

Crystallization-driven Self-assembly of Isotactic Polystyrene in *N, N*-Dimethylformamide^{*}

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Abstract Herein we demonstrate crystallization-driven self-assembly of isotactic polystyrene (*i*PS) with high isotacticity and narrow molecular weight distribution and crystallization-induced switching of the morphology of *i*PS aggregates in *N, N*-dimethylformamide (DMF). The formation and morphology switching of the self-assembled aggregates of *i*PS are investigated by means of dynamic light scattering (DLS), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WXR). The results reveal that cooling DMF solution of *i*PS promotes *i*PS chains to self-assemble into spherical aggregates with a gelled core cross-linked by microcrystals, which is surrounded by solvent-swollen corona. Furthermore, crystallization induces the deformation of *i*PS aggregates from spherical to plate-like or nest-like.

Keywords: Isotactic polystyrene; *N, N*-Dimethylformamide; Crystallization-driven; Self-assembly.

INTRODUCTION

The solution properties of non-polar and weakly-polar crystalline polyolefins such as high density polyethylene (HDPE)^[1], isotactic polypropylene (*i*PP)^[2], syndiotactic polypropylene (*s*PP)^[3], isotactic polystyrene (*i*PS)^[4] and syndiotactic polystyrene (*s*PS)^[5] have attracted a great deal of attention due to the theoretical research as well as potential applications. Note that the dissolution of crystalline polyolefins always requires a higher temperature to destroy the crystal lattice. Moreover, cooling the molecular solution usually gives rise to crystallization of polyolefins and drives further either gelation or precipitation^[6–8]. The competition between gelation and precipitation depends upon the solution crystallization behavior of polyolefins which is dominated by their chemical structure^[9, 10], molecular weight^[11] and stereo-regularity^[12], as well as conditions such as cooling rate^[13], solvent properties^[14] and concentration^[15]. Generally, low cooling rates and concentration would rather yield a crystal precipitation, whereas high cooling rates and concentration would promote gelation^[13].

*i*PS was considered as a semi-crystalline polymer characterized by slow crystallization rates and low crystallinity^[16]. Therefore, the solution crystallization and gelation of *i*PS have caused great interest. For gelation of *i*PS, most of the previous reports focus on concentrated solution or semidilute solution^[17], there are even

^{*} This work was financially supported by the National Natural Science Foundation of China (Nos. 21174167 and 20974123), the Guangdong Province Higher School Science and Technology Innovation Key Project and the Natural Science Foundation of Guangdong Province (No. S2013030013474).

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Received August 13, 2014; Revised September 3, 2014; Accepted September 12, 2014

doi: 10.1007/s10118-015-1615-1

fewer studies concerning dilute solution^[18]. This study, which employs a combination of dynamic light scattering (DLS), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD) to characterize the morphology and structure of *i*PS aggregates, is the first to investigate the crystallization-driven self-assembly of *i*PS and crystallization-induced switching of the morphology of the self-assembled aggregate from dilute solutions less than 1.0 mg/mL in DMF.

EXPERIMENTAL

Synthesis of iPS

*i*PS with high isotacticity and narrow molecular weight distribution could be synthesized *via* living isospecific styrene polymerization catalyzed by chiral benzyl titanium complexes with a tetradentate [OSSO]-type bis(phenolato) ligand^[19]. In this case, *i*PS samples with molecular weight ranging from 5.0×10^3 to 5.0×10^5 and polydispersity (M_w/M_n) less than 1.3 were prepared using 1,4-dithiabutandiy-2,2(-bis(6-tertbutyl-4-methylphenoxy) titanium dibenzyl in the presence of $[C(Ph_3)][B(C_6F_5)_4]$ as cocatalyst and trioctylaluminum as scavenger in toluene at 25 °C^[20, 21]. The triad isotacticity (mm) of the obtained *i*PS samples was evaluated to be over 98% by ¹³C-NMR.

Crystallization-driven Self-assembly of iPS in DMF

40.0 mg of *i*PS and 20 mL of DMF were placed into a 50 mL flask. The mixture was stirred at 150 °C for 30 min to ensure the *i*PS dissolved completely and then cooled to 25 °C. Next, 10 mL of the mixture was added to 50 mL deionized water and transferred to dialysis bag at room temperature for one week to remove DMF. Moreover, the *i*PS/DMF dispersion was aged at room temperature.

Measurements

¹³C-NMR (300 MHz) spectra were recorded in CDCl₃ at 25 °C on a Varian Unity Inova 300 spectrometer. Molecular weight and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) against narrow molecular weight distribution polystyrene standards on a Waters Alliance GPC2000 equipped with three types of Styragel columns (Styragel HT3, Styragel HT4, Styragel HT5) and a Waters 2410 differential refractive index detector at 135 °C with 1,2,4-trichlorobenzene (TCB) as the eluent.

