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Oligomerization of Vinyl Monomers. 12. Anionic Oligomerization of 4-Isopropenylpyridine. Preparation and ^{1}H-NMR Spectroscopic Analysis of Stereoisomeric Oligomers

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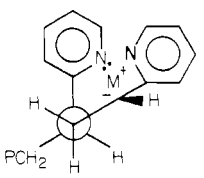
ABSTRACT: Living anionic oligomerization of 4-isopropenylpyridine (4-IP) was carried out by addition of 4-IP monomer to a THF solution of the lithium salt of 2-(4-pyridyl)propane at −78 °C, followed by termination with methyl iodide at the same temperature. The resulting oligomers from the dimer to the hexamers were separated by preparative medium-pressure liquid chromatography, and their structure was determined by ^{1}H and ^{13}C NMR. Syndiotactic-like oligomers, and other minor stereoisomers such as the meso tetramer and the heterotactic pentamer, were shown to be present. The stereoselectivity of monomer addition to the trimeric anion was estimated to be 90% racemic. The 4-IP polymer prepared under similar conditions was also found to be mostly syndiotactic.

Introduction

We recently reported that the anionic stereoregular oligomerization of 2-isopropenylpyridine (2-IP) in the presence of Li ion in THF gives rise to highly syndiotactic oligomers.[2] These results were in sharp contrast to those reported for the oligomerization of the analogous 2-vinylpyridine, where predominantly isotactic oligomers were found.[3] In the latter case, the stereochemistry was shown to be consistent with intramolecular coordination of metal (Li or Na) ion with the penultimate pyridine nitrogen (as shown in 1). For the case of 2-IP, such a



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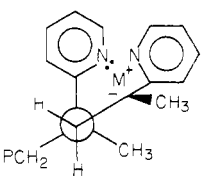

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chelate is less likely due to steric restraints in the oligomer chain. It is therefore possible that the stereochemistry may be dominated by steric and/or dipolar effects. In order to probe these possibilities, the stereochemistry of oligomerization of 4-IP is of interest. Domination of steric effects would ensure a stereochemistry similar to that of 2-IP, whereas the operation of dipolar effects or intramolecular chelation by the 2-pyridine group (as shown in **2**) would give rise to differences in oligomerization stereochemistry of the two monomers.

Experimental Section

Preparation of 4-Isopropenylpyridine (4-IP). To the Grignard reagent, prepared from 51.5 g of methyl iodide and 9.1 g of dry magnesium turnings, was added a solution of 38.6 g of dry 4-acetylpyridine in dry benzene, and it was refluxed for 7 h. Hydrochloric acid solution was dropped into the cooled reaction mixture in order to dissolve all the solids. After neutralization with ammonium hydroxide, organic components were extracted with diethyl ether. After evaporation of organic solvents, yellow crystals were obtained from the residue; yield 36.4 g (83%). The crude 2-(4-pyridyl)-2-propanol was recrystallized from its benzene solution; mp 134–136 °C (lit.[4] mp 136 °C).

The purified alcohol (17.8 g) was dissolved in 45 mL of 98% sulfuric acid at room temperature and the mixture was heated at 90–95 °C for 10 min. After cooling to room temperature, the reaction mixture was dropped into a cold 29% ammonium hydroxide aqueous solution. The resulting free base was salted out with sodium chloride and extracted with diethyl ether. The ether phase was dried over anhydrous magnesium sulfate for 1 day. The solvent was removed, and the residue was distilled under reduced pressure to give 12.1 g (79%) of 4-IP; bp 60–62 °C (4.6 mmHg) [lit.[4] bp 82 °C (15 mmHg)]. The structure of 4-IP was identified by ^{1}H NMR. Gas chromatography failed to show evidence of impurities (<0.1%).

Preparation of 4-Isopropylpyridine. 4-Ethylpyridine, α-methylstyrene, and methyl iodide were purified in vacuo by repeated distillation after drying over calcium hydride. THF was purified by rectification distillation over sodium–potassium alloy, followed by drying over the alloy in vacuo.

