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Synthesis and characterization of cross-type vinylurethane macromonomer (C-VUM) and their application in the dispersion polymerization of styrene

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Abstract

The cross-type vinylurethane macromonomers (C-VUMs) were successfully synthesized using trimethylolpropane (TMP) as a cross-agent, and applied to the dispersion polymerization of styrene in ethanol. The existence and the structural identification of the reactants and the products were verified using the FT-IR and ^{1}H NMR spectra. The molecular weight of C-VUM increased, but the polydispersity index of C-VUM decreased with that of PEG. Structural verification of PS spheres synthesized from C-VUMs is carried out using ^{1}H NMR. However, the molecular weight of polyethylene glycol (PEG) in C-VUM does not affect the particle size of the PS particles, whereas enhanced the uniformity of the PS particles. Thus, C-VUMs act not only as reactive stabilizers, but also as grafting agents

Keywords: Cross-vinylurethane macromonomer; Stabilizer; Grafting agent

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1. Introduction

The preparation of macromolecules with controlled structures has received extensive attention due to their interesting chemical and physical properties [1–3]. Various complicated structures including block, graft, and star copolymers fall into this category. Telechelic macromolecular monomers, so-called telechelic macromonomers, provide a facile route to design sophisticated polymer molecular structures [4,5]. Macromonomers are usually linear polymeric species having one or more reactive end groups which can participate in polymerization reaction [6,7]. Such end groups can be built up with acrylic, vinylic, allylic, propenylic, or isopropenylic functionality [8,9].

In the synthesis of polymer colloids, various stabilizing agents are essentially used, e.g. surfactants in emulsion, dispersants in suspension and steric stabilizers in dispersion polymerization. Steric stabilizers in dispersion polymerization serve as a precursor in particle nucleation and give stability to the formed particles in organic media [10]. Although such stabilizing agents play a crucial role in the production and applications of the colloid dispersions, they also impart various adverse effects including foaming [11], destabilization of latex by migration in paints or films [12,13], and alteration of hardness of products [14].

Macromonomers have been widely and successfully used as building blocks for the synthesis of various branched polymer architectures. Thus, the macromonomer is an important intermediary for constructing super-macromolecular structures. Macromonomers can readily be copolymerized with conventional monomers to afford graft copolymers with well-defined structures. The structure of the polymer chain of the macromonomer affects the properties of the graft copolymer while the end group controls the reactivity in polymerization. Many functional groups having a chemical reactivity for polymerizations have been studied in detail and include conventional free radical [15,16], group transfer [17,18], anionic [19], cationic [20], controlled free radical [21,22], ring opening metathesis [23,24] and metallocene [25,26] polymerizations.

In our previous work the linear-type vinylurethane macromonomer (L-VUM) by the reaction of isocyanate-terminated prepolymer with methacrylamide was prepared and applied to the dispersion polymerization of styrene [27] and methylmethacrylate [28]. The L-VUM was successfully employed as a steric stabilizer and a possibility of the cross-linking agent in the dispersion polymerization of styrene. The urethane and methyl

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Table 1
Abbreviation of the samples and the chemical constituents of C-VUM

Sample name	Reactants			
	Monomer	Polyol	Isocyanate	Cross-agent
C-VUM(1)	MAAm	PEG-400	HDI	TMP
C-VUM(2)	MAAm	PEG-1000	HDI	TMP
C-VUM(3)	MAAm	PEG-2000	HDI	TMP
C-VUM(4)	MAAm	PEG-4000	HDI	TMP
C-VUM(5)	MAAm	PEG-8000	HDI	TMP

