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Novel Macromonomer as a Reactive Stabilizer in the Dispersion Polymerization of Methylmethacrylate

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Abstract: We have synthesized a novel macromonomer of vinyl-terminated bifunctional polyurethane having a molecular weight of 37,000 g/mol and successfully applied it to the dispersion polymerization of methylmethacrylate (MMA). We verified the presence of the vinyl terminal group and the macromonomer grafted onto the poly(ethylene glycol)(PEG) block in the PMMA particles by using ^{1}H and ^{13}C NMR spectroscopies. Monodisperse PMMA microspheres that have good uniformity of 1.01 were prepared at 20 wt% macromonomer content; we investigated the characteristics of the PMMA particles in terms of their molecular weight, molecular weight distribution, size of the particles, thermal properties, and glass transition temperature. We have found that the synthesized polyurethane macromonomer is an effective stabilizer.

Keywords: polyurethane, macromonomer, stabilizer, dispersion polymerization, poly(methyl methacrylate) microspheres.

Introduction

In the synthesis of polymer colloids, various stabilizing agents are essentially used such as surfactants in emulsion, dispersants in suspension, and steric stabilizers in dispersion polymerization. Their working mechanisms are different in each polymerization. In emulsion polymerization, the surfactants provide not only a colloidal stability but also a polymerization locus in aqueous media. In suspension polymerization, protective stabilizers are used to endow colloidal stability of the monomer droplets by physical adsorption in aqueous media. Steric stabilizers in dispersion polymerization serve as a precursor in particle nucleation and give stability of the formed particles in organic media. Although such stabilizing agent plays a crucial role in the production and applications of the colloid dispersions, they also encounter various adverse effects including foaming,[1] destabilization of latex by migration in paints or films[2,3] and alteration of hardness of products.[4]

In order to make such stabilizers more effective, reactive stabilizers which was named "macromolecular surfactant" have been developed.[5] These surfactants contain a polymerizable group on the chain end, so that they can either homopolymerize to give a regular comb-like polymer or copolymerize with a conventional monomer to give a graft copolymer. Use of macromolecular surfactants, or macromolecular monomer (now generally called macromonomer) gives easy route to well-defined branched polymers since the molecular weight of the branch or side chain is predetermined by controlling degree of polymerization of the macromolecular surfactants.

Macromonomers or macromers, have been studied in more detail in the dispersion polymerization by the Imperial Chemical Industries (ICI) in the mid 1970s.[6] Macromonomers are relatively new category of functionalized polymer materials donating one or more polymerizing end groups, thus use of this provides an alternative route to stabilize polymer colloids in replacement of surfactants or steric stabilizers in emulsion or dispersion polymerizations.[7-12]

In the dispersion polymerization, effective macromonomers must be amphiphatic to act as a stabilizer in aqueous (water/alcohol mixture) or non-aqueous media. An anchor segment has a good affinity for the formed polymer particles and a solvent-soluble segment provides a good dispersion of the macromonomer in the media, thereby, it is also referred to *surfmer* (*surf*actant + mono*mer*).[13,14] Unlike conventional steric stabilizers such as homopolymers in dispersion polymerization, the macromomomers provide a useful pathway to control the final properties of the polymer colloids since they contain chemically distinct blocks in the main chains. Therefore, the structural design of macromonomer is of quite importance in order to endow the satisfactory stability of polymer colloids.

The most intensively studied macromonomers are based on poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG) blocks functionalized with styryl, methacryloyl, thiol, maleate, vinyl, and *p*-vinylphenylalkyl reactive groups.[15-17] The use of PEO or PEG, which bears a monofunctionality,

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has the merit of good solubility in water as well as various alcohols. Since bifunctional macromoners possess an additional capability of potential crosslinkers, more versatile applications can be expected. In general, crosslinking agent in the dispersion polymerization is limited to quite low concentration, approximately below 0.5 wt% relative to a main monomer. Thus the addition of a crosslinking agent such as divinylbenzene at a higher level has been led to a coarse surface of the final polymer particles or even popcorn-shaped particles because of the different local degree of crosslinking in microscale.[18-20]

