

Reverse Atom Transfer Radical Polymerization of Stearyl Methacrylate Using 2,2'-Azobisisobutyronitrile as the Initiator

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ABSTRACT: The living/controlled radical polymerization of stearyl methacrylate was carried out with a conventional radical initiator (2,2'-azobisisobutyronitrile) in *N,N*-dimethylformamide in the presence of a 2,2'-bipyridine complex of hexakis(*N,N*-dimethylformamide)iron(III) perchlorate. The polymerization mechanism was thought to proceed through a reverse atom transfer radical polymerization. The molecular weights of resulting poly(stearyl methacrylate) increased with conversion, and the resulting molecular weight distributions were quite narrow. The rates of polymerization exhibited first-order kinetics with respect to the monomer. A probable reaction mechanism for the polymerization system is postulated to explain the observed results. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1236–1245, 2002

Key words: atom transfer radical polymerization (ATRP); glass transition; differential scanning calorimetry (DSC); gel permeation chromatography (GPC); X-ray diffraction

INTRODUCTION

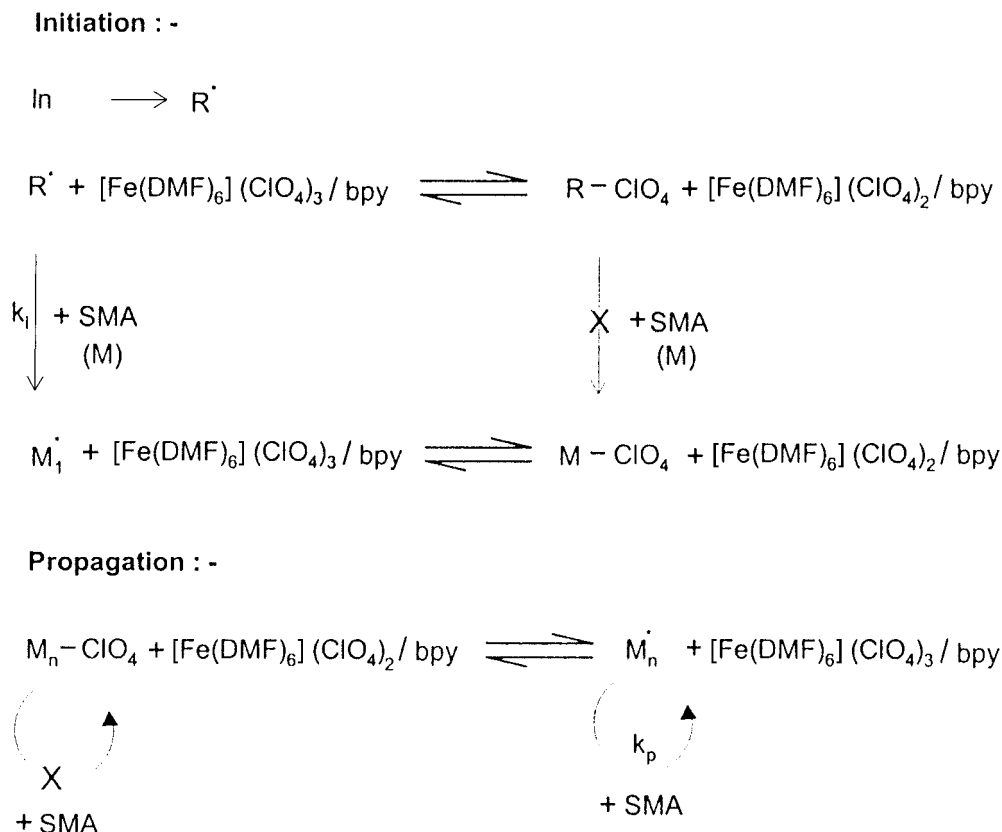
A linear polymer with a pendent alkyl side chain of specific length is one of the general structural characteristics of flow improvers (FIs) and pour point depressants (PPDs) for crude oils.^{1,2} A number of patents describe the use of polymers of higher alkyl acrylates and methacrylates as PPDs and FIs. The large demand for poly(*n*-alkyl acrylate)s and poly(*n*-alkyl methacrylates) with narrow polydispersities has prompted researchers to improve processes for the polymerization of *n*-alkyl (meth)acrylates. We recently investigated the polymerization behavior of higher alkyl acrylates and methacrylates to derive their structure–

reactivity relationships.^{3,4} As for many industrial polymers, polymerizations to synthesize PPDs and FIs are conducted by free-radical polymerization. The high-conversion free-radical polymerization of *n*-alkyl (meth)acrylates shows a strong Trommsdorff effect or gel effect even though the polymerization is carried out above the glass-transition temperature.³ Because of the gel effect, a considerable deviation from the normal kinetic parameters with a broadening of the molecular weight distribution is observed in high-conversion polymerization. Although acrylates can be polymerized anionically, the preparation of well-defined polymers is hindered by a number of side reactions.⁵ Several methods have been developed to overcome this problem,^{6,7} but most poly(meth)acrylates are still produced by free-radical polymerization. However, in comparison with ionic polymerization, free-radical polymerization is difficult to control.