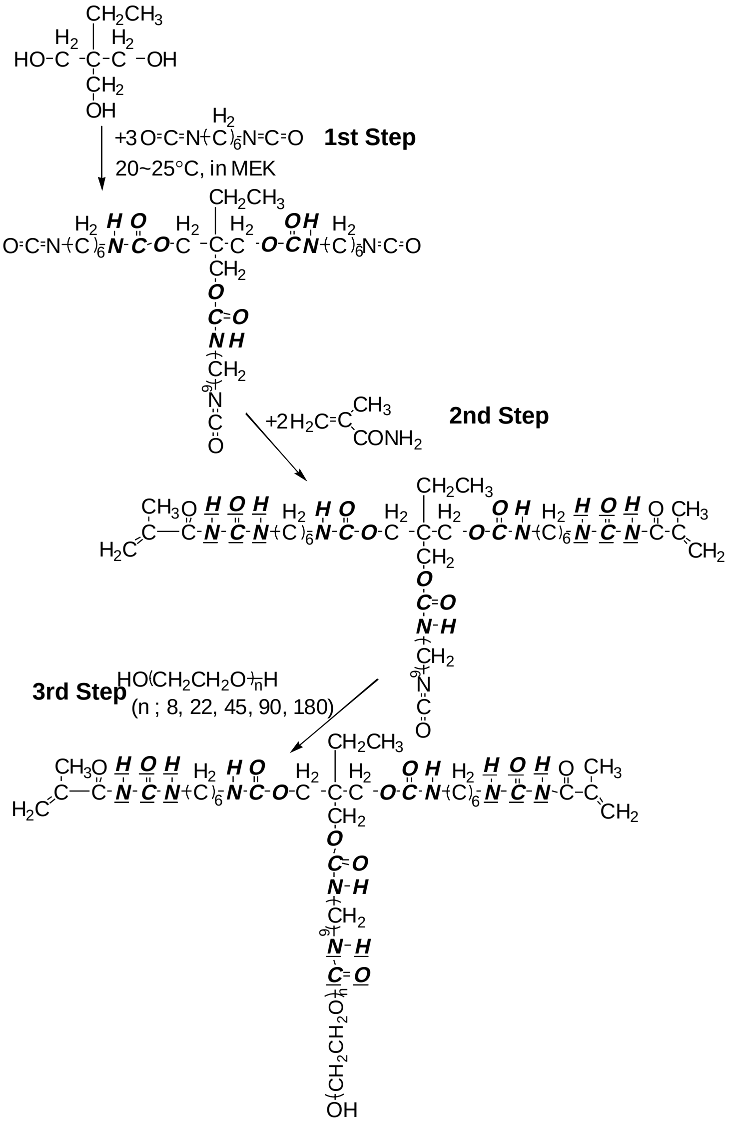
groups in L-VUM are found in the spectrum of PS microspheres and the reactive double bonds of L-VUM were disappeared after polymerization with styrene. Finally, the molecular weight of L-VUM due to various molecular weight of PEG affects to the particle size of PS and PMMA [29].

In this article, the extension to synthesize the cross-type vinylurethane macromonomer (C-VUM) and the characterization of the properties between the L-type and cross-type macromonomers and their applications in the dispersion polymerization of styrene were carried out. This is the first report to prepare the cross-type macromonomer and apply in the dispersion polymerization of styrene.

2. Experimental

2.1. Synthesis of cross-type vinylurethane macromonomers

The C-VUM was synthesized by reacting a trimethylolpropane (TMP) with a diisocyanate (hexamethylene diisocyanate), which were supplied by Aldrich Co. (USA) and used as received. The employed monomeric unit was methacrylamide (MAAm; Aldrich Co., USA). Poly(ethylene glycol) having number-average molecular weights 400 (PEG 400), 1000 (PEG 1000), 2000 (PEG 2000), 4000 (PEG 4000), and 8000 g/mol (PEG 8000) were obtained from Aldrich Co., USA and used as received. Highly pure methyl ethyl ketone (MEK; Samchun, Korea) and acetone (Samchun, Korea) were used as the reaction medium for the isocyanate-terminated



Scheme 1. Synthesis of cross-vinylurethane macromonomer [C-VUM(1) to C-VUM(5)].

Table 2
Typical formula used for the synthesis of dispersion polymerization of styrene (St) (CPS-1–CPS-5)

	Monomer (St) (g)	Stabilizer		Initiator (AIBN) (g)	Solvent (EtOH) (g)
CPS-1	2.0	C-VUM(1)	0.2 g	0.02	20
CPS-2	2.0	C-VUM(2)	0.2 g	0.02	20
CPS-3	2.0	C-VUM(3)	0.2 g	0.02	20
CPS-4	2.0	C-VUM(4)	0.2 g	0.02	20
CPS-5	2.0	C-VUM(5)	0.2 g	0.02	20

preurethane and C-VUM. The abbreviation of the samples and chemical constituents of the C-VUM is shown in detail in Table 1.

