

Supporting information for
**Synthesis of Double-Bonds-Containing Diblock
Copolymers via RAFT Polymerization**

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Experimental Section

Materials

Methyl acrylate (MA, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over CaCl₂ and distilled twice under reduced pressure prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from anhydrous ethanol. Phenol (97%, Aladdin), 3-bromopropyne (Aladdin, 97%), potassium *tert*-butylate (*t*-BuOK, Aladdin, 97%), potassium carbonate (K₂CO₃, Aladdin, 98%), 4-dimethylaminopyridine (DMAP, 97%, Aladdin), *N,N'*-dicyclohexylcarbodiimide (DCC, 97%, Aladdin) and poly(ethylene glycol methyl ether) (PEG-OH, $M_n = 2,000$ g/mol, TCI) were used as received. 1,4-Dioxane (99.5%, J&K), *N,N*-dimethylformamide (DMF, 99.5%, J&K), toluene (99.5%, J&K), tetrahydrofuran (THF, 99.5%, J&K) and dichloromethane (DCM, 99.5%, J&K) were distilled from sodium and benzophenone under Ar prior to use.

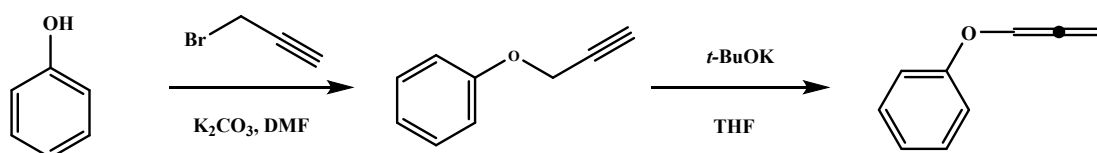
Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FTIR spectrophotometer with a 4 cm⁻¹ resolution. All ¹H and ¹³C NMR analyses were performed on a JEOL resonance ECZ 400S spectrometer (400 MHz) in CDCl₃. Tetramethylsilane (TMS) and CDCl₃ were used as internal standards for ¹H and ¹³C NMR, respectively. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters

1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000), and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μm). GPC measurements were carried out at 35°C using THF as eluent with a flow rate of 1.0 mL·min⁻¹. The system was calibrated with linear polystyrene standards. GC analyses were performed on a Shimadzu GC-2014 spectrometer with a flame ionization detector (FID).

Synthesis of phenoxyallene

Phenoxyallene (POA) was synthesized from phenol as shown in Scheme S1.



Scheme S1. Synthesis of phenoxyallene.

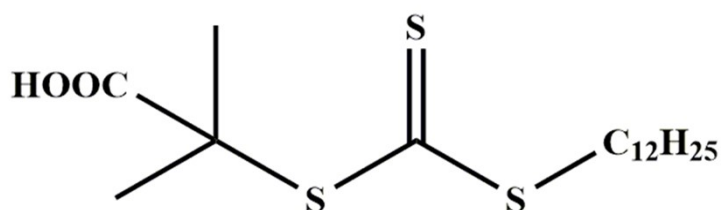
Phenol (20.2 g, 214 mmol), 3-bromopropyne (30.6 g, 257 mmol), K₂CO₃ (77.0 g, 557 mmol) and DMF (250 mL) were firstly added to a 500 mL flask under Ar followed by stirring at room temperature for 24 h. Subsequently, water (50 mL) was added and the resulting mixture was extracted with diethyl ether (150 mL×4) followed by drying over anhydrous Na₂SO₄. After concentration, the residue was purified by flash chromatography (silica gel column, eluent: ethyl acetate/*n*-hexane (v:v = 1:100)) to give phenyl propargyl ether (22.4 g, 79.2%) as a colorless liquid. ¹H NMR: δ (ppm): 7.34 (d, 3H, *J* = 13.0 Hz), 6.99 (t, 2H, *J* = 8.6 Hz), 4.69 (s, 2H), 2.51 (s, 1H). ¹³C NMR: δ (ppm): 157.6, 129.3, 121.3, 115.1, 78.5, 75.5, 55.8.

