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Preparation and Characteristics of Well-defined Polyethylene/Poly(ethylene glycol) Hybrid Materials of Different Molecular Architectures

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New well-defined polyethylene/poly(ethylene glycol) AB_3-type hybrid materials have been developed, and the materials form nanosized particles in water (water dispersion, average particle size 18 nm) as a result of the self-assembly. This is the first example of nanosized particles comprised of polyolefin/polar polymer hybrid materials, which display unprecedented material properties.

One of the crucial goals in polymer synthesis is the preparation of well-defined block or graft copolymers comprised of polyolefin and polar polymer segments (polyolefin/polar polymer hybrid materials). In principal, these hybrid materials should exhibit unique characteristics due to the copresence of both nonpolar and polar segments in the same molecule and thus have a broad range of applications including, but not limited to, compatibilizers, resin modifiers, coating agents, and additives for cosmetics and paints. Thus, a lot of research has been devoted to the synthesis of these hybrid materials, the results of which have been the creation of a wide array of polyolefin/polar polymer hybrid materials.[1–6] At present, however, only a limited number of examples of well-defined hybrid materials composed of polyolefins and water-soluble polymers exist.[3b,7]

In our own work, we have recently prepared well-defined epoxy-, diol-, and acid anhydride-terminated low-molecular-weight polyethylenes (PEs) from vinyl-terminated PE that was produced by the polymerization of ethylene with bis(phenoxyimine)Zr complexes (a.k.a. FI catalysts).[8,9] In the course of the development of new materials based on the above terminally functionalized PEs, we have succeeded in the creation of well-defined PE/poly(ethylene glycol) (PEG) hybrid materials that can display unprecedented material properties. We, therefore, report the synthesis and properties of these new PE/PEG hybrid materials in this communication, thus revealing the significant effect of polymer structure on material properties.[10]

The epoxy- and diol-terminated low-molecular-weight PEs (e-t-PE; $M_n = 1100$, $M_w/M_n = 1.8$, epoxy selectivity 94 mol %, $T_m = 121$ °C, d-t-PE; $M_n = 1100$, $M_w/M_n = 1.8$, diol selectivity 94 mol %, $T_m = 121$ °C) that were used in this research were prepared according to literature procedures.[9b] With these terminally functionalized PEs in hand, we have successfully synthesized well-defined PE/PEG AB_2- and AB_3-type hybrid materials (Figure 1).

The reaction of the d-t-PE with ethylene oxide using KOH as a catalyst resulted in the formation of PE/PEG AB_2-type hybrid materials (AB_2 hybrid materials, PE; $M_n = 1100$, PEG; average $M_n = 600 \times 2$, $T_m = 120$ °C) in practically quantitative yield. Likewise, PE/PEG AB_3-type hybrid materials (AB_3 hybrid materials, PE; $M_n = 1100$, PEG; average $M_n = 400 \times 3$, $T_m = 120$ °C) were prepared by the reaction of triol-terminated PE (which was obtained from the reaction of the e-t-PE with

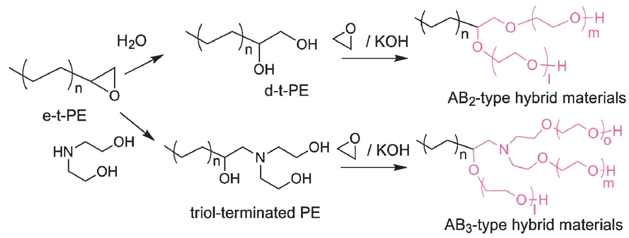

Figure 1. PE/PEG AB_2- and AB_3-type hybrid materials.

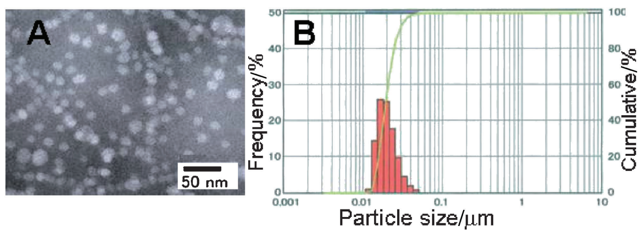

Figure 2. TEM image (A) and particle size distribution of a 5 wt % water dispersion of AB_3 hybrid materials (B).

diethanolamine) and ethylene oxide. We were thus able to acquire PE/PEG AB_2- and AB_3-type hybrid materials that possess about the same PE/PEG compositions (PE/PEG = ca. 1) though their polymer structures are different (AB_2 and AB_3), as shown in Figure 1.

