Helical Configuration of Poly(iminomethylenes). Synthesis and CD Spectra of Polymers Derived from Optically Active Isocyanides[1]

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ABSTRACT: Each of nine chiral isocyanides, R*–N≡C, in enantiomerically pure or almost pure form, is polymerized to the corresponding poly(iminomethylene), [R*–N≡C<]$_n$. The group R* either contains at least one substituent (carboxylic ester, phenyl, phosphinyl) or is unsaturated (C=C, C≡C). The polymers are of the rigid-rod type with a helical main chain of carbon atoms. Because of the chirality of R*–N≡C either the P or the M helix is preferentially formed. CD spectra and optical rotation at 578 nm are determined and compared with those of the model compounds R*–N≡CH(t-C$_4$H$_9$) and the monomers. This comparison and earlier calculations on [t-C$_4$H$_9$–N≡C<]$_n$ allowed the assignment to each polymer of the excess screw sense. The screw sense is also theoretically predicted by two approaches, a thermodynamic and a kinetic one. The latter approach gives an appreciably better fit with the experimental results.

Introduction

Stereoisomerism due to restricted rotation around single bonds (atropisomerism) is a well-known phenomenon in organic chemistry.[3] In polymer chemistry this type of isomerism is very rare. Restricted rotation around the single bonds connecting the main-chain carbon atoms of a macromolecule can give rise to the formation of a stable helix. One condition is that the polymer is highly isotactic; that is, the configuration around all main-chain single bonds should be the same, e.g., all R or all S.

As far as we know, only three examples of atropisomerism in polymers have been reported in the literature. There is indirect evidence that polychloral prepared from chloral with a chiral initiator forms a stable helix with preference of one helical screw sense over the other.[4] It has been shown that triphenylmethyl methacrylate, when polymerized by chiral anionic catalysts, yields an isotactic, optically active polymer.[5] The optical activity is attributed to the presence of a rigid helix, which is stable because of the bulky triphenylmethyl ester functions. The third example of atropisomerism is found in polymers of isocyanides.[6,39] These polymers, also called poly(iminomethylenes) or, more properly, poly(carbonimidoyls), are obtained by polymerization of isocyanides with several catalysts, among them nickel(II) catalysts.

$$nR-N\equiv C \xrightarrow{\text{Ni(II)}} (R-N=C<)_n$$
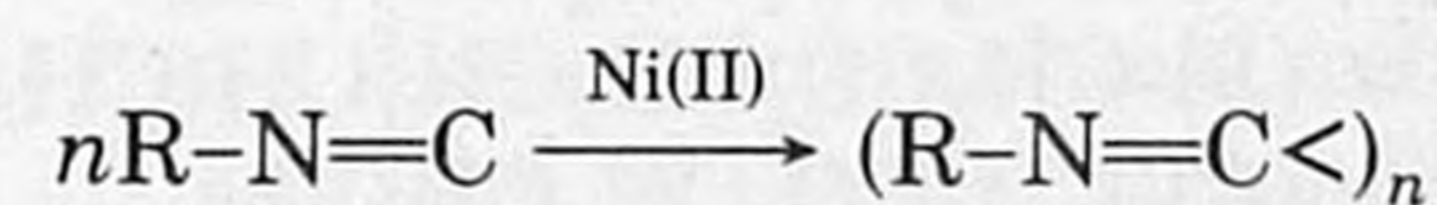
The polymers have a rigid helical structure with four monomeric units per helical turn.[6,7] Poly(*tert*-butyliminomethylene) has been resolved into right-handed (P) and left-handed (M) helices by column chromatography.[8] These helices show negative and positive signs of optical rotation at λ = 578 nm, respectively.[9] The resolution of poly(*tert*-butyliminomethylene) indicates that polymerization of isocyanides is stereoselective with respect to screw sense. Thus, when the monomer is nonchiral a racemic mixture of P and M screws is formed. However, when the monomer is one enantiomer of a chiral isocyanide, its polymer will be a mixture of diastereoisomers, and P and M screws will not be obtained in equal amounts. In a previous paper[10] we compared the CD spectra of polymers of optically active alkyl isocyanides with those of model compounds. This comparison, although restricted to three examples, supported the hypothesis that optically active isocyanides yield polymers with an excess of one helical chain over the other. In the present paper[11] we describe the synthesis and CD spectra of an additional number of nine optically active poly(iminomethylenes), compounds **3a–i** (Scheme I), which have different side chains R. The CD spectra of these polymers are compared with the CD

spectra of representative model compounds. A major goal of our investigations is the development of chiral supports, such as deoxygenated **3i**, which can bind metal complexes. These polymeric systems are of interest as chiral catalysts, e.g., in hydrogenation reactions.[12]
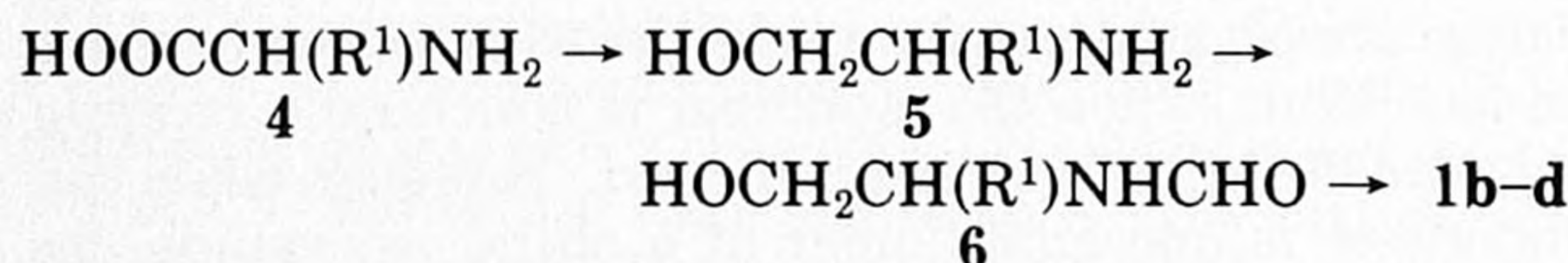
Results and Discussion

Synthesis. Polymers **3a–i** were prepared according to the general procedure of Scheme I. Optically active *N*-formylamines served as starting materials. L(*S*)-*N*-Formylalanine ethyl ester (**1a**) was obtained from L-alanine by esterification with HCl and subsequent reaction with sodium formate, formic acid, and acetic anhydride. (*S*)-*N*-Formyl-*O*-acetyl-2-aminopropanol (**1b**), (*S*)-*N*-formyl-*O*-acetyl-2-amino-3-methyl-1-butanol (**1c**), and (*R*)-*N*-formyl-*O*-acetyl-2-amino-2-phenylethanol (**1d**) were prepared from L-alanine, L-valine, and D-phenylglycine, respectively, as outlined in Scheme II. The carboxylic function of the latter compounds was esterified and subsequently reduced to the hydroxymethyl group with Li-AlH$_4$. In order to facilitate the isolation of alcohols **5j** and **5k** from the reaction mixtures, we attached a benzoyl group to the amino group of **4j** and **4k**.[10] This benzoyl group is converted into a benzyl group during the reduction process. The latter group was removed by hydrogenolysis with palladium on carbon. The unprotected alcohols **5j** and **5k** were treated with formic acid–acetic anhydride to give N,O-diformylated products. The latter compounds were selectively deformylated at oxygen by reaction with sodium hydrogen carbonate in 10% aqueous methanol to give **6j** and **6k**. Formamide **6l** was obtained from **5l** with excess of ethyl formate. Compounds **6** were O-acetylated using acetic anhydride and pyridine. (*S*)-*N*-Formyl-1-amino-1-phenylethane (**1e**) and (*S*)-*N*-formyl-2-amino-1-phenylpropane (**1f**) were prepared from (*S*)-1-amino-1-phenylethane and (*S*)-2-amino-1-phenylpropane (*S*-amphetamine), respectively, using ethyl formate.

Scheme I

$$RNHCHO \rightarrow R-N{=}C \rightarrow (R-N{=}C{<})_n$$
$$\quad \mathbf{1} \qquad\qquad \mathbf{2} \qquad\qquad \mathbf{3}$$
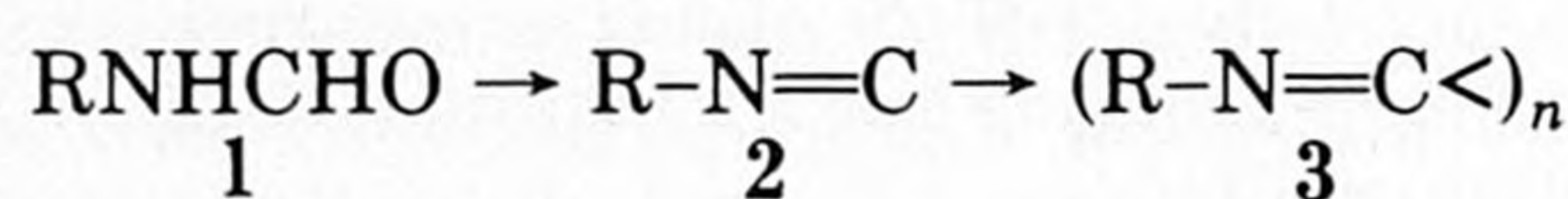
a, R = (*S*)-C$_2$H$_5$O$_2$CCH(CH$_3$)
b, R = (*S*)-CH$_3$CO$_2$CH$_2$CH(CH$_3$)
c, R = (*S*)-CH$_3$CO$_2$CH$_2$CH[CH(CH$_3$)$_2$]
d, R = (*R*)-CH$_3$CO$_2$CH$_2$CH(Ph)
e, R = (*S*)-PhCH(CH$_3$)
f, R = (*S*)-PhCH$_2$CH(CH$_3$)
g, R = (*S*)-HC≡CCH(C$_2$H$_5$)
h, R = (*S*)-H$_2$C=CHCH(C$_2$H$_5$)
i, R = (*S*)-Ph$_2$P(O)CH(CH$_3$)CH$_2$

Scheme II

$$HOOCCH(R^1)NH_2 \rightarrow HOCH_2CH(R^1)NH_2 \rightarrow$$
$$\qquad \mathbf{4} \qquad\qquad\qquad \mathbf{5}$$
$$HOCH_2CH(R^1)NHCHO \rightarrow \mathbf{1b{-}d}$$
$$\qquad\qquad \mathbf{6}$$

4j, R^1 = CH$_3$, L-alanine
 k, R^1 = (CH$_3$)$_2$CH, L-valine
 **l**, R^1 = Ph, D-phenylglycine

Formamides **1g** and **1h** were synthesized from (*S*)-3-amino-1-pentyne and (*S*)-3-amino-1-pentene, respectively. The latter amines were obtained according to Scheme III. Reaction of sodium acetylide in liquid ammonia with propionaldehyde provided alcohol **7**. Compound **7** was converted with *p*-toluenesulfonyl chloride into the corresponding tosylate **8**. When **8** was treated with excess liquid ammonia in an autoclave at room temperature for 24 h,

amine **9** was formed in 85% yield. No reaction was observed at the boiling temperature of ammonia (−33 °C). In the literature, the reaction of a tosylate similar to **8** with sodium amide in liquid ammonia has been described.[13] This procedure gives amine in a much lower yield (40%). The racemic amine **9** was resolved through crystallization of its bitartrate from water. After two crystallizations ^{1}H NMR shift experiments showed that **9** was optically pure with $[\alpha]^{20}_D$ +14.2°. After we had completed this experiment, Scandinavian workers[14] published the resolution of **9** by a similar procedure. Their optically pure amine had $[\alpha]^{22}_D$ +14.4°, and its absolute configuration was established to be *S*. A sample of optically pure (*S*)-**9** was converted into amine (*S*)-**10** by catalytic hydrogenation using a deactivated Lindlar catalyst.[15]

Scheme III

$$HC{\equiv}CNa,\ C_2H_5CHO \rightarrow HC{\equiv}CCH(C_2H_5)OH \rightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{7}$$
$$HC{\equiv}CCH(C_2H_5)OTs \rightarrow HC{\equiv}CCH(C_2H_5)NH_2 \rightarrow$$
$$\qquad \mathbf{8} \qquad\qquad\qquad\qquad\qquad \mathbf{9}$$
$$H_2C{=}CHCH(C_2H_5)NH_2$$
$$\mathbf{10}$$
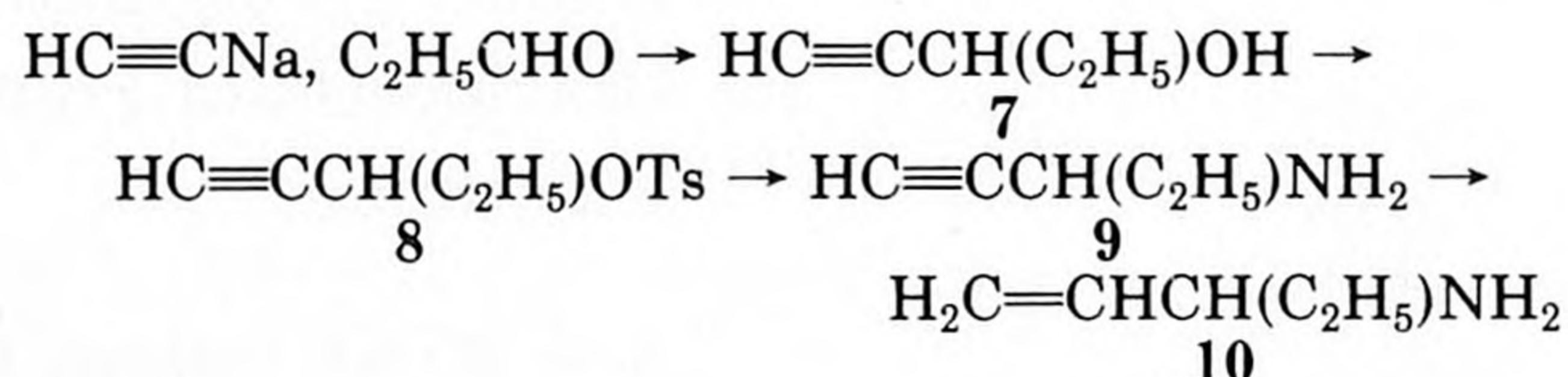
(*S*)-*N*-Formyl-1-amino-2-(diphenylphosphinyl)propane (**1i**) was prepared according to Scheme IV. L-Alanine (**4j**) was converted into its methyl ester and, subsequently, protected at its amine function with two benzyl (Bn) groups. For the introduction of the latter groups we used the combination benzyl bromide and solid sodium carbonate in acetonitrile as solvent. We found this procedure more convenient than the literature procedure,[16] which makes use of benzyl chloride and KOH in ethanol–water as solvent. The double-protected L-alanine ester was reduced with LiAlH$_4$ to give alcohol **11**. Compound **11** was treated with *p*-toluenesulfonyl chloride in pyridine with the purpose of preparing the *O*-tosyl derivative **15**. However, the expected reaction product was not formed. Instead the chloride **12** and pyridine salt **16**[17] were obtained in approximately 45% and 30% yield, respectively. Substitution of *N*-methylimidazole for pyridine gave chloride **12** in an even higher than 95% yield. The latter compound could also be obtained by using thionyl chloride as reagent, albeit in lower yields (<70%) and longer reaction time. The rearrangement, which takes place during the synthesis of **12** from **11** by the procedures mentioned above, is not unexpected and has some precedents in literature.[18] It probably proceeds via the following three-membered-ring intermediate:

