Synthesis and Characterization of Star Polymers and Cross-Linked Star Polymer Model Networks Containing a Novel, Silicon-Based, Hydrolyzable Cross-Linker

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ABSTRACT: An acid-labile dimethacrylate cross-linker, dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES), was synthesized by the reaction of 2-hydroxyethyl methacrylate (HEMA) and dichlorodimethylsilane in the presence of triethylamine. Group transfer polymerization (GTP) was employed to use this cross-linker in the preparation of six hydrolyzable polymer structures: one neat cross-linker network, one randomly cross-linked network of methyl methacrylate (MMA), two star-shaped polymers of MMA, and two cross-linked star polymer model networks (CSPMNs) of MMA. A nonhydrolyzable CSPMN of MMA, based on a stable cross-linker, was also synthesized. Gel permeation chromatography (GPC) in tetrahydrofuran (THF) confirmed the narrow molecular weight distributions (MWDs) of the linear polymer precursors and demonstrated the increase in molecular weight (MW) upon each successive addition of cross-linker or monomer. Characterization by static light scattering (SLS) and GPC showed that star polymers with DMDMAES cores bear a relatively small number of arms, around 7. All star polymers and polymer networks were hydrolyzed using hydrochloric acid in THF. While the MWs of the products from the hydrolysis of the star polymers, the neat cross-linker network, and the randomly cross-linked network were as expected, those from the CSPMNs were of a much higher than expected MW, indicating extensive star−star coupling.

Introduction

Star,[1] graft,[2] and hyperbranched[3] polymers, polymer surfaces,[4] and polymer networks with cleavable branches are unique materials whose molecular weight (MW) and properties dramatically change upon branch removal. A particular category of these materials is that whose labile component is a cleavable divinyl cross-linker. Such materials can be exploited in various applications. For example, hydrolyzable polymer networks can be used as biodegradable orthopaedic implants[5,6] and as drug[7] and protein[8] delivery matrices. Thermally cleavable polymer networks can be applied for the "reworking" of components in electronics and optics industries, where defective parts may be easily replaced or components may be held firmly in place during manufacture but may be removed if so desired.[9]

The preparation of these polymeric systems can be performed either by "living" polymerization methods[10] that secure better structural control or by "nonliving" methods which are synthetically easier. From the "nonliving" methods, free radical polymerization is the most common. For example, Mikos and co-workers[5,6] prepared by free radical cross-linking poly(propylene fumarate) diacrylate networks with main-chain hydrolyzable ester bonds. Ulbrich and colleagues[7] prepared degradable networks based on a cross-linker containing −COONHCO− groups, hydrolyzable at neutral and alkaline pH. Fréchet and co-workers[8] synthesized, using free radical polymerization, polyacrylamide networks cross-linked randomly via a diacrylamide methoxybenzaldehyde acetal, cleavable at acidic pH. Horkay and colleagues[11] prepared dextran hydroxyethyl methacrylate hydrogels with labile carbonate ester bonds. Ober and colleagues[9] polymerized by free radical polymerization diacrylate and dimethacrylate diesters of the ditertiary diols 2,5-dimethyl-2,5-hexanediol, 2,7-dimethyl-2,7-octanediol, and 2,9-dimethyl-2,9-decanediol to obtain highly cross-linked networks, which were subsequently thermolyzed at temperatures above 180 °C. This resulted in networks with anhydride cross-links, which were hydrolyzed in alkaline aqueous solutions to give soluble linear polymers of acrylic or methacrylic acid.

Examples of synthesis of polymers bearing hydrolyzable cross-linkers using "living" polymerization methods are the anionic polymerizations reported by Ruckenstein and Zhang[12] and Long et al.[13] Ruckenstein and Zhang[12] synthesized star polymers, branched polymers, and randomly cross-linked polymer networks of methyl methacrylate (MMA) using the cross-linker ethylene glycol di(1-methacryloyloxy)ethyl ether (EGDMOEE). Because of the presence of acetal groups in this cross-linker, the polymers of Ruckenstein and Zhang were readily hydrolyzed in acetone or tetrahydrofuran (THF) by the addition of aqueous hydrochloric acid solutions to give lower molecular weight products. Long and co-workers[13] prepared, via anionic polymerization, star polymers of MMA, isobutyl methacrylate, and *tert*-butyl methacrylate cross-linked with 2,5-dimethyl-2,5-hexanediol dimethacrylate and dicumyl alcohol dimethacrylate, whose core was subsequently hydrolyzed using *p*-toluenesulfonic acid in dioxane at 100 °C.

Another interesting type of polymeric materials is that of polymer model networks,[14] which are also prepared using "living" polymerization techniques to ensure precise lengths of the chains between cross-links (known as elastic chains), which is the main distinguishing feature of these materials. However, to the best of our knowledge, no polymer model networks with hydrolyzable cross-links have been reported to date. A new type of polymer model networks, again based on nonhydrolyzable cross-links, is that of cross-linked star polymer model networks (CSPMNs)[15−17] developed re-

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cently by our research team, using a "living" polymerization technique, group transfer polymerization (GTP).[18−21] The characteristic feature of CSPMNs is the presence of a large number of dangling chains in addition to the elastic chains. These networks are prepared by the sequential addition of monomer−cross-linker−monomer−cross-linker under GTP conditions. The dangling chains are formed upon the first addition of monomer, whereas the elastic chains are formed upon the second addition of monomer. The two additions of cross-linker give rise to the formation of two different types of cores, the primary cores and the secondary cores, formed upon the first and second additions of cross-linker, respectively. Primary cores are only connected to secondary cores, and secondary cores are only connected to primary cores. The secondary cores bear only elastic chains, while the primary cores bear an equal number of dangling and elastic chains.

The purpose of this investigation was the synthesis of CSPMNs containing a hydrolyzable cross-linker and the examination of their hydrolysis. To this end, the preparation and purification of a novel, acid-labile, silicon-containing dimethacrylate cross-linker were necessary. A nonhydrolyzable cross-linker was also employed in the syntheses. Thus, one type of core of the CSPMNs, primary or secondary, was based on the hydrolyzable cross-linker, while the other type of core was based on the nonhydrolyzable one. To the best of our knowledge, this is the first report on the GTP of a hydrolyzable cross-linker, and this is also the first report on hydrolyzable CSPMNs.

Experimental Section

Materials and Methods. 2-Hydroxyethyl methacrylate (HEMA, 97%) was purchased from Merck, Germany. Dichlorodimethylsilane (99%), triethylamine (Et_3N, 99.5%), tetrabutylammonium hydroxide (40% w/w solution in water), benzoic acid (99.5%), MMA (99%), ethylene glycol dimethacrylate (EGDMA, 98%), 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS, 95%), and 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%) were purchased from Aldrich, Germany. Tetrahydrofuran (THF, 99.8%) was purchased from Labscan, Ireland, and was used as the mobile phase in chromatography (HPLC grade) and as a solvent (reagent grade) both in the reaction for the synthesis of the cross-linker and for the polymerizations.