Recently, crosslinkable macromonomers composed of ethylene-butylene aliphatic hydrophobic chain and difunctional terminal acrylic acid moiety were synthesized by El-Aasser's group,[19,20] then used as a both costabilizer and crosslinking agent in the miniemulsion polymerization of *n*-butyl methacrylate. The most recent examples are methacryloxypropyl-[21] and vinyl-terminal[22] polysiloxanes used in the dispersion polymerization of methyl methacrylate in non-polar media. However, the development of bifunctional macromonomers based on PEO or PEG block is still unexploited.

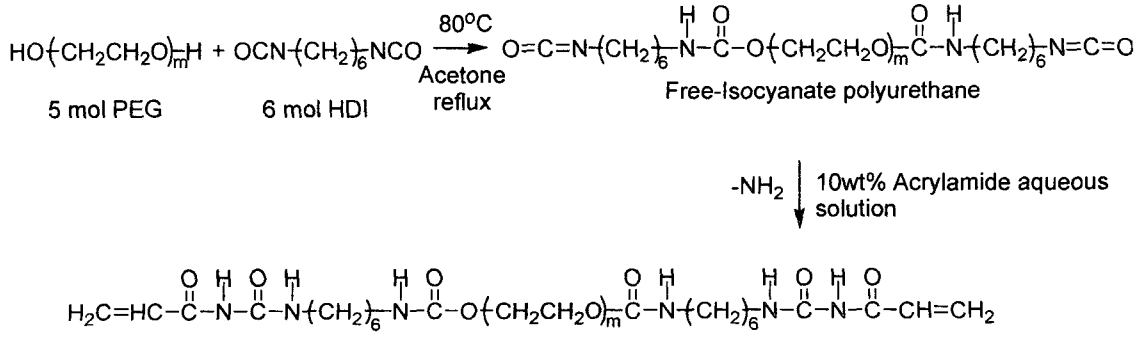
In this article, a difunctional vinyl terminated polyurethane macromonomer having PEO blocks and urethane group was successfully synthesized by polycondensation reaction of PEO and hexamethylenediisocyanate. Then, this novel material was used as a reactive stabilizer to give stable PMMA particles in the dispersion polymerization in ethanol media and the change in thermal properties of the microspheres was investigated.

Experimental

Materials. Poly(ethylene glycol) (PEG) having number-average molecular weights of 1,000 (PEG 1000) and 4,600 g/mol (PEG 4600) and hexamethylenediisocyanate (HDI) were supplied by Aldrich Co. (USA) and used as received. Acrylamide (Am; Aldrich) was purified by recrystallization in methanol twice prior to use. Highly pure acetone (Samchun Co., Korea) was used as the reaction medium for the polyurethane synthesis and double distilled deionized water (DDI) was used. Methyl methacrylate (MMA; Junsei, Japan) as the monomer and absolute ethanol (99%; Samchun, Korea) as the medium were used for the dispersion polymerization. A conventional steric stabilizer, poly(*N*-vinylpyrrolidone) (PVP-40K; weight-average molecular weight = 40,000; Aldrich), was used for a comparison to the synthesized macromonomer. Analytical grade of 2,2-azobisisobutyronitrile (AIBN; Junsei) was used as an initiator and it is used as received.

Synthesis of Macromonomer. Scheme I is the synthetic procedure of the macromonomer in detail. The bifunctional macromonomer, based on free-isocyanate polyurethane precursor, was synthesized using PEG and HDI. A 3:2 molar ratio of PEG 4600 (69 g): PEG 1000 (10 g) was simply mixed to match the M_w of 40,000 g/mol of PVP. A molar ratio of 5:6 of PEG (79 g) to HDI (5.05 g) was mixed in acetone medium and the reaction mixture was refluxed for 4 hrs at 80 °C. The free-isocyanate polyurethane product was dissolved in DDI water at 10 °C and this low temperature was carefully maintained in order to prevent the side reaction of isocynate groups with water. Excess amount of 10 wt% acrylamide (2 mol; 0.7 g) aqueous solution was dropped in the polyurethane aqueous solution in order to introduce vinyl groups at the chain end of the macromonomer.