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Scheme 1

Recently, the transition-metal-catalyzed atom transfer radical polymerization (ATRP) of vinyl monomers has been introduced as a versatile chemistry enabling the synthesis of a wide range of tailor-made polymers with predetermined degrees of polymerization and narrow polydispersities.⁸⁻¹⁰ In ATRP, organic halides (R-X) are used as initiators, and transition-metal compounds in their lower oxidation states are used as catalysts. Electron-donating compounds are frequently used as ligands. In this process, a dynamic equilibrium is established in which the dormant polymer chains are reversibly activated via a halogen atom transfer reaction. A fast equilibrium between growing radicals and dormant species is mandatory for a successful ATRP. This equilibrium between growing and dormant chains is shifted toward the dormant species, giving an extremely low radical concentration that effectively minimizes bimolecular termination. These systems have been applied to a wide range of monomers, including many different functional monomers for the synthesis of a diverse array of polymers with varied compositions and architec-

tures. It also provides a functional end group to prepare well-defined block,¹¹ comb and graft,¹² star,^{13,14} dendritic,¹⁵ and hyperbranched¹⁶ polymers. Presently, attention has been shifted toward iron-catalyzed ATRP because of its lower cost and activity similar to that of ruthenium analogues.¹⁷⁻²¹ To synthesize polymers of higher alkyl acrylates and methacrylates with controlled architectures and narrow molecular weight distributions, recently we reported the ATRP of stearyl methacrylate (SMA).²² The initiator system consisted of a catalytic amount of 2,2'-azobisisobutyronitrile (AIBN) as the source of a reducing agent and a suitable alkyl halide (CBr₄) as the initiator in the presence of a hexakis(*N,N*-dimethylformamide)iron(III) perchlorate {[Fe(DMF)₆](ClO₄)₃}/2,2'-bipyridine (bpy) catalyst system.

However, transition-metal-catalyzed ATRP has two major drawbacks: the toxicity of the halide species RX and the oxidation of the catalyst M_n^t/LX by oxygen in air. To overcome these drawbacks, Matyjaszewski and coworkers^{23,24} and Teyssie et al.²⁵ reported the reverse and alternative ATRP systems, respectively. Recently, a new

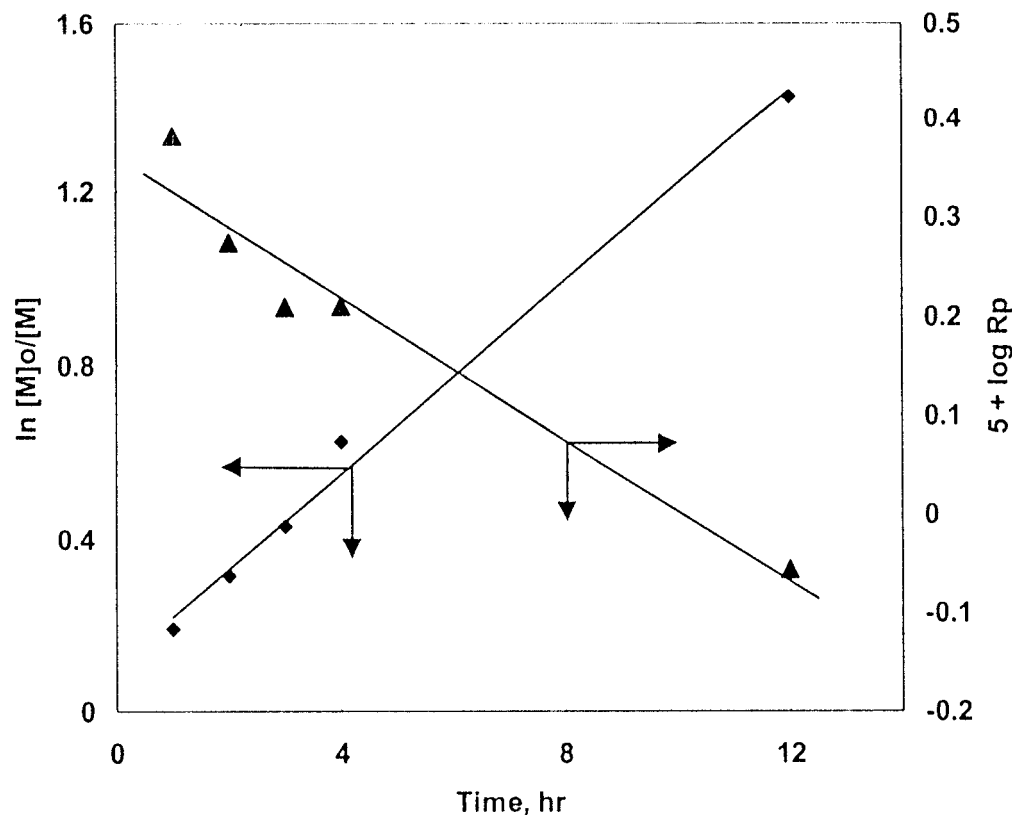


Figure 1 R_p and $\ln([M]_0/[M])$ plots versus time for the reverse ATRP of SMA at 80°C in DMF in the presence of AIBN as an initiator. [SMA] = 0.500M; [AIBN] = 5.00 $\times 10^{-4}$ M; [Fe(III)] = 1.00 $\times 10^{-3}$ M; [bpy] = 3.00 $\times 10^{-3}$ M.

