# Bismethacrylate-Based Hybrid Monomers via Michael-Addition Reactions

**Ekkehard Müh,[†] Jürgen Marquardt,[†] Joachim E. Klee,*,[‡] Holger Frey,*,[†] and Rolf Mülhaupt[†]**

*Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum der Albert-Ludwigs-Universität, Stefan-Meier-Strasse 21/31, D-79104 Freiburg im Breisgau, Germany; and Dentsply DeTrey GmbH, De-Trey-Strasse 1, D-78467 Konstanz, Germany*

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ABSTRACT: Bismethacrylate monomers and macromonomers bearing various alkoxysilyl units were prepared by convenient Michael addition of ethylene glycol acrylate methacrylate (EGAMA) and ethylene glycol bisacrylate (EGBA) to various α,*ω*-alkoxysilylamines. The resulting monomers and macromonomers have been characterized in detail by NMR spectroscopy, VPO measurements and FAB−MS. Average molecular weights $M_n$ ranged between 530 and 1600 (VPO) in addition reactions with bisacrylates. FAB−MS evidenced the formation of a homologous macromonomer series. Viscosities of the liquid monomers are relatively low, ranging from 52 to 305 mPa·s. This renders these compounds interesting as reactive diluents in dental composite formulations. Polymerization of the monomers and macromonomers resulted in low volumetric shrinkage in the range of $\Delta V = 2.2-7.8\%$ at high methacrylate conversion. Cross-linking was monitored by photo-DSC. Furthermore, composites were prepared by mixing Bis-GMA with the new hybrid monomers, initiator and glass filler. The composites showed compressive strengths of 190−329 MPa, flexural strengths from 23 to 53 MPa and Young's moduli between 2090 and 5060 MPa. Low volumetric shrinkage was observed also for the composites upon photopolymerization, ranging from only 0.8% to 2.2% in comparison to over 3% shrinkage of commercially available composites. Besides the viscosity reducing effect due to the branched structure, the pendant alkoxysilyl groups of the synthesized hybrid monomers can be polymerized to form nanoparticles with reactive acrylate surface, permitting the in situ preparation of nanocomposites.

## 1. Introduction

Hybrid organic−inorganic monomers are materials that can be polymerized both at their "organic" functionality as well as at the "inorganic" reactive group, usually an alkoxysilyl moiety. Such compounds offer the possibility of simultaneous or successive radical polymerization and alkoxysilane condensation due to their orthogonal cross-linking chemistry.

Currently, hybrid monomers are considered to be advantageous for the development of advanced dental composites,[1] characterized by low thermal conductivity, elimination of galvanic currents, improved aesthetics, and good mechanical properties compared to traditional amalgams or glass−ionomer cements. Furthermore, advanced composite materials may serve to avoid key problems, such as the undesired volume shrinkage during polymerization that leads to cracks and secondary caries in the contact zone of tooth and filling. Volume shrinkage is caused mainly by two effects: on one hand, the replacement of van der Waals interactions by covalent bonds and, on the other hand, the increased packing density of polymer chains compared to monomer density. Besides the application of fillers, there are several possibilities to reduce volume shrinkage; e.g., by use of monomers with high molecular weight and large steric bulk the number of new covalent bonds formed upon cross-linking can be lowered. However, this often results in an undesired increase of the viscosity. An additional problem can result from the interaction of the inorganic filler with the organic matrix resin.

The commercially available methacryloxypropyltrimethoxysilane is the key monomer in several studies related to these problems.[2,3,4] Wei et al. reported on organic−inorganic hybrid fillers obtained by radical polymerization of methacryloxypropyltrimethoxysilane and successive alkoxysilane condensation.[5] In another work, they introduced the condensable alkoxysilyl groups by hydrosilylation of an allyl methacrylate−methacrylate copolymer.[6] Furthermore, methods to functionalize silica filler particles[7] and the preparation of polymerizable hybrid nanoparticles with methacryloxypropyltrimethoxysilane[8] or hydroxyethyl methacrylate[9,10,11] by convenient sol−gel processes[12,13,14] are well investigated. Novak et al. studied the simultaneous sol−gel condensation and free radical polymerization of tetraalkenylorthosilicates possessing polymerizable groups. In this manner, they obtained semiinterpenetrating networks of linear organic polymers in low-density $SiO_2$ networks.[15] The studies of Wolter et al. focused on the preparation of organic−inorganic copolymers, the so-called ORMOCER ("organically modified ceramics") materials,[16] applying multifunctional methacrylate alkoxsilanes derived from hydrosilylation or isocyanate addition.[17]

Michael addition reactions have been used for the synthesis of polyfunctional methacrylate-terminated monomers in a few recent works.[18] Dendrimers with methacrylic end groups were prepared by modification of aminofunctional poly(propyleneimine) dendrimers with ethylene glycol acrylate methacrylate.[19] However, in this context, the costly synthesis and problems associated with the high functional group density on the surface of dendrimers should be mentioned. In a similar

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[†] Albert-Ludwigs-Universität.
[‡] Dentsply DeTrey GmbH.

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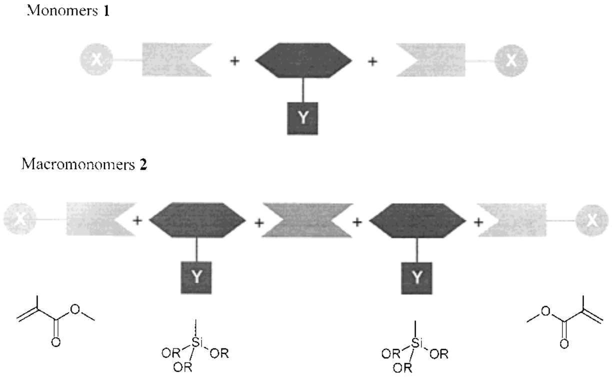


**Figure 1.** General synthetic strategy employed for all monomers **1** and macromonomers **2** prepared via Michael addition in this work: "construction kit".

manner Klee et al. obtained branched methacrylates by addition of ethylene glycol acrylate methacrylate to diamines and studied their application in dental composites.[20] An early work from Yoda and Toda described the addition polymerization of different bisacrylates with amines leading to linear polyamines.[21]

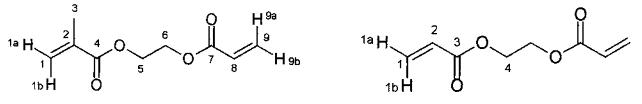
In this paper, we would like to report the synthesis of a series of novel, branched bismethacrylate hybrid monomers as well as macromonomers with pendant alkoxysilane moieties, prepared via convenient Michael addition of $\alpha,\omega$-alkoxysilane−amines to acrylate−methacrylates. Our investigation focuses on the relationship between molecular structure and viscosity and volume shrinkage as well as mechanical properties of the respective composites. By variation of the structure of, e.g., the alkoxysilyl groups as well as the spacer employed, a molecular "construction kit" was developed, which permits us to tailor the properties of the resulting polymer networks as well as the composites. This is schematically shown in Figure 1, which illustrates the strategies employed for the preparation of monomers (**1**) and macromonomers (**2**).[22] The condensation behavior of the alkoxysilyl groups of the hybrid monomers in different media has also been investigated.