Polymerization. Dispersion polymerization was carried out in a 50 mL capped vial with magnetic stirring under nitrogen atmosphere. 25 g of ethanol was first introduced in the vial and 10 wt% MMA (2.5 g) of the medium and 1 wt% of AIBN (0.025 g) relative to the monomer were charged. The concentration of the macromonomer varied between 0, 6, 12, 20, 30 and 40 wt% (0.75 g) relative to MMA and the polymerization temperature in oil bath was fixed at 55 °C. For a comparison, the same amounts of PVP were incorporated instead of macromonomer with maintaining the other polymerization parameters same. After completion of the polymerization, the resultant was rinsed off with DDI water and methanol, then centrifuged repeatedly to remove the non-reacted materials.



Scheme I. Synthetic route to prepare vinyl-terminated polyurethane macronomomer.

Analysis. The structure of the macromonomer and polymer was verified using Varian 400 MHz ^{1}H-NMR and ^{13}C-NMR. The molecular weights of the synthesized macromonomer and PMMA particles were measured using Waters GPC (Gel Permeation Chromatography) equipped with 510 differential refractometer and Viscotek T50 differential viscometer. The macromonomer and PMMA dissolved in THF were injected at a flow rate of 1.0 mL/min and the calibration was carried out using ten polystyrene standard samples (Polymer Laboratories, UK). Philips SEM (Scanning Electron Microscopy) 515 was used to investigate the morphology and size of the PMMA particles. The conversion from monomer to polymer was determined gravimetrically, then the weight-average ($\overline{D_w}$) and number-average ($\overline{D_n}$) diameter, and the uniformity ($\overline{D_w}/\overline{D_n}$) were obtained by counting about 100 particles in SEM photographs using Scion Image Analyzer®. The thermal properties of the prepared PMMA particles were studied using the Perkin-Elmer TGA-7 (thermal gravimetric analysis) at a heating rate of 20 °C/min from 0 to 600 °C under nitrogen environment. The degradation temperature was measured at the transition point as the curve passes the maximum negative slope. 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 and quench cooled at a maximum cooling rate, then reheated in the second time. The glass transition temperature (T_g) was collected at the midpoint of the transition region in the second scan.

Results and Discussion

Synthesis of Macromonomer. Figure 1 exhibits the GPC traces of the synthesized macromonomer. In order to compare the characteristics of the synthesized PMMA particles using the macromonomer and a model stabilizer (PVP), the molecular weight of the targeted macromonomer was designed and controlled. The number- and weight-average molecular weights of the synthesized macromonomer were 12,487 and 38,707 g/mol, respectively, and this material was used for the dispersion polymerization. Under an assumption of complete reaction of each ingredient in the synthesis of macromonomer, the expected number-average molecular weight of it would be approximately 16,800 g/mol (3 mol PEG× 4,600 g/mol + 2 mol PEG× 1,000 g/mol + 6 mol HDI × 170 g/mol = 16,820 g/mol).

Figure 2 shows the ^{1}H-NMR spectrum of the synthesized macromonomer as shown in Scheme I. The strong signal at 3.6 ppm is a characteristic peak of PEO block (-CH_2CH_2O-)$_n$ and the weak signals at 1.3, 1.5 and 3.2 ppm represent the aliphatic chain of (-CH_2-)$_6$ in HDI. The important characteristic signal of the proton in vinyl-terminated polyurethane macromonomer is weakly detected between 5.7 and 6.3 ppm (this range is magnified in the figure) representing the existence of the terminal vinyl groups in the polyurethane macromonomer. This group is expected to act as a stabilizer in the dispersion polymerization.