reverse ATRP process with diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS), a hexasubstituted ethane thermal iniferter, was successfully carried out. The polymerization mechanism belongs to a new reverse ATRP process in which the initiator DCDTS reversibly decomposes into primary radicals in the initiation step.²⁶ More recently, a third ATRP process,^{21,27} *in situ* ATRP, was reported in which neither an organic halide nor a radical initiator is used. In the *in situ* ATRP process, RX and M^{n+1} are both reacted *in situ* for the reaction between a radical initiator and transition-metal ion. Reverse ATRP differs from conventional ATRP in the initiation step, in which the initiating active species or propagating active species can abstract a halogen atom from the oxidized transition-metal complex to form the dormant species and the reduced transition-metal species.^{17,27}

In this article, we describe the well-controlled reverse ATRP of SMA with a conventional radical initiator, AIBN, and a transition-metal complex of iron at a higher oxidation state complexed with bpy as a catalyst.

EXPERIMENTAL

The polymer synthesis and almost all the purification techniques were performed *in vacuo* with a break-seal. SMA was recrystallized three times from hexane at a low temperature. The solid masses were placed in ampules and were thoroughly dried *in vacuo* for at least 24 h.²⁸ *N,N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were purified by standard methods. AIBN was recrystallized from methanol and dried in a desiccator. bpy was used without further purification. The complex $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ was prepared as described before.^{29,30}

The polymerization of SMA was carried out in a dry glass ampule with nitrogen (99.99% pure). The solution was deaerated by three freeze-pump-thaw cycles and sealed with a rubber septum. The tubes were placed in a thermostat at desired temperatures for a definite period of time. After the desired time period, precipitation with acetone containing traces of hydroquinone isolated the polymers. The polymers were then filtered and dried *in vacuo*.

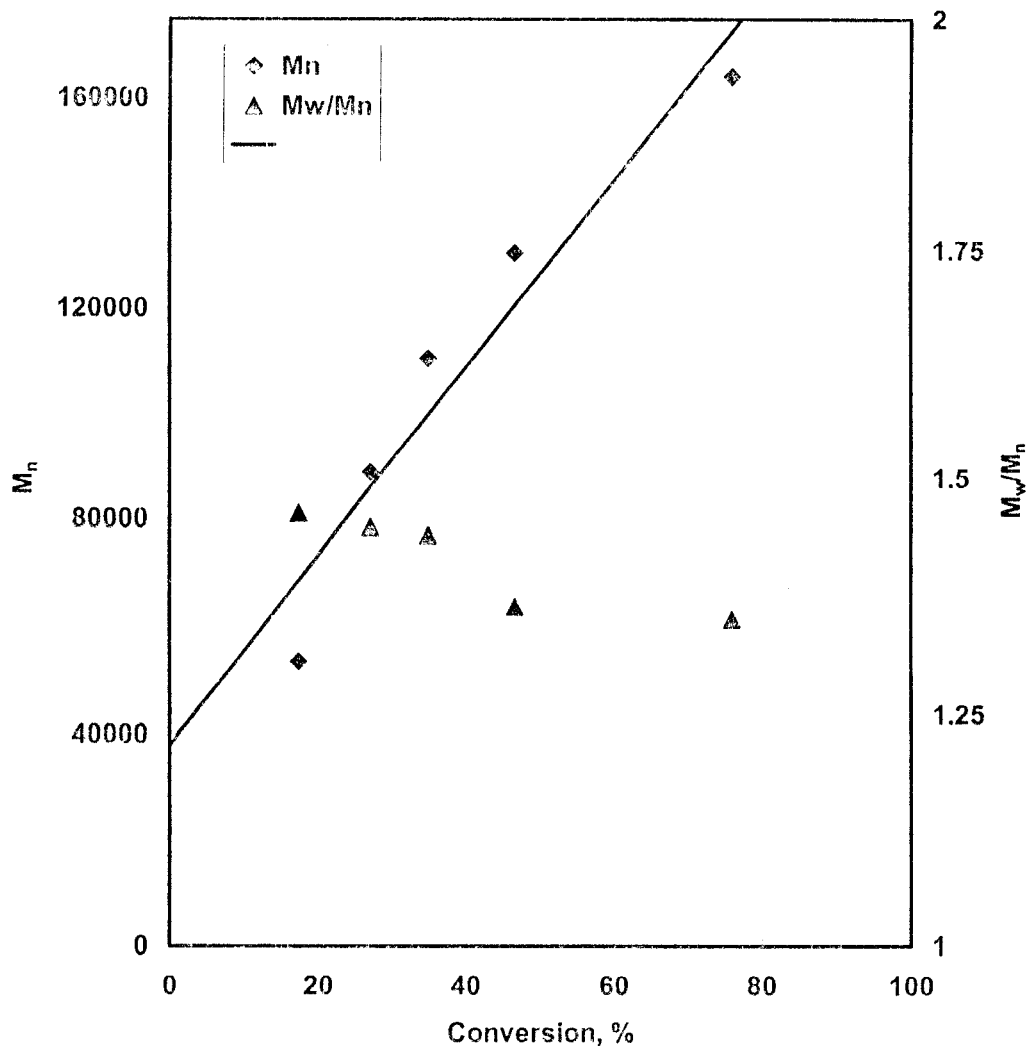


Figure 2 PSMA molecular weight (M_n) and polydispersity index (M_w/M_n) as functions of conversion in the reverse ATRP of SMA at 80°C in DMF in the presence of AIBN as an initiator. [SMA] = 0.500M; [AIBN] = $2.00 \times 10^{-2}M$; [Fe(III)] = $1.00 \times 10^{-3}M$; [bpy] = $3.00 \times 10^{-3}M$.

