Polymer Bulletin 30, 243–248 (1993)

Polymer Bulletin

New diethyl phosphonoalkyl acrylates and their reactivity in copolymerization

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Summary

Two new diester phosphonoalkyl acrylate monomers were synthesized and their reactivity in copolymerization was determined. The selective hydrolysis of diester homologues was performed. The polymerization of the diacid homologue produced a non soluble gel. On the contrary, the polymer of the monoacide/mono salt homologue was soluble in methanol.

Introduction

Phosphorus compounds as flame retardants have been used for many years, and have first been introduced in additives as halogenated compounds, aluminium or magnesium hydroxyles. However, these additives raise problems of migration and compatibility ; these effects reduce the mechanical properties. For these reasons, phosphorus monomers in which phosphorus atom is linked to the backbone were prepared.

Thus, in 1940, Toy (1) prepared $\emptyset$-P(O)(O-CH_2-CH=CH_2)$_2$. Such a monomer, and the triallyl phosphate exhibit good flame retardant properties.

Later, the vinyl phosphorus monomers were synthesized, one of the most known being the bis(2-chloroethyl) vinyl phosphonate (2) from Stauffer Chemical.

However, these monomers lead to low molecular weight polymers. This phenomenon can be explained by transfer reaction onto alkoxy groups. Nevertheless, the monomers have been used in wood (3) or cellulose (4) coatings.

More recently, Rabinowitz et al. (5) have prepared styrenic monomers which exhibit the following chemical structure :

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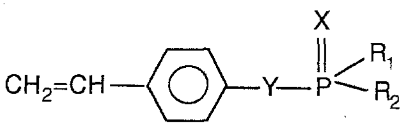


with X = O, S, or nothing
Y = O, CH_2, or nothing
R_1 = alkyl, aryl, alkoxy (6), or amine
R_2 = alkyl, aryl, alkoxy (6), amine or hydroxyl.

These substituted styrenic polymers exhibit flame retardant properties (7).

The styrenic phosphonamides are particularly attractive for formulation of intumescent paints (8).

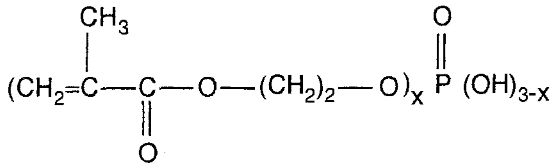
In the sixties, great interest was given for the synthesis of phosphorus acrylic monomers (9). In this case, the phosphorus group can be linked by C-O-P or C-P bonds to the backbone.

It has been shown that the polymerization of these phosphorus monomers is slower than that of their non phosphorus homologous monomers (10, 11).

Besides their flame retardant properties, phosphorus derivatives are very interesting compounds for their adhesive properties onto metals. But in this case, they are required to be in the acidic form.

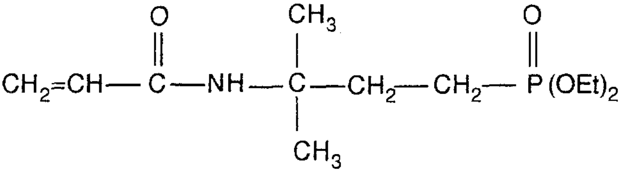
Usually, the hydrolysis of phosphonic esters can be performed either in the presence of strong acids (12) or bases (13), or in milder conditions by using chloro or bromotrimethylsilane (14,15).

Presently, commercially available (meth)acrylic have the following structures :



$$(CH_2{=}\overset{CH_3}{\overset{|}{C}}-\underset{O}{\underset{\|}{C}}-O-(CH_2)_2-O)_x\,\overset{O}{\overset{\|}{P}}\,(OH)_{3-x}$$

(Ebecryl 169, Radure UCB)



