



Synthesis and performance of organophosphorus fire retardants from the reaction of trimethylolpropane and dimethyl methylphosphonate

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Abstract. Organophosphorus fire retardants were synthesised from transesterification reaction of a bicyclic phosphite and dimethylmethyl phosphonate. Different reaction times were tested with the aim to reduce duration of the reactions. It was observed that 11 hours of heating at 200°C was enough for reaction completion, in contrast to previous studies where heating was performed for 24 hours at the same temperatures. Differential scanning calorimetry studies were performed and relevant thermal changes were identified. Infrared spectra were also registered and compared for the obtained substances. Finally, fire retardancy of oligomer phosphonates synthesised was verified testing polyurethane treated samples.

Keywords: Fire retardants, oligomeric phosphonates, propylene oxide, differential scanning calorimetry, infrared spectroscopy

1. Introduction

In 2005, flame retardant (FR) chemical market sales was estimated to be \$3,500 million worldwide. This figure reached \$4.600 million by the year 2010, representing an average annual growth rate of 5.6% [1]. Phosphorus-based FRs can be subdivided into phosphates, phosphoniums, alkyl phosphonates and dialkylphosphinates. Some of the most utilized FR for textiles are dimethyl phosphonopropionamide and tetrakis hydroxymethyl phosphonium chloride or sulphate. At the cheaper

end of the phosphorus flame retardants, ammonium phosphates and ammonium polyphosphates are employed for less demanding applications in cellulose and cellulosic-rich fabrics [2].

The first commercial product trade names for cyclic alkylphosphonates were Antiblaze 19, Antiblaze 1045, and Amgard CU, which are made through an intermediate toxic phosphite and then a Michaelis Arbusov reaction with dimethylmethyl phosphonate (DMMP), except for 1045, which is made by direct transesterification [3]. In particular, a number of phosphonates with flame retardant properties have been described in the literature, including vinyl and diene phosphonates [4] and monomeric cyclic phosphonate for cotton and polypropylene [5]. Although claimed high toxicity of the reaction intermediate bicyclic phosphite has been early reported [6, 7] and procedures for the synthesis of oligomer phosphonates have been patented in the seventies, research has been continued, as these products proved still to be useful. These are categorized among novel FRs, which replace old ones such as brominated or halogenated salts, due to environmental concerns. Permanence of FR in test pieces has been studied to determine how many laundering cycles it can resist without losing fire retardancy. In that sense, many fixation systems have been developed by many authors for synthetic/cotton blends [8, 9].

In this work we have synthesized a fire retardant for textiles by reaction of trimethylolpropane (TMP_r) and trimethyl phosphite (TMP) or phosphorus trichloride at high temperatures and long reaction time, following an esterification with dimethyl methylphosphonate. The final products proved to confer flame retardancy to cotton fabric test pieces. This characteristic is associated with six membered cyclic moieties containing phosphorus [10]. Additionally, fire retardancy of synthesized fire retardant was tested in polyurethane foams to check its effectiveness. Cyclic phosphonate compounds are believed to work in the vapour phase rather than the condensed phase. Most literature citations, however, are focused on their effectiveness in the condensed phase [16]. Flame retardancy needs a catalyst, a charring and a blowing agent. In case of polyurethane foams, the charring agent is the polymer itself [17]. Although cyclic phosphonates are proven fire retardant additives, it is necessary to bear in mind that fire retardancy depends on applied heat. For many polymers, the retardant effect is entirely removed at high heat fluxes [18].

2. Experimental

2.1. Materials and methods

Batch synthesis was performed in 250 ml-rounded bottom flasks with 3 inlets for agitation, temperature measurement and reactant addition or product collection in a Dean Stark collection tube, when applicable. Distillations of heavier fractions were

made in Hickman stillpots under high vacuum (2-5 mm Hg). The Hickman stillpot is a molecular distillation equipment. It is based on the principle of placing, as close as possible, evaporation and condensation surfaces under high vacuum, so as the distance between both surfaces is in the order of the mean free path of the molecules.

