A Versatile Synthetic Route to Macromonomers via RAFT Polymerization

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ABSTRACT: We describe a facile route to prepare functional macromonomers using reversible addition−fragmentation chain transfer (RAFT) polymerization. This was demonstrated in the synthesis of α-functionalized norbornenyl, vinyl, and cinnamyl macromonomers using functional chain transfer agents bearing these end groups. Various homopolymer macromonomers of well-controlled molecular weights were synthesized with near-quantitative incorporation of the end group functionality. The use of norbornenyl and vinyl CTA's resulted in a highly quantitative polymerization of styrene and methyl methacrylate (MMA) monomers yielding well-defined linear macromonomers. On the other hand, monomers with a lower reactivity such as methyl acrylate (MA) exhibited a broader polydispersity. The cinnamyl-functionalized telechelics proved the most challenging due to a competitive chain transfer between the cinnamyl group and the RAFT CTA at higher conversions. To demonstrate utilization of the macromonomer functionality, we synthesized the poly(norbornene-*g*-PMMA) copolymer based on the ring-opening metathesis polymerization (ROMP) of the norbornenyl-functionalized PMMA macromonomer. The main advantage of this new approach should be in the ability to prepare a variety of macromonomer structures utilizing the mild and tolerant conditions of RAFT polymerization.

Introduction

Telechelic polymers are generally low molecular weight polymers with selectively positioned functional groups at any given termini or, in the case of semi-telechelics, precisely at one terminus of the polymer chain. Telechelic polymers have been a subject of intense interest for a variety of applications including precursors for the synthesis of block copolymers, use as cross-linking agents, and in the preparation of polymeric networks.[1] More specifically, macromonomers represent an important class of telechelic polymers that carry polymerizable entities at one or both ends of the polymer chain providing a useful precursor for the supramolecular fabrication of more complex macromolecular architectures.[2−8] The macromonomer approach has been utilized extensively in the syntheses of a great number of branched and complex polymeric structures including graft copolymers,[8] star polymers,[9] and dendronized polymers.[10] Of course, one's ability to construct many of the aforementioned polymeric architectures depends greatly on the availability of well-defined macromonomers. The synthesis methods and their application in macromolecular engineering have recently been summarized;[3] Hadjichristidis et al. outlined the three most common methodologies for the preparation of well-defined macromonomers.[2] The first strategy involves coupling of preformed end-functionalized polymers with polymerizable capping agents possessing complementary functional groups for the coupling chemistry. Although this approach has been extensively employed and has many advantages, the drawback lies in the difficulty of obtaining quantitative end group transformation. The second method involves a termination or end-capping of a "living" polymer chain with an appropriate linking agent containing the polymerizable moiety.[11] This method typically involves some aspect of "living" ionic polymerization, resulting in well-defined and quantitatively functionalized macromonomers. Here the disadvantage lies in the stringent conditions associated with most ionic polymerization methods and the low tolerability of monomer functional groups. The third strategy and perhaps the most studied in recent years involves the initiation of a living polymerization with an initiator functionalized with a polymerizable group.[12] Characteristic of most living polymerization techniques, polymerization from functional initiators yields macromonomers with quantitative α- or α,ω-functionalization depending on the type of initiator (mono- or difunctional) employed. The confining requirement of this strategy is the necessity of inertness or at least negligible reactivity of the initiator-bound functional group under the desired polymerization conditions. This said, various living polymerization techniques, including anionic,[13] cationic,[14] and ring-opening polymerization,[15] have been utilized to obtain well-defined macromonomers under this methodology. More recently, controlled radical polymerization (CRP) has emerged as a class of polymerization techniques with great promise for the synthesis of macromonomers with functionality often difficult to obtain by the previously mentioned techniques. The appeal of CRP techniques, including nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition−fragmentation chain transfer polymerization (RAFT), is evidenced by the explosion of literature accounts published since the mid-1990s and is mostly attributable to the mild reaction conditions and high functional group tolerability typically associated with these methods. Among the CRP techniques, perhaps atom transfer radical polymerization (ATRP) has received the most attention with regard to macromonomer synthesis. ATRP has been employed in the synthesis of a number of macromonomers with polymerizable groups including pyrrole,[15] thiophene,[16] lactone,[17] vinyl ester,[18−21] epoxy,[22] vinyl ether,[23,24] allyl,[24−26] and norbornene,[27] by means of which each of these functional groups exhibits a low susceptibility to polymerization under ATRP conditions.

Reversible addition−fragmentation chain transfer (RAFT) polymerization represents the most recently developed CRP method and is a powerful technique for macromolecular

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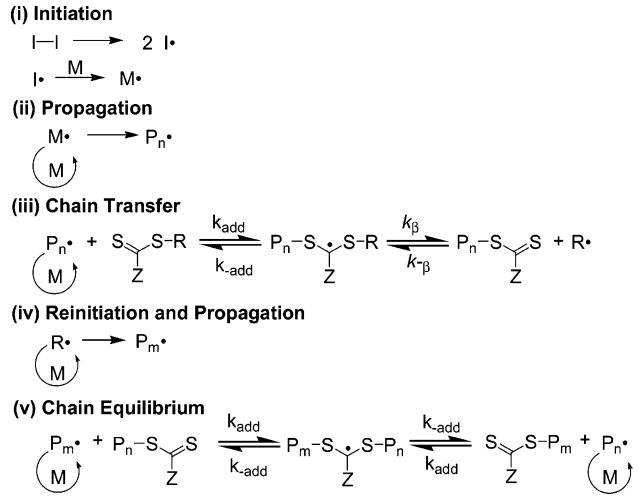

Figure 1. RAFT mechanism.

synthesis of a broad range of well-defined polymers.[28] RAFT polymerization has evolved as one of the more versatile CRP methods due to the high degree of tolerance for a wide range of functional monomers and the mild reaction conditions associated with this technique.[29,30] Nevertheless, the RAFT technique has received little attention in the realm of macromonomer synthesis. By virtue of the accepted mechanism for RAFT-mediated polymerization (Figure 1), the degenerative transfer process involving a chain transfer agent (CTA) (typically a thiocarbonylthio compound S═C(Z)−SR) allows one to prepare polymers that carry the respective Z and R groups at the termini of the polymer chains.[29] Thus, by synthetically modifying the R group of the chain transfer agent, a variety of end-functionalized polymers can be obtained including those of interest for macromonomers. Using a similar approach, we recently reported the synthesis of α,ω-functionalized thiol telechelics resulting from the use of a difunctional CTA possessing the dithioester groups at each end.[31]

In an effort to extend our work on telechelic synthesis and expand the utility of the RAFT polymerization technique, we propose the use of functional chain transfer agents as a facile method in the synthesis of a variety of macromonomers. In this work, we designed a series of CTAs that carry norbornenyl-, vinyl-, and cinnamyl functionalities incorporated within the R group of the dithioester-based compounds. The norbornene and vinyl end groups were chosen on the basis of continued interest of these groups as macromonomers for the further construction of complex macromolecules via ROMP and metathesis polymerization. Likewise, the cinnamate functional group has proven to be an effective means for the preparation of photo-crosslinkable polymer networks and stabilized polymer nanostructures,[32−35] yet few methods have been reported for the synthesis of cinnamyl end-functionalized polymers.[36,37] The CTAs were designed for versatility and application to a range of monomers. Here, we report the polymerization of various monomers including styrene, methyl methacrylate, and methyl acrylate in the presence of the various functional CTAs yielding, in most cases, well-defined macromonomers and telechelics.

