Electronic Supporting Information (ESI)

Pseudo helix-sense-selective polymerisation (PHSSP) of achiral substituted acetylenes

Yu Zang[1], Toshiki Aoki[1]*, Lijia Liu[1], Yunosuke Abe[1],

Yuriko Kakihana[1], Masahiro Teraguchi[1], Takashi Kaneko[1]

[1] Graduate School of Science and Technology, Niigata University, Ikarashi 2-8050, Nishi-Ku, Niigata 950-2181, Japan

* Author to whom correspondence should be addressed; E-Mail: toshaoki@eng.niigata-u.ac.jp; Tel.: +81-25-262-7280; Fax: +81-25-262-7280.

Contents of ESI

1. Notes and references about terminology

(1)**Asymmetric polymerisation**: Asymmetric polymerisation is a polymerisation method for synthesizing a chiral polymer having newly produced chiral structures from an achiral monomer. Asymmetric polymerisation is divided into two categories: one is asymmetric synthesis polymerisation where new asymmetric centres (configurational chirality) are produced in the main chain during polymerisation, and the other is helix-sense-selective polymerisation (**HSSP**) where chiral structures based on one-handed helical main chains (conformational chirality) are newly produced. Enantiomer-selective polymerisation is also categorized as asymmetric polymerisation, but since no new chiral structures are produced, it is not a synthetic method.

(2) **Helix-sense-selective polymerisation** (**HSSP**; Schemes S1, 1B and S3B'): Chiral structures based on one-handed helical main chains (conformational chirality) are newly produced during **HSSP**. Only a few examples have been reported.

For the **HSSP** we developed of monosubstituted acetylene monomers, see reference 2 in the text.

For **HSSP** of other monomers reported: (*a*) R. J. M. Nolte, A. J. M. v. Beijnen and W. Drenth, *J. Am. Chem. Soc.*, 1974, **96**, 5932-5933; (*b*) Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada and H. Yuki, *J. Am. Chem. Soc.*, 1979, **101**, 4763-4765; (*c*) T. Nakano, Y. Okamoto and K. Hatada, *J. Am. Chem. Soc.*, 1992, **114**, 1318-1329; (*d*) T. Nakano and Y. Okamoto, *Macromolecules*, 1999, **32**, 2391-2393; (*e*) N. Hoshikawa, Y. Hotta and Y. Okamoto, *J. Am. Chem. Soc.*, 2003, **125**, 12380-12381; (*f*) T. Nakano, O. Nakagawa, M. Tsuji, M. Tanikawa, T. Yade and Y. Okamoto, *Chem. Commun.*, 2004, 144-145; (*g*) M.

Tsuji, A. K. M. F. Azam, M. Kamigaito and Y. Okamoto, *Macromolecules*, 2007, **40**, 3518-3520; (*h*) T. J. Deming and B. M. Novak, *J. Am. Chem. Soc.*, 1992, **114**, 7926-7927; (*i*) G. Tian, Y. Lu and B. M. Novak, *J. Am. Chem. Soc.*, 2004, **126**, 4082-4083; (*j*) H. Z. Tang, P. D. Boyle and B. M. Novak, *J. Am. Chem. Soc.*, 2005, **127**, 2136-2142; (*k*) H. Z. Tang, E. R. Garland, B. M. Novak, J. He, P. L. Polavarapu, F. C. Sun and S. S. Sheiko, *Macromolecules*, 2007, **40**, 3575-3580; (*l*) C. A. Khatri, Y. Pavlova, M. M. Green and H. Morawetz, *J. Am. Chem. Soc.*, 1997, **119**, 6991-6995; (*m*) G. M. Miyake and E. Y. X. Chen, *Macromolecules*, 2008, **41**, 3405-3416.

(3) **Asymmetric-induced polymerisation** (**AIP**; Schemes S4D and S5D'): Polymerisation inducing a second new chiral structure in the resulting polymers obtained from chiral monomers is also categorized as asymmetric polymerisation in a broad sense.[1d] However, in this communication, it was called asymmetric-induced polymerisation (**AIP**).

For examples of general **AIP**: (*a*) T. Oishi, K. Kagawa and H. Nagata, *Polymer*, 1997, **38**, 1461; (*b*) T. Nakano, D. Tamada, J. Miyazaki, K. Kakiuchi and Y. Okamoto, *Macromolecules*, 2000, **33**, 1489; (*c*) T. Sakaguchi, G. Kwak and T. Masuda, *Polymer*, 2002, **43**, 3937; (*d*) G. Wulff, *Angew. Chem. Int. Ed. Engl*., 1989, **28**, 21; (*e*) T. Kakuchi, A. Narumi, H. Kaga, T. Ishibashi, M. Obata and K. Yokota, *Macromolecules*, 2000, **33**, 3964 ; (*f*) J. Cui, X. Lu, A. Liu, X. Wan and Q. Zhou, *Macromolecules,* 2009, **42**, 7678; (*g*) D. B. Amabilino, E. Ramos, J. L. Serrano, T. Sierra and J. Veciana, *J. Am. Chem. Soc.*, 1998, **120**, 9126.

For examples of **AIP** of substituted acetylenes: (*a*) T. Aoki, M. Kokai, K. Shinohara and E. Oikawa, *Chem. Lett*., 1993, 2009; (*b*) H. Nakako, R. Nomura, M. Tabata and T. Masuda, *Macromolecules*, 1999, **32**, 2861; (*c*) E. Yashima, Y. Maeda and Y. Okamoto, *J. Am. Chem. Soc*., 1998, **120**, 8895; (*d*) I. Otsuka, T. Hongo, H. Nakade, A. Narumi, R. Sakai, T. Satoh, H. Kaga and T. Kakuchi, *Macromolecules*, 2007, **40**, 8930; (*e*) B. S. Li, K. K. L. Cheuk, F. Salhi, J. W. Y. Lam, J. A. K. Cha, X. Xiao, C. Bai and B. Z. Tang, *Nano Lett*., 2001, 323.

(4) ***In-situ*** **asymmetric-induced polymerisation** (***in-situ*** **AIP**; Scheme 1C): When an achiral monomer containing a dynamic covalent bond, such as monomers **1a** and **2a**, was polymerized in the presence of a chiral amine, the exchange reaction between the chiral amine and the achiral amine residues in the monomer, oligomer, and (co) polymer and the (co) polymerisation proceed simultaneously. Therefore, asymmetric-induced polymerisation (**AIP**) can occur**.** It was confirmed by isolating the corresponding CD-active copolymer. In this communication, we refer to it as ***in-situ*** **AIP.**

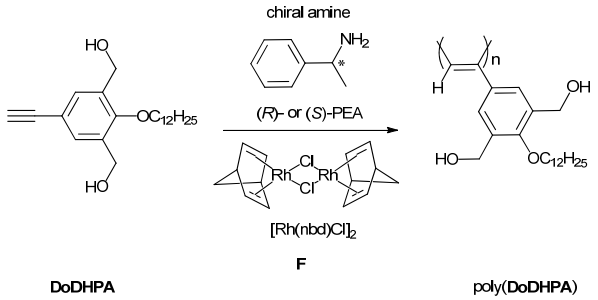
(5) **Pseudo helix-sense-selective polymerisation** (**PHSSP**; Schemes 1A and S3A'): We propose and define **PHSSP** as follows: **PHSSP** is a new asymmetric polymerisation using the same starting compounds (monomers, initiators, and chiral sources) under the same conditions, such as the molar ratio, temperature and solvents, as those used in **HSSP**, but the chiral source is not a catalyst but is a reagent (Scheme 1(A & B)). The overall reaction contains two or three steps, but the practical experimental procedure is simple and almost the same as that in **HSSP**. In addition, because of introduction of the chiral source *via* covalent bonds, the relative optical purity (the strength of the CD

peaks of the final polymers) and the efficiency ([chiral source] / [monomer])in the chiral induction are expected to be higher in **PHSSP** than those in **HSSP**.

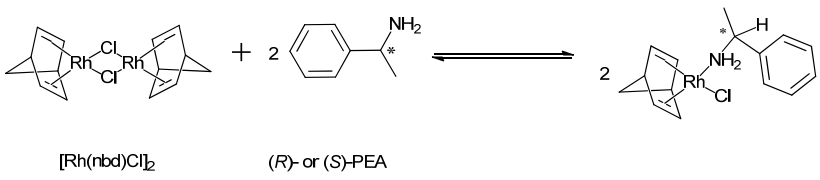
2. Supplemental schemes, tables and figures for the text and this ESI.

Supplemental schemes.

(1) Previous study (Supplemental for introduction)

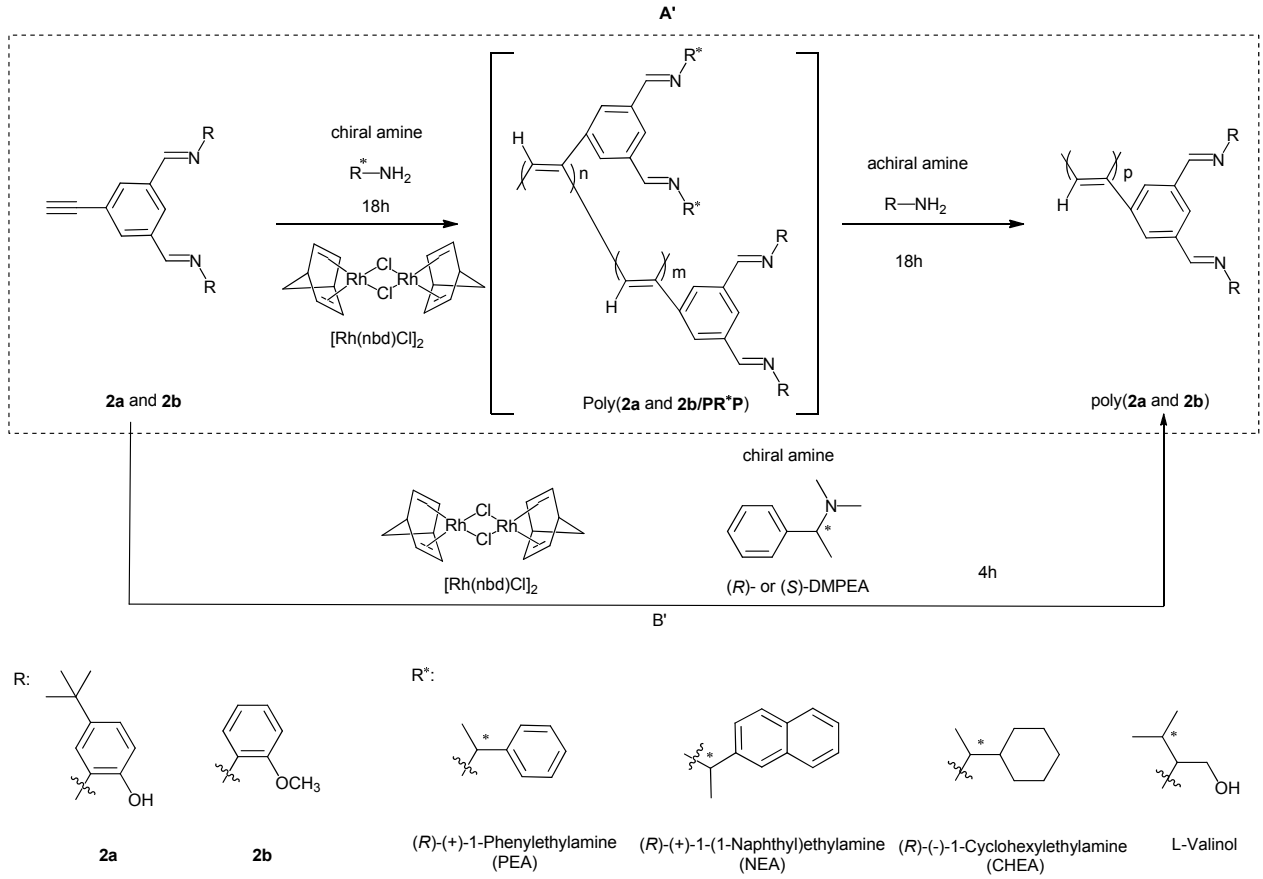


Scheme S1 F: Helix-sense-selective polymerisation (**HSSP**) of **DoDHPA** by using (*R*)- or (*S*)-PEA as a cocatalyst in our previous study.

