

# Chemical Degradation of Polyurethanes: Degradation of Flexible Polyester Polyurethane Foam by Phosphonic Acid Dialkyl Esters

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**ABSTRACT:** Flexible polyurethane foam based on toluene diisocyanate and polyester polyol has been liquefied by treatment with either dimethyl phosphonate  $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$  or diethyl phosphonate  $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{H}$  at  $160^\circ\text{C}$ . The product degraded has been studied by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectroscopy. The likely reaction mechanism is presented. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2565–2573, 2000

**Key words:** chemical recycling; flexible polyester polyurethane foam; chemical degradation; dimethyl phosphonate; diethyl phosphonate

## INTRODUCTION

Recycling of polymer waste materials and used polymers is one of the ways to conserve natural resources and to reduce environmental stress. The chemical degradation of polyurethanes—rigid, flexible, or polyurethane elastomers, involves well-known methods of hydrolysis,<sup>1</sup> glycolysis<sup>2–4</sup> and aminolysis.<sup>5,6</sup>

The primary aim of these studies is to develop a new method for converting polyurethane waste materials and used polyurethanes by treatment with esters of phosphonic and phosphoric acids into reusable products that can be used in the preparation of polymers, including polyurethanes, with reduced flammability. Hereby we report on the chemical degradation of flexible polyurethane foam based on toluene diisocyanate (Desmondur T-80) and polyester polyol (Varalux HL 106) performed by treatment with phosphonic acid diesters.

## EXPERIMENTAL

### Materials and Methods

Flexible polyester polyurethane foam based on polyester polyol Varalux HL, TDI-T-80,  $\text{H}_2\text{O}$ , Sn-octocat, B-Y (amino catalyst), and Sil. stab. BF-2370, was used.

The flexible polyester polyurethane foam was cut into small pieces and placed into the glass appliances. 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) was commercially available.

### Instruments

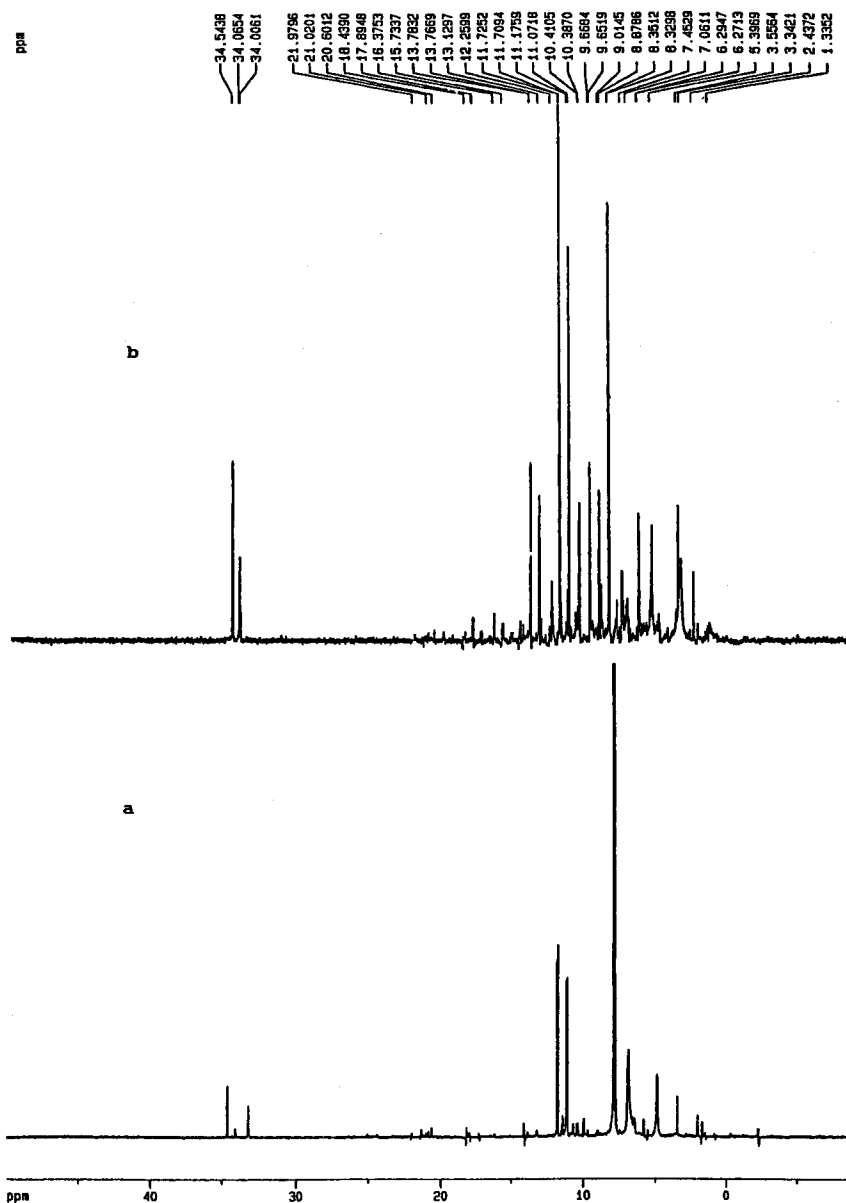
$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectra were recorded on a Bruker apparatus, 500 MHz, in  $\text{CDCl}_3$  solvent. The viscosity was measured on a Brookfield LV viscometer. Phosphorus content was determined on a Specol spectrophotometer, 420 nm wave length. Molecular weight was determined on a GPS Waters apparatus in  $\text{CH}_2\text{Cl}_2$  solvent, using polystyrene as a standard.

