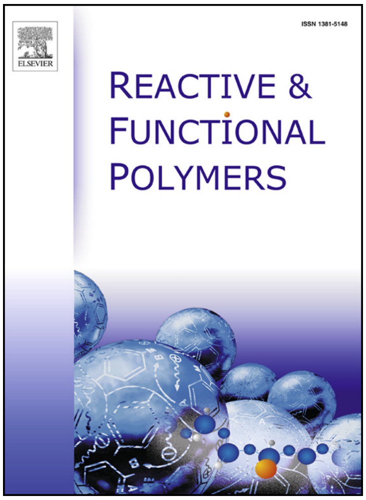

A novel click-chemistry approach to flame retardant polyurethanes

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A novel click-chemistry approach to flame retardant polyurethanes

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ABSTRACT

The low thermo-oxidative properties of PU foams somewhat limits their practical application, particularly as heat sensitive materials. The introduction of a covalently linked flame retardant organophosphonate ester into the PU foam was achieved using the CuAAC 'click' reaction of an alkyne-polyol and azidoalkylmonophosphonate. These functionalised materials were prepared in four steps: first, a number azidoalkyl monophosphonate compounds were formed *via* nucleophilic substitution of bromoalkylphosphonates with NaN_3; next, polyols bearing terminal alkyne groups were prepared by anionic ring opening copolymerization between propylene oxide and glycidyl propargyl ether; followed by 'clicking' the azidoalkylphosphonate to the polyol and finally, synthesis of the PU foam with 2.4wt% of "click-polyol". The functionalised PU foam demonstrated a well-formed polyhedral cell structure and an increase in the fire resistance, according to the SEM and thermogravimetric analysis, respectively. Even after thermal treatment at 400 ºC, the new PU foam material displayed enhanced flame resistant properties by forming a char layer on the surface of the polymer, which, maintaining its polyhedral structure.

Keywords: polyurethane, polyol, click reaction, flame retardant, phosphorus.

1. INTRODUCTION

The unique structural and mechanical properties of polyurethane (PU) polymers have led to their wide-spread application in material products such as: building insulation, domestic mattresses, furniture, sealants, adhesives, leathers and various biomedical products [1]. However, the low thermo-oxidative properties of PU-foams present a serious draw-back, since these materials are readily flammable unless treated. To this end, various modifications of PU foams have been introduced to improve their flame resistance properties including: chemical modification of the surface and core of the polymers, or more commonly, inclusion of an additive. For example, nitrogen and phosphorus bearing compounds as in the phosphazine polymer [2,3], halogen-laced substrates as radical quenchers [4], minerals such as aluminum trihydroxide, magnesium hydroxide [4] or melamine derivatives [6] are just a few of the routinely used additives.

Unfortunately, the compromise of structural and mechanical properties [1-7] associated with most modification techniques, as well as the environmental and human health hazards associated with bio-accumulation of halogenated additives, warrants the development of new strategies.

Stabilised and erosion resistant PU materials can be achieved by the covalent modification of the polymer back-bone with a suitable auxiliary. This approach has several advantages over conventional flame retardant PU foam materials, , allowing lower concentrations of the additive to be employed, with better mechanical properties and resistance to leaching [8].

Organophosphonate esters are routinely employed as flame retardant additives owing to their low toxicity and almost smoke-free burning. They are generally used in combination with radical quenchers such as bromine or along with other phosphorous and nitrogen based polymers (e.g. phosphazine) [8,9]. However, though the use of phosphonate esters as flame retardants is widespread, few methods are reported for their robust and reliable incorporation into PU foams [10].

Here we report the development of a new class of organophosphonate ester functionalised PU-foam with flame retardant properties. The key to our approach was the use of the copper catalysed azide-alkyne cycloaddition (CuAAC) reaction [11], or 'click'-reaction for covalently introducing the organophosphonate into the PU-foam [12-24].

In our design, we reasoned that in addition to the phosphorus functionality, the presence of nitrogen in the triazole group could further improve the flame retardant properties to the PU-foams. At elevated temperature the decomposition of triazole could technically provide a blanket of nitrogen [25].

We have previously demonstrated the successful generation of alkyne-decorated polyols (**5**), by anionic ring opening of propylene oxide (**3**) and glycidylpropargyl ether (**4**), along with their copolymerization (Scheme 1) [26]. It was anticipated that these alkyne-polyols would readily 'click' to an azide bearing organophosphonate compound using the Cu(I) catalysed process.

