Star Polymers and Polymer Networks Containing a Novel, Hydrolyzable Diacetal-Based Dimethacrylate Cross-Linker: Synthesis, Characterization, and Hydrolysis Kinetics

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Introduction

Branched polymer structures comprising degradable branching points[1−4] represent modern materials of great interest for the biomedical field[5−8] (supports in controlled drug delivery and tissue engineering) and for the electronics industry[9−12] (for facilitating the removal and reattachment of components). We have recently embarked on a research involving the preparation of polymer networks and star polymers bearing degradable dimethacrylate cross-linkers as the branching points.[13−15] In addition to their degradability, the particular polymeric materials have the attractive feature of containing (nondegradable) linear chains of narrow molecular weight distributions, afforded by employing for the synthesis a controlled polymerization method, group transfer polymerization (GTP).[16−20] The well-defined nature of these polymers enables the derivation of accurate structure−property relationships for the materials both before and after cross-linker degradation.

To date, we prepared three dimethacrylate cross-linkers[13−15] with different ease of degradation under acidic conditions (2 M DCl/d_6-DMSO solution).[21] The most unstable of the three cross-linkers is dimethyldi(methacryloyloxy-1-ethoxy)silane (DMDMAES),[13] bearing a labile siloxy group that hydrolyzes very rapidly with a pseudo-first-order half-life ($t_{1/2}$) = 0.1 day. At the other extreme is 2-methyl-2,4-pentanediol dimethacrylate (MPDMA),[14] an asymmetric cross-linker bearing one tertiary ester group that hydrolyzes with $t_{1/2}$ = 93 days.[21] The third cross-linker is di(methacryloyloxy-1-ethoxy)methane (DMOEM),[15] bearing an acetal group that hydrolyzes with $t_{1/2}$ = 1.7 days,[21] thus presenting an ease of hydrolysis intermediate between those of the two previous cross-linkers. However, the preparation in pure form of this cross-linker was plagued by low yields because of the presence of side products of similar polarity that eluted near the desired product. By carefully analyzing these side products, we recently identified one of them as a higher homologue of DMOEM, which can, therefore, also act as a degradable cross-linker. The particular compound bears two, rather than one, oxymethylene groups and will be referred to as the diacetal cross-linker. The aim of the present investigation is twofold: first, to fully characterize this novel diacetal cross-linker, polymerize it to obtain star polymers and networks, and study the hydrolysis kinetics of the star polymers; second, to study the hydrolysis kinetics of a star polymer based on the lower homologous cross-linker (not systematically performed in our previous study[15]) and compare it with the new cross-linker.

Experimental Section

Cross-Linker Synthesis. The two acid-labile acetal cross-linkers, DMOEM and bis[(2-methacryloyloxy)ethoxymethyl] ether (MOEME), were prepared as a mixture by the reaction of 2-hydroxyethyl methacrylate (HEMA) with paraformaldehyde in toluene and in the presence of *p*-toluenesulfonic acid (*p*TSA) as catalyst under reflux, as described before.[15] The two cross-linkers were separated by column chromatography (silica gel/hexane:ethyl acetate = 85:15).

Kinetic Study of Cross-Linker Hydrolysis. The kinetics of the hydrolysis of the cross-linkers at a 0.1 mol L^{-1} concentration in deuterium chloride (DCl)-containing (methyl sulfoxide)-d_6 (d_6-DMSO) was followed using ^{1}H NMR spectroscopy. The molar ratio of DCl to the labile cross-linkers was 20, allowing for the calculations to be made under pseudo-first-order conditions.