The synthesis of the C-VUM was carried out under nitrogen atmosphere in a 500 mL jacketed glass reactor. Scheme 1 shows the synthetic procedure of the C-VUMs from C-VUM(1) to C-VUM(5) through a three-step addition reaction in detail. At first, trimethylolpropane (TMP; 0.00625 mol) in methyl ethyl ketone (MEK; 200 g) was placed in a four-necked reactor with a mechanical stirrer, a reflux condenser, a dropping funnel, and an inlet system for nitrogen gas and heated in an oil bath. When the temperature reached to 50 °C, diisocyanate (HDI; 0.01875 mol) was added by drop-wise with stirring and the reaction mixtures were refluxed for 20 h. The degree of reaction was verified with a hydroxyl peak (nearby 3480 cm^{-1}) that disappears as a result of the reaction with diisocyanate using FT-IR spectra of the intermediate. In the second step, the monomeric unit (MAAm; 0.0125 mol) solution (10 wt%) dissolved in acetone was introduced to the reaction medium by drop-wise addition at room temperature under nitrogen atmosphere. Low temperature was carefully maintained at this stage in order to prevent the side reaction of the monomeric unit. In the last step, 0.00625 mol of each polyethylene glycol (PEG 400, PEG 1000, PEG 2000, PEG 4000, and PEG 8000) solution (25 wt%) dissolved in acetone was added into the reactor and reacted for an additional 4 h. The degree of the reaction was verified with an isocyanate group (nearby 2267 cm^{-1}) that disappears as a result of reaction with amine group using FT-IR spectra of the intermediate product.

2.2. Dispersion polymerization

Styrene monomer (Aldrich, USA) was purified to remove residual inhibitor prior to polymerization using an inhibitor-removal column (Aldrich, USA) and stored at −5 °C before use. The 2,2-azobisisobutyronitrile (AIBN; Junsei) was used as an initiator and absolute ethanol (99%; Samchun, Korea) was used as a medium for the dispersion polymerization. The polymerization recipe is shown in detail in Table 2.

The dispersion polymerization of styrene in the presence of C-VUM was carried out in a 50 mL vial with magnetic stirring under nitrogen atmosphere at 70 °C. 20 g of ethanol was first poured in the vial, and 10 wt% of styrene monomer (St; 2.0 g) relative to the medium was charged. The amount of AIBN (0.02 g) was fixed at 0.1 wt% relative to the medium. The concentration of each macromonomer was fixed at 1.0 wt% (0.2 g) relative to the medium.

2.3. Analysis

In order to confirm the structure of the reactants (isocyanate-terminated polyurethane and monomeric unit) and the products (macromonomer and PS particle), Fourier transform infrared (FT-IR) spectroscopy (Bruker 48 series) was employed. The data was obtained at 4 cm^{-1} resolution