The solvent, THF, was dried by refluxing it over a potassium−sodium mixture for 3 days and was freshly distilled prior to use. Et_3N was dried by stirring it for 3 days over calcium hydride and was vacuum-distilled just before its use. HEMA and dichlorodimethylsilane were freshly distilled under vacuum just before their use and kept under a dry nitrogen atmosphere. The polymerization catalyst TBABB was synthesized by the reaction of tetrabutylammonium hydroxide and benzoic acid in water, following the procedure of Dicker et al.,[20] and was kept under vacuum until use. MMA and EGDMA were passed through basic alumina columns to remove protonic impurities and polymerization inhibitors. They were subsequently stirred over calcium hydride (to remove the last traces of moisture and protic impurities) in the presence of an added free-radical inhibitor, DPPH, and stored in the fridge at about 5 °C. Both MMA and EGDMA were freshly distilled under vacuum just before their use and kept under a dry nitrogen atmosphere. The initiator was distilled once prior to the polymerization, but it was neither contacted with calcium hydride nor passed through basic alumina columns because of the risk of hydrolysis. All glassware was dried overnight at 120 °C and assembled hot under dynamic vacuum prior to use.

Cross-Linker Synthesis. The acid-labile cross-linker, dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES), was prepared by the etherification reaction of HEMA with dichlorodimethylsilane in THF and in the presence of Et_3N base. A typical synthesis is detailed in the following. THF (100 mL), Et_3N (24.7 mL, 17.9 g, 0.177 mol), and HEMA (18.3 mL, 19.6 g, 0.151 mol) were syringed to a 250 mL round-bottom flask, kept under a dry nitrogen atmosphere, and equipped with a mechanical stirrer and a thermometer. The contents were stirred and cooled to 0−5 °C. Then, dichlorodimethylsilane (7.3 mL, 7.8 g, 0.060 mol) was added slowly under stirring, giving an exotherm (3.2−10.8 °C). The reaction mixture was stored in the refrigerator overnight, after the addition of the free radical inhibitor DPPH to avoid thermal polymerization. The reaction mixture was filtered in order to remove the precipitated salt of triethylamine hydrochloride. THF (50 mL) was added to wash the filtrate. THF and unreacted Et_3N were subsequently removed under reduced pressure using a rotary evaporator at room temperature. The resulting oily residue was purified by column chromatography (silica gel/CH_2Cl_2:hexane 75:25). An oily liquid was obtained (yield 7.2 g, 40.1%), which was then distilled under vacuum. The high purity of the cross-linker was confirmed by ^1H NMR spectroscopy, and the relevant spectrum is displayed in Figure 1. ^1H NMR: 0.16 [s, $(CH_3)_2Si$, 6 H], 1.94 [s, 2 (CH_3C), 6 H], 3.92 [t, $(OCH_2CH_2O)_2Si$, 4 H], 4.24 [t, $(OCH_2CH_2O)_2Si$, 4 H], 5.58 (s, olefinic H trans to CO_2, 2 H), 6.13 (s, olefinic H cis to CO_2, 2 H). Anal. ($C_{14}H_{24}O_6Si$) C, H, Si: calcd 53.16, 7.59, 8.86: found 53.34, 7.59, 8.47.

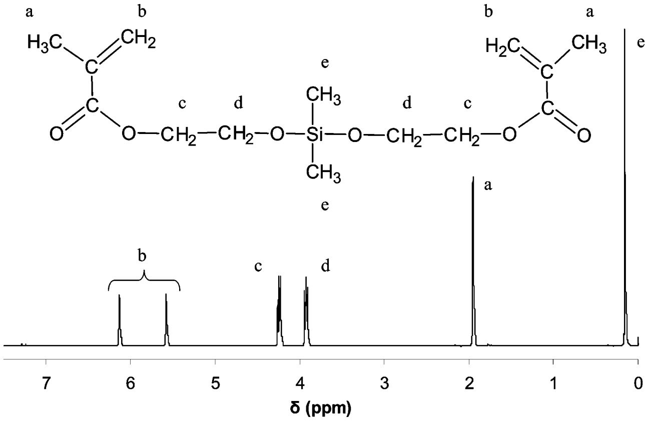

Figure 1. ^1H NMR spectrum of the dimethyldi(methacryloloxy-1-ethoxy)silane (DMDMAES) cross-linker in $CDCl_3$.

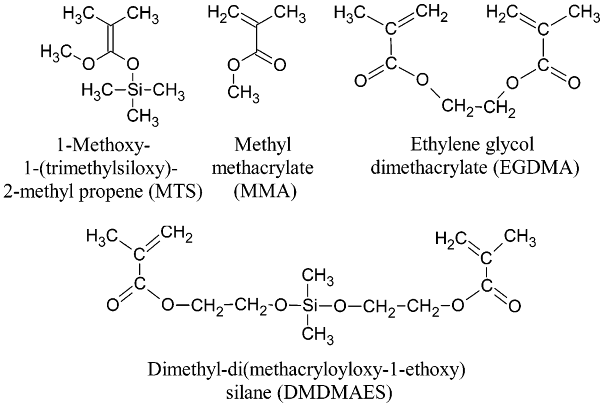

Figure 2. Chemical structures and names of the main reagents used for the polymer synthesis: the monofunctional initiator MTS, the monomer MMA, and the cross-linkers EGDMA and DMDMAES.

Polymer Synthesis. Figure 2 shows the chemical structures and names of the main reagents used for the synthesis of the star polymers and the polymer networks. All syntheses were performed using GTP. The following polymeric materials were prepared: one neat DMDMAES network, one MMA−DMDMAES randomly cross-linked network, two "arm-first" star polymers of MMA−DMDMAES, two CSPMNs of MMA−DMDMAES-EGDMA, and one CSPMN of MMA−EGDMA. The synthetic sequences employed for the preparation of these materials are summarized in Figure 3.

$$(1)\quad \begin{array}{l}\text{TBABB}\\ \text{THF}\\ \text{4 DMDMAES}\end{array} \xrightarrow{\text{1 MTS}} \text{Neat DMDMAES hydrolyzable network}$$

$$(2)\quad \begin{array}{l}\text{TBABB}\\ \text{THF}\\ \text{30 MMA}\\ \text{8 DMDMAES}\end{array} \xrightarrow{\text{1 MTS}} \text{MMA}_{30}\text{-}co\text{-DMDMAES}_{8}\ \text{Hydrolyzable randomly cross-linked MMA network}$$

$$(3)\quad \begin{array}{l}\text{TBABB}\\ \text{THF}\\ \text{1 MTS}\end{array} \xrightarrow{\text{20 MMA}} \text{MMA}_{20} \xrightarrow{\text{4 DMDMAES}} \text{MMA}_{20}\text{-}b\text{-DMDMAES}_{4}\ \text{Core-hydrolyzable MMA star polymer}$$

$$(4)\quad \begin{array}{l}\text{TBABB}\\ \text{THF}\\ \text{1 MTS}\end{array} \xrightarrow{\text{20 MMA}} \text{MMA}_{20} \xrightarrow{\text{2 DMDMAES}} \text{MMA}_{20}\text{-}b\text{-DMDMAES}_{2} \xrightarrow{\text{2 DMDMAES}} \text{MMA}_{20}\text{-}b\text{-DMDMAES}_{4} \xrightarrow{\text{2 DMDMAES}}$$
$$\text{MMA}_{20}\text{-}b\text{-DMDMAES}_{6} \xrightarrow{\text{2 DMDMAES}} \text{MMA}_{20}\text{-}b\text{-DMDMAES}_{8}\ \text{Core-hydrolyzable MMA star polymer}$$