Trimethyl phosphite and trimethylolpropane were of technical grade (Quimex Sudamericana, Bs. As.). Triphenyl phosphite and dimethyl methylphosphonate were purchased from Aldrich Chemicals Argentina. Pentaerithrytol was manufactured in our own laboratory from the aldolic condensation of acetaldehyde and formaldehyde in basic media and its purity was determined by comparing melting point against a standard. Bicyclic phosphite was obtained by reaction of trimethyl phosphite and trimethylpropane. Preliminary characterization of crude extracts was made by FT-IR spectroscopy. A Hewlett Packard 5890 series II gas chromatograph equipped with a split— splitless injector and a flame ionization detector, coupled to a FTIR spectrometer through a light pipe type interphase was utilized. Differential scanning calorimetry (DSC) studies were made using a Universal t3.va TA Instrument.

2.2. Evaluation of fire retardancy properties

Fire retardancy tests were kindly performed by the Construction Department of the Argentine National Industrial Technology (INTI) according to the California Technical Bulletin 117 test. In this test, samples are time exposed to an open flame in a defined test chamber, and the propagation of the open flame and char length is measured. Although this test is limited to be a method of technical evidence as if a fibre or product may be in market turnover, it is similar to worldwide accepted standards such as ASTM E 1590. Test conditions are identical, except that California 117 is solely used when polyurethane is part of upholstery furniture and the ASTM E 1590 for polyurethane mattresses only. Also, ASTM E 1590 measures the rate of heat release (RHH) but California 117 standard does not. For this reason, we point out that initial signs of inflammability, determined during low energetic exposure, may be used for assessment of inhibition properties of an antipyrene, but not as a method decisive for assessment of the behaviour of polyurethane retarded polymer during bulk burning.

2.3. Synthesis of phosphonate fire retardants

Although the synthesis of this phosphonate fire retardants, we studied, is described in the literature [2, 3, 11], we investigated in detail reaction conditions in order to essay if drastic temperature and long time reactions could be diminished. The main reaction scheme is depicted in Figure 1.

Several attempts were made for optimizing parameters for oligomeric phosphonate fire retardant synthesis. Parameters of reaction experimented were

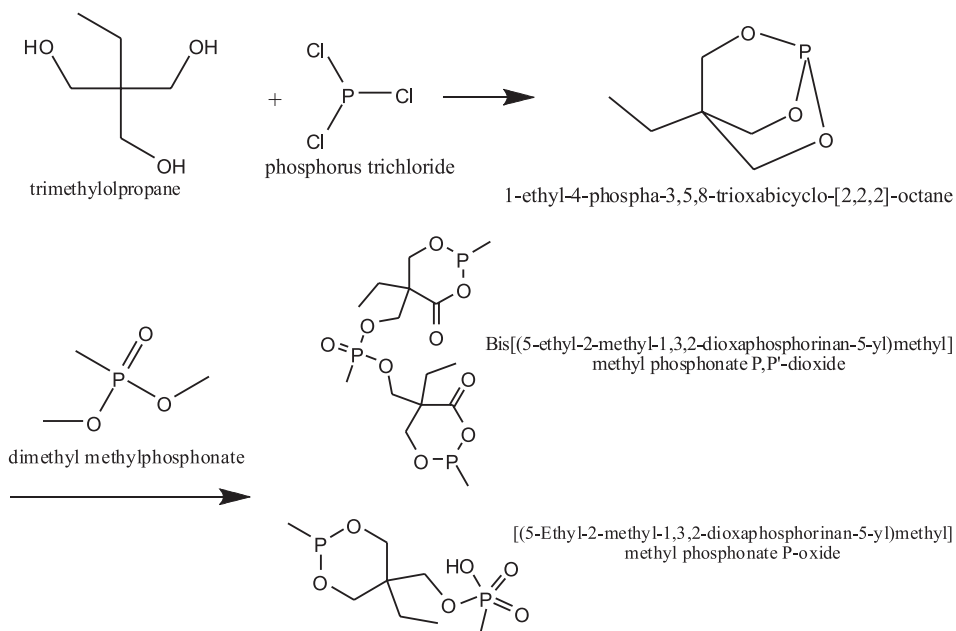


Fig. 1. General scheme of reactions involved

molar ratio of reactants, temperature, and heating time. Several conditions were tested, as patents in this subject usually gives a wide range of possible synthetic conditions, we attempted to optimize temperatures and heating time. Table 1 gives the scheme of synthesis reactions.

