

## Atom Transfer Radical Polymerization of Hexadecyl Acrylate Using CuSCN as the Catalyst

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**Abstract:** The atom transfer radical polymerization (ATRP) of hexadecyl acrylate (HDA) was carried out in *N,N*-dimethylformamide (DMF) in the presence of CuSCN/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA). The results indicate that the polymerization is well-controlled: a linear increase of molecular weights occurs with respect to conversion and the polydispersities are relatively low. In particular, the use of CuSCN as the catalyst resulted in faster polymerization rates for hexadecyl acrylate than did those using either CuBr or CuCl; the polydispersity, however, was larger than those obtained in the cases when CuBr and CuCl were used. In addition, we report the thermodynamic data and activation parameters for the solution ATRP of hexadecyl acrylate.

**Keywords:** atom transfer radical polymerization, hexadecyl acrylate, CuSCN.

### Introduction

Atom transfer radical polymerization (ATRP) is a useful method for a controlled/"living" radical polymerization. A wide variety of monomers including styrene,<sup>1-4</sup> acrylates,<sup>5-8</sup> methacrylates,<sup>9-14</sup> acrylonitrile,<sup>15,16</sup> (meth)acrylamides,<sup>17-19</sup> sodium methacrylate<sup>20</sup> and 4-vinyl pyridine,<sup>21</sup> *et al.* have been polymerized in a well-controlled manner.

Poly(hexadecyl acrylate) is an important functional material for its long pendant alkyl side chain,<sup>22,23</sup> and most PHDA are produced by free radical polymerization. This is because under high conversion, free radical polymerization of *n*-alkyl acrylates shows a strong Trommsdorff effect. A considerable deviation from the normal kinetic parameters with a broadening of the molecular weight distribution is observed. Saikia<sup>24</sup> found that during the ATRP of stearyl methacrylate in *N,N*-dimethylformamide using the carbon tetrabromide/Fe(III)/2,2'-bipyridine initiator system in the presence of 2,2'-azobisisobutyronitrile, the rate exhibited first order kinetic in monomer with a controlled molecular weight, but molecular weight distribution was higher than 1.5. Beer<sup>25</sup> used a soluble catalyst instead of one which has poor solubility, improved both molecular weight control and polydispersities in the ATRP of lauryl acrylate. Recently, CuSCN has been reported as the catalyst for ATRP and it can induce faster polymerization compared to CuBr and CuCl.<sup>26</sup> In this article, we describe the well-controlled ATRP of HDA with

ethyl 2-bromopropionate (EBP) as the initiator and CuSCN/PMDETA as the catalyst.

### Experimental

**Materials.** Hexadecyl acrylate (HDA) was synthesized and confirmed the structure by <sup>1</sup>H-NMR,  $\delta$ 0.88(t, 3H),  $\delta$ 1.25-1.57(m, 29H),  $\delta$ 1.57-1.70(m, 2H),  $\delta$ 4.13-4.17(t, 2H),  $\delta$ 5.8(dd, 1H),  $\delta$ 6.1(m, 1H),  $\delta$ 6.38(dd, 1H). The purity was 99.3% analyzed by GC; *N,N*-dimethylformamide (analytic reagent, Shanghai Chemical Reagent Co., LTD.) was used as received without purification; Ethyl 2-bromopropionate (> 98%) was used as received from Merck; CuBr (chemically pure, Shanghai Chemical Reagent Co., LTD.) was purified by stirring in acetic acid, washing with methanol and then drying under vacuum; CuCl (chemically pure, Shanghai Chemical Reagent Co., LTD.) was dissolved in HCl, precipitated into a large amount of water, and then dried under vacuum; CuSCN(98.04%, Yixing Liaoyuan Chemical Co., LTD.) was purified by washing with acetic acid and acetone, then dried under vacuum; *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (chemically pure, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4 Å molecular sieve and distilled under vacuum. All other reagents used in this study were of analytic reagents.

