Synthesis and Characterization of Star Polymers and Cross-Linked Star Polymer Model Networks with Cores Based on an Asymmetric, Hydrolyzable Dimethacrylate Cross-Linker

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Received July 21, 2005. Revised Manuscript Received October 21, 2005

A hydrolyzable dimethacrylate cross-linker, 2-methyl-2,4-pentanediol dimethacrylate (MPDMA), was synhesized by the reaction of 2-methyl-2,4-pentanediol and methacryloyl chloride in the presence of triethylamine. This cross-linker was used to prepare a neat cross-linker network and three cross-linked star polymer model networks (CSPMNs) of methyl methacrylate (MMA), as well as star-shaped polymers of MMA, by group transfer polymerization (GTP). 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) on each successive addition of cross-linker or monomer. Characterization of the star polymers by static light scattering (SLS) in THF showed that star polymers with MPDMA cores bear a relatively small number of arms, between 7 and 35. All star polymers and polymer networks containing the MPDMA cross-linker were hydrolyzed at room temperature in neat trifluoroacetic acid to yield lower-MW products.

Introduction

Star and branched polymers and polymer networks bearing cleavable divinyl cross-linkers are unique materials that, under the appropriate chemical or physical conditions, can be converted to lower-molecular weight (MW) products with properties different from those of the parent materials. This reduction in MW can be exploited in various applications. For example, hydrolyzable polymer networks can be used as matrixes for tissue scaffolding[1−3] and protein[4] and drug[3,5,6] delivery. Thermally cleavable polymer networks can be applied to the "reworking" of components in electronics and optics industries, where defective parts may be easily replaced or components may be firmly held in place during manufacturing but may be removed if so desired.[7−10] Furthermore, cleavage of the core of star-block copolymers may lead to the loss of their elastomeric behavior,[11] whereas hydrolysis of the branches of pressure-sensitive branched polymers can result in the reduction of their peel strength.[12]

The preparation of these polymeric systems can be performed either by "living" polymerization methods[13] that secure better structural control, or by "nonliving" methods, which are synthetically easier. For the nonliving methods, free-radical polymerization is the most common. For example, Fréchet and co-workers[4] used free-radical polymerization to synthesize polyacrylamide networks cross-linked randomly via a diacrylamide methoxy benzaldehyde acetal, and they subsequently studied the release of protein albumin from them at pH 5.0 and 7.4. At pH 5.0, at which the network started to hydrolyze, albumin was fully released within 5 h. In contrast, at pH 7.4, at which the network was chemically stable, less than 20% of the protein was released after 20 h. Horkay et al.[14] free-radically polymerized dextran hydroxyethyl methacrylate to prepare hydrogels with labile carbonate ester bonds. Ober and colleagues[7] polymerized 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 by free-radical polymerization 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. Finally, Long and co-workers[12] used free-radical polymerization to prepare branched polymers of 2-ethylhexyl acrylate branched with dicumyl alcohol dimethacrylate, which were subsequently hydrolyzed with the aid of a *p*-toluenesulfonic acid catalyst in dioxane at 100 °C.

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10.1021/cm051604a CCC: $33.50
Published on Web 12/02/2005

Examples of the synthesis of polymers bearing hydrolyzable cross-linkers using living polymerization methods are the anionic polymerizations reported by Ruckenstein and Zhang[6] and by Long et al.[3,11] Ruckenstein and Zhang[6] 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 acetal groups were present 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-MW products. Long and co-workers[3,11] prepared, via anionic polymerization, star polymers of MMA and isobutyl methacrylate cross-linked with 2,5-dimethyl-2,5-hexanediol dimethacrylate, whose core was subsequently hydrolyzed using *p*-toluenesulfonic acid in dioxane at 100 °C. Finally, Hawker[15] used living free-radical polymerization and a trifunctional initiator to prepare three-arm polystyrene stars, which were subsequently hydrolyzed with potassium hydroxide back to their constituting arms.

Another interesting type of polymeric material is that of polymer model networks,[16] 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 (regular) polymer model networks with hydrolyzable cross-links have been reported to date. A new type of polymer model network, again based on nonhydrolyzable cross-links, is that of cross-linked star polymer model networks (CSPMNs)[17−19] developed recently by our research team using the living polymerization technique group transfer polymerization (GTP).[20−24] 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, and cross-linker under GTP conditions. The dangling chains are formed on the first addition of monomer, whereas the elastic chains are formed on the second addition of monomer. The two additions of cross-linkers give rise to the formation of two different types of cores, the primary and the secondary, formed on the first and second additions of cross-linker, respectively. Primary cores are connected only to secondary cores, and secondary cores are connected only to primary cores. The secondary cores bear only elastic chains, whereas the primary cores bear an equal number of dangling and elastic chains.

The purpose of this investigation was to synthesize CSPMNs containing a hydrolyzable cross-linker, and to examine their hydrolysis. To this end, the preparation and purification of a novel, asymmetric, dimethacrylate cross-linker containing an ester group of a tertiary alcohol was necessary. A nonhydrolyzable cross-linker was also employed in the syntheses. Thus, one type of CSPMN core, primary or secondary, was based on the hydrolyzable cross-linker, whereas the other type was based on the nonhydrolyzable, resulting in two different isomeric networks. Moreover, the two networks, one with both cores comprising the hydrolyzable cross-linker and the other with both cores based on the nonhydrolyzable cross-linker, were also prepared.

