8808 *Macromolecules* **2004,** *37,* 8808−8811

One-Pot, One-Catalyst Synthesis of Graft Copolymers by Controlled ROMP and ATRP Polymerizations

Richard Charvet and Bruce M. Novak*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695

Received April 19, 2004
Revised Manuscript Received August 13, 2004

Introduction

Because of tremendous progress made in the development of living and stereoselective polymerization processes,[1] complex polymeric molecules with well-defined architectures[2] can now be readily prepared. This provides avenues to obtaining precise structure−property relationships and engineer materials with new and controllable properties. Of the various architectures known, graft copolymers are attractive materials for a wide range of applications[3] due to their numerous structural variables that can be modified. A common route to well-defined graft copolymers relies on macromonomer polymerization that initially requires the preparation of a well-defined polymeric chain functionalized at one end by a polymerizable monomer.[4] To simplify the overall preparation procedure, a one-step approach would be desirable. Here we report the first example of a one-pot synthesis of graft copolymers based on a metathesis skeleton with poly(methyl methacrylate) (PMMA) grafts using a single catalyst.

Experimental Section

General Procedures and Characterizations. All manipulations involving air- and moisture-sensitive compounds were carried out under an atomosphere of prepurified nitrogen using standard Schlenk techniques. ^{1}H NMR spectra were obtained at 300 MHz with a GE NMR Omega spectrometer and at 300 and 400 MHz with Varian-Mercury NMR spectrometers. Infrared spectra were obtained using a Jasco FT/IR-410 spectrometer as thin films on NaCl disks or neat samples between NaCl disks and are uncalibrated. IR data are reported in units of wavenumber (cm^{-1}) for characteristic peaks. Before sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 0.05 Torr). Column chromatography was carried out with Selecto Scientific 63-200 mesh silica gel. Molecular weight and molecular weight distribution were measured via gel permeation chromatography using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector. The stationary phase consisted of two PL-Gel mixed C columns. Chloroform was used as the mobile phase. Molecular weights are relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.). Thermal analyses were performed using Hi-Res TGA 2950 and DSC 2920 TA instruments using a nitrogen purge and heating/cooling rates of 10 °C/min. Elemental analyses were performed by Atlantic Microlab, Inc. Toluene and CH_2Cl_2 were used for polymerization reactions, and reactions with air- and moisture-sensitive materials were purified by passing through one column filled with activated A2 Alumina catalyst and one column filled with activated Q5 copper catalyst under a nitrogen atmosphere (MBraun solvent system). $CDCl_3$ was dried over CaH_2, distilled under nitrogen, and after three freeze−pump−thaw cycles stored into the drybox and used no more than 1 month later. Toluene-d_8 was dried over CaH_2, distilled trap-to-trap after three freeze−pump−thaw cycles, and stored into the drybox. Naphthalene used as a reference in the ^{1}H NMR kinetic experiments was purified by sublimation and stored in the drybox. DPTS was prepared according to the literature.[5] MMA was dried over CaH_2 and stored in the fridge under nitrogen after three freeze−pump−thaw cycles. A small amount was transferred to a Schlenk tube by trap-to-trap distillation, put in the drybox, and used immediately.

7,8-*N*-4-Hydroxyphenylsuccinimide *endo*-Tricyclo[4.2.2.0^{2,5}]deca-3,9-diene. To 1,3,5,7-cyclooctatetraene (1.04 g, 0.01 mol) under N_2 was added *N*-4-hydroxyphenyl maleimide[6] (1.89 g, 0.01 mol), and the resulting neat mixture was progressively heated with an oil bath. At 140 °C, the maleimide had not melted so 1.5 mL of chlorobenzene was added, and the reaction mixture was heated at 170 °C for 1 h, during which crystallization occurred in the flask. After cooling, the mixture was dried under vacuum and the resulting beige solid washed with hexane and dried under vacuum. Recrystallization with ethyl acetate yielded a white duvetlike solid (1.75 g, 60%). This compound is not soluble in $CHCl_3$, partially soluble in acetone, and soluble in THF and DMSO. ^{1}H NMR (DMSO-d_6) δ: 9.72 (s, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 5.92 (s, 2H), 5.91 (s, 2H), 3.04 (s, 2H), 2.99 (s, 2H), 2.85 (s, 2H). ^{13}C {^{1}H} NMR δ: 178.12, 157.27, 138.03, 128.20, 128.09, 123.42, 115.39, 43.60, 42.79, 36.59.

