

Synthesis Characterization And Photopolymerization Of Novel Phosphonated Materials

O. Senhaji^{1,2*}, E. Derwich³, M.K. Skalli³, A.H.Benali⁴, M. Achchoubi¹,
J.J. Robin², M. Filali-Baba³, R. Taouil⁵

¹ Laboratoire de Chimie Physique Appliquée (LCPA), Faculté des Sciences et Techniques.

Université Moulay Ismaïl, Errachidia. Maroc. E-mail : ossenahaji@yahoo.fr.

² Laboratoire de Chimie Macromoléculaire (LCM), UMR 5076 – Hétérochimie Moléculaire et Macromoléculaire, USTL, ENSCM, 8, rue de l'Ecole Normale, 34 296 Montpellier cedex 5. France.

³ Université Sidi Mohammed Ben Abdellah, Fès, Maroc.

⁴ Faculté des Sciences - Oujda – Morocco

⁵ Physique Faculté des Sciences et Techniques, Errachidia. Maroc.

New phosphonated cross-linked materials were synthesized from telomers obtained by reaction between 10-undecenol and dialkyl hydrogenphosphonates. Telomers were then converted to materials resins by methacrylation reactions. Finally, photopolymerization of the different materials synthesized was achieved and influence of the nature of the phosphonate group (diester, monoacid and diacid) was also evaluated.

Keywords : Materials, Oligomers, Photopolymerization.

I. Introduction

Photopolymerization is a very flexible process that can be used in various technological applications because of its high curing rate, reduction of volatile organic compounds (VOC), and low cost.^[1] In this process, monomers react to produce polymeric structures by light-induced initiation (excitation of a photoinitiator) and subsequent

polymerization.^[2,3] A growing interest for this technique has been developed as it allows the cross-linking of resins in a short time under UV radiation. Among all possible monomers, polyols which are widely used in polyurethane chemistry can be used as reagents to produce three dimensional networks by photo polymerization. In that case, their alcohol functions are previously converted in unsaturations by (meth)acrylation^[4-6] before photocross-linking.^[7,8]

Phosphorus-containing polymers are of great interest because of their broad application areas. Generally used as flame retardants, polymers with phosphonate or phosphate functions also exhibit excellent adhesive properties to metal, bone, and dentin.^[9-11]

For example, kinetics of photo polymerization of phosphorus-containing acrylate/ (di)methacrylate monomers based on 3-(acryloyloxy)-2- hydroxypropyl methacrylate (AHM) were investigated^[12] and led to a new family of phosphate-containing crosslinkers based on commercially available AHM potentially usable in applications in adhesives and flame retardant formulations where high local concentrations of active groups are necessary. Synthesis and photopolymerization of monomers from ortho-hydroxyaryolphosphonates were also described in the

literature^[13]. Aromatic mono- and di-phosphonate monomers based on tert-butyl α -bromomethacrylate were prepared for use in dental composites^[14]. Shi and coworkers^[1] have reported the photopolymerization of phosphate diacrylate and triacrylate used as flame retardant monomers. It has been proved that the thermal stability of the UV-cured resins materials and the flame retardency of the cured films could be improved by the addition of tri(acryloyloxyethyl)phosphonate.

and di(acryloyloxyethyl) ethylphosphonate.

In a previous work, we reported the synthesis of polyols obtained from the telomerization of 10-undecenol^[15]. The transfer agent used was methyl- or ethyl-hydrogenphosphonate (DMHP and DEHP, respectively). Radical addition Of DMHP or DEHP on unsaturated compounds was achieved according to Figure 1^[16-18]. The reaction was carried out without solvent at 135 °C with $R_0=[T]_0/[M]_0=1.1$, with $[T]_0$ and $[M]_0$, initial molar concentrations of telogen and monomer, respectively. Telomers with different molecular weights were obtained despite the fact that the double bond has a low reactivity.

