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Synthesis and characterization of (co)polymers containing a phosphonate function for use in dental composites

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Abstract

Novel monomers **1a**, **1b**, in which a phosphonate function is incorporated in both aromatic rings, were synthesized from the addition reaction of tetraisopropyl [2,2′-disulfanyl-5,5′-thiodiphenyl]-1,1′-diphosphonate and diisopropyl (2-sulfanylphenyl)-1-phosphonate with the glycidylmethacrylate. Free radical homo- and copolymerizations of phosphonate monomers containing methacrylate groups were first carried out in bulk and in THF solution. They offered (co)polymers for potential use in dental resins, in high yields and moderate to high inherent viscosities. The components and structure of the (co)polymers were confirmed by FTIR, SEC, ^{1}H, ^{31}P NMR spectra.

Thermal analysis by using differential scanning calorimetry indicated an amorphous structure of the (co)polymers obtained by polymerization in solution. Upon UV-radiation the composite resins have been synthesized by cross-linking reaction.

Keywords: Dental composites; Glycidyl methacrylate-sulfanylphenylphosphate; Free radical co-polymerization

1. Introduction

Dimethacrylate networks are widely used as dental bonding agents [1–4]. Most commercial dental composites contain liquid dimethacrylate monomers (including bis(glycidylmethacrylate) (BIS-GMA; Scheme 1) or variation of it) and silica-containing compositions such as inorganic reinforcing filled particles coated with methyl methacrylate-functional silane coupling agents to bond the resin to the filler. They also contain initiators, accelerators, photoinitiators, photosensitizers, polymerization inhibitors, and UV absorbers. Durability is a major problem with these composites.

Recently, some authors [5–9] have reported advanced epoxy resins-containing phosphorus compounds. According to a recent study [10] the incorporation of a phosphonic function, to monomer structures such as **A** (Scheme 2) should be able to increased biocompatability and adhesion to the tooth due to chelation with calcium ions in the tooth surface. Generally, aliphatic monomers containing acid-function have relatively poor mechanical properties [11,12]; Mou, Singh and Nicholson [10] have anticipated that aromatic monomers will yield materials with improved mechanical properties, because of the similarity with the aromatic dimethacrylate monomers such as BIS-GMA, currently used extensively in dentistry.

Few years ago, our group has shown that *ortho*-sulfanyl arylphosphonates such as **4b** can be easily prepared from the *ortho*-lithiation of *S*-arylphosphorothioates, reaction which is followed by the S–C migration of the phosphono group [14,15]. This lithiation-rearrangement was applied to *O*,*O*,*O*′,*O*′-tetraisopropyl-*S*,*S*′-(thiodi-4,1-phenylene) bis(phosphorothioate) **3a** (Scheme 3) and *O*,*O*′-diisopropyl-*S*-phenylphosphorothioate **3b** (Scheme 4) leading, respectively, to bis-thiol **4a** and thiol **4b.**

Although it is, a priori, difficult to predict the effect of the replacement in compound **A** of the *para*-oxygen atoms and of the bulky dimethylmethylene linkage by sulfur atoms on the physical properties of dentine resins, we decided to initiate a study on the reactivity of such thiols or bis-thiols with GMA and of the polymerization of the resulting monomers. Herein, the first part of this study describes the preparation of the new aromatic methacrylate monomers **1a** and **1b** (Scheme 2) starting from the bis(thiol) **2a** and thiol

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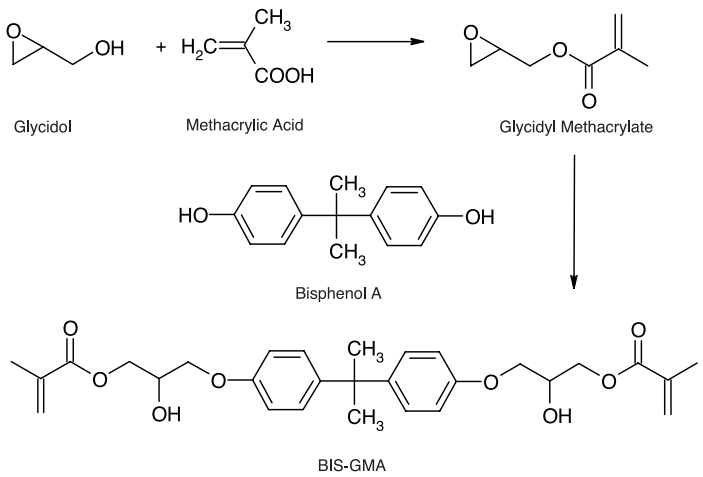


Scheme 1. Synthesis of bis(glycidylmethacrylate) (BIS-GMA), monomer used in dental restorative materials.

2b together with their free radical homo- and copolymerization. The microstructural study of (co)polymers prepared in bulk and in tetrahydrofuran (THF) solution using azobisisobutyronitrile (AIBN) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as free radical initiator is detailed. Due to the presence of phosphonate functions, their adhesive bonding properties should be better to that of the bisphenol A type epoxy resin [13].

2. Results and discussion

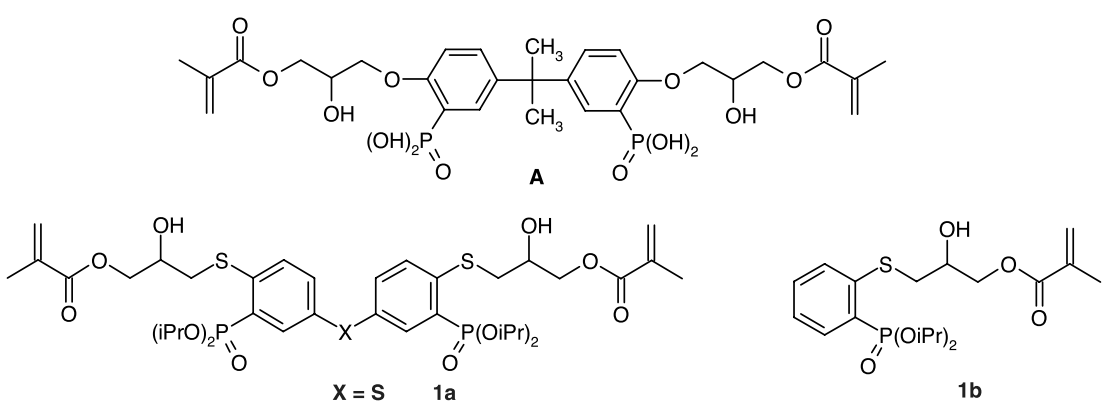
2.1. Preparation of monomers

The synthetic pathway of monomers **1a**, **1b** are shown in Schemes 3 and 4.

