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Synthesis and Controlled Cross-Linking of Polymers Derived from Ring-Opening Metathesis Polymerization (ROMP)

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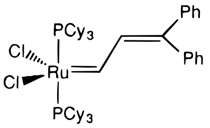
ABSTRACT: The ROMP of 5-methacryloyl-1-cyclooctene and the copolymerization of this monomer with cyclooctadiene were investigated to produce polymers with cross-linkable side chains. The impact of concentration, monomer to catalyst ratio, and the amount of inhibitor in the polymerization was examined. These polymers were cross-linked through the methacrylate side chains with either thermal or photochemical initiation, and the incorporation of these polymers into poly(methyl methacrylate) (PMMA) to produce AB cross-linked materials was accomplished. A comparison of the physical properties of PMMA and these new materials demonstrated that these materials had higher thermal stability and solvent resistance than pure PMMA.

Introduction

In recent years, cross-linkable polymers have found a wide demand in the areas of interpenetrating polymer networks,[1] nonlinear optical materials,[2] macro- and microlithography,[3] and the formation of more thermally and chemically resistant materials.[4] Polymers with siloxane,[5] vinyl,[6] acrylate,[7] and phosphazene[8,9] backbones are but a few examples of materials that have been synthesized with reactive cross-linkable side chains.

One of the most widely employed cross-linkable side chains is the cinnamate group, which undergoes controlled photoinduced [2 + 2] dimerization, as demonstrated in the above examples. However, a more versatile cross-linkable side-chain is the methacrylate group, which polymerizes both thermally and photochemically in the presence of free-radical initiators and photosensitizers, respectively. The methacrylate group has found many applications in the UV curing of photoresists,[10] coatings, and printing inks.[11−13] Due to the sensitivity of many metathesis catalysts to functional groups, the use of ROMP in the formation of these cross-linkable polymers has been limited. However, the development of the new functional group tolerant catalysts $(PCy_3)_2Cl_2Ru{=}CHR$ [14−16] has allowed for the ROMP of a series of functionalized cyclooctenes.[16,17] The high functional group tolerance of these catalysts has prompted an investigation of the use of ROMP in the formation of cross-linkable polymers.

In this study, 5-methacryloyl-1-cyclooctene was synthesized and polymerized by catalyst **1** resulting in an



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alternating terpolymer of polybutadiene, polyethylene, and poly(vinyl methacrylate) with cross-linkable side chains spaced on average every eight carbons. In addition, this monomer was copolymerized with cyclooctadiene (COD), the homopolymer of which is polybutadiene, at varying feed ratios to systematically vary the number of methacrylate groups per chain. Cross-linking of these polymers was carried out both thermally and photochemically. Reaction of this multifunctionalized methacrylate polymer with methyl methacrylate under free-radical polymerization conditions has led to the formation of AB cross-linked systems of poly(methyl methacrylate) (PMMA).

Results and Discussion

Synthesis of 5-Methacryloyl-1-cyclooctene. Synthesis of 5-methacryloyl-1-cyclooctene (**4**) was accomplished in three steps from commercially available COD (Scheme 1). Epoxidation with *m*-chloroperbenzoic acid (MCPBA) in chloroform afforded compound **2** in 83% yield. Reduction of **2** to the alcohol **3** using lithium

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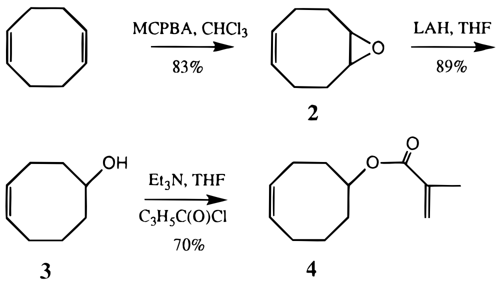
Scheme 1



Scheme 2

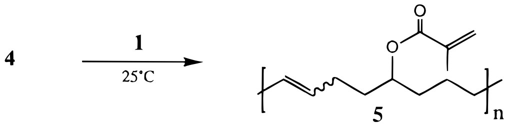


Table 1. Effect of mol % MEHQ on the Polymerization

[M] (M)	[M]:[cat]	rxn time (h)	mol % MEHQ	yield (%)	$\bar{M}_n$[a]	PDI
0.75	1383	12	18	44	21200	3.15[b]
0.75	1329	12	9	47	14000	13.9[c]
0.76	1344	12	0	42	16500	14.9[c]

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodisperse polystyrene standards. [b] Monomodal molecular weight distribution. [c] Multimodal molecular weight distribution.

aluminum hydride (LAH) proceeded in 89% yield. Subsequent esterification of **3** using methacryloyl chloride and triethylamine provided 5-methacryloyl-1-cyclooctene (**4**) in 70% yield. With an overall yield of 52% in only three steps, this synthesis allowed for the large scale preparation of **4**.