2. EXPERIMENTAL

2.1. Materials

Sodium azide (>99.5%, Fischer Scientific), 1,3-dibromopropane (98%, Acros Organics), 1,5-dirbomopentane (98%, Alfa Aesar), 1,10-dibromodecane (>97%, Sigma-Aldrich), 1,4-bis(bromomethyl)benzene (>98%, Alfa Aesar), acetone (reagent grade, Fischer Chemical). Copper (II) sulfate pentahydrate (>99.5%, PANREAC), sodium ascorbate (>99%, PANREAC), tetrahydrofuran (THF) (reagent grade, Fischer Chemical), ethanol (96%, Sigma-Aldrich), ethyl acetate (EtAc) (reagent grade, Fischer Chemical), dichloromethame (DCM) (reagent grade, Fischer Chemical), deionised water, diethyl ether (>99.8 %, Sigma Aldrich).

Glycerol (≥ 86%, Sigma-Aldrich), potassium hydroxide (KOH) (85%, PANREAC), propylene oxide (OP) (100%, PRAXAIR) and glycidyl propargyl ether (GPE) (>90%, Sigma-Aldrich) were used in the synthesis of the polyol as received. Methanol according to Karl Fischer (99.5%, PANREAC) and ion exchange resin Amberlite 252 (Rohm and Hass) were used for catalyst removal from the "click polyols".

For the PU foams synthesis, Alcupol R-458 from Repsol YPF S.A. and the synthesised click polyol were used. As isocyanate, diphenylmethane-4,4'-diisocyanate (MDI), supplied by Merck Group, was used. Catalyst Tegoamin ZEI and surfactant Tegostab B8404 were supplied by Evonik Degussa International AG. Deionised water was used as blowing agent.

2.2. Physico-chemical characterisation

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV400 or Bruker DPX400 (400 MHz for ^{1}H and 100 for ^{13}C). Fourier Transform Infrared (FT-IR) spectra were obtained on Bruker Tensor 27 spectrometer as a solution in chloroform. Thermogravimetric analyses (TGA) were performed in TA Instruments SDT Q600 Simultaneous DSC-TGA at a heating rate of 10 ºC min^{-1} under nitrogen atmosphere from room temperature to 700 ºC. Synthesised PU foams were depicted by scanning electron microscope (SEM, Quanta, FEI Company) in order to observe the possible changes in their cellular structure when the 'click' polyol was added in the recipe, using a large field detector (LFD) with an accelerating voltage of 10 kV and with magnification x 100. Heat treatment of the PU foams samples was carried out in a muffle type furnace at 400 ºC for 15 minutes for further analysis of their char residues, observing their structure by SEM analysis.

2.3. Synthesis of the diethyl azidoalkylphosphonates

The synthesis of the diethyl azidoalkylphosphonates was carried according to Scheme 2. The azidophosphonate compounds **8a-c** was synthesised using Michaelis-Arbuzov conditions [27]. Thus, the commercially available dibromo-alkanes (**6a-c**) were readily transformed into the corresponding phosphonate compounds **7a-c** in the presence of triethylphosphite under elevated temperature and further purified by means of flash silica gel chromatography (CH_2Cl_2) [28]. Nucleophilic substitution of the remaining bromo-group with sodium azide rendered the azidoalkylphosphonates **8a-c** in good to excellent yields (Scheme 3). The azioalkylphosphonate products were separated from the excess of azide by cooling the suspension, filtering and evaporating the solvent under vacuum.

2.4. Synthesis of diethyl-4-(azidomethyl)benzylphosphonate

The synthesis of the diethyl-4-(azidomethyl)benzylphosphonate was carried out according to Scheme 3.

The procedure to obtain diethyl-4-(bromomethyl)benzylphosphonate (**10**) was similar to that explained above for the diethylbromoalkylphosphonates. Next, the resulting diethyl-4-(bromomethyl)benzylphosphonate (1.0 equiv), *N*,*N*'-dimethylethylenediamine (0.15 equiv), CuI (0.1 equiv) and sodium ascorbate (0.5 equiv) were added to a mixture of EtOH/H_2O [70/30]. The reaction flask was flushed with argon, NaN_3 added, and the reaction mixture was heated to reflux for 3h [29]. The product was obtained by removing the volatiles from the reaction mixture *in vacua*, extracting the 4-azidobenzylphosphonate (**11**) with ethyl acetate, extracting the organic layer with water and drying the organic layer over anhydrous $MgSO_4$, filtration and removing the solvent *in vacua* Finally, the product was purified by flash silica gel column chromatography (CH_2Cl_2/EtAc, 10:1).

2.5. Click reaction

With the alkyne-decorated polyol (**5**) and azidophosphonate compounds (**8a-c, 11**) in hand, the key 'click' reaction to render the triazole-polyols (phos-triz-polyol) were performed. A solution of the respective azidophosphonate (1 equiv) and the alkyne-polyether polyol (1 equiv of alkyne groups) in THF:Ethanol:H_2O [1:2:2] were taken in a round bottom flask [30]. Then, the catalyst mixtuire, copper sulphate pentahydrate (0.01 equiv) in water and sodium ascorbate (0.1 equiv) in water were added [31]. The reaction mixture was stirred under microwave irradiation for 1 h at 75 ºC (Scheme 4).