Polymer Synthesis. The syntheses of the polymer structures of this study were performed using GTP. The following polymeric materials were prepared: one neat network of MOEME, one randomly cross-linked methyl methacrylate (MMA)−MOEME network, one "arm-first" MMA−MOEME star polymer (prepared by the sequential addition of MMA and MOEME), and one "in-out" MMA−MOEME star polymer (prepared by the sequential addition of MMA, MOEME, and again MMA). Detailed procedures for these syntheses are provided in our previous publications.[13−15]

Polymer Hydrolysis and Study of Hydrolysis Kinetics of Star Polymers by GPC. The hydrolysis kinetics of the hydrolyzable star polymers MMA_{20}-*b*-$MOEME_4$-*star*, MMA_{20}-*b*-$MOEME_4$-*b*-MMA_{20}-*star*, and MMA_{20}-*b*-$DMOEM_4$-*star* (synthesized in our previous study) was studied by analyzing their molecular weights (MWs) using gel permeation chromatography (GPC) in a mixture of hydrochloric acid (HCl) and THF at room temperature. A 20-fold molar ratio of HCl (final concentration of 1 M) to the labile cross-linkers (0.05 M) was used. The final hydrolysis products were analyzed using GPC and ^{1}H NMR. For instance, 0.21 g of the vacuum-dried "arm-first" star polymer MMA_{20}-*b*-$MOEME_4$-*star* (0.25 mmol of MOEME units) was dissolved in 5 mL of THF and was hydrolyzed by the addition of 0.42 mL of concentrated HCl, 12 M (0.49 g of HCl solution, 5 mmol of neat HCl). Samples were withdrawn regularly and analyzed using GPC. The hydrolysis reaction was left to proceed for 46 h at which point it reached completion (100% conversion by ^{1}H NMR: theoretically expected mol % HEMA = 27.4, experimental = 28.6; theoretically expected MW = 3140 g mol^{-1}, GPC M_n = 5020 g mol^{-1}, M_w/M_n = 1.12; GPC M_n is the number-average MW, GPC M_w is the weight-average MW, and M_w/M_n is the polydispersity index, PDI).

To ensure the complete hydrolysis of all the networks of MOEME, all the samples were hydrolyzed using a 20-fold molar ratio of HCl to the labile cross-linkers and for a longer time period than that used in the kinetic study (4 days rather than 2 days). The final hydrolysis products were analyzed using GPC and ^{1}H NMR.

Polymer Characterization. The MWs and the molecular weight distributions (MWDs) of the star polymers and their precursors and the polymer hydrolysis products were determined using a Polymer Laboratories chromatograph equipped with a refractive index detector. The absolute MWs of the star polymers were measured by static light scattering (SLS) in a GPC configuration, by the simultaneous monitoring of the scattering intensity (BI-MwA Brookhaven detector) and the refractive index (PL-RI 800 detector). NMR spectra were recorded using a 300 MHz Avance Bruker spectrometer.

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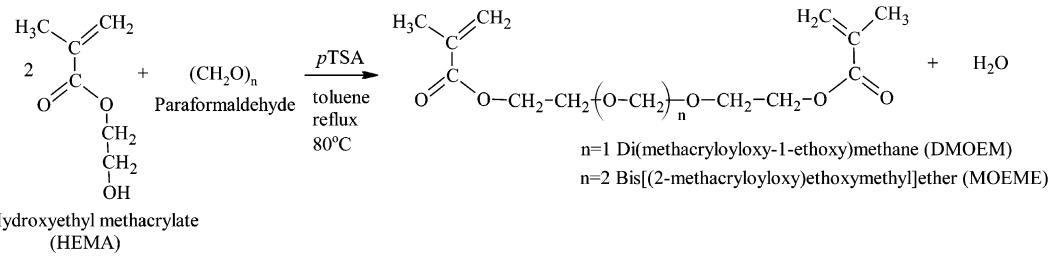

Figure 1. Reaction for the synthesis of the labile cross-linkers di(methacryloyloxy-1-ethoxy)methane and bis[(2-methacryloyloxy)ethoxymethyl] ether in the presence of the *p*-toluenesulfonic acid (*p*TSA) catalyst. Conditions: 1 M 2-hydroxyethyl methacrylate, 1 M $-CH_2O-$ groups, 3.3 mM *p*TSA, toluene solvent at 80 °C for 3 h.