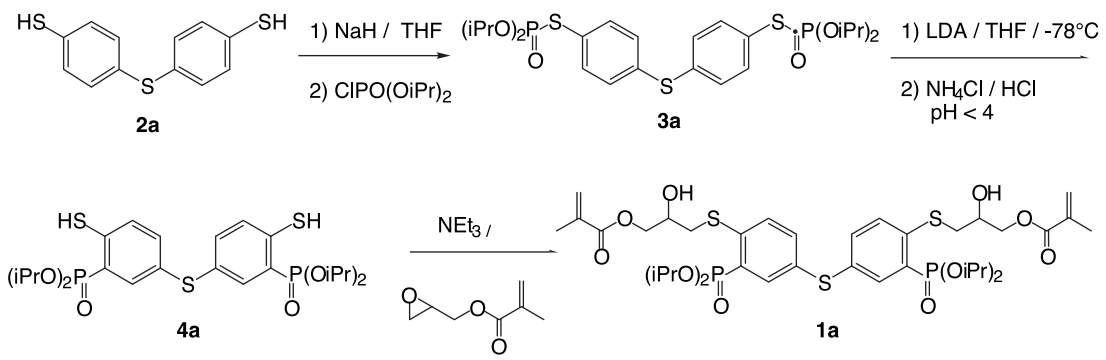
In the sulfur series X = S, starting material **2a** is commercial [22–27]. The treatment of 4,4′-thiodi(benzenethiol) **2a** with 2.5 equiv. of sodium hydride NaH in THF, followed by addition of diisopropyl chlorophosphate [28] led to the tetraisopropyl-*S*,*S*′-(4,4′-thiodiphenyl) bis(thiophosphate) **3a** [14,15] (Scheme 3). This was easily performed on a 20 g scale with 86% yield.

Based on an efficient method for the preparation of *ortho*-substituted thiophenols [14–19], reaction of bis(thiophosphate) **3a** in the presence of an excess (~7 equiv.) of lithium diisopropylamide (LDA) in THF induces the cleavage of the sulfur–phosphorus bond and formation of the carbon–phosphorus bond yielding **4a**. Due to the easy oxidation of the resulting tetraisopropyl [2,2′-disulfanyl-5,5′-thiodiphenyl]-1,1′-diphosphonate **4a** into disulphides during the work-up, several experiments gave yields in the range 60–91% after purification. However, the chemioselective reduction of these disulphides to disulfanyl thiodiphenyl diphosphonate **4a** can be achieved in quantitative isolated yield, with the use of sodium borohydride in THF methanol [29].

Alkylation of tetraisopropyl [2,2′-disulfanyl-5,5′-thiodiphenyl]-1,1′-diphosphonate **4a** was accomplished with GMA in the presence of triethylamine (Et_3N) to afford the new monomer **1a** in moderate yield after purification by flash chromatography. Fortunately, the ring-opening of the epoxide function is faster than the possible 1,4-addition of the thiol to the methacrylic ester (as already reported for other case [20,21], the Michael type addition was not observed). The FTIR analyses of these samples showed the characteristic absorption at $\nu = 1712\ cm^{-1}$ for ester carbonyl groups.



Scheme 2. Phosphonated analogues of BIS-GMA: **1a**, **1b**.



Scheme 3. Synthesis of monomer **1a**: tetraisopropyl [2,2′-bis(2-hydroxy-4-oxa-5-oxo-6-methylhept-6-enylsulfanyl)-5,5′-thiodiphenyl] diphosphonate.

On the other hand, in order to exert some control over the reactivity of (co)polymers towards common cross-linkers through the used of the monomer **1a**, it was also desirable to prepare a mono methacrylate model compound: the diisopropyl-2-(2-hydroxy-4-oxa-5-oxo-6-methylhept-6-enyl sulfanyl) phosphonate **1b** from the benzenethiol **2b** (Scheme 4), according to the method used in the thiodiphenyl series.

The formation of monomers **1a**, **1b** was strongly confirmed by their spectral properties (IR, NMR, masse spectra); in particular the ^{1}H, ^{13}C, 2-D H–H, *J* mod and ^{31}P NMR were most informative (Table 1).

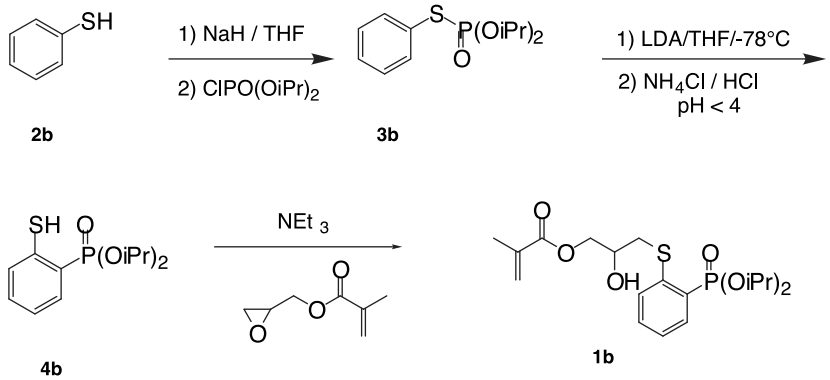
At the same time the characteristic absorption peak of the ν as (–COC–) appeared at 1166 cm^{-1}. Furthermore, the characteristic band assigned to the $-CH_2-$ stretching of the olefin chain was observed at 2800–3060 cm^{-1} and an additional absorption at around 3200–3400 cm^{-1} revealed the existence of an alcohol function in **1a**, **1b**. Likewise, characteristic absorption at $\approx$1260 cm^{-1} (νP=O) and $\approx$996 cm^{-1} (νP–O*i*Pr) are detected and the weak absorption at $\nu = 1638$ cm^{-1} is due to the stretching of C=C bond present at the chain ends.

The characteristic bands in the FTIR spectra, the characteristic peaks in the ^{1}H, ^{13}C and ^{31}P NMR and the mass spectrometric analysis correlate sufficiently well with the proposed structure of **1a**, **1b**. The assignments of ^{1}H NMR signals shown in Fig. 1a were obtained by 2-D H–H spectra of **1a** cast from $CDCl_3$. Cross-communication between different moieties generates off diagonal or cross-peaks which confirmed the structure of monomers **1a**. The multiplet for the $SCH_2(CHOH)$ obtained by the ring-opening reaction of epoxide of GMA, observed at δ 3.78 ppm is correlated with the doublet of doublet at δ 2.85 and 3.12 ppm [SCH_2(CHOH), 2H] (these latter signals are together correlated), and with the doublet–doublet at δ 4.05 and 4.11 ppm [OCH_2(CH–OH), 2H]. The assignment of ^{13}C NMR signals were obtained by *J* mod spectra, (the spectrum of **1a** is shown in Fig. 1b).

2.2. Polymerization

Monomers **1a**, **1b** have been homo- and copolymerized and the nature of (co)polymers is markedly affected by the mode of polymerization. The study is divided into two parts.

A preliminary investigation was carried out with diisopropyl hydroxysulfanyl phosphonate **1b** as a model compound. At first, homopolymer **10b** was prepared by free-radical polymerization of **1b** (Scheme 5) at 60 °C, using *N*,*N*′-azobis-isobutyronitrile as initiator in THF (Method 1). The product formed was isolated in good yield by dissolution and precipitation in dichloromethane/cyclohexane. The absence of the characteristic ^{1}H NMR singlet signal at δ 5.55 and 6.09 ppm for the methylene proton of the methacrylic group indicates that the homopolymerization is complete. The microstructural study of photo-polymerized composite resin **10b**′ in bulk polymerization of **1b**, using 2,2-dimethoxy-2-phenylacetophenone as free radical initiator (Method 2, Scheme 5, Table 2) upon



Scheme 4. Synthesis of diisopropyl 2-(2-hydroxy-4-oxa-5-oxo-6-methylhept-6-enylsulfanyl) phenyl phosphonate **1b**.

