

PREPARATION AND PROPERTIES OF MMA/1-PROPYLMETHACRYLATE-POSS COPOLYMER WITH ATOM TRANSFER RADICAL POLYMERIZATION*

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Abstract The methyl methacrylate (MMA)/1-propylmethacrylate-polyhedral oligomeric silsesquioxane (PM-POSS) copolymers were synthesized *via* atom transfer radical polymerization with CuBr as catalyst. The unreacted PM-POSS monomer could be removed completely by washing the copolymerization product with *n*-hexane. The copolymers were characterized with ¹H-NMR, X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis and gel permeation chromatography. With increasing PM-POSS feed ratio, the total conversion increased while the glass transition temperatures of copolymer decreased. The thermogravimetric analysis demonstrated that the thermal stability of copolymer improved slightly with PM-POSS addition. The molecular weight of copolymers increased with incorporation of PM-POSS.

Keywords: Methyl methacrylate (MMA); Polyhedral oligomeric silsesquioxane (POSS); Copolymer; ATRP.

INTRODUCTION

The atom transfer radical polymerization (ATRP) is today one of the most effective protocols available to achieve controlled/living radical polymerizations of a wide range of monomers^[1]. In ATRP, the reaction is initiated by an alkyl halide activated by a copper catalyst, and termination reactions are mostly suppressed because a rapid equilibrium occurs between dormant and active propagating species^[2]. Different vinylic monomers, *e.g.*, styrenes^[3], acrylates and methacrylates^[4] have been successfully polymerized and copolymerized in a controlled fashion using ATRP techniques, providing polymers with low polydispersities.

Recently, a novel class of hybrid polymers has been developed by using various polyhedral oligomeric silsesquioxane (POSS) derivatives. These materials have shown the novel and often improved mechanical, thermal, electronic, magnetic, and optical properties^[5, 6]. A typical POSS nanoparticle contains an inorganic Si₈O₁₂ nanostructured skeleton surrounded by eight organic groups labeled R (*e.g.* isobutyl, cyclopentyl, or cyclohexyl) on the corners, where one at least is reactive. This reactive group has afforded the opportunity to incorporate inorganic POSS cages into organic matrices through copolymerization^[7].

In this paper, the methacrylate-functional POSS monomer was applied to copolymerization with MMA using ATRP method. The structure and properties of copolymers were characterized with ¹H-NMR, X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis and gel permeation chromatography.

EXPERIMENTAL

Materials

3-(3,5,7,9,11,13,15-Heptaisobutylpentacyclo[9.5.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxan-1-yl)propylmethacrylate (shortly, 1-

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propylmethacrylate-POSS and PM-POSS, Aldrich, U.S.A.) was purchased and used after drying. Methyl methacrylate was purified by distillation from CaH_2 . CuBr (Shinyo Pure Chemicals Co., Ltd., Japan) was purified according to literature procedure^[8]. 2,2'-Bipyridine (BPY) and methyl 2-bromopropionate (MBP) (Tokyo Chemical Industry Co., Ltd., Japan) were purchased and used as received.

Polymerization

The monomers (MMA and PM-POSS) were dissolved in toluene and was injected respectively followed by catalyst, CuBr and ligand, BPY^[8] to glass reactor. Then the initiator, MBP^[2] was added and the polymerization started. After 12 h, polymerization was terminated by the addition of methanol. The copolymer was recovered by filtering, washed with *n*-hexane to remove the unreacted PM-POSS and dried in vacuum at 60°C for 24 h.

Characterization

The ^1H -NMR spectra were taken on a 400 MHz NMR spectrometer (Avance Digital, U.S.A.) at room temperature with chloroform-*d* as solvent.

The X-ray diffraction patterns of copolymers were recorded on an X-ray diffractometer (PW1830, Philips, Netherlands) with $\text{CuK}\alpha$ radiation.

The melting temperatures were determined by differential scanning calorimetry (DSC, DuPont TA 2000, TA Instruments, U.S.A.) operating at a heating rate of 10 K/min. The materials were cooled down from melt (200°C) to 30°C at a rate of 10 K/min, and the melting point was determined in the second scan. Thermogravimetric analysis (TGA, TGA-50, Shimadzu, Japan) was carried out at a heating rate of 10 K/min from 25°C to 650°C under a continuous nitrogen purge (20 mL/min).

Gel permeation chromatography (GPC, Alliance GPC V2000) was used to analyze polymers molecular weight, and the analysis was carried out at 25°C with THF as solvent.

RESULTS AND DISCUSSION

Preparation and Structure of MMA/PM-POSS Copolymer

The ATRP of MMA with PM-POSS was carried out in toluene with CuBr, BPY and MBP at 90°C ([monomer]:[MBP]:[CuBr]:[BPY] = 200:1:1:1). For the exact physical characterization of polymeric material, the purification procedure of copolymer product is critical in removal of the unreacted PM-POSS monomers and impurity.

