

Dispersion polymerization of styrene and Methylmethacrylate using macromonomers as a reactive stabilizer

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Introduction

Dispersion polymerization is a type of precipitation polymerization in which one carries out the polymerization of a monomer in the presence of a second polymer that is soluble in the reaction medium [1, 2]. Macromonomer as one of the second polymer possess mono or bifunctional polymerizable end groups and capable of copolymerizing with the principle monomer to rapidly generate graft copolymer species [3, 4]. It must be amphiphilic so that it contains both an anchor segment, with an affinity for the final polymer particles, and a solvent soluble segment. The hydrophilic part of the macromonomers is often a poly(ethylene oxide) (PEO) chain, and the C=C double bond is located in the hydrophobic part. Recently, hydrophilic macromonomers have been used to prepare polymer particles instead of using a homopolymer as a stabilizer in the dispersion polymerization. In this study, we synthesized a bifunctional vinyl-terminated polyurethane macromonomer having PEO blocks and stabilized to polystyrene and methylmethacrylate particles in dispersion polymerization. Moreover, the effect of structure and molecular weights of macromonomers were investigated in synthesis of micron sized particles.

Experimental

Materials. Poly(ethylene glycol) (PEG) having M_n 400, 1000, 2000, 4000, 8000 g/mol and hexamethylene diisocyanate (HDI) were supplied by Aldrich Co. (USA) and used as received. Allyl alcohol (AOH; Aldrich) and acrylamide (Am; Aldrich) were introduced to make vinyl terminated Linear-type vinylurethane macromonomers (L-VUM). Trimethylolpropane (TMP; Aldrich Co.) having a three-alcohol group was used as a supporting structure for cross-type vinylurethane macromonomer (C-VUM). Methyl ethyl ketone (MEK) (99 %, Samchun Co., Korea) was the reaction medium for the polyurethane synthesis.

Synthesis & Polymerization.

The macromonomer having a molecular weight (M_w) of 40,000 g/mol is synthesized by reacting a molar ratio of 5:6 of PEG to HDI in acetone medium for a comparison with PVP of 40,000 g/mol. Another macromonomer, C-VUM was synthesized with the molar ratio of TMP, HDI, and PEG was 1:3:1 while the ratio of HDI to PEG was 2:1 for L-VUM, respectively. The rest of the synthetic procedure and the confirmation of chemical structure of the macromonomer are described elsewhere [5].

Analysis. In order to confirm the structure of the synthesized macromonomers, Varian 400 MHz ¹H NMR was used using CDCl₃ as a solvent. SEM (Hitach4300, Japan) 515 was used to investigate the morphology and size of the polystyrene particles. The molecular weights of the synthesized macromonomer, polystyrene and PMMA were measured using a Waters GPC. To investigate the stabilizing effects of the particle surface, the surface analysis was carried out using XPS.

Results and discussion

Synthesis of macromonomer. Figure 1 shows the ¹H NMR spectrum of the synthesized macromonomer. The strong signal at 3.6 ppm is a characteristic peak of PEO block (-CH₂CH₂O-)_n and the weak signals at 1.3, 1.5 and 3.2 ppm represent the aliphatic chain of (-CH₂-)₆ in HDI. The important characteristic signal of the proton in vinyl-terminated polyurethane macromonomer is weakly detected between 5.7 and 6.3 ppm representing the existence of the terminal vinyl groups in the polyurethane macromonomer.

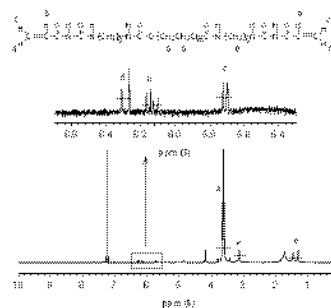


Figure 1. ¹H NMR spectrum of the poly urethane macromonomer (M_w :40,000 g/mol)

Comprison between PS and PMMA particles. The synthesized macromonomer (M_w :40,000 g/mol, terminal group:acrylamide) is applied in the dispersion polymerization of styrene and MMA as a stabilizer. Figure 2 represents the SEM photographs of the synthesized PS and PMMA prepared by macromonomer of 40,000 g/mol at 12 and 20 wt% relative to monomer.