Table 1
Data of starting materials

Compound	^{1}H NMR ($CDCl_3$/TMS) δ (ppm), J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ (ppm), J (Hz)	^{31}P NMR ($CDCl_3$/TMS) δ (ppm)	IR ($CHCl_3$) ν (cm^{-1})	Masse (m/z)	Yield (%)	Aspect
1a	1.22 and 1.29 [2d, $^{3}J_{HH} = 6.20$, 24H, CH_3(iPr)], 1.85 (s, 6H, $H_{8'}$), 2.85 (dd, $^{2}J_{HH} = 14.00$, $^{3}J_{HH} = 9.40$, 2H, $H_{1'a}$), 3.12 (dd, $^{2}J_{HH} = 14.00$, $^{3}J_{HH} = 2.50$, 2H, $H_{1'b}$), 3.78 (m, 2H, $H_{2'}$), 4.05 (dd, $^{2}J_{HH} = 11.40$, $^{3}J_{HH} = 5.20$, 2H, $H_{3'a}$), 4.11 (dd, $^{2}J_{HH} = 11.40$, $^{3}J_{HH} = 5.50$, 2H, $H_{3'a}$), 4.81 [dhept, $^{3}J_{HH} = {}^{3}J_{HP} = 6.20$, 4H, C$H$($i$Pr)], 5.50 and 6.00 (2s, 2H, $H_{7'}$), 7.34 (m, 2H, H_4), 7.51 (dd, $^{3}J_{HH} = 8.16$, $^{4}J_{HP} = 5.50$, 2H, H_3), 7.64 (dd, $^{3}J_{HP} = 14.00$, $^{4}J_{HH} = 2.10$, 2H, H_6)	18.28 (s, $C_{8'}$), 23.78 and 24.12 [2d, $^{3}J_{CP} = 5.50$ and $^{3}J_{CP} = 2.60$, CH$_3$(iPr)], 42.52 (s, $C_{1'}$), 66.90 (s, $C_{3'}$), 67.07 (s, $C_{2'}$), 71.71 and 72.10 [2d, $^{2}J_{CP} = 6.50$, CH(iPr)] 125.84 (s, $C_{7'}$), 135.09 (d, $^{4}J_{CP} = 3.15$, C_4), 135.11 (d, $^{2}J_{CP} = 15.75$, C_2), 135.60 (d, $^{1}J_{CP} = 196.00$, C_1), 136.41 (s, $C_{6'}$), 136.42 (d, $^{2}J_{CP} = 13.90$, C_6), 138.75 (d, $^{3}J_{CP} = 10.00$, C_5) 167.10 (s, $C_{5'}$)	+14.28 (s)	3200–3500 (OH), 2920–3030 (CH_2), 1712 (C=O), 1638 (CH_2=C), 1260 (P=O), 1166 (O–C), 996 (P–OiPr)	864 (M + 2, 0.04), 845 (M − 17, 0.05), 826 (M − 2 × 18), 0.05)	18	Yellow oil
1b	1.33 and 1.41 [2d, $^{3}J_{HH} = 620$, 12H, CH_3(iPr)], 1.92 (s, 3H, $H_{8'}$), 2.91 (dd, $^{3}J_{HH} = 14.00$, $^{3}J_{HH} = 920$, 1H, $H_{1'a}$), 3.23 (dd, $^{2}J_{HH} = 14.00$, $^{3}J_{HH} = 2.50$, 1H, $H_{1'b}$), 3.78 (m, 1H, $H_{2'}$), 4.11 (dd, $^{2}J_{HH} = 11.20$, $^{3}J_{HH} = 5.30$, 1H, $H_{3'a}$), 4.17 (dd, 1H, $^{2}J_{HH} = 11.20$, $^{3}J_{HH} = 5.50$, 1H, $H_{3'b}$), 4.92 [dhept, $^{3}J_{HH} = 6.20$, $^{3}J_{HP} = 7.25$, 2H, CH(iPr)], 5.55 and 6.09 (2s, 1H, $H_{7'}$), 7.31–728 (m, 1H, H_5), 741–752 (m, 1H, H_4), 7.62–7.68 (m, 1H, H_3), 7.82 (ddd, $^{3}J_{HP} = 14.00$, $^{3}J_{HH} = 7.60$, $^{4}J_{HH} = 1.60$, H_6)	18.24 (s, $C_{8'}$), 23.59 and 24.10 [2d, $^{3}J_{CP} = 5.50$, CH$_3$(iPr)], 42.62 (s, $C_{1'}$), 66.82 (s, $C_{2'}$), 66.90 (s, $C_{3'}$), 71.50 [d, $^{2}J_{CP} = 6.60$, CH(iPr)], 125.72 (s, $C_{7'}$), 127.33 (d, $^{3}J_{CP} = 13.90$, C_5), 132.62 (d, $^{4}J_{CP} = 3.15$, C_4), 133.24 (d, $^{3}J_{CP} = 8.20$, C_3), 134.95 (d, $^{1}J_{CP} = 135.00$, C_1), 135.75 (d, $^{2}J_{CP} = 13.20$, C_6), 135.99 (s, $C_{6'}$), 138.77 (d, $^{2}J_{CP} = 8.80$, C_2), 167.52 (s, $C_{5'}$)	+16.95 (s)	3200–3500 (OH), 2920–3030 (CH_2), 1706 (νC=O), 1638 (CH_2=C), 1242 (P=O), 1168 (νO–C), 1058 (νP–OiPr)	416 (M^+, 0.5), 398 (M − 18, 3.4), 357 (0.4), 317 (4): 300 (2), 128 (100), 6.9 (43)	53	Yellow oil
4a	1.27 and 1.37 [2d, $^{3}J_{HH} = 6.20$, 24H, CH_3(iPr)], 4.79 [dhept, $^{3}J_{HH} = 6.20$, $^{3}J_{HP} = 7.70$, 4H, CH(iPr)], 5.59 (s, 2H, SH), 7.19–7.27 (m, 4H, H_3, H_4), 7.79 (dd, $^{4}J_{HH} = 1.60$, $^{3}J_{HP} = 13.80$, 2H, H_6)	23.60 and 23.90 [d, $^{3}J_{CP} = 4.00$, $^{3}J_{CP} = 5.50$, CH_3 (iPr)], 71.69 [d, $^{2}J_{CP} = 250$, CH(iPr)], 127.75 (d, $^{1}J_{CP} = 189.00$, C_1), 131.15 (d, $^{3}J_{CP} = 14.50$, C_3), 132.12 (d, $^{3}J_{CP} = 15.00$, C_5), 134.62 (d, $^{4}J_{CP} = 2.50$, C_4), 136.79 (d, $^{2}J_{CP} = 9.40$, C_6), 137.40 (d, $^{2}J_{CP} = 8.80$, C_2)	+15.62 (s)			99	Yellow oil
4b	1.19 and 1.31 [2d, $^{3}J_{HH} = 6.20$, 12H, CH_3(iPr)], 4.64 [dhept, $^{3}J_{HH} = 6.20$, $^{3}J_{HP} = 7.80$, 2H, CH(iPr)], 5.39 (s, 1H, SH), 7.13–7.23 (m, 1H, H_5), 7.30–7.34 (m, 2H, H_3, H_4), 7.76 (dd, $^{3}J_{HH} = 7.60$, $^{3}J_{HP} = 14.20$, 1H, H_6)	23.53 and 23.95 [d, $^{3}J_{CP} = 3.70$, and $^{3}J_{CP} = 3.90$, CH$_3$(iPr)], 71.32 [d, $^{2}J_{CP} = 5.70$, CH(iPr)], 124.35 (d, $^{3}J_{CP} = 13.90$, C_5), 126.30 (d, $^{1}J_{CP} = 189.00$, C_1), 129.80 (d, $^{3}J_{CP} = 12.60$, C_3), 132.10 (d, $^{4}J_{CP} = 3.15$, C_4), 134.56 (d, $^{2}J_{CP} = 8.80$, C_6), 137.78 (d, $^{2}J_{CP} = 8.80$, C_2)	+18.20 (s)			87	Yellow liquid
3a	1.21 and 1.28 [2d, $^{3}J_{HH} = 6.20$, 12H, CH_3(iPr)], 4.73 [dhept, $^{3}J_{HH} = 6.20$, $^{3}J_{HP} = 8.70$, 4H, CH(iPr)], 6.87–6.94 (m, 4H, H_3, H_5), 7.47–7.54 (m, 4H, H_2, H_6)	22.60 and 22.85 [2d, $^{3}J_{HH} = 6.20$, 12H, CH_3(iPr)], 4.64 [d, $^{3}J_{CP} = 5.60$ and $^{3}J_{CP} = 4.00$, CH$_3$(iPr)], 72.40 [d, $^{2}J_{CP} = 7.00$, CH(iPr)], 118.70 (d, $^{4}J_{CP} = 2.50$, C_3, C_5), 120.50 (d, $^{3}J_{CP} = 7.00$, C_2, C_6), 135.3 (d, $^{2}J_{CP} = 5.00$, C_1), 156.40 (d, $^{5}J_{CP} = 3.15$, C_4)	+23.73 (s)			93	Yellow oil
3b	1.24 and 1.32 [2d, $^{3}J_{HH} = 6.20$, 12H, CH_3(iPr)], 4.77 [dhept, $^{3}J_{HH} = 6.20$, $^{3}J_{HP} = 8.7$, 2H, CH(iPr)], 7.31–7.37 (m, 3H, H_3, H_4, H_5), 7.37–7.67 (m, 2H, H_2, H_6)	23.39 and 23.75 [2d, $^{3}J_{CP} = 5.60$ and $^{3}J_{CP} = 2.60$, C_4), CH$_3$(iPr)], 73.25 [d, $^{2}J_{CP} = 6.90$, CH$_3$(iPr)], 127.21 [d, $^{2}J_{CP} = 7.00$, C_1], 128.57 (d, $^{5}J_{CP} = 3.15$, C_4), 129.08 (d, $^{4}J_{CP} = 1.90$, C_3, C_5), 134.14 (d, $^{3}J_{CP} = 5.70$, C_2, C_6)	+21.38 (s)			97	Yellow liquid
2a	3.42 (s, 2H, SH), 6.85–6.92 (m, 2H, H_3, H_5), 7.24–7.31 (m, 2H, H_2, H_6)	119.53 (s, C_3, C_5), 124.07 (s, C_1), 131.72 (s, C_2, C_6), 155.60 (s, C_4)		3082 (C–H arom.), 2550 (SH), 1530 and 1582 (C=C arom.)		94	Yellow solid

