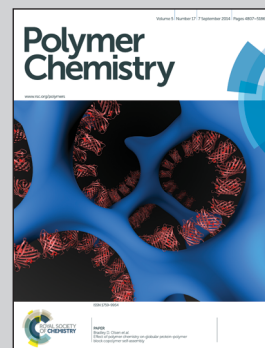


Highlighting research from Dr. Jeanne Crassous's group at CNRS-Université de Rennes, France and Dr. Eiji Yashima's group at Nagoya University, Japan.

Title: Synthesis and chiral recognition ability of helical polyacetylenes bearing helicene pendants

A novel helical polyacetylene bearing optically active [6]helicene units as the pendants was prepared, which exhibited excellent chiral recognition ability toward racemates such as 1,1'-binaphthyl analogues, and enantioselectively adsorbed one of the enantiomers.

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Synthesis and chiral recognition ability of helical polyacetylenes bearing helicene pendants†

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Novel polyacetylenes bearing an optically active or racemic [6]helicene unit as the pendant groups directly bonded to the main-chain (poly-1s) were prepared by the polymerisation of the corresponding acetylenes (1-*rac*, 1-*P* and 1-*M*) using a rhodium catalyst. The optically active polyacetylenes (poly-1-*P* and poly-1-*M*) formed a preferred-handed helical conformation biased by the optically active helicene pendants, resulting in the induced circular dichroism (ICD) in their π -conjugated polymer backbone regions. The optically active helical polymers, when employed as an enantioselective adsorbent, showed a high chiral recognition ability towards racemates, such as the monomeric [6]helicene and 1,1'-binaphthyl analogues, and enantioselectively adsorbed one of the enantiomers.

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Introduction

Helicenes are unique polycyclic aromatic compounds that are inherently chiral because of their nonplanar screw-shaped skeletons.¹ Due to such intriguing features of the helicenes that involve helical chirality, conjugated π -systems and fluorescent and chiroptical properties,^{1,2} optically active helicene-containing polymers have the potential to be used in many fields of the materials science including optoelectric materials, asymmetric catalysts and chiral separation and sensing materials. To date, several groups have attempted to introduce helicene units into macromolecules,³ but the applications of optically active helicene-containing polymers as chiral materials are quite limited.^{1a,b,e} In particular, the application of optically active helicene-containing polymers as enantioselective adsorbents and chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC) has not been previously reported, in spite of the recent significant advance in chromatographic enantioseparation that has become an essential technique for the development of chiral drugs in the pharmaceutical industry.⁴

On the other hand, the development of artificial helical polymers with a controlled helical sense has significantly advanced over the past decades because of their possible applications to chiral materials.⁵ Among the synthetic helical polymers prepared so far, polyacetylenes are one of the most extensively studied helical polymers,^{5,6} and some of them have been successfully utilised as asymmetric catalysts,⁷ chiral adsorbents⁸ and CSPs,^{9,10} in which the preferred-handed helical structures appear to be important for their enantioselectivities and resolving abilities.

We anticipated that an optically active [6]helicene derivative might be a suitable chiral component as the pendant group to develop a novel optically active helical polyacetylene, since the helicene residues, once covalently introduced to the polyacetylene backbone, could induce a preferred-handed helical structure in the polymer accompanied by a one-handed helical array of the helicene pendants, thus showing an intriguing chiral recognition ability originating from the helical chiralities of the helicene itself and polymer main-chain as well. To this end, we have designed and synthesised a series of novel optically inactive (poly-1-*rac*) and active polyacetylenes (poly-1-*P* and poly-1-*M*) (Scheme 1) bearing a racemic or optically active helicene unit as the pendant groups directly connected to the polymer backbone, and also investigated the chiroptical properties of poly-1-*P* and poly-1-*M* and their chiral recognition abilities were evaluated on the basis of an enantioselective adsorption method toward several racemates.¹¹

