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Helical polymer brushes with a preferred-handed helix-sense triggered by a terminal optically active group in the pendant†‡

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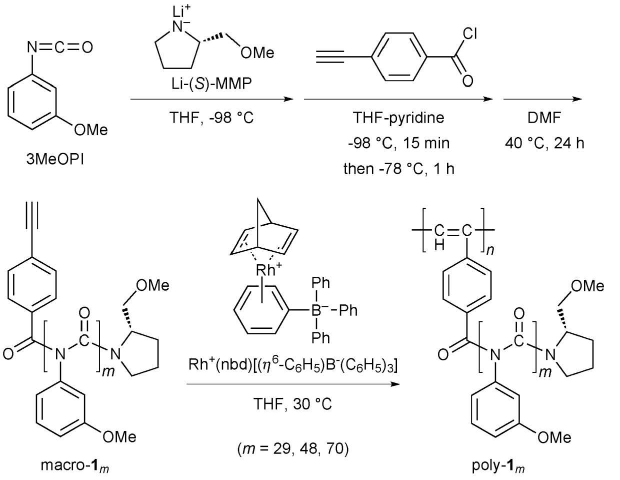
Helical polymer brushes with a preferred-handed helix-sense composed of a poly(phenylacetylene) backbone and poly(phenyl isocyanate) pendants are synthesized. The helix-sense of the backbone is effectively controlled by the helical chirality of the pendants, which is triggered by an optically active group introduced at the pendant terminal.

Biological macromolecules, such as DNA and proteins, adopt one-handed helical structures predetermined by the chirality of their constituent units, which further self-assemble into supramolecular structures responsible for their elaborate biological functions.[1] A large number of artificial helical polymers and oligomers with controlled helicity have been synthesized, not only to mimic biological helices, but also to develop chiral materials with functionality.[2] Among them, dynamic helical polymers, represented by polyisocyanates and polyacetylenes, consist of interconvertible right- and left-handed helical conformations separated by occasional helix reversals. A preferred-handed helical conformation can be induced by introducing a small amount of optically active groups by copolymerization with a small number of optically active monomers, initiating polymerization with an optically active initiator, or interaction with chiral compounds.[2b,d,f,h,j,m] However, optically active groups need to be introduced close to the polymer backbone to effectively control helicity. It has been demonstrated that introduction of stereocenters into pendants at positions removed from the polymer backbone results in an almost racemic helical conformation.[3]

Very recently, Yashima *et al.* reported unique remote control of the dynamic chirality of metal complexes containing *tris*-bidentate ligands by the helical chirality of the oligopeptides attached to the ligands, which was induced by a terminal optically active unit.[4] In this study, we have designed and synthesized a series of poly(phenylacetylene)-based polymer brushes bearing poly(phenyl isocyanate) pendants with an optically active group only at the chain end (poly-$\mathbf{1}_m$), as shown in Scheme 1. We anticipated that the helix-sense bias of the polyacetylene backbone in the polymer brushes would be hierarchically induced by the helical chirality of the pendant polyisocyanate chains triggered by the terminal optically active group based on the covalent-bonding "chiral domino effect",[5,6] which further results in a helical array of helical polyisocyanate pendants with a preferred-handed helix-sense (Fig. 1).



Scheme 1 Synthesis of polymer brushes poly-$\mathbf{1}_m$.

Poly(phenyl isocyanate) compounds bearing an optically active group at the initial chain end (α-end) and a polymerizable phenylacetylene residue at the other (ω-end) with various degrees of polymerization (DP) were first synthesized as macromonomers (macro-$\mathbf{1}_m$: *m* represents DP) by anionic polymerization of

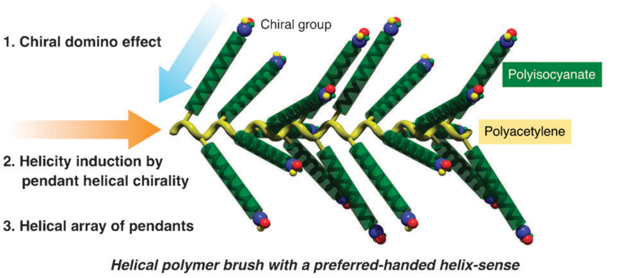


Fig. 1 Schematic illustration of hierarchical chiral amplification in helical polymer brushes composed of dynamic helical polymer chains triggered by a terminal optically active group in the pendant.

