Macromol. Rapid Commun. **20,** *303–307 (1999)*

Kinetics of heterogeneous atom transfer radical polymerization of styrene by using bis(1,10-phenanthroline)copper bromide[a]

*Guang Lou Cheng, Chun Pu Hu, Sheng Kang Ying**

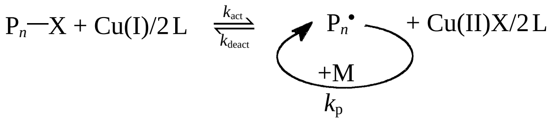
Laboratory of Living Polymerization, East China University of Science and Technology, Box 289,
130 Meilong Road, Shanghai 200237, P. R. China

(Received: June 18, 1998; revised: September 14, 1998)

SUMMARY: The kinetics of atom transfer radical polymerization (ATRP) of styrene using bis(1,10-phenanthroline)copper bromide was investigated. The concentration of the copper catalyst does not affect the propagation rate but does affect the termination process of polymerization appreciably. With increasing reaction temperature the molecular weight distribution of the produced PS becomes more narrow. The apparent activation energy was found to be 75 kJ/mol.

Introduction

Free radical polymerization is one of the most important commercial processes because of the wide scope of suitable monomers and the simplicity of polymerization conditions[1)]. However, it is always considered to be unable to afford polymers with well-defined structures and controlled molecular weights because of the unavoidable irreversible termination of propagating polymer chains such as radical recombination and/or disproportionation[2)]. On the other hand, if a fast equilibrium between propagating radicals and some polymers, which is similar to an equilibrium between propagating cations and non-propagating halogen terminated polymers in living carbocationic polymerizations[3–5)], was established in free radical polymerization, the impact of the termination upon the final product of radical polymerization would be minimized. In fact, many controlled radical polymerizations have been achieved based on this idea[6–13)]. One of them was atom transfer radical polymerization (ATRP)[6–8)]. In this case, a cuprous complex, *in-situ* formed from the coordination reaction of 2,2′-bipyridine (bpy) or 4,4′-di-(5-nonyl)-2,2′-bipyridine (dNbpy) with cuprous halide during polymerization, was used as a catalyst, and an organic halide was used as an initiator to promote the controlled radical polymerization, and to produce polymers with predetermined molecular weights as well as narrow polydispersities. The ‘living’ nature of the ATRP was ascribed to a fast equilibrium between the propagating radicals ($P_n^\bullet$) and non-propagating halogen terminated polymers (P_n–X) accompanied by a Cu(I)/Cu(II) redox equilibrium, as indicated in Eq. (1), where M and L stand for monomer and bpy or dNbpy:



$$P_n\text{—X} + \text{Cu(I)/2L} \underset{k_\text{deact}}{\overset{k_\text{act}}{\rightleftharpoons}} P_n^\bullet \;(+\text{M},\, k_p) + \text{Cu(II)X/2L} \qquad (1)$$

The equilibrium constant and the overall rate of polymerization for such an ATRP system can be expressed as in Eq. (2) and Eq. (3), respectively.

$$K_\text{e} = \frac{k_\text{act}}{k_\text{deact}} = \frac{[P_n^\bullet][\text{Cu(II)X}]}{[P_n\text{X}][\text{Cu(I)}]} \qquad (2)$$

$$[P_n^\bullet] = \frac{K_\text{e}[P_n\text{X}][\text{Cu(I)}]}{[\text{Cu(II)X}]} = \frac{K_\text{e}[\text{RX}][\text{Cu(I)}]}{[\text{Cu(II)X}]}$$

$$R_\text{p} = k_\text{p}[\text{M}][P_n^\bullet] = k_\text{p}\frac{K_\text{e}[\text{RX}][\text{Cu(I)}]}{[\text{Cu(II)X}]}[\text{M}] \qquad (3)$$

Kinetic studies on styrene (St) polymerization by using the heterogeneous 1-phenylethyl chloride (1-PECl)/CuCl/bpy system[7)] showed kinetics of order 1, 0.4, and 0.6 with respect to the concentrations of RX, Cu(I) and bpy, respectively. The homogeneous 1-PEBr/CuBr/dNbpy/St system[8)] exhibited first-order kinetics with respect to both RX and Cu(I) concentrations but the polymerization kinetics were not simply inverse first-order with respect to the initial Cu(II) concentration.