The JSM-6510 SEM is purchased from Japan with an accelerating voltage of 10.0 kV. A drop from the previously prepared colloidal solution was deposited onto a cover glass which was dried at room temperature for several hours before examination by SEM.

The crystal structures of all aggregates were characterized by WAXD, the model was known as D/max2200 vpc, Japan, Cu target, K α radiation ($\lambda = 0.154056$ nm). All samples were obtained after dialysis and subsequent vacuum freeze-drying.

DLS measurements were conducted on a Brookhaven BI-200SM apparatus with a BI-9000AT digital correlator and a He-Ne laser at 532 nm. The angle was fixed to be 90°. The samples were placed in an index-matching decaline bath with temperature control within (± 2) K. Each solution passed through a 0.45 μ m polytetrafluoroethene (PTFE) filter to remove dust. The data were analyzed by CONTIN algorithm, while the hydrodynamic diameter (D_h) and size polydispersity of the particles were obtained by a cumulant analysis of the experimental correlation function.

RESULTS AND DISCUSSION

It is noteworthy that *i*PS and *s*PS belong to weakly-polar crystalline polyolefins. Their dissolution temperatures may be much lower than the T_m of *i*PS (~250 °C) and *s*PS (~260 °C) resulting from that some heat can be produced by the interaction of solvent with amorphous parts to destroy the crystal lattice^[21]. Previous works have reported that the molecular solution of *i*PS and *s*PS can be prepared at temperatures higher than 120 °C in DMF^[22]. Cooling the dilute DMF solution of *i*PS from 150 °C to room temperature, the dispersion was still uniform and transparent and appeared slight bright blue which corresponded to the characteristic of colloidal solution. Information about the D_h and distribution of *i*PS colloidal particles in DMF detected at 25 °C and a

concentration (C) of 1.0–0.2 mg/mL was provided by DLS. As shown in Fig. 1, the D_h distribution demonstrates an aggregation of i PS3 chains with $M_w = 2.9 \times 10^5$ because the average D_h ($\langle D_h \rangle$) of ~ 400 nm is much larger than that of individual chains ~ 50.0 nm in 1,2,4-trichlorobenzene which was determined by gel permeation chromatography (GPC) at 135 °C. And only one peak was detected on the D_h distribution, indicating the aggregation of almost all i PS3 chains. To detect the process of crystallization-driven self-assembly of i PS in DMF, DLS was employed to measure the changes of $\langle D_h \rangle$ as a function of temperature. Due to the used laser light scattering (LLS) apparatus just equipped a circulating water bath, DLS measurements were conducted at different temperatures ranging from 90 to 25 °C as the following procedure. First, the mixture of i PS and DMF was heated to 150 °C and kept the temperature for 30 min ensuring i PS dissolving completely to form a molecular solution. Subsequently, the solution was placed in the DLS cell surrounded by decalin at 90 °C preheated by circulating water bath. The $\langle D_h \rangle$ was recorded once every five minutes at the same temperature during cooling. As shown in the upper right inset in Fig. 1, i PS3 chains begin to aggregate at ~ 70 °C and the $\langle D_h \rangle$ of the aggregates remains unchanged after ~ 35 °C. Figure 2 shows that SEM micrographs of the i PS particles formed upon cooling a 0.05% DMF solution of i PS from 150 °C to room temperature. Spherical aggregates with an average diameter of ~ 400 nm are clearly observed. Figure 3 shows SEM micrographs of the i PS aggregates after aging the i PS/DMF dispersions for 24 h at room temperature. The aggregate morphology changed from spherical to plate-like for the i PS2 with lower molecular weight ($M_w = 2.5 \times 10^4$) and nest-like for i PS3 with higher molecular weight ($M_w = 2.9 \times 10^5$).

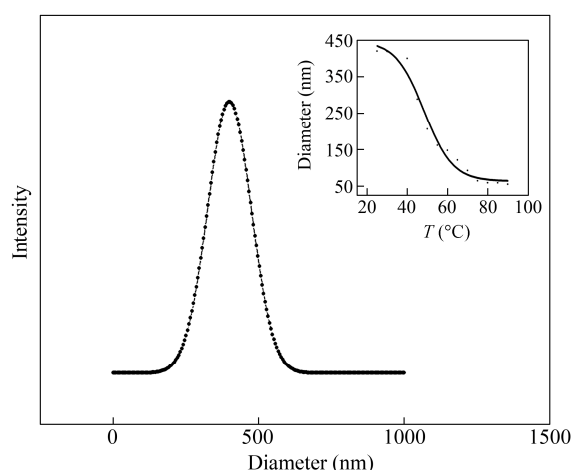


Fig. 1 The D_h distribution of the self-assembled i PS3 ($M_w = 2.9 \times 10^5$) aggregates in DMF at 25 °C. The inset shows the changes of $\langle D_h \rangle$ as a function of temperature cooled from 90 to 25 °C.

