

Hyperbranched Copolymers of *p*-(Chloromethyl)styrene and *N*-Cyclohexylmaleimide Synthesized by Atom Transfer Radical Polymerization

XULIN JIANG,¹ YALAN ZHONG,¹ DEYUE YAN,¹ HUI YU,¹ DEZHEN ZHANG²

¹ College of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

² Department of Polymer Materials, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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ABSTRACT: The hyperbranched copolymers were obtained by the atom transfer radical copolymerization of *p*-(chloromethyl)styrene (CMS) with *N*-cyclohexylmaleimide (NCMI) catalyzed by CuCl/2,2'-bipyridine (bpy) in cyclohexanone (C₆H₁₀O) or anisole (PhOCH₃) with CMS as the inimer. The influences of several factors, such as temperature, solvent, the concentration of CuCl and bpy, and monomer ratio, on the copolymerization were subsequently investigated. The apparent enthalpy of activation for the overall copolymerization was measured to be 37.2 kJ/mol. The fractional orders obtained in the copolymerization were approximately 0.843 and 0.447 for [CuCl]₀ and [bpy]₀, respectively. The monomer reactivity ratios were evaluated to be $r_{\text{NCMI}} = 0.107$ and $r_{\text{CMS}} = 0.136$. The glass transition temperature of the resultant hyperbranched copolymer increases with increasing f_{NCMI} , which indicates that the heat resistance of the copolymer has been improved by increasing NCMI. The prepared hyperbranched CMS/NCMI copolymers were used as macroinitiators for the solution polymerization of styrene to yield star-shaped poly(CMS-co-NCMI)/polystyrene block copolymers by atom transfer radical polymerization. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1992–1997, 2000

Key words: ATRP; “living”/controlled radical copolymerization; *p*-(chloromethyl)styrene; *N*-cyclohexylmaleimide; hyperbranched copolymer; heat-resistance

INTRODUCTION

In recent years, hyperbranched polymers have been attracting much interest because of their unique structures and potential applications.^{1–6} Whereas the majority of hyperbranched polymers have been based on the condensation-type reac-

tion polymerization, Fréchet et al.⁷ described a new synthetic method for the preparation of hyperbranched macromolecules based on the self-condensing vinyl polymerization from a vinyl monomer, 3-(1-chloroethyl)ethenylbenzene, by a “living” cationic polymerization.

The increasing development in “living” free radical polymerization has been reported in many articles.^{8–13} Among a variety of methods thus reported, atom transfer radical polymerization (ATRP), which was first reported by Wang and Matyjaszewski⁸ and Kato et al.,⁹ is a very important method for the controlled radical polymeriza-

Correspondence to: D. Yan (dyyan@mail.sjtu.edu.cn).
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tion. Matjaszewski and coworkers adapted self-condensing vinyl polymerization to the synthesis of hyperbranched polymers by ATRP.¹⁴ These approaches have also been used in the simultaneous copolymerization of vinyl monomers to form statistical copolymers.^{15–17}

On the other hand, *N*-substituted maleimides have become interesting monomers because of the superiority of their polymers or copolymers in thermal stability.^{18–21} To get heat-resistant transparent hyperbranched polymers, the copolymerization of 4-(chloromethyl)styrene (CMS) and *N*-cyclohexylmaleimide (NCMI) using ATRP with CMS as inimer was studied in this work.

EXPERIMENTAL

Materials

CMS [4-(Chloromethyl)styrene] (Aldrich, USA), and 2,2'-bipyridine (bpy) (Aldrich) were used as obtained without further purification. Copper (I) chloride (CuCl, A. R. grade) was purified by stirring in acetic acid, washing with methanol, and then drying. NCMI, a commercial product (Zhuozhou Haihui Chemicals Co. Ltd., Hebei Province), recrystallized twice from dry acetone, was dried in vacuum before use. Anisole, cyclohexanone, and benzene, A. R. grades, were used without further purification.

