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Effect of Polyelectrolyte Function on Helical Structures of Optically Active Poly(phenylacetylene) Derivatives Bearing Basic or Acidic Functional Pendant Groups

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S *Supporting Information*

INTRODUCTION

Helical polymers with a controlled helix sense have become one of the emerging research topics in polymer chemistry[1] and supramolecular chemistry[2] because of their attractive applications in the chiral material sciences for separating enantiomers as chiral stationary phases in chromatography[3] and also for producing one of the enantiomers as a polymeric asymmetric catalyst.[4] The fully synthetic helical polymers prepared so far can be classified into two categories with respect to their helix inversion barriers, i.e., static helical polymers with a sufficiently high helix inversion barrier and dynamic helical polymers with a low helix inversion barrier, although there are certain helical polymers exhibiting both features depending on the structures of the repeating monomer units.[1n] Stereoregular (cis-transoidal) poly(phenylacetylene)s[1g−p] as well as polyisocyanates[1a,b] and polysilanes[1c,f] generally belong to a class of dynamic helical polymers. An extremely high sensitivity to a chiral environment is the most important characteristic of these dynamic helical polymers because a small chiral bias can induce a main-chain conformational change with a large amplification through covalent or noncovalent bonding with a high cooperativity, thus producing optically active helical polymers with a large helical sense excess.[1a,b,g,i,l,n]

In a series of studies, we reported that optically inactive, cis-transoidal poly(phenylacetylene)s bearing basic or acidic functional pendant groups, such as *N*,*N*-diisopropylaminomethyl (poly-**1**)[5] or phosphonate monoethyl (poly-**2**)[6] and carboxy (poly-**3**)[6d,e,7] groups (Chart 1), formed a predominantly one-handed helix by the acid−base complexation with optically active acids or amines, respectively, in water and organic solvents, thus showing a characteristic induced circular dichroism (ICD) in the UV−vis regions of the polymer backbones. During the course of our study, we found that a dynamic helical polyelectrolyte, the hydrochloride salt of poly-**1** (poly-**1**-HCl), was highly sensitive to the chirality of acids and could detect a small enantiomeric imbalance in the chiral acids in water.[5c−e] For example, the ICD intensities of the second Cotton effect of poly-**1**-HCl increased with an increase in the concentration of the chiral acids and reached an almost constant value even at [chiral acid]/[poly-**1**-HCl] = 0.3.[5d] In contrast, the noncharged poly-**1** required a large amount of chiral acids (>500 equiv) to induce a full ICD in organic solvents, such as tetrahydrofuran (THF).[5b] A similar strong chiral amplification has been observed for poly(phenylacetylene)s having bulky crown ether pendants with amino acids in organic solvents,[8] but the noncharged, neutral crown ether-bound poly(phenylacetylene)s were not sensitive to the chirality of the amino acids in water.[9] These observations suggest that the polyelectrolyte character of the poly-**1**-HCl appears to be essential for the powerful chirality-sensing with a high sensitivity in water.