**Polymerization.** The general procedure was as follows: an ampule tube was filled with CuSCN (2.20 mg,  $1.80 \times 10^{-5}$  mol), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (11.3  $\mu$ L,  $5.4 \times 10^{-5}$  mol), ethyl 2-bromopropionate (EBP) (2.32  $\mu$ L,  $1.78 \times 10^{-5}$  mol), DMF(190  $\mu$ L), HDA(1 mL,

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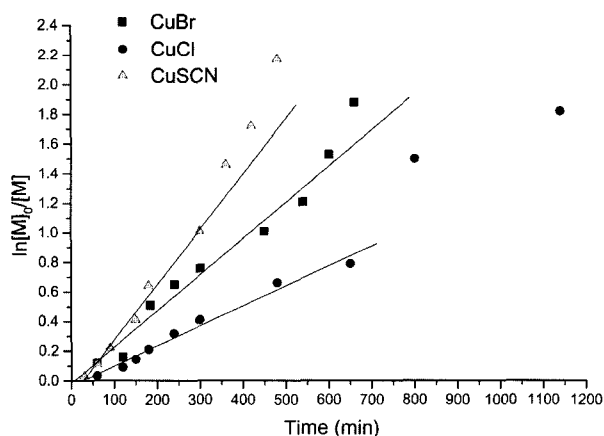
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$2.91 \times 10^{-3}$  mol) in sequence. The tube was purged with argon for 15 min to deplete oxygen in the solution, sealed with argon and then placed into the oil bath at the desired polymerization temperature. The polymerization was stopped after a desired period of time by cooling the tube under cold water. Afterwards, the tube was opened. The contents were transferred and dissolved in tetrahydrofuran (THF), and precipitated in a large amount of methanol. The dried polymer was then characterized by gravimetry.

**Characterization.** Conversion of monomer was determined by gravimetry. Molecular weights and the molecular weight distributions were measured using Waters 1515 GPC with THF as the mobile phase and at a column temperature of 30°C. Polystyrene standards were used to calibrate the columns.  $^1\text{H-NMR}$  spectrum was recorded in  $\text{CDCl}_3$  with an INOVA 400 MHz spectrometer at ambient temperature.

## Results and Discussion

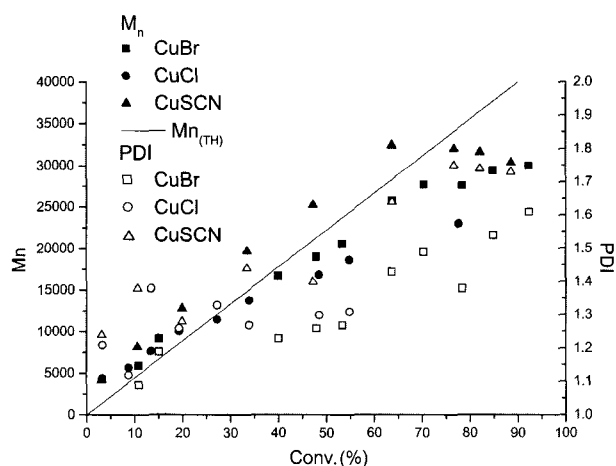
**Effects of Different Catalysts on Polymerization.** HDA was polymerized in DMF with EBP as the initiator using CuBr, CuCl and CuSCN as catalysts and PMDETA as the ligand. As shown in Figure 1, the plots of  $\ln([M]_0/[M])$  versus time are linear indicating first order kinetics in all cases. The propagating radical concentration is constant during the course of polymerization. But when the monomer conversion is above 60%, the plots deviate from linearity. One possible explanation is that as the conversion increased, the concentration of copper(II) decreased due to the low solubility of the Cu(II)-PMDETA complex.<sup>27</sup> The rate of polymerization of HDA with different Cu catalyst was in the order  $\text{CuSCN} > \text{CuBr} > \text{CuCl}$ . In Figure 2, the molecular weights increase with conversion, and the molecular weight distribution of ATRP of HDA using CuSCN is broader than those using CuBr and CuCl. It is hypothesized<sup>26</sup> that the higher rate of



