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Template Polymerization of Multi-Vinyl Monomer with Poly(2-hydroxyethyl methacrylate) Backbone

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Summary: In order to investigate the propagation of polymerization in the template with linear polymer chain, ATRP of methacryloyl type multi-vinyl monomers of pol(2-hydroxyethyl methacrylate) backbone with and without styryl groups on the chain ends was carried out. Change of hydrodynamic radii of products and conversion of vinyl group were analyzed by GPC and FT-IR, respectively.When the multi-vinyl monomer concentration was less than 0.3 wt%, gelation was completely hindered. The kinetic plots of polymerization of multi-vinyl monomers with and without styryl group on the chain ends agreed well.

Keywords: atom transfer radical polymerization; multi-vinyl monomer; poly(2-hydroxyethyl methacrylate); Template polymerization

Introduction

Fine controls of molecular weight and molecular weight distribution by convenient polymerization techniques are very important for macromolecular synthesis. Based on this purpose, controlled/living radical polymerization has been well investigated.[1–9] Well-defined macromolecules with not only linear structure but also more complicated structures, such as brush,[10–12] branched,[13–15] etc. were synthesized. Template polymerization is another simple approach to control the molecular weight and molecular weight distribution.[16–24]

Many types of multi-vinyl monomer in which vinyl groups are combined with the template chain through covalent bonds have been synthesized and polymerized.[16,22–24] When the polymerization proceeds along template polymer, molecular weight, molecular weight distribution and architecture of product depend on those of the template molecule. For example, linear and cyclic poly(methacrylic acid) [PMAA] oligomers with degree of polymerization (DP = 6, 7 and 14) were finely synthesized by using cyclodextrins as templates.[25–27] Ladder-like macromolecule was expected by template polymerization with long chain templates. The template polymerization of poly(2-methacryloyloxyethyl methacrylate), multi-vinyl monomer [MVM] with poly(2-hydroxyethyl methacrylate) [PHEMA] backbone, was carried out by conventional radical polymerization[24,28,29] and atom transfer radical polymerization [ATRP][30] (Scheme 1). The solution viscosity of product showed strong shear dependence, the glass transition temperature, Tg, of products was higher than 200 °C, indicating the products were ladder-like. It was possible to synthesize thermally resistible polymer, which was soluble in good solvent, by radical polymerization. This also suggests the possibility of synthesis of thermally resistible polymer without aromatic groups. Kinetic analysis indicated that the vinyl groups were highly concentrated around activated radical as well as bulk state, the apparent polymerization rate of template polymerization in dilute solution was very close to that in bulk.[30]

However, there was no evidence that the polymerization proceeded along backbone. When the template is a linear polymer chain with soft sequence, the backbone

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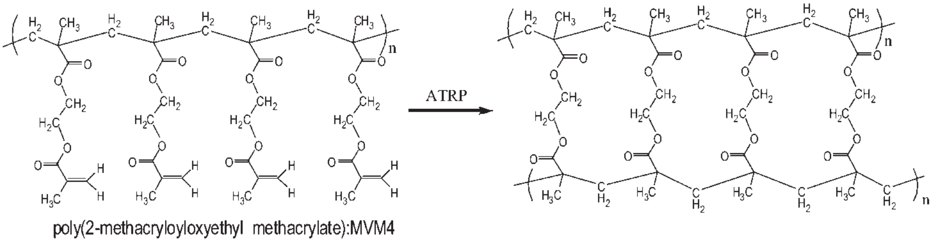


Scheme 1.
Template polymerization of multi-vinyl monomer with poly(2-hydroxyethyl methacrylate) backbone.