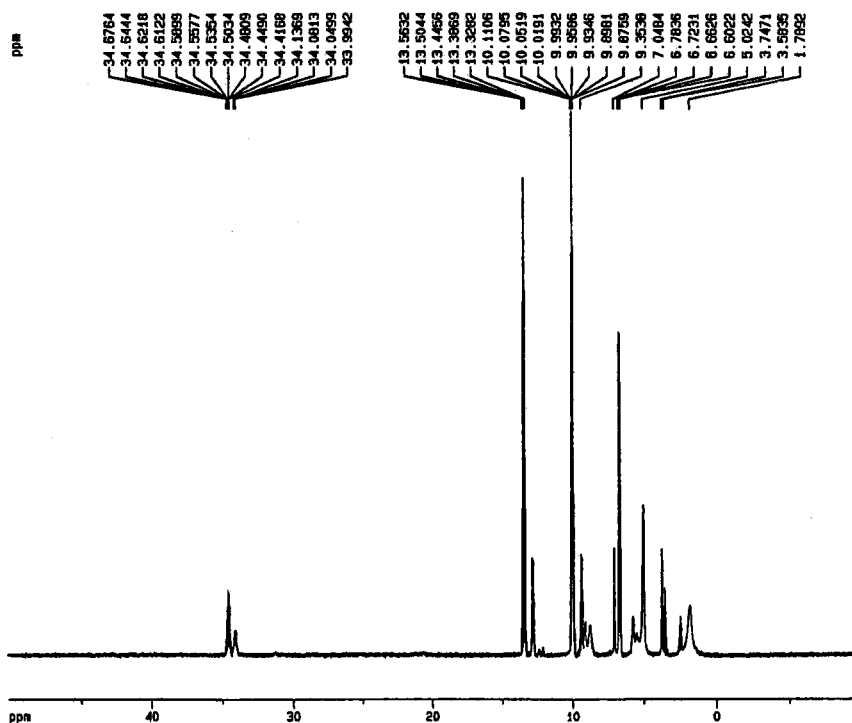
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**Table I** Conditions for Flexible Polyester Polyurethane Foam (PU) Chemical Degradation by Dimethyl Phosphonate (DMP) at 160°C

DMP (g)	PU (g)	Duration of Degradation (h)	Reacted DMP (g)	Unreacted DMP <sup>b</sup> (g)	Degree of Degradation (%)	Yield (g)	Upper Layer (g)	Lower Layer (g)	P (%)	
									Upper Layer	Lower Layer
362.4	120	1 (1) <sup>a</sup>	105.6	256.8	100	214.9	106.3	108.6	4.52	19.00
361.9	120	2 (1)	113.2	248.7	100	222.4	123.2	99.2	7.10	18.80
365.4	120	3 (1)	115.8	249.6	100	224.2	119.4	104.8	4.35	19.30

<sup>a</sup> Duration of addition of PU.<sup>b</sup> Unreacted DMP was removed by vacuum distillation and was reused for degradation.**Figure 1** <sup>31</sup>P{H} NMR spectrum of degraded flexible polyester polyurethane foam by dimethyl phosphonate, upper layers obtained after degradation. (a) 1 h; (b) 3 h.



**Figure 2**  $^{31}\text{P}$  NMR Spectrum of degraded flexible polyester polyurethane foam by dimethyl phosphonate, upper layer. Duration of degradation: 3 h.

