**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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**To cite this Article** Molero, Carolina , Mitova, Violeta , Troev, Kolio and Rodriguez, Juan F.(2010) 'Kinetics and Mechanism of the Chemical Degradation of Flexible Polyurethane Foam Wastes with Dimethyl H-phosphonate with Different Catalysts', Journal of Macromolecular Science, Part A, 47: 10, 983 — 990

**To link to this Article: DOI:** 10.1080/10601325.2010.506408

**URL:** http://dx.doi.org/10.1080/10601325.2010.506408

*Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* (2010) **47**, 983–990
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ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2010.506408

# Kinetics and Mechanism of the Chemical Degradation of Flexible Polyurethane Foam Wastes with Dimethyl H-phosphonate with Different Catalysts

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Received April 2010, Accepted May 2010

Flexible polyurethane foams (PU) based on toluene diisocyanate and polyether polyol have been degraded by dimethyl H-phosphonate (DMP) in the presence of catalysts such as potassium *tert*-butoxide, potassium and azobisisobutyronitrile (AIBN). The structure and molecular weight of the degraded products were monitored by $^{31}$P-NMR and GPC. The degradation process was controlled by the polydispersity (PD) of the reaction product. Potassium *tert*-butoxide enhances interchange reactions compared to the non catalyzed process. The product of degradation contains mainly the original polyol capped with a phosphonate group and a phosphorous dimmer of the original polyol.

**Keywords:** Dimethyl H-phosphonate, polymer degradation, polyurethanes, phosphorous containing oligourethanes

## 1 Introduction

Polyurethanes (PUs) represent an important class of thermoplastic and thermoset polymers as their mechanical, thermal and chemical properties can be tailored by the reaction of various polyols and polyisocyanates. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances to thermoplastic polyurethane used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interiors Polyurethanes (PUs) make ca. 5% of the total amount of plastics (1). Flexible PU foams represent the biggest part of the PU market—around 33 wt% (2). The goal of chemical recycling of flexible foams is to obtain polyols suitable for manufacturing new PU foam (either flexible or rigid). Numerous studies on chemical recycling of flexible foams are described in the literature. Recently, H. Bhatti et al. (3) published an excellent review devoted to the methods for polyurethane recycling and recovery. The most important methods of chemical recycling of PURs are hydrolysis (4), glycolysis (5–7), hydroglycolysis (8), aminoalcoholysis (9, 10), and methanolysis (11). Glycolysis of PU gives a mixture of original polyol, low-molecular-weight urethanes with hydroxy-end groups and secondary products such as aromatic amines (5, 6, 12). The glycolysis of commercially manufactured flexible foams has been studied in order to obtain directly the polyol that can be used in the production of new foams.

A novel strategy for the chemical degradation of polymer materials – polyurethanes (13–19), polycarbonate (20) and polyamide (21) - by esters of H-phosphonic and phosphoric acids was developed. For the first time, it was established that alkyl esters of H-phosphonic and phosphoric acids can be used as degrading agents for polymers. Polyurethanes can be converted into liquid phosphorus-containing oligourethanes by treatment with dimethyl H-phosphonate, or diethyl H-phosphonate, or triethyl phosphate, or tris(1-methyl-2-chloroethyl) phosphate at elevated temperatures. Some of the phosphorus-containing degradation products formed are transformed into reactive intermediates by treatment with propylene oxide and are used for the preparation of rigid polyurethane foams (22). These new materials have higher density and better mechanical properties compared to the standard rigid polyurethane foams. Up to now, the process has been carried out in absence of catalysts. The main advantage of the introduction of phosphorous moiety is the possibility telechelic oligourethanes and polyols with reduced flammability (3–5, 23–24). This is especially desirable in the case of flexible

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foams because of their application in furniture, mattresses and automotive seats.

In this work, chemical degradation of flexible polyurethane foam with DMP has been studied in the presence of different catalysts such as potassium *tert*-butoxide, potassium and azobisisobutyronitrile (AIBN) with the main goal of improving the degradation process via the acceleration of the degradation rate and hence the reduction of the reaction time.

## 2 Experimental

### 2.1 Materials and Methods

Industrial wastes of flexible PU foam based on polyether polyol (Mw= 3500, PD=1.06) and toluene diisocyanate (TDI) were obtained from slabstock manufacturing. The flexible polyether polyurethane foam was cut into small pieces and placed into the glass apparatus. Dimethyl H-phosphonate $(CH_3O)_2P(O)H$, and 2,2-azobisisobutyronitrile (AIBN) was purchased from Fluka. DMP was used without further purification.