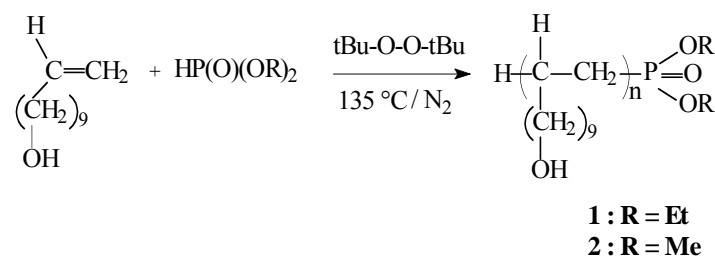


Figure 1: General scheme of radical addition of DMHP or DEHP, on unsaturated compound.

In the present contribution, we report the synthesis, characterization, and photo polymerization of new phosphonated resins derived from the previously obtained telomers. The principal aim of the work is to show that new phosphonated long alkyl chain monomers can be successfully used to produce photopolymerizable resins materials. Resulting derivatives might present interesting applications. As materials used in the field of adhesives, paintings, electronics,^[19] etc. In general, multifunctional oligomers are exposed to UV irradiation in the presence of a photoinitiator and reactive diluent to produce a solid film in a very short time^[20]. This technique is largely spread in industry as it is possible to work without solvent and at room temperature. Here, the previously synthesized telomers were functionalized with (meth)acryloyl groups and fully characterized using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectroscopy measurements. Photopolymerization under UV irradiation of the various phosphonated telomers bearing unsaturations was achieved by varying the nature of the phosphonated group (diester, mono-, and diphosphonic acid) to determine the influence of the oligomer functionality on the rate of polymerization.

II. Experimental Part

II-1. Materials

Allyl alcohol (Aldrich, 99%), DMHP (Aldrich, 98%), DEHP (Aldrich, 98%), di-tert-butyl peroxide (Aldrich, 95%), methacryloyl chloride (Aldrich, 97%), tripropylene glycol diacrylate (Aldrich), Darocur[®] 1173 (CIBA), and all other reagents were used without any further purification.

Size exclusion chromatography (SEC) analyses were performed with a Spectra Physics equipment using two identical Polymer Laboratories columns (PLgel 5 μ m Mixed-C) (Mw 200–30 000) and a precolumn (PL 5 μ m Guard), and a Spectra Physics SP8430 refractive-index (RI) detector. The eluent was THF (T=30 °C, flow rate 0.8 mL min⁻¹). PMMA standards were purchased from Polymer Laboratories. SEC was used to determine molecular weights and molecular weight distributions of the obtained telomers. ¹H and ³¹P NMR spectroscopy were achieved at room temperature on a Bruker AC200 spectrometer using deuterated chloroform, methanol, or DMSO as a solvent and TMS or H₃PO₄ as a reference, respectively. The letters s, d, t, q, and m correspond respectively to singlet, doublet, triplet, and multiplet. The chemical shifts were expressed in ppm. MALDI-TOF mass spectrometry (MS) experiments were conducted at the Service Central d'Analyse du CNRS (Solaize, France) using a Voyager DE STR from Perkin-Elmer equipped with a

