ELSEVIER

Polymer 42 (2001) 6385–6391

polymer

www.elsevier.nl/locate/polymer

Atom transfer radical copolymerization of styrene and poly(THF) macromer

Guo Yan-Ming, Wang Ting, Zou Yin-Fang, Pan Cai-Yuan*

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Received 23 October 2000; received in revised form 22 January 2001; accepted 1 February 2001

Abstract

The graft copolymer with polytetrahydrofuran (PTHF) as branch chain was prepared by atom transfer radical copolymerization of styrene (St) and PTHF with an end-standing methacrylate (MA-THF). GPC and ^{1}H NMR were used to characterize PTHF macromers and copolymers. The straight line on the profile of the molecular weight versus yield of copolymer was obtained, and the molecular weight distribution is relative narrow, supporting that the copolymerization is controllable. The relative reactivity ratio ($1/r_{St}$) of MA-PTHF to St was measured, and is independent of polymerization degree of the macromer. Atom transfer radical polymerizations (ATRP) of PTHF macromer were also investigated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Macromer; Graft copolymer; ATRP

1. Introduction

Graft copolymers represent a valuable class of polymeric materials, which have potential applications in the fields of impact-resistant plastic, thermoplastic elastomers, surface modifiers, polymeric emulsifiers, etc. [1–6]. They are composed of a main polymer chain to which one or more side chains are connected through covalent bonds, and the branches are usually randomly distributed along the backbone. Compared to block copolymers, graft copolymers offer all properties of block copolymers, but are usually easier to synthesize. Moreover, the branched structure of the copolymer leads to the decrease of melt viscosity, which is a great advantage for process of polymer materials. According to the theory of Eruhimovich [7], graft copolymers should show better phase separation than triblock copolymers do.

As we know, controlling polymer properties through design and synthesis of copolymers and macromolecular architectures is a continuing theme for polymer chemistry [8,9]. Recent attention has focused on nonlinear architectures such as graft copolymers, dentrimers, hyperbranch derivatives, and star (co)polymers [10–14]. In order to study the influence of polymer structure on its properties and compare with theoretical models, it is essential to use well-defined materials. However, very little is known about the influence of chain architecture on properties until now due to the difficulties associated with the synthesis of well-defined polymeric materials with special architecture [14]. In previous work [15–18], we prepared several kinds of well-controlled PTHF/PSt copolymers, such as triblock copolymer (PTHF–PSt–PTHF), star block copolymer [*S*-(PTHF–PSt–PMMA)$_4$], A_nB_n miktoarm star copolymers [(PTHF)$_n$(PSt)$_n$, $n = 2$ or 4], by combination of cationic ring-opening polymerization (CROP) and ATRP. For investigating the difference in properties of copolymers with the same composition, but different structure, so we prepared another kind of copolymer with nonlinear structure, graft copolymers of PSt with PTHF.

Graft copolymers are generally prepared by the following three methods [1]: (1) 'grafting from' techniques, that is, more or less active sites on a polymer backbone initiate polymerization of a second monomer, forming a graft copolymers; (2) 'grafting onto' methods, this involves the reaction of functional group (such as, COOH) at the end of polymer with another reactive group (such as OH) distributed randomly or regularly on a polymer backbone; (3) 'grafting through' techniques, in which macromers copolymerize with vinyl monomers. The third method is considered as an effective method of preparing well-defined graft copolymers, and offers better control of copolymerization than grafting from and grafting onto techniques [19]. Here, so-called 'control' includes the control of molecular

* Corresponding author. Fax: +86-551-3631760.
E-mail address: pcy@ustc.edu.cn (Pan C-Y).

PII: S0032-3861(01)00110-0

weights and molecular weight distributions of the polymer backbone and the branch chain as well as average chain length between two branching points.

Synthetic methods initially developed for graft copolymers led to the formation of rather ill-defined polymers. These techniques are mainly based on traditional free radical polymerization techniques. For example, the graft copolymers of styrene and PTHF macromer were prepared by conventional free-radical polymerization [20,21]. However, there is no report on the controlled polymerization of PTHF macromers.

Recently, the development in the controlled/'living' radical polymerization based on the use of reversibly blocking agents, such as sulfur compounds [22,23], stable nitroxyls [24–27], organometal complexes [28,29], and halogens [30–33], has provided possibilities for synthesizing well-defined polymers with narrow polydispersity and/or novel architecture. Some of these techniques have been used to the preparation of well-defined graft copolymer by means of macromer [34–36]. Among these methods, the transition metal-catalyzed ATRP [30–34] was proved to be a versatile route for the synthesis of polymers with well-defined structure from a variety of radical polymerization of macromers. Here, we report the preparation and characterization of graft copolymers of PSt with MA-PTHF.