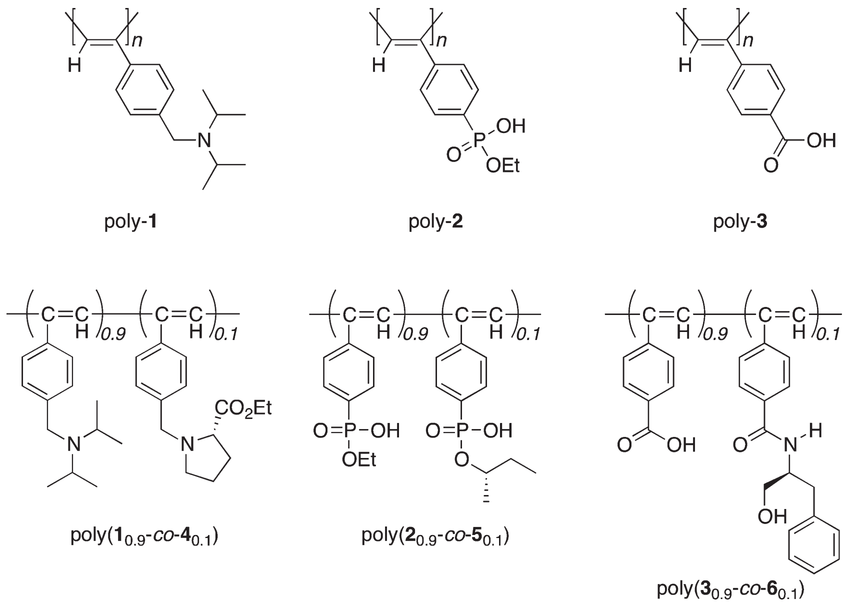
Theoretically, the cooperative change in the enantiomeric excess of a single-handed helical state in dynamic helical polymers is described by the Ising model.[1a,b,10] This model possesses two thermodynamic parameters governing the cooperative enantiomeric excess change, the Gibbs energy difference, $2\Delta G_h$, between the right- and left-handed helical states and the Gibbs energy of the helix reversal, ΔG_r (both per monomer unit). While the discrimination of the opposite-handed helical states is caused by ΔG_h, the high sensitivity of the helical polymer to a chiral environment arises from the difficult helix reversal within the polymer chain, i.e., high ΔG_r.

In the previously mentioned poly(phenylacetylene)s complexed with optically active acids or amines, the chiral interaction between the optically active acids or amines and polymer chain changes, ΔG_h, from zero to a nonzero value, and the intramolecular electrostatic repulsion of the polymer chain may increase the ΔG_r. In the above examples, the ionization of the polymer chain and the association or dissociation of chiral pendant groups simultaneously takes place, so that the experimental check of the contributions of ΔG_h and ΔG_r to the sensitivity during the chirality sensing was difficult.

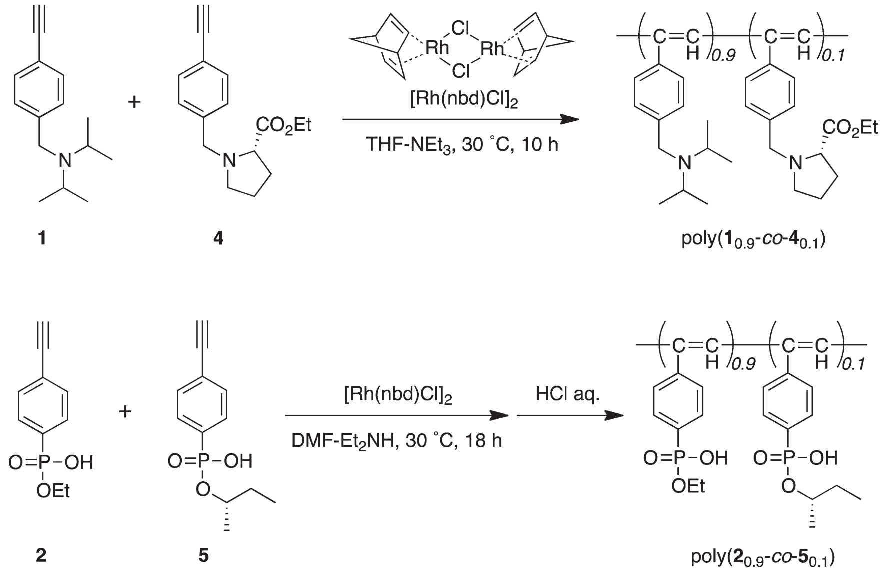
In the present study, we synthesized three novel chiral−achiral random copolymers of phenylacetylene derivatives: (poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$), poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$), and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$)) (Chart 1). These poly(phenylacetylene)s separately bear ionizable groups and a small amount of optically active groups as the pendants. Therefore, we can change only the intramolecular electrostatic interaction of the helical copolymer chains mostly affecting only ΔG_r, while keeping the chiral interaction or

Received: August 22, 2011
Revised: September 14, 2011
Published: September 28, 2011

Chart 1. Structures of Optically Inactive Homopolymers and Optically Active Copolymers Bearing Basic or Acidic Functional Pendant Groups



Scheme 1



ΔG_h constant. Using these copolymers, we have examined the polyelectrolyte effects on the temperature dependence of the circular dichroism (CD) for the copolymers by changing the solvent polarity and also doping an achiral amine to poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in organic solvents.