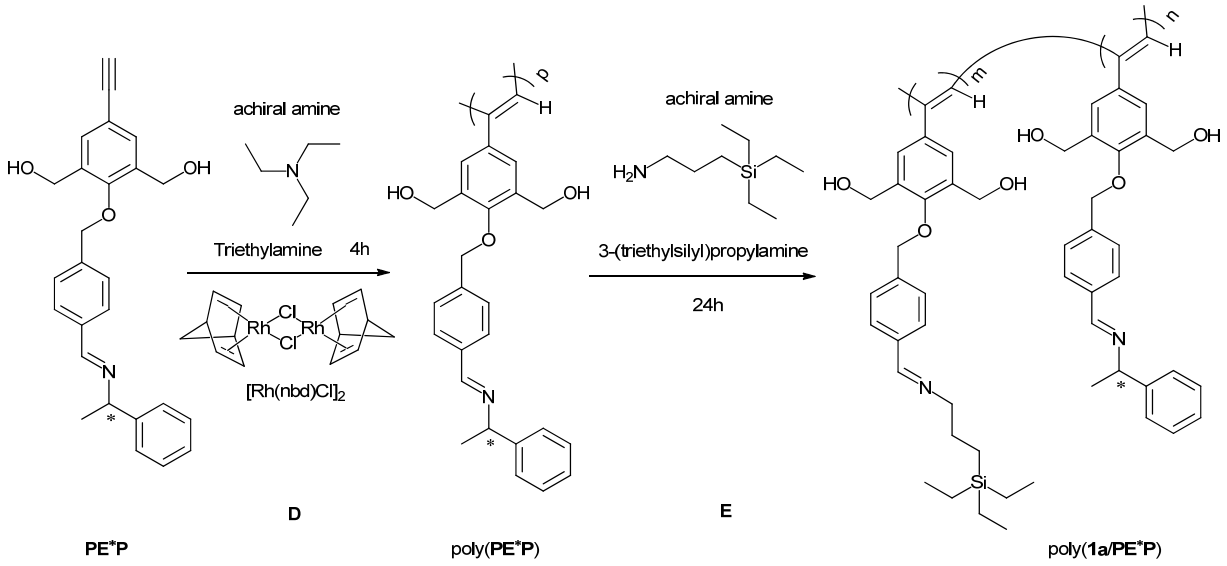


Scheme S2 Equilibrium between $[Rh(nbd)Cl]_2$ and (*R*)- or (*S*)-PEA.

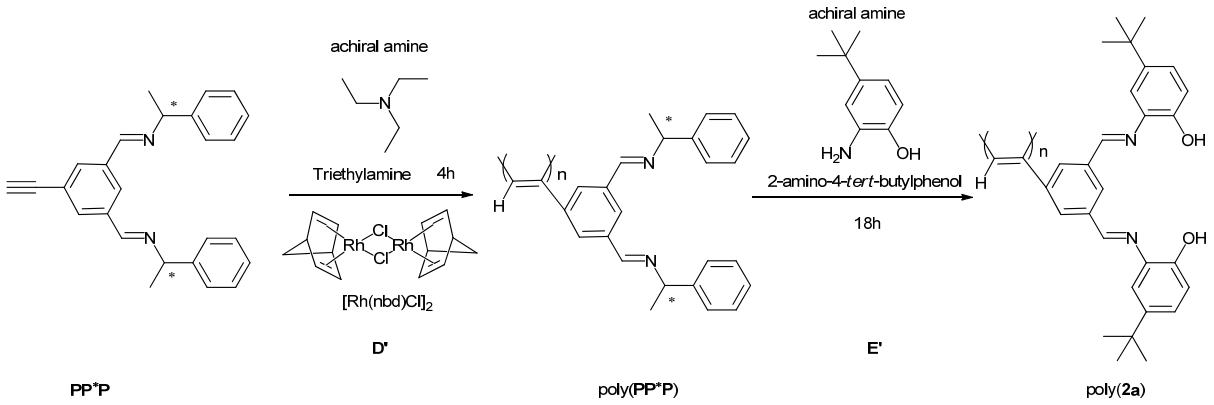
(2) This study



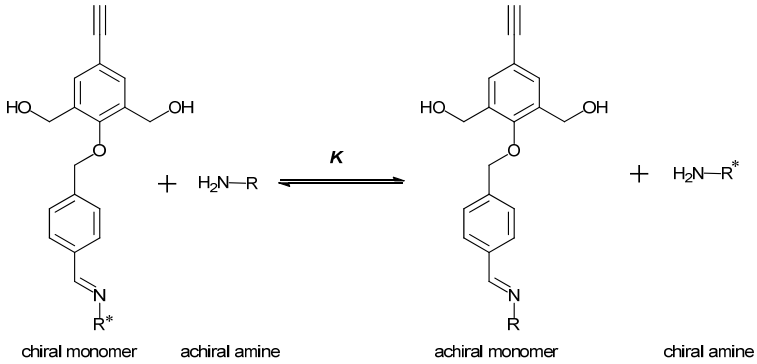
Scheme S3 **A'**: Pseudo helix-sense-selective polymerisation (**PHSSP**) by using various chiral amines as chiral sources, **B'**: Helix-sense-selective polymerisation (**HSSP**) by using (*R*)- or (*S*)-DMPEA as a cocatalyst of monomers **2a** and **2b** in this study.



Scheme S4 **D**: Asymmetric-induced polymerisation (**AIP**) of **PE*P**, **E**: Exchange reaction (**ER**) of PEA residues in poly(**PE*P**) with 3-(triethylsilyl)propylamine (For comparison of **PHSSP** of **1a**).



Scheme S5 D': Asymmetric-induced polymerisation (**AIP**) of **PP*P**, **E'**: Exchange reaction (**ER**) of PEA residues in poly(**PP*P**) with 2-amino-*tert*-butylphenol (For comparison of **PHSSP** of **2a**).



Scheme S6 Equilibrium constant (*K*) for a model exchange reaction of a chiral amine residue (R*-N=) in a monomer with an achiral amine(R-NH_2) for **PHSSP** of **1**.

Supplemental tables.

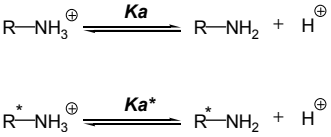
(1) Selection of monomer and optimisation of the condition of **PHSSP** (ESI-3)

Table S1 Attempt of pseudo helix-sense-selective polymerisation (**PHSSP**) of various monomers **1a-c** [a], **2a** [b] and **2b** [b] by using (*R*)-(+)-1-phenylethylamine (PEA), (*R*)-(+)-1-(1-naphthyl)ethylamine (NEA), (*R*)-(-)-1-cyclohexylethylamine (CHEA) and L-valinol as a chiral source to select monomers for **PHSSP**

No.	Monomer [c]	Chiral amine [d]	Yield (%)	M_w [e] ($\times 10^5$)	Achiral [f] amine unit (mol %)	g_{310nm} [g] ($\times 10^{-5}$)	g_{430nm} [g] ($\times 10^{-5}$)	Ka^* [h] ($\times 10^{-10}$)	Ka [h] ($\times 10^{-10}$)	K [i]
1	**1a**	(R)-PEA	72.2	4.60	100 [j]	-2.70	2.07	9.12	0.15	4.69
2	**1b**	(R)-PEA	30.6	1.50	96.0	(-0.09) [k]	(0.06) [k]	9.12	0.20	5.01
3	**1c**	(R)-PEA	65.8	0.47	45.0	(-0.34) [k]	(0.20) [k]	9.12	1.10×10^5	0.14
4	**2a**	(R)-PEA	20.8	3.60	97.3	—	(-0.02) [k, l]	9.12	1.44×10^5	—
5	**2b**	(R)-PEA	45.8	4.70	47.9	—	(0.20) [k, l]	9.12	0.43×10^5	—
6	**2a**	(R)-NEA	10.3	0.36	67.7	—	(-7.3×10^{-3}) [k, l]	4.37	1.44×10^5	—
7	**2a**	(R)-CHEA	2.3	0.27	63.9	—	(5×10^{-4}) [k, l]	0.13	1.44×10^5	—
8	**2a**	L-valinol	trace	—	—	—	—	1.50×10^{-3}	1.44×10^5	—

[a] In THF for 48 h, [monomer]=0.1mol/L, [monomer]/[Rh(nbd)Cl]$_2$=50, [chiral amine]/[monomer]=2.5, [achiral amine]/[monomer]=10. [b] In toluene for 36 h, [monomer]=0.1mol/L, [monomer]/[Rh(nbd)Cl]$_2$=100, [chiral amine]/[monomer]=2.5, [achiral amine]/[monomer]=10. [c] For the codes, see Schemes 1 and S3. [d] For the codes, see Scheme S3. [e] By GPC (polystyrene, THF). [f] Determined by ^{1}H-NMR in the final polymers. [g] g=([θ]/3300/ε)$\times$0.001 in $CHCl_3$. [h] See Equations 1, Ka^* for the chiral amines, Ka for the corresponding achiral amines calculated using Advanced Chemistry Development Software V11.02 from SciFinder. [i] See Equations 2 and Scheme S6, equilibrium constant of exchange reaction determined by ^{1}H-NMR. [j] By elemental analysis. [k] The polymers contain the chiral monomer units. [l] Calculated from the peak at 440nm.

