

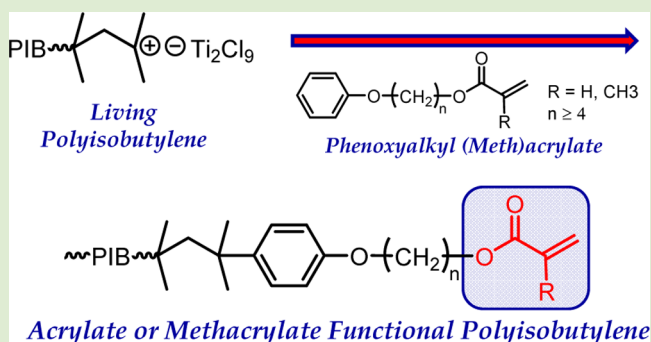
Direct Chain End Functionalization of Living Polyisobutylene Using Phenoxyalkyl (Meth)acrylates

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Supporting Information

ABSTRACT: Phenoxyalkyl acrylates and methacrylates were studied as quenching (capping) agents for living carbocationic polymerization of isobutylene (IB) at $-70\text{ }^{\circ}\text{C}$ in 40/60 (v/v) hexane/methyl chloride, catalyzed by TiCl_4 . Quenching reactions were carried out by reactivation by TiCl_4 of preformed difunctional *tert*-chloride-terminated polyisobutylene (PIB) or by a one-step method in which IB polymerization and quenching were conducted sequentially in the same reactor. Chain-end concentrations ranged from 0.02 to 0.1 M, and quenchers were used at concentrations of 1.5–2.5 times the chain ends. The phenoxyalkyl (meth)acrylates were synthesized by reaction of (meth)acryloyl chloride with the corresponding phenoxyalkanol; alkylene tethers from two to eight carbons were examined. Quenched polymers were characterized by ^1H and ^{13}C NMR, MALDI-TOF mass spectrometry, and size exclusion chromatography (SEC). Alkylation was observed to occur exclusively at the *para* position of the phenoxy moiety, and SEC showed no coupling or molecular weight degradation as a result of quenching. For short tethers of two or three carbons, quenching was slow and incomplete due to competing loss of living chain ends presumably by carbocation rearrangement. For tethers of four, six, or eight carbons, quenching was much faster and yielded quantitative (meth)acrylate chain-end functionality (number-average functionality ≥ 1.98 by ^1H NMR). MALDI-TOF-MS results were consistent with the expected end group structures. The carbonyl group of the quencher consumes one equivalent of Lewis acid in formation of a 1:1 complex; thus, the highest rate of quenching at a given Lewis acid concentration is achieved by using only a modest excess of quencher relative to living chain ends.



Polyisobutylene (PIB) macromonomers and telechelic polymers possessing (meth)acrylate end groups are of great scientific and technological interest for the preparation of graft copolymers,¹ amphiphilic conetworks,^{2–5} and various UV and/or thermally cured networks for sealants, encapsulants, adhesives, and coatings.^{6,7} PIB is advantageous in these applications due to its low-temperature flexibility, adhesive strength, exceptional gas-barrier and energy damping properties, chemical, thermal, and oxidative stability, and biocompatibility.³

The aim of this work was to develop a single-step synthesis of telechelic PIB (meth)acrylates using direct end quenching of living PIB. In the past, PIB (meth)acrylates have been synthesized by reaction of (meth)acryloyl chloride with primary hydroxyl-terminated PIB (PIB-OH)^{1,8,9} or by reaction of alkali metal (meth)acrylates with primary bromine-terminated PIB (PIB-Br).^{6,7,10–12}

The PIB-OH routes involve either *exo*-olefin- or allyl-terminated PIB as an intermediate. In the 1980s, PIBs carrying *tert*-chloride end groups became available via the inifer method¹³ and were converted to the *exo*-olefin derivatives by dehydrochlorination using potassium *tert*-butoxide.^{14,15} More recently, *exo*-olefin-terminated PIB has been obtained by end-

quenching living PIB with methallyltrimethylsilane,¹⁶ hindered nucleophiles,¹⁷ alkoxy silanes,¹⁸ dialkyl sulfides,^{19,20} or dialkyl ethers.^{18,21} Allyl PIB is obtained by end-quenching of living PIB with allyl trimethylsilane.²² The intermediate olefin thus obtained is converted to hydroxyl-terminated PIB through hydroboration–oxidation.^{22,23} Esterification of PIB-OH to the (meth)acrylate typically follows a standard route:⁸ PIB-OH in THF is reacted with an excess of the acid chloride in the presence of a tertiary amine at $0\text{ }^{\circ}\text{C}$.^{1,9}