RESULTS AND DISCUSSION

Synthesis of Optically Active Copolymers of Phenylacetylenes Bearing Basic or Acidic Functional Pendant Groups. Cis-transoidal optically active copolymers bearing a basic diisopropylaminomethyl group (poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$)) and an acidic phosphonate monoethyl ester group (poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$)) were prepared by the copolymerization of **1** with **4** and **2** with **5**, respectively, with a rhodium catalyst, [Rh(nbd)Cl]$_2$, in a method similar to that previously reported as outlined in Scheme 1.[5b,6c,7a,7b] The optically active monomers (**4** and **5**) were designed and synthesized by introducing the chiral substituents with a similar bulkiness to the achiral monomers **1** and **2** in order to exclude the effect of the bulkiness during the copolymerization. The monomer feed ratios were set at [**1**]/[**4**] = 9/1 and [**2**]/[**5**] = 9/1 to minimize the contiguous sequence of the chiral monomer units. The ^{1}H NMR spectra of these copolymers showed sharp singlets centered at around 5.8 ppm due to the main chain protons, indicating that these polymers possess a highly cis-transoidal, stereoregular structure (Figure S1).[5e,6c,11]

To confirm that poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) and poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) are random copolymers, the monomer reactivity ratios during the copolymerizations were estimated using the Kelen–Tüdös method[12] from the copolymerization results at varying monomer feed ratios, followed by termination at low conversions ($\leq$10%) (Tables S1 and S2 and Figure S3). The products of the monomer reactivity ratios for the copolymerizations of **1** with **4** and **2** with **5** are 0.73 and 1.24, respectively, suggesting that the monomer distributions in the copolymers are mostly random. On the other hand, poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) bearing a carboxy group was prepared by the macromolecular reaction of cis-transoidal poly-**3**[7d] with L-phenylalaninol (Scheme S3 and Figure S2) using the condensing agent, 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM),[13] because the copolymerization of the corresponding monomers with a rhodium catalyst produced blocklike copolymers.[14] The contents of the chiral units of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$), poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$), and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) were determined to be ~10% based on ^{1}H NMR and elemental analyses. The molecular weighs of the copolymers are summarized in Table 1.

Chiroptical Properties of the Copolymers. Figure 1A shows the CD and absorption spectra of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) in aqueous 0.1 N HCl at various temperatures. An intense split-type CD is observed in the UV–vis region of the polymer backbone, which decreases with the increasing temperature, but the absorption spectrum only slightly changes with the temperature. These results indicated that the copolymer takes a preferred-handed helical conformation induced by the covalent-bonded chiral pendant groups. The Cotton effect pattern is similar to that of the cis-transoidal poly-**1**-HCl complexed with optically active carboxylic acids as previously reported.[5d,e] Moreover, the CD intensity of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) in aqueous 0.1 N HCl below 25 °C was comparable to the maximum CD intensity ($[\theta]_{2nd} = 5.7 \times 10^4$) of poly-**1**-HCl complexed with optically pure phenyllactic acid estimated from the CD titration profile at which the polymer is anticipated to have a complete single-handed helical conformation,[5e] suggesting that poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) most likely possesses an almost one-handed helical conformation in aqueous 0.1 N HCl below 25 °C.

In Figure 1B, a similar CD pattern is observed in THF, but its CD intensity is much weaker than that in aqueous 0.1 N HCl even below 0 °C. The CD intensity in THF gradually increases with the decreasing temperature, but the absorption spectrum only slightly changes. The temperature-dependent CD change was reversible. Thus, the small amount of chiral units (10 mol %) incorporated in the poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) chain can sufficiently amplify the chirality to induce the overall main chain helical conformation with an almost one-handedness in aqueous 0.1 N HCl, which is not the case in the organic solvent THF.