Results and discussion

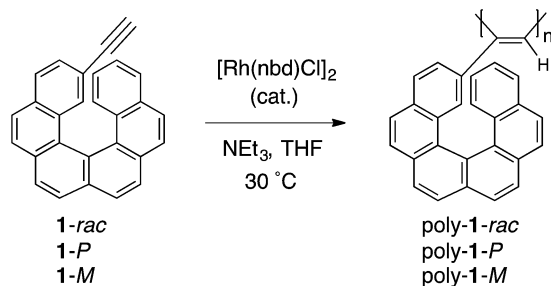
The helicene monomer, 2-ethynyl-carbo[6]helicene (1-*rac*), was prepared and resolved into enantiomers by chiral HPLC

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† Electronic supplementary information (ESI) available: The synthesis and characterisation of poly-1s, the enantioselective adsorption on poly-1-*M* and poly-1-*P* and the molecular modeling and calculations of poly-1-*M*. See DOI: 10.1039/c4py00692e

Scheme 1 Rhodium-catalysed polymerisation of **1**.

separation according to a previously reported method^{2h} (**1-P** and **1-M** with right- and left-handed screw senses, respectively; enantiomeric excess (ee) >99%) (ESI).†

Helically twisted helicene molecules are known to form self-associated supramolecular aggregates through noncovalent, face-to-face π - π interactions, which frequently trigger spontaneous resolution; *P*- and *M*-helicenes favorably form homochiral assemblies over heterochiral ones due to a greater π - π overlap between the helicenes with the same configuration.^{1a,b,e,12} If this is the case, we anticipated that the enantiomerically pure **1-P** and **1-M** could polymerise faster than their racemic mixture (**1-rac**), producing higher molecular weight (MW) homochiral polymers (poly-**1-P** and poly-**1-M**, respectively) or the racemic **1-rac** could polymerise in a stereoselective manner (poly-**1-rac**) via a growing chain-end control mechanism, thus producing a mixture of polymers rich in either **1-P** or **1-M**.¹³

In order to investigate this possibility, we first polymerised **1s** on a small scale under various conditions, namely, in

different solvents (tetrahydrofuran (THF) and chloroform) in the presence of NEt₃, different concentrations of **1s** (0.02–0.2 M) and rhodium catalysts (1–6 mol%) (neutral [Rh(nbd)Cl]₂ and cationic [Rh(nbd)₂BF₄] (nbd: norbornadiene), respectively) based on previously reported results.¹⁴ However, the polymers precipitated during the polymerisation reactions independent of the conditions, affording polymers with relatively low MWs in moderate yields. Therefore, the difference in the polymerisation reactivity between **1-rac** and **1-P** or **1-M** was difficult to investigate.

Typical polymerisation results in THF in the presence of NEt₃ using [Rh(nbd)Cl]₂ as a catalyst, yielding stereoregular (*cis*-*trans*oidal) polyacetylenes,¹⁵ poly-**1-rac**, poly-**1-P** and poly-**1-M** (Scheme 1) are shown in Table 1 (entries 1–3, 4, 9, and 14). The number-average molecular weights (*M*_n) of poly-**1-P** and poly-**1-M** (*M*_n = 2.6 × 10³) estimated by size exclusion chromatography (SEC) using polystyrene standards were higher than that of poly-**1-rac** (*M*_n = 1.6 × 10³) (entries 1–3). However, this tendency was not reproducible (see entries 4, 9 and 14 in Table 1), because the polymers precipitated during the polymerisation as already mentioned. The SEC profiles of poly-**1s** showed multimodal peaks, thus we fractionated poly-**1s** (Table 1, entries 4, 9 and 14) into four fractions (indicated by a subscript notation using A–D) based on the MW by SEC (Fig. S4† and Table 1)^{17,18} and their chiroptical properties were investigated.