## 2. Experimental Section

The following commercial products were used: 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), acryloyl chloride, (aminopropyl)triethoxysilane, aminopropylmethyldiethoxysilane, aminopropyltrimethoxysilane, aminopropyl[2-(2-methoxyethoxy)ethoxy]silane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane, camphor quinone, dimethylaminobenzoic acid ethyl ester, di-*tert*-butyl-*p*-cresole (BHT) (all of Fluka),2,2-bis[*p*-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]-propane (Bis-GMA) (Röhm), and triethylamine (Aldrich).

**Synthesis of Ethylene Glycol Acrylate Methacrylate (EGAMA)[23] and Ethylene Glycol Bisacrylate (EGBA).** A mixture of either 89.88 g (0.691 mol) of HEMA or 80.24 g (0.691 mol) of HEA and 76.88 g (0.760 mol) of triethylamine in 500 mL of absolute toluene was dissolved in a three-necked bottle equipped with stirrer, thermometer, and dropping funnel. Under cooling (0−5 °C), 68.75 g (0.760 mol) of acryloyl chloride dissolved in 50 mL of toluene were added during 4 h. After the mixture was allowed to stand overnight, the precipitate was filtered off and washed twice with 25 mL of toluene. Then the reaction mixture was extracted twice with 150 mL of water, 100 mL of 1 N HCl, and 100 mL of 1 N $Na_2HCO_3$ and dried over $Na_2SO_4$. Subsequently, toluene was evaporated (32 mbar, 40 °C) and 100 mg of BHT were added. Yield (EGAMA): 105.86 g (83%); Bp: 55 °C/3 mbar. IR: 1726 cm$^{-1}$ (s, C=O), 1638 cm$^{-1}$ (m, C=C). $^{1}$H NMR: $\delta = 6.42$ (9a, d), 6.11 (1b, 8, m), 5.83 (9b, d), 5.57 (1a, s), 4.39 (5, 6, s), 1.93 (3, s). $^{13}$C NMR: $\delta = 167.1$ (4), 165.9 (7), 135.9 (2), 131.4 (9), 128.0 (8), 126.1 (1), 62.4 (6), 62.2(5), 18.3 (3).

Yield (EGBA): 93.81 g (80%). Bp: 56 °C/4 mbar; IR: 1728 cm$^{-1}$ (s, C=O), 1637 cm$^{-1}$ (m, C=C); $^{1}$H NMR: $\delta = 6.38$ (1b, d), 6.09 (2, dd), 5.81 (1a, d), 4.35 (4, s); $^{13}$C NMR: $\delta = 165.8$ (3), 131.3 (1), 127.9 (2), 62.1 (4).



*EGAMA and EGBA*

**Addition Product 2a.** First, 9.20 g of EGAMA (0.05 mol) and 4.25 g (0.025 mol) of EGBA were dissolved in 25 mL of absolute ethanol. To this mixture was added 11.07 g (0.05 mol) of 3-aminopropyltriethoxysilane dissolved in 25 mL ethanol at 0−5 °C and stirred for 2 h. Subsequently, ethanol was evaporated and the mixture was reacted for a further 72 h at 23 °C.

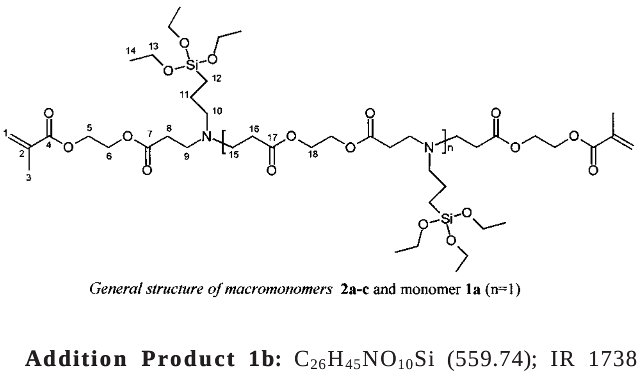
Following the same procedure, the addition products **1a**,**b** and **2b,c** were prepared. The ratios of the mixtures for the macromonomers **2** are summarized in Table 2.

**Addition Product 1a (*n* = 0):** $C_{27}H_{47}NO_{11}Si$ (589.76); IR 1738 cm$^{-1}$, 1724 cm$^{-1}$ (s, C=O), 1638 cm$^{-1}$ (m, C=C); $^{1}$H NMR $\delta = 6.01/5.48$ (1), 4.22 (5,6), 3.79 (13), 2.66 (9), 2.35 (8, 10), 1.83 (3), 1.41 (11), 1.11 (14), 0.45 (12); $^{13}$C NMR $\delta = 172.1$ (7), 166.8 (4), 135.8 (2), 125.8 (1), 62.2 (5), 61,8 (6), 58.2 (13), 56.4 (10), 49.0 (9), 32.4 (8), 20.1 (11), 18.1 (3, 14), 7.6 (12); $^{29}$Si NMR $\delta = -43.4$.

**Addition Product 2a (*n* = 1):** $C_{43}H_{80}N_2O_{18}Si_2$ (981.30); $^{1}$H NMR $\delta = 6.08/5.55$ (1), 4.28 (5,6), 4.21 (18), 3.76 (13), 2.73 (9, 15), 2.42 (8, 10, 16), 1.89 (3),1.47 (11), 1.18 (14), 0.51 (12); $^{13}$C NMR $\delta = 172.2$ (7, 17), 166.9 (4), 135.8 (2), 125.9 (1), 62.3 (5), 62.0 (18), 61,9 (6), 58.2 (13), 56.4 (10), 49.1 (9, 15), 32.5 (8, 16), 20.2 (11), 18.1 (3, 14), 7.7 (12); $^{29}$Si NMR $\delta = -43.4$.