N₂ laser (λ =337 nm). The matrix was made of dithranol containing Ag⁺ cations. The weight concentration of polymer was 0.1%. The spectra were recorded in reflectron mode over an m/z range of 250–2200 Da. The ultraviolet (UV) photopolymerization of phosphonated oligomers, tripropylene glycol diacrylate, and Darocur[®] 1173 as the photoinitiator was studied by real time FT-IR spectroscopy with a Nicolet Nexus apparatus with 2 cm⁻¹ accuracy using OMNIC software. The UV radiations were provided by a Novacure Effos apparatus (EFOS, Ontario, Canada) equipped with a 250–450 nm filter. The UV intensity was measured using a Solatell UV spectroradiometer apparatus (4-D Controls Limited, Cornwall, UK) (light intensities=500 mW cm⁻²). The samples were coated on a polished aluminum plate and protected by a 6- μ m thick poly(propylene) (PP) film to prevent air inhibition. The thickness of the coating was controlled by a poly-(tetrafluoroethylene) (PTFE) thickness gauge (25 μ m) inserted between the PP film and the KBr plate. The UV source was placed perpendicularly to the sample surface. The conversion of methacrylate double band was followed by IR spectroscopy, using the disappearance of the bands at 810 cm⁻¹ (elongation of the C=C bond). Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris 1 apparatus. The sample (around 15 mg) was weighted in an aluminum sample holder that was heated at a rate of 10°C min⁻¹ from -120 up to 50 °C. Two rising scans were taken in the row.

Telomerization of 10-Undecenol with DEHP

Synthesis of telomer from 10-undecenol was previously reported^[15]. Mono- and diadduct were isolated passing the crude material through a column of silica gel.

Telomerization of Allyl Alcohol with DEHP

For $R_0 = [M]_0/[DEHP]_0 = 1.1$, and $C_0 = [Initiator]_0/[Monomer]_0 = 5\%$, allyl alcohol (20 mL, 0.294 mol), DEHP (44.65 g, 0.324 mol), and di-tert-butyl peroxide (2.15 g, 0.015 mol) were introduced to a 500mL three-necked flask equipped with a condenser and then flushed with nitrogen.

The nitrogen was bubbled through the solution at 135 °C in an oil bath. The reaction mixture was stirred at this temperature until the monomer was totally consumed. After cooling to room temperature, the mixture was distilled under vacuum (10⁻² mm Hg, 60 °C) to eliminate the light fractions and unreacted DEHP. Product was obtained with a quantitative yield.

Methacrylation of Side-Phosphonated Telomers Obtained During the Synthesis of 2 from Radical Addition of DMHP on 10-Undecenol (Scheme 1)

Side-phosphonated products obtained during the synthesis of telomer 2 (20 g, 0.029 mol) and

triethylamine (3.4 g, 0.034 mol) were introduced with 100 mL of dichloromethane in a 250 mL three-necked flask fitted with a condenser, a nitrogen flux, and pressure-equalizing dropping funnel. The reaction mixture was purged with nitrogen and cooled at 0 °C. Then methacryloyl chloride (3.6 g, 0.034 mol) dissolved in 10 mL dichloromethane was added dropwise. The reaction mixture was stirred for 48 h at room temperature.

The obtained mixture was filtered and the white precipitate was washed with dichloromethane. The organic phase was washed with dichloromethane.

The organic phase was washed with basic water (5 wt.-% NaHCO₃) and then with water up to neutral pH. Methacrylated dimethylphosphonate ester **6** (21.7 g ≈ 90% yield) was obtained after evaporation of the solvent.

¹H NMR (CDCl₃) : δ = 1.10-1.80 (m, nH, n(CH₂)₉-P) ; 1.95 [s, 3H, CH₂=C(CH₃)] ; 3.75 [d, 6H, P(OCH₃)₂] ; 5.80 and 6.30 [dd, 2H, CH₂=C] . ³¹P NMR (CDCl₃) : δ = 35.39 R-P(O)(OCH₃)₂.

Synthesis of Monophosphonic Acid Resin 7a

Dimethylphosphonic ester **6** (10 g, 0.012 mol) was introduced with sodium iodide (1.9 g, 0.0126 mol) and 50 mL of anhydrous acetone in a 100 mL three-necked flask, equipped with reverse condenser. The mixture was kept under reflux for 12 h and then stirred at room temperature for 6 h. Monophosphonic salt (7.8 g, ≈ 70 % yield) was obtained after filtration and washing with anhydrous acetone.