Results and Discussion

Preparation and Characterization of the DMOEM and MOEME Cross-Linkers. The two acid-labile acetal-based dimethacrylate cross-linkers DMOEM and MOEME were prepared by the reaction between HEMA and paraformaldehyde in the presence of *p*TSA catalyst in toluene,[15,22,23] shown in Figure 1. Reaction yields for the DMOEM and MOEME preparation were high, typically 40% and 46%, respectively, while overall yields after column chromatography and distillation were only 15% and 4%, respectively. Thus, the similar polarities of the two compounds lead to high losses during purification. The high purity of the cross-linkers was confirmed by ^{1}H and ^{13}C NMR spectroscopies (relevant ^{1}H and ^{13}C NMR spectra of MOEME are displayed in Figure S1 in the Supporting Information) and elemental analysis. For MOEME, anal. ($C_{14}H_{22}O_7$) C, H: calcd 55.63, 7.28: found 55.77, 7.28.

Comparing the ^{1}H and ^{13}C NMR spectra of the two homologous acetal-based cross-linkers, DMOEM[15] and MOEME, they are almost identical, with very small differences: In the ^{1}H NMR spectrum of the diacetal MOEME cross-linker, the four protons of its oxymethylene groups (e) appeared at slightly higher δ values (4.78 ppm) than the two protons of the oxymethylene group of the DMOEM cross-linker (4.74 ppm). An analogous shift was also found to occur in their ^{13}C NMR spectra where there was a shift to higher δ values (96 ppm) for the two carbons of the oxymethylene groups (e) of MOEME compared to the carbon of the oxymethylene group of DMOEM (92 ppm).

Rates of Acid Hydrolysis of the Cross-Linkers. The kinetics of acid (20-fold molar ratio of DCl to the cross-linker) hydrolysis of the DMOEM and MOEME cross-linkers was followed using ^{1}H NMR (Figure S2 in the Supporting Information). The semilogarithmic concentration vs time plots (insets to Figure S2) gave straight lines, confirming pseudo-first-order kinetics. The pseudo-first-order hydrolysis rate constants, *k*, were determined by least-squares analysis at early reaction times (up to 6000 min) and found to be 0.40 ± 0.10 day^{-1} for DMOEM and 0.32 ± 0.10 day^{-1} for MOEME, corresponding to the same (within experimental error) values of $t_{1/2}$ ($=$ (ln 2)/*k*) for both cross-linkers of $\sim$2 days. Thus, the two cross-linkers hydrolyze under acidic conditions at similar rates. It is noteworthy that a benzaldehyde acetal bis(acrylamide) cross-linker was hydrolyzed much faster ($t_{1/2} = 5.5$ min) even at milder acidic conditions (aqueous buffer at pH $= 5$)[24] than the present aliphatic acetal cross-linkers.

Preparation and Hydrolysis of the Neat Cross-Linker Network and the Randomly Cross-Linked Network of MMA. The cross-linking ability and hydrolyzability of MOEME were demonstrated by preparing via GTP and decomposing two simple network structures: a MOEME "homopolymer" (neat cross-linker) network and a randomly cross-linked MMA−MOEME network. In both cases, successful gelation took place a few seconds after the addition of the last reagent, the MTS initiator, demonstrating the action of MOEME as cross-linker. These networks were subsequently hydrolyzed using excess HCl in THF solution. Both network samples were fully hydrolyzed and dissolved in THF within 2−3 days, giving transparent solutions. The hydrolysis products displayed MWs and compositions reasonably close to the theoretically expected values for the full hydrolysis of the cross-linker residues and their complete conversion to HEMA units. In particular, the hydrolysis products of the neat cross-linker network exhibited an $M_n = 1730$ g mol^{-1} (theoretically expected MW $= 1140$ g mol^{-1}) with an $M_w/M_n = 1.24$, while the hydrolysis products of the randomly cross-linked network presented an $M_n = 5020$ g mol^{-1} (theoretically expected MW $= 3140$ g mol^{-1}) with an $M_w/M_n = 1.12$. Moreover, the former network was composed 100% of HEMA units, as expected, whereas the latter contained 26.9 mol % HEMA, as compared to the theoretically calculated content of 28.6 mol %.

