fication II in the plane perpendicular to the fiber axis. Feature (2) suggests that in the *b* projection the disorder also has the same structure as modification II, i.e., the $(h0\ell)$ behaves as if no disorder is present. On the other hand, poly(vinylidene fluoride) can take the planar zigzag conformation (modifications I and III) in addition to the $(\mathrm{TGT\overline{G}})_n$ conformation in modification II (T, trans; G and $\overline{\mathrm{G}}$, gauche and minus gauche).

The following proposed structure is consistent with the above facts. A segment of a molecular chain in modification II changes to the planar zigzag conformation, for example, from . . . $\mathrm{TGT\overline{G}TGT\overline{G}}$ . . . to . . . $\mathrm{TGT\overline{G}TTTTGT\overline{G}}$ . . . . All the molecules in a crystallite take the same planar zigzag conformation at the same level, forming a band (Figure 2). In the *b* projection, the planar zigzag part has the same structure as modification II, though it deviates from modification II in the *ac* plane, and in the section perpendicular to the fiber axis it has the same periodicity as modification II. This type of disorder is known as "kink bands" (Figure 3).[3] The intensity distribution (called feature (3) above) was calculated on the basis of the theory for stacking faults[4,5] and found to agree with the observed intensity. This work will be published in detail elsewhere.

The Bragg reflections from modification II containing the kink bands are not appreciably different from the usual ones. This suggests that the $\mathrm{TGT\overline{G}}$ sequences are as long and regular as in the usual modification II. On the other hand, the kink bands can be predicted to be short and disordered because there are some short intermolecular distances in the kink bands. Modification II transforms into the planar zigzag modifications by stretching (to modification I) and by heat treatment under high pressure (to modifications I and III).[6] It can be expected that the kink bands play an important role in these crystal transformation processes.

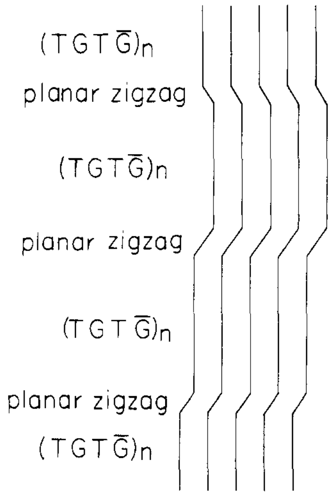

Figure 3. Kink bands in modification II of poly(vinylidene fluoride) in the *a* projection.

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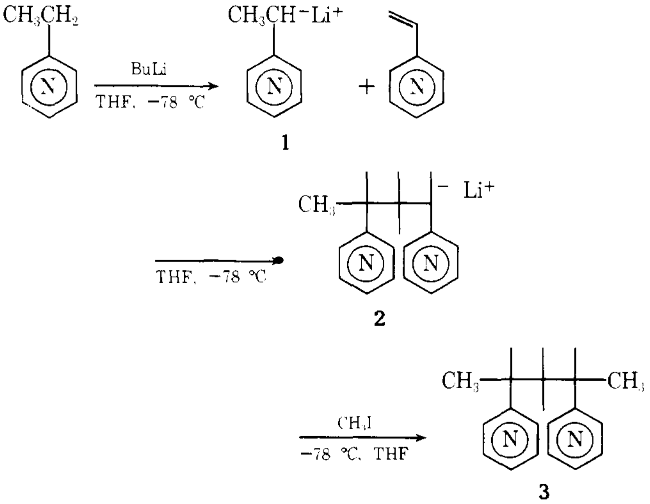
Communications to the Editor

Oligomerization Stereochemistry of Vinyl Monomers. 1. A Stereoselective Synthesis of *meso*-2,4-Di(2-pyridyl)pentane

Studies of the oligomerization of vinyl derivatives, dienes, etc., are frequently of interest since they provide a simplified picture of the corresponding polymerization process. Thus, the stereochemistry of anionic oligomerization of dienes has been studied over the past several years.[1] Though the anionic oligomerization of vinyl monomers has been explored,[2,3] the stereochemistry of this process, to our knowledge, has not been reported.

We now wish to report the addition of α-lithiated-2-ethylpyridine (1) to 2-vinylpyridine with sequential stereoselective methylation of the lithiated adduct (Scheme I). The reaction was carried out by a slow in vacuo distillation of 2-vinylpyridine onto a vigorously stirred THF solution of the 2-ethylpyridyl Li salt that was in turn formed by metallation of 2-ethylpyridine using *n*-BuLi. The methylation was similarly carried out by vacuum distillation of CH_3I onto the carbanion solution at −78 °C. After workup of the reaction mixture, the product **3a** was obtained by vacuum distillation, bp 106–108 °C (0.15 mm). Product yield was about 60%. A small amount of polymer was also formed. The dimer stereochemistry was determined by 60 MHz NMR (*meso*-**3a**: $\delta(CH_2)$ 1.77 and 2.25, $\delta(CH)$ 2.80, $\delta(CH_3)$ 1.25 ppm; *racemic*-**3a**: $\delta(CH_3)$ 1.19). Diastereomeric dimer mixtures were analyzed by determining the ratio of CH_3 doublet absorptions. The product stereochemistry was found to be independent of the temperature of vinyl pyridine addition and time and temperature of storage of the dimer anion (**2a**). Hence, the stereoselection is most