The synthesised phos-triz-polyol and the ion exchange resin Amberlite 252 were stirred together at 100 ºC in order to eliminate the remaining catalyst [32].

2.6. Polyurethane foam synthesis

One of the functionalised phos-triz-polyol (**12b,** 5C-phos-triz-polyol) was next used as reagent in the synthesis of PU foams in order to check the feasibility of using these functionalized polyols as PU foams raw material. PU foams were synthesised by mixing the required masses of the 5C-phos-triz-polyol and a commercial polyol (Alcupol R-458), silicone Tegostab B8404, deionised water and amine Tegoamin ZEI and further stirring the mixture for 1 min. Next, an adequate quantity of isocyanate was added to the mixture and the resulting solution was stirred for just 5 seconds, moment at which the foam started to grow up. Finally, the obtained foams were cured at room temperature. Table 1 shows the foam synthesis recipe.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the foam material

The syntheses of all the flame retardant components were achieved as described and the strucutres confirmed using complementary spectroscopic techniques. The presence of azide clearly apparent by the characteristic peaks at 2100 cm^{-1} in the IR.. The yields of the products obtained are shown in Table 2, with poorer conversions achieved with increase in hydrocarbon chain complexity. To the best of our knowledge, the synthesis of these compounds has not previously been reported.

3.2. Click reaction

The 'click' reaction was followed by IR and monitoring the decrease in azide peak (at 2100 cm^{-1}) [21,33,34]. The corresponding flame retardant monomer was confirmed by ^1H NMR analysis in D_2O, observing the triazole peak at 8.3 ppm (Figure 1) [21,34].

3.3. Synthesis of PU foams

The addition of small amounts of phosphorous (1.0 wt%) into rigid polyurethane foams produce an important improvement of the foams fire resistance [35]. In the present work a 2.4 wt% of the functionalised 5C-phos-triz-polyol (**12b**) was incorporated in PU foam during its formation (phos-triz-PU). For comparative purposes, a PU foam was prepared without any covalent fire retardant.

Figures 2a and 2b show the cell structure of the pure PU and the phos-triz-PU foams, respectively. Both materials exhibited polyhedral closed-cell structures with pentagonal or hexagonal faces containing nodes formed by the junction of four struts, but with higher sizes when adding the 5C-phos-triz-polyol. The increase in cell size can be attributed to the larger volume of the 5C-phos-triz-polyol due to the pendant triazole groups with the flame retardant compounds or because of the modification in recipe for PU formation. It is known that unadjusted foam formulation can modify the nucleation rate and the final cell size [36].

To test the improvement in the fire resistance of the phos-triz-PU foam compared to the pure-PU, thermo gravimetric analyses (TGA) and thermal treatment in furnace were performed. The flame retardant property of polymer is directly related the char formation during the combustion process [37-39] and, the char percentage measured by TGA is accepted as an indirect way of measuring this property [8,40].

Figure 3 compares the TG and DTG analyses of pure-PU and phos-triz-PU foams. The thermal degradation of both samples took place in two main steps, the first one is attributed to the crosslinked polymer degradation including its hard and soft segments and the second is due to the stabilized structures that can be formed during the previous degradation processes [8,41]. It can be observed that just a small addition of flame retardant reduced the temperature at which the maximum degradation occurred from 340 ºC to 324 ºC (Figure 3b) but increased the char yield an 18.2%, from 10.9 wt% to 12.9 wt% (Figure 3a), which confirms the enhancement of the fire resistance.

On the other hand, naked eye visualisation of photos of the char residues for the pure-PU and phos-triz-PU foams after the thermal treatment in the furnace under 400 ºC in air, showed black and brown porous solids for the pure-PU and the phos-triz-PU, respectively (see Figures 4a and 4b). It was clear that the phos-triz-PU foam char residue was covered by a black and bright char layer (See Figures 4c and 4d) whereas no such appearance was recorded for pure-PU.

SEM analyses of these char residues showed that the cell structure of the pure-PU foam was quite degraded, without a defined cell structure (Figure 5a), while the char of the click-PU foam conserved a well defined cell structure with pentagonal or hexagonal faces (Figure 5b). Hence, it can be concluded that the covering char layer acted as protecting barrier, hampering the mass and heat transfer during the combustion [40].