$$CH_3CH{-}CH_2$$
$$\backslash \ \ /$$
$$N^+$$
$$/ \ \ \backslash$$
$$Bn \ \ Bn$$
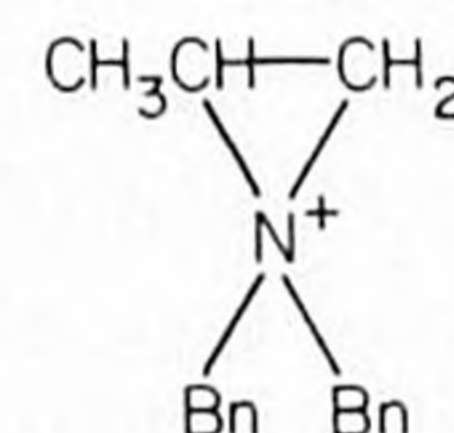
The optical rotation of chloride **12** amounted to $[\alpha]^{20}_D$ +19.3°. The structure of **12** was confirmed by ^{1}H and ^{13}C NMR and mass spectrometry. Chiral shift reagents gave no signal splitting in the ^{1}H NMR of **12**, which might indicate that this compound is optically pure. The absolute configuration of **12** would be *R* if during the conversion **11** → **12** inversion occurs at the chiral center. Chloride **12** was treated with Ph$_2$PLi in THF to give its phosphine derivative, which was oxidized with hydrogen peroxide to yield phosphine oxide **13**. The benzyl groups in the latter compound were removed by hydrogenolysis with palladium on carbon as the catalyst. Attempts to remove the benzyl groups in the phosphine stage were unsuccessful, probably because the phosphine–amine acts as a strong bidentate
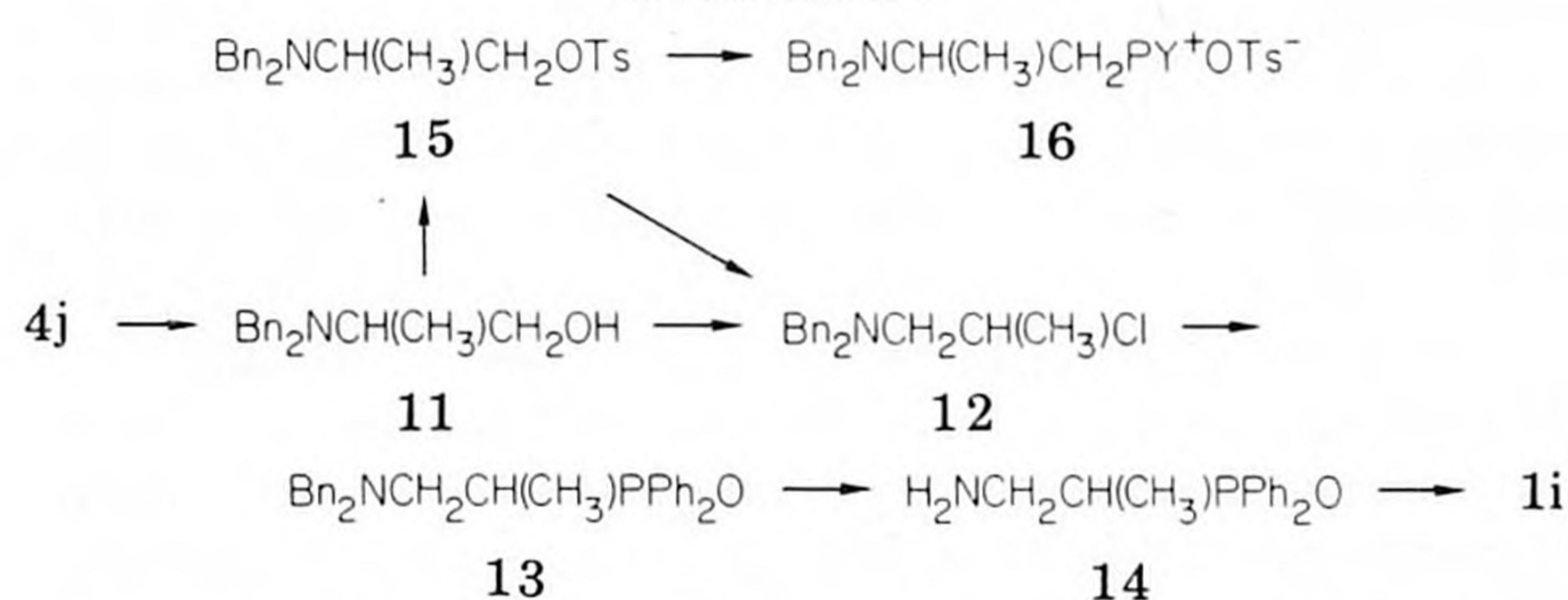
Table I
Molar Optical Rotations of Poly(iminomethylenes) 3, (R—N=C<)$_n$, Their Monomers 2, R—N=C, and Some Model Imines 17, R—N=CH(t-C$_4$H$_9$)

R	$[M]^{20}_{578}$ ^{a,b}		
	2	17	3
a, (S)-C$_2$H$_5$O$_2$CCH(CH$_3$)	+21.2	−175	−355
b, (S)-CH$_3$CO$_2$CH$_2$CH(CH$_3$)	+74.0	+14.3	−190
c, (S)-CH$_3$CO$_2$CH$_2$-CH[CH(CH$_3$)$_2$]	+72.5		−172
d, (R)-CH$_3$CO$_2$CH$_2$CHPh	−129		−156
e, (S)-PhCH(CH$_3$)	−55.0^c	−133	−458
f, (S)-PhCH$_2$CH(CH$_3$)	+70.6	+114^d	+22
g, (S)-HC≡CCH(C$_2$H$_5$)	−11.9^e		−102
h, (S)-H$_2$C=CHCH(C$_2$H$_5$)	+90.2^f	−7.2	+27.6
i, (S)-Ph$_2$P(O)CH(CH$_3$)CH$_2$	+35.3	−234^g	−910

^{a} In (deg·cm^2)/g. The molar rotations of the polymers are expressed per polymer repeat unit. ^{b} In chloroform as solvent, unless otherwise stated; 2, c 1–4; 17, c 1–3; 3, c 0.005–1.0. ^{c} In methanol, c 5. ^{d} Model compound is R—N=C(CH$_3$)$_2$.^{26} ^{e} Neat. ^{f} Both neat and in methanol, c 1. ^{g} A low molecular weight polymer sample serves as model compound, $\overline{MW} \simeq 1100$ (tetramer).

ligand to the metal catalyst. Compound **14** was converted into formamide **1i** using formic acid as formylating agent.

Scheme IV

Bn$_2$NCH(CH$_3$)CH$_2$OTs ⟶ Bn$_2$NCH(CH$_3$)CH$_2$PY$^+$OTs$^-$

15　　　　　　　　　　　　　**16**

4j ⟶ Bn$_2$NCH(CH$_3$)CH$_2$OH ⟶ Bn$_2$NCH$_2$CH(CH$_3$)Cl ⟶

11　　　　　　　　　　　　**12**

Bn$_2$NCH$_2$CH(CH$_3$)PPh$_2$O ⟶ H$_2$NCH$_2$CH(CH$_3$)PPh$_2$O ⟶ **1i**

13　　　　　　　　　　　　**14**

Isocyanides **2** were obtained from formamides **1** by dehydration with trichloromethyl chloroformate (ClCOO-CCl$_3$) and N-methylmorpholine at low temperatures (compounds **2a–d**),[19] by (Ph$_3$PCl)CCl$_3$ in situ from triphenylphosphine and carbon tetrachloride (compound **2e**),[20] and by phosphorus oxychloride and triethylamine or N-methylmorpholine (compounds **2f–i**).[21] The yields varied from 50 to 75%. The infrared absorption spectra of compounds **2a–i** showed characteristic isocyanide stretching vibrations in the region 2140–2145 cm^{-1}. The molar optical rotations of the isocyanides are given in Table I.

The monomers were polymerized at room temperature by 0.1–5 mol % of NiCl$_2$·6H$_2$O either in methanol solution or without solvent. The yields of isolated polymer ranged from 60 to 95%. The polymers were pale yellow or yellow solids. Polymer **3g** was a brown solid. In general, the solids were soluble or sparingly soluble in apolar solvents (chloroform, benzene, petroleum ether) and insoluble in polar solvents (alcohols, water). The intrinsic viscosities [η] of the polymers varied from 0.06 to 0.70 dL/g (toluene or chloroform, 30.00 °C). If we apply the Mark–Houwink equation $[\eta] = 1.4 \times 10^{-9}\bar{M}_w^{1.75}$, determined for poly(2-octyliminomethylene),[10] to the present polymers, we estimate that their viscosity-average molecular weights range from 25 000 to 95 000. We did not aim at high molecular weights. On the other hand, the samples should fulfill the condition that the optical rotation and CD spectrum are independent of molecular weight. The latter situation is attained when the average chain length of the polymers is larger than approximately 20 monomeric units (molecular weight >2000), as we showed in a previous study.[8] We observed that the molecular weight of the polymers strongly depends on the amount of catalyst used. For
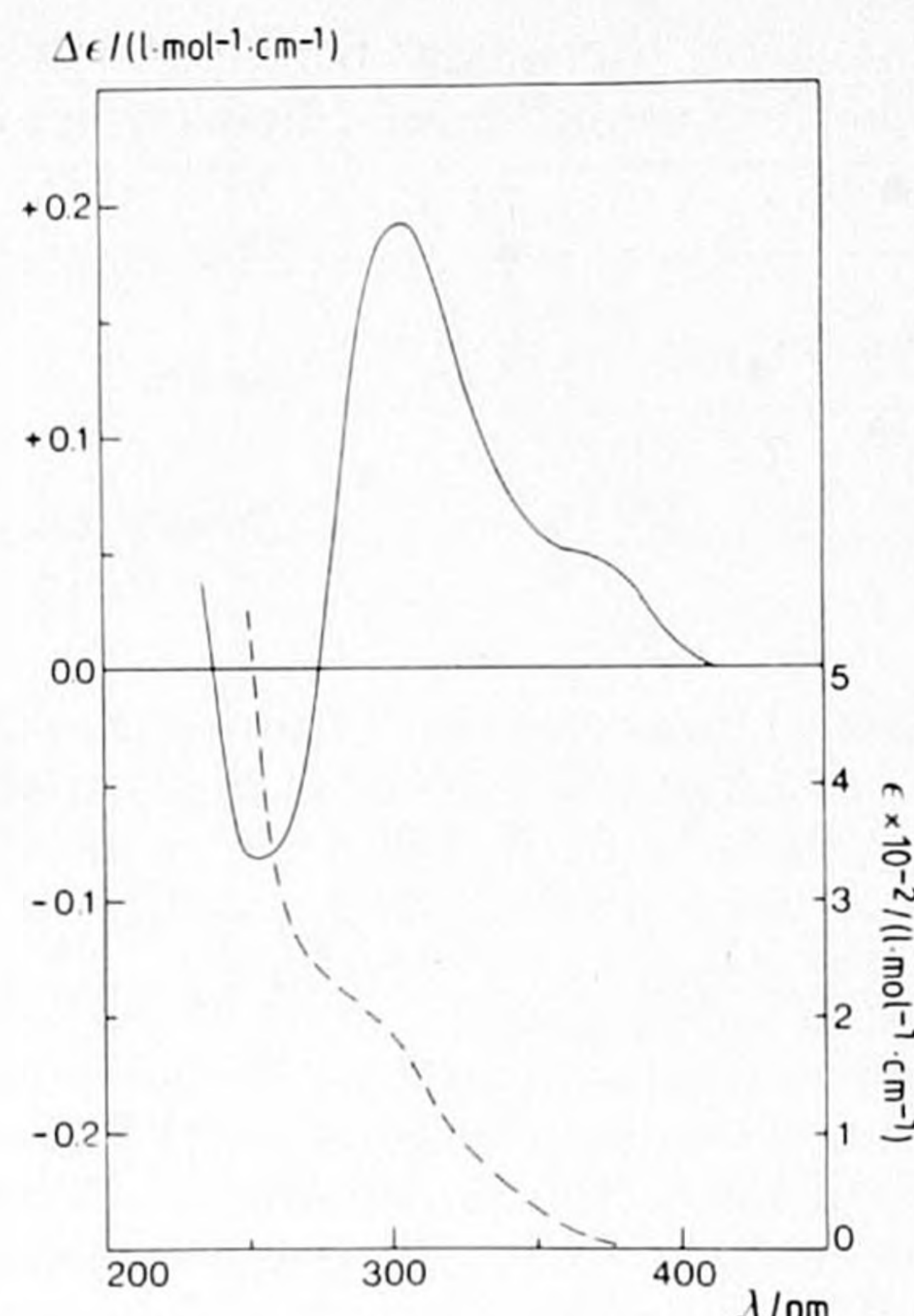

Figure 1. CD (—) and UV (---) spectra of (M)-(+)-poly(tert-butyliminomethylene).

instance, if α-phenylethyl isocyanide (**2e**) is polymerized neat with 0.015, 0.2, 2, and 100 mol % of nickel chloride, the molecular weights of the polymer samples amount to $\bar{M}_v = 175\,000$, $\bar{M}_v = 95\,000$, $\bar{M}_v = 30\,000$, and $\bar{M}_n$(VPO) = 2000, respectively. Polymers **3a–i** showed N=C stretching vibrations in the infrared spectrum at 1620–1650 cm^{-1}. Their optical rotation values are given in Table I.

As low molecular weight model compounds for the polymers a number of N-neopentylidene amines, RN=CH(t-C$_4$H$_9$) (**17**), were synthesized. The molar optical rotations of these compounds are also included in Table I.