Potassium *tert*-butoxide was prepared by the reaction of dry *tert*-butanol with potassium metal.

### 2.2 Instruments

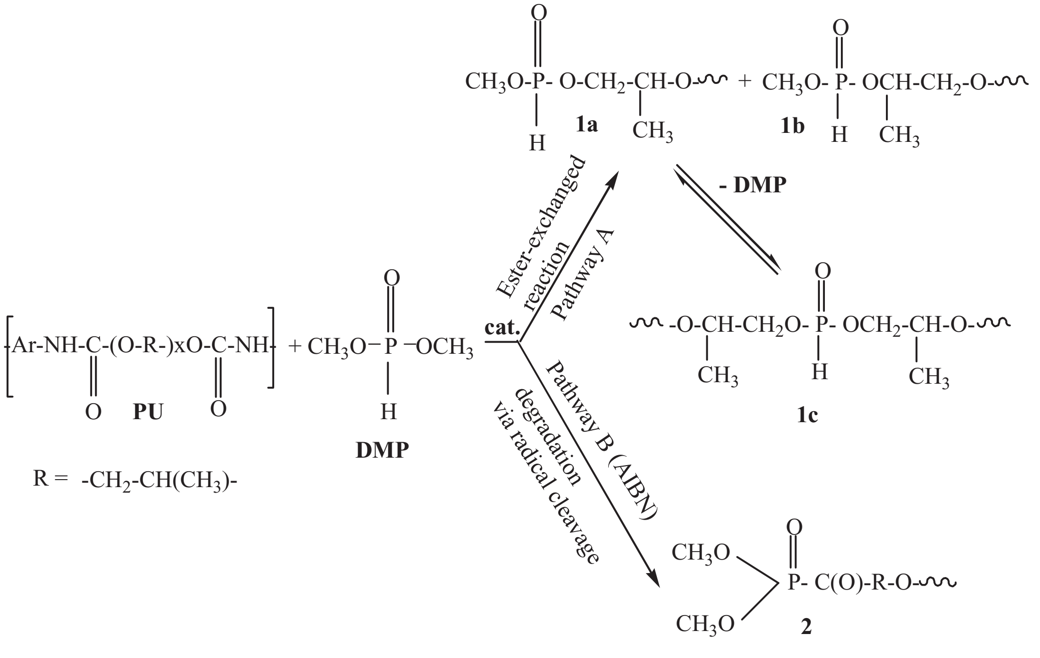
$^{31}$P-NMR spectra were recorded on a Bruker apparatus, 250 MHz, in $CDCl_3$ solvent. Gel Permeation Chromatography (GPC) was used to determine molecular weight distribution (MWD) of the resulting products. Measurements were performed with a Shimadzu chromatograph, equipped with two columns (Styragel HR2 and Styragel HR0.5) using THF at 40°C as eluent and a refractive index detector. PEG standards were used as MWD standards.

### 2.3 Method for Chemical Degradation of Flexible Polyurethane Foam by Dimethyl Phosphonate

Into a three-necked flask equipped with a stirrer, thermometer and reflux condenser were put 12 g of dimethyl H-phosphonate and 4 g of flexible polyether polyurethane foam cut into small pieces (3±5 mm in size). The degradation was carried out under inert atmosphere. The system was submerged in a thermostatic bath. Temperature was set at 140°C to collapse the foam to a gel. After that, the reaction proceeded at 160°C. Potassium *tert*-butoxide- 0.5 and 1.0% of PU weight, potassium- 0.17 and 0.35% of PU weight, and azobisisobutyronitrile (AIBN) -1% of PU weight were used as catalysts. Experiments were performed with heating for 300 min. The reaction mixture was periodically sampled and analyzed.

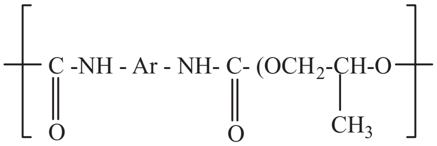
## 3 Results and Discussion

Alkali-metal alkoxides show high activity as catalysts for the ester interchange reactions (25). This fact justifies the employment of potassium *tert*-butoxide as catalyst for chemical degradation of polyurethanes with dimethyl H-phosphonate, and taking into account the ability of potassium to promote the formation of alkoxide type compounds was also chosen. AIBN was also assayed because it was previously proven that the product **2** (shown in Scheme 1) is formed as the result of participation of P-H group *via*