PIB-Br has been produced by several methods. Living PIB may be reacted with 1,3-butadiene to yield allyl chloride end groups (PIB-allylCl), catalyzed by either BCl_3 ²⁴ or TiCl_4 ,²⁵ however, in a separate step the chloride must be converted to bromide by halogen exchange.²⁵ PIB-OH has been converted to primary bromide by reaction with carbon tetrabromide.²⁶ Anti-Markovnikov addition of HBr to PIB olefins has been shown to quantitatively yield primary bromide PIB.^{10–12,27} Finally, PIB can be end-quenched with nucleophilic aromatic

Received: October 18, 2014

Accepted: November 11, 2014

Published: November 17, 2014

substrates, which are substituted with haloalkyl groups, such as *N*-(ω -bromoalkyl)pyrrole²⁸ and 3-bromopropoxybenzene.^{29–32} Once obtained, PIB-Br may be directly converted to PIB-(meth)acrylate by reaction with sodium or potassium (meth)acrylate in THF or mixtures of THF and NMP at reflux temperature.^{6,7,10–12}

All of the above methods involve multistep syntheses. Methods yielding PIB-Br directly by end-quenching^{28–33} require only two steps; however, the second step, nucleophilic substitution of bromide for (meth)acrylate, is typically carried out at elevated temperature (THF reflux) to obtain practical rates. Under these conditions, radical consumption of (meth)acrylate double bonds generally must be suppressed by inhibitors,⁷ which may not be completely effective. Herein, we report a one-step, low-temperature method toward (meth)acrylate-functionalized PIB, involving direct functionalization of living PIB with phenoxyalkyl (meth)acrylate quenchers.^{32,34}

Several considerations informed our approach. Basic functionalities such as carbonyls, hydroxyls, amines, etc., interact strongly with Lewis acids and are known to interfere with quenching.^{29,35} This causes disappearance of *tert*-chloride chain ends that is more rapid than the appearance of quenched product, indicating accumulation of slowly reacting intermediates, presumably via carbenium ion rearrangement.³⁶ Although rearranged structures will slowly alkylate phenoxy quenchers,²⁹ in general, carbocation rearrangement is a useful indicator that the rate constant for alkylation for a given quencher is too low to be practically useful. We have shown that increasing the tether length between the interfering group and the quenching site can eliminate or lessen these problems.²⁹ Regardless of tether length, quenchers with interfering groups alkylate more slowly than noninterfering quenchers and require higher Lewis acid concentrations to achieve satisfactory results.

Quenching reactions catalyzed by TiCl₄ in 40/60 (v/v) hexane/methyl chloride at -70 °C were conducted on difunctional *tert*-chloride PIB ($M_n = 4000$ g/mol, PDI = 1.15 by SEC) synthesized from 1,3-di(1-chloro-1-methylethyl)-5-*tert*-butylbenzene, which provides an internal NMR reference (aromatic ring protons) to which the integrated peak areas of the *tert*-chloride, (meth)acrylate olefinic, and tether protons may be quantitatively compared. We examined phenoxyalkyl (meth)acrylate quenchers with tether lengths from C2–C8: 2-phenoxyethyl acrylate (PEA), 1-phenoxy-2-propyl acrylate (PiPA), 3-phenoxy-1-propyl acrylate (PPA), 4-phenoxy-1-butyl acrylate (PBA), 4-phenoxy-1-butyl methacrylate (PBMA), 6-phenoxy-1-hexyl acrylate (PHA), and 8-phenoxy-1-octyl acrylate (POA).