Experimental Section

Materials. 2-Methyl-2,4-pentanediol (MP), methacryloyl chloride (MAC), triethylamine (Et_3N), tetrabutylammonium hydroxide, benzoic acid, MMA, ethylene glycol dimethacrylate (EGDMA), 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), 1,1′-azobis(cyclohexanecarbonitrile), and calcium hydride were all purchased from Aldrich (Germany). Tetrahydrofuran (THF) was purchased from Labscan (Ireland). It was used as the mobile phase in chromatography (HPLC grade); it was also used as a solvent (reagent grade), both in the reaction for the synthesis of the cross-linker and for the polymerizations.

Methods. The solvent, THF, was dried by being refluxed over a potassium−sodium mixture for 3 days, and was freshly distilled prior to use. Et_3N was dried by being stirred for 3 days over calcium hydride, and was vacuum distilled just before use. MP and MAC were freshly distilled under vacuum just before their use, and were 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.,[22] and was kept under vacuum until use. MMA and EGDMA were passed through basic alumina columns to remove protic 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 were stored in the fridge at about 5 °C. Both MMA and EGDMA were freshly distilled under vacuum just before use, and were 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 was assembled hot under a dynamic vacuum prior to use.

Cross-Linker Synthesis. The hydrolyzable cross-linker, 2-methyl-2,4-pentanediol dimethacrylate (MPDMA), was prepared by the esterification reaction of MP with MAC in THF and in the presence of Et_3N base. A typical synthesis is detailed in the Supporting Information. The product mixture was subsequently purified by column chromatography (silica gel, hexane:ethyl acetate = 95:5). An oily liquid was obtained (overall yield 11.42 g, 28.7%), which was then distilled under vacuum over calcium hydride in the presence of added DPPH. The high purity of the distilled cross-linker was confirmed by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. ^1H NMR ($CDCl_3$, δ): 1.25 (d, CH_3CH, 3 H), 1.48 (s, $(CH_3)_2C$, 6 H), 1.90 (two s, $2(CH_3C)$, 6 H), 2.08−2.33 (dd, q, $(CH_3)_2CCH_2CHCH_3$, 2 H), 5.22

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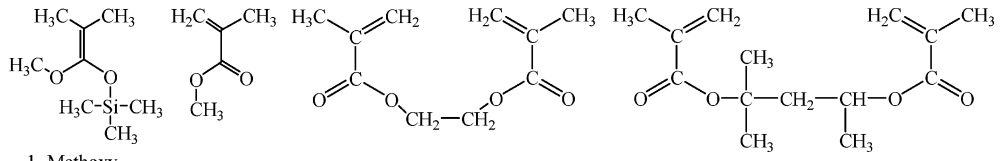

Figure 1. Chemical structures and names of the main reagents used for the polymer synthesis: monofunctional initiator MTS, monomer MMA, and cross-linkers EGDMA and MPDMA.

(m, C*H*CH_3, 1 H), 5.51 (two s, olefinic H trans to CO_2, 2 H), 5.99 (two s, olefinic H cis to CO_2, 2 H). ^{13}C NMR ($CDCl_3$, δ): 18 (s, *C*H_3C(=CH_2), 2 C), 22 (s, CH*C*H_3, 1 C), 26−27 (two s, (*C*H_3)$_2$C, 2 C), 46 (s, C*C*H_2CH, 1 C), 68 (s, *C*H, 1 C), 81 (s, *C*$(CH_3)_2$, 1 C), 125 (two s, *C*H_2=C, 2 C), 137−138 (two s, CH_3*C*(=CH_2), 2 C), 167 (s, O*C*(=O)C, 2 C). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66. Found: C, 65.88; H, 8.47. The relevant ^{1}H and ^{13}C NMR spectra are provided in the Supporting Information as Figures S1 and S2.

Retrieval of the Monosubstituted Monomer. In addition to the desired dimethacrylate product MPDMA, we also obtained the monomethacrylate resulting from the esterification of the secondary hydroxyl with MAC at a yield of typically 25%. The name of this byproduct is (4-hydroxy-4-methyl)-2-pentyl methacrylate (HMPMA). Because of its more-polar character, this product was the slower-moving band in chromatography, from which it was also obtained in pure form. ^{1}H NMR (d_6-DMSO, δ): 1.07 (d, (C*H*$_3$)$_2$COH, 6 H), 1.18 (d, C*H*$_3$CH, 3 H), 1.56−1.81 (dd, q, $(CH_3)_2$CC*H*$_2$CHCH_3, 2 H), 1.86 (s, C*H*$_3$CH, 3 H), 4.29 (s, O*H*, 1 H), 5.08 (m, C*H*CH_3, 1 H), 5.64 (s, olefinic H trans to CO_2, 1 H), 5.99 (s, olefinic H cis to CO_2, 1 H). HMPMA was subsequently polymerized via free-radical polymerization (see below).

Kinetic Study of Cross-Linker Hydrolysis. The kinetics of the hydrolysis of the MPDMA cross-linker were followed using ^{1}H NMR spectroscopy in a 2:1 w/w trifluoroacetic acid−$CDCl_3$ mixture at a 0.91 mol L^{-1} MPDMA concentration. In this experiment, the trifluoroacetic acid concentration was at a 7.4-fold molar excess with respect to MPDMA (6.78 mol L^{-1}), allowing for the calculations to be made under pseudo-first-order conditions. The hydrolysis reaction was studied for 4 h. NMR spectra were recorded every 5 min at the beginning of the hydrolysis, and every 1 h at the later stages.