CD Spectra. Polymers **3a–i** have various side chains R. For convenience, we will divide these polymers into classes that have ester functions only in their side chain (compounds **3a–c**, model compounds are **17a,b**), compounds that have a phenyl substituent or a phenyl substituent in addition to an ester function in their side chain (compound **3d–f**, model compound is **17e**), compounds that have a triple or double bond in their side chain (compounds **3g,h**, model compound is **17h**), and a compound that has a diphenylphosphinyl substituent in its side chain (compound **3i**, model compound is a corresponding low molecular weight polymer sample **17i**). The CD spectra of the various polymers and model compounds will be discussed below. Before doing so, we will recall some features of the CD spectrum of (M)-(+)-poly(tert-butyliminomethylene), which serves as a general reference spectrum.[9] This spectrum is presented in Figure 1 together with the UV absorption spectrum. The shoulder in the latter spectrum at about 290 nm corresponds to the n–π* transition of the imino group.[9] This n–π* transition is responsible for the CD spectrum in the region 240–400 nm. Two CD bands centered at the wavelength of this shoulder are observed, forming a so-called "exciton couplet".[22] The sign sequence of this couplet is characteristic of the screw sense of the polymer. It was shown that a positive band at higher and a negative band at lower wavelength (positive couplet) in poly(iminomethylenes) corresponds to an M-helical configuration.[9] The reverse situation (negative couplet) corresponds to a P-helical configuration.

The UV and CD spectra of the first class of polymers (**3a–c**) are presented in Figure 2a–c. The UV and CD data of model compounds **17a** and **17b** are listed in Table II. Both **17a** and **17b** show an absorption band in the UV at 220–230 nm. These bands probably include the n–π* transition of the imino group as well as that of the carbonyl
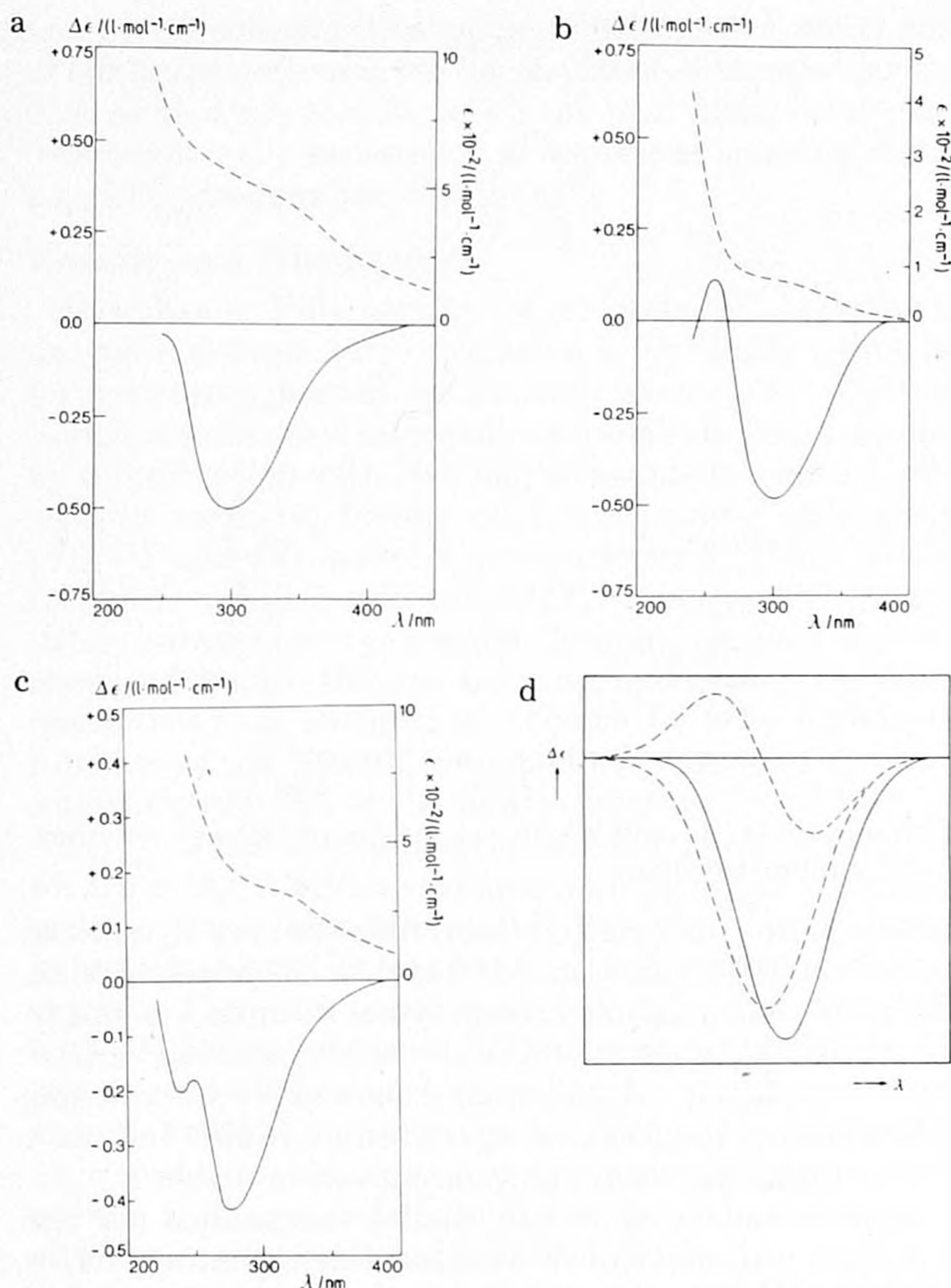
Figure 2. (a) CD (—) and UV (---) spectra of polymer **3a** in chloroform solution. (b) CD (—) and UV (---) spectra of polymer **3b** in chloroform solution. (c) CD (—) and UV (---) spectra of polymer **3c** in methanol solution. (d) Simulated CD spectrum of polymer **3a**. The broken lines represent a negative couplet and a negative, symmetrical Cotton effect; the full line represents the resultant curve.

Figure 3. (a) CD (—) and UV (-·-) spectra in *n*-hexane solution and CD (---) spectrum in chloroform solution of (S)-*N*-neo-pentylidene-α-phenylethylamine (**17e**). (b) CD (—) and UV (---) spectra of polymer **3d** in acetonitrile solution. (c) CD (—) and UV (---) spectra of polymer **3e** in chloroform solution. (d) CD (—) and UV (---) spectra a polymer **3f** in tetrahydrofuran solution. (e) Simulated CD curve of polymer **3e**: (---) negative couplet and single negative Cotton effect; (···) positive phenyl band; (—) resultant curve.

group. The transition of the latter group should be at the shorter wavelength side, as carbonyl groups normally show their n–π* transition at about 210–220 nm ($\epsilon \simeq 50$ L·mol⁻¹·cm⁻¹).[23] In the CD spectra of **17a** and **17b** a Gaussian band centered at 235 nm is visible with Δε values of −4.0 and −0.29 L·mol⁻¹·cm⁻¹, respectively. The relatively high wavelength position of the band suggests that the chirality of the carbonyl group is not pronounced in the CD.

The UV spectra of polymers **3a–c** reveal the n–π* transition of the imino group as a broad band in the region 290–330 nm. This transition is considerably shifted to longer wavelengths with respect to the model compounds. Such a shift has also been observed for poly(imino-methylenes) derived from simple alkyl isocyanides.[10] In polymers of optically active isocyanides both the chiral center in the side chain of the helical structure of the main chain will induce rotational power in the imino chromo-phore. The contribution by the chiral side chain in polymers **3a–c** is manifested in the CD spectrum as a relatively large negative band at 240–400 nm. The helicity of the main chain is obscured due to overlap with this negative band. Careful inspection of the curves, however, shows that negative couplets are present for compounds **3b** and **3c**. The positive parts of these couplets are lowered by the negative band of the side chain. Also for polymer **3a** a negative couplet might well be present; the asymmetry of the CD curve is an indication, as is supported by a simulated spectrum (Figure 2d). For an accurate curve analysis the CD spectra should also be recorded and interpreted in the short-wavelength region. However, this
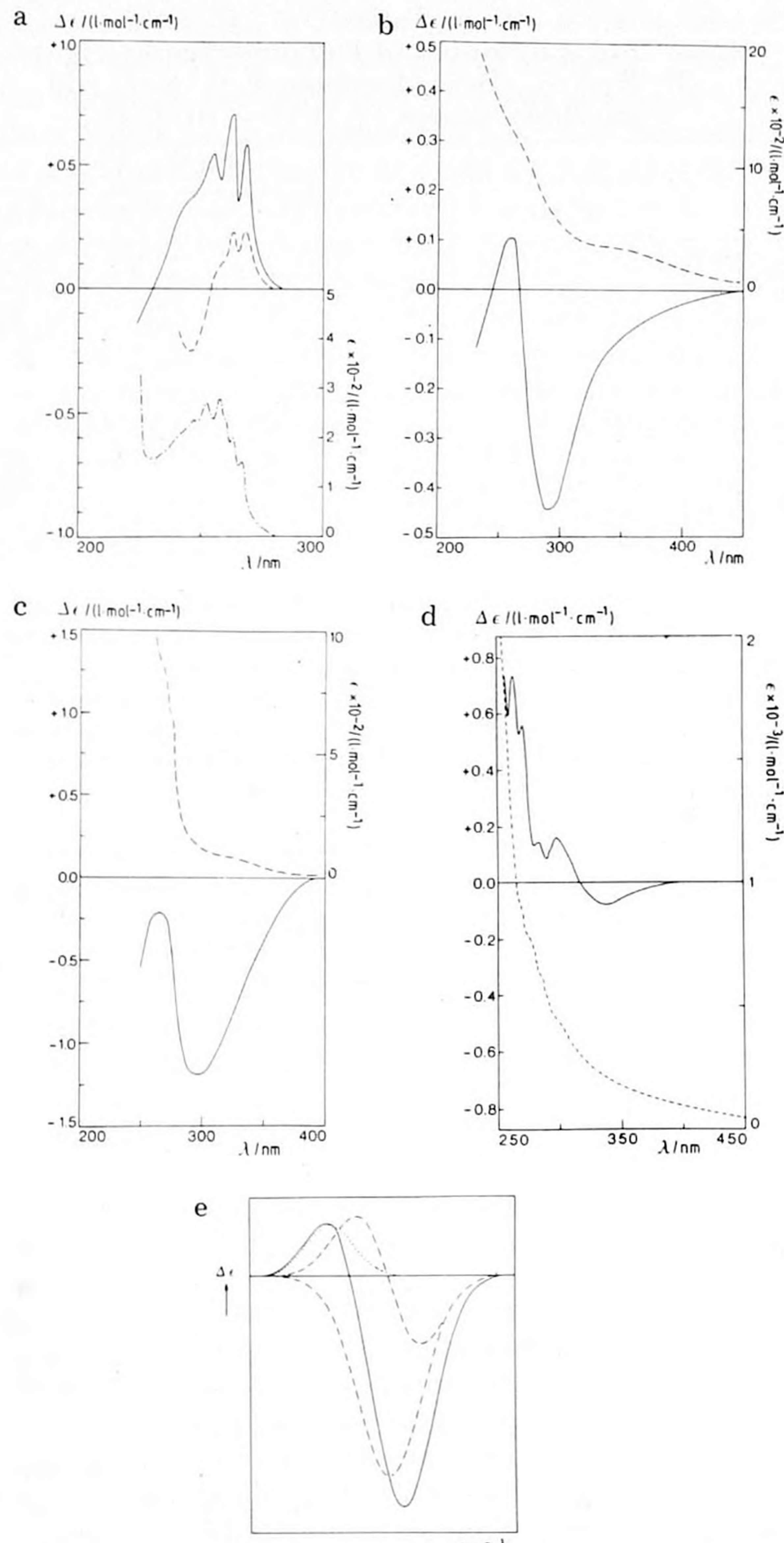
is difficult to realize because of solvent absorption and unfavorable Δε/ε ratios. The occurrence of negative couplets in **3a–c** indicates an excess of right-handed or *P* helices in these polymers. An estimate of the excess percentage from the intensity of the couplets, as we were able to make in case of polymers of simple optically active alkyl isocyanides,[10] would be too unreliable at this time. The molar rotation data for polymers **3a–c** show appreciable shifts to negative values as compared to the rotations of the model imines and also to the rotations of the isocyanide monomers. These shifts to negative rotations suggest a levorotatory contribution by the helices. The combination of *P* screw and negative optical rotation was found earlier for poly(*tert*-butyliminomethylene) (vide supra).

The UV and CD spectra of the model compound of polymers **3d–f**, compound **17e**, are presented in Figure 3a. In these spectra the typical pattern of a phenyl group is
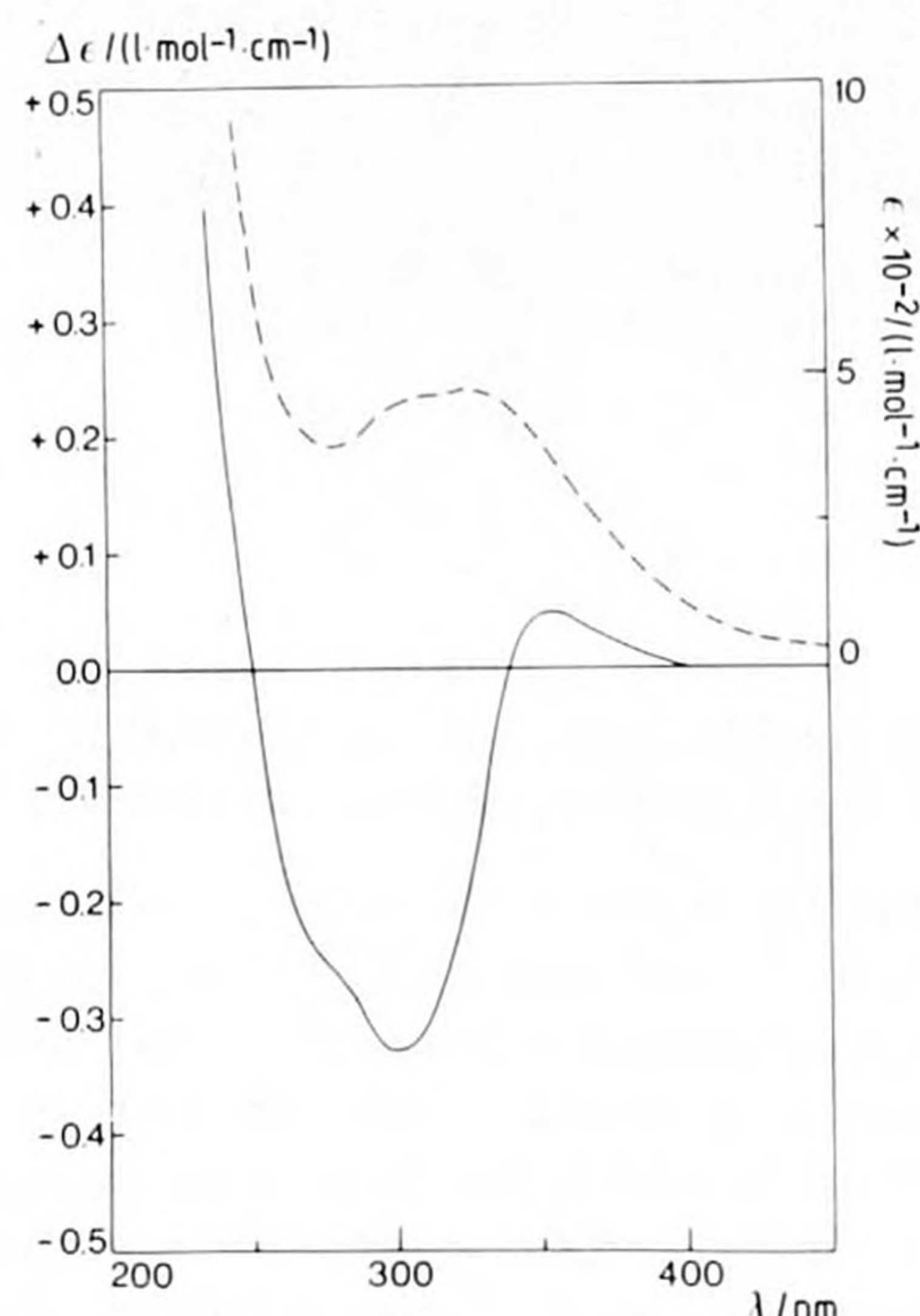
Figure 4. CD (—) and UV (---) spectra of polymer **3h** in *n*-hexane solution.

visible between 250 and 280 nm.[24] The band due to the n–π^* transition of the imino chromophore is partly masked by the phenyl pattern. This n–π^* transition can be located at about 250 nm. In *n*-hexane as well as in chloroform as solvent it gives rise to a negative CD band. The intensity of the latter band in *n*-hexane is lower than in chloroform. This difference in intensity might be caused by conformational changes due to solvation.