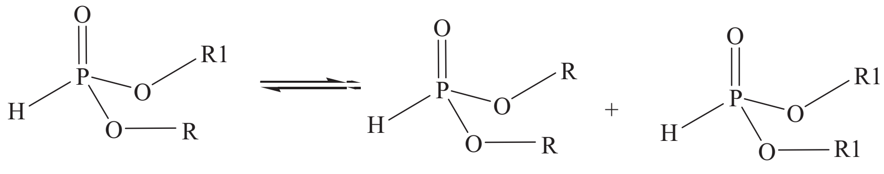
**Sch. 1.** Chemical degradation of polyurethanes with diesters of the H-phosphonic acid.

radical reactions, even though potassium was used as a third catalyst for this study. The polymer chain of the used flexible polyurethane foam is built by the following repeating units:



$$\left[\underset{\underset{O}{\|}}{C}\text{-NH-Ar-NH-}\underset{\underset{O}{\|}}{C}\text{-(OCH}_2\text{-}\underset{\underset{CH_3}{|}}{C}\text{H-O}\right]$$

When heating a mixture of flexible polyurethane based on toluene diisocyanate and polyether polyol and dimethyl H-phosphonate (1:3 ratio) at 160°C in the presence of catalysts–potassium tert-butoxide the polyurethane is completely degraded and two non-mixable layers are formed. The data from the $^{31}$P-NMR studies of the upper layer show that the following products are formed in the result of the chemical degradation of PU with DMP (Table 1). $^{31}$P-NMR spectrum of the upper layer obtained in the presence of 0.5% K-*t*-butoxide showed signals at 9.39 ppm, 10.14 ppm and 10.61 ppm, (Fig. 1). The signal at 9.39 ppm represents a doublet of sextets and can be assigned to the phosphorus atom in the product **1a**. The doublet of quintets at 10.14 ppm can be assigned to the phosphorus atom in the product **1c**. The value of the $^1$J(P,H) = 715.0 Hz is characteristic for such structures (26). The signal at 10.61 ppm, which represents a doublet of quintets, can be assigned to the phosphorus atom in the product **1b**. The experimental data revealed that product **2** is formed in the presence of 1% K-*t*-butoxide. The signal at 8.38 ppm, which represents a septet with $^3$J(P,H)=11.10, can be assigned to the phosphorus atom in the product **2**. The experimental results showed that the content of the degradation products depends on the type and amount of the catalyst.



**product 1a**

R = $CH_3$; $R^1$ = virgin polyol

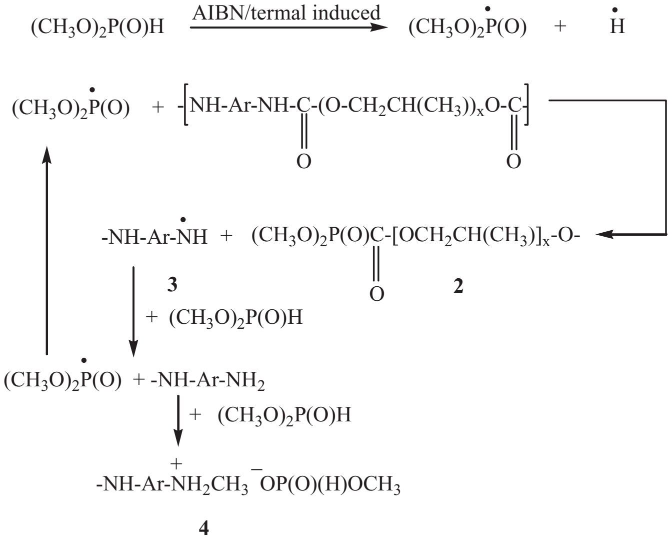
**DMP**

R= $CH_3$

**product 1c**

$R^1$ = virgin polyol

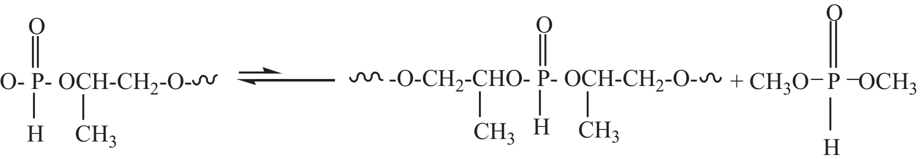
The products obtained in the result of the treatment of the flexible polyether polyurethanes with dimethyl H-phosphonate in the presence of catalysts allow us to assume the following reaction scheme for this interaction (Sch. 1).



**Sch. 2.** Radical degradation of PU by dimethyl H-phosphonate.

The exchange reaction between methoxy groups of dimethyl H-phosphonate and urethane groups –Ar-NH-C(O)-OCH$_2$-CH(CH$_3$)-O- resulted in the formation of products **1a** and **1b**. Both products (**1a** and **1b**) represent asymmetric diesters of H-phosphonic acid. It is well known that the asymmetric diesters of H-phosphonic acid undergoes disproportionation to symmetric diesters (27).