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Table 1 Results of anionic polymerization of 3MeOPI with Li-(*S*)-MMP in THF at −98 °C[a]

Run	[3MeOPI]/[Li-(S)-MMP]	Polymer[b]				
		Sample code	Yield (%)	m^c	$M_n \times 10^{-3d}$	$M_w/M_n{}^d$
1	10	macro-$\mathbf{1}_{29}$	43	29	3.8	1.2
2	20	macro-$\mathbf{1}_{48}$	23	48	6.0	1.3
3	30	macro-$\mathbf{1}_{70}$	23	70	9.4	1.2

[a] [3MeOPI] = 0.67 M. [b] Hexane–EtOH (3/1, v/v) insoluble component after standing at 40 °C for 24 h in DMF. [c] DP determined by ^{1}H NMR in $CDCl_3$. [d] Determined by SEC (polystyrene standard, eluent: $CHCl_3$).

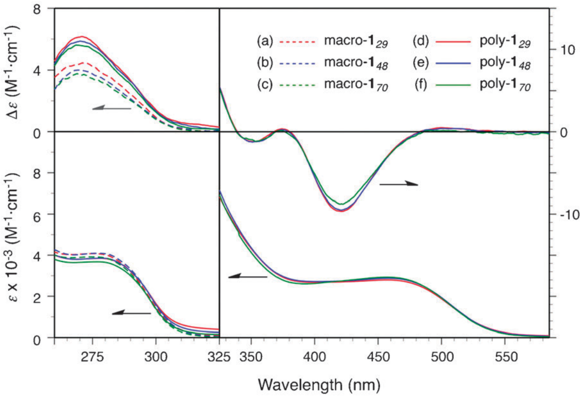

Fig. 2 CD and absorption spectra of macro-$\mathbf{1}_m$ (a–c, dotted lines) and poly-$\mathbf{1}_m$ (d–f, solid lines) in DMSO at 25 °C. The molar ellipticity (Δε) and molar absorption coefficient (ε) were calculated using the molar concentrations of 3MeOPI (250–325 nm: polyisocyanate-backbone chromophore region) and macro-$\mathbf{1}_m$ (>325 nm: polyacetylene-backbone chromophore region).

3-methoxyphenyl isocyanate (3MeOPI) with the lithium amide of (*S*)-2-(methoxymethyl)pyrrolidine (Li-(*S*)-MMP) as the initiator in THF at −98 °C with different molar ratios of [3MeOPI] to [Li-(*S*)-MMP], followed by termination with 4-ethynylbenzoyl chloride (Scheme 1 and Table 1).[5b,7] The –NH terminated polymers that had not been end-capped with a 4-ethynylbenzoyl group were completely removed by selective depolymerization in DMF.[7b] The DP of the obtained macro-$\mathbf{1}_m$ were determined by ^{1}H NMR analysis to be 29 (macro-$\mathbf{1}_{29}$), 48 (macro-$\mathbf{1}_{48}$), and 70 (macro-$\mathbf{1}_{70}$) (Fig. S1, ESI‡). As expected from previous reports,[7] the circular dichroism (CD) spectra of macro-$\mathbf{1}_m$ in DMSO at 25 °C showed a positive Cotton effect in the absorption region of the polyisocyanate backbone (*ca.* 265 nm) because of the formation of a predominantly right-handed helical conformation[8] induced by the chiral group covalently attached to the α-end (Fig. 2a–c). In agreement with previous results,[7] the CD intensities decreased in the order macro-$\mathbf{1}_{29}$ > macro-$\mathbf{1}_{48}$ > macro-$\mathbf{1}_{70}$, *i.e.*, with an increase in the DP of macro-$\mathbf{1}_m$, suggesting that the helical sense bias of macro-$\mathbf{1}_m$ can persist only in a rather short range from the α-end because of helix reversal.

