Synthesis of Regioregular Poly(para-phenylene)s and the Effect of the Structure and Solvents on Circular Dichroism

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We have reported that cross-coupling polymerization of bromo(chloro)benzene bearing different substituents at 2- and 5-positions takes place successfully with nickel(II) catalyst to synthesize the unprecedented regioregular poly (para-phenylene) (PPP).[1] Recently, we have modified the ligand structure of nickel to afford the polymer with large average degree of polymerization (DP).[2] Herein, we describe the CD property of the regioregular PPPs bearing a chiral substituent suggesting chirality-induced higher order orientation of the polymer such as helix structure.

Synthesis of polyphenylene was performed by the cross-coupling polymerization of the monomer with a nickel catalyst bearing chiraphos as a ligand[2] to obtain PPP **1** with the average DP up to 217, which was ca. 4 times higher than that previously prepared. We measured the CD property of **1** (DP=109) in a mixed solution of 1, 2-dichloroethane (DCE)/MeOH and showed the highest CD intensity at the ratio of DCE/MeOH = 5:5 (g factor = 2.4x10^{-2}), which was higher than that of **1** (DP=45) as represented in Figure 1. It was also found that the high CD intensity was observed as the increment of the DP value. However, the CD intensity of PPP **1** of higher DP (> ca. 150) changed to much lower (Figure 1(b)). Effects of the side-chain structure on the CD behavior of polyphenylene **1** and CD and fluorescence properties as a cast film of **1** were also studied.

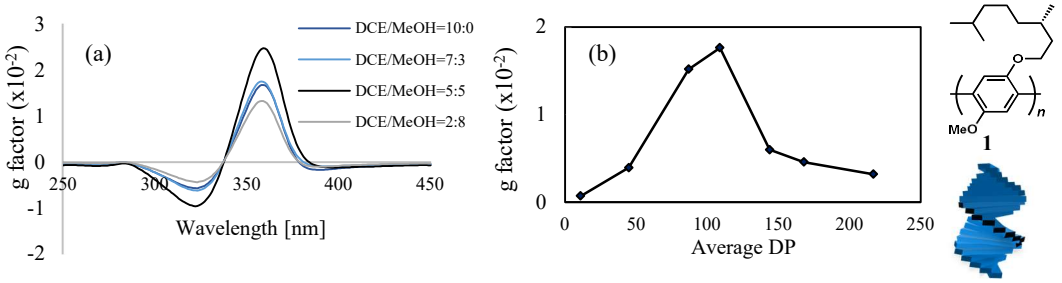

Figure 1. (a) CD spectra of **1** (DP=109) in a mixed solution of 1, 2-dichloroethane (DCE)/MeOH and (b) the relationship of the CD intensity (DCE/MeOH=7:3) to the DP value.

(1) Shibuya, Y.; Nakagawa, N.; Miyagawa, N.; Suzuki, T.; Okano, K.; Mori, A. *Angew. Chem. Int. Ed.* **2019**, *58* (28), 9547–9550. (2) Fukuoka, H.; Susami, K.; Shibuya, Y.; Okano, K.; Mori, A. *The 101st CSJ Annual Meeting*, (2021).