Obviously, the formation of product **1c** can be explained with the assumption that at the reaction conditions there proceeds disproportionation of **1a** to DMP and **1c**. The data from the $^{31}$P-NMR studies revealed that only product **1a** undergoes disproportionation. If **1b** undergoes disproportionation in the $^{31}$P-NMR spectrum of the reaction mixture a doublet of triplets will appear, but in the $^{31}$P-NMR spectrum of the reaction mixture there is no doublet of triplets.

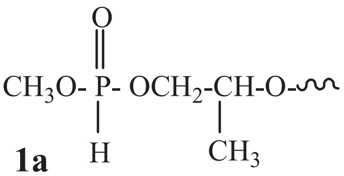
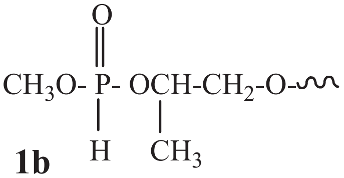
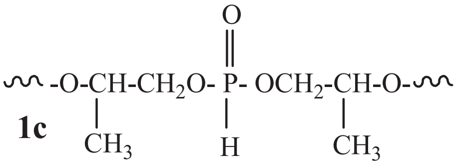
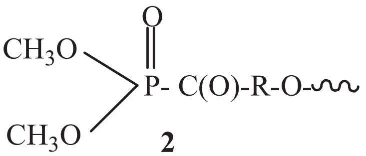


**1b**

**1d**

**DMP**

**Table 1.** Phosphorus containing products from the chemical degradation of flexible polyether polyurethane foam by dimethyl H-phosphonate without and in the presence of 0.5% K-*t*-butoxide

| *N Structure* | $^{31}$*P NMR δ, ppm; J, Hz* | *Content, %* (Without cat./K-*t*-butoxide) Upper layer | Lower layer |
|---|---|---|---|
|  $\mathrm{CH_3O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}\text{-}OCH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}O\text{-}}\sim$ **1a** | 9.39, dsextets $^3$J(P,H)=11.4 $^1$J(P,H)=693.5 | 6.21/18.08 | <1 |
|  $\mathrm{CH_3O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}\text{-}O\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\text{-}O\text{-}}\sim$ **1b** | 10.61, dquintets $^3$J(P,H)=11.86 $^1$J(P,H)=708.5 | 5.14/12.93 | <1 |
|  $\sim\mathrm{\text{-}O\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}\text{-}OCH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}O\text{-}}\sim$ **1c** | 10.14, dquintets $^3$J(P.H)=10.11 $^1$J(P,H)=715.0 | 7.89/10.74 | <1 |
|  **2** | 8.38, septet $^3$J(P,H)=11.10 | 0.8/0.0 | 4.1 |

This can be explained by the fact that the disproportion has been shown to be reversible (28, 29). It can be accepted that this equilibrium is shifted to the asymmetric diesters **1b,** that's why there is no doublet of triplets in the $^{31}$P-NMR spectrum of the reaction mixture.

Based on the data from $^{31}$P-NMR studies, we accept that the radical degradation of PU in the presence of dimethyl H-phosphonate proceeds via reaction scheme 2.

The initial step of the free radical reaction is the AIBN or thermal-induced generation of phosphonyl radical (Sch. 2). The interaction of phosphonyl radical with PU resulted in the formation of product **2** and radical **3**. Radical **3** abstracts the hydrogen from the P-H group of dimethyl H-phosphonate to form phosphonyl radical (30) and amino-containing oligomer which reacts with dimethyl H-phosphonate to form salt **4** (29). The data from the $^{31}$P-NMR spectroscopy of the bottom layer confirm the formation of product **4**. The signal of the phosphorus atom at 7.59 ppm represents a doublet of quartets with $^1$J(P,H) = 657.4 Hz, characteristic for such ionic structures (31). The signal for the phosphorus atom in $^{31}$P-NMR spectrum of the product **2** represents a septet. The data from the $^{31}$P-NMR spectroscopy showed that the content of product **2** is lower- 4.1%.

The molecular weight of the PU decreases with increasing the reaction time in the result of the exchange reaction which takes place between methoxy groups of dimethyl H-phosphonate and urethane groups, pathway A, and radical degradation, pathway B. As an example, the evolution of molecular weight of the glycolisis products in the experiments using K tert-butoxide, AIBN and without catalyst are shown in Figure 2.