1,10-Phenanthroline (phen) is a less expensive ligand and it is a more rigid molecule as compared to bpy with a flexible C(2)–C(2′) bond concerning the rotation. In addition, the oxidation-reduction potentials for bpy and phen complexes (the redox potentials of $\text{Cu(bpy)}_2\text{Cl}$ and $\text{Cu(phen)}_2\text{Cl}$ are +120 mV and +174 mV, respectively) show that phen stablizes the Cu(I) state rather than bpy possibly because the former has a more delocalized electronic structure whose π^* orbitals contribute accordingly more to the π-back-bonding interaction[14)]. However, Hàjek et al. concluded that phen/CuCl showed a higher catalytic activity and selectivity than bpy/CuCl in atom transfer radical addition (ATRA) reactions[15)]. Regarding the aforementioned background, it is encouraging to

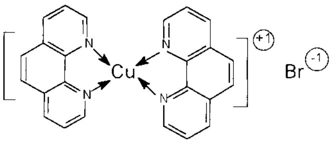
---

[a] Project “Study of copolymerization methods and molecular design of copolymers” supported by NNSFC.

1022-1336/99/0606–0303$17.50+.50/0

investigate the feasibility of ATRP catalyzed by the CuX/phen complex. We and Destarac et al. have reported that RX/CuX/phen is also an effective system to control the polymerization of styrene[16–18] or methyl methacrylate[19].

It should be pointed out that in both bpy(dNbpy)/CuX and phen/CuX systems studied, the ligands and the cuprous halides were separately added to the ATRP system. In such a case, the coordination reactions between the cuprous halides and ligands should take place during the polymerization process, giving rise to complicated kinetic analysis of the ATRP. In this communication, in order to avoid the effect of this coordination reaction on ATRP, bis(1,10-phenanthroline)copper bromide [Cu(phen)$_2$Br] was pre-synthesized, and was directly used as a catalyst in kinetic studies of styrene ATRP initiated with a model compound, 1-phenylethyl bromide (1-PEBr). The experimental results show that the amount of the catalyst has little effect on propagation rate but has an appreciable effect on deviations from the first-order kinetics. Some other kinetic parameters such as the reaction order with respect to the initiator and the apparent activation energy for this system are also reported.



Experimental part

Materials

Styrene (99.0%, Shanghai No.1 Chemicals Factory) was vacuum distilled two times from CaH_2 just before use. CuBr (99.5%, Shanghai No.3 Chemicals Factory) was purified according to a known procedure[20]. 1,10-Phenanthroline (phen) (99.5%, Beijing Chemicals Factory) was recrystallized two times from acetone and dried under argon. 1-Phenylethyl bromide (1-PEBr) (98.5%, Aldrich) was vacuum distilled under argon before use. Bis(1,10-phenanthroline)-copper bromide [Cu(phen)$_2$Br] was prepared according to a known procedure[21].

$C_{12}H_{16}N_4BrCu$ (359.8)	Calc.	C 57.14	N 11.11	H 3.17
	Found	C 57.01	N 11.14	H 3.18

Polymerization

To a previously dried round bottom flask, the solid catalyst was added. After the flask was degassed three times, the liquid reagents, i.e. styrene and initiator were introduced via a syringe. The flask was then immersed in an oil bath thermostatted at the desired temperature and the heterogeneous system was magnetically stirred under argon atmosphere. As soon as the system was heated to the desired temperature, a certain amount of sample was taken from the flask and recorded as a starting point of polymerization. At timed schedule, the same amount of sample was withdrawn from the flask and was injected directly into gel permeation chromatography to measure the molecular weight and polydispersity of the produced polystyrene (PS). Samples for kinetic experiments were dissolved in tetrahydrofuran (THF) and then precipitated in methanol. The PS was then filtered off and evaporated to dryness in vacuum to calculate the styrene conversion.