The as-prepared phenyl propargyl ether (22.4 g, 170 mmol) *t*-BuOK (9.5 g, 85

mmol) and THF (300 mL) were firstly added to a 500 mL flask under Ar at 0°C. The mixture was stirred at room temperature for 36 h followed by filtration over a pad of celite. The celite was washed with dry THF several times. After concentration, the crude product was purified by flash chromatography (silica gel column, eluent: *n*-hexane) to afford phenoxyallene (9.5 g, 42.3%) as a colorless liquid. ¹H NMR: δ (ppm): 7.32 (d, 3H, $J = 13.0$ Hz), 7.07 (d, 2H, $J = 10.5$ Hz), 6.85 (dd, 1H, $J = 21.2$ Hz), 5.45 (s, 2H). ¹³C NMR: δ (ppm): 202.6, 157.1, 129.7, 122.8, 118.1, 116.7, 89.9.

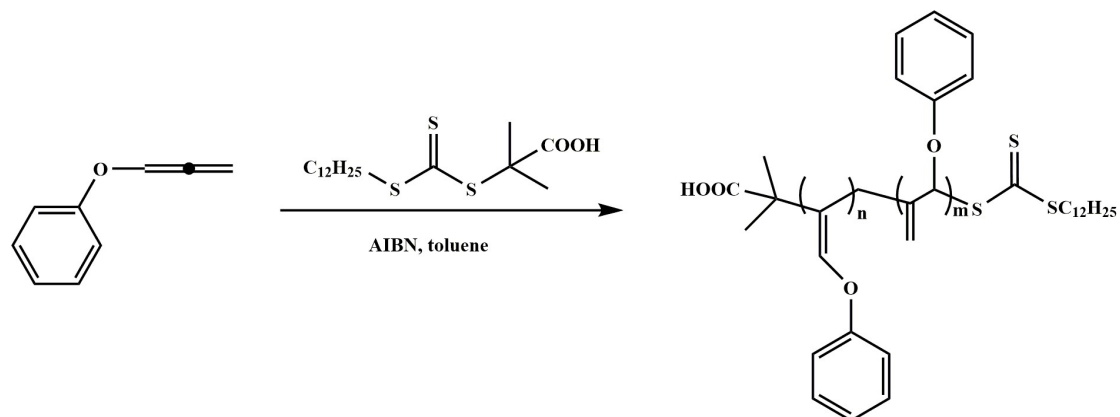
Synthesis of chain transfer agents

Chain transfer agent (CTA) was synthesized according to a previous literature¹ as shown in Scheme S2.



Scheme S2. Chain transfer agent used in RAFT polymerization of phenoxyallene.

RAFT homopolymerization of POA



Scheme S3. RAFT homopolymerization of phenoxyallene.

In a typical procedure, AIBN (7.3 mg, 0.044 mmol), POA (1.03 g, 7.8 mmol) and 2-(dodecylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (47.3 mg, 0.13 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N₂. Next, dry toluene (2.0 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. The polymerization lasted 16 h and it was terminated by putting the flask into liquid N₂. The reaction mixture was precipitated into *n*-hexane. The crude product was purified by repeated dissolution in THF and precipitation in *n*-hexane followed by drying *in vacuo* overnight to give 0.29 g of polyphenoxyallene (PPOA) as a yellow solid. GPC: $M_{n, \text{GPC}} = 4,200$ g/mol, $M_w/M_n = 1.26$. FT-IR: ν (cm⁻¹): 3445 (-COOH), 3062, 3038, 2927, 1780 (C=O), 1639, 1593 (-CH=CH₂), 1491, 1445, 1225, 894, 752, 690. ¹H NMR: δ (ppm): 7.38-6.44 (5H, C₆H₅ and 1H \times n, C=CHOC₆H₅), 5.30-4.48 (2H \times m, CH₂=CCHO and 1H \times m, CH₂=CCHO), 3.32 (2H, SCH₂(CH₂)₁₀CH₃), 3.00-1.99 (2H \times n, =C-CH₂), 1.86 (2H, SCH₂CH₂(CH₂)₉CH₃ and 6H, SC(CH₃)₂CO₂), 1.26 (18H, SCH₂CH₂(CH₂)₉CH₃), 0.88 (3H, SCH₂CH₂(CH₂)₉CH₃). ¹³C NMR: δ (ppm): 158.1, 155.8, 129.6, 122.8, 120.9, 115.4, 73.9, 34.8, 32.0, 29.6, 22.7, 13.9.