4. CONCLUSIONS

Different diethyl azidoalkylphosphonates and the diethyl 4-(azidomethyl)benzylphosphonate were successfully synthesized via a Michaelis-Arbuzov reaction and linked to polyols containing terminal alkyne groups via Cu(I)-catalysed Huisgen 1,3-dipolar cycloaddition. The functionalized polyol containing the (5-azidopentyl) phosphonate was used as raw material for a PU foam synthesis (phos-triz-PU foam). The phos-triz-PU foam showed an improved flame resistance property when compared to pure-PU. TGA results showed that the addition of a small percentage of phos-triz-polyol (2.4 wt%) increases an 18.4% in the char layer residue. Finally, the residues obtained by firing the foams in a furnace allowed to conclude that the resistance enhancement of the click PU foam was achieved by the formation of a char layer that covered the rest of the PU foam, and prevented its degradation. Therefore, the present design of flame retardant based on robust, easy to perform and reliable click chemistry technology could be a real advancement in the field of polyurethane foams synthesis with flame retardant properties.

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FIGURE CAPTIONS

Figure 1. ^{1}H NMR analyses in D_2O of the phos-triz-polyols derived from diethyl (3-azidopropyl) phosphonate (a), diethyl (5-azidopropyl) phosphonate (b), diethyl (10-azidopropyl) phosphonate (c) and diethyl 4-azidobenzylphosphonate (d).

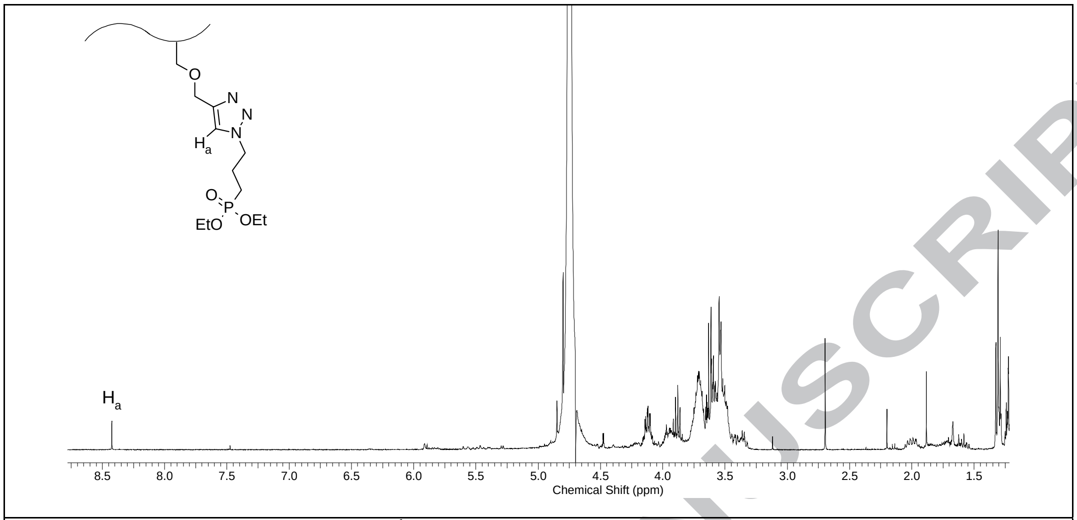
Figure 2. SEM analysis of pure-PU (a) and phos-triz-PU (b) foams.

Figure 3. TG (a) and DTG (b) analyses of the pure-PU and the phos-triz-PU foams.

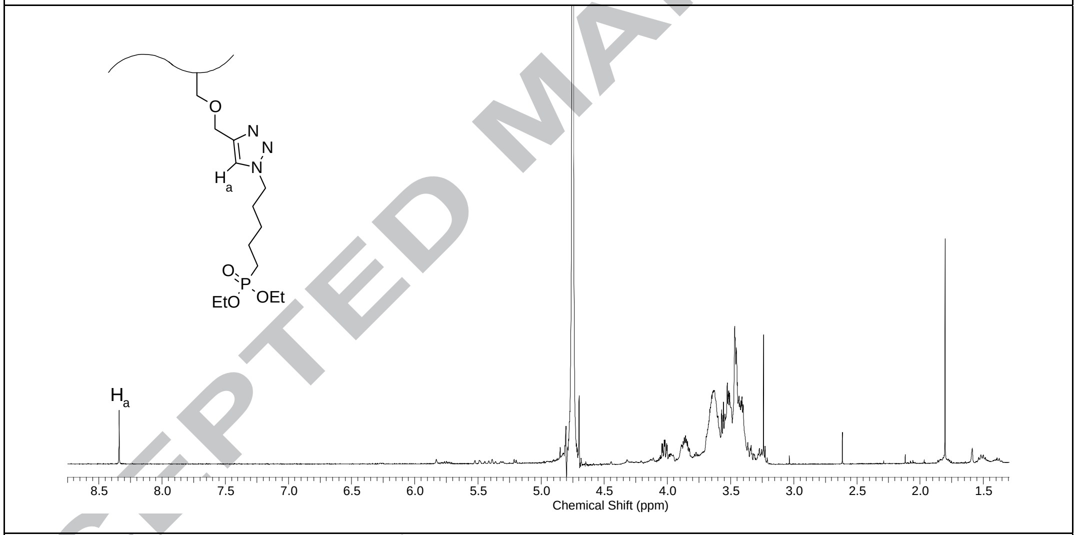
Figure 4. Photos of the char residues of: pure-PU; b) phos-triz-PU; c) phos-triz-PU (covering layer, front view); d) phos-triz-PU (covering layer, side view).