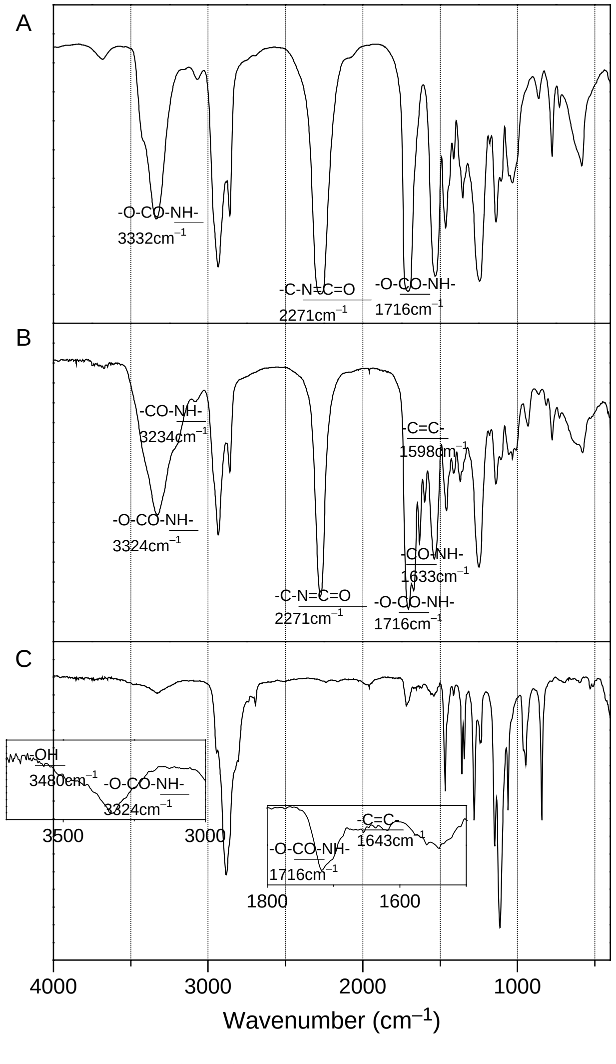


Fig. 1. FT-IR spectra of (A) first step, (B) second step, and (C) third step of C-VUM(5).

and 16 scans were accumulated in 20 s for each specimen. Varian 400 MHz ^{1}H NMR using $CDCl_3$ containing TMS (tetramethylsilane) as the solvent was also utilized to determine the structure of the isocyanate-terminated polyurethane, C-VUM, and the synthesized polystyrene. The molecular weight and polydispersity index (PDI) were measured using Waters gel permeation chromatography (GPC) equipped with 510 differential refractometer and Viscotek T50 differential viscometer. 10^5, 10^3, and 10^2 Å μ-Styragel packed high-resolution columns were employed. A universal calibration curve was obtained based on ten PS standard samples (Polymer Laboratories, UK) with molecular weights ranging 7,500,000 ∼580 g/mol. In order to prepare the GPC sample, an aliquot of the sample taken from the reaction vessel was washed with excess methanol and centrifuged at 13,000 rpm, repeatedly. The final obtained PS dissolved in THF as the mobile phase was injected at a flow rate of 1.0 ml/min. Scanning electron microscopy (SEM; Hitachi S-4300) was used to study the morphology of the PS particles. The number-average particle diameter (D_n) was obtained using Scion Image Analyzer Software by counting the individual 100 particles from SEM microphotographs and the particle size was determined by using a particle size analyzer (Beckman Counter® LS 13 320, USA). The monomer conversion to a polymer was determined gravimetrically after precipitating the polymerized resultant in methanol and followed by a centrifugation.

The glass transition temperature of the sample was measured using the Perkin–Elmer DSC-7 (Differential Scanning Calorimeter), USA. The samples were heated at a heating rate of 20 °C/min under nitrogen atmosphere, quench cooled at a maximum cooling rate, then reheated at the same heating rate used in the first scan. The glass transition temperature (T_g) was collected at the midpoint of the transition region in the second scan.

3. Results and discussion

3.1. Structural verification

The structural verification is carried out using FT-IR and ^{1}H NMR. The FT-IR spectra of the intermediates, the first step and second step in Scheme 1, and the C-VUM (5) of C-VUM in the third step are drawn in Fig. 1, respectively. In Fig. 1(A), the peaks observed at 3332 and 1716 cm^{-1} are characteristic peaks of the N–H and C=O stretching from the urethane group, respectively. The strong peak observed at 2271 cm^{-1} is a characteristic peak of the isocyanate group (–N=C=O) from the first step intermediate (tri-isocyanate) in Scheme 1. In Fig. 1(B), the peaks observed at 3234 and 1633 cm^{-1} are the characteristic peaks of the N–H and C=O stretching from the urea group, respectively. In addition, the peaks of the isocyanate group (–N=C=O) from the second step intermediate (divinyl-isocyanate) in Scheme 1, N–H, and C=O stretching from the urethane group are observed at 2271, 3324, and 1716 cm^{-1}, respectively, in Fig. 1(B). The C=C double bond of the monomeric unit (MAAm), which is used to endow the vinyl group to the second step in Scheme 1, occurs very weakly at 1598 cm^{-1}. The FT-IR spectrum of C-VUM(5) is represented in Fig. 1(C) and the peaks of the N–H and C=O stretching from the urethane group are observed at 3332 and 1716 cm^{-1}, respectively, as seen in Fig. 1(A) and (B). The characteristic peaks of C=O stretching and C=C double bond are also depicted at 1716 and 1643 cm^{-1}, respectively. In addition, the characteristic peak of the isocyanate group (–N=C=O) associated with the first and second step (Fig. 1(A) and (B)) at 2271 cm^{-1} is disappeared in Fig. 1(C) and this