The first soluble oligomers in THF are the trimer molecules of the original polyol with a Mw around 10000. In the case of K tert-butoxide, the kinetic of the process is faster than in the other cases and Mws greater than 7000

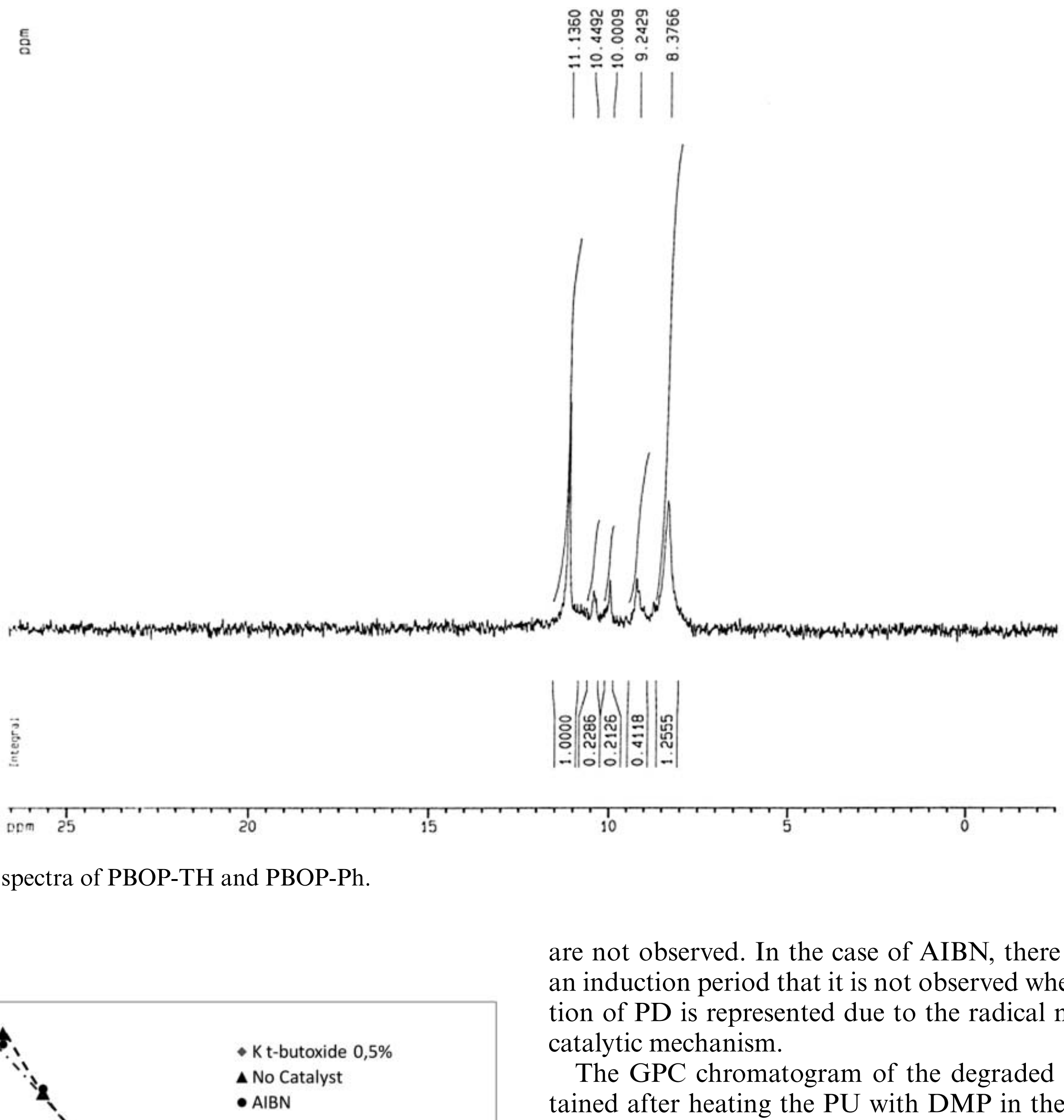


**Fig. 1.** FTIR spectra of PBOP-TH and PBOP-Ph.

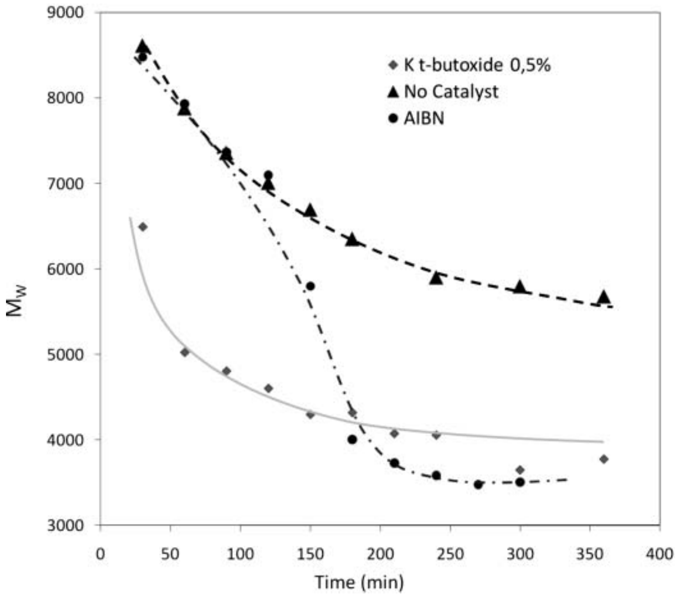


**Fig. 2.** Evolution of the Mw of the products in the upper phase during the glycolysis reaction of PU foams for different catalysts in presence of DEP as glycolysis agent. Tr = 160°C; $W_{DMP} = 12$ g; $W_{PU} = 4$ g; Cat: K-*t*-butoxide 0.5%, AIBN 1%.

are not observed. In the case of AIBN, there seems to be an induction period that it is not observed when the evolution of PD is represented due to the radical nature of the catalytic mechanism.

The GPC chromatogram of the degraded product obtained after heating the PU with DMP in the presence of 0.5% of K tert-butoxide revealed that the reaction product is composed of a mixture of products with two main components, whose molecular weights are 3458 Da and 6955 Da, respectively (Fig. 3).

The product with molecular weight 3458 Da obviously corresponds with recovered polyol-products**1a** and **1b** (Sch. 1), while the product with molecular weight 6955 Da can be assigned to the product **1c** (Sch. 1) which represents dimmers. The