Chirality

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Helix-Sense-Selective Polymerization of Achiral Substituted Acetylenes in Chiral Micelles**

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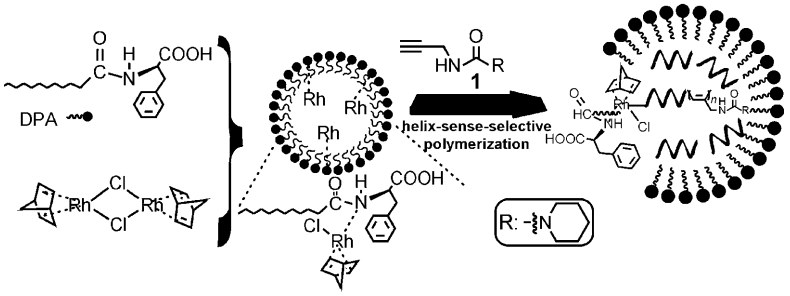
Helix-sense-selective polymerizations have been developed to control the screw sense of helices, by which optically active helical polymers can be formed from achiral monomers.[1–10] The current methodologies for helix-sense-selective polymerizations can be grouped into three categories: 1) by using chiral initiators[1] or chiral catalysts (cocatalysts),[2–6] well exemplified by the leading studies from the groups of Okamoto,[1] Nakano,[2] Masuda,[3] Novak,[4] Chen,[5] and Aoki;[6] 2) by using a chiral structure-directing agent, as demonstrated by the excellent work from Meijer and co-workers;[7] and 3) by using external asymmetric field effects creatively developed by the Akagi[8] and Shirakawa[9] groups.

Chiral micelles[11,12] have been widely applied for chiral recognition,[13] chiral separation,[14] and enantioselective synthesis.[15–18] The latter is of particular significance and promise, as chiral micelles provide an alternative for effectively controlling chiral stereostructures,[16] and thus they can be expected to provide asymmetric environments for performing helix-sense-selective polymerizations. To confirm this hypothesis, we prepared optically active nanoparticles consisting of substituted helical polyacetylenes by asymmetric polymerization of achiral monomers in chiral micelles,[19] whereas nonasymmetric polymerizations occurred in achiral micelles and provided nanoparticles without optical activity.[20] Unfortunately, in the asymmetric polymerizations,[19] even though the helical polymers forming the nanoparticles adopted one predominant handedness, they lost optical activity in solution. In the present study, a novel strategy was created by which helical-sense-selective polymerizations were achieved in chiral micelles; moreover, the as-prepared helical polymers kept their preferential helicity even in solution.

The strategy for helix-sense-selective polymerizations in chiral micelles is outlined schematically in Scheme 1. A chiral emulsifier, dodecylphenylalanine (D- or L-DPA), was synthesized from phenylalanine and dodecanoyl chloride.[21,22] DPA



Scheme 1. Schematic representation of the helix-sense-selective polymerization of achiral acetylenes in chiral micelles.

formed micelles in water and then underwent coordination to form a complex with the hydrophobic catalyst $[(nbd)RhCl]_2$ inside the micelles (nbd = 2,5-norbornadiene). The complex aqueous solutions exhibited optical activity according to the positive (assigned to D-DPA) and negative (L-DPA) circular dichroism (CD) signals at around 400 nm in Figure S1 (Supporting Information), while D- and L-DPA showed CD signals at approximately 230 nm (D-DPA, positive; L-DPA, negative; inset in Figure S1). The difference in the wavelength of the CD signals between DPA and the corresponding coordination complex is due to the coordination of Rh by N in the latter case, which causes charge transfer between the two atoms.[23] Herein, it is important to note that when aqueous NaOH solution was added, for example, to the D-DPA–Rh catalyst solution (e.g., NaOH/D-DPA, 1.5:1, mol%), the positive CD signal at around 400 nm almost disappeared (Figure S1), resulting from destruction of the coordinative bonds between D-DPA and Rh by OH^-. Achiral substituted acetylene monomer **1** (see Scheme 1) was then added and underwent helix-sense-selective polymerization inside the micelles, where the chiral complex acted simultaneously as emulsifier and chiral catalyst. It should be noted that a large amount of emulsifier was needed to obtain stable polymer emulsions from substituted acetylenes.[19,20] This is also true

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for the present helix-sense-selective polymerization of substituted acetylenes.