The “absolute” molecular weight was determined by ¹H NMR: $M_{n, \text{NMR}} = 4,600$ g/mol, $DP_{\text{POA}} = 35$. The composition of 1,2- and 2,3-polymerized repeat unit was evaluated according to eq 1 ($S_{(c+f)}$: the integration area at 7.38-6.44 ppm, $S_{(b+d)}$: the

integration area at 5.30-4.48 ppm; m: 2,3-polymerized repeat unit, n: 1,2-polymerized repeat unit) (Figure S1) and the ratio of $S_{(c+f)}$ to $S_{(b+d)}$ was 13.6. Thus, the resulting PPOA homopolymer obtained from RAFT polymerization consisted of 14.3% of 1,2-polymerized units and 85.7% of 2,3-polymerized units ($m = 5$, $n = 30$).

$$S_{(c+f)}/S_{(b+d)} = [5(m+n) + n]/3m \quad (1)$$

Table S1. RAFT Homopolymerization of Phenoxyallene^a

[POA]/[CTA]	conv. ^b (%)	M_{theo}^c (g/mol)	$M_{n,\text{GPC}}^d$ (g/mol)	M_w/M_n^d	$M_{n,\text{NMR}}^e$ (g/mol)	n/m^e
60	65	5,000	4,200	1.26	4,600	6

^a Polymerization temperature: 60°C, polymerization time: 16 h, solvent: toluene (2 mL). ^b Measured by GC. ^c Calculated from the conversion of monomer. ^d Measured by GPC in THF at 35°C. ^e Obtained from ¹H NMR.

Table S2. Effect of Temperature on RAFT Homopolymerization of POA

entry	temperature (°C)	$M_{n,\text{GPC}}^a$ (g/mol)	M_w/M_n^a
1	60	4,200	1.26
2	70	3,900	1.39
3	80	4,200	1.41

^a Measured by GPC in THF at 35°C.

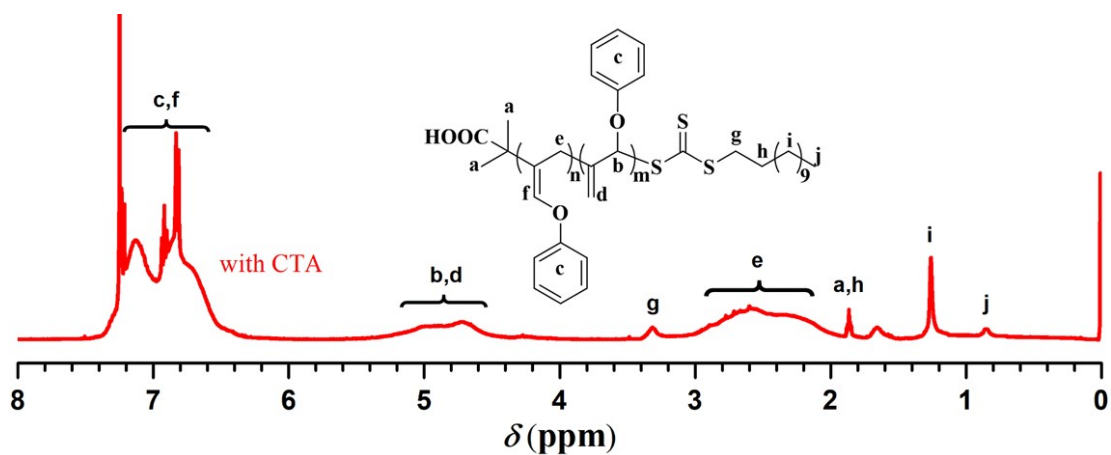


Figure S1. ^1H NMR spectrum of PPOA obtained in the presence of CTA in CDCl_3 .