α-Methylstyrene (10.6 g) was reacted in vacuo with a potassium mirror (4 g) in 300 mL of THF at room temperature for 2 h. After the resulting α-methylstyrene tetramer dianion solution was separated from the excess potassium mirror, 4.3 g of 4-ethylpyridine was added into the dianion solution, and the solution was stirred at room temperature for 30 min. Methyl iodide was subsequently distilled into the resulting 4-ethylpyridyl anion solution at −78 °C with stirring until the color disappeared. After excess methyl iodide was distilled off on the vacuum line, the reaction mixture was evaporated, and the residue was dissolved in 100 mL of diethyl ether. The ether phase was extracted with

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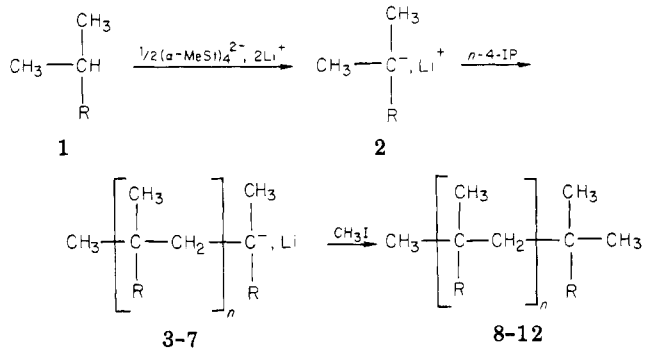
Scheme I



1 2

3-7 8-12

3, 8, $n = 1$; 4, 9, $n = 2$
5, 10, $n = 3$; 6, 11, $n = 4$; 7, 12, $n > 5$
a, R = 2-pyridyl; b, R = 4-pyridyl

1 N hydrochloric acid aqueous solution. The aqueous layer was neutralized with a 29% aqueous ammonium hydroxide solution. The resulting free base was salted out with sodium chloride and extracted with diethyl ether. After drying over anhydrous magnesium sulfate for 1 day, the ether phase was evaporated, and the residual liquid was distilled under reduced pressure to give 4.0 g (85%) of colorless liquid of 4-isopropylpyridine; bp 50 °C (4.5 mmHg) [lit.[5] bp 173 °C (760 mmHg)]. The structure was confirmed by ^{1}H NMR. No evidence of impurities was found by gas chromatography (<0.10%).

Oligomerization (Scheme I). Before use, 4-IP and 2-(4-pyridyl)propane were purified by distillation in vacuo after drying over calcium hydride.

Fresh lithium metal (0.3 g) was placed into a 200-mL round-bottomed flask connected to the vacuum line, THF (100 mL) was distilled into the flask, α-methylstyrene (0.93 g) was added, and the mixture was stirred at 0 °C for 3 h. After separation of the α-methylstyrene tetramer dianion solution from excess lithium metal, 2-(4-pyridyl)propane (0.53 g) was added to the solution at room temperature. Into the resulting yellow solution of 2-(4-pyridyl)propyl anion, 1.50 g of 4-IP was distilled slowly at −78 °C with stirring for 3 h. The reaction was terminated by subsequent distillation of CH_3I into the reaction mixture at −78 °C until the color disappeared. The volatile fraction was evaporated, and the residue was dissolved in a mixture of diethyl ether (50 mL) and 1 N hydrochloric acid aqueous solution (60 mL). The aqueous phase was separated and neutralized with 29% ammonium hydroxide solution (15 mL). The resulting organic compounds were extracted with chloroform. After drying over anhydrous magnesium sulfate, the chloroform layer was evaporated, and the residual sticky solid was dried in vacuo. Crude oligomers were obtained as off-white solids; yield 1.4 g.

Oligomerization of 2-IP was carried out by a similar method using *n*-butyllithium instead of α-methylstyrene tetramer dianion.

Separation of Oligomers. The resulting crude 4-IP oligomers (0.3–0.5 g) were injected into a preparative silica column [Merck, Lobar prepacked column siz B, LiChroprep Si 60 (40–63 μm)] using an Altex Model 332 programmable gradient liquid chromatograph fitted with a constant-wavelength (254 nm) UV Model 153 UV detector. Solvent was passed into the column with a linear gradient from hexane–methylene chloride–methanol mixture (90:8:2) to methylene chloride–methanol (4:1) during 180 min at 5 mL/min.

In some cases, the oligomer mixture was pretreated with a short silica column in order to remove the higher oligomers and/or polymer from the low molecular weight oligomers. All fractions were condensed, and the residual white solids (4–80 mg) were dried in vacuo and weighed prior to their characterization.

