Synthesis and Characterization of Well-Defined Poly(2-hydroxyethyl methacrylate-*co*-styrene)-graft-poly(ε-caprolactone) by Sequential Controlled Polymerization

XUEWEI XU, JUNLIAN HUANG

Department of Macromolecular Science, Fudan University, The Key Open Laboratory of Molecular Engineering of Polymer, State Education Ministry of China, Shanghai, China

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ABSTRACT: A new graft copolymer, poly(2-hydroxyethyl methacrylate-*co*-styrene) -graft-poly(ϵ-caprolactone), was prepared by combination of reversible addition-fragmentation chain transfer polymerization (RAFT) with coordination-insertion ring-opening polymerization (ROP). The copolymerization of styrene (St) and 2-hydroxyethyl methacrylate (HEMA) was carried out at 60 °C in the presence of 2-phenylprop-2-yl dithiobenzoate (PPDTB) using AIBN as initiator. The molecular weight of poly (2-hydroxyethyl methacrylate-*co*-styrene) [poly(HEMA-*co*-St)] increased with the monomer conversion, and the molecular weight distribution was in the range of 1.09 ~ 1.39. The ring-opening polymerization (ROP) of ϵ-caprolactone was then initiated by the hydroxyl groups of the poly(HEMA-*co*-St) precursors in the presence of stannous octoate ($Sn(Oct)_2$). GPC and ^{1}H-NMR data demonstrated the polymerization courses are under control, and nearly all hydroxyl groups took part in the initiation. The efficiency of grafting was very high. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 5523–5529, 2004

Keywords: graft copolymers; radical polymerization; ring-opening polymerization; ϵ-caprolactone; 2-hydroxyethyl methacrylate

INTRODUCTION

Graft copolymerization via functional groups of an exiting polymer main chain offers an easy and effective approach to incorporating new properties into the parent polymer. Compared with the original polymer, graft polymers often exhibit improved physicochemical properties, such as enhanced compatibility with other polymers, adhesion to metallic and inorganic substrates, and dye retention.[1] Recent advances in the area of controlled radical polymerization, including atom transfer radical polymerization (ATRP),[2] nitroxide-mediated polymerization (NMP),[3,4] and reversible addition-fragmentation chain transfer polymerization (RAFT),[5,6] allow us to synthesize easily copolymers with complex architecture and well-defined structures.

Poly(ϵ-caprolactone) (PCL) is an important environmentally friendly and biocompatible material with some special properties such as biodegradability and miscibility toward some commodity polymers, including polyethylene and polypropylene.[7] It was also often used to improve the mechanical properties of the polymers by graft copolymerization, and the resulting graft copolymer could be used as compatibilizer in polymer blends. In the preparation of polymeric hollow nanospheres, graft or block copolymers would play very important roles,[8] especially the biodeg-

Correspondence to: J. Huang (jlhuang@fudan.edu.cn).

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Table 1. RAFT Copolymerization of St and HEMA (Mole Ratio PPDTB:AIBN = 3:1, Reaction Temperature 60 °C)

Sample	f_H[a]	F_H[b]	Time (h)	Mn	Mw/Mn	Conv (%)	N_{OH}[c]
1a	0.1	0.241	5	2,200	1.08	1.98	4.8
1b	0.1	0.253	15	15,100	1.09	11.81	34.5
1c	0.1	0.254	25	25,000	1.11	22.53	57.3
1d	0.1	0.238	50	37,700	1.19	37.74	81.3
2a	0.05	0.151	5	4,000	1.12	2.48	5.6
2b	0.05	0.158	10	10,900	1.14	7.41	15.9
2c	0.05	0.148	15	18,200	1.20	11.24	24.9
2d	0.05	0.151	20	26,950	1.19	16.62	37.7
2e	0.05	0.127	30	35,500	1.39	24.72	42.0
2f	0.05	0.149	40	45,300	1.35	30.57	62.5

[a] Mole fraction of HEMA feed.
[b] Mole fraction of HEMA units on the copolymers measured by ^{1}H NMR spectrum using eq. (1).
[c] Average number of hydroxyl groups per backbone P(HEMA-co-St) chain obtained from eq. (2).

radated segment-containing copolymers as PCL, by which the "core" could be removed easily with enzyme after crosslinking of the shell.