### Degradation by Dimethyl Phosphonate

Flexible polyester polyurethane foam (120 g) cut into small pieces 3–5 mm large and 362.4 g of dimethyl phosphonate were put into a three necked-flask equipped with a stirrer, thermometer, and reflux condenser. The degradation proceeded at 160°C, then the temperature was lowered to 60°C, and the unreacted dimethyl phosphonate was removed under vacuum (0.1 m Hg) and reused for degradation. Experiments on the chemical degradation of flexible polyester polyurethane foam were performed with heating for 1, 2, and 3 h. The results from the degradation are presented in Table I.

### Degradation by Diethyl Phosphonate

The degradation with diethyl phosphonate was run under the same conditions: 18 g of flexible polyester polyurethane foam cut into small pieces 3–5 mm large were added to 53.5 g of diethyl phosphonate. The degradation proceeded at 160°C for 1 h. The reaction mixture was studied without removing the unreacted diethyl phosphonate.

## RESULTS AND DISCUSSION

The reason to choose phosphonic acid dialkyl esters as degradation agents of polyurethanes is the exchange reactions between ester groups proceeding during the synthesis of poly(ethylene terephthalate)<sup>7,8</sup> and the exchange reaction between ester groups of phosphonic acid diesters.<sup>9,10</sup>

### Degradation by Dimethyl Phosphonate

When heating a mixture of flexible polyester polyurethane foam based on toluene diisocyanate, polyester polyol, and dimethyl phosphonate at a 1:3 ratio at 160°C the polyurethane is liquefied. Two liquid layers are formed after removing the unreacted dimethyl phosphonate. We have studied the structure of the products in both layers obtained after 3 h and 1 h of degradation by means of  $^{31}\text{P}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy.

### Study on the Upper Layer

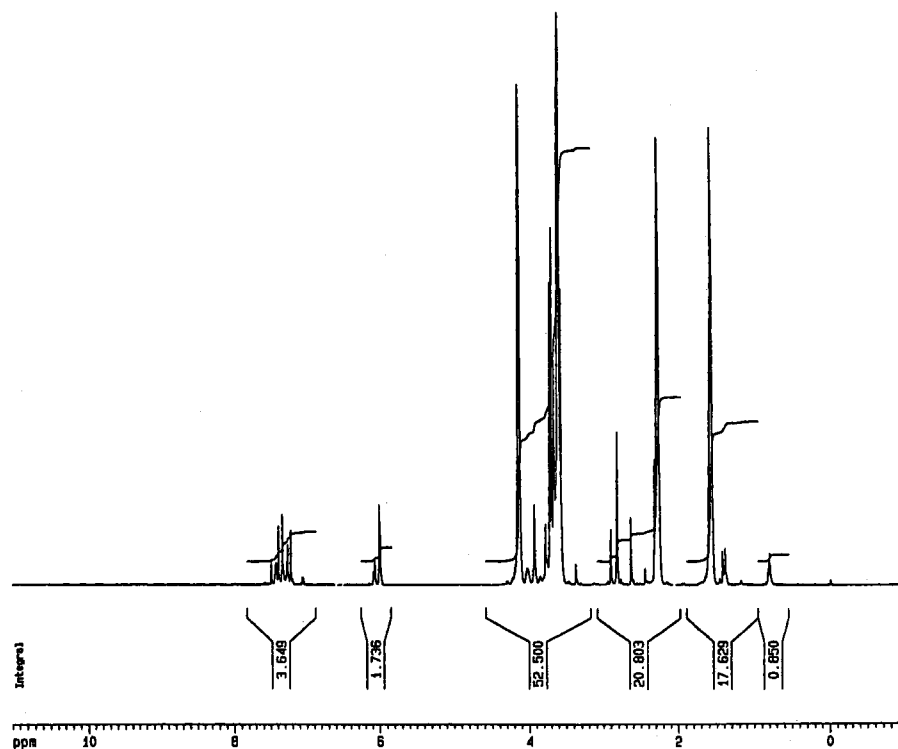
$^{31}\text{P}\{\text{H}\}$  NMR spectra of the upper layer products obtained after degradation for 1 h (Fig. 1a) and for

**Table II Phosphorus-Containing Products from the Chemical Degradation of Flexible Polyester Polyurethane Foam by Dimethyl Phosphonate**