Equations 1



Equations 2

$$K = \frac{[\text{achiral monomer}][\text{chiral amine}]}{[\text{chiral monomer}][\text{achiral amine}]} \qquad r = \frac{[\text{achiral amine}]_0}{[\text{chiral monomer}]_0}$$

Table S2 Exchange reaction of PEA residues in poly(**PP*P**) with achiral amine 2-amino-4-*tert*-butylphenol to optimise condition for PHSSP of **2a** [a]

No.	[2-Amino-4-*tert*-butylphenol] / [poly(**PP*P**)]	Yield (%)	M_w [b] ($\times 10^5$)	Achiral [c] amine unit (mol %)
1	100	42.4	6.19	87.9
2	50	50.0	15.7	87.6
3	10	19.7	7.61	85.9
4	2	45.0	10.0	47.3
5	1	63.6	8.33	7.16
6	0	79.3	5.88	0

[a] In toluene for 18h, [poly(**PP*P**)]=0.1mol/L, see scheme S5E' and Fig.S1. [b] By GPC (polystyrene, THF). [c] In the final polymers determined by ^{1}H-NMR.

(2) The results of **PHSSP**

Table S3 (Supplemental table for Table 1) Pseudo helix-sense-selective polymerisation (**PHSSP**) by using (*R*)- or (*S*)-PEA as a chiral source and helix-sense-selective polymerisation (**HSSP**) by using (*R*)- or (*S*)-DMPEA as a cocatalyst of monomers **1a** [a] and **2a** [b] with other related asymmetric polymerisation

No.	Monomer	Code [c]	Method [c]	[chiral amine] / [monomer]	Yield (%)	M_w [d] ($\times 10^5$)	Achiral [e] amine unit (mol %)	g_{310nm} [f] ($\times 10^{-5}$)	g_{430nm} [f] ($\times 10^{-5}$)	Final polymer	Relative O. P. [g] (%)
1 [a]	**1a**	A	PHSSP	0.50	27.0	1.0	100	-0.96	0.80	poly(**1a**)	38
2 [a]	**1a**	A	PHSSP	0.10	24.5	1.3	100	-0.39	0.40	poly(**1a**)	19
3 [h]	**PE*P**	D	AIP	— [i]	96.3	4.9	0	(-6.1) [j]	(3.6) [j]	poly(**PE*P**)	—
4 [h]	**PE*P**	D+E	AIP+ER	— [i]	62.1	3.8	89	(-4.6) [j]	(2.5) [j]	poly(**1a/PE*P**)	—
5 [k]	**PP*P**	D'+E'	AIP+ER	— [i]	78.4	1.6	100	—	-0.020 [l]	poly(**2a/PP*P**)	1.0
6 [m]	**DoDHPA**	F	HSSP	0.50	67.3	11	100	0.40	0.30	poly(**DoDHPA**)	14
7 [m]	**DoDHPA**	F [n]	HSSP	0.50	85.3	0.30	100	0.40	0.30	poly(**DoDHPA**)	14
8 [m]	**DoDHPA**	F	HSSP	0.25	69.8	33	100	0.060	0.060	poly(**DoDHPA**)	2.9

[a] In THF, [**1a**]=0.1mol/L, [**1a**]/[Rh(nbd)Cl]$_2$=50, [achiral amine]/[**1a**]=10, for the abbreviations, see the notes and scheme 1. [b] In toluene, [monomer]=0.1mol/L, [monomer]/[Rh(nbd)Cl]$_2$=100, [achiral amine]/[monomer]=10, see scheme S3. [c] For the codes and abbreviations, see Chart 1. [d] By GPC (polystyrene, THF). [e] Determined by ^{1}H-NMR in the final polymers. [f] $g=([\theta]/3300/\varepsilon)\times 0.001$ in $CHCl_3$. [g] Relative optical purity based on the g_{430nm} value of No. 1 in Table 1. [h] See Scheme S4, in THF, [**PE*P**]=0.1mol/L, [**PE*P**]/[Rh(nbd)Cl]$_2$=50, [triethylamine]/[**PE*P**]=2.5, [achiral amine]/[poly(**PE*P**)]=10. [i] Triethylamine was used as a cocatalyst. [j] The polymers contain the chiral monomer units. [k] See Scheme S5 in toluene, [**PP*P**]=0.1mol/L, [**PP*P**]/[Rh(nbd)Cl]$_2$=100, [triethylamine]/[**PP*P**]=1.0, [achiral amine]/[poly(**PP*P**)]=10. [l] Calculated from the peak at 440nm. [m] See scheme S1 in toluene [**DoDHPA**]=0.1mol/L, [**DoDHPA**]/[Rh(nbd)Cl]$_2$=200. [n] (*R*)-DMPEA was used as a cocatalyst.

Supplemental figures.

(1) Optimisation of the condition for **PHSSP** (ESI-3)

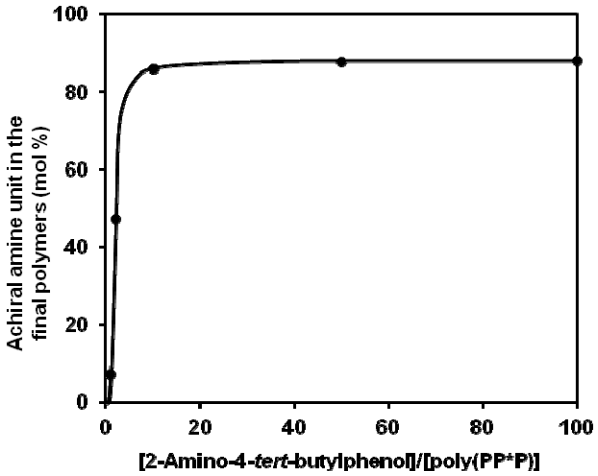


Fig. S1 Plots of the achiral amine units in the final polymers *vs* [2-amino-4-*tert*-butylphenol]/[PEA units in poly(**PP*P**)] in **ER** to optimise the condition in **PHSSP** of **2a** (Scheme S5E' and Table S2).

(2) Comparison between **PHSSP** and **HSSP**

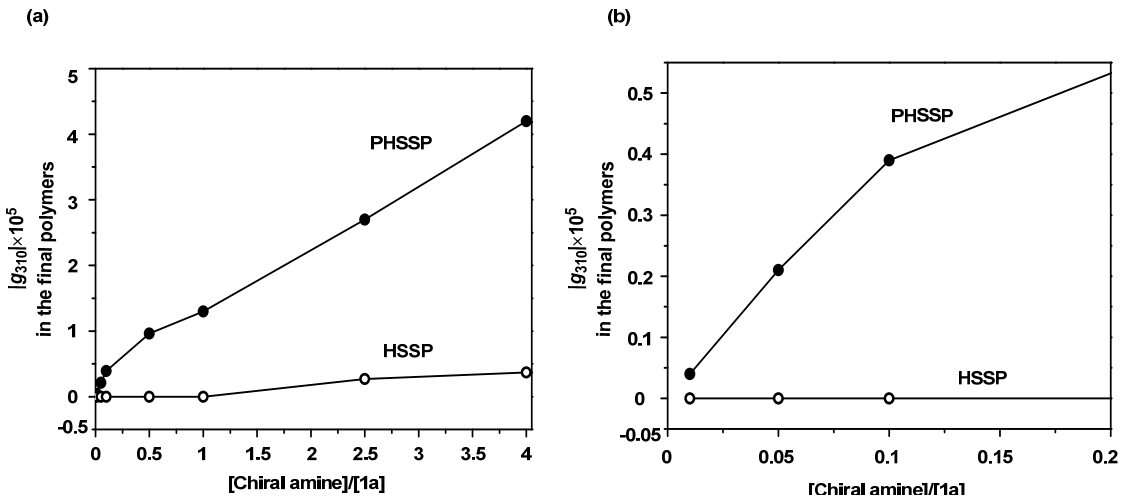


Fig. S2 Plots of **g** values *vs* [chiral amine]/[**1a**] in the feed of poly(**1a**)s prepared by pseudo helix-sense-selective polymerisation (**PHSSP**) and helix-sense-selective polymerisation (**HSSP**) (a), and its enlarged one (b).

(3) Non-linear relationship

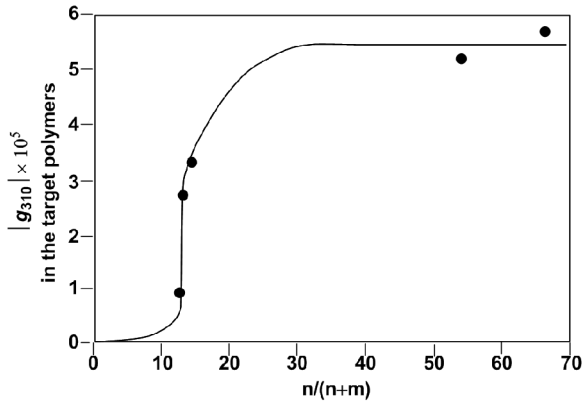


Fig. S3 Plots of ***g*** values vs **n**/(**n+m**) of poly(**1a**/**PE*P**) prepared by *in-situ* asymmetric-induced polymerisation (***in-situ* AIP**) by using different amount of (*R*)- or (*S*)-PEA as a chiral source.

(4) Change of poly(**1a**) by changing polarity of the solvent

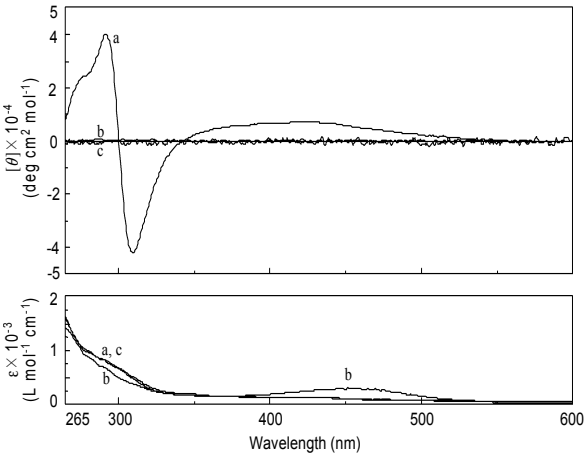


Fig. S4 CD and UV-vis spectra of poly(**1a**) prepared by pseudo helix-sense-selective polymerisation (**PHSSP**) of monomer (**1a**) ([chiral amine]/[**1a**]=2.5) in (a) $CHCl_3$, (b) $CHCl_3$/DMSO=55/45 (v/v), (c) $CHCl_3$/DMSO=95/5 (v/v) ((c) was the solution prepared by addition of $CHCl_3$ to the solution of (b)).

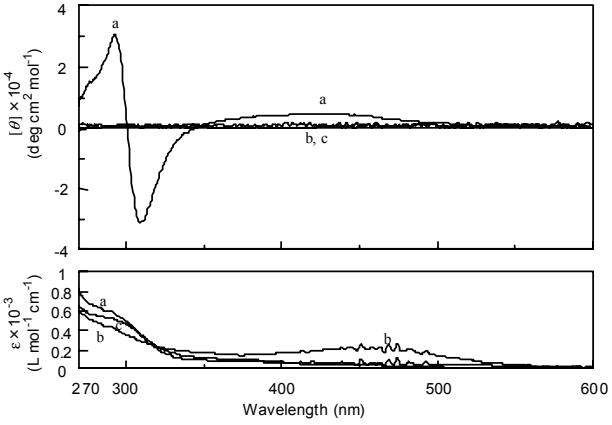


Fig. S5 CD and UV-vis spectra of poly(**1a**) prepared by ***in-situ* AIP** of monomer (**1a**) ([chiral amine]/[**1a**]=0.1) in (a) $CHCl_3$, (b) $CHCl_3$/DMSO=55/45 (v/v), (c) $CHCl_3$/DMSO=95/5 (v/v) ((c) was the solution prepared by addition of $CHCl_3$ to the solution of (b)).