With a new Lobar B column, retention times were generally long, but resolution was excellent. Thus, not only oligomers having different degrees of polymerization but also the tetramer, pentamer, and hexamer stereoisomers could be completely or partially separated (Figure 1)

However, when the column was used a second time, these stereoisomers could not be completely separated. Perhaps absorption of small quantities of water contained in the methanol sharply decreased the resolving power of the column.

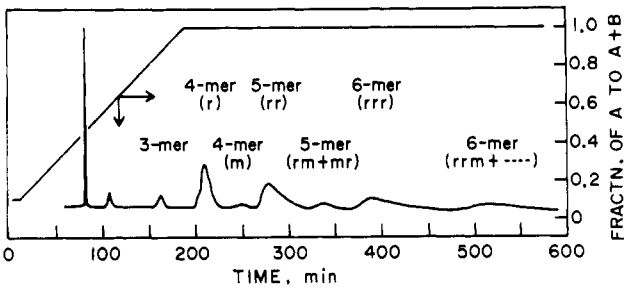


Figure 1. Liquid chromatogram of 4-isopropenylpyridine oligomers through new preparative silica column (Merck, Lobar prepacked column size B). Solvent: A, methylene chloride + methanol (4:1 (v/v)); B, hexanes; rate, 5 mL/min.

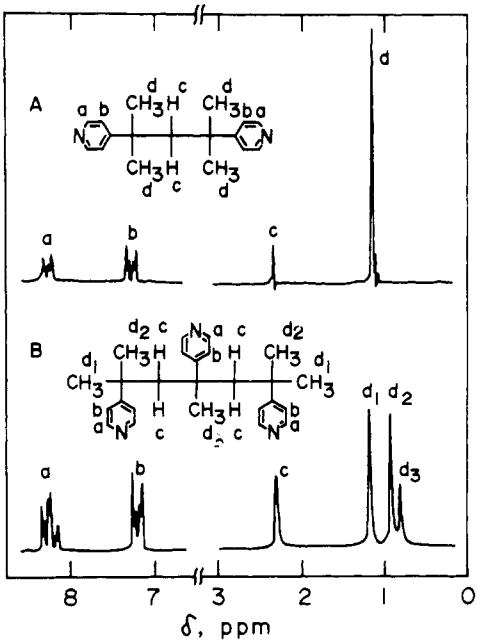


Figure 2. ^{1}H-NMR spectra of dimer (A) and trimer (B) of 4-isopropenylpyridine in methanol-d_4. Room temperature, 60 MHz.

Characterization. ^{1}H- and ^{13}C-NMR spectra of the separated oligomers in methanol-d_4 with added Me_4Si were taken with Varian A-60 and JEOL FT-100 high-resolution nuclear magnetic resonance spectrometers.

Results and Discussion

The mixture of the crude 4-IP oligomers was fractionated by using a preparative silica Lobar B column (see Experimental Section) (Figure 1). The fractions were identified by ^{1}H and ^{13}C NMR, for instance, by comparing the relative absorptions of outer and inner CH_3 groups and by integration of the absorptions due to aromatic, methylene, and methyl protons.

Figure 2 shows the ^{1}H-NMR spectra of the 4-IP dimer and trimer, 2,4-dimethyl-2,4-di(4-pyridyl)pentane and 2,4,6-trimethyl-2,4,6-tri(4-pyridyl)heptane, respectively. The dimer and trimer have no asymmetric centers and hence do not show configurational isomerism. In the spectrum of the trimer, however, three methyl absorptions are observed, assignable to two diastereotopic terminal methyl groups and the interior methyl group. A virtually identical spectrum has been observed for the trimer **9a** derived from 2-IP.[2] The interior methyl protons are observed at the highest magnetic field, presumably due to the ring current effects. Interestingly, in contrast to trimer **9a**,[2] the expected nonequivalency of the methylene protons is not observed (see below).