Figure 5. SEM analysis of PU foams char residues of pure-PU (a) and phos-triz-PU (b) foams.

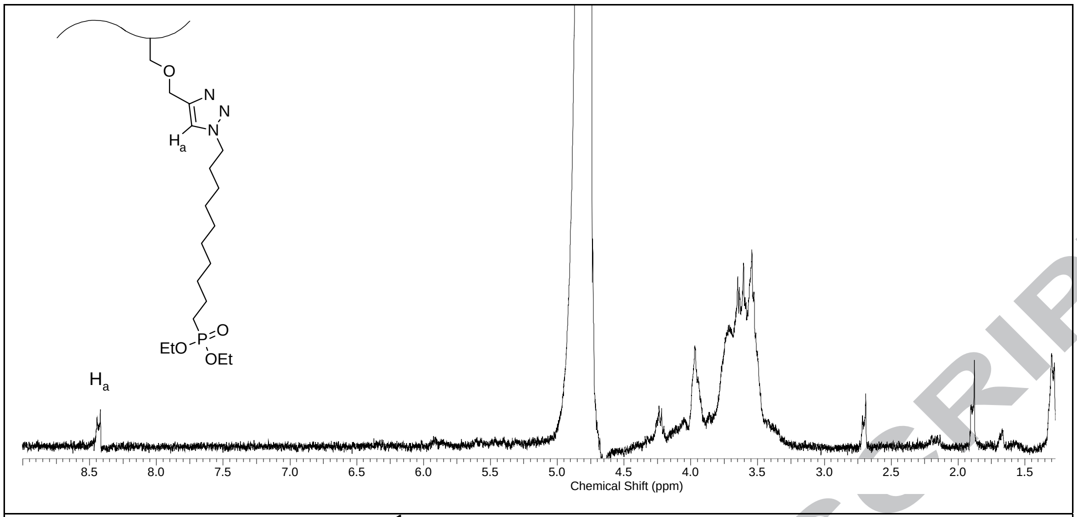
FIGURES



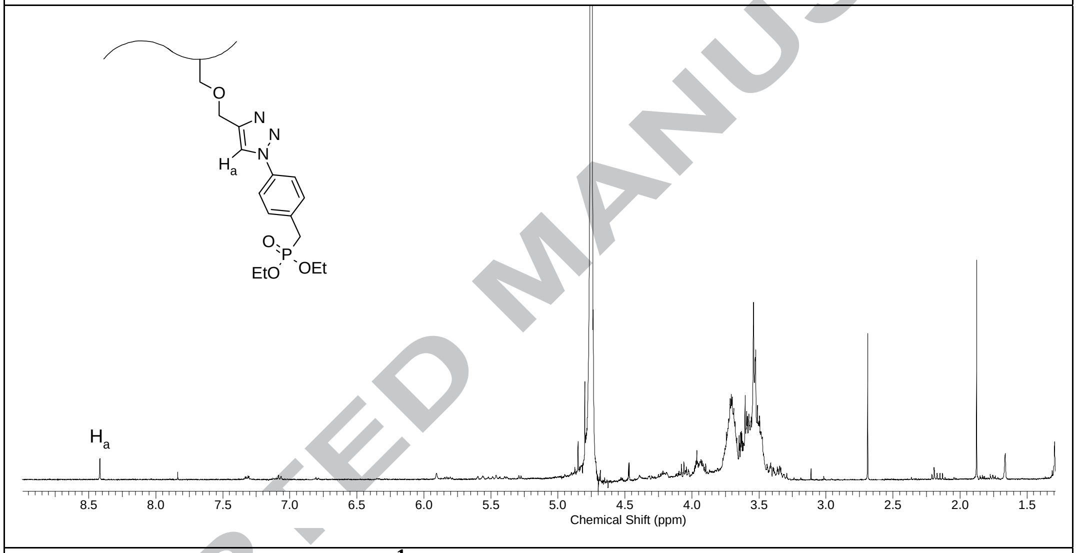
a) ^{1}H NMR (400 MHz, D_2O)



b) ^{1}H NMR (400 MHz, D_2O)