$$(5)\quad \begin{array}{l}\text{TBABB}\\ \text{THF}\\ \text{1 MTS}\end{array} \xrightarrow{\text{20 MMA}} \text{MMA}_{20} \xrightarrow{\text{6 DMDMAES}} \text{MMA}_{20}\text{-}b\text{-DMDMAES}_{6} \xrightarrow{\text{20 MMA}} \text{MMA}_{20}\text{-}b\text{-DMDMAES}_{6}\text{-}b\text{-MMA}_{20} \xrightarrow{\text{4 EGDMA}}$$
$$\text{MMA}_{20}\text{-}b\text{-DMDMAES}_{6}\text{-}b\text{-MMA}_{20}\text{-}b\text{-EGDMA}_{4}\ \text{First-core-hydrolyzable MMA cross-linked star polymer model network}$$

$$(6)\quad \begin{array}{l}\text{TBABB}\\ \text{THF}\\ \text{1 MTS}\end{array} \xrightarrow{\text{20 MMA}} \text{MMA}_{20} \xrightarrow{\text{4 EGDMA}} \text{MMA}_{20}\text{-}b\text{- EGDMA}_{4} \xrightarrow{\text{20 MMA}} \text{MMA}_{20}\text{-}b\text{-EGDMA}_{4}\text{-}b\text{-MMA}_{20} \xrightarrow{\text{6 DMDMAES}}$$
$$\text{MMA}_{20}\text{-}b\text{-EGDMA}_{4}\text{-}b\text{-MMA}_{20}\text{-}b\text{-DMDMAES}_{6}\ \text{Second-core-hydrolyzable MMA cross-linked star polymer model network}$$

$$(7)\quad \begin{array}{l}\text{TBABB}\\ \text{THF}\\ \text{1 MTS}\end{array} \xrightarrow{\text{20 MMA}} \text{MMA}_{20} \xrightarrow{\text{4 EGDMA}} \text{MMA}_{20}\text{-}b\text{- EGDMA}_{4} \xrightarrow{\text{20 MMA}} \text{MMA}_{20}\text{-}b\text{-EGDMA}_{4}\text{-}b\text{-MMA}_{20} \xrightarrow{\text{4 EGDMA}}$$
$$\text{MMA}_{20}\text{-}b\text{-EGDMA}_{4}\text{-}b\text{-MMA}_{20}\text{-}b\text{-EGDMA}_{4}\ \text{Non-hydrolyzable MMA cross-linked star polymer model}$$

Figure 3. Synthetic sequences employed for the preparation of the polymers of this study. TBABB = tetrabutylammonium bibenzoate, polymerization catalyst; THF = tetrahydrofuran, polymerization solvent; DMDMAES = dimethyldi(methacryloyloxy-1-ethoxy)silane, hydrolyzable cross-linker (prepared in this study); MTS = 1-methoxy-1-(trimethylsiloxy)-2-methyl propene, monofunctional initiator; MMA = methyl methacrylate, monomer; EGDMA = ethylene glycol dimethacrylate, nonhydrolyzable cross-linker.

A typical polymerization yielding the first-core-hydrolyzable MMA CSPMN $\text{MMA}_{20}\text{-}b\text{-DMDMAES}_{6}\text{-}b\text{-MMA}_{20}\text{-}b\text{-EGDMA}_{4}$ is detailed in the following. TBABB catalyst (~10 mg, ~20 μmol), freshly distilled THF (27 mL), and MTS initiator (0.2 mL, 0.17 g, 0.98 mmol) were added, in this order, to a 100 mL round-bottom flask kept under a dry nitrogen atmosphere and sealed with a rubber septum. Subsequently, MMA (2.1 mL, 2.0 g, 20 mmol) was syringed slowly under stirring, giving a polymerization exotherm (25.7−33.2 °C), which abated within 5 min. A sample of 0.1 mL was extracted from the reaction solution for GPC analysis (full monomer conversion, polymer $M_n = 6260$ g mol^{-1} and $M_w/M_n = 1.06$), and DMDMAES (1.9 mL, 1.9 g, 5.9 mmol) was added. The reaction temperature rose from 30.1 to 32.9 °C. After sampling for GPC (full cross-linker conversion, apparent star polymer $M_n = 13\,100$ g mol^{-1} and $M_w/M_n = 1.99$), MMA (2.1 mL, 2.0 g, 20 mmol) was added again slowly, which produced an exotherm (30.3−34.9 °C), and a sample was withdrawn again for GPC analysis (full monomer conversion, apparent star polymer $M_n = 33\,300$ g mol^{-1} and $M_w/M_n = 1.58$). Finally, EGDMA (0.74 mL, 0.77 g, 3.9 mmol) was added, which promoted the gelation of the solution within seconds and caused a temperature increase from 32.4 to 33.1 °C.

Determination of the Sol Fraction (Extractables) of the CSPMNs. The networks were taken out of the polymerization flasks by breaking the flasks, and they were transferred in glass bottles, where they were washed in 200 mL of THF for 1 week to remove the sol fraction. Subsequently, the THF solution was recovered by filtration, and the solvent was removed using a rotary evaporator. The sol fraction was calculated as the ratio of the mass of the dried extracted polymer to the theoretical dry mass of the network, estimated as the sum of monomer, cross-linkers, and initiator used for its synthesis. The extractables were characterized in terms of their MWDs using GPC (for the extractables of the H−N network whose synthesis was described above, their weight fraction was 12.7%, whereas their $M_n = 6680$ g mol^{-1} and $M_w/M_n = 1.62$).

Polymer Hydrolysis. All polymers formed using the hydrolyzable cross-linker DMDMAES were hydrolyzed successfully in THF in the presence of a small amount of hydrochloric acid, at room temperature. For instance, 0.3 g of the CSPMN $\text{MMA}_{20}\text{-}b\text{-DMDMAES}_{6}\text{-}b\text{-MMA}_{20}\text{-}b\text{-EGDMA}_{4}$ (0.27 mmol DMDMAES) in THF was hydrolyzed after 5 min in a solution in 0.25 mL of THF, to which a drop of concentrated HCl (12 M) (0.48 mmol) was added. The hydrolyzed polymers were recovered by precipitation in *n*-hexane and were subsequently dried in a vacuum oven at room temperature.

Polymer Characterization. *Gel Permeation Chromatography.* Molecular weights (MWs) and molecular weight distributions (MWDs) of the star polymers and their precursors, of the network precursors, of the extractables from the CSPMNs, and of the hydrolyzed polymer products were determined by gel permeation chromatography (GPC) using a single Polymer Laboratories PL-Mixed "D" column (bead size = 5 μm; pore sizes = 100, 500, 10^3, and 10^4 Å). The mobile phase was THF (flow rate 1 mL min^{-1}), delivered using a Polymer Laboratories PL-LC1120 isocratic pump. The refractive index signal was measured using an ERC-7515A refractive index detector supplied by Polymer Laboratories. The calibration curve was based on eight narrow MW (630, 4250, 13 000, 28 900, 50 000, 128 000, 260 000, and 520 000 g mol^{-1}) linear polyMMA standards supplied by Polymer Laboratories, which provided accurate MW calculations for the linear precursors but only qualitative estimates of the MWs of the star polymers. In particular, the following quantities were calculated: the number-average MWs, M_ns, the polydispersity indices (PDIs) M_w/M_n, where M_w is the weight-average MW, and the peak MWs, M_ps, which are the MWs at the peak maximum.

