Functionalized D-Sorbitol-Based Organogelators for Dental Materials (I)

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Functionalized organogelators derived from 1,3;2,4-bis-O-benzylidene-D-sorbitol with methoxy and carbonylaminoethyl methacrylate moieties were prepared, characterized and their gelation ability was evaluated in order to be utilized as additives for dental materials obtained by photopolymerization of several dimethacrylate (DMA) monomers.

Keywords: 1,3:2,4-bis-O-(p-methoxybenzylidene)-D-sorbitol, 1,3:2,4-bis-O-benzylidene-5,6-bis-carbonylamino -ethyl methacrylate-D-sorbitol, isocyanatoethyl methacrylate

1,3 :2,4-*Bis-O*-benzylidene-D-sorbitol (**DBS**) is known as a versatile gelling agent for a wide range of organic solvents. Recently the gelation ability of **DBS** was extended to more complex systems such as isotactic polypropylene, poly(propylene-glycol), silicone fluids and liquid crystals [1] and is reported to reduce volumetric shrinkage and to increase vinyl conversion for photopolymerization of DMA-derived monomers used for dental materials [2].

Following our interest in D-sorbitol based organogelators [3-6] and their use in the preparation of nanostructured materials [7] we report here the synthesis and characterization of two functionalized derivatives of **DBS**: 1,3:2,4-bis-O-(p-methoxybenzylidene)-D-sorbitol, (**MeO-DBS)**, 1,3:2,4-bis-O-benzylidene-5,6-bis-carbonylamino-ethylmethacrylate-D-sorbitol (**IEM-DBS**), respectively (fig. 1). These compounds are intended to be utilized as additives in the photopolymerization of several DMA monomers - bisphenol A glycidyl dimethacrylate (**bis-GMA**), urethane dimethacrylate (**UDMA**) and triehyleneglycol dimethylacrylate (**TEGDMA**) - for obtaining improved dental materials.

Experimental part

^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer. Approximatively 0.2M (for ^{1}H-NMR spectra) solution in DMSO-d_6 with TMS as internal standard was used. Reported data refer to chemical shifts (ppm, TMS), multiplicity, intensity of the signal and attribution.

FTIR-ATR and FT-RAMAN spectra were recorded on a VERTEX 70 BRUCKER FT-IR spectrometer coupled to a RAM II FT-Raman module. All FTIR measurements were performed in an ATR-FTIR cell on Ge crystal, at room temperature. The FTIR spectra were recorded using 32 scans with a resolution of 4 cm^{-1} in 600-4000 cm^{-1} region. The FT-Raman module was equipped with standard Nd:YAG laser source (1064 nm). All measurements were done using 50 scans, 100 mW of power and a 4 cm^{-1} resolution. The FT-RAMAN configuration provides a spectral range of 3600 – 50 cm^{-1}. The Raman spectra were obtained from compacted fine powder samples.

Differential Scanning Calorimetry (DSC)

The thermotropic behaviour of the gel samples was investigated by high-sensitivity DSC using NETZCH equipment. Gels obtained from **MeO-DBS** in dioxane and **IEM-DBS** in cyclohexane (prepared as mentioned below) were allowed to set overnight at 0°C. A sample of 20 mg of the cooled gel was carefully transferred into DSC pan and sealed. The measurement was carried out in the range temperature of -40 to 50 °C at a scan rate of 5 °C/min under nitrogen atmosphere. Baseline thermograms were obtained using the same amount of pure solvent.

X-Ray Photoelectron Spectroscopy

The XPS Spectra were recorded on Thermo Scientific K-Alpha equipment, fully integrated, with an aluminum anode

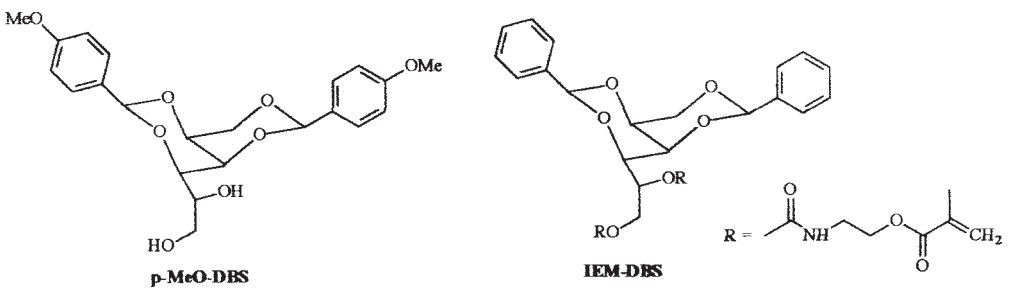

Fig. 1. Structures of methoxy and carbonylaminoethyl methacrylate functionalized organogelators derived from D-sorbitol

