Synthesis and Characterization of Polyurethane-Derived Telechelic Macromonomer Cross-Linkable Stabilizer (TMCS)

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ABSTRACT: The telechelic macromonomer cross-linkable stabilizer (TMCS) was synthesized by the reaction of isocyanate-terminated prepolymer with methacrylamide and was successfully employed as a steric stabilizer and possible cross-linking agent in the dispersion polymerization of styrene. The urethane and methyl groups in TMCS are found in the spectrum of PS microspheres, and the reactive double bonds in TMCS disappear after polymerization with styrene. The qualitative analysis reveals that the symmetric molecular structure with vinyl group in TMCS takes part in the reaction with styrene, and it is proposed that the PS microspheres are substantially cross-linked. In reality, for the 100 wt % TMCS system, the PS is not totally soluble in THF, remaining as a translucent fully-swollen gel in THF. Thus, these qualitative structural investigations suggest that the TMCS serves as a reactive stabilizer as well as a cross-linking agent.

Introduction

Recently, the preparation of macromolecules with a controlled structure has received in 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]

In the synthesis of polymer colloids, various stabilizing agents are essentially used such as surfactants, dispersants, and steric stabilizers in various heterogeneous polymerizations. Although such stabilizing agents play a crucial role in the production and applications of the colloid dispersions, they also encounter various adverse effects including foaming,[6] destabilization of latex by migration in paints or films,[7,8] and alteration of hardness of products.[9] The use of telechelic macromonomers in free-radical heterogeneous polymerizations not only provides for the replacement of steric stabilizers but they also can be used for the synthesis of cross-linked and branched copolymers including comb, star, brush, and graft types.[10−13] The manufacture of such copolymers can be carried out either by homogeneous or heterogeneous copolymerizations.[14,15] The reactive block copolymer having terminal styrenic groups, for example, polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) prepared by anionic polymerization, was used as a steric stabilizer macromonomer in the emulsion polymerization of styrene. Poly(ethylene oxide) (PEO) macromonomers were employed in aqueous emulsion or nonaqueous dispersion polymerization of styrene as a reactive steric stabilizer.[16−18] Lightly cross-linked polymer microspheres were produced using bifunctional urethane acrylate (UA) as a cross-linking agent in the presence of conventional stabilizer in dispersion polymerization.[19,20] The cross-linkable telechelic macromonomers consisting of ethylene-butylene aliphatic hydrophobic chain and difunctional terminal acrylic groups were used as a both co-stabilizer and cross-linker in the miniemulsion polymerization of *n*-butyl methacrylate.[21] However, the development of bifunctional cross-linkable macromonomers based on PEO block is still unexploited. Therefore, this paper describes the synthesis and characterization of a polyurethane-derived bifunctional telechelic macromonomer cross-linkable stabilizer (TMCS) which is a combination of a cross-linker and steric stabilizer in dispersion polymerization of styrene.

Experimental Section

a. Synthesis of Telechelic Macromonoer Cross-Linkable Stabilizer (TMCS). The synthesis of TMCS was carried out in a 500 mL jacketed glass reactor fitted with a reflux condenser, Teflon stirrer, and nitrogen inlet tube. Then 0.05 mol (100 g) of PEG (PEG 2000; Aldrich Co.) is melted at 80−85 °C, and a molar ratio of 2:1 of diisocyanate (0.1 mol; 16.82 g, HDI; Aldrich) to polyol (0.05 mol) was reacted in methyl ethyl ketone (MEK; Samchun Co., Korea) medium. The temperature was raised to 80−85 °C and the reaction was refluxed for 4 h. After finishing this reaction, diethylene glycol (0.025 mol; 2.653 g; DEG, Aldrich) was added for a chain extending of isocyanate-terminated prepolymer and the synthesis progressed for 2 h more under the same conditions. The degree of reaction was verified with a hydroxyl peak (nearby 3480 cm^{-1}) that disappears as a result of reaction with diisocyanate using FT-IR spectra of the intermediate product.