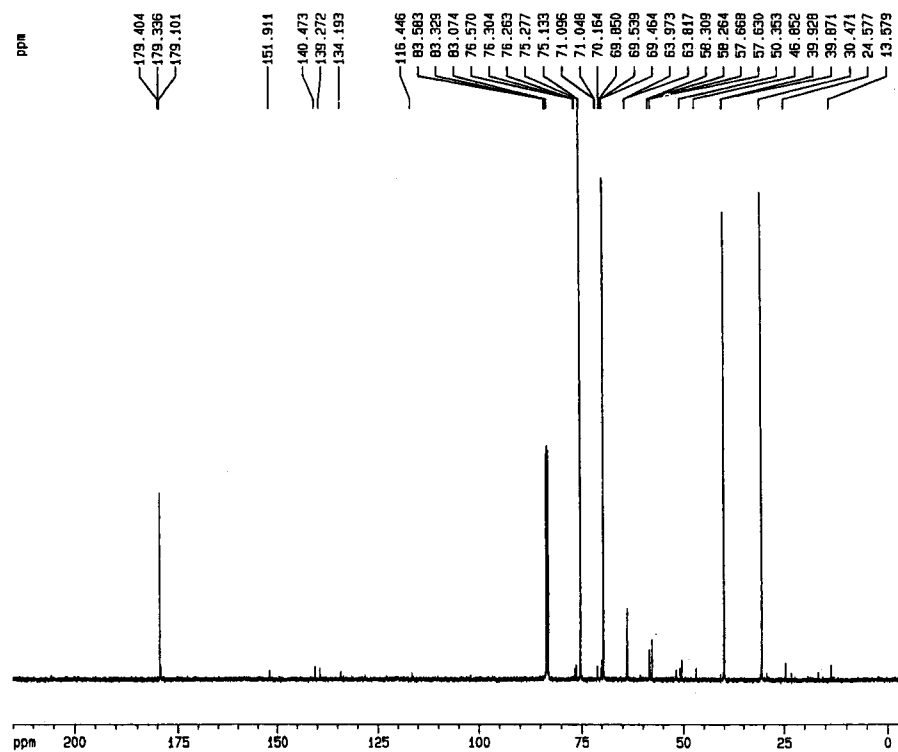
N	Structure	$^{31}\text{P}$ NMR, $\delta$ ppm, J, Hz	Content (%)	
			Upper Layer	Lower Layer
1	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{O}-\text{X} \\   \\ \text{H} \end{array}$ $\text{X} = \begin{array}{ c } \hline \text{---C(O)NH---} \\   \\ \text{CH}_3 \\ \hline \end{array} \text{ or } \begin{array}{ c } \hline \text{---HN---C(O)---NH---} \\   \\ \text{CH}_3 \\ \hline \end{array}$	8.32, dq, $^3\text{J}(\text{P,H}) = 12.2$ $^1\text{J}(\text{P,H}) = 665.9$	18.4	54.8
2	$\begin{array}{c} \text{O} \\ \parallel \\ \text{X}^-\text{O}-\text{P}-\text{O}^-\text{X} \\   \\ \text{H} \end{array}$	5.04, d, $^1\text{J}(\text{P,H}) = 670.3$	14.9	168.8
3	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{O}(\text{CH}_2)_x\text{---} \\   \\ \text{H} \end{array}$	11.07, dsex, $^3\text{J}(\text{P,H}) = 11.8$ $^1\text{J}(\text{P,H}) = 708.7$	31.5	4.7
4	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{NH}-\text{C}_6\text{H}_4-\text{NHC(O)-} \\   \\ \text{H} \end{array}$	3.55, septet, $^3\text{J}(\text{P,H}) = 11.1$	15.8	17.0
5	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{OCH}_3 \\   \\ \text{CH}_3 \end{array}$	34.2–34.8 m	4.2	<1
6	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{O}-\text{P}-\text{O}^-\text{X} \\   \\ \text{CH}_3 \end{array}$	33.9–34.2 m	5.2	<1

3 h (Fig. 1b) have one and the same signals. The integral intensities recorded for the phosphorus atoms showed that with increasing the duration of the degradation process the contents of the products changed. As seen from  $^{31}\text{P}$  NMR spectrum (Fig. 2) the signal at  $\delta = 11.72$  ppm is a doublet of septets with  $^3\text{J}(\text{P,H}) = 11.78$  Hz and  $^1\text{J}(\text{P,H}) = 698.5$  Hz, which is typical for the phosphorus atom in the molecule of dimethyl phosphonate.<sup>11</sup> The content of the dimethyl phosphonate is 3.8%. The signal at 8.32 ppm is a doublet of

