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Atom Transfer Radical Polymerization of Menthyl Acrylate

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ABSTRACT: Atom transfer radical polymerization (ATRP) of menthyl acrylate (MnA) was performed with different catalytic systems. ATRP of MnA proceeds in a controlled/living manner as evidenced by narrow polymer polydispersity ($<$1.20), but with a very slow polymerization rate using 1-phenylethyl bromide (1-PEBr) or ethyl 2-bromopropionate (2-EBP) as initiators (monomer/initiator = 100/1) and *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) as ligand. Only 5.7% and 14.8% monomer conversion were obtained within 4 h using 1-PEBr and 2-EBP, respectively. In contrast, replacing the PMDETA ligand with 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4cyclam) promotes a very fast but uncontrolled polymerization (97.1% conversion in 1 h with a polydispersity as broad as 1.70). However, a controlled/living polymerization system of MnA (with a relatively fast polymerization rate, 78.4% conversion in $^1/_2$ h; $M_n = 14\,000$ g/mol; $M_w/M_n = 1.11$) was achieved by using tris[2-(dimethylamino)ethyl]amine (Me_6TREN) as ligand. The controlled/living feature of this system allowed the chain extension polymerization of methyl acrylate (MA) to synthesize the block copolymer, poly(menthyl acrylate)-*block*-poly(methyl acrylate) [PMnA-*b*-PMA]. The thermal stability of PMnA was investigated by thermogravimetric analysis (TGA) and gas chromotography/mass spectrometry (GC/MS). The pyrolysis of PMnA (with the release of menthenes) provides an alternative route to synthesize poly(acrylic acid) with controlled structures from PMnA (prepared by ATRP of MnA).

Introduction

Controlled/living free radical polymerization has attracted much attention during the past 10 years because it provides access to polymeric materials with well-defined compositions and molecular weights, low polydispersities, and novel architectures. Typical living/controlled polymerizations include atom transfer radical polymerization (or metal-mediated living polymerization) (ATRP),[1−6] nitroxide-mediated polymerization,[7−12] reversible addition−fragmentation transfer polymerization,[13−17] and degenerative transfer polymerization,[18−22] all of which are based on establishing a rapid equilibration between the low concentration of propagating free radicals and a large amount of dormant species. Although a number of vinyl monomers have been polymerized by living/controlled free radical processes, there is no report concerning the polymerization of menthyl acrylate, possibly due to a very slow polymerization rate and the difficulty in synthesizing highly pure monomers.

More than 30 years ago Matsuzaki et al.[23−25] reported the polymerization of menthyl acrylate (MnA) using free radical and γ-radiation processes. For example, using benzoyl peroxide (BPO) as an initiator (with a molar ratio of MnA/BPO = 30/1), only 12% of MnA was converted to polymer at 60 °C after 5.5 h. The conversion of MnA was significantly improved and could reach up to 98% by γ-radiation polymerization within a wide temperature range but required a long reaction time ($>$20 h).

In this paper we report the ATRP of MnA (including the kinetic studies using different catalytic systems), the chain extension polymerization to synthesize the block copolymer poly(menthyl acrylate)-*block*-poly(methyl acrylate) [PMnA-*b*-PMA], and the thermal stability studies of PMnA.

Experimental Section

Materials. All chemicals and reagents were obtained from Aldrich unless stated otherwise. Acrylic acid (99%), (−)-menthol (99%), anisole (99.7%), CuBr (99.999%), and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4cyclam) (98%) were used as received. 1-Phenylethyl bromide (1-PEBr), ethyl 2-bromopropionate (2-EBP), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA), and methyl acrylate (MA, 99%) were vacuum-distilled from CaH_2 and stored in a freezer. Tris[2-(dimethylamino)ethyl]amine (Me_6-TREN) and menthyl acrylate were synthesized according to the literature procedures.[26,27] The unreacted menthol was carefully removed by repeated vacuum distillation until the characteristic peak at 3.40 ppm for free menthol was not observed in the ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$, ppm): 6.32 (d, H, CH_2=CH−), 6.18 (t, H, CH_2=*CH*−), 5.74 (d, H, CH_2=CH−), 4.68 (m, H, from menthyl group adjacent with ester group), 0.6−2.0 ppm (CH_3, CH_2, and CH from menthyl group).