In the UV spectra of polymers **3d–f** (Figure 3b–d) the n–π^* transitions are located as very weak bands in the range from 300 to 350 nm. The absorption bands of the phenyl group can be recognized as shoulders at about 275 nm. The CD spectrum of polymer **3f** (Figure 3d) clearly reveals the CD bands of the phenyl group, as found in the model compound, and a negative couplet at 320 nm, indicative of a *P* helix. Very remarkably, no negative CD band due to the side-chain induction in the imino chromophore is visible. On the contrary, polymers **3d** and **3e** do show the side-chain bands. The latter bands in **3d** and **3e** probably are of opposite sign, as judged by the intensity difference of the CD spectra, in line with the opposite *R* and *S* absolute configuration of the side chains of the polymers. No clear-cut couplets are present for **3d** and **3e**. However, the CD spectra are rather asymmetric, just as in case of polymers **3a–c**. This asymmetry in the CD spectrum of polymer **3e** is simulated in Figure 3e by the summation of a negative couplet, a negative CD band due to the side-chain induction in the imino chromophore, and a positive phenyl band. Thus, also **3d** and **3e** will have *P*-helical structures. The optical rotation data of polymers **3d–f** are in agreement with these structure assignments: going from monomer or model compound to polymer the molar optical rotation becomes more negative (see Table I, entries **d–f**).

The CD spectrum of polymer **3g** in the region around 300 nm could not be measured due to a very unfavorable $\Delta\epsilon/\epsilon$ ratio (the polymer has a dark brown color). The molar optical rotation of this polymer shows a shift to negative value as compared to the isocyanide monomer (Table I). Assuming the isocyanide to be a correct reference for this polymer, the presence of an excess of *P* helices can be derived.

The UV and CD spectra of polymer **3h** and the corresponding data for model compound **17h** are given in Figure 4 and Table II, respectively. The model compound shows a UV n–π^* absorption band at 247 nm and a single negative Cotton effect at the same wavelength position in the

Table II
UV and CD Data of Model Imines R—N=CH(t-C$_4$H$_9$)[a]

compd	UV		CD
	λ_{max}/nm	ϵ/ (L·mol^{-1}·cm^{-1})	$\Delta\epsilon_{max}$/ (L·mol^{-1}·cm^{-1})
17a	≃220[b,c]	≃100	−4.0[b,c]
17b	≃230[b,c]	≃100	−0.29[b,c]
17e	≃250	d	d
17h	247	94	−1.57

[a] Compound, solvent (concentration in mol·L^{-1}): **17a**, *n*-hexane (2.45×10^{-3}), CHCl$_3$ (2.14×10^{-3}); **17b**, *n*-hexane (3.48×10^{-3}), CHCl$_3$ (5.56×10^{-3}); **17e**, *n*-hexane (3.67×10^{-3}), CHCl$_3$ (2.96×10^{-3}); **17h**, *n*-hexane (7.02×10^{-3}). [b] In chloroform the UV and CD cannot be measured below 245 nm. Down to the latter wavelength the intensities in this solvent are of the same order of magnitude and of the same sign as when *n*-hexane was used as solvent. [c] The bands due to the n–π^* transition of the imino group and the carbonyl group are not completely separated in the UV spectrum. In the CD spectrum, $\Delta\epsilon_{max}$ lies at 235 nm. [d] The band due to the n–π^* transition of the imino group is masked by the phenyl bands. See Figure 3a.

CD. The polymer has an absorption band at 320 nm in the UV spectrum. The CD spectrum reveals a negative band due to the side-chain contribution as well as a positive couplet due to the helical main chain. The latter couplet indicates the presence of an excess of *M* helices in polymer **3h**. A comparison of molar optical rotation values (Table I, entry **h**) leads to the same conclusion, provided imine **17h** is used as model compound. Taking isocyanide **2h** as a reference, the wrong screw sense is predicted. This demonstrates that an isocyanide occasionally is an inadequate model for its polymer (compare also ref 11).

Polymers **3g** and **3h** have side chains from which, in principle, the chirality can be removed by reduction. With (*M*)-(+)-poly(*tert*-butyliminomethylene) as a calibration standard, the chiroptical properties of the "dechiralized" polymers will give information about the excess *P* or *M* screw present in the original polymers. Unfortunately, however, we were not able to get this information, as polymers **3g** and **3h** resisted all reduction methods tried. These methods included catalytic hydrogenations with 10% palladium on carbon, platinum oxide, W-6 Raney nickel, and Rh(PPh$_3$)$_3$Cl (Wilkinson catalyst) and dissolving-metal reductions with lithium in ethylenediamine and sodium in liquid ammonia. Probably, the unsaturated groups in **3g** and **3h** are well protected against reduction by steric hindrance.

The UV and CD spectra of polymer **3i** and its model compound, a low molecular weight polymer sample, **17i** (Table I), are given in Figure 5. In these spectra the pattern of the phenyl group is visible between 250 and 280 nm (compare also Figure 3a). The chirality of the main chain in **3i** is manifested by the positive couplet at 320–420 nm, indicating the presence of an excess of *M* helix. Inspection of Table I (entry **i**) indicates that this *M* helix has a negative contribution to the total optical rotation. In this respect polymer **3i** is different from the other optically active poly(iminomethylenes) studied so far. At the moment we cannot offer an explanation for this deviating behavior.

Control of Screw Sense Formation. The induction of screw sense in polymers of chiral isocyanides may be a thermodynamically controlled process, leading to the thermodynamically most stable helix or a kinetically controlled process governed by the relative energies of the diastereomeric transition states. First we will consider the
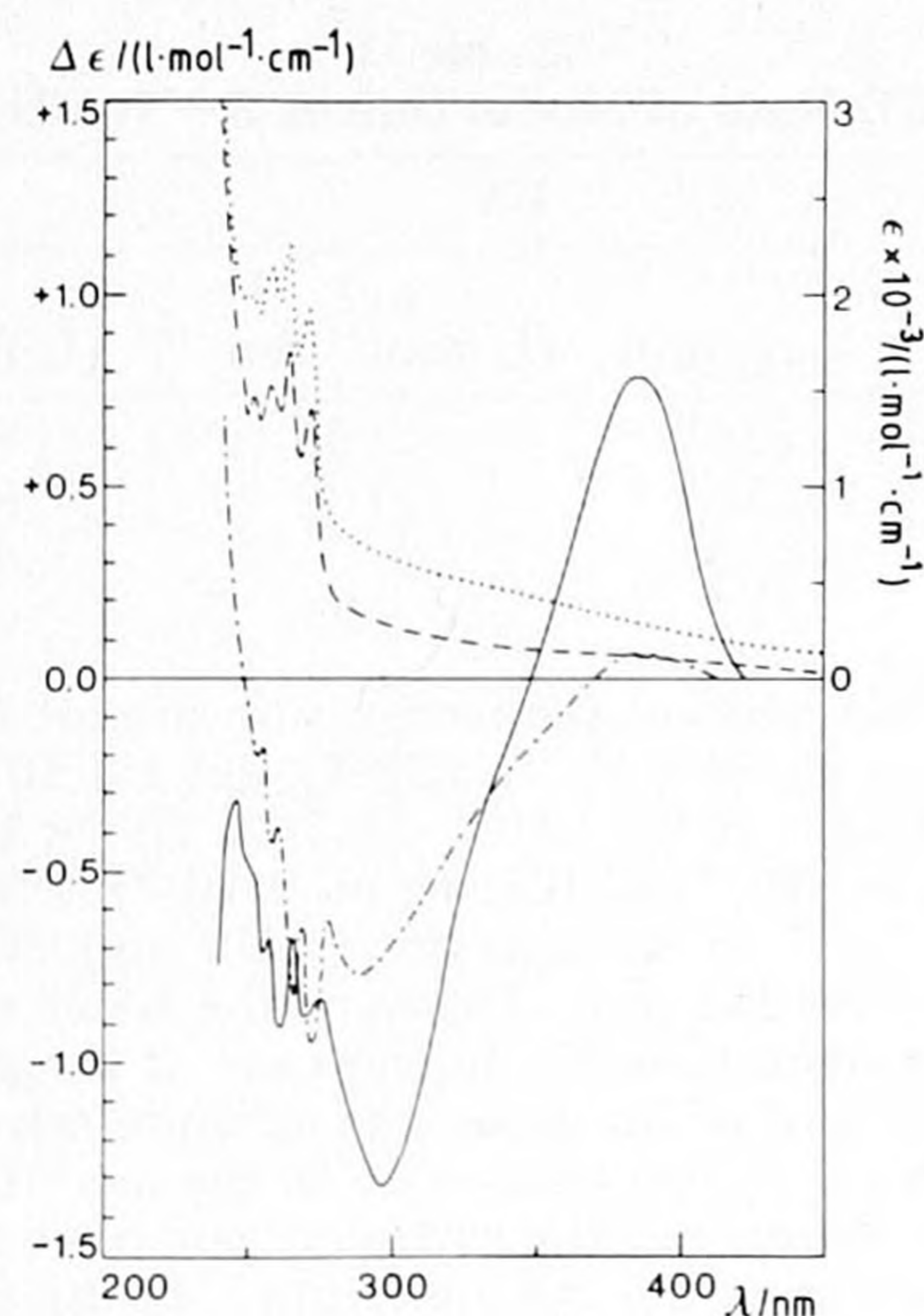
Figure 5. CD (−·−) and UV (···) spectra of model compound 17i and CD (—) and UV (−−−) spectra of polymer 3i in chloroform solution.

Figure 6. Projection of the side chain (SML)C–N= along the C–N= bond in a *P*-helical poly(iminomethylene).

thermodynamically controlled process. The question which screw, *P* or *M*, is the most favorable one for a given chiral side chain R, can be answered by inspecting Figure 6. In this figure a projection along the C–N= bond of a side chain, $R^1R^2R^3C-N=$, of a *P*-helical poly(imino-methylene) is given. The relative steric requirements of the substituents R^1, R^2, and R^3 at the chiral carbon atom are denoted by S (small), M (medium), and L (large), respectively. Poly(iminomethylenes) have four repeating units per helical turn.[7,9] The most severe steric hindrance for a substituent at the chiral carbon atom of repeating
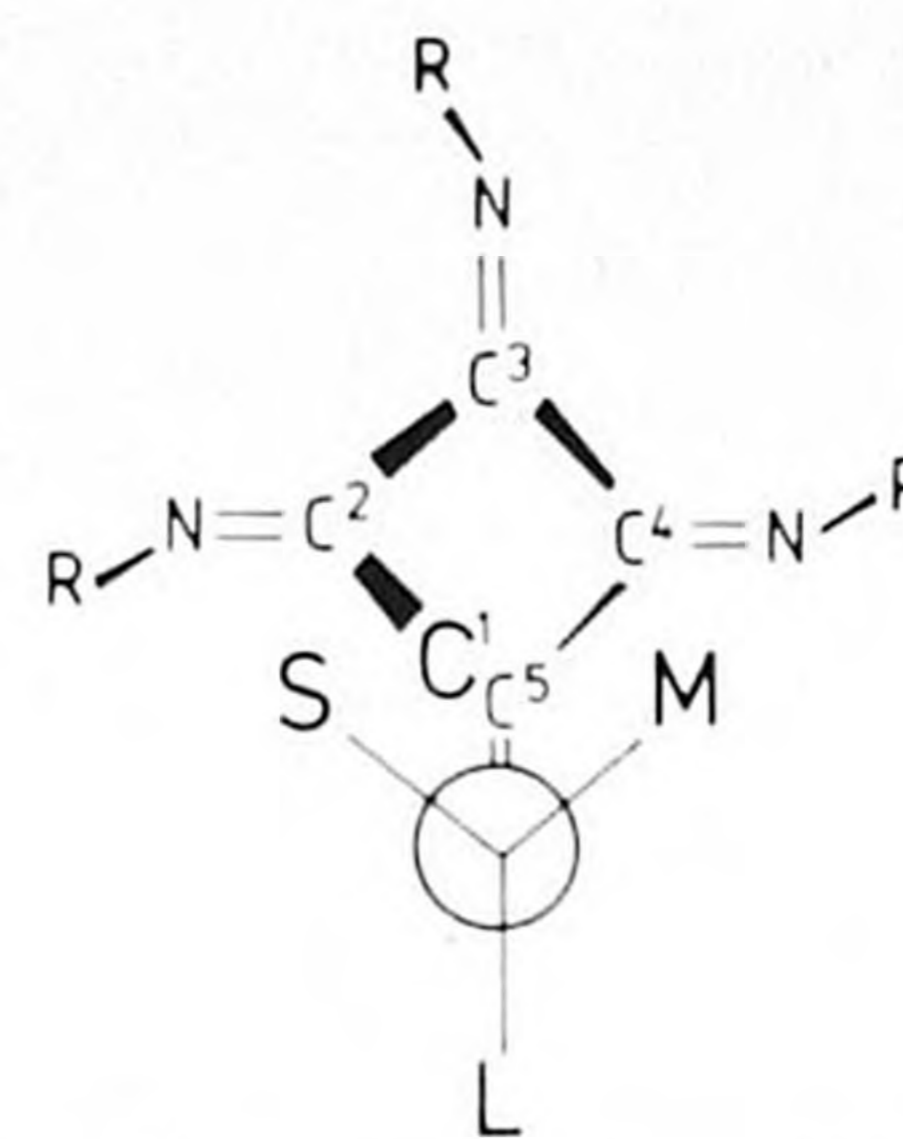
unit C^5 comes from the $R-N=C^2-C^1=N-$ moiety. This moiety is close to and has its C^1 nearly on top of C^5. A lesser but still important hindrance is that with the vicinal $C^4=N$ moiety. The most favorable side-chain position will be that position in which the largest substituent L points away from the helix, while substituents S and M are placed in the direction of C^2 and C^4, respectively. Vice versa one can conclude that an arrangement of substituents as shown in Figure 6 will favor a *P*-helical main chain. In Table III the thermodynamically predicted screw senses are derived by following the procedure outlined above. Also given in Table III are the experimentally determined screw senses. A comparison of the two reveals that there are many disagreements. This result suggests that the induction of screw sense is not a thermodynamically governed process.