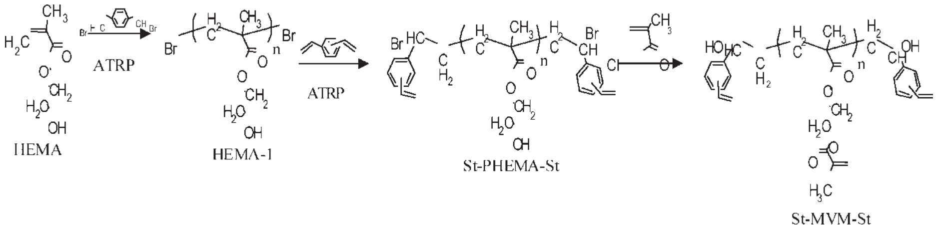
forms globule. It may be possible to propagate polymerization at random in globule. The purpose of this study is to clarify whether the propagation proceeds along the backbone or not. Authors have been synthesized α,ω-styryl terminated PHEMA [St-PHEMA-St] by ATRP with divinyl benzene [DVB] by using the difference of cleavage temperature of Br-methacrylate and Br-styryl bonds.[31] Since the cleavage temperature of Br-styryl bond, >90 °C, is much higher than that of Br-methacrylate bond by copper-mediated ATRP, polymerization of methacrylate was terminated with DVB when the polymerization was carried out at lower than 30 °C.

α,ω-Styryl terminated poly(2-methacryloyloxyethyl methacrylate) [St-MVM-St] will be obtained by esterification of St-PHEMA-St with methacryloyl chloride. The synthetic scheme of St-MVM-St is shown in Scheme 2. If the polymerization proceeds along the backbone, the kinetic plots of MVM and St-MVM-St containing styryl groups will be similar. If the polymerization proceeds at random in the globule, the polymerization of St-MVM-St will terminate earlier than that of MVM. In this study, St-MVM-St was synthesized from the same precursor PHEMA of MVM, the kinetic behavior of St-MVM-St was compared with the previous results.

Experimental Part

Materials

HEMA (95%) and DVB (m- and p- mixture, ca 55% in a mixture of ethylvinyl benzene and diethylbenzene, 50%) were purified by distillation under vacuum. 1,4-Dioxane (99 %), 2,2′-dipyridyl (Bpy, 99%), methanol (99.5%), hydroquinone (99.0%), tetrahydrofuran (THF, 99%), potassium hydroxide (85.5%), sodium sulfate (99.0%), dimethyl sulfoxide (DMSO, 98.0%), lithium hydroxide (95.0 %), acetone (95%) and n-hexane (98%) were used as received. α,α'-Dibromo-*p*-xylene (DBX: Aldrich, 97%), CuBr (99.9%), methacryloyl chloride (80%), chloroform-d_1 with 1% TMS (d = 99.8 %), methanol-d_4 and dimethyl sulfroxide-d_6 (99.9%) were used as received. Tris(2-dimethylaminoethyl)amine [Me_6TREN, 99.5%] was prepared based on the literature.[32] Toluene (99%) and pyridine



Scheme 2.
Synthesis of multi-vinyl monomer, St-MVM-St.

Table 1.
Esterification of poly(2-hydroxyethyl methacrylate)s.

Code	PHEMA	Polymer weight (g)	Solvent[a] (mL)	[COCl]/[OH] [b] (mol/mol)	Temp. (°C)	Time (h)	Estn.[c] (mol%)
MVM4[30]	PHEMA-1	0.650	10.0	1.2	−8	2.0	90.0
St-MVM-St	St-PHEMA-St	0.650	10.0	1.2	−8	2.0	86.0

Precursor polymers. PHEMA-1: $\overline{Mn} = 2.36 \times 10^4$ and $\overline{Mw}/\overline{Mn} = 1.52$, St-PHEMA-St: $\overline{Mn} = 2.36 \times 10^4$ and $\overline{Mw}/\overline{Mn} = 1.52$.[31];

[a] Solvent: THF/water mixture with 40 vol% of water;

[b] Molar ratio of methacryloyl chloride to a 2-hydroxyethyl methacrylate unit;

[c] Degree of esterification determined by ^{1}H-NMR resonances of 4.11–4.26 and 5.56–6.08 ppm.

(99.5%) were dried over calcium hydride (95%) for overnight and distilled under vacuum, immediately prior to use.

α,ω-Br Terminated poly(2-hydroxyethyl Methacrylate) [PHEMA1]

PHMA1 was previously synthesized by copper-mediated ATRP with DBX/Bpy/CuBr and analyzed elsewhere.[30] Conversion of HEMA was about 50 wt%. Number-average molecular weight [$\overline{Mn} = 2.36 \times 10^4$] and molecular weight distribution [$\overline{Mw}/\overline{Mn} = 1.52$] were measured by GPC.

