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Synthesis and Stereochemistry of Helical Polyurethanes Based on 2,2'-Dihydroxy-1,1'-binaphthyl and Diisocyanatobenzenes

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Abstract:

Polyaddition between 2,2'-dihydroxy-1,1'-binaphthyl (BINOL) and 1,4-diisocyanatobenzene (14DIB) and that between BINOL and 1,3-diisocyanatobenzene (13DIB) were conducted to lead to optically active, helical polyurethanes, poly(BINOL-*alt*-14DIB) and poly(BINOL-*alt*-13DIB), respectively. In the BINOL-14DIB systems, cyclic dimers were formed along with helical, linear poly(BINOL-*alt*-14DIB) where the content of dimers was higher at a lower e.e. of BINOL and the yield of higher-molar-mass, linear polymers was higher at a higher e.e. of BINOL in feed. (R,R)-, (R,S)-, and (S,S)-Cyclic dimers were completely resolved and separated by chiral HPLC. (R,S)-Cyclic dimer was preferred over (R,R)- and (S,S)-cyclic dimers In the reaction using racemic BINOL while (R,R)-cyclic dimer was preferred over the other isomers at 25-75% e.e. of (R)-BINOL in feed. Poly(BINOL-*alt*-14DIB) is proposed to compose of sequences with rather contiguous (R)-BINOL units as the majority component with rather sporadically incorporated (S)-units as the minor component. Helical sense excess appears to be greater than expected from the e.e. of BINOL units in the chain, suggesting that (S)-BINOL units sporadically incorporated in a rather contiguous (R)-BINOL units sequence become a part of left-handed helical conformation controlled by the chiral influence of contiguous (R)-BINOL units. In addition, chiral conformation of poly(BINOL-*alt*-14DIB) and BINOL-14DIB cyclic dimer appeared to be stabilized or enhanced in the solid state. The BINOL-13DIB systems produced linear dimers as major components of dimer whose content was almost constant regardless of e.e. of BINOL in feed. Poly(BINOL-*alt*-13DIB) is proposed to compose of sequences with rather randomly distributed (R)- and (S)-BINOL units and may be characterized by sharp, left-handed turns based on BINOL chirality forming a longer-pitched, left-handed helix.

Introduction

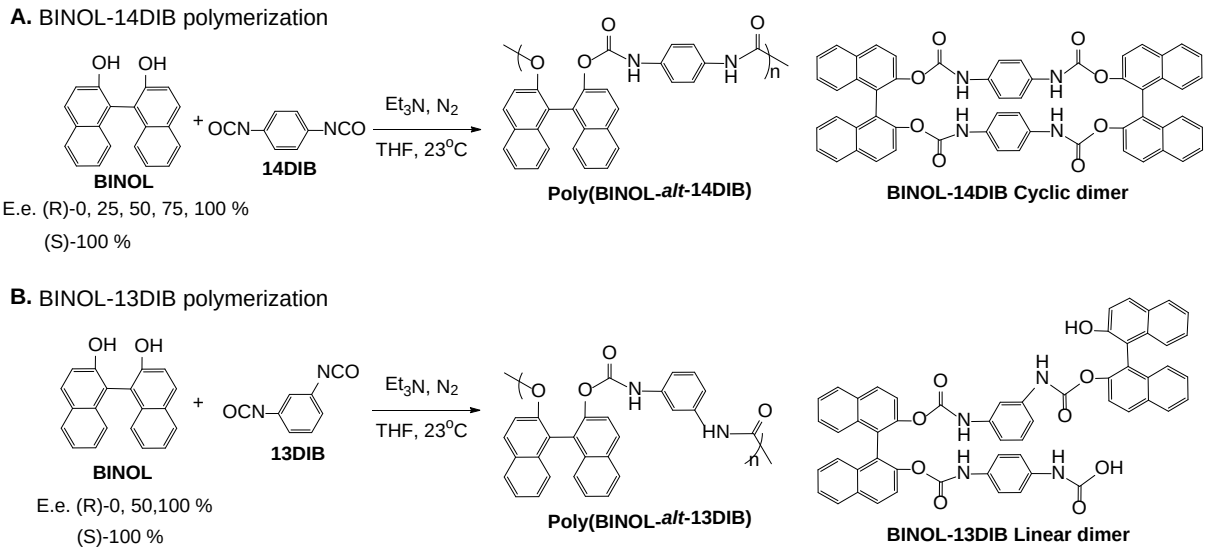
Chiral polymers are an important class of materials that find a wide variety of applications based on their chiral structures and properties.[1-10] Among various methods of chiral polymer synthesis, the most straightforward way is the polymerization of an optically active monomer where the chirality of the monomer is maintained in the resulting polymer structure and the polymer is therefore optically active. In such a polymerization, additional chiral conformation that is not present in the monomer structure may be induced through the polymerization. If a preferred-handed helical conformation is induced through the polymerization of an optically active monomer, the polymerization is not just a reaction connecting chiral units into a chain but is a helix-sense-selective polymerization (asymmetric helix-chirogenic polymerization).

As a novel example of helix induction through polymerization of optically active monomer, we recently introduced asymmetric polyaddition (copolymerization) of optically pure (*R*)-2,2'-dihydroxy-1,1'-binaphthyl ((*R*)-1,1'-bi(2-naphthol), BINOL) with 1,4-diisocyanatobenzene (14DIB) leading to a polyurethane.[11] The resulting polymer was proposed to adopt a left-handed 2/1-helical conformation which is based on the axial chirality of the BINOL units composing the chain (**Fig. S7 C** in ESI). Though polyurethanes are widely used in various polymeric materials,[12-15] the focus of polyurethane development is generally on novel chemical structures leading to new properties, and stereochemical studies of polyurethanes are very rare.[16,17] In addition, an importance aspect involved in the finding of the helical polyurethane lies in the fact that this polymer had a helical conformation with a 2/1-pitch; such a helix is known for only limited polymers including this polyurethane, syndiotactic polystyrene, poly(*p*-methylstyrene), syndiotactic polyprolylene, and syndiotactic polybutane in the solid state.[18-26] The helical conformation of poly(BINOL-*alt*-14DIB) is also characterized by a π-stacked conformation in which the aromatic groups comprising the main chain; this feature may open a way to use polymers for photo electronic applications.[27-30] WAXD profile of poly(BINOL-*alt*-14DIB) shows a diffraction peak at 2θ of 20.0 deg which supports that it has a π-stacked,

2/1-helical conformation with a stacking distance of 4.44 Å (**Fig. S18** in ESI). Further, the polymer does not show any clear melting point in differential scanning calorimetry (DSC) analysis which may mean that the 2/1-helical chains are not crystallized or packed in the solid state possibly due to the variation of chain lengths and supports that the diffraction peak is ascribed to intra-molecular π-stacking (**Figs. S16** and **S17** in ESI).

Binaphthyl is an often-used chiral backbone which is effective in inducing a specific structure to polymer chain.[31-33] Although BINOL and its derivatives are known to racemized in excited states,[34,35] their chirality is robust and stable in the ground state; they are convenient building blocks of chiral polymeric structures.

In this work, polyurethanes were synthesized using 14DIB and BINOL having various enantiomeric excesses (e.e.'s), and the effects of chirality of BINOL on polymerization stereochemistry were investigated in detail (Scheme 1 A). Cyclic dimer was formed as well as linear polymer at all e.e.'s of BINOL, and the ratio of the cyclic dimer changed sensitively depending on e.e. of BINOL and was highest when racemic BINOL was used. The polymer chains were suggested to comprise of sequences with rather contiguous (*R*)-BINOL units rather than sequences with rather randomly distributed enantiomeric BINOL units. In addition, polyurethane was prepared also by polyaddition of BINOL at various e.e.'s with 1,3-diisocynanatobenzene (13DIB) (Scheme 1 B); poly(BINOL-*alt*-13DIB) was suggested to possess a helical conformation which is distinguished from that of poly(BINOL-*alt*-14DIB) in the shape and in chiroptical properties. In the systems with 13DIB, the production of cyclic dimer was not confirmed, while linear dimer was identified as major oligomeric species.



Scheme 1. Syntheses of polyurethanes and dimers from BINOL and 14DIB (A) and from BINOL and 13DIB (B).