This product was dissolved in acetone at 20 °C. Low temperature was carefully maintained at this stage in order to prevent the reaction of MAAm. The 0.05 mol of MAAm solution (10 wt %) dissolved in acetone was dropped in the isocyanate-terminated prepolymer solution to introduce vinyl groups at the chain ends of the TMCS. An amine group of methacrylamide (MAAm; Aldrich) is reacted to the isocyanate of the isocyanate-terminated prepolymer. Throughout this procedure, the end groups of the TMCS can carry the vinyl groups. The degree of the reaction was verified with isocyanate group (nearby 2267 cm^{-1}) that disappears as a result of reaction with amine group using FT-IR spectra of the intermediate product. The synthesis procedure of the TMCS is shown in Scheme 1 in detail. The M_n and PDI of the TMCS measured by GPC were 5460 g/mol and 1.56, respectively.

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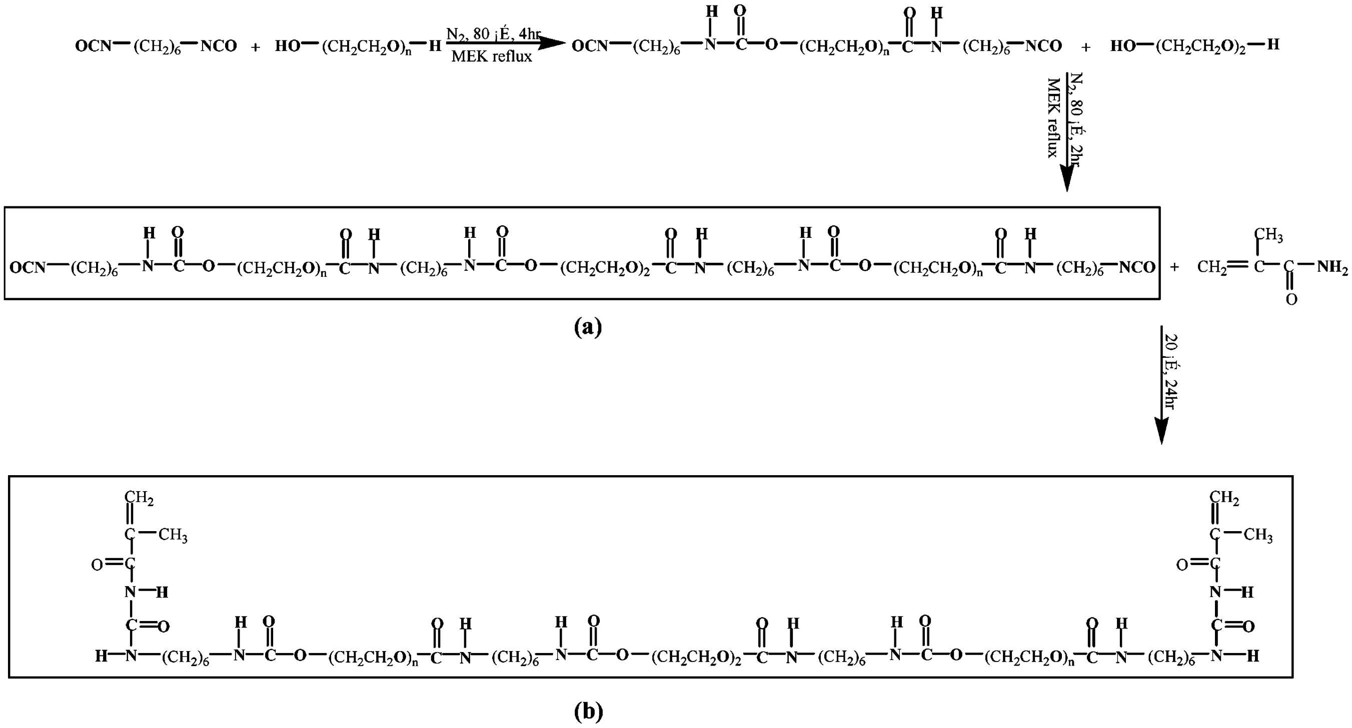
Scheme 1. Synthetic Route Used To Prepare the Synthesis of (a) Isocyanate-Terminated Prepolymer and (b) Telechelic Macromonomer Cross-Linkable Stabilizer (TMCS)



b. Dispersion Polymerization. The dispersion polymerization of styrene (Aldrich) in the presence of TMCS was conducted at 65 °C in ethanol with 2,2-azobis(isobutyronitrile) (AIBN; Junsei, Japan) as an initiator. The polymerization was carried out in a 50 mL vial with magnetic stirring under nitrogen atmosphere. 20 g of ethanol (99%; Samchun) was first poured into the vial and 0.1 or 0.05 wt % of styrene (2.0 or 1.0 g) relative to the medium was charged. The amount of AIBN (0.02 g) was fixed at 0.001 wt % relative to the medium. The concentration of the TMCS was varied 0.01 or 0.05 wt % (0.2 or 1.0 g) relative to the medium, respectively. The polymerization temperature in oil bath was fixed at 65 °C. After completion of the polymerization, the resultant was rinsed off with DDI water and methanol and then centrifuged repeatedly to remove the residual TMCS.