¹H NMR (CD₃OD) : δ = 1.10-1.80 (m, nH, n(CH₂)₉-P) ; 1.95 [s, 3H, CH₂=C(CH₃)] ; 3.75 [d, 3H, P(OCH₃)(ONa)] ; 5.80 and 6.30 [dd, 2H, CH₂=C] . ³¹P NMR (CD₃OD) : δ = 29.03 R-P(O)(OCH₃)(ONa).

The latter (5 g, 5.9 mmol) was dissolved in 100 mL of methanol. The solution was filtered through a glass column filled with a proton-exchange resin (Amberlite IR120). The proton-exchange resin was washed with methanol up to neutral pH. The monophosphonic acid **7a** was recovered in quantitative yield after evaporation of the solvent.

¹H NMR (CD₃OD) : δ = 1.10-1.80 (m, nH, n(CH₂)₉-P) ; 1.95 [s, 3H, CH₂=C(CH₃)] ; 3.45 [d, 3H, P(OCH₃)(OH)] ; 5.80 and 6.30 [dd, 2H, CH₂=C] ; 11.50 [s, 1H, P(O)(OH)] . ³¹P NMR (CD₃OD) : δ = 37.25 R-P(O)(OCH₃)(OH) . ³¹P NMR (DMSO-d₆) : δ = 31.79 R-P(O)(OCH₃)(OH).

Synthesis of Diphosphonic Acid 7b

Trimethylsilyl bromide (4 g, 0.026 mol) was added dropwise at 0 °C under nitrogen to dimethylphosphonated resin **6** (10 g, 0.012 mol) dissolved in 70 mL of dichloromethane. The mixture was kept at 40 °C for 3 h and then maintained under stirring at room temperature for 6 h. After evaporation

of the solvent the recovered solid was dissolved in methanol and then precipitated in pentane. Diphosphonic acid **7b** (8.3 g, ≈ 85 % yield) was obtained after filtration and washing with anhydrous pentane.

¹H NMR (CD₃OD) : δ = 1.10-1.80 (m, nH, n(CH₂)₉-P) ; 1.95 [s, 3H, CH₂=C(CH₃)] ; 5.80 and 6.30 [dd, 2H, CH₂=C] ; 11.90 [s, 2H, P(O)(OH)₂].

¹H NMR (DMSO-d₆) : δ = 1.10-1.70 (m, nH, n(CH₂)₉-P) ; 1.70 [s, 3H, CH₂=C(CH₃)] ; 5.65 and 6.00 [dd, 2H, CH₂=C] ; 8.90 [s, 2H, P(O)(OH)₂]. ³¹P NMR (CD₃OD) : δ = 31.54 R-P(O)(OH)₂. ³¹P NMR (DMSO-d₆) : δ = 29.39 R-P(O)(OH)₂.

Photopolymerization by FT-IR

Phosphonated resin **6**, **7a** or **b** (0.7 g) and tripropyleneglycol diacrylate (0.26 g) were introduced in a glass tube. Then, Darocur 1173 (40 mg) was added via a syringe. The solution was stored under nitrogen atmosphere safe from the light. The UV photo-polymerization was followed by real time FT-IR spectroscopy.

III. Results and Discussion

The usual synthesis of photo-cross-linkable resins is achieved by (meth)acrylation of polyols. Here, the synthesis of polyol by telomerization is described as well as the conversion of alcohol functions to unsaturations. The resulting products were cross-linked under UV irradiation.