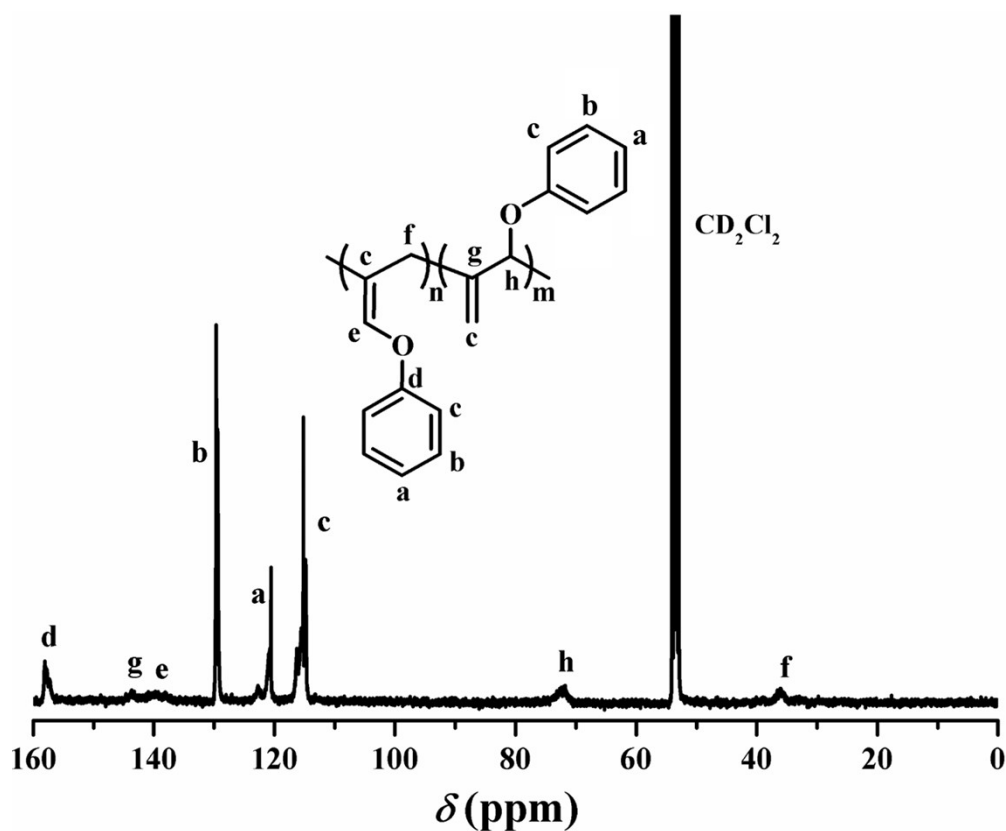


Figure S2. ^{13}C NMR spectrum of PPOA homopolymer in CD_2Cl_2 .