c. Analysis. To confirm the structure of the reactants (isocyanate-terminated polyurethane and methacrylamide), and the products (TMCS and cross-linked polystyrene (PS)), FT-IR spectroscopy (Bruker 48 series) was employed. Varian 400 MHz ^{1}H NMR using $CDCl_3$ containing TMS (tetramethylsilane) as the solvent and ^{13}C NMR also was utilized to determine the structure of isocyanate-terminated polyurethane, the TMCS, and the synthesized PS. The molecular weights of the PS were measured using a Waters GPC (gel permeation chromatography) equipped with a 510 differential refractometer and a Viscotek T50 differential viscometer by flowing PS-dissolved THF at a flow rate of 1.0 mL/min. A Philips SEM (scanning electron microscopy) 515 was used to investigate the morphology of the synthesized PS particles. The weight-average (D_w) diameter, number-average (D_n) diameter, and the uniformity (D_w/D_n) were obtained by counting 100 particles in SEM photographs using a Scion image analyzer.

Results and Discussion

The synthetic route of the TMCS was traced by observing the characteristic peaks of FT-IR spectra of the isocyanate-terminated prepolymer (Scheme 1a), the MAAm, and the TMCS as shown in Figure 1. The peaks observed at 3332 and 1716 cm^{-1} in Figure 1A are characteristic peaks of the N−H and C=O stretching from the urethane group, respectively. The strong peak of isocyanate group ($-N=C=O$) of the isocyanate-terminated prepolymer is observed at 2271 cm^{-1}. The peaks observed at 3382 and 3193 cm^{-1} in Figure 1B are characteristics of asymmetric and symmetric NH_2 stretching, respectively. The characteristic peaks of C=O stretching and NH_2 deformation are illustrated at 1666 and 1604 cm^{-1}, respectively. The C=C bond of MAAm, which is used to attach the vinyl group to TMCS, occurs very weakly at 1643 cm^{-1}. After TMCS is produced by reacting the prepolymer and MAAm, the peaks of the N−H and C=O stretching from the urethane group are observed at 3324 and 1716 cm^{-1}, the same as in Figure 1A. The characteristic peaks of C=O stretching and C=C double bond are also depicted at 1671 and 1635 cm^{-1}, respectively. However, the C=C bond and NH group at 1635 and 3324 cm^{-1}, respectively, in Figure 1C are found to shift to lower frequencies of 8 cm^{-1} than that of pure MAAm (1643 cm^{-1} in Figure 1B) and prepolymer (3332 cm^{-1} in Figure 1A). More importantly, the NH_2 peaks observed at 3382 cm^{-1} (asymmetric stretching) and 3193 cm^{-1} (symmetric stretching) in Figure 1B and the characteristic peak of the isocyanate group at 2271 cm^{-1} from the prepolymer in Figure 1A are not further observed in the FT-IR spectrum of the TMCS. Therefore, it is possible to verify the synthesis of the TMCS by comparing the FT-IR spectra of reactants prepolymer/MAAm and resultant TMCS.

Figure 2 shows the ^{13}C NMR spectra of the prepolymer and TMCS. The signals at 63.4 and 70.7 ppm (a7 and a8) in Figure 2A are a characteristic carbons peak of repeating EO (ethylene oxide) unit ($-\boldsymbol{C}H_2\boldsymbol{C}H_2O-$) from PEG and three methyl carbons peaks of the short aliphatic chain ($-\boldsymbol{C}H_2-$) from HDI are observed at 26.5, 30.3, and 41.0 ppm (a2, a4, and a6), respectively. The carboxyl carbon ($\boldsymbol{C}=O$) of urethane group is observed at 156.6 ppm (a10). Since the isocyanate group sensi-