Synthesis of Diphosphonic Ester and Mono- and Diphosphonic Acid Resins

The telomerization of 10-undecenol with DMHP led to phosphonated polyol telomers following side reactions previously explained. These phosphonated polyols reacted with methacryloyl chloride (Figure 2) to produce resin **6**

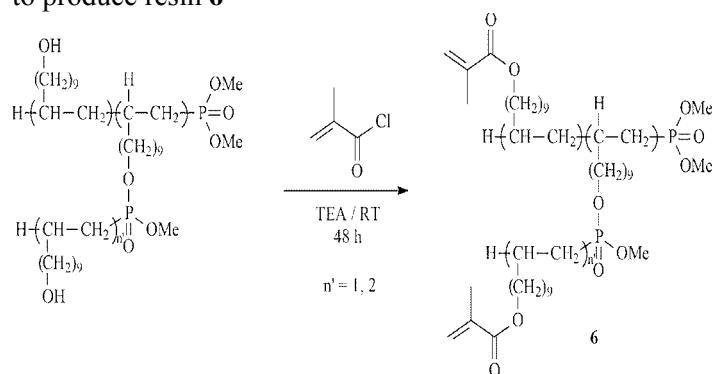


Figure 2 : Reaction of phosphonated telomers with methacryloyl chloride

The chemical structure of **6** was confirmed by ¹H NMR and FT-IR measurements. ¹H NMR (Figure 3) showed the methacrylic protons at 5.80 and 6.30 ppm and of the methyl group at 1.95 ppm. Infrared (IR) spectrum confirmed this result with the disappearance

of the large band at 3600 cm^{-1} assigned to the alcohol function while new at 1635 and 1721 cm^{-1} bands observed corresponding to the $\text{C}=\text{C}$ double bond and to the carbonyl of the methacrylic group introduced, respectively.

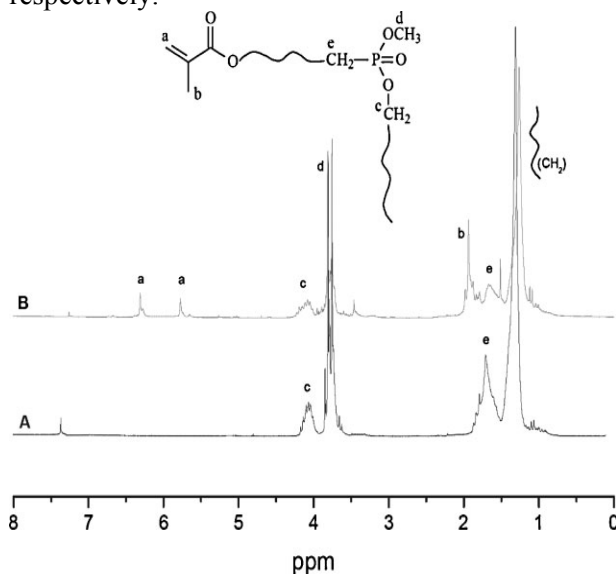


Figure 3 : ^1H NMR spectra of phosphonated polyols prepared from 10-undecenol with DMHP before (A) and after (B) methacrylation reaction.

The dimethyl ester material **6** were then transformed into mono- and diphosphonic acid **7a** and **b** following a procedure developed by Boutevin et al.^[21] Monoacid resins were prepared from dimethylphosphonated ester **6** in two steps. First step allowed the synthesis of the monophosphonic salt by reaction with sodium iodide in acetone. Mono phosphonic acid was then obtained using exchanging ion resin (Amberlite) Figure 4. Chemical structure of the monoacid resin was confirmed by ^1NMR which notably showed the acidic protons at 11.50 ppm and signals at 5.80 and 6.30 ppm , characteristic of the meth acrylic double bond. We also observed, with ^{31}P NMR in deuterated methanol, the disappearance of the signal at 35.51 ppm of the dimethylphosphonate while a new signal at 37.25 ppm characteristic of the mono phosphonic acid was noticed.

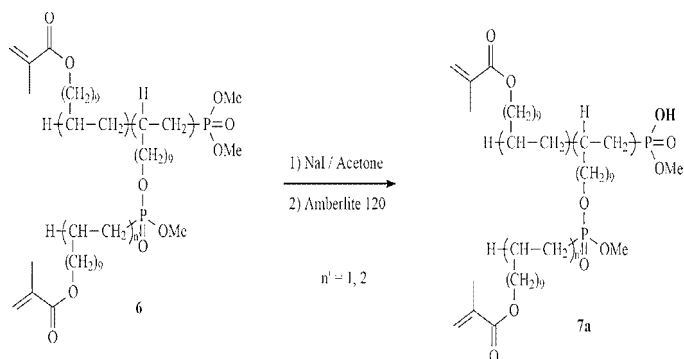


Figure 4 : Synthesis of monophosphonic acid resins **7a**.