PCL is generally synthesized by ring-opening polymerization in the presence of various initiators or catalysts.[9] There are generally two approaches to obtain the graft copolymer of PCL: one is the macromonomer technique in which PCL, bearing a terminal double bond, was copolymerized with other monomers; the other is the "grafting from" technique in which the polymerization of ϵ-CL is (co)initiated by pendent hydroxyl groups of a polymer backbone. For example, some natural macromolecules with multi-hydroxyl groups, such as starch[10,11] and hydroxycellulose,[12] as well as synthetic polymers, such as polyvinyl alcohol[13] and poly(ethylene-*co*-vinyl alcohol) (EVOH),[14,15] could be used to initiate the ring opening polymerization of ϵ-CL.

In this article, the preparation of a well-defined poly(2-hydroxyethylmethacrylate-*co*-styrene)-graft-poly(ϵ-caprolactone) is described by combination of RAFT with ring-opening polymerization, and the controllability of the copolymerization procedure is discussed.

EXPERIMENTAL

Materials

Styrene (St) and ϵ-caprolactone (ϵ- CL) were dried over calcium hydride for 48 h and distilled under reduced pressure just before use. 2-Hydroxyethyl methacrylate (HEMA) was dried over molecular sieves 4 Å and distilled under reduced pressure (68 °C, 50pa) prior to use. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol twice. The RAFT agent, 2-phenylprop-2-yl dithiobenzoate(PPDTB), was prepared as described in the reference[16] in the yield of 28.6%, ^{1}H-NMR($CDCl_3$) d(ppm): 2.01 (s, 6H); 7.16–7.55 (m, 8H) and 7.85 (m, 2H). All other reagents were purified by common purification procedures.

Preparation of Parent Copolymers

An ampoule charged with AIBN (0.04 mmol 6.6 mg), PPDTB (0.12 mmol 32.7 mg), St (0.09 mol 9.374g), and HEMA (0.01 mol 1.302g) was vacuumed by three freeze-thaw-cycles at the temperature of liquid nitrogen, then sealed and placed in a constant temperature oil bath at 60 °C for a given time (see Table 1, series 1), then the ampoule was cooled half a hour in an ice bath and precipitated in cold dried methanol. The product was purified by dissolution/precipitation with THF/methanol, and then dried to constant weight under vacuum at 60 °C.

Synthesis of Graft Copolymers

A typical process was as follows: a dried ampoule containing the ϵ-caprolactone (6.01 mmol, 0.685g) and the copolymer 1b (0.0066 mmol, 0.1g) was bubbled with nitrogen for 1 h at room temperature. Then the proper catalyst ($[Sn(Oct)_2]/[OH] = 0.5$, [OH], calculated from the molecular weight of the copolymer poly(HEMA-*co*-St) and the contents of HEMA in the copolymer) was injected

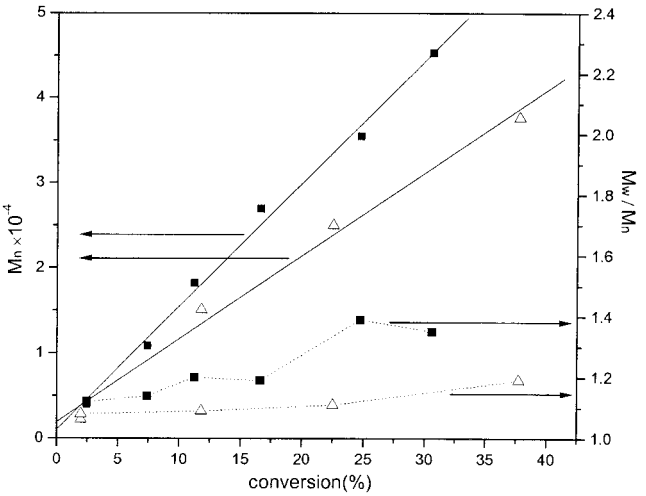

Figure 1. Dependence of M_n and M_w/M_n on the conversion of styrene and HEMA (△: 10% HEMA in feed; ■: 5% HEMA in feed).

under nitrogen, and the reaction was allowed to proceed for a given time at 130 °C. After cooling to room temperature, the products were dissolved in THF and precipitated in cold methanol. The copolymers were purified twice by dissolution/precipitation with THF/methanol. The procedure of solution graft copolymerization of ϵ-caprolactone was similar to the bulk except the reaction temperature was at 100 °C.