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monochromatic source. Survey scans (0-1200 eV) were performed to identify constitutive elements.

SEM images of the xerogels were recorded on a Hitachi S2600N scanning electron microscope. Melting points were determined using a Boetius type microscope with electric plate and are uncorrected. Dibenzylidenesorbitol (**DBS**) was kindly supplied by Milliken Chemical Europe. Commercially available D-sorbitol, 4-methoxybenzaldehyde and isocyanatoethyl methacrylate were used as purchased without any further purification. Solvents were purified according to procedures described in literature and kept on 4Å molecular sieves.

1,3:2,4-bis-O-(p-methoxybenzylidene)-D-sorbitol, MeO-DBS, was prepared from p-methoxybenzaldehyde and D-sorbitol in acid catalysis according to a procedure described in literature for alcoxy-substituted benzaldehydes [8]. A mixture of 3 g (16 mmoles) D-sorbitol, 3.15 g (22 mmoles) p-methoxybenzaldehyde and 0.16 g (0.016 mmoles) dodecylbenzene sulfonate were stirred at room temperature for 1hr. A solution of 4.2 mL (4.956 g, 51 mmoles) concentrated hydrochloric acid and 3.15 mL water was added to the reaction mixture and stirring was continued for 22 h. After neutralization with 2.25 g (56 mmoles) sodium hydroxide dissolved in 12 mL water, the resulted precipitate was filtered and washed successively with water and dichloromethane and finally dried in vacuum. Thus 3.17 g (69%) **MeO-DBS** were obtained as a white solid, m.p. 158°C.

^{1}H-NMR (δ, ppm, DMSO-d_6): 3.40 (dd, J= 10Hz, J=6Hz) and 3.58 (d, J=10Hz), 2H (CH_2 - sugar, H^6); 3.75 (s, 3H, OCH_3); 3.78 (m, 1H ,CH - sugar, H^5); 3.80 (d, J=10Hz, 1H, CH – sugar, H^2); 3.88 (s, 1H, CH – sugar, H^4); 4.09 (s, 1H, CH_2 - sugar, H^3); 4.12 (m, 2H, CH_2 – sugar, H^1); 5.59 (s, 2H, Ph-CH); 6.92 (d, J=8.4Hz, 4H, p-CH_3O-Ph - H^m); 7.39 (d, J=8.4 Hz, 2H, p-CH_3O-Ph - H^o) and 7.37 (d, J=8.4 Hz, 2H, p-CH_3O-Ph - H^o).

^{13}C-NMR (δ, ppm, DMSO-d_6): 55.11 ($O\underline{C}H_3$); 62.60 (CH_2-sugar, $\underline{C}^6$); 67.70 (CH-sugar-$\underline{C}^5$); 68.30 (CH-sugar- $\underline{C}^3$); 69.30 (CH_2-sugar-$\underline{C}^1$); 77.62 (CH-sugar- $\underline{C}^4$) 99.28 and 99.22 ($\underline{C}$H-Ph); 113.21 and 113.27 (p-CH_3O-Ph, $\underline{C}^m$); 127.44 and 127.48 (p-CH_3O-Ph, $\underline{C}^o$); 130.93 and 131.19 (p-CH_3O-Ph, $\underline{C}^{ipso}$); 159.34 and 139.40 (p-CH_3O-Ph, $\underline{C}^p$).

