

Notes

Effect of 3rd Monomer Addition on Styrene/Styryl-Polyhedral Oligomeric Silsesquioxane (POSS) Copolymerization

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Introduction

Many studies on organic-inorganic nanocomposite materials have shown dramatic improvement of physical properties compared with pure materials by introducing inorganic particles into an organic polymeric matrix at the nanometer scale.¹⁻⁴ In particular, the use of polyhedral oligomeric silsesquioxane (POSS) nanoparticles has been demonstrated to be an efficient method in the design of hybrid materials.⁵⁻⁷ The cage-shaped POSS molecules have an empirical formula $(\text{RSiO}_{1.5})_n$ with R groups that can be hydrogen or an organic group. A typical POSS nanoparticle contains an inorganic Si_8O_{12} nanostructured skeleton surrounded by seven unreactive organic groups (e.g. isobutyl, cyclopentyl) on the corners to promote solubility in conventional solvents and one reactive group for polymerization.⁸

It was found that the syndiotactic polystyrene (sPS) can be obtained with half-titanocene complexes⁹ as well as dinuclear titanocene.¹⁰ A few works have been reported so far for the copolymerization of styrene (St) and polymerizable POSS monomer initiated with AIBN¹¹ or cyclopentadienyltitanium trichloride (Cp^*TiCl_3).⁷ On the other hand, the norbornene content could be improved by addition of 1-hexene as 3rd monomer for the copolymerization of ethylene and norbornene.¹² In this report, the effect of 4-methylstyrene (4-MeSt) as 3rd monomer had been studied for the copolymerization of St and St-POSS initiated with tetramethylcyclopentadienyltitanium trichloride (Cp^*TiCl_3).¹³ The

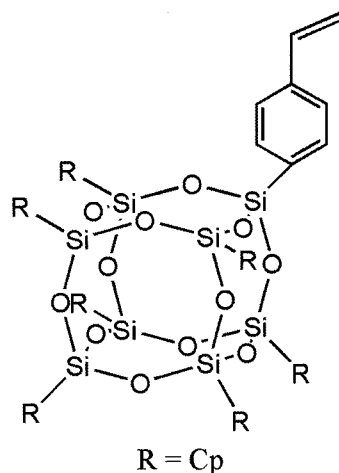
prepared polymer had been characterized in details with ¹H NMR, ¹³C NMR, XRD, DSC, TGA and GPC to examine the physical properties of polymer.

Experimental

Materials. The half-titanocenes of Cp^*TiCl_3 (Aldrich, U.S.A.) as catalyst and modified methylaluminoxane (MMAO, type-3, Al 6.9 wt% in toluene, Akzo Nobel, U.S.A.) cocatalyst were purchased and used directly. The monomers of St, 4-MeSt (Junsei Chem. Co., Japan) and toluene medium were purified with distillation. The St-POSS monomer, 1-(4-vinylphenyl)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (St-POSS, Aldrich, U.S.A.) was purchased and prepared by the described procedure.¹⁴ The structure of POSS materials was shown in Scheme I.

Procedure. The monomers, St and St-POSS without and with 4-MeSt were dissolved in toluene and were injected respectively followed by MMAO cocatalyst to glass reactor under nitrogen atmosphere. Then the half-titanocene solution was added and the polymerization started. After a fixed time, the polymerization was terminated by the addition of HCl/methanol. The copolymerization product was recovered by filtering, washed with *n*-hexane to remove the unreacted St-POSS and dried in vacuum at 60 °C for 24 h. From the weight of obtained copolymer, the catalyst activity (kg-polymer/mol-Ti·h) was estimated.

Characterization. The ¹H and ¹³C NMR spectra were taken on a NMR spectrophotometer (Bruker Avancel, 400 and 100 MHz, U.S.A.) at room temperature with chloroform-*d* as solvent. With ¹H NMR spectra the copolymer composition was decided,¹⁵ while the racemic triad [rr] of copolymer was estimated with ¹³C NMR spectra.¹⁶ The syndiotactic index (SI) of copolymer was measured by the extraction of copolymer with methylethylketone (MEK) for



Scheme I. Structure of St-POSS.

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10 h.¹⁷

The X-ray diffraction patterns of copolymers were recorded on an X-ray diffractometer (PW1830, Philips, Netherlands) with Cu K α -Ni filtered radiation at $2\theta=5^\circ$ - 40° in step angle $=0.02^\circ$.

