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# Chiral/Achiral Copolymers of Biphenylacetylenes Bearing Various Substituents: Chiral Amplification through Copolymerization Followed by Enhancement/Inversion and Memory of the Macromolecular Helicity

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## ABSTRACT

A series of dynamic helical homo- and copolymers of chiral and/or achiral biphenylacetylenes (PBPA)s bearing achiral methoxymethoxy or acetyloxy groups at the 2,2'-positions along with a chiral or achiral alkyl ether or alkoxy carbonyl group at the 4'-position of the biphenyl pendants were synthesized. The effects of the chiral/achiral substituents at the different positions on their helical structures and amplification of the helicity through covalent and further noncovalent chiral interactions followed by the memory of the helicity were investigated. The chiral homopolymers formed a preferred-handed helical structure as revealed by their circular dichroism (CD) spectra, whose Cotton effect signs and intensities were significantly dependent on the chiral/achiral pendant groups introduced at the 2,2',4'-positions of the biphenyl units as well as the solvents and temperatures, while the corresponding poly(phenylacetylene)s carrying the identical chiral substituents exhibited negligible CDs. Among the chiral homopolymers, a PBPA bearing the 2,2'-methoxymethoxy and 4'-chiral alkyl ether groups showed a unique helix-inversion/switching in aliphatic hydrocarbons according to whether they are cyclic or acyclic. The chiral/achiral copolymers displayed a moderate amplification of the helicity due to the chiral units covalently bonded to the pendants (the sergeants and soldiers effect). The macromolecular helicity of the copolymers with imperfect or no helical sense excesses were, however, significantly enhanced to the almost completely one-handed helices or inverted to the opposite ones through

noncovalent chiral interactions with enantiomeric alcohols, which could be further memorized after complete removal of the chiral alcohols.

## **INTRODUCTION**

The origin of homochirality in biological systems is most likely associated with some type of amplification of chirality through which optical purities of chiral molecules could be significantly amplified.<sup>1-4</sup> Green et al., for the first time, demonstrated the amplification of chirality in synthetic helical polymer systems<sup>5</sup> and proposed two seminal concepts for amplification of the macromolecular helicity in dynamic helical polyisocyanates, that is, the “sergeants and soldiers” effect<sup>6</sup> and the “majority rule” principle,<sup>7</sup> through which an excess one-handed helical polyisocyanate can be produced by the copolymerization of achiral monomers with a small amount of a chiral monomer and nonracemic monomers with a low optical purity, respectively. Thus far, a variety of helical polymers<sup>8-22</sup> and supramolecular helical polymers<sup>2,23-27</sup> with an excess one-handedness has been produced based on the “sergeants and soldiers” effect and the “majority rule” principle.

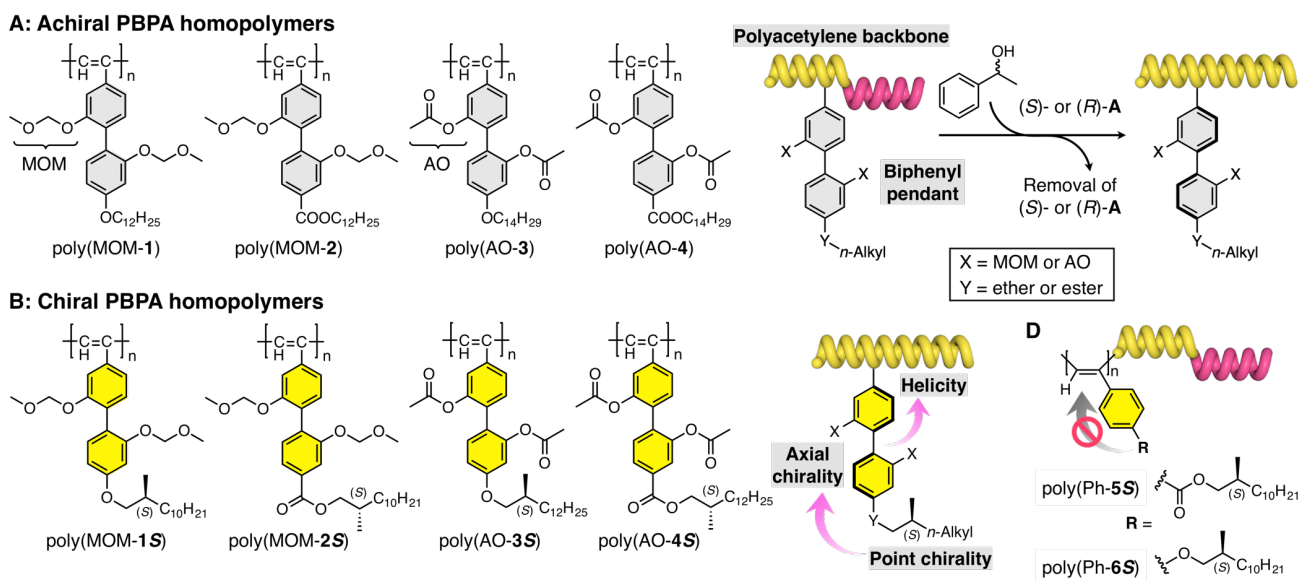
We previously reported unique helical polymers, poly(biphenylacetylene)s (PBPA)s, such as poly(MOM-1),<sup>28,29</sup> poly(MOM-2),<sup>30-32</sup> and poly(AO-4)<sup>30</sup> (Figure 1A). These polymers consist of achiral monomer units and are inherently optically inactive, but formed a preferred-handed helical conformation

through noncovalent chiral interactions with optically active 1-phenylethanol ((*R*)-**A** and (*S*)-**A**). Being significantly different from a number of previously reported helical polymers,<sup>33-37</sup> including polyacetylenes,<sup>14,17,20-22,38-42</sup> the macromolecular helicity induced in the PBPA backbones could be retained (i.e., memorized) after complete removal of the optically active alcohols. The observed unique static memory of the helicity of PBPA relies on the axially chiral biphenyl pendants with a twist-sense bias induced by (*R*)-**A** or (*S*)-**A** and subsequent memory, which may contribute to the memory of the main-chain helicity. Taking advantage of such a helicity induction and its subsequent memory of the main-chain helicity and axial chirality, we successfully developed the first chiral stationary phases<sup>28,31</sup> and asymmetric catalysts<sup>43,44</sup> capable of switching the elution orders of enantiomers and enantioselectivities in the asymmetric reactions, respectively. Suginome *et al.* has recently applied this “helicity induction and memory” strategy to dynamic helical poly(quinoxaline-2,3-diyl)s and developed powerful asymmetric catalysts.<sup>45</sup>