FT-IR (ATR, cm^{-1}): 3200-3400, broad (ν_{OH}); 2830 ($\nu_{Calif-H}$); 1615, 1517, 1401, 1342 ($\nu_{Car=Car}$); 1251 ($\nu_{Car-O-C}$, asym); 1019 ($\nu_{Car-O-C}$, sym); 1095 (ν_{CH-OH}); 1051 (ν_{CH2-OH});

FT-Raman (compacted powder, cm^{-1}): 3023, 3076 (ν_{Car-H}); 2903, 2871, 2835 ($\nu_{Calif-H}$); 1614 (2), 1256 (9), 837 (5), 642 (10), (in plane ring modes for 1,4-disubstituted benzenes); 1221 (sym C-O-C streching); 979 (asym C-O-C streching); 791 (out of plane C_{ar}-H deformations for 1,4 disubstituted benzenes).

1,3:2,4-bis-O-benzylidene-5,6-bis-carbonylamino-ethylmethacrylate-D-sorbitol, IEM-DBS, was prepared from **DBS** and isocyanatoethyl methacrylate according to a procedure described in literature for alcohols [9]. To a stirred solution of 1 g (2.8 mmoles) **DBS** in 45 mL THF at 60°C under argon, 1 mL (1.1 g, 7 mmoli) 2-isocyanatoethyl methacrylate and 0.1 mL dibutyltin dilaurate were added in drops. The viscous reaction mass was stirred overnight and then the resulted **IEM-DBS** was precipitated with an appropriate volume of hexane. The precipitate was separated by vacuum filtration, washed several times with hexane and dried in vacuum. Thus 1.77 g (95%) **IEM-DBS** were obtained as white solid with m.p. >315°C (decomp.).

^{1}H-NMR (δ, ppm, DMSO-d_6): 1.84, s, 6H (CH_3, methacrylate); 3.25, m, 4H, (CH_2-NH); 4.19, m, 4H (CH_2-OCO, methacrylate); 3.90-4.40, m, 7H and 5.10, m, 1H (CH, CH_2, sorbitol); 5.63, s, 2H (CH-Ph); 5.75, s, 2H and 6.04, s, 2H (vinyl, CH_2=); 7.37, m, 6H (Ph, H^m, H^p); 7.40, m, 4H (Ph, H^o).

^{13}C-NMR (δ, ppm, DMSO-d_6): 18.07 ($\underline{C}H_3$, allylic); 40.47 ($\underline{C}H_2$-NH); 63.34 ($\underline{C}H_2$-OCO); 63.29, 68.75, 69.32, 69.73, 76.24, 79.20 ($\underline{C}$H, $\underline{C}H_2$, sorbitol0; 99.10 and 99.39 ($\underline{C}$H-Ph); 125.86 ($\underline{C}H_2$=); 126.02, 126.17 (Ph, $\underline{C}^o$); 128.18 and 128.01 (Ph, $\underline{C}^p$); 128.90 and 128.56 (Ph, $\underline{C}^m$); 135.89 (-$\underline{C}$=, vinyl); 138.03 and 138.22 (Ph, $\underline{C}^{ipso}$), 158.71 ($\underline{C}$O-NH); 166.60 ($\underline{C}$O, methacrylate).

FT-IR (ATR, cm^{-1}): 3200-3400, broad (ν_{NH}); 1720 (ν_{CO}, methacrylate); 1695 (ν_{CO}, amide I); 1541 (ν_{CO}, amide II); 1638 ($\nu_{C=C-COO}$); 1266 (ν_{C-N}); 1210 (ν_{C-O}, vinyl ester); 1099 (ν_{C-O}, acetal).

FT-Raman (compacted powder, cm^{-1}): 3067 ($\nu_{=CH}$); 2959, 2929, 2898 ($\nu_{Calif-H}$); 1719 ($\nu_{C=O}$); 1639 ($\nu_{C=C}$); 1002 (ring mode vibration for monosubstituted benzenes).

Gelation test. A sample of gelator (15 mg) was mixed with the dried organic solvent (0.5 mL) in capped test tube, sonicated and heated on an oil bath at 60°C until a solution was obtained. The solution was cooled at room temperature for 1h and the tube was inverted. Gelation was considered successful if no sample flow occurred.

Xerogels for SEM measurements. The gel (3%wt/vol) was prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was evaporated by a vacuum pump for 6 h. The dried sample thus obtained was coated with silver.