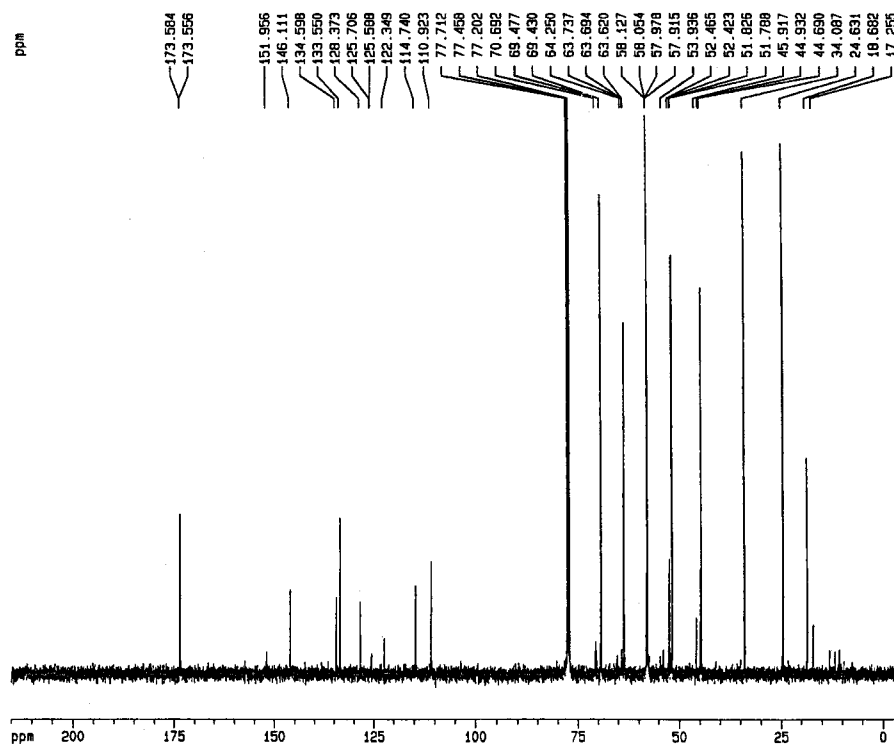
quartets with  $^3\text{J}(\text{P,H}) = 12.22$  Hz and  $^1\text{J}(\text{P,H}) = 665.9$  Hz. The above data can be assigned to the phosphorus atom in product 1 (Table II). The signal at 5.40 ppm is a doublet with  $^1\text{J}(\text{P,H}) = 670.3$  Hz and can be assigned to the phosphorus atom in product 2 (Table II). The signal at 11.07 ppm is a doublet of sextets with  $^3\text{J}(\text{P,H}) = 11.80$  Hz and  $^1\text{J}(\text{P,H}) = 708.7$  Hz. These data can be assigned<sup>12</sup> to the phosphorus atom in product 3 (Table II). The signal at 3.55 ppm is a septet with  $^3\text{J}(\text{P,H}) = 11.11$  Hz and can be assigned to the phosphorus



**Figure 3**  $^1\text{H}$  NMR spectrum of degraded flexible polyester polyurethane foam by dimethyl phosphonate, upper layer. Duration of degradation: 3 h.



**Figure 4**  $^{13}\text{C}$  NMR spectrum of degraded flexible polyester polyurethane foam by dimethyl phosphonate, upper layer. Duration of degradation: 3 h.



**Figure 5**  $^{13}\text{C}$  NMR spectrum of degraded flexible polyester polyurethane foam by dimethyl phosphonate, lower layer. Duration of degradation: 3 h.

atom in product 4 (Table II). The signals at 33.06 and 34.56 ppm are multiplets at 32.71–31.50 ppm and 34.35–34.80 ppm and can be assigned to the phosphorus atoms in products 5 and 6 (Table II).

The  $^1\text{H}$  NMR spectrum (Fig. 3) shows signals that can be attributed to the above products. There are four types of P-H protons at 6.71 ppm, 6.69 ppm, 6.76 ppm, and 6.80 ppm that are  $^1\text{J}(\text{P,H})$ : 698.6 Hz, 665.1 Hz, 670.1 Hz, and 671.0 Hz, respectively, and can be assigned to P-H protons of dimethyl phosphonate, in products 1, 2, and 3, respectively. Several doublets are observed in the region 3.57–3.74 ppm having  $^3\text{J}(\text{POCH}) = 11.96$  Hz, which should be assigned to P- $\text{OCH}_3$  protons. Because the spectrum is rather complicated it is difficult to assign the doublets for the respective structures. The signal at 2.94 ppm could be assigned to  $^+\text{N-CH}_3$  protons.