More recently, we have found an unexpectedly strong chiral amplification of PBPA-based chiral/achiral copolymers (poly(MOM-**2**<sub>1-*r*</sub>-*co*-MOM-**2S**<sub>*r*</sub>) in Figure 1C) of the biphenylacetylenes. In contrast, an analogous phenylacetylene-based homopolymer carrying the identical optically pure pendants (poly(Ph-**5S**) in Figure 1D) showed a negligible optical activity due to a small helical sense bias.<sup>32</sup> Although the helical handedness excesses of the poly(MOM-**2**<sub>1-*r*</sub>-*co*-MOM-**2S**<sub>*r*</sub>) copolymers

composed of a smaller amount of chiral monomer units (< 20 mol %) were imperfect, their helical sense excesses were found to be further enhanced or inverted to an opposite helix through noncovalent interactions with the enantiomeric (*R*)-**A** or (*S*)-**A**, which could be memorized after complete removal of the chiral alcohols. Although there is a huge number of studies on the amplification of chirality (helicity),<sup>2,8-27</sup> we are not aware of any helical polymers and supramolecular helical systems showing such a unique hierarchical amplification and memory of the macromolecular helicity by the covalent and further noncovalent chiral interactions.

To gain further insight into the dynamic control of the macromolecular helicity utilizing the combination of the covalent and noncovalent chiral interactions, in this study, we synthesized a series of dynamic helical PBPA homo- and copolymers of chiral and/or achiral biphenylacetylenes carrying methoxymethoxy (MOM) or acetyloxy (AO) groups at the 2,2'-positions along with a chiral or achiral alkyl ether or alkoxy carbonyl group at the 4'-position of the biphenyl pendants (Figure 1A–C). The effects of the chiral/achiral substituents at the different positions on their helical structures and amplification of the helicity through covalent (the sergeants and soldiers effect) and further noncovalent chiral interactions using (*R*)-**A** and (*S*)-**A**, resulting in the helicity enhancement/inversion followed by the static memory of the enhanced/inverted macromolecular helicities, were investigated (Figure 1C).



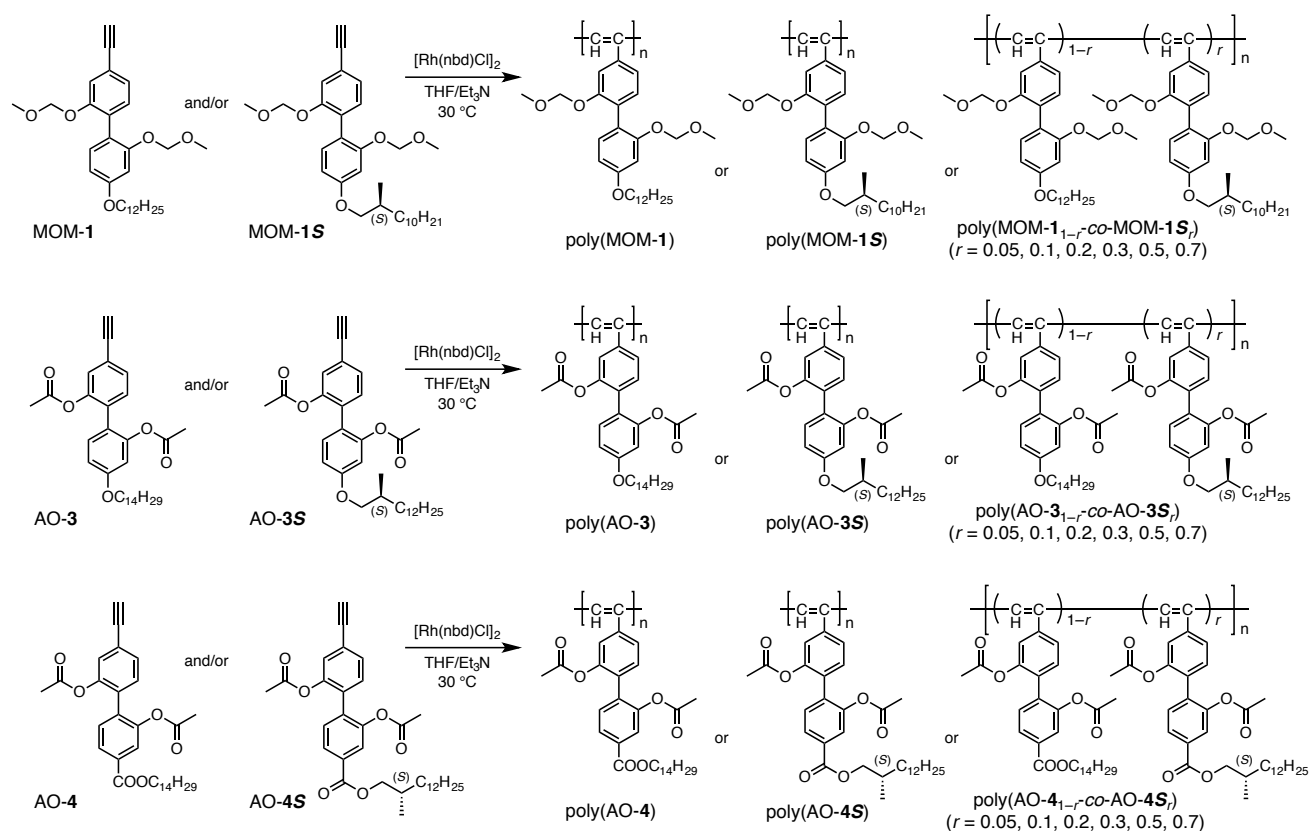
**Figure 1.** (A) Schematic illustration of a sequential induction of axial chirality at the biphenyl pendants of PBPA composed of achiral monomer units (poly(MOM-1), poly(MOM-2), poly(AO-3), and poly(AO-4)) and their macromolecular helicity accompanied by chiral amplification through noncovalent chiral interactions with an optically pure alcohol ((*R*)-A or (*S*)-A) and subsequent memory of the induced axial chirality and helicity of these polymers after complete removal of A. (B) Chiral information transfer in PBPA composed of chiral monomer units (poly(MOM-1S), poly(MOM-2S), poly(AO-3S), and poly(AO-4S)) from optically active pendants with point chirality to biphenyl units with dynamic axial chirality and further to the polyacetylene backbones with dynamic helical chirality. (C) Chiral amplification of the helical chirality in PBPA composed of chiral/achiral monomer units (poly(MOM-1<sub>1-r</sub>-co-MOM-1S<sub>r</sub>), poly(MOM-2<sub>1-r</sub>-co-MOM-2S<sub>r</sub>), poly(AO-3<sub>1-r</sub>-co-AO-3S<sub>r</sub>), and poly(AO-4<sub>1-r</sub>-co-AO-4S<sub>r</sub>)) through the sergeants and soldiers effect and further enhancement and/or inversion of the macromolecular helicity through noncovalent bonding interactions with (*R*)-A or (*S*)-A followed by their static memory of the helicity after removal of (*R*)-A or (*S*)-A. (D) Structures of poly(Ph-5S) and poly(Ph-6S).