Fig. 1A shows the circular dichroism (CD) and absorption spectra of the optically active **1-P**, **1-M**, poly-**1-P**_B and poly-**1-M**_B measured in THF at 25 °C. The monomers **1-P** and **1-M** gave rise to the typical absorption signals centered at around 270 and 320 nm assigned to the helicene moiety (g and h in Fig. 1A) and characteristic intense Cotton effects in the regions (c and d).^{2h}

Table 1 Polymerisation of **1-rac**, **1-P** and **1-M** with [Rh(nbd)Cl]₂ and SEC fractionation results of poly-**1-rac**, poly-**1-P** and poly-**1-M**^a

Entry	Monomer	Polymer					
		Code	Yield ^d (%)	<i>M</i> _n × 10 ⁻³	<i>M</i> _w / <i>M</i> _n ^e	$\Delta\epsilon_{1st}^f$ (M ⁻¹ cm ⁻¹)	$\Delta\epsilon_{2nd}^f$ (M ⁻¹ cm ⁻¹)
1	1-rac	poly- 1-rac	50	1.6	3.4	—	—
2 ^b	1-P	Poly- 1-P	25	2.6	5.3	0.98	-0.88
3	1-M	Poly- 1-M	17	2.6	7.1	-0.94	0.82
4 ^c	1-rac	poly- 1-rac	46	1.8	3.6	—	—
5		poly- 1-rac _A	—	5.8	2.0	—	—
6		poly- 1-rac _B	—	11	1.3	—	—
7		poly- 1-rac _C	—	3.0	1.6	—	—
8		poly- 1-rac _D	—	0.74	1.1	—	—
9 ^c	1-P	Poly- 1-P	52	1.7	2.7	1.22	-1.13
10		poly- 1-P _A	—	— ^g	— ^g	— ^g	— ^g
11		poly- 1-P _B	—	7.0	1.4	1.27	-1.12
12		poly- 1-P _C	—	2.7	1.3	1.29	-1.14
13		poly- 1-P _D	—	0.73	1.4	1.32	-1.25
14 ^c	1-M	Poly- 1-M	47	1.8	2.7	-1.16	1.07
15		poly- 1-M _A	—	— ^g	— ^g	— ^g	— ^g
16		poly- 1-M _B	—	5.2 ^h	1.3	-1.24	1.07
17		poly- 1-M _C	—	2.1 ^h	1.6	-1.25	1.10
18		poly- 1-M _D	—	0.79 ^h	1.4	-1.31	1.23

^a Polymerised under nitrogen; [monomer] = 0.2 M, [Rh]/[monomer] = 100. ^b [Rh]/[monomer] = 33. ^c [Rh]/[monomer] = 17. ^d Diethyl ether-insoluble part. ^e Estimated by SEC (polystyrene standards) with THF as the eluent. ^f The intensities of the first ($\Delta\epsilon_{1st}$) and second Cotton effects ($\Delta\epsilon_{2nd}$) at around 250 and 330 nm, respectively, measured in THF (0.02 mg mL⁻¹) at 25 °C. ^g Not measured because the amounts of poly-**1-P**_A and poly-**1-M**_A obtained by SEC fractionation were too small. ^h For their MALDI-TOF MS spectra, see Fig. S5.†