2. Experimental

2.1. Materials

Styrene (St), CuBr (AR, The First Shanghai Chemical Reagent Factory, 98%), and 2.2′-bipyridine (bpy, Aldrich) was of analytical grade and purified by the method described in our previous paper [37]. Ethyl 2-bromobutyrate (EBB) was synthesized in this laboratory [38]. The reagents used for the cationic ring-opening polymerization of THF were purified as before [39]. Methacryloyl chloride (95% Aldrich) was purified by distillation in vacuum before use. All other reagents were of analytical grade, and used as received.

2.2. Synthesis of MA-PTHF

MA-PTHF was synthesized according to the method described in reference [40] with a slight modification. A typical procedure was as follows: a 50 ml two-necked flask with a magnetic bar was evacuated and purged with pure nitrogen alternatively three times, 10.5 ml of methylene chloride and 0.181 g (1.73 mmol) of methacryloyl chloride were then added, stirring was commenced. Under nitrogen atmosphere, 0.374 g (1.73 mmol) of silver perchlorate was transferred into the flask at −15°C. After one hour, 19.5 ml (240 mmol) of THF was added with a syringe. The samples used for measurements of polymerization conversion and molecular weight (MW) was withdrawn from the polymerization system at prescribed time intervals. The polymerization was stopped by adding excess distilled water. The mixture was filtered to remove AgCl, and the solution was added into methanol at −30°C. The product MA-PTHF was precipitated, collected by filtration, and finally dried at 40°C/0.2 Torr for 24 h.

2.3. Copolymerization of St and MA-PTHF by ATRP

A glass tube with a magnetic bar was charged with 3.48 g of MA-PTHF (1 mmol), 0.028 g (0.143 mmol) of EBB, 0.020 g (0.143 mmol) of CuBr, 0.067 g of bpy (0.429 mmol) and 5.20 g of St (50 mmol) and 2 ml THF. The mixture was immediately degassed by three freeze-evacuate-thaw cycles. The tube was then sealed under vacuum and placed in an oil bath at 105°C. After a prescribed time, the reaction mixture was cooled to room temperature, dissolved in THF, and passed through a short neutral alumina column to remove the copper complexes. The copolymers were obtained by precipitating polymer solution in excess methanol three times to remove unreacted macromer, and the filtrates were combined and distilled under vacuum to recover macromer. All samples were then dried at 40°C/0.1 Torr for 24 h, and 3.63 g of copolymer and 1.75 g of unreacted macromer were obtained.

2.4. Homopolymerization of MA-PTHF by ATRP method

With a similar procedure of copolymerization, homopolymerization of MA-PTHF was carried out in a sealed tube. After polymerization was finished, copper complexes was removed, the polymer solution in THF was subjected to GPC measurement.

