Shape-Directed Assembly of a “Macromolecular Barb” into Nanofibers: Stereospecific Cyclopolymerization of Isopropylidene Diallylmalonate

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Ordered molecular assembly in solution generally requires sufficiently strong and directional forces given by, e.g., hydrogen-bonding,1 π-electronic,2 and/or metal-ligating interactions.3 In contrast, van der Waals interactions are inherently weak and nondirectional and by themselves hardly induce ordered assembly if not assisted by directional forces. Peptide amphiphiles4a and paraffinic oligoethylenes4b are typical examples that self-assemble regularly into nanofibers by combining a directional interaction with a van der Waals force.4 These nanofibers can eventually be cross-linked to cause physical gelation of solvents.4 Here we report that a “barb”-shaped polymer self-assembles into regular nanofibers solely by a van der Waals interaction. This work was prompted by our serendipitous finding that a physical gel forms when isopropylidene diallylmalonate (1)6 is allowed to polymerize in CH2Cl2 using newly designed α-dimine Pd(II) complex 3 (Figure 1a). Unprecedentedly, the produced cycloolefinic polymer (2) is highly rich in threo-disyndiotactic sequences (st–st–2) and, on the basis of a molecular model of its stereochemically pure 16-mer, likely adopts a barb shape (Figure 1b) with its cyclic malonate pendants sticking out alternately up and down along the main chain. Polyolefins such as branched polyethylene and isotactic polypropylene are known to form physical gels. However, in these cases, the polymer molecules self-assemble not into nanofibers but into spherulites, which are responsible for the formation of a cross-linked 3D network structure essential for physical gelation.6 Apart from polyolefins, poly(lactic acid)7 and poly(methyl methacrylate) (PMMA)8,9 are known as rare examples that give rise to physical gelation only by van der Waals interactions. However, in the former case, spherulites are again responsible for the formation of a 3D network.7 Although the latter example is similar to our system in that nanofibers are formed solely by van der Waals interactions, this particular assembly occurs only when isotactic and syndiotactic PMMAs are mixed together.8,9

Initiator 3 features a cyclic ligand with an azobenzene strap on one side and an α-dimine unit10 that accommodates a chloro-(methyl) palladium(II) species on the other. We succeeded in crystallographic determination of the structure of as-synthesized 3 and confirmed that the azobenzene unit adopts a trans form (Figure 2). The crystal structure also shows that trans-3 possesses C1 symmetry, with one side of the Pd(II) center sterically blocked by the azobenzene strap. The initial purpose of the present study was to develop an initiator that is capable of photochemically switching its polymerization activity. We chose polymerization of 1, which has been reported by Osakada et al.5 to proceed stereospecifically

Figure 1. (a) Polymerization of diallylmalonate 1 initiated by α-dimine Pd(II) complexes 3 (this work) and 4 (ref 5). Also shown are structures and computer-generated CPK models of 16-mers of 1 composed exclusively of (b) threo-disyndiotactic (st–st–2) and (c) threo-diisotactic (it–it–2) sequences.

Figure 2. Crystal structure (ORTEP diagram) of trans-3, showing 50% probability thermal ellipsoids. H atoms have been omitted for clarity.

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10.1021/ja910901e © 2010 American Chemical Society
was unavailable photochemically.12 The polymerization of tacticity. Accordingly, in 13C NMR spectroscopy, polymer rene standards (Table 1, run 1). For evaluating the activity of 3 obtained with (Figure 3b). Hence, the intense CH signal at 47.0 ppm for polymer -ducted at lower temperatures, such as 0 °C (Table 1, run 1) showed a highly enhanced CH signal at 47.0 ppm. Such an activity monomer conversion in 48 h (Table 1, run 6). With the this mixed initiator system took place sluggishly, reaching quantita-

Table 1. Polymerization of 1 Initiated with α-Diimine Complexes trans-3, cis-3 (80%), and 4 in CH2Cl2.a

<table>
<thead>
<tr>
<th>run</th>
<th>Initiator (Ini)</th>
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<td>8400</td>
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<tr>
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<td>48</td>
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<td>0</td>
<td>168</td>
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<td>6500</td>
</tr>
</tbody>
</table>

[a][NaBARF]0/[Ini]0 = 1.2. b The value in parentheses is [Ini]0 (in mM). c Syndiotactic tetrad content (in %).

Using C2-symmetric α-diimine Pd(II) initiator 4 in conjunction with NaBARF,11 affording polymer 2 that is rich in three-syndiotactic sequences (i.e., 3).5 When 1 was allowed to polymerize with trans-3 in CH2Cl2 at 25 °C ([I]0/[3]/[NaBARF]0 = 100/1/1.2), the polymerization system entirely underwent gelation within 12 h. After 24 h, 1 was consumed completely, affording 2 with Mn and Mw/Mn of 4300 and 1.92, respectively, as estimated using poly styrene standards (Table 1, run 1). For evaluating the activity of cis-3, we used a 20/80 mixture of trans-3 and cis-3, since pure cis-3 was unavailable photochemically.12 The polymerization of 1 with this mixed initiator system took place sluggishly, reaching quantitative monomer conversion in 48 h (Table 1, run 6). With the assumption of pseudo-first-order kinetics, the activity of cis-3 for the polymerization of 1 was estimated as only 2% that of trans-3.12 Thus, the geometry of the azobenzene strap significantly affects the polymerization activity of 3.