Kinetics of RAFT homopolymerization of POA

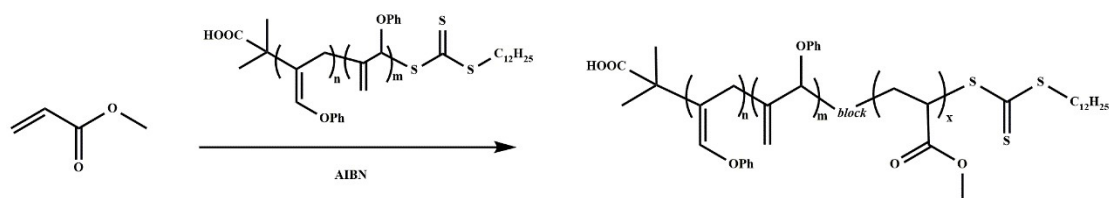
For kinetics study, AIBN (7.3 mg, 0.044 mmol), POA (1.03 g, 7.8 mmol) and 2-(dodecylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (47.3 mg, 0.13 mmol)

were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N₂. Next, dry toluene (2.0 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. At appropriate time intervals, 0.10 mL of aliquots were removed from the reaction mixture and added to 1.00 mL of acetone for terminating the reaction. The quenched solution in acetone taken at different time interval was injected into GC to determine the conversion of POA compared to the time = 0 data point. The remaining solution was used for GPC measurement to determine the molecular weight and molecular weight distribution.

RAFT block copolymerization of MA using PPOA-CTA

PPOA-*b*-PMA diblock copolymer was synthesized by RAFT block copolymerization of MA mediated by PPOA-CTA in toluene (Scheme S4). PPOA (0.20 g, 0.045 mmol, $M_{n, GPC} = 4,400$ g/mol, $M_w/M_n = 1.20$, $M_{n, NMR} = 4,100$ g/mol), AIBN (2.4 mg, 0.015 mmol) and methyl acrylate (0.234 mL, 2.58 mmol) were first added to a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N₂. Next, dry toluene (1.0 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. After 24 h, the polymerization was terminated by immersing the flask into liquid N₂. Toluene was then evaporated under reduced pressure and the crude product was

purified by dissolving in THF and precipitating in methanol three times followed by drying *in vacuo* overnight to give 325 mg of PPOA-*b*-PMA as a white solid. GPC: $M_{n,GPC} = 5,800$ g/mol, $M_w/M_n = 1.39$. FT-IR: ν (cm^{-1}): 3518, 3050, 2920, 1725, 1656, 1443, 1240, 1161. ^1H NMR (CDCl_3): δ (ppm): 7.51-6.26 (5H, C_6H_5 and $1\text{H} \times m$, $\text{C}=\text{CHOC}_6\text{H}_5$), 5.58-4.46 (2H, $\text{CH}_2=\text{CCHO}$ and 1H, $\text{CH}_2=\text{CCHO}$), 3.61 (3H, $-\text{OCH}_3$), 3.46 (2H, $\text{SCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 2.81-2.21 (2H, $=\text{C}-\text{CH}_2$ and 1H, CH_2CH), 1.95-0.74 (2H, CH_2CH ; 23H, $-\text{SCH}_2\text{C}_{11}\text{H}_{23}$ and 6H, $\text{C}(\text{CH}_3)_2\text{CO}_2$).



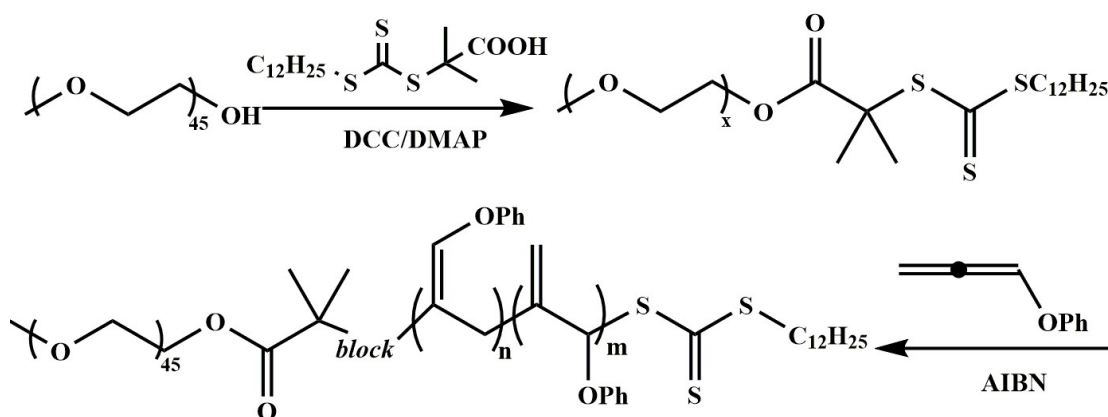
Scheme S4. RAFT block copolymerization of methyl acrylate using PPOA-CTA.