Polymer Synthesis. Figure 1 shows the chemical structures and names of the main reagents used for the synthesis of the polymers in this study. All syntheses were performed using GTP. The polymerizations were carried out in 100 mL round-bottom flasks that were fitted with a rubber septum. Catalytic amounts of TBABB were transferred to the flask, which was immediately purged with dry nitrogen. Freshly distilled THF was subsequently transferred directly into the flask via a glass syringe, followed by the addition of the initiator. Finally, the monomer and the dimethacrylate cross-linkers were added in the appropriate order to the flask to prepare the polymers. The reactions were carried out at ambient temperature (∼25 °C) without thermostating the polymerization reactor. The polymerization exotherms were monitored by a digital thermometer, and were used to follow the progress of the reaction.

The following polymeric materials were prepared: one neat MPDMA network, one arm-first and one in−out MMA−MPDMA star polymer, and four MMA CSPMNs with different combinations of the MPDMA and EGDMA cross-linkers. A typical polymerization yielding the first-core-hydrolyzable CSPMN MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}-*b*-$EGDMA_4$ is detailed in the following. Freshly distilled THF (32 mL) and freshly distilled MTS initiator (0.3 mL, 0.26 g, 1.5 mmol) were added, in this order, to a 100 mL round-bottom flask, sealed with a rubber septum, and kept under a dry nitrogen atmosphere; the reaction mixture contained a small amount (∼10 mg) of TBABB catalyst (∼20 μmol). MMA (3.2 mL, 3.0 g, 30 mmol) was added slowly under stirring, giving a polymerization exotherm (26.3−43.6 °C) that abated within 5 min. A 0.1 mL sample was extracted from the reaction solution for gel permeation chromatography (GPC) analysis, and MPDMA (1.4 mL, 1.5 g, 6.0 mmol) was added. The reaction temperature rose from 37.9 to 42.8 °C. After sampling for GPC, we again slowly added MMA (3.2 mL, 3.0 g, 30 mmol), which produced an exotherm (37.9−50.1 °C), and a sample was withdrawn again for GPC analysis. Finally, EGDMA (1.1 mL, 1.2 g, 6.0 mmol) was added, which promoted the gelation of the solution within seconds and caused a temperature increase from 44.7 to 46.1 °C.

The other three CSPMNs were prepared by altering the order of addition of the two different cross-linkers (one network), or by exclusively using either the MPDMA or the EGDMA cross-linker (two networks). The hydrolyzable in−out star polymer was prepared by the sequential addition of MTS, MMA, MPDMA, and MMA, whereas the hydrolyzable arm-first star polymer was prepared by MTS, MMA, and MPDMA sequential addition. The neat MPDMA network was prepared by MPDMA and MTS sequential addition. The synthetic sequences employed for the preparation of all these materials are summarized in Figure S3 in the Supporting Information.

The monosubstituted monomer HMPMA (0.75 mL, 0.74 g, 3.97 mmol) was polymerized by free-radical polymerization using 1,1′-azobis(cyclohexanecarbonitrile) (0.097 g, 0.39 mmol) as the initiator and toluene (5.1 mL) as the solvent at 90 °C for 24 h. The polymerization product was recovered by precipitation in *n*-hexane, dried in a vacuum oven for 72 h at room temperature, and characterized by GPC and ^{1}H NMR.

Determination of the Sol Fraction (Extractables) and Degree of Swelling of the CSPMNs. We removed the networks from the polymerization flasks by breaking the flasks. Photographs of the three hydrolyzable CSPMNs right after they were removed from the flasks are shown in Figure S4 in the Supporting Information. The CSPMNs 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 from the sol fraction solution using a rotary evaporator. The recovered extracted polymer was further dried for 72 h in a vacuum oven at room temperature. 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 the mass of the monomer, cross-linkers, and initiator used for its synthesis. The extractables were characterized in terms of their MWDs, using GPC, and in terms of their composition, using ^{1}H NMR. To determine the degree of swelling (DS) of the CSPMNs in THF, we cut ∼1 cm^3 pieces from the THF-equilibrated and washed networks, and weighed the pieces. They were subsequently placed in a vacuum oven, where they were dried at 40 °C for 72 h. The dried masses were determined, and the DS was calculated as the ratio of the swollen THF divided by the dried masses.

Polymer Hydrolysis. All polymers formed using the hydrolyzable cross-linker MPDMA were hydrolyzed in neat trifluoroacetic acid at room temperature. For the neat cross-linker network and the CSPMNs, the products after 3 days of hydrolysis were precipitated by adding their trifluoroacetic acid solution dropwise to water. The precipitates were recovered by filtration, washed in the filter with more water, dried in a vacuum oven for 72 h at room temperature, and characterized using GPC and ^{1}H NMR.

The hydrolysis of the two MPDMA-containing star polymers was followed kinetically for 4 days. To this end, 0.5 g of star polymer was dissolved in 5 g of trifluoroacetic acid. Samples (0.5 g of solution) were withdrawn every 30 min in the beginning of the hydrolysis and every day at the later stages of the reaction. The samples were recovered by precipitation in water, and were dried as described for the network hydrolysis samples above. The dried samples were characterized using GPC.