The short-tether quenchers PEA, PiPA, and PPA were found to alkylate so slowly that chain end rearrangement could not be avoided. PPA performed the best of these three, and at chain end concentration [CE] = 0.02 M, [PPA] = 0.05 M, and [TiCl₄] = 0.12 M, we observed 42% depletion of *tert*-chloride chain ends but only 31% yield of acrylate chain ends after 4 h. After 20 h, we observed 100% depletion of *tert*-chloride but a final acrylate chain end yield of only 48%. In the ¹H NMR spectrum of the final product (Figure S1, Supporting Information), acrylate vinyl, trimethylene tether, and phenoxy aromatic proton intensities are consistent with one another but low relative to those of the initiator aromatic ring, and carbenium ion rearrangement can be observed as a multitude of small peaks in the 1.70–2.25 ppm region. Under the same or more moderate conditions, however, quenchers possessing

tether lengths of four carbons or greater yielded quantitative (meth)acrylate functionality in far shorter times (1–2 h). Figures 1 and 2 show ¹H NMR spectra of difunctional PIB

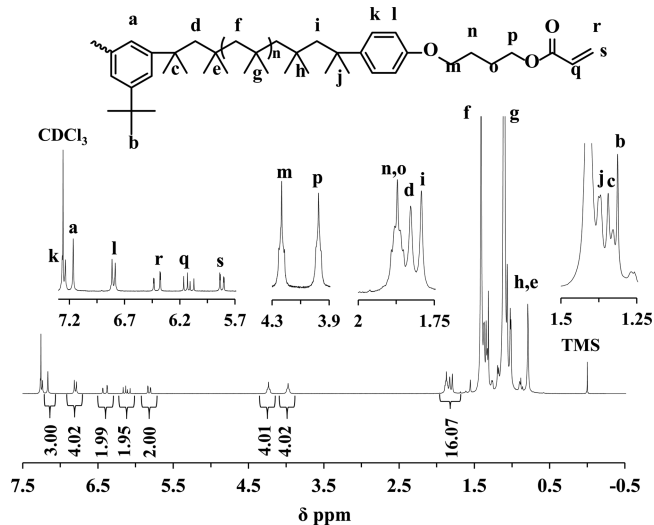


Figure 1. ¹H NMR (300 MHz, CDCl₃, 23 °C) spectrum of difunctional PIB (4000 g/mol) quenched with PBA for 120 min. -70 °C; 40/60 (v/v) hexane/methyl chloride; [CE] = 0.02 M, [PBA] = 0.05 M, [TiCl₄] = 0.12 M, [2,6-lutidine] = 0.005 M.

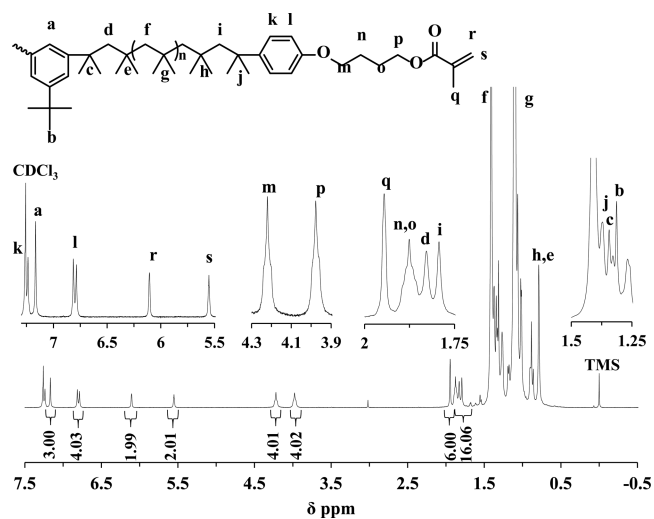


Figure 2. ¹H NMR (300 MHz, CDCl₃, 23 °C) spectrum of difunctional PIB (4000 g/mol) quenched with PBMA for 90 min. -70 °C; 40/60 (v/v) hexane/methyl chloride; [CE] = 0.02 M, [PBMA] = 0.05 M, [TiCl₄] = 0.10 M, [2,6-lutidine] = 0.005 M.

