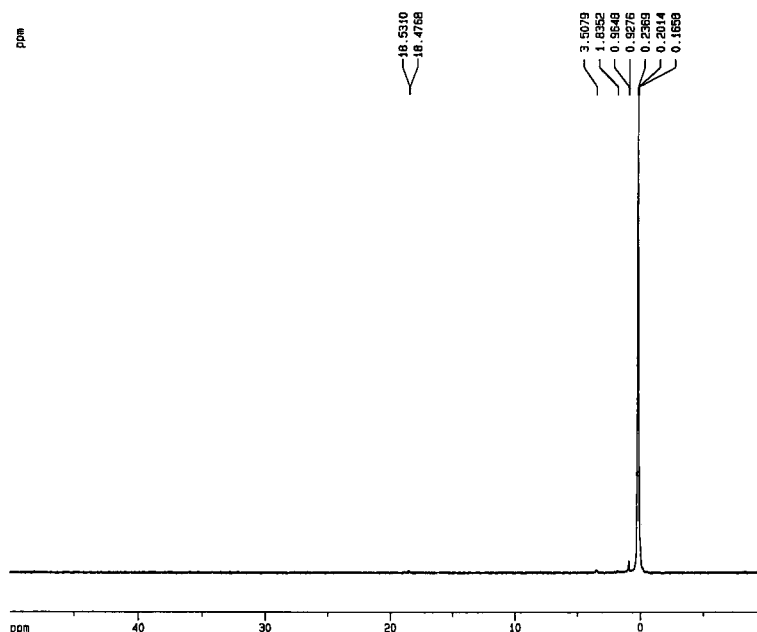
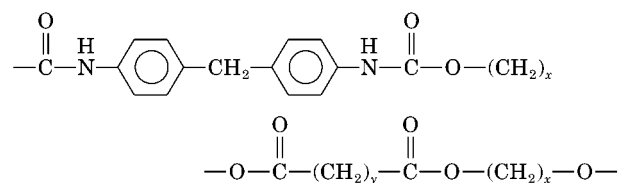
Into a three-necked flask equipped with a stirrer, thermometer, and reflux condenser was placed 40 g of microporous polyurethane elastomer cut into small pieces (3–5 mm in size) and 119.4 g of tris(2-chloroethyl) phosphate. The degradation proceeded at 180°C for 5 h. Then the temperature was lowered to 90°C and unreacted tris(2-chloroethyl) phosphate was removed under vacuum (0.1 mmHg). The final product is liquid. At these con-

ditions in the condenser, which was cooled by liquid nitrogen, was obtained 7.8 g of liquid.

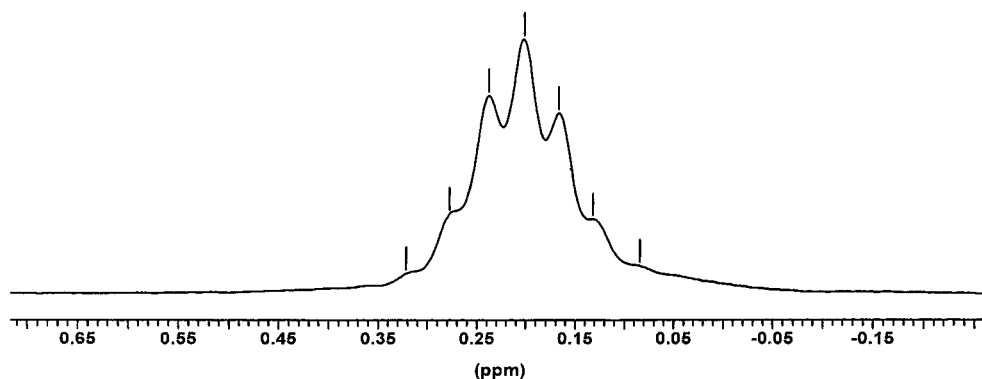
## RESULTS AND DISCUSSION

Results of the flexible polyester polyurethane foam chemical degradation by phosphonic acid esters<sup>1</sup> is the basis for suggesting phosphoric acid trialkyl esters to be used as degradation agents for polyurethanes.