Characterization. *Nuclear Magnetic Resonance*. ^{1}H NMR (500 MHz) spectra were recorded at room temperature on a Varian-500 spectrometer. $CDCl_3$ was used as the solvent. The chemical shifts were referenced relative to the solvent.

Gel Permeation Chromatography (GPC). Molecular weights and polydispersities were measured by an Agilent high-pressure liquid chromatography system consisting of two-column bed (PolyPore 7.5 × 300 mm and PolyPore Guard 7.5 × 50 mm columns with 5 μm bead size: 200−2000 000 g/mol), Agilent 1100 differential refractometer, and UV detector. GPC samples were run in THF at ambient temperature (using a flow rate of 1 mL/min) and calibrated with poly(methyl methacrylate) standards obtained from Polymer Laboratories Ltd. UK.

Thermogravimetric Analysis (TGA). The thermogravimetric analyses were performed on a Hi-Res TGA 2959 from TA Instruments, using helium as purge gas. Spectra were recorded from 50 to 500 °C with a heating rate of 10 °C/min.

Differential Scanning Calorimetry (DSC). Thermal analysis of polymer was conducted on a Perkin-Elmer DSC-7 operating from 25 to 300 °C with a heating rate of 20 °C/min. Thermal history differences were erased by reheating sample and recording a second DSC scan.

FT-IR Measurements. FT-IR spectra were obtained with 4 cm^{-1} resolution on a FT-IR 870 spectrometer (Thermo Nicolet). Polymer sample (fine powder, 30 mg) was mixed with KBr (100 mesh, 300 mg) and ground in an agate mortar until it became a uniform powder which was then pressed to form a pellet.

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Table 1. Atom Transfer Radical Polymerization of Menthyl Acrylate (MnA)[a]

run	initiator	ligand	MnA/initiator (molar ratio)	time (h)	conv[b] (%)	M_n[d]	PDI (M_w[e]/M_n)
1	1-PEBr	PMDETA	100	4.0	5.70	1900	1.14
2	2-EBP	PMDETA	100	4.0	14.8	n.d.	n.d.
3	2-EBP	PMDETA	100	7.0	30.2	5400	1.15
4	2-EBP	Me_4Cyclam	100	1.0	97.1	21000	1.70
5	1-PEBr	Me_4Cyclam	200	3.0	60.2	56000	2.18
6[c]	2-EBP	Me_6TREN	200	1.0	36.4	8600	1.06
7	2-EBP	Me_6TREN	200	0.5	67.9	16000	1.22
8	2-EBP	Me_6TREN	100	0.125	44.2	7500	1.07
9	2-EBP	Me_6TREN	100	0.5	78.4	14000	1.11

[a] Conditions: 95 °C; [CuBr] = [ligand] = [initiator] = 0.0474 M, 1-PEBr = 1-phenylethyl bromide, 2-EBP = ethyl 2-bromopropionate, PMDETA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine, Me_4Cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, Me_6TREN = tris[2-(dimethylamino)ethyl]amine, [b] Based on 500 MHz ^{1}H NMR. [c] 50 °C. [d] Number-average molecular weight. [e] Weight-average molecular weight.

Table 2. Atom Tranfer Radical Polymerization of Menthyl Acrylate (MnA) by 2-EBP/CuBr + $CuBr_2$/Me_4Cyclam[a]

run	$CuBr_2$/CuBr (molar ratio)	time (h)	conv[b] (%)	M_n[c]	PDI (M_w[d]/M_n)
1	0	1.0	97.1	21000	1.70
2	0.25	0.5	24.4	5600	1.34
3	0.25	1.0	54.7	6900	1.51
4	0.50	1.0	46.6	5100	1.33
5	0.50	4.0	63.7	10300	1.34
6	0.75	1.0	9.1	5600	1.40
7	1.0	2.0	0		

[a] Conditions: 80 °C, [CuBr] = [Me_4Cyclam] = [2-EBP] = 0.006 M, [MnA] = 0.600 M, 2-EBP = ethyl 2-bromopropionate, Me_4Cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. [b] Based on 500 MHz ^{1}H NMR. [c] Number-average molecular weight. [d] Weight-average molecular weight.