quenched with PBA and PBMA, which are representative. In both spectra, the intensity of the olefinic protons (acrylate 5.7–6.5 ppm, methacrylate 5.55 and 6.11 ppm) relative to either the tether protons (triplets at 3.98 and 4.22 ppm) or the aromatic quencher protons (doublet at 6.80 ppm) matches the theoretical prediction, indicating no loss of (meth)acrylate double bonds to radical side reactions, as expected since these groups are not exposed to elevated temperatures in the direct quenching process. The aromatic quencher protons are crisp doublets, indicating exclusively *para* substitution and no coupling via double alkylation of a single phenoxy moiety. Integration of the olefinic protons relative to the aromatic protons of the initiator (7.16 ppm) allowed calculation of the

absolute (meth)acrylate functionality of each sample: $F_n = 1.98$ for the PIB diacrylate and 2.00 for the PIB dimethacrylate. SEC traces of PIB samples before and after quenching were essentially identical, confirming the absence of coupling or chain degradation reactions (Figure S2, Supporting Information). A high-resolution ^{13}C NMR (150 MHz, CDCl_3 , 23 °C) spectrum with comprehensive peak assignments of the PIB diacrylate sample is shown in Figure S3 (Supporting Information).

Figure 3 shows progress of quenching versus time (^1H NMR data) for the sample shown in Figure 1. It may be observed that

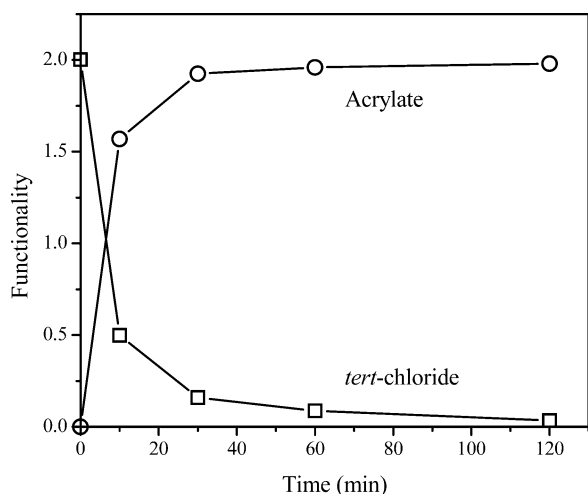


Figure 3. PIB functionality versus time for the quenching reaction of difunctional *tert*-chloride PIB (4000 g/mol) with PBA. -70 °C; 40/60 (v/v) hexane/methyl chloride; $[\text{CE}] = 0.02$ M, $[\text{PBA}] = 0.05$ M, $[\text{TiCl}_4] = 0.12$ M, $[\text{2,6-lutidine}] = 0.005$ M.

the quenching reaction reached 96.5% conversion after 30 min and was essentially complete after 120 min. The disappearance of *tert*-chloride end groups was found to be inversely related to the appearance of acrylate end groups, indicating that accumulation of slowly reacting intermediates (carbocationic rearrangement) was absent or negligible.

We hypothesize that the poor performance of quenchers with short, i.e., C2 and C3, tethers is due to the likelihood of cyclic conformers that bring the TiCl_4 -carbonyl complex in close proximity to the phenoxy aromatic ring and thereby reduce its reactivity toward the PIB carbenium ion. Longer tethers apparently reduce the likelihood of these interactions and lead to dramatically enhanced reactivity.

The quenched products were characterized by matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF MS); Figure 4 shows the spectrum of difunctional PIB quenched with PHA, which is representative. The spectrum displays a single distribution corresponding to sodiated PIB diacrylate molecules. From regression analysis of a plot of the masses of the peaks vs their degree of polymerization, a linear relationship with a regression slope of 56.04 and intercept of 734.16 was obtained. Thus, each peak represents a PIB molecule consisting of a number of isobutylene repeat units plus a residual mass of 734.16 Da, representing initiator residue, end groups, and sodium cation ($\text{I}+\text{EG}+\text{Na}$). The theoretical exact mass of this residue for the target structure ($\text{C}_{46}\text{H}_{62}\text{O}_6\text{Na}^+$) totals 733.42 Da. The difference is only 0.1%, providing strong evidence that the target structure was achieved. MALDI-TOF MS results for all