Results and Discussions

Synthesis, structure and properties of poly(BINOL-*alt*-14DIB)

The polymerization of 14DIB with (*R*)-BINOL at 0, 25, 50, 75, and 100 % e.e. or (S)-BINOL of 100% e.e. was conducted in tetrahydrofuran (THF) containing 5 % of Et_3N as a reaction promoter at [BINOL] = [14DIB] = 0.154 M at 23°C. At all e.e.'s BINOL was consumed at high conversion ratios. **Fig. 1** shows the size-exclusion chromatography (SEC) profiles of the reaction products obtained using (R)-BINOL monomers at different e.e.'s. All products contained significant amounts of cyclic dimer, and the dimer content was found to be higher at a lower e.e. of BINOL as estimated by wave-form analysis of the chromatograms (**Fig. S8** in ESI). The SEC curves also indicate that higher molar-mass products are formed in a higher yield at a higher e.e. of BINOL in feed.

These results imply the following characteristics about monomeric sequences of polymer: (1) a random sequence of (R)- and (S)-BINOL units involving (R)-(S) junction does not grow to a longer chain, and (2) a longer chain tends to be composed of contiguous (R)-BINOL units. The former character is consistent with the fact that only a low-molar-mass polymer was produced

in a low yield at 0% e.e. of BINOL in feed, and the latter character accounts for the fact that a higher-molar-mass polymer was produced in a higher yield at a higher e.e. of BINOL in feed. An actual polymer chain produced in the systems with (R)-BINOL in excess in feed would have a sequence structure composed of rather contiguous (R)-BINOL units as the majority component with sporadically incorporated, rather isolated (S)-BINOL units as the minority component. Production of chains consisting only of (R)-BINOL units and one consisting only of (S)-BINOL units at the same time may not be plausible even when racemic BINOL was used ("racemate-forming enantiomer-differentiating polymerization").

In connection with the sequence structure (distribution of enantiomeric BINOL units), three polymer models having different monomeric sequences were simulated by molecular dynamics and mechanics (MD and MM) calculations; the models are 20-mers composed of an alternating sequence of (R)- and (S)-BINOL units, composed of a random sequence of (R)- and (S)-BINOL units, and composed only of (R)-BINOL units having the proposed 2/1-helical conformation[11] (**Fig. S7** in ESI). The alternating and random chains have significantly different conformations from the 2/1-helix. In addition, the alternating and random chains had higher total steric energies (2826 kcal mol^{-1} and 2709 kcal mol^{-1}, respectively) than the proposed 2/1-helical structure (2474 kcal mol-1). These results support the conclusion based on the SEC curves that sequences composed of rather contiguous (R)-BINOL units would be preferred over random sequences.

When racemic BINOL was used, more than 80% of the products was the cyclic dimer. This observation may suggest that cyclic dimer tend to be composed of (R)- and (S)-BINOL molecules ((R,S)-dimer) rather than those composed of two (R)-BINOL molecules and two (S)-BINOL molecules ((R,R)-dimer and (S,S)-dimer). This aspect was assessed by HPLC separation of the three cyclic dimers (**Fig. 2**).

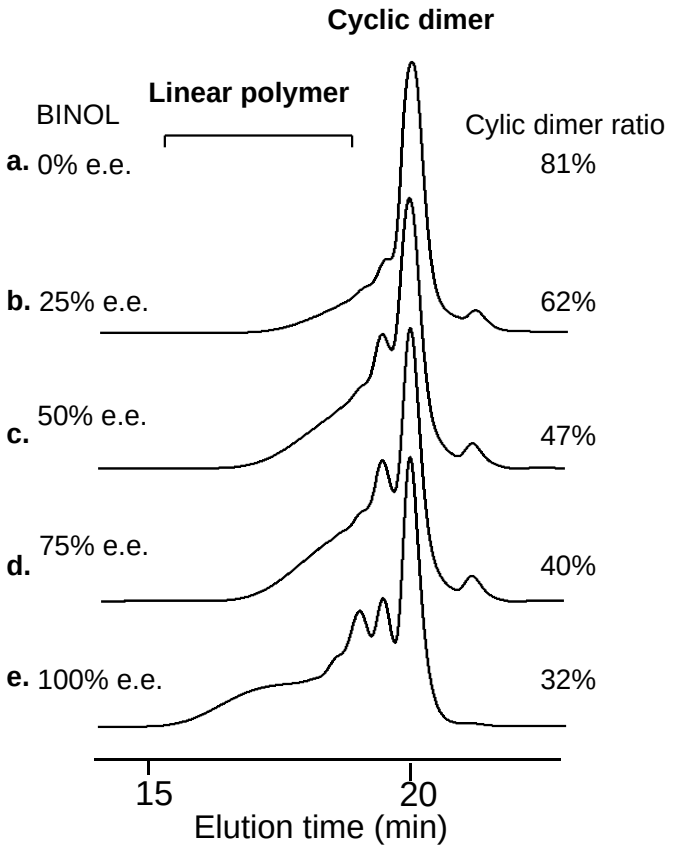


Fig. 1. SEC profiles of polymerization products obtained from 14DIB and (R)-BINOL at 0% e.e. (a), 25% e.e. (b), 50% e.e. (c), 75% e.e. (d), and 100% e.e. (e) with cyclic dimer contents estimated by wave-from analysis (Fig. S8 in ESI) [detection by UV at 254 nm]

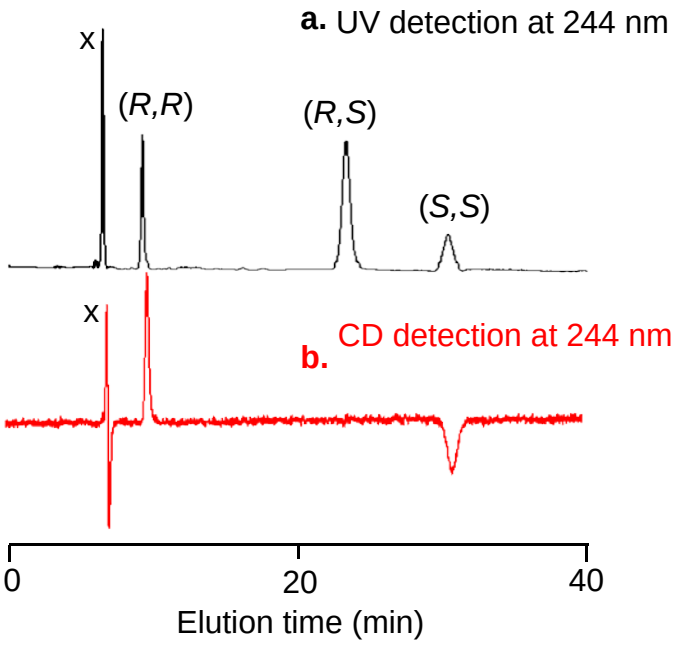


Fig. 2. HPLC separation/resolution of cyclic dimer obtained from racemic BINOL and 14DIB.

x denotes solvent signals at void volume. [column = Chiralpak IA, eluent = CH_2Cl_2-hexane (95/1), flow rate 0.5 mL/min]

As shown in **Fig. 2**, clear, base-line separation/resolution by chiral HPLC was attained for the cyclic dimer under the chromatographic conditions noted in the figure legend. Among the three signals, the one at 23.3 min was assigned to (R,S)-cyclic dimer since this species did not show any CD detector responses. The absolute configurations of (R,R)- and (S,S)-cyclic dimers were assigned using the (R,R)-cyclic dimer sample available from our recent work.[11] The accurate ratios of the three cyclic dimer species were determined by the HPLC analyses; the ratios are plotted against e.e. of BINOL in feed along with the theoretical (statistical) ratios of the three isomers calculated according to the ratios of (R)-BINOL to (S)-BINOL in feed (**Fig. 3**).

There is clear deviation of the observed ratios from the theoretical ratios; at 25%, 50%, and 75% e.e. of BINOL in feed, the ratio of (R,R)-isomer tends to be greater and that of (S,S)-isomer smaller than the corresponding theoretical values, suggesting that (R)-BINOL is incorporated into cyclic dimer more preferentially than expected from its concentration bias. Such preference could occur through autocatalysis[36,37] where (R,R)-isomer formed in the earlier stage of reaction might enhance the formation of the same species in the latter stages while the extent of preference is moderate and the mechanism elucidation needs further studies.

On the other hand, in the reaction using racemic BINOL where there is no concentration bias on either enantiomer of BINOL, the ratio of (R,S)-cyclic dimer (60 %) is clearly higher than the corresponding theoretical value (50%). Under this condition, (R,S)-cyclic dimer was selected over (R,R)- and (S,S)-cyclic dimers in the reaction. This observation is in line with the conclusion about the monomeric sequence that a random sequence involving (R)-(S) junction does to grow to a high polymer; such the combination of (R)- and (S)-BINOL units tend to form a cyclic dimer.