Measurements

The monomer conversion was measured gravimetrically. The molecular weight and the molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) (HP1100) using three Waters Styragel columns (pore size: 102 Å, 103 Å, and 104 Å in series) and a Waters 410 refractive-index detector, and THF as eluent with a flow rate of 1 mL min^{-1} at 35 °C, the monodistributed polystyrene was used as the calibration standard. ^{1}H-NMR measurement was carried out on a Bruker (500 MHz) spectrometer with tetramethylsilane as the internal standard, DMSO and $CDCl_3$ as the solvents.

RESULTS AND DISCUSSION

Synthesis and characterization of the parent copolymers [poly(HEMA-*co*-St)]

The copolymerization of HEMA and St was carried out by a RAFT process in which the PPDTB was used as chain transfer agent. Two copolymers was prepared by the variation of the HEMA mole fraction in feed ratio as portrayed in Table 1 to synthesize different branch density graft copolymers. The relationship of monomer conversion with molecular weight and molecular weight distribution is portrayed in Figure 1, in which the molecular weight increased with the conversion, and in all cases the molecular weight distribution of copolymer was less than 1.4. Therefore, in our system the copolymerization of HEMA and St in the presence of PPDTB was controllable.

Figure 2 illustrates the GPC traces of the samples 1a, 1b, 1c, and 1d with different polymerization time. It is worth noting that obvious bimodal peaks were detected for the samples of 1b, 1c, and 1d with high conversion, but not for 1a with low conversion. The number average molecular weight of the peak with short retention time for these samples was twice as much as the main peak with long time, and the weight fraction of the former is approximately 2%, 4%, and 7%, respectively. It means that the probability of coupling termination in copolymerization increased with the monomer conversion, so the molecular weight distribution was widened from 1.08 for sample 1a to 1.19 for 1d.

Figure 3 shows a typical NMR spectrum of a copolymer. The copolymer composition can be readily obtained by using following formula:

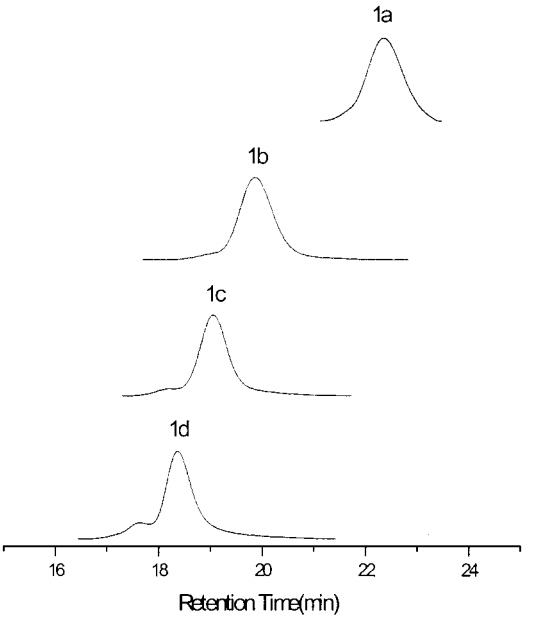

Figure 2. GPC traces of the copolymer P(HEMA-*co*-St) (reaction time for 1a: 5h, 1b: 15h, 1c: 25h, 1d: 50h).

$$F_H = \frac{A_T - \frac{3}{5}A_H}{A_H + (A_T - \frac{3}{5}A_H)} \qquad (1)$$

where F_H is the mole fraction of HEMA in copolymer; A_T and A_H represent the peak area sum of a, b, e, and f of the protons of the main chain and the peak areas of the aromatic protons, respectively.

F_H values of 0.241 for 1a and 0.151 for 2a in the different feed ratios were calculated, which was very similar to the theoretical values ($F_{Htheo1a} = 0.235$, $F_{Htheo2a} = 0.143$, respectively) calculated by the reported monomer reactivity ratios of St and HEMA ($r_H = 0.49$, $r_S = 0.27$) of conventional bulk radical polymerization.[17] So, the RAFT polymerization had little influence on the reactivity ratios in our system.

To determine the grafting efficiency, the number of hydroxyl groups (N_{OH}) per P(HEMA-*co*-St) backbone chain could be calculated by the following equation:

$$M_n = N_{OH} \bullet \left(M_H + \frac{(1 - F_H)}{F_H} M_S\right) \qquad (2)$$

where M_H and M_S are the mole masses of HEMA and styrene, and F_H is the mole fraction of HEMA units in the copolymers, respectively. The results are listed in Table 1.