Pyrolysis−Gas Chromotography/Mass Spectrometry (GC/MS). A microfurnace pyrolyzer was directly attached to a gas chromotograph (Agilent 6890) equipped with a 5973N series mass selective detector and a high-resolution fused-silica capillary column (model no.: Agilent 122-5563, 0.25 mm i.d. × 60 m long) coated with immobilized dimethylsiloxane (1 μm thick). About 0.3 mg of the sample was pyrolyzed at 400 °C under a flow of helium carries gas (45 mL/min) which was reduced to 1.0 mL/min at the capillary column by a splitter. The GC column temperature was programmed from 50 to 290 °C at a rate of 25 °C/min and then held at 290 °C. The mass spectra were compared against the entire National Institute of Standards and Technology Mass Spectral Library for matches of greater than 90% similarity.

ATRP of Menthyl Acrylate. In a typical experiment (Table 1, run 8), a 20 mL glass vial was charged with anisole (5 mL), Me_6TREN (0.0546 g, 0.237 mmol), MnA (4.98 g, 23.7 mmol), and 2-EBP (0.0429 g, 0.237 mmol). The contents of the vial were then transferred to a 100 mL nitrogen-filled Schlenk flask containing CuBr (0.0340 g, 0.237 mmol). Three cycles of freeze−pump−thaw were used to degas the system. The flask was charged with N_2 at room temperature and then placed in an oil bath at 95 °C. Samples were taken out from the reaction mixture with a degassed syringe at the desired period for 500 MHz ^{1}H NMR and GPC analyses. The conversion was determined from the integration ratio of resonances at 2.30 ppm for the CH unit in polymer backbone and 6.18 ppm for the =CH unit in monomer (reaction time: 7.5 min; conversion: 44.2%; M_n: 7500; PDI: 1.07).

ATRP of Menthyl Acrylate by the 2-EBP/(CuBr + $CuBr_2$)/Me_4Cyclam System. In a typical experiment (Table 2, run 5), a 20 mL glass vial was charged with ethanol (10 mL), MnA (1.26 g, 6.00 mmol), and 2-EBP (0.0109 g, 0.0600 mmol). The contents of the vial were then transferred to a 100 mL nitrogen-filled Schlenk flask containing CuBr (8.61 mg, 0.0600 mmol) and $CuBr_2$ (6.70 mg, 0.0300 mmol). Three cycles of freeze−pump−thaw were used to degas the system. The flask was charged with N_2 at room temperature and then placed in an oil bath at 80 °C. Samples were taken out from the reaction mixture with a degassed syringe at the desired period for ^{1}H NMR and GPC analyses (reaction time: 4 h; conversion: 63.7%; M_n: 10 300; PDI: 1.34).

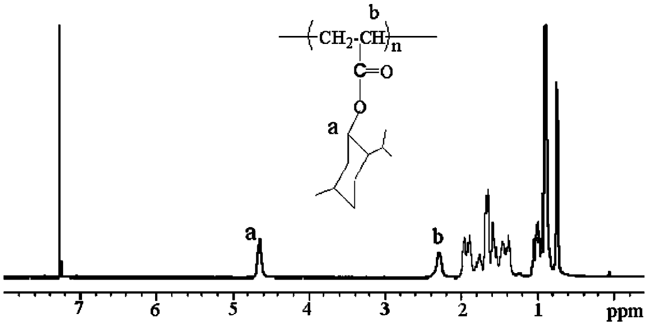

Figure 1. ^{1}H NMR (500 MHz) spectrum of poly(menthyl acrylate) prepared by 2-EBP/CuBr/Me_6TREN (conditions: 95 °C; [CuBr] = [Me_6TREN] = [2-EBP] = 0.0474 M, [menthyl acrylate] = 4.74 M, 2-EBP = ethyl 2-bromopropionate, Me_6TREN = tris[2-(dimethylamino)ethyl]amine).

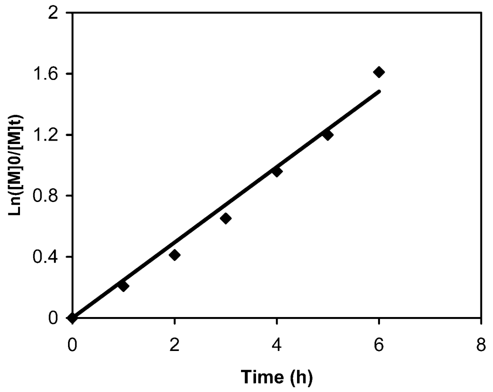

Figure 2. Kinetic plot of atom transfer radical polymerization of menthyl acrylate (MnA) by by 2-EBP/CuBr/PMDETA (conditions: 95 °C, [CuBr] = [PMDETA] = [2-EBP] = 0.0474 M, [MnA] = 2.37 M, 2-EBP = ethyl 2-bromopropionate, PMDETA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine).