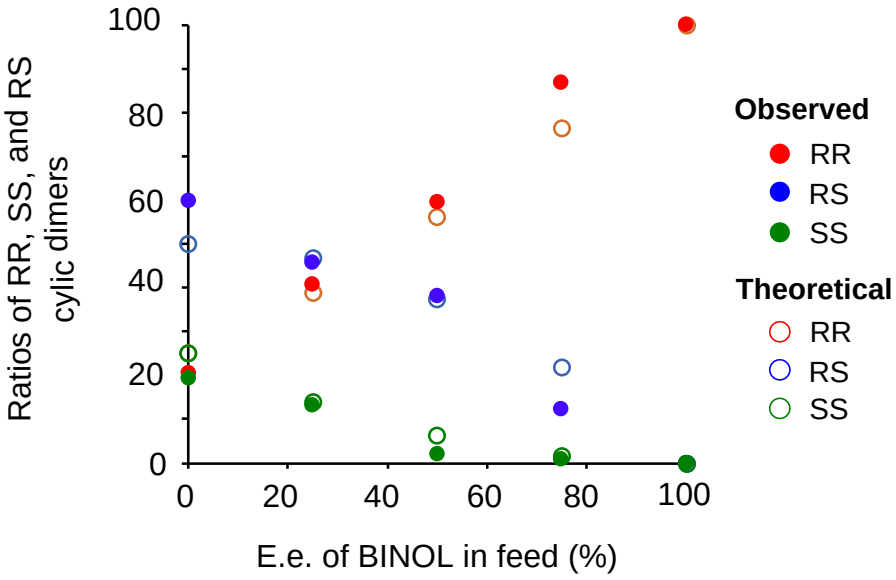


Fig. 3. Ratios of (R,R)-, (R,S)-, and (S,S)-cyclic dimers of BINOL and 14DIB plotted against e.e. of BINOL in feed: observed values [filled circles] and theoretical (statistical) values calculated based on e.e. of BINOL in feed [open circles].

With this result, a question may be whether or not (R,S)-cyclic dimer is substantially more stable over (R,R)- and (S,S)-cyclic dimers. In order to obtain information on this aspect as well as on the fact that cyclic dimers, not "linear dimers", are obtained, molecular dynamics and mechanics (MD and MM) calculations were conducted on cyclic dimers as well as "linear dimers" having a structure similar to the BINOL-13DIB linear dimer in **Scheme 1 B** is discussed later (**Fig. S5** in ESI). The total steric energies for (R,R)-cyclic dimer, (R,S)-cyclic dimer, (R,R)-linear dimer, and (R,S)-linear dimer were 409.5 kcal mol^{-1}, 390.69 $kcalmol^{-1}$, 288.56 $kcalmol^{-1}$, and 278.47 $kcalmol^{-1}$, respectively (COMPASS force field). (R,S)-cyclic dimer is indeed more stable than (R,R)-cyclic dimer, which may account for the preference of (R,S)-cyclic dimer over (R,R)-cyclic dimer in the racemic BINOL system. However, it is intriguing that the linear dimers are much more stable than the cyclic dimers in spite of the experimental fact that the cyclic dimers, not the linear dimers, are exclusively formed as dimers.

Static energies of the dimes species hence cannot explain the formation cyclic dimers; they may be preferentially formed through kinetic control.

The structure of (R,S)-dimer was unambiguously clarified by single crystal X-ray analysis where the presence of both (R)- and (S)-BNOL units connected to the central benzene rings through urethane bonds is clear (**Fig. 4**). The crystal was obtained by recrystallization from a mixture of $CHCl_3$, tetrahydrofuran, ethyl acetate and hexane; a $CHCl_3$ and a THF molecules are co-crystallized with the dimer. In the crystal, the two benzene rings are almost completely co-facially and closely π-stacked with a spacing distance of ca. 3.8 Å. This structure is in a sharp contrast to that of the (R,R)-cyclic dimer already reported where the two benzene rings are arranged in a perpendicularly twisted manner.

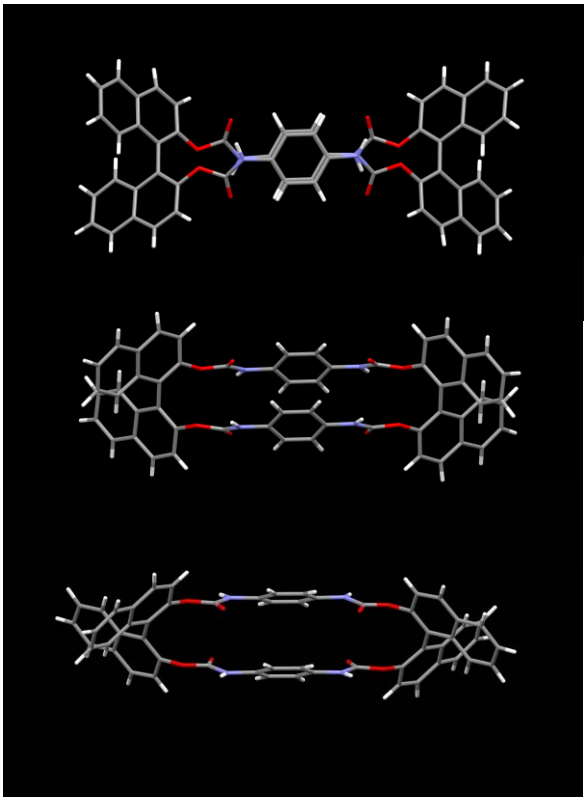


Fig. 4. Crystal structure of (R,S)-cyclic dimer obtained from rac-BINOL and 14DIB viewed from three different angles.

On the basis of the ratios of the three cyclic dimers and the contents of the cyclic dimers at

different e.e. of BINOL, e.e.'s of BINOL units in polymers (all species excepting for the cyclic dimer in this context) as well as those of cyclic dimers were estimated and plotted against e.e. of BINOL in feed (**Fig. 5**). E.e.'s of BINOL units in cyclic dimer were slightly higher and those in polymer were slightly lower than the diagonal theoretical line connecting the data points at e.e. of BINOL in feed = 0% and 100%. These results may mean that (i) the cyclic dimers were formed prior to the linear polymers, (ii) (R)-BINOL was preferentially than incorporated into cyclic dimers where the extent of preference was more than expected from the concentration bias between the enantiomers, and (iii) the polymer was formed from the remaining BINOL having a lower e.e. that that in feed. In the BINOL-14DIB systems, chiral non-linear effects were thus observed in the selection of BINOL enantiomers. Chiral non-linear effects have been reported for various polymer systems including polyisocyanates as representing examples of dynamic systems.[38]

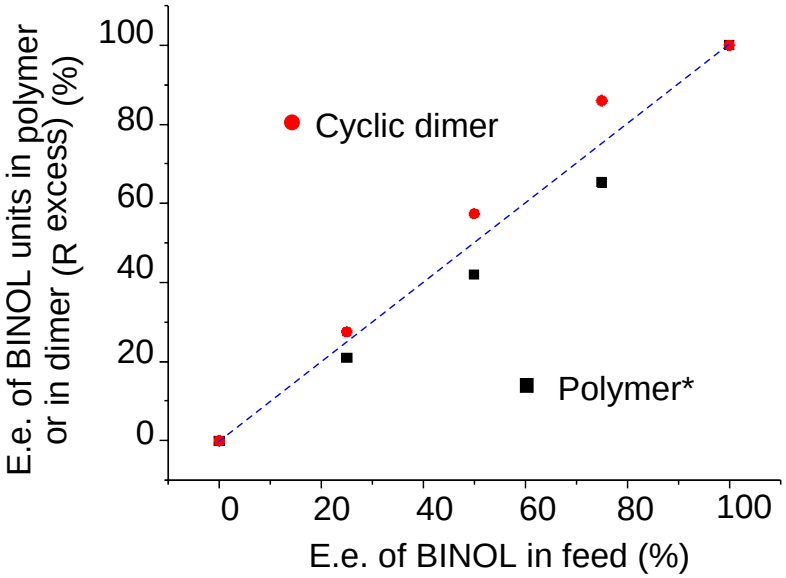


Fig. 5. E.e. of BINOL units in polymer and in cyclic dimer (R excess) plotted against e.e. of BINOL in feed. E.e. of units in polymer was calculated on the basis of e.e. in cyclic dimer and dimer content. *"Polymer" means all species excepting for the cyclic dimer.