data from the GPC analysis (Fig. 1) confirms the data from the $^{31}$P-NMR spectroscopy (Table 1). According to the $^{31}$P-NMR spectroscopy (Table 1), the reaction mixture includes recovered polyol - products **1a** and**1b** and dimmer - products **1c**. These products according to the GPC analysis have molecular weights 3458 and 6955 Da, respectively.

As the degradation of PU network with DMP advances, the observed Mw of the polymer decreases and the PD of the resulting products does as well. In general, it was observed that although the advance of the reaction could

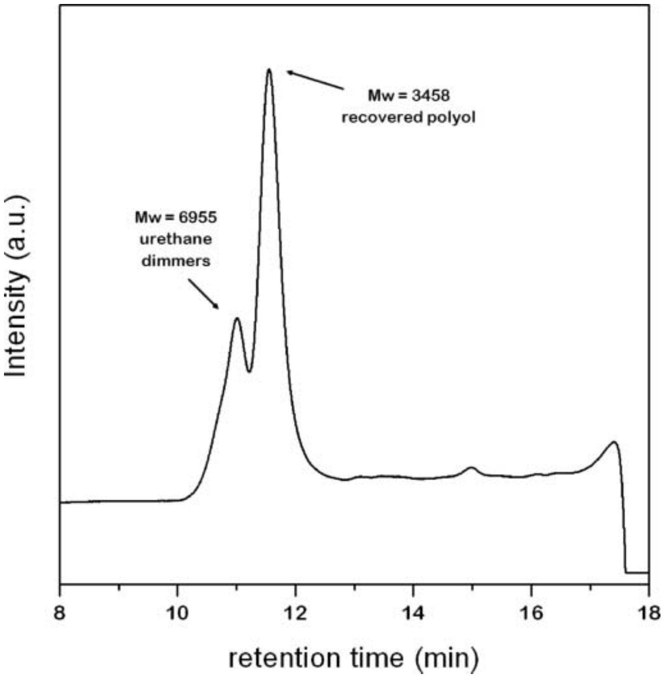


**Fig. 3.** GPC chromatogram of degradation products (polyol phase-upper phase) Reaction time: 240 min. Catalyst: K *tert*-butoxide 0.5% by weight of PU. Tr = 160°C; $W_{DMP} = 12$ g; $W_{PU} = 4$ g; Cat: K-*t*-butoxide 0.5%.

be followed by the molecular weight, it was easier to understand following the variation of polydispersity whose evolution was more stable and predictable. Therefore, the degradation progress was monitored using the polydispersity (PD) of the reaction products. The PD value of the recovered products will decrease with the increase of the reaction time reaching finally that value of the raw polyol (1.06), which is the typical value that exhibits the original commercial polyol (Mw = 3500, PD = 1.06).