Initial Polymerization Studies. Initial polymerizations were carried out as shown in Scheme 2. Gel formation was observed during the polymerization when THF, benzene, toluene, or methylene chloride was used as solvent. The polymer isolated from this gel was insoluble in all common organic solvents and was presumed to be highly cross-linked. Free radical cross-linking of this side chain was one plausible explanation for the observed gelation. Another possible mechanism of cross-linking was the catalyst mediated dimerization of the pendant methacrylate groups. Polymerizations under dilute concentration (0.75 M) afforded a 40% yield of polymer. This polymer had a broad, multimodal molecular weight distribution with a $\bar{M}_n$ of 16 500 and a PDI of 14.9, much broader than the PDI of ~2.0 expected for this polymerization. A PDI of ~2.0 should result for this type of polymerization in which the polymer chains are in equilibrium through chain transfer and backbiting reactions.[4] This polymer cross-linked on standing overnight at room temperature to yield an insoluble solid regardless of whether stored neat or in solution, even when shielded from light in an inert atmosphere.

***p*-Methoxyphenol (MEHQ) as a Free Radical Inhibitor.** To establish the free-radical nature of the cross-linking process, the polymerizations were studied in the presence of a free-radical inhibitor. The effect of the inhibitor MEHQ on the polymerization was thus examined (Table 1).[18] When 18 mol % MEHQ was used, polymers with monomodal molecular weight distributions were formed in moderate yields.[19] Use of less than 18 mol % MEHQ in the polymerization again resulted in broad, multimodal molecular weight distributions.

Table 2. Effect of [M]:[cat] Ratio on the Polymerization

[M] (M)	[M]:[cat]	rxn time (h)	mol % MEHQ	yield (%)	$\bar{M}_n$[a]	PDI[a]
0.75	850	12	18	52	13800	13.9[b]
0.75	1383	12	18	44	21200	3.15[c]
0.75	1574	12	18	30	15700	4.02[c]

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodisperse polystyrene standards. [b] Multimodal molecular weight distribution.

Scheme 3

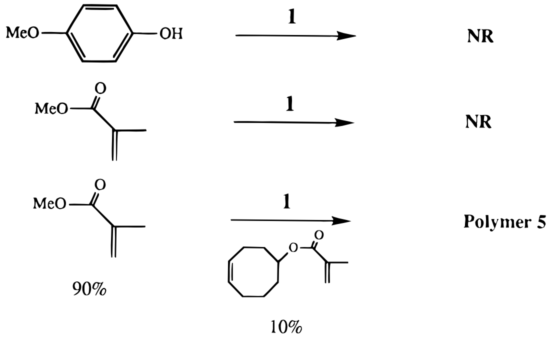


Table 3. Effects of Catalyst on a Monomodal Sample of Homopolymer 5

condition	$\bar{M}_n$[a]	PDI[a]
1	900	9.39
2	1100	12.7
3	13300	3.10
4	12700	3.13

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodisperse polystyrene standards.

These results supported the free-radical mechanism of cross-linking.

The effect of the monomer to catalyst ([M]:[cat]) ratio on the polymers was studied (Table 2). Only in the case of high [M]:[cat] ratios were monomodal polymers obtained which were stable to cross-linking.

Exclusion of the Metathesis Based Mechanism of Cross-Linking. To conclusively exclude the mechanism of cross-linking through metathesis mediated dimerization of the pendant methacrylate groups, several control experiments were run. A mixture of the catalyst and methyl methacrylate (MMA) (**6**) in toluene showed no reaction over 12 h at room temperature. The possibility that the propagating catalyst species, not the starting vinyl carbene, was reacting with the methacrylate side chain was ruled out by the addition of 10% of **4** to the MMA and catalyst reaction mixture. Over 12 h, the polymerization of **4** was observed while no reaction of the MMA occurred. The reaction of the catalyst with MEHQ was also examined to ensure that no side reaction occurred between the catalyst and inhibitor. Again, no reaction was observed over 12 h.

