Atom Transfer Radical Copolymerization of *N*-Phenylmaleimide and Styrene Initiated with Dendritic Polyarylether 2-Bromoisobutyrate

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ABSTRACT: Dendritic polyarylether 2-bromoisobutyrates with different generations (Gn-Br, $n = 1$–3) were prepared by reaction of the Fréchet-type hydroxyl-terminated polyarylether with 2-bromoisobutyryl bromide and triethylamine. Gn-Br as a macroinitiator for the controlled free-radical polymerization of *N*-phenylmaleimide (PhMI, M_1) and styrene (St, M_2) was investigated. The copolymerization carried out in anisole with CuBr/bpy catalyst afforded polymers with well-defined molecular weights and low polydispersities ($1.12 < M_w/M_n < 1.35$). When the molar fraction of PhMI was 0.50, the apparent activation enthalpy of copolymerization was 38.2 kJ/mol. The effects of monomer feed on the apparent activation enthalpy and copolymer composition were also studied. The monomer reactivity ratios were determined to be $r_1 = 0.0325$ and $r_2 = 0.0524$ according to the Kelen–Tüdős method. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 3960–3966, 2001

Keywords: block copolymer; *N*-phenylmaleimide; styrene; atom transfer radical copolymerization (ATRP)

INTRODUCTION

Because well-defined polymer microstructures promise new material properties, the control of the macromolecular architecture has become an important topic of contemporary polymer science.[1] Recently, significant progress has been made in the field of living free-radical polymerization such as nitroxide-mediated stable free-radical polymerization,[1–4] atom transfer radical polymerization (ATRP),[5–12] reverse ATRP,[13–16] and reversible addition–fragmentation chain transfer.[17–20] Among them, ATRP has been extensively investigated and successfully applied to the synthesis of well-defined macromolecular architectures such as comb,[21–23] star,[24–26] hyperbranched, and dendritic macromolecules.[27–30]

Meanwhile, rapidly increasing attention has been paid to dendrimers because of their highly regular three-dimensional structures and potential applications.[31,32] Furthermore, dendritic macromolecules are suitable building blocks for the design and synthesis of novel functional materials. Of these macromolecular structures, dendritic-linear block copolymers consisting of covalently bound linear and dendritic segments have been shown to exhibit interesting solution, solid-state, and interfacial properties. Up to this point, many of the dendritic-linear block copolymers have been synthesized by dendritic initiators;[33–36] however, reports on dendrimer as a functional macroinitiator for the synthesis of well-defined alternating copolymers are scarce.

In this study, three kinds of dendritic polyarylether 2-bromoisobutyrates (Gn-Br, $n = 1$–3)

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derived from the Fréchet-type polyarylether (Gn-OH) were synthesized. The copolymerization of *N*-phenylmaleimide (PhMI) and styrene (St) by ATRP initiated with Gn-Br was investigated. In addition, the monomer reactivity ratios were determined by the Kelen–Tüdős method.

EXPERIMENTAL

Materials

PhMI and the hydroxyl-terminated polyarylether (Gn-OH, $n = 1$–3) were prepared according to the literature.[37,38] St was distilled under reduced pressure after removal of the inhibitor and stored at low temperatures. CuBr was purified by stirring in acetic acid, washing with ethanol, and then drying *in vacuo*. Toluene was dried over Na, distilled, and stored under N_2. Anisole was distilled before use. 2,2′-Bipyridine (bpy) and other reagents were of analytical grade and used as received.

Synthesis of Dendritic Polyarylether 2-Bromoisobutyrate (Gn-Br)

G3-OH (3.19 g, 2.0 mmol) was dissolved in 40 mL of dry toluene. To this solution was added triethylamine (0.25 g, 2.5 mmol); then 2-bromoisobutyryl bromide (0.55 g, 2.4 mmol) was added dropwise over a 10-min period. The mixture was stirred 48 h at room temperature before it was washed with water. The combined organic layer was then dried and concentrated. The crude product was purified by flash chromatography, eluted with 1:1 hexane/chloroform gradually increasing to 1:2. After precipitation into hexane, 2.80 g (yield: 80%) of G3-Br were obtained as a yellowish glass. G1-Br and G2-Br were prepared according to the similar procedure.