Chain Extensions to Synthesize Poly(menthyl acrylate)-*block*-poly(methyl acrylate). A 100 mL Schlenk flask was charged with PMnA-Br (0.530 g, 0.150 mmol; M_n: 2300 g/mol; PDI: 1.15) solution in anisole (10 mL), CuBr (0.0210 g, 0.150 mmol), PMDETA (0.0250 g, 0.140 mmol), and MA (1.50 g, 17.4 mmol). Three cycles of freeze−pump−thaw were used to degas the system. The flask was charged with N_2 at room temperature and then placed in an oil bath at 90 °C. Samples were taken out from the reaction mixture with a degassed syringe at desired periods for GPC analyses (reaction time: 22 h; M_n: 4800; PDI: 1.10).

Results and Discussion

ATRP of Menthyl Acrylate. ATRP of MnA using 1-PEBr or 2-EBP as initiators (monomer/initiator = 100/1) and PMDETA as ligand showed controlled/living characteristics as evidenced by very narrow polydispersities (1.14 and 1.15), as

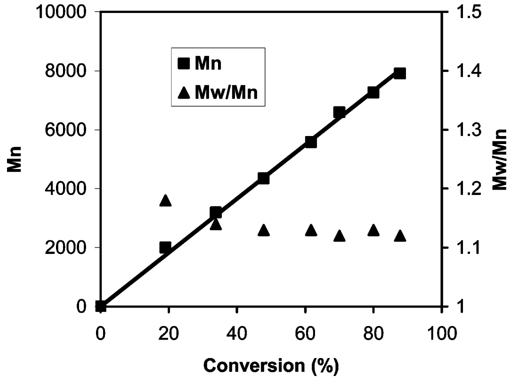

Figure 3. Dependence of number-average molecular weight (M_n) and polydispersity (M_w/M_n) on monomer conversion (conditions: 95 °C, [CuBr] = [PMDETA] = [2-EBP] = 0.0474 M, [menthyl acrylate] = 2.37 M, 2-EBP = ethyl 2-bromopropionate, PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine).

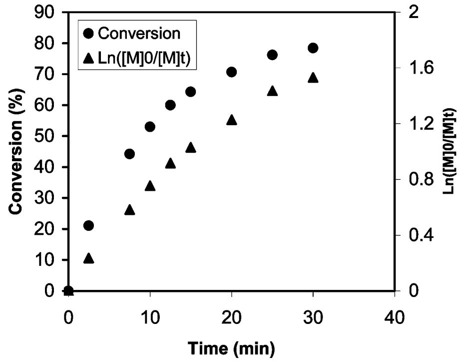

Figure 4. Kinetic plot of atom transfer radical polymerization of menthyl acrylate (MnA) by 2-EBP/CuBr/ Me_6TREN (conditions: 95 °C, [CuBr] = [Me_6TREN] = [2-EBP] = 0.0474 M, [MnA] = 4.74 M, 2-EBP = ethyl 2-bromopropionate, Me_6TREN = tris[2-(dimethylamino)ethyl]amine).

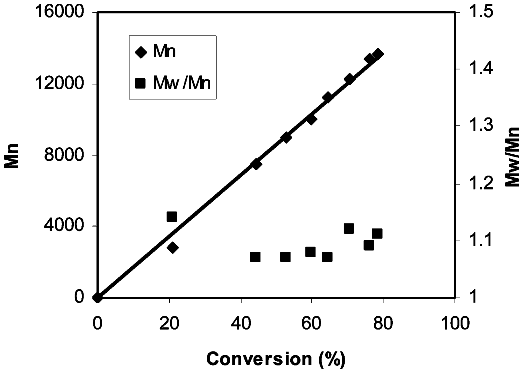

Figure 5. Dependence of number-average molecular weight (M_n) and polydispersity (M_w/M_n) on monomer conversion (conditions: 95 °C, [CuBr] = [Me_6TREN] = [2-EBP] = 0.0474 M, [menthyl acrylate] = 4.74 M, 2-EBP = ethyl 2-bromopropionate, Me_6TREN = tris[2-(dimethylamino)ethyl]amine).