Analogous to reported α-diimine Pd(II) initiators,5 trans-3 and 20/80 trans-3/cis-3 allowed for complete cyclization of the two allylic groups of 1 to afford, in the polymer main chain, trans-1,2-disubstituted cyclopentane units (2) whose relative configurations give rise to tacticity. Accordingly, in 13C NMR spectroscopy, polymer 2 could in principle show eight singlet CH signals corresponding to eight possible tetrads.5,12 Of particular interest, 2 obtained with cis-3 (Table 1, run 1) showed a highly enhanced CH signal at 47.0 ppm. Such an enhancement was more explicit when the polymerization was conducted at lower temperatures, such as 0 °C (Table 1, run 3; Figure 3c) and −10 °C (Table 1, run 5). Among the eight possible tetrads,12 only the disotactic or disyndiotactic tetrad content can be enhanced when the polymerization proceeds stereospecifically. With reported initiator 4,5 it was prepared as a reference (Table 1, run 7), which allowed us to confirm a marked enhancement of the CH signal at 46.7 ppm (Figure 3b). Hence, the intense CH signal at 47.0 ppm for polymer 2 obtained with trans-3 (Figure 3c) can be assigned to the three-disyndiotactic sequence.13 On the basis of a fitted spectrum using Lorentz functions,12 the three-disyndiotactic diad, triad, and tetrad contents in the polymer chain were evaluated as 84, 71, and 60%, respectively (Table 1, run 3).12

Size-exclusion chromatography using a refractive index/UV−vis dual detector suggested that stich-2 as-synthesized using trans-3 carried at its active end an initiator fragment, which was successfully cleaved off using Et3SiH.12 We confirmed that the resultant polymer bearing no initiator fragment can also induce gelation of halogenated solvents such as CH2Cl2 upon heating followed by cooling (Figure 4c inset and Table S2 in the SI).12 Using a smaller amount of stich-2 for the heating/cooling treatment in CH2Cl2 resulted in the formation of a weak gel. When this weak gel was subjected to centrifugation, a liquid phase clearly separated from a gel phase, indicating a critical gelation concentration (CGC). As the polymer molecular weight increased (Mn = 4200 → 8400 → 15800), the CGC decreased (22 → 14 → 10 wt %). In contrast, no gelation of CH2Cl2 occurred when stich-2 prepared using initiator 4 (Table 1, run 7) was used in place of stich-2 (Figure 4d, inset). Thus, the tacticity of polymer 2 plays a critical role in the gelation of CH2Cl2.

The physical gelation of CH2Cl2 indicates that stich-2 self-assembles to form a 3D network structure. As shown in Figure 4b,c, nanofibers with an average diameter of ∼10 nm were visualized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) of an air-dried sample of stich-2 (Table 1, run 4) prepared from its CH2Cl2 solution. Nanofiber formation also occurred with lower-molecular-weight stich-2 (Table 1, run 2).12 By means of cryogenic TEM, we confirmed that such nanofibers form even in dilute solution (Figure 4a). Consistently, dynamic light-scattering (DLS) analysis at 20 °C (Figure 5a) of a 2 wt % CH2Cl2 solution of stich-2 (dashed curve) showed the presence of light-scattering species whose hydrodynamic diameters increased as the concentration of stich-2 increased (8 wt %; solid curve). Its solution viscosity was highly sensitive to the concentration of stich-2 (Figure 5b, blue) even when it was lower than the CGC. In sharp contrast, as shown in Figure 4d, no nanofibers were observed for stich-2 (Table 1, run 7). Its CH2Cl2 solution (8 wt %) was virtually DLS-silent. Furthermore, the viscosity remained almost constant as the concentration of stich-2 increased from 0 to 2 wt % (Figure 5b, inset).
digitation has never been reported for polymers with rigid side chains on a rigid backbone.14 Prompted by unexpected physical gelation of solvents, we noticed that cyclic α-diamine Pd(II) complex trans-3 is the first initiator to cause syndiospecific cyclopolymerization of isopropylidene diallylmalonate (1),5 affording a barb-shaped polymer (Figure 1b). In halogenated solvents, this polymer, in contrast to its isotactic reference, self-assembles into nanofibers, eventually leading to the formation of a 3D network structure essential for physical gelation. This is in sharp contrast to known polymer physical gels, where polymer molecules assemble into spherulites rather than fibers for cross-linking.5,7 Further studies are in progress to elucidate the origin of syndiospecificity of trans-3 and tailor barb-shaped st-2 to develop particular functions.

Acknowledgment. We thank Dr. M. Yamashita for supporting X-ray crystallography, Profs. K. Osakada and D. Takeuchi for generous discussions, and Prof. M. Shimomura, Dr. H. Yabu, and Mr. M. Ara for viscosity measurements. The synchrotron radiation experiments were performed at BL44B2 at SPring-8 with the approval of RIKEN (Proposal 20090021). This work was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan, Grants-in-Aid for Scientific Research on Innovative Areas to K.K. (Photochromism 471) and T.A. (Emergence in Chemistry 2010).

Supporting Information Available: Synthesis of 3, X-ray crystallographic data for trans-3 (CIF), polymerization of 1, SEM and TEM micrographs of 2 and a derivative, DLS profiles of CH2Cl2 solutions of 2, DSC and TGA profiles of 2, and the WAXD profile of st-2. This material is available free of charge via the Internet at http://pubs.acs.org.

References