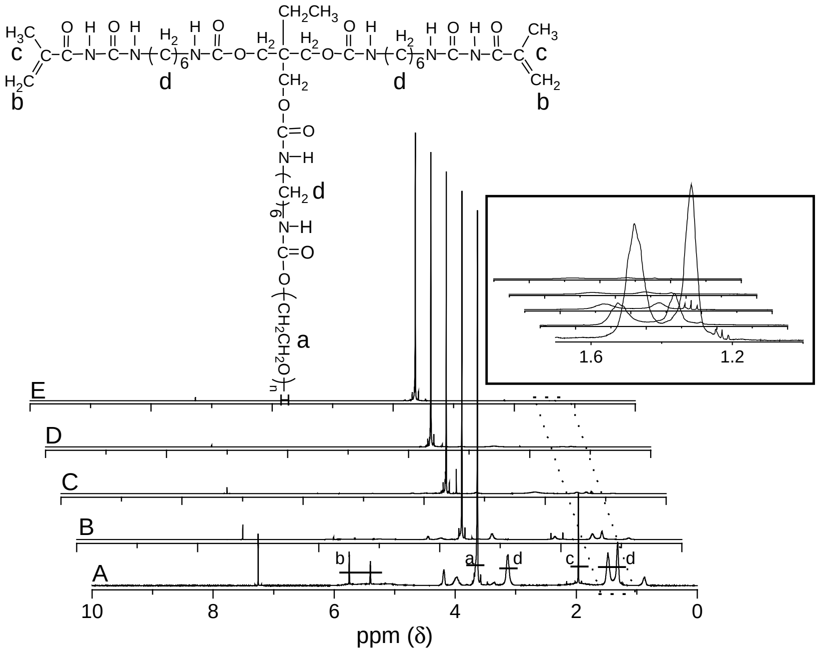
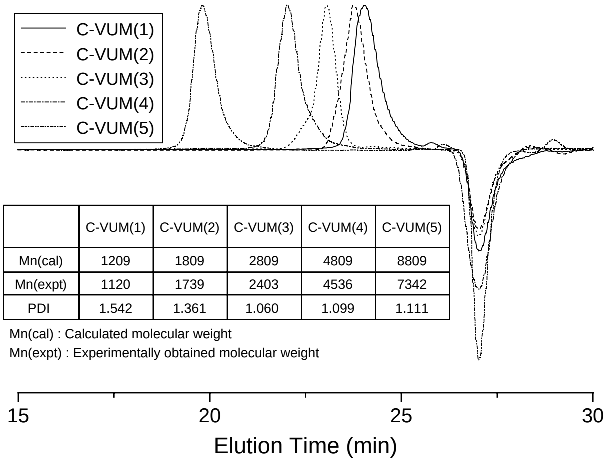


Fig. 2. ^{1}H NMR spectrum of (A) C-VUM(1), (B) C-VUM(2), (C) C-VUM(3), (D) C-VUM(4), and (E) C-VUM(5). Box areas are magnified in top.



	C-VUM(1)	C-VUM(2)	C-VUM(3)	C-VUM(4)	C-VUM(5)
Mn(cal)	1209	1809	2809	4809	8809
Mn(expt)	1120	1739	2403	4536	7342
PDI	1.542	1.361	1.060	1.099	1.111

Mn(cal) : Calculated molecular weight
Mn(expt) : Experimentally obtained molecular weight

Fig. 3. GPC trace of the synthesized macromonomers from C-VUM(1) to C-VUM(5).

confirms that they react with PEG together to form the urethane group. Thus, it is possible to verify the synthesis of C-VUM(5) by comparing the FT-IR spectra.