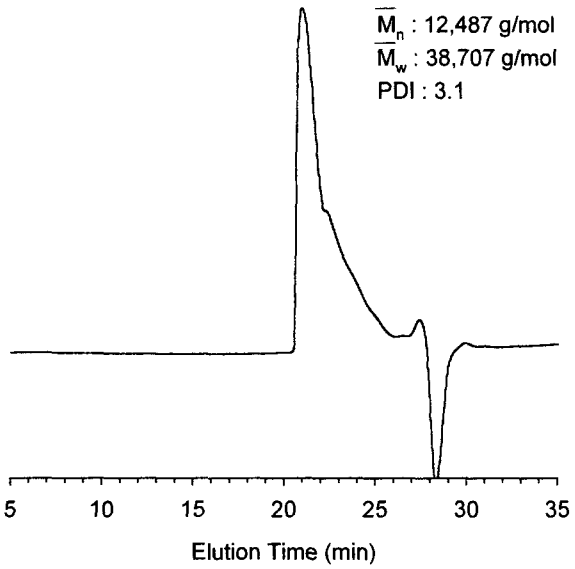


Figure 1. ^{1}H-NMR spectrum of the vinyl-terminated polyurethane macromonomer.

Macromonomer as a Reactive Stabilizer. The synthesized bifunctional macromonomer was applied in the dispersion polymerization of MMA as a stabilizer and the PMMA microspheres were successfully prepared by varying the macromonomer concentrations from 0 to 40 wt% relative to MMA. In general, ^{1}H-NMR or ^{13}C-NMR techniques are frequently used to determine the existence or ratio of the grafted macromonomer with polymer.[23,24]

Although the reactivity of the macromonomer with monomer was investigated using ^{1}H-NMR spectra in this study, 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. Thus, ^{13}C-NMR is used to verify the existence of the vinyl terminated PEG block in polyurethane macromonomer and the grafted macromonomer with PMMA. Figure 3(a) shows the vinyl terminated PEG block in macromonomer at 70.8 ppm and Figure 3(b) also exhibits the PEG block in the 40 wt% macromonomer involved PMMA particles at the same region, 70.8 ppm, as in Figure 3(a). This confirms that the grafting reaction between the vinyl terminated macromonomer and PMMA occurs during the polymerization.

The SEM pictures of the resultant particles synthesized with various concentrations of macromonomer are drawn in Figure 4. As usual, spherical particles were obtained, implying that the macromonomer acts as a stabilizer in the dispersion polymerization. In addition, the average particle size decreased with the macromonomer content and the monodisperse particle size was obtained at 20 wt% macromonomer. It is noted

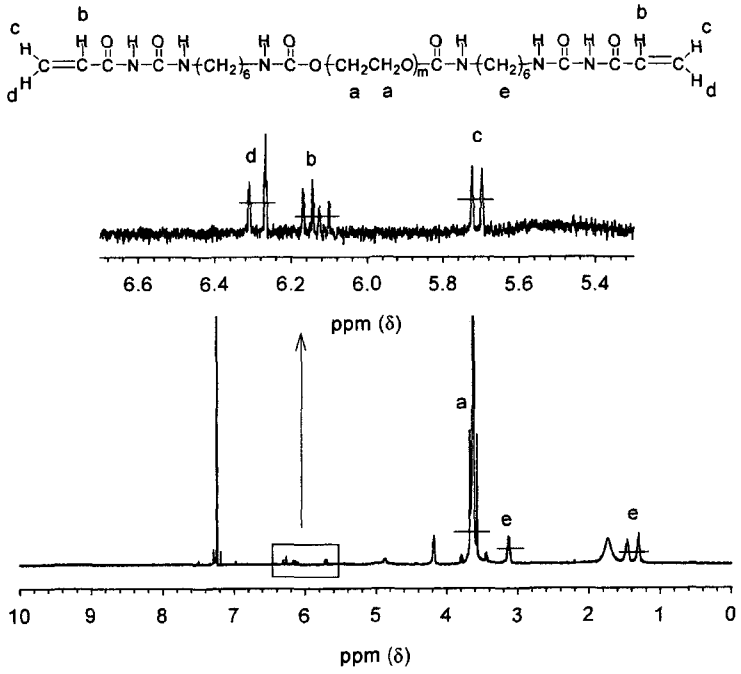


Figure 2. ^{1}H-NMR spectrum of the vinyl-terminated polyurethane macromonomer.