Experimental Section

Materials. Reagent chemicals were purchased from Aldrich and used without further purification unless otherwise indicated. Tetrahydrofuran (THF) used in synthesis was distilled from sodium/benzophenone ketyl. Styrene (99+%), methyl methacrylate (MMA, 99+%), and methyl acrylate (MA, 99%) were passed through a column of activated basic alumina to remove the inhibitor, distilled, and stored at −20 °C. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol and stored at 5 °C in an amber bottle. Bis(tricyclohexylphosphine)benzylidine ruthenium(IV) chloride (Grubb's first generation catalyst) was purchased from Aldrich and used as received. Dithiobenzoic acid (DTBA)/sodium dithiobenzoate was prepared and subsequently oxidized to bis(thiobenzoyl)-disulfide according to the literature.[38]

Characterization. Gel permeation chromatography (GPC) was conducted on a Viscotek 270 (Viscotek, Inc.) equipped with an RI detector and a three-column series including two GMHHR-M and one GMHHR-L Mixed Bed ViscoGel column. THF (Omnisolve, HPLC grade) served as the polymer solvent and eluent at a flow rate of 1 mL min^{-1}. Samples were prepared at a known concentration (ca. 1−3 mg/mL), and an injection volume of 100 μL was used. Monodisperse poly(styrene) and poly(methyl methacrylate) standards (EZ Vials, Polymer Laboratories) were used to construct the calibration curves. NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR.

The thermal properties of the polymers were measured by thermogravimetric analysis (TGA) on a TA Instruments TGA 2920. The samples were heated to 800 °C at a heating rate of 10 °C/min under a dry nitrogen atmosphere (flow rate 80 mL/min) on a TA Instruments 2950 thermogravimetric analyzer. T_g was determined by DSC from the midpoint of the inflection tangent from the second heating at 5 °C/min. TGA and DSC data were analyzed using TA Instruments Universal Analysis software.

Synthesis of 4-Cyano-4-((thiobenzoyl)sulfanyl)pentanoic Acid (1).[38] 4,4′-Azobis(4-cyanovaleric acid) (4.19 g, 0.0149 mol) and bis(thiobenzoyl)disulfide (3.07 g, 0.01 mol) were dissolved in ethyl acetate (200 mL) in a 500 mL round-bottom flask equipped with a condenser. The mixture was degassed by bubbling through with N_2 and heated to reflux for 20 h under N_2. The reaction was allowed to cool to room temperature, and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel) with ethyl acetate:hexanes 2:3 as the eluent. After removal of solvent, the red fraction gave 4-cyano-4-((thiobenzoyl)sulfanyl)-pentanoic acid as a red oil. The product solidified upon sitting at −20 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.95 (s, 3H, CH_3); 2.40−2.80 (m, 4H, CH_2CH_2); 7.42 (m, 2H, *m*-ArH); 7.60 (m, 1H, *p*-ArH); 7.91 (m, 2H, *o*-ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.1, 29.5, 32.9, 45.6, 118.4, 126.7, 128.6, 133.1, 144.4, 177.3, 222.1.

Synthesis of 4-Hydroxybutyl Cinnamate (2). To a 250 mL round-bottom flask was added 1,4-butanediol (1.62 g, 0.018 mol) and triethylamine (1.82 g, 0.018 mol) in 50 mL of dry THF. The mixture was cooled to 0 °C under N_2, and cinnamoyl chloride (3.0 g, 0.018 mol) in 10 mL of dry THF was added dropwise over the course of 1 h. The reaction mixture was allowed to warm to room temperature and stirred overnight. The precipitated triethylamine salt was removed by filtration, and the solvent was removed by rotary evaporation. The oily residue was then taken up in 50 mL of diethyl ether and washed with sodium bicarbonate (2 × 20 mL) and water (2 × 20 mL) and then dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the crude product as a yellow oil, which was further purified by column chromatography on silica gel with 3:2 hexane/ethyl acetate as eluent (1.95 g, 49%). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.66−1.83 (m, 4H); 3.70 (t, 2H); 4.24 (t, 2H); 6.41 (d, 1H); 7.36−7.39 (m, 3H); 7.50−7.54 (m, 2H); 7.66 (d, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 25.2, 29.1, 62.3, 64.4, 118.0, 128.0, 128.9, 130.3, 134.4, 144.8, 167.1.

Synthesis of Bicyclo[2.2.1]hept-5-en-2-ylmethyl 4-Cyano-4-(phenylcarbonothioylthio)pentanoate (Norbornenyl-Functionalized CTA, 3). In a 100 mL round-bottom flask equipped with a stir bar and an addition funnel, a solution of **1** (0.675 g, 2.42 mmol), 5-norbornene-2-methanol (mixture of endo and exo) (0.36 g, 2.90 mmol), and 4-(dimethylamino)pyridine (DMAP) (30 mg, 0.245 mmol) in 30 mL of dry CH_2Cl_2 was cooled to 0 °C under N_2. DCC (0.598 g, 2.89 mmol) was dissolved in 5 mL of CH_2Cl_2 and added dropwise to the reaction flask under stirring. After complete addition of DCC, the reaction was stirred for 5 min at 0 °C and then allowed to warm to room temperature overnight. Then, the solid was

removed by filtration, and the filtrate was washed with dilute sodium bicarbonate (20 mL) and water (2 × 20 mL) and finally dried over anhydrous $MgSO_4$. The solution was filtered and the solvent removed to yield the crude product mixture as a red oil, which was further purified by column chromatography on silica gel using 2:1 hexane/ethyl acetate as the eluent. The final product was obtained as a viscous red oil (0.439 g, 47.1%). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.8−1.51 (m, 4H); 1.89 (s, 3H); 2.30−2.49 (m, 1H); 2.55−2.76 (m, 4H); 2.78−2.91 (m, 2H); 3.63−3.93 (m, 1H); 3.95−4.23 (m, 1H); 5.90−6.19 (m, 2H); 7.36−7.45 (m, 2H); 7.53−7.51 (m, 1H); 7.88−7.99 (m, 2H).

Synthesis of Dec-9-enyl 4-Cyano-4-(phenylcarbonothioylthio)-pentanoate (Vinyl-Functionalized CTA, 4). In a 100 mL round-bottom flask equipped with a stir bar and an addition funnel, a solution of **1** (1.0 g, 3.58 mmol), 9-decen-1-ol (0.614 g, 3.94 mmol), and 4-(dimethylamino)pyridine (DMAP) (40 mg, 0.327 mmol) in 30 mL of CH_2Cl_2 was cooled to 0 °C under N_2. DCC (0.812 g, 3.94 mmol) was dissolved in 5 mL of CH_2Cl_2 and added dropwise to the reaction flask under stirring. After complete addition of DCC, the reaction was stirred for 5 min at 0 °C and then allowed to warm to room temperature overnight. Then, the precipitated solid was removed by filtration, and the filtrate was washed with dilute sodium bicarbonate (20 mL) and water (2 × 20 mL) and finally dried over anhydrous $MgSO_4$. The solution was filtered and the solvent removed to yield the crude product mixture as a red oil, which was further purified by column chromatography on silica gel using 2:1 hexane/ethyl acetate as the eluent. The final product was obtained as a viscous red-pink oil (1.05 g, 70.3%). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.23−1.44 (m, 10H); 1.63 (q, 2H); 1.94 (s, 3H); 1.99−2.08 (m, 2H); 2.37−2.74 (m, 4H); 4.10 (t, 2H); 4.89−5.04 (m, 2H); 5.73−5.89 (m, 1H); 7.35−7.45 (m, 2H); 7.53−7.61 (m, 1H); 7.87−7.95 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 24.1, 25.8, 28.5, 28.8, 29.0, 29.1, 29.3, 29.8, 33.5, 33.7, 45.8, 65.3, 114.2, 118.5, 126.7, 128.6, 133.0, 139.1, 144.4, 171.6, 222.4.