The polymers derived from **1** adopted helical conformations but without optical activity.[24] In the helix-sense-selective polymerizations of **1** in the presence of L-DPA-Rh or D-DPA-Rh, the monomer conversions were 92% and above. The number-average molecular weight (M_n) of poly(**1**) (from **1**) obtained in L- and D-DPA–Rh micelles was 43800 and 37400, the molecular weight distribution (M_w/M_n) 1.52 and 1.53, respectively. The difference in M_n values of the two polymers may be attributed to the varied chiral stereostructure of the catalyst.

The polymer emulsions were found to be quite stable for at least three months. A transmission electron microscopy (TEM) image of D-DPA-poly(**1**) is shown in Figure 1 and clearly demonstrates the formation of nanoparticles. The average particle diameter was 135 nm. The TEM images of D-DPA micelles, D-DPA-**1** emulsions, and D-DPA-poly(**1**) are shown in Figure S2 in the Supporting Information. The polymer particle size was much larger than that of the initial micelles (47 nm) and the monomer micelles (51 nm). It is indicated that the polymerizations occurred inside the micelles, as will be discussed below.

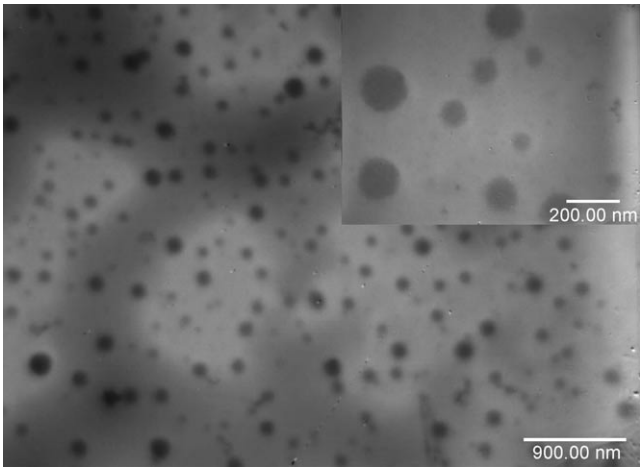

Figure 1. TEM images of a D-DPA-poly(**1**) emulsion. The diameter of the particles was about (135 ± 17) nm.

Our previous investigations demonstrated that CD spectroscopy is applicable to identify the secondary structures of polymers constituting nanoparticles.[19,20] The present polymer emulsions were thus characterized by CD spectroscopy, and the obtained CD spectra are displayed in Figure 2, where positive and negative Cotton effects are observed at about 370 nm for poly(**1**) emulsions prepared in the presence of D-DPA and L-DPA, respectively (spectra 1 and 6 in Figure 2). Meanwhile, D- and L-DPA-poly(**1**) emulsions present UV/Vis absorptions in a wavelength range of 300–500 nm with $\lambda_{max} =$ 330 nm (Figure S3). It is worthy to note that emulsions of monomer **1** in the presence of D-DPA–Rh (D-DPA-**1**) or L-DPA–Rh (L-DPA-**1**) did not exhibit CD signals and UV/Vis absorptions at the investigated wavelength from 300 to 500 nm. Therefore, according to the observations above and