In order obtain information on chiroptical properties of the polymers and dimers, CD and UV spectra of the samples prepared using (R)-BINOL at different e.e.'s and (S)-BINOL at 100% e.e were measured in a THF solution and in a cast film (**Fig. 6**). The polymer samples were obtained by purification by preparative SEC, and had e.e.'s of BINOL units and following molar masses (vs. polystyrene): **a.** (S)-100% e.e., M_n 2960; **b.** (R)-21% e.e., M_n 2920 (25% e.e of (R)-BINOL in feed), **c.** (R)-42% e.e., M_n 2740 (50% e.e of (R)-BINOL in feed); **d.** (R)-65% e.e., M_n 2890 (75% e.e of (R)-BINOL in feed); **e.** (R)-100% e.e., M_n 3520. In a THF solution (**Fig. 6 A and B**), the polymers and dimers indicated intense Cotton splitting centered at 225 nm which is considered to be contributed mainly by the BINOL units; the (S)-BINOL-based polymer and cyclic dimer exhibited positive splitting and the (R)-BINOL-based polymers and cyclic dimers negative splitting, which accounts for the absolute chirality of BINOL units. On the other hand, the CD bands in the range of about 250-350 nm which may be contributed mainly by the -CO-NH-C_6H_4-NH-CO chromophore are considered to reflect helical chirality of the polymers and conformation of the cyclic dimers. This conclusion is supported by the fact that CD spectrum of BINOL in this range has a spectral pattern completely different from those of the polymers and dimers (**Fig. S4** in ESI).

The CD spectra of the cyclic dimers have more intense and clearer splitting bands in the range of 250-350 nm compared with the polymers which may reflect a twisted relative arrangement of the two CO-NH-C_6H_4-NH-CO chromophores connecting BINOL units leading to intra-chromophore exciton coupling effects. The distance the two CO-NH-C_6H_4-NH-CO chromophores is considered short enough to exert exciton coupling interactions.

In order to obtain further information from the CD spectra, the plots were made between relative CD intensity of the polymers and cyclic dimers obtained at different e.e.'s of BINOL in feed against e.e. of BINOL units in these species (**Fig. 7**). As for the polymers (**Fig. 7 A**), the relative CD intensity corresponding to BINOL units e.e. of 65, 42, and 21 % corresponding to

the e.e. of 75%, 50%, and 25% of BINOL in feed were greater than expected from the linear, theoretical line connecting the data at 100% e.e. and 0% e.e., at all examined wavelengths (220, 231, 251, and 295 nm). Non-linearity was especially remarkable for the CD band at 295 nm which mainly reflects helical chirality of the chain while it was moderate at the other wavelengths. The relative CD intensity at 295 nm seems to approach to the 100%-e.e. value even at a low e.e. of BINOL units while the deviation at the other three wavelengths are moderate. These results suggest that helical sense excess of the polymers is not proportional to e.e. of BINOL units, and a high helical sense excess is achieved even at a low e.e., implying that a sequence consisting of (S)-BINOL units as minority is forced to assume left-handed helicity due to chirality effects of a sequence consisting of contiguous (R)-BINOL units as majority through polymerization.

In a sharp contrast, the relative CD intensity for the cyclic dimers were only moderately lower than the values expected from the linear, theoretical line at all examined wavelengths (228, 244, 265, and 291 nm) and showed only slight non-linearity (**Fig. 7 B**). The moderate deviation from the theoretical could be attributed to intermolecular interactions among the three isomeric cyclic dimers though details of this aspect are not yet clear.

Fig. 8 shows the ^{1}H NMR spectra of poly(BINOL-*alt*-14DIB) having different e.e.'s of BINOL units. All polymers exhibit rather broad signals which are consistent with the presence of rigid helical conformation. The up-field shifted aromatic signals in the range of 6-7 ppm may be base on π-stacking of benzene-1,4-diyl moieties. Also, it can be confirmed that the relative intensities of the signals at around 7.8 ppm, 7.3, and 6.6 ppm those in the range of 5.6-6.2 ppm marked by downward arrows tended to decrease and the relative intensity of the signals at around 7.3 ppm marked by an upward arrow tended to increase with an increase in e.e. of BINOL units. These observations may be ascribed to the change in the ratio of (R)-BINOL units to (S)-BINOL units which are considered to be diastereomeric to each other in a left-handed helix. This is consistent with the aforementioned conclusion that the polymers have

left-handed helical sense excess which is much higher than expected from e.e. of BINOL units due to non-linear chirality effects.

The polymers and cyclic dimers exhibited clearer CD spectra also in a cast film made from $CHCl_3$ solution than in solution (**Fig. 6 C and D**). The intensity of CD bands in the range of about 250-350 nm relative to those in the range of 200-250 nm was much higher in film than in solution, suggesting that chiral conformations of the polymers and cyclic dimers are stabilized and enhanced in the solid state. In order to take advantage of the chirality-enhanced helical structure of the linear polymers, circular polarized light (CPL) emission measurements were attempted. Although the polymers exhibited an emission band centered at around 370 nm on phot excitation at 270 nm both in solution and film (**Figs. S12 and S13** in ESI), they did not show any detectable CPL. Chirality of the polymers in excited states may not be significant even in the solid state.

Additional experiments were conducted to obtain information on the effects of molar mass and reaction time on UV and CD spectra of poly(BINOL-*alt*-14-DIB). As for the molar mass effects, three samples having M_n's of 2580, 1940, and 1540 were separated from the polymerization product obtained at 50% e.e. of BINOL in feed by preparative SEC showed very similar CD spectra and slightly different UV spectra (**Fig. S13** in ESI). These results may mean that the three samples have slightly different ratios of (R)- and (S)-BINOL units and imply that the enantiomeric BINOL monomers have different reactivities not only at the stage of cyclic dimer formation but also at the stage of polymer formation. As for the reaction time effects, samples obtained in 10 min and 24 h of polymerization at 50% e.e. of BINOL in feed showed very similar CD spectra and slightly different UV spectra (**Figs. S14** and **S15** in ESI). These results also appear consistent with the conclusion that enantiomeric BINOL monomers have different reactivities in the formation of polymer.