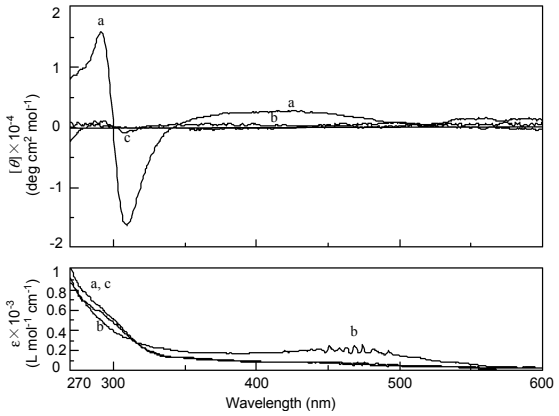


Fig. S6 CD and UV-vis spectra of poly(**1a**) prepared by ***in-situ*** **AIP** of monomer (**1a**) ([chiral amine]/[**1a**]=1.0) in (a) $CHCl_3$, (b) $CHCl_3$/DMSO=55/45 (v/v), (c) $CHCl_3$/DMSO=95/5 (v/v) ((c) was the solution prepared by addition of $CHCl_3$ to the solution of (b)).

(5) NMR of the final polymer prepared by **PHSSP** of **1a**

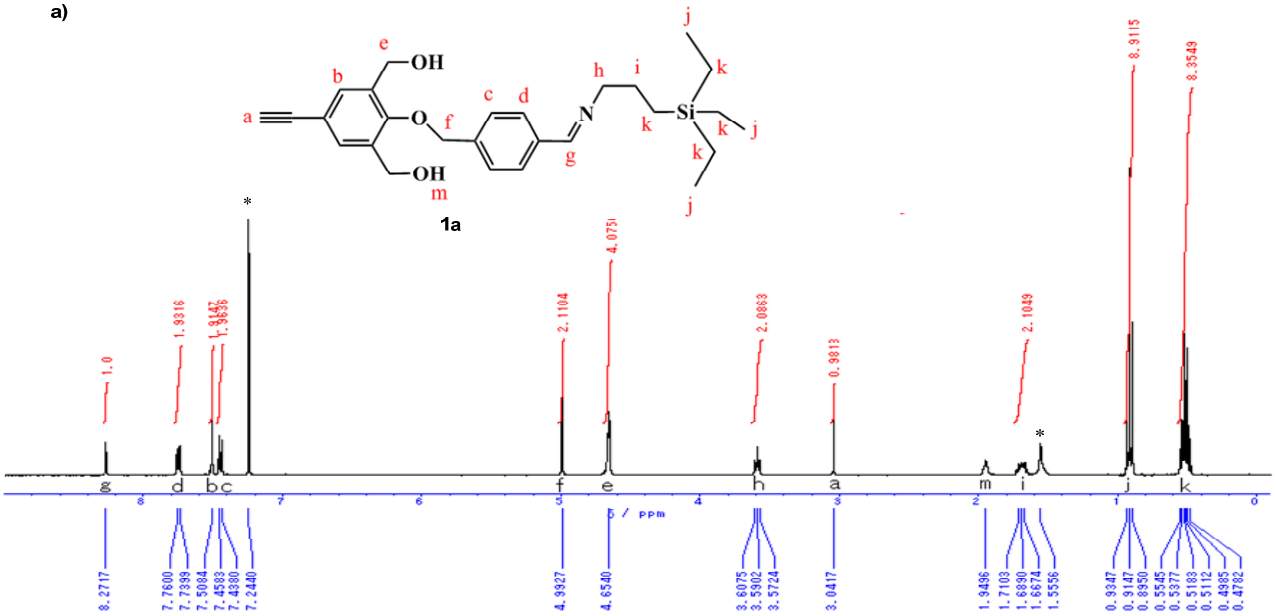


Fig. S7 ^{1}H-NMR spectra of **a**) monomer (**1a**), **b**) helix-sense-selective polymerisation (**HSSP**) of monomer (**1a**) by using (*R*)- or (*S*)-DMPEA as a cocatalyst, **c**) pseudo helix-sense-selective polymerisation (**PHSSP**) of monomer (**1a**) by using (*R*)- or (*S*)-PEA as a chiral source (No. 2 in table 1), **d**) pseudo helix-sense-selective polymerisation (**PHSSP**) of monomer (**1a**) by using (*R*)- or (*S*)-PEA as a chiral source (No. 1 in table 1), **e**) monomer (**PE*P**), **f**) asymmetric-induced polymerisation (**AIP**) of chiral monomer **PE*P**, **g**) the enlargement of b), c) and d).

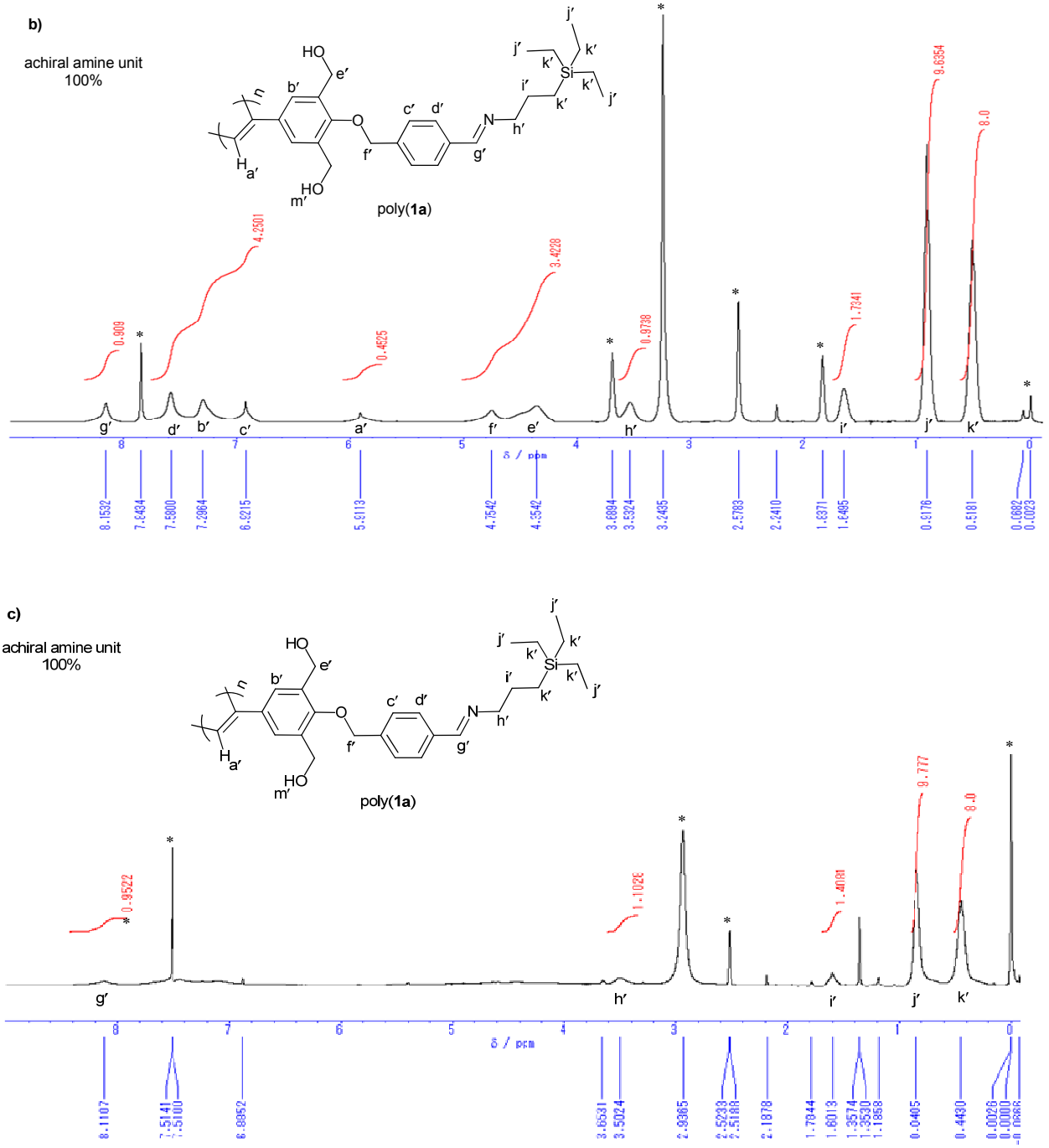
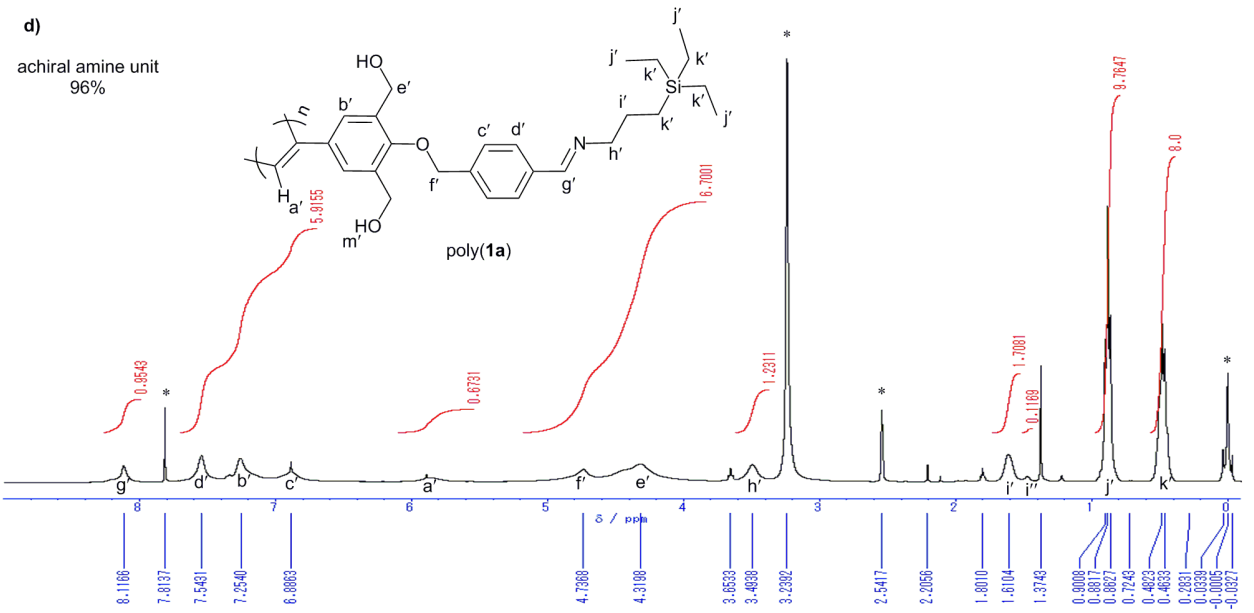


Fig. S7 (Continued).