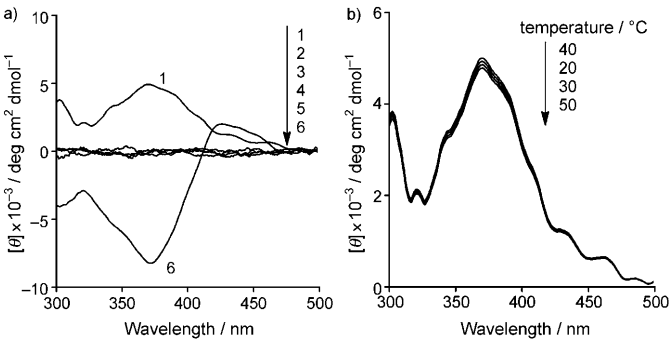

Figure 2. CD spectra of poly(**1**) emulsions. a) Spectrum 1: D-DPA-poly(**1**) emulsion; spectrum 2: D-DPA-**1** emulsion; spectrum 3: L-DPA-**1** emulsion; spectrum 4: SDS-poly(**1**) emulsion; spectrum 5: poly(**1**) obtained from solution polymerization emulsified by D-DPA; spectrum 6: L-DPA-poly(**1**) emulsion. The spectra were recorded at 20°C. b) CD spectra of D-DPA-poly(**1**) emulsions measured at various temperatures. The concentration of all the polymers was approximately 0.15 M (determined by the monomer unit); for measuring CD spectra, all the original solutions were diluted 15 times with deionized water.

referring to our earlier investigations,[19,20] both D- and L-DPA-poly(**1**) emulsions possess optical activities, which originate from the preferential helical conformations of the polymers constituting the nanoparticles. This consideration is also supported by further investigations of poly(**1**) in $CHCl_3$ solution, as will be discussed below.

It is considered that the preferential helical structures of D- and L-DPA-poly(**1**) are formed by helix-sense-selective polymerization of achiral **1** rather than by "chiral induction" toward poly(**1**) by D- and L-DPA after polymerization. This conclusion is made on the basis of the following observations. Firstly, no Cotton effects were observed in the CD spectra of the poly(**1**) emulsion in the presence of D-DPA (300–500 nm; spectrum 5 in Figure 2a), which was prepared by emulsification of poly(**1**) by D-DPA in an aqueous system under similar conditions to prepare D-DPA-poly(**1**) in chiral micelles (L-DPA provided the same results; herein, poly(**1**) was pre-prepared by solution polymerization of **1** in THF). Secondly, no Cotton effects were observed in the emulsion of SDS-poly(**1**), which was prepared by monomer polymerization in achiral micelles consisting of SDS and $[(nbd)RhCl]_2$ (SDS–Rh; spectrum 4 in Figure 2a; SDS = sodium dodecylsulfate). Moreover, D- and L-DPA-poly(**1**) emulsions present CD effects of the same sign as that of the corresponding D- and L-DPA–Rh (Figure S1). It hence seems that the chirality of the chiral micelles was transferred to the helical polymers.

The helical structures of D- and L-DPA-poly(**1**) in the nanoparticles had high thermal stability, which was supported by the little change in the CD signals and UV/Vis absorptions of the D-DPA-poly(**1**) emulsion from 20 to 50°C (taking D-DPA-poly(**1**) as an example; Figure 2b and Figure S4 in the Supporting Information).

To further understand the helix-sense-selective polymerizations in chiral micelles, poly(**1**) in the nanoparticles was collected by repeatedly centrifugal separation with a rotational speed of 20000 rpm and washed with 10% aqueous NaOH solution several times. OH^- ions destroyed the coordinative bonds between DPA and the Rh catalyst, as

mentioned above, and hence pure poly(**1**) was obtained. This consideration is supported by the ^{1}H NMR spectrum of poly(**1**) (from D-DPA-poly(**1**)) in Figure S5, which is highly similar to that of pure poly(**1**) obtained in organic solvents.[24] The residual product of pure poly(**1**) was then dissolved in $CHCl_3$ for measuring CD and UV/Vis absorption spectra. The results are presented in Figure 3. The UV/Vis absorptions and