Polymerization

Catalyst, ligand, inimer, monomer, and solvent were added to a dry flask with stirrer. The flask was sealed with a rubber septum and was cycled between vacuum and nitrogen three times to remove the oxygen. The flask was then immersed in an oil bath held by a thermostat at the required temperature. After polymerization for a given time, the flask was cooled to room temperature and the contents of the flask were poured into a large amount of methanol with rapid stirring to precipitate the products. The precipitated polymer was filtered and washed thoroughly with methanol, purified by reprecipitation from the tetrahydrofuran solution into excess methanol. Dried at room temperature for several hours first, the samples were heated in a vacuum oven at 50°C for at least 24 h. The monomer conversion was determined gravimetrically.

Analysis and Characterization

The molecular weights of the resulting copolymers were determined using size exclusion chro-

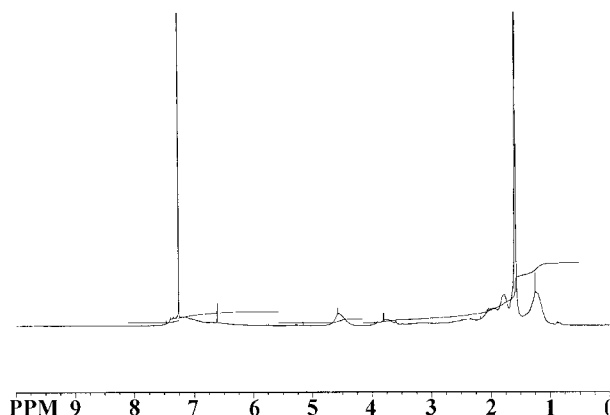


Figure 1 ¹H-NMR spectrum of the copolymer of CMS with NCMI obtained with CuCl/bpy in cyclohexanone.

motography (SEC) (Waters 150, USA) apparatus equipped with single RI detector (Waters 410) calibrated by linear polystyrene standards. Furthermore, the actual molar masses of the resultant hyperbranched copolymers were determined by using a Waters 150 SEC apparatus equipped with dual detector Viscotek T60A and Differential Refractometer Waters 410 (triple detection SEC, differential refractometer, on-line viscometer, 90° light scattering detector). ¹H-NMR spectra were taken on 500-MHz spectrometers at room temperature in CDCl₃. UV/Vis spectra were recorded on a PE Lambda 20 spectrophotometer. The glass transition temperature (*T_g*) of copolymer was measured by differential scanning calorimetry (DSC) (PE Pyris-1 Series) in a flowing nitrogen atmosphere (the heating rate was 10°C/min). The copolymer composition was calculated from nitrogen elemental analysis (Heraeus Rapid CHN-O). The chlorine content in the star-branched polymers was determined by elemental analysis.

RESULTS AND DISCUSSION

Hyperbranched Copolymers of CMS and NCMI by ATRP

The copolymerization of CMS [*p*-(chloromethyl)styrene] with NCMI, by ATRP, was performed in cyclohexanone (C₆H₁₀O) or anisole (PhOCH₃) with CMS as both initiator and monomer (inimer). The hyperbranched copolymers can be prepared by the approach described in literature.¹⁴ Figure 1 shows ¹H-NMR spectrum of the copolymer of CMS with NCMI obtained therefrom with CuCl/bpy as catalyst system in cyclohexanone. In

Table I Characterization of Resulting Hyperbranched poly(St-co-NCMI)s^a

Time (h)	Conv (%)	$M_{w,c}^b$	$M_{n,t}^c$	$M_{w,t}^c$	PD _c ^b	PD _t ^c	Radius of Gyration (nm)	Intrinsic Viscosity (dL/g)
2	40.2	1640	2660	3510	1.37	1.32	1.61	0.0362
9.5	69.4	5000	4720	10,100	2.37	2.14	2.27	0.0409
20.5	83.0	5300	6050	11,300	2.70	1.87	2.39	0.0419
33	86.2	7420	6540	18,300	3.20	2.80	2.61	0.0434

^a The polymerization condition: [CMS]₀ = [NCMI]₀ = 1.5M, [bpy]₀ = 2[CuCl]₀ = 0.36M; temperature, 110°C; solvent, PhOCH₃.