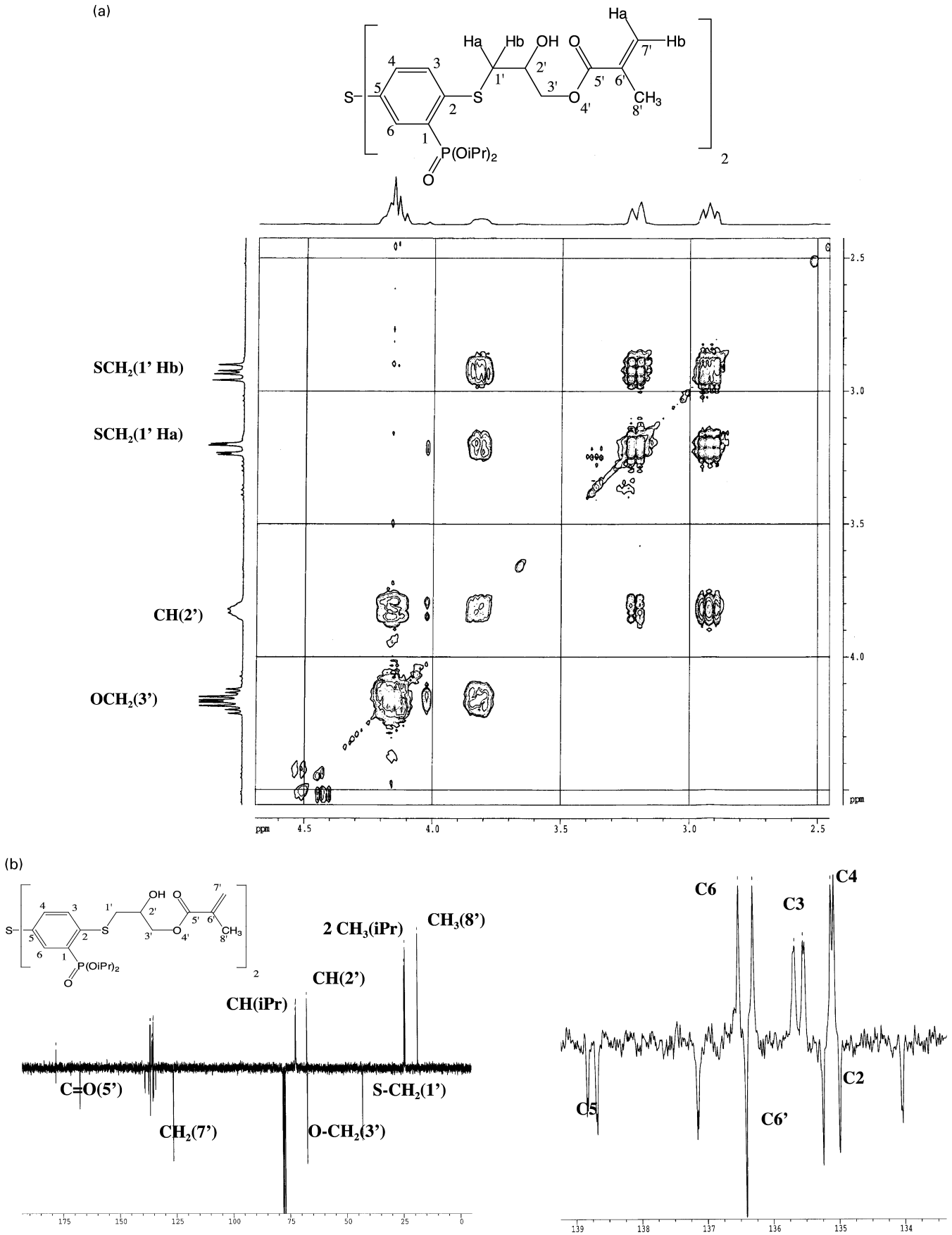
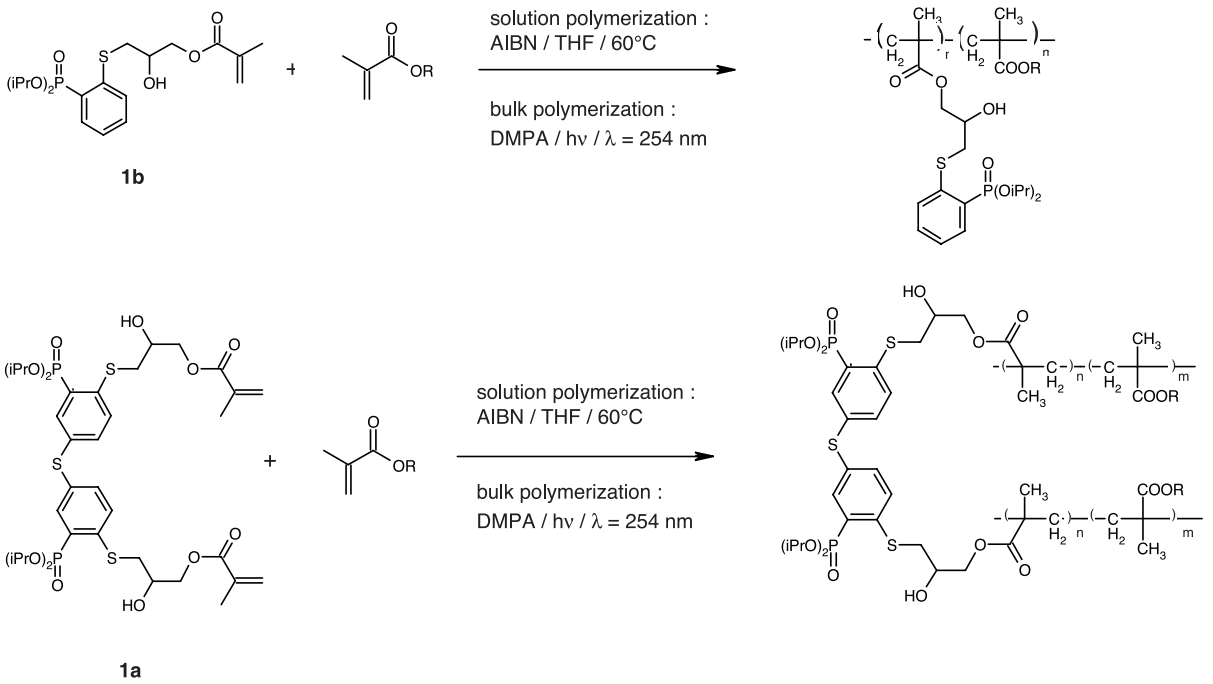