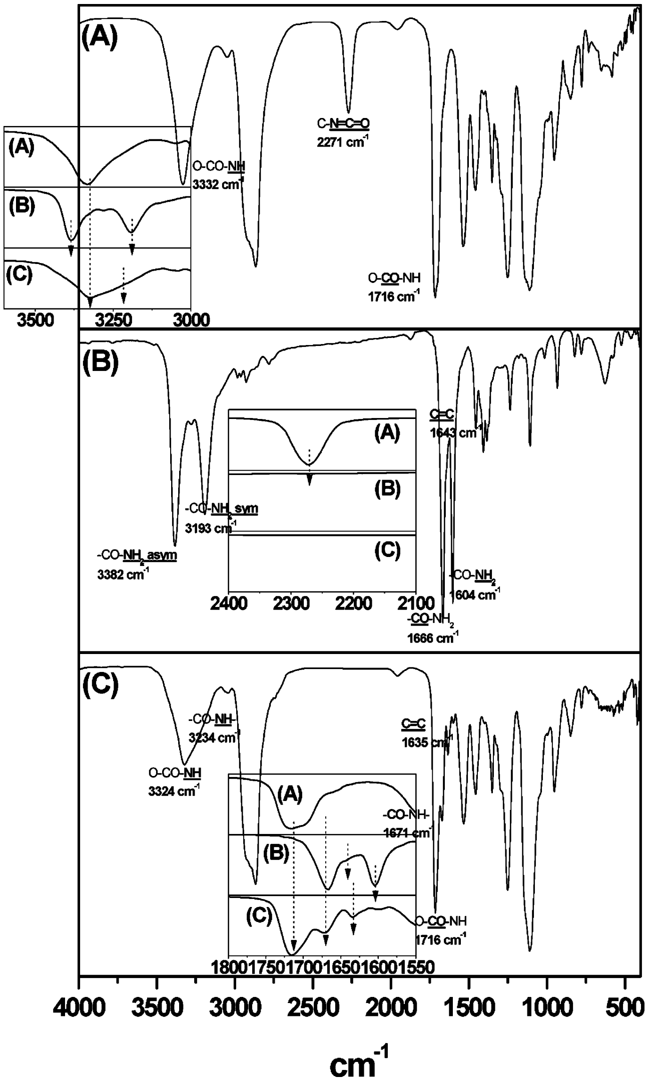


Figure 1. FT-IR spectra of (A) isocyanate-terminated prepolymer, (B) MAAm, and (C) TMCS.

tively reacts with moisture in atmosphere, the prepolymer dissolved in MEK was used to confirm its structure using ^{13}C NMR. The most important characteristic carbon signal ($-N=\boldsymbol{C}=O$) in terminal isocyanate functional group of prepolymer is detected at 122.1 ppm (a9). In Figure 2B, the ^{13}C NMR spectrum of the synthesized TMCS is represented. The characteristic signal of methyl carbon from MAAm is observed at 18.9 ppm (b1) in this spectrum. The carbon peaks of the EO repeating unit from PEG and short aliphatic chain from HDI are observed at the same position (b2, b4, b5, and b6) as found in the prepolymer (a2, a6, a7, and a8) in Figure 2A. The carboxyl carbon in urethane groups both in prepolymer and TMCS is detected at the same 156.6 ppm (a10 and b9). Since the isocyanate group was participated in the reaction with MAAm, the carbon signal in isocyanate terminal group in prepolymer observed at 122.1 ppm (a9) in Figure 2A disappears in the spectrum of TMCS. The important characteristic signals of the vinyl carbon in TMCS are detected in the range between 120 and 140 ppm. The signals at 120.9 and 139.3 ppm (b7 and b8) are attributed to methyl carbons ($\boldsymbol{C}H_2=\boldsymbol{C}H-$) of the terminal vinyl groups of TMCS. Therefore, Figure 2B clearly confirms the existence of the terminal vinyl groups in the synthesized TMCS.

The synthesized TMCS was applied in the dispersion polymerization of styrene. The TMCS-stabilized PS microspheres were successfully prepared by varying TMCS concentrations at 10 and 100 wt % relative to styrene. It is noted that the use of a high amount of TMCS of 100 wt % was to investigate the chemical structure of the resultant PS-*co*-TMCS and feasibility of the TMCS as a cross-linking agent. The formation of stable and monodisperse PS microspheres reveals that the TMCS works as a steric stabilizer by means of chemical and physical adsorption. The D_n/uniformity of the PS microspheres in Figure 3 parts A and B, are 2.59/1.018 and 1.64/1.003, respectively.

