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Well-Defined Networks with Precisely Located Cleavable Sites: Structure Optimization and Core Functionality Determination

Maria D. Rikkou and Costas S. Patrickios*

Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus

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Covalent polymer networks represent a unique class of materials consisting of chemically interconnected polymer chains,[1] insoluble in all solvents but capable to swell in various solvents to different degrees.[2] One type of these networks is called responsive or "intelligent" as they exhibit dramatic changes in their swelling upon a change in the environmental conditions, including temperature and pH changes and also introduction of electromagnetic fields.[3] This environmental responsiveness secures many of the modern applications of networks, including uses as actuators, valves, sensors, controlled release systems for drugs, artificial muscles for robotics, chemical memories, optical shutters, and molecular separation systems.[4]

Despite the rich functional behavior of intelligent networks, their molecular structure is poorly controlled, with the length and composition of the segments between cross-links (the so-called elastic chains) varying widely. The recent use of controlled polymerization methods[5] with the sequential/stepwise polymerization of monomers and cross-linker[6] allowed the preparation of responsive networks with improved molecular structure[7] which exhibited supramolecular organization as evidenced by characterization using scattering and microscopy techniques.[8] In these networks, the elastic chain length and composition were well-controlled and precisely known, but the core functionality, *that is, the number of arms radiating out from each cross-link*, was an unknown characteristic of the system.

The aim in this investigation is to determine the core functionality in these well-controlled networks. The strategy implemented is outlined in Scheme 1 and involves the use of a cleavable bifunctional initiator for network synthesis.[9] The fragment of the initiator would be incorporated in the middle of the polymer chain and would also be carried over in the resulting networks. Cleavage of the initiator fragment in the networks would convert them to carboxylic acid end-functional star polymers whose absolute molecular weight (MW) and number of arms could be readily determined by static light scattering (SLS). This number of arms is equal to the core functionality of the star and also equal to that of the network.

The first step in this study was the design of an appropriate degradable bifunctional initiator. Since our previous synthetic work involved network preparation by group transfer polymerization (GTP),[10] a controlled polymer synthesis method for methacrylates using silyl ketene acetal initiating groups, the present bifunctional initiator should possess two such groups for initiation. Two further regular (carbon-based) acetal groups were also engineered into this initiator since such groups are well-behaving degradable groups,[11] readily hydrolyzed under mildly acidic conditions. Thus, the compound bearing four acetal groups, two for initiation and two for degradation, shown in Figure 1a, was prepared in our laboratories at 74% yield. The reaction scheme for the synthesis of this initiator and its ^{1}H and ^{13}C NMR spectra as well as those of the intermediate diisobutyryl diester are shown in the Supporting Information (Figure S1).

Before the preparation of the degradable networks, degradable linear polymers of methyl methacrylate (MMA) were synthesized by GTP to test the tetraacetal initiator both for polymerization and hydrolysis. Three linear polyMMAs with nominal degrees of polymerization (DPs) 10, 20, and 50 were prepared. GPC analysis indicated that these materials were highly homogeneous with polydispersity indices (PDIs, M_w/M_n) around 1.2 (Table S1 in the Supporting Information). The initiator fragment is located in the middle of the polymers, flanked by the two polyMMA segments (Figure 1a). Upon hydrolysis, effected 10 min after the addition of a small volume of a 2 M HCl aqueous solution to a polymer solution in tetrahydrofuran (THF), the chains are cut in half. This is supported by GPC analysis which showed that the MWs after hydrolysis were exactly one-half of those before hydrolysis, while the PDIs remained low (Table S1). Figure 1b plots the GPC traces of MMA_{20} before

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* To whom correspondence should be addressed. E-mail: costasp@ucy.ac.cy.

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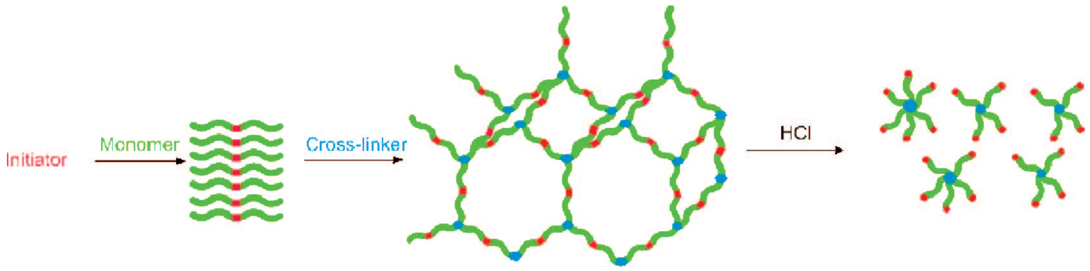
Scheme 1. Synthesis and Hydrolysis of Well-Defined Networks Based on a Degradable Bifunctional Initiator



and after hydrolysis. Upon hydrolysis, the molecular weight distribution (MWD) was shifted to larger retention volumes, consistent with lower MWs. Successful hydrolysis was also confirmed by ^{1}H NMR analysis which indicated the complete removal of the acetal protons at 5.8 ppm after hydrolysis (Figure 1c,d). Thus, these experiments clearly show that we can use the hydrolyzable bifunctional initiator to prepare linear MMA polymers which can be cleaved in the middle.