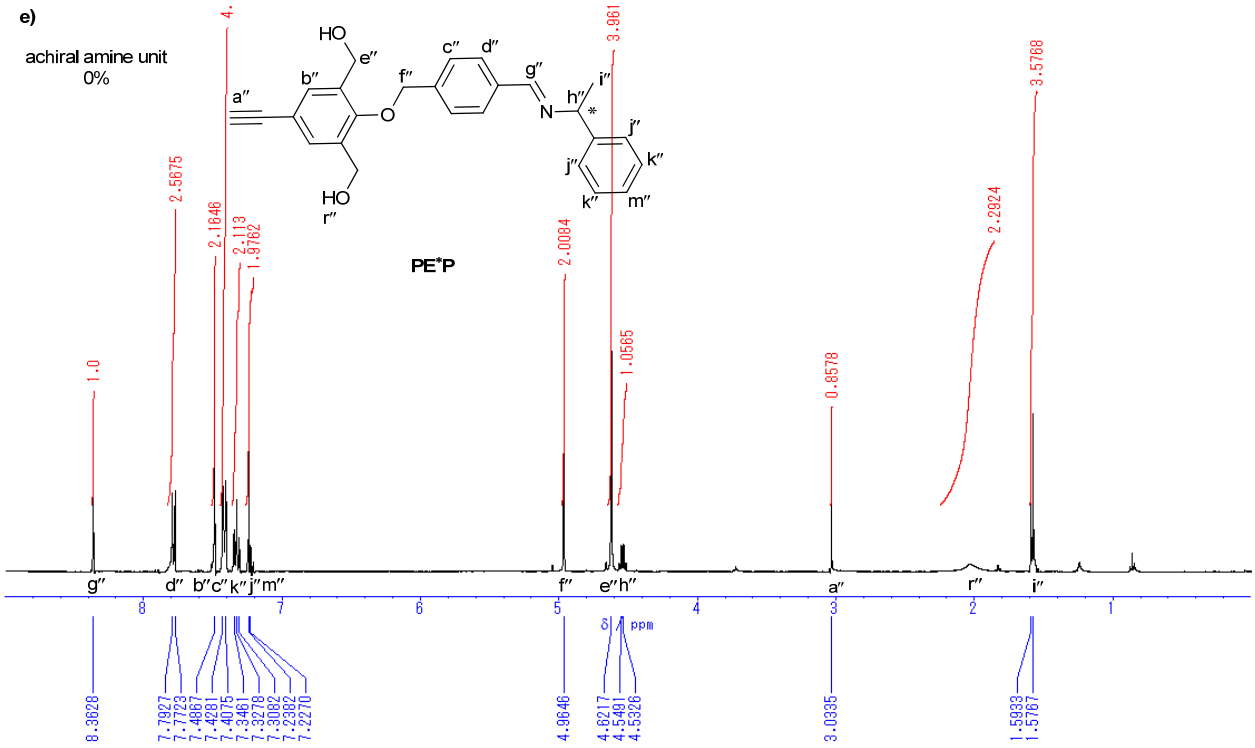


Fig. S7 (Continued).

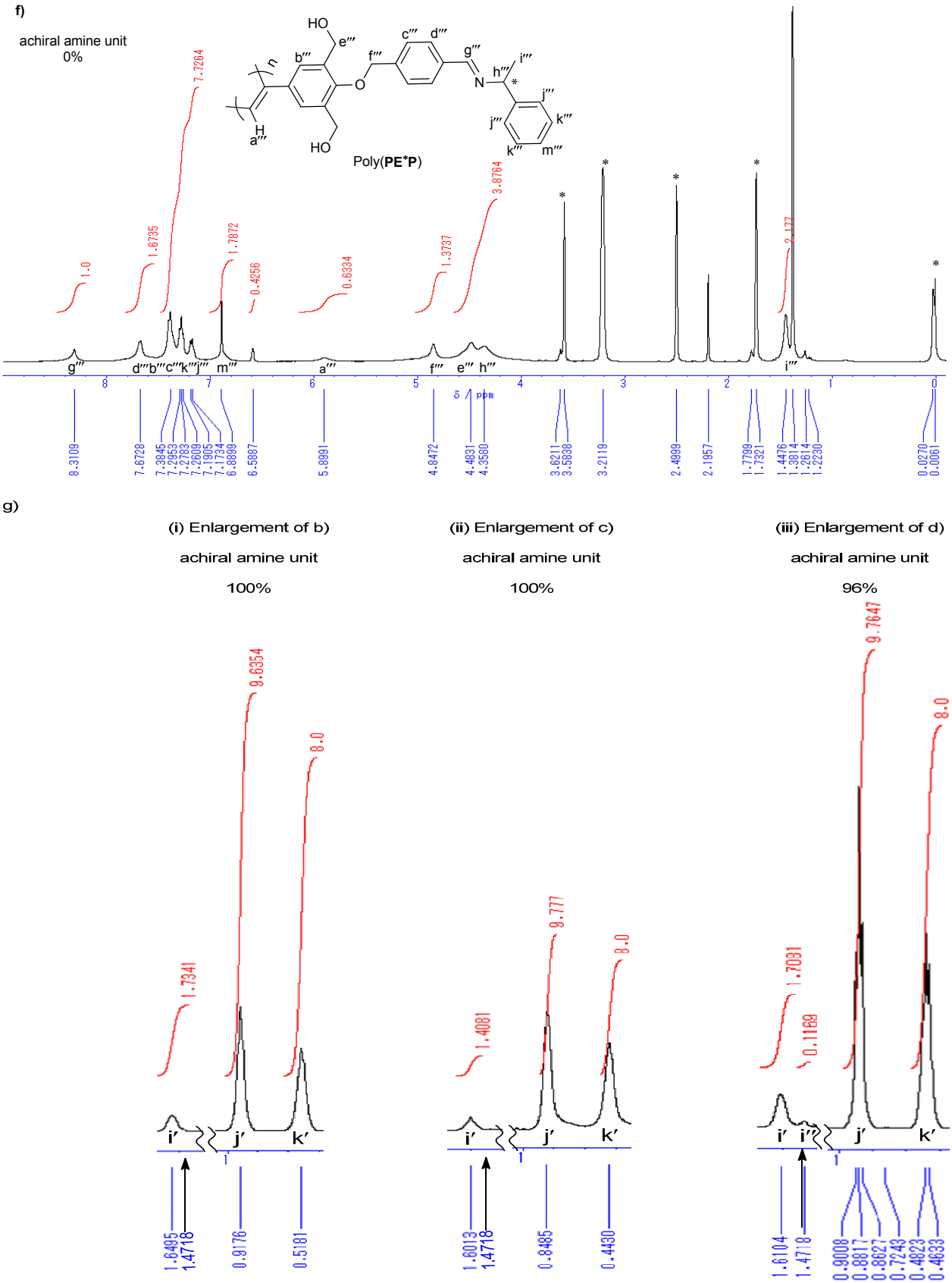


Fig. S7 (Continued).

3. Selection of compounds and optimisation of the conditions for PHSSP

(1) Monomer design

Two kinds of achiral monomers having one or two achiral amine residues *via* dynamic covalent imine bonds (**1a-c** in Scheme 1 and **2a** and **2b** in and Scheme S3) were designed and synthesized for **PHSSP**. The former (**1a-c**) was expected to be suitable for not only **PHSSP** but also **HSSP** because **1a-c** contain two hydroxyl groups which can make intramolecular hydrogen bonds to maintain one-handed helicity of the resulting polymers, while suitability of the latter (**2a** and **2b**) for **PHSSP** and **HSSP** was not clear although they contain two planer bulky substituents which can maintain one-handed helicity.

(2) Selection of the best chiral amine by preliminary experiments (Table S1)

The chiral amines should have a low basicity to keep low conversion in the exchange reaction at the first step of **PHSSP** (Scheme S3), because they should be removed completely at the second step. We attempted to carry out **PHSSP** (for the detail procedure, see the experimental part of ESI-4(3)1)) of **2a** using four chiral amines, PEA, NEA, CHEA, and L-valinol (Scheme S3). As the results, when PEA was used, the content of the chiral units was lowest (Table S1, nos.4, 6-8). It was reasonable because PEA had the lowest basicity (the highest *Ka** value) among them. About chiral induction ability of the chiral amines, since the final polymers in the **PHSSP** procedure showed the biggest ***g*** value assigned to the main chain (Table S1, nos.4, 6-8) in spite of the lowest content of the chiral amine units, we decided to select PEA as the best chiral amine for **PHSSP**.

(3) Selection of the best achiral amine by preliminary experiments (Tables S1 and S2)

The achiral amines should have a higher basicity and higher conversion to attain complete removal of the chiral amine units from the intermediate chiral polymers in the re-exchange reaction at the second step of **PHSSP** (Schemes 1 and S3). We attempted to carry out **PHSSP** (for the detail procedure, see the experimental part of ESI-4(3)1)) of **1a-c** using PEA (Scheme 1, Table S1, nos.1-3). As results, when **1a** and **1b** were used, the contents of the chiral units were almost zero (Table S1, nos.1 and 2). In particular in the case of **1a**, it had no chiral units, *ie*, an ideal result was achieved (Table S1, no.1). It was reasonable because the corresponding amine of **1a** had the highest basicity (the lowest *Ka* value) among them. Since poly(**1a**) from **1a** showed the biggest ***g*** value assigned to the main chain (Table S1, no.1) in spite of the no content of the chiral amine units, we decided to select the corresponding achiral amine of **1a** (= 3-triethylsilylpropylamine) as the best achiral amine for **PHSSP**. Similarly to the case of **1a**, the corresponding amine of **2a** was selected as the better achiral amine between **2a** and **2b** (Table S1, nos.4 and 5).