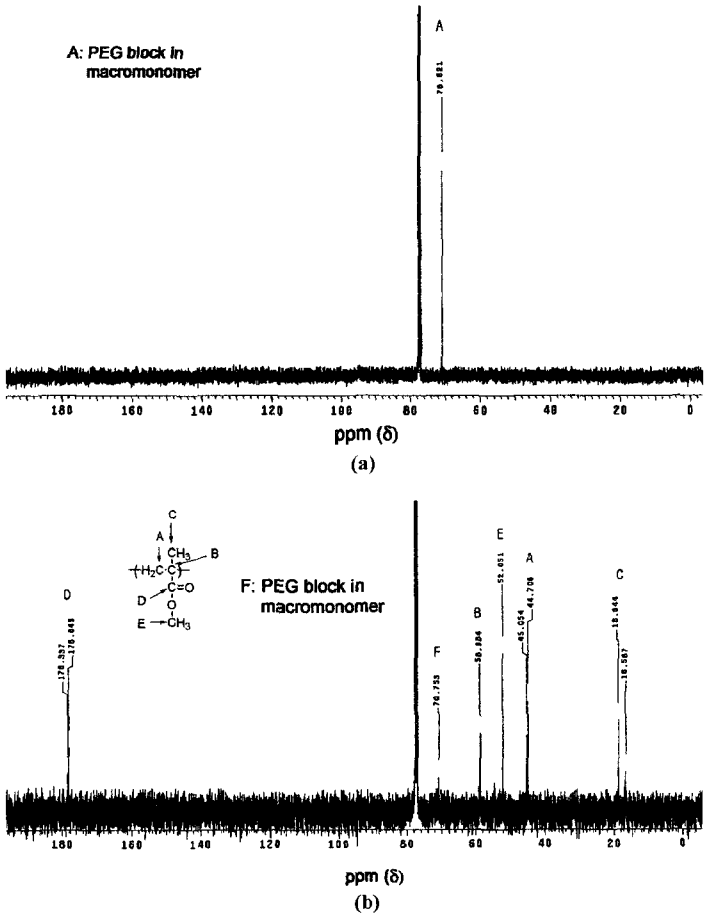


Figure 3. ^{13}C-NMR spectra of (a) vinyl-terminated polyurethane macromonomer and (b) PMMA prepared with 40 wt% macromonomer.