7,8-*N*-(4-(2-Bromo-2-methylpropionic acid)phenyl ester)succinimide *endo*-Tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (1). To 7,8-*N*-4-hydroxyphenylsuccinimide *endo*-tricyclo[4.2.2.0^{2,5}]-deca-3,9-diene (1 mmol, 293.1 mg), 2 bromo-2 methylpropionic acid (1.04 mmol, 173.6 mg), and DPTS (0.2 mmol, 64 mg) dissolved in dry THF (16 mL) was added DCC (1.25 mmol, 258 mg), and the mixture was stirred at room temperature for 24 h. The solution was then filtered and concentrated. The desired compound (200 mg, 46%) was recovered as a white crystalline solid after silica gel column chromatography (hexane/ethyl acetate, 1/1). ^{1}H NMR ($CDCl_3$) δ: 7.28 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 6.02 (m, 2H), 5.93 (s, 2H), 3.28 (bs, 2H), 2.97 (s, 2H), 2.89 (s, 2H), 2.07 (s, 6H). ^{13}C {^{1}H} NMR δ: 177.83, 169.96, 150.53, 138.18, 129.84, 128.64, 127.79, 121.86, 55.39, 44.23, 43.52, 37.18, 30.73. IR 3041, 2955, 2901, 1754, 1698, 1506, 1400, 1290, 1264, 1235, 1188, 1158, 1136, 1103, 878, 789, 732, 684. Anal. Calcd for $C_{22}H_{20}O_4NBr$: C, 59.74; H, 4.56; N, 3.17. Found: C, 60.09; H, 4.56; N, 3.23.

7,8-*N*-4-(11-Hydroxyundecyl-1-oxy)phenylsuccinimide *endo*-Tricyclo[4.2.2.0^{2,5}]deca-3,9-diene. 7,8-*N*-4-Hydroxyphenylsuccinimide *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (490 mg, 1.67 mmol) was dissolved with acetone (26 mL), and the solution was degassed with N_2 for 15 min. K_2CO_3 (820 mg, 5.85 mmol) and 18-crown-6 (12 mg) were then added, and the mixture was degassed again. 11-Bromo-1-undecanol (504 mg, 2.0 mmol) was added, and the mixture was heated to reflux. The reaction was monitored using ^{1}H NMR ($CDCl_3$/DMSO-d_6 and $CDCl_3$) by following the disappearance of the aromatic phenol (δ = 6.80 ppm, doublet) and appearance of the aromatic phenol ether (δ = 7.08 ppm, doublet). After 64 h, the starting phenol derivative had been completely consumed. After cooling, the reaction mixture was filtered. It was dissolved with CH_2Cl_2 and washed with 0.5 N HCl and water until neutral pH. After drying with $MgSO_4$ and concentration, a white solid was obtained (680 mg). The excess of 11-bromo-1-undecanol was removed by washing the crude powder with hexane. After drying, a pure fine white powder was obtained (572 mg, 74%). ^{1}H NMR δ: 7.08 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.01 (m, 2H), 5.92 (s, 2H), 3.95 (t, J = 6.4 Hz, 2H), 3.64 (t, J = 6.4 Hz, 2H), 3.27 (s, 2H), 2.94 (s, 2H), 2.87 (s, 2H), 1.77 (m, 2H), 1.57 (m, 2H), 1.44 (m, 2H), 1.30 (m, 12H). ^{13}C {^{1}H} NMR δ: 178.36, 159.17, 138.09, 128.51, 127.83, 127.78, 115.03, 68.29, 63.03, 44.21, 43.39, 37.09, 32.85, 29.65, 29.59, 29.57, 29.50, 29.39, 29.21, 26.05, 25.84. IR: 3382 (br), 3050, 3019, 2924, 2851, 1768, 1714, 1699, 1608, 1514, 1470, 1251, 1183,

---

* Corresponding author: e-mail novak@chemdept.chem.ncsu.edu.

10.1021/ma049244k CCC: $27.50

1047, 839, 821, 791, 739, 718. Anal. Calcd for $C_{29}H_{37}NO_4$: C, 75.13; H, 8.04; N, 3.02. Found: C, 74.44; H, 8.13; N, 2.99.