Characterization of the graft copolymer P(HEMA-co- St)-g-PCL

The graft polymerization of ϵ-CL in our system was carried out by ring-opening of ϵ-CL initiated

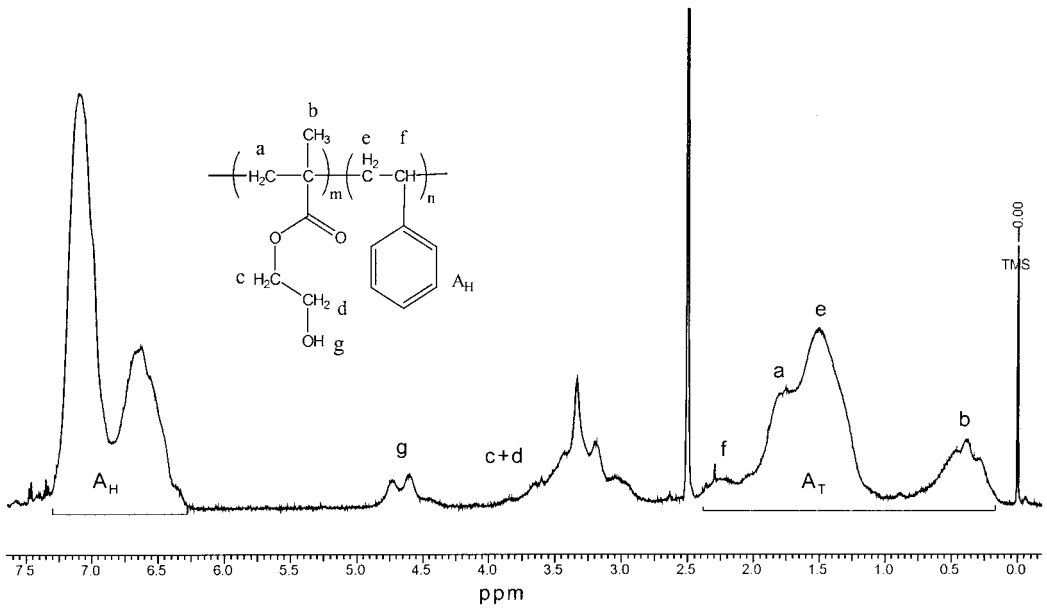

Figure 3. ^{1}HNMR spectrum of P(HEMA-*co*-St) (1b: Mn 1.51×10^4) with a mole fraction of HEMA (F_H) of 0.253 (solvent: DMSO).

Table 2. Bulk and Solution Ring-opening Polymerization of the ϵ-CL Initiated by Copolymer P(HEMA-co-St) ([$Sn(Oct)_2$]:[OH] = 1:2: Solution System: [OH] = 0.1 mol/L, Toluene as Solvent)

Graft copolymer	P(HEMA-co-St)	P(HEMA-co-St) (g)/ϵ-CL(g)	Time (h)	Conv (%)[a]	Mn[b]	Mw/Mn	Mn_g[c]	Mn_n[d]
1b1(bulk)	1b	0.1/0.685	24	0.97	105,500	1.22	2620	2861
1c1(bulk)	1c	0.1/0.344	24	0.96	108,800	1.39	1460	1413
1c2(bulk)	1c	0.1/0.458	24	0.96	141,100	1.34	2030	1870
2d1(bulk)	2d	0.1/0.445	24	0.98	152,400	1.34	3330	3602
1b2(solution)	1b	0.1/0.137	24	0.97	38,800	1.21	687	696
1b3(solution)	1b	0.1/0.274	24	0.98	58,700	1.21	1264	1117
1b4(solution)	1b	0.1/0.412	24	0.98	77,300	1.16	1803	1733
1c3(solution)	1c	0.1/0.229	24	0.98	80,600	1.18	970	923
2d2(solution)	2d	0.1/0.157	24	0.99	71,500	1.26	1182	1083

[a] ϵ-CL monomer conversion measured gravimetrically.
[b] Number average molecular weight measured by GPC using PS as standard.
[c] Number average molecular weight of each grafted PCL chain calculated using eq. (3).
[d] Number average molecular weight of the grafted PCL chain calculated from the ^1H NMR data.

by hydroxyl groups of the HEMA segment in copolymers; the contents of HEMA on the copolymers is rather low (around 25% for series 1 and 14% for series 2). The data of graft polymerization both in bulk and solution are listed in Table 2. As is well known, when the ring-opening polymerization of ϵ-CL was initiated by hydroxyl groups of the HEMA segment of copolymers, the end groups of grafted PCL chains should also be hydroxyl, so it was generally very difficult to directly determine how many hydroxyl groups of original copolymers took part in the initiation. Here the average molecular weight of each grafted PCL was calculated by the following equation first:

$$M_{ng} = \frac{M_{nCL}}{N_{OH}} \tag{3}$$

Here Mn_g is the number average molecular weight of each grafted PCL chain; Mn_{CL} is the total molecular weight of all the grafting PCL chains, which could be obtained by GPC; N_{OH} is the average hydroxyl number of poly(HEMA-*co*-St).