## RESULTS AND DISCUSSION

### Synthesis

Novel optically active biphenylacetylene monomers (MOM-**1S**, AO-**3S**, and AO-**4S**) bearing MOM or AO groups at the 2,2'-positions and an alkyl ether or an alkoxy carbonyl pendant with a stereogenic center at the 4'-position of the biphenyl unit were synthesized as outlined in Scheme S1. These monomers were then homopolymerized or copolymerized with the corresponding achiral monomers (MOM-**1**, AO-**3**, and AO-**4**), respectively, at different feed monomer ratios using a rhodium catalyst ([Rh(nbd)Cl]<sub>2</sub>, nbd: norbornadiene) in a tetrahydrofuran (THF)/triethylamine (Et<sub>3</sub>N) mixture at 30 °C according to our previously reported procedure (Scheme 1),<sup>28,30-32</sup> affording optically active homopolymers (poly(MOM-**1S**), poly(AO-**3S**), and poly(AO-**4S**)) and copolymers (poly(MOM-**1**<sub>1-*r*</sub>-*r*-co-MOM-**1S**<sub>*r*</sub>), poly(AO-**3**<sub>1-*r*</sub>-*r*-co-AO-**3S**<sub>*r*</sub>), and poly(AO-**4**<sub>1-*r*</sub>-*r*-co-AO-**4S**<sub>*r*</sub>) (*r* = 0.05–0.7)) in good yields (Tables 1 and 2). The number-average molar masses, *M*<sub>n</sub>, of the resulting homo- and copolymers were estimated to be more than 2.2 × 10<sup>5</sup> by size-exclusion chromatography (SEC). The compositional ratios of the chiral/achiral units in the copolymers were confirmed to be nearly in accordance with those in the feed. For a comparative study, optically inactive poly(biphenylacetylene)s (poly(MOM-**1**),<sup>28</sup> poly(AO-**3**), and poly(AO-**4**)<sup>30</sup>) consisting entirely of achiral units and an optically active poly(phenylacetylene) (poly(Ph-**6S**), see Figure 1D) bearing the identical chiral pendant to that in

poly(MOM-1S) were also prepared in the same way (runs 1, 3, 5, and 7 in Table 1). The stereoregularities of the obtained homo- and copolymers were almost completely *cis-transoidal*, confirmed by their typical laser Raman spectra (Figure S1).



**Scheme 1.** Syntheses of homopolymers of achiral (poly(MOM-1), poly(AO-3), and poly(AO-4)) and chiral (poly(MOM-1S), poly(AO-3S), and poly(AO-4S)) monomer units and copolymers of chiral/achiral monomer units (poly(MOM-1<sub>1-r</sub>-co-MOM-1S<sub>r</sub>), poly(AO-3<sub>1-r</sub>-co-AO-3S<sub>r</sub>), and poly(AO-4<sub>1-r</sub>-co-AO-4S<sub>r</sub>)).



**Table 1.** Homopolymerization results of MOM-1, MOM-1S, AO-3, AO-3S, AO-4, AO-4S, and Ph-6S with [Rh(nbd)Cl]<sub>2</sub> in THF/Et<sub>3</sub>N at 30 °C for 3 h<sup>a</sup>

run	monomer	polymer			
		sample code	yield (%) <sup>b</sup>	$M_n \times 10^{-5}$ <sup>c</sup>	$M_w/M_n$ <sup>c</sup>
1 <sup>d</sup>	MOM-1	poly(MOM-1)	98	4.9	1.8
2	MOM-1S	poly(MOM-1S)	97	2.7	1.7
3	AO-3	poly(AO-3)	96	6.0	1.8
4	AO-3S	poly(AO-3S)	91	6.0	1.9
5 <sup>e</sup>	AO-4	poly(AO-4)	96	6.1	1.9
6	AO-4S	poly(AO-4S)	97	4.4	1.8
7	Ph-6S	poly(Ph-6S)	88	5.5	1.9

<sup>a</sup> [Monomer] = 0.5 M, [Rh(nbd)Cl]<sub>2</sub> = 0.005 M, [Et<sub>3</sub>N]/[monomer] = 3. <sup>b</sup> Methanol insoluble part. <sup>c</sup> Determined by SEC (polystyrene standards) with THF as the eluent. <sup>d</sup> Cited from ref. 28. <sup>e</sup> Cited from ref. 30.

**Table 2.** Copolymerization results of MOM-1 with MOM-1S, AO-3 with AO-3S, and AO-4 with AO-4S using [Rh(nbd)Cl]<sub>2</sub> in THF/Et<sub>3</sub>N at 30 °C for 3 h<sup>a</sup>