7,8-*N*-4-(11-(2-Bromo-2-methylpropionic acid)undecyl ester-1-oxy)phenylsuccinimide *endo*-Tricyclo[4.2.2.0^{2,5}]-deca-3,9-diene (2). To 7,8-*N*-4-(11-hydroxyundecyl-1-oxy)-phenylsuccinimide *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (0.43 mmol, 200 mg), 2-bromo-2-methylpropionic acid (0.45 mmol, 75 mg), and DPTS (0.09 mmol, 28 mg) dissolved in dry CH_2Cl_2 (4 mL) was added DCC (0.54 mmol, 114 mg), and the mixture was stirred at room temperature for 24 h. The solution was then filtered and concentrated. The desired compound (200 mg, 46%) was recovered as a white crystalline solid after silica gel column chromatography (hexane/ethyl acetate, 1/1). ^1H NMR ($CDCl_3$) δ: 7.08 (d, $J = 8.8$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 6.00 (m, 2H), 5.92 (s, 2H), 4.17 (t, $J = 6.6$ Hz, 2H), 3.95 (t, $J = 6.6$ Hz, 2H), 3.27 (bs, 2H), 2.94 (s, 2H), 2.87 (s, 2H), 1.94 (s, 6H), 1.77 (m, 2H), 1.69 (m, 2H), 1.5−1.3 (m, 14H). ^{13}C {^1H} NMR δ: 178.33, 171.88, 159.21, 128.14, 128.56, 127.82, 124.42, 115.07, 68.32, 66.31, 56.19, 44.25, 43.44, 37.13, 30.93, 29.64, 29.59, 29.47, 29.29, 29.27, 28.47, 26.12, 25.91. IR 3041, 2921, 2851, 1733, 1713, 1698, 1607, 1514, 1467, 1388, 1253, 1182, 1165, 1108, 838, 821, 791, 716, 682. Anal. Calcd for $C_{33}H_{42}O_5NBr$: C, 64.70; H, 6.91; N, 2.29. Found: C, 64.47; H, 7.01; N, 2.33.

Preparation of a 20-mer Polymer from 1 with Ru-I. To **1** (0.067 mmol, 29.8 mg) in CH_2Cl_2 (0.3 mL) was added a CH_2Cl_2 solution (0.140 mL) of **Ru-I** (3.4 μmol, 2.8 mg), and the mixture was stirred at room temperature for 16 h. After quenching with a few drops of ethyl vinyl ether and stirring for 1 h, the solution was added dropwise to 75 mL of methanol. After centrifugation and several washing with methanol, the polymer was recovered as a white powder (quantitative yield). ^1H NMR ($CDCl_3$) δ: 7.15 (m, 4H), 6.50, 6.39 (m, 2H), 5.29, 5.20 (m, 2H), 3.39, 3.29, 3.06, 2.80 (m, 6H), 2.07 (s, 6H). GPC: $M_n = 6943$, PDI = 1.12. DSC: $T_g = 37.1$ °C.

Preparation of a 20-mer Polymer from 2 with Ru-I. To **2** (0.052 mmol, 31.7 mg) in CH_2Cl_2 (0.25 mL) was added a CH_2Cl_2 solution (0.10 mL) of **Ru-I** (2.45 μmol, 2.0 mg), and the mixture was stirred at room temperature for 16 h. After quenching with a few drops of ethyl vinyl ether and stirring for 1 h, the solution was added dropwise to 75 mL of methanol. After centrifugation and several washing with methanol, the polymer was recovered as a white powder (quantitative yield). ^1H NMR ($CDCl_3$) δ: 6.98, 6.83 (m, 4H), 6.50, 6.37 (m, 2H), 5.25, 5.17 (m, 2H), 4.17 (t, $J = 6.6$ Hz, 2H), 3.92 (m, 2H), 3.31, 3.25, 3.03 (m, 6H), 1.93 (s, 6H), 1.77 (m, 2H), 1.68 (m, 2H), 1.43, 1.31 (m, 14H). GPC: $M_n = 11\,770$, PDI = 1.14.