Polymer Characterization. *Gel Permeation Chromatography.* Molecular weights (MWs) and molecular weight distributions (MWDs) of the star polymers and their precursors, the network precursors, the extractables from the CSPMNs, and the hydrolyzed polymer products were determined by GPC using a single Polymer Laboratories PL-mixed D column. The mobile phase was THF (flow rate of 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 created on the basis of 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_n, the polydispersity indices (PDI, M_w/M_n, where M_w is the weight-average MW), and the peak MWs, M_p, which are the MWs at the peak maximum.

Static Light Scattering. Absolute M_w values 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 multi-angle detector that determines the intensity of scattered light at seven different angles (35, 50, 75, 90, 105, 130, and 145°). Polymer samples were dissolved in HPLC-grade THF at different polymer concentrations (typically seven), and were filtered through 0.45 μm pore size syringe filters. From this information, we constructed a Zimm plot 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) of the polymer solutions in THF were determined using an ABBE refractometer.

NMR Spectroscopy. The MPDMA cross-linker and the HMPMA monomer (monosubstituted product) and its homopolymer were characterized using 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.

Results and Discussion

Preparation and Hydrolysis of the MPDMA Cross-Linker. The hydrolyzable dimethacrylate cross-linker MPDMA was prepared by an esterification reaction between diol MP and MAC in the presence of triethylamine base in absolute THF. Stoichiometric amounts of MP (1 equiv) and MAC (2 equiv) were used in our later syntheses. Use of excess MAC (up to 20%) was not sufficient for the full conversion of both hydroxyl groups of the diol. In particular, there were difficulties in the esterification of the tertiary hydroxyl group due to steric hindrance,[25] always leading to the production of the monosubstituted product as well. It was thus decided that the use of excess MAC be avoided because it would result in a greater amount of unreacted MAC/methacrylic acid. We removed the unreacted MAC by passing the product mixture twice through a column of basic alumina. The desired product was easily separated from the monosubstituted byproduct by column chromatography. Typical yields of the reaction for the MPDMA preparation were 77%, whereas overall yields after column chromatography and distillation were 29%. The synthesis of the MPDMA cross-linker has recently been reported in the patent literature.[26] However, because of the industrial nature of that work (free-radical polymerization and subsequent cleavage by thermolysis), no care was taken to purify the cross-linker.

^{1}H NMR spectroscopy showed that the hydrolysis of MPDMA in a 7.4-fold molar excess of trifluoroacetic acid followed pseudo-first-order kinetics, giving a straight line in the semilogarithmic concentration vs time plot. The pseudo-first-order half-life under these conditions was 560 min (pseudo-first-order hydrolysis rate constant $= 2.05 \times 10^{-4} \pm 5 \times 10^{-7}$ s^{-1}), whereas the second-order hydrolysis rate constant was calculated to be 3.03 ± 0.07 M^{-1} s^{-1}, where the molarity units M refer to the trifluoroacetic acid concentration. On the basis of the cross-linker half-life determined above, 90, 99, and 99.9% hydrolysis is predicted to occur after approximately 31, 62, and 93 h, respectively, in almost neat trifluoroacetic acid. Thus, complete hydrolysis of the MPDMA-containing polymers should last 3−4 days. Trifluoroacetic acid has similarly been used for the removal of *tert*-butyl groups in polymers and their conversion to polycarboxylic acids.[27]

Polymerization of the HMPMA Monomer. The HMPMA monomer was successfully polymerized by free-radical polymerization. The resulting homopolymer was obtained at a 100% yield, and had a GPC M_n of 10 100 g mol^{-1} and a PDI of 1.91 ($M_p = 15\,700$ g mol^{-1}). ^{1}H NMR (d_6-DMSO, δ): 0.95 (CH_3C, 3 H), 1.12 ((CH_3)$_2$COH, 6 H), 1.24 (CH_3-CH, 3 H), 1.62−1.76 ((CH$_3$)$_2$CCH_2CHCH$_3$ and CH_2CCH$_3$, 4 H), 4.29 (OH, 1 H), 4.81 (CHCH$_3$, 1 H).

Preparation and Hydrolysis of the Neat Cross-Linker Network. To prove the efficiency of the hydrolyzable cross-linker in forming networks via GTP, we performed preliminary experiments in which we prepared the simplest network structure: a MPDMA homopolymer (neat cross-linker) network. As explained in Polymer Synthesis in the Experimental Section, the MTS initiator was added last for the synthesis of this network. Successful gelation took place a few seconds after the MTS addition, demonstrating the action of MPDMA as a cross-linker.

Next, to prove the hydrolyzability of the MPDMA cross-linker, we subjected a sample from this network to hydrolysis in neat trifluoroacetic acid. After 72 h, the sample was

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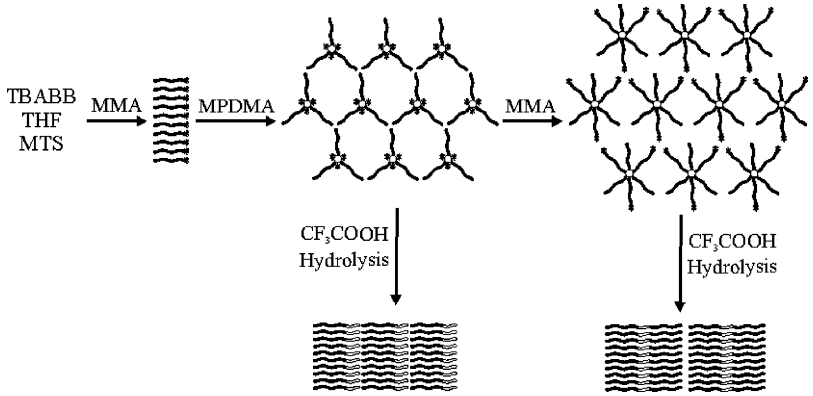

Figure 2. Schematic representation of the synthesis and hydrolysis of the arm-first and in−out star polymers with a core composed of the hydrolyzable MPDMA cross-linker.