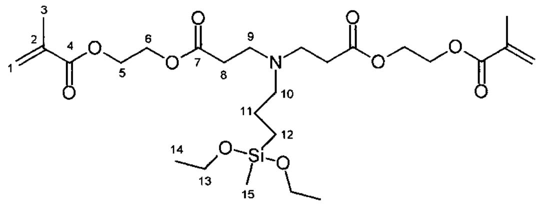
**Addition Product 2b (*n* = 2):** $C_{61}H_{113}N_3O_{25}Si_3$ (1372.84);$^{1}$H NMR $\delta = 6.08/5.55$ (1), 4.28 (5,6), 4.21 (18), 3.76 (13), 2.73 (9, 15), 2.42 (8, 10, 16), 1.89 (3), 1.47 (11), 1.18 (14), 0.51 (12); $^{13}$C NMR $\delta = 172.3$ (7, 17), 167.0 (4), 135.9 (2), 125.9 (1), 62.4 (5), 62.1 (18), 62,0 (6), 58.3 (13), 56.5 (10), 49.1 (9, 15), 32.5 (8, 16), 20.3 (11), 18.2 (3, 14), 7.8 (12); $^{29}$Si NMR $\delta = -43.3$.

**Addition Product 2c (*n* = 3):** $C_{78}H_{146}N_4O_{32}Si_4$ (1764.37); $^{1}$H NMR $\delta = 6.08/5.55$ (1), 4.28 (5,6), 4.21 (18), 3.76 (13), 2.73 (9, 15), 2.42 (8, 10, 16), 1.90 (3), 1.47 (11), 1.18 (14), 0.51 (12); $^{13}$C NMR $\delta = 172.3$ (7, 17), 167.0 (4), 135.9 (2), 126.0 (1), 62.4 (5), 62.1 (18), 62,0 (6), 58.3 (13), 56.5 (10), 49.1 (9, 15), 32.5 (8, 16), 20.3 (11), 18.2 (3, 14), 7.8 (12); $^{29}$Si NMR $\delta = -43.3$.



*General structure of macromonomers* **2a-c** and monomer **1a** (n=1)

**Addition Product 1b:** $C_{26}H_{45}NO_{10}Si$ (559.74); IR 1738 cm$^{-1}$, 1723 cm$^{-1}$ (s, C=O), 1638 cm$^{-1}$ (m, C=C); $^{1}$H NMR $\delta =$ 6.00/5.51 (1), 4.25 (5,6), 3.67 (13), 2.69 (9), 2.38 (8, 10), 1.87 (3), 1.40 (11), 1.13 (14), 0.46 (12), 0.03 (15); $^{13}$C NMR $\delta = 172.2$ (7), 166.9 (4), 135.8 (2), 125.9 (1), 62.3 (5), 61,9 (6), 58.0 (13), 56.7 (10), 49.1 (9), 32.5 (8), 20.3 (11), 18.2 (3, 14), 11.2 (12), −5.0 (15); $^{29}$Si NMR $\delta = -3.0$.

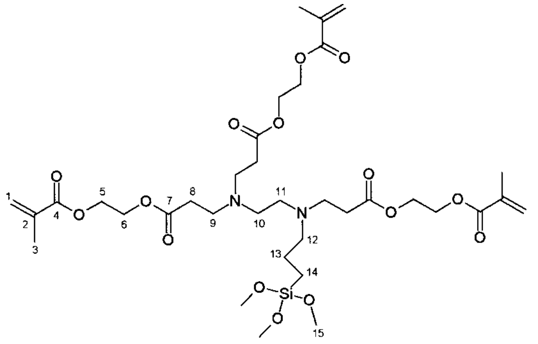


*Structure of addition product* **1b**

**Addition Product 1c.** First, 11.04 g of EGAMA (0.060 mol) was dissolved in 25 mL of absolute methanol. To this mixture was added 4.47 g (0.020 mol) of 3-(2-aminoethylamino)-propyltrimethoxysilane dissolved in 25 mL of methanol at 0−5 °C and stirred for 2 h. Subsequently, methanol was evaporated and the mixture was reacted for a further 36 h at 23 °C.

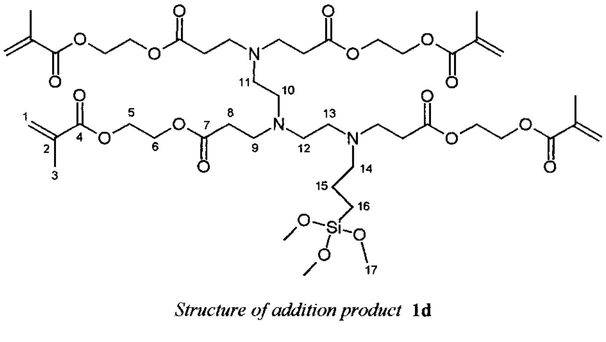
Following the same procedure, the addition products **1d**−**f** were prepared.

**Addition Product 1c:** $C_{35}H_{58}N_2O_{15}Si$ (774.94); IR 1719 cm$^{-1}$ (s, C=O), 1638 cm$^{-1}$ (m, C=C); $^1$H NMR $\delta$ = 6.04/5.50 (1), 4.25 (5,6), 3.46 (15), 2.69 (9), 2.40 (8, 10, 11, 12), 1.86 (3), 1.43 (13), 0.50 (14); $^{13}$C NMR $\delta$ = 172.2 (7), 166.9 (4), 136.1 (2), 125.8 (1), 62.2 (5), 61,9 (6), 57.0 (12), 52.1 (10, 11), 50.3/49.7 (9), 49.5 (15), 32.4 (8), 20.1 (13), 18.1 (3), 6.4 (14); $^{29}$Si NMR $\delta$ = −41.8.