Synthesis of 4-(Cinnamoyloxy)butyl 4-Cyano-4 (Phenylcarbonothioylthio)pentanoate (Cinnamate-Functionalized CTA, 5). In a 100 mL round-bottom flask equipped with a stir bar and an addition funnel, a solution of **1** (0.8 g, 2.86 mmol), **2** (0.662 g, 3.0 mmol), and 4-(dimethylamino)pyridine (DMAP) (30 mg, 0.245 mmol) in 30 mL of CH_2Cl_2 was cooled to 0 °C under N_2. Dicyclohexylcarbodiimide (DCC) (0.619 g, 3.0 mmol) was dissolved in 5 mL of CH_2Cl_2 and added dropwise to the reaction flask under stirring. After complete addition of DCC, the reaction was stirred for 5 min at 0 °C and then allowed to warm to room temperature overnight. Then, the precipitated solid was removed by filtration, and the filtrate was washed with dilute sodium bicarbonate (20 mL) and water (2 × 20 mL) and finally dried over anhydrous $MgSO_4$. The solution was filtered and the solvent removed to yield the crude product mixture as a pink oil, which was further purified by column chromatography on silica gel using 2:1 hexane/ethyl acetate as the eluent. The final product was obtained as a viscous pink oil (0.79 g, 57.3%). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.78−1.81 (m, 4H); 1.93 (s, 3H); 2.38−2.76 (m, 4H); 4.18 (t, 2H); 4.24 (t, 2H); 6.41 (d, 1H); 7.36−7.42 (m, 5H); 7.51−7.59 (m, 3H); 7.66 (d, 1H); 7.87−7.94 (m, 2H).

General Polymerization Procedures. All polymerizations were performed in a Schlenk apparatus under homogeneous conditions. AIBN was employed as the initiator in all polymerizations. In general, a solution of the respective monomer, initiator, chain transfer agent (CTA), and solvent was prepared in an oven-dried Schlenk tube fitted with a rubber septum and a stir bar. The specific concentrations and conditions for each reaction are noted in Tables 1 and 2. The mixtures were thoroughly deoxygenated by 3−5 freeze−pump−thaw cycles, backfilled with nitrogen, and placed in a thermostated water bath at preset temperature. At specific time intervals, aliquots were removed and rapidly quenched by lowering the temperature to 0 °C. Portions of these aliquots were used directly for analysis by GPC for molecular weight characteristics and ^{1}H NMR for monomer conversion. Purified polymer samples were obtained by repeated precipitation into a 10-fold excess of non-solvent (methanol for PS; hexane for MMA; 50% mixture water/methanol for MA). The polymer was collected either by centrifugation or by filtration and dried under vacuum for a minimum of 2 days prior to analysis.

Table 1. Results and Conditions for the Polymerization of Sty, MMA, and MA in the Presence of 3

CTA polymer	time (h)	% conv[a]	$M_{n,GPC}$[b]	$M_{n,theory}$[c]	PDI
NB−PS[d]	2	2.92	1110	2210	1.07
	4	6.94	3700	4720	1.10
	8	10.5	8380	6950	1.06
	12	15.9	12300	10300	1.09
	24	27.7	20170	17700	1.23
NB−PMMA[e]	1	5.66	4210	3790	1.19
	2	11.5	6860	7300	1.18
	3.5	20.6	11400	12800	1.16
	7	36.3	21200	22200	1.17
	9	41.5	24700	25400	1.20
NB−PMA[f]	0.5	2.90	689	1630	1.13
	1	5.66	1950	2820	1.11
	2	10.7	6450	4990	1.08
	4	21.9	12000	9800	1.17
	8	36.3	20270	16000	1.34
	12	50.0	22700	21900	1.47

[a] Conversion determined by RI response for Sty and by NMR for MMA and MA. [b] Calculated using OmniSec software vs PS or PMMA standards. [c] $M_{n,theory}$ = [M]/[CTA] × conv × MW_M + MW_{CTA}. [d] Sty 4.53 M, [M]:[CTA], 600:1; [CTA]:[I], 5:1; 65 °C. [e] MMA 5.83M, [M]:[CTA], 600:1; [CTA]:[I], 1.9:1; 65 °C. [f] MA 5.68 M, [M]:[CTA], 500:1; [CTA]:[I], 2.1:1; 65 °C

Table 2. Results and Conditions for the Polymerization of Sty, MMA, and MA in the Presence of 4

CTA polymer	time (h)	% conv[a]	$M_{n,GPC}$[b]	$M_{n,theory}$[c]	PDI
V−PS[d]	1	1.47	1300	1340	1.03
	2	2.73	2160	2120	1.07
	4	5.44	4240	3820	1.06
	8	11.4	8830	7550	1.09
	22	26.5	19980	16960	1.21
V−PMMA[e]	0.5	4.76	4760	3280	1.16
	1	9.09	6700	5880	1.15
	2	18.0	10960	11250	1.11
	4	31.0	18300	19000	1.13
	8	49.5	26400	30140	1.25
V−PMA[f]	0.5	2.91	720	1670	1.04
	1	5.66	1570	2850	1.09
	2	12.3	4670	5700	1.07
	4	23.7	9780	10600	1.14
	8	36.7	16800	16200	1.32
	12.5	49.8	21400	21800	1.41

[a] Conversion determined by RI response for Sty and by NMR for MMA and MA. [b] Calculated using OmniSec software vs PS or PMMA standards. [c] $M_{n,theory}$ = [M]/[CTA] × conv × MW_M + MW_{CTA}. [d] Sty 4.53 M, [M]:[CTA], 600:1; [CTA]:[I], 5:1; 65 °C. [e] MMA 5.83M, [M]:[CTA], 600:1; [CTA]:[I], 1.9:1; 65 °C. [f] MA 5.68 M, [M]:[CTA], 500:1; [CTA]:[I], 2.1:1; 65 °C.

Determination of Monomer Conversion. Monomer conversion was determined by one of two methods depending on the monomer of interest. For styrene, the monomer conversion was obtained by integration of the RI response for the monomer and for the polymer in the crude reaction mixture as defined by eq 1. $A(M_{RI})$ is the area under the RI response for the monomer and must be corrected based on the monomer/solvent ratio used in the reaction. $A(P_{RI})$ denotes the area under the RI response for the polymer. Monomer conversion for methyl methacrylate and methyl acrylate was obtained by ^{1}H NMR and calculated on the basis of eq 2.

$$\text{conversion} = 1 - \frac{A(M_{RI})}{A(M_{RI}) + A(P_{RI})} \quad (1)$$

$$\text{conversion} = 1 - \frac{I(M_{-OCH_3})}{I(P_{-OCH_3}) + I(M_{-OCH_3})} \quad (2)$$

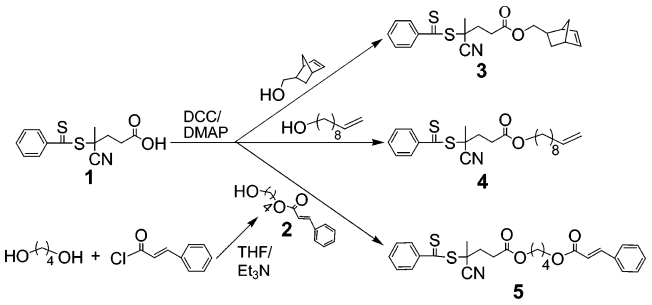

Figure 2. Synthesis scheme for the preparation of the (**3**) norbornene-, (**4**) vinyl-, and (**5**) cinnamate-derivatized chain transfer agents.

$I(M_{-OCH_3})$ is the chemical shift for the methoxy protons of the monomer which resonate at a slightly higher field than the methoxy protons of the polymer, denoted $I(P_{-OCH_3})$. This procedure was adapted from the methods reported by Saricilar et al. for similar polymers.[39] Similar values of conversion were obtained by either method.