Finally, the reaction of monomodal homopolymer **5** with catalyst under four conditions was studied. The homopolymer $\bar{M}_n$ = 14 200 and a PDI = 3.15 was dissolved in toluene and combined with catalyst (condition 1), with catalyst and MEHQ (condition 2), with MEHQ only (condition 3), and with no additives (condition 4) for 12 h. As shown in Table 3, no significant change in the polymer was observed for conditions 3 and 4 where no catalyst was employed, while a significant reduction in the molecular weight was observed for conditions 1 and 2, presumably due to depolymerization and backbiting. If the catalyst was reacting with the methacrylate side chains, this would have resulted in

Table 4. Polymerization Results for the Homopolymerization of 4 and Its Copolymerization with COD

polymer	[M] total (M)	% COD in feed	[M]:[cat]	mol % MEHQ	% COD in prod[a]	rxn time (h)	yield (%)	$\bar{M}_n$[b]	PDI[b,c]
5	0.8	0	1383	18	0	12	44	21200	3.15
6	1.2	30.4	1490	4	37	6	60	30300	2.37
7	2.9	50.6	1660	4	56	6	72	36500	2.89
8	5.8	79.7	1673	4	84	5	86	34600	2.56
9	6.0	89.4	1865	4	92	6	84	37100	2.39
10	5.7	94.8	1777	4	95	7.5	87	32900	2.14

[a] Determined by ^{1}H NMR integration. [b] Determined by Gel Permeation Chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [c] Monomodal molecular weight distribution.

chain coupling, and higher molecular weights would have been observed. These results showed that the proposed side reaction of the catalyst with the methacrylate group to give chain coupling and cross-linked products was not significant. The dominant side reaction of the catalyst was with the polymer backbone olefins, resulting in depolymerization and backbiting.

The free-radical mechanism of cross-linking was most consistent with these results. This conclusion also explained the results from Table 2, which showed the effect of [M]:[cat] ratio on the polymerization. These results showed that low [M]:[cat] ratios resulted in multimodal molecular weight distributions. It has been observed that the yields of polymer increased with the amount of catalyst used. So, as lower [M]:[cat] ratios were used, the reaction mixture became more viscous due to higher conversion to polymer, and this more viscous solution formed lowered the efficiency of MEHQ in solution. The effect of reaction concentration on the polymerizations paralleled these results. The higher the concentration, the more gelation and multimodal molecular weight distributions were observed.

Copolymerization of 4 with COD. To systematically control the concentration of cross-linkable groups on the polymer backbone, **4** was copolymerized with COD in several feed ratios. Homopolymerization of **4** and its copolymerization with cyclooctadiene yielded polymers **5**−**10** in Table 4. Two significant differences between the homopolymerization and copolymerizations were immediately recognized. First, it was possible to run the copolymerizations at higher concentrations, resulting in higher yields than in the case of the hompolymerization. As the amount of **4** in the feed ratio was decreased, the more the concentration of the polymerization could be increased. Second, the amount of MEHQ needed in the reaction was drastically reduced for the copolymerizations without the formation of any cross-linked side products.

These copolymers (**6**−**10**) could have consisted of either a random, alternating, or blocky type composition. Attempts to determine the composition through analysis of the ^{1}H and ^{13}C NMR spectra of the homopolymer and copolymers have been inconclusive. Analysis of the alkyl region between 20 and 40 ppm in the ^{13}C NMR was used to exclude a perfect diblock structure; however, this analysis has been unable to rule out tapered or multiple block materials. A highly blocky composition is unlikely due to the relative stability of these copolymers to cross-linking relative to the homopolymer. Such blocky copolymers should have exhibited similar difficulties with cross-linking as in the case of the homopolymer. One experiment to probe this question was the polymerization of a 1:1 ratio of **4**:COD in toluene-d_8 monitored by ^{1}H NMR. At 10% conversion, the ratio of **4**:COD in the polymer was 39:61, determined by NMR integration. These percentages were within experimental error of the 44:56 ratio observed for the isolated 1:1 copolymer (Table 3), demonstrating that the polymer composition was relatively invariant during the reaction. Although this did not conclusively rule out a blocky composition, these results were in agreement with a more alternating or random composition. The polymer composition could only have been determined conclusively through an extensive study of the reactivity ratios for the copolymerization.[20]