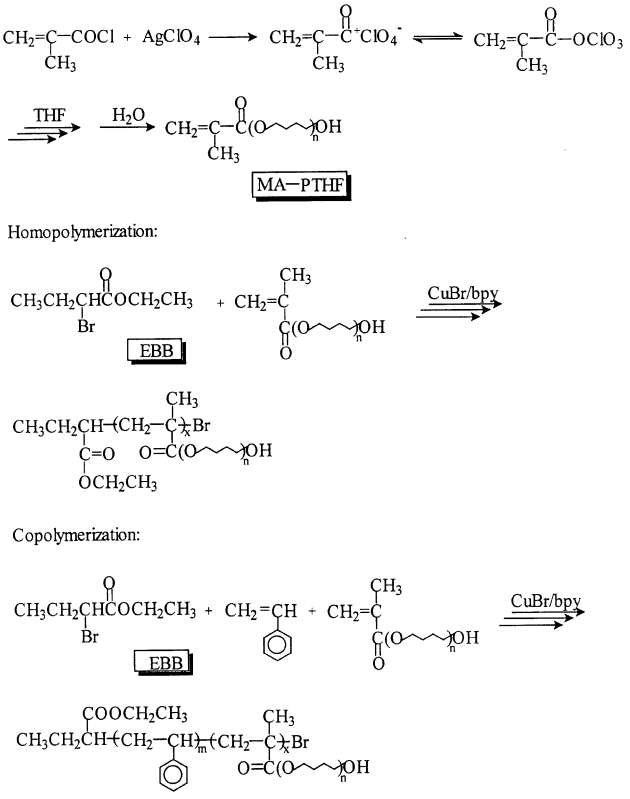
2.5. Characterization

The conversion measurements of THF were carried out on a 102G gas chromatography (Shanghai Analysis Instrument) equipped with 3 m long column in which a 101 white support coated with 15 wt % OV-17 was filled. ^{1}H NMR spectra were recorded on a Bruker DMX-500 nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard. Molecular weight (MW) and molecular weight distribution (MWD) were determined on a Waters 150C gel permeation chromatography (GPC) equipped with microstyragel columns (500, 10^3, and 10^4 Å) using polystyrene standards, and THF as eluent at a flow rate of 1.0 ml min^{-1}.

3. Results and discussions

3.1. Macromer synthesis by cationic ring-opening polymerization

The basic outline for the synthesis of PTHF terminated with methacrylate group (MA-PTHF), its homopolymerization and copolymerization of MA-PTHF with St is shown in Scheme 1. The conditions and results for



Scheme 1. 'Atom transfer radical copolymerization'.

cationic ring-opening polymerization (CROP) of THF initiated by acrylium ions, which was formed in situ by the reaction of methacryloyl chloride with $AgClO_4$, are listed in Table 1.

In order to confirm the structure of the macromer carrying a methacrylate group at the end of chain, a typical ^1H NMR spectrum of MA-PTHF is shown in Fig. 1.

The absorption peaks at 5.54, 6.09 and 1.94 ppm correspond to methylene protons of the double bond and methyl protons in the MMA unit, respectively. The signal at 4.17 ppm is ascribed to the methylene protons adjacent to the oxygen of the ester group. The peak at 3.62 ppm originates from the methylene protons next to the end-standing

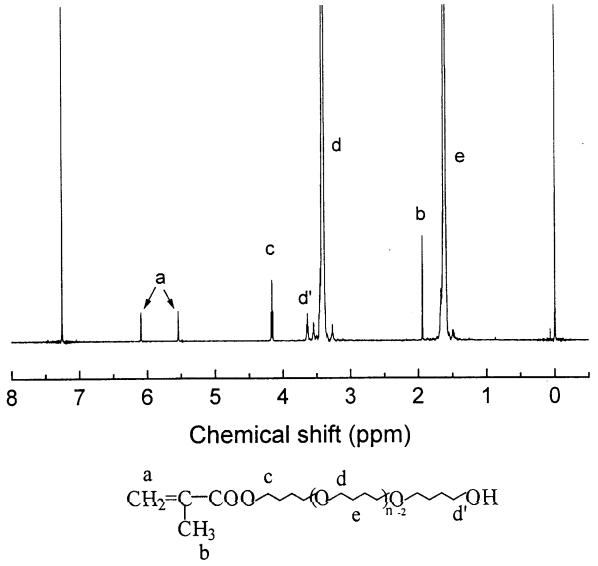


Fig. 1. ^1H NMR of PTHF macromer (No. 1 in Table 1).

hydroxyl group. For estimating whether every macromer contains one methacrylate group, the number-average end functionality (F_n) was derived from the intensity ratio of the peaks at 5.54 and 6.09 ppm (I_6) to that at 3.62 ppm ($I_{3.6}$) as described by Eq. (1)

$$F_n = I_6/I_{3.6}. \quad (1)$$

The values of F_n listed in Table 1 are all close to 1 within ±5% experimental errors, indicating that the macromer contains one methacrylate group. The number-average molecular weight of polymerization, M_n(NMR) is determined by the intensity of the peaks at 1.63 ppm ($I_{1.6}$), corresponding to the two middle methylene protons in the tetramethylene group, and at 1.94 ppm ($I_{1.9}$)

$$M_n(\text{NMR}) = (I_{1.6}/4)/(I_{1.9}/3) \times 72 + 86, \quad (2)$$

where 72 and 86 are the molar masses of THF and mathacrylic acid, respectively.