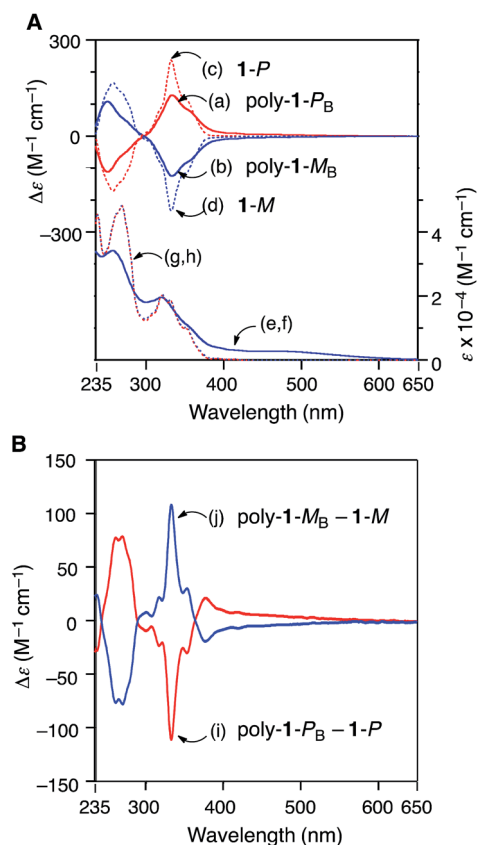


Fig. 1 (A) CD (a–d) and absorption (e–h) spectra of poly-1- P_B (a and e), poly-1- M_B (b and f), 1- P (c and g) and 1- M (d and h) recorded in THF at 25 °C. (B) Differential CD spectra between poly-1- P_B and 1- P (i) and poly-1- M_B and 1- M (j), where the CD spectra of 1- P and 1- M are subtracted from the observed CD spectra of poly-1- P_B and poly-1- M_B , respectively, without normalisation. The concentrations of polymers and monomers were 0.02 and 0.1 mg mL⁻¹, respectively.

On the other hand, poly-1- P_B and poly-1- M_B showed an apparent CD in the π -conjugated main-chain region (380–600 nm) induced by the chiral helicene pendants as well as CDs in the helicene chromophore region (235–380 nm) (a and b), whose CD spectral patterns were different from those of the monomers 1- P and 1- M . Fig. 1B shows the differential CD spectra in which the contributions arising from the CD absorption due to the enantiomerically pure 1- P and 1- M themselves are subtracted from the observed CD spectra of poly-1- P_B and poly-1- M_B , respectively (i and j in Fig. 1B). The differential CD spectral patterns seem to be like those of helical polyacetylenes with optically active pendant groups,¹⁹ suggesting that poly-1- P and poly-1- M most likely possess an excess of a one-handed helical conformation induced by the optically active helicene pendants, which may further result in a preferred-handed helical array of the helicene pendants along the single-handed helical polymer backbone.

The CD and absorption spectra of the fractionated poly-1- $P_{C,D}$ and poly-1- $M_{C,D}$ were also recorded in THF at 25 °C (Fig. S6A, C and D[†]), which, together with the differential CD spectra (Fig. S6B[†]) indicated that the CD intensities more or less depended on the MW of the polymers, but their difference was

not significant, probably because poly-1- P and poly-1- M likely possess a rather stable helical conformation with an excess one-handedness stabilised by the attractive intramolecular π - π interaction between the helically arranged helicene pendants with the same configuration. This speculation was supported by the facts that the CD spectra of poly-1- $P_{B,C}$ and poly-1- $M_{B,C}$ hardly changed over the temperature range of -10 to 55 °C in THF and remained unchanged after heating at 55 °C for 2 h (Fig. S7[†]). Such a thermal stability of the present helical poly-1- P and poly-1- M is noticeable, since most of the reported helical polyacetylenes are dynamic in nature and highly sensitive to temperature, which frequently exhibits an inversion of the macromolecular helicity with temperature.^{5d,6a,c,f}

Fig. 2A and B display a possible right-handed helical structure of poly-1- M (20 mer) based on molecular mechanics calculations with a 23 unit per 10 turn (23/10) helical poly-(phenylacetylene) whose helical structure was determined by X-ray diffraction measurements (see ESI[†]).²⁰ The calculated structure revealed that the helicene pendant units are closely packed and the neighboring helicene pendant units are overlapped *via* π - π interactions, resulting in the formation of the one-handed helical array along the helical polymer backbone.²¹