There is an amount of unreacted PM-POSS in the products after copolymerization and the pure PM-POSS could dissolve in *n*-hexane and THF, so the copolymers were washed with *n*-hexane to remove the unreacted PM-POSS monomer. After washing with *n*-hexane, the solid product was analyzed with GPC as shown in Fig. 1.

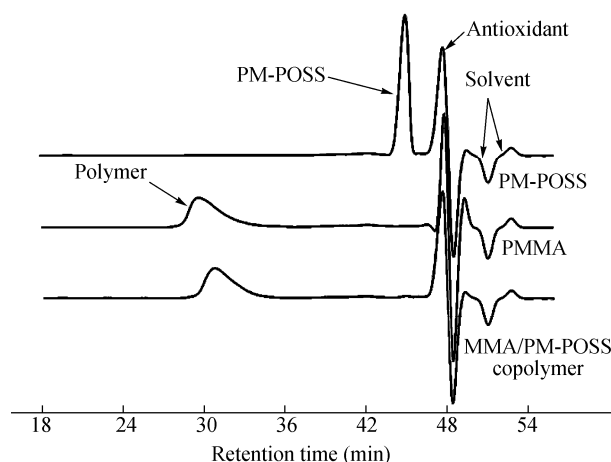


Fig. 1 GPC chromatograms of PM-POSS, PMMA and MMA/PM-POSS copolymer

For MMA/PM-POSS copolymer after treating with *n*-hexane, no peak of PM-POSS comonomer was observed indicating that the unreacted PM-POSS was removed completely by washing with *n*-hexane.

The experimental data of PM-POSS feed ratio, yields, copolymer composition and molecular weight are shown in Table 1. With the addition of PM-POSS, the yield and the total conversion of copolymers increased slightly. The composition of copolymer was obtained with 3-H peak^[9] relative to 9,10-H ones^[10] of ¹H-NMR spectrum of Fig. 2. As expected, the incorporation of PM-POSS in copolymers increased with PM-POSS feed ratio. The PM-POSS mol% of final copolymer was systematically less than the feed mol%, even though the difference was not so big. Such a trend has already been observed with AIBN initiation^[11]. The monomer reactivity ratio obtained by Fineman-Ross method^[12] was found to be $r_{\text{MMA}} = 1.19$ and $r_{\text{PM-POSS}} = 0.68$. On the other hand, the reported values^[13] were $r_{\text{MMA}} = 1.61$ and $r_{\text{PM-POSS}} = 0.58$.

Table 1. Copolymerization of MMA and PM-POSS with ATRP^a

Feed ratio (mol%)		Yield (g)	Total conversion (wt%)	POSS content (mol%) ^b	POSS conversion (wt%)	T_{dm} (°C)	$M_w (\times 10^3)$	PDI
MMA	PM-POSS							
100.0	—	2.26	48	—	—	365	36	1.1
98.9	1.1	2.60	53	0.97	44	368	55	1.2
97.7	2.3	3.46	60	1.81	51	367	64	1.2
96.7	3.3	3.74	61	3.04	57	360	68	1.3
95.5	4.5	4.05	62	3.85	56	371	65	1.2

^aExperimental conditions: [Monomer] = 4.7 mol/L, [monomer]:[MBP]:[CuBr]:[BPY] = 200:1:1:1, Temperature = 90°C, Reaction time = 12 h; ^bAs determined by ¹H-NMR