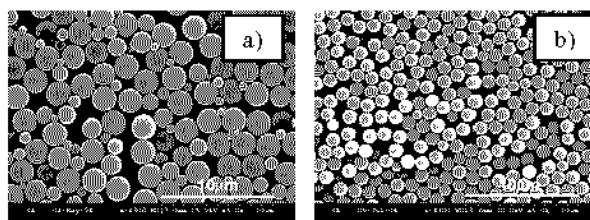
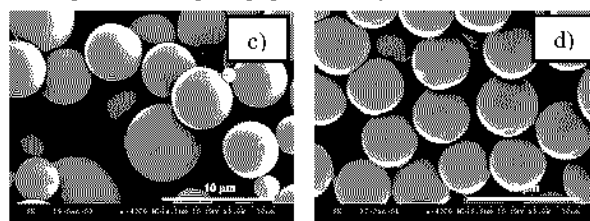


Figure 2. SEM photographs of the synthesized PS and PMMA



microspheres prepared by macromonomer. a) 12 wt%, PS, b) 20 wt %, PS, c) 12 wt%, PMMA, d) 20 wt%, PMMA.

The particle size decrease with the macromonomer concentration and PMMA particles are larger than PS. The Table 1 shows the D_w , M_w and PDI of PMMA and PS particles. The GPC analysis and particle size of synthesized macromonomer were exhibited in Table 1. The M_w increased with macromonomer concentration and decreased D_w . This is a typical phenomenon observed in dispersion polymerization. Pain et al. reported the inverse relationship between the molecular weight and the size of the polymer beads: the smaller the particles, the higher the molecular weight obtained [6].

Table 1. Analysis of stabilized PS and PMMA particles at 12 wt% and 20 wt% macromonomer concentrations.

Stabilized particle	Concentration of macromonomer	D_w (μm)	Uni.	M_w (g/mol)	Grafting ratio
PS	12 wt%	2.09	1.05	304,195	0.0213
	20 wt%	1.23	1.01	501,272	0.0475
PMMA	12 wt%	5.09	1.31	161,306	Impossible conform
	20 wt%	5.03	1.007	180,266	

¹H NMR technique has been used to verify the PEO macromonomers grafted with polymer latex particles [7]. The grafting ratio of the PS particle calculated from ¹H NMR. However, it is impossible to

confirm the grafting ratio of stabilized PMMA due to that the signals originated between macromonomer and PMMA were not distinguishable since the PEG block in the macromonomer and the methoxy group in the PMMA side chain coexist between 3.5 and 3.7 ppm. Unusually, high molecular weights up to 501,300 g/mol of PS particles were obtained by the dispersion polymerization because of the grafting reaction of the macromonomer with PS. These result verify that the vinyl urethane macromonomer act as an effective reactive stabilizer working as a grafting agent.

Stabilizing mechanism of the cross-type macromonomers.

The GPC analysis of the synthesized C-VUM and L-VUM with various PEG molecular weights and the abbreviation of macromonomer and stabilized PS were exhibited in Table 2.

Table 2. Abbreviation of two types of macromonomer with various PEG molecular weight and stabilized PS particles and analysis.

M_n of PEG	Synthesized macromonomer		Stabilized PS		
	Abbrev.	M_w^a (g/mol)	Abbrev.	M_w^a (g/mol)	D_w^b (μm)
400	C-VUM-400	2070	C-PS-400	34129	4.4
1000	C-VUM-1K	2738	C-PS-1K	48778	2.8
2000	C-VUM-2K	3157	C-PS-2K	63302	2.26
4000	C-VUM-4K	4928	C-PS-4K	76217	1.65
8000	C-VUM-8K	11776	C-PS-8K	100487	1.36
400	L-VUM-400	945	L-PS-400	32208	-
1000	L-VUM-1K	1623	L-PS-1K	42586	3.56
2000	L-VUM-2K	3305	L-PS-2K	53937	2.75
4000	L-VUM-4K	4815	L-PS-4K	66519	2.23
8000	L-VUM-8K	10970	L-PS-8K	71883	1.52