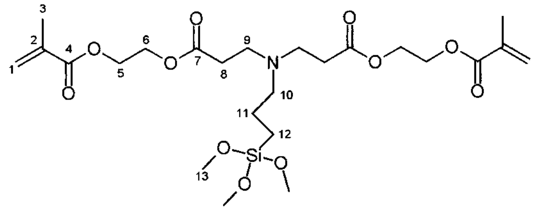
*Structure of monomer* **1c**

**Addition Product 1d:** $C_{46}H_{75}N_3O_{19}Si$ (1002.21); IR 1723 cm$^{-1}$ (s, C=O), 1638 cm$^{-1}$ (m, C=C); $^1$H NMR $\delta$ = 6.05/5.52 (1), 4.26 (5,6), 3.48 (17), 2.71 (9), 2.40 (8, 10, 11, 12, 13, 14), 1.87 (3), 1.44 (15), 0.51 (16); $^{13}$C NMR $\delta$ = 172.2 (7), 166.9 (4), 135.9 (2), 125.9 (1), 62.3 (5), 62,0 (6), 57.1 (14), 52.7/52.2 (10, 11, 12, 13), 50.3/49.7 (9), 49.5 (17), 32.4 (8), 20.2 (15), 18.1 (3), 6.5 (16); $^{29}$Si NMR $\delta$ = −42.0.



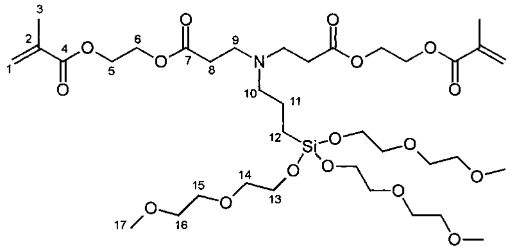
*Structure of addition product* **1d**

**Addition Product 1e:** $C_{24}H_{41}NO_{11}Si$ (547.68); IR 1723 cm$^{-1}$ (s, C=O), 1638 cm$^{-1}$ (m, C=C); $^1$H NMR $\delta$ = 6.00/5.47 (1), 4.21 (5,6), 3.43 (13), 2.65 (9), 2.34 (8, 10), 1.82 (3), 1.39 (11), 0.48 (12); $^{13}$C NMR $\delta$ = 171.8 (7), 166.5 (4), 135.6 (2), 125.5 (1), 62.0 (5), 61.7 (6), 56.0 (10), 50.0 (9), 48.8 (13), 32.2 (8), 19.8 (11), 17.8 (3), 6.1 (12); $^{29}$Si NMR $\delta$ = −42.1.



*Structure of monomer* **1e**

**Addition Product 1f:** $C_{36}H_{65}NO_{17}Si$ (812.00); IR 1722 cm$^{-1}$ (s, C=O), 1637 cm$^{-1}$ (m, C=C); $^1$H NMR $\delta$ = 6.00/5.50 (1), 4.18 (5,6), 3.76 (13), 3.56−3.41 (14, 15, 16), 3.23 (17) 2.62 (9), 2.31 (8, 10), 1.79 (3), 1.37 (11), 0.44 (12); $^{13}$C NMR $\delta$ = 172.0 (7), 166.7 (4), 135.6 (2), 125.7 (1), 71.9 (14), 71.6 (16), 71.6 (15), 62.1 (5), 61.7 (6), 61.3 (13), 58.6 (17), 56.1 (10), 50.1 (9), 48.8 (17), 32.2 (8), 19.8 (11), 17.9 (3), 6.7 (12); $^{29}$Si NMR $\delta$ = −44.9.



*Structure of monomer* **1f**

**Photochemical Polymerization.** First, 0.035 g of camphor quinone and 0.035 g of dimethylaminobenzoic acid ethyl ester were added to 10 g of the hybrid monomers **1** or **2**. This mixture was homogenized by stirring at 40 °C for 30 min and then degassed at 200 mbar and 60 °C for 30 min. Photochemical polymerization of these samples was carried out in a Triad photochemical curing unit (Dentsply De Trey, Konstanz, Germany) within 20 min.

**Mixtures of the Monomers with Bis-GMA.** First, 0.035 g of camphor quinone and 0.040 g of dimethylaminobenzoic acid ethyl ester were added to 3 g of the new hybrid monomers and 7 g of Bis-GMA. The sample preparation was similar to the preparation of the pure addition products. The curing time was 4 min.

**Preparation of the Composites.** To the described mixtures of the respective hybrid monomers and Bis-GMA was added silanized Spectrum glass (Schott, average particle size 1.6 $\mu$m) in such a manner that composites with 70 wt % filler were obtained. The mixture was stirred until it was homogeneous and then degassed at 200 mbar and 60 °C for 15 min.

**Methods. NMR.** $^1$H, $^{13}$C, and $^{29}$Si NMR spectra were recorded in $CDCl_3$ at concentrations of 250 g/L on a Bruker ARX 300 spectrometer, operating at 300, 75.4, and 59.6 MHz, respectively. Chemical shifts are given in ppm.

**IR.** IR spectra were measured using a Vector 22 FTIR spectrometer (Bruker).

**VPO.** Vapor pressure osmometry was carried out using a Knauer vapor pressure osmometer K7000 in dimethylformamide at 90 °C in the concentration range 10−40 mg/mL. Glucose pentaacetate (Merck) was used for calibration.

**FAB−MS.** Fast atom bombardment mass spectra were obtained with a double focusing Finnigan MAT 312/AMD 5000 mass spectrometer equipped with a Cs ion source.

**Photo-DSC.** Photocalorimetric measurements were carried out with a Perkin-Elmer DSC7/DPA7 photocalorimeter. Calibration of the photocalorimeter was achieved by irradiating a sample of each addition product for 30 min to determine the maximum photochemical conversion. The heat flow per weight measured in these experiments was set as 100% conversion. The following measurements of samples of the appropriate addition product were compared with this value.

**Viscosities.** Viscosities were measured using a Bohlin rheometer CS50.

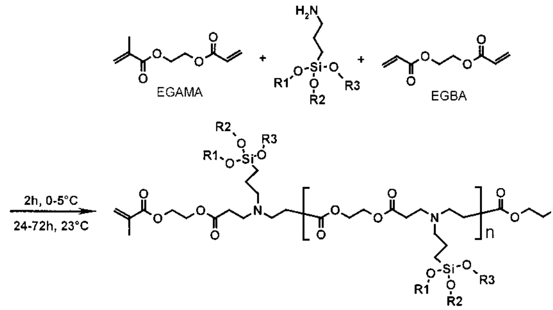


**Figure 2.** Synthesis and general structure of monomers and macromonomers prepared via Michael addition, based on EGAMA and EGBA.

**Volume Shrinkage.** The volumetric shrinkage was determined by the method of Archimedes.

**Mechanical Data.** Compressive and flexural strengths were measured according to ISO 9917 and 4049, respectively, using a Zwick instrument.