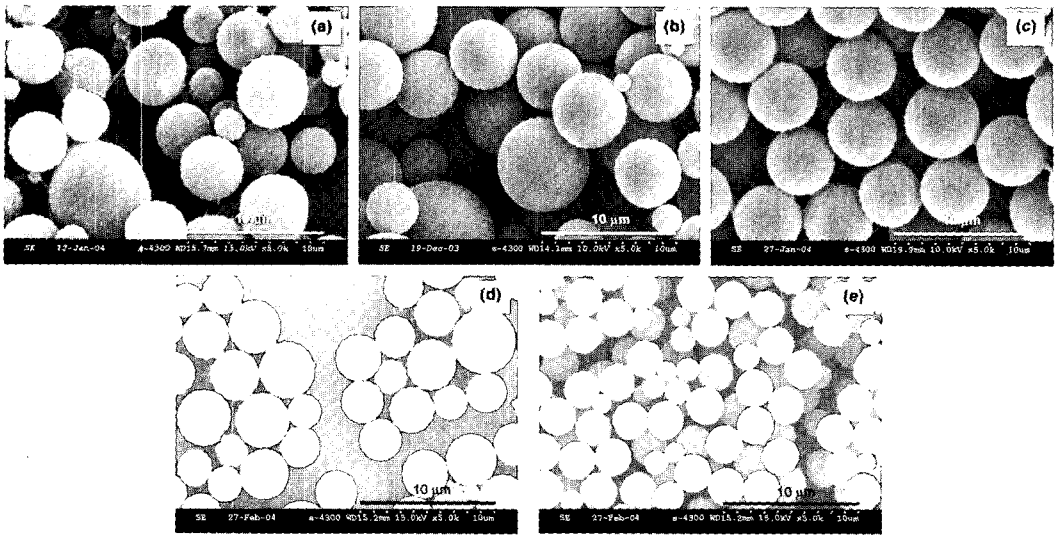


Figure 4. SEM photographs of the synthesized PMMA particles prepared with (a) 6, (b) 12, (c) 20, (d) 30, and (e) 40 wt% polyurethane macromonomer.

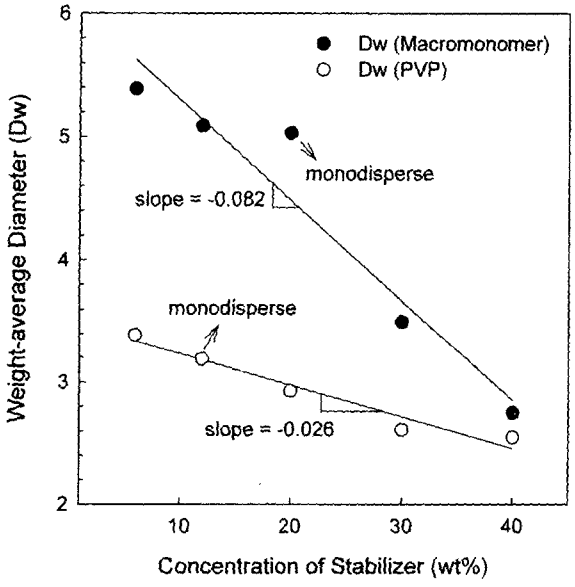


Figure 5. The weight-average diameter ($\overline{D_w}$) of the PMMA particles prepared by varying concentration of polyurethane macromonomer (solid symbols) and PVP (open symbols).

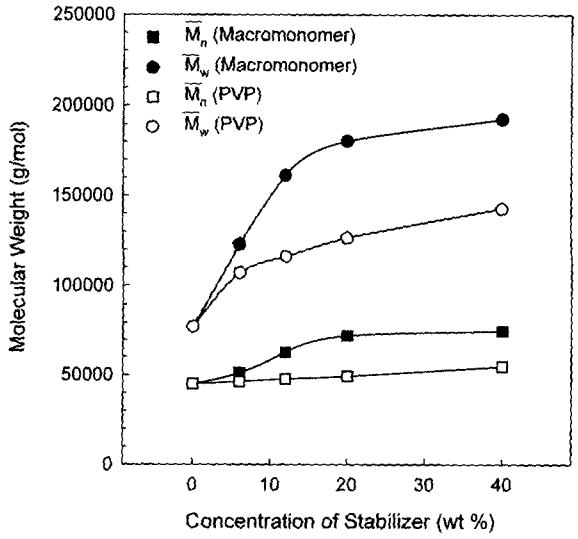


Figure 6. Number- (open symbol)s and weight-average molecular weight(solid symbols) of PMMA microspheres prepared at various concentrations of macromonomer (circle symbols) and PVP (square symbols).

that the final conversion of the polymerization lies between 84 and 87% after 24 hrs, showing a negligible dependence on the amount of macromonomer. Furthermore, coagulum of the products was not observed in the presence of the macromonomer.

In order to verify the role of the macromonomer other than stabilizer in the dispersion polymerization of MMA, the commercial stabilizer, PVP ($\overline{M_w}$ = 40,000 g/mol) was used for polymerizing the PMMA particles using the same conditions as used with macromonomer. In Figure 5, the number- ($\overline{D_n}$) and weight-average diameter ($\overline{D_w}$) of the PMMA particles prepared at various concentrations of polyurethane macromonomer and PVP are compared. The slope (= -0.082) between the $\overline{D_w}$ and the stabilizer concentration with macromonomer is three times higher than that (= -0.026) of PVP stabilized PMMA. This may imply that the macromonomer is more effective to stabilize the surface area to highly reduce the particle size. This result tells us that the macromonomer is acting as a reactive stabilizer.