Results and Discussion

Synthesis of the Functional Chain Transfer Agents. The chain transfer agents containing the norbornene (**3**), vinyl (**4**), and cinnamate (**5**) functionalities were designed by coupling the dithioester compound, **1**, with the hydroxyl derivatives of the respective functional group. The synthetic scheme for these CTAs is shown in Figure 2. The coupling chemistry based on DCC/DMAP-mediated esterification provided the target compounds in good yield under mild reaction conditions.

We chose to incorporate the 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (**1**) functional group mainly due to proven effectiveness of this compound and its derivatives as RAFT agents for the polymerization of styrene, methyl methacrylate, and a variety of other monomers,[40,41] though a similar strategy could be designed to accommodate other monomer types. As designed, the polymerizable moiety functions as part of the R group and thus remains at one end of the polymer chain. The other end of the polymer chain contains the dithioester group which remains active opening the possibility for the synthesis of block copolymer macromonomers. Because of the spacer length between the functional group and the point of fragmentation, it is expected that these CTAs would behave similarly when exposed to identical polymerization conditions. The main difference in behavior should be attributed to the various reactivities of the incorporated functional group (i.e., norbornene, vinyl, and cinnamate).

General Considerations in the Synthesis of Macromonomers by RAFT. Styrene (Sty), methyl methacrylate (MMA), and methyl acrylate (MA) were the three monomers investigated for the preparation of the various macromonomers and telechelics by RAFT polymerization. The monomers above were chosen to have a broad range and substantially higher reactivity relative to the norbornenyl, vinyl, and cinnamate functional groups incorporated in the CTAs. In addition, the reaction conditions were optimized to minimize the undesirable polymerization or chain transfer involving the norbornenyl, vinyl, and cinnamate groups by utilizing a high initial monomer to CTA ratio as well as maintaining a relatively low monomer conversion.

Synthesis of Norbornenyl Macromonomers. The homopolymerization of styrene (Sty), methyl methacrylate (MMA), and methyl acrylate (MA) was carried out in the presence of **3** under typical homogeneous RAFT conditions. The polymerizations were performed in benzene at 65 °C using AIBN as a radical initiator. The specific conditions utilized for each monomer system are detailed in Table 1. A point of interest in the preparation of the macromonomers presented in the present work is determining the extent of involvement of the functional group (i.e., norbornene, vinyl, or cinnamate) in the RAFT polymerization process. In the case of **3**, the copolymerization of the norbornenyl group with styrene, MMA, or MA could lead to either linear polymer chains of approximately twice the MW if reinitiation did not occur from the polymerized norbornenyl site or a branched structure if reinitiation and propagation were to occur at the norbornenyl site. Both of these pathways would undoubtedly lead to an uncontrolled M_n and a broadened molecular weight distribution (PDI). In this regard, we investigated the extent of reactivity of the norbornenyl group under the RAFT conditions employed for each macromonomer system by monitoring the kinetic profiles of each system. Aliquots were taken from the reaction vessel at specific time intervals to monitor the monomer conversion vs time and the evolution of M_n and PDI as a function of monomer conversion.

An initially high monomer to CTA ratio (styrene, [M]:[CTA] 600:1; MMA, [M]:[CTA] 600:1; MA, [M]:[CTA] 500:1) was employed in these reactions to minimize the unwanted occurrence of norbornenyl copolymerization. The GPC chromatograms for each monomer polymerized in the presence of **3** are shown in Figure 3. For (a) NB−PS and (b) NB−PMMA, the chromatograms were observed to be narrow and unimodal. However, in the case of NB−PMA, as conversion increased a high-MW shoulder was observed with a peak molecular weight (M_p) approximately twice that of the M_p of the majority product, suggesting that a small portion of the norbornenyl group copolymerizes with the MA monomer. This result is further discussed below. As shown in Figure 4a, all three macromonomers, (■) NB−PS, (○) NB−PMMA, and (Δ) NB−PMA, showed characteristics of a well-controlled polymerization with a constant radical concentration as indicated by the linearity between $\ln([M]_0/[M])$ and the time of polymerization. The controlled nature of the polymerization is further demonstrated by the linear increase in M_n vs conversion shown in Figure 4b for (■) NB−PS, (○) NB−PMMA, and (Δ) NB−PMA. A deviation from linearity was observed in the case of NB−PMA at higher conversions (>40%), again indicating some copolymerization or termination events involving the norbornenyl group, although the contribution of other side reactions or termination events cannot be neglected. The deviation in linearity is also reflected as an increase in the PDI of the NB−PMA rising to ∼1.5 at 50% conversion. This result is in contrast to the NB−PS and the NB−PMMA systems, which maintain a PDI of ≤1.2 at 27.7% and 41.5% conversion, respectively. Furthermore, an excellent agreement between the experimentally determined M_n (GPC) and the theoretical M_n was observed, indicating the norbornenyl group on **3** remains essentially intact over the course of the reaction.

Synthesis of Vinyl-Terminated Macromonomers. The same approach was employed to evaluate the effectiveness of **4** to yield well-defined vinyl macromonomers. Similar results were obtained for the synthesis of the vinyl-terminated macromonomers under similar conditions as the norbornenyl system. The specific conditions are summarized in Table 2. Figure 5 shows the GPC chromatograms for (a) styrene, (b) MMA, and (c) MA as polymerized using **4** as the chain transfer agent. The results resemble those obtained for the norbornenyl macromonomers with V−PS and V−PMMA yielding narrow and unimodal molecular weight distributions within the range of conversions investigated. For methyl acrylate, the GPC exhibited narrow and unimodal distributions at conversions less than 24%;

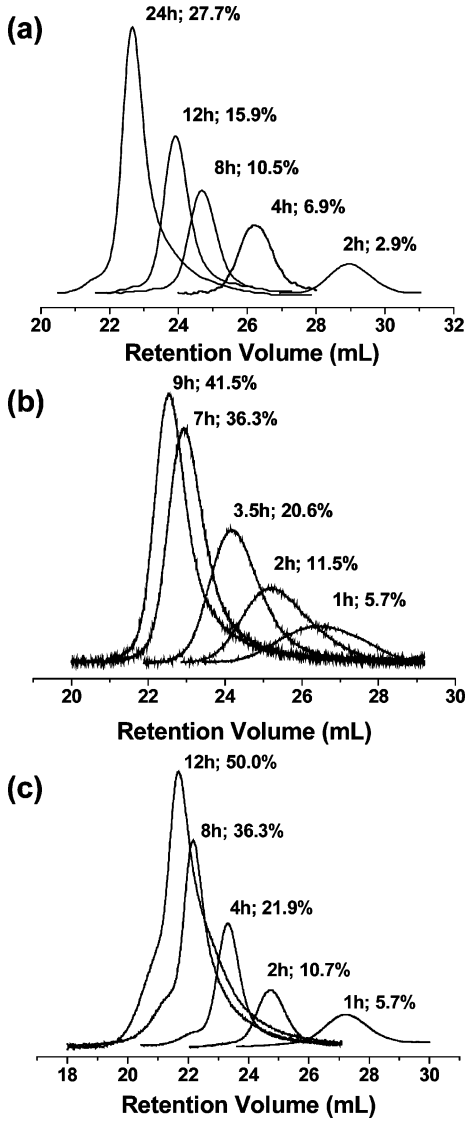

Figure 3. Gel permeation chromatograms collected over time for (a) NB−PS, (b) NB−PMMA, and (c) NB−PMA. The chromatograms are scaled according to the observed conversion.