Characterization

Gel permeation chromatography (GPC) analysis of polymer was performed at a flow-rate of 1.0 ml/min in THF at 25 °C by using a Waters 150 component system (refractive index detector) equipped with Ultra-*u*-Stragel columns (100 Å, 1000 Å and 10000 Å) after calibration with standard polystyrenes. ^1H NMR spectra of PS were recorded at 20 °C in $CDCl_3$ with a Brucker DPX-300 spectrometer operating at 300.13 Hz. Peaks in ^1H NMR spectra were assigned according to ref.[22]

Results and discussion

Dependence of the propagation rate on Cu(phen)$_2$Br catalyst concentration

We started our studies with the investigation of the dependence of reaction rates on catalyst concentration. The copper catalyst concentration was varied from 6.78×10^{-3} M to 4.52×10^{-2} M (i.e., 0.15 to 1.0 with respect to initiator concentration) and the other polymerization parameters were kept constant. Fig. 1 presents the dependence of ln$[M]_0/[M]$ on reaction time for the 1-PEBr/Cu(phen)$_2$Br/St system. Within an experimental error, the apparent rate constants (k_p^{app}), estimated from the maximum slopes of the first-order kinetics curves, are nearly identical for all catalyst concentrations. This result differs from the 1-PECl/CuCl/bpy/St system[7] in which

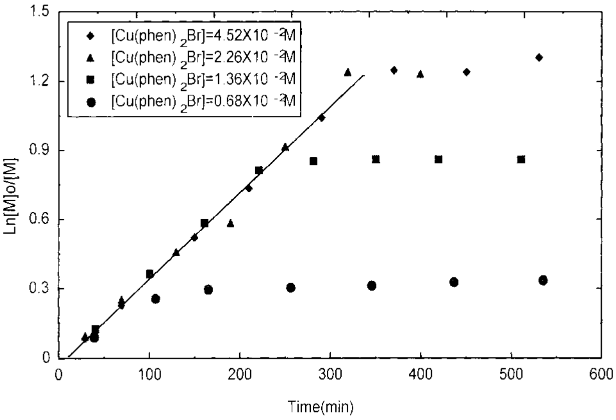


Fig. 1. First-order time-conversion plots for bulk ATRP of styrene at 135 °C. [RBr] = 4.52×10^{-2} M. Parameter is the initial catalyst concentration

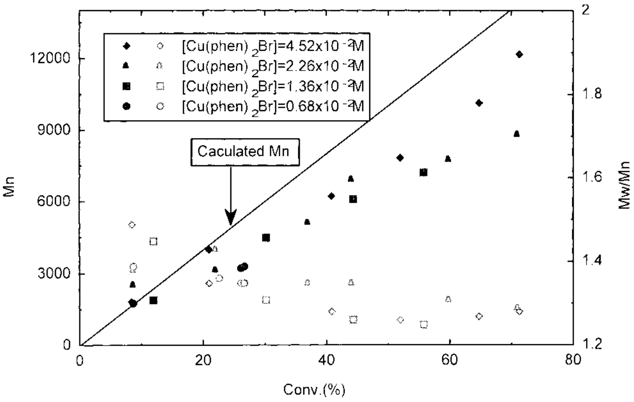


Fig. 2. The dependence of molecular weight ($\overline{M}_n$, solid points) and polydispersity index (P.I. = $\overline{M}_w/\overline{M}_n$, open points) upon the monomer conversion for bulk ATRP of styrene at 135 °C. [RBr] = 4.52×10^{-2} M. Parameter is the initial catalyst concentration

the orders of kinetics with respect to CuCl and bpy were 0.4 and 0.6, respectively, and may be attributed to the different catalyst used. For example, in the system studied here, $Cu(phen)_2Br$ was directly used, while in ref.[7] CuCl and bpy were separately added to the polymerization system. However, in the RBr/CuBr/4,4′-di-*tert*-butyl-2,2′-bipyridine (dTbpy) heterogeneous system, Matyjaszewski et al.[23] have also found that changes in concentration of the initial catalyst (CuBr/dTbpy) showed little effects on propagation rate of ATRP of methacrylate and suggested that it was due to the solubility limit of the catalyst. Thus, it seems that the solubility limit of ionic $[Cu(phen)_2]^+Br^-$ in non-polar styrene may be also responsible for the independence of k_p^{app} of Cu(I) concentration.