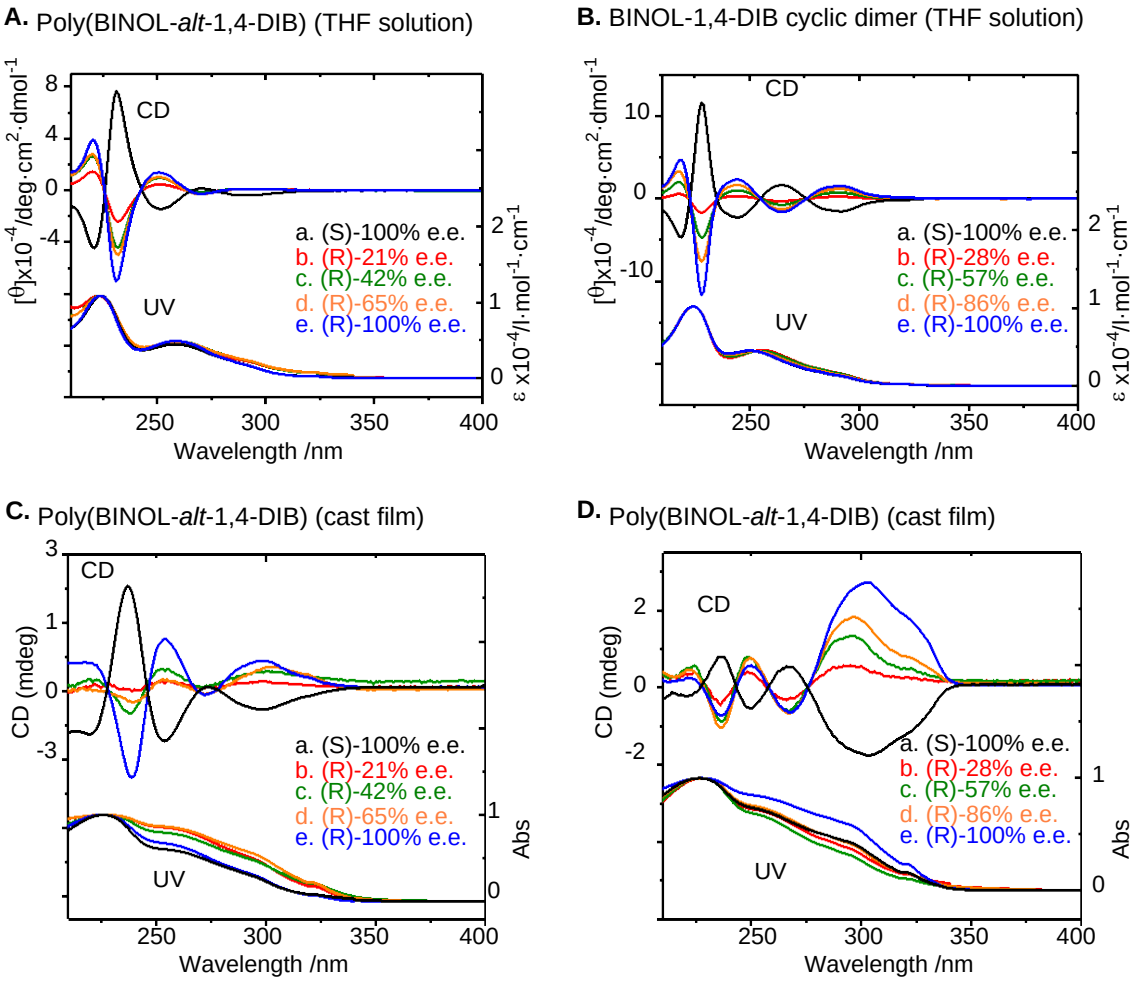


Fig. 6. UV and CD spectra of poly(BINOL-*alt*-14DIB) in THF (A) and in film (C) and those of cyclic dimer in THF (B) and in film (D). The solid-state spectra were obtained by averaging those recorded at four (90° interval) different film orientations (angles) with the film face positioned vertically to the incident light beam for measurement. The polymers samples were purified by preparative SEC and had following e.e.'s of BINOL units and molar masses (vs. polystyrene): **a.** (S)-100% e.e., M_n 2960; **b.** (R)-21% e.e., M_n 2920 (25% e.e of (R)-BINOL in feed), **c.** (R)-42% e.e., M_n 2740 (50% e.e of (R)-BINOL in feed); **d.** (R)-65% e.e., M_n 5 (75% e.e of (R)-BINOL in feed); **e.** (R)-100% e.e., M_n 3520. The polymers in b, c, and d in A contained a small amount of THF-insoluble part; concentrations of the solutions of these samples were normalized using the UV spectrum of a in A at 224 nm.

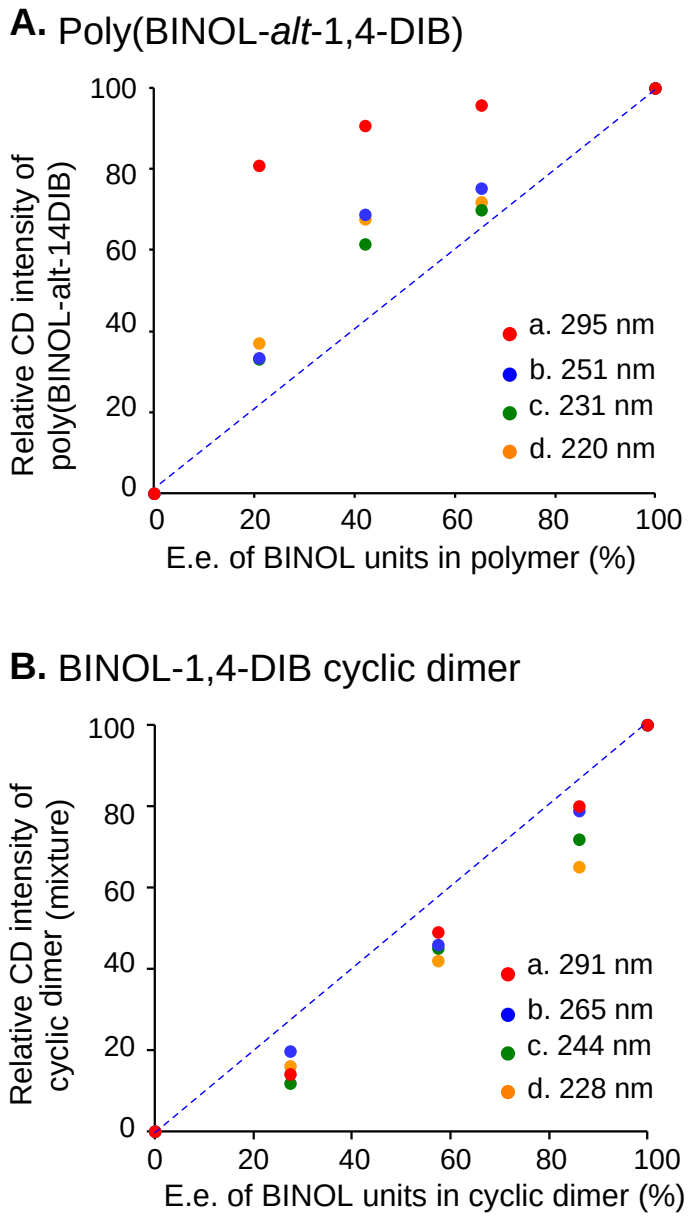


Fig. 7. Relation between relative CD intensities (absolute values of molar ellipticities) of poly(BINOL-*alt*-14DIB) in solution and e.e. of BINOL units in polymer at 310 nm (a), 251 nm (b), 231 nm (c), and 219 nm (d). In calculating relative CD intensities, molar ellipticities of the polymer and the cyclic dimer consisting only of (R)-BINOL units were set to 100.

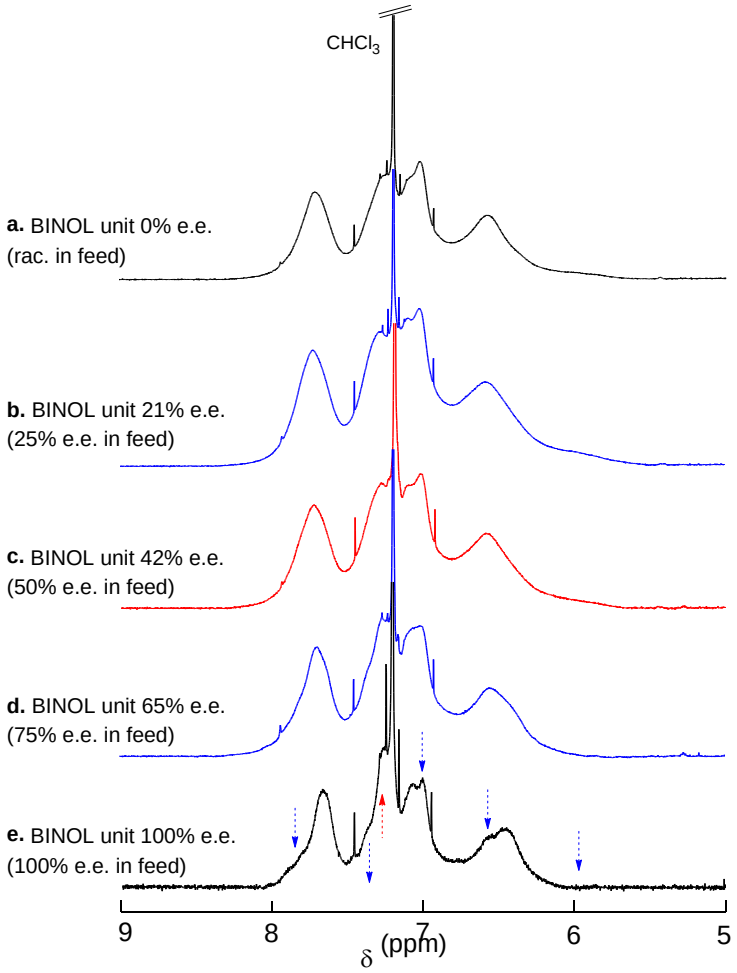


Fig. 8. ^{1}H NMR spectra of poly(BINOL-*alt*-14DIB)s having different e.e.'s of BINOL units: 0% (a), 21% (b), 42% (c), 65% (d), and 100% (e). [400 MHz, r.t., $CDCl_3$]

Synthesis, structure and properties of poly(BINOL-*alt*-13DIB)

Poly(BINOL-*alt*-13DIB)s were prepared from racemic BINOL and (R)-BINOL at 50% and 100% e.e. with 13DIB in the same manner applied for the poly(BINOL-*alt*-14DIB) synthesis. The subtle difference in the substitution position of the diisocyanate monomers remarkably was found to significantly alter the polymerization behavior and the product structure. The polymerization was conducted in in THF containing 5 % of Et_3N at [BINOL] = [13DIB] = 0.154 M at 23°C, and the monomers were almost completely consumed. **Fig. 9** shows the SEC curves the polymerization products obtained at different e.e.'s of BINOL in feed. In a sharp

contrast to the polymerization systems with 14DIB, the shapes of SEC curves were very similar to each other regardless and the ratio of the largest peak which is assigned to a "linear dimer" as discussed later was almost constant regardless of e.e. of BINOL in feed. Although it is difficult to assume a sequence structure of poly(BINOL-*alt*-13DIB), ^{1}H NMR spectra lead to relevant information.