We next investigated if the racemic 1-*rac* could polymerise in a stereoselective fashion to produce a mixture of poly-1s rich in either 1- P or 1- M by an enantioselective adsorption technique¹¹ using optically active (-)-poly(triphenylmethyl methacrylate) ((-)-PTTrMA) with a one-handed helical conformation.^{5a-c,24} The optically active helical PTTrMA is a practically useful chiral packing material for HPLC and has been used to resolve a variety of aromatic racemic compounds including [6]helicene as well as racemic helical polymers such as (\pm)-PTTrMA.^{5a-c,25} In fact, (-)-PTTrMA selectively adsorbed poly-1- M from an equimolar mixture of poly-1- P and poly-1- M in hexane-THF (80 : 20, v/v), and its supernatant solution exhibited a CD whose spectral pattern and intensity were identical to those of poly-1- P (ee = 36.5%) (for more detailed experimental procedures, see ESI, Table S1 and Fig. S8[†]). In the same way, an enantioselective adsorption experiment was performed for poly-1-*rac* with (-)-PTTrMA. However, the supernatant solution showed almost no CD due to poly-1- P or poly-1- M (Table S1 and Fig. S8[†]), suggesting that 1-*rac* polymerised in an almost random way, or a highly stereoselective polymerisation (racemate-forming

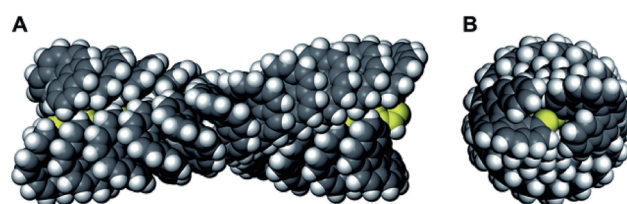
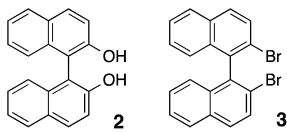


Fig. 2 (A) Side view and (B) top view of a possible right-handed helical structure of poly-1- M (20 mer). The structure is shown using the space-filling model; the main-chain atoms are shown in yellow for clarity. The pendant helicene residues are arranged in a left-handed helical array along the right-handed helical poly-1- M backbone. The helix-sense of the main-chain is assumed from the Cotton effect sign in the main-chain region (>380 nm) according to the literature.¹⁹



Table 2 Enantioselective adsorption of racemates on poly-1-*P* and poly-1-*M*^a


Entry	Analyte	Polymer	Yield of adsorbed analyte ^b (%)	ee of adsorbed analyte ^b (%)	Separation factor ^c (α)
1	1	poly-1- <i>P</i>	5.0	3.6 (<i>P</i>)	1.08
2 ^d		poly-1- <i>M</i>	5.0	3.7 (<i>M</i>)	1.08
3 ^d	2	poly-1- <i>P</i>	0.64	37 (<i>S</i>)	2.18
4 ^d		poly-1- <i>M</i>	0.66	35 (<i>R</i>)	2.09
5 ^d	3	poly-1- <i>P</i>	2.1	26 (<i>S</i>)	1.71
6 ^d		poly-1- <i>M</i>	2.3	29 (<i>R</i>)	1.84

^a Experimental conditions for entries 1 and 2: poly-1-*P* or poly-1-*M*, 2.0 mg; analyte, 0.04 mg (1 mL portion from a 0.04 mg mL⁻¹ solution in methanol). Experimental conditions for entries 3–6: poly-1-*P*, 2.0 mg or poly-1-*M*, 3.5 mg; analyte, 0.4 mg for poly-1-*P* or 0.7 mg for poly-1-*M* (1 mL or 1.75 mL portion from a 0.4 mg mL⁻¹ solution in methanol). ^b Determined by chiral HPLC analysis of analytes adsorbed on poly-1-*P* or poly-1-*M* using a UV-visible detector. ^c Calculated according to the equation $\alpha = (F_{\text{major}}(\%)/F_{\text{minor}}(\%))/(A_{\text{major}}(\%)/A_{\text{minor}}(\%))$, where F_{major} and F_{minor} are the percentages of major and minor enantiomers of the free analyte in the supernatant solutions, respectively, and A_{major} and A_{minor} are those of major and minor enantiomers of the adsorbed analyte, respectively. ^d Average values of two runs.

enantiomer-differentiating polymerisation) may not occur during the present polymerisation of 1-*rac*.