Results and discussion

Synthesis of 1,3:2,4-bis-O-(*p*-methoxybenzylidene)-D-sorbitol, **MeO-DBS** was performed in good yield (69%) by treating an excess of D-sorbitol with *p*-methoxy-benzaldehyde in the presence of dodecylsulfonate and diluted hydrochloric acid according to a procedure described in literature for acetals of D-sorbitol with other alcoxy-substituted benzaldehydes [8]. The initial attempt to synthesize the desired compound according to previously reported method [3] under phase-transfer conditions - water/ dicloromethane, cetyltrimethylammonium bromide- and acid catalyst -sulfuric acid - was less successful (5%).

Functionalization of the hydroxyl groups of the **DBS** in order to obtain 1,3:2,4-*bis*-O-benzylidene-5,6-bis-carbonylaminoethylmethacrylate-D-sorbitol (**IEM-DBS**) was performed in very good yield (95%) by the reaction of the former with an excess of 2-isocyanatoethyl methacrylate catalyzed by dibutyltindilaurate in tetrahydrofurane according to a procedure described in literature for alcohols [9].

The structure and purity of the synthesized products were confirmed by ^{1}H-NMR, ^{13}C-NMR, FT-IR and FT-Raman spectra (Experimental section). In addition, XPS spectroscopy was used to identify the surface elements and carry out a quantitative analysis for parent compound **DBS** and the functionalized derivatives **MeO-DBS** and **IEM-DBS**, respectively, by recording survey spectra in the binding energy range from 0 eV to 1200 eV (fig. 2). Distinct carbon and oxygen peaks representing the major constituents of the investigated compounds are present in all the survey spectra. Taking as reference the survey spectra of **DBS** (fig. 2a), an increased ratio oxygen:carbon for **MeO-DBS** (fig. 2b) and the appearance of the nitrogen peak for **IEM-DBS** (fig. 2c) are observed.

The high resolution XPS spectra for the DBS compounds, in the region of C 1s are shown in figure 3 and the assignments of the deconvoluted peaks are presented in table 1.