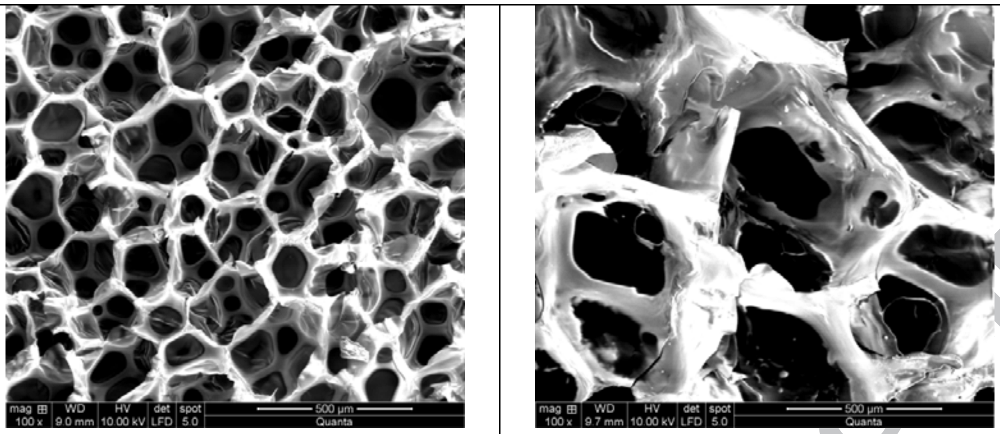


c) ^{1}H NMR (400 MHz, D_2O)



d) ^{1}H NMR (400 MHz, D_2O)

FIGURE 1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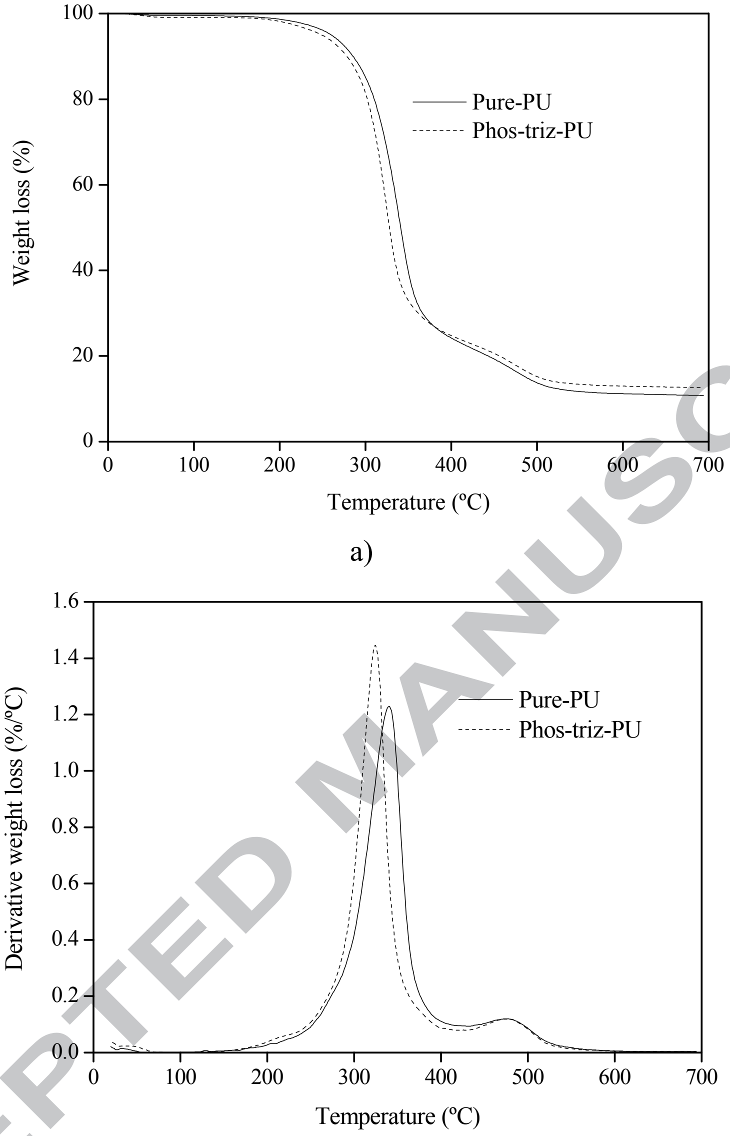
spot 5.0
500 µm
Quanta

a) b)