Typical ^{1}H NMR spectra of vinyl-terminated TMCS and PS prepared with 100 wt % TMCS are demonstrated in Figure 4, parts A and B, respectively. It is noted that PS microspheres prepared with 100 wt % TMCS were partially soluble CDCl$_3$ for the NMR measurement. In Figure 4A, the strong signal at 3.6 ppm (a5) characterizes EO unit ($-C\boldsymbol{H_2}C\boldsymbol{H_2}O-$) of PEG, whereas the methylene protons ($-C\boldsymbol{H_2}-$) of HDI are observed at 1.3, 1.5, and 3.2 ppm (a1, a2, and a4). The magnified view near 8.0 ppm verifies the existence of amine proton ($-N\boldsymbol{H}COO-$) of urethane group at 8.07 ppm (a8). The methylene protons ($=C\boldsymbol{H_2}$) of the vinyl

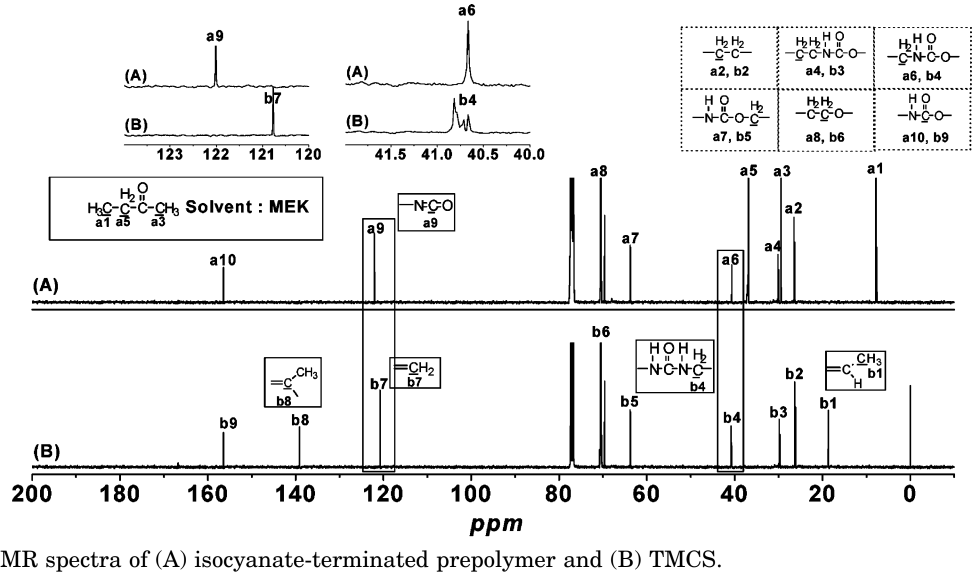


Figure 2. ^{13}C NMR spectra of (A) isocyanate-terminated prepolymer and (B) TMCS.

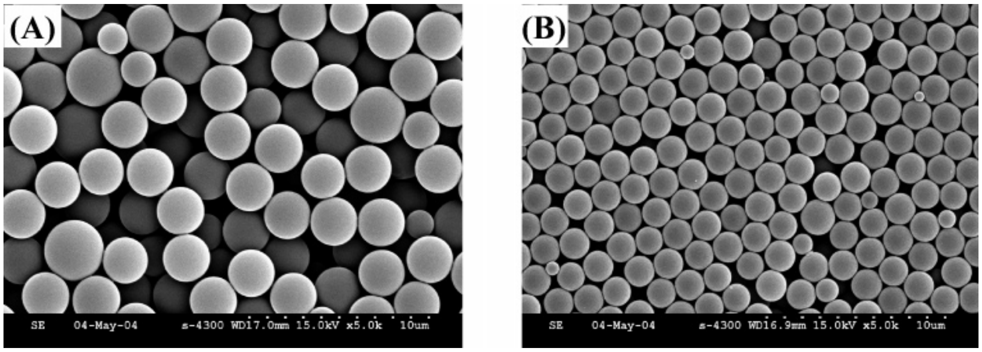


Figure 3. SEM photographs of the synthesized PS microspheres using different amounts of TMCS via dispersion polymerization, (A) 10 wt % and (B) 100 wt % relative to styrene.