monomer in feed (mol%)		copolymer				
		sample code	yield (%) <sup>b</sup>	$M_n$ (10 <sup>5</sup> ) <sup>c</sup>	$M_w/M_n$ <sup>c</sup>	chiral units (mol%) <sup>d</sup>
MOM-1 (95)	MOM-1S (5)	poly(MOM-1 <sub>0.95-co</sub> -MOM-1S <sub>0.05</sub> )	96	2.7	1.8	4
MOM-1 (90)	MOM-1S (10)	poly(MOM-1 <sub>0.9-co</sub> -MOM-1S <sub>0.1</sub> )	95	2.5	1.7	9
MOM-1 (80)	MOM-1S (20)	poly(MOM-1 <sub>0.8-co</sub> -MOM-1S <sub>0.2</sub> )	95	2.3	1.8	18
MOM-1 (70)	MOM-1S (30)	poly(MOM-1 <sub>0.7-co</sub> -MOM-1S <sub>0.3</sub> )	94	2.5	1.7	28
MOM-1 (50)	MOM-1S (50)	poly(MOM-1 <sub>0.5-co</sub> -MOM-1S <sub>0.5</sub> )	95	2.3	1.9	47
MOM-1 (30)	MOM-1S (70)	poly(MOM-1 <sub>0.3-co</sub> -MOM-1S <sub>0.7</sub> )	95	2.2	1.7	67
AO-3 (95)	AO-3S (5)	poly(AO-3 <sub>0.95-co</sub> -AO-3S <sub>0.05</sub> )	54	6.5	1.7	3
AO-3 (90)	AO-3S (10)	poly(AO-3 <sub>0.9-co</sub> -AO-3S <sub>0.1</sub> )	96	5.9	1.5	8
AO-3 (80)	AO-3S (20)	poly(AO-3 <sub>0.8-co</sub> -AO-3S <sub>0.2</sub> )	65	6.3	1.7	16
AO-3 (70)	AO-3S (30)	poly(AO-3 <sub>0.7-co</sub> -AO-3S <sub>0.3</sub> )	99	4.7	2.0	26
AO-3 (50)	AO-3S (50)	poly(AO-3 <sub>0.5-co</sub> -AO-3S <sub>0.5</sub> )	89	3.8	2.1	45
AO-3 (30)	AO-3S (70)	poly(AO-3 <sub>0.3-co</sub> -AO-3S <sub>0.7</sub> )	68	4.3	2.1	64
AO-4 (95)	AO-4S (5)	poly(AO-4 <sub>0.95-co</sub> -AO-4S <sub>0.05</sub> )	99	6.5	1.7	5
AO-4 (90)	AO-4S (10)	poly(AO-4 <sub>0.9-co</sub> -AO-4S <sub>0.1</sub> )	99	5.9	1.5	11
AO-4 (80)	AO-4S (20)	poly(AO-4 <sub>0.8-co</sub> -AO-4S <sub>0.2</sub> )	99	6.3	1.7	23
AO-4 (70)	AO-4S (30)	poly(AO-4 <sub>0.7-co</sub> -AO-4S <sub>0.3</sub> )	99	7.2	1.6	30
AO-4 (50)	AO-4S (50)	poly(AO-4 <sub>0.5-co</sub> -AO-4S <sub>0.5</sub> )	99	5.2	1.8	49
AO-4 (30)	AO-4S (70)	poly(AO-4 <sub>0.3-co</sub> -AO-4S <sub>0.7</sub> )	99	6.9	1.7	68

<sup>a</sup> [Monomer] = 0.5 M, [[Rh(nbd)Cl]<sub>2</sub>] = 0.005 M, [Et<sub>3</sub>N]/[monomer] = 3. <sup>b</sup> Methanol insoluble part.

<sup>c</sup> Determined by SEC (polystyrene standards) with THF as the eluent. <sup>d</sup> Estimated by <sup>1</sup>H NMR.

## Chiroptical Properties of the Chiral Homopolymers

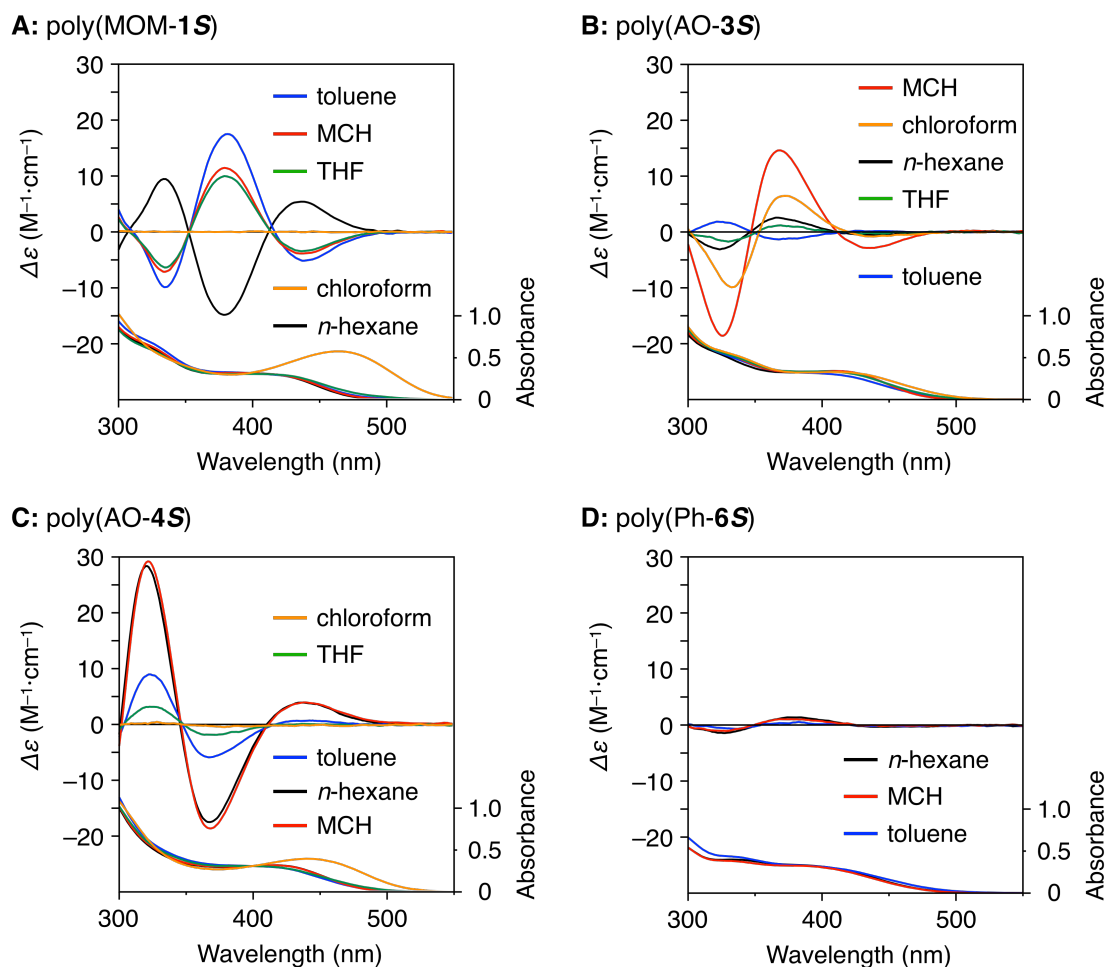
The combinational effects of the achiral and chiral pendants introduced at the 2,2'-positions and the 4'-position of the biphenyl pendants in the PBPA, respectively, on their preferred-handed helix-forming abilities were first investigated by measuring their CD spectra of poly(MOM-1S), poly(AO-3S), and poly(AO-4S) in various solvents at different temperatures (Figures 2 and S2–S5) and comparing the results with those of the previously reported poly(MOM-2S) (Figure S6).<sup>32</sup> Poly(AO-4S) with the AO groups displayed intense CD signals in the absorption region of the  $\pi$ -conjugated main-chain in methylcyclohexane (MCH) and *n*-hexane at 25 °C (Figure 2C), and their spectral patterns and intensities were similar to those of poly(MOM-2S) carrying the MOM groups with an almost perfect right-handed helical conformation in MCH (Figure S6A),<sup>32,46-50</sup> indicating that poly(AO-4S) efficiently formed a right-handed helical conformation through the chiral information transfer from the chiral substituents at the pendant groups. Compared to the results in the alkane solvents, poly(AO-4S) showed lower Cotton effects in toluene and THF at 25 °C (Figure 2C) and mostly lost the CD signals in chloroform at 25 °C and even at –10 °C along with a red-shift of the absorption spectra (Figure S5). These results were inconsistent with those of poly(MOM-2S) showing strong Cotton effects in toluene and THF at 25 °C and in chloroform at –10 °C being comparable to that in MCH (Figure S6).<sup>32</sup> These results implied that

the AO groups instead of the MOM groups at the 2,2'-positions of the biphenyl units would destabilize the preferred-handed helix formation in toluene, THF, and chloroform.