Reactions 1 and 2 (not shown in the table) were performed according to Ref. 11, with the modification that DMMP was added in the same pot where TMP and TMP_r reacted to form bicyclic phosphite and lower reaction times were utilized, but the viscosity of crude substance increases noticeably. However, in reaction 3, we followed the same temperature and time conditions described in the patent, with the exception that methyl pyrophosphate was chosen as catalyst. After distillation of crude substance, final product showed fire retarding properties in tests performed with cotton fabrics added at 6% (w/w) of fabric, using a pad-dry-cure process (2 minutes at 150°C after the piece was embedded and dried) withstanding periods of more than 5 minutes under direct flame application with a Mecker burner.

As still reactions experimented required long reaction times and high temperatures and also because colour of final products is very sensitive to minor changes in reaction temperature at around 190°C, we decided to assay two of the available techniques in literature for obtaining first the intermediate bicyclic phosphite 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.1]octane at lower temperatures (80-100°C) and then add afterwards the DMMP for completing the reaction at a higher temperature.

TABLE 1

The conditions and results of synthesis reactions

Reaction	Molar ratio of substrates	Heating time [h]	Temperature [°C]	Characteristics of final product	Stripping	Yield [%]
3 ^[11]	TMP/TMP _r /DMMP 1:1:1.5, one pot plus catalyst	25	190	Viscous brownish liquid	50°C/3.5 mbar and 95°C/3.5 mbar	n.d.
4 ^[12]	TMP/TMP _r 1:1	8	100	White acicular crystals	27-30°C/6 mbar	38
5 ^[11]	BiPh /DMMP 1:0,5	11	200	Viscous clear liquid	No fraction after 6 h 70-120°C/4 mbar	26
6 ^[11]	BiPh /DMMP 1:3.5	10	200	Viscous clear liquid	120°C /4.5 mbar	48
7	TMP/TMP _r /DMMP 1:1:1, one pot	24	100			
		10	190	Viscous light brown liquid		59
8 ^[13]	TPPh/PE 1:1	2	100	White crystals		66
9	Product from 3 + propylene oxide	13	55 up to 80	Viscous transparent liquid	180°C /4.5 mbar	69

TMP — trimethyl phosphite; TMP_r — triphenyl phosphite; TMP_r — trimethylolpropane, PE — pentaerythritol; DMMP — dimethyl methylphosphonate; BiPh — bicyclic phosphite.

The first procedure utilized for the synthesis of bicyclic phosphite (reaction 4) consisted in the reaction of trimethylolpropane and trimethyl phosphite with triethylamine as a catalyst. This mixture was heated 8 hours at 100°C at which point alcohol began to distil off [12]. This is a direct transesterification of trimethyl phosphite and trimethylolpropane. Transesterification of trialkyl phosphites with aliphatic alcohols has been described, indicating possible catalysts, and the necessity of a leaving alcohol of lower boiling point than the transesterified alcohol [14].

The second procedure, comprised the reaction of trimethylolpropane and phosphorous trichloride (first stage of reaction 5) [12]. Immediately, hydrogen chloride evolved and the reaction was held for 8 hours, during which time the temperature was gradually raised to 70°C. At the end of the reaction period, the thick white paste obtained was distilled in a Hickman still pot at 60°C and 4 mbar for 8 hours, yielding transparent acicular crystals of a product which had a melting

point of 55–56°C. This corresponds to the melting point of ethyl bicyclic phosphite. This procedure was adopted further on for its simplicity and good yield.

Then, in a separate stage, the purified bicyclic phosphite was heated with DMMP for 11 hours at 200°C in a proportion of 2 moles of bicyclic phosphite: 1 mol DMMP. Thick amber oil was obtained, which was stripped under vacuum without recovering any fraction. This suggested that the reactants were completely consumed.

In reaction 6, molar ratio DMMP/bicyclic phosphite was increased 7 fold (BiPh: DMMP 1:3,5), condition which corresponded to the formation of the diphosphonate [11]. After the heating period, 6 g of DMMP were recovered after stripping in a Hickman pot from 11.7 g of reaction crude. Comparing reactions 5 and 6, it is possible to elucidate the effect of increasing the molar ratio DMMP/bicyclic phosphite on the course of the reaction.