As shown in Figure 6, the number- and weight-average molecular weight increased as the macromonomer concen-

tration augmented and the molecular weight of the PMMA stabilized with the macromonomer is higher than that with PVP. Paine *et al.*[25] reported the inverse relationship between the molecular weight and size of the polymer beads in the conventional dispersion polymerization: the smaller the particles, the higher the molecular weight was obtained due to an increased radical capturing ability and reduced termination rate.

The effects of the high molecular weight of the PMMA microspheres prepared with the macromonomer on the thermal properties of the PMMA particles were investigated using TGA and DSC. The TGA thermograms of the PMMA microspheres by macromonomer (Figure 7(a)) and PVP (Figure 7(b)) are compared. In general, the weight loss of the macromonomer stabilized PMMA is much less, indicating their thermal properties is much enhanced. Especially, in the region between 260 and 400 °C, the thermal properties of the macromonomer stabilized PMMA are enhanced due to the increased molecular weight of PMMA. In Figure 8, the TGA onset point of the PMMA resin without either stabilizer is 235 °C and that of the PMMA particles synthesized with 6, 12, 20, 30, and 40 wt% macromonomer is 303, 330, 334, 345, and 349 °C, and that with PVP is 299, 307, 312, 324, and 327 °C, respectively. This result reveals that the thermal stability of the PMMA particles is improved due to the increase in the molecular weight.

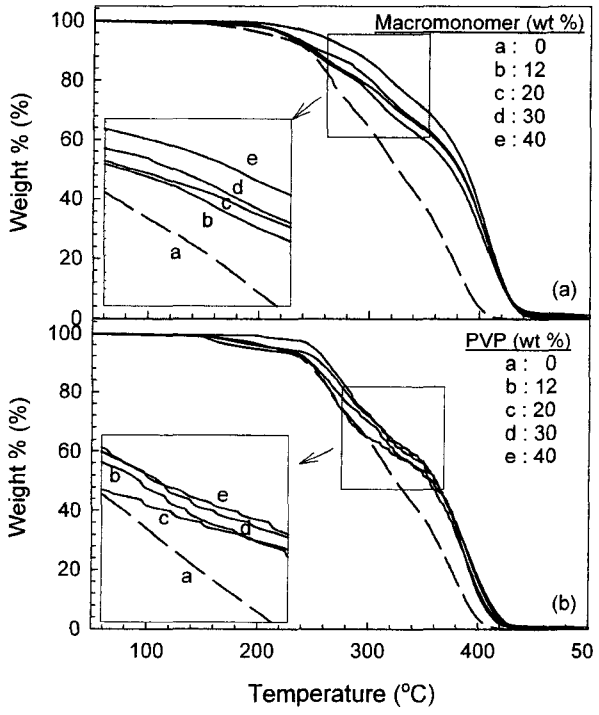


Figure 7. TGA thermograms of PMMA microspheres prepared by (a) macromonomer as a crosslinkable stabilizer and (b) a conventional PVP stabilizer. Dashed line denotes PMMA resin prepared in the absence of a stabilizer.

The influence of the concentrations of the macromonomer and PVP on the T_g of the PMMA particles is represented in Figure 9. The T_g of the PMMA prepared without stabilizer is obtained at 104.3 °C, and those of the PMMA particles with 6 and 40 wt% PVP are observed at 103.6 and 105.2 °C, respectively, which means that no distinctive influence of T_g upon PVP content is observed. On the other hand, the PMMA particles prepared with 6 and 40 wt% macromono-