Fig. 1. (a) 2-D proton spin diffusion spectrum of monomer **1a** cast from $CDCl_3$. (b) *J* mod spectrum of **1a** cast from $CDCl_3$.



Scheme 5. Free-radical (co)polymerization of monomers **1a**, **1b**. (AIBN: *N*,*N*′-azobis-isobutyronitrile; DMPA: 2, 2-dimethoxy-2-phenylacetophenone).

UV-irradiation ($\lambda = 254$ nm), showed that the photopolymerized composite resin **10b′** has been synthesized by light-induced cross-linking polymerization of **1b**. No T_g was obtained in this case.

Under similar conditions (co)polymers **11b**–**13b** and **11b′**–**13b′** were synthesized from monomer **1b**, and characterized by their IR data, ^{1}H, ^{31}P NMR spectra and SEC. The chemical shifts and signal assignments are summarized in Table 3 and in Section 3.

In a second step, similar polymerizations were realized with compound **1a** containing either bis(phosphonate) functions and dimethacrylate groups.

Diphosphonate (co)polymers **10a**–**14a** have been prepared by free radical homo- and copolymerizations of **1a** using AIBN in THF at 60 °C, according to Scheme 5, Table 2. Yields, inherent viscosities and glass transition temperature of (co)polymers **10a**–**14a** are summarized in Table 3.

Good to high yields (after purification by precipitation) were obtained and inherent viscosities lying in the range 0.20–2.34 dl g^{-1} were observed. The number average molecular weight of these polymers was estimated to be in the range 437–8721 g mol^{-1} from size exclusion chromatography (SEC) measurements (according to polystyrene (PS) standards) with a polydispersity index of 1.3–4.9. (Co)polyphosphonates **10a**–**14a** were found amorphous (T_g ranged from 53 to 106 °C, respectively) and did not crystallize. The structure and purity of (co)polyphosphonates were confirmed in each case by ^{1}H, ^{31}P NMR and FTIR. The absence of CH_2=C singlet signal at 5.50 and 6.00 ppm in ^{1}H NMR spectra of **10a**–**14a** shows

Table 2
Free-radical (co)polymerization of monomers **1a**, **1b**

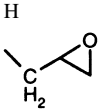
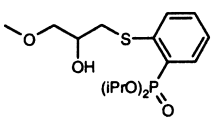
Comonomer	R	Solution polymerization		Bulk polymerization	
		Monomer **1a**	Monomer **1b**	Monomer **1a**	Monomer **1b**
Homopolymer		**10a**	**10b**	**10a′**	**10b′**
Methyl methacrylate	Me	**11a**	**11b**	**11a′**	**11b′**
Methacrylic acid	H	**12a**	**12b**	**12a′**	**12b′**
Glycidyl methacrylate		**13a**	**13b**	**13a′**	**13b′**
Monomer **1b**		**14a**		**14a′**	