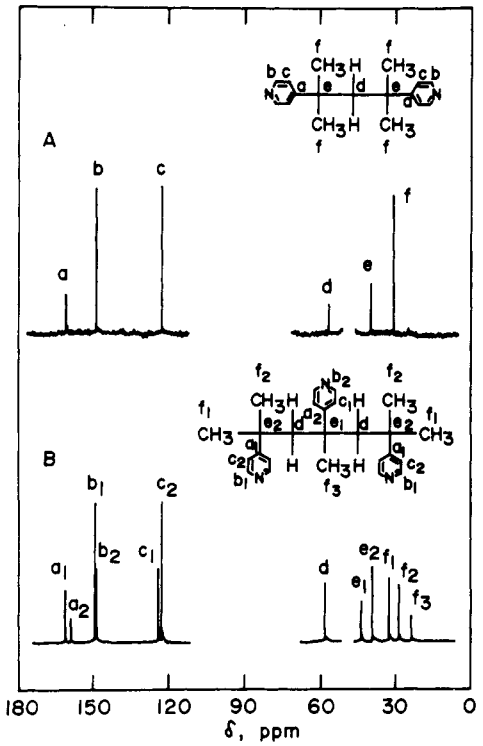


Figure 3. ^{13}C-NMR spectra of dimer (A) and trimer (B) of 4-isopropenylpyridine in methanol-d_4. Room temperature, 25 MHz.

The ^{13}C-NMR spectra of dimer and trimer of 4-IP are shown in Figure 3. The CH_3 absorptions show a pattern similar to that observed in the corresponding ^{1}H-NMR spectrum. The upfield shift of the quaternary carbon (e) compared to that of the methylene carbon (d) (checked by off-resonance decoupling) is noteworthy. The same relative chemical shift of methine and methylene carbon is observed for syndiotactic poly(methyl methacrylate).[6]

Figure 4 shows the ^{1}H-NMR spectra of the racemic and meso 4-IP tetramers **10b** obtained by liquid chromatography in the ratio of 9:1. The spectrum of a roughly 2:1 mixture of the racemic and meso tetramer is shown in Figure 4C. The spectrum (A) of the major isomer strongly resembles that of the racemic isomer of 2-IP (**10a**),[2] identified by X-ray crystallography and shown to exist in a translike conformation.[2] The chemical shifts of the three methyl singlets are virtually the same as those of *rac*-**10a** and are well upfield from the minor isomers for both **10a** and **10b**.[7] The spectra of both *rac*-**10a** and that in Figure 4A show a closely spaced AB quartet and a singlet for the external and internal methylene protons, respectively. Moreover, Figure 4B, in contrast with Figure 4A, shows a pronounced nonequivalency of the internal and external aromatic protons. Such a pattern would be consistent with a translike conformation of *meso*-**10b**. Thus both types of protons of the internal pyridine groups would be shifted upfield due to pyridine–pyridine shielding. In *rac*-**10b**, the corresponding trans conformation is expected to lead to more similar magnetic environments for internal and external aromatic protons, and this is observed. Furthermore, the relative chemical shifts of the internal CH_3 group for the racemic and meso isomer are in accord with that of the corresponding syndiotactic and isotactic polymer of poly(2-IP)[8] and poly(α-methylstyrene).[9] It is plausible therefore that Figure 4A is that of *rac*-**10b**.

The ^{1}H-NMR spectra of the major and minor pentamer stereoisomers are shown in spectra A and B of Figure 5, respectively. Consistent with the above, spectrum 5A is

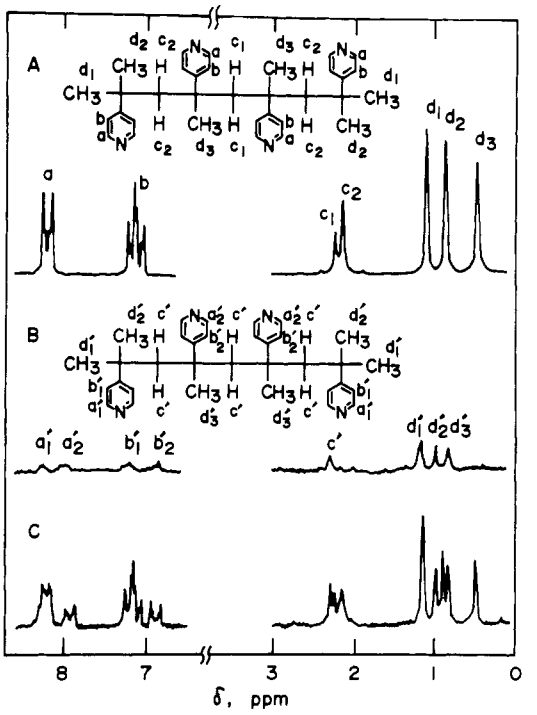


Figure 4. ^{1}H-NMR spectra of 4-isopropenylpyridine tetramers in methanol-d_4. Room temperature, 60 MHz. A, racemic tetramer; B, meso tetramer; C, tetramer mixture ([r]:[m] = 0.54:0.46).