thereafter, a high molecular weight shoulder was observed with an M_p, indicating a molecular weight approximately twice that of the major product as shown in the inset in Figure 5c. This shoulder might be attributed to the copolymerization of the vinyl functional group with methyl acrylate. The results of the kinetic analysis for styrene, MMA, and MA in the presence of **4** are shown in Figure 6. Figure 6a shows the pseudo-first-order kinetic plots for each monomer, indicating a constant radical concentration throughout the polymerization characteristic of a well-controlled polymerization. Excellent control over the polymer chain growth is evident by the linear increase in M_n as a function of conversion and the close agreement between the experimental and theoretical M_n values in the case of each monomer as shown in Figure 6b. The molecular weight distribution remained low (<1.25) for styrene and MMA, whereas the PDI for MA gradually increased with conversion up to 1.41. This increase was observed in conjunction with the appearance of the high-MW shoulder in the GPC chromatograms. The same observation was documented for the NB−PMA macromonomers. However, it is worth noting that well-defined V−PMA macromonomers were obtained for molecular weights up to ~10K by carefully controlling the conversion. This MW range is typical for the preparation of graft copolymers

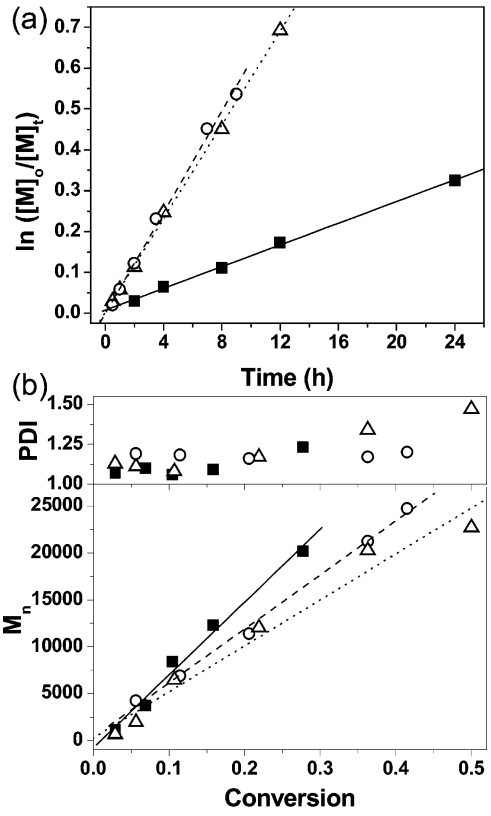

Figure 4. (a) Kinetic plots and (b) evolution of molecular weight and PDI with conversion, respectively, for the polymerization of styrene (■; linear fit, —), MMA (○; linear fit, - - -), and MA (△; linear fit, ···) in the presence of **3**.

since the reactivity of the vinyl end group has been shown to be deficient for larger MWs.

Synthesis of α-Functionalized Cinnamyl Telechelics. Although not thought of as a macromonomer, the cinnamyl-functionalized telechelics are an interesting class of photoreactive end-functionalized polymers. The cinnamyl functionality has been extensively employed as polymer pendant groups for photolithography applications and as a method for photoinduced stabilization of polymer nanostructures based on the well-known [2 + 2] cycloaddition reaction common to this class of compounds.[32] However, few examples have demonstrated the synthesis of cinnamate-functionalized telechelics,[36,37,42] and to our knowledge, none have been prepared directly by controlled radical polymerization techniques. It would be expected that cinnamate esters exhibit a low reactivity toward radical polymerization in light of the fact that 1,2-disubstituted alkenes generally function poorly as monomers in free radical polymerization.[43] However, a few examples have been reported in which cinnamate esters were shown to undergo polymerization both by thermal and radical initiation.[44,45] More recently, Esen and co-workers reported the copolymerization of a cinnamate ester derivative with styrene and methyl methacrylate. Furthermore, Colombani et al. have employed cinnamate derivatives as chain transfer agents in the polymerization of styrene, butyl acrylate, and MMA. These examples seem to complicate the process of obtaining well-defined telechelics due to the possibility of copolymerization and competitive chain-transfer activity in the RAFT technique.In order to probe the extent of reactivity of the cinnamyl-functionalized CTA (**5**) and its ability to yield well-defined polymers, a similar approach was adopted as described for **3** and **4**. The GPC chromatograms taken of the crude reaction mixtures over time for the polymerization of styrene, MMA, and MA in the presence of **5** are shown in Figure

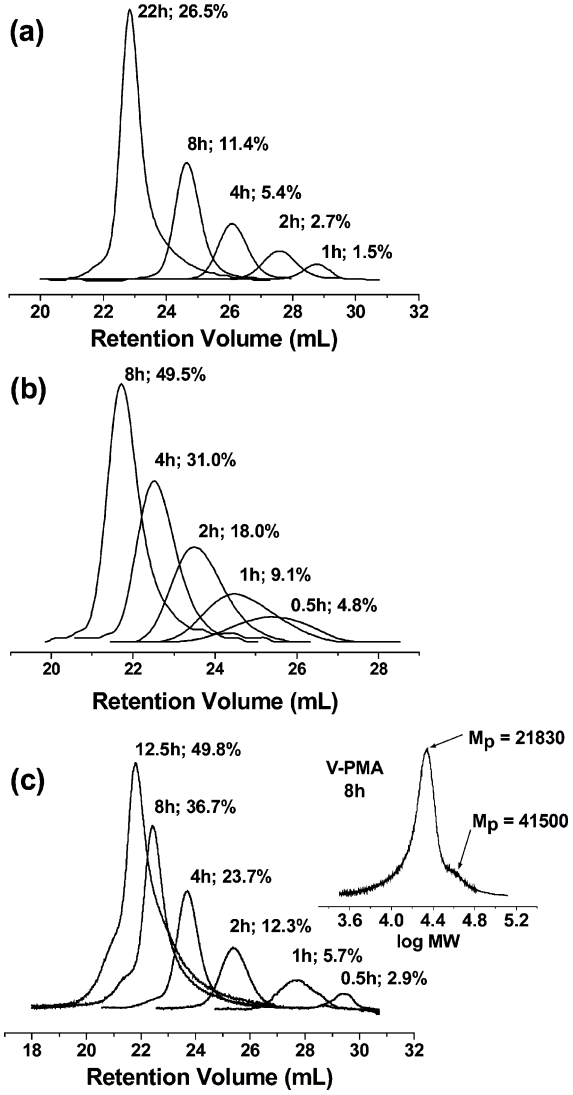

Figure 5. Gel permeation chromatograms collected over time for (a) V−PS, (b) V−PMMA, and (c) V−PMA. The chromatograms are scaled according to the observed conversions. The MW values shown in the (c) inset indicate the peak MW values.