On the other hand, poly(MOM-1S) with MOM groups at the 2,2'-positions and a chiral alkyl ether pendant at the 4'-position of the biphenyl pendant showed a unique solvent- and temperature-dependent helix inversion that was not observed for poly(MOM-2S)<sup>32</sup> and poly(AO-4S) (Figures 2A, S2, and S3). In linear alkanes, including *n*-pentane, *n*-hexane, and *n*-heptane, poly(MOM-1S) showed the CD signals with a negative second Cotton effect derived from a right-handed helix formation, while the mirror-imaged CDs due to the opposite left-handed macromolecular helicity was induced in solvents with a cyclic shape, such as cyclopentane, cyclohexane, MCH, toluene, and THF, with varying degrees of CD intensity (Figures 2A and S2). A similar macromolecular helicity inversion in response to the molecular shapes of solvents (linear or cyclic) has also been observed for poly(quinoxaline-2,3-diyl)s bearing optically active side chains.<sup>51,52</sup> The origin of this inversion phenomena is not clear at present, but may be relevant to the aspect ratios of the solvent molecules. Moreover, the heating of the cyclic alkane and toluene solutions of poly(MOM-1S) resulted in the macromolecular helicity inversion, whereas such a helix inversion did not occur upon heating of the linear alkane solutions (Figure S3). These results clearly indicated that both the right- and left-handed helices of poly(MOM-1S) could be produced and switched by a delicate tuning of the solvent/temperature conditions.

Poly(AO-3S) with the same chiral pendant as poly(MOM-1S), except for the alkyl chain length at the 4'-position of the biphenyl pendant, also showed the solvent- and temperature-dependent helix inversion, although the helix-sense excess before and/or after inversion was low (Figures 2B and S4D). Based on the structural identity between the poly(MOM-1S) and poly(AO-3S) carrying MOM and AO substituents at the 2,2'-positions, respectively, a chiral alkyl ether pendant introduced at the 4'-position of the biphenyl pendant most likely played an important role in the helicity switching depending on the surrounding environment. We also found that poly(AO-3S) showed a clear CD signal in chloroform and its intensity at -10 °C reached a comparable level to that of the single-handed helical poly(MOM-2S) (Figures 2B, S4E, and S6).<sup>32</sup> This is a significant difference from the chiroptical properties of poly(MOM-1S) and poly(AO-4S) possessing an elongated  $\pi$ -conjugated backbone in chloroform that was not appropriate for a preferred-handed helix formation (Figures S3E and S5E). In sharp contrast, very weak or almost no Cotton effects appeared in the backbone region of poly(Ph-6S) (Figure 2D), which is consistent with the result of the CD silent poly(Ph-5S).<sup>32</sup> Therefore, the dynamic axial chirality inherent in the biphenyl moieties is considered indispensable for the efficient transfer of chiral information from the optically active pendant to the polyacetylene backbone. Given the solvent-dependent chiroptical properties of poly(MOM-1S), poly(AO-3S), and poly(AO-4S), the following chiral amplification and helicity control/memory experiments with the

MOM-1/MOM-1S-based (co)polymers were performed in *n*-hexane, while MCH was used as a solvent for the AO-3/AO-3S- and AO-4/AO-4S-based (co)polymers.

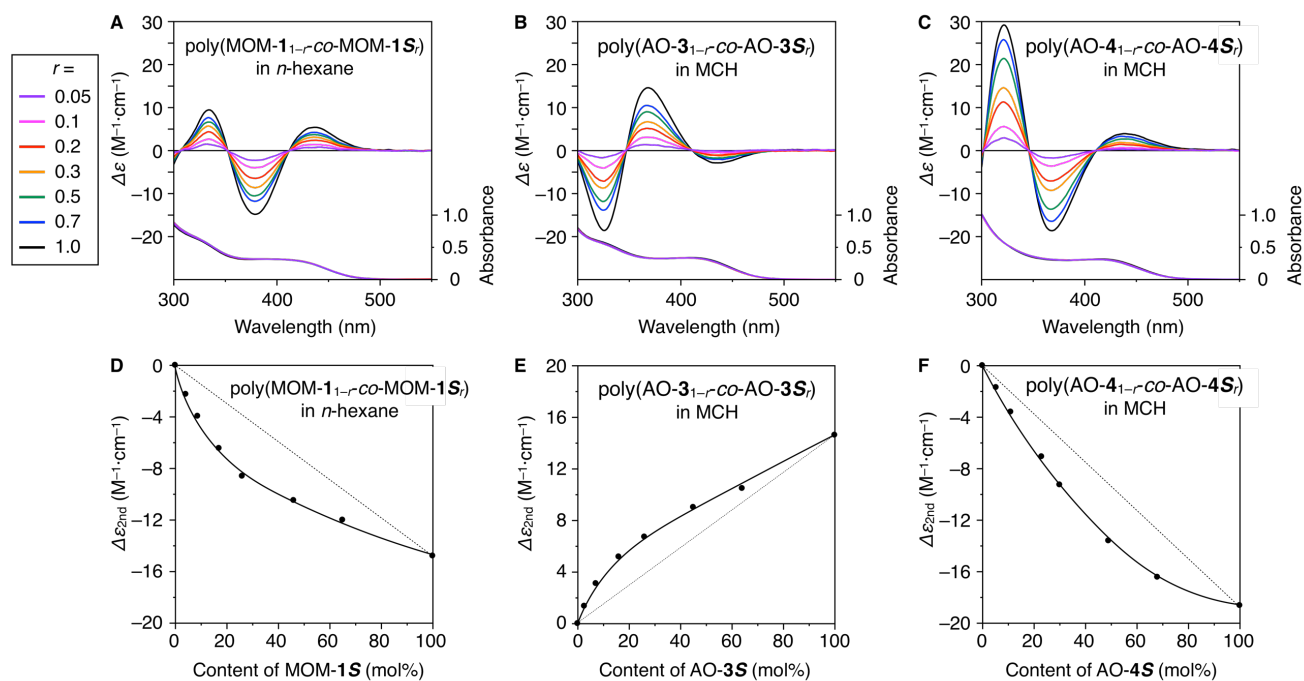


**Figure 2.** CD and absorption spectra of poly(MOM-1S) (A), poly(AO-3S) (B), poly(AO-4S) (C), and poly(Ph-6S) (D) in various solvents (*n*-hexane, MCH, toluene, THF, and chloroform) measured at 25 °C after allowing to stand at 25 °C for 24 h. [Polymer] = 1.0 mM. The polymer concentration was calculated based on the monomer units.