Gel permeation chromatography (GPC) was performed with a Waters model 515 solvent delivery system (Milforde, MA) at a flow rate of 1.0 mL min⁻¹ through a combination of Waters HR1, HR3, and HR4 Styragel columns. The analysis was performed at room temperature with purified high-performance-liquid-chromatography-grade THF as an eluent. A Waters model 2410 differential refractometer was used as the detector. Calibration was based on nine narrow molecular weight distribution polystyrene standards with the Waters Millennium 2.0 software package.

Differential scanning calorimetry (DSC) was performed on a TA series DSC 2010 instrument (New Castle, DE) with 2–5-mg polymer samples

weighed in aluminum pans. The samples were analyzed in a nitrogen atmosphere at a heating rate of 10°C min⁻¹.

IR spectra of the compounds were measured (4000–200 cm⁻¹) with a PerkinElmer IR 883 spectrophotometer (Beaconsfield, England).

The X-ray diffractograms of polymers were recorded on a JEOL model JDX-11P3A diffractometer (Tokyo, Japan) with a solid sample with a Ni filter with Cu K α radiation at 35 kV and 10 mA in the wide-angle range $2^\circ < 2\theta < 60^\circ$.

The ¹H-NMR spectrum was recorded on a Bruker 300-MHz spectrometer (Fallanden, Switzerland) in CDCl₃ with tetramethylsilane as an internal reference.

Table I Effects of the Concentrations of SMA, Fe(III), and AIBN on the Molecular Weight and Polydispersity Index of PSMA Prepared by Reverse ATRP in a Nitrogen Atmosphere at 80°C in DMF

[SMA] (mol/L)	$10^3 \times$ [Fe(III)] (mol/L)	$10^3 \times$ [AIBN] (mol/L)	$10^5 \times R_p$ (mol/L s)	M_n	M_w/M_n	mp (°C)	ΔH_m (kJ/mol)	ΔS_m (J/K mol)
1.00	1.00	2.00	4.18	22700	1.67	44.5	28.74	90.52
0.75	1.00	2.00	3.08	15700	1.59	43.3	26.19	82.80
0.50	1.00	2.00	2.03	13000	1.54	42.9	26.30	83.25
0.30	1.00	2.00	1.18	9900	1.46	42.3	24.76	78.54
0.50	10.00	2.00	2.21	11700	1.80	41.5	19.24	61.20
0.50	5.00	2.00	2.20	13400	1.77	43.6	28.63	90.43
0.50	3.00	2.00	2.19	14500	1.63	43.4	29.23	92.41
0.50	0.67	2.00	2.16	16100	1.62	42.9	23.80	75.33
0.50	1.00	10.00	2.09	15900	1.55	42.3	24.29	77.03
0.50	1.00	7.50	2.02	18900	1.65	42.6	24.51	77.66
0.50	1.00	5.00	2.00	22500	1.59	42.5	24.74	78.41
0.50	1.00	3.00	1.81	30700	1.50	42.8	25.39	80.40
0.50	1.00	2.00	1.70	34100	1.63	42.5	26.84	85.07
0.50	1.00	1.00	1.78	122200	1.39	42.8	28.12	89.04
0.50	1.00	0.75	1.19	148000	1.36	43.2	28.34	89.62

RESULTS AND DISCUSSION

The criterion of a controlled radical polymerization is to maintain the fast equilibrium between the growing radicals and dormant species. In ATRP or reverse ATRP, such equilibrium is achieved with a metal complex that changes between n and $n + 1$ oxidation states. Reverse ATRP has already been established for both copper and iron complexes. Here, a conventional radical initiator such as AIBN was used as a source of radicals, and a transition-metal complex was employed in its higher oxidation states. At higher temperatures and in the presence of the monomer, the initiator system became a conventional ATRP initiating system by decomposition of the radical initiator, forming radicals that then reacted with the higher transition-state metal to form the polymeric halide and the complex of the transition metal in its lower oxidation state. However, the reverse ATRP of acrylates and methyl methacrylate is not controlled.²³ The polymerization was very fast and led to gelation at approximately 40% monomer conversion with a very broad multimodal molecular weight distribution. To cope with such a problem, in a transition-metal-mediated reverse ATRP system, a catalytic amount of AIBN as a radical source is used to maintain the low concentration of growing radicals, and a suitable alkyl halide is used as a coinitiator to control the molecular weight of the

final product.²³ Studies reveal that the transition-metal complex of bpy plays a significant role in vinyl polymerization under usual reaction conditions.^{29,30} The same metal ion can accelerate, retard, and initiate the polymerization reaction. The effect changes depending on the method of initiation, the ligand associated or coordinated with the metal ion, and the mechanism of the reaction.^{31,32}

The proposed polymerization mechanism as depicted in Scheme 1. In the initiation step, it consists of the homolytic decomposition of the initiator to form the primary free radical ($R \cdot$) and the addition of the $R \cdot$ radical to the monomer to produce the monomeric radical ($M \cdot$). The monomer radical abstracts the chlorate atom from the high-oxidation-state transition-metal species, Fe(III), to form the reduced transition-metal species, Fe(II), and the dormant species. The subsequent propagation steps proceed via an ATRP process.