(4) Determination of the amount of achiral amines by preliminary experiments (Table S2 and Fig.S1)

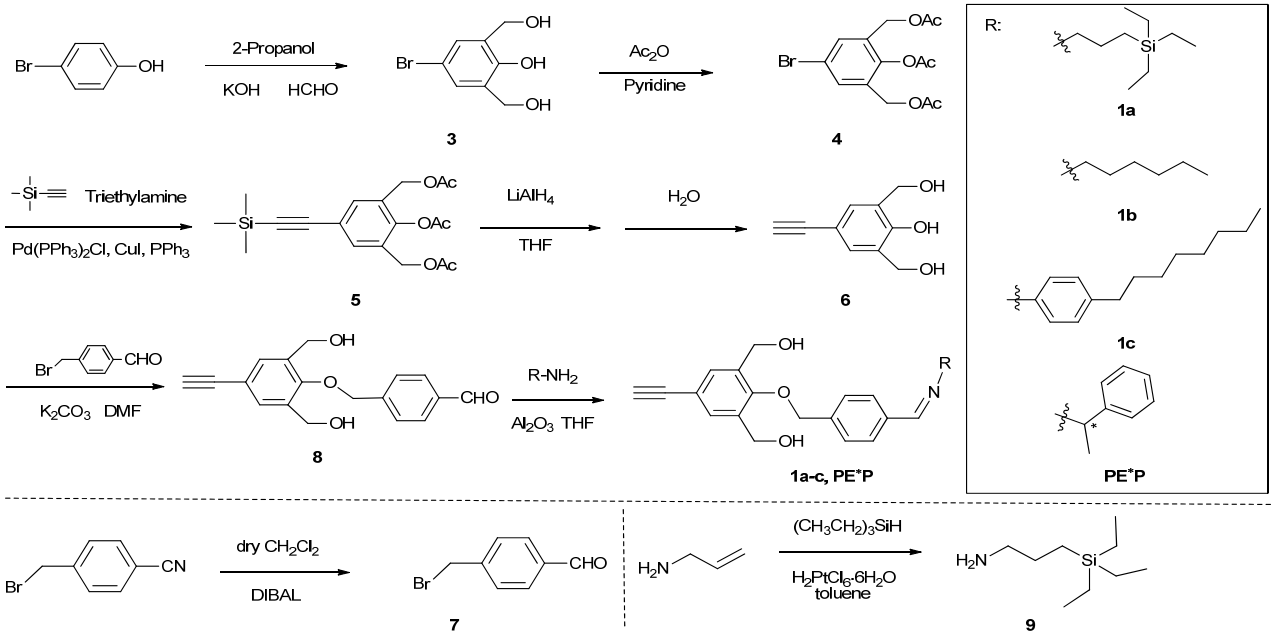
To optimise the ratio of the amount of achiral amines to the amine residues in the polymer for **PHSSP**, an exchange reaction (Scheme S5E') between the corresponding achiral amine to **2a** (= 2-amino-4-*tert*-butylphenol) and the chiral amine(PEA) residues in poly(**PP*P**) as a model reaction of the 2nd step in **PHSSP**. As a result (Table S2 and Fig.S1), when the ratio of 2-amino-4-*tert*-butylphenol to the PEA residues in poly(**PP*P**) exceeded 10, the content of the chiral unit in the final polymer became almost constant. Therefore we decided to use 10 for the ratio in **PHSSP**.

4. The detail of experimental procedures for synthesis and polymerisation

Materials

All the solvents used for monomer synthesis and polymerisation were distilled as usual. The polymerisation initiator, $[Rh(nbd)Cl]_2$ (nbd=2,5 norbornadiene), purchased from Aldrich Chemical Co., Inc., was used as received. The silicon-containing reagent, trimethylsilylacetylene was purchased from Shinetsu Chemical Co., Ltd., and used as received.

(1) Synthetic procedures of the monomers 1a-c and PE*P (Scheme S7)



Scheme S7. Synthetic route to the monomers **1a-c** and **PE*P**

1) 4-Bromo-2, 6-bis(hydroxymethyl)-1-phenol (**3**) [S1]

According to the literature procedure, **3** was prepared as a white solid. Yield: 80.9% (136g). ^{1}H NMR (DMSO-d_6): δ = 8.76 (s, 1H, PhO*H*), 7.29 (s, 2H, Ph*H*), 5.31 (t, 2H, J = 5Hz, CH_2O*H*), 4.51 (d, 4H, J = 5Hz, C*H*$_2$OH).

2) 2,6-Bis(acetoxymethyl)-4-bromo-1-phenyl acetate (**4**) [S2]

To a pyridine solution (100mL) of **3** (20g, 85.8mmol), acetic anhydride (48.6mL, 515mmol) was added dropwise at 0°C. The solution was stirred for 1.5h at room temperature and then ethyl acetate (200mL) was added to the mixture. Then the mixture was washed with saturated aqueous solution of $CuSO_4 \cdot 5H_2O$ to remove pyridine.

The organic layer was dried over anhydrous $MgSO_4$. After concentration, the crude product was purified by silica-gel column chromatography to give **4** as a white solid. Yield: 70% (21.5g). Rf = 0.36 (ethyl acetate/hexane = 1/2). ^{1}H NMR (DMSO-d_6): δ= 7.68 (s, 2H, Ph*H*), 4.97 (s, 4H, Ph(CH_2O)$_2$, 2.31 (s, 3H, PhOCOCH_3), 2.03 (s, 6H, Ph(CH$_2$OCOCH_3)$_2$).

3) 2, 6-Bis(acetoxymethyl)-4-(trimethylsilylethynyl)-1-phenyl acetate (**5**) [S2]

A mixture of **4** (10.76g, 30mmol), triphenylphosphine (550mg, 2.1mmol), copper (I) iodide (690mg, 3.6mmol), bis(triphenylphosphine)palladium(II)dichloride (420mg, 0.6mmol) and trimethylsilylacetylene (6.2mL, 45mmol) in triethylamine (120mL) was refluxed for 24h. After the mixture was filtered, the solvent was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **5** as a brown liquid. Yield: 87.7% (9.9g). Rf = 0.32 (ethyl acetate/hexane = 1/3). ^{1}H NMR ($CDCl_3$, TMS): δ= 7.50 (s, 2H, Ph*H*), 4.98 (s, 4H, Ph(CH_2OAc)$_2$), 2.32 (s, 3H, PhOCOCH_3), 2.06 (s, 6H, Ph(CH$_2$OCOCH_3)$_2$), 0.22 (s, 9H, Si(CH_3)$_3$).

4) 2, 6-Bis(hydroxymethyl)-4-ethynylphenol (**6**) [S2]

To a mixture of lithium aluminum hydride (2.0g, 52.4mmol) and tetrahydrofuran (87.0mL), a tetrahydrofuran solution (15.0mL) of **5** (9.87g, 26.2mmol) was added dropwise at 0°C. After the mixture was stirred for 2h at room temperature, deionized water (72.0mL) was added dropwise to the reaction mixture at 0°C. The mixture was stirred for 12h at room temperature. The reaction mixture was treated with 2N HCl aq. to precipitate aluminum salts. After the mixture was filtered, tetrahydrofuran was removed by evaporation. The product was dissolved in ethyl acetate and the solution was washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give **6** as a white solid. Yield: 81.4% (3.8g). Rf = 0.27 (ethyl acetate/hexane = 1/1). ^{1}H NMR (DMSO-d_6): δ= 8.98 (s, 1H, PhO*H*), 7.27 (s, 2H, Ph*H*), 5.29 (s, 2H, Ph(CH$_2$O*H*)$_2$), 4.52 (s, 4H, Ph(CH_2OH)$_2$), 3.91 (s, 1H, *H*C≡C).

5) 4-Bromomethylbenzaldehyde (**7**) [S3]

4-Cyanobenzyl bromide (14g, 71.4mmol) was dissolved in dry CH_2Cl_2 (260mL) and the solution was stirred at 0℃. 1.0M diisobutylaluminium hydride hexane solution (DIBAL, 70mL, 70mmol) was added dropwise to the solution at 0℃. The solution was stirred for 15min and then DIBAL solution (35mL) was added dropwise again. The mixture was stirred for 15min at 0℃ and then 30min at room temperature. The reaction mixture was treated

with 50% H_2SO_4 (150mL) aq. to precipitate the aluminium salt. After the mixture was filtered, the solution was washed with water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated to give aim product **7** as a white solid. Yield: 56.3% (8.0g). ^{1}H NMR ($CDCl_3$, TMS): δ= 10.0 (s, 1H, PhC*H*O), 7.85 (d, 2H, J=8Hz, BrCH$_2$Ph*H*), 7.54 (d, 2H, J=8Hz, *H*PhCHO), 4.50 (s, 2H, BrC*H*$_2$Ph).

6) 4-(4'-Formylbenzyloxy)-3,5-bis(hydroxymethyl)phenylacetylene (**8**)

A mixture of **6** (3.79g, 21.3mmol), **7** (4.23g, 21.3mmol) and K_2CO_3 (8.8g, 63.9mmol) in DMF (107mL) was stirred for 50h at 70℃. After the mixture was filtered, the solvent was removed. The residue was washed with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give aim product **8**. Rf = 0.7 (chloroform/methanol = 95/5). ^{1}H NMR ($CDCl_3$, TMS): δ= 10.0 (s, 1H, PhC*H*O), 7.94 (d , 2H, J=8Hz, *H*PhCHO), 7.63 (d , 2H, J=8Hz, OCH$_2$Ph*H*), 7.54 (s, 2H, HC≡CPh*H*), 5.08 (s, 2H, PhOC*H*$_2$Ph), 4.69 (d, 4H, J=6Hz, Ph(C*H*$_2$OH)$_2$), 3.07 (s, 1H, *H*C≡C), 1.74 (t, 2H, J=6Hz, Ph(CH$_2$O*H*)$_2$).

7) 3-(Triethylsilyl)propylamine (**9**)

$H_2PtCl_6 \cdot 6H_2O$ (26mg, 0.05mmol), toluene (15mL) was added to the flask and stirred at 80℃ until $H_2PtCl_6 \cdot 6H_2O$ was dissolved completely. Triethylsilane (8mL, 50.2mmol) and allylamine (4.2mL, 55.2mmol) was added dropwise to the solution at 40℃ separately and stirred at 85℃ for 120h. The crude product was purified by vacuum distillation at 54℃ (250Pa) to give aim product **9** as a colorless liquid. Yield: 67.7% (5.89g). ^{1}H NMR ($CDCl_3$, TMS): δ= 2.65 (t, 2H, J=7Hz, NH$_2$C*H*$_2$), 1.42 (m, 2H, NH$_2$CH$_2$C*H*$_2$CH$_2$), 1.27(s, 2H, N*H*$_2$), 0.92 (t, 9H, J=8Hz, Si(CH$_2$C*H*$_3$)$_3$), 0.59 (t, 2H, J=8Hz, NCH$_2$CH$_2$C*H*$_2$Si), 0.49 (q, 6H, J=8Hz, Si(C*H*$_2$CH$_3$)$_3$).

8) 4-[4'-{(3-Triethylsilyl)propyliminomethyl}benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene **(1a)**

A mixture of **8** (500mg, 1.68mmol), **9** (586mg, 3.36mmol) and Al_2O_3 (10g) in dry THF (16mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to yield a white solid. The crude product was purified by recrystallization in $CHCl_3$/hexane to give monomer **1a** as a white solid. Yield: 56.5% (428mg). ^{1}H NMR ($CDCl_3$, TMS): δ= 8.21 (s, 1H, PhC*H*=N), 7.76 (d, 2H, J=8Hz, NCHPh*H*), 7.50 (s, 2H, C≡CPh*H*), 7.45 (d, 2H, J=8Hz, PhOCH$_2$Ph*H*), 4.99 (s, 2H, PhOC*H*$_2$Ph), 4.65 (d, 4H, J=6Hz, Ph(C*H*$_2$OH)$_2$), 3.59 (t, 2H, J=7Hz, NC*H*$_2$CH$_2$), 3.04 (s, 1H, *H*C≡C), 1.90 (t, 2H, J=6Hz, Ph(CH$_2$O*H*)$_2$), 1.68 (m, 2H, NCH$_2$C*H*$_2$CH$_2$),

0.91 (t, 9H, J=8Hz, $Si(CH_2CH_3)_3$), 0.53 (t, 2H, J=8Hz, $NCH_2CH_2CH_2Si$), 0.49 (q, 6H, J=8Hz, $Si(CH_2CH_3)_3$). IR (cm^{-1}, KBr): 3322 (OH), 3233 (HC≡C), 1643 (C=N). Anal. Cacld for $C_{27}H_{37}O_3NSi$: C, 71.80; H, 8.26; N, 3.10. Found: C, 71.74; H, 8.17; N, 3.10.