Then the number average molecular weight of each grafted PCL chain could also be obtained by NMR. Figure 4 shows the ^1H-NMR spectra of the graft copolymer 1b3.

Comparing the ^1H-NMR spectra of the parent copolymer 1b P(HEMA-*co*-St), a new signal at 3.64 ppm appeared, which was attributed to the methylene protons (k) adjacent to the hydroxyl end groups of the grafting PCL chains. By comparison of the integration of methylene protons (k) with the methylene protons (j) adjacent to oxygen (-OOC-) in the repeating unit of PCL, the number-average molecular weight of grafted PCL could also be calculated. If all hydroxyl groups of P(HEMA-*co*-St) took part in the initiation, the average molecular weight of PCL grafted chain obtained from eq. (3) should equal or be approximately equal to the value from the NMR. Table 2 lists these data and shows that the molecular weights of grafted PCL obtained by eq. (3) and NMR were rather close, which means in our system nearly all hydroxyl groups of P(HEMA-*co*-St) took part in the initiation, so the grafted efficiency was very high.

Effect of Polymerization Conditions on Grafting Copolymerization

It was found that in the same conditions the conversion of ϵ-CL monomer in the bulk was as high as that in the solution, but the molecular weight distribution of final graft copolymers was slightly wider in the bulk than that in the solution shown in Table 2. This may be attributed to the difficult diffusion of the propagating chains in bulk rather than in solution because of rapid enhancement of bulk viscosity with the conversion of ϵ-CL, more than in solution.

Figure 5 shows the GPC traces of the grafted copolymer P(HEMA-*co*-St)-g-PCL 1b2, 1b3, and 1b4 with different feed ratios and the original copolymer P(HEMA-*co*-St)1b. It was observed that in the same conditions, the molecular

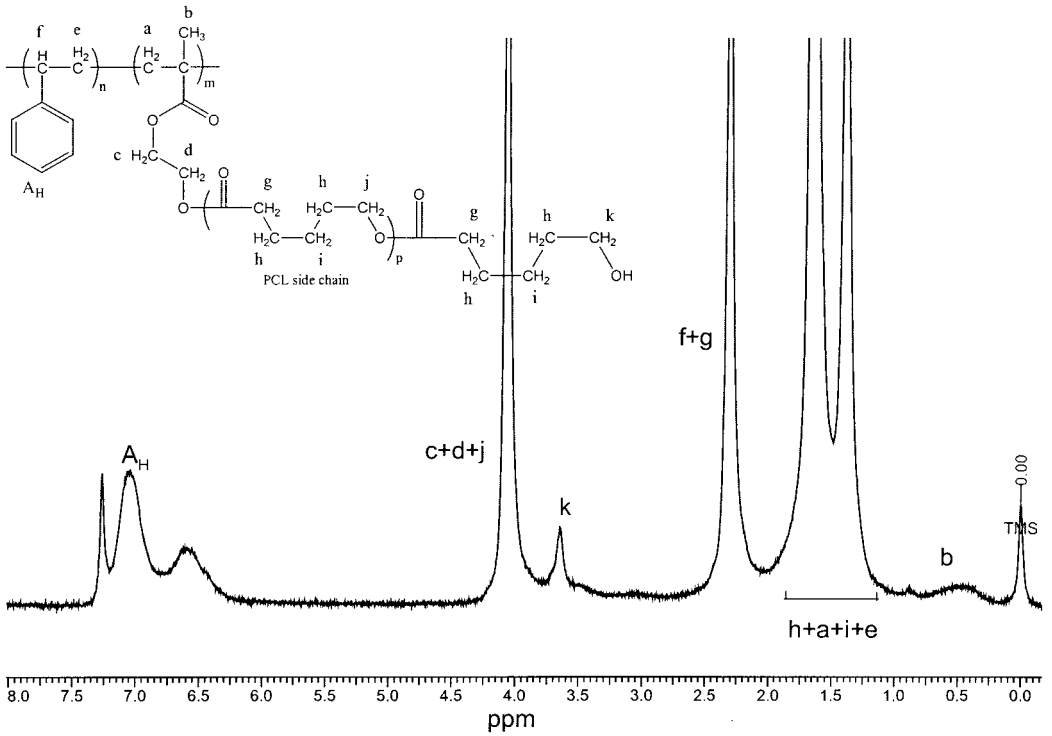

Figure 4. ^{1}HNMR spectrum of graft copolymer (1b3: Mn 5.87×10^4; Mn_g 1.26×10^3) (solvent: $CDCl_3$).