Significant differences between the CD in an aqueous solution and organic solvents were also observed for poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) (Figure S5) and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) (Figure S6) bearing acidic functional groups. Figure 2 shows the CD intensities of the second Cotton effect ($[\theta]_{2nd}$) for the three copolymers as functions of the temperature. In Figure 2A,C, both the CD and their temperature dependences of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) in THF and of poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in methanol (MeOH) are much weaker than those of the same copolymers in an aqueous solution. As shown in Figure 2B, the CD of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) in a MeOH/dimethyl sulfoxide (DMSO) mixture (9/1, v/v) is also much weaker than that in 0.01 N aqueous NaOH above 0 °C, but it sharply increases at low temperatures, eventually reaching the value in the aqueous solution around 0 °C.

Table 1. Characteristics of Copolymers of Achiral Phenylacetylenes Bearing Basic or Acidic Functional Groups with Optically Active Phenylacetylenes

run	copolymer	$M_w \times 10^{-5}$	M_w/M_n	$N_{0,w} \times 10^{-3}$ [a]
1	poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$)	4.46[b]	1.8[b]	1.8
2	poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$)	2.42[b]	1.6[b]	1.0
3	poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$)	4.97[c]	4.5[c]	3.1

[a] Weight-average degree of polymerization estimated from M_w. [b] Calculated from the number-average molecular length (L_n) and weight-average molecular length (L_w) estimated by AFM (Figure S4). [c] Determined by SEC (polystyrene standards) with chloroform as the eluent as its methyl ester of the original poly-**3**.

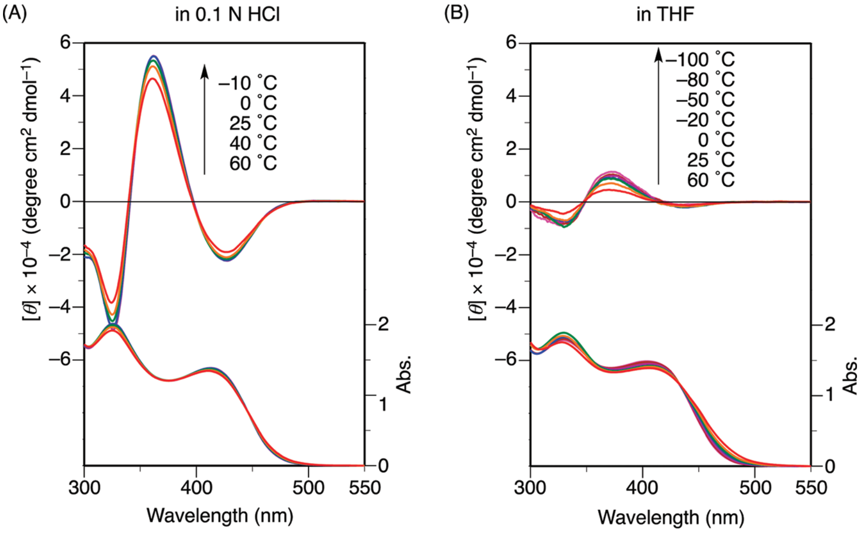


Figure 1. Temperature-dependent CD and absorption spectra of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) in aqueous 0.1 N HCl (pH 1.4) (A) and in THF (B). [Polymer] = 0.2 (<−10 °C) and 1.0 mg/mL (≥−10 °C).

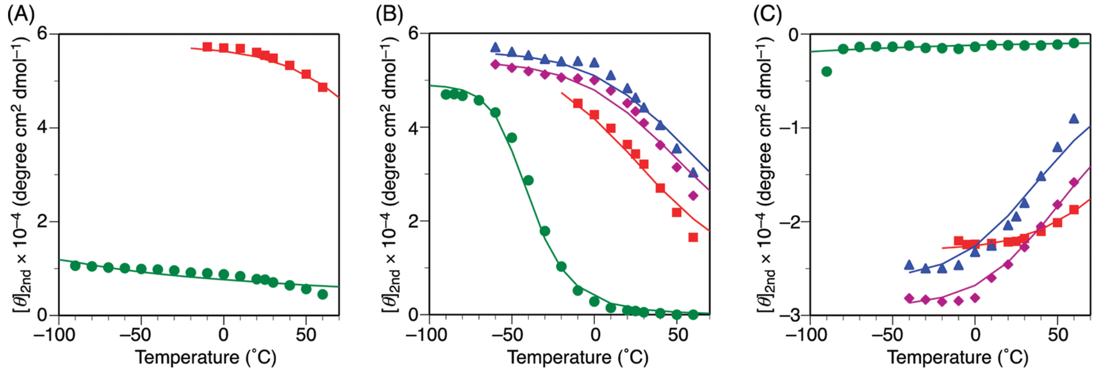
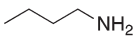
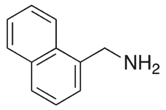