Reaction 7 was performed again in one pot, adding DMMP directly to the reaction mixture of TMP and TMP_r. Again, coloured products were obtained, as reported above with reactions 1 and 2. Consequently, one pot synthesis was left aside as synthetic procedure.

In reaction 8, we used pentaerythritol instead of trimethylolpropane as polyhydric condensation alcohol. Pentaerythritol phosphite [4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane] was obtained, as confirmed by CG-MS analysis (not shown). The product is white and crystalline. Although a similarity of the reactions of pentaerythritol with triphenyl phosphite and trimethylolpropane with trimethyl phosphite exist, the conditions for formation of the condensation product with pentaerythritol required 4 times less time for completion than in reaction 4, at the same temperature of 100°C. This suggests the existence of a more pronounced steric hindrance effect for trimethylolpropane than for pentaerythritol when they are used as reactant polyols.

All the final products obtained from reactions in Table 1 were of high acidity (90 mg KOH/g, pH 2). In reaction 9, propylene oxide was mixed with final product from reaction 3 (tab. 1). Thus, 12.3 g of purified product from reaction 3 was mixed with an excess of 8.34 g of propylene oxide and heated 9 h at 55°C, at which time pH of crude was 3.1. From 9 to 13 h of reaction, while temperature was slowly raised up to 80°C, pH increased to 3.4. Reaction was stopped and crude substance was stripped at 4.5 mbar and 180°C, recovering 69% of a viscous transparent liquid, with an acidity of 60 mg KOH/g. These values are of the order of the recommended for the commercial product Antiblaze 19 (Amgard CU) of 0.2 meq/g or less.

3. Results and discussion

The substances obtained were investigated using IR spectroscopy and differential scanning calorimetry (DSC). FT-IR spectra of reactions 2 and 3 products were almost

identical, suggesting that reaction time could be diminished (see tab. 1) and that the catalyst chosen contributed to control polymerization and thus, viscosity. FT-IR of final products of reactions 3 and 9 are shown in Figures 2 and 3, respectively. This is for assaying the effect of propylene oxide final treatment. They are identical to the FT-IR spectra of a commercial sample of a standard (Pekoflam PES, obtained from Clariant Argentina). The peak at 1315 cm^{-1} in all samples could correspond to hydroxymethyl phosphonium formed from side undesired reactions. Broad peak at 1026 cm^{-1} in product from reaction 3 is not seen in propylene oxide treated