Fig. 2 shows the ^{1}H NMR spectra of the synthesized C-VUM(1) to C-VUM(5) by the reaction of the isocyanate-terminated urethane prepolymer and MAAm. The representative confirmation of C-VUM(1) is shown in Fig. 2(A) and the peak assignment is the following. The strong signal at 3.6 ppm (a) characterizes EO unit ($-CH_2CH_2O-$) of PEG, whereas the methylene protons ($-CH_2-$) of HDI are observed at 1.3, 1.5, and 3.2 ppm (d). The methylene protons ($=CH_2$) of the vinyl group in C-VUM are detected at 5.4 and 5.7 ppm (b) and the signal at 1.9 ppm (c) is a characteristic peak of the methyl protons ($-CH_3$) in C-VUMs. Although the protons of the urethane group (–N*H*COO–) of C-VUM are expected to appear at 8.07 ppm in this spectrum, they are not observed since the number of urethane groups in a gigantic C-VUM molecule is quite small. However, we were able to detect these protons in the urethane macromonomers having a similar structure in our previous study [27]. Since, the macromonomers were prepared by the polyaddition reaction of polyol and isocynate, it is thought that urethane groups are inevitably developed. As the number-average molecular weight of PEG increased from 400, 1000, 2000, 4000, to 8000 g/mol, the peak intensity of 1.5 ppm ($-CH_2-$) decreased due to the increased molar mass (as shown in Fig. 2(A)–(E)). Throughout the investigation using ^{1}H NMR spectrum, the structures of each macromonomer were successfully verified as an evidence of the reaction of the isocyanate-terminated urethane prepolymer and MAAm.

3.2. Characterization of C-VUM and PS particles

Fig. 3 exhibits the GPC traces of the synthesized C-VUM(1), C-VUM(2), C-VUM(3), C-VUM(4), and C-VUM(5). The molecular weights of C-VUMs increased

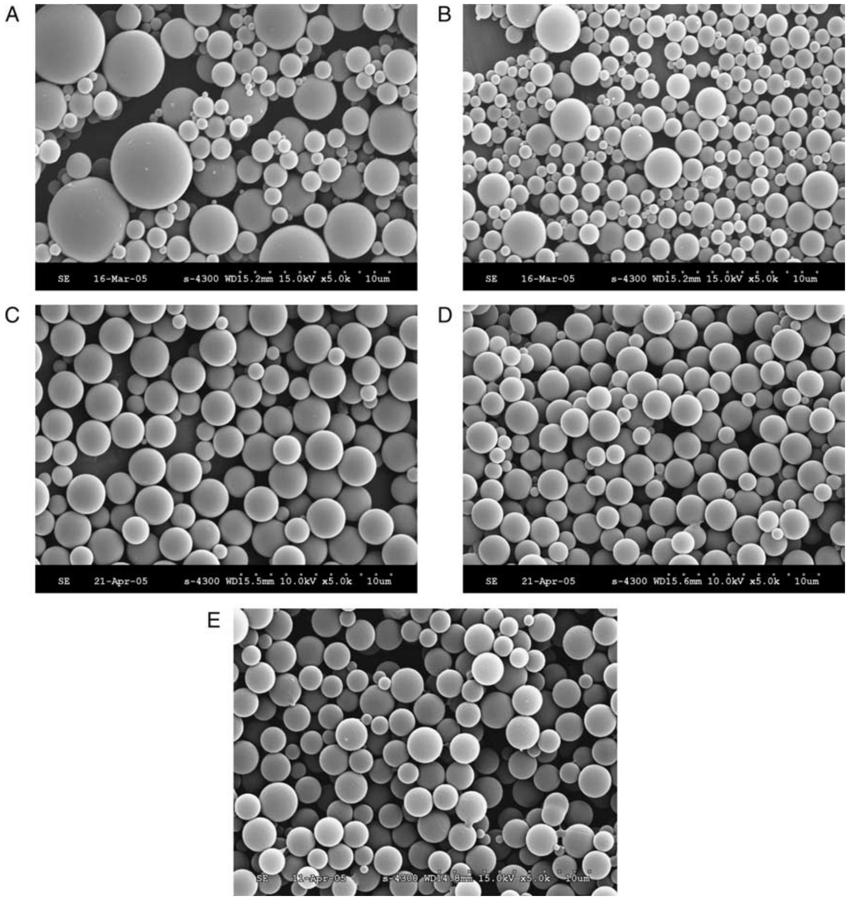
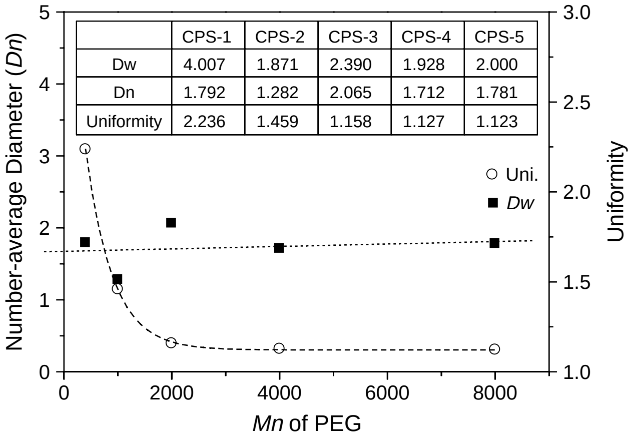