^{1}H NMR Spectroscopy. The compositions of the hydrolyzed polymer products were determined by proton nuclear magnetic

Table 1. Results of GPC and ^{1}H NMR Characterization of the Hydrolysis Products of the Neat DMDMAES Network and the Randomly Cross-Linked MMA−DMDMAES Network

			GPC results		composition (mol % HEMA)	
initial network	hydrolysis product	theoretical MW[a]	M_n	M_w/M_n	theoretical	by ^{1}H NMR
DMDMAES$_4$	HEMA$_8$	1140	1270	1.38	100.0	100.0
MMA$_{30}$-*co*-DMDMAES$_8$	MMA$_{30}$-*co*-HEMA$_{16}$	5180	11100	1.22	34.8	39.1

[a] The molecular weight of the initiator fragment of 100 g mol^{-1} has also been included in the calculation.

resonance (^{1}H NMR) spectroscopy in deuterated chloroform (CDCl$_3$) or in deuterated dimethyl sulfoxide (d_6-DMSO). The spectra were recorded using a 300 MHz Avance Bruker spectrometer equipped with an Ultrashield magnet.

Static Light Scattering. Absolute M_ws were measured by static light scattering (SLS) using a Brookhaven molecular weight analyzer, BI-MwA, equipped with a 30 mW red diode laser emitting at 673 nm and a multiangle detector which determines the intensity of scattered light at seven different angles (35°, 50°, 75°, 90°, 105°, 130°, 145°). Polymer samples were dissolved in HPLC-grade THF at different polymer concentrations and were filtered through 0.45 μm pore size syringe filters. From this information, a Zimm plot was constructed using standard BI-MwAZP software from which the absolute M_w was calculated as the inverse of the intercept. The refractive index increments (dn/dc) in white light of the polymer solutions in THF were determined using an ABBE refractometer.

Results and Discussion

Preparation of Cross-Linker. The acid-sensitive cross-linker DMDMAES was prepared by an etherification reaction between HEMA and a dichlorosilane in the presence of triethylamine base in absolute THF. A 25% mol excess of HEMA was used relative to the reactive chlorines of dichlorodimethylsilane to ensure a high conversion of the latter. Use of excess of the dichlorosilane was avoided as it would lead to the formation of the monosubstituted product as well. The excess HEMA was removed by column chromatography, which was used for product purification. The preparation of DMDMAES is similar to the synthesis of trimethylsilyl-protected HEMA, 2-(trimethylsiloxy)ethyl methacrylate (TMSEMA).[22,23] In the latter, however, an excess of trimethylsilyl chloride is used to ensure complete conversion of HEMA to TMSEMA, while the volatile unreacted trimethylsilyl chloride is easily removed by evaporation. Thus, the purification of TMSEMA is simply accomplished by vacuum distillation, requiring no column chromatography. Typical yields of the reaction for the DMDMAES preparation were 75%, while overall yields after column chromatography and distillation were 41%.

Preparation and Hydrolysis of the Neat Cross-Linker Network and the Randomly Cross-Linked Network of MMA. To prove the efficiency of the hydrolyzable cross-linker in forming networks via GTP, we performed preliminary experiments in which we prepared two simple network structures. First, a DMDMAES "homopolymer" (neat cross-linker) network and, second, a randomly cross-linked MMA−DMDMAES network. As shown in reactions 1 and 2 of Figure 3, for these syntheses, the MTS initiator was added last. In both cases, successful gelation took place a few seconds after the MTS addition, demonstrating the action of DMDMAES as a cross-linker.

Next, to prove the hydrolyzability of the DMDMAES cross-linker, samples from both of these networks were subjected to hydrolysis in excess THF after the addition of HCl. Within 5 min, both network samples were dissolved in THF, giving transparent solutions. The ease of hydrolysis of the networks based on this cross-linker was better than that of the tertiary esters of Long and co-workers[13] and Ober et al.[9] and comparable to the acetal-based cross-linkers of Ruckenstein and Zhang[12] and Fréchet and co-workers.[8]

The resulting soluble polymer samples were recovered by precipitation in n-hexane and were vacuum-dried at room temperature. They were subsequently characterized in terms of their MWs and compositions by GPC and ^{1}H NMR, respectively. Each DMDMAES cross-linker unit is expected to be converted upon hydrolysis to two HEMA units. Thus, the neat DMDMAES network should be converted to a linear HEMA homopolymer, while the randomly cross-linked MMA−DMDMAES network should yield a linear MMA−HEMA random copolymer. Given that the DMDMAES/initiator molar ratio upon synthesis was 4/1, the former polymer should be the linear 8-mer of HEMA, while the latter should have the formula MMA$_{30}$-*co*-HEMA$_{16}$. Table 1 displays the experimental molecular weights and compositions of the hydrolysis products, which appear to be along the lines expected from the basis of the "livingness" of GTP and the full hydrolysis of DMDMAES. The M_n of the hydrolyzed neat DMDMAES network is very close to the theoretically expected, while its PDI is somewhat high (~1.4), but still within the limits for a "living" polymerization, especially for these low MWs. On the other hand, the M_n of the hydrolyzed randomly cross-linked MMA−DMDMAES network is higher (by a factor of 2) than the theoretically expected, indicating some initiator deactivation, while its PDI is sufficiently low (~1.2); the HEMA content (calculated from the area of the peak of the methoxy protons of MMA and the methylene esteric protons of HEMA) of the hydrolysis products is very close to the theoretically expected.

Preparation and Hydrolysis of Star Polymers of MMA. After demonstrating the cross-linking ability of DMDMAES from the network formation mentioned above, we pursued the synthesis of "arm-first" star polymers by the sequential GTP of MMA and DMDMAES, which are shown in reactions 3 and 4 in Figure 3. Subsequently, we pursued the hydrolysis of the star polymers. The synthesis and hydrolysis are depicted schematically in Figure 4, and both proved to be successful. The synthesis of the star polymer is based on the ability of this polymerization method to produce linear "living" polymers upon the addition of a methacrylate monomer to a THF solution of monofunctional initiator and catalyst and the conversion of these linear polymers to star polymers upon the addition of a dimethacrylate cross-linker. The labile nature of the present cross-linker leads to its hydrolysis and its separation into two HEMA units, thus eliminating the interconnection between different linear chains and converting the star polymers into linear polymers.

Table 2 shows the results for the synthesis and hydrolysis of such a MMA−DMDMAES star polymer

Table 2. Results of GPC and ^{1}H NMR Characterization of the "Arm-First" Star Polymer MMA_{20}-*b*-$DMDMAES_4$ and Its Hydrolysis Products

		GPC results			composition (mol % HEMA)		static light scattering	
polymer sample	theor MW[a]	M_n	M_w/M_n	M_p	theor	by ^{1}H NMR	M_w	no. of arms
MMA_{20}	2100	4680	1.06	4870	N/A[b]	N/A[b]	N/D[c]	N/A[b]
MMA_{20}-*b*-$DMDMAES_4$	N/A[b]	9710	1.55	8650, 19500	N/A[b]	N/A[b]	34600	7
MMA_{20}-*b*-$HEMA_8$	3140	6900	1.12	7850	28.6	31.7	N/D[c]	N/A[b]

[a] The molecular weight of the initiator fragment of 100 g mol^{-1} has also been included in the calculation. [b] Not applicable. [c] Not determined.

