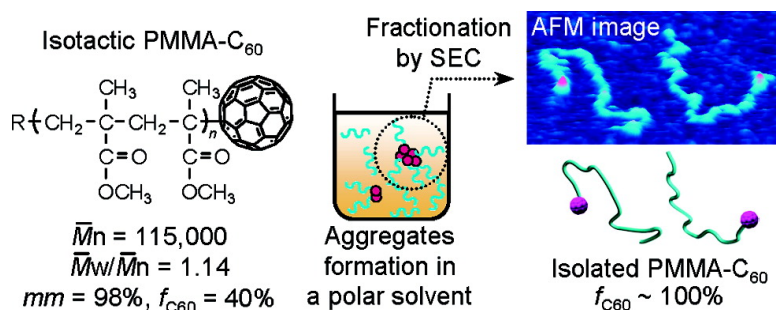Communication

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# Synthesis, Isolation via Self-Assembly, and Single-Molecule Observation of a [60]Fullerene-End-Capped Isotactic Poly(methyl methacrylate)

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The design and synthesis of $C_{60}$-containing polymers with a well-defined structure has been of great interest because of their possible applications as advanced materials.[1] Varieties of $C_{60}$-bound molecules have been incorporated into polymer backbones, pendants, or the terminal groups as components.[1d,2] Among them, the $C_{60}$-end-capped polymers are particularly interesting, because the hydrophobic $C_{60}$ core self-assembles on a nanometer scale into the micelle or vesicle-like aggregates in polar solvents.[3] However, previous studies of the $C_{60}$-end-capped polymers have mainly focused on their syntheses, structures, and morphology of their aggregates in solution or in the solid. Living radical and anionic polymerizations have often been used to produce $C_{60}$-end-capped polymers including polystyrene[4] and poly(methyl methacrylate) (PMMA)[5] with a controlled molecular weight (MW), but stereoregular $C_{60}$-end-capped polymers with a narrow molecular weight distribution (MWD) have not yet been prepared. Stereoregular PMMAs are known to supramolecularly assemble into higher-order structures, for instance, the double-stranded helices of isotactic (*it*)-PMMA[6] and a stereocomplex of the *it*- and syndiotactic (*st*)-PMMAs.[7] Therefore, stereoregular PMMAs having $C_{60}$ at the controlled chain end combined with crystallization and stereocomplex formation will provide a new sophisticated self-assembly system, for constructing two- and three-dimensional arrangements of the $C_{60}$ molecules or clusters in polymer materials.

To this end, we report here the preparation and single-molecule observation of a high molecular weight $C_{60}$-end-capped, stereoregular PMMA (PMMA-$C_{60}$) with a precisely controlled structure. The highly isotactic PMMA-$C_{60}$ (*mm* = 98%) with a narrow MWD was synthesized by the stereospecific anionic living polymerization of a methacrylate followed by end-capping with $C_{60}$. Although the functionality of $C_{60}$ ($f_{C60}$) of the as-prepared isotactic PMMA was imperfect (ca. 40%), the completely $C_{60}$-end-capped PMMA ($f_{C60} \approx 100\%$) was successfully isolated through self-assembly of the $C_{60}$-end-capped PMMA in a polar solvent by size exclusion chromatography (SEC) (Scheme 1). Furthermore, the individual PMMA chains together with the covalently bonded terminal $C_{60}$ molecules were clearly visualized by atomic force microscopy (AFM), which definitely showed the structure of the isolated PMMA-$C_{60}$.

*tert*-Butyl methacrylate (*t*-BuMA) was first living and anionically polymerized with (1,1-diphenyl-3-methylpentyl)lithium (*s*-BuDPE-Li) in toluene at −78 °C to give a high MW isotactic polymer with a narrow MWD.[8] After completion of the polymerization, a solution of $C_{60}$ in toluene was added to the mixture, yielding poly-(*t*-BuMA)-$C_{60}$, which converted to PMMA-$C_{60}$ by hydrolysis of the pendant esters, followed by complete methylation with $CH_3I$ in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU).[9] The resulting polymer (PMMA-$C_{60}$) and its prepolymer (PMMA) obtained by quenching the living polymer with $CH_3OH$ were then analyzed by SEC using refractive index (RI) and UV (330 nm)