We will now consider a kinetically controlled process at the catalyst center. Polymerization of isocyanides by nickel(II) salts proceeds via a sequence of insertion reactions around the nickel center (Scheme V).[6] Reaction starts from the square-planar complex $Ni(CNR)_4^{2+}$. A coordinated isocyanide in the latter complex is easily attacked by a nucleophile X (e.g., Cl$^-$ of nickel chloride) to

Table III
Experimental and Predicted Screw Sense of Poly(iminomethylenes) $(R^1R^2R^3CN=C<)_n$

polymer	R^1, R^2, R^3 [a]	exptl	pred kinetically	pred thermodynamically
3a	H (S), CH$_3$ (L), COOC$_2$H$_5$ (M, Y)	*P*	*P*	*P*
3b	H (S), CH$_3$ (M), CH$_2$O$_2$CCH$_3$ (L, Y)	*P*	*P*	*M*
3c	H (S), *i*-C$_3$H$_7$ (L), CH$_2$O$_2$CCH$_3$ (M, Y)	*P*	*P*	*P*
3d	H (S), CH$_2$O$_2$CCH$_3$ (M, Y), Ph (L, Y)	*P*	*P/M* [b]	*M*
3e	H (S), CH$_3$ (M), Ph (L, Y)	*P*	*P*	*M*
3f	H (S), CH$_3$ (M), CH$_2$Ph (L, Y)	*P*	*P*	*M*
3g	H (S), C$_2$H$_5$ (L), C≡CH (M, Y)	*P*	*P*	*M*
3h	H (S), C$_2$H$_5$ (L), CH=CH$_2$ (M, Y)	*M* [c]	*P*	*P*
3i	H (S), PPh$_2$O (L, Y), CH$_3$ (M) [d]	*M*	*M*	*M*

[a] In parentheses are the relative bulkiness and coordinative property. The substituents R^1, R^2, and R^3 are ranked according to their anticlockwise sequence in Newman projection i. They are numbered according to their relative steric requirements as expressed by the λ-steric parameters (see ref 27); R, λ_R: H, 0.00; CO$_2$C$_2$H$_5$, 0.90; CH$_3$, 1.00; C$_2$H$_5$, 1.05; CH$_2$O$_2$CCH$_3$, ≈1.1; CH$_2$Ph, 1.15; Ph, 1.23; *i*-C$_3$H$_7$, 1.27; PPh$_2$O, >1.27; the steric parameters for CH=CH$_2$ and C≡CH are unknown, but will be <1, with $\lambda_{C≡CH} < \lambda_{CH=CH_2}$ (see ref 28). [b] *P* screw if Ph coordinates to nickel, *M* screw if CH$_2$O$_2$CCH$_3$ coordinates to nickel. [c] In a previous paper[11] we reported a *P* screw for this polymer based on a comparison of optical rotation data (see also text). Both the kinetically and thermodynamically predicted screw sense disagree with the experimental one. At the moment, we cannot give a satisfactory explanation for this result. [d] $R^1R^2R^3$ are the substituents at the chiral β-carbon atom. The kinetically predicted screw sense is derived from the Newman projection ii of **18z** along the =NCH$_2$-CH(CH$_3$)PPh$_2$O bond.

i

ii

Scheme V

18

19

20

18z
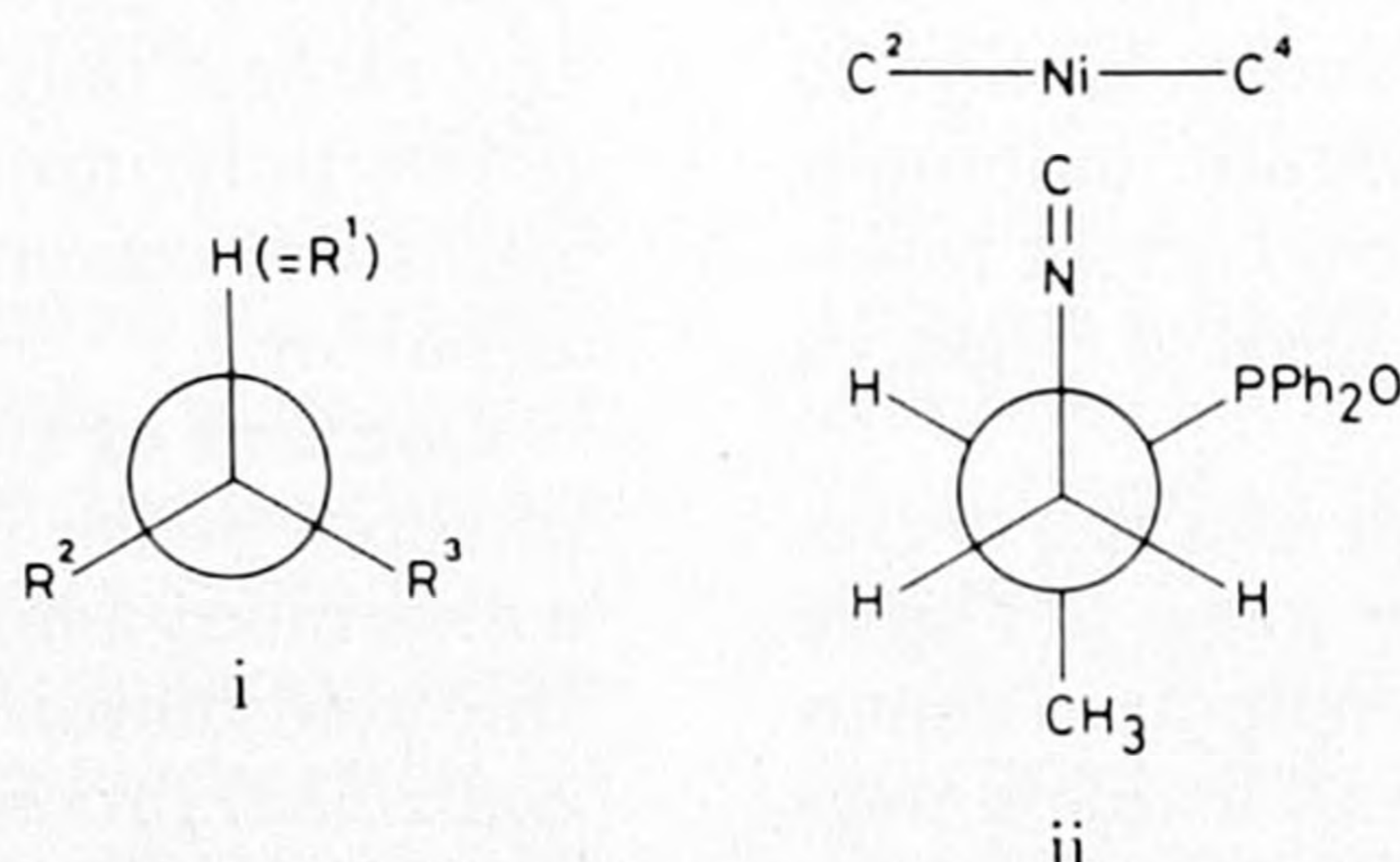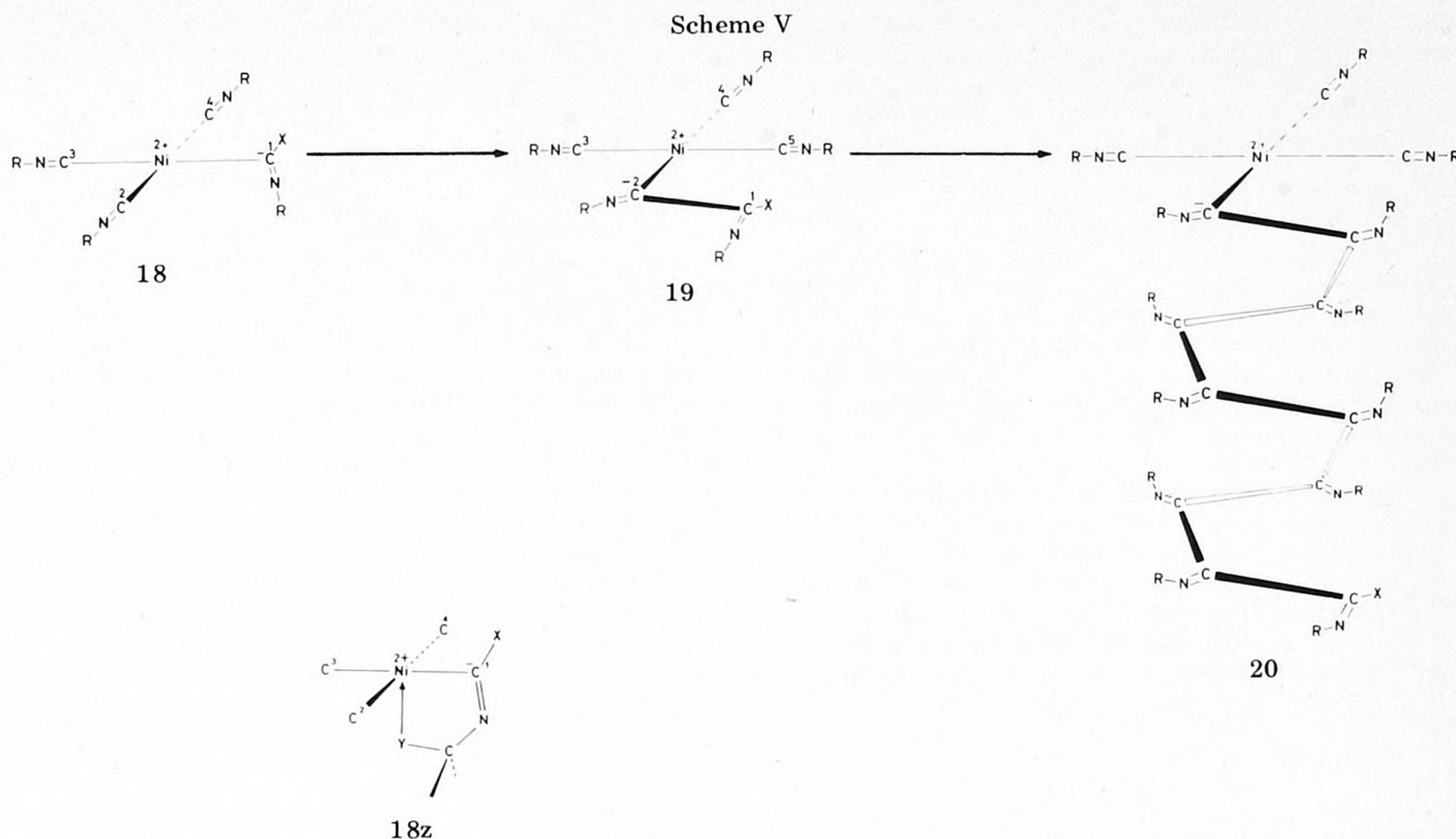
give ion **18**. The plane of the ligand C(X)=NR in **18** is approximately perpendicular to the plane of the isocyanide carbons and nickel, with R either in the E or in the Z position with respect to the nickel center. There is no free rotation around the bond from C^1 to nickel for steric reasons. Carbon atom C^1 has gained in nucleophilicity, allowing it to attack a neighboring ligand. Such an attack is facilitated when a new isocyanide ligand C^5=NR is substituted for C^1(X)=NR. Attack can occur on either C^2 or C^4. In **19** it has occurred on C^2. When the sequence of attacks continues in the direction C$^1 \rightarrow$ C$^2 \rightarrow$ C$^3 \rightarrow$ C^4, a left-handed helix is obtained (**20**). In a similar way the sequence of attacks C$^1 \rightarrow$ C$^4 \rightarrow$ C$^3 \rightarrow$ C^2 will result in a right-handed helix.

In the case of an achiral isocyanide the transition states for attack of C^1 on C^2 and on C^4 are the same. On the contrary, in case of a chiral isocyanide these transition states differ and will depend on the steric interactions between ligands C^1 and C^2, and C^1 and C^4, respectively. With regard to these interactions the E or Z position of –CR^{1}R^{2}R^3 in C^1(X)=NCR^{1}R^{2}R^3 is of interest as well as the relative sizes and arrangement of the substituents R^1, R^2, and R^3 on the chiral carbon atom. It is known from the literature[25] that in metal complexes comparable to **18** as well as in imines, the E/Z ratio varies with temperature, solvent, and substituents. The present ligands C^1(X)=NCR^{1}R^{2}R^3 all contain substituents (denoted by Y) that can interact with the nickel center and thus favor a Z position (**18z**) over an E position. In **18z** Y is coordinated to the nickel center and the remaining substituents at the chiral carbon atom are S and M or L. For a given arrangement of substituents attack by C^1 will preferentially occur on the least hindered side. In **18z** with S pointing backward this is on C^4 and with S pointing to the front this is on C^2. A P screw and an M screw will be formed, respectively. In Table III the kinetically predicted screw senses, based on intermediate **18z**, of polymers **3a–i** are given. In general, these screw senses are in good agreement with experiment. In view of this finding we can say that the induction of screw sense in the polymerization of optically active isocyanides is most likely a process kinetically controlled at the catalyst center.

Experimental Section

Analytical Techniques. Infrared (IR) spectra were recorded on Perkin-Elmer 297 and 283 spectrophotometers. Ultraviolet (UV) spectra were obtained on a Perkin-Elmer 200 spectrophotometer. CD spectra were recorded on a home-built apparatus. This instrument measures the differential absorbance (ΔA) with a sensitivity better than 1×10^{-6}. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. ^{1}H, ^{13}C, and ^{31}P spectra were obtained on a Varian EM 390, a Varian CFT 20, and a Bruker WH 90 instrument, respectively. Chemical shifts (δ) are given in ppm from internal tetramethylsilane or external H$_3$PO$_4$. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under the supervision of W. J. Buis. Melting points were determined on a Mettler FP5/FP51 photoelectric melting point apparatus. Solution viscosity data were obtained with a Cannon-Ubbelohde viscometer. Mass spectra were recorded on an AEI MS-902 spectrometer. Field desorption (FD) mass spectra were obtained with a Varian MAT 711 mass spectrometer with a combined EI/FI/FD ion source and coupled to a spectrosystem MAT 100 data acquisition unit.