Fig. 4. SEM photographs of the PS prepared by Table 2. (A) CPS-1, (B) CPS-2, (C) CPS-3, (D) CPS-4, and (E) CPS-5.



	CPS-1	CPS-2	CPS-3	CPS-4	CPS-5
Dw	4.007	1.871	2.390	1.928	2.000
Dn	1.792	1.282	2.065	1.712	1.781
Uniformity	2.236	1.459	1.158	1.127	1.123

Fig. 5. The number-average diameter (D_n) (solid symbols) and uniformity (open symbols) of the PS particles prepared by various C-VUMs. (Uni. = D_w/D_n)

with the molecular weight of PEG ranging from several hundred to a few thousand and these values are similar to the calculated ones.

Fig. 4 represents the SEM photographs of the PS particles prepared by various C-VUMs and styrene. As usual, spherical particles are obtained, implying that the macromonomer acts as a stabilizer in the dispersion polymerization. In addition, as seen in Fig. 5, the D_n of PS particles is negligible change around 1.7 μm, thus, the molecular weight of PEG (macromolecular unit of C-VUM) does not affect the size of the PS particle. This is a contrast result to our previous study using L-VUM; PS particles increased, but PMMA spheres decreased with the molecular weight of L-VUM [29]. In addition, the uniformity of the PS particles was enhanced with the molecular weight of PEG.

The existence of C-VUM in PS microspheres and reaction of C-VUM with styrene monomer are further verified using the characteristic protons in urethane and vinyl groups, respectively. Fig. 6(A) shows the ^{1}H NMR spectrum of the CPS-1 polymerized as listed in Table 2. The signals at 1.9 and 2.3 ppm are the repeating vinyl protons ($–CH_2CH–$) of styrene main chain and phenyl protons of styrene side group are observed at 7.0 and 6.5 ppm. The EO unit ($–CH_2CH_2O–$) of PEG is characterized in 3.6 ppm and methylene protons ($–CH_2–$) of HDI are also observed at 1.3 and 1.5 ppm as also detected in Fig. 2(A). Furthermore, it is clearly seen that the vinyl protons in C-VUM at 5.4 and 5.7 ppm in Fig. 2(A) are absent after polymerization, which means that the C-VUM participates in the reaction with styrene during the polymerization. This phenomenon would indicate that C-VUMs work as reactive stabilizer and grafting agent as well [28,30].

The comparison of the glass transition temperature (T_g) of the PS particles prepared with the C-VUMs and PVP (polyvinylpirrolidone) is represented in Fig. 7. The T_g of the PS particle in the absence of any stabilizer (e.g. soap-free emulsion polymerization) and in the presence of PVP is observed at 98 and 104 °C, respectively. In addition, those of the PS particles with C-VUMs (CPS-1, CPS-2, CPS-3, CPS-4, and CPS-5) are observed around 101, 100, 102, 102, and 102 °C, respectively, which means that no distinctive influence of T_g upon the molecular weight of PEG is observed. When 6–20 wt% PVP contents relative to styrene