Table 1. Results of GPC and SLS Characterization of Arm-First and In−Out Star Polymers MMA_{20}-*b*-$MPDMA_4$ and MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20} and Their Hydrolysis Products

		GPC results			static light scattering	
polymer sample	theoretic MW[a]	M_n	M_w/M_n	M_p	M_w	no. of arms
MMA_{20}	2100	2570	1.42	4250		
MMA_{20}-*b*-$MPDMA_4$		33600	1.46	51100, 5200	39 700	7
MMA_{20}-*b*-(MAA-*co*-HMPMA)$_4$	3120	2780	1.11	3100		
MMA_{20}	2100	6250	1.16	7760		
MMA_{20}-*b*-$MPDMA_4$		21 100	2.08	51300, 10400		
MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}		45 200	4.10	101000, 8670	314000	35
MMA_{20}-*b*-(MAA-*co*-HMPMA)$_4$-*b*-MMA_{20}	5120	7560	1.38	14500, 5250		

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

dissolved, giving a brown solution. The resulting soluble polymer sample was recovered by precipitation in water followed by filtration, and was then vacuum-dried at room temperature. The GPC M_n and PDI of the hydrolysis product were 520 g mol^{-1} and 1.18, respectively.

Preparation and Hydrolysis of Star Polymers of MMA. After demonstrating the cross-linking ability of MPDMA, we pursued the synthesis of arm-first and in−out star polymers by the sequential GTP of MMA and MPDMA. The cross-linker:initiator molar ratio used was 4:1, following our previous work on the GTP synthesis of star polymers with EGDMA cores.[28] Subsequently, we pursued the star polymer's hydrolysis, and studied its kinetics. The synthesis and hydrolysis of both arm-first and in−out"star polymers are depicted schematically in Figure 2, and both processes proved to be successful.

Table 1 lists the MWs of the arm-first and in−out MMA−MPDMA star polymers and their hydrolysis products. The table shows that a linear MMA homopolymer of narrow MWD was obtained in the first step of the polymerization. On addition of the MPDMA cross-linker to the living MMA_{20} linear homopolymer, the apparent M_n increased more than 10-fold, which is consistent with the interlinking of the linear polymer to a starlike structure. This is the arm-first star polymer MMA_{20}-*b*-$MPDMA_4$, whose GPC chromatogram is plotted in Figure 3. The MWD of this polymer is bimodal, with the two M_p values, listed in Table 2, corresponding to 10 times and 1 time the M_p of the arm.

For comparison, Figure 3 also shows the GPC chromatogram of an arm-first star polymer with arms bearing 20

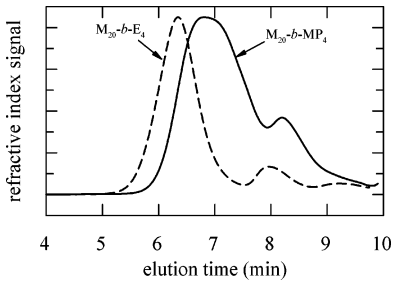

Figure 3. GPC chromatograms of the arm-first star polymers of MMA with hydrolyzable MPDMA and nonhydrolyzable EGDMA cores.

MMA units as well, but the units are cross-linked with the nonhydrolyzable cross-linker EGDMA (this was a precursor to one of the CSPMNs). This EGDMA-containing star polymer had a slightly higher MW and a narrower MWD than the MPDMA-containing arm-first star polymer, indicating that EGDMA was a slightly more efficient cross-linker than MPDMA. This was probably due to the structure of MPDMA being bulkier than that of EGDMA (MW values of 254 and 198 g mol^{-1}, respectively), which led to a greater percentage of unreacted methacrylate groups in the case of MPDMA than in EGDMA. Lower reactivities of other bulky dimethacrylate cross-linkers have also been reported in both GTP[29] and anionic polymerization.[30]

SLS on THF solutions of star polymers MMA_{20}-*b*-$MPDMA_4$ and MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20} allowed for the determination of their absolute M_w and weight-average number of arms, both presented in Table 1. The absolute M_w determined by SLS was greater than the M_w determined

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Table 2. Results of GPC Characterization of the Precursors to the Cross-Linked Star Polymer Model Networks, Extractables from the Networks, and Hydrolysis Products of the Networks