The macromonomers were then polymerized with a zwitterionic rhodium complex,[9] $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ (nbd = 2,5-norbornadiene), in THF at 30 °C to convert them into polymer brushes consisting of a poly(phenylacetylene) backbone and polyisocyanate pendants (Scheme 1).[10] The results of the polymerization of macro-$\mathbf{1}_m$ are summarized in Table 2. All of the polymerization reactions proceeded homogeneously and afforded stereoregular (*cis–transoid*) poly(phenylacetylene)-based polymer brushes (poly-$\mathbf{1}_m$) in high yield except for poly-$\mathbf{1}_{70}$.[11] The low yield of poly-$\mathbf{1}_{70}$ is probably caused by the decrease in the concentration of macro-$\mathbf{1}_{70}$ in the feed because of its limited solubility. The obtained polymer brushes were soluble in THF, DMSO, and $CHCl_3$.

Table 2 Polymerization of macromonomers (macro-$\mathbf{1}_m$) with $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ in THF at 30 °C for 5 h[a]

Run	Macromonomer	[macro-$\mathbf{1}_m$] (mM)	Polymer			
			Sample code	Yield[b] (%)	$M_n \times 10^{-4c}$	$M_w/M_n{}^c$
1	macro-$\mathbf{1}_{29}$	105	poly-$\mathbf{1}_{29}$	93	5.9	2.0
2	macro-$\mathbf{1}_{48}$	42	poly-$\mathbf{1}_{48}$	85[d]	12.0	1.7
3	macro-$\mathbf{1}_{70}$	26	poly-$\mathbf{1}_{70}$	25[e]	15.0	1.3

[a] [macro-$\mathbf{1}_m$]/[Rh] = 70 (run 1) or 85 (runs 2 and 3). [b] MeOH insoluble component. [c] Determined by SEC (polystyrene standard, eluent: $CHCl_3$). [d] MeOH–THF (3 : 2, v/v) insoluble component. [e] MeOH–THF (1 : 1, v/v) insoluble component.

The chiroptical properties of the polymer brush with the shortest polyisocyanate pendants (poly-$\mathbf{1}_{29}$) were first investigated by CD and absorption spectral measurements. Poly-$\mathbf{1}_{29}$ exhibited a similar CD pattern to that of the corresponding macromonomer macro-$\mathbf{1}_{29}$ in the absorption region of the pendant polyisocyanate (<325 nm) in DMSO at 25 °C (Fig. 2d). Interestingly, its intensity significantly increased compared with that of macro-$\mathbf{1}_{29}$. In addition, the differential CD spectral pattern between poly-$\mathbf{1}_{29}$ and macro-$\mathbf{1}_{29}$ was consistent with the CD pattern of macro-$\mathbf{1}_{29}$. Therefore, this enhancement in the CD intensity means that the helix-sense excess of the pendant polyisocyanate chains was amplified after conversion to the polymer brush. Under these conditions, only very small absorption and CD signals were observed in the absorption region of the polyacetylene backbone above 325 nm because of the very low concentration of the polyacetylene chromophore in poly-$\mathbf{1}_{29}$. However, absorption and CD signals from the polyacetylene backbone were observed above 325 nm for poly-$\mathbf{1}_{29}$ when measurements were performed using a cell that was 5 times longer at a concentration that was 2.5 times higher (Fig. 2d). This observation indicates that a preferred-handed helical conformation was induced in the polyacetylene backbone of poly-$\mathbf{1}_{29}$ despite the fact that the optically active group attached to the pendant terminals is separated from the backbone by twenty-nine achiral isocyanate units. As illustrated in Fig. 1, this helicity induction triggered by a remote optically active group simultaneously results in a helical array of pendant helical polyisocyanate chains along the polyacetylene backbone with a preferred-handed helix-sense. It should be noted that the CD intensity of poly-$\mathbf{1}_{29}$ in the polyacetylene chromophore region (>325 nm) as well as the polyisocyanate chromophore region (260–325 nm) increased reversibly with decreasing temperature. This suggests that both the polyacetylene backbone and polyisocyanate pendants of the polymer brush have a dynamic nature (Fig. S5, ESI‡).[12]

To investigate the effect of the chain length of the pendant polyisocyanates bearing a terminal chiral group on the induction of helicity in the polyacetylene backbone of the polymer brushes, CD spectra were obtained for poly-$\mathbf{1}_{48}$ and poly-$\mathbf{1}_{70}$ with longer pendant chains under the same conditions.[13]