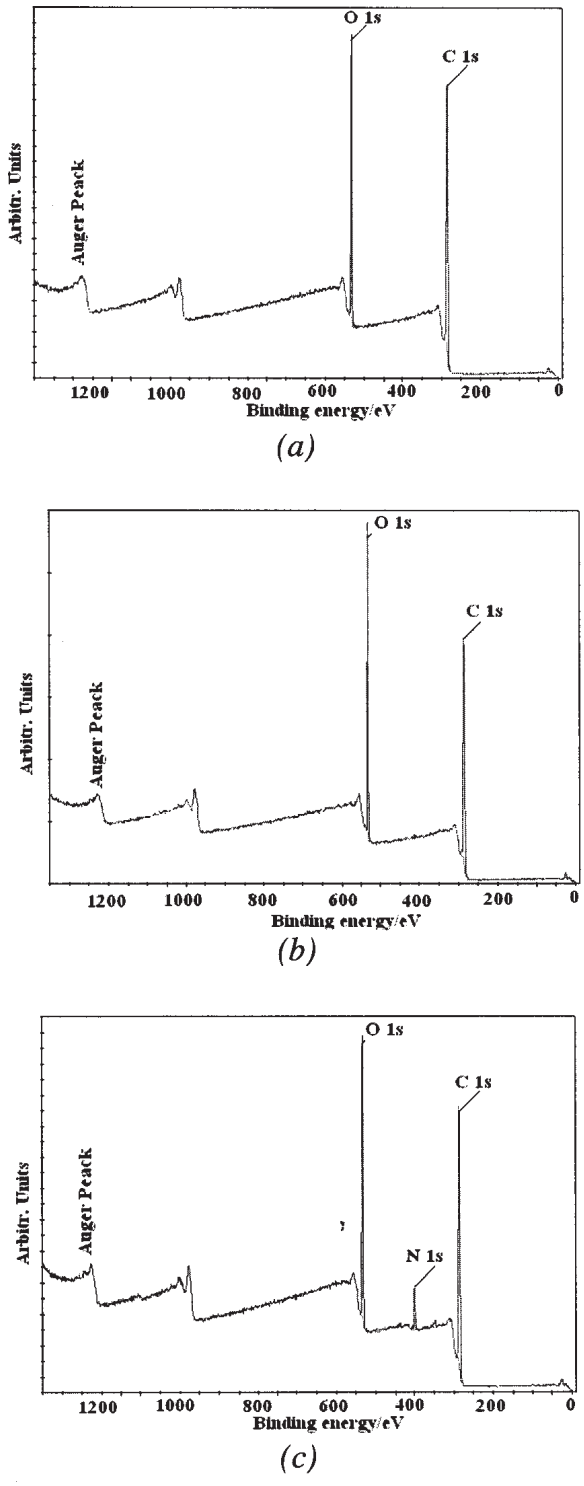


Fig. 2. XPS survey spectra for **DBS** (a), **MeO-DBS** (b) and **IEM-DBS** (c)

In all the high resolution spectra shown in figure 3 the low energy peak, denoted as **D**, ~ 284 eV was assigned to C=C bonds in aromatic rings, the peak denoted as **C**, ~ 287 eV was assigned to C-C/C-H bonds and the peak denoted as **B**, ~ 287 eV was assigned to C-O-C or C-O bonds respectively. The highest energy peak denoted as A at 288.8 eV which appear only in high resolution spectra of **IEM-DBS** was assigned to C-O-C=O and to N-C=O groups [10-12] introduced by functionalization of **DBS** with carbonylaminoethyl methacrylate moieties.

The gelation tests for the synthesized compounds were carried out for 17 typical organic solvents according to a method previously described [13] and the results are shown in table 2.

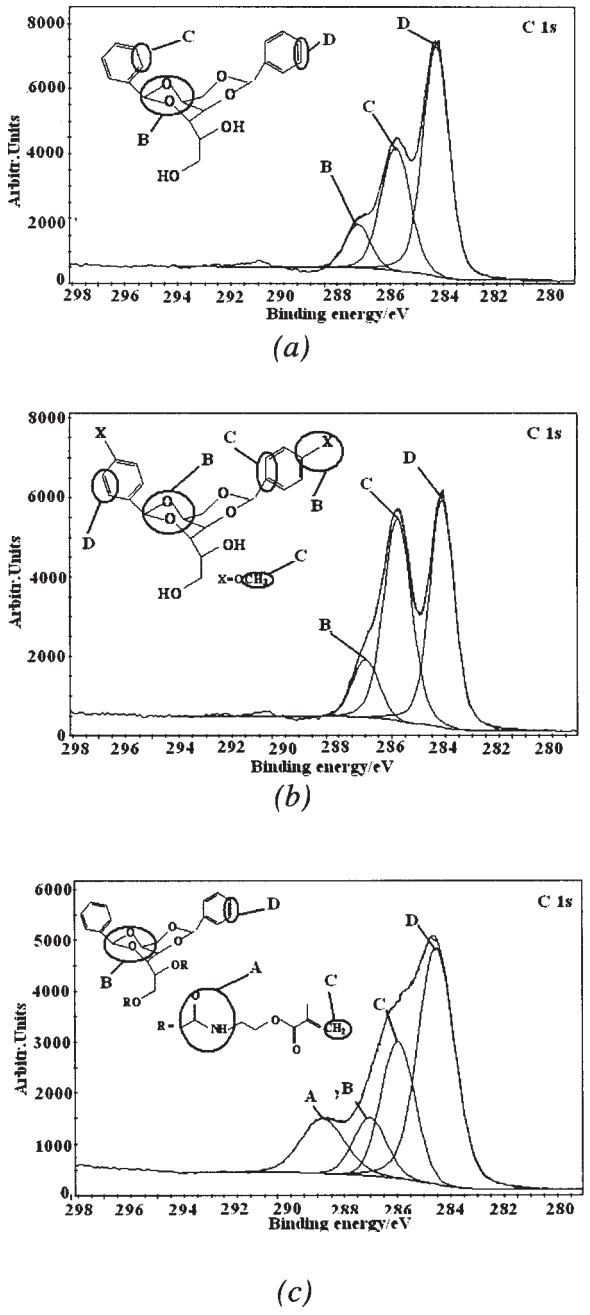


Fig.3. High resolution XPS spectra for **DBS** (a), **MeO-DBS** (b) and **IEM-DBS** (c)

The results presented in table 2 show that in the case of **MeO-DBS** substitution of benzene rings from the parent **DBS** with methoxy moieties does not affect the overlapping of benzylidene groups, proved previously to be the main driving force in the mechanism of gelation of **DBS** [14, 3]. As a consequence gels were obtained in the case of ten of the tested solvents. In the case of **IEM-DBS** by the functionalization of the remaining hydroxyl groups of **DBS** with carbonylaminoethyl methacrylate, introducing additional hydrogen bonding by amide and ester moieties, improves either the gelation ability or the solubility in the tested solvents.