α,ω-Styryl Terminated poly(2-Hydroxyethyl Methacrylate) [St-PHEMA-St]

St-PHEMA-St was previously prepared with PHEMA1 and DVB at 20 °C for 420min, and characterized elsewhere.[31] $\overline{Mn} = 2.13 \times 10^4$ and $\overline{Mw}/\overline{Mn} = 1.52$ were measured by GPC. The number of styryl group per PHEMA chain estimated by ^{1}H-NMR was 1.9.

Multi-vinyl Monomer MVM4

MVM4 was previously synthesized from PHEMA1 by the Shotten-Baumann method and analyzed elsewhere.[30]

α,ω-Styryl Terminate Multi-Vinyl Monomer, St-MVM-St

St-MVM-St, was synthesized by the Shotten-Baumann method[24] as well as MVM4.[30] Conditions are listed in Table 1. The conversion of esterification was determined by ^{1}H-NMR measurements (JEOL, GLX-400, 400 MHz) with chloroform-d_1 at room temperature by comparison with the resonances of –COO –CH_2–CH_2 (4.11–4.26) and CH_2=C (5.56– 6.08 ppm).

ATRP of Multi-Vinyl Monomer

The polymerization was carried out with and without a initiator by ATRP at in a range from 25 to 40 °C for in a range from 2 to 48 h under vacuum. The ATRP conditions are listed in Table 2. The product was white powder. The reaction between template monomer molecules was determined by GPC. The conversion of reacted vinyl

Table 2.
Atom transfer radical polymerization of multi-vinyl monomers in 1,4-dioxane/water (= 9/1 v/v) mixture at 25 °C.

Code	MVM type	MVM conc. (wt%)	[Initiator]/[MVM] (mol/mol) [a]	time (h)	V % [b] (mol%)	Remarks
PMVM4-3[30]	MVM4	0.30	1.0	6.0	77.8	
PMVM4-7	MVM4	0.50	1.0	2.0	58.9	gel
P(St-MVM-St)-1	St-MVM-St	0.30	1.0	4.0	85.3	
P(St-MVM-St)-2	St-MVM-St	0.50	1.0	2.0	62.0	gel

[DBX] : [CuBr] : [Me_6TREN] = 1 : 4 : 8;

[a] Molar ratio of DBX to multi-vinyl monomer;

[b] Conversion of vinyl groups determined by FT-IR spectroscopy with the absorption at 1730 and 1636 cm^{-1}.

group was determined by FT-IR (Jasco, FT/IR-410) by KBr method by using the absorption of carboxyl and vinyl groups observed at 1730 and 1636 cm^{-1}, respectively.

Hydrolysis of Polymerized Product of St-MVM-St

P(St-MVM-St)-1 (0.10 g) and lithium hydroxide (10 mmol) was dissolved in a mixture of DMSO (10 mL) and water (3 mL). The solution was stirred at 40 °C for 180 h, and then poured into 0.5 N-HNO_3 aq. (30 mL). The precipitate, PMAA, was collected by centrifugation (400 rpm, 10 min), washed with water (20 mL) for three times and dried under vacuum. The degree of hydrolysis was determined by ^{1}H-NMR spectroscopy (JEOL, GLX-400, 400 MHz) with deuterated methanol. ^{1}H-NMR (methanol-d_4): δ [ppm] = 0.8–1.2 (3.00H, CH_3), 1.9–2.0 (2.29 H, CH_2), 3.6 (0.53 H, CH_2), 3.9 (0.97 H, CH_2), 7.05 (0.19 H, phenyl-H).

Measurement of GPC

For specimen preparation, 0.1 wt% of THF solutions were prepared. In case of PHEMA-1, acetic anhydride was added to the solution to cap the hydroxyl groups. $\overline{Mn}$ and $\overline{Mw}/\overline{Mn}$ were measured at 35 °C with a gel permeation chromatography (HITACHI, L-7100 series) doubly detected with a refractive index detector (HITACHI, L-2490) and a UV spectrometer (TOSOH, UV-8011) at 254 nm. Column: TSK-GEL G5000HHR, an eluent: THF, flow rate: THF, 0.6 mL/min. The calibration curves were prepared using poly(methyl methacrylate) with various molecular weights.