The plot of $\ln[M]_0/[M]$ versus time is linear (Fig. 1), indicating first-order kinetics. The apparent rate constant was $2.23 \times 10^{-5} \text{ s}^{-1}$ at 80°C. This means that the propagating radical concentration is constant during the course of polymerization. This observation together with the linear increase in the molecular weight with conversion (Fig. 2) indicates that initiation is fast and that the effect of the chain-transfer and termination reaction during the course of polymerization is

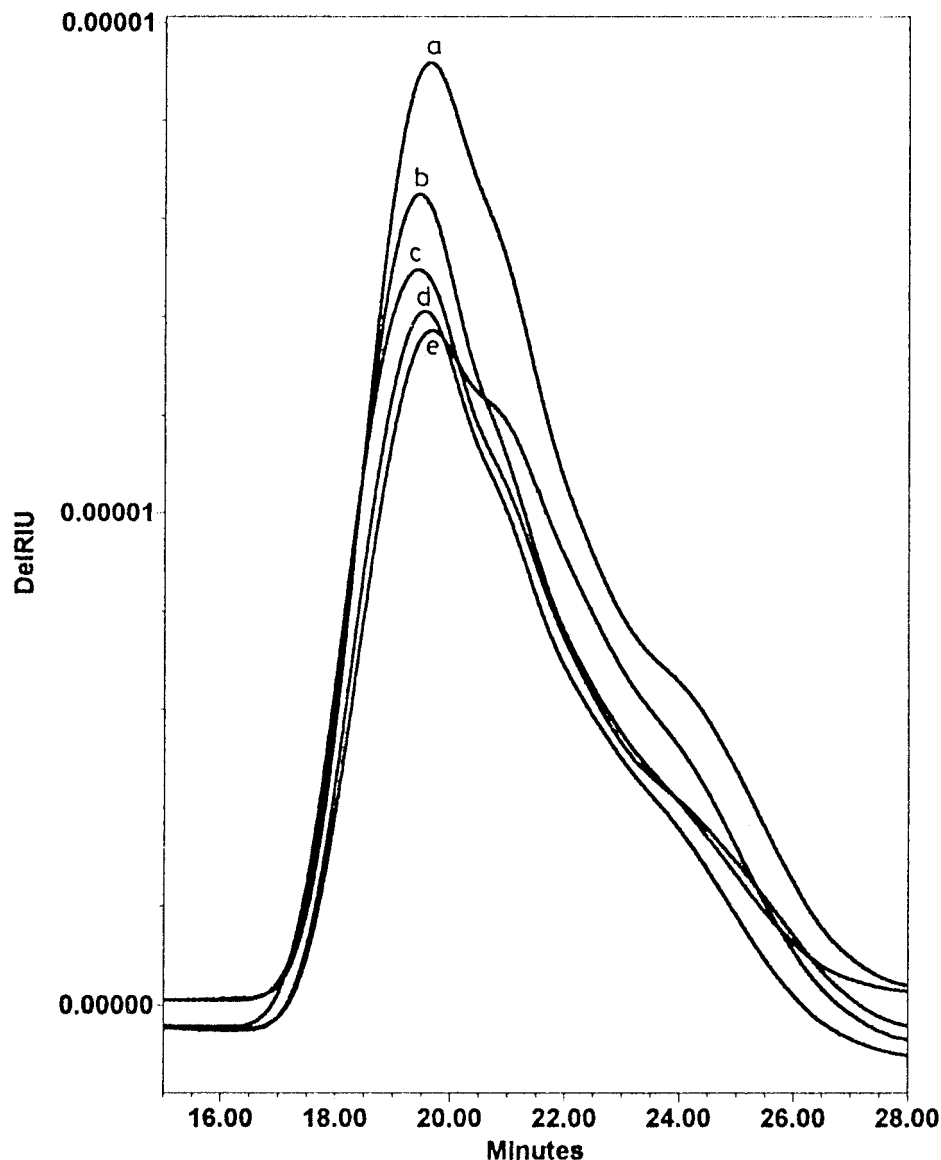


Figure 3 GPC traces (refractive-index detector) of PSMA synthesized by the reverse ATRP of SMA at 80°C in DMF in the presence of AIBN as an initiator with the following conversions: (a) 17.2, (b) 27.1, (c) 34.9, (d) 43.6, and (e) 75.9%. [SMA] = 0.500M; [AIBN] = $2.00 \times 10^{-2}M$; [Fe(III)] = $1.00 \times 10^{-3}M$; [bpy] = $3.00 \times 10^{-3}M$.