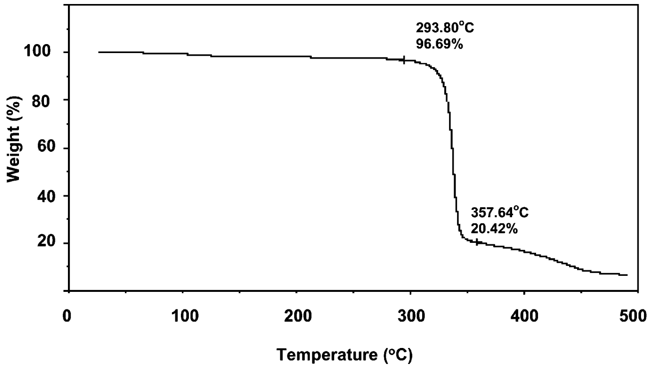

Figure 6. TGA curve of poly(menthyl acrylate) prepared by 2-EBP/CuBr/Me_6TREN (conditions: 95 °C; [CuBr] = [Me_6TREN] = [2-EBP] = 0.0474 M, [menthyl acrylate] = 4.74 M, 2-EBP = ethyl 2-bromopropionate, Me_6TREN = tris[2-(dimethylamino)ethyl]amine).

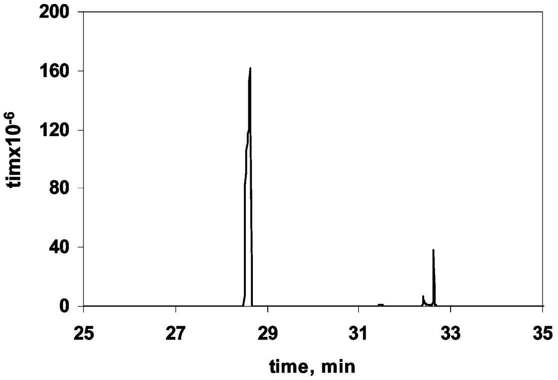

Figure 7. GC/MS pyrolysis (400 °C) of poly(menthyl acrylate) prepared by 2-EBP/CuBr/Me_6TREN (conditions: 95 °C; [CuBr] = [Me_6TREN] = [2-EBP] = 0.0474 M, [menthyl acrylate] = 4.74 M, 2-EBP = ethyl 2-bromopropionate, Me_6TREN = tris[2-(dimethylamino)ethyl]amine).

summarized in Table 1 (runs 1−3). However, the polymerization rates were extremely slow with 5.7% and 14.8% conversions in 4 h for 1-PEBr and 2-EBP, respectively. These results are consistent with those of traditional free radical initiated MnA polymerization in which MnA showed much less reactivity than methyl acrylate (MA). Replacing PMDETA with Me_4Cyclam (run 4) promotes a very fast but uncontrolled polymerization. The polymerization reached 97.1% within 1 h to produce polymer with M_n = 21 000 and M_w/M_n = 1.70. On the other hand, the 1-PEBr/Me_4Cyclam system proceeded with a slightly slower rate with a 60.2% conversion in 3 h and yielded polymer with more broad polydispersity (M_w/M_n = 2.18).

The controlled/living system with fast polymerization rate was achieved by using tris{2-(dimethylamino)ethyl]amine (Me_6TREN) as ligand (Table 1, runs 6−9). For runs 8 and 9 (with a monomer/initiator = 100/1) the conversion reached 44.2% in 7.5 min and 78.4% in 30 min to yield polymers of M_n = 7500 (M_w/M_n = 1.07) and M_n = 14 000 (M_w/M_n = 1.11), respectively. Increasing the ratio of monomer/initiator to 200/1 (Table 1, run 7), the polymerization reached 67.9% conversion with M_n = 16 000 and M_w/M_n = 1.22. Moreover, this system for MnA polymerization can be carried out at 50 °C (Table 1, run 6) with 36.4% conversion within 1 h to afford polymer of M_n = 8600 and M_w/M_n = 1.06.