The signals in  $^{13}\text{C}\{\text{H}\}$  NMR spectrum (Fig. 4) are (1) at 30.47 ppm and can be attributed to carbon atoms in the  $\text{N-CH}_3$  group; (2) at 50.35 ppm and can be assigned to carbon atoms in  $\text{CH}_3\text{O-C(O)}$  group and to the carbon atom in P- $\text{OCH}_3$ ; and (3) at 63.97 ppm and should be assigned to carbon atoms in the P-O- $\text{CH}_2$  group.

The content of the aromatic carbon atoms is very low.

#### Study on the Lower Layer

$^{31}\text{P}\{\text{H}\}$  NMR spectra of the lower layer products obtained after degradation for 1 and 3 h shows the same signals as the upper layer. The integral intensities registered showed that the product having highest content gives a chemical shift at 8.32 ppm. The content of the phosphorus-containing products is given in Table II.

It should be noted that the lower layer consists of aromatic carbon atoms (Fig. 5).

#### Degradation 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 as in the case of dimethyl phosphonate. The  $^{31}\text{P}$  NMR spectrum shows that the signal at 8.43 ppm is a doublet of quintets with  $^3\text{J}(\text{P,H}) = 9.25$  Hz and  $^1\text{J}(\text{P,H}) = 692.2$  Hz, which could be assigned to

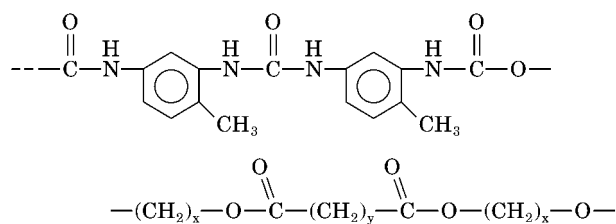
**Table III Phosphorus-Containing Products from the Chemical Degradation of Flexible Polyester Polyurethane Foam by Diethyl Phosphonate<sup>a</sup>**

N	Structure	<sup>31</sup> P NMR, δ ppm, J, Hz	Content (%)
7	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{O}(\text{CH}_2)_x- \\   \\ \text{H} \end{array}$	8.68, dq, quintets <sup>3</sup> J(P,H) = 9.24 <sup>1</sup> J(P,H) = 692.2	45.0
8	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{O}-\text{P}-\text{O}-\text{X} \\   \\ \text{H} \end{array}$	5.50, d <sup>3</sup> J(P,H) = 8.32 <sup>1</sup> J(P,H) = 655.2	10.0
$\text{X} = \begin{array}{c} -\text{C}(\text{O})\text{NH}- \\   \\ \text{CH}_3\text{CH}_2 \end{array} \quad \text{or} \quad \begin{array}{c} -\text{NHC}(\text{O})\text{NH}- \\   \\ \text{CH}_2\text{CH}_3 \end{array}$			

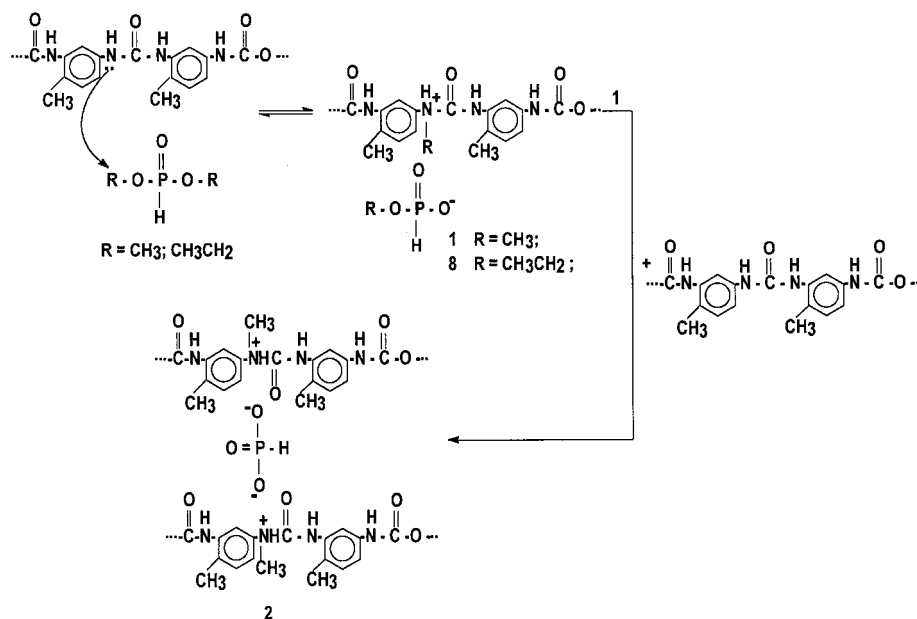
<sup>a</sup> The content of the unreacted diethyl phosphonate was 45%.