negligible. These results convincingly reveal that the polymerization of SMA with the AIBN/Fe(III)/bpy system at 80°C is a living/controlled radical polymerization process. Increasing the [SMA]/[AIBN] ratio results in the expected increase in the number-average molecular weight (M_n). The effect of varying the SMA, Fe(III), and AIBN concentrations on M_n and the molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of poly(stearyl methacrylate) (PSMA) is presented in

Table I. With an increasing SMA concentration, both the rate of polymerization (R_p) and M_n increased. The higher value of M_w/M_n may be attributed to branching reactions or a gel effect.²⁵ The branching may be due to the extraction of a large number of hydrogen atom from the long alkyl group of the alkyl chain. The polydispersity index also decreases with increasing conversion. Molecular weights determined from GPC were lower than the theoretically predicted value. This disparity may be due to the difference in hydro-

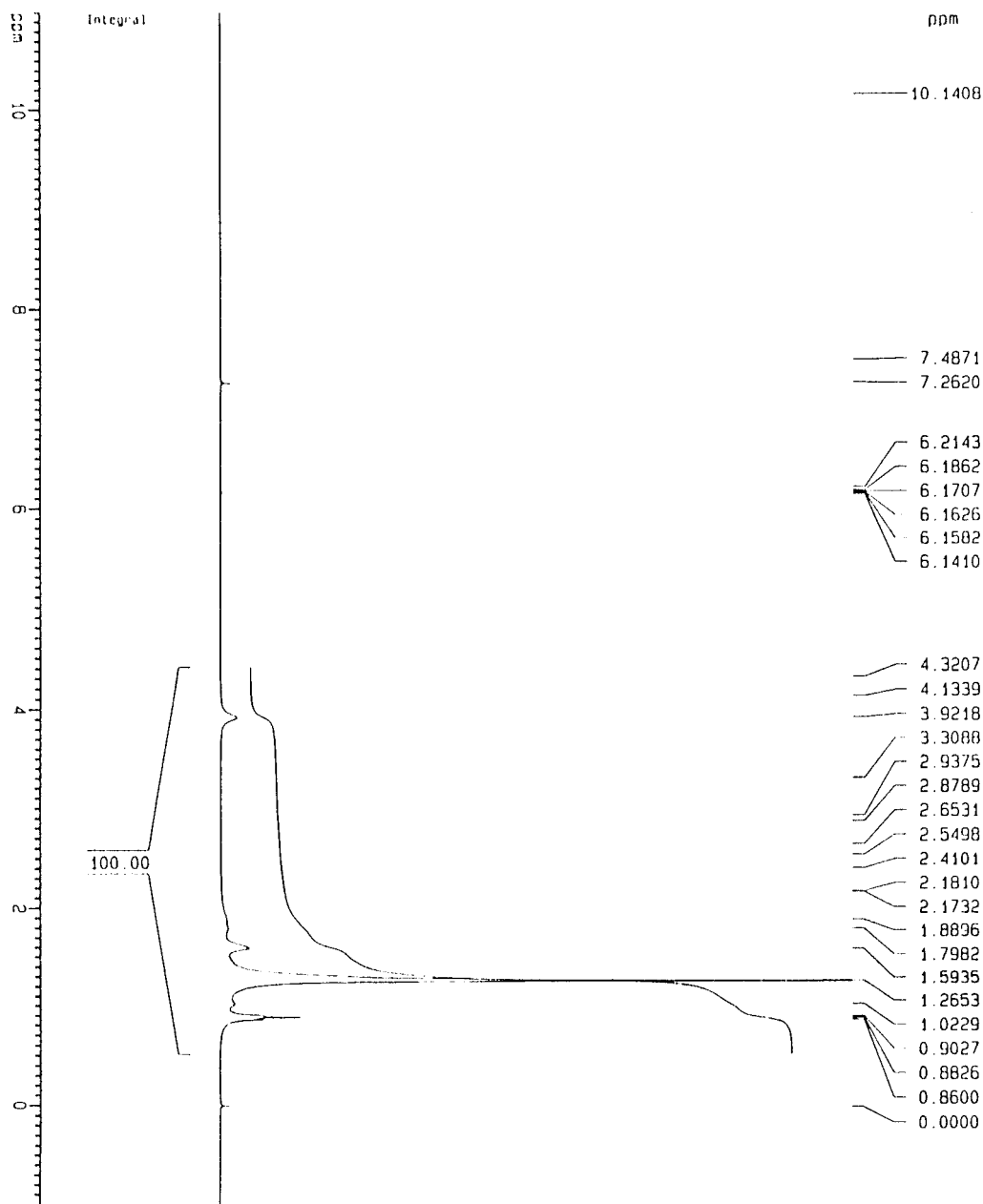


Figure 4 $^1\text{H-NMR}$ spectrum of PSMA synthesized by the reverse ATRP of SMA at 80°C in DMF in the presence of AIBN as an initiator. $[\text{SMA}] = 0.500\text{M}$; $[\text{AIBN}] = 2.00 \times 10^{-2}\text{M}$; $[\text{Fe(III)}] = 1.33 \times 10^{-3}\text{M}$; $[\text{bpy}] = 4.00 \times 10^{-3}\text{M}$.

dynamic volumes between the PSMA polymer and polystyrene standards. Because branched polymers have a lower hydrodynamic volume than linear ones, the polymers will elute later in GPC, leading to apparently lower M_n values. The GPC curves of PSMA in Figure 3 show sharp peaks, and molecular weight distributions are uniform throughout the polymerization, indicating a controlled polymerization.