sample name	polymer formula	theoretic MW[a]	GPC results		
			M_n	M_w/M_n	M_p
	H−N Network				
homopolymer	MMA_{20}	2100	2050	1.31	2800
arm-first star	MMA_{20}-*b*-$MPDMA_4$		4770	2.19	10900
in−out star	MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}		8050	2.04	16600
extractables	MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}-*b*-$EGDMA_4$		2900	3.33	64400, 7920, 3360
hydrolysis product	MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$-*b*-MMA_{20}-*b*-$EGDMA_4$		5200	1.49	63200
	N−H Network				
homopolymer	MMA_{20}	2100	6300	1.14	7560
arm-first star	MMA_{20}-*b*-$EGDMA_4$		81500	1.34	93300, 7560
in−out star	MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}		168000	1.69	166000, 8290
extractables	MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}-*b*-$MPDMA_4$		128000	1.24	129000, 7560
hydrolysis product	MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$		957000	1.43	811000, 141000
	N−N Network				
homopolymer	MMA_{20}	2100	6950	1.15	8620
arm-first star	MMA_{20}-*b*-$EGDMA_4$		99300	1.36	112000, 8670
extractables	MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}-*b*-$EGDMA_4$		160000	1.54	146000, 8290
	H−H Network				
homopolymer	MMA_{20}	2100	6880	1.14	8180
arm-first star	MMA_{20}-*b*-$MPDMA_4$		19700	2.36	63000, 9500
in−out star	MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}		112000	2.25	128000, 8670
extractables	MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}-*b*-$MPDMA_4$		7510	1.75	31100, 7970
hydrolysis product	MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$-*b*-MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$	6130	21000	1.34	27500

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

by GPC (MW calibration on the basis of linear polyMMA standards) due to the compact nature of the star structure. The weight-average number of arms was calculated by dividing the SLS M_w of the star polymer by the effective GPC M_w of the arms. The latter was estimated by adding the contribution from the MPDMA cross-linker (4 times the mole content of the MTS initiator) to the GPC M_w of the arms. Thus, the weight-average numbers of arms were found to be 7 and 35 for the arm-first and in−out star polymers, respectively. The value of 7 is less than the values of 20,[31] 30,[18] 50,[17] and 15−40[32] reported in the literature for the number of arms in arm-first star polymers with EGDMA cores also prepared by GTP. Furthermore, the value of 35 is less than the range of values between 60[18] and 100[17] determined in previous work by our group on in−out star polymers.

Following the above characterization, we proceeded to the hydrolysis of these star polymers. The progress of hydrolysis was followed by GPC. The relevant chromatograms are overlaid in Figure 4. The figure shows that the MWs decreased with time. In particular, in 4 h, both star polymers were broken down to much smaller products. The product of the complete hydrolysis of the arm-first star polymer should be the arm plus the residues from the hydrolyzed cross-linker (Figure 2). Indeed, the calculated MW of the hydrolysis product shown in Table 1 was close to that of the arm. On the other hand, the product of the hydrolysis of the in−out star polymer should be approximately twice that of the arm (Figure 2). The GPC chromatogram of this product presents a bimodal size distribution in Figure 4a, with the lower-MW species corresponding to the initial unattached arm and the higher-MW species corresponding to the hydrolysis product. The M_p of the main peak of the hydrolysis product listed in Table 1 (14 500 g mol^{-1}) was

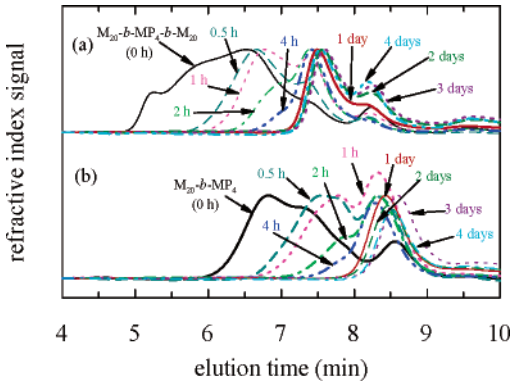

Figure 4. GPC chromatograms of samples obtained at different times in the hydrolysis of the (a) in−out and (b) arm-first star polymers having MPDMA hydrolyzable cores.

approximately twice that of the linear precursor (7760 g mol^{-1}).

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[17−19] of MMA. The synthesis of these materials involved one extra step compared to that of the in−out star polymers, namely a second addition of cross-linker to interlink the in−out star polymers to a network. The synthesis and hydrolysis of one such network is represented schematically in Figure 5, where both the hydrolyzable and nonhydrolyzable cross-linkers were used. In particular, the hydrolyzable MPDMA 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 interconnected the in−out star polymers to networks (secondary cores). In Figure 5, the hydrolyzable MPDMA cores were drawn in white, whereas the nonhydrolyzable EGDMA cores were painted black. The molar ratio of cross-

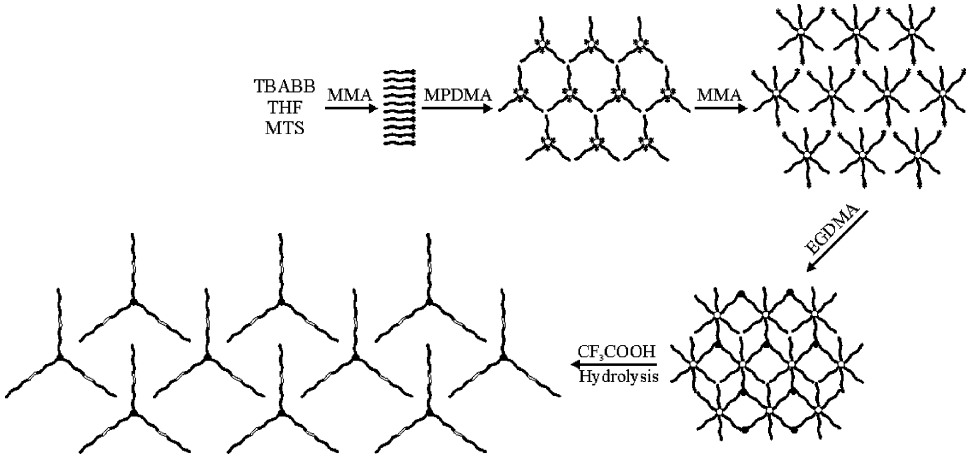

Figure 5. Schematic representation of the synthesis and hydrolysis of the H−N CSPMN MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}-*b*-$EGDMA_4$, which contains hydrolyzable (MPDMA) and nonhydrolyzable (EGDMA) cross-linkers in the primary and secondary cores, respectively.