Figure 2. Temperature dependence of the molar ellipticity $[\theta]_{2nd}$ at the second Cotton peak of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) (A), poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) (B), and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) (C) in water (■) (aqueous 0.1 N HCl (A) and 0.01 N NaOH (B, C)) and organic solvents (THF (A), MeOH-DMSO (9/1, v/v) (B), and MeOH (C)) in the absence (●) and presence of *n*BA (▲) and NMA (◆). Solid curves represent theoretical values calculated by the Ising model theory with parameters listed in Table 2.

The CD intensities of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in the organic solvents dramatically increased and become comparable to those in the aqueous solutions by the addition of the achiral amine *n*-butylamine (*n*BA) or 1-naphthalenemethylamine (NMA), as shown in Figure 2B,C. The changes in the CD intensities are almost independent of the bulkiness of the amines added for both copolymers. Previously, we have demonstrated by viscometry that poly-**3** was converted from a neutral polymer to a polyelectrolyte in DMSO with the addition of (1-(1-naphthyl)ethyl)amine. Although we have not done the viscometric check for the copolymers under the solvent conditions shown in Figure 2B,C, we can expect the ionization for the two copolymers by the addition of the achiral bases in organic solvents and that the remarkable amplifications of the helical chirality by the bases result from generation of the charged pendant groups upon complexation with bases.



*n*BA



NMA

Theoretical Analysis of CD Data. To provide more quantitative arguments, we compared the temperature dependences of the CD shown in Figure 2 with the Ising model,[1a,b,10] in which each monomer unit in the helical polymer chains can take a right-handed (*P*) helical state, left-handed (*M*) helical state, or helix reversal state. The model is characterized by four parameters, i.e., the Gibbs energy difference, $2\Delta G_h$, between the *P* and *M* states, the Gibbs energy, ΔG_r, of the helix reversal state, the degree of polymerization, N_0, and the chiral monomer content, x. We used the weight-average degree of the polymerization listed in Table 1 as N_0, neglecting the effect of the polydispersity in N_0, and $x = 0.1$. In general, ΔG_h for chiral−achiral copolymers depends on the type of chirally interacting neighboring monomer units,[15] but the ΔG_h value for the chiral−chiral monomer units is not important for our present samples with $x = 0.1$ because the chiral−chiral monomer unit sequence seldom appears. We assumed the same value for ΔG_h for the chiral−chiral and chiral−achiral monomer units.

According to the previously reported procedure,[16] we calculated the average conformational partition function to obtain the fraction f_M of the units in the *M* helix state in the routine procedure by generating many sequences of the chiral−achiral random copolymer with a given N_0 and the mole fraction of the chiral unit (10%) on a computer.[10b] The molar ellipticity of the second Cotton effect ($[\theta]_{2nd}$) was calculated from the helical sense excess ($2f_M - 1$) of the *M* helix state multiplied by the maximum molar ellipticity $[\theta]_{max}$ of the intact *M* helix at $2f_M - 1 = 1$. Here, a positive $[\theta]_{2nd}$ can be assigned to the left-handed helix on the basis of the relation between the CD sign and the handedness of the helix determined by the direct visualization of the helical structure of analogous optically active poly(phenylacetylene) derivatives by atomic force microscopy (AFM).[11f−h,17]