General Procedure for the Copolymerization of 1 (or 2) with MMA Using Ru-I. To the desired ATRP initiator dissolved in toluene in a screw-cap vial equipped with a stirring bar was added the desired amount of freshly distilled MMA with a syringe. To the stirred mixture a monomer was then added to an aliquot of a freshly prepared toluene solution of **Ru-I** at room temperature. The vial was taken out of the drybox, sealed with Parafilm, and place in a preheated giggler with a temperature set at 65 °C. After 24 h, the vial was cooled to room temperature. The visquous solution was diluted with a few drops of CH_2Cl_2 and added dropwise to a methanol solution under vigorous stirring. After centrifugation and several washing with methanol, the polymer was dried under high vacuum at 40 °C for 12 h and recovered as a white filament-like solid.

Preparation of Poly(2-*co*-3)-*graft*-PMMA Polymers. The desired amounts of **2** and **3** were dissolved with toluene in a screw-cap vial. To this solution was added an aliquot of a freshly prepared toluene solution of **Ru-I**. The conditions were adjusted so that [**2**] = 0.1 M and [**2**]/[**Ru-I** = 20. After a complete copolymerization as indicated by the ^1H NMR analysis of a quenched aliquot (13 h, overnight), freshly distilled MMA was added via a syringe to the yellow slightly visquous copolymer solution ([MMA]/[**2**] = 40). The vial was taken out of the drybox, sealed with Parafilm, and place in a preheated giggler with a temperature set at 65 °C. After 30 h, the vial was cooled to room temperature. The orange viscous solution was diluted with a few drops of CH_2Cl_2 and added dropwise to a methanol solution under vigorous stirring. After centrifugation and several washing with methanol, the polymer was dried under high vacuum at 40 °C for 12 h and recovered as a white fibrous solid. GPC data (for **2**:**3** = 1:3.1; yield: 68%): ROMP copolymer (aliquot) $M_n = 26\,000$, PDI = 1.12; poly(**2**-*co*-**3**)-*graft*-PMMA $M_n = 81\,000$, PDI = 1.62.

Determination of the Kinetics of the Copolymerization by ^{1}H NMR. In a vial were mixed **2** (15.4 mg, 25.1 μmol), MMA (105 μL, 0.98 mmol), and naphthalene (4.7 mg). The mixture was diluted with 420 μL of toluene-d_8 and transferred with a pipet in a NMR tube equipped with a Teflon valve. To this mixture was then added 80 μL of a freshly prepared **Ru-I** stock solution (2.5 mg, 100 μL of toluene-d_8), and a timer was started. The NMR tube was rapidly taken out of the drybox and immersed in oil bath thermostated at 65 °C. At repeated intervals, the NMR tube was removed from the oil bath for ^1H NMR analysis. The conversion of MMA was measured by following the disappearance of the olefinic proton signal at 5.98 ppm vs the naphthalene reference signal at 7.6 ppm.

Results and Discussion

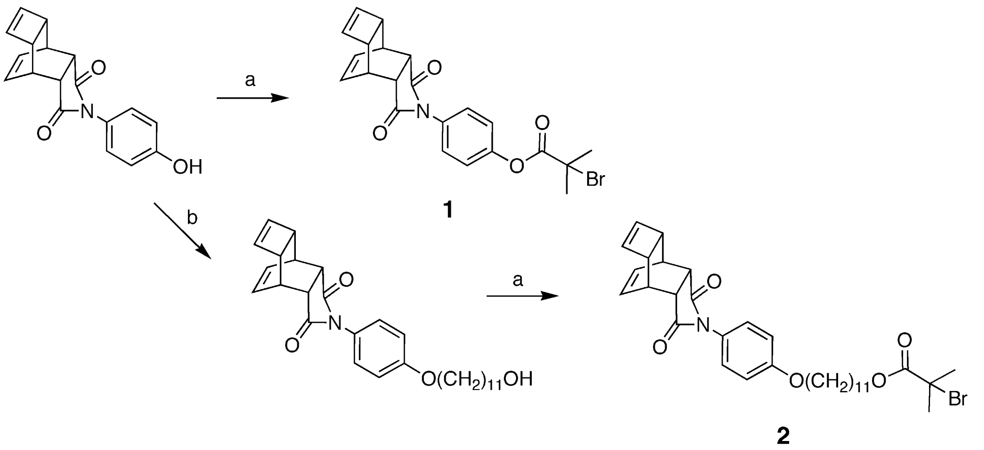
We previously reported the living ring-opening metathesis polymerization (ROMP) of cyclobutene derivatives based on the *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene structure with fused functionalized rings at the 7,8-positions using the Grubbs catalyst $Cl_2Ru(CHPh)(PCy_3)_2$ (**Ru-I**).[7] In the presence of an appropriate initiator, this catalyst has recently been shown to promote the controlled atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA).[8] Also, this unique specificity has then been used for the preparation of block copolymers, the ATRP initiator being incorporated on the ruthenium catalyst.[9] Inspired by these developments, we decided to functionalize our polycyclic monomer structure with an ATRP initiator and investigated the possible one-pot synthesis of graft copolymers with PMMA chains as the sidearms.