Table 3
Data of copolymers

Monomer	Polymers								Polymerization in solution				Bulk polymerization	
	Comonomer	r	No.	Yield[a] (%)	T_g (°C)	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w$ (g mol^{-1})	I	η_{inh} (dl g^{-1})	^{1}H NMR ($CDCl_3$/TMS) δ (ppm), J (Hz)	^{31}P NMR ($CDCl_3$/TMS) δ (ppm)	IR ($CHCl_3$) ν (cm^{-1}) (OH), (C=O), (P=O), (O–C), (P–OR)	No.	T_g (°C)
1a			**10a**	67	53, 93	8721	11,621	1.79	0.25	0.80–0.90 (m, 4H, H_3), 1.36–1.44 [m, 24H, CH_3(*i*Pr)], 1.79 (s, 6H, H_4), 2.90–3.23 (m, 4H, $H_{3'}$), 3.40–4.20 (m, 6H, $H_{1'}$, $H_{2'}$), 4.65–4.90 [m, 4H, CH(*i*Pr)], 7.20–8.00 (m, 6H, H arom.)	+14.19 (s)	3200–3600, 1726, 1238, 1100, 1050	**10a′**	No
1a	Methyl methacrylate	1/4	**11a**	83	52, 84	6354	7352	1.40	0.16	0.70–0.85 [m, 4H, H_2 (MMA)], 0.90–0.97 [m, 2H, H_2 (**3b**)], 1.10–1.40 [m, 12H, CH_3(*i*Pr)], 1.65 [s, 6H, H_4 (MMA)], 2.03 [s, 3H, H_4 (**3b**)], 2.50–3.40 (m, 2H, $H_{3'}$), 3.44–3.86 (m, 9H, $H_{2'}$, $H_{3'}$, OCH_3), 4.70–4.95 [m, 2H, CH(*i*Pr)], 7.32–8.20 (m, 3H, H arom.)	+14.16 (s)	3200–3600, 1730, 1218, 1196, 996	**11a′**	No
1a	Methacrylic acid	1/4	**12a**	70	109	Insoluble in THF			0.77	0.85–1.15 [m, 6H, H_3], 1.18–1.47 [m, 12H, CH_3(*i*Pr)], 1.75–2.10 (m, 9H, H_4), 2.70–3.50 [m, 3H, $H_{3'}$, $H_{2'}$], 3.75–4.10 (m, 2H, $H_{1'}$), 4.65–5.05 [m, 2H, CH(*i*Pr)], 7.25–8.0 (m, 3H, H arom.), $H_{3'}$, OCH_3), 4.70–4.95 [m, 2H, CH(*i*Pr)], 7.32–8.20 (m, 3H, H arom.)	+14.12 (s)		**12a′**	No
1a	Glycidyl methacrylate	1/4	**13a**	50	106	1176	4728	3.90	0.27	0.93 [s, 2H, H_3 (**3b**)], 1.00–1.68 [m, 16H, H_3 (GMA), CH_3(*i*Pr)], 1.57–2.20 (m, 9H, H_4), 2.32–3.15 (m, 6H, $H_{1'}$), 3.10–3.32 [m, 2H, $H_{2'}$ (GMA)], 3.34–4.58 [m, 7H, $H_{1'}$ (GMA), $H_{2'}$ (**3b**), $H_{1'}$, (**3b**)], 5.60–5.95 [m, 2H, CH(*i*Pr)], 7.25–8.15 (m, 3H, H arom.)	+15.05 (s)		**13a′**	No
1a	Monomer **1b**	1/1	**14a**	80	No	978	1404	1.88		0.52–0.95 (m, 4H, H_3), 1.00–1.47 [m, 24H, CH_3(*i*Pr)], 1.52–2.5 (m, 6H, H_4), 2.60–3.32 (m, 4H, $H_{3'}$), 3.42–4.24 (m, 6H, $H_{1'}$, $H_{2'}$), 4.50–4.95 [m, 4H, CH(*i*Pr)], 7.10–8.00 (m, 7H, H arom.)	+14.15(s), +15.74(s)		**14a′**	No
1b			**10b**	59	No	7185	9471	1.45		0.80–0.95 (m, 2H, H_3), 1.05–1.40 [m, 12H, CH_3(*i*Pr)], 1.73 (s, 3H, H_4), 2.72–3.23 (m, 2H, $H_{3'}$), 3.60–425 (m, 3H, $H_{2'}$, $H_{3'}$), 4.65–5.00 [m, 2H, CH(*i*Pr)], 7.10–7.95 (m, 4H, H arom.)	+16.93 (s)		**10b′**	No
1b	Methyl methacrylate	1/2	**11b**	31	153, 232	5728	7299	1.28	0.37	0.84 [s, 4H, H_3 (MMA)], 1.02 [s, 2H, H_3 (**3c**)], 1.27–1.43 [m, 12H, CH_3(*i*Pr)], 1.83–2.02 (m, 9H, H_4), 2.63–2.84 (2s, 2H, $H_{3'}$), 3.05–3.15 (m, 1H, $H_{2'}$), 3.60 [s, 6H, OCH_3 (MMA)], 3.95–3.99 (m, 2H, $H_{1'}$), 4.68–4.95 [m, 2H, CH(*i*Pr)], 7.35–7.82 (m, 4H, H arom.)	+13.25 (s)	3200–3600, 1716, 1206; 1102, 994	**11b′**	No
1b	Methacrylic acid	1/2	**12b**	55	172, 227	437	660	1.51		1.26–1.43 [m, 18H, H_3, CH_3(*i*Pr)], 1.83–2.06 (m, 9H, H_4), 2.78–3.31 (m, 2H, $H_{3'}$), 3.83–3.87 (m, 1H, $H_{2'}$), 3.94–3.99 (m, 2H, $H_{1'}$), 4.78–4.80 [m, 2H, CH(*i*Pr)], 7.50–8.25 (m, 4H, H arom.)	+13.23 (s)		**12b′**	141, 169
1b	Glycidyl methacrylate	1/2	**13b**	54	152, 160	4276	4810	1.35	2.34	0.90 [s, 2H, H_3 (**3c**)], 1.17–1.44 [m, 16H, H_3 (GMA), CH_3(*i*Pr)], 1.81–2.00 (m, 9H, H_4), 2.65 and 2.85 [2s, 2H, $H_{3'}$ (GMA)], 3.24 [s, 2H, $H_{2'}$ (GMA)], 3.70–383 [m, 1H, $H_{2'}$ (**3c**)], 3.87–3.93 [m, 2H, $H_{1'a}$ (GMA)], 3.95–4.09 [m, 2H, $H_{1'}$ (**3c**)], 4.29–4.35 [m, 2H, $H_{1'b}$ (GMA)], 4.70–488 [m, 2H, CH(*i*Pr)], 7.25–8.28 (m, 4H, H arom.)	+13.02 (s)	3200–3600, 1712, 1212; 1090, 994	**13b′**	170

r, molecular rate monomer/comonomer; T_g, glass transition temperature; $\bar{M}_n$, $\bar{M}_w$, number average molecular weight; I, polydispersity; η_{inh}, inherent viscosities.

[a] The yields reported are for purified compunds.

that the precipitated polymers were monomer-free. The ^{31}P NMR also provided convincing support for the assignment, as the resonance due to the phosphonate monomers was observed at $\delta + 14.28$ and $+16.95$ ppm for **1a** and **1b**, respectively, whilst in the phosphonate polymers **10b–13b** and **10a–14a** these signals were found to be at $\delta + 13.02$ and 15.74 ppm, respectively. The 1:4 copolymeric structure of **10a–14a** has been elucidated spectroscopically for the first time. Table 1 summarizes the fundamental IR frequencies and bond assignments of the monomers **1a**, **1b** and Table 3 for homopolymers and (co)polymers. For the homopolymers, IR spectra the band at 1726 cm^{-1}, together with the strong bond absorption centred at 1100 cm^{-1}, is in accordance with the presence of the ester group. The C=O vibration show a relatively large shift with respect to the vibration in the monomer. The olefinic band indicated by the sharp absorption at 3062 and 1638 cm^{-1} in the IR spectrum of the monomer is absent in the spectra of the homopolymers. The bands at $\approx 1250\ cm^{-1}$ (νP=O) and $\approx 1000\ cm^{-1}$ (νP–OiP) correspond to the phosphonate group in agreement with the literature reports [15].

An other easy way to produce (co)polymers **10a′–14a′** and **11b′–13b′** is by bulk photoinitiated polymerization of a monomer mixture in the presence of DMPA as free radical photoinitiator. UV-radiation has already been used to produce composite resin of dimethacrylate monomers in various polymer matrix [30–36]. The main interest of using UV-light to induce the polymerization lies in the high polymerization rates, which can be reached under intense illumination, together with the advantage of a solvent-free formulation curable at ambient temperature.

