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NOTE

Inclusion of fullerene in polymer chains grafted on silica nanoparticles in an organic solvent

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Fullerene has received much interest for applications in smart and functional materials owing to its characteristic properties, such as electron-accepting or -releasing capacity, high refractive index, high heat conductivity and absorption in the UV region. So far, a number of papers have reported fundamental and practical studies employing modified or unmodified fullerenes in applications such as solar cell devices, fillers and semiconductors.[1–4] In most cases, a surface modification of fullerenes was performed to promote dispersion or to increase the solubility of the fullerenes in solution.[5] However, surface modification by a covalent bond sometimes spoils the innate properties of fullerene. Furthermore, the addition of surfactants causes fullerene to leak from the final products and contaminate the environment. In this regard, in our previous study we showed that a polymer dispersant, poly(methyl methacrylate-co-2-naphthyl methacrylate) (poly(MMA-NMA)), effectively disperses fullerene in an organic solvent without spoiling the original properties of fullerene.[6]

Silica is widely used as a raw material in many applications, including paints, fillers of plastics, carriers of catalysts, supports in heterogeneous organic synthesis and stationary phase of chromatography, owing to its nontoxicity, stability and availability. A recent development in colloid chemistry also made it possible to control the size of the colloidal inorganic particles ranging from nanometer to micrometer size.[7] Nanometer-sized colloidal silica is an especially attractive material owing to its spherical shape, colorlessness and high stability in an aqueous solution. An aqueous solution containing colloidal silica $< 20\,nm$ is usually transparent. Therefore, polymer composites consisting of fairly well-dispersed fullerene and silica nanoparticles can result in the fabrication of unique functional materials, that is, silica-reinforced and heat-conductive transparent composites. In this study, the inclusion of fullerene (C_{60}) into poly(MMA-NMA) chains grafted on silica particles 12 nm in diameter in tetrahydrofuran (THF) without formation of C_{60} clusters and fabrication of transparent hybrid films composed of C_{60} and poly(MMA-NMA)-grafted silica composite were investigated.

According to our previous study,[6] the poly(MMA-NMA)s to MMA/NMA mole ratio of 1/6 to 1/15, and around number average molecular weight (M_n) = 10 000 was effective as a dispersant of C_{60} in methyl methacrylate (MMA); therefore, the grafting copolymers were employed at a mole ratio ranging from 1/7 to 1/14.

EXPERIMENTAL PROCEDURE

Materials
A colloidal silica aqueous sol, containing 30 wt% SiO_2 9.1 nm in diameter and with a polydispersity index of 0.127, was kindly provided by Nikki Catalysts & Chemical Co. Ltd, Kanagawa, Japan. Colloidal silica suspended in ethanol was prepared by solvent exchange with azeotropic evaporation of water after the addition of ethanol to the original aqueous solution. Fullerene (C_{60}), Nanom purple ST, was purchased from Frontier Carbon Co. Ltd, Tokyo, Japan. MMA and other chemicals were obtained from Wako Chemicals Co. Ltd, Osaka, Japan. (3-Aminopropyl) trimethoxysilane was purchased from Kanto Chemicals Co. Ltd, Tokyo, Japan.

Measurements
The M_n and polydispersity (M_w/M_n) of the synthesized polymers were determined by gel permeation chromatography on columns containing TSK gels G4000H$_6$ and G5000H$_6$ (Tosoh Co. Ltd, Yamaguchi, Japan) at 35 °C, using THF as an eluent at a flow rate of 0.8 ml min^{-1} and calibrated with a polystyrene standard. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 400 (400 MHz), Karlsruhe, Germany. The amounts of grafted polymer were determined by a thermal gravimetric analysis on a TG-50, Shimadzu Co. Ltd, Kyoto, Japan, while elevating the temperature up to 800 °C at a heating rate of 10 °C min^{-1}. The particle size was determined by dynamic light scattering on an Otsuka Electronics DLS-7000 spectrophotometer equipped with a He-Ne laser (10 mW, 633 nm). The transmission spectra of the hybrid films were recorded on a multichannel spectrometer, Ohtsuka MCPD-3700, Osaka, Japan.