***N*-Formyl-L-alanine Ethyl Ester (1a).** L-Alanine (**4j**) was esterified with ethanol and dry HCl, according to a standard procedure.[29,30] Subsequent reaction with formic acid, sodium formate, and acetic anhydride[31] afforded **1a** as a colorless liquid in quantitative yield: $[\alpha]^{21}_{578}$ −69.0° (c 4, ethanol); IR (neat) 1740 (CO), 1675 (NCO) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.24 (s, 1 H, CHO), 7.75 (br, 1 H, NH), 4.61 (m, 1 H, CH), 4.22 (q, 2 H, CH$_2$), 1.43 (d, 3 H, CH$_3$), 1.25 (t, 3 H, CH$_3$).

(*S*)-1-Carbethoxyethyl Isocyanide (2a). This isocyanide was synthesized from **1a** according to a modification of the method of Skorna and Ugi.[19] The procedure was as follows: Into a round-bottomed flask, equipped with a magnetic stirrer and a CO$_2$/acetone reflux condenser kept at −30 °C were brought 4.35 g (30 mmol) of **1a**, 7.05 mL (63.0 mmol) of dry *N*-methylmorpholine, and 50 mL of dry CH$_2$Cl$_2$ as a solvent. At a temperature of −30 to −40 °C, 1.81 mL (15.0 mmol) of diphosgene in 10 mL of dry CH$_2$Cl$_2$ was introduced into the stirred reaction mixture over a period of approximately 2 h. The reaction was followed by TLC (silica gel, CHCl$_3$). The chromatograms were developed with a NiCl$_2$·6H$_2$O solution in ethanol; with this reagent isocyanides give a red-brown spot. In this way it could be determined that the minimum temperature for reaction was between −30 and −40 °C. After reaction was complete (3 h) the cooling

bath was removed, and immediately 25 mL of water was added to the mixture. The still cold organic layer was separated, shaken with 35 mL of an aqueous 7.5% NaHCO₃ solution, again separated, and dried over Na₂SO₄. The crude reaction product was purified by column chromatography (silica gel, CHCl₃): yield 2.86 g (75%); $[\alpha]^{21}_{578}$ +16.7° (c 3.7, chloroform); IR (CCl₄) 1740 (C=O), 2140 (N=C) cm⁻¹; ¹H NMR (CCl₄) δ 4.30 (q, 2 H, CH₂), 4.25 (m, 1 H, CH), 1.65 (d, 3 H, CH₃), 1.37 (t, 3 H, CH₃). In order to check the optical purity of the racemization-sensitive compound **2a** we hydrolyzed a sample with a solution of 0.01 mol/L HCl in water–tetrahydrofuran (1:2 (v/v)). The thus obtained formamide had, after chromatographic purification, almost the same optical rotation value, viz., $[\alpha]^{21}_{578}$ –68.0° (c 1.7, ethanol), as the formamide **1a** from which the isocyanide was prepared. Thus racemization had not occurred during the formation and purification of the isocyanide.

Poly[(S)-(1-carbethoxyethyl)iminomethylene] (3a). Isocyanide **2a** was polymerized with 0.2 mol % of NiCl₂·6H₂O at ambient temperature and without solvent. After 5 days the glassy reaction mixture was dissolved in a small amount of chloroform and added dropwise to an excess of vigorously stirred methanol–water (4:1 (v/v)). The precipitated yellow-colored polymer was collected by filtration, washed with methanol–water, and dried at reduced pressure at 50 °C over KOH: yield 70%; [η] = 0.44 dL/g (toluene, 30.0 °C); $[\alpha]^{22}_{578}$ –280° (c 0.36, chloroform); IR (KBr) 1740 (CO), 1638 (CN) cm⁻¹. Anal. Calcd for C₆H₉NO₂: C, 56.68; H, 7.14; N, 11.02; O, 25.17. Found: C, 56.14; H, 7.22; N, 10.95; O, 25.70.

(S)-2-Aminopropanol (L-Alaninol (5j)). N-Benzoyl-L-alanine and N-benzoyl-L-alanine methyl ester were prepared starting from L-alanine (**4j**) according to standard procedures.[29,30] N-Benzyl-L-alaninol was prepared from the above ester with an excess of LiAlH₄ in boiling diethyl ether.[29,32] After hydrogenolysis in water–ethanol (1:4 (v/v)) at 60 °C, compound **5j** was isolated as its HCl salt in an overall yield of 90%: $[\alpha]^{22}_D$ +19.8° (c 2.5, methanol); ¹H NMR (CD₃OD) δ 4.8 (br, 4 H, NH₃⁺ and OH), 3.5–3.9 (m, 3 H, CH₂ and CH), 1.30 (d, 3 H, CH₃).

(S)-N-Formyl-2-aminopropanol (6j). The N,O-diformylated product was obtained from the HCl salt of **5j** by treatment with formic acid, sodium formate, and acetic anhydride, according to a literature method.[31] The yield of bright yellow syrup was almost quantitative: IR (neat) 1735 (OCHO), 1665 (NCHO) cm⁻¹; in the ¹H NMR (CD₃OD) peaks at δ 8.10 and 8.13 were visible for the N-formyl and the O-formyl protons. The O-formyl group was selectively removed by the following procedure: 30 g (0.229 mol) of syrup was dissolved in 100 mL of 10% aqueous methanol, and 3 g of NaHCO₃ was added. The mixture was stirred and kept at 60 °C for 2 h. Subsequently, the solvent was evaporated under vacuum and the residue was taken up in 100 mL of acetone. After the precipitated salts had been removed by filtration, the acetone was evaporated at reduced pressure. The product was obtained as a yellow syrup in a yield of 90%: IR (neat) 1665 (NCHO) cm⁻¹; the ¹H NMR (CDCl₃) showed in the low-field region a single peak at approximately δ 8.12 (NCHO).

(S)-N-Formyl-O-acetyl-2-aminopropanol (1b). Alcohol **6j** was acetylated by dissolving it in an excess of acetic anhydride with a catalytic amount of pyridine. The mixture was kept at 50 °C during 24 h. The excess of volatile reagents was removed at reduced pressure. Compound **1b** was obtained as a yellow syrup in a quantitative yield: $[\alpha]^{22}_{578}$ –39.9° (c 2.5, CHCl₃); IR (neat) 1735 (OCO), 1675 (NCO) cm⁻¹; ¹H NMR (CDCl₃) δ 8.15 (s, 1 H, CHO), 7.15 (br, 1 H, NH), 4.33 (m, 1 H, CH), 4.04 (m, 2 H, CH₂O), 2.05 (s, 3 H, COCH₃), 1.18 (d, 3 H, CH₃). Another route to **1b** started from a sample of commercially available optically pure (S)-2-aminopropanol. This was converted with an excess of ethyl formate[33] into the (S)-N-formyl-2-aminopropanol and subsequently, with acetic anhydride and pyridine, into compound **1b**. This sample and the sample of which the synthesis is described above had an identical optical rotation.

(S)-O-Acetyl-2-isocyano-1-propanol (2b). This isocyanide was prepared from **1b** as described for the synthesis of **2a**. The reaction temperature was kept between –15 and –20 °C. After distillation **2b** was obtained as a colorless liquid: yield 75%; bp 50 °C (0.02 mm); $[\alpha]^{22}_{578}$ +58.3° (c 3.3, chloroform); IR (CCl₄) 2145 (NC), 1735 (CO) cm⁻¹; ¹H NMR (CCl₄) δ 3.7–4.2 (m, 3 H, CH₂ and CH), 2.08 (s, 3 H, COCH₃), 1.37 (m, 3 H, CH₃).

Poly[(S)-(1-(acetoxymethyl)ethyl)iminomethylene] (3b). Monomer **2b** was polymerized with 0.3 mol % of NiCl₂·6H₂O in methanol. Polymer **3b** was obtained as a yellow solid in a yield of 90%: [η] = 0.42 dL/g (chloroform, 30.00 °C); $[\alpha]^{22}_{578}$ –150° (c 1.2, chloroform); IR (KBr) 1735 (CO), 1630 (CN) cm⁻¹. Anal. Calcd for C₆H₉NO₂: C, 56.68; H, 7.14; N, 11.02; O, 25.17. Found: C, 56.20; H, 6.87; N, 11.08; O, 25.85.

(S)-2-Amino-3-methylbutanol (L-Valinol (5k)). This compound was obtained starting from L-valine (**4k**) as indicated for the synthesis of **5j** and isolated as its HCl salt from methanol–ether: mp 120 °C [lit.[34] mp 117–118 °C]; $[\alpha]^{20}_D$ +14.5° (c 2.0, H₂O) [lit.[34] $[\alpha]^{20}_D$ +14.25° (c 5.5, H₂O)]; ¹H NMR (CD₃OD) δ 4.8 (s, 4 H, NH₃⁺ and OH), 3.5–3.9 (m, 2 H, CH₂), 2.95 (m, 1 H, CHN), 1.96 (m, 1 H, CH), 1.06 and 0.98 (2 d, 6 H, (CH₃)₂C).

(S)-N-Formyl-2-amino-3-methylbutanol (6k). This compound was obtained from **5k** as described for the synthesis of **6j**. It was used directly for the synthesis of **1c**.

(S)-N-Formyl-O-acetyl-2-amino-3-methylbutanol (1c). Alcohol **6k** was acetylated with acetic anhydride and pyridine in quantitative yield. The resulting oil had the following properties: $[\alpha]^{22}_{578}$ –48.6° (c 2.5, chloroform); IR (neat) 1745 (CO), 1670 (NCO) cm⁻¹; ¹H NMR (CDCl₃) δ 7.0–8.5 (m, 2 H, NHCHO), 4.0–4.6 (m, 3 H, CH₂ and CH), 2.05 (s, 3 H, CH₃), 1.9 (m, 1 H, CH), 0.97 (d, 6 H, (CH₃)₂C).

(S)-O-Acetyl-2-isocyano-3-methylbutanol (2c). This isocyanide was obtained from the latter formamide as described for **2a**. The reaction temperature was kept between –20 and –25 °C. After chromatographic purification (silica gel, CHCl₃) the yield was 70% of a colorless liquid: $[\alpha]^{22}_{578}$ +46.8° (c 1.6, chloroform); IR (CHCl₃) 2148 (NC), 1745 (CO) cm⁻¹; ¹H NMR (CDCl₃) δ 4.14 (m, 2 H, CH₂), 3.63 (m, 1 H, CHN), 2.07 (s, 3 H, CH₃), 1.9 (m, 1 H, CH), 1.01 (d, 6 H, (CH₃)₂C).

Poly[(S)-(1-(acetoxymethyl)-2-methylpropyl)iminomethylene] (3c). Monomer **2c** was polymerized with 0.5 mol % of NiCl₂·6H₂O in methanol. The polymer was obtained as a yellow powder: yield 75%; $[\alpha]^{22}_{578}$ –111° (c 0.15, chloroform); IR (KBr) 1741 (CO), 1624 (CN) cm⁻¹.

(R)-2-Amino-2-phenylethanol (5l). This compound was prepared starting from (R)-(-)-α-aminophenylacetic acid (D-phenylglycine (**4l**)). The amino acid was esterified in methanol with dry HCl. The resulting ester was liberated from its HCl salt by dissolving it in an aqueous Na₂CO₃ solution; the free amine was extracted with benzene and dried over Na₂SO₄. After the solvent was evaporated, the residue was dissolved in diethyl ether and added dropwise to an excess of LiAlH₄ in ether. Subsequently, the mixture was refluxed for 2 h. After workup, the desired compound was obtained as light yellow crystals from ether–hexane: yield 65%; mp 76.0–76.5 °C [lit.[35] 77–78 °C]; $[\alpha]^{22}_D$ –26.2° (c 1.0, methanol) [lit.[35] $[\alpha]^{25}_D$ –27.2° (c 9.9, methanol)]; ¹H NMR (CDCl₃) δ 8.32 (s, 5 H, C₆H₅), 3.98 (m, 1 H, CH), 3.35–3.85 (m, 2 H, CH₂), 2.66 (s, 3 H, NH₂ and OH).

(R)-N-Formyl-2-amino-2-phenylethanol (6l). This formamide was synthesized from **5l** by treatment with a 25% excess of ethyl formate:[33] yield 90%; mp 100 °C; $[\alpha]^{22}_{578}$ –149° (c 0.7, methanol); IR (KBr) 1660 (NCO) cm⁻¹.

(R)-N-Formyl-O-acetyl-2-amino-2-phenylethanol (1d). This compound was obtained from **6l** by O-acetylating with acetic anhydride and a catalytic amount of pyridine at 50 °C during 24 h. The product was obtained as white crystals from ether in a yield of 95%: mp 67 °C; $[\alpha]^{22}_{578}$ –89.6° (c 1.0, chloroform); IR (KBr) 1745 (OCO), 1655 (NCO) cm⁻¹; ¹H NMR (CDCl₃) δ 8.15 (s, 1 H, CHO), 7.65 (br, d, 1 H, NH), 7.33 (s, 5 H, C₆H₅), 5.35 (m, 1 H, CH), 4.30 (d, 2 H, CH₂), 1.97 (s, 3 H, CH₃).

(R)-O-Acetyl-2-isocyano-2-phenylethanol (2d). Formamide **1d** was converted into isocyanide **2d** at a reaction temperature of –20 °C as described for the synthesis of **2a**. Column chromatography (silica gel, CHCl₃) of the crude product afforded the pure isocyanide as a colorless liquid: yield 60%; $[\alpha]^{22}_{578}$ –68.5° (c 2.1, CHCl₃); IR (CCl₄) 2138 (NC), 1748 (CO) cm⁻¹; ¹H NMR (CCl₄) δ 7.37 (s, 5 H, C₆H₅), 4.91 (m, 1 H, CH), 4.0–4.3 (m, 2 H, CH₂), 2.02 (s, 3 H, CH₃).

Poly[(R)-(2-acetoxy-1-phenylethyl)iminomethylene] (3d). Monomer **2d** was polymerized with 0.15 mol % of NiCl₂·6H₂O in methanol. The polymer was obtained as a bright yellow powder in a yield of 70%: [η] = 0.076 dL/g (chloroform, 30.00 °C); $[\alpha]^{22}_{578}$ –82° (c 0.5, chloroform); IR (KBr) 1745 (CO), 1622 (CN) cm⁻¹.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40; O, 16.91. Found: C, 68.98; H, 5.92; N, 7.38; O, 17.72.

(S)-N-Formyl-1-phenylethylamine (1e). 1-Phenylethyl-amine was resolved into its optical antipodes by a standard method.[36] The specific optical rotation of the S enantiomer was $[\alpha]^{22}_D$ −38.6° (neat) [lit.[36] $[\alpha]^{29}_D$ −39.4 (neat)]. This amine was N-formylated with a 10% excess of ethyl formate[33] in an almost quantitative yield: mp 46–48 °C [lit.[37] mp 46–47 °C]; $[\alpha]^{22}_D$ −190 (c 1, methanol) [lit.[37] $[\alpha]^{19}_D$ −178° (c 4.25, 96% ethanol)].