The agreement of M_n(NMR) with M_n(th) demonstrates that molecular weight can be controlled. In addition, the

Table 1
Conditions and results of CROP of THF initiated by methacryloyl chloride in combination with $AgClO_4$ (the polymerization were performed at −15°C; $[THF]_0 = 8.0$ mol l^{-1})

No.[a]	$[I]_0$ (mmol l^{-1})	$[AgClO_4]$ (mmol l^{-1})	Time (h)	Conv[b] (%)	F_n[c]	M_n		M_w/M_n (GPC)
						(NMR)[d]	(th)[e]	
1	57.7	57.7	6	32	1.05	3480	3290	1.22
2	96.3	96.3	5	38	0.97	2590	2360	1.26
3	96.3	96.3	3	26	1.04	1710	1650	1.40

[a] Sample Nos. 1 and 2 were precipitated from excess of methanol at −30°C one time. Sample No. 3 was obtained after evaporation of THF in vacuum.
[b] Determined by GC.
[c] The number-average end functionality was calculated by Eq. (1).
[d] The number-average molecular weight was calculated by Eq. (2).
[e] Theoretical molecular weight of poly(THF) macromers M_n(th), was calculated according to $M_n(\text{th}) = ([THF]_0/[I]_0) \times 72 + 86$.

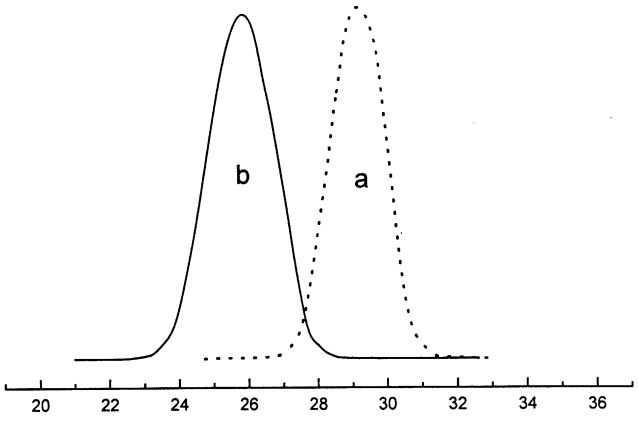


Fig. 2. GPC curves of PTHF macromer (a) (No. 1 in Table 1) and copolymer (b) (No. 6 in Table 2).

results listed in Table 1 show narrow molecular weight distribution (1.22–1.40). The symmetric and unimodal GPC curve as shown in Fig. 2a and the controlled molecular weight indicate that the cationic ring-opening polymerization of THF initiated by methacryloyl chloride in combination with $AgClO_4$ is of living nature.

3.2. Copolymerization of styrene and MA-PTHF by ATRP

The conditions and results for the copolymerization of St with MA-PTHF are summarized in Table 2. In general, M_ns determined from GPC are obvious underestimated due to different hydrodynamic volume of the graft copolymer from that of the polystyrene standard. So the number of branch in graft copolymer calculated from GPC data are also underestimated. In spite of these, from Table 2 we can see the trends that M_n and the branch number of copolymers increased with the increase of conversion.

The conversions of St or MA-PTHF versus time are shown in Fig. 3a. The polymerizations took place smoothly without induction time. It was found that the polymerization of macromer was faster than that of St in the preliminary stage due to more reactive methacrylate group, then the conversion of MA-PTHF increased slowly. This might be attributed to the increasingly high viscosity of the polymerization system rather than to irreversible termination reactions, such as combination of growing radicals. It was suggested for homopolymerization of macromers [41,42] that as the polymerization proceeds and the viscosity of medium increases, the propagation mechanism can change from a chemical controlled to a diffusion controlled process. This phenomenon for MA-PTHF is more serious comparison with St (see Fig. 3a).

Fig. 3b gives plot of the molecular weight of copolymer versus total conversion of St and MA-PTHF. The linear relationship shows no chain-transfer reaction during the copolymerization.

As shown in Fig. 2b, the GPC curve of the copolymer is symmetric and unimodal. No shoulder peaks corresponding to the PTHF macromer or its homopolymer were observed. The GPC curves of the products obtained from filtration solution are similar to that of macromers (see Fig. 2a), indicating that the homopolymers of MA-PTHF are negligible,

Table 2
Conditions and results of ATRP of St and MA-PTHF (the polymerization was performed at 105°C, $[St]_0 = 4.59\ mol\ l^{-1}$, $[MA\text{-}PTHF]_0 = 9.18 \times 10^{-2}\ mol\ l^{-1}$)