7, a, b, and c, respectively. The polymerization of styrene in the presence of **5** initially showed a narrow and unimodal molecular weight distribution, but quickly developed a high-MW shoulder even at conversions as low as ~7%. At higher conversions, a distinguishable high-MW product was observed with a peak molecular weight (M_p 50 850) twice that of the major product (M_p 25 330) as indicated in the inset of Figure 7a. This higher molecular weight product could be due to chain transfer to the cinnamate functionality yielding a linear chain if propagation does not occur at the resulting radical site. However, if propagation occurs, a branched product could be obtained. Interestingly, the polymerization of MMA in the presence of **5** showed a unimodal molecular weight distribution for the entire range of conversions studied (up to 50%). This result is in contrast to the MA case that gave bimodal distributions at relatively low conversions (16%) and showed a more significant reactivity of the cinnamate functional group. Again, the high molecular weight product showed an M_p (47 320) approximately twice that of the major product (M_p 25 620) observed by GPC (inset Figure 7c). The variation in the polymerization behavior of these three monomers in the presence of **5** might be explained in terms of the ability of the various propagating radicals to undergo chain transfer with the

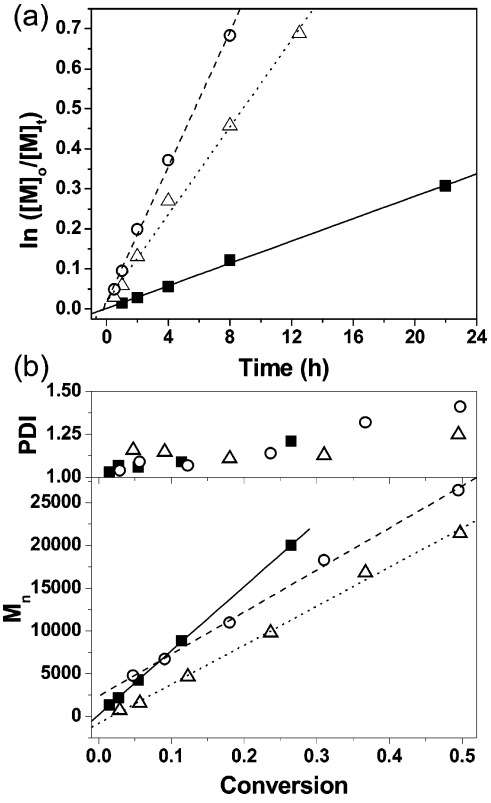

Figure 6. (a) Kinetic plots and (b) evolution of molecular weight and PDI with conversion, respectively, for the polymerization of styrene (■; linear fit, —), MMA (○; linear fit, - - -), and MA (△; linear fit, ···) in the presence of **4**.

Table 3. Results and Conditions for the Polymerization of Sty, MMA, and MA in the Presence of 5

CTA polymer	time (h)	% conv[a]	$M_{n,GPC}$[b]	$M_{n,theory}$[c]	PDI
C−PS[d]	0.75	1.46	1180	1400	1.03
	2	3.40	2400	2600	1.07
	4	6.59	4810	4600	1.08
	8	12.7	9260	8430	1.13
	21	27.9	20600	17900	1.35
C−PMMA[e]	0.5	5.66	4360	3880	1.19
	1	10.7	6520	6910	1.17
	2	19.4	10500	12100	1.15
	4	33.8	18300	20770	1.14
	6	43.8	22900	26800	1.14
	8	48.2	24450	29400	1.16
C−PMA[f]	0.5	3.85	855	2140	1.07
	1	6.54	2080	3300	1.11
	2	16.0	5230	7350	1.10
	4	25.9	11340	11600	1.22
	8	37.9	19600	16790	1.48
	12.5	41.2	21650	18200	1.54

[a] Conversion determined by RI response for Sty and by NMR for MMA and MA. [b] Calculated using OmniSec software vs PS or PMMA standards. [c] $M_{n,theory}$ = [M]/[CTA] × conv × MW_M + MW_{CTA}. [d] Sty 4.53 M, [M]:[CTA], 600:1; [CTA]:[I], 5:1; 65 °C. [e] MMA 5.83 M, [M]:[CTA], 600:1; [CTA]:[I], 1.9:1; 65 °C. [f] MA 5.68 M, [M]:[CTA], 500:1; [CTA]:[I], 2.1:1; 65 °C

cinnamate functionality. On the basis of the *Q* and *e* values for these monomers, a sensible trend cannot be established. Solely on the basis of reactivity ratios, it would be expected that the order of reactivity (chain transfer or copolymerization) with the cinnamate functionality would increase following the trend MA > MMA > styrene. However, the expected order was not observed. A better explanation can be made in terms of steric hindrance of the polymeric propagating radicals where the degree of hindrance follows the trend MMA > styrene > MA.

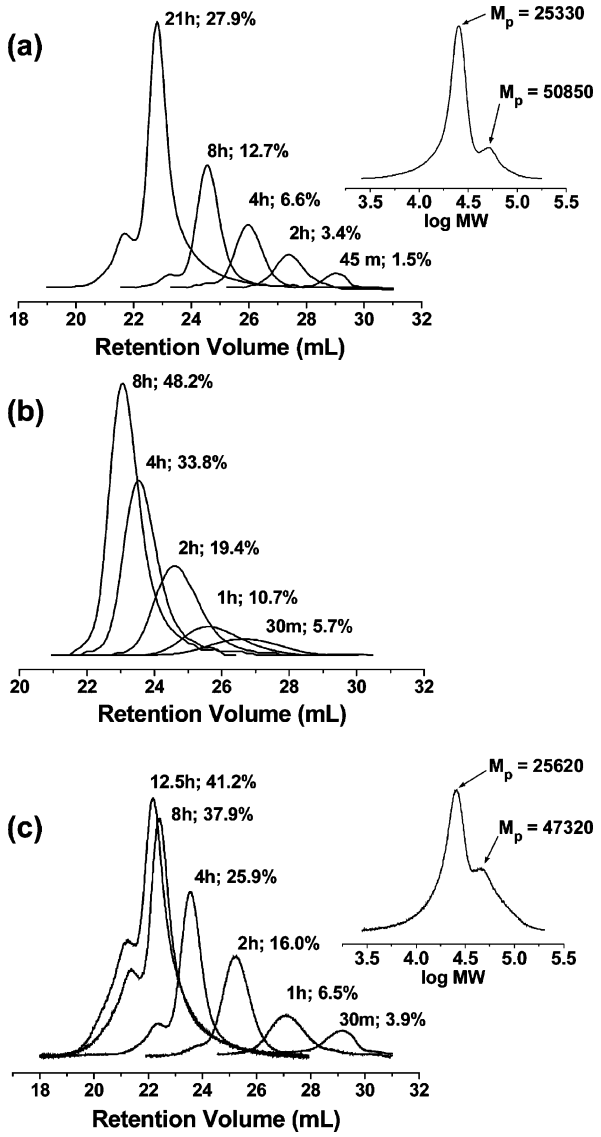

Figure 7. Gel permeation chromatograms collected over time for (a) C−PS, (b) C−PMMA, and (c) C−PMA. The chromatograms are scaled according to the observed conversions. The MW values shown in the insets indicate the peak MW values.

This could explain the absence of chain transfer (or copolymerization) to the cinnamate group in the case of MMA, while styrene and MA show greater reactivity depending on the bulkiness of the propagating radical. A similar trend was reported by Colombani et al.,[46] in which MMA showed the lowest chain transfer constant to ethyl cinnamate derivatives.

The trends observed in the GPC chromatograms correlate well with the kinetic profiles of the three monomers in the presence of **5**. Figure 8a shows the pseudo-first-order kinetic plots for styrene (■), MMA (○), and MA (△). The plots for styrene and MMA exhibit a linear relationship between $\ln([M]_0/[M])$ and polymerization time, indicating a constant radical concentration over the course of the reaction. Apparently, the formation of the higher MW product observed in the GPC for styrene does not significantly alter the kinetic profile. MA, on the other hand, deviates from linearity at higher conversions suggesting a decrease in the radical concentration due to termination and/or side reactions that correlate with the significant presence of the high-MW side product observed by GPC. Similarly, the evolution of the M_n showed typical characteristics of a living polymerization indicated by the linear increase in molecular weight with conversion for styrene (■) and MMA (○) (Figure 8b). The presence of the high molecular weight product in the case of styrene is reflected as an increase in PDI (1.35) at higher conversions (>25%), although at conversions <15% well-defined telechelics are obtainable (PDI < 1.15). The polymerization of MMA/**5** yields well-defined telechelics over the course of the reaction evident by the low PDI (<1.20) and excellent agreement between the experimental and theoretical M_n values. In the case of MA (Figure 8b, △), the relationship of M_n vs conversion shows two regimes of linearity with an inflection point observed as a result of the high-MW product indicated by GPC analysis. Thereafter, the M_n values are skewed to the higher side of the theoretical M_n values. In addition, the PDI increases from ∼1.10 to 1.54 with the increasing contribution of the high-MW side product.