Controlled Thermal and Photochemical Cross-Linking of Polymers 5−10. The controlled cross-linking of monomodal samples of the homopolymer **5** and copolymers **6**−**10** was achieved in all cases. Both thermal initiation with benzoyl peroxide or AIBN at 80 °C as well as photochemical initiation using 2,2-dimethoxy-2-phenylacetophenone resulted in cross-linked polymers in less than 5 min. However, solutions of these polymers in toluene containing 5% (w/w) MEHQ were stable to cross-linking conditions. MEHQ is an excellent free-radical inhibitor for this system. Removal of the solvent *in vacuo* resulted in a rubbery, clear solid which was insoluble in all common organic solvents. IR spectra exhibited a sharp decrease in the C=C stretch at approximately 1640 cm^{-1} as compared to the starting polymers due to the cross-linking of the pendant methacrylate groups.

Synthesis of AB Cross-Linked Systems of Polymer 9 and PMMA. The success that has been observed in these experiments has led to an investigation of the formation of AB cross-linked systems with PMMA. Despite the many current industrial applications of PMMA, there are problems with impact resistance, thermal stability, and chemical resistance.[21,22] The incorporation of a rubbery polymer through chemical cross-links in PMMA could improve many of these limitations. By polymerizing MMA in the presence of one of the methacrylate polymers **5**−**10**, cross-links should form with the methacrylate side chains of these polymers, thus yielding AB cross-linked materials.

Two different materials were made in this study. Copolymer **9** was dissolved in MMA as a 5% (w/w) and as a 10% (w/w) solution. Benzoyl peroxide, 1% (w/w), was added to both solutions as a free-radical initiator. When heated above 80 °C, MMA polymerized and cross-links were formed simultaneously with **9**. The result was a hard, clear solid which molded to the shape of the container. While PMMA was soluble in benzene, toluene, chloroform, or methylene chloride, the new materials were insoluble in these organic solvents and exhibited only minor swelling in chloroform and methylene chloride. The thermal properties were also compared with those of pure PMMA using the T_d, temperature at 10% weight loss, determined by thermogravimetric analysis (TGA). Increases in thermal stability of 41.5 °C (95% PMMA) and 108.7 °C (90% PMMA) were observed for these new materials relative to pure PMMA (Table 5). As shown in Figure 1, the TGA results clearly demonstrated the difference in thermal stability be-

Table 5. Comparison of Thermal Decomposition for the New Materials with PMMA

wt % of copolymer **9** used in polymerization	T_d (°C)[a]
0% (100% PMMA)	229.9
5% (95% PMMA)	271.4
10% (90% PMMA)	328.6

[a] All values are obtained under an atmosphere of argon at a scan rate of 10 °C/min.

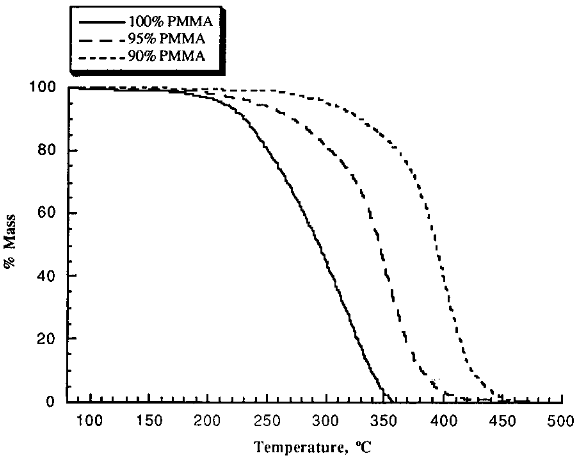


Figure 1. Comparison of thermal stability between PMMA and the new AB cross-linked materials in an argon atmosphere with a scan rate of 10 °C/min.

tween these materials.