Dimethacrylate monomers, which are known for their high reactivity, polymerize rapidly in the presence of photogenerated free radicals upon UV exposure ($\lambda = 254$ nm). In our case during polymerization of the dimethacrylate diphosphonate, the dimethacrylate functions react with the residual unsaturation on the surface of the splinter particles to produce a relatively uniform yellow pale (colourless), hard, brittle solid **10a′–14a′**. However, glass transition of (co)polymers **10a′–14a′** cannot be detected at the used experimental conditions. The T_g values obtained with DSC are also summarized in Table 3 as a function of blend composition. The tendency for cross-linking to occur either during bulk free radical photoinitiated polymerization has been observed for homo-and copolymerization of **1a** with methyl methacrylate, methacrylic acid, glycidyl methacrylate and monomer **1b**.

3. Experimental

3.1. General

All reactions were run under a positive nitrogen pressure. THF was distilled over sodium benzophenone ketyl. Monomers **1a**, **1b** were purified by flash chromatographies (silica gel). Eluent is cyclohexane or cyclohexane–ethyl acetate or cyclohexane–dichloromethane mixture in the ratio indicate below.

^{1}H, ^{13}C and ^{31}P NMR spectra were run on a Bruker AC 250 (250 MHz) spectrometer with TMS as an internal reference. The products were dissolved in the mentioned solvent. Data are given in the following order: chemical shift in ppm, multiplicity (s, singulet; d, doublet; t, triplet; q, quartet; hept, heptuplet; m, multiplet), coupling constant in hertz, assignment broad band ^{1}H decoupling. The solvent used is indicated below ($CDCl_3$ as solvent in most cases).

IR absorption spectra were recorded as liquid thin films between NaCl plates or as solids in KBr pellets, or dissolved in $CDCl_3$ on a Perkin Elmer 1760 16 PC Fourier transform spectrophotometer. The mentioned IR-absorptions were observed as strong bands in cm^{-1}.

Mass spectra were recorded with a Nermag P 1010 H spectrometer, electronic impact at 70 eV (the molecular ion and the most abundant ion are reported).

Molecular weights were determined by SEC. A waters 515 HPLC apparatus, fitted with a refractive index and UV detectors was used. It was equipped with a Styragel HR 0.5 and HR 4E (THF) columns calibrated with standard PS samples using tetrahydrofuran at 30 °C as the mobile phase at a flow rate of 0.6 ml min^{-1}. The volume of injected sample solution (1 mg ml^{-1}) was 20 μl.

Intrinsic viscosity measurement were carried out by using an Ubbelohde capillary viscometer having an internal diameter of 0.5 mm and a length of 15 cm. The flow times were measured by using a viscotimer Schott Gerate AVS 400. Because the flow times were relatively long (to >100 s), the correction for kinetic energy could be ignored. The samples were dissolved by adding fresh solvent and the solutions were then introduced into the viscosimeter reservoir at 25 °C.

Thermal properties of the (co)polymers and homopolymers were studied by differential scanning calorimetry (DSC) on a Perkin Elmer DSC-7 calibrated with an indium standard. The values of glass transition temperature (T_g) are obtained from the second heating run, at 20 °C min^{-1} under a nitrogen atmosphere and a least 10 mg of the sample used for DSC measurement.

3.2. Monomers synthesis

Diisopropyl chlorophosphate was prepared according to Ref. [28] from diisopropyl phosphite (66 ml; 0.39 mol) and 1.1 equiv. of sulfuryl chloride (34 ml; 0.42 mol) at ≤ 0 °C. The crude product formed was sufficiently pure for use without purification (diisopropyl chlorophosphate was damaged by distillation).

O,O,O′,O′-Tetraisopropyl *S,S′*-(thiodi-4,1-phenylene) bis(phosphorothioate) **3a** and *O,O′*-diisopropyl-*S*-phenyl-phosphorothioate **3b** were synthesized according to the method described by Masson [14,15].

Tetraisopropyl 2,2′-disulfanyl-5,5′-thiodi(phenylphosphonate) **4a** was prepared by reaction of bis(phosphorothioate) **3a** with LDA, according to the procedures described earlier by Masson [14,15].

3.2.1. General method

Under nitrogen atmosphere a solution of bis(phosphorothioate) **3a** (7 g, 12 mmol) in dry THF (10 ml) was slowly added at −78 °C, to a solution of LDA prepared from diisopropylamine (13 ml, 90 mmol, 7.5 equiv.) *n*-butyllithium (53 ml, 1.6 M in hexane, 84 mmol, 7 equiv.) and THF (50 ml) at −20 °C for 1 h. After 5 min, the mixture was allowed to warm to 0 °C for 30 min and stirred again for 3 h. The mixture was then added under N_2 to a stirred ice-cold solution of NH_4Cl/HCl (pH = 1) in diethyl ether.

A solution of 1 M HCl was added if necessary (solution pH must be ≤4) then the mixture was allowed to warm to room temperature and extracted with diethyl ether. The organic layer was washed with water, dried over $MgSO_4$. The solvent was removed in vacuo to give a yellow oil as crude product **4a**. Yield = quantitative.

3.2.2. Diisopropyl (2-sulfanylphenyl) phosphonate *4b*

According to the method described above, the reaction was carried out with phosphorothioate **3b** (5.003 g, 18 mmol), diisopropylamine (10 ml, 72 mmol, 4 equiv.) and *n*-butyllithium (40 ml, 1.6 M in hexane, 64 mmol, 3.5 equiv.). Evaporation of the solvent in vacuo furnished the product **4b** (4.31 g, 16 mmol) as a yellow liquid. Yield = 87%.

3.2.3. Tetraisopropyl [2,2′-bis(2-hydroxy-4-oxa-5-oxo-6-methylhept-6-enylsulfanyl)-5′,5′-thiodiphenyl] diphosphonate *1a* and diisopropyl [2-(2-hydroxy-4-oxa-5-oxo-6-methylhept-6-enylsulfanyl)] phosphonate *1b*

The experimental procedure employed here were the same as those reported by Sharpless [21].

In a round-bottomed, three-necked flask equipped with a nitrogen inlet, a condenser and a mechanic stirred were placed the phosphonate **4a** or **4b** and the glycidyl methacrylate in freshly distilled triethylamine. The mixture was stirred under nitrogen at 50 °C over 5 h and Et_3N was distilled of *under vacuum*. Monomers **1a** and **1b** were purified by flash chromatography on silicagel with the eluting solvent: ethyl acetate/cyclohexane mixture 3/1 for **1a** and 1/1 for **1b**.

1a (1.804 g, 2.1 mmol) was obtained by reaction of **4a** (6.974 g, 12 mmol), glycidyl methacrylate (3.8 ml, 28 mmol, 2.3 equiv.) and triethylamine (60 ml). Yield = 18%, yellow-orange oil.

1b (3.54 g, 8.5 mmol) was prepared analogously from **4b** (4.31 g, 16 mmol), glycidyl methacrylate (2.6 ml, 19 mmol, 1.2 equiv.) and triethylamine (25 ml). Yield = 53%, yellow oil.