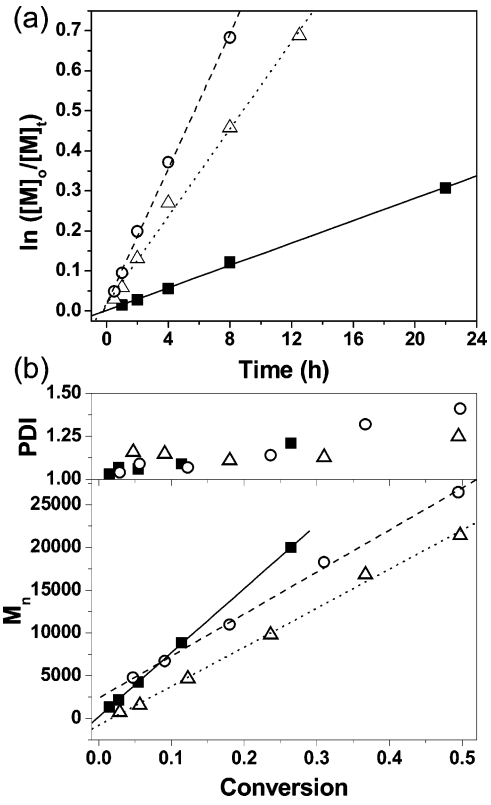

Figure 8. (a) Kinetic plots and (b) evolution of molecular weight and PDI with conversion, respectively, for the polymerization of styrene (■; linear fit, —), MMA (0; linear fit, - - -), and MA (△; linear fit, ···) in the presence of **5**.

Characterization of the Macromonomers and Telechelics. Theoretically, all of the PS, PMMA, and PMA macromonomers prepared in the presence of **3**, **4**, and **5** should be quantitatively α-terminated with norbornenyl, vinyl, and cinnamyl functional groups, respectively. In addition, the ω-terminal should carry the dithioester functionality originating from the CTA. These assumptions neglect the small portion of initiator-derived chain ends and other chain ends that might result from termination by disproportionation. The macromonomers were characterized by ^{1}H NMR in order to verify the proposed structure and to evaluate the degree of terminal functionality by end group analysis. Figure 9 shows the exemplary ^{1}H NMR spectra for the (a) NB−PMMA, (b) V−PMMA, and (c) C−PMMA macromonomers with the corresponding assignments.

In the case of NB−PMMA, the characteristic resonances of the norbornenyl alkene protons were observed at 5.9−6.2 ppm. Similarly, the vinylic protons were observed at 4.88−5.04 and 5.76−5.86 ppm for the vinyl-functionalized macromonomer. For the C−PMMA, the characteristic resonance peaks of the

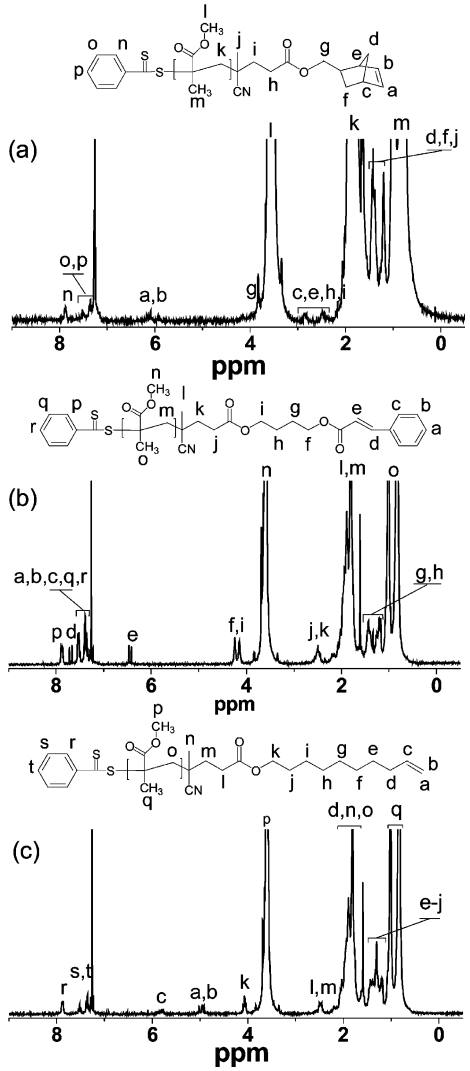

Figure 9. Exemplary ^{1}H NMR spectra of the macromonomers (a) NB−PMMA, 20.6% conversion; (b) V−PMMA, 4.8% conversion; and (c) C−PMMA, 5.7% conversion. Similar results were obtained for styrene and methyl acrylate.

cinnamyl alkene were detected as two doublets centered at 6.44 and 7.69 ppm, respectively. In addition, the aromatic protons attributed to the phenyl ring adjacent to the dithioester in the CTA could be clearly identified, indicating the presence of the RAFT end group. In each of these systems, the proton resonances of interest are well separated from all other peaks, allowing end group analysis to be performed. It should be noted that the accuracy of the end group analysis was limited by the poor signal-to-noise ratio of the obtained spectra. However, the results obtained for each macromonomer system show an excellent correlation between the M_n^{GPC} and the M_n^{NMR} (NB−PMMA: M_n^{GPC} 11 400, M_n^{NMR} 11 700; V−PMMA: M_n^{GPC} 4760, M_n^{NMR} 4900; C−PMMA, M_n^{GPC} 4360, M_n^{NMR} 4700), indicating quantitatively that one functional group was present per macromonomer chain. This was further confirmed by integrating the characteristic resonances of the α-phenyl and ω-(functional group) chain ends by which a close correlation was observed (assuming an error in integration of ∼5−6%). Similar results were obtained in the analysis of the PS and PMA macromonomers.

The thermal stability of the macromonomers was evaluated by TGA under a nitrogen atmosphere. Cheng and co-workers recently reported an improvement in the thermal stability of norbornenyl macromonomers (prepared by ATRP) with increasing NB content (i.e., low M_n), which was attributed to a thermally induced radical polymerization of the norbornene moieties.[27] This observation was contradictory to the fact that a higher molecular weight polymer typically shows improved thermal properties. In contrast, we observed deterioration in the thermal stability for the low-MW analogues in the case of all macromonomers investigated in the current work. The TGA profiles for the (a) NB−PMMA, (b) V−PMMA, and (c) C−PMMA macromonomers are shown in Figure 10. For comparison, two molecular weights were evaluated for each macromonomer with corresponding variations in the functional group content.