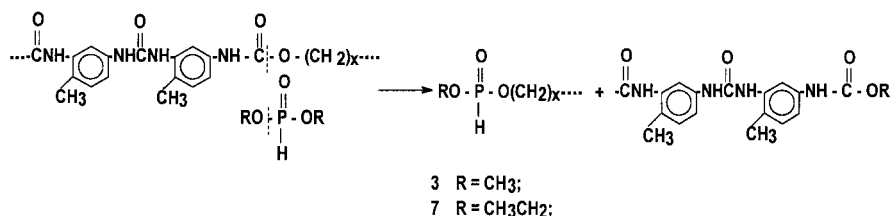
the phosphorus atom of diethyl phosphonate. The signal at 8.68 ppm is a doublet of quintets that could be assigned to the phosphorus atom of product 7 (Table III). The signal at 5.50 ppm is a doublet of triplets that could be assigned to the phosphorus atom of product 8 (Table III). <sup>13</sup>C{H} NMR spectrum shows signals that support the above mentioned structures.

The following repeating units build the flexible polyester polyurethane foam.



The NMR data from the studies performed on the products from the chemical degradation of flexible

**Scheme 1**



Scheme 2

polyester polyurethane foam with dimethyl diethyl phosphonates give grounds to suggest that products 1, 2, and 8 were formed as a result of the proceeding of alkylation reaction (Scheme 1) in which the electrophilic center is  $\alpha$ -carbon atom of the methoxy or ethoxy groups whereas the nitrogen atom of the urea (water was used as a blowing agent) or urethane groups is the nucleophile.

When  $\alpha$ -carbon atom from product 1 participates in the same reaction with the urea or urethane groups, the resulting product is 2 (Scheme 1).

It is known<sup>13-15</sup> that the nitrogen atom, being a nucleophilic center, prefers to attack the weaker electrophilic center in the molecule of dialkyl esters of phosphonic acid, namely the  $\alpha$ -carbon atom of alkoxy group. The data from the <sup>31</sup>P NMR studies showed that the content of product 8 is about 10% whereas the content of product 1 is 46.5%. It is known that the  $\alpha$ -carbon atom of the ethoxy group of diethyl phosphonate has a lower positive charge than that of the  $\alpha$ -carbon atom of the methoxy group of dimethyl phosphonate due to the donor character of -CH<sub>3</sub> group. That is why the alkylation reaction does not go to completion with diethyl phosphonate.

Products 3 and 7 are obtained as a result of the exchange reaction with the participation of ester

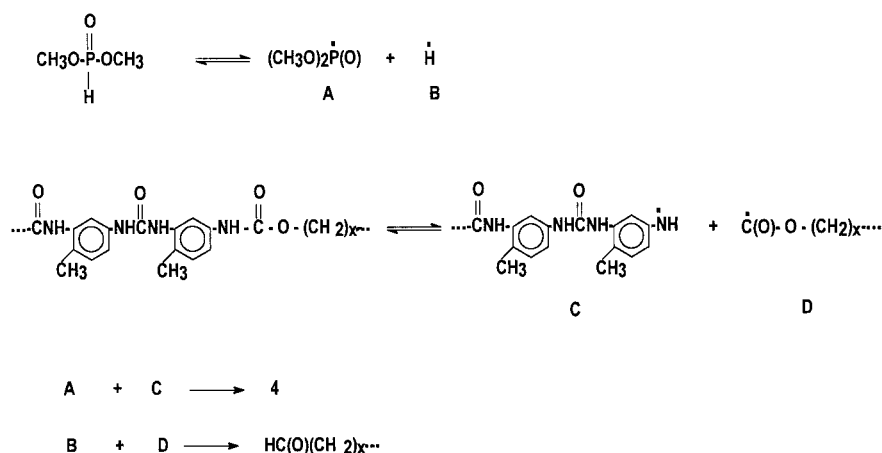
groups of dimethyl or diethyl phosphonate and urethane groups (Scheme 2).