The microporous polyurethane elastomer is built by the following repeating units:



**Figure 1** <sup>31</sup>P{H}-NMR spectrum of degraded polyurethane elastomer by triethyl phosphate (duration 6 h).



**Figure 2**  $^{31}\text{P}$ -NMR spectrum of degraded polyurethane elastomer by triethyl phosphate (duration 6 h).

### Degradation by Triethyl Phosphate

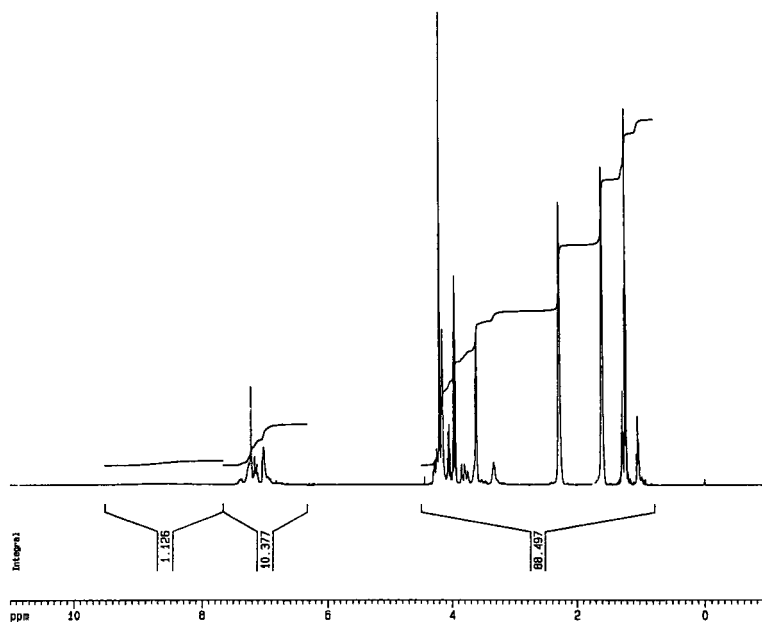
When heating a mixture of microporous polyurethane elastomer, (based on MDI and polyester polyol Baiflex 2003) and triethyl phosphate  $(\text{RO})_3\text{P}(\text{O})$  at a 1 : 3 ratio at  $180^\circ\text{C}$  the elastomer is liquified. Degradation products were investigated by means of  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{31}\text{P}$ -NMR spectroscopy.

$^{31}\text{P}\{\text{H}\}$ NMR spectrum of the product, obtained after 6 h of heating (Fig. 1) shows signals at  $\delta$

$= 0.24$  and  $\delta = 0.96$  ppm. The integral intensities show that the phosphorus containing degraded product has a signal at 0.24 ppm and is the major product, obtain in 97.3% yield. The signal at 0.24 ppm in  $^{31}\text{P}$ -NMR spectrum (Fig. 2) is a septet with  $^3J(\text{P},\text{H}) = 7.23$  Hz that could be assigned to phosphorus atom in product **1** (Table II). The signal at 0.96 ppm is a multiplet that could be assigned to phosphorus atom in product **2** (Table II).

**Table II** Phosphorus Containing Compounds from the Chemical Degradation of Microporous Polyurethane Elastomer by Triethyl Phosphate and Tris(2-chloroethyl) Phosphate

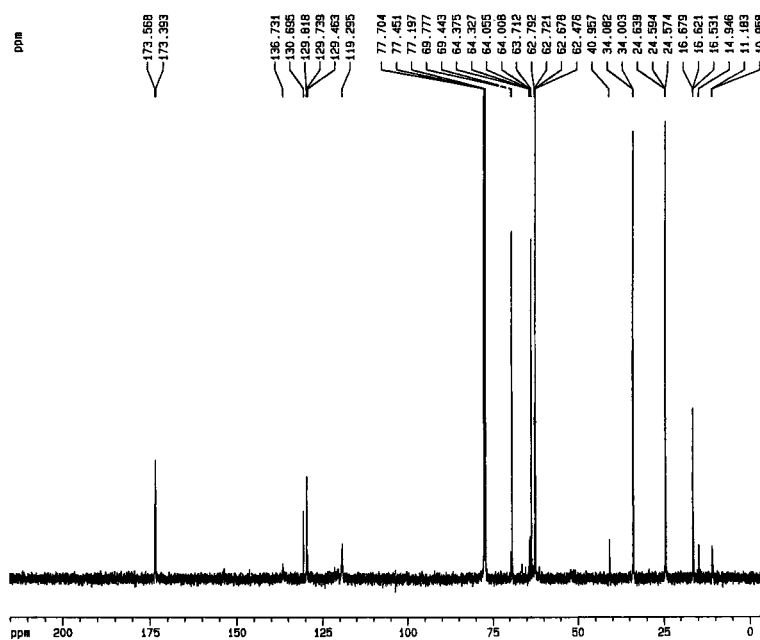
N	Structure	$^{31}\text{P}$ -NMR $\delta$ , ppm; $J$ , Hz	Content, %
Triethyl phosphate			
<b>1</b>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{OCH}_2\text{CH}_3 \\   \\ \text{OCH}_2\text{CH}_2-\text{~~~~} \end{array}$	0.24 septet $^3J(\text{P}, \text{H}) = 7.04$	97
<b>2</b>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{OCH}_2\text{CH}_2-\text{~~~~} \\   \\ \text{OCH}_2\text{CH}_2-\text{~~~~} \end{array}$	0.97, m	3
Tris(2-chloroethyl) phosphate			
<b>3</b>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{ClCH}_2\text{CH}_2\text{O}-\text{P}-\text{OCH}_2\text{CH}_2\text{Cl} \\   \\ \text{OCH}_2\text{CH}_2-\text{~~~~} \end{array}$	- 0.98 septet $^3J(\text{P}, \text{H}) = 7.95$	83
<b>4</b>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{ClCH}_2\text{CH}_2\text{O}-\text{P}-\text{OCH}_2\text{CH}_2-\text{~~~~} \\   \\ \text{OCH}_2\text{CH}_2-\text{~~~~} \end{array}$	- 0.73 septet $^3J(\text{P}, \text{H}) = 7.78$	17



