

Transition Metal-Catalyzed Atom Transfer Radical Polymerization of Stearyl Methacrylate in the Presence of Carbon Tetrabromide and a Conventional Radical Initiator

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ABSTRACT: Atom transfer radical polymerization of stearyl methacrylate (SMA) was successfully carried out in *N,N*-dimethylformamide using the carbon tetrabromide/*Fe*(III)/2,2'-bipyridine initiator system in the presence of 2,2'-azobisisobutyronitrile (AIBN) as the source of the reducing agent to maintain the equilibrium between growing radicals and dormant species. The molecular weights of the resulting poly(stearyl methacrylate) (PSMA) increased with the conversion and the molecular weight distribution of PSMA was quite narrow. The rates of polymerization exhibit

first-order kinetics with respect to the monomer. A probable reaction mechanism for the polymerization system was postulated to explain the observed results. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 386–394, 2002

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

INTRODUCTION

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 a predetermined degree of polymerization and narrow polydispersity.^{1–3} This approach has been developed as an extension to atom transfer radical addition (ATRA), in particular to atom transfer radical cyclization of α,α -trichlorinated carbonyl compounds.⁴ The presence of a catalytic amount of growing radicals (P_n^{\cdot}) and a fast equilibrium between growing radicals and dormant (P_n-X) species are mandatory for a transition metal-mediated ATRP.^{5,6} This equilibrium between growing and dormant chains is shifted toward the dormant species, giving an extremely low radical concentration which effectively minimizes bimolecular termination. A fast halide exchange process ensures that all polymer chains grow at the same rate, giving excellent control over the radical polymerization.¹ A number of efficient living radical polymerization systems have been reported with a wide range of transition metal complexes including copper,^{1,7} rhodium,⁸ palladium,⁹ ruthenium,^{10,11} and nickel,^{6,12} since they are capable of coordinating a wide range of li-

gands. Presently, attention has been shifted toward iron-catalyzed ATRP due to its lower cost and similar activity to their ruthenium analogs.^{5,13–16} Most of the complexes are known as catalysts for Kharasch or ATRA reactions.¹⁷ 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 architecture. They also provide a functional end group to prepare well-defined block,¹² comb and graft,¹⁸ star,^{19,20} dendritic,^{21,22} and hyperbranched²³ polymers. Recently, a steady effort has been directed toward the combination of conventional ATRP with other polymerization methods, such as ring-opening metathesis polymerization (ROMP), anionic and cationic polymerization, and nitroxide mediated radical polymerization (NMRP), to yield homopolymers and block copolymers with predictable molecular weights (MWs) along with a narrow molecular weight distribution (MWD).^{24–26}

In contrast to other living/controlled radical polymerizations, the features of these transition metal-catalyzed radical polymerizations include not only the use of a redox reaction of transition metal complexes but also the simple structure of halide-type initiators that may enable the synthesis of end-functionalized polymers. The main advantage of ATRP is its tolerance to most functional groups present in reagents, solvents, and impurities, precluding the extensive use of protecting group chemistry and laborious reagent and solvent purification. This has enabled the synthesis of an impressive array of novel polymers. The rate

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of polymerization can be enhanced by the presence of certain polar impurities, by the use of aliphatic multidentate tertiary amines, or in aqueous media which can allow the reaction to be carried out even at ambient temperatures or with reduced catalyst concentration by changing the nature of the active catalyst present during polymerization. In copper-catalyzed ATRP, replacement of 2,2'-bipyridine (bpy) ligands with alkyl amines lowers the redox potential of the copper halide catalyst and accelerates the polymerization.²⁷ A similar phenomenon was also observed in ruthenium and iron-catalyzed ATRP when triphenylphosphine and bpy were replaced with tributylphosphine and tributylamine, respectively.¹⁵ However, the stability of Fe(III) complexes may depend on the reaction conditions. Apparently, the nature of the ligands strongly affects the kinetics of polymerization and the polydispersity by influencing the thermodynamics and kinetics of the exchange process.¹⁵

In ATRP, organic halides (R—X) are used as initiators, transition metal compounds in their lower oxidation states are used as catalysts, and electron-donating compounds are used as ligands. In this process, a dynamic equilibrium is established where the dormant polymer chains are reversibly activated via a halogen atom transfer reaction.