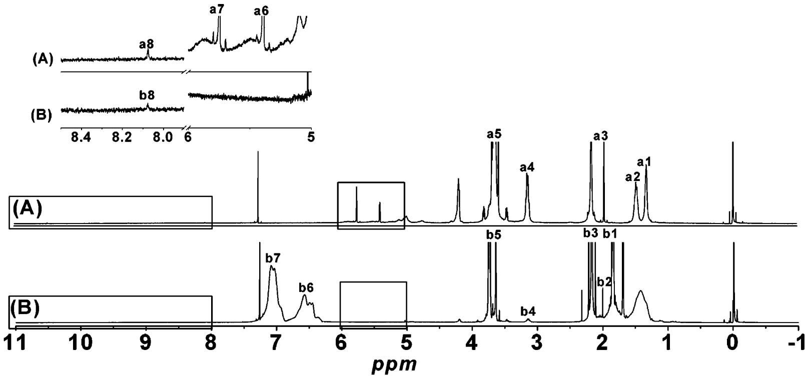


Figure 4. ^{1}H NMR spectra of (A) TMCS and (B) PS prepared with 100 wt % of TMCS. Box areas are magnified in top.

group in TMCS are detected at 5.4 and 5.7 ppm (a6 and a7) and the signal at 1.9 ppm (a3) is a characteristic peak of the methyl protons ($-\mathrm{C}\boldsymbol{H_3}$) in TMCS. The existence of TMCS in PS microspheres and reaction of TMCS with styrene monomer are further verified using the characteristic protons in urethane and vinyl groups, respectively as shown in Figure 4B. The EO unit ($-\mathrm{C}\boldsymbol{H_2}\mathrm{C}\boldsymbol{H_2}\mathrm{O}-$) of PEG is characterized in 3.6 ppm (b5) and methylene protons ($-\mathrm{C}\boldsymbol{H_2}$-) of HDI are observed at 3.2 ppm (b4) as also detected in Figure 4A. The weak signal of the urethane group ($-\mathrm{N}\boldsymbol{H}\mathrm{COO}-$) of TMCS is also observed at 8.07 ppm (c8) in ^{1}H NMR spectrum of the PS in Figure 4B. The urethane group in ^{1}H NMR spectrum of PS indicates that TMCS is reacted with styrene. Furthermore, it is clearly seen that the vinyl protons in TMCS at 5.4 and 5.7 ppm (a6 and a7 in Figure 4A) are absent after polymerization, which means that the TMCS participates in the reaction with styrene during the polymerization. In addition, the methyl protons ($-\mathrm{C}\boldsymbol{H_3}$) of TMCS at 1.9 ppm (a3) exist in Figure 4B.

The molecular weight of the PS microspheres prepared with both 10 and 100 wt % TMCS shown in Figure 3, parts A and B, are measured. In the case of 10 wt % TMCS, the resultant PS microspheres have the M_w of 201 750 g/mol and PDI of 2.57. For the 100 wt % TMCS system, the PS microspheres are not totally soluble in THF, remaining as a translucent fully swollen gel in THF. It is thought that the PS microspheres have a cross-linked structure owing to the reaction of bifunctional TMCS with styrene during the polymerization.

Conclusions

The telechelic macromonomer cross-linkable stabilizer (TMCS) was synthesized by the reaction of isocyanate-terminated prepolymer with methacrylamide. The TMCS was successfully employed as a steric stabilizer and cross-linking agent in the dispersion polymerization of styrene. The urethane and methyl groups of TMCS are found in the spectrum of PS microspheres prepared by means of TMCS. Meanwhile, the reactive double bonds of TMCS disappear after polymerization with styrene. The qualitative analysis reveals that the terminal vinyl groups of TMCS take part in the reaction with styrene during the dispersion polymerization. Since the synthesized TMCS has a symmetric molecular structure with vinyl group at chain ends, it is thought that the PS microspheres are substantially cross-linked. In reality, for the 100 wt % TMCS system the PS is not totally soluble in THF, remaining as a translucent fully swollen gel in THF. Finally, these qualitative structural investigations indicate that the TMCS serves as a reactive stabilizer as well as a cross-linking agent so that the cross-linked PS microspheres could be prepared using the bifunctional TMCS.

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