Table 2 summarizes the results of ATRP by MnA by the 2-EBP/(CuBr + $CuBr_2$)/Me_4Cyclam system. The significant effect of addition of $CuBr_2$ on polymerization is observed, and the reaction shows some "controlled" features. Comparison of runs 1, 3, 4, and 6 reveals that the conversions of MnA decrease from 97.1% to 54.7%, 46.6%, and 9.1% while polydispersities change from 1.70 to 1.51, 1.33, and 1.40 when the ratios of $CuBr_2$/CuBr increase from 0 to 0.25, 0.50, and 0.75. These observations demonstrate that the addition of $CuBr_2$ slows the polymerization rate and improves the control of molecular weights and polydispersities. However, the polymerization of MnA was completely suppressed when 1 equiv of $CuBr_2$ was added to the system (Table 2, run 7) due to the extremely low concentration of propagating free radicals and high concentration of dormant species generated by the reaction of $CuBr_2$ with free radicals.

Scheme 1. Formation of Menthenes from Pyrolysis of Poly(menthyl acrylate)

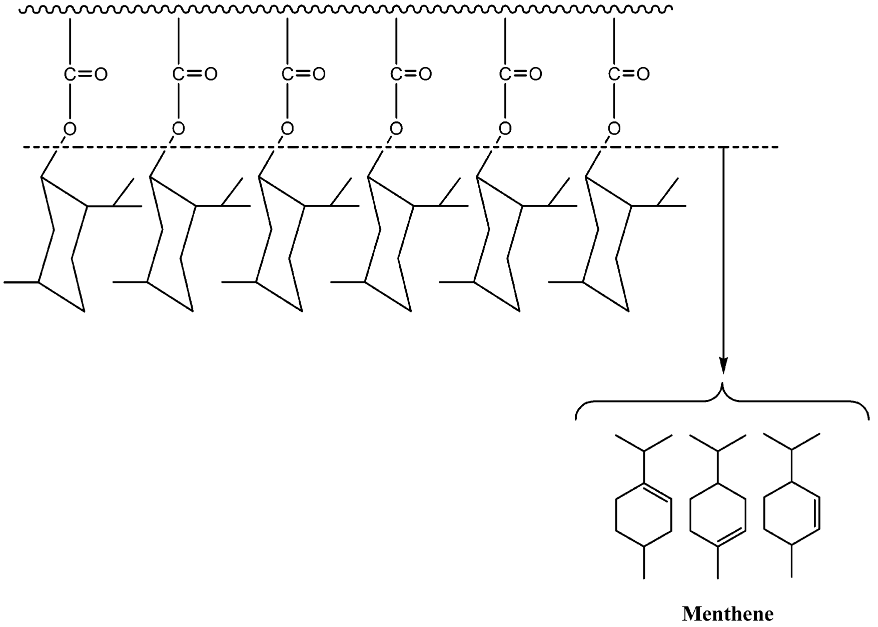

Figure 1 shows the 500 MHz ^{1}H NMR spectra of poly(menthyl acrylate) prepared by ATRP. The resonance at 4.65 ppm is assigned to the proton from menthyl group adjacent to the ester unit. The chemical shift at 2.30 ppm is assigned to CH units in backbone. The resonances at 0.6−2.0 ppm are due to CH_3, CH_2, and CH units of menthyl groups.

The ATRP of MnA with 2-EBP as initiator and PMDETA as ligand displays the typical characteristics of a "living" system. A linear plot of $\ln([M]_0/[M]_t)$ vs time was observed throughout the polymerization, indicating that the number of propagating species remained constant (Figure 2). The molecular weight increased linearly with overall conversion while the polydispersities remain below 1.15 (Figure 3). When using Me_6TREN as ligand, the conversion increased rapidly with polymerization time, and a linear kinetic plot of $\ln([M]_0/[M]_t)$ vs time was obtained before 50% conversion (Figure 4). After that, the slight curvature from first-order kinetics that was noticed was attributed to the termination of small amounts of propagating chains. However, the "living" features are still sufficient as demonstrated by Figure 5, in which the molecular weight increased linearly and the polydispersities were relatively narrow (<1.12).

