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The design and synthesis of C₆₀-containing polymers with a well-defined structure has been of great interest because of their possible applications as advanced materials. Varieties of C₆₀-bound molecules have been incorporated into polymer backbones, pendents, or the terminal groups as components. Among them, the C₆₀-end-capped polymers are particularly interesting, because the hydrophobic C₆₀ core self-assembles on a nanometer scale into the micelle or vesicle-like aggregates in polar solvents. However, previous studies of the C₆₀-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 C₆₀-end-capped polymers including polystyrene and poly(methyl methacrylate) (PMMA) with a controlled molecular weight (MW), but stereoregular C₆₀-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 (ι-) and syndiotactic (σ-) PMMAs. Therefore, stereoregular PMMAs having C₆₀ 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 C₆₀ molecules or clusters in polymer materials.

To this end, we report here the preparation and single-molecule observation of a high molecular weight C₆₀-end-capped, stereoregular PMMA (PMMA-C₆₀) with a precisely controlled structure. The highly isotactic PMMA-C₆₀ (mm = 98%) with a narrow MWD was synthesized by the stereospecific anionic living polymerization of a methacrylate followed by end-capping with C₆₀. Although the functionality of C₆₀ (f₆₀) of the as-prepared isotactic PMMA was imperfect (ca. 40%), the completely C₆₀-end-capped PMMA (f₆₀ ≈ 100%) was successfully isolated through self-assembly of the C₆₀-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 C₆₀ molecules were clearly visualized by atomic force microscopy (AFM), which definitely showed the structure of the isolated PMMA-C₆₀.

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. After completion of the polymerization, a solution of C₆₀ in toluene was added to the mixture, yielding poly-(t-BuMA)-C₆₀, which converted to PMMA-C₆₀ by hydrolysis of the pendant esters, followed by complete methylation with CH₃I in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The resulting polymer (PMMA-C₆₀) and its prepolymer (PMMA) obtained by quenching the living polymer with CH₃OH were then analyzed by SEC using refractive index (RI) and UV (330 nm) dual detectors in toluene. Figure 1 shows the SEC curves of the obtained PMMA-C₆₀ (b), together with those of the PMMA prepolymer (a). The PMMA showed a unimodal SEC curve detected by both the RI and UV; the MWD remained unimodal and narrow (Mₘ = 115 000, Mₘ/Mₙ = 1.14), indicating that the reaction of the living polymer with C₆₀ proceeded bimolecularly without the formation of bisadducts. However, the f₆₀ value estimated by the absorption spectrum of the PMMA-C₆₀ on the basis of the molar absorptivity (ε) of a model compound (MIB-C₆₀) 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 C₆₀ at −78 °C (Supporting Information).

C₆₀-based amphiphilic derivatives and polymers were found to self-assemble in polar solvents due to their hydrophobic characteristics. We then used this peculiar feature to isolate the monosubstituted C₆₀-bound PMMA via self-assembly. Regardless of the high molecular weight of the PMMA-C₆₀ of more than 10⁵, we found that the PMMA-C₆₀ self-aggregated into clusters in a CH₃OH/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-C₆₀ 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 10⁸−10⁹, and the shift in the UV trace was significant. These results indicate that the PMMA-C₆₀ self-aggregates into large clusters with C₆₀ as the core and the polymer chain as the shell, while the unreacted PMMA exists as individual polymer chains, because the PMMA prepolymer showed no aggregation under the...
identical conditions (Figure 1d). The PMMA-C₆₀ aggregates were spin-cast from a dilute solution in chloroform on mica. The height of PMMA-C₆₀ [(CH₃)₂C(CO₂CH₃)₅]C₆₀ (MIB-C₆₀), and could not be resolved in the SEC traces in Figure 1c, the RI (solid line) and UV (330 nm, dotted red line) detected SEC curves of PMMA (a, d) and PMMA-C₆₀ before (f(C₆₀) = 40%) (b, e) and after (f(C₆₀) ≈ 100%) (c) purification by SEC fractionation using toluene (a–c) and CH₂OH/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 1. RI (solid line) and UV (330 nm, dotted red line) detected SEC curves of PMMA (a, d) and PMMA-C₆₀ before (f(C₆₀) = 40%) (b, e) and after (f(C₆₀) ≈ 100%) (c) purification by SEC fractionation using toluene (a–c) and CH₂OH/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-C₆₀ [(CH₃)₂C(CO₂CH₃)₅]C₆₀ (100%) (c) purification by SEC fractionation using toluene (a–c) and CH₂OH/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).

identical conditions (Figure 1d). The PMMA-C₆₀ 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 CH₂OH/THF mixture were found to completely disassociate 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-C₆₀ 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-C₆₀ was estimated to be almost 100%. In more polar solvents, such as H₂O/THF (1/9, v/v), DLS measurement results, and ¹³C NMR spectra of low MW PMMA and PMMA-C₆₀. This material is also available free of charge via the Internet at http://pubs.acs.org.

Supporting Information Available: Experimental details, a polymerization table, ¹H NMR and UV–vis spectra of PMMA-C₆₀ and MIB-C₆₀, time-dependent SEC changes of PMMA-C₆₀ in CH₂OH/THF (7/3, v/v) and H₂O/THF (1/9, v/v), DLS measurement results, and ¹³C NMR spectra of low MW PMMA and PMMA-C₆₀. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(8) (a) Müller, A. H. E.; Jeuck, H.; Johann, C.; Kilz, P. Polym. Prepr. 1986, 27, 153–154. (b) Varsney, S. K.; Gao, Z.; Zhong, X. F.; Eisenberg, A. Macromolecules 1994, 27, 1076–1082. We also polymerized MMA with the initiator, but the polymerization was not living and its tacticity was rather low (mn = 80%).


(10) A low MW PMMA-C₆₀ was also prepared in the same way, but its MWD was broad as previously reported in ref 8b. However, the ¹³C NMR clearly showed the existence of the C₆₀ unit (Supporting Information).


(12) The hydrodynamic diameter of the aggregates was estimated to be ca. 120 nm based on the dynamic light scattering (DLS) measurements (Supporting Information).


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