Preparation and Characterization of Star Polymers of MMA. Table 1 presents the structures of the MOEME−MMA star polymers synthesized in this study (one "arm-first" star polymer and one "in-out" MMA star polymer with MOEME cores) as well as of the "arm-first" MMA star polymers with DMOEM[15] and EGDMA[13] cores prepared in our previous studies. The same table also displays the characterization results for these star polymers, including their MWs and compositions. The MWs of all the star polymers were greater than the MWs of their linear precursors, confirming the interconnection of the arms to star structures and indicating the adequacy of the employed 4/1 cross-linker/initiator molar ratio.[25,26] The MWDs of all the star polymers were bimodal, and the MWs at the maxima (peak MWs, M_ps) of the two distributions are given in Table 1. The lower MW peak corresponded to unattached linear polymer, whose fraction was estimated from the relative peak areas in the chromatograms and is also provided in Table 1. This fraction was ca. 30% for the star polymers based on the degradable cross-linkers, as compared to the fraction of $\sim$10% corresponding to the star polymer based on the more efficient, nondegradable EGDMA cross-linker. The fraction of unattached chains for star polymers based on other degradable cross-linkers reported in literature was similarly high and ranged between 30%[27] and 50%.[28]

The absolute weight-average MWs, M_ws, of all the star polymers were determined by SLS (and found greater than the GPC M_ws), from which the absolute numbers of arms were calculated and are also listed in Table 1. The number of arms of the "in-out" MOEME-MMA star polymer was greater than that of its "arm-first" counterpart, 13 vs 9, as expected. These values were comparable to the number of arms of the "arm-first" DMOEM−MMA star of 11, and much lower than that of the star polymer based on the more compact and more efficient EGDMA cross-linker of 107.

Table 1. Molecular Weights, Fractions of Unattached Arms, Numbers of Arms, and Compositions of the Star Polymers

		GPC results				SLS results[c]		composition (mol % cross-linker)	
sample formula	theoretical MW[a]	M_n	M_w/M_n	M_p	% linear polymer	M_w	no. of arms	theory	by ^{1}H NMR
MMA_{20}	2100	2680	1.39	3860					
MMA_{20}-*b*-$MOEME_4$-*star*	N.A.[b]	22300	1.81	3860, 26900[c]	31.2	51100	9	16.7	16.3
MMA_{20}	2100	3720	1.15	4330					
MMA_{20}-*b*-$MOEME_4$-*star*	N.A.[b]	20600	1.39	5790, 22600[c]					
MMA_{20}-*b*-$MOEME_4$-*b*-MMA_{20}-*star*	N.A.[b]	31000	1.50	10000, 28500[c]	32.2	72000	13	9.1	7.9
MMA_{20}	2100	1450	1.39	2280					
MMA_{20}-*b*-$DMOEM_4$-*star*	N.A.[b]	5480	2.36	3100, 16100[c]	33.0	32400	11	16.7	15.6
MMA_{20}	2100	3650	1.29	5440					
MMA_{20}-*b*-$EGDMA_4$-*star*	N.A.[b]	110000	1.98	5760, 115000[c]	10.6	694000	107	16.7	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] Calculated for the main star peak.

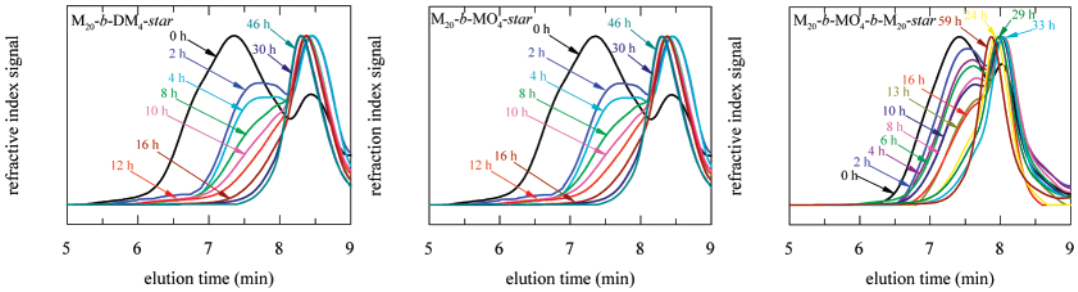

Figure 2. GPC traces of the hydrolysis products of the star polymers of methyl methacrylate (MMA or M) with the hydrolyzable di(methacryloyloxy-1-ethoxy)methane (DMOEM or DM) and bis[(2-methacryloyloxy)ethoxymethyl] ether (MOEME or MO) cross-linkers at various times of their hydrolysis reaction. Conditions: 1 M HCl, 0.05 M labile cross-linker, ambient temperature (~25 °C).