Synthesis of NMA
This compound was synthesized by the usual method that employs 2.8 g 2-naphthol, 3.0 ml methacryloyl chloride, 10.0 ml N,N,N-triethylamine and 18 ml chloroform. Recrystallization from the methanol/water cosolvent (80/

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20 vol) and drying under reduced pressure yielded 3.3 g 2-naphthyl methacrylate (NMA). ^{1}H NMR (CDCl$_3$): 2.10 (*s*, CH$_3$), 5.79 (*d*, CH$_2$), 6.40 (*d*, CH$_2$), 7.26 (*d*, 3-*H* (naphthyl)), 7.46 (*t*, 8-*H* (naphthyl)), 7.49 (*t*, 7-*H* (naphthyl)), 7.59 (*s*, 11-*H* (naphthyl)), 7.80 (*d*, 6-*H* (naphthyl)), 7.85 (*d*, 4-*H* (naphthyl)), 7.86 (*d*, 9-*H* (naphthyl)) p.p.m.

Synthesis of trimethoxysilyl-terminated poly(MMA-NMA)

The polymer silanes were synthesized by following three methods, shown in Scheme 1.

Method 1.[8] A mixture of 2.6 ml MMA, 0.40 g NMA and 10 ml THF solution containing 14 mg (3-mercaptopropyl)trimethoxysilane and 5 mg 2,2′-azobis(isobutylonitrile) was put into a 50-ml flask thoroughly purged with nitrogen. The mixture was stirred at 75 °C for 8 h. Precipitating with diethyl ether and drying under reduced pressure produced 1.5 g polymer silane **1** of MMA/NMA with a mole ratio = 14/1, $M_n = 7400$ and $M_w/M_n = 2.02$. ^{1}H NMR (CDCl$_3$): 0.84 (*s*, CH$_3$), 1.02 (*s*, CH$_3$), 1.34–1.67 (broad, CH$_2$), 1.71–2.22 (broad, CH$_2$), 3.59 (*s*, CH$_3$), 7.26 (*m*, 3-*H* (naphthyl)), 7.40–7.54 (broad, 8-*H*, 9-*H* (naphthyl)), 7.58 (broad, 10-*H* (naphthyl)), 7.55–7.90 (broad, 4-*H*, 6-*H*, 9-*H* (naphthyl)) p.p.m.

Method 2.[9] A mixture of 3.6 ml MMA, 0.70 g NMA and 10 ml THF solution containing 12 mg 4,4′-azobis(cyanovaleric acid) was put into a 50-ml flask thoroughly purged with nitrogen. The mixture was stirred at 55 °C for 12 h.

Precipitating with methanol and drying under reduced pressure produced 2.4 g carboxyl-terminated polymer of MMA/NMA mole ratio = 7/1, $M_n = 48\,000$ and $M_w/M_n = 2.28$. ^{1}H NMR (CDCl$_3$): 0.85 (*s*, CH$_3$), 1.02 (*s*, CH$_3$), 1.46–1.60 (*m*, CH$_2$), 1.73–2.17 (*m*, CH$_2$), 3.60 (*s*, CH$_3$), 7.26 (*m*, 3-*H* (naphthyl)), 7.40–7.54 (broad, 8-*H*, 9-*H* (naphthyl)), 7.58 (broad, 10-*H* (naphthyl)), 7.55–7.90 (broad, 4-*H*, 6-*H*, 9-*H* (naphthyl)) p.p.m. A mixture of 2.4 g carboxyl-terminated poly(MMA-NMA), 15 mg *N,N*′-dicyclohexylcarbodiimde and 30 ml chloroform was put into a 50-ml flask. The mixture was stirred in an ice bath for 30 min. After the addition of 50 mg (3-aminopropyl)trimethoxysilane to the mixture, the resultant solution was stirred at room temperature for 5 h. After removing *N,N*′-dicyclohexylurea by filtration, precipitating with methanol and drying under reduced pressure produced 1.9 g polymer silane **2**. ^{1}H NMR (CDCl$_3$): 0.84 (*s*, CH$_3$), 1.02 (*s*, CH$_3$), 1.31–1.68 (broad, CH$_2$), 1.71–2.18 (broad, CH$_2$), 3.60 (*s*, CH$_3$), 7.26 (*m*, 3-*H* (naphthyl)), 7.40–7.54 (broad, 8-*H*, 9-*H* (naphthyl)), 7.58 (broad, 10-*H* (naphthyl)), 7.55–7.90 (broad, 4-*H*, 6-*H*, 9-*H* (naphthyl)) p.p.m.

