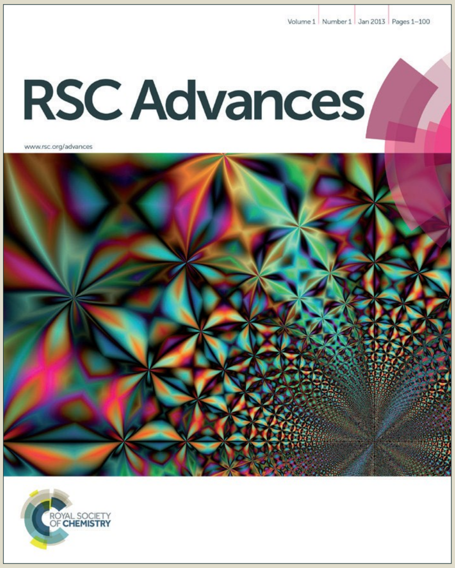
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Catalytic Helix-Sense-Selective Polymerisation of Achiral Substituted Acetylenes Containing Bulky π-Conjugated Planar Substituents Yielding Soluble and Statically Stable One-Handed Helical Polymers

Y. Zang,*[a] X. Wang, [b] W.Zhang,[b] T. Aoki,*[a,c] M. Teraguchi,[c] T. Kaneko,[c] L. Ma[a] and H. Jia[a]

Helix-sense-selective polymerisation of three new achiral substituted acetylenes containing two bulky π-conjugated planar substituents via imino groups by using *catalytic amounts* of chiral source yielded soluble and *statically stable* one-handed helical polymers which was stabilized by intramolecular *steric hindrance*.

π-Conjugated polymers like polyacetylenes have aroused interest because of their noteworthy physical properties such as conductivity, organomagnetism, and optical non-linear susceptibility. Recently chiral polyacetylenes[1] have attracted much attention since the chiral structure can enhance the unique properties and add new functions.

Several kinds of asymmetric polymerisations of achiral monomers to yield chiral polymers having their chiral structures in their main chains have been reported. Among them, a direct synthetic method of *soluble and stable chiral π-conjugated* polymers whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains (therefore, they have no asymmetric carbons) and are *stable alone in solution* was so far only the helix-sense-selective polymerisation (HSSP) of an achiral phenylacetylene monomer by using a chiral catalytic system developed in our laboratory. [2]

In general for all kinds of polymers prepared by addition polymerization, there exist two methods to synthesize soluble chiral polymers whose chiral structures are present *alone* in the main chain as asymmetric carbons and/or as a one-handed helical conformation. One is HSSP [3] of an *achiral* monomer by using a chiral catalyst as a chiral source and the other is asymmetric-induced polymerization (AIP), by using achiral catalysts, of monomers having a chiral group as a chiral source, followed by removing the chiral groups by a polymer reaction(R) *in solution* where the chiral groups were desubstituted from the resulting one-handed helical polymers (AIP-R). [4]

However, the examples of application of the two methods ,*i.e.*,HSSP and AIP-R to *π-conjugated polymers* were very few. [2, 5] In fact there have been only one example of HSSP by our group[2] and only one example of AIP-R *in a solid state* by our group[5] for obtaining *soluble and stable* chiral conjugated polymers. Therefore, so far our HSSP and AIP-R synthesis were the only two methods available to obtain *soluble and stable* chiral conjugated polymers whose chiral structures arise only from the one-handed helical conformation of their conjugated main chains.

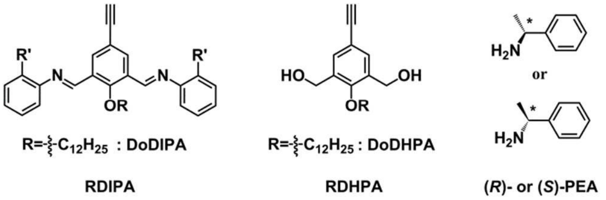
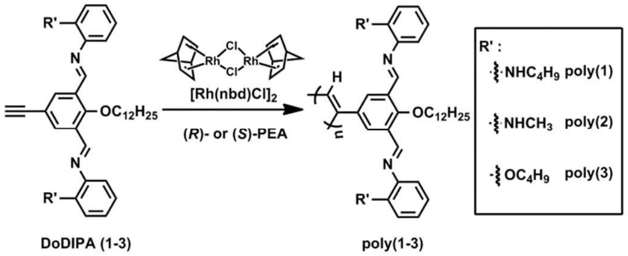


Chart 1. Chemical structures of achiral monomers and a chiral amine.