G1-Br: yield: 84%; mp 71–72 °C, white crystalline solid. IR (KBr): 3066, 3036, 2932, 1737, 1595, 1498, 1450, 1376, 1275, 1168, 1067, 842, 745, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.29–7.42 (m, 10H, PhH), 6.60 (s, 2H, ArH), 6.58 (d, 1H, ArH), 5.13 (s, 2H, $ArCH_2O$), 5.03 (s, 4H, $PhCH_2O$), 1.93 (s, 6H, CH_3). ELEM. ANAL. Calcd. for $C_{25}H_{25}BrO_4$: C, 63.97%; H, 5.37%; Br, 17.02%. Found: C, 63.95%; H, 5.36%; Br, 16.98%.

G2-Br: yield: 75%, yellowish glass. IR (NaCl): 3066, 3033, 2931, 1736, 1597, 1498, 1453, 1375, 1296, 1160, 1057, 840, 738, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.29–7.42 (m, 20H, PhH), 6.56–6.67 (m, 9H, ArH), 5.12 (s, 2H, $ArCH_2O$), 5.01 (s, 8H, $PhCH_2O$), 4.96 (s, 4H, $ArCH_2O$), 1.93 (s, 6H, CH_3). ELEM. ANAL. Calcd. for $C_{53}H_{49}BrO_8$: C, 71.15%; H, 5.48%; Br, 8.93%. Found: C, 71.19%; H, 5.49%; Br, 8.93%.

G3-Br: yield: 80%, yellowish glass. IR (NaCl): 3066, 3033, 2926, 1735, 1597, 1499, 1451, 1374, 1296, 1157, 1051, 833, 737, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.28–7.41 (m, 40H, PhH), 6.52–6.68 (m, 21H, ArH), 5.11 (d, 2H, $ArCH_2O$), 5.00 (s, 16H, $PhCH_2O$), 4.95 (s, 12H, $ArCH_2O$), 1.91 (s, 6H, CH_3). ELEM. ANAL. Calcd. for $C_{109}H_{97}BrO_{16}$: C, 75.12%; H, 5.61%; Br, 4.58%. Found: C, 75.14%; H, 5.60%; Br, 4.56%.

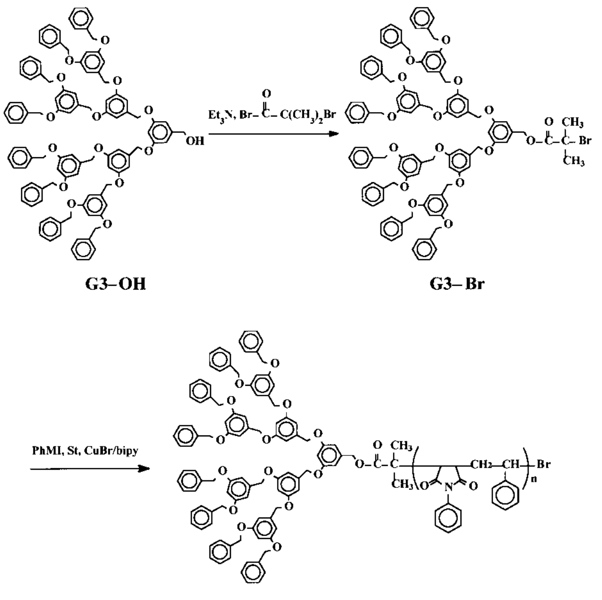
Atom Transfer Radical Polymerization from the Dendritic Initiator

The polymerization was conducted in a sealed glass tube. A representative feed was [PhMI]:[St]:[G3-Br]:[CuBr]:[bpy] = 50:50:1:1:2, and the total monomer concentration ($[M]_T$) was 4.0 mol/L. The materials were accurately weighed and placed into a dried glass tube, and then anisole was added. The polymerization mixture was degassed with three freeze-evacuate-thaw cycles and polymerized in a sealed tube at the required temperature. At a given time, the glass tube was removed and cooled to room temperature. The polymerization solution was dissolved in chloroform and precipitated from a large amount of methanol. The crude product was dissolved in chloroform again, and then the solution was passed through a short silica column to remove the catalyst. The polymer was recovered by precipitating it into methanol and then dried under vacuum to constant weight. The copolymer G3-Poly(PhMI-*co*-St) obtained was white fine powders.

IR (KBr): 3062, 3028, 2926, 1777, 1712, 1598, 1497, 1453, 1383, 1185, 1069, 756, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.28–7.60 (m, PhH in dendron and PhMI monomer unit), 6.2–7.2 (m, PhH in St monomer unit and ArH in dendron), 4.8–5.3 (m, $ArCH_2O$ and $PhCH_2O$ in dendron), 4.2–4.5 [m, CH(Ph)Br], 2.5–4.0 (br m, CH in imide ring), 0.9–2.4 (br m, CH and CH_2 in St monomer unit). The other copolymers were synthesized according to the similar approach, using G1-Br and G2-Br as macroinitiators, respectively.