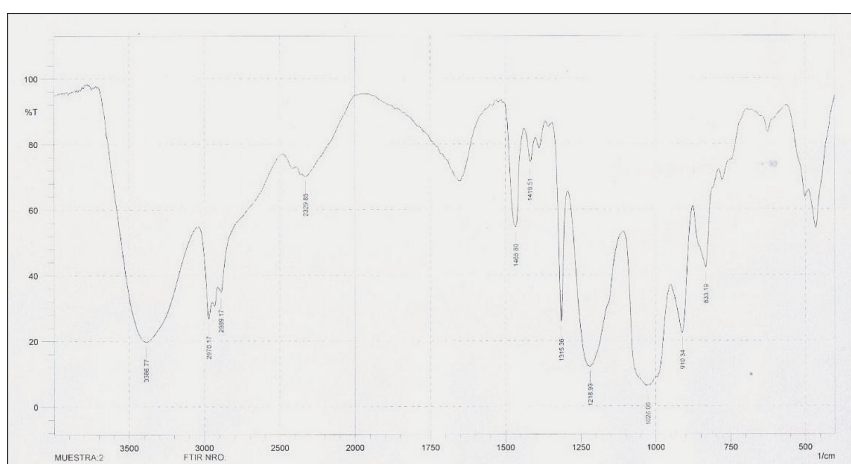


Fig. 2. FT-IR spectrum of product from reaction 3

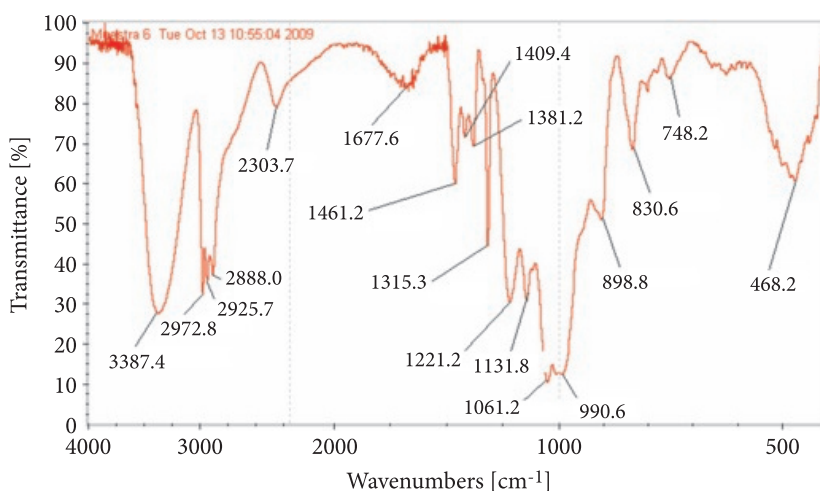


Fig. 3. FT-IR spectrum of product from reaction 9 (propylene oxide treated oligomer phosphonate)

product. Also FT-IR spectra of product from reaction 9 (fig. 3) was similar to Pekoflam standard, only showing a peak at 1131 cm^{-1} , not seen in the standard.

FT-IR of the product from reaction 6 showed a distinctive peak at 1110 cm^{-1} , almost not noticeable in reaction product 5, in which monophosphonate was expected, according to the molar ratio of reactants.

FT-IR spectra of reaction 7 products showed that many side reactions and polymerization occurred, considering that all absorption bands are very broad (figure not shown). However, reactions 1 and 2 were performed in one pot, and spectra peaks of their products were quite clear. This could be related to the higher molar fraction of DMMP in reaction 7, which promoted a higher degree of polymerization.

FT-IR analysis of reaction 2, 3, 5, and 6 products (tab. 1) showed that all samples shared the spectra identical to a commercial product (Pekoflam PES, Clariant) except for a distinctive large peak at $2310\text{--}2320\text{ cm}^{-1}$, only slightly noticeable in the commercial sample. This signal corresponds to P-H bond [15], and suggested the formation of some monomethyl acid methyl phosphonite in our experiments. Transesterification is complicated with O,O-dialkyl phosphonates by side reactions in which the phosphonate acts as an alkylating agent. This is not the case for O,O-diaryl phosphonates, in which case ester interchange is an effective route to polymeric phosphonates [4].

Then, product from reaction 3 of Table 1 was analysed by DSC, and later embedded into a $5 \times 10\text{ cm}$ cotton fabric. DSC analysis was also later performed on the fabric against untreated cotton fabric as a control. Figure 4 shows the

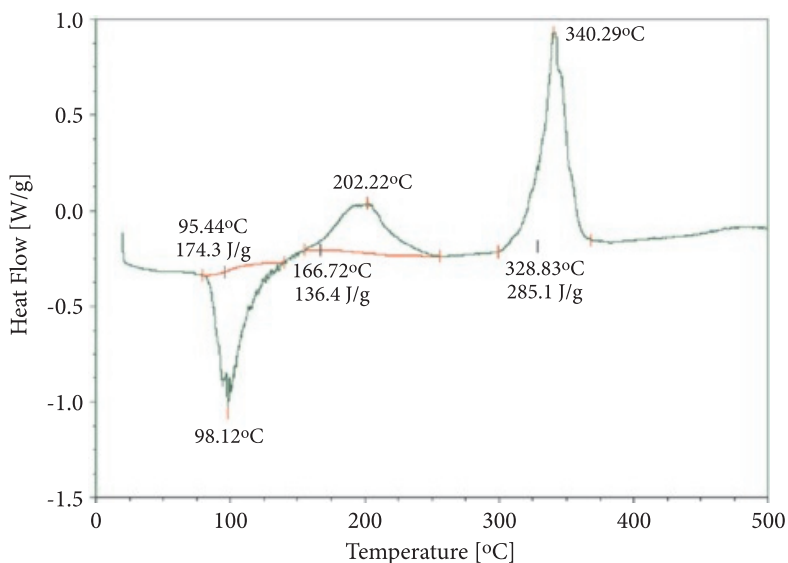


Fig. 4. Differential scanning calorimetry of product from reaction 3 (see Table 1)