The thermal stability of the gels formed by the functionalized organogelators was investigated by Differential Scanning Calorimetry (DSC). In figure 4 are shown DSC curves for gels formed in dioxane at increasing concentrations of **MeO-DBS** (a) and gels formed in cyclohexane at increasing concentrations of **IEM-DBS** (b), respectively. As the gel was heated (upscan), a peak due to transition from gel to sol ($T_{g\text{-}s}$) was observed. When

Deconvoluted peak for C1s	Assignments	Binding energy (eV)		
		DBS	MeO-DBS	IEM-DBS
A	C-O-C=O / N-C=O	-	-	288.8
B	C-O-C / C-O	287.22	286.99	287.03
C	C-C / C-H	285.79	285.78	285.97
D	C=C	284.27	284.12	284.53

Table 1
THE XPS ASSIGNMENTS FOR **DBS** AND FUNCTIONALIZED DERIVATIVES **MEO-DBS** AND **IEM-DBS**

Ent.	Organic solvent	MeO-DBS	IEM-DBS
1.	Hexane	I	S
2.	Cyclohexane	G	G
3.	Benzene	G	pG
4.	Toluene	P	pG
5.	Chloroform	G	G
6.	Dichloromethane	G	G
7.	Carbon tetrachloride	G	G
8.	Methanol	G	pG
9.	Ethanol	G	pG
10	Diethylether	I	I
11.	*n*- Butanol	P	vS
12.	Dioxane	P	S
13.	Tetrahydrofurane	S	G
14.	Ethyl acetate	G	G
15.	Acetone	G	pG
16.	Acetonitrile	G	G
17.	Dimethylsulfoxide	S	pG

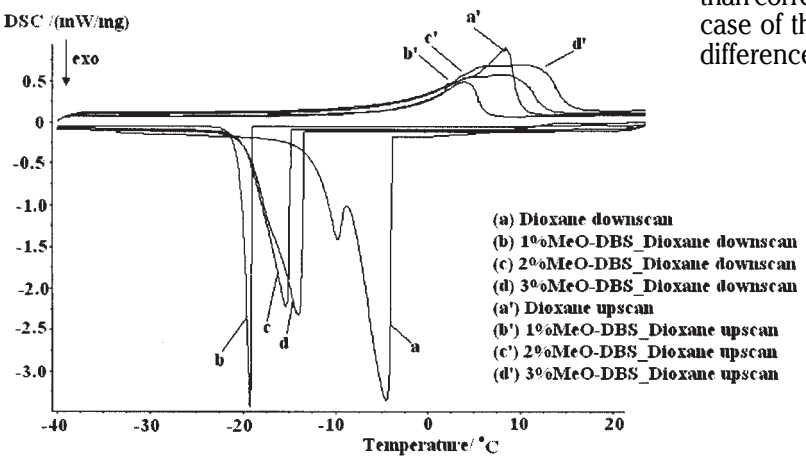
Table 2
GELATION TESTS FOR **MEO-DBS** AND **IEM-DBS** IN ORGANIC LIQUIDS (3.0% (WT/VOL)) AT 25°C

G = gel; pG = partial gel, I = insoluble; P = precipitation; S = solution, vS = viscous solution