Conclusions

An efficient synthesis of 5-methacryloyl-1-cyclooctene was accomplished, and the controlled ROMP of this monomer to create a linear polymer with methacrylate side chains was demonstrated. The copolymerization of this monomer with cyclooctadiene allowed for the incorporation of a varying number of methacrylate side chains on the polymer backbone. The effect of reaction concentration, solvent, amount of inhibitor, and [M]:[cat] ratio on the polymerization was elucidated. In addition, both thermal and photochemical initiated cross-linking of these materials was accomplished, as well as the determination of an efficient inhibitor for these cross-linking processes. These successful cross-linking reactions led to a study of AB cross-linked systems of these polymers with PMMA resulting in new PMMA materials that had higher thermal stability and solvent resistance than pure PMMA.

Future studies will focus on the synthesis of even more thermally and chemically resistant materials by increasing the amount of copolymer relative to MMA and by utilizing the copolymers with higher methacrylate content. The mechanical properties of these materials will be examined as well in an attempt to develop higher impact resistance PMMA.

Experimental Section

General Procedure. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on GE QE-300 Plus (300.1 MHz; 75.49 MHz ^{13}C) spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system using an Altex Model 110A pump, a Rheodyne Model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 μm mixed bed columns, and a Knauer differential refractometer using CH_2Cl_2 as eluent at a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported versus monodisperse polystyrene standards. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA-2. Photolysis was accomplished with a 450 W medium-pressure mercury Hanovia lamp.

Materials. The toluene used in polymerizations was distilled from CaH_2 under vacuum. Dry THF was obtained by distillation under atmospheric pressure from CaH_2. All other solvents were reagent grade and used without purification. Cyclooctadiene, *m*-chloroperbenzoic acid, methacryloyl chloride, *p*-methoxyphenol, lithium aluminum hydride, triethylamine, and 2,2-dimethoxy-2-phenylacetophenone were purchased from the Aldrich Chemical Co. and used without further purification.

Preparation of Cyclooctadiene Monoepoxide (2) and 5-Hydroxy-1-cyclooctene (3). The preparation of these compounds was carried out using a recent modification[17] of a literature procedure.[23]

Preparation of 5-Methacryloyl-1-cyclooctene (4). Compound **3** (16.2 g, 129 mmol, 1 equiv) was mixed with THF (100 mL) and triethylamine (14.3 g, 142 mmol, 1.1 equiv) in a 500 mL round-bottom flask under argon. To the reaction flask 90% methacryloyl chloride (17.9 g, 154 mmol, 1.2 equiv) was added by syringe over 45 min at 0 °C. The ice bath was then removed and the reaction was left to stir for 3 h at room temperature. The solid was removed by filtration and washed with diethyl ether (300 mL). The organics were then washed with 15% NaOH (3 × 200 mL), deionized water (200 mL), and brine (200 mL). The organics were then dried over $MgSO_4$ and concentrated *in vacuo*. The product was then distilled at 1 mmHg/78 °C to give 17.5 g (70%) of pure product. ^{1}H NMR ($CDCl_3$) δ 6.04 (dt, $J_1 = 1.5$ Hz, $J_2 = 0.9$ Hz, 1H), 5.67 (m, 2H), 5.50 (q, $J = 1.5$ Hz, 1H), 4.88 (m, 1H), 2.40−2.04 (m, 4H), 1.90 (dd, $J_1 = 0.9$ Hz, $J_2 = 1.5$ Hz, 3H), 1.89−1.54 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 166.8, 136.9, 129.8, 129.7, 124.8, 75.7, 33.7, 33.3, 25.5, 24.8, 22.2, 18.3; IR (neat) 3017, 2933, 2859, 1710, 1638, 1467, 1450, 1402, 1381, 1328, 1318, 1294, 1174, 1038, 972.6, 932, 885, 815, 727 cm^{-1}; HRMS (FAB) calcd for $C_{12}H_{18}O_2$ $(M)^+$ 194.1307, found 194.1311.