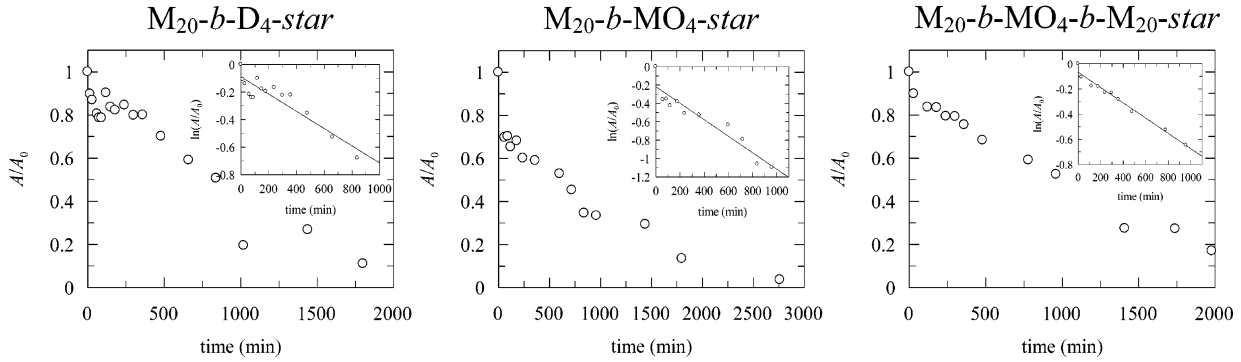

Figure 3. Time dependence of the fraction of the nonhydrolyzed star polymers of methyl methacrylate (MMA or M) with the hydrolyzable di(methacryloyloxy-1-ethoxy)methane (DMOEM or DM) and bis[(2-methacryloyloxy)ethoxymethyl] ether (MOEME or MO) cross-linkers during the course of their hydrolysis. Conditions: 1 M HCl, 0.05 M labile cross-linker, ambient temperature (~25 °C).

The star polymer compositions in MOEME cross-linker were measured using ^{1}H NMR by ratioing the areas of the characteristic peaks of the cross-linker and the monomer. The peak of the methylene protons of MOEME at ~4.9 ppm and that of the methyl protons of MMA at 3.6 ppm were used as characteristic peaks. These compositions are also shown in Table 1 along with the composition of MMA_{20}-*b*-$DMOEM_4$-*star*[15] and the theoretically expected compositions. There was a good agreement between the theoretical and the ^{1}H NMR compositions, with the experimental ones being systematically slightly lower than the theoretical, reflecting the broadening of the peaks of the cross-linker (MOEME or DMOEM) units which were immobilized in the core of the stars, whereas for the same reason, it was impossible to calculate the composition of MMA_{20}-*b*-$EGDMA_4$-*star* based on the more compact EGDMA cross-linker.

Hydrolysis of Star Polymers of MMA. Following their synthesis and characterization, the star polymers based on the hydrolyzable MOEME and DMOEM cross-linkers were subjected to hydrolysis using a solution of HCl in THF. An HCl to cross-linker molar ratio of 20 was used for the hydrolysis, as in the experiments of the hydrolysis of the (low-MW) cross-linkers. The progress of the hydrolysis was followed by GPC. The relevant chromatograms of the samples obtained during the course of the hydrolysis of star polymers MMA_{20}-*b*-$DMOEM_4$-*star*, MMA_{20}-*b*-$MOEME_4$-*star*, and MMA_{20}-*b*-$MOEME_4$-*b*-MMA_{20}-*star* are overlaid in Figure 2.