**Transmission Electron Microscopy (TEM).** TEM measurements of films on carbon grids were carried out with a LEO CEM 912 transmission electron microscope applying an acceleration voltage of 120 kV. Silicon specific imaging (Si-ESI) was performed using the five-window method with energy losses of 135, 120, 105, 94, and 70 eV (L-edge) and 1885, 1870, 1855, 1840, and 1740 eV (K-edge). (Software: Esi-Vision by SIS). Films were prepared by dropping the nanoparticle suspensions obtained from the alkoxysilane condensation on carbon grids and drying in high vacuum at 100 °C.

## 3. Results and Discussion

**A. Monomers.** The novel class of organic−inorganic hybrid monomers was prepared according to the general synthetic route shown in Figure 2. The synthesis of monomers (**1a**−**f**) and macromonomers (**2a**−**c**) was achieved via Michael addition of a variety of alkoxysilylamines to the acrylate group of ethylene glycol acrylate methacrylate (EGAMA) and ethylene glycol bisacrylates (EGBA), respectively. EGAMA and EGBA were prepared according to a procedure published by Luchtenberg and Ritter in 1994.[23]

By variation of the pendant alkoxysilyl groups and the chain length of the amine a versatile molecular "construction kit" for monomers and macromonomers with tailored properties was obtained, as schematically depicted in Figure 1. The average chain length of the macromonomer series can be controlled simply by the molar ratio of the monomers used.

For all monomer syntheses, the conversion of acrylate groups in the course of the Michael addition was monitored by $^{1}$H and $^{13}$C NMR spectroscopy. The addition reaction was commonly complete after 36−72 h at 23 °C, as evidenced by the disappearance of the $^{1}$H NMR signals of the acrylate group at 6.42, 6.11, and 5.83 ppm as well as the $^{13}$C NMR signals at 131.4 and 128.0 ppm. Typical new signals were observed at 2.70 and 2.40 ppm in the $^{1}$H NMR spectra and at 49.0 and 32.4 ppm in the $^{13}$C NMR spectra, respectively. $^{1}$H and $^{29}$Si NMR spectroscopies provide evidence that no addition to methacrylate groups took place and that the ethoxy-substituted alkoxysilane groups remained uncondensed during monomer synthesis. However, in the case of methoxysilanes, weak signals indicative of condensation products were observed.

In previous work, we had already studied branched bismethacrylates, showing that branching significantly lowers viscosity.[24] In the current work, all monomers were obtained as clear liquids. Their viscosities are relatively low, ranging from 52 to 305 mPa·s, and are clearly correlated to the molecular weight of the monomers (cf. Tables 1 and 2). The addition product **1f** with aminopropyl[2-(2-methoxyethoxy)ethoxy]silane possessed the lowest viscosity of all samples studied. With respect to their low viscosity, monomers **1a**, **b**, **e**, and **f**, in particular, are of practical interest as reactive diluents in dental composite formulations.

The FAB−MS spectra show molecular ions [MH$^{+}$] at *m*/*z* 590 (**1a**), 560 (**1b**), 775 (**1c**), 1002 (**1d**), 548 (**1e**), and 812 (**1f**) for the series of monomers **1** and at *m*/*z* 590, 981, 1372, and 1764 for the series of macromonomers **2**, evidencing the formation of a homologous series. This is exemplified in Figure 3 by the FAB−MS spec-

**Table 1. Monomers 1a−1f Prepared ($n$ = 0) with Calculated and Determined Molecular Weights (FAB−MS and Vapor Pressure Osmometry) as Well as Dynamic Viscosities $\eta$**

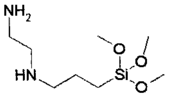
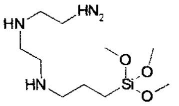
| addition product | R (amine) | $M_n$(calcd) | *m*/*z* (FAB−MS) | $M_n$(VPO) | viscosity $\eta$ [Pa·s] |
|---|---|---|---|---|---|
| **1a** | $R_1 = R_2 = R_3 = OC_2H_5$ | 589.76 | 590 | 580 | $5.76 \times 10^{-2}$ |
| **1b** | $R_1 = R_2 = OC_2H_5$<br>$R_3 = CH_3$ | 559.74 | 560 | 540 | $5.35 \times 10^{-2}$ |
| **1c** | $R_1 = R_2 = R_3 = OCH_3$<br> | 774.94 | 775 | 610 | $1.70 \times 10^{-1}$ |
| **1d** | $R_1 = R_2 = R_3 = OCH_3$<br> | 1002.21 | 1002 | 720 | $1.65 \times 10^{-1}$ |
| **1e** | $R_1 = R_2 = R_3 = OCH_3$ | 547.68 | 548 | 530 | $6.15 \times 10^{-2}$ |
| **1f** | $R_1 = R_2 = R_3 = O(CH_2)_2O(CH_2)_2CH_3$ | 811.98 | 812 | 800 | $5.24 \times 10^{-2}$ |

**Table 2. Macromonomers 2a−2c Prepared ($n \geq 1$) with Calculated and Determined Molecular Weights (FAB−MS and Vapor Pressure Osmometry) as Well as Dynamic Viscosities $\eta$**

| addition product | R (amine) | mol ratio[a] | $M_n$(calcd) | *m*/*z* (FAB−MS) | $M_n$(VPO) | viscosity $\eta$ [Pa·s] |
|---|---|---|---|---|---|---|
| **2a** | $R_1 = R_2 = R_3 = OC_2H_5$ | 2:2:1 | 981.30 | 981 | 900 | $1.03 \times 10^{-1}$ |
| **2b** | $R_1 = R_2 = R_3 = OC_2H_5$ | 2:3:2 | 1372.84 | 1372 | 1200 | $2.31 \times 10^{-1}$ |
| **2c** | $R_1 = R_2 = R_3 = OC_2H_5$ | 2:4:3 | 1764.37 | 1764 | 1600 | $3.05 \times 10^{-1}$ |

[a] EGAMA:amine:EGBA.