The dimethylphosphonic ester **6** was also used to produce diphosphonic acid by silylation with trimethylsilylbromide followed by methanolysis according to Scheme 10. Chemical structure of diphosphonic acid resin was confirmed by ^1H NMR in DMSO-d_6 where we observed the disappearance of the methyl signal of phosphonated ester $[\text{P}(\text{O})(\text{OMe})_2]$ and the presence of the signal at 8.90 ppm characteristic of diacid proton (Figure 5).

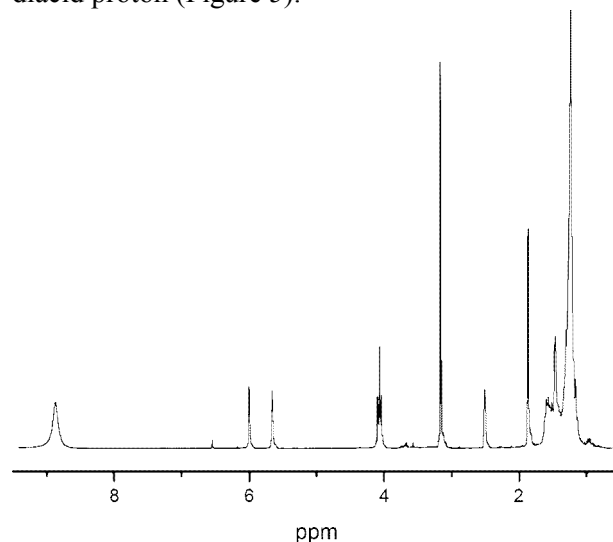


Figure 5 : ^1H NMR spectrum of diphosphonic acid **7b**.

We also checked by ^{31}P NMR in deuterated DMSO that the signal corresponding to the phosphorus atom shifted from 35.39 ppm for the diester to 31.79 and 29.39 ppm for the phosphonated mono- and diacid, respectively (Figure 6).

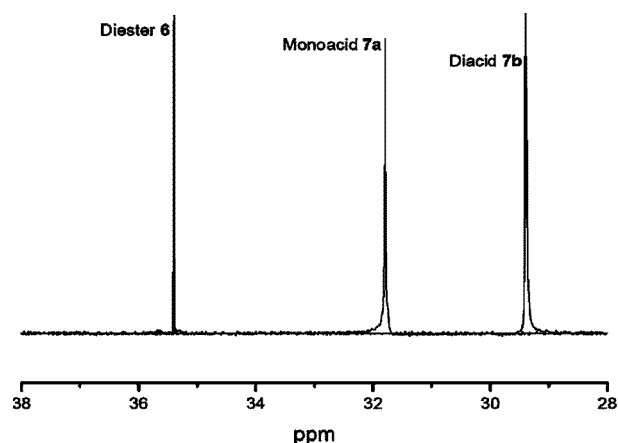


Figure 6 : ^{31}P NMR spectra of diphosphonic ester **6** and mono- and diphosphonic acid resins (**7a** and **b**, respectively) in deuterated DMSO .

Finally, FT-IR spectroscopy showed characteristic bands of the methacrylic group at 1631 and 1720 cm^{-1} ($\text{C}=\text{C}$ double bond and carbonyl of the ester function, respectively) and a large band around 3300 cm^{-1} due to the hydroxyl groups of the acidic function (Figure 7).