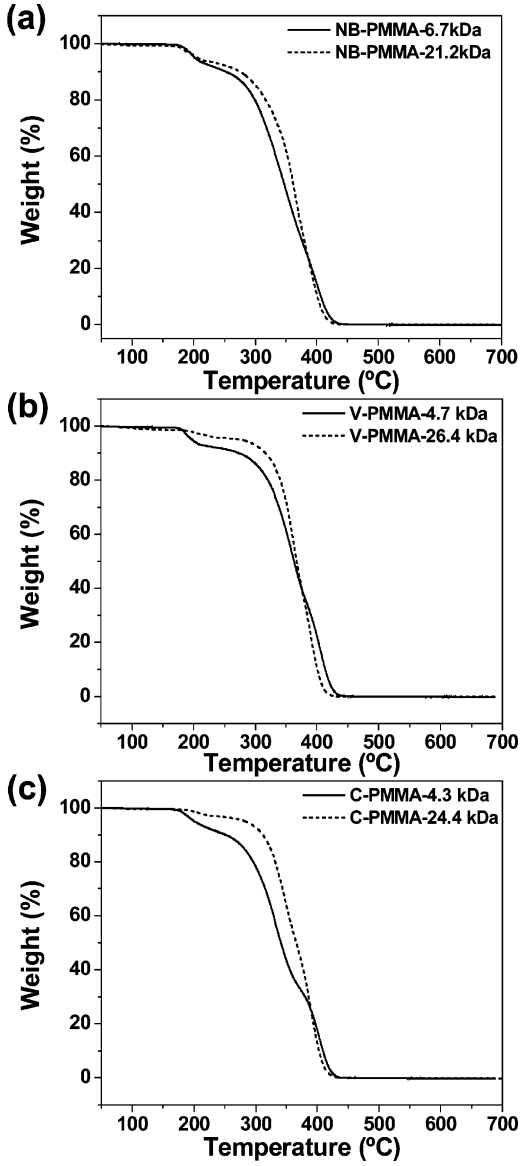

Figure 10. TGA thermolytic profiles for (a) NB−PMMA (M_n^{GPC} = 21.2 kDa, 0.59 wt % NB: $T_{d,20}$ = 317 °C, $T_{d,50}$ = 362 °C; M_n^{GPC} = 6.7 kDa, 1.84 wt % NB: $T_{d,20}$ = 299 °C, $T_{d,50}$ = 348 °C); (b) V−PMMA (M_n^{GPC} = 26.4 kDa, 0.47 wt % V: $T_{d,20}$ = 340 °C, $T_{d,50}$ = 367 °C; M_n^{GPC} = 4.7 kDa, 2.6 wt % V: $T_{d,20}$ = 320 °C, $T_{d,50}$ = 362 °C); (c) C−PMMA (M_n^{GPC} = 24.4 kDa, 0.51 wt % cinnamate: $T_{d,20}$ = 332 °C, $T_{d,50}$ = 366 °C; M_n^{GPC} = 4.3 kDa, 2.9 wt % cinnamate: $T_{d,20}$ = 296 °C, $T_{d,50}$ = 341 °C). $T_{d,50}$ and $T_{d,20}$ represent the temperature at 50% and 20% weight loss.

In each system, a minor degradation was observed at an onset temperature of ∼160 °C that is likely due to the presence of the thermally labile dithioester end group resulting from the RAFT process. From these results, it can be concluded that an increase in the functional group content has little effect on

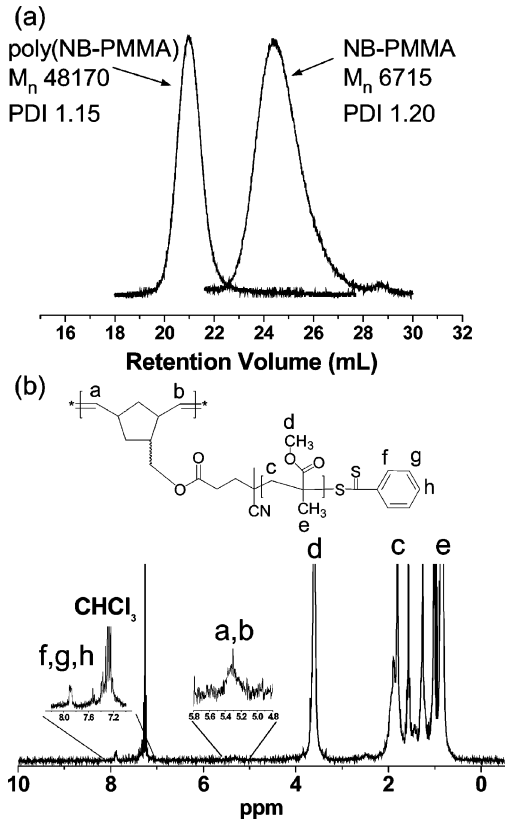

Figure 11. GPC chromatogram for a (a) NB−PMMA (M_n 6715) macromonomer and the resulting graft copolymer (M_n = 48 170) prepared by ROMP. (b) ^{1}H NMR spectrum of the poly(NB-*g*-PMMA) copolymer confirming the incorporation of the macromonomer into the final graft copolymer.

improving the thermal stability of the macromonomers. In the present study, it appears that the molecular weight of the polymer is the dominant factor in determining the decomposition temperature. Interestingly, we did observe a small improvement in the thermal stability toward the end of the decomposition for the lower MW analogues indicated by the higher temperature at 90% weight loss. This observation is presumably due to some occurrence of thermally induced cross-linking of the functional end groups.

Polymerization of the Macromonomers. In order to demonstrate the utility of these macromonomers for linear polymerization, we carried out ring-opening metathesis polymerization (ROMP) on the norbornene macromonomer system. Depending on the graft length and degree of polymerization, the macromonomers may adapt various conformations in solution including comblike and bottle-brush structures.[47−49] As an example, we prepared a poly(norbornene-*g*-PMMA) copolymer from a norbornene-functionalized PMMA macromonomer (M_n 6715) with Grubb's first generation catalyst ($RuCl_2$(=CHPh)-(PCy_3)$_2$) using standard ROMP conditions.[50] We chose to target a low degree of polymerization (DP = 8) to avoid steric hindrance effects which have been reported in the ROMP of norbornenyl macromonomers of modest MW.[47] Figure 11a shows the GPC chromatograms of the NB−PMMA macromonomer and of the resulting graft copolymer (poly(NB−PMMA)). Under these conditions, near-quantitative conversion was obtained, and a good agreement between the target M_n and the experimental M_n^{GPC} (48 170, PDI 1.15) was observed, indicating a well-controlled polymerization. A minute amount of the starting macromonomer could be observed in the crude GPC, although this was easily removed by careful precipitation. ^{1}H NMR confirmed the structure of the graft copolymer by the observation of a broad peak at 5.3 ppm due to the protons of the double bond in the ring-opened polymer backbone. The characteristic resonances of the PMMA graft were also identified as shown in Figure 11b. In addition, the presence of the RAFT derived end group was confirmed by the observation of the aromatic protons of the CTA phenyl ring. As such, the graft copolymer shown here could further act as a macroCTA in subsequent RAFT polymerizations.

Conclusions

A new and versatile approach for the synthesis of α-functionalized norbornenyl, vinyl, and cinnamyl macromonomers by reversible addition−fragmentation chain transfer polymerization has been demonstrated on the basis of the use of functional chain transfer agents. This synthetic method was employed for the preparation of various homopolymer macromonomers with near-quantitative incorporation of the polymerizable moieties. In the case of the norbornenyl and vinyl CTAs, polymerization of monomers with a high reactivity, such as styrene and MMA, yielded well-defined linear macromonomers whereas monomers with a lower reactivity (MA) exhibited a broader polydispersity attributed to copolymerization or bimolecular coupling between the propagating polymer and the α-functional group. However, it should be noted that well-defined structures could be prepared in all cases at low conversions. The cinnamyl-functionalized telechelics proved the most challenging due to a competitive chain transfer between the cinnamyl group and the RAFT CTA at higher conversions. The degree to which the unwanted side product occurred seems dependent on the bulkiness of the propagating radical rather than its reactivity. In addition, each of the macromonomers prepared by the current technique carries the dithioester moiety at the ω-termini and, therefore, can further serve as macro-chain-transfer agents for preparation of block copolymer macromonomers. To demonstrate the macromonomer applicability, we synthesized a poly(norbornene-*g*-PMMA) copolymer based on the ROMP polymerization of the norbornenyl-functionalized PMMA macromonomer. Thus, the advantage of this new approach lies in the ability to prepare a variety of macromonomer structures utilizing the mild and tolerant conditions of RAFT polymerization. Furthermore, a generalized approach can be envisioned on the basis of the current methodology and made available by facile modifications of the functional chain transfer agents.

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