This type of ATRP, however, 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 the drawbacks, Matyjaszewski et al.^{28,29} and Teyssie et al.³⁰ reported "reverse" and "alternative" ATRP systems, respectively. Recently, a new reverse ATRP process with diethyl 2,3-dicyano-2,3-di(*p*-tolyl)succinate (DCDTS), a hexa-substituted ethane thermal iniferter, was successfully carried out. The polymerization mechanism belongs to a new reverse ATRP process, with the initiator DCDTS reversibly decomposed to primary radicals in the initiation step.³¹ More recently, a third ATRP process,^{16,32} that is, *in situ* ATRP, was reported where neither an organic halide nor a radical initiator was 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. In reverse ATRP or *in situ* ATRP, a radical initiator and a higher oxidation state transition metal catalyst complex $M^{n+1}XL_m$ (where *m* is the number of ligands) are used. Reverse ATRP defers from the conventional ATRP in the initiation step, where the initiating active species or the 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.^{5,32} In an ATRP, the initiating system must be either an organic halide or a radical initiator in reverse ATRP.³¹

A linear polymer with a pendent alkyl side chain of specific length is one of the general structural characteristics of flow improvers (FI)/pour-point depres-

sants (PPD) for crude oils.^{33,34} A number of patents describe the use of polymers of higher alkyl acrylates and methacrylates as PPDs and/or FIs. We recently investigated the polymerization behavior of higher alkyl acrylates and methacrylates to derive their structure–reactivity relationship.^{35,36} The large demand for poly(*n*-alkyl acrylates) with narrow MWDs prompted research toward improving processes for the polymerization of *n*-alkyl acrylates. Like many industrial polymers, polymerizations to synthesize PPDs/FIs are conducted by free-radical polymerization. However, in comparison with anionic and cationic polymerization, free-radical polymerization is difficult to control. The polymerization of alkyl acrylates/methacrylates in bulk and in solution shows a strong Trommsdorff effect or gel effect even though the polymerization is carried out above the glass transition temperature (T_g).³⁵ This results in the broadening of the MWD of the resulting polymers. Due to the gel effect, considerable deviation from the normal kinetic parameters is observed in high-conversion polymerization. To synthesize polymers of higher alkyl acrylates/methacrylates with a controlled architecture and narrow MWD, we investigated the polymerization of stearyl methacrylate (SMA) with a novel ATRP initiator system. The initiator system comprises a catalytic amount of AIBN as the source of the reducing agent, a suitable alkyl halide (CBr_4) as the initiator, in conjunction with the $[Fe(DMF)_6](ClO_4)_3/bpy$ catalyst.

EXPERIMENTAL

The polymer synthesis and almost all the purification techniques were performed in a vacuum, in all-glass reactors provided with break seals and constrictions. SMA was recrystallized three times from hexane at low temperature. The solid masses were placed in ampules and were thoroughly dried in a vacuum for at least 24 h.³⁷ *N,N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were purified by the standard methods. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried in a desiccator; bpy and carbon tetrabromide (CBr_4) were used without further purification. The complex $[Fe(DMF)_6](ClO_4)_3$ (A) was prepared as before.³⁸

The polymerization of SMA was carried out by the following general procedure: First, a tris(2,2'-bipyridine)iron(III) complex $[Fe(bpy)_3]^{3+}$ was synthesized *in situ* in a glass ampule from the complex A, and bpy, by the method reported in the literature³⁹; then, AIBN, as the source of the reducing agent, the initiator CBr_4 , and SMA were added to the glass ampule that was purged 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 the desired temperatures for a definite period of time. After the desired time period, precip-

itating with acetone containing traces of hydroquinone isolated the polymers. The polymers were then filtered and dried under a vacuum.

Gel permeation chromatography (GPC) was performed using a Waters Model 515 solvent delivery system 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 using purified high-performance liquid chromatography (HPLC)-grade THF as the eluent. A Waters differential refractometer Model 2410 was used as the detector. The sample concentration was 0.2% (w/v), and the volume injected was $50 \mu\text{L}$. The GPC curves were analyzed with the calibration curve obtained by nine narrow MWD polystyrene samples (Waters). Data were recorded and processed using the Millennium 2.0 software package.

Differential scanning calorimetry (DSC) was performed on a TA series DSC 2010 instrument with 2–5 mg of polymer samples weighed in aluminum pans. All experiments were carried out under a nitrogen atmosphere and the measurement was started as soon as the heat flow in the DSC cell was stabilized. The samples were analyzed in a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$.

IR spectra of the compounds were measured ($4000\text{--}200 \text{ cm}^{-1}$) using a Perkin-Elmer IR 883 spectrophotometer. The X-ray diffractogram of the polymers were recorded on a model JDX-11P3A JEOL diffractometer with a solid sample using a Ni filter with $\text{CuK}\alpha$ radiation at 35 kV and 10 mA in the wide-angle range of $2^\circ < 2\theta < 60^\circ$. The $^1\text{H-NMR}$ spectrum was recorded on a Bruker 300 MHz spectrometer in CDCl_3 using tetramethylsilane (TMS) as the internal reference.