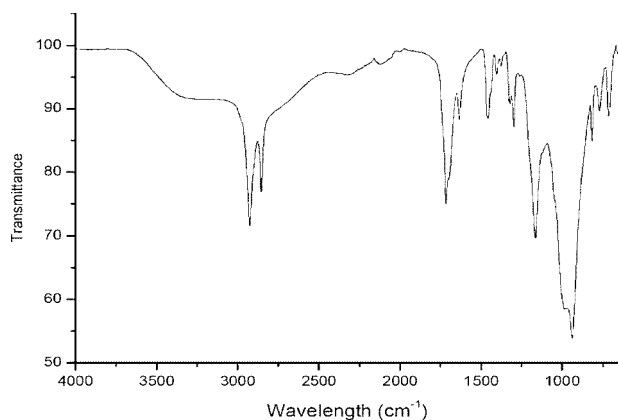


Figure 7 : FT-IR spectrum of diphosphonic acid 7b. Resins **6**, **7a**, and **b** have been synthesized with good yields and are fully characterized by ^1H NMR, ^{31}P NMR, and FT-IR measurements.

These resins, slightly yellow very viscous liquids, were then used formulations to try producing different final cross-linked compounds with Different functionalities (phosphonated diester, phosphonated mono-, and diacids). Influence of the phosphonate group has been evaluated to determine kinetic parameters such as rate of polymerization.

Photopolymerization of Resins **6**, **7a**, and **b**

Possibility to photopolymerize previously obtained resins **6**, **7a** and **b** was evaluated. Irrespective of the resin formulation was prepared using 70 wt.-% of the phosphonated resin, 26 wt.-% of diluents (tripropylene glycoldiacrylate) to adjust the viscosity of the reaction mixture and 4% of hydroxyalkylacetophenone (Darocur 1173) added as initiator.

In these conditions, the ratio [double bond]/[initiator] was almost constant since the starting unsaturated resins had very close molecular weights. Photopolymerization was followed with real time IR spectroscopy^[22-25] using bands attributed to acrylate function (810 cm^{-1}). The conversion of methacrylate double bonds was followed by IR spectroscopy, using the decrease of the absorption band at 810 cm^{-1} (elongation of the C=C bond) versus that of 1725 cm^{-1} (carbonyl absorption) which remained constant during photo-cross-linking (Figure 8). The conversion rate was given by the general formula

$$N = [A]_n \left[1 - \frac{(DO)_{810}^t}{(DO)_{810}^0} \right]$$

$(DO)^0$ and $(DO)^t$ being the the absorbances at 810 cm^{-1} at $t = 0$ and t , respectively. The infrared spectrometer permitted to evaluate polymerization recording a spectrum every 0.03 s. The curve $\alpha = f(t)$ permitted to reach polymerization rate R_p at a given time^[26]. The polymerization rate was evaluated using the slope of the recorded curves. The influence of the nature of the phosphonated function on the polymerization rate was determined (Figure9).

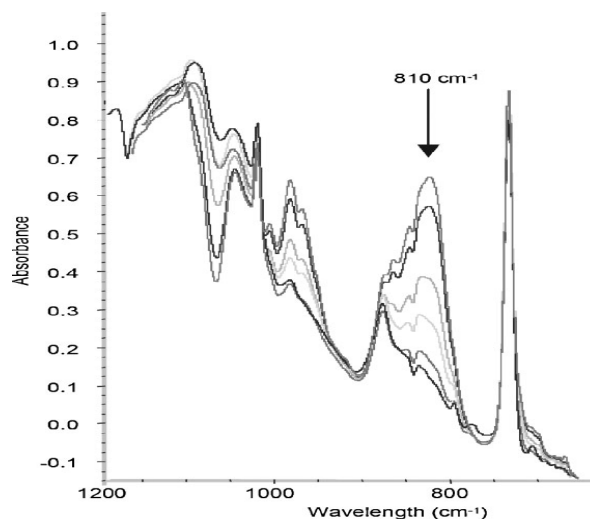


Figure 8 : Zoom between 650 and 1200 cm^{-1} of the IR spectra at different times for the photopolymerization of **6**.