For our studies, we prepared two monomers functionalized with 2-bromo-2-methyl propionate, a common initiator for the ATRP of MMA with ruthenium-based promoters (Scheme 1).[8,10] Monomers **1** and **2** differ by the proximity of the initiator vis-à-vis the ROMP cyclic structure, a factor that could influence the polymerization kinetics as the consumption of MMA could be rapidly slowed down due to increased steric hindrance around the main polymer chain.

Both functionalized monomers could be polymerized in a controlled fashion using **Ru-I**, indicating that the introduced ATRP initiator was not interfering with the ROMP process. Narrow dispersity 20-mer samples (PDI = 1.12) were obtained in quantitative yields. Whereas no transition was observed by DSC analysis of poly-**2**, a low T_g (37°C) was present for poly-**1**. This turns out to be a unique characteristic among the 7,8-succinimide-*endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene ROMP polymers we have strudied: in no other cases has a T_g been observed. The T_g of poly-**1** proved to be a useful handle for the characterization of graft copolymers with a poly-**1** backbone. The ^1H NMR of both polymers show well-resolved resonances for the gem dimethyl groups of the 2-bromo-2-methyl propionate initiators at 2.07 and 1.93 ppm for poly-**1** and -**2**, respectively. These downfield shifts indicate that the electron-withdrawing bromine is still intact in both cases.

The polymerization of mixtures of the functionalized monomers **1** or **2** and MMA with **Ru-1** was investigated in toluene at 65 °C under a nitrogen atmosphere for 24 h. In all experiments, the solution initially turned from purple-pink—the color of the catalyst solution—to dark

Scheme 1. Monomer Synthesis[a]



[a] a: 2-bromo-2-methylpropionic acid, DCC, DPTS; b: 11-bromoundecanol, K_2CO_3.

Table 1. Selected Graft Polymerization Results[a]

entry	initiator (I)	[I] (M)	yield (%)	GPC data
1	**1**	0.04	70	M_n = 53600, PDI = 2.62
2	**1**	neat	66	bimodal M_w distribution
3	**2**	0.01	100	ROMP homopolymer only
4	**2**	0.05	88	M_n = 23800, PDI = 1.67
5	**2**	0.1	30	M_n = 27800, PDI = 1.80
6	**2**	0.15	53	M_n = 34000, PDI = 1.89
7	**2**	0.2		bimodal M_w distribution

[a] Conditions: toluene, 65 °C, N_2 atmosphere, 24 h, [**Ru-1**]:[I]:[MMA] = 1:20:800 (entry 1, 3, 5−7), 1:20:100 (entry 4), neat: 13.6 mg (I)/mL (MMA).

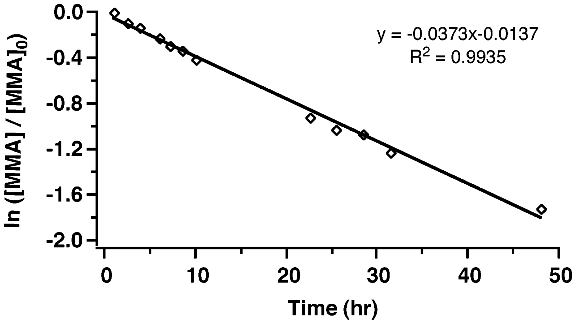


Figure 1. Logarithm plot of the kinetic data of the ATRP of MMA during a copolymerization with **2** and **Ru-I** (toluene-d_8, 65 °C, N_2 atmosphere, [**2**] = 0.05 M, [**Ru-1**]:[**2**]:[MMA] = 1:10:400).