^b The apparent molar masses determined using SEC versus linear polystyrene standards.

^c The actual molar masses determined using triple detection SEC (differential refractometer, on-line viscometer, 90° light scattering detector).

Figure 1, there are evident signals of NCMI repeat units, besides the signals from the aromatic protons and methylene and methine protons adjacent to the chlorine atoms, which indicates the formation of the copolymer of CMS and NCMI by ATRP.²² The signals, at 5.2 and 5.7 ppm, arising from the two methylene protons of the double bond at the chain end¹⁴ (or unreacted monomers CMS) are very weak, which indicates the formation of macromolecules and the absence (or very little) of unreacted monomer CMS.

It can be seen from Table I that the molecular weight of the resulting copolymer increases with conversion because of the "living" character of the investigated free radical polymerization. Also seen from Table I, the apparent molar masses of the resulting copolymers determined using SEC versus linear polystyrene standards are much

lower than the actual molar masses obtained using triple detection SEC (differential refractometer, on-line viscometer, 90° light scattering detector). This demonstrates that the resulting copolymer of CMS with NCMI by ATRP exhibits a branched structure.¹⁴ When the copolymers obtained were purified by reprecipitation from the tetrahydrofuran solution into excess methanol, the polymers precipitated very slowly, which indicated a certain solvation of the resulting highly branched copolymers in methanol.

Influence of the Polymerization Conditions

Several solvents were investigated for the ATRP of CMS with NCMI using the CuCl/bpy catalyst

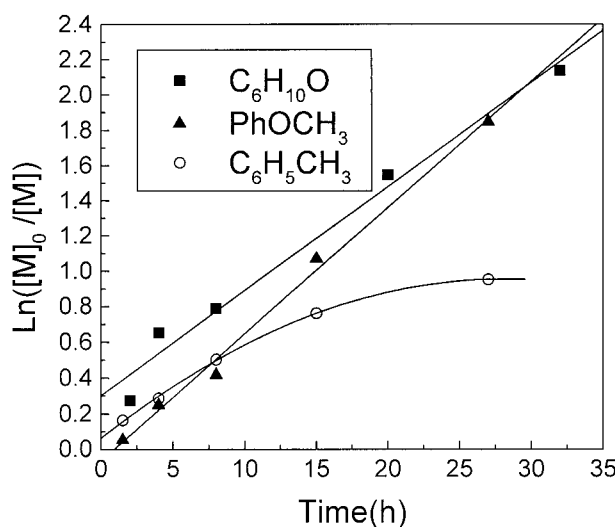


Figure 2 Semilogarithmic kinetic plots for the ATRP of CMS and NCMI in various solvents at 110°C. [CMS]₀ = [NCMI]₀ = 1.0M, [bpy]₀ = 3[CuCl]₀ = 0.24M.

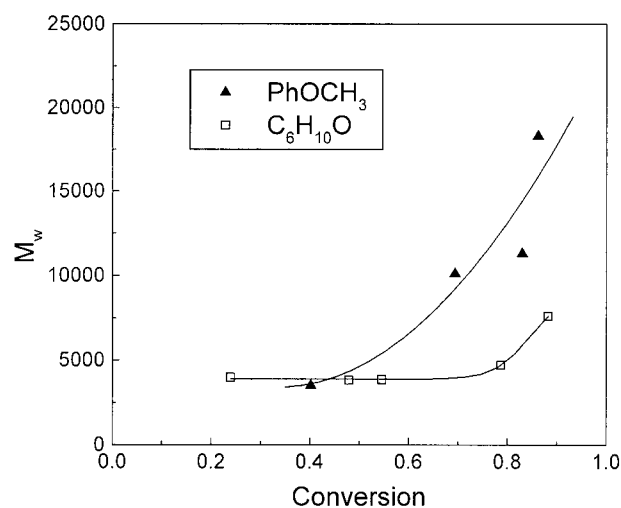


Figure 3 The dependence of M_w determined using a triple detector SEC upon conversion for the hyperbranched copolymerization of CMS/NCMI at 110°C. (a) Using PhOCH₃ as solvent, [CMS]₀ = [NCMI]₀ = 1.5M, [bpy]₀ = 2[CuCl]₀ = 0.36M (▲); (b) using cyclohexanone as solvent, [CMS]₀ = [NCMI]₀ = 1.0M, [bpy]₀ = 3[CuCl]₀ = 0.24M (□).

