Nanoparticle Formation by Irreversible In situ Aggregation of Rigid π-Stacked Segments of a Flexible–Rigid Block Copolymer

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Block copolymers of dibenzofulvene and methyl methacrylate obtained by living anionic polymerization formed stable, soluble nanoparticles by in situ molecular aggregation of the poly(dibenzofulvene) segments having a rigid π-stacked conformation; the nanoparticles indicated red-shifted absorption bands and reduced oxidation potential relative to a single chain poly(dibenzofulvene).

Controlled spatial arrangement of chromophoric groups and molecules often plays an important role in obtaining electronic and photophysical organic materials with desired properties.[1] As an example of chromophore ordering along a polymer chain, poly(dibenzofulvene) (poly(DBF)) and its derivatives have been reported by us and others;[2–6] these polymers have a regulated π-stacked conformation in which the main-chain C–C bonds are nearly all trans and the side-chain fluorene moiety are stacked on top of each other. Poly(DBF) has a potential for a novel electronic material.[7,8] In this study, a block copolymer consisting of rigid poly(DBF) segment and flexible poly(methyl methacrylate) (poly(MMA)) segment was prepared to control molecular ordering of the π-stacked poly(DBF) chains. The obtained flexible–rigid copolymer was found to form stable particles by irreversible in situ aggregation of the poly(DBF) segments.

The block copolymers were synthesized by first polymerizing MMA in tetrahydrofuran (THF) at −78 °C using 9-fluorenyllithium (FlLi) under a living anionic condition and then adding DBF to the living growing anion at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/15$, 1/30/10, and 1/30/3 (Scheme 1). Both monomers were nearly quantitatively consumed in the polymerization. The fact that DBF effectively reacted with the living poly(MMA) anion indicates unusually high reactivity of DBF as a hydrocarbon monomer. This is in stark contrast with the inactivity of styrene toward poly(MMA) anion.[9]

The block formation was confirmed by means of SEC analyses. As an example, Figure 1 shows the curves for the reaction at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/10$. SEC analyses also indicated that the block copolymerization products at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/10$ and 1/30/15 contained major fractions (70 and 90%, respectively) whose molecular weights were much larger than the theoretical value expected for a block copolymer (observed M_ns: 82×10^3 and 140×10^3 (vs PSt), respectively; calculated M_ns for block copolymers: 4.9×10^3 and 5.8×10^3, respectively). These fractions are considered to be aggregates of the block copolymer formed by the interchain interaction of the rigid poly(DBF) segments because poly(DBF) with a higher degree of polymerization (DP) tends to be insoluble in solvents due to molecular aggregation[2a] while poly(MMA) has good solubility. This is supported by the fact that a higher $[\mathrm{DBF}]_o$ concentration leading to a longer theoretical DBF segments produced larger aggregates in a higher content. In addition, the product at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/3$ containing a short poly(DBF) segment (theoretical segment DP = 3) contained no aggregated fraction. The aggregates may have a core–shell structure with poly(DBF) segments in the core and poly(MMA) segments in the shell (Scheme 2).

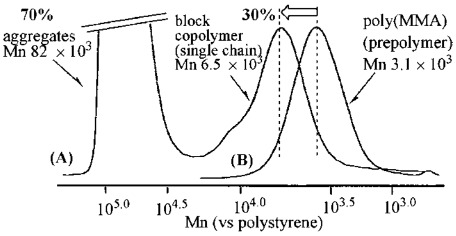
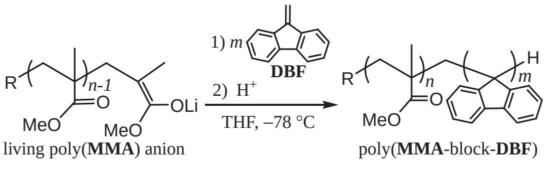


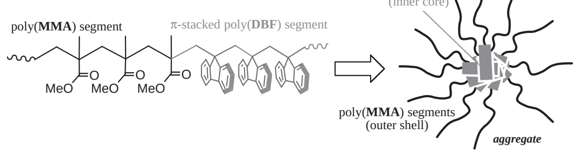
Figure 1. SEC curves of MMA-DBF block copolymerization products at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/10$ (A) and prepolymer (PMMA) (B).



Scheme 1. Synthesis of MMA–DBF block copolymer.

M_w of the aggregates obtained at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/15$ was determined to be 5.3×10^6 by SEC using THF as eluent with on-line multiangle light-scattering (MALLS) detection, meaning that ca. 900 block copolymer chains form one cluster based on the theoretical molecular weight of a single block copolymer chain[8] (5.8×10^3). The radius of gyration of the aggregates was estimated to be 33 nm by the SEC-MALLS analysis.

The size and amount of the aggregates did not decrease on heating them in a THF solution, indicating that the aggregation



Scheme 2. Nanoparticle formation by in situ molecular aggregation of poly(DBF) segment of a block copolymer.