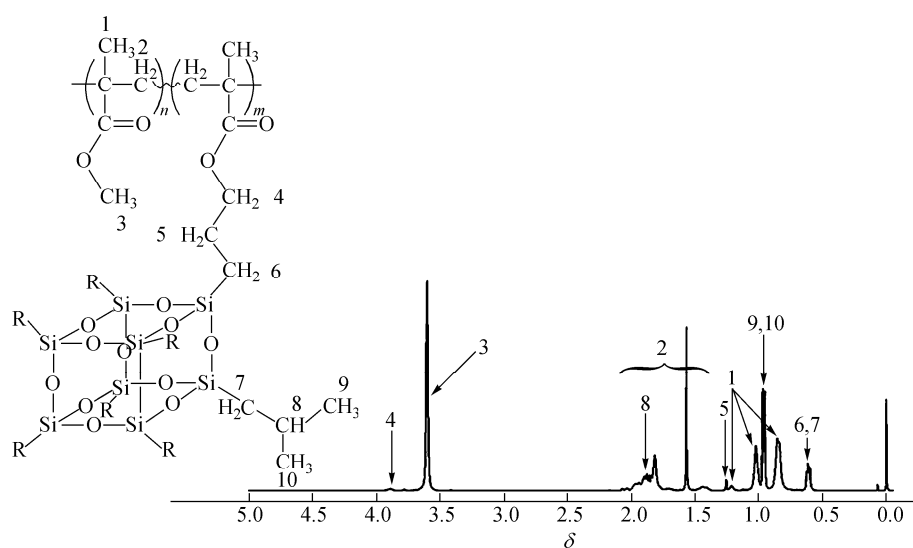


Fig. 2 ¹H-NMR spectrum of MMA/PM-POSS copolymer

The X-ray scattering profiles of PMMA, PM-POSS and MMA/PM-POSS copolymers are shown in Fig. 3. The pure PMMA exhibited reflections at 2θ 's of 12° and 30° and PM-POSS at 3°–4° respectively. The shape of the first most intense peak reflects the ordered packing of polymer chains while the second peak denotes the ordering inside the main chains^[14]. As the PM-POSS content increased, the reflections ($2\theta = ca. 5^\circ$) from PM-POSS component increased in intensity and sharpness while the PMMA reflections became weaker and broader. From this observation, it was confirmed that the PM-POSS cages formed the aggregation to crystalline domain^[15].

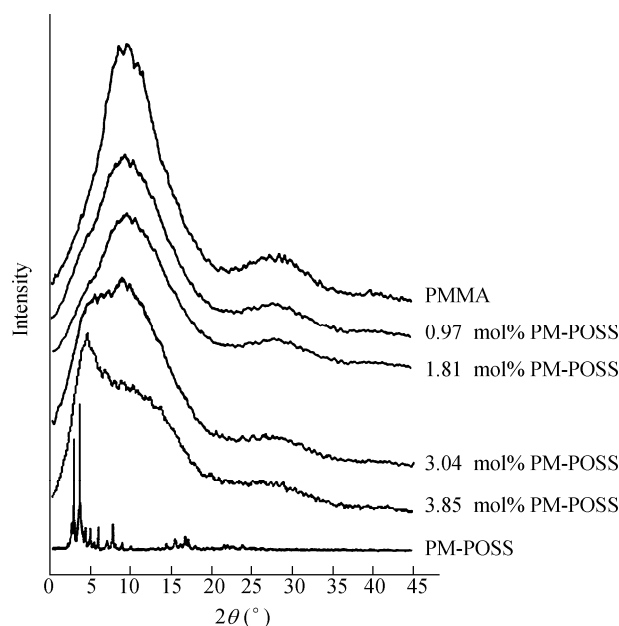


Fig. 3 X-ray diffraction patterns of PMMA, PM-POSS and MMA/PM-POSS copolymers

Properties of MMA/PM-POSS Copolymers

The thermal analysis of MMA/PM-POSS copolymers revealed that the glass-transition temperature (T_g) of copolymers decreased with increasing of PM-POSS content as shown in Fig. 4. The T_g of MMA/PM-POSS copolymer decreased with increasing of PM-POSS feed ratio because of the diluent effect of PM-POSS comonomer to reduce the self-association of MMA. This observation was similar to the result for MMA/PM-POSS copolymers prepared with AIBN^[11].

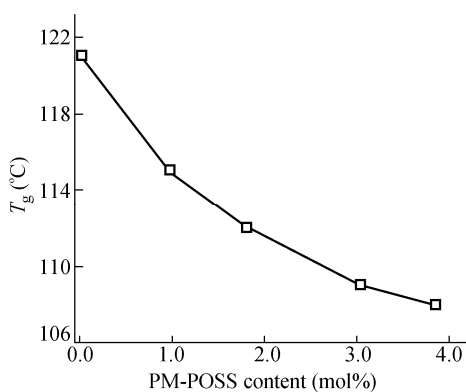


Fig. 4 Effect of PM-POSS content on T_g

The maximum degradation temperature (T_{dm}) obtained with TGA operated under nitrogen atmosphere increased slightly with PM-POSS content as given in Table 1, and the onset temperature of degradation was found in the range of 310–350°C.

The weight-average molecular weight of copolymer was higher than that of PMMA and increased with PM-POSS content. The polydispersity index (PDI) was found to be 1.1–1.3 and no significant change was observed as the typical ATRP system.

CONCLUSIONS

The hybrid copolymer of MMA and PM-POSS was synthesized *via* ATRP method. By washing the copolymerization product with *n*-hexane, the unreacted PM-POSS could be removed completely. The yield of copolymers increased with incorporation of PM-POSS comonomer. With increasing PM-POSS contents, the T_g of copolymers decreased while T_{dm} improved slightly. The molecular weights of copolymers increased with incorporation of PM-POSS and PDI of copolymer exhibited the narrow molecular weight distribution.

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