(S)-1-Phenylethyl Isocyanide (2e). This isocyanide was synthesized from 1e according to the method of Appel et al.:[20] yield 50%; bp 95–96 °C (16 mm) [lit.[38] bp 93–94 °C (13 mm)]; $[\alpha]^{20}_D$ −40.9° (c 5, methanol) [lit.[39] $[\alpha]^{27}_D$ −35.8° (neat)]; IR (CCl₄) 2140 (NC) cm⁻¹; ¹H NMR (CCl₄) δ 7.30 (s, 5 H, C₆H₅), 4.75 (m, 1 H, CH), 1.59 (m, 3 H, CH₃).

Poly[(S)-(1-phenylethyl)iminomethylene] (3e). Isocyanide 2e was polymerized neat with 0.015 mol% of NiCl·6H₂O at 0–5 °C: yield 90%; [η] = 0.70 dL/g (toluene, 30.00 °C); $[\alpha]^{20}_D$ −350° (c 1, chloroform). Anal. Calcd for C₉H₉N: C, 82.41; H, 6.92; N, 10.68. Found: C, 81.97; H, 7.04; N, 10.12; O, 0.87 (corrected to C + H + N = 100%: C, 82.69; H, 7.10; N, 10.21). Thus the polymer contains a small amount of O; compare ref 10.

(S)-N-Formyl-1-benzylethylamine (1f). This compound was synthesized starting from a sample of optically pure (S)-1-benzylethylamine·¹/₂H₂SO₄ [(S)-amphetamine sulfate], which had $[\alpha]^{20}_D$ +22.5° (c 2, H₂O) [lit.[40] $[\alpha]_D$ +22° (c 8, H₂O)]. The amine was liberated from its salt with an excess of aqueous NaOH solution and subsequently converted into the formamide with a 50% excess of ethyl formate.[33] The product was obtained as a white solid in almost quantitative yield: mp 44–46 °C; $[\alpha]^{22}_{578}$ −17.0° (c 2.0, chloroform); IR (KBr) 1670 (CO) cm⁻¹; ¹H NMR (CCl₄) δ 7.89 (s, 1 H, CHO); 7.5 (br, d, 1 H, NH), 7.13 (s, 5 H, C₆H₅), 4.18 (m, 1 H, CH), 2.4–2.9 (m, 2 H, CH₂), 1.07 (d, 3 H, CH₃).

(S)-1-Benzylethyl Isocyanide (2f). Formamide 1f was converted into the isocyanide according to a modified literature method.[21] Instead of triethylamine, N-methylmorpholine was used as the base. The reaction temperature was kept at −10 °C. The isocyanide was obtained as a colorless liquid in 55% yield after column chromatography (silica gel, CHCl₃): bp 46 °C (0.1 mm); $[\alpha]^{22}_{578}$ +48.7° (c 3.5, chloroform); IR (CCl₄) 2141 (NC) cm⁻¹; ¹H NMR (CCl₄) δ 7.20 (s, 5 H, C₆H₅), 3.72 (m, 1 H, CH), 2.79 (m, 2 H, CH₂), 1.28 (m, 3 H, CH₃).

Poly[(S)-(1-benzylethyl)iminomethylene] (3f). Isocyanide 2f was polymerized with 0.1 mol% of NiCl₂·6H₂O in methanol. After 48 h the methanol was evaporated at reduced pressure. A yellow solid (95%) resulted. The product was sparingly soluble in chloroform and tetrahydrofuran. The soluble fraction had a specific optical rotation of $[\alpha]^{22}_{578}$ +15° (c 0.4, chloroform); IR (KBr) 1631 (CN) cm⁻¹. Anal. Calcd for C₁₀H₁₁N: C,, 82.72; H, 7.64; N, 9.65. Found: C, 81.84; H, 7.69; N, 9.59; O, 0.88 (corrected to C + H + N = 100%: C, 82.58; H, 7.76; N, 9.67 (compare also 3e)).

1-Ethyl-2-propynol (7). This alcohol was prepared from sodium acetylide and propionaldehyde in liquid ammonia in an approximately 50% yield [lit.[41] yield 50%]; ¹H NMR (CCl₄) δ 4.25 (m, 1 H, CH), 4.00 (s, 1 H, OH), 2.39 (d, 1 H, ≡CH), 1.65 (m, 2 H, CH₂), 1.00 (t, 3 H, CH₃).

1-Ethyl-2-propynyl p-Toluenesulfonate (8). This tosylate was made according to a literature method[42] in a yield of 95%: mp 41 °C; ¹H NMR (CCl₄) δ 7.77 and 7.30 (2 d, 4 H, C₆H₄), 4.96 (m, 1 H, CH), 2.46 (d, 1 H, ≡CH), 2.40 (s, 3 H, ArCH₃), 1.78 (m, 2 H, CH₂), 0.95 (t, 3 H, CH₃).

1-Ethyl-2-propynylamine (9). Under a N₂ atmosphere 220 g (0.8 mol) of the powdered tosylate 8 was brought into a 1-L autoclave that was cooled to −40 °C. Then 0.75 L of liquid ammonia was introduced, and the autoclave was closed. The mixture was shaken for 24 h at room temperature and, subsequently, the excess of ammonia was allowed to evaporate. The reaction product was distilled directly from the autoclave into a cold trap by applying a vacuum. After distillation the pure amine was obtained in a 85% yield: bp 103–104 °C [lit.[14] bp 104 °C]; ¹H NMR (CCl₄) δ 3.38 (m, 1 H, CH), 2.18 (d, 1 H, ≡CH), 1.50 (m, 2 H, CH₂), 1.40 (s, 2 H, NH₂), 0.98 (t, 3 H, CH₃). The optically active amine 9 was obtained by fractional crystallization of the bitartrate in water. The procedure was as follows: 124.5 g (1.5 mol) of the amine was added dropwise to a cooled solution

of 225 g (1.5 mol) of (+)-tartaric acid in 1000 mL of water. The mixture was cooled to 0–5 °C. After a few days the precipitated crystals were collected by filtration and dried under vacuum over P₂O₅. The filtrate was concentrated, and the crystallization was repeated. The first fractions, with a combined weight of 122 g, had a melting point that varied between 182 and 155 °C. The specific optical rotations of these fractions were $[\alpha]^{25}_{578}$ +24 to +23.5° (c 4, H₂O). The residual fractions of crystals, with a combined weight of 227 g, had melting points lower than 110 °C and $[\alpha]^{25}_{578}$ <+16.5° (c 4, H₂O). The first, combined fractions (122 g) were subjected to a second fractional crystallization. The initial amount of solvent was 550 mL of water. The procedure described above was followed. Fractions with a total weight of 110 g showed a melting point of 183 °C [lit.[14] 186–187 °C] and had a specific optical rotation $[\alpha]^{25}_{578}$ of +24.1° and $[\alpha]^{25}_D$ of +23.3° (c 2, H₂O) [lit.[14] $[\alpha]^{22}_D$ +23.3° (c 1, H₂O)]. The (S)-amine was liberated from the bitartrate with a 30% excess of aqueous sodium hydroxide and distilled from powdered K₂CO₃: yield 35.7 g (0.43 mol) of a colorless liquid; bp 104 °C; remarkably, the optical rotation (and Cotton effect) changed sign when the pure sample was dissolved in ethanol: $[\alpha]^{20}_D$ −15.0° (neat, d^{20} 0.816 g/mL), $[\alpha]^{20}_D$ +14.4° (c 1.2, ethanol) [lit.[14] $[\alpha]^{22}_D$ −20.9° (neat, d^{22} 0.813 g/mL, $[\alpha]^{22}_D$ +14.4° (c 1.0, ethanol)].

(S)-N-Formyl-1-ethyl-2-propynylamine (1g). The formamide was obtained in almost quantitative yield from the amine by a literature method:[31] $[\alpha]^{22}_{578}$ −132° (c 20, CCl₄); IR (CCl₄) 1660 (CO) cm⁻¹; ¹H NMR (CCl₄) δ 8.12 (s, 1 H, CHO), 8.1 (br, 1 H, NH), 4.63 (m, 1 H, CH), 2.28 (d, 1 H, ≡CH), 1.70 (m, 2 H, CH₂), 1.02 (t, 3 H, CH₃).

(S)-1-Ethyl-2-propynyl Isocyanide (2g). This compound was prepared from 1g in a yield of 50% according to a standard procedure:[21] $[\alpha]^{22}_{578}$ −12.8° (neat, d^{22} 0.834 g/mL); IR (CCl₄) 3300, 650 (CCH), 2140 (NC) cm⁻¹; ¹H NMR (CCl₄) δ 4.37 (m, 1 H, CH), 2.50 (d, 1 H, ≡CH), 1.90 (m, 2 H, CH₂), 1.12 (t, 3 H, CH₃). The colorless liquid became dark on standing at room temperature or in a refrigerator at −20 °C under a N₂ atmosphere.

Poly[(S)-(1-ethyl-2-propynyl)iminomethylene] (3g). Isocyanide 2g was polymerized with 0.3 mol% of NiCl₂·6H₂O in methanol. After 24 h the reaction mixture was concentrated under vacuum. The residual solid was dissolved in chloroform, washed with water, dried over MgSO₄, and concentrated to a small volume. The polymer was obtained as a static brown solid after precipitation in pentane: yield 90%; $[\alpha]^{22}_{578}$ −110 ± 10° (c 0.005, chloroform); IR (KBr) 3300, 650 (CCH), 1650–1600 (br, CN) cm⁻¹; the ¹H NMR (CDCl₃) gave only broad signals in the region 0.5–5.0 ppm. Anal. Calcd for C₆H₇N: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.70; H, 7.02; N, 15.27. On exposure to air at room temperature the polymer slowly takes up oxygen (compare also 3e).

(S)-1-Ethyl-2-propynylamine (10). A solution of 12.5 g (0.15 mol) of optically pure (S)-1-ethyl-2-propynylamine, (S)-9, in 300 mL of ether, 700 mg of a deactivated Lindlar catalyst,[15] and 3 g of quinoline was brought into a H₂ atmosphere. The mixture was stirred and the hydrogen uptake was followed. When the theoretical amount of H₂ was consumed, the rate of the gas consumption decreased. Subsequently, stirring was stopped and the volatile compounds were distilled into a cold trap (CO₂/ acetone). On cooling, dry HCl gas was led through the distillate. The precipitated white amine hydrochloride salt was collected and dried. The yield amounted to 17.2 g (95%): mp 192–194 °C [lit.[43] mp 194–195 °C]; $[\alpha]^{20}_D$ +21.6° (c 2.5, methanol) [lit.[43] $[\alpha]^{20}_D$ +21.1° (c 1.1, ethanol)]. A sample of the amine was liberated from its salt by treating it with an excess of aqueous KOH solution and, subsequently, by extraction with CCl₄. The solution was dried over Na₂SO₄; ¹H NMR (CCl₄) δ 5.50–5.90 (m, 1 H, =CH), 4.85–5.20 (m, 2 H, =CH₂), 3.13 (m, 1 H, CH), 1.35 (m, 2 H, CH₂), 1.20 (s, 2 H, NH₂), 0.90 (t, 3 H, CH₃).

(S)-N-Formyl-1-ethyl-2-propenylamine (1h). This form-amide was obtained from the HCl salt of 10 with sodium formate, formic acid, and acetic anhydride:[31] yield almost 100% of light yellow oil; $[\alpha]^{20}_{578}$ −24.1° (c 2.4, methanol); IR (neat) 3080, 990, 925 (CH=CH₂), 1650–1690 (CO and CH=CH₂) cm⁻¹; ¹H NMR (CCl₄) δ 7.5–8.2 (br, 1 H, NH), 8.1 (s, 1 H, CHO), 5.6–6.0 (m, 1 H, =CH), 5.0–5.3 (m, 2 H, =CH₂), 4.34 (m, 1 H, CH), 1.53 (m, 2 H, CH₂), 0.92 (t, 3 H, CH₃).

(S)-1-Ethyl-2-propenyl Isocyanide (2h). This isocyanide was obtained from 1h in 70% yield according to a literature

method:[21] $[\alpha]^{20}_{578}$ +95° (neat and also *c* 1, methanol); IR (CCl$_4$) 3090, 1655, 990, 925 (CH=CH$_2$), 2141 (NC) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 5.55–5.95 (m, 1 H, =CH), 5.2–5.5 (m, 2 H, =CH$_2$), 4.10 (m, 1 H, CH), 1.65 (m, 2 H, CH$_2$), 1.02 (t, 3 H, CH$_3$).

Poly[(S)-(1-ethyl-2-propenyl)iminomethylene] (3h). Isocyanide **2h** was polymerized with 0.4 mol % of NiCl$_2$·6H$_2$O in methanol. The yellow, static polymer was obtained in 80% yield: [η] = 0.064 dL/g (chloroform, 30.00 °C), $[\alpha]^{20}_{578}$ +29° (*c* 0.2, chloroform); IR (KBr) 3090, 1659, 990, 925 (CH=CH$_2$), 1641 (CN) cm^{-1}. Anal. Calcd for C$_6$H$_9$N: C, 75.74; H, 9.53; N, 14.72. Found: C, 75.51; H, 9.57; N, 14.92. On exposure to air at room temperature the polymer slowly takes up oxygen (compare also **3e**).

(S)-N,N-Dibenzyl-2-aminopropanol (L-N,N-Dibenzylalaninol (11)). L-Alanine was esterified with methanol and dry HCl gas.[29] The amino acid ester was dibenzylated by stirring with 2.1 equiv of benzyl bromide and 5 equiv of solid Na$_2$CO$_3$ in CH$_3$CN during 1 h at room temperature. The salts were filtered off, and the solvent was evaporated under vacuum. After distillation L-N,N-dibenzylalanine methyl ester was obtained in a yield of 90%: bp 140–150 °C (0.005 mm); $[\alpha]^{22}_{D}$ −110.8° (*c* 1.8, chloroform); ^{1}H NMR (CDCl$_3$) δ 7.3 (m, 10 H, aromatic H), 3.2–3.9 (m, 5 H, NCH$_2$, CH), 3.61 (s, 3 H, OCH$_3$), 1.25 (d, 3 H, CH$_3$). The latter ester was reduced with an excess of LiAlH$_4$ in THF to give **11** in a yield of 95%: bp 160 °C (0.001 mm); $[\alpha]^{22}_{D}$ +86.9° (*c* 1.4, chloroform); ^{1}H NMR (CDCl$_3$) δ 7.3 (m, 10 H, aromatic H), 3.31 and 3.79 (J_{gem} = 13.2 Hz, 2 d, 4 H, NCH$_2$), 3.25 and 3.48 (*J* = 5.1 and 9.1 Hz, J_{gem} = 13.5 Hz, 2 H, CH$_2$O), 3.1 (s, 1 H, OH), 3.0 (m, 1 H, CH), 0.91 (*J* = 6.8 Hz, d, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 139.63, 129.17, 128.69, 127.41 (aromatic C), 63.07 (CH), 54.47 (CH$_2$O), 53.25 (CH$_2$N), 9.08 (CH$_3$).