weight of the grafter increased with the contents of ϵ-CL in feed; it is characteristic of controlled polymerization; at the same time, no traces of homopolymer of ϵ-CL and remaining 1b could be detected. The molecular weight distributions of all graft copolymers are less than 1.21. Thus, it is clearly indicated that whether the graft copolymerization of ϵ-CL was performed in bulk or solution, all the parent copolymers took part in the initiation.

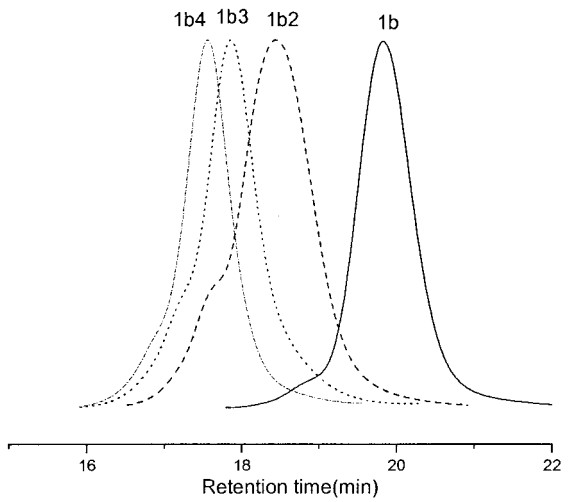

Figure 5. GPC traces of the P(HEMA-*co*-St) (1b: Mn 1.51×10^4) and the P(HEMA-*co*-St)-g-PCL. (feed ratio-[P(HEMA-*co*-St)(g)/ ϵ-CL (g)]of 1b2: 0.1/0.137, 1b3: 0.1/0.274, 1b4:0.1/0.412).

Controllability of Grafting Copolymerization of ϵ-CL

The kinetic investigation of the ROP of ϵ-CL initiated by the parent copolymer P(HEMA-*co*-St) was completed in the presence of catalyst $Sn(Oct)_2$. Figure 6 shows the nice linear relationship between the number average molecular weight of graft copolymer and the conversion of ϵ-CL, so the grafted copolymerization was under control.

CONCLUSION

A new graft copolymer poly(2-hydroxyethyl methacrylate-*co*-styrene)-graft-poly(ϵ-caprolactone) was successfully prepared by combination of reversible addition-fragmentation chain transfer polymerization (RAFT) with ring-opening poly-

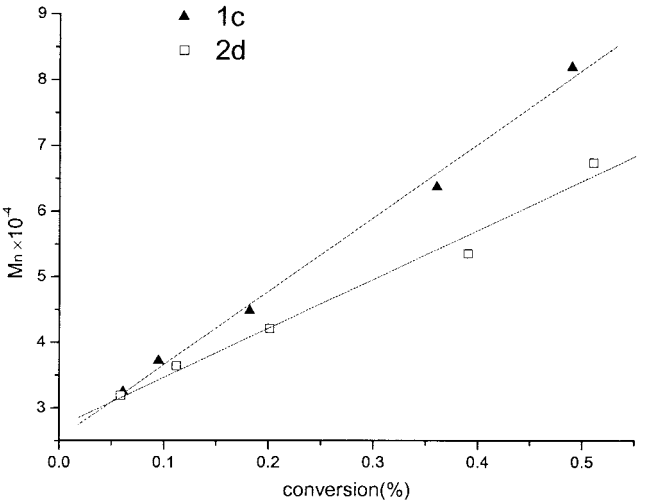

Figure 6. Dependence of M_n of graft copolymer P(HEMA-*co*-St)-g-PCL on the conversion of ϵ-CL (experimental condition: $[Sn(Oct)_2]$:[OH] = 1:2, [OH] = 0.1mol/L, toluene as solvent).

merization (ROP). The copolymerization of St and HEMA and then grafted polymerization of ϵ-CL were controllable. It was confirmed that in our system all hydroxyl groups of P(HEMA-*co*-St) took part in the initiation, and the grafted efficiency of ϵ-CL was very high.

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