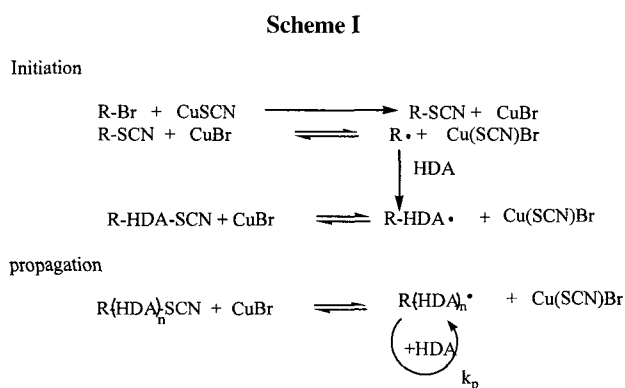
**Figure 1.** Effect of different catalyst on ATRP of HDA in DMF at 100°C.  $[\text{HDA}]_0 = 2.43 \text{ M}$ ;  $[\text{EBP}]_0 = 0.0148 \text{ M}$ ;  $[\text{CuBr}]_0 = [\text{CuCl}]_0 = [\text{CuSCN}]_0 = 0.015 \text{ M}$ ;  $[\text{PMDETA}]_0 = 0.045 \text{ M}$ ;  $V_{\text{HDA}}/V_{\text{DMF}} = 1:0.19$ .

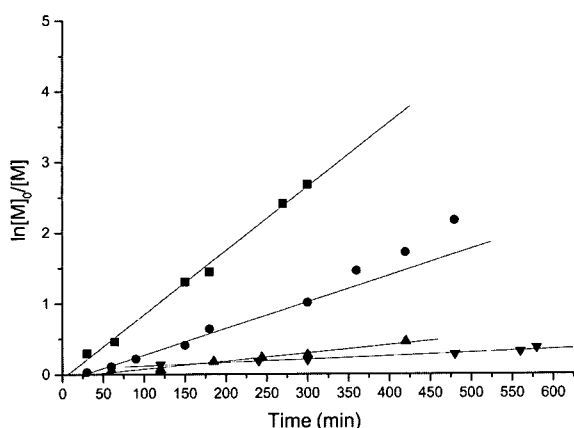
polymerization in this case is due to a slower deactivation reaction. This effect is greater than that of slower activation which results in an overall shift in equilibrium. In addition, due to the slower dynamics of equilibrium, multiple monomer additions may take place per activation-deactivation cycle that results in a broadening of the molecular weight distribution. Scheme I shows the mechanism of the ATRP of HDA. Singha<sup>26</sup> used the MALDI-TOF MS to confirm the presence of SCN at the end of the polymer.

**Effects of the Concentration of Initiator and Catalyst on Polymerization.** The kinetics of different concentrations of initiator are shown in Figure 3. It can be found that the rate of polymerization increases with the concentration of initiator. Plots of  $\ln k_p^{\text{app}}$  vs.  $\ln[\text{EBP}]_0$  and  $\ln k_p^{\text{app}}$  vs.  $\ln[\text{CuSCN}]_0$  show that the rate of polymerization is 0.46 order and 1.77 order with respect to the concentration of the initiator (Figure 4) and catalyst (Figure 5), respectively. The apparent external orders of the reactants deviate from the typical first orders. This may be contributed by the poor solubility of the catalyst complex formed with PMDETA and Cu(I)SCN in HDA. Figures 6 and 7 show the molecular weight,  $M_n$ , and molec-