## Chiral Amplification Based on the Sergeants and Soldiers Effect

We next investigated chiral amplification in the chiral/achiral copolymers based on their CD spectral analyses (Figure 3A–C), related to the “sergeants and soldiers” effect. Figure 3D–F show the plots of the induced CD (ICD) intensities at the second Cotton effect ( $\Delta\epsilon_{2nd}$ ) of poly(MOM-**1**<sub>1-*r*</sub>-*co*-MOM-**1S**<sub>*r*</sub>), poly(AO-**3**<sub>1-*r*</sub>-*co*-AO-**3S**<sub>*r*</sub>), and poly(AO-**4**<sub>1-*r*</sub>-*co*-AO-**4S**<sub>*r*</sub>) in *n*-hexane or MCH at 25 °C versus the content of the chiral units in the copolymers. As is the case for the previously reported chiral/achiral PBPA copolymers (poly(MOM-**2**<sub>1-*r*</sub>-*co*-MOM-**2S**<sub>*r*</sub>)),<sup>32</sup> the present three types of copolymers with different combinations of chiral/achiral pendants also showed a positive nonlinear relationship; in other words, the ICD intensities nonlinearly increased with an increase in the mole fraction of the chiral units. This means that the chiral information on the chiral pendant units was transferred and amplified to the dynamically racemic helical segments composed of achiral units, resulting in the amplification of the helical chirality in PBPA through the sergeants and soldiers effect. The nonlinearities observed for the three types of copolymers were more or less similar to each other,<sup>53</sup> but lower than that of poly(MOM-**2**<sub>1-*r*</sub>-*co*-MOM-**2S**<sub>*r*</sub>), in which 20 mol % of the chiral unit was sufficient to show the full ICD as intense as that of a single-handed helical homopolymer, poly(MOM-**2S**).<sup>32</sup> The combination of chiral/achiral pendant units introduced at the 2,2',4'-positions of the biphenyl units in the PBPA affected the chiral amplification in the manner of an AND logic gate; that is, the combination of the MOM groups

at the 2,2'-positions and the chiral alkoxy carbonyl pendant at the 4'-position would be especially preferable to achieve the high degree of chiral amplification compared to the others.<sup>32</sup>



**Figure 3.** (A–C) CD and absorption spectra of poly(MOM-1<sub>1-*r*</sub>-co-MOM-1S<sub>*r*</sub>) in *n*-hexane (A) and poly(AO-3<sub>1-*r*</sub>-co-AO-3S<sub>*r*</sub>) (B) and poly(AO-4<sub>1-*r*</sub>-co-AO-4S<sub>*r*</sub>) (C) in MCH measured at 25 °C after allowing to stand at 25 °C for 24 h. *r* = 0.05 – 1.0. (D–F) Plots of ICD intensity ( $\Delta\epsilon_{2nd}$ ) of poly(MOM-1<sub>1-*r*</sub>-co-MOM-1S<sub>*r*</sub>) (D), poly(AO-3<sub>1-*r*</sub>-co-AO-3S<sub>*r*</sub>) (E), and poly(AO-4<sub>1-*r*</sub>-co-AO-4S<sub>*r*</sub>) (F) versus the content of the corresponding chiral monomer units. [Polymer] = 1.0 mM.



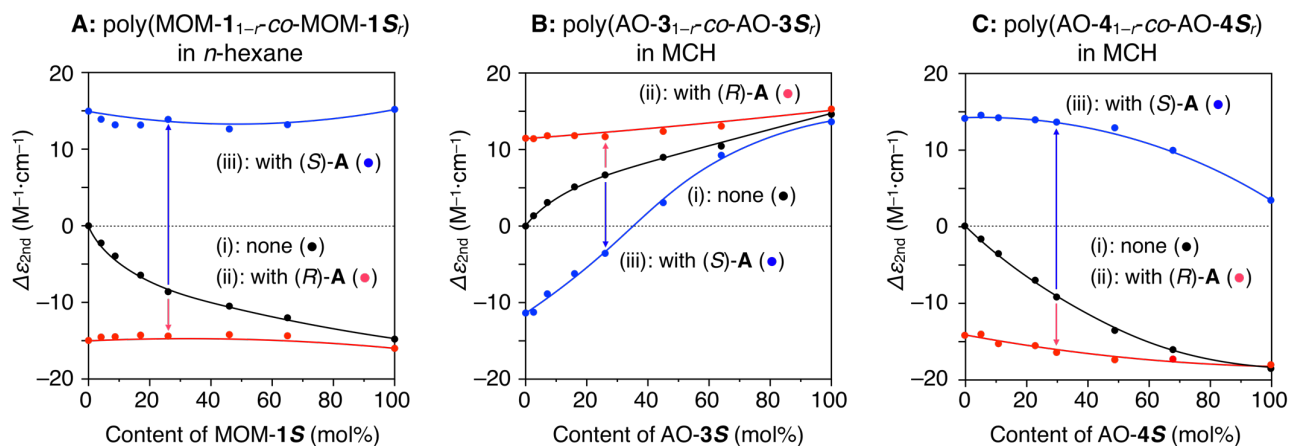
## Enhancement and Inversion of the Macromolecular Helicity through Noncovalent Interactions with Chiral Alcohols

We then investigated if the macromolecular helicity of the PBPA homopolymers and copolymers could be further enhanced and/or inverted through noncovalent chiral interactions with optically active guests ((*R*)- and (*S*)-**A**). The ICD intensities of poly(MOM-**1**<sub>0.7-co-MOM-1S</sub><sub>0.3</sub>) gradually increased with time in an *n*-hexane/(*R*)-**A** mixture (80/20, v/v) at 25 °C and reached a plateau value being identical to that of poly(MOM-**1S**) (Figure S8A). We also found that all the chiral/achiral copolymers (poly(MOM-**1**<sub>1-r-co-MOM-1S</sub><sub>r</sub>), poly(AO-**3**<sub>1-r-co-AO-3S</sub><sub>r</sub>), and poly(AO-**4**<sub>1-r-co-AO-4S</sub><sub>r</sub>)) and optically inactive homopolymers (poly(MOM-**1**), poly(AO-**3**), and poly(AO-**4**)) with imperfect and no helical sense excesses, respectively, showed the similar amplification/enhancement of the macromolecular helicity with (*R*)-**A**, through which the ICD intensities increased to the levels comparable to or slightly less than those of the corresponding chiral homopolymers within 1 h (red circles in Figures 4, S9A, and S10A). It should be noted that the time required to enhance the macromolecular helicity was significantly shortened compared to that of poly(MOM-**2**<sub>1-r-co-MOM-2S</sub><sub>r</sub>), which required ca. 12 h to induce a fully one-handed helix by (*R*)-**A**.<sup>32</sup>