The figure shows that in all three cases the MW decreased with time. In particular, within 1 day, the star polymers were almost fully hydrolyzed, giving products with much lower MWs than the initial star polymers, approaching the MW of the initial MMA arm. Kinetic analysis of the GPC traces is presented in Figure 3 where the fraction of nonhydrolyzed star polymer is plotted against time. The pseudo-first-order hydrolysis rate constants (k) were calculated from the straight lines in the semilogarithmic fraction vs time plots (insets in Figure 3). These rate constants were used to calculate the corresponding $t_{1/2}$ (= (ln 2)/k). The "arm-first" star polymer MMA_{20}-*b*-$MOEME_4$-*star* was found to hydrolyze faster (with $t_{1/2} = 0.53 \pm 0.08$ day) than both the "arm-first" star polymer MMA_{20}-*b*-$DMOEM_4$-

Table 2. Molecular Weights and Compositions of the Final Hydrolysis Products of the Star Polymers

polymer sample	hydrolyzed polymer	theoretical MW[a]	GPC results			composition (mol % HEMA)	
			M_n	M_w/M_n	M_p	theory	by ^{1}H NMR
MMA_{20}-*b*-$MOEME_4$-*star*	MMA_{20}-*b*-$HEMA_8$	3140	5020	1.12	5960	28.6	28.0
MMA_{20}-*b*-$MOEME_4$-*b*-MMA_{20}-*star*	MMA_{20}-*b*-$HEMA_8$-*b*-MMA_{20}	5140	9740	1.09	10900	16.7	17.6
MMA_{20}-*b*-$DMOEM_4$-*star*	MMA_{20}-*b*-$HEMA_8$	3140	2560	1.20	3210	28.6	27.4

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

star (with $t_{1/2} = 0.80 \pm 0.09$ day) and the "in-out" star polymer MMA_{20}-*b*-$MOEME_4$-*b*-MMA_{20}-*star* (also with $t_{1/2} = 0.80 \pm 0.04$ day), probably due to its lower number of arms, leading to decreased steric hindrances during hydrolysis. It is interesting to note that the $t_{1/2}$ values for the hydrolysis of these star polymers were shorter than those for the hydrolysis of the low-MW cross-linkers by 2.5−4 times, which might be due to the different solvents employed in the two studies (THF in the former and d_6-DMSO in the latter).

After their full hydrolysis, the resulting polymer samples were recovered by precipitation in *n*-hexane and were vacuum-dried at room temperature. The results of the GPC and ^{1}H NMR characterization of the hydrolysis product of all the star polymers along with the theoretically expected results are summarized in Table 2. The product of the complete hydrolysis of the "in-out" star polymer MMA_{20}-*b*-$MOEME_4$-*b*-MMA_{20}-*star* should be an MMA−HEMA−MMA triblock copolymer with an MW twice that of the arm plus the residues from the hydrolyzed cross-linker MOEME. Indeed, the calculated M_n of this hydrolysis product, shown in Table 2 (9740 g mol^{-1}), was more than twice that of the linear precursor shown in Table 1 (3720 g mol^{-1}). The product of the hydrolysis of the "arm-first" star polymers of MOEME or DMOEM should consist of the arm plus the residues from the hydrolyzed cross-linker; i.e., it should be an MMA−HEMA diblock copolymer. The calculated MW of the hydrolysis products of the "arm-first" star polymers MOEME and DMOEM, shown in Table 2, were 5020 and 2560 g mol^{-1}, respectively, and were much higher than those of the arms of the star polymers, 2680 and 1450 g mol^{-1}, respectively (Table 1), indicating the formation of MMA−HEMA diblock copolymers due to the incorporation of the residues of the hydrolyzed cross-linker to the arm. The PDIs of the hydrolysis products of all the star polymers varied between 1.09 and 1.20, within the limits for a "living" polymerization. ^{1}H NMR confirmed the presence of the expected percentage of HEMA units in the hydrolyzed product. Thus, both the MWs and the compositions of the hydrolysis products were close to those expected on the basis of the full hydrolysis of the cross-linkers.