linker to initiator was 4:1 for both cross-linkers, as determined in previous studies.[28] The asterisks in the figure indicate the active (living) polymerization sites. The CSPMN in Figure 5 will be henceforth abbreviated as H−N, indicating the order of addition of the hydrolyzable (H) and nonhydrolyzable (N) cross-linkers. There are three more possible combinations of H and N cross-linkers in the primary and secondary cores: N−H, N−N, and H−H. The CSPMNs with these combinations were also prepared and studied.

The network hydrolysis products of the H−N network are also shown in Figure 5. The black and white colors in the linear segments of the hydrolysis products denote the MMA units and the MPDMA cross-linker hydrolysis fragments, respectively. The hydrolysis products of both the 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-*b*-(HMPMA-*co*-MAA)-*b*-MMA, whereas the latter copolymers are hetero-arm copolymers based on MMA homopolymer arms and diblock (HMPMA-*co*-MAA)-*b*-MMA copolymer arms with (HMPMA-*co*-MAA) outer blocks. The hydrolysis products of the H−H networks are linear tetrablock MMA-*b*-(HMPMA-*co*-MAA)-*b*-MMA-*b*-(HMPMA-*co*-MAA) copolymers.

Samples of the three precursors (linear MMA homopolymer, arm-first star polymer, and in−out star polymer) to the four (N−N, N−H, H−N, and H−H) CSPMNs were withdrawn during synthesis, and were characterized by GPC. The GPC chromatograms are plotted in Figure 6, and the calculated MWs and PDIs are listed in Table 2. The chromatograms show that with each addition of monomer or cross-linker the MWDs moved to higher MWs, as expected. The calculations of the average MWs in Table 2 confirmed this trend.

For all four networks, the chromatograms of the linear MMA_{20} precursors in Figure 6 were narrow and unimodal. In contrast, the MWDs of all the arm-first and in−out star polymers, based on both the hydrolyzable and nonhydrolyzable cross-linker, were broader, exhibiting in most cases

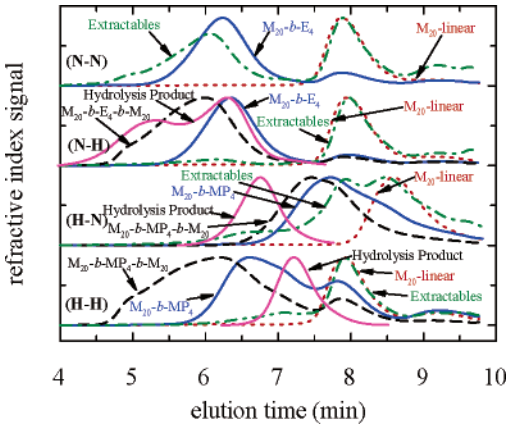

Figure 6. GPC chromatograms of the precursors, extractables, and hydrolysis products of cross-linked star polymer networks N−N, N−H, H−N, and H−H.

two peaks: the star polymer peak (which was the main peak) and the unattached linear polymer peak. The M_p values of all these peaks are listed in Table 2.

Sol Fraction and Degree of Swelling of the CSPMNs. Table 3 shows the sol fraction extracted from all four CSPMNs, as well as the content of the sol fraction in the linear polymer and the M_p values in the MWDs of the extractables. The MWDs of the extractables have already been presented in Figure 6, and their calculated MWs in Table 2. Table 3 suggests that the lowest sol fractions were extracted from the N−H and H−H networks, 8.4 and 10.5%, respectively, whose secondary cores were based on the hydrolyzable cross-linker MPDMA. The other two networks, N−N and H−N, presented sol fractions of 15.6 and 14.6%, respectively. The two networks with secondary hydrolyzable cores, N−H and H−H, which have the lowest sol fraction, displayed extractables composed mainly of linear polymers. In contrast, the networks with secondary nonhydrolyzable cores, N−N and H−N, presented a greater percentage of star extractables. This might be due to the high efficiency of this cross-linker, whose high reactivity resulted in a fast reaction, during which not all of the polymer had time to become part of the network. Table 3 also lists the DS in THF of the CSPMNs, the values of which were all around 7, with those of the networks with MPDMA primary cores being slightly greater in value than those of the networks

Table 3. Analysis of the Sol Fraction (extractables) and Degree of Swelling in THF of the Four Cross-Linked Star Polymer Networks

network	network formula	sol fraction (% w/w)	linear content in sol fraction (% w/w)	M_p star	M_p linear	DS in THF
H−N	MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}-*b*-$EGDMA_4$	14.6	58.2	64400, 7920	3360	7.1
N−H	MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}-*b*-$MPDMA_4$	8.4	81.8	129000	7560	5.7
N−N	MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}-*b*-$EGDMA_4$	15.6	49.1	146000	8290	6.8
H−H	MMA_{20}-*b*-$MPDMA_4$-*b*-MMA_{20}-*b*-$MPDMA_4$	10.5	81.5	31100	7970	8.0

Table 4. Absolute M_w Values for Hydrolysis Products of the Networks As Determined by SLS

sample network	hydrolysis product	static light scattering M_w
H−N	MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$-*b*-MMA_{20}-*b*-$EGDMA_4$	149 000
N−H	MMA_{20}-*b*-$EGDMA_4$-*b*-MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$	5 270 000
H−H	MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$-*b*-MMA_{20}-*b*-(MAA-*co*-$HMPMA)_4$	18 400

with EGDMA cores, probably reflecting the smaller number of arms in the primary cores of the former type of networks.