The chiral recognition ability of the optically active poly-1-*P* and poly-1-*M* was then investigated for the aromatic racemic compounds (1–3) including 1-*rac* by enantioselective adsorption experiments (Table 2 and ESI†).^{11,26,27}

poly-1-*P* and poly-1-*M* selectively adsorbed one of the enantiomers of 1–3 in methanol. The adsorbed analytes on the polymers were almost completely recovered by desorption in methanol and subsequently in a methanol–THF (50 : 50, v/v) mixture (ESI†), and their amounts and ee values were estimated by chiral HPLC analysis (Table 2).

As anticipated,^{1a,b,e,12} poly-1-*P* and poly-1-*M* preferentially adsorbed 1-*P* and 1-*M* with the same configuration of the helicene residues, furnishing 3.6 and 3.7% ee, respectively (entries 1 and 2). Interestingly, poly-1-*P* and poly-1-*M* showed a much better and more remarkable chiral recognition toward the racemic 1,1'-binaphthyl analogues (2 and 3), and selectively adsorbed the (*S*)- and (*R*)-enantiomers, respectively, with up to 37% ee (entries 3–6). Based on the amounts and ee values of the analytes (1–3) adsorbed on the polymers, the separation factor (α), which is a useful measure in chiral HPLC to evaluate the chiral resolving ability of optically active hosts toward racemic analytes,¹¹ can be calculated (Table 2).⁴ The calculated α values (1.71–2.18) are high enough for the complete separation of enantiomers when used as a CSP for HPLC,^{4,5a,b} indicating that the helicene-bound helical polyacetylenes possess a practically useful chiral recognition power for aromatic racemic compounds like a commercially available (+)-PTMA column.

The enantioselective adsorption results on the poly-1-*P* and poly-1-*M* (Table 2) revealed insight into the chiral recognition mechanism, in other words, the stereochemistry of the poly-1-analyte interaction; helically arranged helicene-pendant residues along the poly-1 helical backbone (Fig. 2) appear to be responsible for the observed efficient separation of aromatic

analytes (1–3). The two naphthyl rings of the more retained enantiomers of (*R*)-2 and (*R*)-3 on poly-1-*M* may be favorably twisted into a left-handed helix so as to interact with the adjacent *M*-helicene groups arranged in a left-handed helical array through the aromatic interactions, whereas due to a considerable π – π overlap between the helicene pendants, may interfere with the favorable close helicene–helicene interactions between poly-1 and 1-*rac*, resulting in a relatively lower separation factor than we anticipated.

Conclusions

In summary, we have, for the first time, prepared stereoregular helical polyacetylenes bearing optically active and racemic [6] helicene groups as the pendants. Although the molecular weights of the polymers were rather low because of the low solubility of the helicenes, the optically active helicene-bound polymers exhibited an apparent CD in the polymer backbone chromophore region due to a preferred-handed helix formation biased by the chiral helicene residues. Moreover, we found that the optically active helicene-bound polyacetylenes showed a high chiral recognition ability toward racemic 1,1'-binaphthyl derivatives largely arising from a one-handed helical array of the pendant helicene residues.

The present results suggest that a more practically useful chiral material for the separation of enantiomers may be developed based on analogous helicene- and organometallic helicene^{2f}-bound helical polyacetylenes by introducing a long alkyl chain on the helicene residue, which will overcome the solubility problem of polymers, thereby providing a unique chiral stationary phase with a high enantioselectivity composed of one-handed helical polyacetylenes with screw-shaped helicene and organometallic helicene pendants, and further studies along this line are now in progress.



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