The transition temperatures were determined by differential scanning calorimetry (DSC, DuPont TA 4000, TA Instruments, U.S.A.) operating at a heating rate of $10^\circ\text{C}/\text{min}$. The materials were cooled down from melt (300°C) to 30°C , and the glass transition temperature (T_g) and melting point (T_m) were determined in the second scan. Thermogravimetric analysis (TGA, Shimadzu TGA-50, Japan) was carried out at a heating rate of $10^\circ\text{C}/\text{min}$ from 25 to 650°C under a continuous nitrogen purge ($20\text{ mL}/\text{min}$).

The determination of molecular weight and its distribution were carried out by gel permeation chromatography (GPC, Waters 150C) with 1,2,4-trichlorobenzene (TCB) solvent at 140°C . The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were calculated in the reference of standard polystyrene.

Results and Discussion

The copolymerization of St and St-POSS monomer without and with 4-MeSt had been carried out in toluene with half-titanocenes of Cp^{*}TiCl₃ catalysts conjunction with MMAO. For the exact physical characterization of polymeric material, the purification procedure of polymer product is critical in removal of the unreacted monomers and impurity. Although it has inorganic siloxane cage, St-POSS is soluble in *n*-hexane, THF and toluene due to the bulky organic cyclopentyl groups. During the recovery procedure of copolymer from the reaction mixture with methanol, the unreacted St-POSS monomer and polymer was coprecipitated and mixed with each other. Therefore the purification of the polymer was washed the precipitated powder with *n*-hexane to remove the unreacted St-POSS.¹³ After removing the unreacted monomer, the experimental results are shown in Table I.

The St/St-POSS/4-MeSt terpolymerization had a higher activity and conversion than St/St-POSS copolymerization, which could be explained in terms of the electron donating effect of CH₃ substituent of 4-MeSt¹⁸ or the higher monomer reactivity ratio ($r_{St}=0.40$, $r_{4-MeSt}=1.47$) of 4-MeSt.¹⁹ The

St-POSS content in polymer increased with the addition of 4-MeSt as 3rd monomer as reported previously,¹² which could be correspond to the higher reactivity between 4-MeSt and St-POSS than St with St-POSS.

The stereoregularity of sPS could be evaluated with syndiotactic index (SI) and racemic triad [rr], which were determined by MEK extraction¹⁷ and ¹³C NMR,¹⁶ respectively. As given in Table I, SI of polymer having a higher 4-MeSt content (more than 12.4 mol%) could not be measured due to the complete dissolution of copolymer in MEK. The [rr] value of copolymer decreased from 89% to 36% with increasing 4-MeSt content up to 18.7 mol%, which suggested that the stereoregularity of Cp^{*}TiCl₃ catalyst was disturbed by the addition of 3rd monomer.

The crystal structure of St-POSS monomer and St/St-POSS copolymer as well as St/St-POSS/4-MeSt terpolymer was studied, and the obtained XRD patterns were given in Figure 1.

The crystalline sPS is polymorphism and have α -, β -, γ - and δ -forms of crystal.²⁰ As far as XRD analysis is concerned, the α -form is characterized by a diffraction peak at $2\theta=7.7^\circ$, 11.7° , 14.0° , 20.1° , the β -form at $2\theta=6.1^\circ$, 12.3° , 13.6° , 20.2° , the γ -form at $2\theta=9.1^\circ$, 16.3° , 20.1° , 28.0° , and the δ -form at $2\theta=17.4^\circ$, 20.1° , 23.6° , 28.0° .²¹ As shown in Figure 1, the characteristic peaks of St-POSS monomer (a) appeared