Despite the remote location of the chiral group, the CD intensity in the polyacetylene chromophore region of poly-$\mathbf{1}_{48}$ was almost identical to that of poly-$\mathbf{1}_{29}$ (Fig. 2e). Although poly-$\mathbf{1}_{70}$ showed a slight decrease in CD intensity, it can be presumed that the helix-sense excess of the polyacetylene backbone in poly-$\mathbf{1}_{70}$ is still rather high judging from its relatively large $\Delta\varepsilon$ compared with those of previously reported helical poly(phenylacetylene) derivatives (Fig. 2f).[2m,14] On the basis of these results, we can conclude that the preferred-handed helical chirality of the pendant polyisocyanate chains induced by the chiral group at the α-end would play an essential role in the remote control of the helicity of the polyacetylene backbone in the polymer brush. As with poly-$\mathbf{1}_{29}$, the amplification of the helix-sense excess of the pendant polyisocyanate chains after conversion to the polymer brush was also observed for poly-$\mathbf{1}_{48}$ and poly-$\mathbf{1}_{70}$, showing a more intense CD signal in the absorption region of the polyisocyanate ($<$325 nm) than that of the corresponding macromonomers macro-$\mathbf{1}_{48}$ and macro-$\mathbf{1}_{70}$, respectively (Fig. 2b, c, e and f). This amplification may be caused by the chiral interaction between the pendants and/or a reduction in the number of helix reversals in the polyisocyanate chains caused by the interaction between adjacent pendants as observed for polyisocyanates and polyacetylenes in a liquid crystal state.[15]

In conclusion, we have demonstrated that poly(phenylacetylene)-based polymer brushes bearing poly(phenyl isocyanate) pendants form a preferred-handed helical structure when a chiral group is introduced only at the pendant terminal. In these polymers, the pendant helical polyisocyanate chains are arranged in a helical array with a preferred-handed helix-sense along the helical polyacetylene backbone, which is accompanied by amplification of the helix-sense excess of the pendants. This method will be applicable to the combination of other dynamic helical polymers to arrange pendant helical polymer chains in preferred-handed helical arrays using chiral amplification. We believe that such helical polymer brushes may be useful as novel chiral materials for possible application as asymmetric catalysts and enantioselective selectors.

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11 It was difficult to evaluate the stereoregularity of poly-$\mathbf{1}_m$ using ^{1}H NMR spectroscopy because the peak caused by the main chain protons, which are highly useful for assigning the conformation and configuration of the polyacetylene backbone, could hardly be observed because of their very weak intensities relative to those of the protons of the pendant polyisocyanates (Fig. S2, ESI‡). Therefore, the stereoregularity of poly-$\mathbf{1}_m$ was evaluated using laser Raman spectroscopy (Fig. S3, ESI‡).

12 The vibrational CD (VCD) spectra of poly-$\mathbf{1}_{29}$ in THF at 25 and −10 °C were measured in order to clearly demonstrate that the change of the CD intensity of poly-$\mathbf{1}_{29}$ in the polyisocyanate chromophore region with temperature is due to the change of the helical screw sense preference of the polyisocyanate backbone, not due to the change of conformation adoption for the 3-methoxyphenyl side group against the polyisocyanate backbone. The VCD spectra of poly-$\mathbf{1}_{29}$ showed a bisignate couplet in the C=O stretching band region of the polyisocyanate backbone, whose intensity increased reversibly with decreasing temperature (Fig. S6, ESI‡). These VCD results support that the polyisocyanate pendants have a dynamic nature.

13 The CD intensity in the polyacetylene chromophore region (above 325 nm) of poly-$\mathbf{1}_{29}$ was apparently changed by solvents, whereas that in the polyisocyanate chromophore region (260–325 nm) of poly-$\mathbf{1}_{29}$ as well as macro-$\mathbf{1}_{29}$ was almost the same independent of solvent (see Fig. S4 in the ESI‡). Poly-$\mathbf{1}_{29}$ exhibited the most intense CD in the absorption region of the polyacetylene backbone in DMSO. Therefore, the CD and absorption spectra of poly-$\mathbf{1}_{48}$ and poly-$\mathbf{1}_{70}$ with longer pendant chains were measured in DMSO.

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