It was established that the exchange reaction between ester groups of phosphonic acid and ester groups of poly(ethylene terephthalate) proceed at temperatures higher than 175°C (diethyl phosphonate was used) with a very low rate.<sup>16</sup> Obviously, at this condition the exchange reaction between ester groups of phosphonic acid and ester groups of polyester polyol does not proceed.

Product 4 (Table II) probably results of radical processes in which the phosphonate radicals take part (Scheme 3).

Dimethylmethyl phosphonate, product 5 (Table II), forms in the result of the thermal rearrangement of dimethyl phosphonate. Product 6 is formed in the result of alkylation of urea or urethane groups by dimethylmethyl phosphonate.

Running the above processes with heating of flexible polyester polyurethane foam with dimethyl phosphonate leads to a decrease in molecular weight of polyurethane. The polyurethane was converted into a liquid. The proceeding of the degradation was confirmed <sup>31</sup>P NMR and by the determined viscosities of the upper (Fig. 6) and lower layers (Fig. 7), and by gel permeation chromatography (GPC) anal-



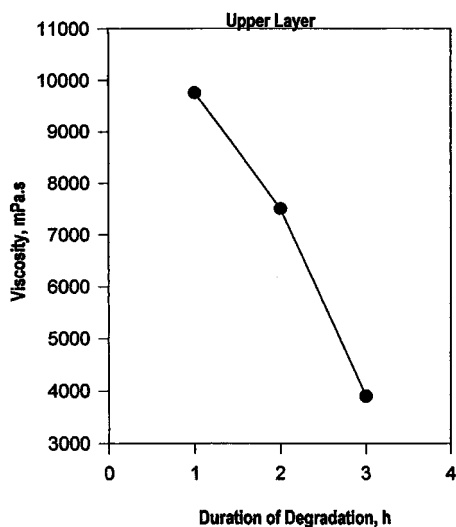
Scheme 3



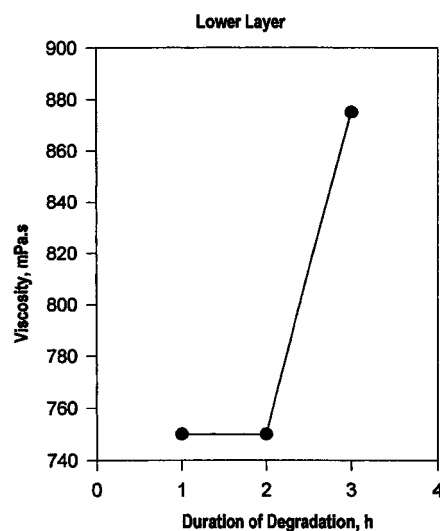
ysis. GPC analysis of the upper layer showed that  $M_n = 2764$  and that it has a dispersity of 2.38 (duration 3 h). It should be noted that the increasing of the duration of the degradation leads to lowering the viscosity of the upper layer, whereas that of the lower layer remains unchanged. On the other hand the phosphorus content of the upper layer is considerably lower than that in the lower layer (Table I). The difference could be explained by the structures of the phosphorus-containing products formed as the result of the degradation. The lower layer is built mainly of aromatic compounds that consist phosphorus (Table II, product 1 and 2).

## CONCLUSION

It has been shown that dimethyl phosphonate and diethyl phosphonate can be used as degradation agents of flexible polyester polyurethane foam. The flexible polyester polyurethane foam was converted into liquid after treatment with dimethyl phosphonate or diethyl phosphonate at 160°C. The products obtained are phosphorus-containing oligomers. These products directly or after chemical treatment can be used for the preparation of polyurethanes with reduced flammability, or can be used as additives to polymers, improving their fire resistance. It is likely that other esters of phosphonic  $[(RO)_2P(O)R]$  and phosphoric  $[(RO)_3P(O)]$  acids could also participate in the above mentioned



**Figure 6** Viscosity vs degradation duration of flexible polyester polyurethane foam by dimethyl phosphonate upper layer.



**Figure 7** Viscosity vs degradation duration of flexible polyester polyurethane foam by dimethyl phosphonate, lower layer.

reactions and could also degrade polyesters, polycarbonates, and phosphorylate polyamide. We are going to prove this assumption experimentally.

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