9) 4-[4'-(Hexyliminomethyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**1b**)

A mixture of **8** (200g, 0.67mmol), hexylamine (177μL, 1.35mmol) and Al_2O_3 (5.0g) in dry THF (7mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to yield a white solid. The crude product was purified by recrystallization in $CHCl_3$/hexane to give monomer **1b** as a white solid. Yield: 58% (148mg). ^{1}H NMR ($CDCl_3$, TMS): δ= 8.28 (s, 1H, PhC*H*=N), 7.74 (d, 2H, J=8Hz, NCHPh*H*CH_2), 7.52 (s, 2H, HC≡CPh*H*), 7.44 (d, 2H, J=8Hz, OCH_2Ph*H*), 5.00 (s, 2H, PhOCH_2Ph), 4.66 (br, 4H, Ph($CH_2OH)_2$), 3.59 (t, 2H, J=7Hz, $NH_2CH_2CH_2$), 3.05 (s, 1H, *H*C≡CPh), 2.00 (br, 2H, Ph($CH_2OH)_2$), 1.70 (m, 2H, $NCH_2CH_2CH_2$), 1.33 (m, 6H, $CH_2(CH_2)_3CH_3$), 0.89 (t, 3H, J=7Hz, CH_2CH_3). IR (cm^{-1}, KBr): 3332 (OH), 3243 (HC≡C), 1637 (C=N).

10) 4-[4'-(4''-n-Octylphenyliminomethyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**1c**)

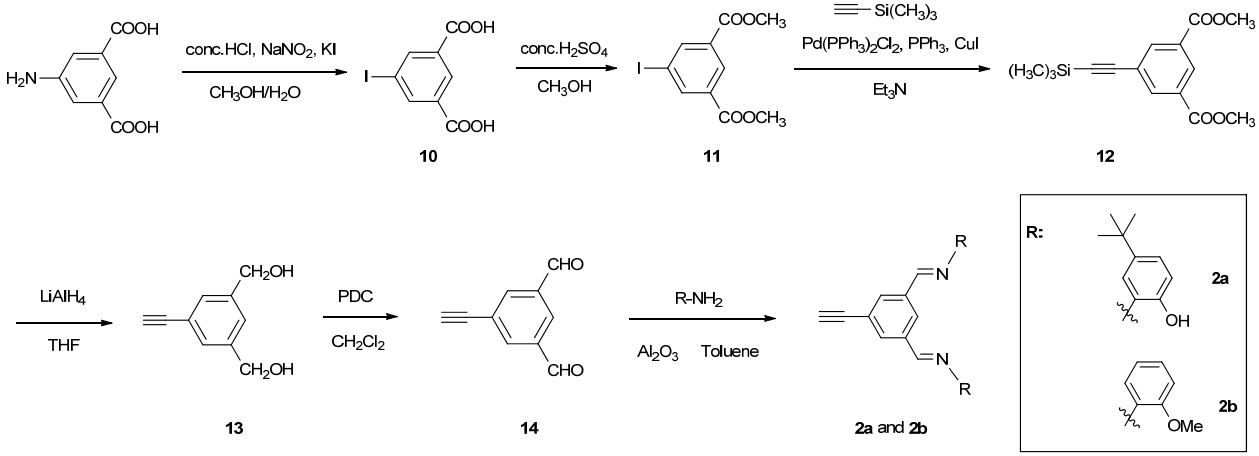
A mixture of **8** (500mg, 1.69mmol), 4-n-octylaniline (520mg, 2.53mmol) and Al_2O_3 (10g) in dry THF (17mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to yield a white solid. The crude product was purified by recrystallization in $CHCl_3$/hexane to give monomer **1c** as a white solid. Yield: 47% (383mg). ^{1}H NMR ($CDCl_3$, TMS): δ= 8.50 (s, 1H, PhC*H*=N), 7.92 (d, 2H, J=8Hz, N=CHPh*H*), 7.53 (s, 2H, HC≡CPh*H*), 7.51 (d, 2H, J=8Hz, OCH_2Ph*H*), 7.20 (d, 2H, N-Ph*H*CH_2 CH_2), 7.16 (d, 2H, CHN-Ph*H*CH_2), 5.05 (s, 2H, PhOCH_2Ph), 4.69 (d, 4H, J=6Hz, Ph($CH_2OH)_2$), 3.06 (s, 1H, *H*C≡CPh), 2.63 (t, 2H, J=8Hz, PhCH_2CH_2), 1.90 (t, 2H, J=6Hz, Ph($CH_2OH)_2$), 1.63 (m, 2H, Ph$CH_2CH_2CH_2$), 1.27 (br, 10H, $CH_2(CH_2)_5CH_3$), 0.88 (t, 3H, J=7Hz, CH_2CH_3). IR (cm^{-1}, KBr): 3355 (OH), 3282 (HC≡C), 1625 (C=N). Anal. Cacld for $C_{32}H_{37}O_3N$: C, 79.47; H, 7.71; N, 2.90. Found: C, 79.36; H, 7.68; N, 2.94.

11) 4-[4'-(Phenylethyliminomethyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**PE*P**)

A mixture of **8** (500g, 1.68mmol), (*R*)-phenylethylamine (432.7μl, 3.37mmol) and Al_2O_3 (10g) in dry THF (16mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to

yield a white solid. The crude product was purified by recrystallization in $CHCl_3$/Hexane to give monomer **PEP** as a white solid. Yield: 53% (210mg). ^{1}H NMR ($CDCl_3$, TMS): δ= 8.36 (s, 1H, PhC*H*=N), 7.77 (d, 2H, J=8Hz, Ph*H*CH=N), 7.48 (s, 2H, HC≡CPh*H*), 7.42 (d, 2H, J=8Hz, OCH_2Ph*H*), 7.40 (d, 2H, J=7Hz, N-CHPh*H*), 7.32 (t, 2H, J=7Hz, N-CHPh*H*), 7.22 (t, 1H, J=7Hz, N-CHPh*H*), 4.96 (s, 2H, PhOCH_2Ph), 4.62 (br, 4H, Ph(CH_2OH)$_2$), 4.53 (q, 1H, J=7Hz, NC*H*Ph), 3.03 (s, 1H, *H*C≡CPh), 2.13 (br, 2H, Ph(CH_2O*H*)$_2$), 1.57 (d, 3H, J=7Hz, CHCH_3).

(2) Synthetic procedures of the monomers 2a and **2b** (Scheme S8)



Scheme S8. Synthetic route to the monomers **2a and 2b**

1) 5-Iodoisophthalic acid (**10**)

5-Aminoisophthalic acid (30.0g, 161.5mmol) and the cold $NaNO_2$ aqueous solution (28.0g/43.0mL, 168.6mmol) were added to a mixture of ice (50g), methanol (200mL), concentrated hydrochloric acid (40mL, 1.35mol) with stirring. Then the mixture was added to a solution of KI aqueous solution. After stirring for 20min at room temperature, the Na_2SO_3 was added to the mixture and stirred for another 20min. The mixture was filtered, the solvent was removed and the crude product was purified by *vacuo* drying to give aim product **10** as a yellow solid. Yield: 67% (31.6g). ^{13}C NMR (DMSO-d_6, TMS): δ= 165.0 (*C*OOH), 141.3 (Ph*C*), 133.0 (Ph*C*), 129.0 (Ph*C*), 94.7 (*C*-I). IR (cm^{-1}, KBr): 3300~2500 (OH), 1716 (C=O).

2) Methyl 5-iodoisophthalate (**11**) [S4]

A mixture of **10** (31.6cg, 108mmol), methanol (900mL, 37.3mol) and concentrated sulfuric acid (31.6mL, 592mmol) was stirred for 24h at 65℃. After the mixture was filtered, the solvent was removed. The residue was washed with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated.

The crude product was purified by silica-gel column chromatography to give aim product **11** as a white solid. Yield: 83.8% (29.0g). Rf = 0.58 (ethyl acetate/hexane = 1/4). ^{1}H NMR ($CDCl_3$, TMS): δ= 8.63 (t, 1H, J=2Hz, Ph*H*), 8.55 (d, 2H, J=2Hz, Ph*H*), 3.95 (s, 6H, OCH_3).

3) Methyl 5-(trimethylsilylethynyl)isophthalate (**12**) [S5]

A mixture of **11** (7.88g, 24.6mmol), triphenylphosphine (41.9mg, 159μmol), copper (I) iodide (31mg, 163μmol), bis(triphenylphosphine)palladium(II)dichloride (43.3mg, 61.7μmol) and trimethylsilylacetylene (6.09mL, 42.3mmol) in triethylamine (300mL) was refluxed for 24 h. After the mixture was filtered, the solvent was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **12** as a white solid. Yield: 99.6% (6.75g). Rf = 0.4 (ethyl acetate/hexane = 1/10). ^{1}H NMR ($CDCl_3$, TMS): δ= 8.60 (t, 1H, J=2Hz, Ph*H*), 8.29 (d, 2H, J=2Hz, Ph*H*), 3.95 (s, 6H, OCH_3), 0.26 (s, 9H, Si(CH_3)$_3$).

4) 3,5-Bis(hydroxylmethyl)phenylacetylene (**13**)

To a mixture of lithium aluminum hydride (0.711 g, 18.7mmol) and tetrahydrofuran (40mL), a tetrahydrofuran solution (8mL) of **12** (3.84 g, 13.9mmol) was added dropwise at 0°C. After the mixture was stirred for 7h at room temperature, deionized water (1mL) was added dropwise to the reaction mixture at 0°C. The mixture was stirred for 8h at room temperature. The reaction mixture was treated with 2N HCl aq. to precipitate aluminum salts. After the mixture was filtered, tetrahydrofuran was removed by evaporation. The product was dissolved in ethyl acetate and the solution was washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give **13** as a white solid. Yield: 80.5% (1.82g). Rf = 0.13 (ethyl acetate/hexane = 1/1). ^{1}H NMR ($CDCl_3$, TMS): δ= 7.42 (s, 2H, Ph*H*), 7.37 (s, 1H, Ph*H*), 4.69 (d, 4H, J=6Hz, Ph(CH_2OH)$_2$), 3.08 (s, 1H, *H*C≡C), 1.73 (t, 2H, J=6Hz, Ph(CH$_2$O*H*)$_2$).