Fig. 1 also shows that a deviation from linear first-order kinetics occurs at a certain conversion for these ATRP systems. A similar phenomenon has also been observed in styrene ATRP by using the 1-PEBr/CuBr/bpy system[24] and it was ascribed to some side reactions including elimination and termination[25]. Furthermore, because termination also reduces [Cu(I)] and increases [Cu(II)], for the system containing a less amount of the initial catalysts, the cuprous catalysts may be depleted earlier, resulting in earlier deviation from linear first-order kinetics, as shown in Fig. 1.

The molecular weight and polydispersity index (P.I. = $\overline{M}_w/\overline{M}_n$) of the produced polystyrenes (PS) under various concentrations of the copper catalyst were further examined, as shown in Fig. 2. In all cases $\overline{M}_n$ increases with the increase of monomer conversion. Narrow polydispersities are observed (1.2 < P.I. < 1.5) and they are not affected by the amount of the copper catalyst used. However, $\overline{M}_n$ tends to deviate from values calculated by assuming that one 1-PEBr initiates one PS chain. In order to gain insight into the nature of this deviation, we investigated the ^1H NMR spetrum of the formed PS as shown in Fig. 3. The peak at 4.5 ppm is attributed to the methine

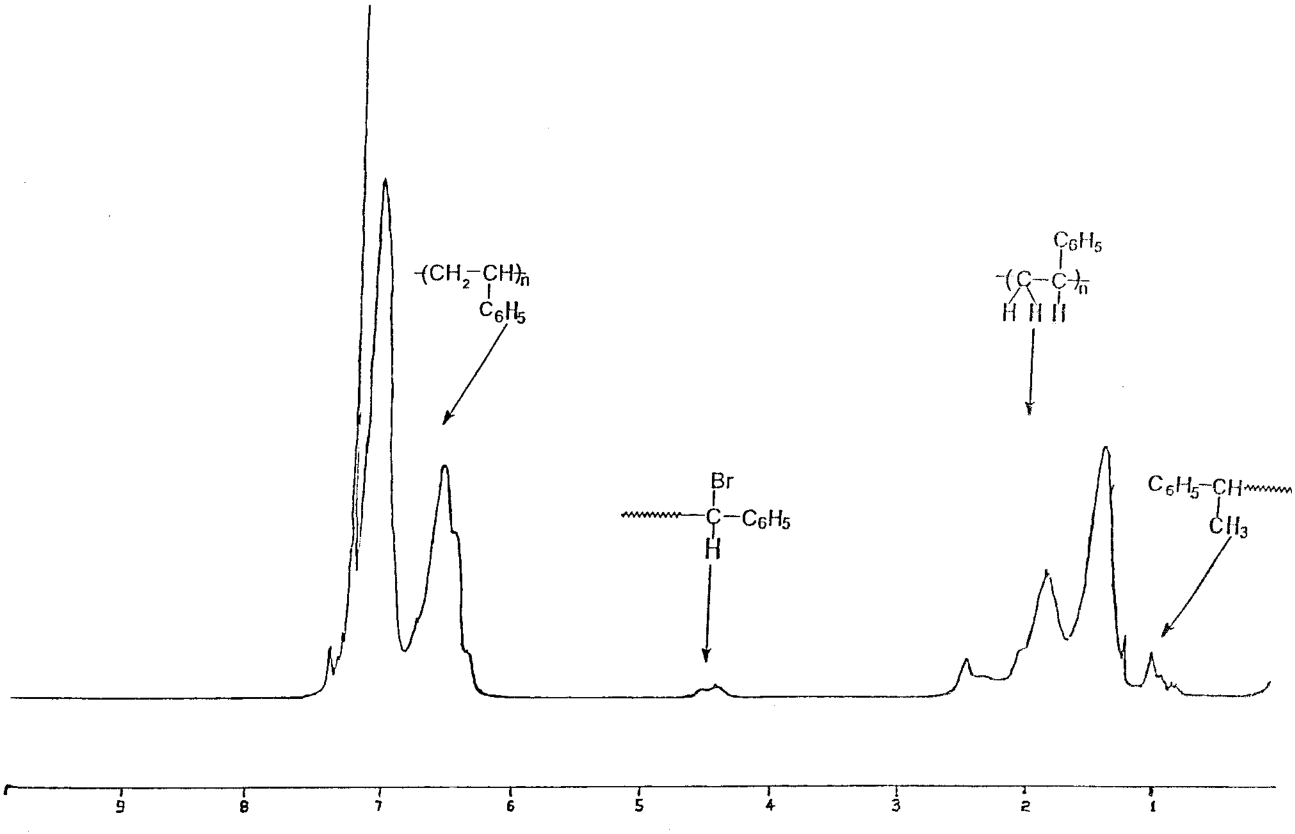


Fig. 3. ^1H NMR spectrum of polystyrene prepared using $[1\text{-PEBr}]/[Cu(phen)_2Br]$ at 135 °C. Polymerization conditions as indicated in Fig. 1

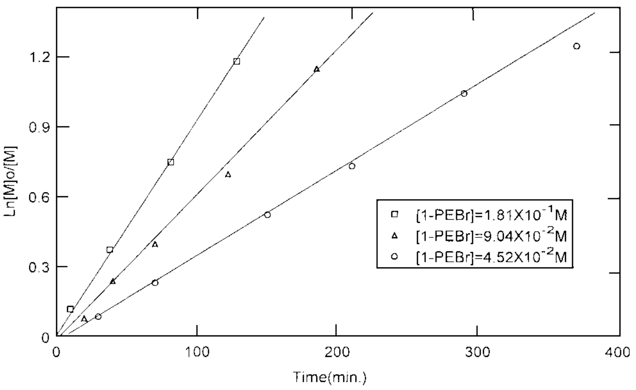


Fig. 4. First-order time-conversion plots for bulk ATRP of styrene at 135 °C. $[Cu(phen)_2Br] = 4.52 \times 10^{-2}$ M. Parameter is the initial initiator concentration