On the other hand, when the antipode (*S*)-**A** was used as a chiral guest instead of (*R*)-**A**, the Cotton effect signs of poly(MOM-**1**<sub>1-r-co-MOM-1S</sub><sub>r</sub>) ( $r < 0.7$  including  $r = 0$ ) and poly(MOM-**1S**) were almost

completely inverted to the opposite ones, while their absolute ICD intensities were comparable to those in *n*-hexane/*(R)*-**A** (80/20, v/v) (Figures 4A and S11), suggesting that both the left- and right-handed helices with almost the same helical sense excess could be induced in these polymers at will by noncovalent interactions with *(S)*- and *(R)*-**A**, respectively. These results also indicated that the helical senses of poly(MOM-**1**<sub>1-*r*</sub>-*co*-MOM-**1S**<sub>*r*</sub>) were unambiguously controlled by the point chirality of the guest alcohols other than that of the covalently linked chiral pendants regardless of the chiral MOM-**1S** contents. In a similar way, the Cotton effect signs of poly(AO-**4**<sub>1-*r*</sub>-*co*-AO-**4S**<sub>*r*</sub>) were inverted to the opposite ones in MCH/*(S)*-**A** (80/20, v/v), but the helical sense excesses in the presence of *(S)*-**A** were not perfectly the same if the AO-**4S** mole fraction was more than 50% (Figures 4C and S13). This is most likely because the helical sense preferences of the copolymers were determined by the competition between the two kinds of point chirality from the covalently bonded optically active pendants and the chiral guest alcohols. A similar, but more marked antagonistic effect in the helix induction was observed in the homo- and copolymer systems containing a chiral AO-**3S** unit, in which the CD inversion (the helix inversion) did not take place unless the proportions of the chiral AO-**3S** unit in the copolymers decreased below 30 mol % (Figures 4B and S12). We also confirmed that the enhancement and inversion of the macromolecular helicity of these chiral/achiral copolymers through noncovalent interactions with *(R)*- and *(S)*-**A**, respectively, were more noticeable at a lower temperature (Figures S8–S10). As

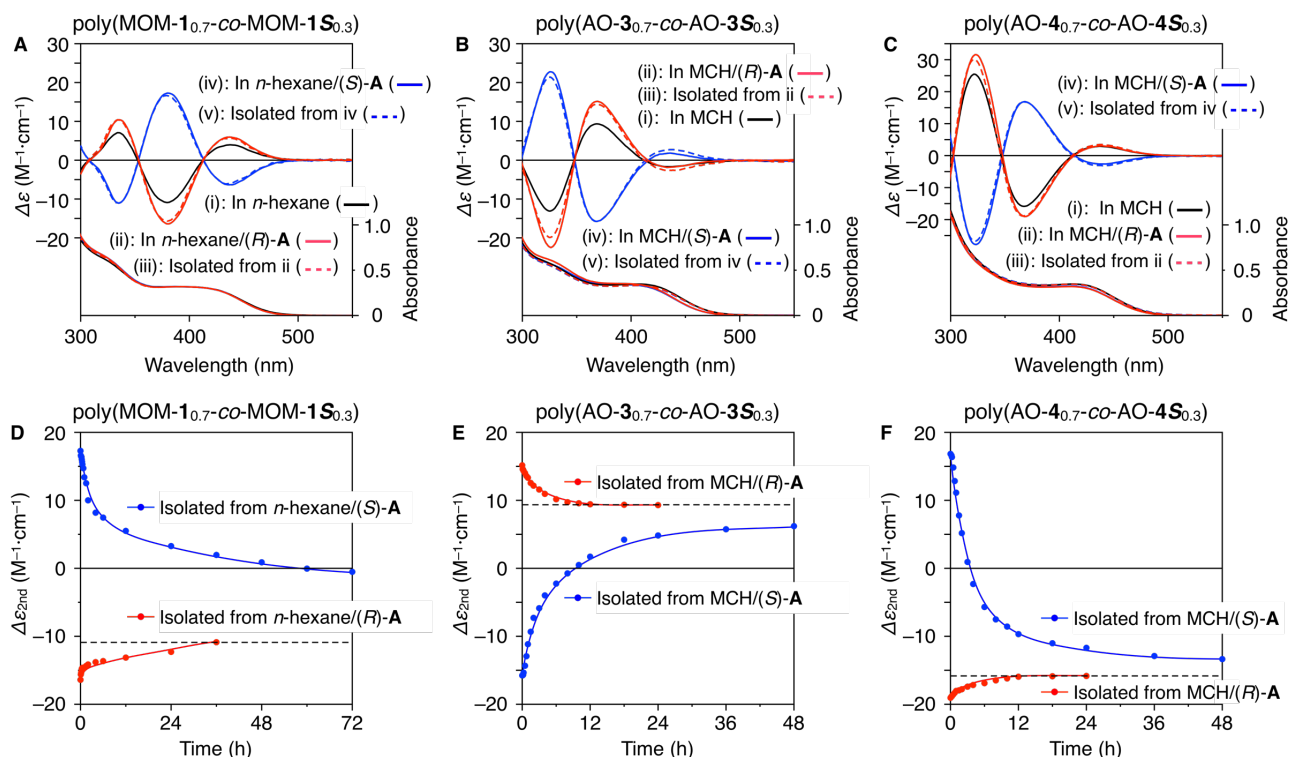
previously reported, the CD signs and intensities of the right-handed poly(MOM- $2_{1-r}$ -co-MOM- $2S_r$ ) ( $r > 0.20$ ) did not change at all in the presence of an opposite-handed helix inducer, (*S*)-**A**.<sup>32</sup> Thus, the ease of the helix inversion of the PBPA s through noncovalent interactions with the chiral alcohol **A** tended to decrease in the following order: poly(MOM- $1_{1-r}$ -co-MOM- $1S_r$ ) > poly(AO- $4_{1-r}$ -co-AO- $4S_r$ ) > poly(AO- $3_{1-r}$ -co-AO- $3S_r$ ) > poly(MOM- $2_{1-r}$ -co-MOM- $2S_r$ ). This difference may be related to the rotational barriers of the biphenyl pendants with an axial chirality.