Results and Discussion

Synthesis of St-MVM-St

St-MVM-St, was synthesized by the Shotten-Bauman method as well as the previous work.[30] The terminal Br groups at the backbone, which were the initiators of ATRP, were readily hydrolyzed with KOH solution by Shotten-Baumann esterification.[30] The initiation from backbone during the template polymerization can be neglected. Thus, Shotten-Bauman method is suitable for synthesis of multi-vinyl monomer. Conditions and results are listed in Table 1. Figure 1 shows ^{1}H-NMR spectra of St-MVM-St. The resonances owing to vinyl group were observed at 5.56 and 6.08 ppm. The resonance at 7.30 ppm originated from styryl group at chain ends and benzene at the center of PHEMA backbone. The conversion of esterification of St-MVM-St calcurated from the resonance areas was 86 mol% and was close enough to that of MVM4.

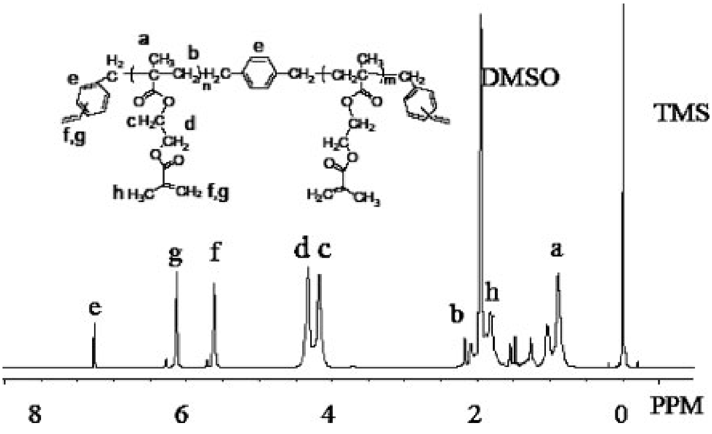


Figure 1.
^{1}H-NMR resonance of St-MVM-St.

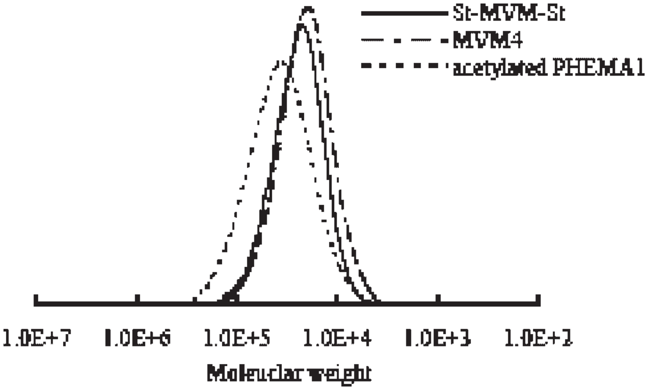


Figure 2.
GPC profiles of St-MVM-St, MVM4 and acetylated PHEMA1.

To investigate the side reaction, such as gelation, during the esterification, GPC measurements were carried out. Figure 2 shows the GPC profiles of St-MVM-St, MVM4 and acetylated PHEMA-1. Hydroxyl groups of PHEMA-1 were capped by acetylation. The peaks agreed well, $\overline{Mn}$ and $\overline{Mw}/\overline{Mn}$ of St-MVM-St were in fair agreement with those of MVM4.

This also indicated that the side reaction was completely prohibited during esterification. In conclusion, St-MVM-St, which was a preferable multi-vinyl monomer for kinetic analysis of template polymerization, was obtained.