proton geminal to bromine, while the peak at 1.0 ppm is assigned to the methyl group from the initiator. The ratio of the integrated areas of the methyl group to the proton geminal to bromine is 3 : 1, indicating that each bromine end group resulted from one initiator 1-PEBr. Furthermore, because this spectrum does not show any peak at 3.9 ppm, which is always assigned to the protons in oligomers produced by self-initiation through the Mayo mechanism[26], so the deviation of experimental $\overline{M}_n$ from the calculated values in Fig. 2 should not originate from self-initiation[18].

Dependence of propagation rate on initiator concentration

Fig. 4 demonstrates the first-order plots for various concentrations of 1-PEBr initiator. It is shown that with increasing initiator concentration the rate of polymerization increases. A bilogarithmic plot of the apparent rate constant k_p^{app} vs. initial initiator concentration $[I]_0$ gives a slope of 0.94, as shown in Fig. 5. This indicates that the reaction order with respect to initiator concentration is approximately unity which is in good agreement with the 1-PECl/CuCl/bpy/St[7] and 1-PEBr/CuBr/dNbpy/St systems[8].

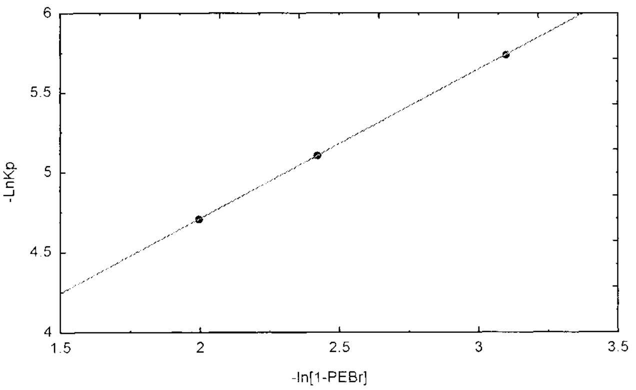


Fig. 5. Reaction orders for the initiator, 1-PEBr, in the bulk ATRP of styrene

Dependence of propagation rate on temperature

The effect of temperature on the rate of polymerization was studied over a temperature range from 110 °C to 135 °C. Fig. 6 shows the first order kinetics plots. The linearity between $\ln[M]_0/[M]$ and time in all cases indicates that the concentration of growing species remains constant and k_p^{app} increases with increasing the temperature of the polymerization. The Arrhenius plot obtained from the experimental results in Fig. 6 is given in Fig. 7. Thus, the apparent activation energy was calculated and found to be at 75 kJ · mol^{-1}. Such an apparent activation energy is higher than that reported for the homogeneous dNbpy/CuBr ATRP system (50 kJ · mol^{-1})[8].