Scheme 1. Helix-sense-selective polymerisation (HSSP) of achiral monomers (DoDIPA (**1**-**3**)) using (*R*)- or (*S*)-PEA as a chiral cocatalyst in toluene at room temperature.

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[a] College of Materials Science and Engineering, Qiqihar University, Wenhua street 42, Qiqihar,Heilongjiang 161006, China. zangyu.25@163.com

[b] College of chemistry and chemical engineering, Qiqihar University, Wenhua street 42, Qiqihar, Heilongjiang 161006, China.

[c] Faculty of Engineering, Niigata University, Ikarashi 2-8050, Nishi-Ku, Niigata 950-2181, Japan; toshaoki@eng.niigata-u.ac.jp

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Table 1 Helix-sense-selective polymerisation (HSSP) of achiral monomers (DoDIPA (**1**-**3**)) using (*R*)- or (*S*)-PEA as a chiral cocatalyst in toluene at room temperature.

No. [a]	Achiral DoDIPA [b]	Chiral Cocatalyst [b]	[Cocatalyst]/ [DoDIPA]	Yield [c] [%]	M_w [d] [$\times10^6$]	M_w/M_n [d]	g_{297nm} [e] [$\times10^6$]
1	**1**	(*S*)-PEA	2.50	94	3.6	6.7	-2.1
2	**1**	(*R*)-PEA	2.50	89	4.5	2.3	2.4
3	**1**	(*R*)-PEA	1.00	89	3.8	12	2.3
4	**1**	(*R*)-PEA	0.0200	72	1.8	11	1.7
5	**1**	(*R*)-PEA	0.00500	76	2.0	6.6	1.4
6	**1**	(*R*)-PEA	0.00300	67	1.5	6.0	0.58
7	**2**	(*R*)-PEA	2.50	69	0.77	5.8	1.6
8	**2**	(*R*)-PEA	1.00	53	0.26	4.1	0.82
9	**2**	(*R*)-PEA	0.0200	4.2	0.030	2.2	0 [f]
10	**3**	(*R*)-PEA	2.50	83	0.36	4.0	2.2
11	**3**	(*R*)-PEA	1.00	65	0.52	3.0	0.90
12	**3**	(*R*)-PEA	0.0200	56	1.0	5.0	0.060
13 [g]	DoDHPA	(*R*)-PEA	2.50	77	5.1	9.9	1.3 [h]
14 [g]	DoDHPA	(*R*)-PEA	1.25	62	1.2	3.2	0.76 [h]
15 [g]	DoDHPA	(*R*)-PEA	0.250	70	3.4	2.0	0.052 [h]

[a] For 18h, [DoDIPA] = 0.100 mol/L, [DoDIPA]/[[Rh(nbd)Cl]$_2$] = 100. [b] For the codes, see Chart 1 and Scheme 1. [c] Methanol insoluble part. [d] Determined by GPC (polystyrene, THF). [e] $g = ([\vartheta]/3300/\varepsilon)\times0.001$, in THF (0.100 mmol/L). [f] Less than 10^{-8}. [g] For 4h, [DoDHPA] = 0.100 mol/L, [DoDHPA]/[[Rh(nbd)Cl]$_2$] = 200. [h] Calculated from the peak at 310nm.

The HSSP to obtain chiral conjugated polymers is more simple procedure than AIP-R. However, the HSSP suitable monomers were limited and needed two functional groups which could make hydrogen bonds like hydroxy groups to stabilize the one-handed helical conformation(Chart 1, DoDHPA).[2a] And therefore the one-handed helical conformation was not stable to polar solvents and heating because it was maintained by intramolecular hydrogen bonds. In addition, the efficiency of the chiral induction was not high, *i.e.*, a high ratio of the chiral cocatalyst to the achiral monomer (Chart 1, (*R*)- or (*S*)-PEA) was needed.

In this communication, we report the *stability* to polar solvents and heating of the resulting one-handed helicity of poly(DoDIPA) (Chart 1) prepared by the HSSP(Scheme 1) and it was kept by intramolecular *steric interaction*. In addition, we report high efficiency of chiral induction of the HSSP of achiral DoDIPA. In other words, it needed only *catalytic amounts* of the chiral source. Because the HSSP of RDHPA(Chart 1) needed a large amount of the chiral source, it is a valuable development. This new HSSP having excellent performance has been achieved by using novel and more general monomers having no groups making hydrogen bonds such as hydroxyl groups[2a,b] and amide groups[2c] but having two *bulky planar conjugated* groups via planar imino groups (Chart 1, DoDIPA). Finally the reason for the suitability of DoDIPA for the HSSP is discussed.