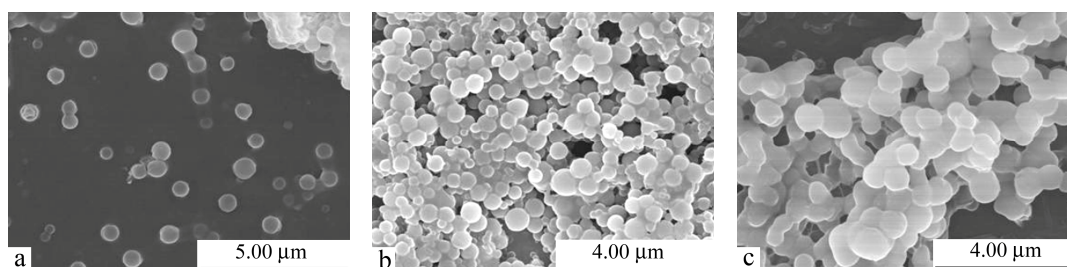


Fig. 2 SEM micrographs of the self-assembled aggregates of i PS with different molecular weights in DMF at 25 °C: (a) $M_w^{iPS1} = 4.6 \times 10^3$, (b) $M_w^{iPS2} = 2.5 \times 10^4$ and (c) $M_w^{iPS3} = 2.9 \times 10^5$

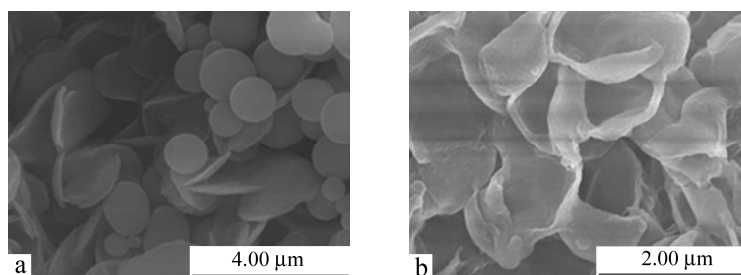


Fig. 3 SEM micrographs of the *i*PS aggregates after aging the DMF dispersions of (a) *i*PS2 and (b) *i*PS3 for 24 h at room temperature

In order to explore the structure of the *i*PS aggregates, the *i*PS/DMF dispersions were rapidly added into numerous deionized water at room temperature, and then the mixture was dialyzed against deionized water to remove DMF. Furthermore, the glass transition temperature (T_g) of the resultant aggregates after dialysis was measured by DSC at a heating scan rate of 5 K/min. The T_g of *i*PS aggregates was $\sim 98^\circ\text{C}$ which is near to the T_g of bulk PS, implying that the DMF in *i*PS aggregates was almost completely removed by dialysis. It should be noted that *i*PS will no longer continue to crystallize when the DMF was removed, because the room temperature is much lower than T_g of *i*PS. The WAXD patterns of *i*PS aggregates obtained after dialysis and subsequent vacuum freeze-drying are shown in Fig. 4. The *i*PS aggregates show the diffraction peaks at $2\theta = 8.2^\circ$, 14.1° , 16.3° , 18.1° , 21.4° and 24.6° attributed to the (110), (300), (220), (211), (410) and (321) reflections as the same as those of bulk *i*PS^[23]. The crystallinity was estimated from the ratio of the integrated intensity of the crystalline peaks to the total integrated intensity of coherent scattering after subtraction of the incoherent background^[24, 25]. In Fig. 4, the crystallinity of *i*PS2 aggregates increases with aging time increasing and approaches to a constant value.