As reported by Matyjaszewski et al.[27] and Haddleton et al.[28], a four-coordinated tetrahedral Cu(I) complex[29] must change to a penta-coordinated distorted square-based-pyramidal Cu(II) complex[30] upon a halogen atom

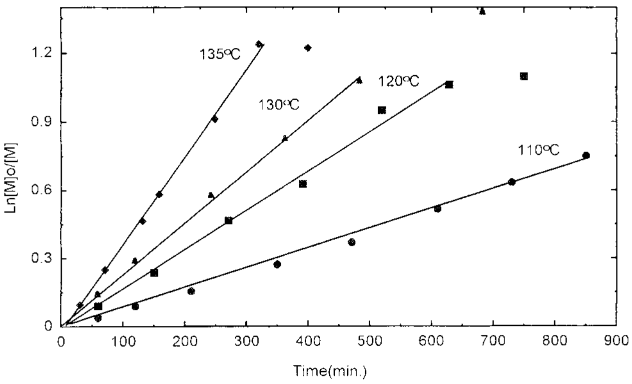


Fig. 6. First-order time-conversion plots for the bulk ATRP of styrene at varying temperature. $[1\text{-PEBr}] = 4.52 \times 10^{-2}$ M, $[Cu(phen)_2Br] = 2.26 \times 10^{-2}$ M

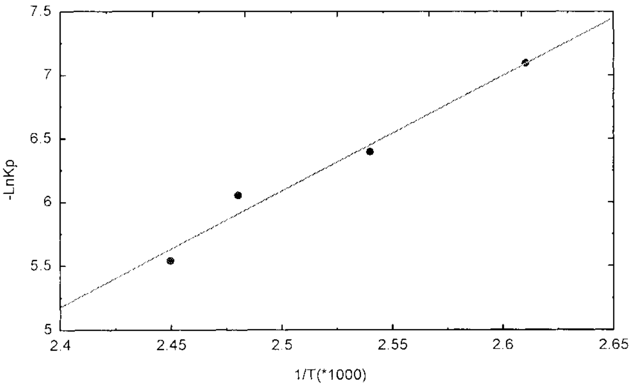


Fig. 7. Temperature dependence plots for the bulk ATRP of styrene. $[1\text{-PEBr}] = 4.52 \times 10^{-2}$ M, $[Cu(phen)_2Br] = 2.26 \times 10^{-2}$ M, slope = 8.98

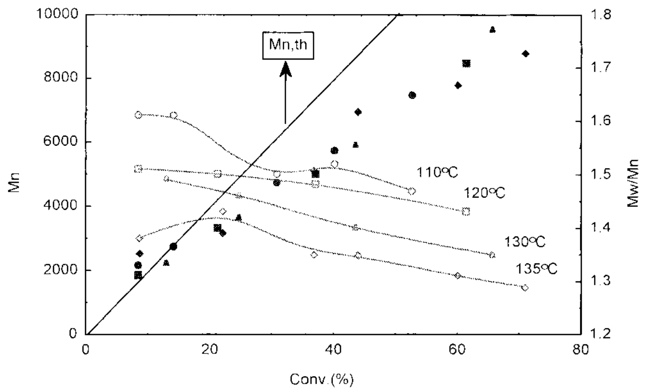


Fig. 8. The dependence of molecular weight ($\overline{M}_n$, solid points) and polydispersity index (open points) upon monomer conversion for bulk ATRP of styrene at varying temperature. [RBr] = 2[Cu(phen)$_2$Br] = 4.52 × 10^{-2} M

transfer from RX to copper center in ATRP. In this case, the steric barrier to the conformational change of Cu(phen)$_2$Br should be larger than that for Cu(dNbpy)$_2$Br since the dNbpy skeleton, in which the two pyridine groups are bound by a single bond, is more flexible than the phen skeleton[21]. In addition, as mentioned before[14], because phen has a more delocalized electronic structure, whose π* orbitals contribute accordingly more to π-back-bonding interaction, than dNbpy, the Cu(I)/phen complex is more stable than the Cu(I)/dNbpy complex. Therefore, the radical reaction of bromine atom transfer by using Cu(phen)$_2$Br should be more difficult than that by using Cu(dNbpy)$_2$Br, contributing to a higher apparent activation energy.