Scheme I



a = 2-pyridyl
b = 4-pyridyl

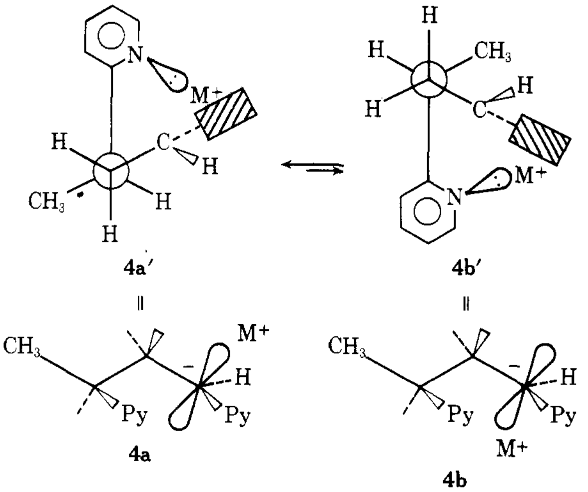
Table I
Methylation Stereochemistry of 1,3-Di(pyridyl)butane Anion as a Function of Temperature, Cation, Solvent, and Carbanion Structure

Carbanion	Cation/solvent	Monomer	T, °C	% meso of **3a/3b**
1a	Li/THF	2-VP	−78	>99
1a	Li/THF	2-VP	0	95
1a	Li/THF, pyridine[a]	2-VP	−78	83
1a	Rb/THF[b]	2-VP	−78	57
1b	Li/THF	4-VP	−78	~50[c]

[a] 50/50 by volume. [b] Carbanion salt was generated using α-methylstyrene tetramer^{2-}, Rb_2^+ salt. [c] Measured by ratio of CH_3 doublets; CH_3 shifts of the diastereomers have not been identified.

likely due to the methylation reaction. Equilibrium epimerization studies with potassium *tert*-butoxide in DMSO as catalyst showed that meso and racemic forms of 3 are of nearly equal stability, a result similar to that obtained by Flory and co-workers for the corresponding epimerization of 2,4-diphenylpentane.[4] The methylation stereochemistry thus appears to be kinetically controlled. A higher methylation temperature slightly decreases the stereoselectivity. The stereoselectivity of methylation is decreased when pyridine (50% by volume) was added after the formation of 2 (Table I). Also the use of Rb α-methylstyrene tetramer as a metallating agent significantly decreases the stereoselectivity of alkylation (Table I). These observations indicate that the high stereoselectivity is due to the strong coordinative ability of the Li ion.

The above results are consistent with the presence of a strongly preferred conformation of the Li salt of **2a.**[5] If the Li ion is present above or below the planar carbanion,[6] two diastereotopic ion pairs (**4a** and **4b**) should exist, each of which may occur in several conformations. The very high stereoselectivity of methylation can, in such a case, only be consistent with the predominant participation of either **4a** or **4b** in the reaction and an alkyl halide approach that is exclusively syn or anti with respect to metal cation.



The pronounced effect of cation size and coordination on the stereochemistry of **3a** strongly suggests Li ion coordination by the penultimate 2-pyridyl group. Several such conformations are possible for each ion pair diastereomer of which **4a′** and **4b′** (corresponding to **4a** and **4b**, respectively) seem most reasonable. From inspection of models, **4a′** is expected to be more stable by several kilocalories on account of CH_3-pyridine gauche and CH_3-nitrogen lone pair interactions in **4b′**. Now, the methylation reaction probably occurs cation side since the approach of the halide from the opposite side would result in the formation of energetically unfavorable product separated ion pairs. This cation side approach of halide also appears to be supported by recent work on stereoselective alkylation.[7] The predominance of the meso form in the methylation product of the Li salt of **2a** is, therefore, consistent with the prevalence of **4a′**. The above interpretation is supported by recent conductometric evidence[8,9] for such 2-pyridyl Na^+ ion coordination in species similar to **2a** and by the fact that the methylation of the Li salt of **2b** is not stereoselective[10] (Table I). Coordination of cation with the 4-pyridyl group of **2b** seems impossible on the basis of inspection of models.

The possible existence of two or more ion pair diastereomers is of interest in the stereochemistry of anionic polymerization processes.[11] The role of ion pairing in the stereochemistry of anionic polymerization of vinyl monomers such as acrylates has been extensively studied but appears to be still incompletely understood. Most proposed descriptions of ion pair type processes focus on some type of coordination of cation with penultimate Lewis base substituent and incoming monomer.[12] The above results tend to support such a model. The data also indicate that the anionic polymerization stereochemistry of 2-vinylpyridines and similar polar monomers may be affected by the relative proportion of the two "configurational" ion pair diastereomers of the carbanion site and by the direction of monomer approach with respect to cation. Oligomerization studies focusing on this aspect are presently underway.

Acknowledgment. This work was supported by NSF through Grant DMR72-03130

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Received April 5, 1976