5) 3,5-Bis(formyl)phenylacetylene (**14**)

To a mixture of pyridinium dichromate (PDC) (8.7g, 23.1mmol) and CH_2Cl_2 (100mL), a CH_2Cl_2 solution (100mL) of **13** (0.75 g, 4.62mmol) was added dropwise at 0°C. After the mixture was stirred for 48h at room temperature, the mixture was filtered, CH_2Cl_2 was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **14** as a yellow solid. Yield: 45.2% (0.33g). Rf = 0.33 (ethyl

acetate/hexane = 1/4). ^{1}H NMR ($CDCl_3$, TMS): δ= 10.0 (s, 2H, C*H*O), 8.34 (t, 1H, J=2Hz, Ph*H*), 8.23 (d, 2H, J=2Hz, Ph*H*), 3.27 (s, 1H, *H*C≡C).

6) 3,5-Bis(*N*-2-hydroxyl-5'-*tert*-butylphenyliminomethyl)phenylacetylene (**2a**)

A mixture of **14** (201mg, 1.27mmol), 2-amino-4-*tert*-butylphenol (467mg, 2.83mmol) and Al_2O_3 (1g) in dry toluene (20mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by Al_2O_3 column chromatography to give **2a** as a yellow solid. Yield: 53.8% (310mg). Rf = 0.52 (ethyl acetate/hexane = 1/6).^{1}H NMR ($CDCl_3$, TMS): δ= 8.76 (s, 2H, N=C*H*), 8.40 (br, 1H, HC≡CPh*H*), 8.17 (d, 2H, J=2Hz, HC≡CPh*H*), 7.34 (d, 2H, J=2Hz, C=NPh*H*), 7.30-7.28 (d, d, 2H, J=8Hz, J=2Hz, C=NPh*H*), 7.03 (s, 2H, PhO*H*), 6.97 (d, 2H, J=8Hz, C=NPh*H*), 3.33 (s, 1H, C≡C*H*), 1.35 (s, 18H, (PhC(CH_3)$_3$)$_2$). IR (cm^{-1}, KBr): 3450 (OH), 3304 (H≡C), 2965 (C-H), 2398 (C≡C), 2000-1800 (Ar-H), 1625 (C=N). Anal. Cacld for $C_{30}H_{32}O_2N_2$: C, 79.61; H, 7.13; N, 6.19. Found: C, 79.36; H, 7.01; N, 6.11.

7) 3,5-Bis(*N*-*o*-methoxylphenyliminomethyl)phenylacetylene (**2b**)

A mixture of **14** (123mg, 0.778mmol), *o*-anisidine (200µl, 1.77mmol)) and Al_2O_3 (0.6g) in dry toluene (15mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by Al_2O_3 column chromatography to give **2b** as a yellow solid. Yield: 45.5% (130mg). Rf = 0.36 (ethyl acetate/hexane = 1/10).^{1}H NMR ($CDCl_3$, TMS): δ= 8.54 (s, 2H, N=C*H*), 8.39 (br, 1H, HC≡CPh*H*), 8.18 (d, 2H, J=2Hz, HC≡CPh*H*), 6.96-7.04 (m, 6H, C=NPh*H*), 3.90 (s, 6H, (PhOCH_3)$_2$), 3.15 (s, 1H, C≡C*H*. IR (cm^{-1}, KBr): 3450 (OH), 3228 (H≡C), 2935 (C-H), 2357 (C≡C), 1624 (C=N), 1246 (C-O-C).

(3) Polymerisation of all the monomers (Schemes 1, S1, S3, S4 and S5)

1) Pseudo helix-sense-selective polymerisation (**PHSSP**) (Schemes 1 and S3, routes **A** and **A'**).

A typical procedure for **1a** was as follows: A solution of [Rh(nbd)Cl]$_2$ (0.8mg, 1.76µmol) and (*S*)- or (*R*)-phenylethylamine (PEA) (28.21µl, 0.22mmol) in dry THF (0.44mL) was added to a dry THF (0.44mL) solution of **1a** (40mg, 88µmol). The reaction solution was stirred at room temperature for 24h. Then the achiral amine **9** (136µl, 0.88mmol) was added to the solution, and continued to stir for 24h. The crude polymer was purified by

reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other pseudo helix-sense-selective polymerisation (**PHSSP**) of the monomers **1a-c**, **2a** and **2b** were carried out similarly (Schemes 1 and S3, routes **A** and **A'**).

Poly(**1a**) 100%: ^{1}H NMR (DMSO-d_6/CCl_4=1/5): δ= 8.11 (br, 1H, PhC*H*=N), 3.50 (br, 2H, NCH_2CH$_2$), 1.60 (br, 2H, NCH$_2$CH_2CH$_2$), 0.84 (br, 9H, Si(CH$_2$CH_3)$_3$), 0.44 (br, 2H, NCH$_2$CH$_2$CH_2Si), 0.44 (br, 6H, Si(CH_2CH$_3$)$_3$) (Fig. S7, c)). IR (cm^{-1}, KBr): 3375 (OH), 1645 (C=N).

Poly(**1a**) 96%: ^{1}H NMR (DMSO-d_6/CCl_4=1/5): δ= 8.11 (br, 1H, PhC*H*=N), 7.54-6.88 (br, 6H, Ph*H*), 5.89 (br, cis proton in the main chain), 4.73 (br, 2H, PhOCH_2Ph), 4.31 (br, 4H, Ph(CH_2OH)$_2$), 3.49 (br, 2H, NCH_2CH$_2$), 1.61 (br, 2H, NCH$_2$CH_2CH$_2$), 1.47 (br, 0.12H, CHCH_3 in poly(PEP)), 0.88 (t, 9H, J=8Hz, Si(CH$_2$CH_3)$_3$), 0.50 (br, 2H, NCH$_2$CH$_2$CH_2Si), 0.46 (q, 6H, J=8Hz, Si(CH_2CH$_3$)$_3$) (Fig. S7, d)). IR (cm^{-1}, KBr): 3336 (OH), 1645 (C=N).

2) Helix-sense-selective polymerisation (**HSSP**) (Schemes 1, S1, and S3, routes **B** and **B'**).

A typical procedure for monomer (**1a**) was as follows: A solution of [Rh(nbd)Cl]$_2$ (0.8mg, 1.76μmol) and (*S*)- or (*R*)-*N*,*N*-dimethylphenylethylamine (DMPEA) (36.3μl, 0.22mmol) in dry THF (0.44mL) was added to a dry THF (0.44mL) solution of **1a** (40mg, 88μmol). The reaction solution was stirred at room temperature for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other helix-sense-selective polymerisation (**HSSP**) of the monomers **1a-c**, **2a** and **2b** were carried out similarly (Schemes 1, S1, and S3, routes **B** and **B'**).

Poly(**1a**) 100%: ^{1}H NMR (DMSO-d_6/CCl_4=1/5): δ= 8.15 (br, 1H, PhC*H*=N), 7.58-6.92 (br, 6H, Ph*H*), 5.91 (br, cis proton in the main chain), 4.75 (br, 2H, PhOCH_2Ph), 4.35 (br, 4H, Ph(CH_2OH)$_2$), 3.53 (br, 2H, NCH_2CH$_2$), 1.65 (br, 2H, NCH$_2$CH_2CH$_2$), 0.88 (br, 9H, Si(CH$_2$CH_3)$_3$), 0.51 (br, 2H, NCH$_2$CH$_2$CH_2Si), 0.51 (br, 6H, Si(CH_2CH$_3$)$_3$) (Fig. S7, b)). IR (cm^{-1}, KBr): 3375 (OH), 1645 (C=N).

3) *In-situ* asymmetric induced polymerisation (***in-situ* AIP**) (Scheme 1, route **C**).

A typical procedure for monomer (**1a**) was as follows: A solution of $[Rh(nbd)Cl]_2$ (0.8mg, 1.76μmol) and (*S*)- or (*R*)-phenylethylamine (PEA) (28.21μl, 0.22mmol) in dry THF (0.44mL) was added to a dry THF (0.44mL) solution of **1a** (40mg, 88μmol). The reaction solution was stirred at room temperature for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other *in-situ* asymmetric induced polymerisation (***in-situ* AIP**) of the monomers **1a-c** were carried out similarly (Scheme 1, route **C**).

4) Asymmetric-induced polymerisation (**AIP**) (Schemes S4 and S5, routes **D** and **D'**).

A typical procedure for monomer (**PE*P**) was as follows: A solution of $[Rh(nbd)Cl]_2$ (1.15mg, 2.5μmol) and triethylamine (TEA) (43.3μl, 0.31mmol) in dry THF (0.625mL) was added to a dry THF (0.625mL) solution of **PE*P** (50mg, 125μmol). The reaction solution was stirred at room temperature for 4h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

The asymmetric-induced polymerisation (**AIP**) of **PP*P** was carried out similarly (Scheme S5, route **D'**).

5) Exchange reaction (**ER**) (Schemes S4 and S5, routes **E** and **E'**).

A typical procedure for monomer (**PE*P**) was as follows: 3-(Triethylsilyl)propylamine (**9**) (0.1mL) was added to a dry THF (1mL) solution of poly(**PE*P**) (22mg) prepared by AIP. The reaction solution was stirred at room temperature for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

The exchange reaction (**ER**) of **PP*P** was carried out similarly (Scheme S5, route **E'**).

(4) Exchange reaction of a chiral amine residue in a monomer with an achiral amine (Scheme S6)

A typical procedure for achiral amine 3-(triethylsilyl)propylamine (**9**) was as follows: Achiral amine **9** (43.3mg, 0.25mmol) was added to a $CDCl_3$ (0.25ml) solution of **PE*P** (10mg, 25μmol). The reaction solution was stirred at room temperature for 24h. The result solution was loaded into a Teflon screw-capped NMR tube. The equilibrium constant was then determined from the ration of the integrated ^1H NMR signals.

Other exchange reactions of a chiral amine residue in a monomer with an achiral amine were carried out similarly (Scheme S6).

(5) Measurements

Average molecular weight (*Mw*) was estimated by gel permeation chromatography (tetrahydrofuran as an eluent, polystyrene calibration) using JASCO Liquid Chromatography instruments with PU 2080, DG 2080 53, CO 2060, UV 2070, CD 2095, and two polystyrene gel columns (Shodex KF 807L). NMR spectra were recorded on a JEOL GSX 270 at 400 MHz for ^{1}H. IR spectra were recorded on a JASCO FTIR 4200 spectrometer. CD spectra were measured with a JASCO J 720 spectropolarimeter.

References

(S1) T. Aoki, T. Kaneko, N. Maruyama, A. Sumi, M. Takahashi, T. Sato and M. Teraguchi, *J. Am. Chem. Soc.*, 2003, **125**, 6346.

(S2) L. Liu, Y. Zang, S. Hadano, T. Aoki, M. Teraguchi, T. Kaneko and T. Namikoshi, *Macromolecules*, 2010, **43**, 9268.

(S3) R. Guilard, M. A. Lopez, A. Tabard, P. Richard, C. Lecomte, S. Brandes, J. E. Hutchison and J. P. Collman, *J. Am. Chem. Soc.*, 1992, **114**, 9877.

(S4) Y. Liu, *Molecules*, 2004, **9**, 725.

(S5) J. J. Hwang and J. M. Tour, *Tetrahedron,* 2002, **58**, 10387.