RESULTS AND DISCUSSION

Reverse ATRP has already been established for both copper and iron complexes. Here, a conventional radical initiator such as AIBN as a source of the reducing agent together with a transition metal complex in its higher oxidation state was used. At higher temperature and in presence of the monomer, the initiator system became a conventional ATRP initiating system by decomposition of the radical initiator to form radicals which then react with the higher transition state metal to form the polymeric halide and the complex of the transition metal in its lower oxidation state. However, as reported in the literature, the reverse ATRP of acrylates and methyl methacrylate (MMA) is not a controlled one.²⁸ The polymerization was very fast and led to gelation at about a 40% monomer conversion with a very broad multimodal MWD. To cope with such a problem, in a transition metal-mediated reverse ATRP system, a catalytic amount of AIBN as a radical source was used to maintain the low concen-

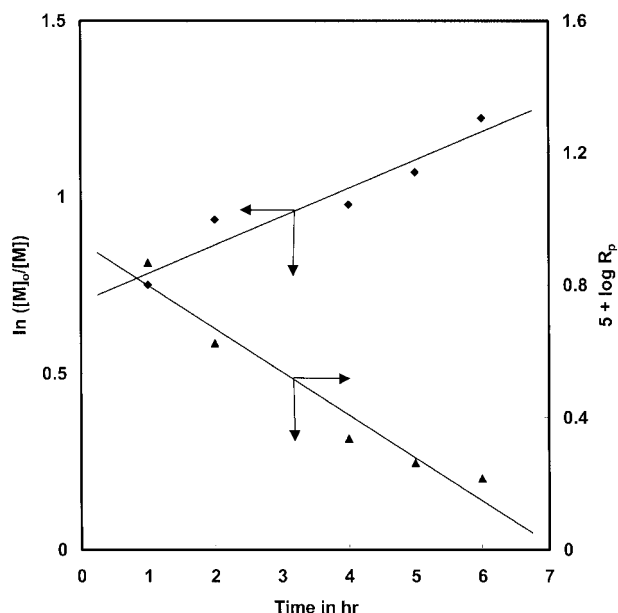


Figure 1 Rate of polymerization (R_p) and $\ln([M]_0/[M])$ plots versus time for ATRP of SMA at 80°C in DMF in the presence of AIBN as the source of the reducing agent. Conditions: $[\text{SMA}] = 0.50\text{M}$; $[\text{AIBN}] = 2.00 \times 10^{-2} \text{ M}$; $[\text{CBr}_4] = 0.10 \text{ M}$; $[\text{Fe(III)}] = 1.33 \times 10^{-3} \text{ M}$; $[\text{bpy}] = 4.00 \times 10^{-3} \text{ M}$.

tration of growing radicals and a suitable alkyl halide as a coinitiator to control the molecular weight of the final product.²⁸ Here, we describe the polymerization of SMA in DMF by a novel ATRP method which is promoted by an Fe(III) complex of bpy in the presence of AIBN as the source of the reducing agent to supply Fe(II) ion throughout the reaction and CBr_4 as the initiator.

The results of the polymerization of SMA in DMF for various conditions are presented in Figures 1–4. The linearity of the semilogarithmic plot of $\ln([M]_0/[M])$ versus time indicates that the polymerization is first-order with respect to the monomer concentration and that the living radical concentration is constant throughout the polymerization (Fig. 1). The apparent rate constant was found to be $2.23 \times 10^{-5} \text{ s}^{-1}$ at 80°C .

Bamford et al.⁴⁰ studied the polymerization of MMA by using metallic carbonyls in the presence of CBr_4 . They assumed that two types of initiating radicals are generated from CBr_4 (i.e., $\dot{\text{C}}\text{Br}_3$ and $\cdot\text{Br}$). By incorporating radioactive ^{13}C -labeled CBr_3 to the polymer chain end, they established that the initiating radicals are $\dot{\text{C}}\text{Br}_3$. CBr_4 is a highly active chain-transfer agent, and since transfer also gives rise to the terminal CBr_3 group in the polymer, it is necessary to use a low concentration of CBr_4 .⁴⁰ For this reason, low concentrations of CBr_4 were used in the present work. CBr_4 is a reactive halide, and with CBr_4 , the rate of secondary radical formation is much higher and the two processes cannot be separated. They also reported that both stages yield $\dot{\text{C}}\text{Br}_3$ radicals for initiation.⁴⁰