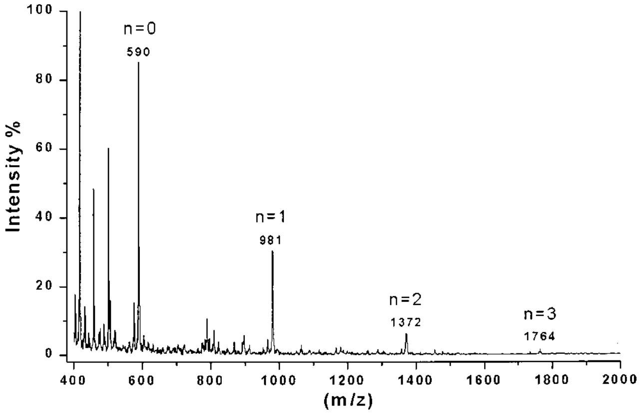


**Figure 3.** FAB−MS spectrum of macromonomer **2a**.

trum of the macromonomer **2a**. Of course, the actual distribution of macromonomer species present is not reflected by the FAB−MS spectrum due to molar mass dependent ionization of this method. Macromonomers with chain lengths $n > 3$ could not be detected by FAB−MS, but they are certainly formed during the Michael addition oligomerization. The fractions expected according to stochastic considerations are 0.167 ($n = 0$), 0.250 ($n = 1$), 0.208 ($n = 2$), 0.146 ($n = 3$), 0.094 ($n = 4$), 0.057 ($n = 5$), etc.[25]

Also, the molecular weights determined by vapor pressure osmometry for the simple 1:2 addition products agreed well with the expected values. The measured molecular weights for the macromonomers are generally somewhat lower than the calculated values. Two possible reasons are traces of solvent which could not be removed after the addition reaction and incomplete conversion, especially for the alkoxysilanes with high number of amino functionalities. In Tables 1 and 2, the calculated and measured molecular weights as well as the viscosities of the monomers prepared are summarized.

The monomers were photochemically cross-linked using 0.75 wt % camphor quinone/*N*,*N*-dimethyl-*p*-aminobenzoic acid ethyl ester (1:1) as photoinitiator in a photocuring unit ($\lambda_{\max} = 470$ nm). During polymerization relatively low volumetric shrinkage occurred, ranging from $\Delta V = 2.2$ to 7.8%, depending on the molecular weight and the number of polymerizable methacrylate groups. As expected, the volume shrinkage decreased with increasing molecular weight of the monomers, due to the decreasing fraction of polymerizable double bonds. The conversion of double bonds was followed by photo-DSC measurements. Calibration of the photocalorimeter was achieved by irradiating a sample of each addition product for 30 min. This was assumed to lead to the maximum photochemical conversion. The obtained heat flow per weight from these experiments was set to 100% conversion as a reference. All subsequent measurements of samples of the appropriate addition products were compared to this value. Of course, 100% conversion of the reactive methacrylate double bonds can only be achieved by thermal polymerization. In summary, the obtained conversion values refer to the photochemically polymerizable fraction of the acrylate functionalities. Figure 4 shows the conversion-vs-time curves for monomer **1a** and the three macromonomers **2** with triethoxysilane groups. It is obvious that the polymerization rate decreases with increasing molecular weight and viscosity of the monomers.

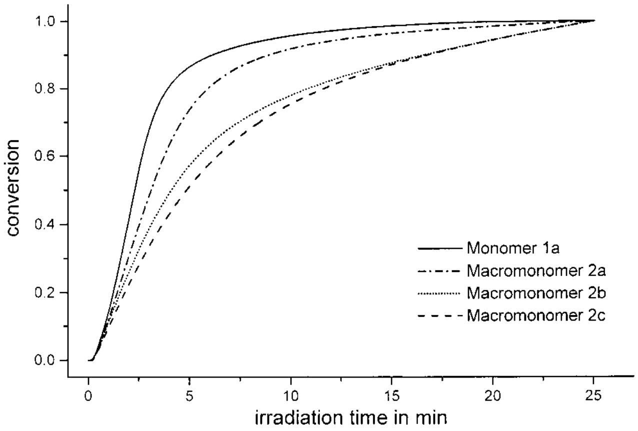


**Figure 4.** Photochemical conversion of methacrylate groups of monomers **1a** and **2a**, **2b**, and **2c** vs irradiation time.

**Table 3. Volumetric Polymerization Shrinkage and Conversion Data for Photopolymerization of Monomers 1a−1f and Macromonomers 2a−2c**

| monomer | **1a** | **1b** | **1c** | **1d** | **1e** | **1f** | **2a** | **2b** | **2c** |
|---|---|---|---|---|---|---|---|---|---|
| vol. shrinkage $\Delta V$ [%] | 7.2 | 7.6 | 7.3 | 6.5 | 7.8 | 5.0 | 4.8 | 3.1 | 2.2 |
| conversion $p$ [%] (DSC) | | | | | | | | | |
| after 2 min | 42 | 52 | 46 | 54 | 31 | 25 | 33 | 33 | 28 |
| after 10 min | 96 | 97 | 94 | 95 | 94 | 89 | 96 | 92 | 88 |

Polymerization times were in the range of 10−20 min. This is considerably longer than for many common bismethacrylates. Clearly, this can be explained by the presence of tertiary amino groups in the monomers that can form temporarily stable radicals. Nevertheless, degrees of conversion $p$ ranging from 88% to 97% after 10 min of irradiation were obtained. In Table 3, volume shrinkage and conversion data at different polymerization times are summarized for monomers **1a**−**2c**.

**B. Composites.** Polymerizable matrix resins were prepared by mixing Bis-GMA with the addition products **1** and **2** (weight ratio: 70:30) and 0.75 wt % of the initiator system camphor quinone/dimethylaminobenzoic acid ethyl ester. The viscosities of these matrix resins ranged from 6.2 to 54.1 Pa·s. For commercially available matrix resins, values of 10−20 Pa·s are common. The volume shrinkage of the matrix materials and the viscosities are correlated to the volume shrinkage and the viscosity of the pure addition products. Clearly, the polymerization behavior of the resins was dominated by the Bis-GMA fraction. Photo-DSC measurements showed that the polymerization is very fast and after 2 min of irradiation in most cases over 70 % conversion was already reached. After 4 min about 85 % of the photochemically polymerizable acrylate groups have reacted. Viscosities and volume shrinkage as well as the conversion data for the prepared matrix resins are summarized in Table 4.

Composites were prepared by adding 71−74 wt % glass filler (silanized Schott glass) to the homogenized matrix resins. The unpolymerized composite material exhibits interesting viscosity behavior. A dilatant effect was observed during mixing of resin and filler, showing a strong increase in the viscosity under shear stress. The polymerized composites were investigated with respect to their mechanical properties and their volume shrinkage.