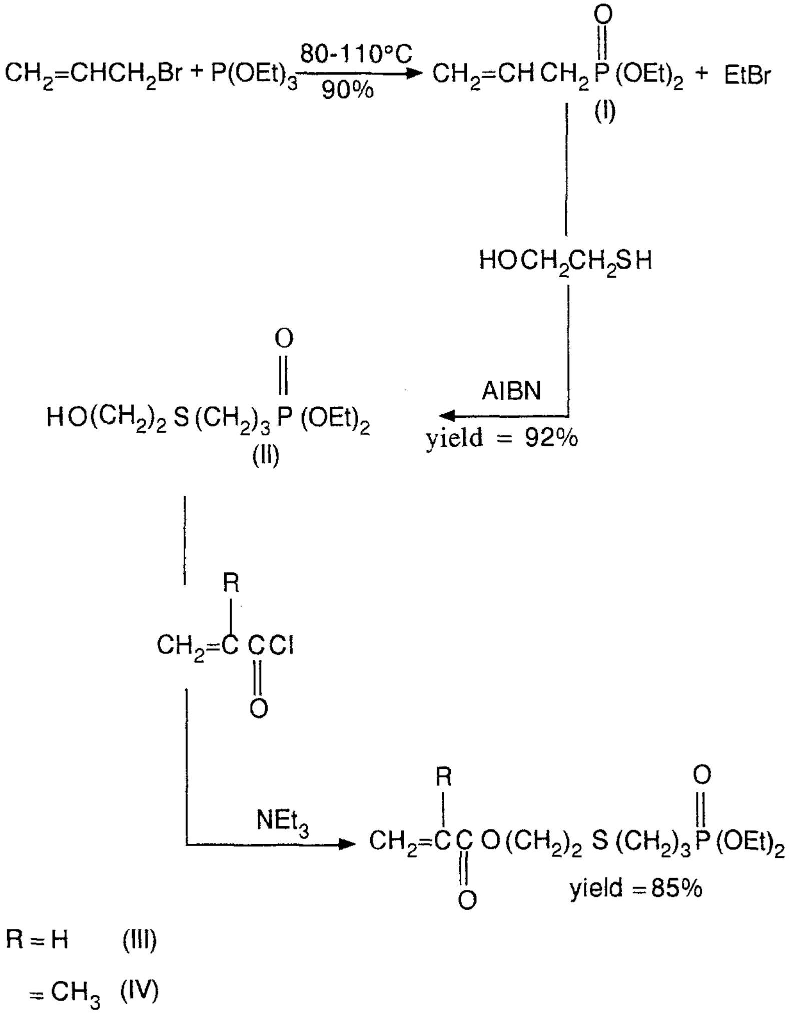
$$CH_2{=}CH-\overset{O}{\overset{\|}{C}}-NH-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_2-\overset{O}{\overset{\|}{P}}(OEt)_2$$

(Chemie Linz)

The aim of this article concerns the synthesis of a new series of acrylic phosphonylated monomers in which the phosphorus group is far from the double bond and which exhibit a carbon phosphorus bond.

Results and Discussion

In previous work, the diethyl allyl phosphonate (12) was synthesized. The free radical addition of mercapto-ethanol onto its allylic double bond was performed then the obtained hydroxyl end-group phosphonoalkyl compound was esterified with (meth)acryloyl chloride and led to phosphonoalkyl (meth)acrylates compounds as follows:



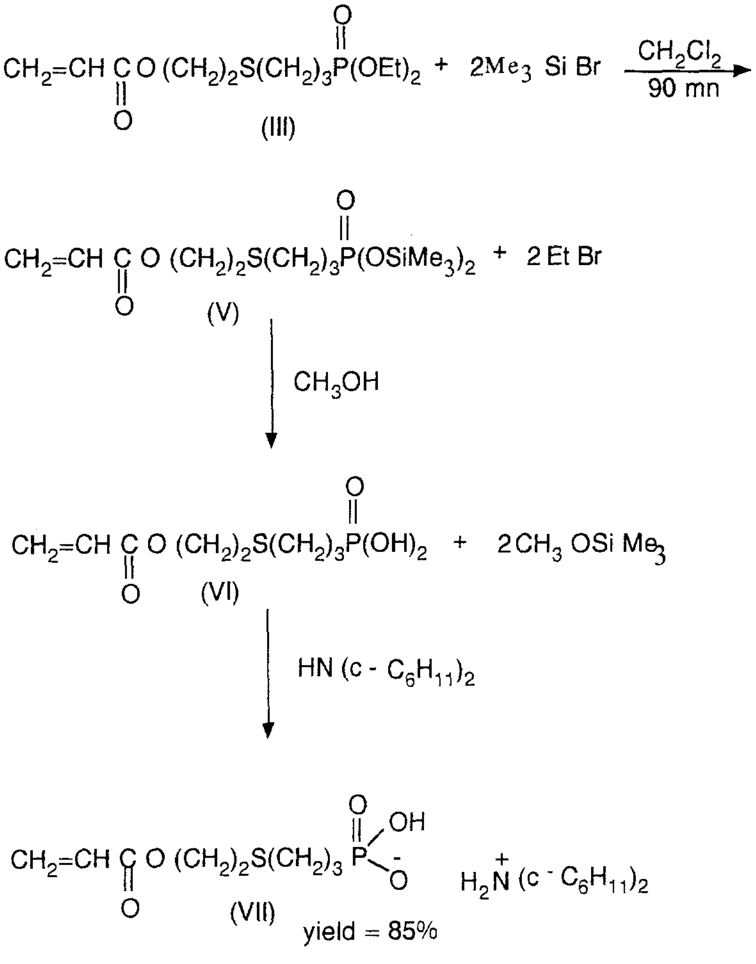
The intermediates were characterized by ^{1}H-NMR (250 MHz, $CDCl_3$).