No.[a]	MW of MA-PTHF	Time (h)	M_n (GPC)	M_w/M_n (GPC)	C_1[b] (%)	C_2[b] (%)	C_t[c] (%)	N_g[d]
1	3480	3	8819	1.30	13.8	20.1	16.3	1.25
2		6.5	15950	1.30	26.2	34.3	29.4	2.14
3		10	24130	1.33	36.5	49.7	41.8	3.31
4		14	27470	1.34	45.3	56.5	49.8	3.59
5		18	30090	1.37	51.1	58.1	53.9	3.74
6		23	33970	1.38	58.2	61.1	59.4	4.02
7		30	35190	1.45	66.8	63.7	65.6	4.13
8	2590	3	10140	1.32	18.2	26.3	21.3	1.85
9		6	18150	1.29	33.0	48.2	38.8	3.3
10		10	25170	1.31	45.6	61.5	51.7	4.43
11		14	29930	1.34	55.1	67.9	60.0	5.02
12		19	33090	1.34	62.3	69.4	65.0	5.23
13		24	34160	1.39	66.7	70.0	67.9	5.22
14		30	36280	1.43	73.4	72.6	73.1	5.33

[a] From No. 1 to 7, $[St]_0/[MA\text{-}PTHF]_0/[EBB]/[CuBr]/[bpy] = 350:7:1:1:3$ (molar ratio); from No.8 to 14, $[St]_0/[PTHF]_0/[EBB]/[CuBr]/[bpy] = 320:8:1:1:3$ (molar ratio).

[b] C_1 and C_2 are the conversions of St and MA-PTHF, respectively, and determined by weight method. $C_2 = (W_{2,0} - W_2)/W_{2,0}$, $C_1 = [W_c - (W_{2,0} - W_2)]/W_{1,0}$, where W_c is weight of the copolymer obtained, $W_{1,0}$ and $W_{2,0}$ are the initial weights of M_1 and M_2, respectively, W_2 is the weight of unreacted macromer.

[c] C_t is total conversion, and was calculated by $C_t\% = [W_c/(W_{1,0} + W_{2,0})] \times 100\%$, where W_c is weight of the copolymer obtained, $W_{1,0}$ and $W_{2,0}$ are the initial weights of M_1 and M_2, respectively.

[d] N_g is average number of branch chain in one macromolecule, and was calculated according to $N_g = M_c W_g/M_2$, here: M_c is molecular weight of the copolymer; W_g is weight percentage of MA-PTHF in copolymer; M_2, is molecular weight of MA-PTHF.

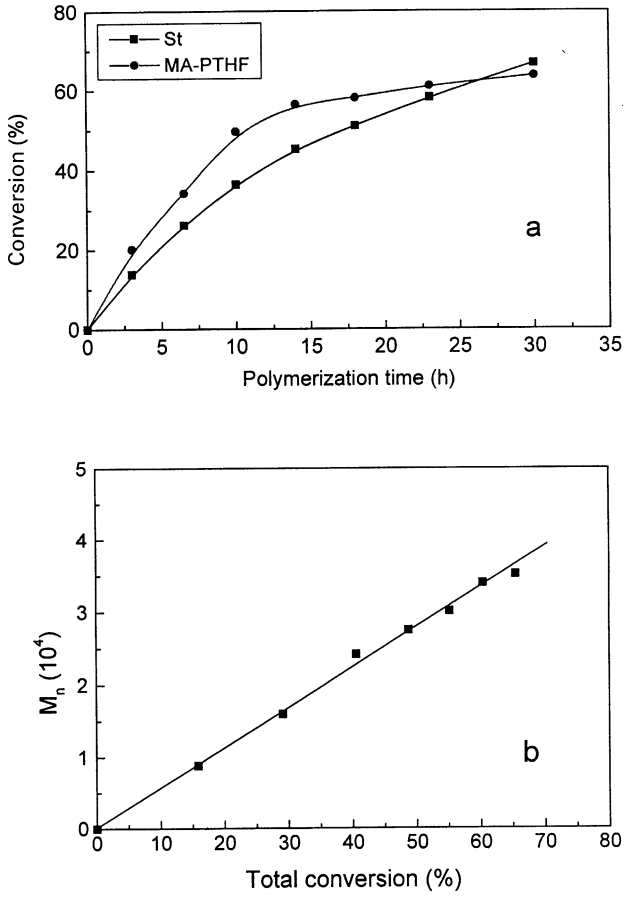


Fig. 3. Conversions of St or MA-PTHF versus polymerization time (a) and M_n versus total conversion (b) for copolymerization of St and PTHF macromer.

and the loss of copolymer during the precipitation is not serious.