After polymerization the compressive strength of the composites ranged from 190 to 329 MPa. The monomers **1c** and **d** and macromonomers **2** resulted in the lowest values. As expected, the compressive strength decreased

**Table 4. Viscosities, Volume Shrinkage and Conversion Data of Matrix Resins with Monomers 1 and Macromonomers 2**

| addition product | viscosity $\eta$ [Pa·s] | vol. shrinkage $\Delta V$ [%] | conversion p [%] (DSC) after | |
|---|---|---|---|---|
| | | | 2 min | 4 min |
| **1a** | 12.8 | 5.4 | 74 | 86 |
| **1b** | 17.7 | 5.4 | 74 | 86 |
| **1c** | 32.3 | 5.2 | 71 | 82 |
| **1d** | 43.9 | 4.9 | 69 | 81 |
| **1e** | 18.9 | 5.6 | 78 | 88 |
| **1f** | 6.2 | 5.3 | 81 | 90 |
| **2a** | 24.2 | 5.1 | 72 | 84 |
| **2b** | 41.0 | 4.6 | 68 | 82 |
| **2c** | 54.1 | 4.3 | 69 | 83 |

with molecular weight in the case of **2**, which is explained by the decreasing network density. Surprisingly, the compressive strength also decreased with presence of more than two acrylate groups in the monomers. Interestingly, the highest value was obtained for the addition product **1e**. A possible explanation lies in the condensation of the trimethoxysilyl groups reacting with itself or the filler surface, leading to an increase of the network density. This may be due to the trimethoxysilyl groups that undergo condensation much faster than the triethoxysilyl group.

Flexural strengths ranged from 23 to 53 MPa and the Young's moduli from 2090 to 5060 MPa. The highest values were obtained with monomers **1a**, **1b**, and especially **1e**. Monomer **1f** showed the lowest measured flexural strength. The bulky [2-(2-methoxyethoxy)ethoxy]silyl group which provided the desired low viscosity unfortunately leads to worse mechanical properties, in particular, to a decrease of the flexural strength of the composite.

It is obvious that—apart from the higher compressive strengths—the mechanical properties cannot compete with values known for commercial composite materials. However, if one takes into account that the investigated systems are not optimized with respect to resin composition and fraction of filler, the obtained values are encouraging. Further condensation of the alkoxy silyl groups present in the material after cross-linking of the methacrylate groups is possible upon prolonged storage, in particular for the methoxysilyl groups, but is very unlikely for the ethoxysilyl moieties. However, this has not been studied in detail in the present work.

The main advantage of the new hybrid monomers is the low volumetric shrinkage of only 0.8–2.2% in comparison to more than 3% shrinkage of commercially available composites. The best values were obtained with the macromonomers **2**, due to the lower number of polymerizable groups. The mechanical data and the volume shrinkage of the composites are listed in Table 5.

**C. Condensation Behavior of Selected Monomers.** Besides their viscosity-reducing qualities, the pendant "inorganic" alkoxysilyl groups of the hybrid monomers prepared can be condensed to form silicate nanoparticles with reactive acrylate surface. Macromonomers with several condensable groups should form networks or microgels in a sol–gel type process. These could then be further polymerized via the methacrylate end groups.

To demonstrate the feasibility of this approach, we studied the condensation behavior of the addition products **1a** and **1e** in ethanol/water or methanol/water mixtures, respectively, applying acid or base catalysis. The water concentration was held constant at 6 mol/L; the monomer concentration was 0.3 mol/L. All condensations were carried out at room temperature, stirring the reaction mixtures for 2 weeks. The long reaction time required is due to the bulky organic substituents at these monomers. The condensation products were investigated by IR spectroscopy and transmission electron microscopy (TEM).

**Table 5. Mechanical Properties and Volume Shrinkage of Composites with Monomers 1a–1f and Macromonomers 2a–2c**

| composite containing addition product | filler content [wt %] | vol. shrinkage $\Delta V$ [%] | flexural strength [MPa] | compressive strength [MPa] | Young modulus [MPa] |
|---|---|---|---|---|---|
| **1a** | 73.7 | 1.9 | 50 ± 4 | 288 ± 2 | 3720 ± 180 |
| **1b** | 73.7 | 1.8 | 53 ± 3 | 291 ± 5 | 3830 ± 210 |
| **1c** | 70.6 | 1.4 | 32 ± 2 | 218 ± 19 | 2420 ± 200 |
| **1d** | 71.2 | 1.2 | 32 ± 3 | 190 ± 17 | 2090 ± 180 |
| **1e** | 73.0 | 2.2 | 53 ± 4 | 329 ± 8 | 5060 ± 110 |
| **1f** | 72.0 | 1.5 | 23 ± 1 | 264 ± 8 | 3000 ± 200 |
| **2a** | 73.5 | 1.7 | 37 ± 3 | 247 ± 10 | 2700 ± 30 |
| **2b** | 71.6 | 1.2 | 33 ± 2 | 213 ± 4 | 2250 ± 60 |
| **2c** | 70.7 | 0.8 | 31 ± 3 | 201 ± 5 | 2210 ± 100 |

In the case of triethoxysilyl groups (monomer **1a**), without acid or base catalysis no remarkable condensation occurred. Ammonia was applied as basic catalyst in a concentration of 2.1 mol/L. TEM images evidenced the formation of particles with an average size of 12.3 nm (Figure 5a). Unfortunately the ester bonds in the hybrid monomers were hydrolyzed in the alkaline condensation medium. Consequently, the polymerizable methacrylate moieties are no longer attached to the particle. However, in the case of acidic catalysis (0.5 mol/L acetic acid) IR spectra evidenced that the esters remained stable. The TEM image (Figure 5b) obtained from the acidic hydrolysis product of **1a** demonstrates the formation of nanoparticles with an average diameter of 14.8 nm.

It can be stated that the triethoxysilyl group is quite stable against hydrolysis under the conditions investigated. However, the trimethoxysilyl moiety is much more hydrolysis sensitive than the triethoxysilyl group.[13] Condensation of this group already takes place in neutral media. The particles formed are relatively small and possess an average diameter of 8 nm. This is explained by the rapid condensation reaction compared to the triethoxysilyl groups. The particle sizes obtained by catalyzed condensation support this conclusion. Base catalysis applying 0.1 mol/L triethylamine afforded particles with an average size of 7.2 nm. The IR spectra of the condensation product showed that the ester groups in the molecules remained unhydrolyzed. The TEM image of the acid-catalyzed condensation product (0.5 mol/L acetic acid; average particle diameter 6.6 nm) and the element-specific TEM image, showing the Si distribution, are depicted in Figure 6. The two images demonstrate that the resulting particles possess high silicon density in the core and thus confirm the formation of functional nanoparticles. As expected, IR spectra showed in this case no reaction of the ester groups.