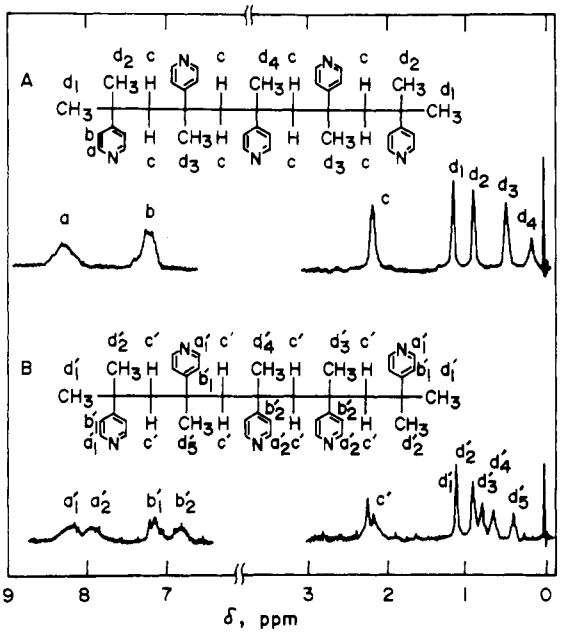


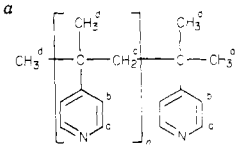
Figure 5. ^{1}H-NMR spectra of 4-isopropenylpyridine pentamers in methanol-d_4. Room temperature, 60 MHz. A, pentamer (rr); B, pentamer (rm + mr).

reasonably assigned to the syndiotactic pentamer. Of interest is the strong upfield shift of the d_4 methyl signal as compared to d_3. This again suggests a trans conformation in which d_4 is shielded by two pyridine moieties. Figure 5B is clearly that of the heterotactic pentamer, showing the expected five nonequivalent methyl signals in a 1:1:1:2:2 ratio in going downfield. Again the a_2' and b_2' aromatic signals characteristic of a meso sequence are clearly visible with an a_1'/a_2' and a b_1'/b_2' ratio of $\sim 3/2$. Isotactic pentamer was not isolated. This is not surprising in view of the preferred racemic placement ($P_r \cong 0.80$–0.90) of the 4-IP monomer in these oligomers. Figure 6 shows the ^{13}C-NMR spectra of the syndiotactic isomers of tetramer and pentamer.

Table I
Chemical Shifts and Assignments of All Proton Peaks in the ^{1}H-NMR Spectra of 4-Isopropenylpyridine Oligomers and Polymer in Methanol-d_4 [a]

oligomer	peak a, ppm	peak b, ppm	peak c, ppm	peak d, ppm
dimer	8.27	7.28	2.37	1.16
trimer	8.22	7.19	2.30	1.18, 0.90, 0.80
tetramer (r)	8.23	7.16	2.27, 2.17	1.13, 0.90, 0.50
tetramer (m)	8.23, 7.94	7.16, 6.90	2.31	1.17, 0.99, 0.83
pentamer (rr)	8.23	7.14	2.13	1.12, 0.88, 0.50, 0.18
pentamer (rm + mr)	8.23, 7.96	7.14, 6.88	2.31, 2.20	1.16, 0.94, 0.83, 0.69, 0.41
hexamer (rrr)	8.28	7.17	2.09	1.12, 0.88, 0.45, 0.16
poly(4-IP)	8.37, 8.03, 7.77	7.14, 6.78, 6.49	1.77	1.11, 0.57, 0.21

[a]



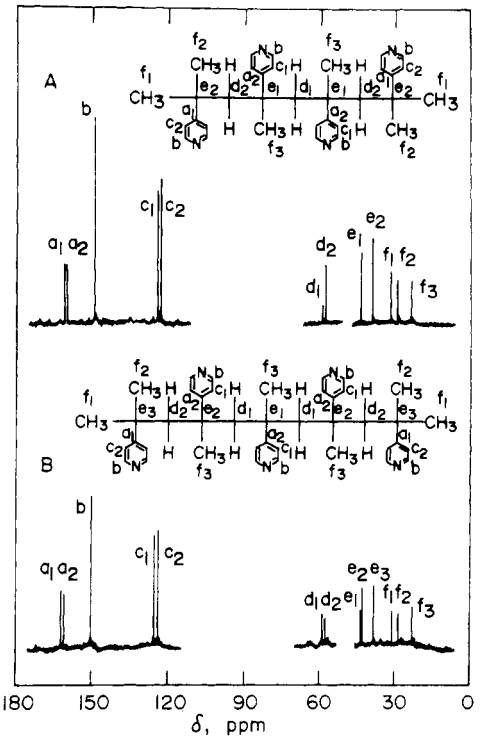


Figure 6. ^{13}C-NMR spectra of racemic tetramer (A) and racemic pentamer (B) of 4-isopropenylpyridine in methanol-d_4. Room temperature, 25 MHz.