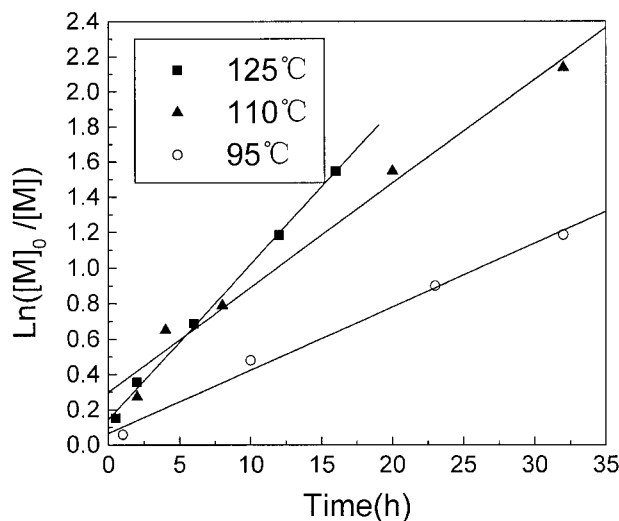


Figure 4 Semilogarithmic kinetic plots for the ATRP of CMS and NCMi in cyclohexanone at different temperatures. $[CMS]_0 = [NCMI]_0 = 1.0M$, $[bpy]_0 = 3[CuCl]_0 = 0.24M$.

system at 110°C. The first-order kinetic plots of the copolymerizations are shown in Figure 2. It can be seen from Figure 2 that a linear plot of $\ln([M]_0/[M])$ versus time using $PhOCH_3$ or $C_6H_{10}O$ as solvent was obtained, indicating that the number of propagating species remained constant. In contrast, the use of benzene as the solvent resulted in a decreased rate of copolymerization as the reaction proceeded, which can be attributed to the termination reactions.¹² As shown

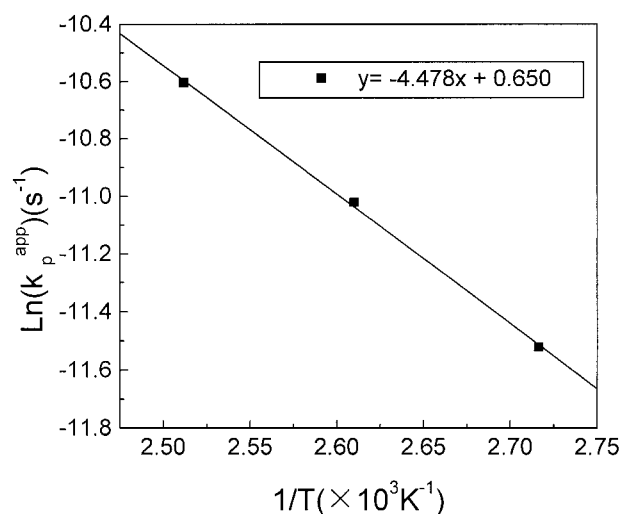


Figure 5 Temperature dependence plot for the ATRP of styrene and NCMi in cyclohexanone. The reaction condition was identical with that of Figure 4.