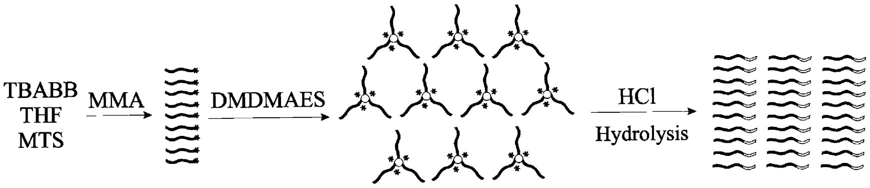

Figure 4. Schematic representation of the synthesis and hydrolysis of an "arm-first" star polymer with a core composed of a hydrolyzable cross-linker. TBABB = tetrabutylammonium bibenzoate, polymerization catalyst; THF = tetrahydrofuran, polymerization solvent; DMDMAES = dimethyldi(methacryloyloxy-1-ethoxy)silane, hydrolyzable cross-linker (prepared in this study); MTS = 1-methoxy-1-(trimethylsiloxy)-2-methyl propene, monofunctional initiator; MMA = methyl methacrylate, monomer; HCl = hydrochloric acid, hydrolysis reagent.

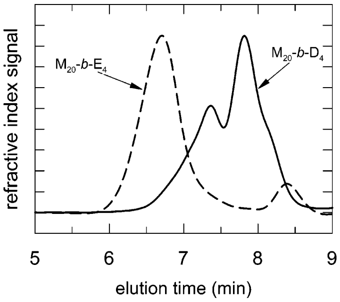

Figure 5. GPC chromatograms of the "arm-first" star polymers of methyl methacrylate (MMA or M) with hydrolyzable dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES or D) and nonhydrolyzable ethylene glycol dimethacrylate (EGDMA or E) cores.

in which the molar ratio of cross-linker/initiator was 4/1, taken from our previous work on EGDMA stars.[24,25] Table 2 shows that a linear MMA homopolymer of narrow MWD was obtained in the first step of the polymerization. Upon the addition of the DMDMAES cross-linker to the "living" MMA_{20} homopolymer, the M_n doubles and the MWD broadens, which is consistent with the interlinking of the linear polymer to a starlike structure. Table 2 also displays the M_ps and reveals that the MWD of the star polymer is bimodal with maxima at MWs corresponding to 2 and 4 times the MW of the arm. Figure 5 shows the GPC chromatogram of this star polymer, where the bimodal nature of the MWD is clear. A similar bimodal distribution was observed by Ruckenstein and Zhang[12] with their MMA star polymers cross-linked with another hydrolyzable cross-linker, ethylene glycol di(1-methacryloyloxy)ethyl ether.

For comparison, Figure 5 also shows the GPC chromatogram of a star polymer with arms bearing 20 MMA units, too, but cross-linked with the nonhydrolyzable cross-linker EGDMA. This EGDMA-containing star polymer exhibits a single peak in the higher MW region (in addition to some linear MMA arm) and has a higher MW than the DMDMAES-containing star polymer. This indicates that EGDMA is a more efficient cross-linker than DMDMAES. This is probably due to the bulkier structure of DMDMAES than EGDMA (MWs 316 and 198 g mol^{-1}, respectively), which leads to a greater percentage of unreacted methacrylate groups in the case of DMDMAES than EGDMA. Some silicon-containing monomethacrylate monomers have also been reported to be less reactive toward oxyanion-catalyzed GTP, which was confirmed to be due to their bulky structure[26] rather than the competition between the alkosiloxy groups of the initiator and the alkosiloxy groups of these monomers for the oxyanion catalyst.[27]

SLS of THF solutions of MMA_{20}-*b*-$DMDMAES_4$ allowed the determination of its absolute M_w and weight-average number of arms, both presented in Table 2. The M_w is greater than the corresponding GPC M_w based on linear PMMA standards due to the compact nature of the star structure. The weight-average number of arms was calculated by dividing the M_w of the star polymer determined by SLS by the M_w of the arms determined by GPC and was found to be 7. This value is lower than the values of 20,[28] 30,[16] 50,[15] 15−40,[29] and 20−100[30] reported in the literature for the number of arms of "arm-first" star polymers with EGDMA cores also prepared by GTP.

Following the above characterization, we proceeded to the hydrolysis of this star polymer. The hydrolysis products were characterized by GPC and ^{1}H NMR, and the results are also displayed in Table 2. GPC showed that, upon hydrolysis, the MW decreased, approaching the value of the arm but remained higher due to the incorporation of eight HEMA units. ^{1}H NMR confirmed the presence of the expected percentage of HEMA in the hydrolyzed product.

To optimize the amount of hydrolyzable cross-linker necessary for the synthesis of the star polymers, further syntheses of star polymers were performed, where the molar ratio of DMDMAES to initiator was varied systematically. Thus, in a single reactor, after the formation of linear MMA homopolymer with 20 units, amounts of DMDMAES were successively added so that the final DMDMAES/MTS molar ratio was 2, 4, 6, and 8. After the polymerization of each successive amount of cross-linker, samples were withdrawn for GPC analysis. The GPC chromatograms of the analyzed samples are overlaid in Figure 6, and the results of the MW calculation are summarized in Table 3.

Figure 6 shows that the linear homopolymer MMA_{20} has a unimodal and narrow molecular weight distribution, with a PDI of 1.07 and an M_n of 4050, listed in

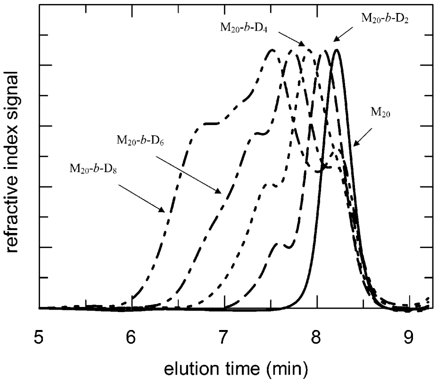

Figure 6. GPC chromatograms of hydrolyzable "arm-first" star polymers of methyl methacrylate (MMA or M) with different loadings of the dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES or D) hydrolyzable cross-linker. The GPC chromatograms of the linear polyMMA precursors and of the linear hydrolysis product poly(MMA-*b*-HEMA) are also shown.

Table 3. Results of GPC Characterization of the "Arm-First" Star Polymers MMA_{20}-*b*-$DMDMAES_x$ and Their Hydrolysis Product

polymer sample	theor MW[a]	GPC results M_n	M_w/M_n	M_p
MMA_{20}	2100	4050	1.07	4310
MMA_{20}-*b*-$DMDMAES_2$	N/A[b]	5680	1.22	5460, 12200
MMA_{20}-*b*-$DMDMAES_4$	N/A[b]	7890	1.41	4740, 8350, 16200
MMA_{20}-*b*-$DMDMAES_6$	N/A[b]	10500	1.73	5460, 11600, 22500
MMA_{20}-*b*-$DMDMAES_8$	N/A[b]	13000	2.32	4970, 16200, 30700, 58000
MMA_{20}-*b*-$HEMA_{16}$	4180	8610	1.12	9560

[a] The molecular weight of the initiator fragment of 100 g mol^{-1} has also been included in the calculation. [b] Not applicable.