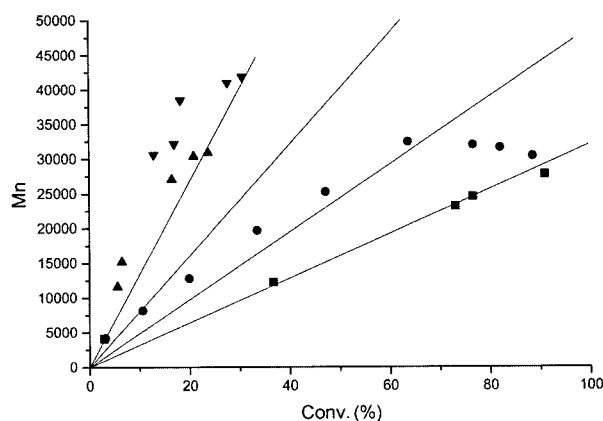


**Figure 2.** Dependence of  $M_n$  and PDI on the conversion with different catalyst.  $[\text{HDA}]_0 = 2.43 \text{ M}$ ;  $[\text{EBP}]_0 = 0.0148 \text{ M}$ ;  $[\text{CuX}]_0 = 0.015 \text{ M}$ ;  $[\text{PMDETA}]_0 = 0.045 \text{ M}$ .

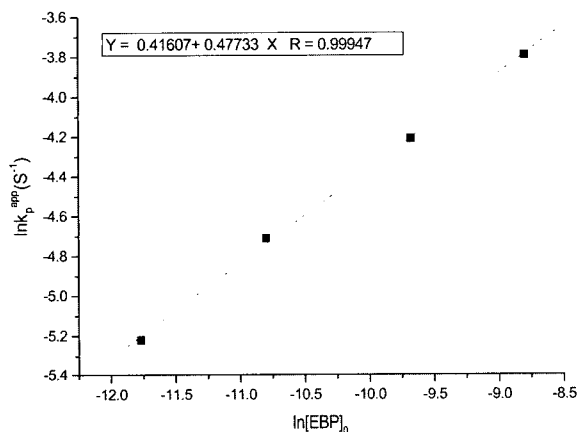




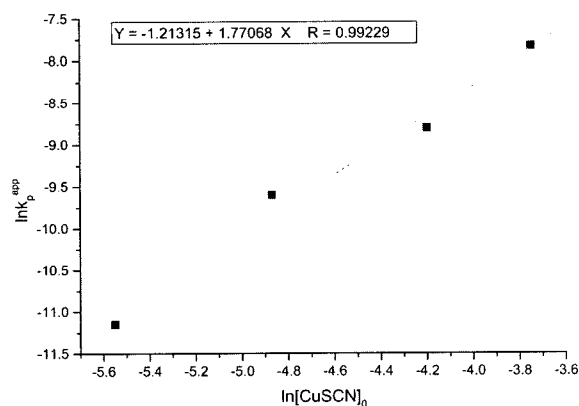
**Figure 3.** Effect of concentration of initiator on ATRP of HDA in DMF at 100 °C.  $[HDA]_0 = 2.43$  M;  $[CuSCN]_0 = 0.015$  M;  $[PMDETA]_0 = 0.045$  M;  $[EBP]_0 = 0.0225$  M (■); 0.0148 M (●); 0.009 M (▲); 0.0054 M (▼)  $V_{HDA}/V_{DMF} = 1:0.19$ .



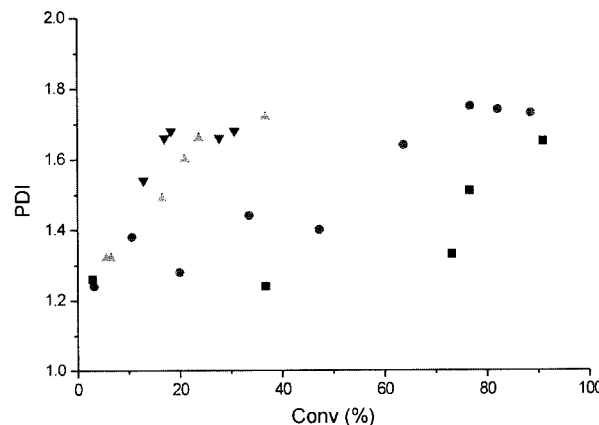
**Figure 6.** Dependence of molecular weight on monomer conversion for the ATRP of HDA in DMF at 100 °C.  $[HDA]_0 = 2.43$  M;  $[CuSCN]_0 = 0.015$  M;  $[PMDETA]_0 = 0.045$  M;  $[EBP]_0 = 0.0225$  M (■); 0.0148 M (●); 0.009 M (▲); 0.0054 M (▼).