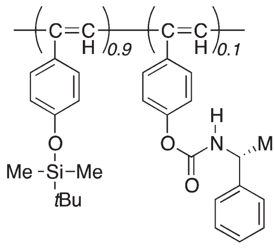
We first tried to fit data for the three copolymers in an aqueous solution, taking ΔG_h, ΔG_r, and $[\theta]_{max}$ as the adjustable parameters. The fitting results are shown in Figure 2 by the red curves, and the selected fitting parameters are listed in Table 2. The values of $|\Delta G_h|$ and ΔG_r are 36 ± 7 J mol^{-1} and 17200 ± 2100 J mol^{-1}, respectively, being intermediate among those already reported for synthetic helical polymers, poly(isocyanate)s[18] and poly(silylene)s.[19] In a previous study,[16] we reported $|\Delta G_h|$ and ΔG_r for optically active homopolymers and chiral−achiral random copolymers of phenylacetylene derivatives in organic solvents. The present ΔG_r values are close to the previous results for poly(phenylacetylene)s bearing bulky substituents. On the other hand, the present $|\Delta G_h|$ values are slightly higher than the previous results (<10 J mol^{-1}). This may be due to the position of the asymmetric carbons, which in the present samples are closer to the main chain than those in the previous ones. The values of $[\theta]_{max}$ for poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) and poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) are close to each other, but that for poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) is considerably smaller than that for the other copolymers. Accordingly, the absorption spectrum for poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) was also slightly different from those of the other two copolymers (cf. Figure S6). These differences are caused by the different stable internal rotation angle of the polyacetylene main chain of the copolymers.

The weak temperature dependences of the CD for poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) in THF and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in MeOH shown in Figure 2 could not be fitted by the theory using the temperature independent ΔG_h and ΔG_r. Similar weak temperature dependences of the CD were previously observed for poly-**7**,

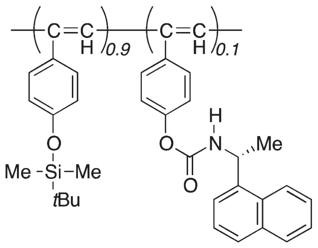
Table 2. Parameters Determined by Fitting CD Data for Poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$), Poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$), and Poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) to the Ising Model Theory

run	polymer	solvent	$[\theta]_{max}$[a]	ΔG_h[b]	ΔG_r[b]
1	poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$)	water[c]	5.7	33	19200
2		THF	5.7	33	$32.5T = 5600$ (−100 °C) $32.5T = 11200$ (70 °C)
3	poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$)	water[d]	5.4	29	15100
4		MeOH−DMSO (9/1, v/v)	4.9	30	$26900-69.9T = 14800$ (−100 °C) $26900-69.9T = 2900$ (70 °C)
5		MeOH-DMSO (9/1, v/v)[e]	5.6	38	16300
6		MeOH-DMSO (9/1, v/v)[f]	5.4	33	16300
7	poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$)	water[g]	2.3	−42	17600
8		MeOH	2.6	−15	$30.0T = 5200$ (−100 °C) $30.0T = 10300$ (70 °C)
9		MeOH[e]	2.6	−21	16300
10		MeOH[h]	2.9	−25	16700

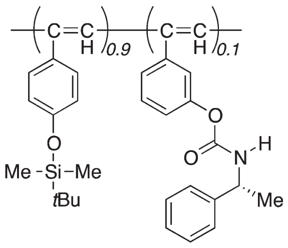
[a] In units of 10^4 deg cm^2 dmol^{-1}. [b] In units of J mol^{-1}. [c] 0.1 N HCl, pH 1.4. [d] 0.01 N NaOH, pH 12.3. [e] In the presence of *n*BA ([*n*BA]/[polymer] = 10). [f] In the presence of NMA ([NMA]/[polymer] = 10). [g] 0.01 N NaOH, pH 11.8. [h] In the presence of NMA ([NMA]/[polymer] = 500).