Method 3.[10] A mixture of 2.0 ml MMA, 0.35 g NMA, 1.5 ml dry anisol containing 10 mg 4-(1-bromoethyl)benzoic acid, 5.0 ml *N,N,N″,N″,N″*-pentamethyldiethylenetriamine and 1.2 mg CuBr was put in a test tube. The test tube was purged with nitrogen during four freeze-and-thaw cycles. After sealing the tube, the solution was stirred at 85 °C for 14 h. Precipitating with methanol and drying under reduced pressure produced 1.1 g carboxyl-terminated poly(MMA-NMA) of MMA/NMA with a mole ratio = 8/1,
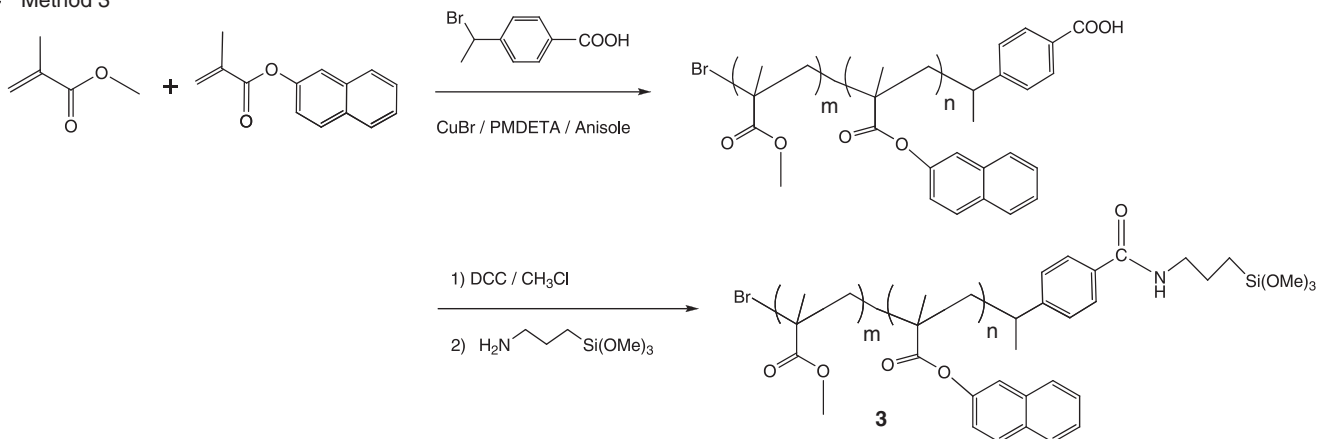
a Method 1
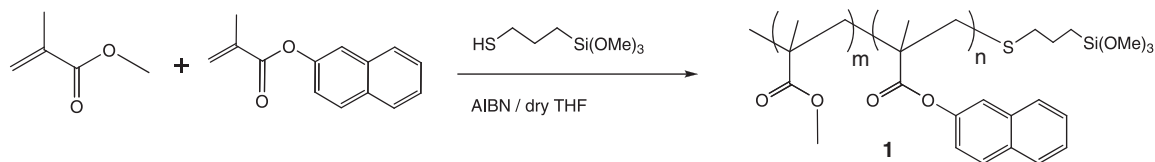
b Method 2
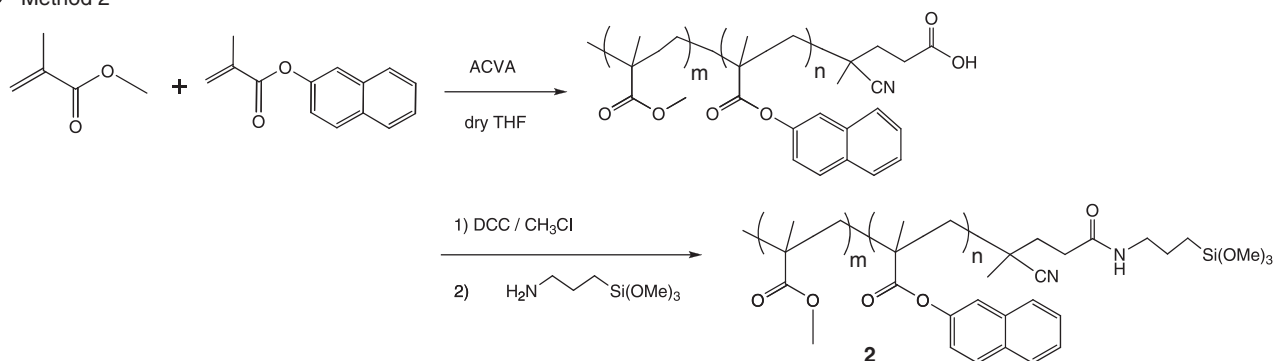
c Method 3

Scheme 1 Syntheses of polymeric silanes **1**, **2** and **3**.