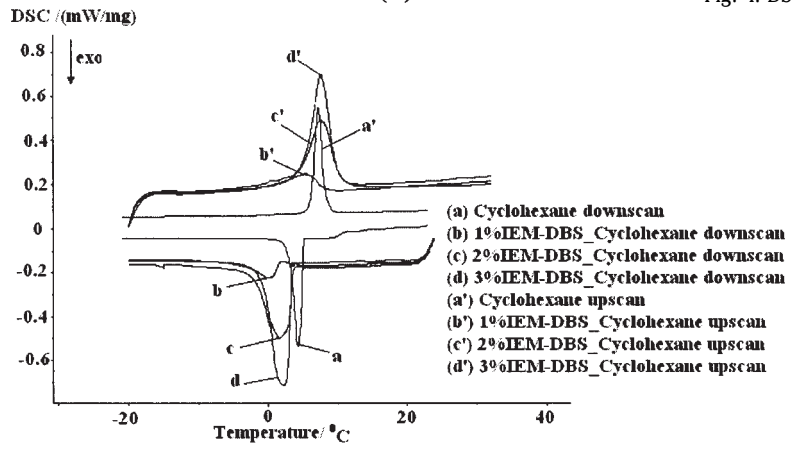
cooling the sol (downscan), a peak due to transition from sol to gel (T_{s-g}) was observed [15]. The gel-to-sol melting transitions of the gels were found to be broader than the corresponding solidification transitions of sol-to-gel. The sharp exothermic peaks for the solidification transitions indicate a "discontinuous" enthalpy change, implying that the transition is first order [16]. The broad melting peaks for gelation suggest that the gel-to-sol transition is weakly first order or possibly even second order [17].

Transition temperatures (T_{g-s}, T_{s-g}) and calorimetric enthalpies (ΔH) of the transitions deduced from the DSC curves are shown in tables 3 and 4.

The melting temperatures (T_{g-s}) for the gels formed by **MeO-DBS** in dioxane were found to be ~10-15°C higher than corresponding solidification temperatures (T_{s-g}). In the case of the gels formed by **IEM-DBS** in cyclohexane the differences between T_{g-s} and T_{s-g} are lower, ~ 4-5°C.



(*a*)



(*b*)

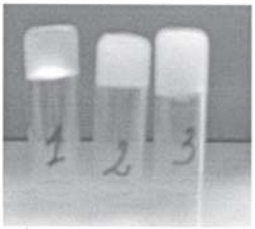
Fig. 4. DSC curves for gels formed by **MeO-DBS** in dioxane (a) and **IEM-DBS** in cyclohexane(b), respectively

Table 3
TRANSITION TEMPERATURES AND CALORIMETRIC ENTHALPIES (ΔH) FOR GELS FORMED BY **MeO-DBS** IN DIOXANE

MeO-DBS (%) in dioxane	upscan		downscan	
	T_{g-s} [°C]	ΔH [J/g]	T_{s-g} [°C]	ΔH [J/g]
0	**8.5**	**63.84**	**-4.5**	**61.15**
1	3.9	31.76	-19.2	37.92
2	8.1	69.95	-15.3	41.68
3	10.3	94.35	-14	60.07

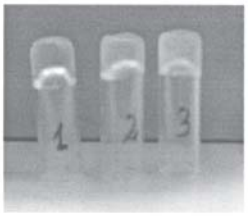
Table 4
TRANSITION TEMPERATURES AND CALORIMETRIC ENTHALPIES (ΔH) FOR GELS FORMED BY **IEM-DBS** IN CYCLOHEXANE

IEM-DBS (%) in cyclohexane	upscan		downscan	
	T_{g-s} [°C]	ΔH [J/g]	T_{s-g} [°C]	ΔH [J/g]
0	**7.3**	**6.36**	**4.3**	**16.75**
1	5.4	4.03	0.2	1.79
2	7.6	16.51	1.5	12.09
3	7.7	19.76	1.7	15.16



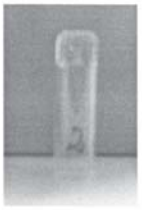
UDMA with 1%, 2%, 3% wt/vol **MeO-DBS**

(a)



UDMA with 1%, 2%, 3% wt/vol **IEM-DBS**

(b)