poly-**7**



poly-**8**



poly-**9**

poly-**8**, and poly-**9** in THF, which were not theoretically analyzed in a previous paper.[16] The above-mentioned strong temperature dependences in aqueous solutions mainly arise from the temperature dependence of the probability of the helix reversal, which is proportional to $\exp(-\Delta G_r/RT)$ (R: the gas constant; T: the absolute temperature), so that the temperature insensitivity of the CD in organic solvents may be attributed to the temperature independence of the probability. If the entropic contribution ΔS_r is predominant in ΔG_r, we can write $\Delta G_r \approx -\Delta S_r T$, and the probability of the helix reversal becomes temperature independent. On the basis of the assumption of a purely entropic ΔG_r, the theory can fit the CD data for poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in organic solvents as demonstrated by the green curves in Figure 2A,C. The used values of ΔS_r were −32.5 J K^{-1} mol^{-1} for poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) in THF and −30.0 J K^{-1} mol^{-1} for poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in MeOH. As listed in Table 2, the ΔG_r values calculated from ΔS_r are considerably smaller than ΔG_r of the same copolymers in aqueous solutions in the investigated range from −100 to 70 °C and comparable to those previously estimated for the copolymers of nonbulky phenylacetylene with a small amount of optically active phenylacetylene derivatives in THF (runs 2, 7, and 11 in Table 2 of ref 16). If the helix reversal is prohibited by some steric hindrance within the copolymer chain, ΔG_r may be purely entropic, while the intramolecular electrostatic interaction may provide an enthalpic ΔG_r.

Although poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) exhibits the strong temperature dependence of the CD in the MeOH/DMSO mixture, the temperature dependence could not be fitted by the theory using the constant ΔG_r because the CD and its temperature dependence were very weak above 0 °C. If we assume a linear temperature dependence of ΔG_r given in Table 2 (run 4), the theory fits the experimental data, as shown by the green curve in Figure 2B. This temperature dependence of ΔG_r assumed is opposite to those for poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in organic solvents; i.e., ΔG_r is small at high temperatures and increases with the decreasing temperature. The ΔG_r value becomes comparable to that in 0.01 N NaOH at −100 °C. This implies that poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) likely behaves as a polyelectrolyte at low temperature and neutral at higher temperatures, although we have no direct evidence for this hypothesis. The ionization of phosphate groups may need a specific solvation to the charged groups, which is destroyed at higher temperatures.

The temperature dependences of the CD for poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$) in organic solvents in the presence of achiral bases were fitted by the theory using parameters comparable to those chosen for the aqueous solutions (Figure 2B,C and Table 2).

In summary, optically active copolymers of achiral phenylacetylenes bearing basic or acidic functional pendant groups and a small amount of optically active phenylacetylenes were synthesized and the temperature dependence of their CDs was investigated. The thermodynamic parameters featuring the dynamic helical structures for the copolymers with charged and noncharged pendants in water and organic solvents were estimated by the theoretical analysis of their temperature-dependent CD changes. The results revealed a significant contribution of the charged pendant groups that increased the ΔG_r values, leading to remarkable amplification of the helical chirality by reduction of the helical reversal population, which further results in the increased CD intensities. These phenomena would be applicable to other dynamic helical polymers bearing basic or acidic functional pendant groups. Therefore, the present results should be useful for designing novel optically active dynamic helical polymers with unique amplification of the helical chirality induced by a very small amount of chiral bias.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details of the synthesis and characterization of **4**, **5**, poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$), poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$), and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$); ^{1}H NMR spectra of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$), poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$), and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$), determination of monomer reactivity ratios and the copolymerization results of **1** with **4** and **2** with **5**; Kelen−Tüdös plots for the copolymerizations; AFM images of poly($\mathbf{1}_{0.9}$-*co*-$\mathbf{4}_{0.1}$) and poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$), and temperature-dependent CD and absorption spectra of poly($\mathbf{2}_{0.9}$-*co*-$\mathbf{5}_{0.1}$) and poly($\mathbf{3}_{0.9}$-*co*-$\mathbf{6}_{0.1}$). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported in part by Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS). We thank Dr. K. Terao (Osaka University) for kind use of the program to calculate the average conformational partition function.

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(14) The monomer **3** has a carboxy group that inhibits the polymerization activity of a rhodium catalyst, and therefore, the copolymerization was performed in the presence of bases such as triethylamine.[7d] However, as anticipated, the pendant carboxy group of **3** likely dissociates into a charged carboxylate anion in part, while the monomer **6** is neutral. Therefore, the polymerizability of the charged **3** might be significantly lower than that of the neutral **6** due to the electrostatic repulsion during the copolymerization, thus producing a blocklike copolymer.

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