Then, we proceeded to the networks. The procedure involved the preparation of the linear polymer first and then the addition of ethylene glycol dimethacrylate (EGDMA) at an 8:1 molar ratio relative to the initiator to form the network. Again, we prepared materials of three different DPs, 10, 20, and 50. To our surprise, when we added HCl for hydrolysis, none of the networks were dissolved to give a solution. This was not due to lack of initiator hydrolysis (already proved with the experiments on the linear polymers) but due to the formation of extra linkages between the cores by the cross-linker (yielding practically infinitely large core clusters) because, when less cross-linker was used for gelation, the networks could be readily dissolved upon acid addition. In particular, after a systematic study, we determined that the optimal cross-linker:initiator molar ratio was 2:1 (in line with the predictions of Flory and Stockmayer[12]), because for higher ratios the networks would not dissolve upon hydrolysis, whereas for lower ratios only mechanically poor networks would form (Table S2 and Figure S2 in Supporting Information).

Then, we went on to prepare again the networks using the optimal cross-linker to initiator molar ratio of 2 to 1 (Table 1). Before hydrolysis, the networks were fully characterized in terms of their degree of swelling (DS) in THF, defined as the ratio of the mass of the THF-equilibrated network divided by that of the dry network, and also in terms of their sol fraction. These results are shown in Table 1, too, and were as expected: as the elastic chain length increased, both the DSs in THF and the sol fraction increased.

Subsequently, the networks were hydrolyzed, and the hydrolysis products were characterized in terms of their MWs (Figure 1b and Table 1). To our surprise, these traces were not monomodal but bimodal. We expected them to be monomodal, as the linear extractable material was washed out before hydrolysis. The higher MW peaks, at lower retention volumes, were due to the anticipated star polymers as their MWs were much higher than those of the linear precursor chains. The lower MW peaks, at larger retention volumes, had MWs lower than those of the linear precursor chains and approximately equal to those of the linear hydrolysis products, implying that the peaks in question originated from hydrolyzed dangling (singly attached) chains. The fraction of these chains, estimated from the relative peak areas in the chromatograms, was about 15% for all three network hydrolysis products, indicating a relatively small percentage of this defect in the parent networks. To the best of our knowledge, this is the first time that the fraction of dangling chains in networks is quantified.

The hydrolysis products of the networks were also characterized in terms of their absolute weight-average MWs, M_w, using

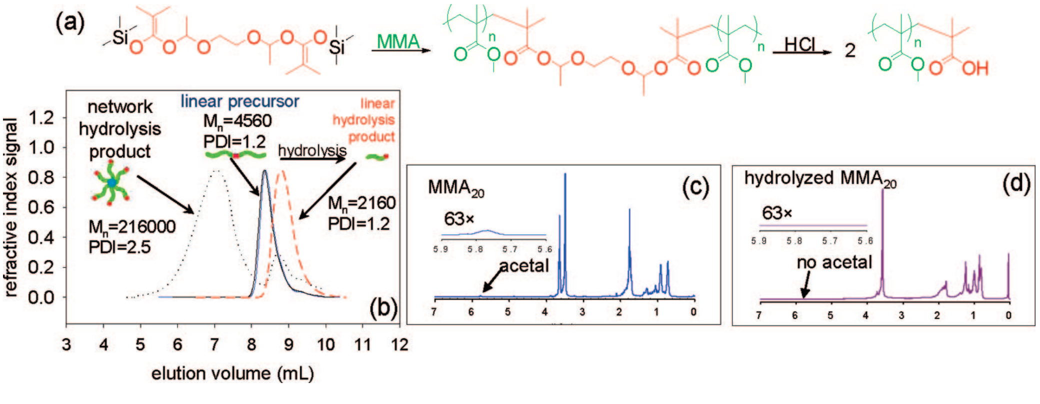


Figure 1. GTP synthesis and hydrolysis of linear MMA_{20}. The GPC trace of hydrolyzed network MMA_{20} is also shown in (b).

Table 1. Molecular Weights and Polydispersities of the Linear Network Precursors and the Network Hydrolysis Products and Degrees of Swelling in THF and Sol Fraction of the Networks

	linear precursor		network		network hydrolysis product			
network formula	M_n (g mol^{-1})	M_w/M_n	extractables (%)	DS	M_n (g mol^{-1})	M_w/M_n	SLS M_w (g mol^{-1})	no. of arms
MMA_{10}-*b*-$EGDMA_2$	2290	1.18	34	4.0 ± 0.4	855	1.20		
					10 800	1.50	156 000	115
MMA_{20}-*b*-$EGDMA_2$	4330	1.17	34	4.4 ± 0.3	1 780	1.10		
					33 100	2.50	216 000	85
MMA_{50}-*b*-$EGDMA_2$	9070	1.17	50	13.1 ± 0.6	4 070	1.10		
					39 700	1.20	88 900	18

SLS in a flow configuration (Table 1). The SLS M_ws were higher than the GPC MWs due to the compact nature of the star polymer compared to the linear polyMMA GPC calibration standards. From the SLS M_ws, the absolute numbers of arms were calculated to be 115, 85, and 18 for the three networks and decreasing with the elastic chain length due to increasing steric hindrances toward core−core coupling. These numbers of arms compare favorably with the number of arms of MMA star polymers prepared by GTP directly as star polymers in solution using a monofunctional, nondegradable initiator,[7g] rather than being prepared from the hydrolysis of model networks synthesized using a bifunctional, degradable GTP initiator.

In conclusion, we present here the first example of a degradable GTP initiator which was used to prepare model networks based on MMA homopolymers. Optimal network synthesis and acid hydrolysis were achieved when the moles of cross-linker used were twice the moles of the initiator used. Future work, within GTP, will involve the introduction of pairs of functional monomers to obtain stimuli-responsive degradable conetworks, such as amphiphilic and ampholytic, which upon hydrolysis will yield the corresponding responsive carboxylic acid end-functional star copolymers. Furthermore, the present chemistry of degradable diacetal initiator will be exported to other controlled polymerization methods, including reversible addition−fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP).

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Supporting Information Available: Synthesis and characterization of the initiator and MWs of the linear polymers before and after hydrolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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