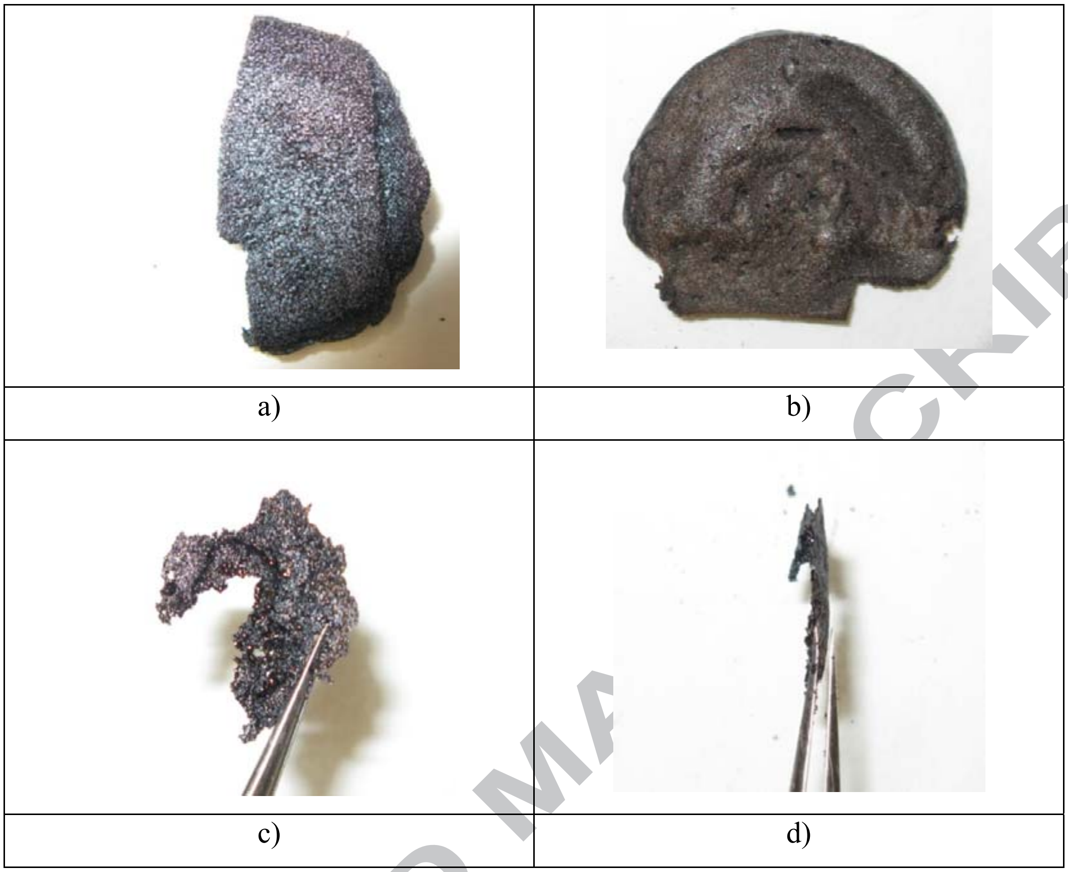
FIGURE 2


100
80
60
40
20
0
Weight loss (%)
0
100
200
300
400
500
600
700
Temperature (ºC)
Pure-PU
Phos-triz-PU
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Derivative weight loss (%/ºC)
Temperature (ºC)
Pure-PU
Phos-triz-PU

a)

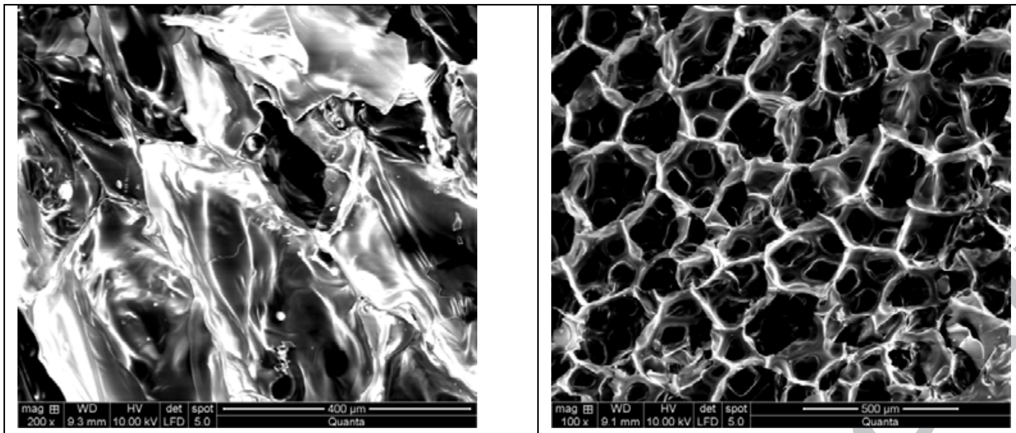
b)

FIGURE 3



a) b) c) d)