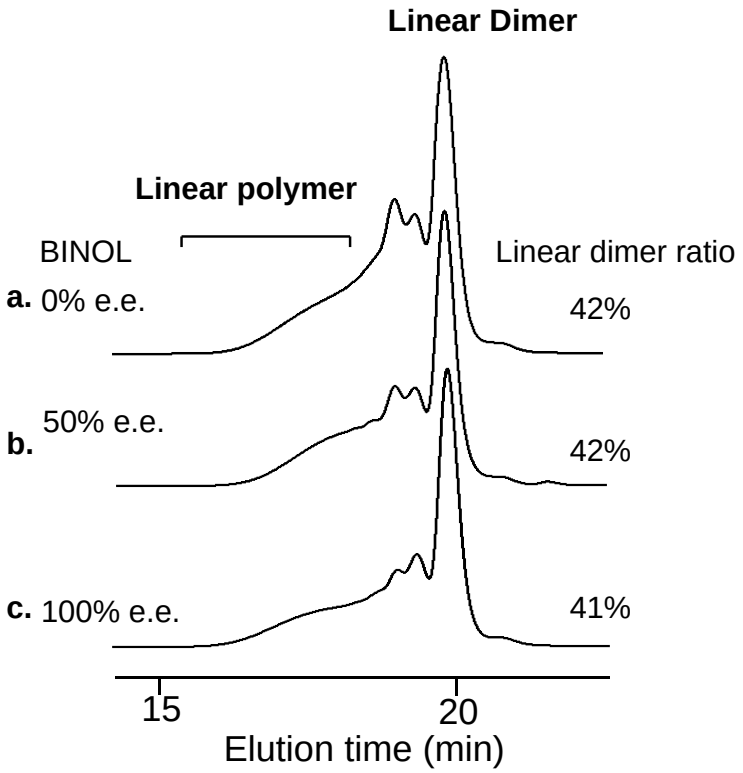


Fig. 9. SEC profiles of polymerization products obtained from 13DIB and (R)-BINOL at 0% e.e. (a), 50% e.e. (b), and 100% e.e. (c) associated with linear dimer contents estimated by wave-from analysis by wave-form analyses (Fig. S9 in ESI). [detection by UV at 254 nm]

Fig. 10 shows the ^{1}H NMR spectra of the poly(BINOL-*alt*-13DIB)s obtained at different e.e's of BINOL. The spectral shape varied depending on 100% e.e. of BINOL in feed where the relative intensity of the signal at 7.7 ppm marked by upward arrows increased and those at around 7.1 ppm and in the range of 5.2-6.8 ppm marked by downward arrows decreased with an increase in e.e. of BINOL unit in feed. The fact that the spectral shapes of the polymers

obtained form racemic BINOL and pure (R)-BINOL are remarkably different rules out independent formation of a chain comprised purely of (R)-BINOL units and one comprised of (S)-BINOL units which would be mirror images having opposite helical senses ("racemate-forming enantiomer-differentiating polymerization") in the system with racemic BINOL. The former chain is formed in the system with pure (R)-BINOL in feed. Sequences comprising of rather randomly distributed (R)-BINOL and (S)-BINOL units may be more plausible for the actual polymer chains; the two units would be diastereomeric to each other in a single-handed helical chain and can show different positions of signals. Production of rather random chains is also in line with the result that SEC profiles were almost unchanged regardless of e.e. of BINOL in feed.

It is noteworthy that poly(BINOL-*alt*-13DIB) made from (R)-BINOL at 100% e.e. lacks the signals in the range of 6-7 ppm while poly(BINOL-*alt*-14DIB) has signals in this range due to π-stacking. This observation suggests that conformation of poly((R)-BINOL-*alt*-13DIB) differs from that of poly((R)-BINOL-*alt*-14DIB), left-handed 2/1-helical structure with π-stacking character.

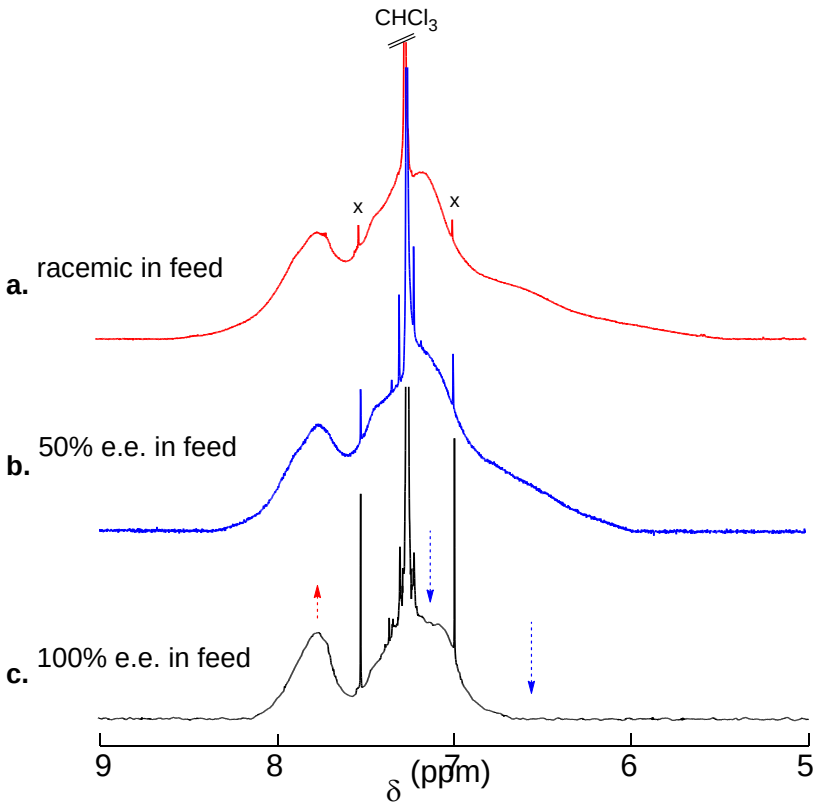


Fig. 10. ^{1}H NMR spectra of poly(BINOL-*alt*-13DIB)s obtained at different e.e.'s of BINOL in feed: 100% (M_n 2840) (a), 50% (M_n 3430) (b), and 0% (M_n 3270) (c). [400 MHz, r.t., $CDCl_3$]

The structure of the dimer was assessed by preparative SEC fractionation from the product mixtures obtained at 50% and 100% e.e. of BINOL in feed and ESI-mass and ^{1}H NMR analyses (**Fig. S3** in ESI). The fractionated dimer sample showed a molar mass of 910.29 corresponding to the "linear dimer" (**Scheme 1 B**, exact mass: 910.40), supporting that this species is a dimer having a linear chain structure, not a cyclic structure. The 1,3-substitution pattern of the benzene of 13DIB ring may make the ring closure difficult.

Molecular dynamics and mechanics (MD and MM) calculations were conducted for the linear dimers and hypothetical cyclic dimers in the same way as applied for the dimers in the BINOL-

14DIB systems (**Fig. S6** in ESI). The linear dimers having (R,R)- and (R,S)-configurations had total steric energies of 262.3 kcal mol^{-1} and 279.0 kcal mol^{-1}, respectively, and the cyclic dimers having (R,R)- and (R,S)-configurations 381.9 kcal mol^{-1} and 396.1 kcal mol^{-1}, respectively. The cyclic dimers were found to be much less stable than the linear dimers probably due to ring strain, which would explain the production of the linear dimers in the BINOL-13DIB systems. The tendency that linear dimers are more stable than cyclic dimers in simulations is common between the BINOL-14DIB systems and the BINOL-13DIB systems while the former led to the cyclic and the latter the linear dimers. Kinetic control over the reactions might have different magnitudes in the two systems.

Unlike the BINOL-14DIB cyclic dimers, the BINOL-13DIB linear dimers were not able to be separated by chiral HPLC and the isomeric ratios are hence not known. The CD/UV spectra of the linear dimers obtained at 50% and 100% of BINOL are shown in **Fig. 11 A**. The CD spectra of the dimers have very similar shapes to each other, and the spectral intensities are closer than expected from the difference in e.e. of BINOL in feed. These results suggest two possibilities, *i.e.*, (i) BINOL unit isomeric ratios are similar in the two linear dimers ((R)-isomer was highly preferred in the formation of linear dimer at 50% of BINOL in feed), or (ii) the CD spectra mainly reflect conformational chirality of linear dimer and the dimer obtained at 50% of (R)-BINOL in feed has a conformation similar to that obtained at 100% of (R)-BINOL in feed. The latter might be more plausible because very high selectivity of enantiomer was not observed in the BINOL-14DIB systems. The fact that the linear dimers' spectral shapes are largely different from that of (R)-BINOL (**Fig. S4** in ESI) also supports that their CD spectra arise mainly from a conformation.