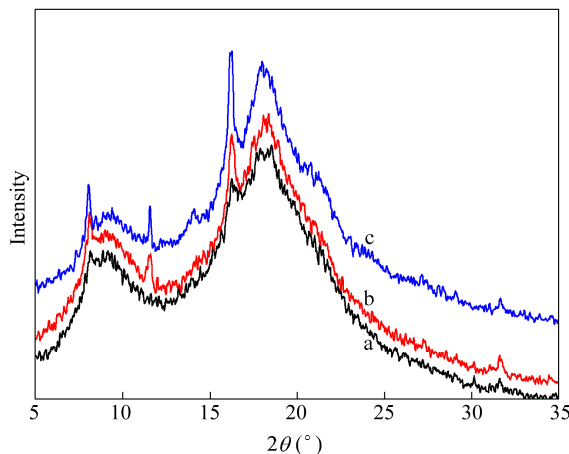


Fig. 4 WAXD patterns of *i*PS2 aggregates obtained from (a) the freshly prepared *i*PS2/DMF dispersions and those aged for (b) 24 h and (c) 48 h

The crystallization-driven self-assembly of *i*PS and crystallization-induced switching of the morphology of *i*PS aggregates in DMF can be schematically shown in Fig. 5. Cooling *i*PS molecular solution promotes the self-assembly into spherical aggregates with a gelled core cross-linked by the microcrystals, in which the crystallinity of *i*PS is very low due to the slow crystallization kinetics of *i*PS in DMF solution, surrounded by a solvent-swollen corona that provides colloidal stability^[26]. With the increase of crystallinity, plate-like aggregates of *i*PS2 with lower molecular weight are formed as a result of the two-dimensional crystalline growth, namely *i*PS chains must fold back and forth to form lamellar crystals, and meanwhile DMF in the gelled cores is gradually extruded out during crystal growth. Moreover, for the *i*PS3 with higher molecular weight, the relatively slow

crystallization rate of *i*PS in flexible cores leads to the formation of twisted lamellae (nest-like aggregates)^[27–29]. In addition, the solubility of *i*PS in DMF decreases as temperature drops. Cooling the *i*PS molecular solution may give rise to both liquid-liquid demixing and polymer crystallization^[30, 31]. Crystal nucleation prefers to occur at the diffuse interfaces and crystallization is enhanced^[30]. Therefore, we suggest that the surface-enhanced crystallization^[30] should be conducive to the deformation of *i*PS aggregates from spherical to plate-like and/or nest-like.

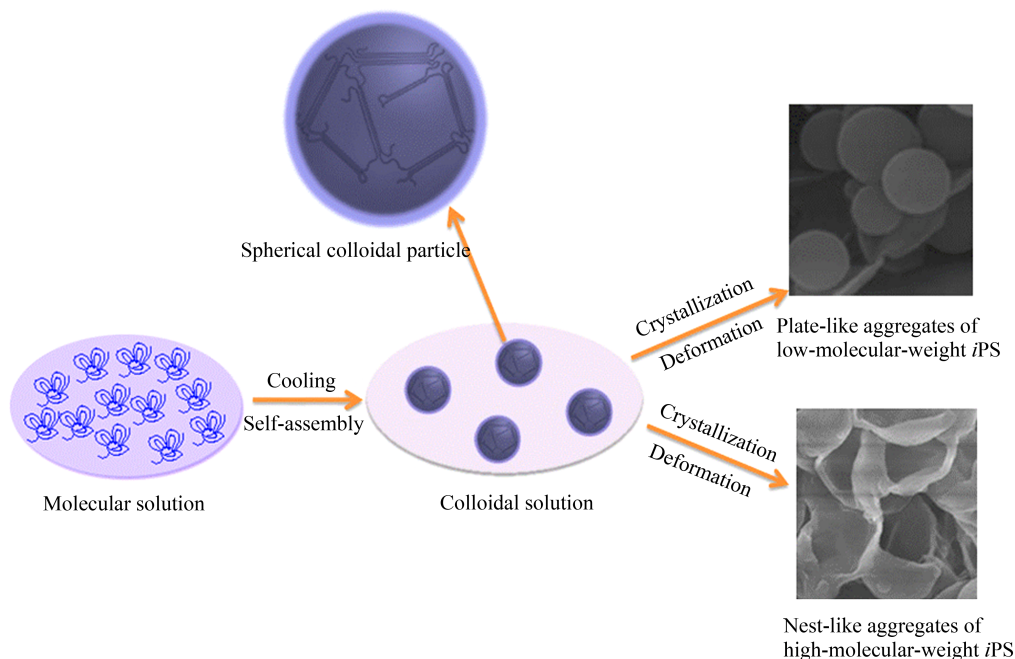


Fig. 5 The schematic representation of the crystallization-driven self-assembly of *i*PS chains and crystallization-induced switching of the morphology of *i*PS aggregates in DMF

CONCLUSIONS

*i*PS with high isotacticity and narrow molecular weight distribution can be dissolved in DMF at 150 °C to form a molecular solution. *i*PS chains can self-assemble into spherical aggregates with a gelled core cross-linked by microcrystals resulting from crystallization upon cooling. Moreover, with the increase of the aging time of *i*PS/DMF dispersion, crystallization induces the deformation of *i*PS aggregates from spherical to plate-like or nest-like.

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