$M_n = 71\ 800$ and $M_w/M_n = 1.16$. ^{1}H NMR (CDCl$_3$): 0.85 (s, CH$_3$), 1.02 (s, CH$_3$), 1.13–1.32 (broad, CH$_2$), 1.71–2.14 (broad, CH$_2$), 3.60 (s, CH$_3$), 7.26 (m, 3-H (naphthyl)), 7.40–7.54 (broad, 8-H, 9-H (naphthyl)), 7.58 (broad, 10-H (naphthyl)), 7.55–7.90 (broad, 4-H, 6-H, 9-H (naphthyl)) p.p.m. Coupling the reaction of 1.1 g carboxyl-terminated polymer with 2.8 g (3-aminopropyl)trimethoxysilane in the presence of N,N'-dicyclohexylcarbodiimde was performed by the same method as described in Method 2. After removing N,N'-dicyclohexylurea by filtration, precipitating with methanol and drying under reduced pressure, 0.90 g polymer silane 3 was produced. ^{1}H NMR (CDCl$_3$): 0.84 (s, CH$_3$), 1.02 (s, CH$_3$), 1.31–1.68 (broad, CH$_2$), 1.71–2.18 (broad, CH$_2$), 3.60 (s, CH$_3$), 7.26 (m, 3-H (naphthyl)), 7.40-7.54 (broad, 8-H, 9-H (naphthyl)), 7.58 (broad, 10-H (naphthyl)), 7.55–7.90 (broad, 4-H, 6-H, 9-H (naphthyl)) p.p.m.

Reaction of copolymer silane with colloidal silica
A typical run went as follows. A mixture of 0.160 g polymer silane 1 (mole ratio MMA/NMA = 14/1), 0.40 ml silica ethanol sol, containing 0.109 g SiO$_2$ and 20 ml THF was stirred at room temperature for 5 h. Next, 1.0 g silica gel, Wako gel C-300, was added to the suspension to remove unreacted polymer silane and its condensed products.[11] After the addition of 100 ml THF and removing the silica gel by centrifugation, the supernatant suspension containing poly(MMA-NMA)-grafted silica was available for the following experiments. After evaporation of the aliquot of the supernatant and drying under reduced pressure, the amount of grafted polymer on the silica was determined by thermal gravimetric analysis. The amounts of grafted polymer and size distribution of the poly(MMA-NMA)-grafted silica were listed in Table 1.

Inclusion of C$_{60}$ into poly(MMA-NMA) chains grafted on silica
A typical run went as follows. The poly(MMA-NMA)-grafted silica of 27.9 mg, composed of 11.2 mg SiO$_2$, was added to the THF suspension (3.00 ml) containing 0.068 mg g C$_{60}$, and the resulting suspension was sonicated at room temperature for 3 days to measure the particle size by dynamic light scattering. In a series of C$_{60}$ inclusion tests, the amount of polymer-grafted silica was adjusted to contain 11.2 mg SiO$_2$ in 3.00 ml THF.

Preparation of a C$_{60}$/silica PMMA hybrid film
To THF solution (3.00 ml) containing 24.6 mg poly(MMA-NMA)-grafted silica included 0.027–0.25 mg C$_{60}$, prepared from poly(MMA-NMA) silane of $M_n = 48\,000$ and MMA/NMA mole ratio = 7/1, 112 mg poly(methyl methacrylate) (PMMA) with a $M_n = 5000$ was added. The solution (0.5 ml) was cast on a cover glass and dried under atmosphere to obtain the hybrid film.