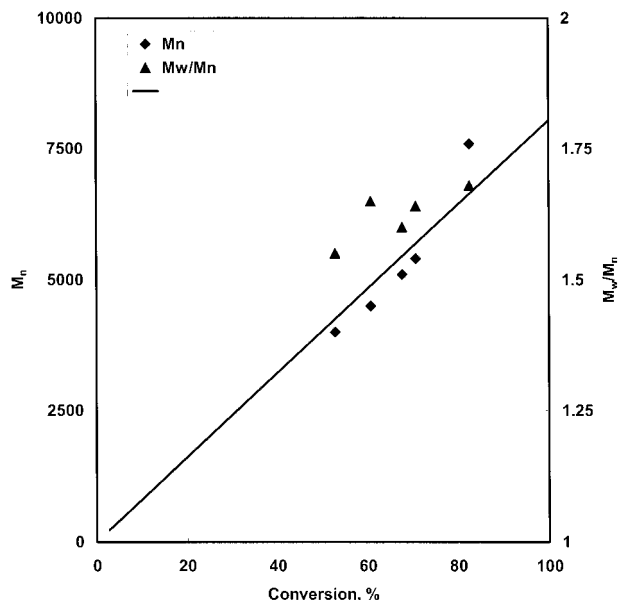


Figure 2 PSMA molecular weight (M_n) and polydispersity index (M_w/M_n) as a function of conversion in the ATRP of SMA at 80°C in DMF in the presence of AIBN as the source of the reducing agent. Conditions: [SMA] = 1.00M; [AIBN] = 2.00×10^{-2} M; [CBr₄] = 0.10M; [Fe(III)] = 1.33×10^{-3} M; [bpy] = 4.00×10^{-3} M.

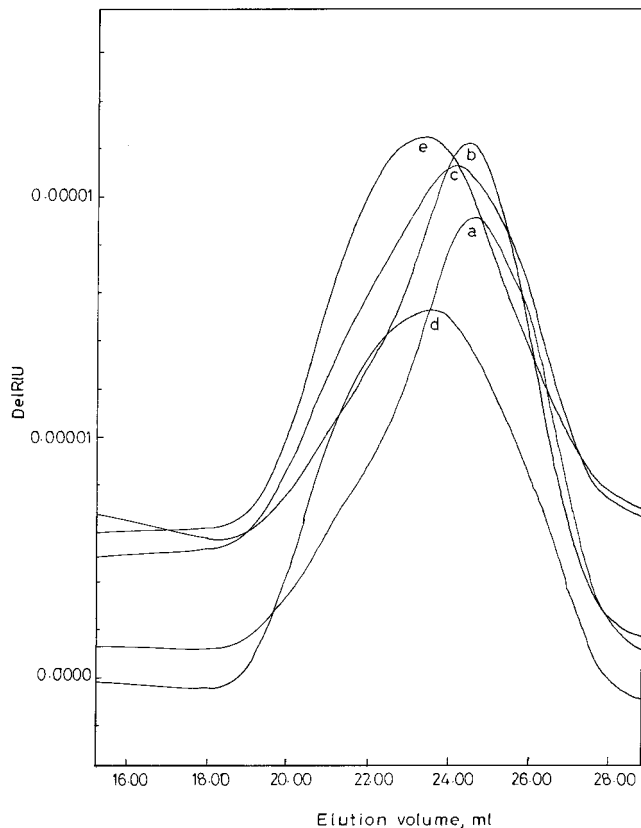


Figure 3 GPC traces (RI detector) of PSMA synthesized by ATRP of SMA at 80°C in DMF in the presence of AIBN as the source of the reducing agent. Conditions: [SMA] = 1.00M; [AIBN] = 2.00×10^{-2} M; [CBr₄] = 0.10 M; [Fe(III)] = 1.33×10^{-3} M; [bpy] = 4.00×10^{-3} M. Conversions for curves: (a) = 52.8%; (b) = 60.7%; (c) = 67.7%; (d) = 70.6%; (e) = 82.5%.

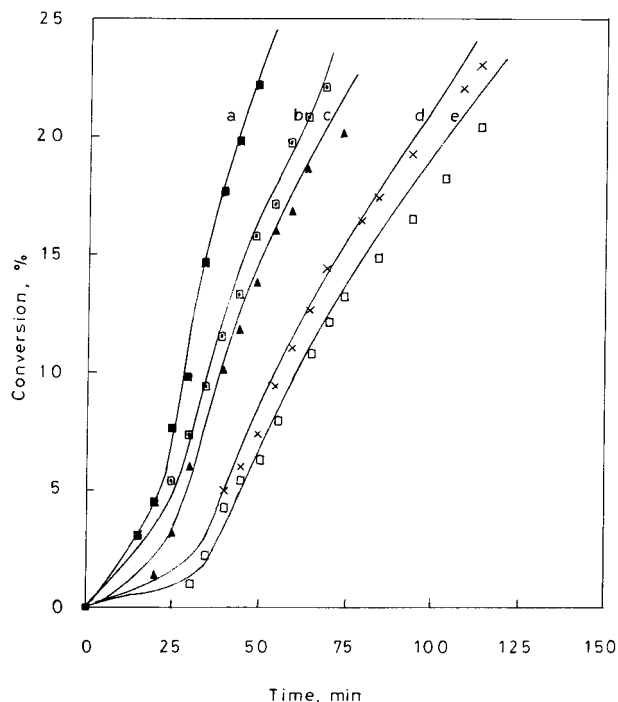


Figure 4 ATRP of SMA 80°C in DMF in the presence of different concentrations of $\text{Fe}(\text{bpy})_3^{3+}$. Conditions: [SMA] = 1.00M; [AIBN] = 2.00×10^{-2} M; [CBr₄] = 0.10M; [Fe(bpy)₃³⁺], for curves: (a) = 3.33×10^{-4} M; (b) = 6.66×10^{-4} M; (c) = 1.00×10^{-3} M; (d) = 1.33×10^{-3} M; (e) = 1.66×10^{-3} M.