**Scheme 1.** Synthetic Route of PMMA-$C_{60}$
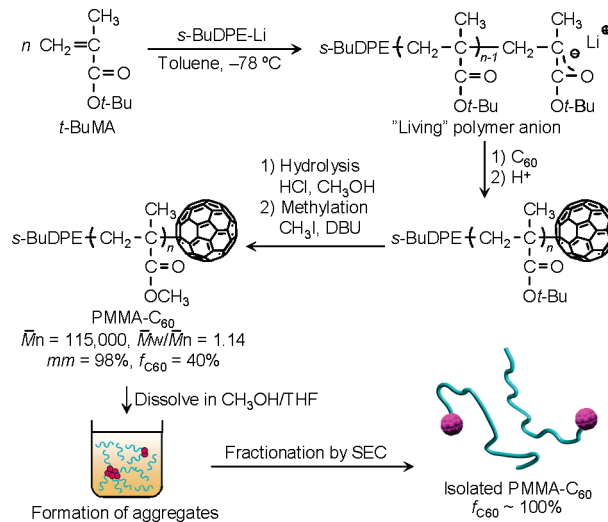


dual detectors in toluene. Figure 1 shows the SEC curves of the obtained PMMA-$C_{60}$ (b), together with those of the PMMA prepolymer (a). The PMMA showed a unimodal SEC curve detected only by RI ($M_n$ = 118 000, $M_w/M_n$ = 1.14), while the PMMA-$C_{60}$ having a chromophoric $C_{60}$ unit at the terminal end exhibited similar SEC curves detected by both the RI and UV; the MWD remained unimodal and narrow ($M_n$ = 115 000, $M_w/M_n$ = 1.14), indicating that the reaction of the living polymer with $C_{60}$ proceeded bimolecularly without the formation of bisadducts.[10] However, the $f_{C60}$ value estimated by the absorption spectrum of the PMMA-$C_{60}$ on the basis of the molar absorptivity ($\epsilon$) of a model compound (MIB-$C_{60}$)[9] of the polymer at 330 nm was rather low (ca. 40%), probably due to the low reactivity of the living poly(*t*-BuMA) enolate anion toward $C_{60}$ at −78 °C (Supporting Information).

$C_{60}$-based amphiphilic derivatives[11] and polymers[3] were found to self-assemble in polar solvents due to their hydrophobic characteristics. We then used this peculiar feature to isolate the monosubstituted $C_{60}$-bound PMMA via self-assembly. Regardless of the high molecular weight of the PMMA-$C_{60}$ of more than $10^5$, we found that the PMMA-$C_{60}$ self-aggregated into clusters in a $CH_3OH$/tetrahydrofuran (THF) (3/7, v/v) mixture. The aggregation process was time-dependent and required a rather long time in the solvent mixture (Supporting Information). Figure 1e shows the RI and UV detected SEC curves of the PMMA-$C_{60}$ solution after the sample had been allowed to stand for 96 h. The apparent MWs detected by the RI and UV shifted toward extremely high MWs on the order $10^6$−$10^8$, and the shift in the UV trace was significant. These results indicate that the PMMA-$C_{60}$ self-aggregates into large clusters with $C_{60}$ as the core and the polymer chain as the shell,[3,12] while the unreacted PMMA exists as individual polymer chains, because the PMMA prepolymer showed no aggregation under the
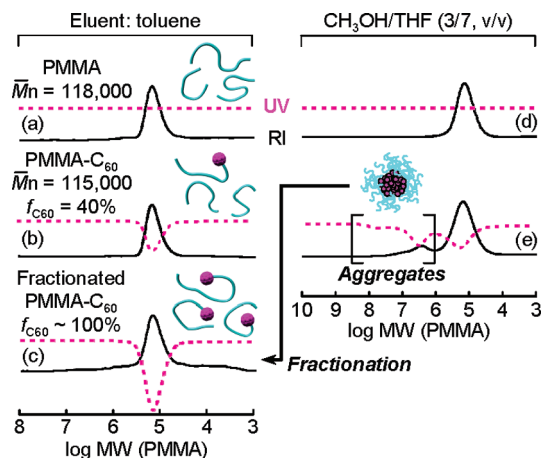
**Figure 1.** RI (solid line) and UV (330 nm, dotted red line) detected SEC curves of PMMA (a, d) and PMMA-$C_{60}$ before ($f_{C60} = 40\%$) (b, e) and after ($f_{C60} \approx 100\%$) (c) purification by SEC fractionation using toluene (a−c) and $CH_3OH$/THF (3/7, v/v) (d, e) as the eluent. The SEC curves (d, e) were obtained after the samples had been allowed to stand at room temperature for 96 h. The fraction marked by brackets in (e) was collected and then injected into the SEC system (c).
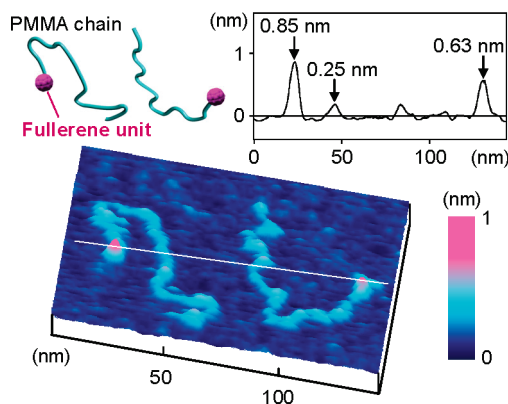