**Figure 4.** Dependence of apparent rate constant of propagation ( $k_p^{app}$ ) on the initiator concentration for ATRP of HDA in DMF at 100 °C.



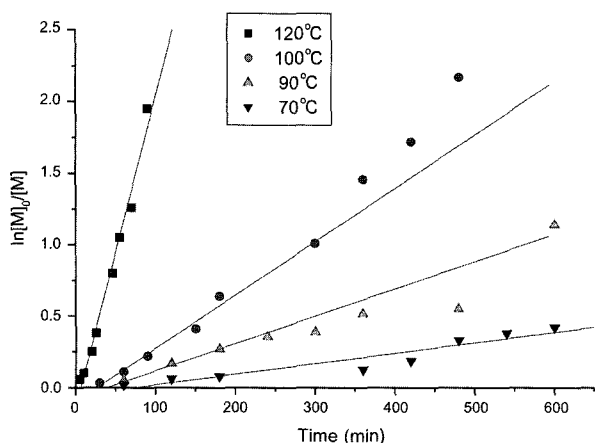
**Figure 5.** Dependence of apparent rate constant of propagation ( $k_p^{app}$ ) on the catalyst concentration for ATRP of HDA in DMF at 100 °C.



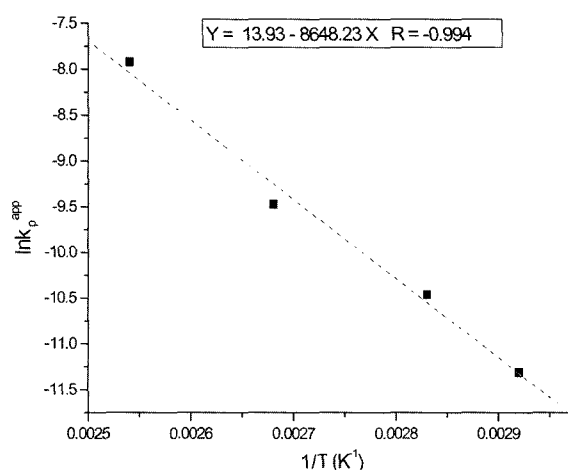
**Figure 7.** Dependence of molecular weight distribution on monomer conversion for the ATRP of HDA in DMF at 100 °C.  $[HDA]_0 = 2.43$  M;  $[CuSCN]_0 = 0.015$  M;  $[PMDETA]_0 = 0.045$  M;  $[EBP]_0 = 0.0225$  M (■); 0.0148 M (●); 0.009 M (▲); 0.0054 M (▼).

ular weight distribution, PDI. When the ratio of  $[HDA]_0$ :  $[EBP]_0 < 150:0.91$ , the experimental values by GPC are close to the theoretical value. Deviation from the theoretical line at higher ratio  $[HDA]_0$ :  $[EBP]_0 > 150:0.56$  indicate transfer of some chains by undefined impurities. Namely, the PDI is narrower at the lower ratios than those at higher ratios.

**Effects of Polymerization Temperature on the Polymerization.** The effect of the reaction temperature on the polymerization was studied over a temperature range of 70–120 °C.  $\ln([M]_0/[M])$  vs. reaction time shows a good linearity at all temperature, indicating that the radical concentration in all these systems is low enough to prevent significant radical termination. From Figure 8, it can be found that even at lower polymerization temperature (70 °C) the ATRP of



**Figure 8.** Effect of polymerization temperature on ATRP of HDA in DMF with CuSCN/PMDETA.  $[HDA]_0 = 2.43$  M;  $[EBP]_0 = 0.0148$  M;  $[CuSCN]_0 = 0.015$  M;  $[PMDETA]_0 = 0.045$  M;  $V_{HDA}/V_{DMF} = 1:0.19$ .