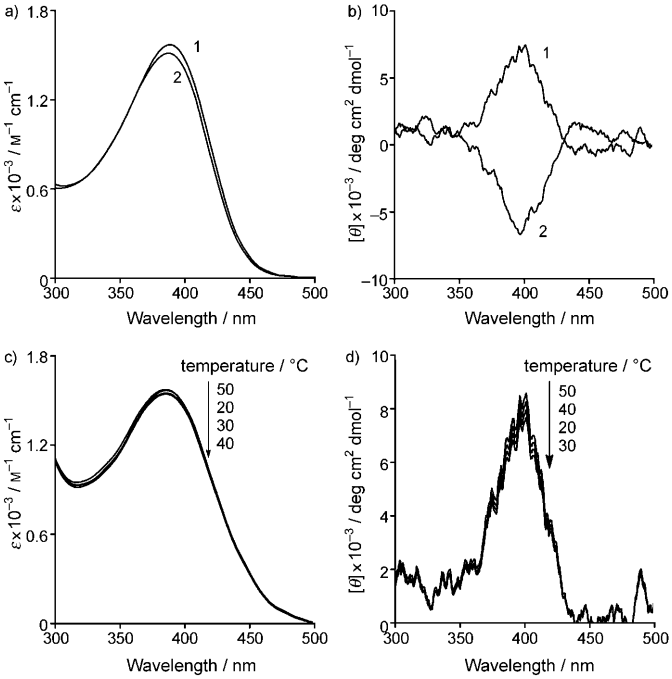

Figure 3. a) UV/Vis spectra and b) CD spectra of poly(**1**) (spectra 1: by D-DPA; spectra 2: by L-DPA) in $CHCl_3$ ($c = 0.1$ mM). The spectra were recorded at 20 °C. c) UV/Vis spectra and d) CD spectra of poly(**1**) (by D-DPA) in $CHCl_3$, measured at various temperatures.

positive and negative CD signals of poly(**1**) samples (by D-DPA and L-DPA) at about 390 nm reflect that both poly(**1**) isomers form predominantly one-handed helical structures[24,25] and more importantly present optical activity. Namely, helicity was retained in the pure helical poly(**1**) samples in solution. Moreover, the UV/Vis absorptions and CD signals of poly(**1**) (by D-DPA, as a representative) in $CHCl_3$ hardly changed with increasing temperature (Figure 3c,d), but a red shift appeared relative to the signals of the corresponding poly(**1**) emulsion (Figure 2), as a result of the highly packed polymer chains and their reduced effective conjugation length inside the nanoparticles.[20]

According to the investigations above, we propose that in the course of the helix-sense-selective polymerizations, the helicity of D- and L-DPA-poly(**1**) was controlled by the chirality of the Rh catalyst/chiral emulsifier coordination complex. The resulting helices were further stabilized by intramolecular hydrogen bonds and steric repulsions of the pendent groups. During the helix-sense-selective polymerization, the helical conformations of the polymer may be under kinetic rather than thermodynamic control.[4] The difference between thermodynamic control and kinetic control led to two results of large difference: Thermodynamic control gave rise to dynamic helices, as observed in our earlier studies,[19] where the helical polymers cannot retain their chirality in solution. In contrast, kinetic control resulted in stable helices, as observed in the present study.[4] For this reason, the helical polymers prepared in this study can retain their optical activity in $CHCl_3$ solution. However, in a highly polar solvent, such as DMF, the polymers lose their original preferential helicity as a result of destruction of hydrogen bonds between neighboring urea groups.

In summary, achiral substituted acetylene **1** underwent helix-sense-selective polymerization inside chiral micelles. The obtained polymer emulsions presented optical activity. The polymer constituted the nanoparticles' adopted predominantly one-handed helical conformation both in the nanoparticle and in solution states, even at an elevated temperature. The present investigations led to a novel strategy to perform helix-sense-selective polymerizations in chiral micelles to prepare preferentially helical polymers and optically active polymer emulsions from achiral monomers. The effective and robust strategy is expected to be applicable to other types of achiral monomers. This study also provides a versatile platform for designing and preparing further novel nanoparticles consisting of preferentially helical polymers and polymeric emulsions.