As described above, the chemical structures of achiral monomers suitable for the HSSP were limited. They were limited to DoDHPA and its related structures (RDHPA; Chart 1) we reported previously.[2b] Therefore, to develop new monomers having more general structures for the HSSP than RDHPA (Chart 1), we designed and synthesized new types of three achiral substituted phenylacetylene monomers (DoDIPA: **1**-**3** in Scheme 1) which contained two *bulky π-conjugated planar* substituents via planar imine bonds and an alkyl group. The monomers were polymerised by using the chiral catalytic system, [Rh(nbd)Cl]$_2$ and chiral phenylethylamine ((*R*)- or (*S*)-PEA) that we previously developed for the HSSP of DoDHPA [2a] as shown in Table 1. A typical polymerisation procedure for **1** was as follows: A solution of [Rh(nbd)Cl]$_2$ (0.220 mg, 0.470 μmol) and (*S*)-phenylethylamine (PEA) (15.0 μL, 0.120 mmol) in dry toluene (0.240 mL) was added to a dry toluene (0.240 mL) solution of **1** (30.0 mg, 47.0 μmol). The reaction solution was stirred at room temperature for 18 h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the formed solid was dried in vacuo to give an orange solid. Poly(**1**): Yield: 94.0% (28.2 mg). M_w = 3.6 $\times10^6$. M_w / M_n = 6.7 (Table 1, No. 1). ^{1}H NMR (400MHz, CDCl$_3$, TMS, δ): 1.27 (br, $\Delta W_{1/2}$ (half width) = 0.13 ppm, 18H, CH$_2$(C*H*$_2$)$_9$CH$_3$), 0.89 (br, $\Delta W_{1/2}$ (half width) = 0.067 ppm, 3H, O(CH$_2$)$_{11}$C*H*$_3$), the other peaks were not detected because they

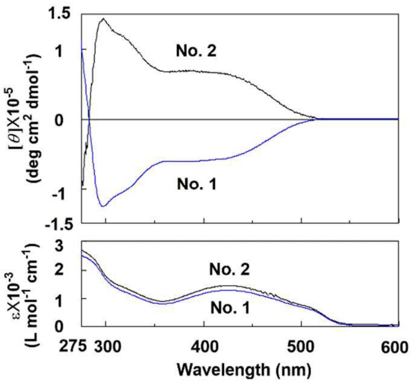

Fig. 1 CD and UV-vis spectra of poly(**1**) (Nos. 1 and 2 in Table 1) in THF.

were very broad; IR (KBr): 2924 (CH), 1593 (C=N), 1445 cm^{-1} (N-C); UV–vis ($CHCl_3$): λ_{max} (ε) = 425 nm (1300). The other polymerisations of the monomers **2** and **3** were also carried out similarly. The results are summarized in Table 1.

The resulting polymers of achiral **1**-**3** having ca. 10^6 of M_W were chiral because they had CD absorption bands although the starting monomers were *achiral* (Fig. 1 and Fig. S1). Since the CD bands were observed at the wavelength assigned to the main chain, the polymers had chirality in the main chain, that is, one handed helical backbone. In addition, the sense of the helicity was controlled by the sign of the chiral amine ((*R*)- or (*S*)-PEA) as shown in Nos.1 and 2 in Fig. 1 and Table 1, and Fig. S1. Therefore, the HSSPs of DoDIPA (**1**-**3**) without any hydroxy groups have been successfully achieved for the first time.

To estimate the stability of one-handed helical conformation of poly(DoDIPA) prepared by the HSSP to polar solvents, a polar solvent, dimethyl sulfoxide (DMSO) was added to the chloroform solution of poly(**1**) (Fig. 2 (a)). The CD spectra showed almost no change (Fig. 2 (b) and (c)). This means the one-handed helical conformation of poly(**1**) was very *stable* and much more stable than that of poly(DoDHPA) whose one handed helicity was kept by intramolecular hydrogen bonds and disappeared completely by adding DMSO to the chloroform solution showing CD peaks.[2] The other two poly(DoDIPA), poly(**2**) and poly(**3**) were also very stable to polar solvents because the CD peaks showed no changes by adding DMSO (Fig. S2). In addition, no change happened in the CD of poly(DoDIPA) by heating at 50℃ (Fig. S3) where the CD peaks of poly(DoDHPA) decreased. In summary, poly(DoDIPA) had an intrinsically stable helical backbone which was completely different from that of poly(DoDHPA). This is the first *stable and static* chiral conformation obtained by HSSP of *achiral* acetylenes.