* The ^{1}H-NMR spectrum of the compound (I) exhibits at 2.60 10^{-6} a doublet dedoubled by the phosphorus atom corresponding to the methylene group in the a position to the phosphorus atom.

* That of the compound (II) shows a triplet at 2.62 10^{-6} characteristic of the methylene group in g to the phosphorus atom and in α to the sulphur atom. This is an evidence of the addition of the thiol onto the allylic double bond.

* For the compounds (III) and (IV), the corresponding spectra show a shift of the triplet at 3.70 10^{-6} corresponding to the methylene adjacent to the hydroxyle in the compound (II) at 4.15 10^{-6} in the acrylic product.

The hydrolysis of the compound (III) was performed in two steps : first, the obtaining of silylated esters (V) form trimethylbromosilane was quantitative and was followed by the addition of an excess of methanol. This led quantitatively and selectively to the corresponding diacid (VI) which by addition of an amine such as the dicyclohexylamine produced a mono acid / mono salt compound (VII) according to the following scheme :



$$CH_2{=}CH\,\underset{\underset{O}{\|}}{C}\,O\,(CH_2)_2S(CH_2)_3\overset{\overset{O}{\|}}{P}(OEt)_2 + 2Me_3\,Si\,Br \xrightarrow[90\ mn]{CH_2Cl_2}$$

(III)

$$CH_2{=}CH\,\underset{\underset{O}{\|}}{C}\,O\,(CH_2)_2S(CH_2)_3\overset{\overset{O}{\|}}{P}(OSiMe_3)_2 + 2\,Et\,Br$$

(V)

$$\Big\downarrow\ CH_3OH$$

$$CH_2{=}CH\,\underset{\underset{O}{\|}}{C}\,O\,(CH_2)_2S(CH_2)_3\overset{\overset{O}{\|}}{P}(OH)_2 + 2CH_3\,OSi\,Me_3$$

(VI)

$$\Big\downarrow\ HN\,(c-C_6H_{11})_2$$

$$CH_2{=}CH\,\underset{\underset{O}{\|}}{C}\,O\,(CH_2)_2S(CH_2)_3\,\overset{\overset{O}{\|}}{P}{\scriptstyle\genfrac{}{}{0pt}{}{OH}{O^-}}\quad H_2\overset{+}{N}\,(c-C_6H_{11})_2$$

(VII)

yield = 85%

The compounds (V), (VI) and (VII) were also characterized by ^{1}H-NMR (250 MHz, $CDCl_3$).

* On the ^{1}H-NMR spectrum of the compound (V), it is noted the absence of the peaks of the phosphonic esters (triplet and quartet at 1.15 and 3.90 10^{-6}, respectively) and the presence of a singlet at 0.3 10^{-6} corresponding to the three methyl groups of the silyl ester.

* For compound (VI), the absence of the singlet at 0.30 10^{-6} characteristic of the silyl ester is observed whereas the presence of the signal at 10.40 10^{-6} is assigned to the acid function.

* As for the compound (VII), the presence of a peak corresponding to the methylene group adjacent to the nitrogen atom in cyclohexyl is observed on the ^{1}H NMR spectrum (Figure 1) at 2.90 10^{-6}.