After heating for 90 min in the presence of 0.5 and 1.0% of potassium *tert*-butoxide, the PD values of the reaction products are 1.35 and 1.33, respectively, while for the non-catalyzed process, the PD is 1.44 (Fig. 4).

Obviously, potassium *tert*-butoxide enhances interchange reactions. The PD values of the reaction products obtained in the presence of catalyst are lower compared to the non-catalyzed experiment. The experimental results showed that after 120 min, heating PD of the products obtained in the presence and without catalyst are the same 1.33. This fact can be explained taking into account that the catalyst can suffer a thermal degradation process. At elevated temperatures (above 160°C), dimethyl H-phosphonate undergoes thermal decomposition to monomethyl H-phosphonate and dimethyl methylphosphonate (32, 33).

$$(CH_3O)_2P(O)H \xrightarrow{\Delta} CH_3OP(O)(OH)H + (CH_3O)_2P(O)CH_3$$

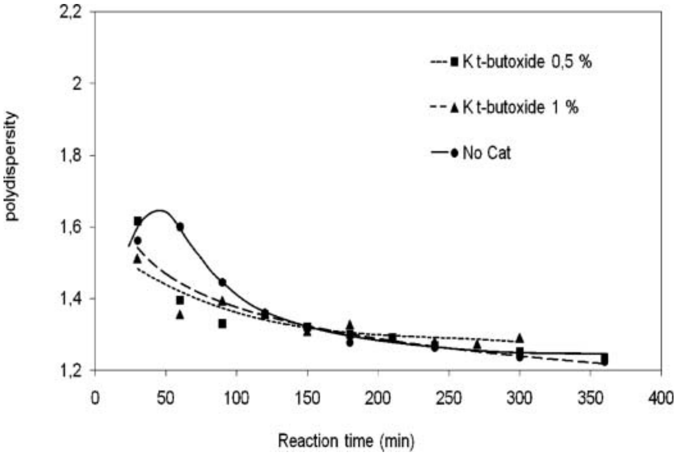


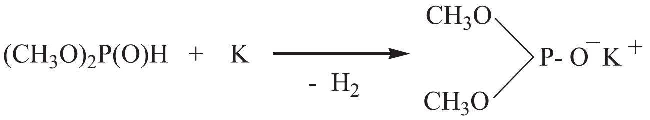
**Fig. 4.** Polydispersity of degradation products by DMP (oligourethanes and polyol) as a function of reaction time in dependence of potassium *t*-butoxide concentration. Tr = 160°C; $W_{DMP} = 12$ g; $W_{PU} = 4$ g; Cat: K-*t*-butoxide.

So, formed monomethyl H-phosphonate reacts with potassium *t*-butoxide to form potassium salt of monomethyl H-phosphonate and *t*-butanol:

$$CH_3OP(O)(H)OH + t = C_4H_9OK \longrightarrow CH_3OP(O)(H)OK + t = C_4H_9OH$$

Proceeding with this reaction resulted in inactivation of the catalyst. The results obtained revealed that the decrease of PD of the reaction products from 150 min to 300 min, heating is rather small from 1.33 to 1.27. Taking into account the evolution of Mw and the PD value of the reaction products, the time required for the complete degradation of the PU matrix can be esstablished. In the case of the non-catalyzed process, the time required is more than 300 min, while for the catalyzed process, the reaction time required for the complete degradation is about 200 min.

In the case of using potassium instead of K t-butoxide at the first stage, interaction between dimethyl H-phosphonate and potassium continues.



$$(CH_3O)_2P(O)H + K \xrightarrow[- H_2]{} \begin{matrix} CH_3O \\ CH_3O \end{matrix}\!\!>\!P\text{-}\,\bar{O}\,K^+$$

Experimental results showed that potassium salt of dimethyl phosphite (tri-coordinate, trivalent form) exhibits no catalytic activity (Fig. 5). Up to 100 min of heating the polydispersity is higher compared to the non-catalyzed process. Obviously, potassium salt of dimethyl phosphite suppresses the exchange reactions. The reaction product still contains non-degraded polyurethane pieces.