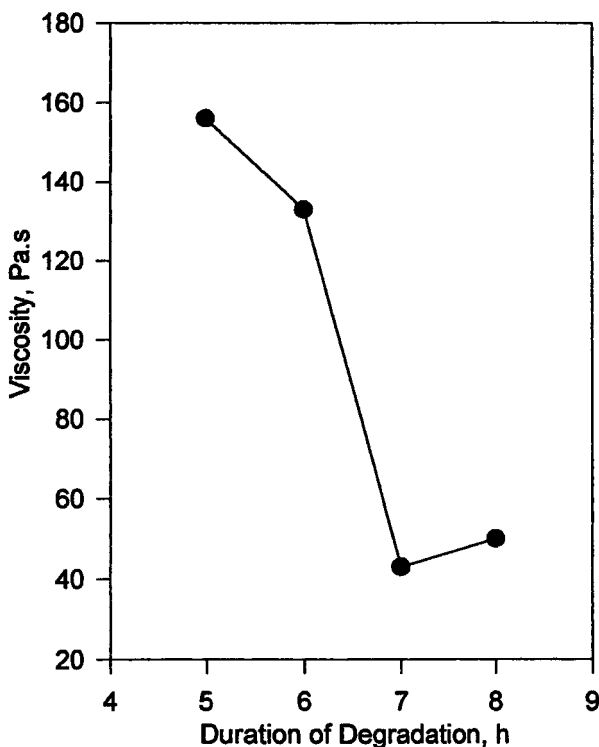
**Figure 3**  $^1\text{H-NMR}$  spectrum of degraded polyurethane elastomer by triethyl phosphate (duration 6 h).

The  $^1\text{H-NMR}$  spectrum (Fig. 3) shows signals at 1.15 ppm, *t*, with  $^3J(\text{H,H}) = 7.8$  Hz that can be assigned to  $\text{CH}_3$  protons; 1.8 and 3 ppm for  $\text{CH}_2$  protons; 4.05–4.12, ppm for  $\text{POCH}_2$ ; 7.03–7.31 ppm for aromatic protons. The  $^{13}\text{C-NMR}$

spectrum (Fig. 4) shows signals at 10.96, 14.95, and 16.62 ppm that could be assigned to  $\text{CH}_3$  carbon atoms in  $\text{CH}_3\text{CH}_2\text{O-P}$ ,  $\text{CH}_3\text{CH}_2\text{OC(O)}$ , and  $\text{CH}_3\text{CH}_2\text{OC(O)NH-}$  groups, respectively, at 63.71 ppm for  $\text{POCH}_2$  carbon atoms, at 62.47 ppm



**Figure 4**  $^{13}\text{C-NMR}$  spectrum of degraded polyurethane elastomer by triethyl phosphate (duration 6 h).



**Figure 5** Viscosity versus degradation duration of degraded polyurethane elastomer by triethyl phosphate (duration 6 h).

for  $\text{CH}_3\text{CH}_2\text{OC}(\text{O})$  carbon atoms, at 119.29–136.73 ppm for aromatic carbon atoms, and at 173.39 ppm for  $\text{OC}(\text{O})$  carbon atoms.