In order to confirm the formation of the graft copolymer of St and MA-PTHF, the ^{1}H NMR spectra of copolymer were measured and a typical ^{1}H NMR spectrum is shown in Fig. 4. The peaks from 6.35 to 7.20 ppm are assigned to

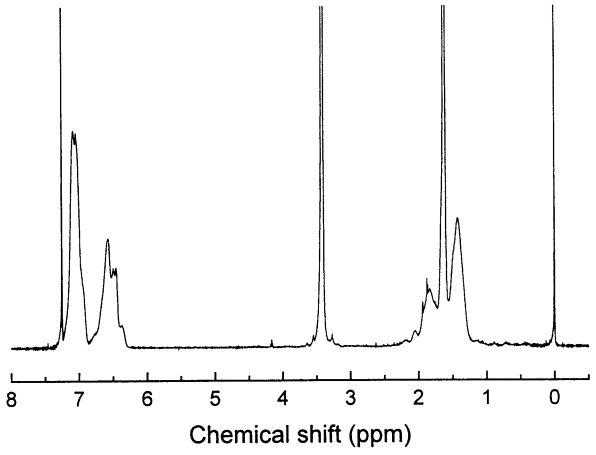


Fig. 4. ^{1}H NMR of graft copolymer (No. 6 in Table 2).

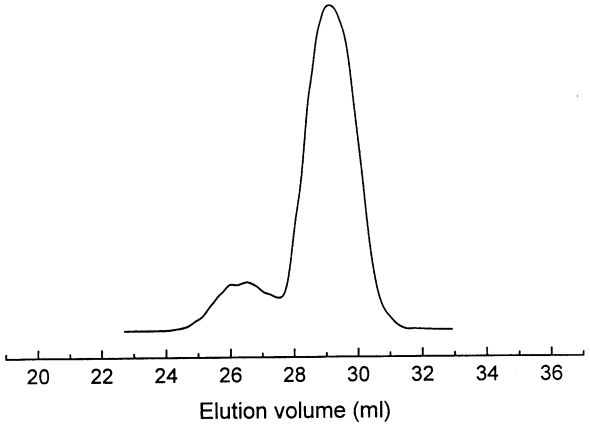


Fig. 5. GPC curves of homopoly(macromer) for the MA-PTHF with molecular weight 3480.

aromatic protons, and the absorption at 3.41 ppm is ascribed to the methylene protons next to oxygen in THF unit, The peaks located between 1.18 and 2.25 ppm correspond to the methylene protons of the two middle methylene groups in THF unit and to the methylene and methine groups on the PSt backbone, respectively. These facts verify the formation of graft copolymer.

The homopolymerization of MA-PTHF was also carried out by ATRP. Because separation of MA-PTHF from its homopolymers is difficult, the polymerization solutions were directly used to GPC measurement as shown in Fig. 5. It is obvious that there are two peaks in this figure. One at lower molecular weight is attributed to MA-PTHF; another is its homopolymers. Comparing the area of the two peaks, only low conversion (~15%) of MA-PTHF was obtained in 20 h, and the molecular weight distribution is relatively wide (about 1.9). This is very different from ATRP of poly(vinyl ether) macromers [43], but similar to the results reported by Sierra-vargas [20]. The probable reason may be due to the very high bulky group of MA-PTHF, and to the low encountering possibility of the active sites. Because of the low molar ratio of the macromer to St, and slow homopolymerization of the macromer, so the random copolymerization can be considered.

3.3. Determining of reactivity ratio in copolymerization system

Copolymerization of a conventional monomer (here is St), M_1, with a macromer (here is MA-PTHF), M_2, gives a graft copolymer with M_1 backbone and M_2 branch chain. The monomer reactivity ratios could be derived from a conventional Mayo–Lewis formula [44] as shown in Eq. (3)

$$\mathrm{d}[M_1]/\mathrm{d}[M_2] = ([M_1]/[M_2])\{(r_1[M_1] + r_2[M_2])/(r_2[M_2] + [M_1])\}, \quad (3)$$

where $\mathrm{d}[M_1]/\mathrm{d}[M_2]$ is the instant molar ratio of M_1 and M_2 in the copoloymer, $[M_1]$ and $[M_2]$ are the concentrations of M_1

and M_2 in the feed at a given time, and r_1 and r_2 are the reactivity ratios of M_1 and M_2, respectively. When $[M_1] \gg [M_2]$, Eq. (3) can be simplified as Eq. (4), which was firstly suggest by Jaacks [45]:

$$d[M_1]/d[M_2] = r_1[M_1]/[M_2]. \quad (4)$$

Integrating Eq. (4), Eq. (5) is obtained

$$\ln([M_2]_t/[M_2]_0) = 1/r_1 \ln([M_1]_t/[M_1]_0), \quad (5)$$

where $[M_1]_0$ and $[M_2]_0$ are the initial concentrations, and $[M_1]_t$ and $[M_2]_t$ are the concentrations of M_1 and M_2 at time t. Eq. (5), so-called Jaacks equation can be used up to high conversions, provide that the large excess of M_1 over M_2 throughout the copolymerization process. Comparing to Mayo–Lewis equation, this proves a decisive advantage in the practical application. If the conversions of M_1 and M_2 at time t are C_1 and C_2, respectively, Eq. (6) can be obtained.

$$\ln(1 - C_2) = 1/r_1 \ln(1 - C_1). \quad (6)$$

Plotting $\ln(1 - C_2)$ against $\ln(1 - C_1)$, $1/r_1$ could be obtained from the slope of the straight line as shown in Fig. 6. As mentioned above, polymerization rate of macromer decreased obviously faster than that of St did in the latter stage (see Fig. 3a) because of the change of propagation mechanism, the relative reactivity obtained would be more accurate at primary polymerization stage. Within 50 or 60% of conversion, the values of $1/r_1$ are 1.41 and 1.46, respectively, for MA-PTHF with molecular weights of 3480 and 2590. The small difference of $1/r_1$ values due to molecular weight of MA-PTHF is in the experimental error. These values are similar with $1/r_{St}$ (1.61) obtained from the copolymerization of St and MMA by the conventional radical polymerization [45]. For the probable explanation of this result, a lower diffusion rate of macromer leads that chain radical and methacrylate group will undergo more collisions before diffusion apart, so its reactivity does not reduce. However, the reactivity of macromer obviously decreases at high conversion (such as >50%, see Fig. 3a), because the diffusion control became more serious in the latter stage.

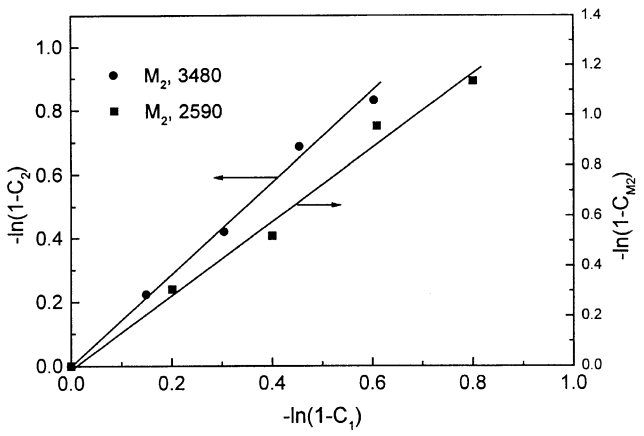


Fig. 6. Jaacks plots of $\ln(1 - C_1)$ as a function of $\ln(1 - C_2)$.

4. Conclusions

A well-defined graft copolymer with PSt-co-PMMA as backbone and PTHF as branch chain was prepared by ATRP. The structures of the graft copolymer obtained were characterized by GPC and ^{1}H NMR spectra. The molecular weight can be controlled by the molar ratio of St and MA-PTHF consumed to initiator; the length of branch chains is determined by the MW of PTHF macromer synthesized from living cationic ring-opening polymerization of THF; the average branch number of every macromolecule can be estimated by the conversions of St and MA-PTHF, and the molar ratio of St and MA-PTHF to initiator. The molecular weight distribution of the grafts is narrow ($M_w/M_n = 1.29$:1.43). The distribution of branch chain along with the backbone is random. The monomer reactivity ratio of macromer ($1/r_1$) obtained by the Jaacks method is independent on the molecular weight of macromer, and is about 1.41 or 1.46, which is similar to the corresponding value of MMA, indicating the independence of $1/r_1$ on the molecular weight of macromer.

Acknowledgements

This research was supported by National Natural Science Foundation of China under contract No. 59773001.