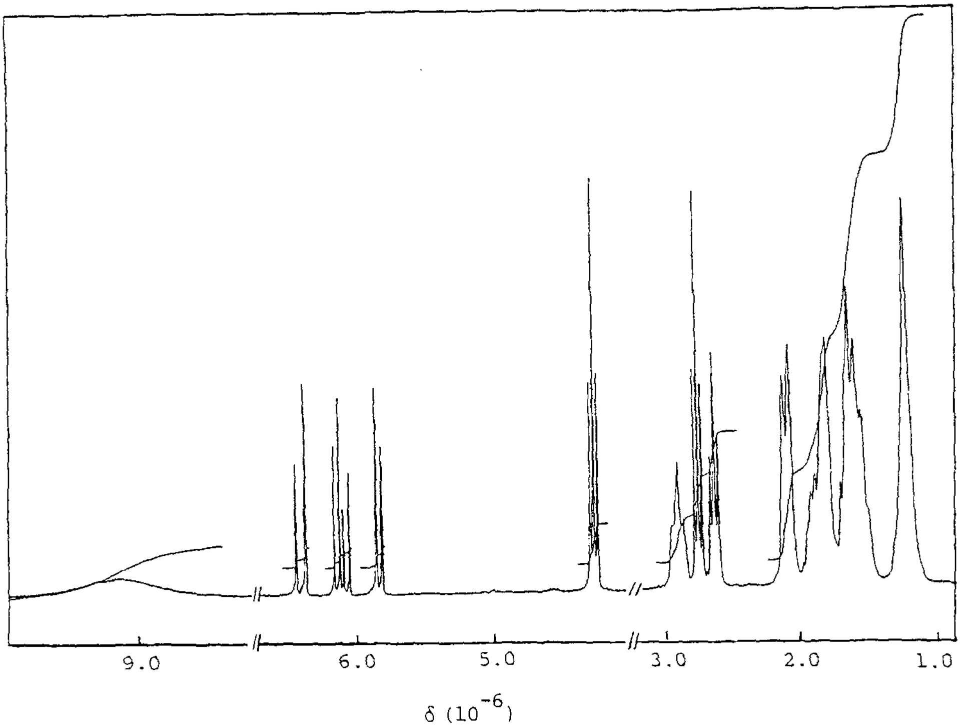


Figure 1 : ^{1}H NMR spectrum of compound VII

1°) Reactivity of phosphonoalkyl acrylates (III), (IV)

In order to determine the reactivity of both monomers by comparison with 2,3-epoxy propyl methacrylate (MAGLY) in copolymerization, a kinetical study for the equimolar stoichiometry only, was perfomed, using the usual YBR method (16).

The copolymerization was carried out at 85°C in acetonitrile, under nitrogen in the presence of AIBN. The reaction was monitored by HPLC with chlorobenzene as internal standard. The results are listed in the Table 1.

M_1	M_2	r_1	r_2
MAGLY	III	2.4	0.4
MAGLY	IV	1.1	0.9

Table 1 : Reactivity ratios of diethyl phosphonoalkyl (III) and (IV) with MAGLY

The obtained values of reactivity ratios are in good agreement with those of the literature (17, 18) for similar couple of monomers.

2°) Homopolymerization of phosphonoalkyl acrylate mono acide / mono salt VII

The reaction was initiated by AIBN and tertiobutyl peroxypivalate at 60°C in chloroform under nitrogen for 16 hours. After addition of initiators, a gel precipitated and could be dissolved in methanol.

The ^{1}H-NMR spectroscopy confirms the obtaining of homopolymer. The yield was 82%. This polymer is soluble only in polar solvants such as methanol and water, without any cross-linking.

The polymerization of diacid homologue monomers was also performed but the obtained polymers were not soluble in these solvents, probably due to the formation of the P-O-P link of P-OH group.

Conclusion

Phosphonylated acrylates which bear one acrylate and one phosphonate functions separated by some carbons atoms, were synthetized. These phosphonylated acrylates have similar reactivities as their organic homologues.

The selective hydrolysis of phosphonic esters was carried out in mild conditions with trimethyl bromosilane. The formation of the mono acid / mono salt was performed in order to broader the fields of applications of phosphorus monomers.

We plan to investigate applications such as flame retardancy, anticorrosive coating for metals immobilization of proteins, and adhesion promotors.

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Accepted January 12, 1993 C