Figure 2 shows the number-average molecular weight (M_n) of PSMA produced an increase with increasing conversion. The molecular weight determined from GPC was lower than the predicted value. The deviation of the theoretical M_n from the experimental M_n is presumably due to the chain transfer to CBr₄. This disparity may be also caused by a hydrodynamic difference between the PSMA polymer and polystyrene standards. The GPC curves of PSMA shown in Figure 3 show sharp peaks and the MWDS (M_w/M_n) are uniform throughout the polymerization, indicating a controlled polymerization. For comparison of the (M_w/M_n), free-radical polymerization of SMA was conducted with AIBN as the initiator in the presence of bpy at 80°C for 6 h. The molecular weight was 3.75×10^4 with an M_w/M_n of 3.22. From these results, we can see that the M_n and M_w/M_n are much higher than those produced by the ATRP mechanism.

The bpy had a pronounced effect on the Lewis acid-catalyzed ATRP of SMA. It was confirmed spectroscopically that complex A with bpy in the molar ratio of [A]:[bpy] = 1:3 produced only ³⁹Fe(bpy)₃³⁺ and no other complex even in the presence of excess bpy. A chelating nitrogen ligand like bpy forms low-spin complexes that are fairly inert to substitution by other ligands.⁴¹ The effect of Fe(III) on the ATRP of SMA at

TABLE I
Effect of Concentrations of [SMA], [Fe(III)], [AIBN], and [CBr₄] on the Molecular Weight, Rate of Polymerization, Polydispersity Index, and Thermal Behavior of PSMA Prepared by ATRP in a Nitrogen Atmosphere at 80°C in DMF

[SMA] (mol L ⁻¹)	10 ³ × [Fe(III)] (mol L ⁻¹)	10 ² × [AIBN] (mol L ⁻¹)	10 ² × [CBr ₄] (mol L ⁻¹)	10 ⁵ × R _p (mol L ⁻¹ s ⁻¹)	M _n	M _w /M _n	mp (°C)	ΔH _m (kJ mol ⁻¹)	ΔS _m (J K ⁻¹ mol ⁻¹)
1.00	1.33	2.00	10.00	3.97	6600	1.51	45.0	26.23	82.51
0.75	1.33	2.00	10.00	2.87	6100	1.66	44.2	26.75	84.35
0.50	1.33	2.00	10.00	1.53	5100	1.64	43.3	27.24	86.12
0.30	1.33	2.00	10.00	0.42	4400	1.30	42.7	27.60	87.45
0.50	1.00	2.00	8.00	2.13	8300	1.80	44.7	27.72	87.26
0.50	1.00	2.00	6.00	2.07	9100	1.77	44.5	26.91	84.79
0.50	1.00	2.00	3.00	2.11	10,200	1.72	44.8	26.73	84.12
0.50	1.00	2.00	2.00	2.20	12,000	1.71	45.7	26.17	82.28
0.50	5.00	2.00	10.00	1.63	5900	1.75	43.5	26.96	85.20
0.50	0.67	2.00	10.00	1.60	6500	1.55	46.8	24.03	75.12
0.50	0.40	2.00	10.00	1.73	6200	1.59	46.0	24.34	76.32
0.50	0.27	2.00	10.00	1.86	5400	1.70	44.1	24.39	76.92
0.50	0.13	2.00	10.00	1.99	5200	1.73	44.0	24.84	78.36

80°C was followed dilatometrically by adding different concentrations of Fe(bpy)₃³⁺ to a constant composition of SMA, CBr₄, and AIBN in DMF. A few rate curves obtained from the dilatometric experiments are shown in Figure 4. Studies^{38,39} revealed that transition metal complexes play a significant role in vinyl polymerization under usual reaction conditions. The same metal ion can accelerate, retard, and initiate the polymerization reaction. The effect depends upon the method of initiation, the ligand associated or coordinated with the metal ion, and the mechanism of the reaction.^{42,43} They may also induce an atom transfer reaction or provide a source of metal-complexed radicals or even initiate a polymerization catalytic cycle that does not involve radical interactions.⁴⁴ Therefore, the reduction of R_p with increasing Fe(III) in the polymerization of SMA may be due to the retarding effect of Fe(III) complexes.