Table 3. With each successive addition of DMDMAES cross-linker, the MWs of the polymer products grew and their MWDs broadened significantly, presenting up to four individual peaks. In particular, as the DMDMAES/MTS ratio increased from 2 to 8, the M_ns of the polymers increased from approximately 5500 to 13 000 g mol^{-1} while the PDIs increased from 1.2 to 2.3. The increase in MW is associated with the interconnection of the linear chains to form star polymers, which are further interconnected and get larger by each successive addition of cross-linker. The individual peaks, observed in the MWDs, are due to star polymers with certain number of arms. For the MWDs of the star polymers with the higher DMDMAES/MTS ratios, 6 and 8, the peak of the linear MMA polymer can be seen on the lower MW side of the chromatograms on the right. From the relative peak areas, the linear polymers contributed 17.5 and 16.0% to the total mass of the samples with 6 and 8 DMDMAES/MTS molar ratio, respectively. Thus, by increasing the DMDMAES/MTS ratio from 6 to 8, no significant incorporation of linear polymer into the star was achieved. It was, therefore, decided that a DMDMAES/MTS ratio of 6 was optimal for the synthesis. Note that the optimal cross-linker/initiator molar ratio may differ from cross-linker to cross-linker. For instance, for the more effective EGDMA cross-linker, a molar ratio of EGDMA/MTS of 4/1 has been determined.[24,25]

Held and Müller[31] also had to use a relatively high (10−15) molar ratio of cross-linker to initiator for the preparation by anionic polymerization of "arm-first" *tert*-butyl acrylate star polymers with EGDMA cores to avert large percentages (>30%) of unattached linear chains and secure a number of arms larger than four. The low efficiency of the EGDMA cross-linker in the work of Held and Müller[31] might be due to its polymerization after that of the more reactive *tert*-butyl acrylate monomer.

Ruckenstein and Zhang[12] also investigated the synthesis of star-shaped poly(MMA) by anionic polymerization using ethylene glycol di(methacryloyloxy)ethyl ether as a hydrolyzable cross-linker. These workers varied the cross-linker to initiator molar ratio from 3 to 8. GPC analysis showed that the MWs increased as the cross-linker ratio increased. Similar to our results, the MWs were always relatively low and the PDIs high. In particular, as the cross-linker to initiator molar ratio increased from 3 to 8, the M_ns increased from 8500 to 15 500 g mol^{-1}, and the PDIs increased from 1.4 to 2.2, again in agreement with our results.

The final star polymer with DMDMAES/MTS molar ratio of 8 was hydrolyzed using HCl. According to the stoichiometry, the hydrolysis products should be MMA−HEMA diblock copolymers with 20 units of MMA and 16 units of HEMA. The results from the GPC analysis are listed in Table 3, indicating that the hydrolysis products have an M_n of approximately 8500 g mol^{-1}, which is twice the value of the M_n of the linear MMA homopolymer precursor, just as expected. Note that these two values of M_n are twice the corresponding theoretical values listed in Table 3, due to partial initiator deactivation.

Preparation and Hydrolysis of CSPMNs of MMA. After establishing our ability to prepare and hydrolyze star polymers of MMA, we proceeded to prepare and hydrolyze model networks based on cross-linked star polymers[15−17] of MMA. The synthesis of these materials involved two extra steps compared to that of the star polymers, namely, a second addition of MMA to grow arms from the center of the star polymers outward and obtain the so-called "in−out" star polymers and a second addition of cross-linker to interlink the "in−out" star polymers to a network. The synthesis and hydrolysis of two such networks are represented schematically in Figures 7 and 8, where both the hydrolyzable and nonhydrolyzable cross-linkers were used. In particular, in Figure 7, the hydrolyzable DMDMAES cross-linker was used for the formation of the cores of the "arm-first" star polymers (primary cores) and the nonhydrolyzable EGDMA cross-linker was used for the formation of the cores that interconnect the "in−out" star polymers to networks (secondary cores), while the reverse was applied in Figure 8. In these figures, the hydrolyzable DMDMAES cores are drawn in white, whereas the nonhydrolyzable EGDMA cores are painted black. The molar ratios of cross-linker to initiator were 6/1 for DMDMAES, as determined in the star polymer synthesis optimization study described above, and 4/1 for EGDMA, as determined in previous studies.[24,25] The asterisks in the figures indicate the active ("living") polymerization sites. The CSPMNs in Figures 7 and 8 will be henceforth abbreviated as H−N and N−H, respectively, indicating the order of addition of the hydrolyzable (H) and nonhydrolyzable (N) cross-linkers. A third CSPMN with both cores based on the nonhydrolyzable EGDMA cross-linker was also synthesized as a control, and this will be abbreviated as N−N.

The network hydrolysis products are also shown in Figures 7 and 8. The black and white colors in the linear

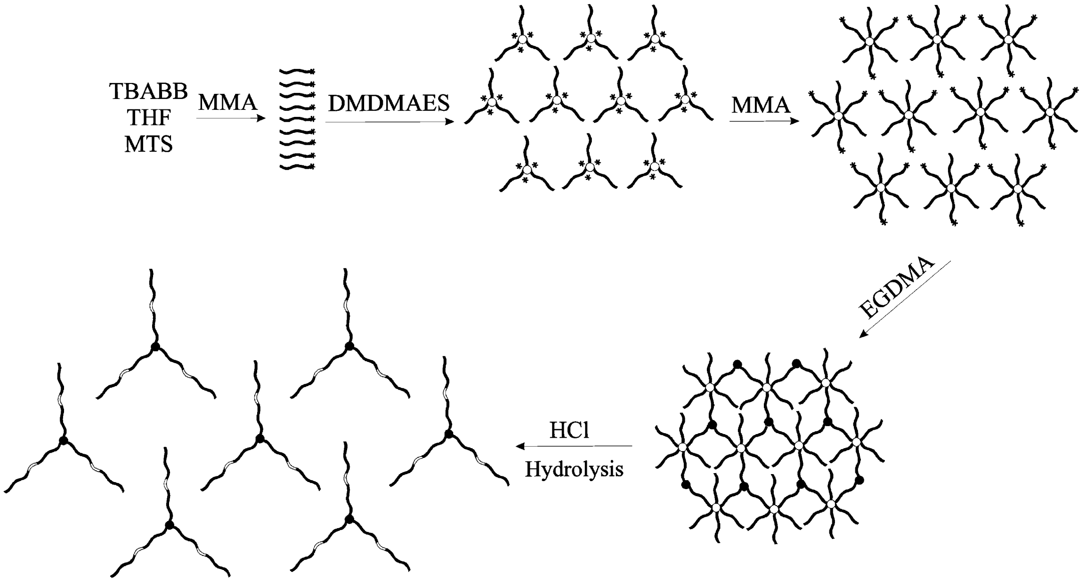

Figure 7. Schematic representation of the synthesis and hydrolysis of the H−N cross-linked star polymer model network (CSPMN) MMA_{20}-*b*-$DMDMAES_6$-*b*-MMA_{20}-*b*-$EGDMA_4$, containing the hydrolyzable dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES) and the nonhydrolyzable ethylene glycol dimethacrylate (EGDMA) cross-linker in the primary and secondary cores, respectively. TBABB = tetrabutylammonium bibenzoate, polymerization catalyst; THF = tetrahydrofuran, polymerization solvent; MTS = 1-methoxy-1-(trimethylsiloxy)-2-methyl propene, monofunctional initiator; MMA = methyl methacrylate, monomer; HCl = hydrochloric acid, hydrolysis reagent.