Viscosity of the degraded polyurethane elastomer (Fig. 5) decreases with increasing of the duration of degradation. This result proves that running the exchange reaction between urethane groups of polyurethane and ester groups of tri-

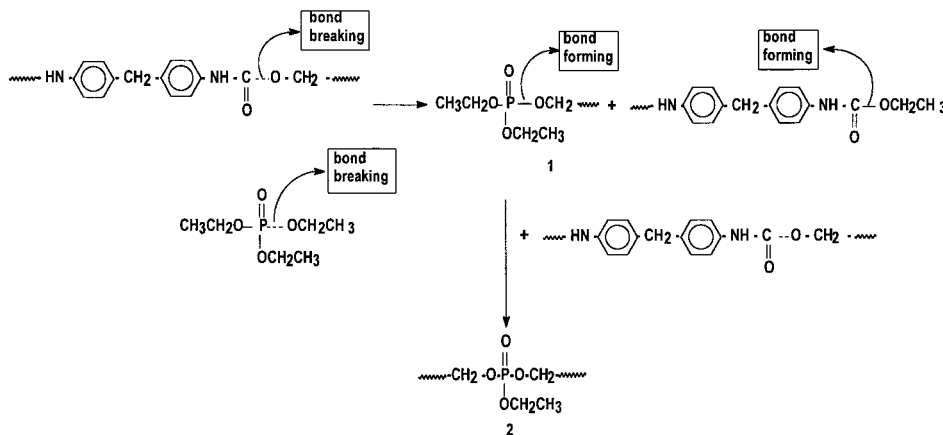
ethyl phosphate leads to breakage of the polymer chain. The viscosity of the degraded product at 8 h of degradation is higher compared to that at 7 h degradation. This can be explained with the running of the exchange reaction, which leads to an increase of molecular weight of the degraded polyurethane (formation of the product **2**, Scheme 1). The same dependence was established between phosphorus content of degraded product and duration of degradation (Table I). The phosphorus content of the degraded product obtained after 8 hours of heating is lower than that at 7 h of heating.

### Degradation by Tris(2-chloroethyl) Phosphate

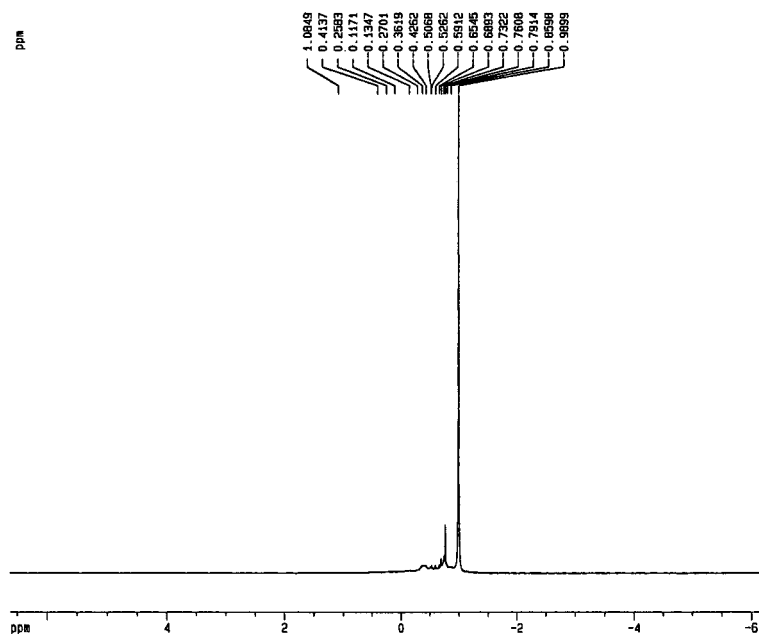
Microporous polyurethane elastomer was converted into liquid by treatment with tris(2-chloroethyl) phosphate.

$^{31}\text{P}(\text{H})$ -NMR spectrum (Fig. 6) of microporous polyurethane elastomer degraded by tris(2-chloroethyl) phosphate polyurethane shows signals at  $-0.98$ ,  $-0.73$ , and  $-0.36$  ppm. Correlation between integral intensities is 5.49 : 1 : 0.1. The signal at  $-0.98$  ppm in the  $^{31}\text{P}$ -NMR spectrum (Fig. 7) is a septet with  $^3J(\text{P},\text{H}) = 7.76$  Hz that could be assigned to phosphorus atom in product **3** (Table II). The signal at  $-0.73$  ppm (Fig. 7) is a septet with  $^3J(\text{P},\text{H}) = 7.78$  Hz that could be assigned to phosphorus atom in product **4** (Table II). The signal at  $-0.36$  ppm has a very low intensity. Its content is lower than 0.5%.