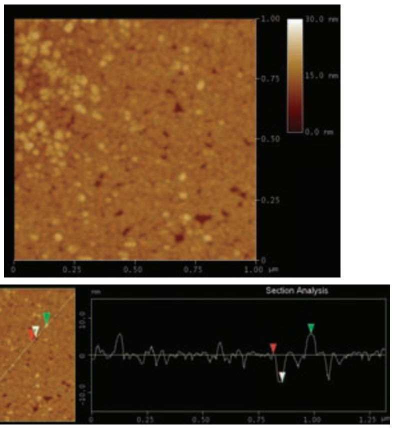


Figure 2. Tapping-mode AFM images of the aggregates isolated by SEC: 1 × 1 µm^2 topographic image (top) and section analysis chart (bottom). The darkest brown parts in the top image are the substrate surface.

is irreversible. Hence, the aggregates are stable and are not unraveled into single chains under studied conditions.

The structure of the aggregates was studied by atomic force microscopy (AFM) (Figure 2). The aggregates were isolated by preparative SEC from the products at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/15$. The isolated aggregates were drop-casted onto a mica surface from a dilute chloroform solution. The image shows a layer formed by particulate objects (brown dots) on the substrate surface (darkest brown parts). In some parts, particles sit on the first layer to form the second layer (whitish brown dots). The height analysis chart indicates that the thickness of the bottom layer corresponding to the particle size is about 7 nm which is smaller than the Rg (33 nm) in solution. This suggests that poly(MMA) segments in the shell part of the particles are shrunk in the dried, solid state on the mica substrate. Interaction between poly(MMA) chains and mica surface appear not to be effective in keeping the shape (conformation) of poly(MMA) in solution.

The absorption spectrum of the isolated aggregates shown in Figure 3 indicated a clear hypochromic effect. In addition, exclusive excimer (dimer) emission[10] was observed in the fluorescence spectra around 400 nm on excitation at 267 nm. These results support that the poly(DBF) segments maintain a π-stacked conformation[2a] in the aggregates. The aggregates indicated significantly red-shifted absorption bands compared with DBF homopolymer. This was especially clear for the lowest-energy peak; the peak wavelength of this band (ca. 314 nm) largely deviated from the DP–peak wavelength relation reported for the DBF homopolymer.[2a] The lowest-energy peak band may possibly reflect chain-to-chain electronic interactions in the aggregates.

Such an interaction was implicated also by cyclic voltammetry (CV) measurements of the isolated aggregates. The half-wave oxidation potential was $E_{p/2}$ 1.03 V vs Ag/AgCl which was much lower than that of the single chain DBF hompolymer (1.49 V[2a]), suggesting that charges can be delocalized over neighboring chains due to close chain packing in the aggregate.

In summary, the MMA–DBF block copolymers prepared by the anionic polymerization formed stable, particulate aggregates. The clustered π-stacked chains in the aggregates may be regarded as a soluble model of the solid-state chains and allow the property measurements in solution. In addition, from a standpoint of synthetic utility, the poly(DBF) segments may be viewed as molecular glue tying poly(MMA) chains in a bundle. The particle formation revealed in this study is not due to covalent bond formation but due to the tight molecular packing of the rigid poly(DBF) segments. The use of DBF for block copolymerization in combination with other monomers may open a convenient way to produce various novel nanoparticles with functional polymer chains sticking out from the aggregated poly(DBF) core because a wide range of comonomers would be applicable to such a synthesis due to the high reactivity of DBF in vinyl polymeriztaions.[2,3]

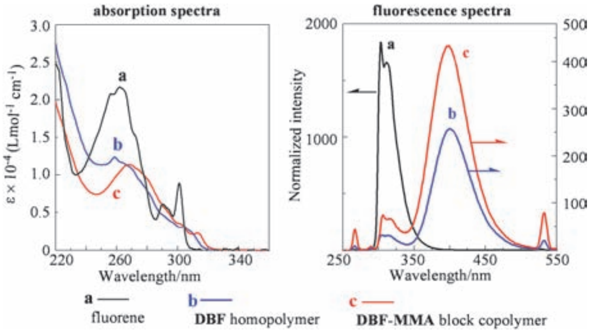


Figure 3. Absorption (left) and fluorescence (right) spectra of fluorene (**a**), a DBF homopolymer having hydrogens at chain terminals ($M_n = 1780$)[2a] (**b**), and the poly(MMA)-block-poly(DBF) aggregates isolated by preparative SEC from the products at $[\mathrm{FlLi}]_o/[\mathrm{MMA}]_o/[\mathrm{DBF}]_o = 1/30/15$ (**c**) (THF, room temp.). ε values in absorption spectra are based on the concentration of DBF unit. Excitation wavelength in fluorescence spectra was 267 nm; spectral intensity was normalized to a constant absorbance at 267 nm.

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