DSC diagram of final product from reaction 3. The sample embedded with this product showed two exothermal peaks at 294°C and 340°C, the first one corresponding to inflammation of cellulose fabric and the second likely to the fire retardant product, according to the data presented in thermogravimetric curves by Hoang et al. [16]. Control fabric showed only a broad peak at 357°C (thermogram not shown). This was similar to those from reactions 3, 5, and 6. Superimposing DSCs of oligomer phosphonates from reactions 3, 5 and 6 with the one reacted with propylene oxide (reaction 9) it is possible to compare their thermal properties (Fig. 5).

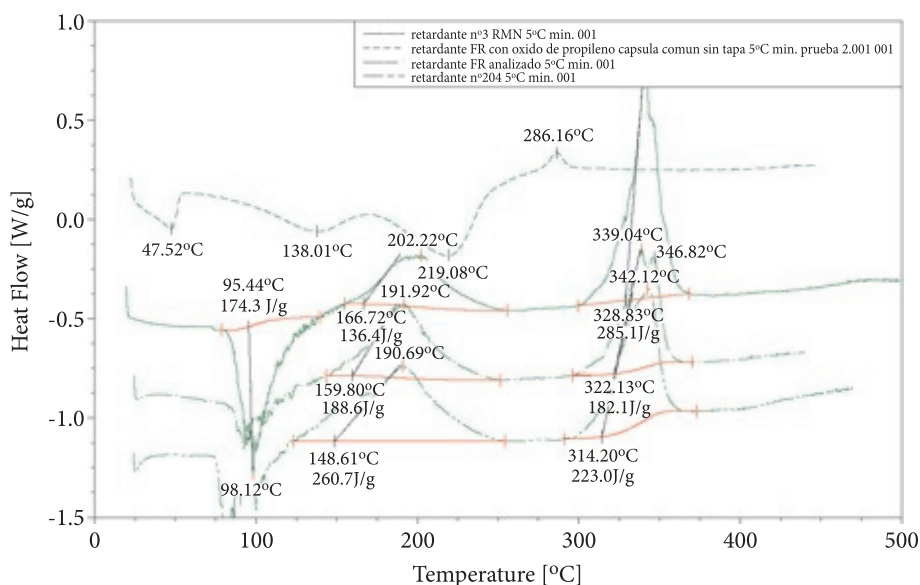


Fig. 5. Differential scanning calorimetry of oligomer phosphonates obtained and propylene oxide treated (dotted line on top of graphs) (see Table 1)

The results from DSC studies were consistent with what was found in the bibliography. In phosphorylated Proban® treated cotton fabric, maximum weight loss as a function of temperature was close to 320°C, as in Figure 4.

On the other side, DSC of propylene oxide treated oligomer phosphonates showed a different pattern than for the others products from reactions of Table 1. Anyway, propylene oxide treated oligomer phosphonates showed a DSC pattern resembling untreated ones, only that peaks shifted to lower temperatures. This suggested that the epoxide polymerized hydroxyl-pendant groups in oligomer phosphonate without linking chains and hence not favouring getting larger polymers. Therefore, DSC general profile is not altered in propylene oxide treated sample.

3.1. Procedure for embedding flame retardants on polyurethane matrix

A polyurethane sample was prepared according to standard methodology, utilizing a polioliol with an hydroxyl number of 56 and toluene diisocyanate (TDI), Petroquímica Río Tercero, Argentina. Catalyzers were tin octoate and amine, with water as blowing agent. Final polyurethane samples have a density of around 30 kg/m^3 . After curing at atmospheric conditions, sample (223 g) was soaked with a solution of 22.3 g of oligomeric phosphonate obtained from reaction 3 in 500 ml of ethanol. Sample was dried in an oven at $140\text{-}160^\circ\text{C}$ for 90 minutes.