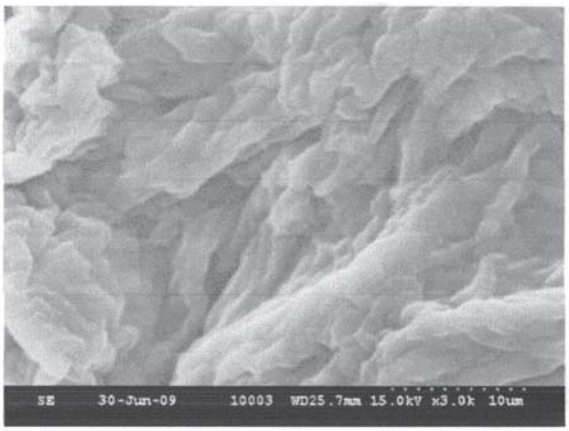
BisGMA with 1% wt/vol **MeO-DBS**

(c)

BisGMA with 1% wt/vol **IEM-DBS**

(d)

Fig. 5.Gelation tests for DMA monomers with **MeO-DBS** and **IEM-DBS**



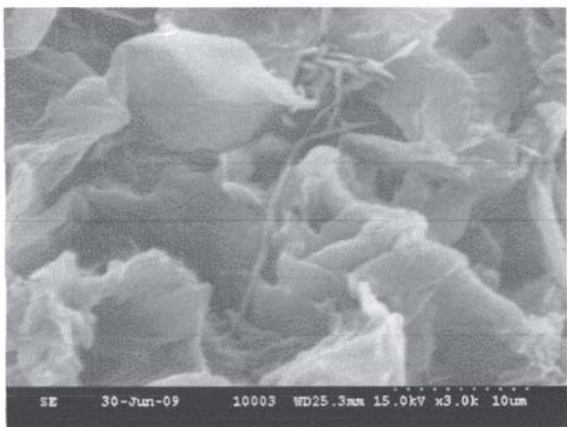


Fig. 6. SEM images of xerogel formed by **MeO-DBS** in dioxane (a) and by **IEM-DBS** in acetonitrile (b)

In order to estimate the maximum amount of the synthesized **DBS** derivatives which can be added to a DMA monomer with no significant changes in the flow properties, several gelation tests for **bis-GMA** and **UDMA** were performed for various concentrations of organogelator.

Gelation tests were run for concentrations of **MeO-DBS** and **IEM-DBS** of 1%, 2% and 3% wt/vol in the case of **UDMA** and only for 1% wt/vol for the highly viscous **Bis-GMA**. The results are shown in the figure 5 indicating that the gelation of **UDMA**

occurs for 2% wt/vol **MeO-DBS** (a) and for >3% wt/vol **IEM-DBS** (b). Due to a higher viscosity, gelation of **Bis-GMA** is obtained at 1% wt/vol concentrations of the both tested gelators (c, d).

Visual insights into the aggregation mode in the gel phase for **MeO-DBS** and **IEM-DBS** were obtained by Scanning Electron Microscopy (SEM) of the dried samples (xerogels). Figure 6(a) is a typical image of the xerogel obtained from **MeO-DBS** in dioxane and exhibits a tightly compacted three dimensional fibrous network with twisted fibrils similar to the structure reported previously for **NH_2-DBS** [3]. The xerogel obtained from **IEM-DBS** in acetonitrile presents a mixture of fibrils of ~300 nm in diameter and more compacted membrane-like aggregates (fig. 6b)

The morphology of xerogels with tightly packed fibrils indicates a high degree of intermolecular association by non-covalent forces for the molecules of the synthesized gelators with no significant influence of the solvent in good agreement with the good gelation ability of both polar and non-polar solvents as shown in table 2.

Conclusions

The synthesis and characterization of two functionalized D-sorbitol based organogelators: 1,3:2,4-bis-O-(p-methoxybenzylidene)-D-sorbitol, **MeO-DBS** and 1,3:2,4-bis-O-benzylidene-5,6-bis-carbonylaminoethyl-methacrylate-D-sorbitol (**IEM-DBS**) were extensively studied. Functionalization of phenyl or hydroxyl groups of dibenzylidene sorbitol (**DBS**) with introduction of additional hydrogen bonding moieties leads to an extended gelation ability and formation of xerogels with tightly compacted three dimensional fibrous networks. The gelation ability was tested on several dimethacrylate monomers in order to estimate the modification of their flow properties when these organolators are used as additives in photopolymerization leading to dental materials.

The subject was discussed also in other paper [18, 19].

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