Atom Transfer Radical Polymerization

Template polymerization of St-MVM-St was carried out under similar polymerization conditions to MVM4 (Table 2). For strict control of radical concentration in solution, copper-mediated ATRP with DBX was chosen. Since DBX is a bifunctional initiator, the initiation place in the chain can be neglected. Because polymerization proceeds toward chain ends from the bifunctional initiator. PMVM4-7 was newly polymerized with MVM4. When the monomer concentration was 0.5 wt%, the solutions gelled within 2.0 h (PMVM4-7 and P(St-MVM-St)-2).

In contrast, when the monomer concentration was 0.3 wt%, the solutions did not gel. The conversions of vinyl group were 77.8 and 85.3 mol% for PMVM4-3 and P(St-MVM-St)-1, respectively. Taking into account the conversions of esterification of St-MVM-St and MVM4 (90.0 and 86.0 mol%, respectively), the degrees of cross-piece of ladder-like stucture were 70.0 and 73.4 mol% for PMVM4-3 and P(St-MVM-St)-1, respectively. Thus, the chemical structures of PMVM4-3 and P(St-MVM-St)-1 are very similar.

Figure 3 shows GPC profiles of St-MVM-St and P(St-MVM-St)-1. The peak positions and peak widths of these profiles completely agreed. Thus, polymerization was completely limited in the St-MVM-St molecules as well as the case of MVM4.[30] If the polymerization proceeds at random in globule of multi-vinyl monomer, the

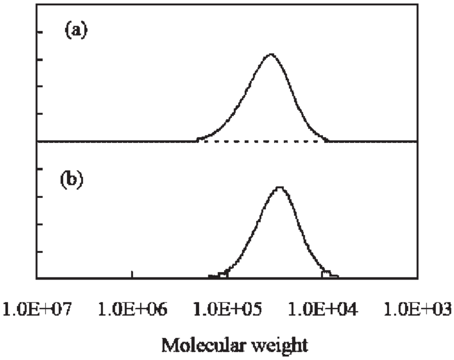


Figure 3.
GPC profiles of St-MVM-St (a), and polymerized product, P(St-MVM-St)-1 (b).

conversion of vinyl group and polymerization rate of P(St-MVM-St)1 will be lower than those of PMVM4-3. Because the possibility of termination of polymerization be reaction with styryl group will large from early stage of polymerization. The similar conversions of vinyl group of P(St-MVM-St)-1 and PMVM4-3 suggest that the polymerization of styryl group did not occur until the late stage of polymerization. Thus, the kinetics of P(St-MVM-St)-1 was analyzed.

Figure 4 shows kinetic plots of P(St-MVM-St)-1 and PMVM4-3 previously reported elsewhere. Again, the random propagation in globule molecule reduces the polymerization rate of P(St-MVM-St)-1 from that of PMVM4-3. The kinetic plots of P(St-MVM-St-)-1 were very similar to those of PMVM4-3. In case of P(St-MVM-St)-1, the induction time of polymerization until 0.2 h was observed. In range from 0.25 to 1.0 h, the first-order kinetic plots showed good linearlity. Over 1.5 h, the conversion was saturated, indicating that the polymerization was completed. Thus, ATRP of St-MVM-St proceeded in a living manner, as well as MVM4. The slopes of P(St-MVM-St)-1 from 0.25 to 1.0 and PMVM4-3 from 0.25 to 1.5 h, apparent polymerization constants, k_{app} ($=k[M]$), were 4.7×10^{-5} and 5.0×10^{-5} s^{-1}, respectively. Here k is the polymerization constant and [M] is the concentration of vinyl group around radical. The similar k_{app} values and kinetic plots of P(St-MVM-St)-1 and PMVM4-3 through template polymerization indicates that the reaction with styryl group did not occur until the late stage of polymerization. In conclusion, the polymerization proceeded along the backbone of template molecule.

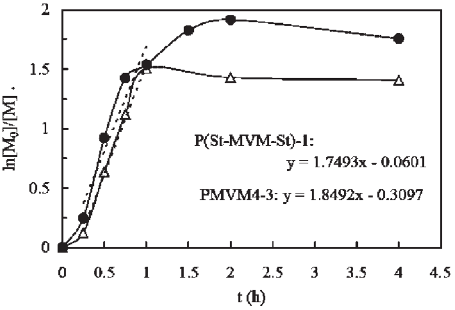


Figure 4.
Kinetic plots of P(St-MVM-St)-1 (circle) and PMVM4-3[30] (triangle).