Fig. 11 B shows the CD/UV spectra of poly(BINOL-*alt*-13DIB)s obtained at 50 and 100% e.e. of BINOL in feed. The CD spectral patterns are remarkably different from those of the linear dimers suggesting that the polymers' CD patterns reflect their helical conformation. Further, the two polymer CD spectra do not only different in intensity but also in spectral pattern from

each other. The polymer obtained at 100% e.e. of BINOL in feed has all negative responses in the range of 225-267 nm while the one obtained at 50% e.e. of BINOL in feed has a clear positive peak at 246 nm. These spectral features mean reflect that (R)- and (S)-BINOL units are in a diastereomeric relation in a helical chain as the same preferred-handed helicity in the two systems would be plausible. The differences in NMR spectra between the two systems (**Fig. 10 b** and **c**) may also arise from diastereomeric (R)- and (S)-BINOL units in a helical chain.

Another important feature of the CD spectra of poly(BINOL-*alt*-13DIB)s is found in intensity. The negative splitting centered at 217 nm is considered to be based mainly on the axial chirality of BINOL units, and the negative trough at 231 nm of the polymer obtained at 100% e.e. of BINOL in feed has a molar ellipticity of -2.6 deg $cm^{-2}dmol^{-1}$ which is about 3 times less in absolute value than that of the same band of poly(BINOL-*alt*-14DIB) obtained at 100% e.e. of BINOL (-7.2 deg $cm^{-2}dmol^{-1}$) and also than that of pure BINOL (-7.3 deg $cm^{-2}dmol^{-1}$) (**Fig. S4** in ESI). These results imply that the CD band of poly(BINOL-*alt*-13DIB) is contributed by helicity formed through the polymerization as well as BINOL unit chirality. The formation of helical conformation seems to create positive Cotton effects at around 231 nm.

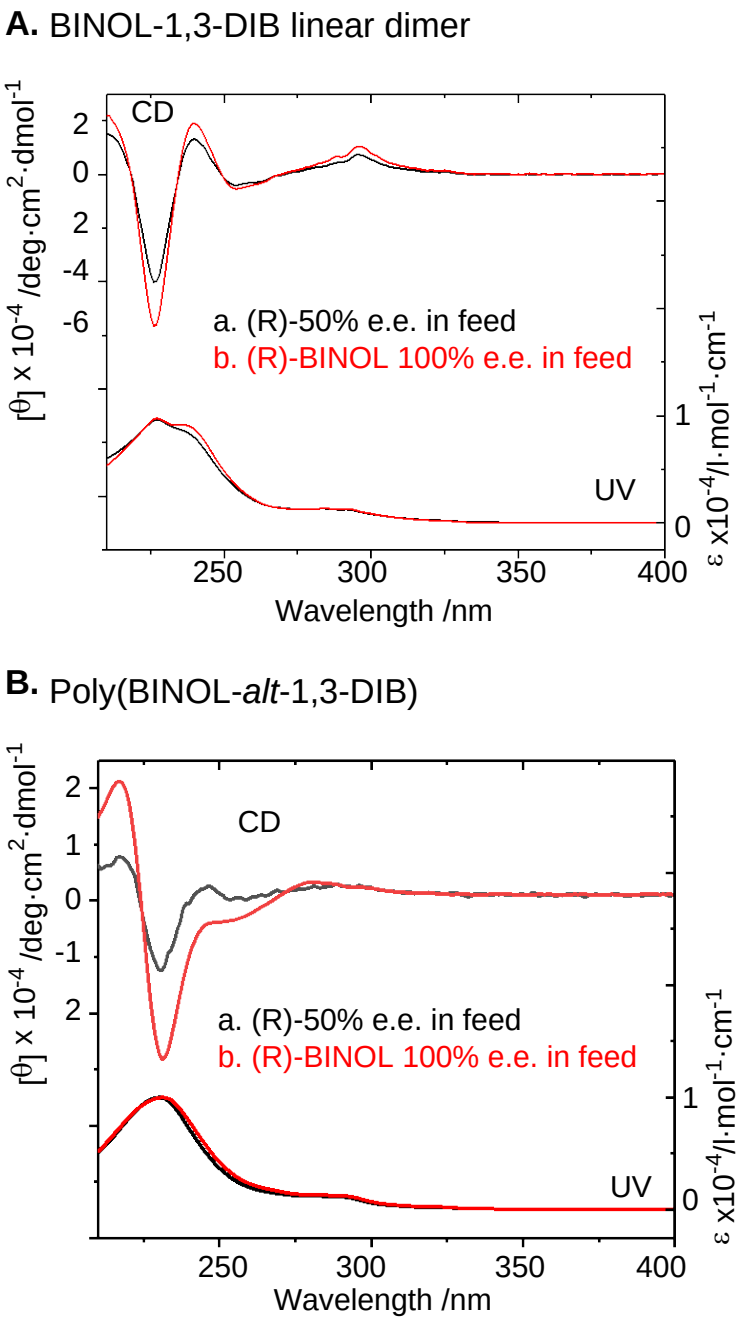


Fig. 11. CD spectra measured in THF solution of BINOL-13DIB linear dimers (A) and poly(BINOL-*alt*-13DIB) (B) obtained at 50% e.e. (M_n 3430) (a) and 100% e.e. (M_n 2840) (b) of (R)-BINOL in feed.

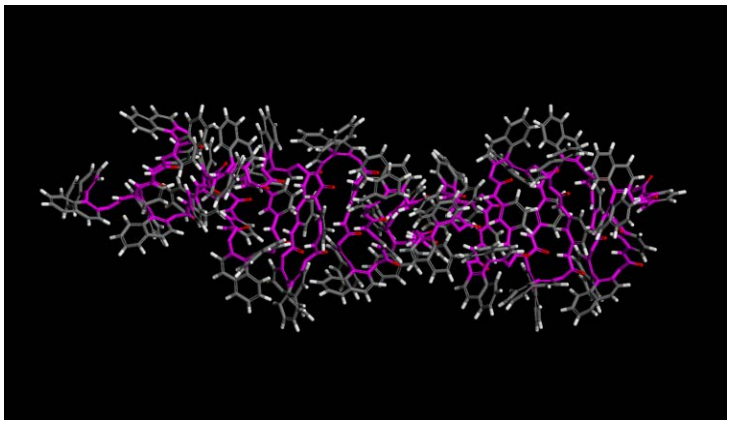
Although the details of helical conformation of poly(BINOL-*alt*-13DIB) are not yet clear, possible conformations obtained by MD and MM calculations for the chain comprised only of (R)-BINOL units are shown in **Fig. 12**. The proposed structures are characterized left-handed helical sharp turns based on chirality of (R)-BINOL (2/1-helical motif) which are arranged also in a left-handed, single-handed helical manner with greater pitches (9/1 in A and 8/1 in B). Although the calculated steric energy of conformation A was lower (2202 kcal mol^{-1}) than that of B (2328 kcal mol^{-1}), the difference seems not large enough to identify A as the most probable structure. However, the sharp turn structures based on BINOL were almost unchanged in the two models through the MD simulations; the actual helical conformation would be characterized by the sharp left-handed, local turns forming a longer-pitched, left-handed helical chain.

The two conformations of poly((R)-BINOL-*alt*-13DIB) are remarkably different from the left-handed 2/1-helical structure of poly((R)-BINOL-*alt*-14DIB) in the fact that average distance between benzene-1,3-diyl moieties appeared too long to form π-stacked structure (5.66 Å for 9/1-helix and 6.37 Å for 8/1-helix in **Fig. 12**) (**Fig. S12** in ESI). The corresponding distance for poly poly((R)-BINOL-*alt*-14DIB) was 4.53 Å.[11] These structural features are in line with the ^{1}H NMR spectral patterns of the two polymers indicating that poly((R)-BINOL-*alt*-14DIB) has π-stacking while poly((R)-BINOL-*alt*-13DIB) does not at least in solution.