Vofsi et al.^{45,46} proposed a chain mechanism for the iron chloride-catalyzed telomerization where the catalyst participated in the chain propagation as a chlorine atom transfer agent. The catalyst in its oxidized form is a much more efficient chlorine atom donor than is the halogen-containing substrate. Fe(III) ions so produced can be instantaneously oxidized by CCl₄ to produce ĊCl₃.

The ATRP mechanism relies on a fast equilibrium between dormant polymeric halide and active species (group radical) as shown in Scheme 1.^{1,2} When used as halogen for redox polymerization, polyhaloalkanes can be divided into two main categories⁴⁷: 1,1,1, trihaloalkanes; tetrahaloalkanes, including 1,1,1,3 tetrahalocompounds resulting from telomerization of an alkene with tetrahalomethane; and tetrahaloalkanes themselves. Among tetrahaloalkanes, CCl₄ has been the most widely used halogen in redox telomerization.⁴⁷ The ability of a —CCl₃ end group in transition metal-catalyzed redox telomerization prompted many researchers to use CCl₄ as a promoter of bis-telomerization.

Therefore, the ATRP of SMA initiated by CBr₄ may follow the same mechanistic pathway. To establish the effect of CBr₄ during the initial stages, we used it at different concentrations in the ATRP of SMA catalyzed by Fe(III)/bpy (Table I).

The homogeneous ATRP of SMA using the Fe(III)/bpy catalyst system has been proposed to occur by the mechanism illustrated in Scheme 1. The polymerization of SMA in the presence of the Fe(III) complex plausibly proceeds by the same ATRP as proposed for the other ATRP systems.

The polymeric halide (P_m—X) may be repeatedly activated by the Fe(II) species to form the growing radical P_m[•] and X—Fe(III). The X—Fe(III) species may rapidly react with a propagating polymeric radical, which has incorporated several monomer molecules to regenerate P_m—X and the Fe(II). Repetition of the reactions results in the formation of well-defined tailor-made polymers. A fast equilibrium between the growing radicals and dormant species is achieved by using a metal complex that changes between *n* and *n* + 1 oxidation states.

The structure of the chain ends of low molecular weight PSMA, synthesized by the ATRP technique, was analyzed by ¹H-NMR spectroscopy. Figure 5 presents the ¹H-NMR spectra of PSMA, which was prepared at 80°C using AIBN as the radical source and CBr₄ as the initiator and in the presence of Fe(bpy)₃³⁺. 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. Similar spectra of PMMA obtained from the reverse ATRP of MMA were reported in the literature such as the signals at 3.72 ppm reported by Qin et al.³¹ and 3.79 ppm by Moineau et al.³⁰ This was ascribed to the effect of the ω-chlorine end group. These results indi-