In the  $^1\text{H}$ -NMR spectrum (Fig. 8) signals corresponding to  $\text{CH}_2$  protons at 1.72 and 2.17 ppm,  $\text{ClCH}_2$  protons at 3.5 ppm,  $\text{POCH}_2$  protons at 4.05–4.12 ppm, aromatic protons in the region



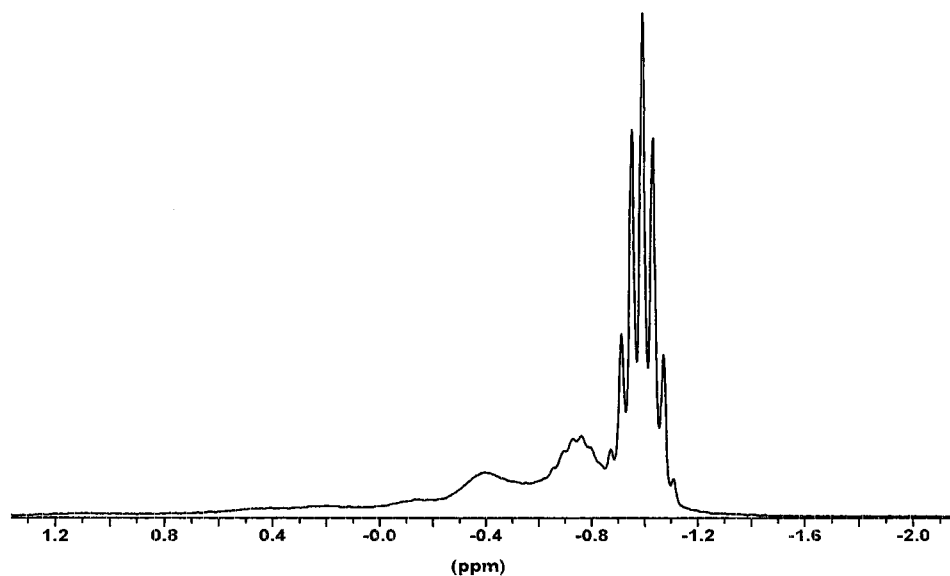
**Scheme 1**



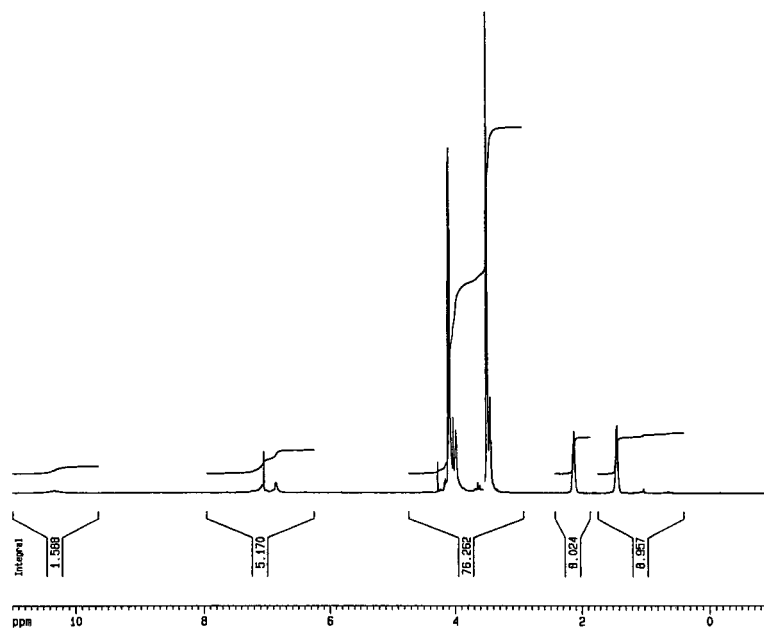
**Figure 6**  $^{31}\text{P}\{\text{H}\}$ -NMR spectrum of degraded polyurethane elastomer by tris(2-chloroethyl) phosphate.