RESULTS AND DISCUSSION
Grafting of poly(MMA-NMA) onto silica particles
Polymeric silanes 1, 2 and 3 for grafting onto silica particles were synthesized by three methods of radical polymerization to control the molecular weight. The polymeric silanes of low molecular weight, that is, 7400 and 16 800, intermediate molecular weight, that is, 33 200 and 48 000, and high molecular weight, that is, 71 200 and 248 000, were synthesized by Methods 1, 2 and 3, respectively, shown in Scheme 1. The grafting of poly(MMA-NMA) onto silica particles was performed by reacting the polymeric silane with silica ethanol sol in THF at room temperature for 5 h. In Table 1, the dosed amounts of each copolymer silane, amounts of grafted polymer and size of resulting composite particles were listed. In reactions of low-molecular-weight polymeric silanes, that is, $M_n = 7400$, 16 800 and 33 200, with silica sol, the grafted polymer increased with an increased dosage of polymer silane, with >90% grafted onto the silica particles. In fact, the surface hydroxyl group on colloidal silica particles <50 nm is active enough to react with polymeric alkoxy silane at room temperature.[11] However, the amounts of grafted polymer decreased with increased molecular weight of the copolymer silane. In the case of the reaction of polymer silane 3 with a $M_n = 248\,000$ with silica sol, 67% of the dosed polymer silane was bound onto the silica, most

likely because of steric hindrance. The polymer grafting obviously increased the size of the poly(MMA-NMA)-grafted silica. However, distinct correlations between molecular weight of the polymer and the size were not observed.

Inclusion of C$_{60}$ into grafted-poly(MMA-NMA)
After the addition of C$_{60}$ to the THF suspension of poly(MMA-NMA)-grafted silica and sonication for 1 h, the resulting solution became clear without the formation of C$_{60}$ clusters, which was due to the inclusion of C$_{60}$ into the polymer chains grafted on silica particles through the π–π interaction between C$_{60}$ and naphthyl group. However, it was observed that the addition of too much C$_{60}$ to the suspension caused aggregation between the poly(MMA-NMA)-grafted silica and C$_{60}$ molecules in the suspension. As fullerenes are significantly insoluble in THF, adding them to THF forms clusters immediately, as expected. The results indicated that C$_{60}$ molecules were included into the polymer chains, because the formation of clusters was never observed in the THF suspension of the polymer-grafted silica after the addition of C$_{60}$. In Figure 1, the dependence of the composite particle size on the amount of C$_{60}$ was shown. In these cases, the grafted-polymer amounts of 1.27, 2.03 and 3.74 g/g-SiO$_2$ corresponded to graft densities of 0.066, 0.108 and 0.194 chains per nm^2, respectively, which were estimated based on the assumption of homogeneous polymer grafting on silica. As shown in Figure 1, the size of composite particles, including C$_{60}$, was mostly independent of the amounts of grafted polymer smaller than 20 nm below the critical 0.2 mg C$_{60}$ addition. However, adding more than 0.2 mg C$_{60}$ to the suspension resulted in the formation of aggregates of the composite particles, most likely due to low polar–low polar interaction between the C$_{60}$-included composite particles. Therefore, it was suggested that the inclusion of C$_{60}$ into the grafted-poly(MMA-NMA) chains through the π–π interaction presumably took place near the outer end parts of the grafted polymer chains on the silica.

Table 1 Preparation of poly(MMA-NMA)-grafted silica^a

Prep. method		Poly(MMA-NMA)-Si(OMe)$_3$				Poly(MMA-NMA)/SiO$_2$	
	M_n	M_w/M_n	m/n	Dosed amount (mg)		Grafted polymer (g/g-SiO$_2$)	Size (nm)
						None	9.1^b
1	7400	2.02	14/1	133		1.53	12.3
				256		2.97	11.8
1	16 800	1.56	12/1	90		0.96	11.1
				170		1.89	12.1
				280		2.93	14.6
2	33 200	1.52	11/1	80		0.94	13.1
				120		1.42	12.4
				230		2.46	11.1
2	48 000	2.28	7/1	129		1.27	13.5
				221		2.03	13.0
				428		3.74	12.7
3	71 800	1.16	8/1	130		1.21	14.8
				220		2.34	10.1
3	248 000	2.19	9/1	250		1.93	16.3