RAFT block copolymerization of POA using PEG-CTA

PEG-OH (2.5 g, 1.25 mmol), 2-(dodecylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (0.95 g, 2.6 mmol) and anhydrous DCM (20 mL) were added to a dry flask under N_2 . Next, a solution of DMAP (0.032 g, 0.26 mmol) and DCC (0.53 g, 2.6 mmol) in anhydrous DCM (10 mL) was added dropwise at 0°C . The esterification reaction lasted 48 h at room temperature. After rotary concentration, the mixture was precipitated by cold diethyl ether. The crude product was purified by flash chromatography (eluent: chloroform/methanol, v:v = 95:5) followed by drying *in vacuo* at 45°C overnight, affording PEG-CTA (2.71 g, 89.7%) as a yellow powder. ^1H NMR: δ (ppm): 4.25 (2H, CO_2CH_2), 3.64 (4H, OCH_2CH_2), 3.25 (2H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.73 (2H, $\text{SCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.68 (6H, $\text{SC}(\text{CH}_3)_2\text{CO}_2$),

1.24 (18H, SCH₂CH₂(CH₂)₉CH₃), 0.86 (3H, SCH₂CH₂(CH₂)₉CH₃).

PEG-*b*-PPOA diblock copolymer was synthesized by RAFT block copolymerization of POA mediated by PEG-CTA in DMF (Scheme S5). POA (2.98 g, 22.5 mmol), AIBN (2.4 mg, 0.015 mmol) and PEG-CTA (106.3 mg, 0.045 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N₂. Next, dry DMF (5.0 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. At appropriate time intervals, 0.10 mL of aliquots was removed from the reaction mixture and added to 1.00 mL of cold methanol for terminating the reaction. The solution was used for GPC measurement to determine the molecular weight and molecular weight distribution of PEG-*b*-PPOA diblock copolymer as summarized in Table S3. ¹H NMR: δ (ppm): 7.30-6.37 (5H, C₆H₅ and 1H×n, C=CHOC₆H₅), 5.15-4.44 (2H×m, CH₂=CCHO and 1H×m, CH₂=CCHO), 3.63 (4H×45, OCH₂CH₂), 3.00-1.98 (2H×n, =C-CH₂), 1.84 (2H, SCH₂CH₂(CH₂)₉CH₃ and 6H, SC(CH₃)₂CO₂), 1.53 (20H, SCH₂(CH₂)₁₀CH₃), 1.24 (18H, SCH₂CH₂(CH₂)₉CH₃), 0.87 (3H, SCH₂(CH₂)₁₀CH₃).



Scheme S5. RAFT block copolymerization of phenoxyallene using PEG-CTA.

Table S3. Synthesis of PEG-*b*-PPOA Diblock Copolymer^a

time (h)	$M_{n, \text{GPC}}^b$ (g/mol)	M_w/M_n^b
0.5	5,000	1.05
1.0	5,400	1.07
2.0	6,000	1.09
3.0	6,900	1.15
4.0	7,500	1.20
6.0	8,000	1.25
8.0	8,500	1.24
24.0	13,000	1.32

^a [POA] : [PEG-CTA] : [AIBN] = 1500 : 3 : 1, polymerization temperature: 60°C. ^b

Measured by GPC in THF at 35°C.

References

1. Lai, J. T.; Filla, D.; Shea, R. Functional polymers from novel carboxyl-terminated trithiocarbonates as highly efficient RAFT agents. *Macromolecules* **2002**, *35*, 6754-6756.