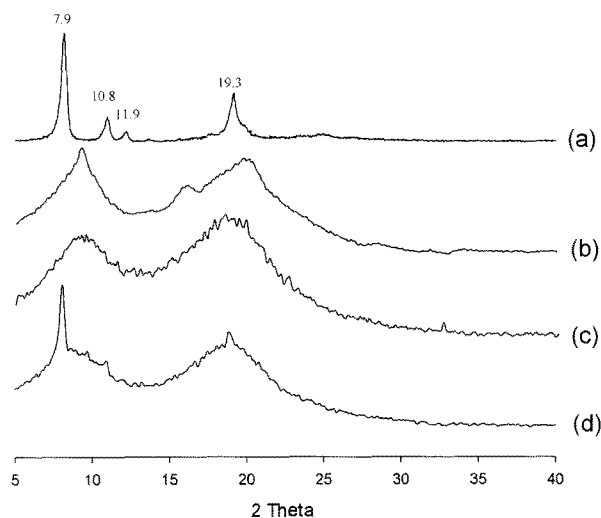


Figure 1. XRD patterns of St-POSS monomer (a), St/St-POSS (0.7 mol%) copolymer (b) and St/St-POSS/4-MeSt terpolymers with various 4-MeSt contents (mol%) of 12.4 (c) and 18.7 (d).

Table I. Addition of 4-MeSt for St/St-POSS Copolymerization Initiated with Cp^{*}TiCl₃ and MMAO

St/St-POSS/4-MeSt (mol/L)	Activity ^a	Conversion (wt%)	St/St-POSS/4-MeSt ^b (mol%)	S.I (wt%)	[rr]
0.99/0.01/0.00	136	15.0	99.3/0.7/-	43	89
0.89/0.01/0.10	343	34.3	86.8/0.8/12.4	27	68
0.88/0.02/0.10	460	42.1	79.4/1.9/18.7	-	36

^aPolymerization conditions: [Ti]= 5.5×10^{-5} mol/L, [Al]/[Ti]=1000, 70°C , 2 h. ^aActivity: kg polymer/(mol-Ti·h). ^b4-MeSt and St-POSS content in copolymer determined by ¹H NMR.

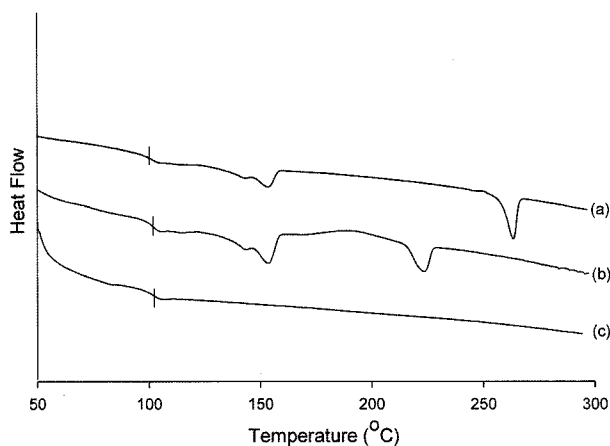


Figure 2. DSC chromatograms of St/St-POSS (a) and St/St-POSS/4-MeSt polymers with various 4-MeSt content (mol%) of 12.4 (b), and 18.7 (c).

at $2\theta=7.9^\circ, 10.8^\circ, 11.9^\circ, 19.3^\circ$. And the St/St-POSS copolymer (b) exhibited diffraction peaks at $2\theta=9.1^\circ, 16.3^\circ, 17.4^\circ, 20.1^\circ, 28^\circ$ suggesting the γ - and δ -form of crystal. For St/St-POSS/4-MeSt (12.4 mol%) terpolymer, the diffraction peak became broader or disappeared meaning that the crystallinity decreased, so the polymorphic behavior of sPS was altered by the introduction of 4-MeSt units. And the XRD patterns of Figure 1(d) (18.7 mol% 4-MeSt), the peak at $2\theta=7.9^\circ, 10.8^\circ, 11.9^\circ, 19.3^\circ$ became clear and sharper that it could be correspond to the higher content of St-POSS in the terpolymer.

To examine the effect of 3rd monomer content on T_g and T_m of the polymer, the polymer was carried out with DSC analysis of polymers was carried out as shown in Figure 2, and it revealed that T_g of terpolymers (from 101 to 102 °C) was slightly higher than copolymer (100 °C) due to the introduction of 4-MeSt as the 3rd monomer.²²