As reported previously, the vinyl groups of MVM were highly concentration in the template molecules in the template polymerization. The k_{app} value of PMVM4-3 showed fair agreement with those of methyl methacrylate on copper-mediated ATRP with Br groups in bulk at 80 °C[33] and in ethylene carbonate with 50 wt% of methyl methacrylate at 60 °C.[34] The vinyl groups of St-MVM-St were also concentration in the template molecule. The polymerization of P(St-MVM-St)-1 terminated in relatively wide range from 1.0 to 1.5 h, the polymerization of PMVM4-3 terminated at 1.5 h. It would be due to the termination by styryl groups near the chain ends at late stage of polymerization.

Hydrolysis of Polymerized Product of St-MVM-St

Next, P(St-MVM-St)-1 was hydrolyzed and analyzed by ^{1}H-NMR. If all styrl groups are reacted in the molecule and the product is completely hydrolyzed, cyclic poly(methacrylic acid) will be obtained. Figure 5 shows ^{1}H-NMR of the hydrolyzed product of P(St-MVM-St)-1. No resonance owing to vinyl group was observed in a range from 5.5 to 6.5 ppm. Vinyl groups of styryl group cannot be removed by hydrolysis because styryl groups were introduced into St-MVM-St by ATRP. Thus, styryl groups at the chain ends were completely reacted by template polymerization. The resonances at 3.6 and 3.9 ppm (c and d) originating from methylene groups of HEMA unit and crosspiece of ladder were observed, the hydrolysis was incompleted. It would be due to the formation of ladder-like structure. Taking into account the resonance area of methyl groups of methacrylate and methacrylic acid units (from 0.6 to 1.0 ppm), the calculated molar contents of methacrylic acid unit, HEMA unit and methacrylate group were 0.507, 0.267 and 0.226, respectively. The degree of decomposed

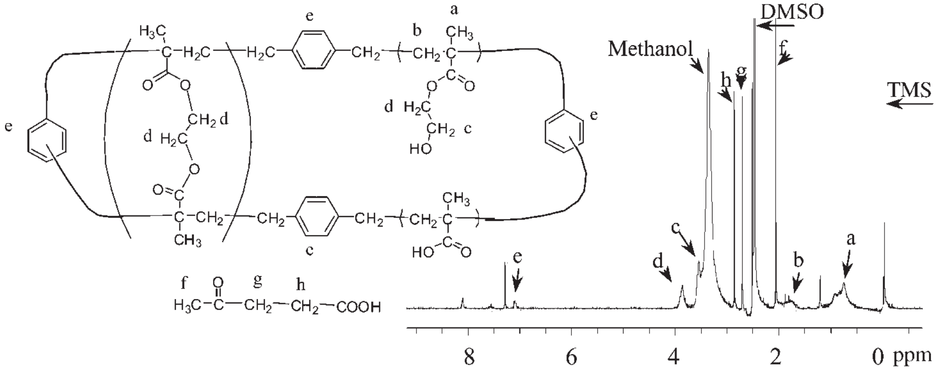


Figure 5.
^{1}H-NMR spectra of hydrolyzed product of P(St-MVM-St)-1.

crosspiece of ladder was 0.774. Again, complete hydrolysis of P(St-MVM-St)-1 will provide cyclic poly(methacrylic acid). Thus, the template polymerization of multi-vinyl monomer is the useful approach to control the architecture of macromolecules.

Conclusion

Template polymerization of St-MVM-St was complared with the case of MVM4. When the monomer concentration was 0.3 wt%, template polymerization was completely limited in the molecules. The k_{app} values of multi-vinyl monomers with and without terminal styryl groups were very close. Template polymerization proceeded toward the chain ends along the backbone of multi-vinyl monomer. From the ^{1}H-NMR measurements of hydrolyzed product of P(St-MVM-St)-1, the complete reaction of styryl groups was found. However the hydrolysis was incompleted because of its ladder-like structure. suggested the synthesis of macrocyclic macromolecule.

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