General Polymerization Procedures. All manipulations were carried out in a drybox. In a 10 mL vial, the correct amount of **4** and cyclooctadiene were weighed out. In a separate vial, the catalyst was weighed out and dissolved in the appropriate amount of toluene with MEHQ. The catalyst solution was then pipetted into the first vial and a small Teflon-coated stirbar was added. The vial was then capped, removed from the drybox, wrapped with aluminum foil, and left to stir for the desired time. Ethyl vinyl ether (600 equiv) was pipetted into the vial along with an equal volume of toluene. This was left to stir for 1 h followed by precipitation into MeOH to isolate the polymer. Polymers **5**−**10** were synthesized by this method and characterized by standard methods including ^{1}H NMR, ^{13}C NMR, IR, and GPC.

Polymer 5: ^{1}H NMR ($CDCl_3$) δ 6.06−6.00 (bm, 1H), 5.51−5.45 (bm, 1H), 5.38−5.22 (bm, 2H), 4.98−4.82 (bm, 1H), 2.00−1.90 (bm, 4H), 1.91 (s, 3H), 1.60−1.42 (bm, 4H), 1.39−1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.67, 130.36, 130.20, 129.92, 129.78, 129.72, 129.62, 129.33, 129.10, 124.99, 74.0, 34.06, 33.98, 33.89, 33.75, 33.69, 33.61, 32.42, 28.44, 27.02, 26.98, 25.29, 25.26, 25.18, 25.13, 23.19, 23.13, 23.11, 18.41; IR (neat) 3002, 2931, 2837, 1719, 1631, 1443, 1402, 1372, 1314, 1290, 1167, 1067, 1008, 967, 932, 814, 719 cm^{-1}.

Polymer 6: ^{1}H NMR ($CDCl_3$) δ 6.06−6.00 (bm, 1H), 5.51−5.45 (bm, 1H), 5.38−5.22 (bm, 4H), 4.98−4.82 (bm, 1H), 2.00−1.90 (bm, 8H), 1.91 (s, 3H), 1.60−1.42 (bm, 4H), 1.39−1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.67, 130.34−128.85 (m, *C* olefin), 124.96, 74.00, 34.05−23.12 (m, *C* alkyl), 18.40; IR (neat) 3006, 2932, 2858, 1716, 1637, 1464, 1401, 1379, 1318, 1295, 1166, 967, 937, 725 cm^{-1}.

Polymer 7: ^{1}H NMR ($CDCl_3$) δ 6.06−6.00 (bm, 1H), 5.51−5.45 (bm, 1H), 5.38−5.22 (bm, 7H), 4.98−4.82 (bm, 1H), 2.00−1.90 (bm, 14H), 1.91 (s, 3H), 1.60−1.42 (bm, 4H), 1.39−1.20 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 167.10, 136.68, 130.33−128.83 (m, *C* olefin), 124.94, 74.01, 34.04−23.18 (m, *C* alkyl), 18.39; IR (neat) 3006, 2925, 2847, 1715, 1636, 1454, 1403, 1379, 1316, 1295, 1164, 966, 729 cm^{-1}.

Polymer 8: ^{1}H NMR (CDCl$_3$) δ 6.06−6.00 (bm, 1H), 5.51−5.45 (bm, 1H), 5.38−5.22 (bm, 23H), 4.98−4.82 (bm, 1H), 2.00−1.90 (bm, 46H), 1.91 (s, 3H), 1.60−1.42 (bm, 4H), 1.39−1.20 (bm, 2H); ^{13}C NMR (CDCl$_3$) δ 167.11, 136.70, 130.37−128.84 (m, *C* olefin), 124.95, 74.03, 34.04−23.19 (m, *C* alkyl), 18.41; IR (neat) 3005, 2921, 2845, 1717, 1638, 1449, 1401, 1316, 1295, 1165, 966, 729 cm^{-1}.

Polymer 9: ^{1}H NMR (CDCl$_3$) δ 6.06−6.00 (bm, 1H), 5.51−5.45 (bm, 1H), 5.38−5.22 (bm, 46H), 4.98−4.82 (bm, 1H), 2.00−1.90 (bm, 92H), 1.91 (s, 3H), 1.60−1.42 (bm, 4H), 1.39−1.20 (bm, 2H); ^{13}C NMR (CDCl$_3$) δ 167.10, 136.71, 130.47−128.2 (m, *C* olefin), 124.94, 74.07, 74.01, 34.06−23.20 (m, *C* alkyl), 18.40; IR (neat) 3006, 2919, 2844, 1717, 1638, 1448, 1402, 1316, 1295, 1165, 966, 727 cm^{-1}.