^{a}The reactions were conducted using 0.40 ml silica ethanol sol, containing 0.109 g SiO$_2$, in 20.0 ml THF.
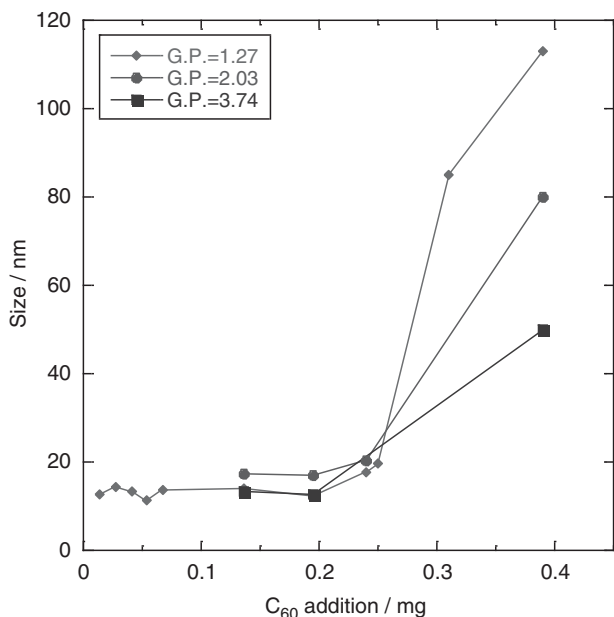^{b}Polydispersity index of original colloidal silica was 0.127.

Figure 1 Changes of polymer-grafted silica size following C$_{60}$ addition. Grafting polymer: poly(MMA-NMA) with a $M_n = 48\,000$, MMA/NMA mole ratio = 7/1. G.P., grafted polymer, and the numeric values correspond to the amount of G.P. in units of g/g-SiO$_2$. A full color version of this figure is available at *Polymer Journal* online.
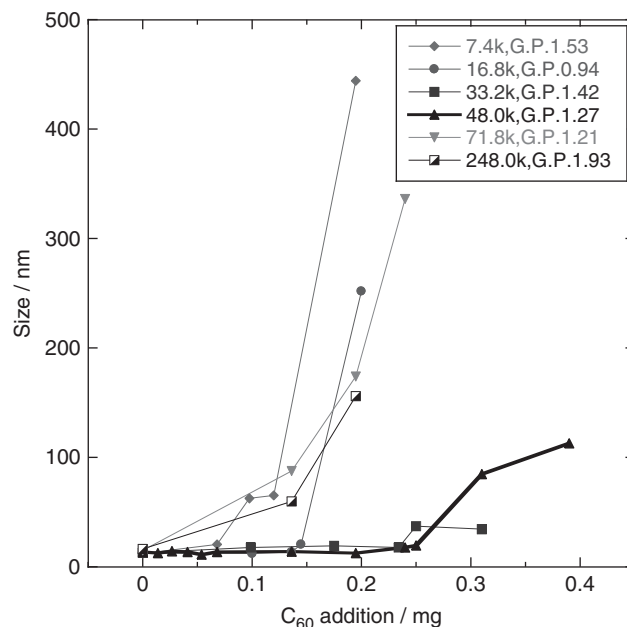

Figure 2 Effect of molecular weight of grafted poly(MMA-NMA) on silica composite size following C$_{60}$ addition. G.P., grafted polymer in units of g/g-SiO$_2$. A full color version of this figure is available at *Polymer Journal* online.