For St/St-POSS copolymer and St/St-POSS/4-MeSt (12.4 mol%) terpolymer, three endothermic peaks were appeared; the lower two peaks (ca. 150 °C) were correspond to the crystalline form transition of polymer that from crystalline δ -form transform into γ -form firstly and subsequently into α -form.²¹ The higher peak (264 °C for St/St-POSS copolymer and 223 °C for St/St-POSS/4-MeSt (12.4 mol%) terpolymer) could be ascribed to the crystallization (melting) peak of sPS unit. For St/St-POSS/4-MeSt (12.4 mol%) terpolymer, the melting peak decreased to 223 °C by introduction of 4-MeSt. For St/St-POSS/4-MeSt terpolymer, the melting peak disappeared for 18.7 mol% 4-MeSt and 1.9 mol% St-POSS content in the terpolymer. This phenomenon was not surprised because the introduction of 4-MeSt and POSS can decrease the melting temperature, and also the melting peaks could disappeared with an increase in 4-MeSt content.^{18,23} The heat of fusion (ΔH) of St/St-POSS copolymer was determined to be 5 J/g, whereas ΔH of St/St-POSS/4-MeSt terpolymer dropped to 3 J/g for 12.4 mol% 4-MeSt. On the

other hand, it had been known that the ΔH of sPS is 27 J/g.¹³ The degree of crystallization calculated with 100% crystalline sPS ($\Delta H=53.2$ J/g)²⁴ was 9%, 6%, 0% for St/St-POSS copolymer incorporated with 0, 12.4, 18.7 mol% of 4-MeSt, respectively.

The influence of 4-MeSt addition on the thermal behavior of St/St-POSS copolymer was evaluated by means of TGA analysis. By introduction of 4-MeSt as the 3rd monomer, the degradation temperature (T_d) and char yield of copolymer increased gradually with the 4-MeSt content; T_d of St/St-POSS copolymer was 444 °C, while T_d of St/St-POSS/4-MeSt terpolymer was 453 and 458 °C for 12.4 and 18.7 mol% of 4-MeSt, respectively. And the char yield recorded under nitrogen increased considerably to be 3 wt% for St/St-POSS copolymer, 5 and 7 wt% for St/St-POSS/4-MeSt (12.4 and 18.7 mol% 4-MeSt) terpolymers.

To know the 3rd monomer effect on molecular weight and its distribution of the copolymers, the copolymers were characterized by GPC chromatograms as shown in Figure 3, and M_n , M_w and PDI were calculated as given in Table II.

From Table II, it could be considered that the effect of 4-MeSt addition on M_n , M_w and PDI of St/St-POSS copolymer was not remarkable. As shown in Figure 3, the GPC chromatogram was bimodal and not changed by the introduction of the 4-MeSt monomer. The bimodal could be ascribed to the catalyst active site supported on POSS.¹³

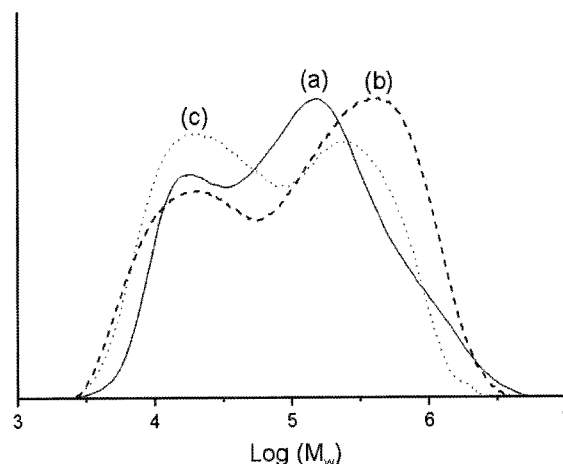


Figure 3. GPC chromatograms of St/St-POSS (a) and St/St-POSS/4-MeSt polymers with various 4-MeSt content (mol%) of 12.4 (b), and 18.7 (c).

Table II. Molecular Weights and PDI of St/St-POSS Copolymers with and Without 4-MeSt

St/St-POSS/4-MeSt Content (mol%)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PDI
99.3/0.7/-	23	105	4.6
79.6/0.8/12.4	26	118	4.6
79.4/1.9/18.7	24	98	4.1

Conclusions

Copolymerization of St and St-POSS with and without 4-MeSt was carried out with half-titanocenes of Cp*TiCl₃ catalyst and MMAO cocatalyst. The activity of catalyst and St-POSS content increased by the addition of 4-MeSt as the 3rd monomer. The characteristic crystalline peak of St/St-POSS copolymer was altered by incorporating of 4-MeSt. With increasing 4-MeSt contents, the glass transition temperature of the polymers increased and the thermal stability was improved. The molecular weight and PDI of the polymers were not changed significantly with the incorporation of 4-MeSt.

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