Characterization

Fourier transform infrared spectroscopic analyses were performed on a PerkinElmer 2000 spectrome-



Scheme 1

ter. ^{1}H NMR spectra were recorded on a Varian 300-MHz spectrometer in $CDCl_3$ at room temperature. The molecular weight and molecular weight distribution were measured on a Waters 150-C gel permeation chromatographer (GPC) equipped with Ultrastyragel columns at 40 °C. Tetrahydrofuran was used as an eluent, and polystyrene standards were used as calibrations. The copolymer composition was determined either by elemental analysis or ^{1}H NMR; both methods gave comparable results. The molar conversion was obtained on the basis of the weight and copolymer composition.

RESULTS AND DISCUSSION

N-Substituted maleimide and St are one of the extensively examined monomer pairs for the exploration of alternating polymerization.[1,39–42] It has been reported with the participation of a charge-transfer complex, the alternating copolymer of *N*-substituted maleimide and St can be formed even at different monomer feeds. In this study, the dendritic initiators with different generations (Gn-Br, $n = 1$–3) were used for the atom transfer radical copolymerization of PhMI and St.

Atom Transfer Radical Copolymerization of PhMI and St Initiated with Various Dendritic Initiators

As shown in Scheme 1, the dendritic polyarylether 2-bromoisobutyrate (Gn-Br) was prepared by reaction of the hydroxyl-terminated polyarylether with 2-bromoisobutyryl bromide and triethylamine. The synthesis of Gn-Poly(PhMI-*co*-St) was accomplished by reaction of Gn-Br with PhMI and St in the presence of a catalytic amount of CuBr and bpy in anisole at 110 °C.

The molar fraction of PhMI (f_1) was 0.50 and dendritic polyarylether 2-bromoisobutyrates with different generations were used as macroinitiators, and the results of copolymerization with different polymerization times are listed in Table I. The number-average molecular weight determined by GPC [M_n (GPC)] was nearly equal to that obtained by ^{1}H NMR spectroscopy [M_n (NMR)], and both are almost consistent with the theoretical calculated molecular weight [M_n (calcd.)]. For instance, the copolymerization initiated with G3-Br in a sealed tube for 8 h afforded the copolymer in 46.0% conversion. The GPC curve of the resulting copolymer is presented in Figure 1, after purification. Figure 1 shows that the copolymer had an M_n (GPC) value of 8700 and a low polydispersity ($M_w/M_n = 1.12$). From ^{1}H NMR spectroscopy, the M_n (NMR) was calculated to be 8570. It is obvious that both M_n (GPC) and M_n (NMR) are in excellent agreement with the calculated value of 8090. From Table I, the initiator efficiency [f, calculated from $f = M_n$ (calcd.)/M_n (GPC)] of dendritic initiators also increases with increasing polymerization time. For example, when G3-Br was used as the initiator, the initiator efficiency varied from 0.75 to 0.98 as the conversion increased from 13.9 to 70.2%.

G3-Br for the ATRP of *N*-Phenylmaleimide and Styrene

As for the copolymerization initiated with the G3-Br/CuBr/bpy catalytic system at 110 °C, the relationship between the molar conversion and polymerization time is demonstrated in Figure 2. The plot of $\ln([M]_0/[M])$ versus time is almost linear, indicating that the polymerization kinetics is of a first-order nature. This means that the concentration of propagating radicals is constant during the polymerization procedure.

The effect of polymerization conversion on the M_n and M_w/M_n of copolymers is depicted in Figure 3. The plots of M_n (GPC) and M_n (NMR) versus the polymerization conversion are nearly a linear relationship and almost consistent with the theoretical calculated values [M_n (calcd.)]. This indicates that the anticipated average molecular weight of the dendritic-linear copolymer can be

Table I. Molecular Weight Results for the ATRP of PhMI and St Initiated with Gn-Br[a]