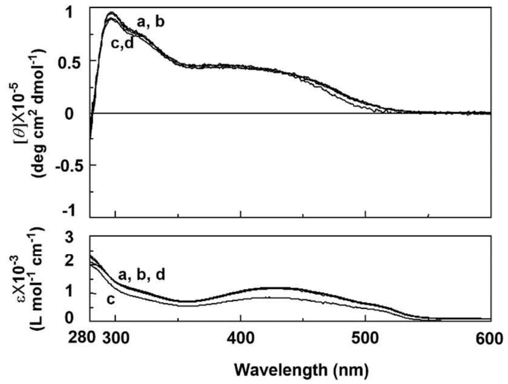

Fig. 2 CD and UV-vis spectra of poly(**1**) in (a) $CHCl_3$; (b) $CHCl_3$ / DMSO = 95 / 5 (v / v); (c) $CHCl_3$ / DMSO = 90 / 10 (v / v); (d) $CHCl_3$ / DMSO = 95 / 5 (v / v) ((d) was the solution prepared by addition of $CHCl_3$ to the solution of (c))[6].

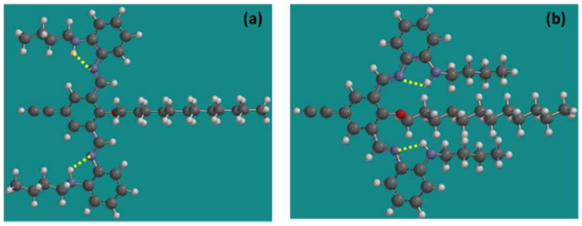

Fig. 3 MMFF-optimized conformation of monomer (**1**) (a) suitable conformation (trans-transoid) to HSSP and (b) unsuitable conformation (cis-transoid) to HSSP (---- : hydrogen bonds). (See Chart S1)

Since the one-handed helicities of the three poly(DoDIPA), poly(**1**) - poly(**3**) were not affected by changing the polarity of the solvents, the helicity was thought to be maintained not by intramolecular hydrogen bonds but by *steric interactions*. This was *directly* proved by the fact that monomer **3** having no functional groups which could make hydrogen bonds was also suitable to the HSSP to give a one-handed helical polymer (Fig. S1(II)), and the one-handed helical main-chain of poly(**3**) was also stable to polar solvents (Fig. S2(II)). Therefore, we successfully found a new type of monomers having no groups making hydrogen bonds which were suitable to the HSSP. Since this type of monomers does not need to have groups making intramolecular hydrogen bonds in the polymers, the monomers RDIPAs are more general and more valuable than RDHPAs.

We previously reported that one-handed helical poly(DoDHPA) prepared by HSSP had *a tight and statistic* helical main chain and this macromolecule was very rigid and its motion was heavily restricted in non-polar solvent.[2a,b, and d] As one of the evidences, the NMR peaks of the macromolecule were very broad compared with those for many other poly(substituted acetylenes) whose peaks are unusually sharp. Therefore, the stability of the one-handed helical conformation was thought to be based on the unusual rigidity of the main chain which was partly estimated by NMR. Judging from the half width of the NMR peaks(see the exp part), the backbone of poly(DoDIPA) in *polar and nonpolar* solvents was thought to be very rigid similarly to that of poly(DoDHPA) in nonpolar solvent. The one-handed helicity of poly(DoDIPA) was not affected by polar solvents and heating and therefore *statically stable*(For details, see ESI-2.1 and 2.2).

Since we reported the HSSP of DoDHPA needed *a large amount* of the chiral source,[2a,b] the efficiency should be improved. The efficiency of the chiral induction during the HSSP of the new monomers (DoDIPA) was much higher than that of the previous monomers having two hydroxy groups (DoDHPA), *i.e.*, the minimum amounts of the chiral source which was needed to obtain CD active polymers by the HSSP of DoDIPA were much lower than those of DoDHPA, as shown in Table 1. For example, to obtain chiral polymers having more than g = 1.0, achiral monomer **1** needed only more than [chiral cocatalyst] / [achiral monomer] = 0.00500 (No.5), while DoDHPA needed [chiral cocatalyst] / [achiral monomer] = 2.50 (No.13). In the case of DoDHPA, to obtain CD-active polymers (g > 0.05), more than 0.250 of [chiral cocatalyst] / [achiral monomer] was necessary (No.15), while monomers **1** and **3** needed only 0.00300 and 0.0200 of [chiral cocatalyst] / [achiral monomer], respectively (Nos. 6 and 12). Therefore, the achiral monomers (**1**-**3**) needed only *catalytic amounts* of chiral source during the HSSP (As described above the HSSP of DoDHPA needed a *large amount* of the chiral source). Since they had higher efficiency in chiral induction during the HSSP, we concluded that they were more suitable to the HSSP than DoDHPA. Since they did not need functional groups which could make hydrogen bonds such as hydroxy groups in DoDHPA, the finding enlarged the range of design of monomers having possibility to be suitable for the HSSP. Therefore, RDIPA is more general and valuable than RDHPA as a HSSP monomer.