The controlled/living free radical polymerizations can provide products with controlled molecular weight and narrow molecular weight distribution; more importantly, the polymer prepared by the controlled/living system can be retreated with monomers for chain extension to form block copolymers. Indeed, the synthesis of block copolymers is widely used to demonstrate the "living" nature of a polymerization.[28−31] The solid sample PMnA-Br (0.530 g, 0.150 mmol; M_n: 2300; PDI: 1.15) was employed as a macroinitiator in chain extension polymerization of methyl acrylate (MA) to form PMnA-*b*-PMA. The PMnA-Br was first dissolved in anisole and then mixed with CuBr (0.0210 g, 0.150 mmol), PMDETA (0.0250 g, 0.140 mmol),

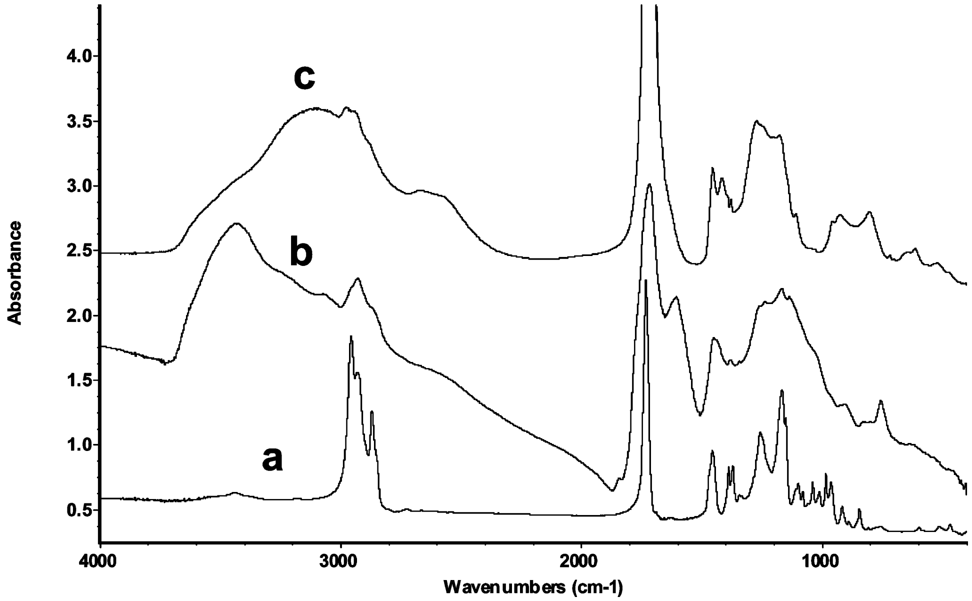

Figure 8. IR spectra of poly(menthyl acrylate) (a), pyrolyzed poly(menthyl acrylate) (b), and standard poly(acrylic acid) (Aldrich, $M_n = 2000$) (c). Poly(menthyl acrylate) was prepared by 2-EBP/CuBr/Me_6TREN (conditions: 95 °C; [CuBr] = [Me_6TREN] = [2-EBP] = 0.0474 M, [menthyl acrylate] = 4.74 M, 2-EBP = ethyl 2-bromopropionate, Me_6TREN = tris[2-(dimethylamino)ethyl]amine).

and MA (1.50 g, 17.4 mmol). The mixture was heated at 95 °C for 22 h to afford the final product of $M_n = 4800$ and $M_w/M_n = 1.10$. The polydispersity of the final product is much lower than that for a conventional radical process, implying efficient chain initiation by the PMnA-Br macroinitiator.

Thermal Stability of Poly(menthyl acrylate). PMnA prepared in this work shows amorphous structure, as evidenced by the absence of melting peak between 20 and 250 °C in DSC curve. Figure 6 shows the TGA thermograms (with a heating rate of 10 °C/min) of PMnA. The PMnA began to decompose at 293.8 °C, and the weight loss reached 76.3% at 357.6 °C. The weight loss during this range of temperature was ascribed to the dissociation of menthyl group from the polymer chain. Further increase of temperature resulted in more weight loss due to the dissociation of carboxylate group from polymer chain and the decomposition of polymer backbone.

The components of PMnA decomposition products can be determined by GC/MS. Figure 7 shows the GC/MS pyrolysis of PMnA at 400 °C. All peaks (28.5, 32.4, and 32.6 min) are corresponding to menthene structures implying the breakage of ester groups, as illustrated in Scheme 1. The formation of poly(acrylic acid) during pyrolysis was confirmed by the characteristic broad stretching absorption of COOH group between 3000 and 3600 cm^{-1} in the IR spectrum of pyrolyzed PMnA (Figure 8b). Therefore, by controlling the decomposition temperature and driving off menthene units from side chains, it is possible to convert poly(menthyl acrylate) to poly(acrylic acid). We have known that it is a challenge to polymerize acrylic acid by ATRP due to the side reaction of monomer with metal catalyst and the quaternization of nitrogen ligand. Therefore, ATRP of MnA also provides an alternative to synthesize poly(acrylic acid) with controlled structures.[32−35]