**Figure 4.** Plots of ICD intensity ( $\Delta\epsilon_{2nd}$ ) of poly(MOM- $1_{1-r}$ -co-MOM- $1S_r$ ) in *n*-hexane (A) and poly(AO- $3_{1-r}$ -co-AO- $3S_r$ ) (B) and poly(AO- $4_{1-r}$ -co-AO- $4S_r$ ) (C) in MCH measured at 25 °C versus the content of chiral monomer units in the absence (i) and presence of (*R*)-**A** (ii) and (*S*)-**A** (iii) (alkane/**A** = 80/20, v/v) after standing at 25 °C for 48 h. For the corresponding CD spectra, see Figures S11–S13. [Polymer] = 1.0 mM. The black solid curves are taken from Figure 3D–F.

More importantly, the macromolecular helicities of poly(MOM- $1_{0.7}$ -co-MOM- $1S_{0.3}$ ), poly(AO- $3_{0.7}$ -co-AO- $3S_{0.3}$ ), and poly(AO- $4_{0.7}$ -co-AO- $4S_{0.3}$ ) enhanced or inverted by chiral guests could

be further automatically memorized after complete removal of the helix inducers (Figure 5A–C) as previously reported for the analogous PBPA.s.<sup>28,30-32</sup> To investigate the stabilities of the static helicity memories of the copolymers, we followed the changes in the CD spectra of the isolated chiral/achiral copolymers in *n*-hexane or MCH at –10 °C (Figure 5D–F). In each case, the  $\Delta\epsilon_{2nd}$  value gradually changed with time and likely converged to the original value of the as-prepared copolymer. We then roughly estimated the apparent half-life period ( $t_{1/2}$ ) of the helicity memory defined as the time required to reach the midpoint between the  $\Delta\epsilon_{2nd}$  values of the as-prepared chiral/achiral copolymers in *n*-hexane or MCH at –10 °C and the corresponding helicity-memorized copolymers just after dissolving them under the same conditions. The  $t_{1/2}$  values of the isolated poly(MOM-**1**<sub>0.7-co</sub>-MOM-**1S**<sub>0.3</sub>), poly(AO-**3**<sub>0.7-co</sub>-AO-**3S**<sub>0.3</sub>), and poly(AO-**4**<sub>0.7-co</sub>-AO-**4S**<sub>0.3</sub>) from their alkane/(*R*)-**A** or (*S*)-**A** (80/20, v/v) solutions were ca. 6, 2, and 3 h or ca. 24, 4, and 3 h, respectively. Combined with the  $t_{1/2}$  values of the helicity-memorized poly(MOM-**2**<sub>1-*r*-co</sub>-MOM-**2S**<sub>*r*</sub>) ( $r = 0.05$  and  $0.1$ ) recovered from MCH/(*R*)-**A** or (*S*)-**A** (80/20, v/v) (>7 days at –10 °C),<sup>32</sup> the MOM groups at the 2,2'-positions of the biphenyl units appear to more efficiently contribute to stabilize the enhanced/inverted helicity memory of the PBPA.s than the AO groups.



**Figure 5.** (A–C) CD and absorption spectra of poly(MOM-1<sub>0.7-co</sub>-MOM-1S<sub>0.3</sub>) (A), poly(AO-3<sub>0.7-co</sub>-AO-3S<sub>0.3</sub>) (B), and poly(AO-4<sub>0.7-co</sub>-AO-4S<sub>0.3</sub>) (C) in the absence (i) and presence of (*R*)-A (ii) and (*S*)-A (iv) in *n*-hexane (A) and MCH (B, C) (alkane/A = 80/20, v/v) measured at  $-10\text{ }^{\circ}\text{C}$  after standing at  $25\text{ }^{\circ}\text{C}$  for 48 h and those of the isolated copolymers in MCH at  $-10\text{ }^{\circ}\text{C}$  recovered from ii (iii) and iv (v). (D–F) Time-dependent ICD intensity ( $\Delta\epsilon_{2\text{nd}}$ ) changes of the isolated poly(MOM-1<sub>0.7-co</sub>-MOM-1S<sub>0.3</sub>) (D), poly(AO-3<sub>0.7-co</sub>-AO-3S<sub>0.3</sub>) (E), and poly(AO-4<sub>0.7-co</sub>-AO-4S<sub>0.3</sub>) (F) with macromolecular helicity memory in *n*-hexane (D) and MCH (E, F) at  $-10\text{ }^{\circ}\text{C}$ . [Polymer] = 1.0 mM.

## CONCLUSIONS

In summary, we have synthesized a series of PBPA homopolymers and copolymers composed of chiral and/or achiral biphenylacetylene units bearing different functional groups, MOM or AO groups at the 2,2'-positions along with an optically active or inactive alkyl ether or alkoxy carbonyl pendant at the 4'-position of the biphenyl units. Based on the systematic studies of their preferred-handed helix

formations of the chiral homopolymers under various solvent/temperature conditions, the following findings can be drawn: (i) the chiral information of the optically active pendants could be efficiently transferred to the polyacetylene backbones only through the biphenyl units with a dynamic axial chirality, but not through the achiral phenyl units, despite the more short-range chiral communication; (ii) the MOM groups at the 2,2'-positions more effectively promoted the preferred-handed helix formation than the AO groups when the same chiral pendants were attached to the 4'-position; and (iii) the chiral alkyl ether pendant at the 4'-position enabled the macromolecular helicity inversion depending on the temperature and solvents, and particularly, poly(MOM-1S) with MOM groups showed unique helicity switching phenomena in response to the shapes of the solvent molecules (linear or cyclic). We also found that the chiral amplification of the macromolecular helicity based on the sergeants and soldiers effect was achieved in any series of chiral/achiral copolymers and that the degree of amplification was significantly influenced by the combinations of the functional chiral/achiral pendant groups introduced at the 2,2',4'-positions of the biphenyl units. When the helical sense preferences of the copolymers were not complete, their macromolecular helicity could be fully enhanced through noncovalent chiral interactions with optically active alcohols. Moreover, the preferred helical senses of the copolymers could be further inverted to the opposite one by tuning the chirality balance between the covalently bonded chiral pendants and the optically active alcohols. Such enhanced and inverted macromolecular helicities of the

present copolymers were further automatically memorized after removing the chiral alcohols. We believe that the present helicity control/memory strategy combining covalent and noncovalent chiral interactions will contribute to the development of novel chiral materials being capable of switching enantioselectivities during asymmetric catalysis<sup>43,44,54</sup> and chiral separation.<sup>28,31</sup>

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX

Experimental procedures, characterizations of polymers and copolymers, and supporting data  
(PDF)

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