Hydrolysis Products of the CSPMNs. The hydrolyzable networks H−N, N−H, and H−H were hydrolyzed by treatment of the vacuum-dried material in trifluoroacetic acid. All three networks gradually dissolved in the acid, giving homogeneous and dark brown solutions. The N−N network was subjected to the same treatment, but did not dissolve (although it broke into small pieces), and the liquid phase turned milky white (not brown). Thus, the N−N network did not hydrolyze. After the hydrolysis treatment of all four networks, the polymer products were recovered by precipitation in water and vacuum-drying at room temperature. With the exception of the trifluoroacetic acid-treated N−N network, the hydrolysis products of the networks readily dissolved in THF for GPC and SLS analysis. The GPC chromatograms of the hydrolysis products of the three networks are presented in Figure 6, whereas the MW calculations are given in Table 2.

The hydrolysis products of the N−H network should be star polymers with a slightly higher MW than their in−out star polymer precursor. Table 2 shows that these two species indeed had similar M_p values, 141 000 and 166 000 g mol^{-1} for the hydrolysis product and the in−out star polymer, respectively. The lower-than-expected M_p value for the hydrolysis product might be due to intrastar linkages, e.g., either re-esterification or hydrogen bond formation[33] between the carboxyl and hydroxyl groups of the hydrolyzed cross-linker, both of which would result in a smaller hydrodynamic volume and lower GPC MW. It is noteworthy that the hydrolysis product displayed a peak with a smaller surface area and a higher M_p value, 811 000 g mol^{-1} (Table 2), indicating the presence of interstar linking with the same origin as the intrastar linking described above.

The hydrolysis products of the H−N network should also be star polymers, but with the HMPMA−MAA units in the middle rather than at the end of the arms (Figure 5), thus preventing extensive intermolecular association. The MWD of the hydrolysis product of the H−N network was unimodal with a M_p value of 63 200 g mol^{-1}, which is higher than the M_p value of the in−out star polymer precursor to the same network. This was because the in−out star polymer precursor had a core based on the less-efficient hydrolyzable MPDMA cross-linker, whereas the hydrolysis product was a star with a core based on the more-efficient nonhydrolyzable EGDMA cross-linker. Moreover, the arms of the hydrolysis product should be more than twice as long as those of its star polymer precursors (Figure 5).

Finally, the hydrolysis products of the H−H network should be linear tetrablock copolymers with the structure MMA-*b*-(HMPMA-*co*-MAA)-*b*-MMA-*b*-(HMPMA-*co*-MAA), and with a MW more than double that of the linear homopolymer precursor. Table 2 lists theoretical MWs of 6130 and 2100 g mol^{-1} for these two polymers. However, according to the same table, the GPC M_n of the linear homopolymer precursor was 6880 rather than 2100 g mol^{-1}, i.e., 3.3 times more than expected. Thus, the M_n of the hydrolysis product should also be 3.3 times more than the theoretically expected value of 6130 g mol^{-1}, i.e., 20 100 g mol^{-1}. Indeed, the measured M_n of the hydrolysis product was 21 000 g mol^{-1}, very close to the expected value.

The absolute M_w values of all the hydrolysis products, as determined by SLS, are listed in Table 4. The absolute M_w values of the hydrolysis products of the N−H networks were higher than those of the H−N networks, as observed by GPC (Table 2). However, the SLS M_w values were in both cases several times higher than the corresponding GPC values, confirming the compact nature of the hydrolysis products. In contrast, the GPC and SLS MWs of the hydrolysis products of the H−H network were close in value to each other, in agreement with their expected linear structure.

Conclusions

A novel hydrolyzable, asymmetric dimethacrylate cross-linker was synthesized, purified, and copolymerized with MMA by GTP to prepare star polymers and CSPMNs. Although the bulkiness of this cross-linker did not allow for a large number of arms at the cores, as with more traditional dimethacrylate cross-linkers such as EGDMA, the resulting polymeric products were of comparable high quality. The star polymers and the CSPMNs were hydrolyzed in neat trifluoroacetic acid to give lower-MW polymer products. The star polymers yielded hydrolysis products with the expected MWs, corresponding to the linear arms. The same was true with the hydrolysis products of the H−N and H−H

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CSPMNs. However, the hydrolysis products of the N−H network were much higher in molecular weight than expected, indicating extensive coupling of the star polymers that are produced.

Acknowledgment. The A. G. Leventis Foundation is thanked for a generous donation, which enabled the purchase of the NMR spectrometer for the University of Cyprus. The University of Cyprus Research Committee (Grant 2000-2003) is thanked for providing funds for the purchase of the static light scattering spectrophotometer.

Supporting Information Available: The protocol for cross-linker synthesis, ^{1}H and ^{13}C spectra for the MPDMA cross-linker, synthetic sequences for the preparation of all polymers, and photographs of the three hydrolyzable networks (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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