Conclusion

In conclusion, we have investigated the atom transfer radical polymerization (ATRP) of menthyl acrylate (MnA) with different catalytic systems. Using 1-PEBr or 2-EBP as initiators and PMDETA as ligand, ATRP of MnA proceeds in a controlled/living manner as evidenced by narrow polymer polydispersity (<1.20), but very slow polymerization rates. Replacing PMDETA with Me_4cyclam promotes a very fast but uncontrolled polymerization with a broad polydispersity product. The controlled/living system with a fast polymerization rate was achieved by using Me_6TREN as a ligand. The polymerization reached 78.4% conversion in half hour to yield polymer of $M_n = 14\,000$ and $M_w/M_n = 1.11$. The living feature of this system allowed chain extension polymerization of methyl acrylate (MA) to synthesize the block copolymer, PMnA-*b*-PMA. The thermal stability of PMnA was investigated by TGA and GC/MS. The release of menthenes during pyrolysis of PMnA makes it possible to synthesize poly(acrylic acid) with controlled structures from PMnA prepared by ATRP of MnA.

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References and Notes

(1) Matyjaszewski, K. Ed. *Controlled Radical Polymerization*; ACS Symposium Series No. 685; American Chemical Society: Washington, DC, 1998.

(2) Matyjaszewski, K. Ed. *Controlled/Living Radical Polymerization Progress in ATRP, NMP, and RAFT*; ACS Symposium Series No. 768; American Chemical Society: Washington, DC, 2000.

(3) Matyjaszewski, K. Ed. *Advances in Controlled/Living Radical Polymerization*; ACS Symposium Series No. 854; American Chemical Society: Washington, DC, 2003.

(4) Liu, S.; Sen, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6175−6192.

(5) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.

(6) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3746.

(7) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.

(8) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(9) Finet, J.; Lemoigne, F.; Grimaldi, S.; Nicol, P.; Plechot, M.; Tordo, P. PCT Int. Appl. WO96/24620, 1996.

(10) Grimaldi, S.; Finet, J.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. *Macromolecules* **2000**, *33*, 1141−1147.

(11) Schierholz, K.; Givehchi, M.; Fabre, P.; Nallet, F.; Papon, E.; Guerret, O.; Gnanou, Y. *Macromolecules* **2003**, *36*, 5995−5999.

(12) Harth, E.; Hawker, C. J.; Fan, W.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 3856−3862.

(13) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.

(14) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071−2074.

(15) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977−6980.

(16) Chong, Y. K.; Krstina, J.; Le, T. P. L.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.

(17) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2283.

(18) Matyjaszewski, K.; Gaynor, S.; Wang, J. S. *Macromolecule* **1995**, *28*, 2093−2095.

(19) Wakioka, M.; Baek, K.-Y.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2002**, *35*, 330−333.

(20) Iovu, M. C.; Matyjaszewski, K. *Macromolecule* **2003**, *36*, 9346−9354.

(21) Lutz, J.-F.; Kirci, B.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 3136−3145.

(22) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Weichold, O. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3283−3299.

(23) Matsuzaki, K.; Tateno, N. *J. Polym. Sci.* **1968**, *C23*, 733−739.

(24) Matsuzaki, K.; Ishida, A.; Tateno, J. *J. Polym. Sci.* **1967**, *C16*, 2111−2120.

(25) Matsuzaki, K.; Hosonuma, K.; Kanai, T.; Kobayashi, K. *Makromol. Chem.* **1975**, *176*, 2853−2860.

(26) Ciampolin, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41−44.

(27) Zhong, G.; He, J. *Tuliao Gongye* **1992**, *1*, 10−12.

(28) Lutz, J-F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986−6993.

(29) Tang, C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 8587−8589.

(30) Shipp, D. A.; Wang, J.-L.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 8005−8008.

(31) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.

(32) Camp, W. V.; Prez, E. D. *Macromolecules* **2004**, *37*, 6673−6675.

(33) Hoogenboom, R.; Schubert, U. S.; Camp, W. V.; Prez, E. D. *Macromolecules* **2005**, *38*, 7653−7659.

(34) Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2003**, *36*, 8260−8267.

(35) Ladaviére, C.; Dörr, N.; Claverie, J. *Macromolecules* **2001**, *34*, 5370−5372.

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