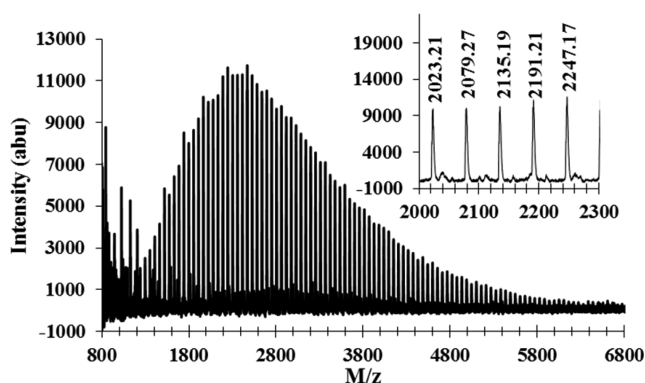


Figure 4. MALDI-TOF mass spectrum of difunctional PIB (4000 g/mol) quenched with PHA for 60 min. -70 °C; 40/60 (v/v) hexane/methyl chloride; $[\text{CE}] = 0.02$ M, $[\text{PBA}] = 0.05$ M, $[\text{TiCl}_4] = 0.08$ M, $[\text{2,6-lutidine}] = 0.005$ M.

of the long-tether quenchers are summarized in Table 1. In all cases, the agreement between the observed and theoretical residual exact mass was excellent.

Quenching reactions were also conducted on preformed difunctional PIB containing mixed *tert*-chloride/*exo*-olefin/*endo*-olefin end groups. We observed that phenoxyalkyl (meth)acrylate quenchers alkylate these various end groups with equal facility, consistent with our experience with phenoxy quenchers generally.²⁹

We next examined phenoxyalkyl (meth)acrylate quenching using a one-step, *in situ* method, in which IB polymerization and quenching were conducted sequentially in the same reactor (see Supporting Information). The *in situ* process was found to work with equal facility to the reactivation process and to yield products that are indistinguishable from those discussed above. One such experiment using PBA as a quencher was designed to demonstrate the practicality of phenoxyalkyl (meth)acrylate quenching under conditions of high $[\text{CE}]$ (0.1 M) and lower $[\text{Q}]/[\text{CE}]$ (1.5). This reaction worked well and did not suggest any problems with phenoxyalkyl (meth)acrylate quenching at higher concentrations. In fact, with increasing $[\text{CE}]$ in an *in situ* process, we predict that the highest practical monomer concentration will be exceeded before the phenoxy quenching reaction fails. The product of reaction at $[\text{CE}] = 0.1$ M was analyzed using high-field ^1H NMR (600 MHz) (Figure S4, Supporting Information). Integration of acrylate protons relative to the aromatic protons of the initiator indicated acrylate functionality of $F_n = 2.00$. We attempted to detect trace amounts of nonacrylate end groups. Very high expansion of the 4.4–5.5 ppm region of the spectrum did reveal weak peaks identifiable as *exo*-olefin end groups at 4.64 and 4.85 ppm, but these resonances were barely resolved above the baseline noise and were unquantifiable by integration (Figure S5, Supporting Information).

Kinetics of phenoxyalkyl (meth)acrylate quenching were examined as a function of the quencher concentration, $[\text{Q}]$, nominal Lewis acid concentration, $[\text{TiCl}_4]_0$, and structure of quencher. The rate of phenoxy quenching, catalyzed by TiCl_4 , may be treated using the integrated form of the standard second-order rate equation²⁹

$$\ln\left(\frac{M-p}{M(1-p)}\right) = k_c K_{\text{eq}} [\text{TiCl}_4]^2 [\text{CE}] (M-1) t$$

Table 1. MALDI-TOF Mass Spectral Data of PIB Di(meth)acrylates Obtained by Quenching Preformed *tert*-Chloride PIB with Phenoxyalkyl Acrylates^a

quencher	theoretical exact mass (Da)		experimental exact mass (Da)		difference	repeat unit
	I+EG+Na	I+EG+Ag	I+EG+Na	I+EG+Ag		
<i>tert</i> -Cl	-	393.02	-	393.07	0.05	56.05
PBA	-	761.28	-	760.86	0.42	56.07
PBMA	705.4	-	705.34	-	0.06	56.06
PHA	733.42	-	734.16	-	0.74	56.04
POA	789.48	-	788.82	-	0.66	56.08

^aQuenching Conditions: $-70\text{ }^{\circ}\text{C}$; 40/60 (v/v) hexane/methyl chloride; $[\text{CE}] = 0.02\text{ M}$, $[\text{Q}] = 0.05\text{ M}$, $[\text{TiCl}_4] = 0.12\text{ (PBA)}$, 0.10 (PBMA) , 0.08 (PHA) , 0.12 M (POA) , $[\text{2,6-lutidine}] = 0.005\text{ M}$.