In the case of using AIBN as catalyst, data from $^{31}$P-NMR spectroscopy revealed that the contribution of the radical processes in the degradation of PU with dimethyl H-phosphonate in the presence of AIBN is not important because the content of product **2** is only 4% and the Mw

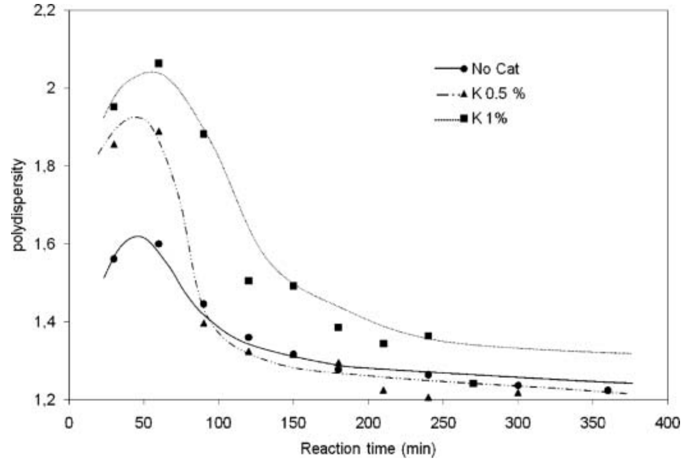


**Fig. 5.** Polydispersity of degradation products by DMP (oligourethanes and polyol) as a function of reaction time in dependence of potassium concentration. Tr = 160°C; $W_{DMP}$ = 12 g; $W_{PU}$ = 4 g; Cat: K.

and the PD of the product obtained with it is quite similar to that obtained with the other catalysts, Figures 2 and 6.

The decrease of the Mw and PD of the reaction products in the case of using AIBN follows a sinusoidal profile quite different from that of the other catalysts with exponential decay profile. This fact could be explained on the basis of an induction period for AIBN that takes about 17min in the absence of tin (II) octoate (SnOc2), whereas it takes only 8 min for the binary system [SnOc2)]/[AIBN]=1, as was observed by Widmaier et al. (34). In this way, it is possible that at this reaction condition, AIBN interacts with the tin (II) octoate that was employed as a catalyst of the polymer network formation (35). The fact that final Mw and PD of the glycolisis product was the same in the case of AIBN and K t-butoxide can be also explained taking into account that the same authors also found that with the exception of the induction period, the kinetics of decomposition of AIBN are not influenced by the presence of SnOc2. Summarizing the radical processes which take place during the heating of PU with dimethyl H-phosphonate are mostly thermal-induced but can also be influenced by the presence of the SnOc2 in the media.

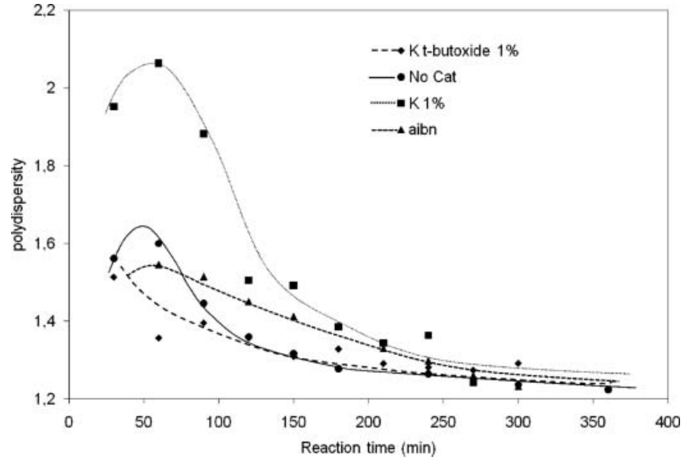


**Fig. 6.** Polydispersity of degradation products by DMP as function of reaction time. Tr = 160°C; $W_{DMP}$ = 12 g; $W_{PU}$ = 4 g; Cat: K-*t*-butoxide, K, AIBN 1%.

## 4 Conclusions

It has been shown that potassium t-butoxide can be used as a catalyst for the degradation of flexible polyether polyurethane foam with dimethyl H-phosphonate. The products obtained are the raw polyol with end phosphonate group and a phosphorus-containing dimmer of the original polyol. The degraded polyol with end phosphonate group undergoes a disproportionation to phosphorus-containing dimmer of the virgin polyol.

Although the degradation process with DMP can be carried out in absence of catalyst, the glycolisis process is greatly enhanced by the presence of catalyst in the media. K t-butoxide is the most active catalyst of the assayed. Using K t-butoxide or AIBN, a complete degradation of the polymer network is accomplished in about 200 min.

The degradation follows different mechanisms depending on the type of catalyst that have been coherently confirmed considering the type of products identified with $^{31}$P-NMR spectra.

## Acknowledgments

Financial support from REPSOL-YPF SA through the General Foundation of the UCLM University and the CICYT project CTQ2005–07315PPQ and a Jose Castillejo grant of JCCM for mobility are gratefully acknowledged.

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