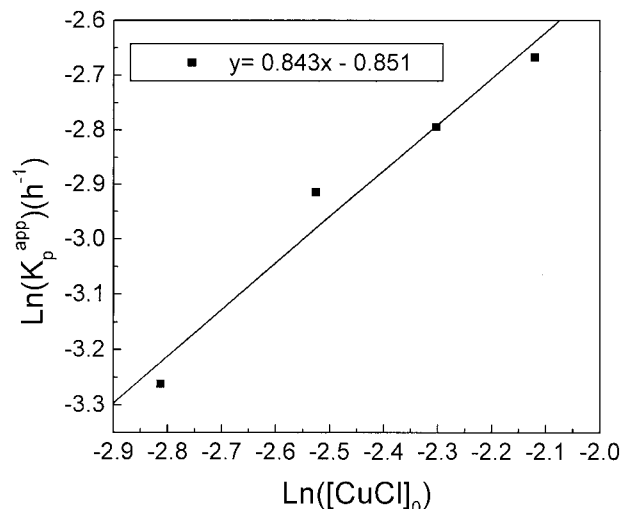


Figure 6 Reaction orders for $[CuCl]_0$ in the ATRP of CMS and NCMi in cyclohexanone at 110°C. $[CMS]_0 = [NCMI]_0 = 1.0M$, $[bpy]_0 = 0.24M$.

in Figure 3, using $PhOCH_3$ or $C_6H_{10}O$ as solvent in the copolymerization the weight-averaged molecular weight (M_w) of the resulting copolymer determined using triple detection SEC increased with conversion, but the M_w of the resulting copolymer using cyclohexanone as solvent increased slowly with conversion. Thus, the copolymerization between CMS and NCMi with the $CuCl/bpy$ catalyst system in $PhOCH_3$ or $C_6H_{10}O$ at 110°C was found to behave in a living fashion and the

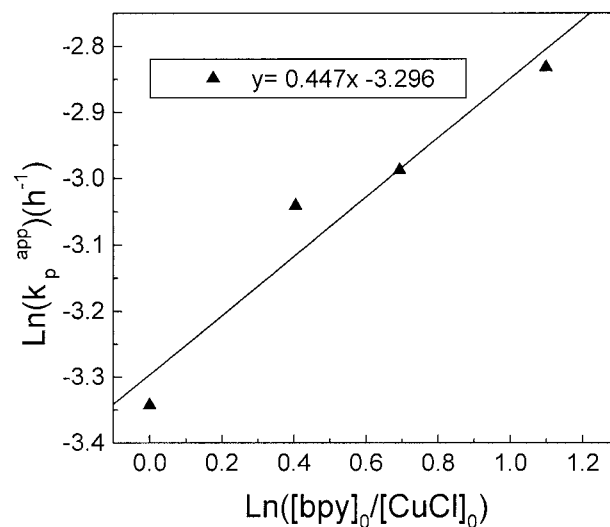


Figure 7 Reaction orders for ligand bpy in the ATRP of CMS and NCMi in cyclohexanone at 110°C. $[CMS]_0 = [NCMI]_0 = 1.0M$, $[CuCl]_0 = 0.08M$.

Table II Copolymerization Data for NCMI and CMS at 110°C in Cyclohexanone

f_{NCMI}	N Content in Copolymer (%)	F_{NCMI}	Conv (%)	T_g (°C)
0.25	3.53	0.412	17.4	178.5
0.33	3.81	0.447	23.1	179.1
0.50	4.22	0.500	29.5	180.0
0.67	4.55	0.543	32.2	186.5
0.75	4.71	0.563	23.4	190.7

$[M]_0 : [\text{CuCl}]_0 : [\text{bpy}]_0 = 50:1:3$, $[M]_0 = [\text{CMS}]_0 + [\text{NCMI}]_0 = 1.0M$, $t = 8$ h.

same copolymerization in benzene displayed poor control.