Polymer 10: ^{1}H NMR (CDCl$_3$) δ 6.06−6.00 (bm, 1H), 5.51−5.45 (bm, 1H), 5.38−5.22 (bm, 84H), 4.98−4.82 (bm, 1H), 2.00−1.90 (bm, 168H), 1.91 (s, 3H), 1.60−1.42 (bm, 4H), 1.39−1.20 (bm, 2H); ^{13}C NMR (CDCl$_3$) δ 167.10, 136.68, 131.39−127.99 (m, *C* olefin), 125.01, 73.70, 73.64, 33.42−24.97 (m, *C* alkyl), 18.35; IR (neat) 3006, 2918, 2844, 1717, 1654, 1448, 1403, 1372, 1316, 1165, 965, 728 cm^{-1}.

Determination of Polymer Composition at 10% Conversion. In a drybox, **1** (1.3 mg, 1.4 μmol, 1 equiv), **4** (225 mg, 1.16 mmol, 825 equiv), COD (122 mg, 1.13 mmol, 804 equiv), and MEHQ (12 mg, 96.8 μmol) were combined in toluene-d_8 (0.8 mL), and this polymerization was monitored by ^{1}H NMR. When the polymerization was at 10% conversion, the reaction mixture was precipitated in MeOH and the polymer composition analyzed by ^{1}H NMR integration.

Reaction of MMA and 1. In a drybox, **1** (7.4 mg, 8 μmol, 1 equiv), MMA (**6**) (48 mg, 479 mmol, 59.9 equiv), and the internal standard, mesitylene, were combined and dissolved in toluene-d_8 (0.5 mL), and the solution was then transferred to a NMR tube and removed from the drybox. The reaction was then monitored by ^{1}H NMR for 12 h for the disappearance of catalyst or MMA. No reaction was observed during this time.

Reaction of MMA, 4, and 1. In a drybox, **1** (7.4 mg, 8 μmol, 1 equiv), MMA (**6**) (43 mg, 347 μmol, 53.8 equiv), compound **4** (9.3 mg, 47.9 μmol, 6.0 equiv), and mesitylene were combined and dissolved in toluene-d_8 (0.5 mL), and the solution was then transferred to a NMR tube and removed from the drybox. Monitoring by ^{1}H NMR showed no reaction over 12 h except for the polymerization of **4**.

Reaction of 1 and MEHQ. In a drybox, **1** (7.4 mg, 8 μmol, 1 equiv), MEHQ (53 mg, 427 μmol, 59.1 equiv), and mesitylene were combined in toluene-d_8 (0.5 mL), and the solution was transferred to a NMR tube and removed from the box. The reaction was monitored by ^{1}H NMR, but no reaction was observed over 12 h.

Reaction of 1 with Homopolymer 5. In a drybox, homopolymer **5** (50 mg, 258 μmol, 99 equiv) was dissolved in toluene (0.75 mL) in each of four vials. In vial 1, **1** (2.4 mg, 2.6 μmol, 1.0 equiv) was added; in vial 2, the same amount of catalyst and MEHQ (10 mg) were added; in vial 3, only MEHQ (10 mg) was added; and in vial 4, nothing else was added. The four vials were removed from the box and allowed to react at room temperature for 12 h. The polymer was then precipitated in MeOH and analyzed by GPC.

General Procedure for PMMA AB Cross-Linked Systems. The desired ratio of MMA and copolymer **9** was combined with benzoyl peroxide and agitated until a solution resulted. This was then heated open to air with stirring at 90 °C. After 15 min, the solution became viscous, and the vial was removed from the 90 °C bath. The stirbar was removed, the vial capped, and then the vial was placed in a 40 °C bath and left for 10 h. After this time, the vial was removed from the bath, and the resulting polymer was isolated by breaking away the glass to obtain a hard, clear solid. Reaction at 90 °C for longer than 15 min led to foamy, brittle materials due to trapping of unreacted monomer in the polymeric solid.

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(19) In the presence of 5 mol % MEHQ, the isolated polymers were stable to cross-linking for short periods (<1 day) neat or indefinitely as a solution in toluene.

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