Conclusions

A novel hydrolyzable diacetal dimethacrylate cross-linker, MOEME, was recovered from the same product mixture where its monoacetal homologue, DMOEM, was synthesized. After purification, MOEME was copolymerized with MMA by GTP to prepare degradable polymer networks and star polymers. The numbers of arms at the cores of the prepared star polymers were limited by the relative bulkiness of MOEME to ∼10, similar to that obtained with DMOEM, but much lower than that obtained with the more traditional, nondegradable and compact, dimethacrylate cross-linker EGDMA. The degradable star polymers containing this acid-labile cross-linker were hydrolyzed in THF using HCl to give lower MW polymer products with the expected MWs. Pseudo-first-order half-lives of the MOEME-based star polymers under the examined conditions ranged between 0.53 and 0.80 day (13 and 19 h), similar to that of the DMOEM-based star polymer of 0.53 day.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of purified MOEME cross-linker (Figure S1) and time dependence of fraction of unreacted DMOEM and MOEME cross-linkers (A/A_0) during their acid hydrolysis (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456−1459.
(2) Inoki, M.; Akutsu, F.; Yamaguchi, H.; Naruchi, K.; Miura, M. *Macromol. Chem. Phys.* **1994**, *195*, 2799−2804.
(3) Kambouris, P.; Hawker, C. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, *22*, 2717−2721.
(4) Yamagishi, H.; Saito, K.; Furusaki, S.; Sugo, T.; Hosoi, F.; Okamoto, J. *J. Membr. Sci.* **1993**, *85*, 71−80.
(5) Ulbrich, K.; Šubr. V.; Podpěrová, P.; Burešová, M. *J. Controlled Release* **1995**, *34*, 155−165.
(6) Timmer, M. D.; Shin, H.; Horch, R. A.; Ambrose, C. G.; Mikos, A. G. *Biomacromolecules* **2003**, *4*, 1026−1033.
(7) Timmer, M. D.; Carter, C.; Ambrose, C. G.; Mikos, A. G. *Biomaterials* **2003**, *24*, 4707−4714.
(8) Stubbe, B. G.; Horkay, F.; Amsden, B.; Hennink, W. E.; De Smedt, S. C.; Demeester, J. *Biomacromolecules* **2003**, *4*, 691−695.
(9) Ogino, K.; Chen, J.-S.; Ober, C. K. *Chem. Mater.* **1998**, *10*, 3833−3838.
(10) Ober, C. K.; Koerner, H. United States Patent 5,948,922, 1999.
(11) Ober, C. K.; Koerner, H. United States Patent 5,973,033, 1999.
(12) Crane, L. N.; Ober, C. K.; Bae, Y. C.; Yu, S.; Park, J.-W. United States Patent 6,657,031, 2003.
(13) Themistou, E.; Patrickios, C. S. *Macromolecules* **2004**, *37*, 6734−6743.
(14) Kafouris, D.; Themistou, E.; Patrickios, C. S. *Chem. Mater.* **2006**, *18*, 85−93.
(15) Themistou, E.; Patrickios, C. S. *Macromolecules* **2006**, *39*, 73−80.
(16) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706−5708.
(17) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473−1488.
(18) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034−4041.
(19) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2855−2860.
(20) Webster, O. W. *Adv. Polym. Sci.* **2004**, *167*, 1−34.
(21) Themistou, E. Ph.D. Thesis, University of Cyprus, 2006.
(22) Goethals, E. J.; De Clercq, R. R.; De Clercq, H. C.; Hartmann, P. J. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 151−162.
(23) De Clercq, R. R.; Goethals, E. J. *Macromolecules* **1992**, *25*, 1109−1113.
(24) Murthy, N.; Thng, Y. X.; Schuck, S.; Xu, M. C.; Fréchet, M. J. M. *J. Am. Chem. Soc.* **2002**, *124*, 12398−12399.
(25) Simmons, M. R.; Yamasaki, E. N.; Patrickios, C. S. *Macromolecules* **2000**, *33*, 3176−3179.
(26) Simmons, M. R.; Yamasaki, E. N.; Patrickios, C. S. *Polymer* **2000**, *41*, 8523−8529.
(27) Ruckenstein, E.; Zhang, H. *Macromolecules* **1999**, *32*, 3979−3983.
(28) Kilian, L.; Wang, Z.-H.; Long, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3083−3093.

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