The kinetic study was implemented in the range of 95–125°C in $\text{C}_6\text{H}_{10}\text{O}$, as showed in Figure 4; the linear time dependence of $\ln([M]_0/[M])$ is consistent with a controlled polymerization that is first order in monomer. In addition, from Figure 4, the apparent propagation rate constants (k_p^{app}) at 95, 110, and 125°C can be calculated from the plots of $\ln([M]_0/[M])$.¹⁷ The plot of $\ln k_p^{\text{app}}$ versus $1/T$ is given in Figure 5 in the range of 95–125°C. From the slope of the straight line the apparent enthalpy of activation for the overall copolymerization, $\Delta H_{\text{app}}^\ddagger$, was calculated to be 37.2 kJ/mol. The value is lower than those of conventional free-radical copolymerizations initiated by thermal initiator decomposition.²³

Figure 6 depicts the effect on the copolymerization rate of CuCl concentration with all other components held constant. A plot of $\ln(k_p^{\text{app}})$ versus $\ln[\text{CuCl}]_0$ reveals that the rate of the copolymerization of CMS and NCMI at 110°C in $\text{C}_6\text{H}_{10}\text{O}$ is proportional to the 0.843 power of the concentration of copper(I).

The concentration of the bpy ligand being varied, a series of copolymerizations were performed while keeping the original concentration of CMS, NCMI, and CuCl constant. A plot of $\ln(k_p^{\text{app}})$ versus $\ln([\text{bpy}]_0/[\text{CuCl}]_0)$ as shown in Figure 7 reveals that the kinetic order with respect to the bpy ligand is 0.447.

Effect of the CMS and NCMI Molar Ratio

The atom transfer radical random copolymerization of CMS and NCMI with the CuCl/bpy catalyst at 110°C for various ratios of NCMI to CMS was performed. Table II shows the influence of the initial molar composition of the comonomer

feed (f_{NCMI}) on the molar fraction of NCMI in the copolymer (F_{NCMI}) and the T_g of the resulting copolymer. Under the identical polymerization condition and after the same reaction time, high reaction conversion (rate) occurred near the equimolar feed composition as shown in Table II. The T_g of the copolymer increases with increasing the content of feed NCMI in the copolymerization system. The T_g of the linear poly[4-(chloromethyl)styrene] (PCMS) is 101°C and the T_g of the branched PCMS is between 58 and 81°C.²⁴ Therefore, adding NCMI can greatly improve the thermal resistance of PCMS.

The monomer reactivity ratios were evaluated to be $r_{\text{CMS}} = 0.136$ and $r_{\text{NCMI}} = 0.107$ in terms of the extended Kelen–Tüdös method²⁵ using the copolymerization data in Table II. Both r_{NCMI} and r_{CMS} are close to zero, which means that the ATRP of CMS and NCMI has a strong tendency toward alternative one and shows little tendency to homopolymerization.

As is known, the copolymerization of charge transfer complex (CTC) comonomers usually leads to an alternative copolymer.²³ For this reason, the ultraviolet spectrometer has been applied to look over whether CMS and NCMI could form a CTC or not. However, no new absorbance peak has been observed after mixing CMS with NCMI in PhOCH_3 , $\text{C}_6\text{H}_{10}\text{O}$, or ethanol solution, respectively, which illustrates that it seems impossible to form a CTC between CMS and NCMI. At least, it is too weak to be detected even if this kind of complex may exist.

Synthesis of Poly(CMS-co-NCMI)/Polystyrene Block Copolymers

To investigate the activity of chlorine groups of the hyperbranched poly(CMS-co-NCMI)s in ATRP, we used the synthesized hyperbranched CMS/NCMI copolymers as macroinitiators for the solution

Table III Chain Extension of Hyperbranched CMS/NCMI Copolymers with Styrene

Sample	Time (h)	Cl (%)	M_n	M_w	PD
1	0	8.09	2560	4170	1.63
2	3	3.04	6150	14,500	2.35
3	9	1.83	11,800	24,500	2.07
4	20	1.30	18,400	49,000	2.66

$[\text{ST}]_0 = 3.0M$, $[\text{CuCl}]_0 = 0.1M$, $[\text{bpy}]_0 = 0.3M$; solvent, anisole; temperature, 130°C.

ATRP of styrene to yield star-shaped poly(CMS-co-NCMI)/polystyrene block copolymers. The almost linear increase of the molecular weight and the decrease of chlorine element content with reaction time (Table III) and the nearly complete conversion of the starting copolymer shown in the comparative SEC elution time plots significantly demonstrate a controlled chain extension reaction.

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