3.3. Preparation of homopolymers and copolymers

3.3.1. Free radical polymerizations in solution (according to Pham [37,38])

3.3.1.1. General procedure. All polymerizations were performed in THF with *N*,*N*′-azobis-isobutyronitrile as an initiation under nitrogen atmosphere. The radical polymerization of phosphonate monomers bearing methacrylate functions was conducted under conditions described below.

In a round-bottomed, two-necked flask equipped with a condenser, a nitrogen inlet and a magnetic stirrer were placed monomer and comonomer dissolved in anhydrous freshly distilled THF (5 ml) and AIBN (2.5 mol% of methacrylate function). The flask was then immersed in an oil bath at 60 °C and the polymerization allowed to proceed during 24 h in refluxing THF before cooling. The mixture was then concentrated under reduced pressure to give the crude polymers. NMR analysis carried out to verify the absence of the signal CH_2=CH of the methacrylate groups, indicated that the polymerization is complete. The product was purified by reprecipitation. After drying in vacuo for ~3 h, the polymers were fully characterized by spectroscopy, SEC and DSC analysis.

*3.3.1.2. Polymerization of monomers **1a** and **1b**.* Homopolymer **10a** was obtained from monomer **1a** (100 mg, 0.12 mmol) and AIBN (1 mg, 6 mmol), according to the general procedure (24 h at the reflux temperature of THF). The crude product was dissolved in dichloromethane and precipitated by adding slowly to pentane then dried. Yield = 67% (67 mg), white powder.

*3.3.1.3. Preparation of copolymer **11a** from **1a** and methyl methacrylate.* According to the general method (24 h in refluxing THF), the copolymer **11a** was prepared by the reaction of monomer **1a** (50 mg, 58 mmol) with methyl methacrylate (25 μl, 233 mmol, 4 equiv.) and AIBN (2.4 mg, 14.5 mmol). The white solid was diluted in CH_2Cl_2 and precipitated by dropwise addition to pentane and dried. Yield = 83% (60.75 mg).

*3.3.1.4. Preparation of copolymer **12a** from **1a** and methacrylic acid.* The reaction of **1a** (45 mg, 52 mmol) with methacrylic acid (20 μl, 0.22 mmol, 4 equiv.) and AIBN (2.4 mg, 15 mmol), according to the general procedure (24 h at the reflux temperature of THF) gave **12a** (49.6 mg). The crude polymer **12a** was purified by reprecipitation from methanol using diethyl ether as the non-solvent and dried in vacuo. Yield = 70%, white powder.

*3.3.1.5. Preparation of copolymer **13a** from **1a** and glycidyl methacrylate.* According to the general method (24 h in refluxing THF), the copolymer **13a** was obtained from monomer **1a** (100 mg, 12 mmol), glycidyl methacrylate

(64 μl, 0.46 mmol, 4 equiv.) and AIBN (2.80 mg, 17 mmol). The crude copolymer was dissolved in CH_2Cl_2 and reprecipitated from diethyl ether. Yield = 50% (83 mg), white powder.

*3.3.1.6. Preparation of copolymer **14a** from **1a** and monomer **1b***. Monomer **1a** (92 mg, 0.22 mmol) reacted with monomer **1b** (195 mg, 22 mmol) in the presence of AIBN (2.3 mg, 14 mmol) to provide the copolymer **14a**, according to the general procedure (24 h at the reflux temperature of THF). The purification was performed by dissolving in dichloromethane, and cyclohexane was used as precipitant. Yield = 80% (233 mg) yellowish powder.

*3.3.1.7. Preparation of homopolymer **10b** from monomer **1b***. Reaction was carried out on monomer **1b** (100 mg, 0.24 mmol) and AIBN (98 mg, 0.06 mmol), according to the general method (24 h in refluxing THF). The polymer was purified by reprecipitation from CH_2Cl_2 using cyclohexane as the non-solvent and dried in vacuo. Yield = 59% (59 mg), white powder.

*3.3.1.8. Preparation of copolymer **11b** from **1b** and methyl methacrylate*. According to the general procedure (24 h at the reflux temperature of THF), monomer **1b** (53 mg, 0.12 mmol), methyl methacrylate (26 μl, 0.24 mmol) and AIBN (1.3 mg, 0.009 mmol) were used to furnish the copolymer **11b**. Purification of the resulting copolymer was accomplished by reprecipitation from CH_2Cl_2 using pentane as the precipitant. Yield = 31% (23.4 mg), white powder.

*3.3.1.9. Preparation of copolymer **12b** from **1b** and methacrylic acid*. Reaction of monomer **1b** (53 mg, 0.12 mmol) with methacrylic acid (20 μl, 0.24 mmol) and AIBN (1.70 mg, 0.010 mmol) affords **12b**, according to the general method (24 h in refluxing THF). The crude copolymer was purified by reprecipitation from CH_2Cl_2 using petroleum ether as precipitating agent and dried in vacuo. Yield = 55% (40 mg), white powder.

*3.3.1.10. Preparation of copolymer **13b** from **1b** and glycidyl methacrylate*. According to the general procedure (24 h at the reflux temperature of THF), the copolymer **13b** was obtained by the reaction of **1b** (52 mg, 0.12 mmol) with glycidyl methacrylate (33 μl, 0.24 mmol) and AIBN (1.5 mg, 0.009 mmol). Purification of the resulting copolymer by reprecipitation from CH_2Cl_2/diethyl ether furnished 47 mg of yellow-colourless resin. Yield = 54%.

*3.3.2. Bulk free radical photoinitiated polymerization. Preparation of homopolymers **10a′**, **10b′** and copolymers **11a′–14a′**, **11b′–14b′***

The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (5% molar of methacrylate function) was dissolved in the mixture of monomers or **1b** (50 mg, 0.06 mmol) and comonomers (0.23 mmol, 4 equiv.) under stirring at room temperature. For the UV-cured materials, the thickness of cure practically realizable was approximately 2 mm, so that a thin layer (1 mm) of this mixture was irradiated on an optical bench set-up utilising a 150 W UV lamp, $\lambda = 254$ nm (Heraeus Noblelight) at 10 cm distance during 2 h. (The UV radiation intensity at 254 nm was 150 W/cm^2 at the sample level.) The insoluble obtained resins were then characterized by DSC.

4. Conclusion

In summary, the monomers selected for this study are close to those typically used in UV-curable resins. Two novel aromatic mono- and di(phosphonate) monomers bearing mono- and di(methacrylate) functions were synthesized from readily available mono- and bis(sulfanyl phenyl phosphonate) and GMA and characterized with moderate to good yields. The proposed structure was confirmed by FTIR and NMR spectra. The free radical homopolymerization and copolymerization of these monomers in THF solution gave predominantly amorphous linear (co)polymers. They exhibited moderate to high glass transition. Some preliminary attempts to produce composite resins in bulk copolymerization led to cross-linking, upon UV-irradiation in the presence of free radical initiator DMPA. Although no tests of biocompatibility and adhesion to the tooth have not yet been done, both of these (co)polymers already constitute a new class of materials for potential use in dental composites.

Further studies related to the corresponding monomers, polymers and (co)polymers bearing the free phosphonic acid function are under way.

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