Since the AB_2- and AB_3-type hybrid materials have multiple hydrophilic (water-soluble) PEG segments in the molecules, we were interested in their behavior in water. As anticipated, the AB_2 and AB_3 hybrid materials were dispersed in water without the aid of surfactants because of their affinity to water. The water dispersions of these hybrid materials were prepared at 130 °C (above the T_m of the PE segment) under pressurized conditions. A photograph of the water dispersion of AB_2 hybrid materials (5 wt %) is shown in Figure S-1A.[11] The average particle size is 2 μm, which is within the range of the water dispersions of conventional maleic anhydride-grafted polyolefins (2–10 μm).[12]

To our surprise, the corresponding water dispersion of the AB_3 hybrid materials seems semitransparent (Figure S-1B),[11] indicative of the distinctive features of these materials. The transmission electron microscope (TEM) image and particle size distribution of the water dispersion of the AB_3 hybrid materials are displayed in Figure 2, and these show that the AB_3 hybrid materials form nanosized particles, the average size being 18 nm with narrow particle size distribution.[13]

The AB_3-type molecular architecture is evidently responsible for this exceptional behavior, providing a clear demonstration that the polymer structure (AB_2 and AB_3) rather than the polymer composition (PE/PEG ratio) plays a crucial role in

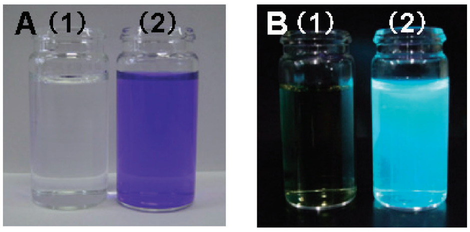

Figure 3. 2,7,12,17-Tetra-*tert*-butyl-5,10,15,20-tetraazaporphyrinatocopper(II) (0.07 mmol) or 8-anilino-1-naphthalene sulfonic acid (0.01 mmol) with water (10 mL) in the absence (A(1) and B(1)) or in the presence of AB_3 nanoparticles (0.2 wt %, A(2) and B(2)).

determining the behavior in water for the PE/PEG hybrid materials.

The nanoparticles are probably produced through the self-assembly of the hydrophobic PE segments as cores and that of the three hydrophilic-PEG-segments at the particle surfaces that efficiently insulate PE segments from water. The inside of the nanoparticles probably possesses a hydrophobic environment since the inside is comprised of semicrystalline PE.

The water dispersion is highly stable and retains its chemical nature for more than one year at room temperature (virtually no aggregation and precipitation). It should be noted that the dispersion is unusually robust under a wide range of temperature and pH conditions (0–100 °C, pH 1–13, the AB_3 hybrid materials content 0.1–40 wt %). The nonionic nature and the presence of the semicrystalline PE segments of the AB_3 hybrid materials are probably responsible for its unprecedented stability. Interestingly, the nanoparticles can be isolated from water as nanopowders by freeze drying or spray drying and are dispersible in organic solvents such as methanol and dimethylformamide. With the above unique features along with a nanosized nature, the AB_3 hybrid materials may expand the utility of polyolefin/polar polymer hybrid materials.

As expected, the nanoparticles showed several characteristic features. For example, they can include 2,7,12,17-tetra-*tert*-butyl-5,10,15,20-tetraazaporphyrinatocopper(II) (a water-insoluble dye) inside the particles in water, leading to the formation of purple-colored water dispersion (Figure 3A). This result indicates that the particles can include fairly large molecules. Additionally, the nanoparticles can also include 8-anilino-1-naphthalene sulfonic acid (an environmentally sensitive fluorescent probe), which does not produce fluorescence in water under UV light irradiation. Interestingly, however, the water dispersion of the AB_3 hybrid materials including this probe is fluorescent under UV light (365 nm) (Figure 3B), demonstrating the hydrophobic nature of the particle interior.

Since the polymer morphologies of the PE/PEG hybrid materials, which are dictated by polymer structures and compositions, can be modified by changing the molecular weights of the PE and/or PEG segments, the development of these hybrid materials provides an opportunity to systematically study the relationship between the polymer morphologies and material properties, which indeed is our current topic of research.

In summary, we have successfully prepared well-defined PE/PEG AB_2- and AB_3-type hybrid materials, starting from the vinyl-terminated PE derived from an FI catalyst. We have demonstrated that the PE/PEG AB_3-type hybrid materials display unprecedented features, thus making these hybrid materials an exciting new product with various potential applications.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

12 The reaction of the e-t-PE ($M_n = 1100$, $M_w/M_n = 1.8$, epoxy selectivity 94%, $T_m = 121$ °C) with PEG ($M_n = 1000$, $M_w/M_n = 1$) in the presence of NaOH produced PE/PEG AB- and ABA-type hybrid materials. A water dispersion of this mixture (5 wt %) resulted in particles having an average particle size of 13 µm.

13 AB_2 hybrid materials can form nanosized particles in water as a result of elaborate material design [e.g., PE: $M_n = 1100$, PEG: $M_n = 2200$ (average $M_n = 1100 \times 2$), average particle size 20 nm].