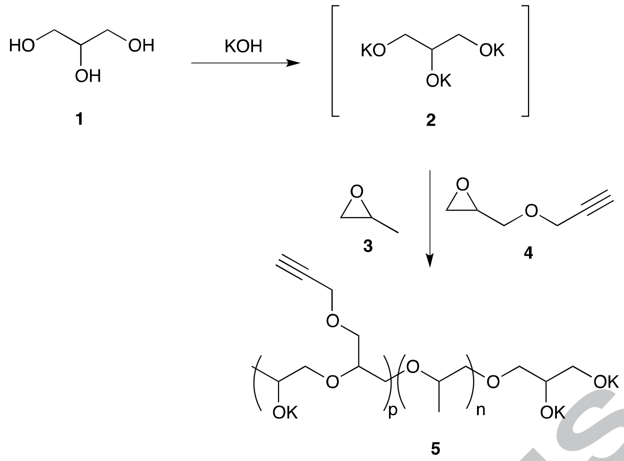
FIGURE 4


mag
200 x
WD
9.3 mm
HV
10.00 kV
det
LFD
spot
5.0
400 μm
Quanta
mag
100 x
WD
9.1 mm
HV
10.00 kV
det
LFD
spot
5.0
500 μm
Quanta

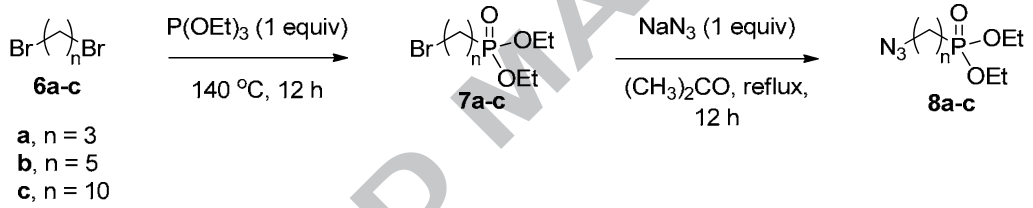
a) b)

FIGURE 5

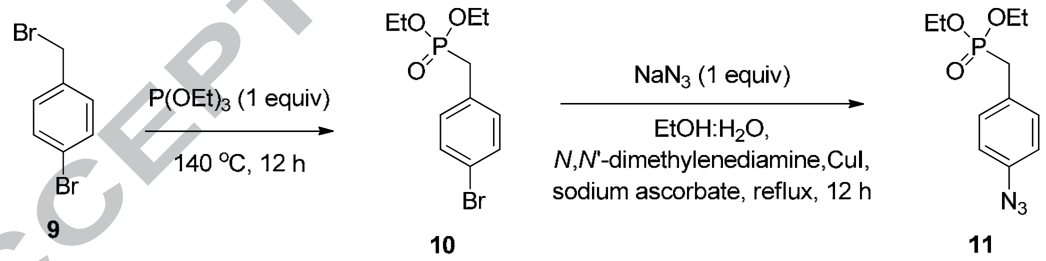
SCHEMES



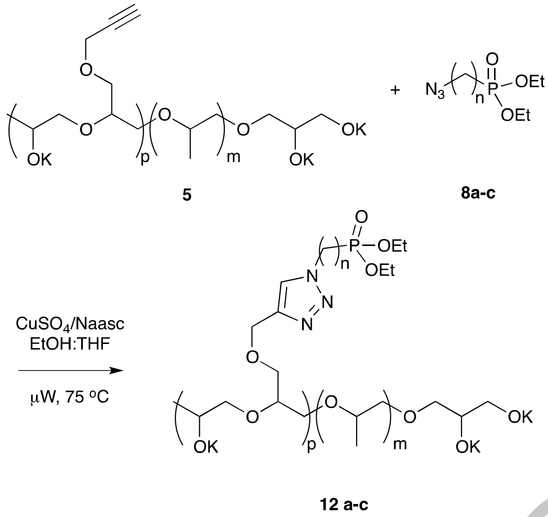
Scheme 1. Anionic ring opening copolymerisation between propylene oxide and glycidylpropargyl ether



Scheme 2. Synthesis of diethyl azioalkylphosphonates



Scheme 3. Synthesis of diethyl 4-(azidomethyl)benzylphosphonate.



Scheme 4. Synthesis of the phos-triz-polyols.

TABLES

Table 1. Weight percentage of raw materials for PU foams synthesis.

Material	Weight percentage
Alcupol R-458	46.01
5C-phos-triz-polyol	2.42
Water	1.21
Silicone	0.73
Amine	1.21
MDI	48.43

Table 2. Yields of the flame retardant synthesis reactions.

Flame retardant	Yield (%)
Diethyl (3-azidopropyl) phosphonate	90.4
Diethyl (5-azidopentyl) phosphonate	85.0
Diethyl (10-azidodecanyl) phosphonate	46.6
Diethyl 4-(azidomethyl)benzylphosphonate	36.1