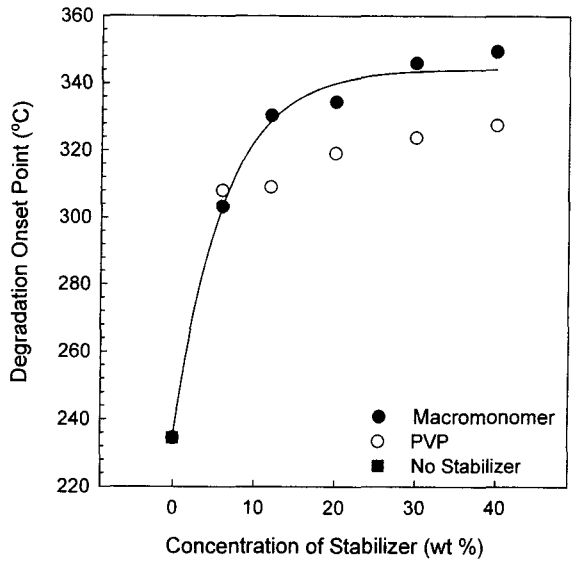


Figure 8. The thermal degradation temperature of the PMMA particles prepared at various concentrations of polyurethane macromonomer (solid symbols) and PVP (open symbols).

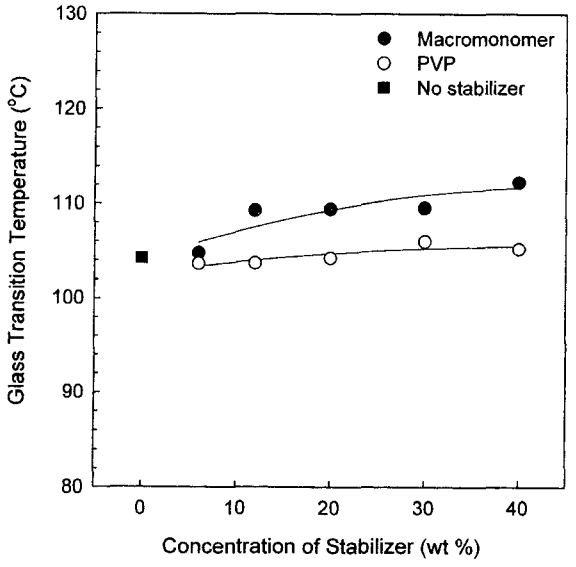


Figure 9. The glass transition temperature the PMMA prepared in the absence of a stabilizer (solid squares) and at various concentrations of the macromonomer (solid circles) and PVP (open circles).

mer increased from 104.8 to 112.3 °C with broad transition, respectively. When PVP is used as the stabilizer, the T_g marginally increases with the amount of the PVP. However, a substantially increase in T_g of the macromonomer-stabilized PMMA particles is clearly observed. This phenomenon would indicate that a novel bifunctional polyurethane macromonomer works as an effective stabilizer. Furthermore, the augmented molecular weight of the PMMA microspheres prepared by the grafting of the macromonomer improves the thermal properties of the PMMA.

Conclusions

A novel macromonomer of vinyl terminated bifunctional polyurethane having a molecular weight of 37,000 g/mol was successfully synthesized in acetone and applied to the dispersion polymerization of MMA in ethanol. The existence of the vinyl terminal group and the grafted macromonomer onto the PEG block in the PMMA particles was confirmed using ^{1}H-NMR and ^{13}C-NMR. The monodisperse PMMA microspheres with good uniformity of 1.01 were prepared using the synthesized polyurethane macromonomer, implying that this is acting as a stabilizer. The increase in molecular weight but the decrease in size of the PMMA particles upon macromonomer concentration just followed the manner of the conventional dispersion polymerization. In order to explore the role of the macromonomer, the characteristics of the PMMA particles prepared between PVP and macromonomer was investigated in terms of the molecular weight, molecular weight distribution, size of the particles, thermal stability, and the glass transition temperature. The study showed that the macromonomer-stabilized PMMA exhibited much higher molecular weight, larger particle sizes, higher thermal stability, and higher glass transition temperature. These results indicate that the macromonomer acts as an effective stabilizer, and therefore the monodisperse stable and crosslinked PMMA microspheres could be prepared using this type of stabilizer.

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