Run	Initiator	Time (h)	Conversion (%)	F_{PhMI}[b]	M_n (Calcd.)[c]	M_n (NMR)[d]	M_n (GPC)[e]	M_w/M_n[e]	f[f]
1	G1-Br	4	28.8	0.492	4,450	6,120	6,400	1.32	0.70
2	G1-Br	8	47.2	0.489	6,980	8,400	8,560	1.28	0.82
3	G1-Br	12	63.5	0.491	9,230	10,100	10,200	1.27	0.90
4	G1-Br	20	75.6	0.490	10,900	11,200	11,800	1.20	0.92
5	G2-Br	2	14.5	0.493	2,900	4,240	4,650	1.33	0.62
6	G2-Br	6	36.8	0.491	5,970	7,180	7,200	1.24	0.83
7	G2-Br	12	60.0	0.491	9,170	10,300	10,500	1.26	0.88
8	G2-Br	16	66.9	0.490	10,100	10,800	11,200	1.17	0.90
9	G3-Br	2	13.9	0.495	3,670	4,500	4,900	1.28	0.75
10	G3-Br	4	26.7	0.492	5,430	6,240	6,470	1.24	0.84
11	G3-Br	8	46.0	0.491	8,090	8,570	8,700	1.12	0.93
12	G3-Br	20	70.2	0.488	11,400	11,200	11,600	1.20	0.98

[a] Conditions of polymerization: [PhMI] : [St] : [Gn-Br] : [CuBr] : [bpy] = 50 : 50 : 1 : 1 : 2, $[M]_T$ = 4.0 mol/L, in anisole at 110 °C.

[b] The copolymer composition was determined either by elemental analysis or by ^{1}H NMR; both methods gave comparable results.

[c] M_n (calcd.) = ([PhMI] × F_{PhMI} × MW_{PhMI} + [St] × F_{St} × MW_{St})/[dendron]) × conversion + $MW_{dendron}$.

[d] Obtained by comparing the signal intensity of $ArCH_2O$ and $PhCH_2O$ protons in dendron (4.8–5.3 ppm) with that of CH protons in the imide ring (2.5–4.0 ppm) and that of CH and CH_2 protons in the St monomer unit (0.9–2.4 ppm).

[e] Determined by GPC in THF at 40 °C.

[f] Initiator efficiency (f) was calculated by $f = M_n$ (calcd.)/M_n (GPC).

manipulated by the control of polymerization conversion. In Figure 3, the resulting copolymers possess relatively narrow polydispersities (1.12 < M_w/M_n < 1.33). The fact suggests that the contribution of chain breaking and transfer as well as termination reactions during copolymerization can be neglected until higher polymerization conversion, which is similar to the result reported by Chen et al.[40] Thus, the copolymerization process of PhMI and St initiated with dendritic polyarylether 2-bromoisobutyrates is controllable and of a "living" polymerization nature.

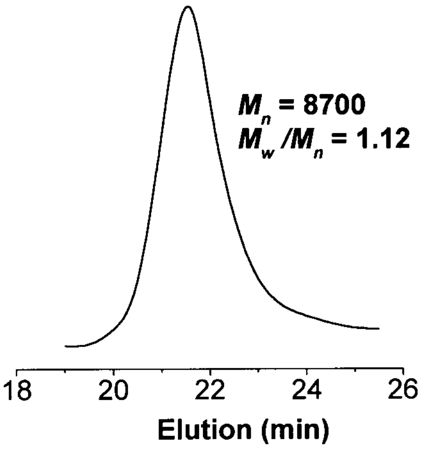


Figure 1. GPC trace of G3-Poly(PhMI-*co*-St) obtained via ATRP.

To investigate the temperature dependence of the copolymerization rate, the ATRP of PhMI and St was conducted in the range of 100–130 °C with anisole as a solvent. As shown in Figure 4, when the molar fraction of PhMI (f_1) is 0.50, the linear time dependence of ln($[M]_0$/[M]) is consistent with a controlled polymerization that is first order in monomer. The apparent rate coefficient k_{app} was determined from the slope of the straight line in a plot of ln($[M]_0$/[M]) versus polymerization time.[43,44] From the Arrhenius plots of lnk_{app} versus 1/T (Fig. 5), the apparent activation enthalpy ($\Delta H^{\neq}_{app}$) was 38.2 kJ/mol. The value is lower than

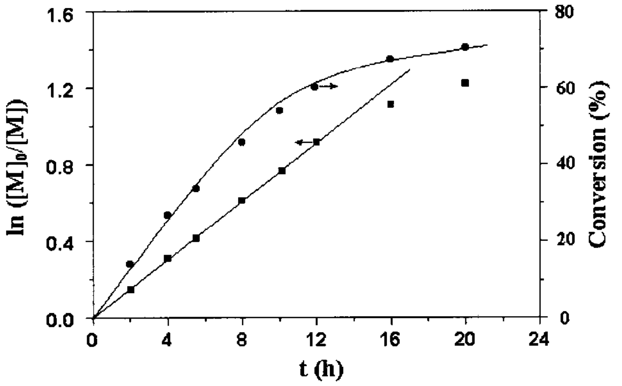


Figure 2. Time dependence of ln($[M]_0$/[M]) and conversion in anisole at 110 °C.