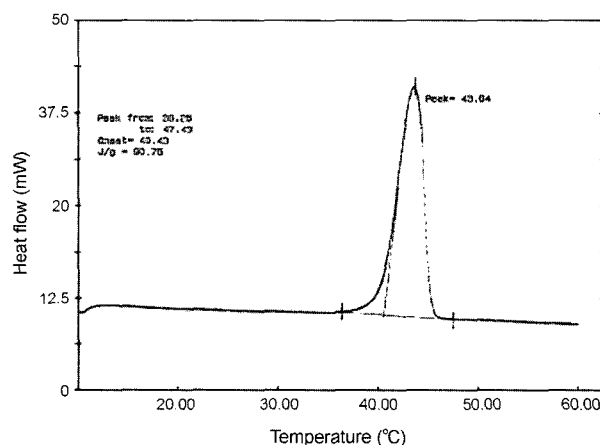
**Figure 9.** Plots of  $\ln k_p^{app}$  vs.  $1/T$  for ATRP of  $[HDA]_0 = 2.43$  M;  $[EBP]_0 = 0.0148$  M;  $[CuSCN]_0 = 0.015$  M;  $[PMDETA]_0 = 0.045$  M.

HDA is well controlled and has a fast rate of polymerization. This indicates that CuSCN/PMDETA/EBP is an effective catalyst system for ATRP of HDA. The Arrhenius plot for the CuSCN/PMDETA catalyzed polymerization of HDA is shown in Figure 9. Based on the slope, an apparent energy of activation,  $E_{app}^\ddagger = 17.1$  kcal/mol was calculated. According to Eq. (1),  $\Delta H_{eq}^0 = 12.2$  kcal/mol was obtained. This value is much lower than the corresponding values for ATRP of BA ( $\Delta H_{eq}^0 = 63.6$  kcal·mol<sup>-1</sup> initiated with ethyl 2-bromoisobutyrate<sup>28</sup> and values for MA<sup>29</sup> ( $\Delta H_{eq}^0 = 23$  kcal·mol<sup>-1</sup> for ATRP initiated by methyl 2-bromopropionate).

$$\Delta H_{eq}^0 = E_{app}^\ddagger - E_{prop}^\ddagger \quad (1)$$

$$\Delta H_{prop}^\ddagger \approx 4.95 \text{ kcal/mol.}^{30}$$

DSC measurements of PHDA were carried out at a heating rate of 5 °Cmin<sup>-1</sup> in a nitrogen atmosphere. Figure 10 shows a typical DSC curve of PHDA. Melting endothermic peaks are observed at 40–46 °C. The melting point and heat fusion are determined from the endothermic peaks. It can be found



**Figure 10.** Typical DSC thermogram (scanning rate = 5 °Cmin<sup>-1</sup>) of PHDA synthesized by ATRP of HDA at 100 °C in DMF in the presence of CuSCN/PMDETA/EBP.

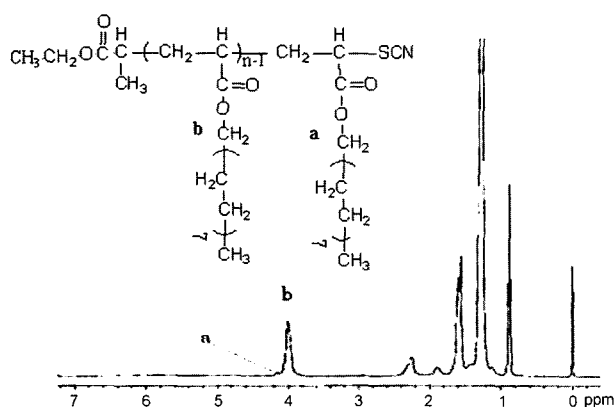
from Table I that the melting point (mp) and heat fusion ( $\Delta H_m$ ) are constant regardless of the monomer conversion and the molecular weights of the polymers. The entropy of

**Table I.** Effect of the Conversion of Monomer and Molecular Weight on the Melting Point and Heat of Fusion of PHDA Prepared by ATRP in DMF at 100 °C