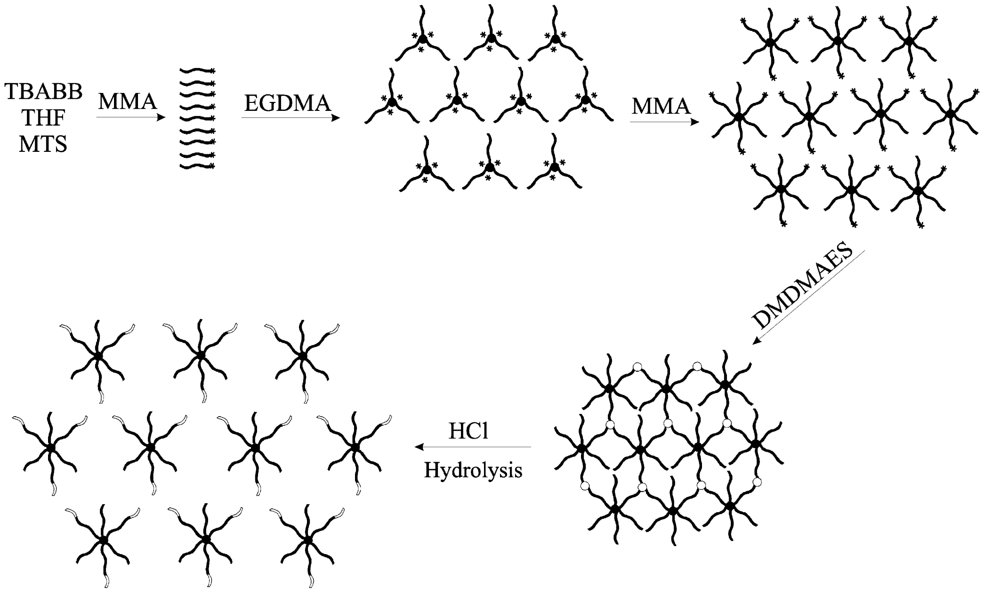

Figure 8. Schematic representation of the synthesis and hydrolysis of the N−H cross-linked star polymer model network (CSPMN) MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}-*b*-$DMDMAES_6$, containing the nonhydrolyzable ethylene glycol dimethacrylate (EGDMA) cross-linker and the hydrolyzable dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES) cross-linker in the primary and secondary cores, respectively. TBABB = tetrabutylammonium bibenzoate, polymerization catalyst; THF = tetrahydrofuran, polymerization solvent; MTS = 1-methoxy-1-(trimethylsiloxy)-2-methyl propene, monofunctional initiator; MMA = methyl methacrylate, monomer; HCl = hydrochloric acid, hydrolysis reagent.

segments of the hydrolysis products denote the MMA and HEMA units (the latter produced after the DMDMAES hydrolysis), respectively. The hydrolysis products of both H−N and N−H networks are star copolymers with EGDMA cores. The star copolymers resulting from the H−N networks comprise arms approximately twice as long as those of the N−H stars. Moreover, the former copolymers are homo-arm star copolymers based on ABA triblock copolymer arms of MMA−HEMA−MMA, while the latter copolymers are hetero-arm copolymers based on MMA homopolymer arms and diblock HEMA−MMA copolymer arms with HEMA outer blocks.

Samples of the three precursors (linear MMA homopolymer, “arm-first” star polymer, and “in−out” star polymer) to the three (H−N, N−H, and N−N) cross-linked star polymer model networks were withdrawn during synthesis and were characterized by GPC. The GPC chromatograms are plotted in Figure 9, and the calculated MWs and PDIs are listed in Table 4. The chromatograms show that, with each addition of monomer or cross-linker, the MWDs move to higher MWs, as expected. The calculations of the average MWs in Table 4 confirm this trend.

The top panel of Figure 9 shows the chromatograms of the three precursors to the H−N network. Whereas the chromatogram of the linear precursor MMA_{20} is narrow and unimodal, the MWDs of the “arm-first” and “in−out” star polymers, both based on the hydrolyzable

Table 4. Results of GPC Characterization of the Precursors to the Cross-Linked Star Polymer Model Networks, the Extractables from the Networks, and the Hydrolysis Products of the Networks

			GPC results		
sample name	polymer formula	theor MW^a	M_n	M_w/M_n	M_p
	H−N Network				
homopolymer	MMA$_{20}$	2100	6260	1.06	6910
"arm-first" star	MMA$_{20}$-*b*-DMDMAES$_{6}$	N/A^b	13 100	1.99	6290, 11600, 23000
"in−out" star	MMA$_{20}$-*b*-DMDMAES$_{6}$-*b*-MMA$_{20}$	N/A^b	33 300	1.58	4740, 19600, 41600, 63700
hydrolysis product	MMA$_{20}$-*b*-HEMA$_{12}$-*b*-MMA$_{20}$-*b*-EGDMA$_{4}$	N/A^b	1540000	1.46	6600, 31100, 1560000
extractables	MMA$_{20}$-*b*-DMDMAES$_{6}$-*b*-MMA$_{20}$-*b*-EGDMA$_{4}$	N/A^b	6680	1.62	6070, 26600
	N−H Network				
homopolymer	MMA$_{20}$	2100	5120	1.06	5460
"arm-first" star	MMA$_{20}$-*b*-EGDMA$_{4}$	N/A^b	73 100	1.21	5210, 80700
"in−out" star	MMA$_{20}$-*b*-EGDMA$_{4}$-*b*-MMA$_{20}$	N/A^b	135 000	1.36	4970, 17000, 123000
hydrolysis product	MMA$_{20}$-*b*-EGDMA$_{4}$-*b*-MMA$_{20}$-*b*-HEMA$_{12}$	N/A^b	7520000	3.89	5020, 106000, 7360000
extractables	MMA$_{20}$-*b*-EGDMA$_{4}$-*b*-MMA$_{20}$-*b*-DMDMAES$_{6}$	N/A^b	77000	1.08	5530, 18500, 79900
	N−N Network				
homopolymer	MMA$_{20}$	2100	4490	1.07	4780
"arm-first" star	MMA$_{20}$-*b*-EGDMA$_{4}$	N/A^b	66200	1.28	4100, 72600
"in−out" star	MMA$_{20}$-*b*-EGDMA$_{4}$-*b*-MMA$_{20}$	N/A^b	155000	1.43	5020, 15000, 135000
extractables	MMA$_{20}$-*b*-EGDMA$_{4}$-*b*-MMA$_{20}$-*b*-EGDMA$_{4}$	N/A^b	6880	1.12	8080, 24200

[a] The molecular weight of the initiator fragment of 100 g mol^{-1} has also been included in the calculation. [b] Not applicable.