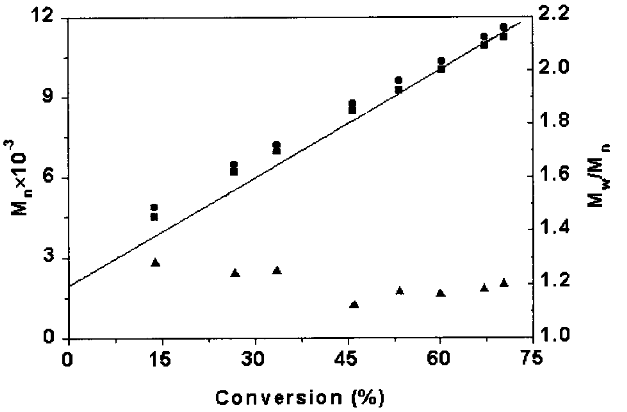


Figure 3. Dependence of the molecular weight and polydispersity of G3-Poly(PhMI-*co*-St) on the monomer conversion [●, M_n (GPC); ■, M_n (NMR); —, M_n (calcd.); ▲, M_w/M_n].

that of conventional free-radical copolymerization initiated by thermal initiator decomposition.[45]

The effect of monomer feed on copolymerization kinetics was also studied. When the monomer feeds were changed from 0.10 to 0.90, the copolymerization of PhMI and St initiated with G3-Br was carried out at various temperatures. According to the preceding approach, the apparent activation enthalpies at different monomer feeds were obtained. As shown in Table II, there is a minimum value of $\Delta H^{\neq}_{app}$ with the change of monomer feed that can be ascribed to the contribution of charge-transfer complex in polymerization.[39,42]

Calculation of Reactivity Ratios of PhMI and St in ATRP

In Table I, the copolymer compositions are always close to 1:1 in equimolar comonomer feed at different polymerization conversions. To further demonstrate that the resulting copolymers possess an alternating structure, the copolymerization of PhMI and St at different monomer feeds was carried out. The relationship between monomer feed and copolymer composition is listed in Table III, containing monomer conversions of less than 10%. The result shows that the copolymers possess a predominantly alternating structure in a wide range of monomer feeds.

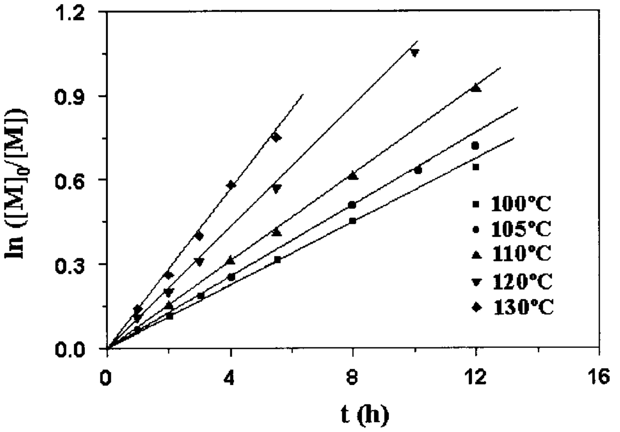


Figure 4. Semilogarithmic kinetic plots for the atom transfer radical copolymerization of PhMI and St in anisole at different temperatures.

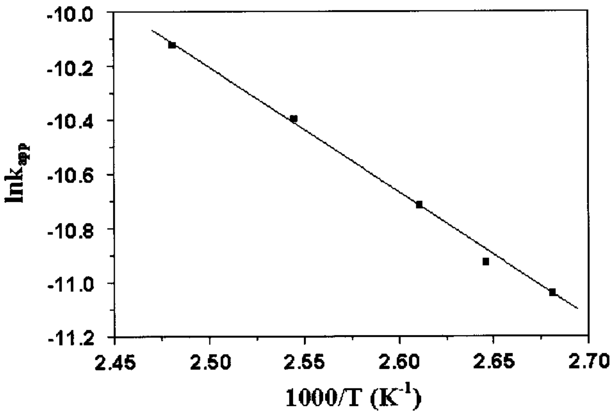


Figure 5. Arrhenius plots for the atom transfer radical copolymerization of PhMI and St in anisole.