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[1] Y. Okamoto, T. Nakano, *Chem. Rev.* **1994**, *94*, 349 – 372.
[2] T. Sakamoto, Y. Fukuda, S. Sato, T. Nakano, *Angew. Chem.* **2009**, *121*, 9472 – 9475; *Angew. Chem. Int. Ed.* **2009**, *48*, 9308 – 9311.
[3] T. Nishimura, Y. Ichikawa, T. Hayashi, N. Onishi, M. Shiotsuki, F. Sanda, T. Masuda, *Organometallics* **2009**, *28*, 4890 – 4893.
[4] G. L. Tian, Y. J. Lu, B. M. Novak, *J. Am. Chem. Soc.* **2004**, *126*, 4082 – 4083.
[5] G. M. Miyake, E. Y. X. Chen, *Macromolecules* **2008**, *41*, 3405 – 3416.
[6] T. Aoki, T. Kaneko, N. Maruyama, A. Sumi, M. Takahashi, T. Sato, M. Teraguchi, *J. Am. Chem. Soc.* **2003**, *125*, 6346 – 6347.
[7] A. J. Wilson, M. Masuda, R. P. Sijbesma, E. W. Meijer, *Angew. Chem.* **2005**, *117*, 2315 – 2319; *Angew. Chem. Int. Ed.* **2005**, *44*, 2275 – 2279.
[8] K. Akagi, *Chem. Rev.* **2009**, *109*, 5354 – 5401.
[9] H. Shirakawa, *Curr. Appl. Phys.* **2001**, *1*, 88 – 89.
[10] Z. Q. Wu, K. Nagai, M. Banno, K. Okoshi, K. Onitsuka, E. Yashima, *J. Am. Chem. Soc.* **2009**, *131*, 6708 – 6718.
[11] J. Skey, R. K. O'Reilly, *J. Polym. Sci. Part A* **2008**, *46*, 3690 – 3702.
[12] L. Z. Zhao, X. Wang, Y. Li, R. J. Ma, Y. L. An, L. Q. Shi, *Macromolecules* **2009**, *42*, 6253 – 6260.
[13] C. Bombelli, C. Bernardini, G. Elemento, G. Mancini, A. Sorrenti, C. Villani, *J. Am. Chem. Soc.* **2008**, *130*, 2732 – 2733.
[14] S. A. A. Rizvi, J. Zhang, R. P. Apkarian, S. N. Dublin, S. A. Shamsi, *Anal. Chem.* **2007**, *79*, 879 – 898.
[15] S. I. Goldberg, N. Baba, R. L. Green, R. Pandian, J. Stower, R. B. Dunlap, *J. Am. Chem. Soc.* **1978**, *100*, 6768 – 6769.

[16] K. Ahlford, J. Lind, L. Maler, H. Adolfsson, *Green Chem.* **2008**, *10*, 832 – 835.
[17] Y. Zhang, P. Sun, *Tetrahedron: Asymmetry* **1996**, *7*, 3055 – 3058.
[18] F. H. Zhang, W. S. Zhao, J. Zou, Y. Liu, R. T. Liand, Y. C. Cui, *Chirality* **2009**, *21*, 492 – 496.
[19] X. F. Luo, L. Li, J. P. Deng, T. T. Guo, W. T. Yang, *Chem. Commun.* **2010**, *46*, 2745 – 2747.
[20] J. P. Deng, B. Chen, X. F. Luo, W. T. Yang, *Macromolecules* **2009**, *42*, 933 – 938.
[21] E. Jungermann, J. F. Gerecht, I. J. Krems, *J. Am. Chem. Soc.* **1956**, *78*, 172 – 174.
[22] S. Miyagishi, M. Nishida, *J. Colloid Interface Sci.* **1978**, *65*, 380 – 386.
[23] W. Choi, A. Termin, M. R. Hoffmann, *J. Phys. Chem.* **1994**, *98*, 13669 – 13679.
[24] J. P. Deng, X. F. Luo, W. G. Zhao, W. T. Yang, *J. Polym. Sci. Part A* **2008**, *46*, 4112 – 4121.
[25] L. Ding, X. F. Jiao, J. P. Deng, W. G. Zhao, W. T. Yang, *Macromol. Rapid Commun.* **2009**, *30*, 120 – 125.