where p is conversion of *tert*-chloride chain ends; k_c is rate constant for alkylation; K_{eq} is ionization equilibrium constant; $[\text{TiCl}_4]$ is effective concentration of TiCl_4 available to catalyze ionization; $M = [\text{Q}]/[\text{CE}]$ is the initial quencher to chain end concentration; and t is time. Regardless of tether length, (meth)acrylate quenchers were found to consume 1 equiv of TiCl_4 due to formation of a 1:1 complex with the carbonyl group. This was revealed by essentially zero alkylation rate when $[\text{TiCl}_4]_0 < [\text{Q}]$; similar loss of catalytic activity has been observed by others when esters were present in carbocationic polymerizations at a concentration exceeding that of the Lewis acid.³⁷ Since rate is determined by the square of available TiCl_4 concentration, the use of excess quencher relative to chain ends, normally an effective strategy for reducing reaction time in a second-order reaction, is predicted in this case to be self-defeating. This prediction was tested by observing the progress of PBA quenching at lower M values of 1.5 and 2.0, compared to the typical value of $M = 2.5$. It was observed that quenching rate is approximately constant for all three M values and probably decreases slightly with increasing M (Figure S6, Supporting Information). This confirmed that at constant $[\text{TiCl}_4]_0$, larger stoichiometric excesses of quencher do not enhance rate and are simply wasteful of quencher.

Figure 5 is a plot of second-order quenching kinetics for several quenchers. The rate of alkylation rises modestly with an increase in tether length in the C4–C8 range. Quenchers with longer tethers cause greater separation between the aromatic

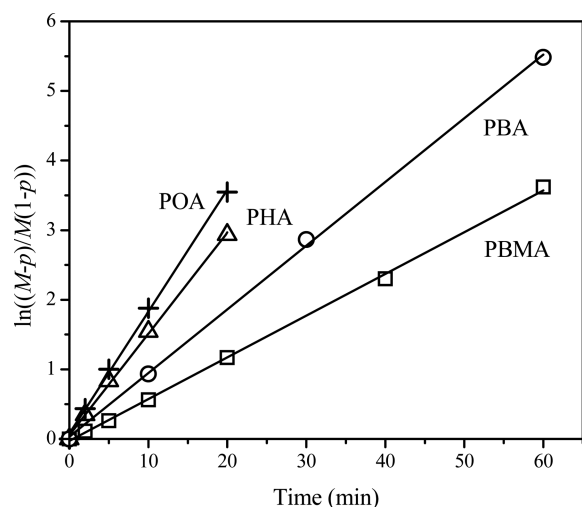


Figure 5. Second-order kinetic plots for quenching reactions of difunctional *tert*-chloride PIB (4000 g/mol) with various phenoxyalkyl (meth)acrylates. $-70\text{ }^{\circ}\text{C}$; 40/60 (v/v) hexane/methyl chloride; $[\text{CE}] = 0.02\text{ M}$, $[\text{Q}] = 0.05\text{ M}$, $[\text{TiCl}_4] = 0.10\text{ M}$, $[\text{2,6-lutidine}] = 0.005\text{ M}$.

substrate and TiCl_4 –carbonyl complex, resulting in less interaction with the phenoxy moiety. This is consistent with the very slow rates observed with C2 tethers. At constant C4 tether length, the methacrylate quencher was less reactive than the acrylate quencher.

In conclusion, phenoxyalkyl (meth)acrylates are effective quenchers (capping agents) for living carbocationic PIB, and their use enables the synthesis of (meth)acrylate telechelic PIBs in one step, directly within the polymerization reactor. If desired, the method can obviously be extended to trifunctional (or higher) PIBs using an appropriate initiator.⁶ An inherent advantage of this process is that the thermally sensitive (meth)acrylate functionality is never exposed to elevated temperatures. A minimum alkyl tether length of at least four carbon atoms is necessary to achieve practical rates of quenching. Because the carbonyl group of the quencher sequesters one equivalent of Lewis acid in the formation of a 1:1 complex, the highest rate of quenching at a given Lewis acid concentration is achieved by using only a modest excess of quencher relative to living chain ends.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental section and additional data (NMR spectra, SEC data, kinetic data). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Office of Naval Research provided financial support of this research (Award N00014-07-1-1057). Stipend support for coauthor Yang was provided by Henkel Corp.

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