The precondensed hybrid monomers can be used as highly cross-linkable nanofillers for composite formulations. The reinforcing effect of the additional inorganic network on the macroscopic mechanical properties is the subject of our current research.

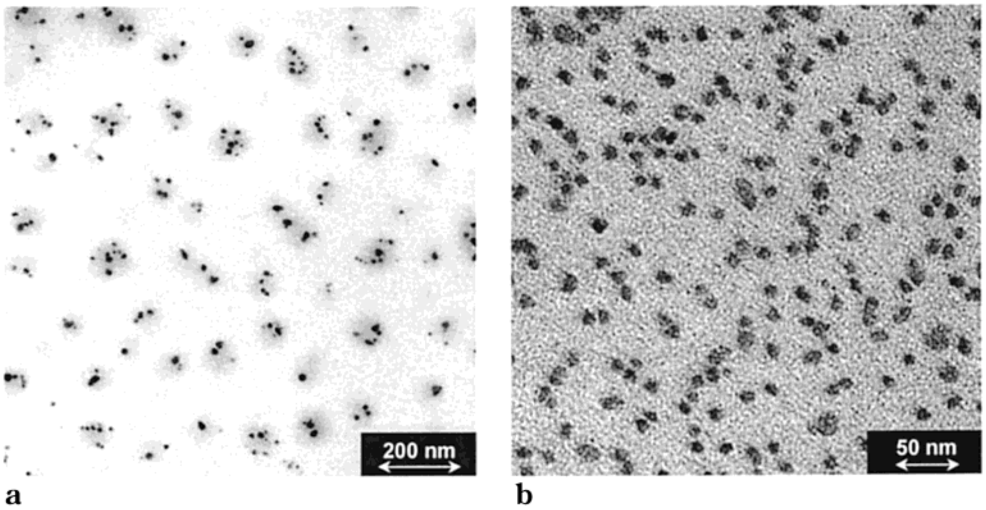


**Figure 5.** (a) Condensation product of monomer **1a**. Ammonia was applied as basic catalyst. (b) Particles obtained from **1a** by acidic catalysis (0.5 mol/L acetic acid). IR spectra demonstrate that the esters remained stable, resulting in nanoparticles with an average diameter of 14.8 nm.

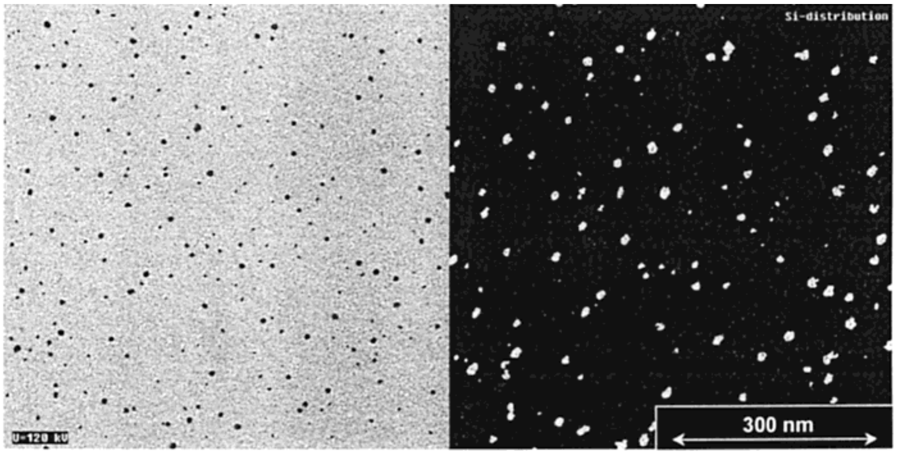


**Figure 6.** Element-specific TEM image, showing the Si distribution in the particles obtained after condensation of **1a**.

## 4. Conclusions

A series of novel bismethacrylate-based hybrid monomers with pendant alkoxysilane moieties has been prepared via convenient Michael addition of $\alpha,\omega$-alkoxysilane−amines to acrylate methacrylates. Furthermore, macromonomers with higher molecular weights could be obtained by combining this synthetic route with bisacrylates. In all cases, the Michael addition led to quantitative conversion. The obtained monomers and macromonomers were characterized in detail by NMR spectroscopy, VPO measurements and FAB−MS. Average molecular weights $M_n$ ranged between 530 and 1600 g/mol (VPO). FAB−MS evidenced the formation of a homologous macromonomer series in addition reactions with bisacrylates.

The viscosities of the liquid monomers are relatively low, ranging from 52 to 305 mPa·s. This renders these compounds interesting as reactive diluents in dental composite formulations. During polymerization of the monomers and macromonomers, low volumetric shrinkage occurred, which was in the range of $\Delta V = 2.2-7.8\%$ at high conversions. Cross-linking was monitored by photo-DSC.

Composites were prepared by mixing Bis-GMA with the new hybrid monomers (weight ratio: 70:30), initiator and 73 wt % glass filler. The composites showed compressive strengths of 190−329 MPa, flexural strengths from 23 to 53 MPa and $E$ moduli between 2090 and 5060 MPa. Thus, the mechanical properties of the prepared composites are very promising, taking into account that the investigated systems are not optimized with respect to resin composition and filler fraction.

The main advantage of the new hybrid monomers is the low volumetric shrinkage of the composites, ranging from only 0.8% to 2.2% in comparison to the over 3% shrinkage of commercially available composites. Besides the viscosity-reducing property due to the branched structure, the pendant alkoxysilyl groups of the synthesized hybrid monomers can be polymerized to form particles with a polymerizable acrylate surface. The condensation reaction was studied, applying acid and base catalysis. The condensation products were investigated by IR spectroscopy and transmission electron microscopy (TEM). Methoxy- and ethoxysilyl groups have been compared with respect to condensation. Depending on the condensation conditions, nanoparticles with average diameters between 6 and 15 nm were formed. A promising application of the precondensed hybrid monomers is the use as highly cross-linkable nanofillers. Such filler particles are expected to show a strong effect on the mechanical properties of the resulting nanocomposites. This question is being studied at present, and results will be reported in due course.

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