^{a)} measured by GPC

^{b)} determined by Scion Image

The average particle size decreased, but the molecular weight increased with the molecular weights of VUM. In addition, the molecular weight of C-PS is higher than that of L-PS. Usually, the resultant particle size decreased when increasing the stabilizer molecular weight under fixed stabilizer concentration. In comparison of the stabilizing effect between C-VUM and L-VUM, the stabilizing ability of the C-VUM is higher than that of L-VUM. This phenomenon suggests that the hydrophilic tail and the electron affinity of C-VUM would enhance the chain mobility to extend the tail toward the particle surface and the reaction medium. Based on the above idea, the ratio of the carbon, oxygen, and nitrogen on the particle surface were analyzed to verify the role of C-VUM and L-VUM in forming PS particles by using XPS. The XPS spectra of the particle surface of C-PS and L-PS are drawn in Figure 3. The integrated peak area of 1Os and C1s of PEG are calculated from the peak in Figure 3, normalized with fixed C1s, and plotted in Figure 4.

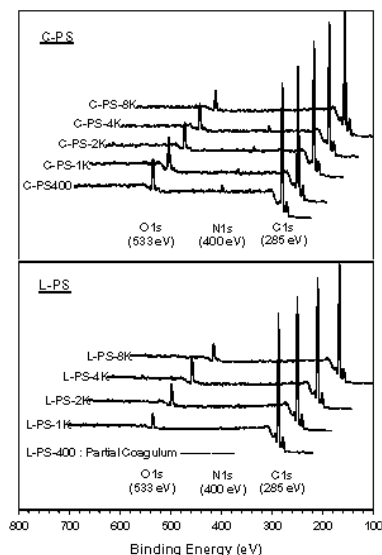


Figure 3. XPS spectra of the C-PS and L-PS particle surface.

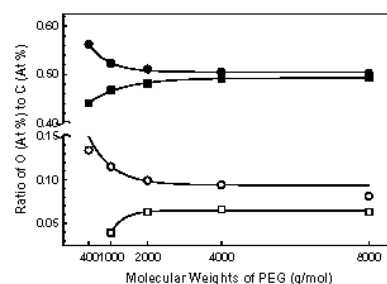


Figure 4. Atomic ratio of oxygen to carbon on the surface of PS particles prepared by C-VUM and L-VUM using XPS. (●) C-PS (cal), (■) L-PS (cal), (○) C-PS (expt), (□) L-PS (expt).

The O1s to C1s ratio of C-VUM decreases from 0.56 to 0.50, while that of L-VUM increases from 0.44 to 0.48. The more C-VUM exists on the particle surface, a more stabilizing effect induces a high molecular weight and smaller particles of C-PS. The part of the stabilizer exists inside of the particles as well as in the medium.

Using the information observed from Table 2 and Figure 3, 4, the reaction and stabilizing mechanism of the PS particles using C-VUM and L-VUM is proposed as given in Figure 5. The L-VUM contains a vinyl urethane end group at both ends, some of the macromonomers may exist on the particle surface as a loop-shape in which both ends are embedded on the surface as drawn in Figure 5. On the other hand, the reaction and stabilizing mechanism of C-PS would be the following. At the final stage of the particle formation, the particle is stabilized due to the surrounded cross-type VUM as given in Figure 5. As seen in the schematic difference between the L-VUM and C-VUM, the stabilizing effect of C-VUM is stronger than that of L-VUM.

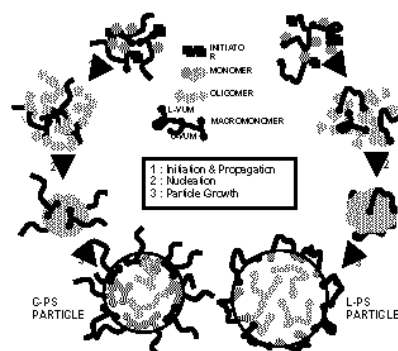


Figure 5. Proposed reaction and stabilizing mechanism of the formation of PS particles with the C-VUM (left) and L-VUM (right)

Conclusions

The vinyl urethane macromonomer act as a reactive stabilizer. The XPS result showed that the C-PS was anchored with a larger amount of PEG than that of the L-PS on the particle surface. Thus, the reaction and stabilizing mechanism of the macromonomers for the formation of PS particles is proposed that the particle surface of the C-PS is surrounded by a large amount of tail shaped macromonomers leading to higher molecular weights and smaller particle sizes.

References

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