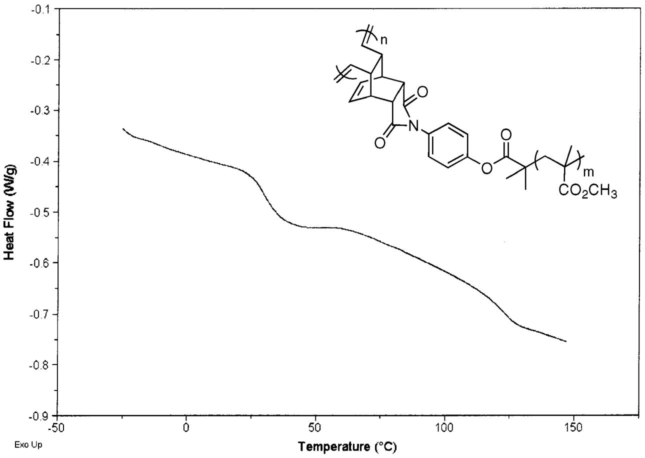


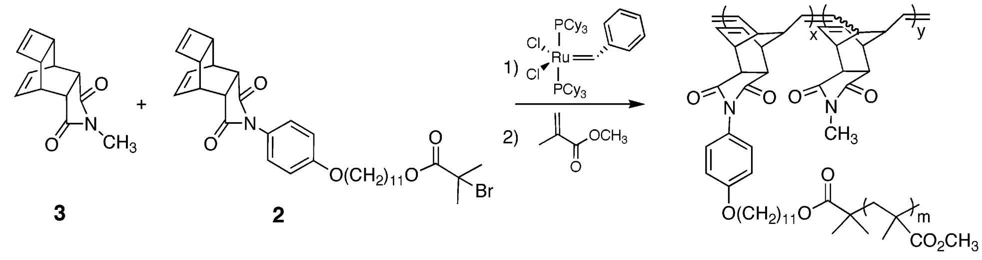
Figure 2. DSC thermogram of (poly-**1**)-*graft*-PMMA (entry 1 in Table 1).

yellow as is commonly observed for the ROMP of this type of functional monomer. With time, however, the color progressively became deep orange, and the viscosity increased dramatically. While the relative molecular weights measured by GPC do not really have meaning because the structure of a graft polymer substantially influences the hydrodynamic volume, no trace of the homo-ROMP or homo-PMMA polymers was present when the initiator concentration was at least 0.04 M (Table 1). Unfortunately, the use of **1** appeared to be unpractical due to its low solubility in toluene. Also, the neat copolymerization of **1** in MMA, a better solvent for **1**, led to a bimodal, polydisperse molecular weight distribution, possibly resulting from the coupling between polymer chains favored by the highly viscous reaction mixture. Compound **2** proved to be the monomer of choice to identify suitable experimental conditions. With 0.05 < [**2**] < 0.2 M ([**Ru-1**]:[**2**] = 20), grafting of PMMA on the partially unsaturated backbone occurred, as indicated by the ^{1}H NMR analysis of the isolated fibrous white solids (Figure S1) and the presence of a unique high molecular weight peak with a smooth Gaussian shape upon GPC analysis (Figure S3). The low yields indicate that the conversion of MMA is not complete after 24 h. With a [**Ru-1**]:[**2**]:[MMA] ratio of 1:20:100, i.e., a small initiator:MMA ratio of 5, a high conversion was obtained within 24 h as confirmed by ^{1}H NMR analysis of the isolated polymer in $CDCl_3$ (4.4 MMA units per unit of **2**, 88% yield).

To better characterize this system, the copolymerization was followed using ^{1}H NMR. While the ROMP process was complete in less than 30 min, the ATRP of MMA had barely started. Followed over 48 h using naphthalene as an internal reference, the MMA consumption was found to be a first-order kinetic process (Figure 1), which indicated the absence of chain termination, the major problem encountered in radical polymerizations. These data support that the ATRP of MMA with **2** as initiator and **Ru-I** as promotor is well-controlled.

^{1}H NMR and quantitative ^{13}C NMR analyses indicated that syndiotactic PMMA blocks had been synthesized (*rr*:*rm*:*mm* = 64:34:2), in agreement with previous synthesis of PMMA via ATRP with ruthenium-based promotors.[8a,10] The graft morphology of the prepared copolymers was evidenced by some differences observed in the ^{1}H NMR spectrum measured in different solvents. The copolymer is not as readily soluble in toluene as in

Scheme 2. One-Pot Synthesis of Poly(2-*co*-3)-*graft*-PMMA



chloroform, which certainly results from the insolubility of the ROMP-polymer backbone in toluene. Significant changes in the chemical shifts of the protons of the PMMA fragments are observed in toluene-d_8 compared to $CDCl_3$: the methylene (1.25 vs 1.02 ppm) and methyl protons (1.15 vs 0.81 ppm) are shifted downfield whereas the methoxy protons (3.30 vs 3.55 ppm) are shielded (Figure S2). Also, as the protons of the ROMP skeleton can hardly be observed, the copolymer may adopt a micelle-like morphology in solution, the ROMP backbone being segregated in the core.