**Figure 2.** Tapping mode AFM height images of isolated PMMA-$C_{60}$ ($f_{C60} \approx 100\%$) spin-cast from a dilute solution in chloroform on mica. The height profile measured along the white line in the image is also shown.

identical conditions (Figure 1d). The PMMA-$C_{60}$ aggregates were then fractionated by SEC (Figure 1e) and subjected to the SEC system using toluene as the eluent (Figure 1c); the aggregates formed in the $CH_3OH$/THF mixture were found to completely dissociate into individual polymers in toluene as evidenced by the nearly identical, unimodal RI and UV SEC curves with a narrow MWD as observed for PMMA-$C_{60}$ before the self-aggregation (Figure 1b). On the basis of the intensity ratio of the RI and UV traces in Figure 1c, the $f_{C60}$ value of the isolated PMMA-$C_{60}$ was estimated to be almost 100%. In more polar solvents, such as $H_2O$/THF (1/9, v/v), PMMA-$C_{60}$ tended to aggregate more rapidly and efficiently, but the aggregates did not completely dissociate (Supporting Information). Although the mechanism of this aggregation and dissociation phenomena in polar solvents has not yet been clearly elucidated,[3] we emphasize that this assembly methodology developed here provides an excellent opportunity to purify other varieties of $C_{60}$-containing polymers.

AFM provided strong evidence for the structure of the isolated PMMA-$C_{60}$. Figure 2 shows typical AFM images of the isolated PMMA-$C_{60}$ spin-cast from a diluted chloroform solution. Individual PMMA long chains and spherical $C_{60}$ molecules attached to the PMMA chain end can be clearly seen in the image; the height profile of the cross section (ca. 0.3 and ca. 0.7 nm thickness for the PMMA chain[13] and the $C_{60}$ molecule, respectively) also supports

the structure of the PMMA-$C_{60}$. Moreover, the AFM studies indicate that $C_{60}$ molecules attached at the polymer end may be used as a novel label of the polymer chains for the AFM observations.

In summary, we have synthesized and characterized a high MW and stereoregular vinyl polymer with a narrow MWD having the one $C_{60}$ unit at the chain end. Although the functionality of $C_{60}$ was low, the completely $C_{60}$-end-capped polymers as clearly visualized by AFM can be obtained by self-assembly of the $C_{60}$ units, which offers a useful method to purify the $C_{60}$-containing polymers. The *it*-PMMA-$C_{60}$ obtained in the present study may be used as an interesting component to construct the supramolecular assemblies with *st*-PMMA-$C_{60}$, which may produce two- and three-dimensional arrangements of the individual $C_{60}$ molecules or self-assembled clusters that will be applicable to the electrooptic materials.[1] This work is now in progress.

**Supporting Information Available:** Experimental details, a polymerization table, ^{1}H NMR and UV−vis spectra of PMMA-$C_{60}$ and MIB-$C_{60}$, time-dependent SEC changes of PMMA-$C_{60}$ in $CH_3OH$/THF (7/3, v/v) and $H_2O$/THF (1/9, v/v), DLS measurement results, and ^{13}C NMR spectra of low MW PMMA and PMMA-$C_{60}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) A low MW PMMA-$C_{60}$ was also prepared in the same way, but its MWD was broad as previously reported in ref 8b. However, the ^{13}C NMR clearly showed the existence of the $C_{60}$ unit (Supporting Information).

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