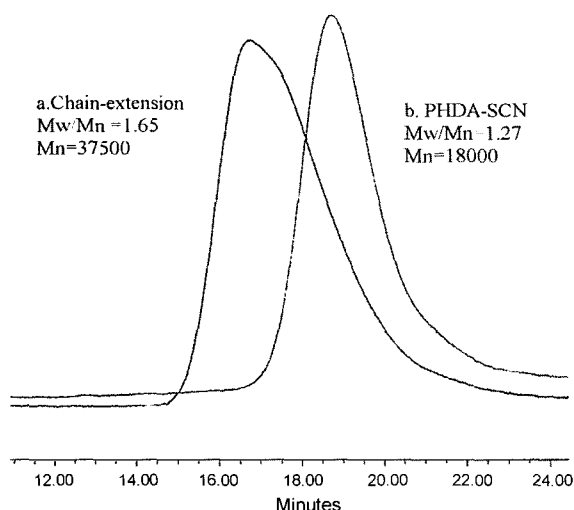
Entry	Conversion(%)	$M_{n(th)}$	$M_{n(GPC)}$	$M_w/M_n$	mp (°C)	$\Delta H_m$ (kJ/mol)	$\Delta S_m$ (J/K mol)
1	10.6	5,100	8,100	1.38	40.6	26.39	84.15
2	19.9	9,700	12,800	1.28	36.4	26.70	86.30
3	33.5	16,300	19,700	1.44	36.9	18.78	60.00
4	47.2	22,900	25,200	1.40	36.8	27.20	87.80
5	63.7	30,900	32,400	1.64	40.6	26.98	86.03
6	88.6	43,000	30,300	1.73	40.4	26.86	85.71

fusion ( $\Delta S_m$ ) is also constant. The changes in melting point are not predominant. Typical values of  $\Delta H_m$  and  $\Delta S_m$  are 26–28 kJ mol<sup>-1</sup> and 84–89 JK<sup>-1</sup> mol<sup>-1</sup>, respectively. Compared with another important monomer with long alkyl chain, stearyl methacrylate, they have similar thermodynamic data and regularity changes.<sup>31</sup>

**End Group Characterization and Chain Extension.** The structure of the chain ends of PHDA synthesized by ATRP was analyzed by <sup>1</sup>H-NMR spectroscopy. Figure 11 presents a signal (a) at 4.15–4.20 ppm corresponding to the hexadecyl ester group at the chain end, which departs from other methylene protons of the repeated hexadecyl esters, because it was effected by an  $\omega$  pseudohalide group in the PHDA chain end. Thus, these demonstrate the quantitative presence of a pseudohalide at  $\omega$  end of the chain. The polymeri-



**Figure 11.** <sup>1</sup>H NMR of PHDA initiated with CuSCN/PMDETA/EBP at 100°C.



**Figure 12.** GPC curves of PHDA a. polymer obtained after chain extension using PHDA-SCN as macroinitiator, CuBr/PMDETA as catalyst; b. macroinitiator.  $[HDA]_0:[macroinitiator]_0:[CuBr]_0:[PMDETA]_0 = 75:0.27:1:3$ ;  $V_{toluene}:V_{HDA} = 1:2$ ; polymerization temperature = 100°C.

zations of HAD in toluene with the obtained PHDA bearing terminal group (PHDA-SCN) acting as a macroinitiator catalyzed by EBP/CuSCN/PMDETA were performed at 100°C. GPC curves (Figure 12) illustrate the changes in  $M_n$  and  $M_w/M_n$  before and after the polymerization.  $M_n$  went from 18,000 up to 37,400, and  $M_w/M_n$  changed from 1.27 to 1.65. All these results demonstrate that the polymerization of HDA in this process is carried out according to the mechanism of ATRP.

## Conclusions

We investigated ethyl 2-bromopropionate as the initiator for ATRP of HDA catalyzed by CuSCN/PMDETA in DMF. A well-defined PHDA with a narrow PDI was obtained. The molecular weight of the polymer increased with monomer conversion. Compared with the catalysts of CuBr/PMDETA and CuCl/PMDETA in the ATRP of HDA, CuSCN can induce a faster rate of polymerization, but a larger polydispersity in the presence of EBP. In addition, the ATRP of HDA in this system has a lower value of  $\Delta H_{eq}^0$  which indicates that radicals are easily obtained at a low reaction temperature.

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