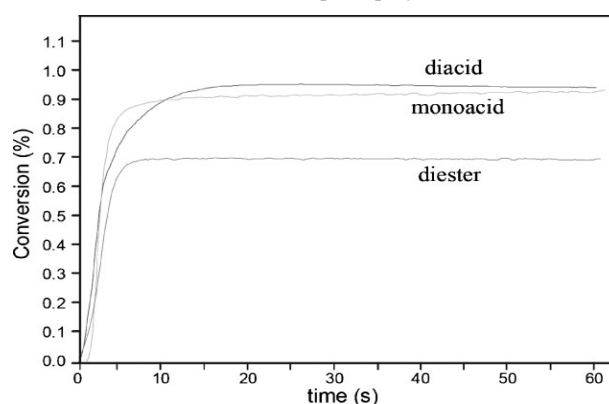


Figure 9 : Conversion versus time for the photopolymerization of resins **6**, **7a**, and **b**.

Irrespective of the phosphonated group, photopolymerization was rapid as conversion was high after a very short time. Nevertheless, it appeared that polymerization reaction was achieved faster using phosphonated diacid resin **7b** whereas the weaker **6** conversion was obtained for the phosphonated diester **6** (Table 1).

Table 1. Kinetic parameters for the hotopolymerization of **6**, **7a**, and **b**.

Phosphonated function	Conversion rate ^{a)}	Vp/[M] s^{-1}	Tg $^{\circ}\text{C}$
Diester (6)	0.70	0.20	- 50
Monoacid (7a)	0.92	0.25	-45
Diacid (7b)	0.98	0.43	-40

^{a)} Determined at $t = 180\text{ s}$.

Final conversion where 0.70, 0.92, and 0.98 for phosphonated diester, monoacid, and diacid, respectively. Here, it seems that the presence of strong Bronsted acid greatly increased the yield of photopolymerization in terms of rate and conversion. It

is also important to notice that the presence of acidic functions on the resin backbone has been previously demonstrated to have an influence on the rate of polymerization^[27]. The hydrogen bonding can be responsible for high local concentration in double bonds, and decrease in termination rate. Furthermore, the coatings were easily removed from the aluminum plates in the case of phosphonated diester whereas it was impossible to separate them for phosphonated monoacid and diacid. This observance comes from phosphonic acid functions well known to improve adhesion of polymer coatings onto metals.

Finally, glass transition temperatures (T_g) were determined by DSC. The observed glass transitions were very close (around -40 to -50 °C) (Table 1). These low temperatures can be explained by the long alkyl chains of the monomer giving some flexibility to the networks and Acting as plasticizers. Nevertheless, slight differences observed between diester, monoacid, and diacid-based materials could be attributed to hydrogen bondings that make glass transition increasing.

IV. Conclusion

Radical addition of dialkylhydrogen phosphonates (DMHP or DEHP) on the 10-undecenol was studied. Characterization of the obtained telomers permitted to highlight a cross-esterification reaction of DEHP on produced phosphonated telomers. This side reaction was followed by another reaction with 10-undecenol leading to polyols with higher molecular weights that those targeted.

Methacrylation of polyols derived from 10-undecenol and DMHP enabled us to synthesize resins. Phosphonated groups were modified to afford three different types of resins : phosphonated diester, mono-, and diacid.

The study of the photopolymerization of the various phosphonated resins under UV irradiation permitted us to observe the influence of the nature of the phosphonated group on the polymerization rate. Diester derivative was less reactive and led to a relatively weak conversion rate of the double bond, whereas both mono- and diacid forms were more reactive. As conversions reached high values.

This new class of cross-linked phosphonated polymers could be used as adhesives as they present good adhesion properties on metal surfaces and low glass transitions.

V. References

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