The inclusion of C$_{60}$ into the poly(MMA-NMA) chains grafted on silica was also affected by the molecular weight of the polymer. Figure 2 showed the relation between the amount of added C$_{60}$ and the size of the composite particles, in which the amount of SiO$_2$ in the composite particle was the same as that in Figure 1, that is, 11.2 mg. In these cases, to compare the effect of the poly(MMA-NMA) molecular weight on the C$_{60}$ inclusion ability of the polymer-grafted silica particles without inducing aggregation and/or formation of C$_{60}$ clusters, inclusion tests were performed by using poly(MMA-NMA)-grafted silica with grafted polymers in the range of 1.2 to 1.9 g/g-SiO$_2$. The inclusion of C$_{60}$ into the grafted-poly(MMA-NMA) chains without aggregation between composite particles was strongly dependent on the molecular weight of the polymer. The silica composite particles grafting the polymer with an $M_n = 33\,200$ and 48 000 afforded a higher capacity of C$_{60}$ inclusion by keeping the particle size <20 nm, compared with composite particles with poly(MMA-NMA) with $M_n = 7400$, 16 800, 71 200 and 248 000. The maximum inclusion of 0.25 mg C$_{60}$ was observed with the addition of C$_{60}$ to the THF suspension of the poly(MMA-NMA)-grafted silica consisting of 11.2 mg SiO$_2$ without particle aggregation, corresponding to 2.7 C$_{60}$ molecules per unit 12 nm SiO$_2$ particle (Figure 2). The reason why composite particles grafted with polymers of molecular weights of 33 200 and 48 000 exhibit higher C$_{60}$ inclusion ability is still unclear. Most likely, in the case of the C$_{60}$ inclusion using the composite particles, grafting of the low-molecular-weight poly(MMA-NMA)s with $M_n = 7400$ and 16 800 was relatively high because the graft density of the grafted polymer forced the C$_{60}$ molecules close together and the high affinity between C$_{60}$ molecules eventually induced the aggregation between the C$_{60}$-included composite particles. Otherwise, when using composite particles to graft high molecular weight poly(MMA-NMA)s, $M_n = 71\,200$ and 248 000, the C$_{60}$-included polymer chains on the silica surface have a high enough mobility to behave as a cross-linker between the C$_{60}$-included composite
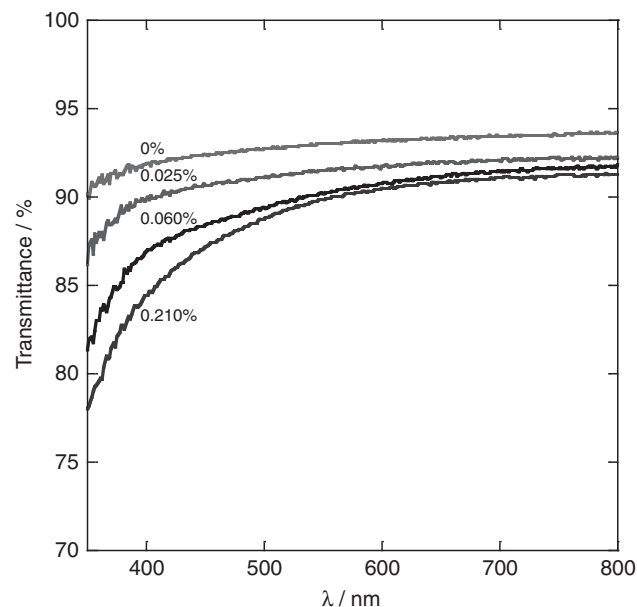
Figure 3 Transmission spectra of C$_{60}$/poly(MMA-NMA)-grafted silica/PMMA hybrid films, 50 μm in thickness. Numeric values signify the C$_{60}$ content of the hybrid film. Grafting polymer: poly(MMA-NMA) with a $M_n = 48\,000$, MMA/NMA mole ratio = 7/1. Content of SiO$_2$: 10 wt%. A full color version of this figure is available at *Polymer Journal* online.

particles through a low polar-low polar interaction; the addition of a relatively small amount of C$_{60}$ induced the aggregation.

C$_{60}$/silica PMMA hybrid film

The hybrid films were prepared by casting the THF solution containing C$_{60}$-included composite particles and PMMA. In

Figure 3, the transmission spectra of the films were shown. The films, composed of 10 wt% SiO$_2$ and C$_{60}$ in the range of 0.025 to 0.21 wt%, showed transmittance >80% in the visible light region, whereas the transmission decreased as the C$_{60}$ content increased. Therefore, the included C$_{60}$ molecules in the grafted poly(MMA-NMA) chains induced a small amount of aggregation between the composite particles during the casting process. Note that the transmittance decreased as the C$_{60}$ content increased at a low wavelength below 500 nm. This observation was most likely due to effective absorption by the C$_{60}$ molecules. Studies related to applications of the hybrid film are now in progress.

SUMMARY

We successfully achieved inclusion of fullerene (C$_{60}$) into the grafted-poly(MMA-NMA) chains in THF without inducing the formation of C$_{60}$ clusters and/or aggregation between the polymer-grafted silica particles. Polymer grafting onto silica was conducted by reacting 12 nm colloidal silica particles with polymeric silane, prepared by radical polymerization, in THF without particle aggregation. Molecules of C$_{60}$ were effectively included into grafted polymer chains in the THF suspension of the poly(MMA-NMA)-grafted silica, prepared from polymers with molecular weights of 33 200 and 48 000, without the formation of C$_{60}$ clusters and without aggregation between the silica composite particles. It was observed that the maximum C$_{60}$ inclusion into poly(MMA-NMA) chains grafted on 11.2 mg silica particles was 0.25 mg, corresponding to 2.7 C$_{60}$ molecules per unit SiO$_2$ particle.

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