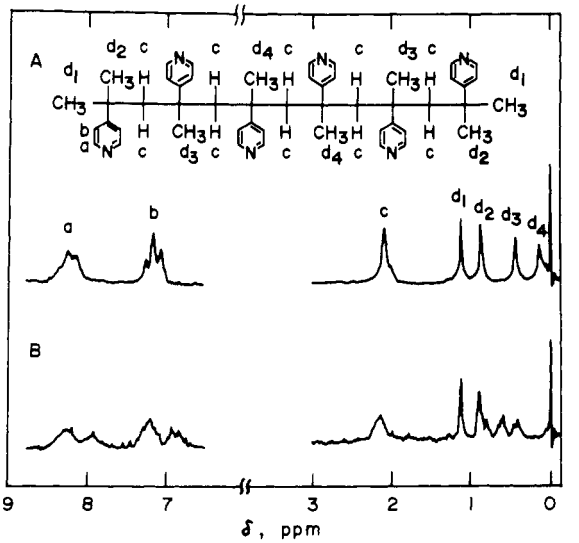


Figure 7. ^{1}H-NMR spectra of 4-isopropenylpyridine hexamers in methanol-d_4. Room temperature, 60 MHz. A, hexamer (rrr); B, other hexamers.

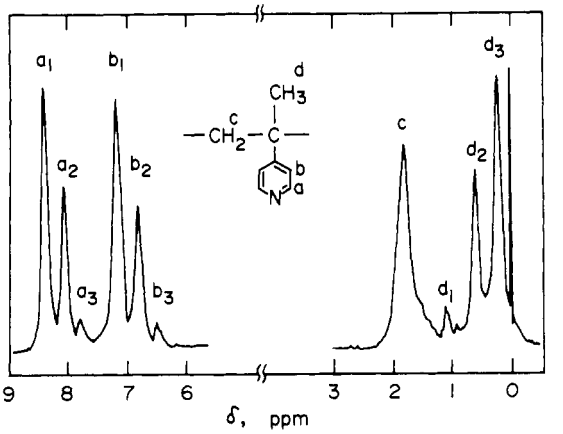


Figure 8. ^{1}H-NMR spectrum of 4-isopropenylpyridine polymer in methanol-d_4. 70 °C; 100 MHz.

In the case of the hexamers, only the rrr (syndiotactic) isomer could be isolated in pure form (Figure 7). Again the d_4 methyl groups are broadened and shifted upfield from the d_3 methyl groups, indicating most probably a predominantly trans conformation in the central portion of the chain. Figure 7B is probably a mixture of rrm (mrr) and rmr isomers, since the racemic monomer placement appears to be strongly preferred.

Figure 8 shows the ^{1}H-NMR spectrum of the 4-IP polymer obtained in THF at −78 °C using (2-(4-pyridyl)-propyl)lithium as initiator. The observed splitting of the a, b, and d peaks is clearly due to the steric microstructures of the 4-IP polymer.

The proton chemical shifts of the 4-IP oligomers and polymer are summarized in Table I. The internal methyl groups d_4 and d_4' of the rr and rm pentamers, respectively (Figure 5), can be regarded as models of syndiotactic and heterotactic polymer triads. The methyl signals in the spectrum of the 4-IP polymer (Figure 8) should therefore be assigned to be syndiotactic, heterotactic, and isotactic triads, in order of decreasing field. A similar triad assignment has been made for poly(2-isopropenylpyridine)[8] and for poly(α-methylstyrene).[9]

The triad distribution for poly(4-IP) appears to be consistent with Bernoullian statistics and yields a P_r value of ~0.78, being somewhat lower than that observed for tetramer **10b**, where P_r was estimated as ~0.90 (obtained from the ^{1}H-NMR spectrum of the unresolved tetramer

and confirmed by the ^{13}C-NMR spectrum of ^{13}C-labeled oligomers[10]).