7.03–7.31 ppm. In the  $^{13}\text{C}$ -NMR spectrum (Fig. 9) signals corresponding to:  $\text{Cl}\text{CH}_2$  carbon atoms at 24.60 ppm,  $\text{POCH}_2\text{CH}_2$  at 24.57 ppm,  $\text{POCH}_2\text{CH}_2$  at 63.71 ppm, aromatic carbon atoms in the region 119.29–129.78 ppm. The signal at 173.23 ppm could be assigned to  $\text{OC}(\text{O})$  carbon atoms and to  $\text{RO}\text{C}(\text{O})\text{—CH}_2$  carbon atoms.

It was established that degradation of microporous polyurethane elastomer by tris(2-chloroethyl) phosphate is accompanied by evolution of 1,2-dichloroethane, as the product, which was cooled by liquid nitrogen. It is known<sup>2</sup> that the condensation of tris(2-chloroethyl) results in the formation of 1,2-dichloroethane. This side reaction



**Figure 7**  $^{31}\text{P}$ -NMR spectrum of degraded polyurethane elastomer by tris(2-chloroethyl) phosphate.

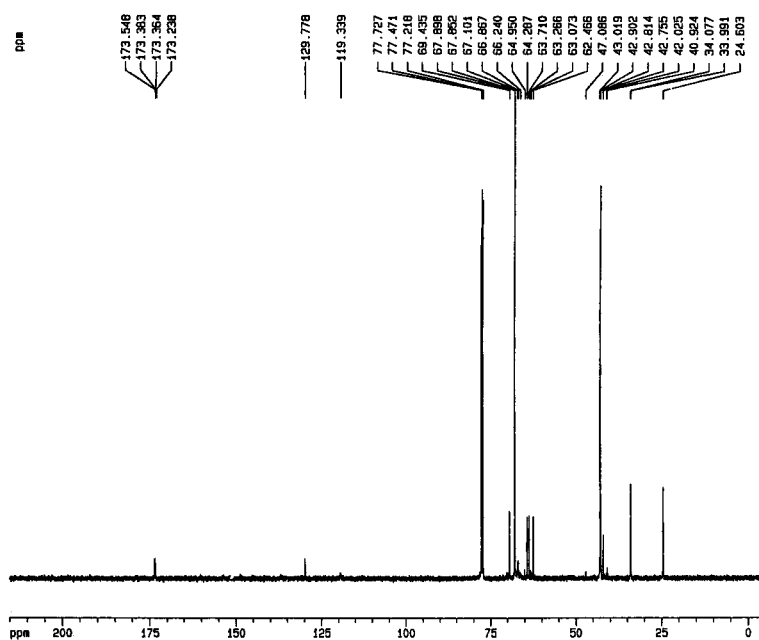


**Figure 8** <sup>1</sup>H-NMR spectrum of degraded polyurethane elastomer by tris(2-chloroethyl) phosphate.

is undesirable because 1,2-dichloroethane is a cancerous-causing compound. This product was the reason we limited our investigations with tris(2-chloroethyl) phosphate to only one experiment.

All products 1–4 are formed as a result of the exchange reaction between ester groups of tri-

ethyl phosphate or tris(2-chloroethyl)phosphate and urethane groups.<sup>1</sup> The data from the <sup>13</sup>C-NMR spectroscopy revealed that the products 1–4 are apparently formed mainly by the exchange reaction between urethane groups and phosphoric acid ester groups. In the <sup>13</sup>C-NMR spectra



**Figure 9** <sup>13</sup>C-NMR spectrum of degraded polyurethane elastomer by tris(2-chloroethyl) phosphate.

(Figs. 4 and 9) the signal for the  $\text{C}(\text{O})\text{NH}$  carbon atoms has a very low intensity while the signals for the  $\text{C}(\text{O})\text{O}$  are too intensive. The experiments from the chemical degradation of poly(ethylene terephthalate) by triethyl phosphate show that the degradation proceeds at 190–195°C. The degree of the completion of the degradation is very low.<sup>3</sup>

Product **2** is formed when product **1** participates in an exchange reaction with urethane groups (Scheme 1).

The same exchange reactions proceed between urethane groups and ester groups of tris(2-chloroethyl) phosphate.

## CONCLUSIONS

Phosphoric acid triesters can successfully be used as degradation agents for microporous polyure-

thane elastomers. Degradation products are phosphorus containing oligomers with terminal phosphate groups. They can be utilized as nonreactive additives or as reactive compounds after treatment by hydroxyl-containing compounds, amines, or metal salts for the preparation or synthesis of polymers, including polyurethane, polyvinylchloride with reduced flammability.

## REFERENCES

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