The structure of the chain ends of low molecular weight PSMA synthesized by a reverse ATRP technique was analyzed with $^1\text{H-NMR}$ spectroscopy. Figure 4 presents the $^1\text{H-NMR}$ spectra of PSMA prepared at 80°C with AIBN as the radical source in the presence of the Fe(III)/bpy catalyst system. A broad multiplet at $\delta = 1.26$ corresponds to the terminal $-\text{CH}_3$ group from the initiator, whereas $-\text{CH}$ and $-\text{CH}_2$ backbone protons cor-

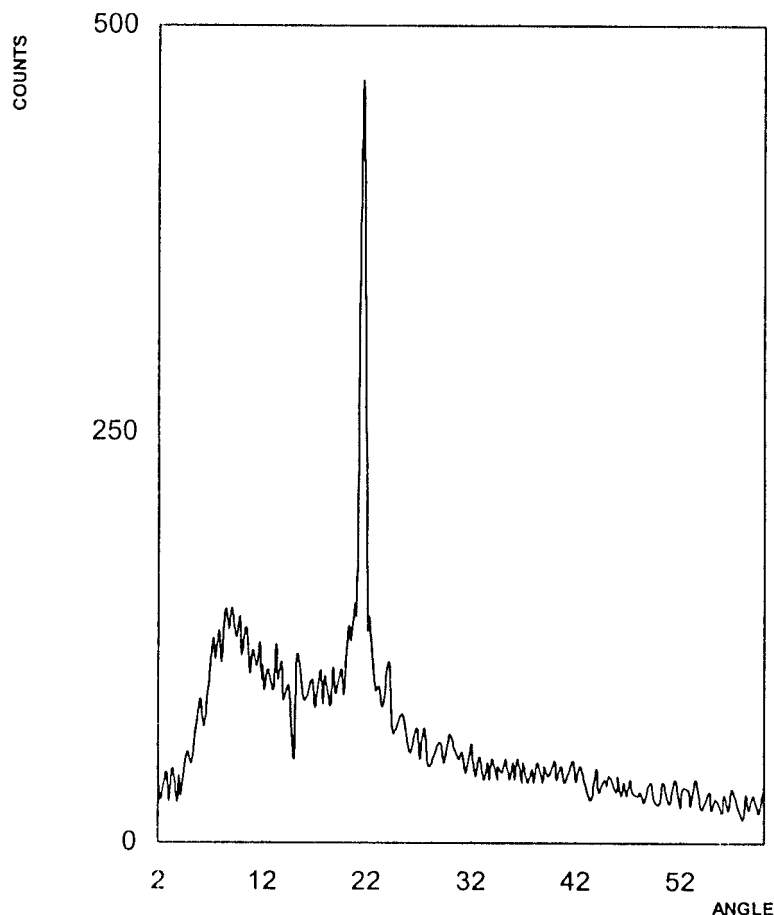


Figure 5 Typical X-ray diffraction pattern of PSMA synthesized by the reverse ATRP of SMA at 80°C in DMF in the presence of AIBN as an initiator.

respond to resonance at 2.88 and 1.56–1.94 ppm, respectively. The signal at 3.92 ppm is assigned to the protons of the terminal methyl ester unit, which is resolved from other methyl protons of the repeated stearyl ester.²² Similar spectra of poly(methyl methacrylate) obtained from the reverse ATRP of methyl methacrylate have been reported in the literature, including signals at 3.72 ppm reported by Qin et al.²⁶ and signals at 3.79 ppm reported by Moineau et al.²⁵ When AIBN is used as the initiator, the polymer end groups remasked by resonance from the polymer chain end, and so M_n cannot be directly calculated from the ¹H-NMR data.

The X-ray diffraction pattern of PSMA shows a peak at about $2\theta = 22^\circ$, which corresponds to 4.16 Å spacing (Fig. 5). This corresponds to the values of several long-chain acrylate and methacrylate comblike polymers³³ attributed to the Van der Waals contraction of nonbonded atoms.³⁴ Besides

this peak, a very sharp peak at a very low angle (between 2 and 3°) is apparent. This indicates the presence of structures other than atom contact structures in the comblike PSMA. For conventional comblike polymers, Yokota et al.³⁵ proposed a peculiar layered structure made up of several parallel alkyl side chains arranged on both sides of the main chain. Polyacrylate and poly(*n*-alkyl methacrylate) crystallize in hexagonal packing (in accordance with X-ray studies) characterized by a single absorption band³⁵ at 720 cm⁻¹. PSMA prepared with this initiation system also shows a single band at 722 cm⁻¹, indicating that the long alkyl side chains of PSMA are hexagonally packed.