Fig. 8 shows that over all temperature ranges studied, the $\overline{M}_n$ of the PS increases linearly with increasing styrene conversion, but the deviation from the calculated values also takes place. Furthermore, Fig. 8 exhibits smaller polydispersities of the polymers at higher temperature. It may be related to a higher k_p/k_t value and/or a faster exchange between the inactive species and active species due to a better solubility of the catalyst/deactivator in the ATRP system at a higher temperature.

[1] G. Moad, D. H. Solomon, "*The Chemistry of Free-radical Polymerization*", Pergamon, Oxford 1995

[2] D. Grestza, D. Mardare, K. Matyjaszewski, *Macromolecules* **27**, 638 (1994)

[3] B. Iván, J. P. Kenndy, *Macromolecules* **23**, 2880 (1990)

[4] B. Iván, *Macromol. Symp.* **88**, 201 (1994)

[5] M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **25**, 2587 (1992)

[6] J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **117**, 5614 (1995)

[7] J. S. Wang, K. Matyjaszewski, *Macromolecules* **28**, 7901 (1995)

[8] K. Matyjaszewski, J. Xia, T. E. Patten, T. Abernathy, *J. Am. Chem. Soc.* **119**, 674 (1997)

[9] V. Percec, H. J. Kim, B. Barbiou, *Macromolecules* **30**, 6702 (1997)

[10] C. Granel, Ph. Dubois, R. Jéròme, Ph. Teyssié, *Macromolecules* **29**, 8576 (1996)

[11] M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, *Macromolecules* **26**, 2987 (1993)

[12] B. B. Wayland, G. Poszmik, S. L. Mukerjee, M. Fryd, *J. Am. Chem. Soc.* **116**, 7943 (1994)

[13] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **28**, 1721 (1995)

[14] B. R. James, R. J. P. Williams, *J. Chem. Soc.* 2007 (1961)

[15] M. Hàjek, P. Šilhavy, *Collect. Czech. Chem. Commun.* **48**, 1710 (1983)

[16] CN 1165828A (1997), East China Univ. of Sci. & Tech., invs.: G. L. Cheng, C. P. Hu; *Chem. Abstr.* **126**, 225600r (1997)

[17] G. L. Cheng, C. P. Hu, S. K. Ying, *China Synth. Rubber Ind.* **(20)2**, 116 (1997)

[18] M. Destarac, J. M. Bessière, B. Boutevin, *Macromol. Rapid Commun.* **18**, 967 (1997)

[19] G. L. Cheng, C. P. Hu, S. K. Ying, *Polymer* **40**, 2167 (1999)

[20] G. M. Whitesides, J. S. Sadowski, *J. Am. Chem. Soc.* **96**, 2829 (1974)

[21] M. Munakata, S. Nishibayashi, H. Sakamoto, *J. Chem. Soc. Chem. Commun.* 219 (1980)

[22] K. Matyjaszewski, Y. Nakagama, S. G. Gaynor, *Macromol. Rapid Commun.* **18**, 1057 (1997)

[23] H. Paik, K. Matyjaszewski, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **37(2)**, 274 (1996)

[24] J. Qiu, K. Matyjaszewski, *Macromolecules* **30**, 5643 (1997)

[25] M. Wei, T. E. Patten, K. Matyjaszewski, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **38(1)**, 683 (1997)

[26] Y. K. Chong, E. Rizzardo, D. H. Solomon, *J. Am. Chem. Soc.* **105**, 7761 (1983)

[27] K. Matyjaszewski, *Macromol. Symp.* **111**, 47 (1996)

[28] D. M. Haddleton, C. B. Jasieczek, M. J. Hannon, A. J. Shooter, *Macromolecules* **30**, 2190 (1997)

[29] P. C. Healy, L. M. Engelhardt, V. A. Patrick, A. H. White, *J. Chem. Soc. Dalton Trans.* 2541 (1985)

[30] P. Nagle, E. O'Sullivan, B. J. Hathaway, *J. Chem. Soc. Dalton Trans.* 3399 (1990)