(R)-N,N-Dibenzyl-2-chloro-1-propanamine (12). This compound was obtained from **11** by treatment with 1.2 equiv of *p*-toluenesulfonyl chloride and N-methylimidazole in chloroform at 0–20 °C. After 15 h the chloroform solution was washed four times with 5% aqueous Na$_2$CO$_3$ and twice with H$_2$O and dried over Na$_2$SO$_4$. After evaporation of the solvent, **12** was obtained in quantitative yield: mp 47 °C; M$^+$ *m/e* 273; $[\alpha]^{22}_{D}$ +19.3 (*c* 0.8, chloroform); ^{1}H NMR (CDCl$_3$) δ 7.35 (m, 10 H, aromatic H), 4.0 (*J* = 6.7 Hz, m, 1 H, HCCl), 3.55 and 3.74 (J_{gem} = 13.5 Hz, 2 d, 4 H, CH$_2$Ph), 2.69 and 2.74 (*J* = 7.5 and 6.3 Hz, J_{gem} = 13.5 Hz, 2 H, CH$_2$N), 1.40 (*J* = 6.6 Hz, d, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 138.94, 128.78, 128.12, 126.97 (aromatic C), 61.89 (CH$_2$N), 59.00 (CH$_2$Ph), 55.34 (HCCl), 22.98 (CH$_3$). Anal. Calcd for C$_{17}$H$_{20}$NCl: C, 74.57; H, 7.36; N, 5.12; Cl, 12.95. Found: C, 74.50; H, 7.32; N, 5.16; Cl, 13.01. Compound **12** was also synthesized from **11** in 70% yield using HCl/SOCl$_2$ in chloroform.[44]

(R)-N,N-Dibenzyl-2-(diphenylphosphinyl)propylamine (13). To a solution of 17 g (0.06 mol) of **12** in 100 mL of THF at 0 °C was slowly added a solution of 1.3 equiv (0.08 mol) of Ph$_2$PLi in 50 mL of THF. The latter solution was made from Ph$_2$PCl and lithium in THF at 20 °C by stirring the reactants for 10 h. After the addition of the Ph$_2$PLi the reaction mixture was heated to 50 °C during 2 h. Subsequently, the mixture was stirred for another 15 h at room temperature.[45] Ether and saturated ammonium chloride solution were added to the THF solution. The organic layer was washed twice with saturated NH$_4$Cl, and the solvent was removed under vacuum. The phosphine was obtained as its HCl salt after crystallization of the crude product from a mixture of methanol, concentrated HCl, and water (15:2:5 (v/v)): yield 90%; $[\alpha]^{22}_{D}$ −89.5° (*c* 1.2, chloroform). A sample was liberated from its HCl salt by treatment with KOH in ethanol. The ethanol was removed under vacuum and the residue was dissolved in THF. After washing and drying, the THF was removed and the resulting phosphine was crystallized from ethanol: $[\alpha]^{22}_{D}$ −75.6° (*c* 0.16, benzene); ^{1}H NMR (C$_6$D$_6$) δ 7.3 (m, 20 H, aromatic H), 3.12 and 3.65 (J_{gem} = 14.3 Hz, 2 d, 4 H, CH$_2$Ph), 2.5 (m, 3 H, CHCH$_2$N), 1.13 (*J* = 6 Hz, ^3J(P–H) = 13.4 Hz, dd, 3 H, CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 139.97, 129.24, 126.78 (aromatic C of Bn), 138.01, 137.66, 134.14, 133.88, 128.75, 128.42, 126.39, 126.01 (aromatic C of PPh$_2$), 59.27 (CH$_2$ of Bn), 57.87 (^2J(C–P) = 26 Hz, CH$_2$N), 29.56 (^1J(C–P) = −11.4 Hz, PCH), 15.62 (^2J(C–P) = 13.6 Hz, CH$_3$), the off-resonance spectrum confirmed this assignment; ^{31}P NMR (C$_6$D$_6$) δ −5.6.

The phosphine hydrochloride was converted into the phosphine oxide hydrochloride with 1.1 equiv of H$_2$O$_2$ in ethanol at 0 °C. The product was crystallized from ethanol; $[\alpha]^{22}_{D}$ −26.6° (*c* 0.7,

chloroform). The amine was liberated from its HCl salt by treatment of a chloroform solution of this compound with NH$_3$ gas. Compound **13** had the following: ^{1}H NMR (CDCl$_3$) δ 7.2–7.7 (m, 20 H, aromatic H), 3.3 and 3.7 (J_{gem} = 13.8 Hz, 2 d, 4 H, CH$_2$Ar), 2.3–2.8 (m, 3 H, CHCH$_2$N), 1.15 (*J* = 6.5 Hz, ^3J(P–H) = 17 Hz, dd, 3 H, CH$_3$); ^{31}P NMR (C$_6$D$_6$–EtOH) δ +31.0.

(R)-2-(Diphenylphosphinyl)propylamine (14). This amine was obtained after debenzylation of **13**·HCl in acidified ethanol using Pd/C as a catalyst.[15] The product was purified by column chromatography over silica gel using CHCl$_3$ and CHCl$_3$–CH$_3$OH (5:1 (v/v)) as eluents: $[\alpha]^{22}_{D}$ +28.0 (*c* 0.7, chloroform); ^{1}H NMR (CDCl$_3$) δ 7.5–8 (m, 10 H, aromatic H), 3.0 (m, 2 H, CH$_2$N), 2.5 (m, 1 H, CHP), 1.83 (s, 2 H, NH$_2$), 1.18 (m, 3 H, CH$_3$).

(R)-N-Formyl-2-(diphenylphosphinyl)propylamine (1i). This compound was obtained in 94% yield from **14** and formic acid in benzene by azeotropic distillation. The formamide was purified by column chromatography: $[\alpha]^{22}_{D}$ +7.7° (*c* 0.7, chloroform); IR (KBr) 1860 (CO), 1440 (PPh) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.1 (s, 1 H, CHO), 7.6–8.0 (m, 10 H, aromatic H), 7.5 (br, 1 H, NH), 3.0–4.0 (m, 2 H, CH$_2$), 2.8 (m, 1 H, CHP), 1.15 (m, 3 H, CH$_3$).

(R)-2-(Diphenylphosphinyl)propyl Isocyanide (2i). Isocyanide **2i** was prepared from **1i** using POCl$_3$ and N-methylmorpholine in CH$_2$Cl$_2$ as solvent.[21] The temperature of the reaction mixture was kept below −20 °C. After workup the isocyanide was purified by column chromatography (silica gel, CHCl$_3$–CH$_3$OH (20:1 (v/v)) and subsequently crystallized from chloroform–*n*-hexane: yield 75%; mp 105.5–106.3 °C; $[\alpha]^{22}_{578}$ +13.1° (*c* 0.6, chloroform); IR (KBr) 2145 (NC), 1438 (PPh) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.5–7.9 (m, 10 H, aromatic H), 3.5 (m, 2 H, CH$_2$), 2.8 (m, 1 H, CHP), 1.35 (m, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 132.32, 132.27 130.94, 130.75, 129.11, 128.98 (aromatic C), 43.36 (CH$_2$N), 33.42 (CHP), 11.12 (CH$_3$), no signal for the isocyano carbon atom was observed; ^{31}P NMR (C$_6$D$_6$–THF) δ +28.6.

Poly[(R)-(2-(diphenylphosphinyl)propyl)iminomethylene] (3i and 17i). Isocyanide **2i** was polymerized with 0.5 mol % of NiCl$_2$·6H$_2$O in ethanol. The polymer was isolated by centrifugation, washed with cyclohexane and EtOH–H$_2$O, respectively, and dried under vacuum: yield 90%; $[\alpha]^{20}_{578}$ −338° (*c* 0.3, chloroform); IR (KBr) 1630 (CN) cm^{-1}; ^{31}P NMR (CDCl$_3$–THF) δ +34.4 ($\Delta\nu_{1/2}$ = 110 Hz). Anal. Calcd for C$_{16}$H$_{16}$NPO·1/2(C$_2$H$_5$OH): C, 69.85; H, 6.55; N, 4.79; P, 10.59; O, 8.21. Found: C, 70.41; H, 6.43; N, 4.61; P, 10.61; O, 7.94. The polymer has a low solubility in organic solvents, probably due to its high molecular weight. A low molecular weight, soluble product (**17i**) was obtained by reacting isocyanide **2i** with 3 mol % of NiCl$_2$·6H$_2$O in ethanol: $[\alpha]^{22}_{578}$ −87.0° (*c* 0.2, chloroform); IR (KBr) 1630 (CN), 1439 (PPh) cm^{-1}; the FD mass spectrum reveals a major peak at 1078 (tetramer, H(CNC$_{15}$H$_{16}$PO)$_4$H).

N-Neopentylidene-L-alanine Ethyl Ester (17a). This compound was synthesized from pivaldehyde and L-alanine ethyl ester according to a procedure described in the literature:[46,47] bp 92 °C (30 mm); $[\alpha]^{22}_{578}$ −94.5° (*c* 3.0, chloroform) and $[\alpha]^{22}_{578}$ −135° (*c* 3.0, hexane); IR (neat) 1745 (CO), 1666 (CN) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.53 (s, 1 H, =CH), 4.10 (q, 2 H, CH$_2$), 3.75 (q, 1 H, CHN), 1.32 (d, 3 H, CH$_3$), 1.23 (t, 3 H, CH$_3$), 1.06 (s, 9 H, *t*-C$_4$H$_9$).

(S)-N-Neopentylidene-O-acetyl-2-aminopropanol (17b). (S)-2-Aminopropanol hydrochloride (L-alaninol hydrochloride, **5j**·HCl) was O-acetylated with acetic anhydride. The free amine was generated in situ with triethylamine and reacted with an excess of pivaldehyde in the presence of molecular sieve at 0 °C. The yield was 70%: bp 86 °C (20 mm); $[\alpha]^{22}_{578}$ +7.7° (*c* 2.3, chloroform) and $[\alpha]^{22}_{578}$ +20.7° (*c* 3.0, hexane); IR (neat) 1745 (CO), 1667 (CN) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.50 (s, 1 H, =CH), 3.94 (m, 2 H, CH$_2$), 3.25 (m, 1 H, CHN), 2.03 (s, 3 H, COCH$_3$), 1.07 (d, 3 H, CH$_3$), 1.04 (s, 9 H, *t*-C$_4$H$_9$).

(S)-N-Neopentylidene-1-phenylethylamine (17e). This compound was synthesized from (S)-1-phenylethylamine and pivaldehyde. The imine had the following properties: bp 99–100 °C (15 mm); $[\alpha]^{22}_{578}$ −70.3° (*c* 2.3, chloroform); IR (neat) 1666 (CN) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.54 (s, 1 H, =CH), 7.2 (m, 5 H, C$_6$H$_5$), 4.15 (q, 1 H, CHN), 1.35 (d, 3 H, CH$_3$), 1.02 (s, 9 H, *t*-C$_4$H$_9$).

(S)-N-Neopentylidene-1-ethyl-2-propenylamine (17h). This compound was synthesized from **10** as indicated for the synthesis of **17a**: bp 48 °C (18 mm); $[\alpha]^{22}_{578}$ +4.7° (*c* 1.0, chloroform) and $[\alpha]^{22}_{578}$ +8.4° (*c* 1.8, hexane); IR (neat) 1668 (CN) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.53 (s, 1 H, N=CH), 5.6–6.1 (m, 1 H,

C=CH), 4.8–5.1 (m, 2 H, =CH$_2$), 3.27 (q, 1 H, CHN), 1.50 (m, 2 H, CH$_2$), 1.02 (s, 9 H, *t*-C$_4$H$_9$), 0.87 (t, 3 H, CH$_3$).

Registry No. L-**1a**, 21683-14-7; (*S*)-**1b**, 87281-01-4; (*S*)-**1b** (SRU), 68810-71-9; (*S*)-**1c**, 87281-02-5; (*R*)-**1d**, 87281-05-8; (*S*)-**1f**, 15547-39-4; (*S*)-**1g**, 87305-63-3; (*S*)-**1h**, 87281-07-0; (*R*)-**1i**, 87281-11-6; (*S*)-**2a**, 68778-13-2; (*S*)-**2a** (homopolymer), 68778-14-3; (*S*)-**2b**, 68794-84-3; (*S*)-**2b** (homopolymer), 68805-52-7; (*S*)-**2c**, 87281-03-6; (*S*)-**2c** (homopolymer), 87281-23-0; (*R*)-**2d**, 87281-06-9; (*R*)-**2d** (homopolymer), 87281-24-1; (*S*)-**2e**, 21872-32-2; (*S*)-**2e** (homopolymer), 26714-26-1; (*S*)-**2f**, 68778-11-0; (*S*)-**2f** (homopolymer), 68778-12-1; (*S*)-**2g**, 68778-40-5; (*S*)-**2g** (homopolymer), 68778-41-6; (*S*)-**2h**, 68778-38-1; (*S*)-**2h** (homopolymer), 68778-39-2; (*R*)-**2i**, 87281-12-7; (*R*)-**2i** (homopolymer), 87281-25-2; (*S*)-**3a**, 68810-70-8; (*S*)-**3c**, 87281-20-7; (*R*)-**3d**, 87281-21-8; (*S*)-**3e**, 68810-68-4; (*S*)-**3f**, 68810-69-5; (*S*)-**3g**, 68810-67-3; (*S*)-**3h**, 68824-01-1; (*R*)-**3i**, 87281-22-9; (*S*)-**5j**, 2749-11-3; (*S*)-**6j**, 40916-85-6; (*R*)-**6l**, 87281-04-7; (*S*)-**11**, 60479-65-4; (*R*)-**12**, 87281-08-1; (*R*)-**13**, 87281-09-2; (*R*)-**13**·HCl, 87281-19-4; (*R*)-**14**, 87281-10-5; L-**17a**, 3417-93-4; (*S*)-**17b**, 87281-13-8; (*S*)-**17e**, 33978-37-9; (*S*)-**17h**, 87281-14-9; (*S*)-**17i**, 87281-15-0; NiCl$_2$, 7718-54-9; L-*N*,*N*-dibenzylalanine methyl ester, 87281-16-1; (*R*)-*N*,*N*-dibenzyl-2-(diphenylphosphino)propylamine hydrochloride, 87281-17-2; (*R*)-*N*,*N*-dibenzyl-2-(diphenylphosphino)propylamine, 87281-18-3.

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