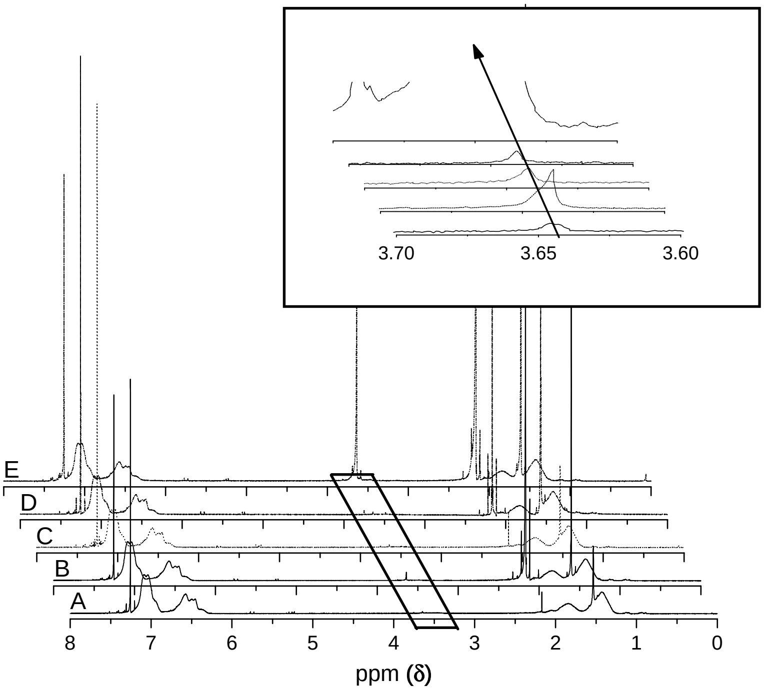
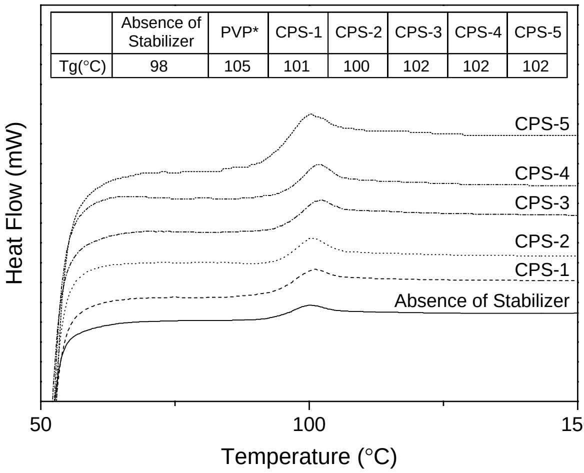


Fig. 6. ^{1}H NMR spectra of the PS prepared by Table 2. (A) CPS-1, (B) CPS-2, (C) CPS-3, (D) CPS-4, and (E) CPS-5. Box areas are magnified in top.



	Absence of Stabilizer	PVP*	CPS-1	CPS-2	CPS-3	CPS-4	CPS-5
Tg(°C)	98	105	101	100	102	102	102

Fig. 7. The DSC thermograms of the PS particles prepared in the absence of stabilizer and presence of macromonomer. *, Ref. [28].

monomer are added, the T_g shows a negligible change around 104 °C due to the slightly increased molecular weight [28]. However, the T_g of the PS microspheres synthesized with the C-VUM is approximately 2–3 °C lower than that of the PVP system.

4. Conclusions

The C-VUMs were successfully synthesized using TMP and applied to the dispersion polymerization of styrene in ethanol. The existence of the vinyl terminal group in the C-VUMs was verified using FT-IR and ^{1}H NMR spectra and the PS particles prepared by the reaction with the macromonomers were confirmed using FT-IR and ^{1}H NMR. Meanwhile, the reactive double bonds of macromonomers disappeared after polymerization of styrene. The qualitative analysis using FT-IR and ^{1}H NMR techniques reveals that the terminal vinyl groups of macromonomers take part in the reaction with styrene during the dispersion polymerization. The polymer (PS) microspheres were successfully obtained using the synthesized macromonomers (C-VUMs). Since, the synthesized macromonomers have a symmetric molecular structure with a vinyl group at chain ends, it is thought that the polymer (PS) is lightly crosslinked or grafted because of the same reactivity of terminal vinyl groups.

Various C-VUMs [from C-VUM(1) to C-VUM(5)] and styrene monomers are used to synthesize the stable PS particles. The PEG molecular weight of C-VUM was not affecting the particle size of the PS particles. However, as the PEG molecular weight of C-VUM increased, the uniformity of the PS particles enhanced. These results verify that C-VUMs act not only as reactive stabilizers, but also as grafting agents

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