In summary, we found new types of monomers which were more suitable, more general, and more valuable to the HSSP because the simple monomers produced *intrinsically stable* one-handed helical polymers using *a catalytic amount* of chiral source. This finding made the HSSP method more valuable and more useful in the field of asymmetric polymerisation of acetylenes.

All the three RDIPA monomers (**1**-**3**) we *newly synthesized* in this study were found to be suitable to the HSSP as described above. When we compared them in the same condition (the same ratio of the chiral cocatalyst to the achiral monomer = 1.00) (Table 1, Nos. 3, 8, and 11), monomer **1** gave a polymer having the highest *g* value (Table 1, No. 3). In addition, the smallest ratio of the chiral cocatalyst to the achiral monomer (= 0.00300) was sufficient for **1** to give the resulting polymer showing clear CD signals (Table 1, No. 6). Therefore, **1** was the best monomer which had the highest efficiency of chiral induction among the three *new* monomers.

To stabilize one handed helical conformation of the resulting polymers of the HSSP of RDIPA, the trans-transoid conformer of the monomer (Fig. 3a)) may keep the helicity more easily than the other conformers like cis-transoid conformer (Fig. 3b)). From the stability of the trans-transoid conformer of **1** calculated by MMFF, the reason for the suitability of RDIPA and monomer **1** to the HSSP could be explained (For the detailed discussion, see the ESI-3.2).

In conclusion, we synthesized and polymerised new types of three *achiral* substituted acetylene monomers (RDIPA), which were suitable to the helix-sense-selective polymerisation (HSSP) by using *catalytic amounts of chiral source*. The new *achiral* monomers contained two *bulky π-conjugated planar* substituents via planar imine bonds and an alkyloxy group. The resulting polymers had a *very stable and static* one-handed helical main chain stabilized by intramolecular *steric hindrance*. The chiral main chains were *very stable to polar solvents and heating* and the minimum amounts of the chiral source needed to obtain CD active polymers were much smaller than those of the previous monomers having two hydroxyl groups. Therefore we found new valuable monomers (RDIPA) which were more suitable and more general to the HSSP. Among RDIPAs (**1**-**3**), **1** was the best monomer because it had the highest efficiency of the chiral induction.

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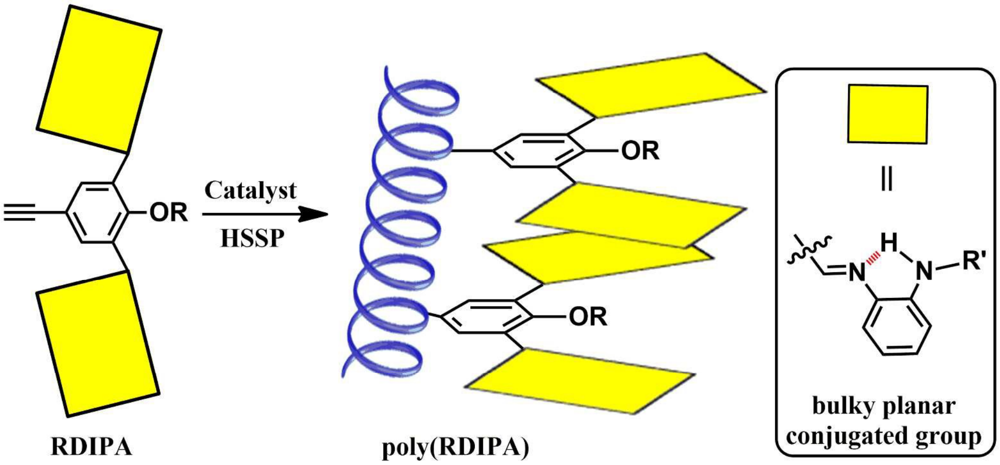
6 It was comparison with that in poly(DoDHPA). When the same procedure was carried out to poly(DoDHPA) prepared by the HSSP, the UV was returned to the original one but CD was not recovered because the hydrogen bonds were recovered as reported previously (ref.2(a)). Therefore, in the case of poly(1), the results support no effective hydrogen bonds to maintain one-handed helicity were present.



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