References

[1] Dreyfuss P, Quirk RP. In: Kroschwitz JI, editor. Encyclopedia of polymer science and engineering, vol. 7. New York: Wiley-Interscience, 1987. p. 551.
[2] Rempp P, Lutz PJ. Adv Polym Sci 1984;58:1.
[3] Maniruzzaman MK, Kawaguchi S, Ito K. Macromolecules 2000;33:1583.
[4] Zen FQ, Shen YQ, Zhu SP, Delton R. Macromolecules 2000;33:1628.
[5] Tsukahara Y, Tsai HC, Yamashita Y, Muroya Y. Polym J 1987;19:1033.
[6] Xie HQ, Zhou SB. J Appl Polym Sci 1991;42:199.
[7] Dobrynin AV, Erukhimovich IY. Macromolecules 1993;26:276.
[8] Webster OW. Science 1994;251:887.
[9] Fréchet JMJ. Science 1994;263:1710.
[10] Matthews OA, Shipway AN, Stoddart JF. Prog Polym Sci 1998;23:1.
[11] Voit B. J Polym Sci, Part A: Polym Chem 2000;38:2505.
[12] Hadjichristidis N. J Polym Sci, Part A: Polym Chem 1999;37:857.
[13] Ishizu K, Uchida S. Prog Polym Sci 1999;24:1439.
[14] Pitsicalis M, Pispass S, Mays JW, Hadjischristidis N. Adv Polym Sci 1998;135:1.
[15] Xu YJ, Pan CY. J Polym Sci, Part A: Polym Chem 2000;28:337.
[16] Xu YJ, Pan CY. Macromolecules 2000;33:4456.
[17] Guo YM, Pan CY. Polymer 2001;42:2863.
[18] Guo, YM, Pan, CY, J Polym Sci Part A: Polym Chem 2001;39:437.
[19] Meijis GF, Rizzardo EJ. Macromol Sci Rev, Macromol Chem Phys 1990;C30:305.
[20] Sierra-Vargas J, Franta E, Remmpp P. Makromol Chem 1981;182:2603.
[21] Asami R, Takaki M. Makromol Chem Suppl 1985;12:163.

[22] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadune RTA, Meijis GF, Moad KL, Moad G, Rizzardo E, Thang SH. Macromolecules 1998;31:5559.
[23] Otsu T, Yoshida M. Makromol Chem Rapid Commun 1982;3:127.
[24] Georges MK, Veregin RPN, Kazmaier PM, Hamaer GK. Macromolecules 1993;26:2987.
[25] Odell PG, Vererin RPN, Michalak LM, Georges MK. Macromolecules 1997;30:2232.
[26] Hawker CJ. J Am Chem Soc. 1994;116:11,185.
[27] Greszta D, Matyjaszewski K. Macromolecules 1996;29:7661.
[28] Wayland BB, Pozmik G, Mukeriee Sl S, Fryd M. J Am Chem Soc 1994;116:7943.
[29] Wayland BB, Basickes L, Mukurjee S, Wei M, Fryd M. Macromolecules 1997;30:8109.
[30] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721.
[31] Wan JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614.
[32] Wan JS, Matyjaszewski K. Macromolecules 1995;28:7901.
[33] Matyjaszewski K, Patten TE, Xia J. J Am Chem Soc 1997;119:674.
[34] Roos SG, Müller AHE. Macromolecules 1999;32:8331.
[35] Hawker CJ, Mecerreyes D, Elce E, Dao JL, Hedrick JL, Barakat I, Dubois P, Jerome R, Volksen W. Macromol Chem Phys 1997;198:155.
[36] Wang Y, Huang J. Macromolecules 1998;31:4057.
[37] Xu YJ, Pan CY, Tao L. J Polym Sci, Part A: Polym Chem 2000;38:436.
[38] Pan CY, Lou XD. Macromol Chem Phys 2000;201:1115.
[39] Xu YJ, Liu Y, Pan CY. J Polym Sci, Part A: Polym Chem 1999;37:3391.
[40] Sierra-Vargas J, Zilliox JG, Rempp P, Franta E. Polym Bull 1980;3:83.
[41] Tsukahara Y, Mizuno K, Segawa A, Yamashita Y. Macromolecules 1989;22:1546.
[42] Tsukahara Y, Tsutsumi K, Yamashita Y, Shimada S. Macromolecules 1990;23:5201.
[43] Yamada k, Miyazaki M, Ohno K, Fukuda T, Minoda M. Macromolecules 1999;32:290.
[44] Mayo FR, Lewis FM. J Am Chem Soc 1944;66:1594.
[45] Jaacks V. Makromol Chem 1972;161:161.