In the DSC thermogram of the graft copolymers, the T_g of the PMMA blocks was present at 124 °C, confirming that syndiotactic blocks had been prepared.[11] While no other transition was seen for (poly-**2**)-*graft*-PMMA copolymers up to 150 °C, the T_g of the poly-**1** backbone could be seen at the lower value of 30 °C, suggesting that the PMMA fragments may behave as a plasticizer (Figure 2). As the glass transition temperatures of both blocks are seen, phase segregation certainly occurs.

The presented strategy was also applied to the preparation of partially grafted copolymers by copolymerizing **2** with a nonfunctionalized ROMP monomer, 7,8-methylsuccinimide-*endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene, **3**. First a random copolymer was prepared with various **2** and **3** contents, **3** being chosen for its good solubility in toluene and the simple ^{1}H NMR spectrum of the resulting polymer (Scheme 2). After 16 h, the copolymerization was complete as indicated by ^{1}H NMR analysis of an aliquot, and GPC analysis confirmed the formation of a well-defined copolymer. MMA was then added to the reaction mixture and heated at 65 °C for 30 h. A similar color change from yellow to orange was observed with time. PMMA grafts were generated as indicated by the ^{1}H NMR and GPC analysis of the isolated polymers. Once again, a Gaussian-type monomodale molecular weight distribution was obtained with no trace of the ROMP copolymer precursor (Figure S4). As the ROMP copolymer was prepared in 16 h, it is interesting to see that the ruthenium catalyst was still able to promote the ATRP of MMA after such a long time in solution. Furthermore, as the initiation for ROMP is complete,[12] this indicates that the active ROMP propagating species can promote ATRP.

In summary, we have presented an original one-pot synthesis approach for the preparation of graft copolymers based on a ROMP skeleton with PMMA grafts using a single catalyst. This methodology relies on the controlled activity of $Cl_2Ru(CHPh)(PCy_3)_2$ for two distinct polymerization processes with the selected monomer structures. As this practical approach can certainly be extended to other monomers suitable for controlled ROMP and ATRP polymerizations, a wide range of materials with tunable properties can be easily prepared.

Acknowledgment. The authors acknowledge financial support of this work from the NSF.

Supporting Information Available: Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Selected reviews: (a) Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT;* ACS Symp. Ser. Vol. 768; American Chemical Society: Washington, DC, 2000. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689. (c) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661. (d) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (e) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.

(2) See for example: (a) Lutz, J. F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986. (b) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747.

(3) (a) Breitenkamp, K.; Emrick, T. *J. Am. Chem. Soc.* **2003**, *125*, 12070. (b) Shinoda, H.; Miller, P. J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 3186.

(4) (a) Mishra, M. K., Ed. *Macromolecular Design: Concept and Practice-Macromonomers, Macroinitiators, etc.*; Polymer Frontier International: New York, 1994. (b) Schulz, G. O.; Milkovich, R. *J. Appl. Polym. Sci.* **1982**, *27*, 4773.

(5) Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65.

(6) Park, O. J.; Jang, S. H. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 723.

(7) (a) Charvet, R.; Novak, B. M. *Polym. Prepr.* **2002**, *43* (1), 728. (b) Charvet, R.; Novak, B. M. *Macromolecules* **2001**, *34*, 7680. (c) Charvet, R.; Novak, B. M. *Polym. Prepr.* **2001**, *42* (1), 496.

(8) (a) Simal, F.; Demonceau, A.; Noels, A. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 538. (b) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 5689.

(9) Bielawski, C. W.; Louie, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 12872.

(10) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* **1997**, *53*, 15445.

(11) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.

(12) Charvet, R. Ring-Opening Metathesis Polymerization of Functionalized Cyclobutene Derivatives. Ph.D. Dissertation, North Carolina State University, Raleigh, NC, 2002.

MA049244K