3.2. Results of flame retardancy test

Samples of polyurethane embedded with oligomeric phosphonates were subjected to the California TB 117 standard test for flammability. All samples passed this standard and synthesized compounds proved to be efficient as flame retardants, showing a similar performance to a same type commercial sample. Sample pieces ($30 \times 7.5 \times 13 \text{ mm}$) were essayed after 48 hours of preconditioning at 23°C and 50% of relative humidity; and also after an ageing 24 hours at 103°C under forced convection. Flame length was 38 mm, and distance to sample pieces was 19 mm. Time of flame contact with sample pieces was 12 seconds. Aged FR-treated samples showed a loss in fire retardancy. Results are given in Table 2.

TABLE 2

The results of flame retardation properties of oligomeric phosphonates

Sample piece	After flame time [s]	Afterglow time [s]	Char length [mm]
Non-aged samples, synthesized FR added			
1	8	0	80
2	43	0	300
3	4	0	80
4	1	0	20
5	2	0	40
Mean average	12	0	104
Standard deviation	17.7	0	112.6
Variation coefficient [%]	147.9	0	108.2
Aged samples, synthesized FR added			
1	2	0	70
2	6	0	60
3	30	0	60
4	3	0	65

cont. Table 2

5	4	0	71
Mean average	9	0	65
Standard deviation	11.8	0	5.2
Variation coefficient [%]	131.4	0	8.0
Non-aged samples, control without FR			
1	37	0	300
2	44	0	300
3	44	0	300
Mean average	41.6	0	300
Standard deviation	4	0	0
Variation coefficient [%]	9.6	0	0
Aged samples, control without FR			
1	130	0	300
2	54	0	300
3	71	0	300
Mean average	85	0	300
Standard deviation	40	0	0
Variation coefficient [%]	46.9	0	0
Non-aged samples, <i>commercial FR added</i> (Pekoflam PES, Clariant Argentina)			
1	0	0	45
2	0	0	36
3	0	0	55
4	0	0	60
Mean average	0	0	49
Standard deviation	0	0	10.6
Variation coefficient [%]	–	0	21.7
Aged samples, <i>commercial FR added</i> (Pekoflam PES, Clariant Argentina)			
1	1	0	57
2	0	0	45
3	1	0	54
4	0	0	66
Mean average	0.5	0	55.5
Standard deviation	0.5	0	8.6
Variation coefficient (%)	115.4	0	15.6

4. Conclusions

Improved conditions for oligomer phosphonate fire retardant synthesis were determined, which utilized reduced reaction times compared to current state of the art. Products were obtained with good properties for making cotton samples and polyurethane flame resistant. However, the product is very viscous and probably difficult to handle in industrial scale, although water soluble. Propylene oxide treated oligomers showed lower acidity and better fluency properties. Calorimetry data of these oligomers were useful to assess which temperatures should be used to calibrate the impregnation and curing process of these modified FRs on the polyurethane samples. Finally, searching for catalysts for direct transesterification of TMPH and DMMP could be a useful strategy to follow, in order to favour transesterification reaction instead of etherification through methylation side reactions and improving synthesis and final product.

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Synteza fosforoorganicznych substancji ogniouodporniających w wyniku reakcji trimetylopropanu i dimetylo metylofosfonianu

Streszczenie. Wykonano syntezę fosforoorganicznych substancji ogniouodporniających. Synteza polegała na reakcji transestryfikacji dicyklicznych fosfonianów. Badano wpływ różnych czasów reakcji w celu zminimalizowania tego czasu. Stwierdzono, że 11 godzin ogrzewania w 200°C było wystarczające do zakończenia reakcji. Z wcześniejszych badań wynikało, że reakcję należy prowadzić przez 24 godziny. Przeprowadzono badania za pomocą różnicowej kalorymetrii skaningowej i określono zmiany zachodzące w otrzymanych substancjach w wyniku ich ogrzewania. Zarejestrowano też i porównano widma w podczerwieni tych substancji. W końcu sprawdzono działanie otrzymanych oligomerów fosfonianowych jako substancji przeciwzapalnych na próbkach poliuretanów w standardowych warunkach.

Słowa kluczowe: fosforoorganiczne substancje ogniouodporniające, oligomery fosfonianowe, tlenek propylenu, różnicowa kalorymetria skaningowa, spektroskopia podczerwieni