On the other hand, WAXD profile of poly(BINOL-*alt*-13DIB) showed a peak at 2θ of 21.5 deg corresponding to a d-spacing of 4.13 Å (**Fig. S18** in ESI). This result may mean that poly((R)-BINOL-*alt*-13DIB) has a π-stacking character in the solid state while stacking was not supported by NMR in solution. The conformation of poly(BINOL-*alt*-13DIB) may be more flexible than that of poly(BINOL-*alt*-14DIB) in solution and may be stabilized in the solid state. It is noteworthy that the WAXD pattern of poly(BINOL-*alt*-13DIB) was broader than that of poly(BINOL-*alt*-14DIB), suggesting that the conformation of poly(BINOL-*alt*-13DIB) is less

ordered that that of poly(BINOL-*alt*-14DIB) in the solid state. In addition, poly(BINOL-*alt*-13DIB) did not show any clear melting point in DSC analysis, suggesting that there is no regular chain packing of the polymer in the solid state (**Figs. S16** and **S17** in ESI). This aspect reinforces that the aforementioned WAXD peak is ascribed to intramolecular π-stacking.

A. Poly(BINOL-*alt*-13DIB) [9/1-helix]



B. Poly(BINOL-*alt*-13DIB) [8/1-helix]

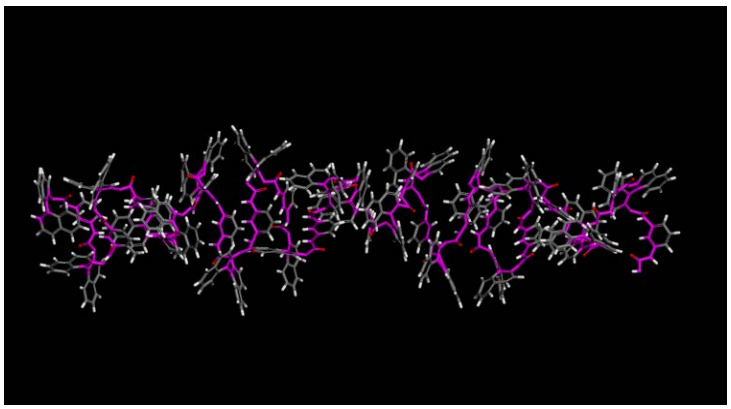


Fig. 12. Possible conformations of poly(BINOL-*alt*-13DIB) consisting of R-BINOL units obtained by MD simulations for 14-16 nsec at 297K followed by MM optimization using COMPASS force field.

Conclusions

Polymerization behavior and properties and structure of products with a focus on stereochemistry were investigated in detail for BINOL-14DIB and BINOL-13DIB systems. In the BINOL-14DIB systems, cyclic dimers were formed along with helical, linear poly(BINOL-

alt-14DIB) where the content of dimers was higher at a lower e.e. of BINOL and the yield of higher-molar-mass, linear polymers tended to be higher at a higher e.e. of BINOL in feed. The three forms of the cyclic dimer, i.e., (R,R)-, (R,S)-, and (S,S)-isomers, were completely resolved and separated by chiral HPLC, and their ratios were unambiguously determined. In the reaction using racemic BINOL, (R,S)-cyclic dimer was preferred over (R,R)- and (S,S)- cyclic dimers while (R,R)-cyclic dimer was preferred the other isomers when (R)-BINOL was present in excess over (S)-BINOL at 25-75% e.e. in feed; the latter observation might mean autocatalysis in the formation in (R,R)-cyclic dimer. As the cyclic dimers were found much less stable than the corresponding linear dimers by molecular simulations, the formation of the cyclic dimers may be based on kinetic control. Poly(BINOL-*alt*-14DIB) is proposed to compose of sequences with rather contiguous (R)-BINOL units as the majority component with rather sporadically incorporated (S)-units as the minor component. Helical sense excess appears to be greater than expected from the e.e. of BINOL units in the chain, suggesting that (S)-BINOL units sporadically incorporated in a rather contiguous (R)-BINOL units sequence become a part of left-handed helical conformation controlled by the chiral influence of (R)-BINOL units. These results may mean that, once a helix with one-handed helicity due to chirality of (R)-BINOL units is formed, the growing species may incorporate (S)-BINOL without changing helicity. Left-handedness of the chain is consistent with the absolute twist hand of (R)-BINOL with a negative dihedral angle, and it may be reinforced by contiguous (R)-BINOL units. While the absolute twist hand of (S)-BINOL would favor right-handed helix, sporadically distributed or isolated (S)-units may not be effective in reversing the left-handed helical chain supported by contiguous (R)-BINOL units. Helicity of chains composed of enantiomeric monomeric units has been studied in detail for for poly(3-methyl-1-pentene).[39,40]

In a sharp contrast to the BINOL-14DIB systems, the BINOL-13DIB systems did not produce cyclic dimers but linear dimers as major components of dimer. The content of linear dimers was almost constant regardless of e.e. of BINOL in feed. In addition, poly(BINOL-*alt*-13DIB) is

proposed to compose of sequences with rather more randomly distributed (R)- and (S)-BINOL units than those in poly(BINOL-*alt*-14DIB). CD spectra of poly(BINOL-*alt*-13DIB)s seem to be contributed by bands reflecting helical chirality which overlaps the negative splitting due to (R)-BINOL chirality. Further, a chain conformation is proposed to be characterized by sharp, left-handed turns based on BINOL chirality forming a longer-pitched, left-handed helix with no intra-chain π-stacking character for poly((R)-BINOL-*alt*-13DIB) in solution which is in sharp contrast to the left-handed 2/1-helical conformation of poly((R)-BINOL-*alt*-14DIB) with intra-chain π-stacking. Both poly((R)-BINOL-*alt*-13DIB) and poly((R)-BINOL-*alt*-14DIB) has p-stacking in the solid state as indicated by WAXD analysis.

Thus, the different substitution positions in the benzene ring which is the only and subtle difference between the BINOL-14DIB and BINOL-13DIB systems results in remarkable differences in polymerization behaviors and sequence structures and chiroptical properties of the reaction products. While reports on polyurethanes from a view of stereostructure are very rare, this work presents the systematic, in-depth studies of helical polyurethanes. Once fine stereochemical control is performed over polyurethanes, they may find a wide rage of applications in advanced chiral materials on the basis of the advantages that polyurethanes can be prepared by simple polyaddition under mild conditions, that chemical structural variations can be readily introduced by changing diol and diisocyanate monomers, and that polyurethanes can interact through hydrogen bonds using the urethane group with external polymers and molecules.

Supporting Information. Experimental details, ^{1}H NMR spectra of dimers, molecular conformations obtained by computer simulations, wave-form analysis results of SEC curves, mass spectra, fluorescence spectra, CD and UV spectra, thermal analysis data, and WAXD profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no conflict of interest.

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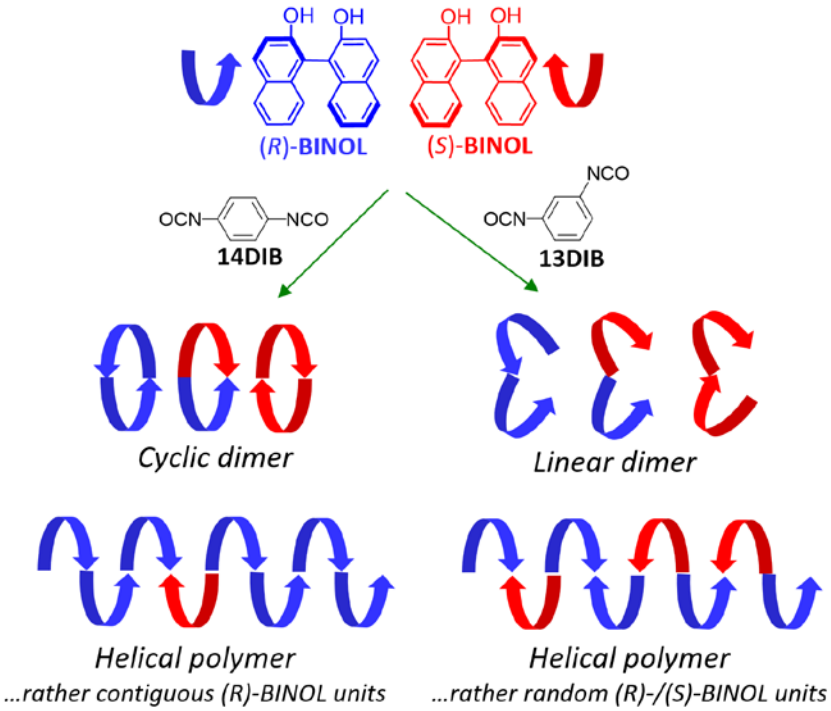
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OH OH
OH OH
(R)-BINOL
(S)-BINOL
OCN NCO
14DIB
OCN NCO
13DIB
Cyclic dimer
Linear dimer
Helical polymer
...rather contiguous (R)-BINOL units
Helical polymer
...rather random (R)-/(S)-BINOL units