DSC measurements of PSMA were carried out at a heating rate of 10°C min⁻¹ in a nitrogen atmosphere. Figure 6 shows a typical DSC curve of PSMA. Melting endothermic peaks were observed at 40–48°C for the polymer samples. The

Sample: Po(Stearyl Macrylate) living
 Size: 4.3100 mg
 Method: 120oC @ 10oC/min
 Comment: Poly(stearyl methacrylate) by reverse ATRP

DSC

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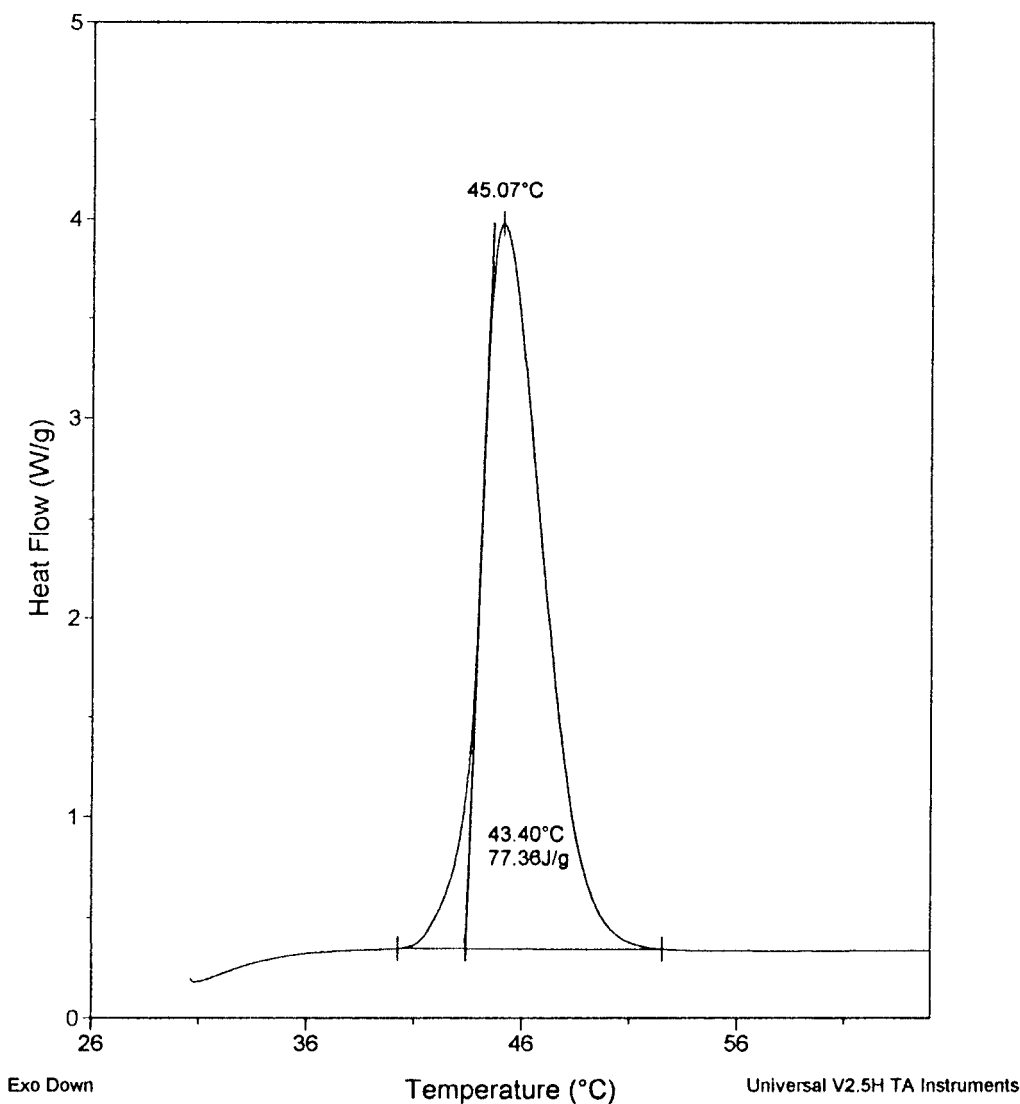


Figure 6 Typical DSC thermogram (scanning rate = $10^{\circ}\text{C min}^{-1}$) of PSMA synthesized by the reverse ATRP of SMA at 80°C in DMF in the presence of AIBN as an initiator.

melting point and heat of fusion (ΔH_m) were determined from the endothermic peaks. The melting point and ΔH_m values were almost constant, regardless of the conversion percentages and molecular weights of the polymers. Like the ΔH_m value, the value of the entropy of fusion (ΔS_m) was also constant, so the melting point changes were not very predominant. Typical values of ΔH_m and ΔS_m were $24\text{--}30 \text{ kJ mol}^{-1}$ and $75\text{--}85 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

CONCLUSIONS

A reverse ATRP was performed with a new initiating system, AIBN/Fe(III)/bpy, for the living/controlled radical polymerization of SMA in DMF at 80°C . A well-defined PSMA with a high molecular weight and a quite narrow polydispersity index was obtained with this system. The M_n values of the polymers increased with increasing monomer conversion, and the polydispersity de-

creased with conversion in agreement with the ATRP process.

Because Lewis acids are good electron acceptors, the complex $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ enhances the electron-donating capacity of bpy, and the formation rate of free radicals becomes rapid. The presence of a catalytic amount of growing radicals and a fast equilibrium between growing radicals and dormant species are mandatory for the reverse ATRP of *n*-alkyl (meth)acrylates with pendant alkyl side chains.

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