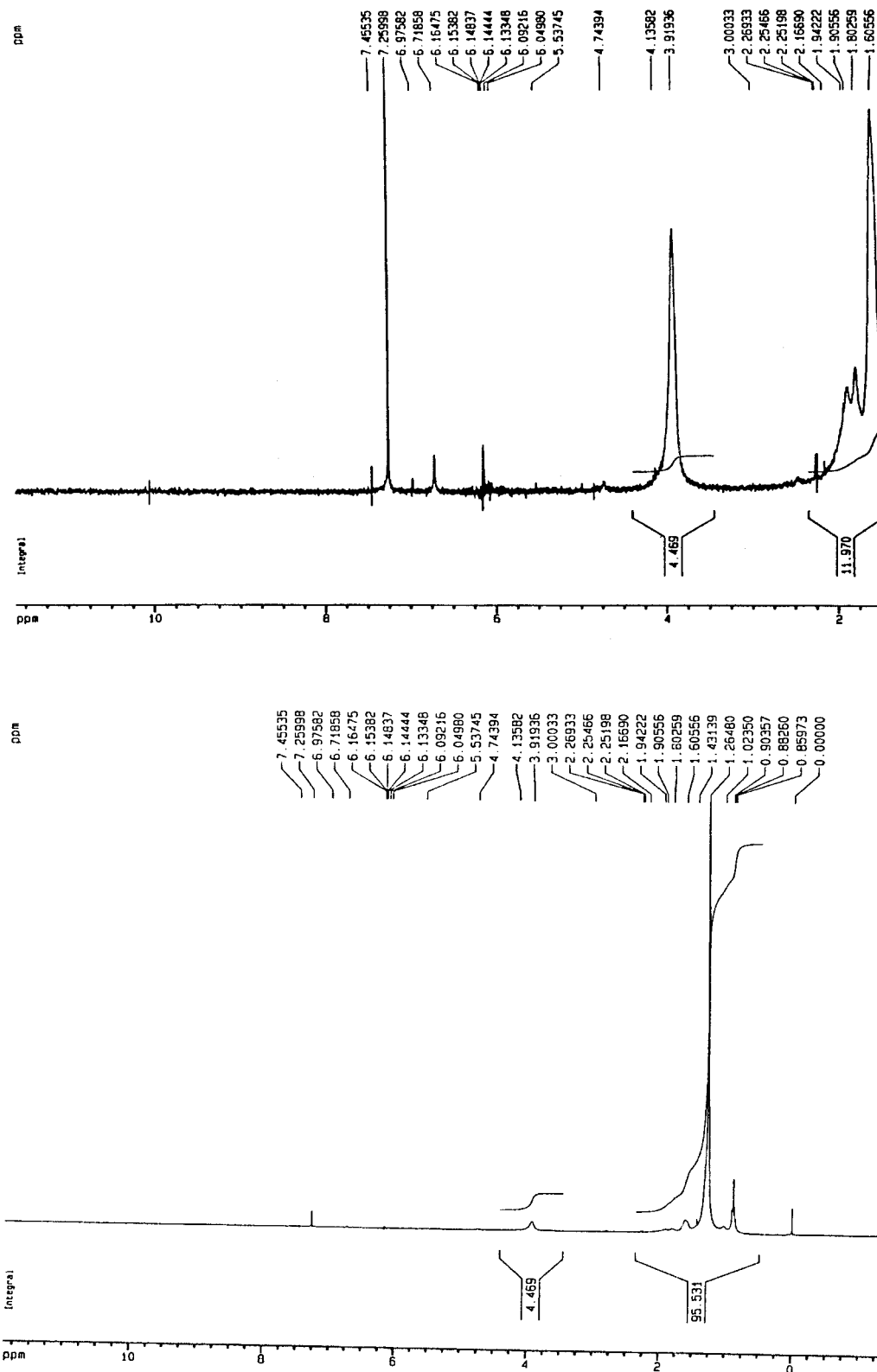
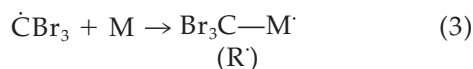
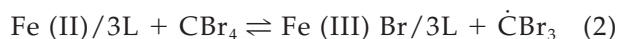
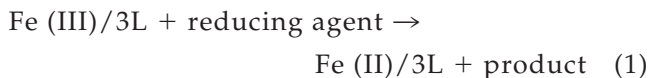
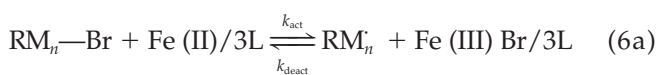
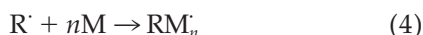


Figure 5 ¹H-NMR of PSMA synthesized by ATRP of SMA at 80°C in DMF in the presence of AIBN as the source of the reducing agent. Conditions: [SMA] = 0.50M; [AIBN] = 2.00 × 10⁻² M; [CBr₄] = 0.10M; [Fe(III)] = 1.33 × 10⁻³ M; [bpy] = 4.00 × 10⁻³ M.

cate that PSMA was end-functionalized with the ω-chlorine group from the catalyst. The molecular weight determined from the ¹H-NMR spectrum is not

same as the one obtained from GPC. This is evident because the *M_n(GPC)* of PSMA was obtained from a polystyrene standard.

Initiation:**Propagation:****Termination:**

Mutual termination by disproportionation through transfer of hydrogen atom:



Mutual termination by combination



The X-ray diffraction pattern of PSMA shows a peak at about $2\theta = 22^\circ$, which corresponds to 4.16 \AA spacing (Fig. 6). This corresponds to the value of several long-chain acrylate and methacrylate comblike polymers,⁴⁸ attributed to the van der Waals contract of nonbonded atoms.⁴⁹ 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 contract structures in the comblike PSMA. On the basis of a detailed study of the conventional comblike polymers, Yokota et al.⁵⁰ proposed a peculiar layered structure made up of several parallel alkyl side chains arranged on both sides of the main chain.

Poly(*n*-alkyl)acrylates and methacrylates crystallize in hexagonal packing (in accordance with the X-ray studies) as characterized by a single absorption band⁵⁰ at 720 cm^{-1} . PSMA prepared by the present initiation system also shows a single band at 720 cm^{-1} , indicating that the long alkyl side chains of PSMA are of hexagonal-type packing.