The P_r values of the corresponding oligo- and polymerization of 2-IP and the polymerization of α-methylstyrene under similar conditions (Li^+, THF/−78 °C) were found to be 0.91[8] and 0.64[9c], respectively. The three systems are thus similar in that predominantly syndiotactic polymer is formed. On the other hand, the polymerization of 2-vinylpyridine leads to predominantly isotactic polymers, and that of 4-vinylpyridine results in random stereochemistry.[11] The difference in stereochemistry between the latter monomers is probably at least partially due to the intramolecular chelation of the counterion with the nitrogen lone pair of the penultimate asymmetric center, occurring in the case of 2-vinylpyridine. Such an interaction is not possible for 4-vinylpyridine. The predominantly syndiotactic content observed for the polymers derived from the three isopropenyl isomers indicates that the mechanism of oligo- and polymerization is quite different and may be largely influenced by steric factors.[9,12] It is, however, clear from the significantly higher syndiotactic content of poly(2-IP) and poly(4-IP) compared to that of poly(α-methylstyrene) that other factors are involved arising from the presence of the heteroatom in the ring. Intramolecular cation coordination of the type discussed above is not plausible on steric grounds. Thus the presence of the methyl group on the penultimate asymmetric center effectively prevents such an interaction. It is more likely that dipolar interactions between monomer and chain end are involved, especially in the case of 2-IP. In view of the relatively small differences in activation energy between the three systems, however, the nature of these interactions is difficult to identify.

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Registry No. 2,4-Dimethyl-2,4-di(4-pyridyl)pentane, 87461-72-1; 2,4,6-trimethyl-2,4,6-tri(4-pyridyl)heptane, 87461-73-2; 2,4,6,8-tetramethyl-2,4,6,8-tetra(4-pyridyl)nonane (isomer 1), 87461-74-3; 2,4,6,8-tetramethyl-2,4,6,8-tetra(4-pyridyl)nonane (isomer 2), 87461-75-4; 2,4,6,8,10-pentamethyl-2,4,6,8,10-penta(4-pyridyl)undecane (isomer 1), 87461-76-5; 2,4,6,8,10-pentamethyl-2,4,6,8,10-penta(4-pyridyl)undecane (isomer 2), 87507-90-2; 2,4,6,8,10,12-hexamethyl-2,4,6,8,10,12-hexa(4-pyridyl)tridecane, 87494-47-1; poly(4-isopropenylpyridine), 87461-77-6.

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Oligomerization of Vinyl Monomers. 13. Anionic Oligomerization of 2- and 4-Isopropenylpyridine. Stereoselectivity on Monomer Addition and Methylation Determined by End-Group ^{13}C Labels

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ABSTRACT: The anionic oligomerization of 2-isopropenylpyridine (2-IP) and 4-isopropenylpyridine (4-IP) was carried out by initiation using the lithium salts of 2- and 4-isopropylpyridine, followed by termination with ^{13}C-enriched methyl iodide. From the ^{13}C NMR spectroscopic analyses of the ^{13}C-enriched terminal methyl carbons, the stereoselectivity on methylation and monomer addition of both oligomeric anions was found to be predominantly racemic-like (~80–90%), decreasing slightly with increasing degree of polymerization. The observed stereoselectivity is apparently not due to intramolecular chelation of the counterion by the pyridyl nitrogen atom but appears to be mainly caused by steric effects at the terminal carbanion. Thus, nonbonded interactions between the methyl and pyridine groups bonded to the carbanion and to the penultimate asymmetric center are expected to lead to a preferred conformation in which the *pro*-racemic face of the carbanion is most accessible to electrophilic attack.

Introduction

Several recent studies have been concerned with the stereochemistry of oligomerization of vinylpyidines,[2,3] acrylates,[4] and other vinyl monomers.[5] For the stereochemistry of anionic oligomerization of 2- and 4-vinylpyridines in THF, the apparent stereoselectivity observed in the oligomerization–methylation sequence of 2-vinylpyridine (predominantly isotactic-like) was concluded to be due to intramolecular chelation of the alkali metal cation and the nitrogen lone pair of the penultimate 2-pyridine ring.

On the other hand, anionic oligomerization of 2-isopropenylpyridine (2-IP) and 4-isopropenylpyridine (4-IP) under similar conditions yielded predominantly syndio-

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