Table 5. Sol Fraction (Extractables) of the Three Cross-Linked Star Polymer Networks

network name	network formula	sol fraction (% w/w)	linear content in sol fraction (% w/w)
H−N network	MMA$_{20}$-*b*-DMDMAES$_{6}$-*b*-MMA$_{20}$-*b*-EGDMA$_{4}$	12.7	72.5
N−H network	MMA$_{20}$-*b*-EGDMA$_{4}$-*b*-MMA$_{20}$-*b*-DMDMAES$_{6}$	20.5	76.3
N−N network	MMA$_{20}$-*b*-EGDMA$_{4}$-*b*-MMA$_{20}$-*b*-EGDMA$_{4}$	6.9	93.0

cross-linker, exhibit three and four peaks, respectively. In both cases, the lowest MW peak corresponds to the unattached linear polymer. The M_ps of all these species are listed in Table 4, where all lower M_ps are around 6000 g mol^{-1}. For the "arm-first" star polymer, the two extra peaks are at around 12 000 and 23 000 g mol^{-1}, which are 2 and 4 times the MW of the linear polymer. Considering the compact nature of the star polymers, confirmed previously by the SLS study, the above numbers do not necessarily imply star polymers with only two and four arms, respectively, but star polymers with a larger number of arms, with the one being the dimer of the other. The last observation is suggestive of a star−star coupling mechanism.[31] Because all three peaks of the "arm-first" star polymer (including that of the linear precursors) were unresolved in the GPC chromatogram, the PDI reported in Table 4 was calculated for the whole distribution and came out to be near 2. The M_ps of the peaks of the "in−out" star polymer are again integer multiples of the lowest of the three peaks: 20 000, 42 000, and 64 000 g mol^{-1}, implying again a star−star coupling mechanism. Unlike the "arm-first" star polymer, the peak of the linear homopolymer was fully resolved from the three peaks of the "in−out" star polymer. Thus, the PDI of the "in−out" star polymer reported in Table 4 was calculated only for the star polymers without the peak of the linear polymer and came out to be near 1.6, lower than that of the "arm-first" star polymer.

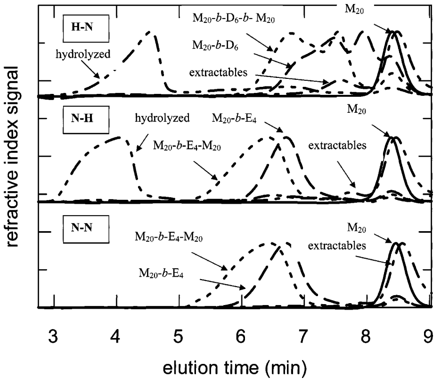

Figure 9. GPC chromatograms of the precursors and the extractables of cross-linked star polymer model networks (CSPMNs) H−N, N−H, and N−N. The GPC chromatograms of the hydrolysis products of the H−N and N−H CSPMNs are also shown. M, D, and E are (further) abbreviations for methyl methacrylate (MMA), dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES), and ethylene glycol dimethacrylate (EGDMA), respectively.

The other two panels in Figure 9 show the chromatograms of the three precursors to the N−H and N−N networks. Again, the chromatograms of the linear precursors MMA$_{20}$ are narrow and unimodal. The MWDs of the "arm-first" and "in−out" star polymers, both based on the nonhydrolyzable cross-linker, are at higher MWs and exhibit higher PDIs compared to their linear precursors and also contain an amount of unattached linear polymer. However, the MWDs of these star polymers are not as broad as the MWDs of the stars based on the hydrolyzable cross-linker, and they exhibit just one main peak, with MW higher than that of the corresponding hydrolyzable stars, and the amount of unattached linear polymer is smaller. All of the above indicate the higher linking efficiency of the nonhydrolyzable cross-linker compared to the hydrolyzable, as explained in a previous section. By going from the "arm-first" star polymer to the "in−out" star polymer, the MW approximately doubles. The minor peak in the chromatograms of the "in−out" star polymers at approximately 16 000 g mol^{-1} has been observed before and has been attributed to a dimer formed by the coupling reaction between two "living" linear chains with one EGDMA molecule[16] or star polymers with a small number of arms.

Sol Fraction of the CSPMNs. Table 5 shows the sol fraction extracted from the CSPMNs H−N, N−H, and N−N, as well as the content of the sol fraction in linear polymer. The MWDs of the extractables are given in Figure 9, and their calculated MWs are listed in Table

4. Table 5 suggests that the lowest sol fraction was extracted from the N−N network, 6.9%, whose both types of cores are based exclusively on the more efficient nonhydrolyzable cross-linker EGDMA. From the other two networks, the N−H network contained a higher sol fraction, 20.5%, because its secondary cores, more essential for gel formation, are based on the hydrolyzable DMDMAES cross-linker. The sol fraction from the H−N network was significantly lower, at 12.7%. From the MWDs in Figure 9, it seems that the extractables from all three networks contain a large percentage of linear chains. Table 5 shows the percentage of the extractables from each network in linear chains, as calculated from the areas under the MWDs in Figure 9. The extractables from the N−N network are almost exclusively linear chains, with 93.0% w/w linear polymer, whereas the linear content of the extractables from the other two networks are approximately 75% w/w, also containing a respectable amount of star polymers. These data are again consistent with the higher cross-linking efficiency of EGDMA compared to that of DMDMAES, which would imply that, once formed, star polymers based on and cross-linked by EGDMA are less likely to remain unattached to the network.

Hydrolysis Products of the CSPMNs. The acid hydrolysis of the H−N and N−H networks was first confirmed qualitatively by observing the dissolution of ~1 cm^3 pieces of the THF-swollen gel in excess THF containing HCl, in approximately 5 min. When the network hydrolysis products were recovered by precipitation in water and vacuum-dried at room temperature, the redissolution in THF of the products from the N−H network was impossible, either due to their very high molecular weight or due to re-formation of some of the network bonds upon drying. Thus, the hydrolysis products were characterized by GPC from the hydrolysis solution, without recovery by precipitation. Their MWDs are displayed in Figure 9, and the calculated MWs are listed in Table 4. Very high MWs, with M_ps at 1 600 000 and 7 400 000 g mol^{-1}, much higher than that of the "in−out" star precursors, were observed, indicating interstar linkage.

In particular, according to Figure 8, the hydrolysis product of the N−H network should be of a slightly higher MW than the "in−out" star precursor having an M_p of 123 000 g mol^{-1}. However, the main peak is at 7 400 000 g mol^{-1}, manifesting interstar linking. It is noteworthy that the hydrolysis product displays a smaller peak at an M_p of 106 000 g mol^{-1}, in fair agreement with the expected value and presumably corresponding to the nonrecombined product. According to Figure 8, the hydrolysis products of the N−H network are star polymers with HEMA units on the periphery of the star. The hydroxyls of the HEMA units can combine physically[32] via hydrogen bonds or chemically through etherification either intermolecularly to give the very high MW product or intramolecularly to give the star polymer with a slightly lower than expected MW.

For the H−N network, Figure 7 shows that the hydrolysis product is again a star polymer, whose HEMA units, however, are in the middle of the arms, preventing extensive intermolecular association. Indeed, the high MW peak of the hydrolysis product is at 1 600 000 g mol^{-1}, lower than that of the N−H network. The MWD of the hydrolysis product of the H−N network has a smaller peak at 31 000 g mol^{-1}, again in fair agreement with the M_ps of the "in−out" star polymer precursor to the network. Characterization by static light scattering was possible only on the hydrolysis product of the H−N network which could dissolve in THF after precipitation and drying. The absolute MW was determined to be 1 220 000 g mol^{-1}, in fair agreement with the GPC MW.

Conclusions

A novel hydrolyzable silicon-containing dimethacrylate cross-linker was synthesized and polymerized by GTP with MMA to prepare star polymers and CSPMNs. The bulkiness of this cross-linker did not allow a large number of arms at the cores as with more traditional dimethacrylate cross-linkers such as EGDMA. The star polymers and the CSPMNs were hydrolyzed in THF using hydrochloric acid to give lower MW polymer products. The star polymers yielded hydrolysis products with the expected MWs, corresponding to the linear arms. Although, upon hydrolysis, the CSPMNs readily dissolved to give homogeneous polymer solutions, the MWs of the resulting polymers were much higher than expected, indicating extensive coupling of the star polymers produced.

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