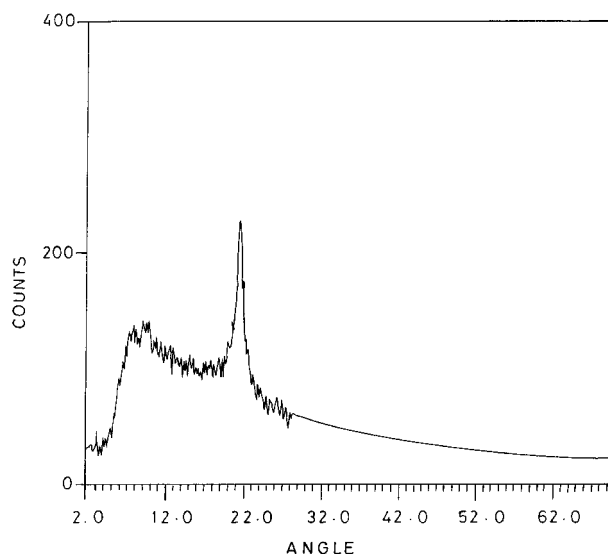


Figure 6 Typical X-ray diffraction pattern of PSMA synthesized by ATRP of SMA at 80°C in DMF in the presence of AIBN as the source of the reducing agent.

The effect of the variation of $[\text{SMA}]$, $[\text{Fe(III)}]$, and $[\text{CBr}_4]$ on the M_n and M_w/M_n of PSMA is presented in Table I. It was found that, with increasing $[\text{SMA}]$, both R_p and M_n increased. Similarly, M_n increases with decreasing $[\text{CBr}_4]$. The higher value of M_w/M_n may be attributed to branching reactions or to the gel effect.²⁵ The branching may be due to the extraction of a large number of hydrogen atoms from the long alkyl group of the alkyl chain.

DSC measurements of PSMA were carried out at a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. Figure 7 shows a typical DSC curve of PSMA. Melting endothermic peaks were observed at $40\text{--}48^\circ\text{C}$ for the polymer samples. The melting point (mp) and heat of fusion (ΔH_m) were determined from the endothermic peaks. These values are shown in Table I. The mp and ΔH_m values were almost constant regardless of the percent conversion and the molecular weights of the polymers. Like the ΔH_m value, the value of the entropy of fusion (ΔS_m) is also constant, which results in the fact that the mp changes are not very predominant.

CONCLUSIONS

We investigated CBr_4 as the initiator for ATRP of SMA in DMF catalyzed by Fe(III)/bpy in the presence of AIBN as the source of the reducing agent. A well-defined PSMA with a quite narrow M_w/M_n was obtained. The M_n of the polymers increased with an increasing monomer concentration and first-order plots were conducted. Polymers with various MW and narrow M_w/M_n were prepared.

Because Lewis acids are good electron acceptors, complex A, therefore, enhanced the electron-donating

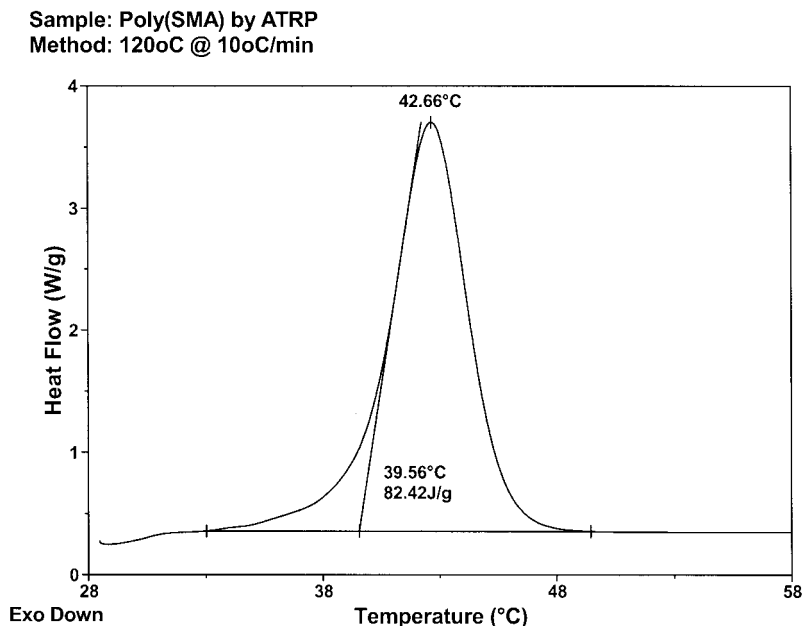


Figure 7 Typical DSC thermogram (scanning rate = $10^{\circ}\text{C min}^{-1}$) of PSMA synthesized by ATRP of SMA at 80°C in DMF in the presence of AIBN as the source of the reducing agent.

capacity of bpy and the rate of formation of free radicals became rapid. Consequently, it tends to maintain the activity of the catalytic system composed to redox telomerization. The presence of a catalytic amount of growing radicals and a fast equilibrium between growing radicals and dormant species are mandatory for ATRP of *n*-alkyl (meth)acrylates having a pendent alkyl side chain.

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