It is well known that reactivity ratios can offer the message of relative reactivity of comonomers.[46–48] To estimate the relative reactivity of PhMI and St in the atom transfer radical copolymerization, the Kelen–Tüdős equation was used to calculate the monomer reactivity ratios

$$\eta = (r_1 + r_2/\alpha)\zeta - r_2/\alpha \qquad (1)$$

where $\eta = G/(\alpha + F)$, $\xi = F/(\alpha + F)$, $G = X(Y - 1)/Y$, $F = X^2/Y$, $X = f_1/(1 - f_1)$, $Y = F_1/(1 - F_1)$, $\alpha = (F_m F_M)^{1/2}$, F_M, and F_m are the maximum and minimum values of F, and f_1 and F_1 are the molar

Table II. Effect of Monomer Feed on the Apparent Activation Enthalpy

f_1	$\Delta H^{\neq}_{app}$ (KJ/mol)
0.10	59.6
0.30	50.4
0.50	38.2
0.70	43.8
0.90	54.5

Conditions of polymerization: $[M]_T$: [G3-Br] : [CuBr] : [bpy] = 100 : 1 : 1 : 2, $[M]_r$ = 4.0 mol/L, in anisole.

fractions of PhMI in the monomer feed and copolymer, respectively.

The plot of η versus ξ is shown in Figure 6 where several monomer feeds ($f_1 = 0.2$–0.6) were chosen to calculate the monomer reactivity ratios. From the slope and intercept of the straight line, the reactivity ratios of PhMI and St were determined to be $r_1 = 0.0325$ and $r_2 = 0.0524$, respectively. The results are close to those obtained at the conventional radical copolymerization with the usual free-radical initiator.[39] The two monomers have a strong tendency to form alternating copolymer because the value of $r_1 \cdot r_2$ is close to 0.

CONCLUSIONS

The dendritic polyarylether 2-bromoisobutyrates (Gn-Br, $n = 1$–3) were prepared by reaction of the hydroxyl-terminated polyarylether with 2-bromoisobutyryl bromide and triethylamine. Gn-Br as a macroinitiator for the controlled free-radical polymerization of PhMI (M_1) and St (M_2) has been investigated. The resulting copolymers possess well-defined molecular weights and low polydispersities ($1.12 < M_w/M_n < 1.35$). When the molar fraction of PhMI was 0.50, the copolymerization kinetics was investigated, and the apparent activation enthalpy of polymerization was 38.2 kJ/mol. In addition, effects of monomer feed on the apparent activation enthalpy and copolymer composition were also studied. By using the Kelen–Tüdős method, the monomer reactivity ratios were determined to be $r_1 = 0.0325$ and $r_2 = 0.0524$, respectively.

Table III. Copolymerization of PhMI and St at Various Monomer Feeds[a]

f_1	Conversion (%)	F_1	M_n (GPC)	M_w/M_n
0.10	9.84	0.414	4240	1.33
0.20	9.57	0.455	3960	1.28
0.30	9.86	0.473	3800	1.21
0.40	8.92	0.485	4080	1.25
0.50	9.43	0.496	4250	1.26
0.60	7.88	0.504	3970	1.22
0.70	8.75	0.514	3640	1.28
0.80	9.33	0.528	3880	1.35
0.90	8.65	0.574	3560	1.32

[a] Conditions of polymerization: $[M]_T$: [G3-Br] : [CuBr] : [bpy] = 100 : 1 : 1 : 2, $[M]_r$ = 4.0 mol/L, in anisole at 110 °C.

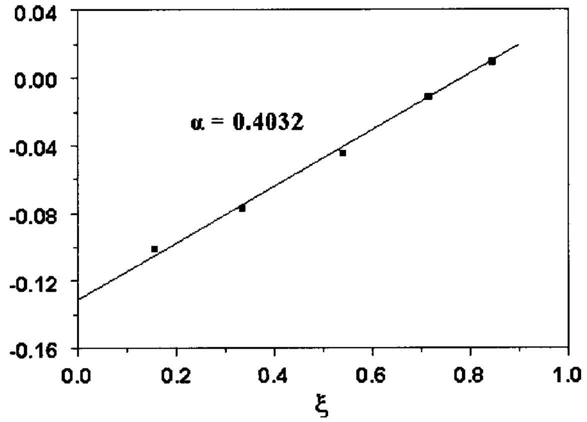


Figure 6. Kelen–Tüdős plots for the ATRP of PhMI and St.

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