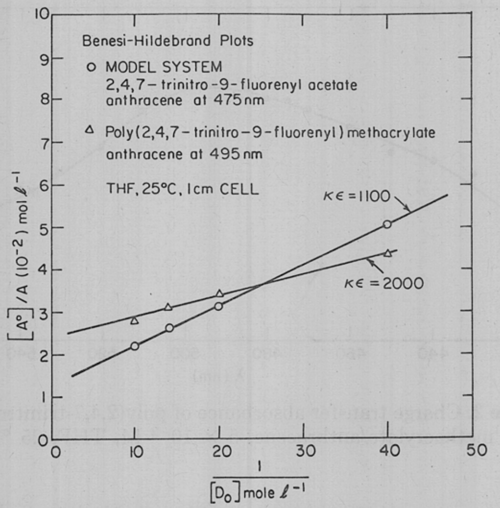

Figure 3. Benesi–Hildebrand plots for 2,4,7-trinitro-9-fluorenyl acetate/anthracene, 475 nm (○), and poly(2,4,7-trinitro-9-fluorenyl) methacrylate/anthracene, 495 nm (△); THF, 25 °C, 1-cm cell.

From these results the polymer charge transfer spectrum is shifted to longer wavelengths and in addition it appears that there may be some slight enhanced complexation in the polymeric acceptor when compared to the small molecule model. Examples of this type of behavior have been observed with polymeric systems before and have been somewhat nebulously described as "polymer effects".[13] Our results are qualified by several factors. The first is that the model acceptor IV is not exactly the repeat unit of the polymer and thus, the comparison may not be exact. A second factor is that the charge transfer bands of both the polymer and model systems have some asymmetry (Figure 2) indicating more complicated processes, other than simple 1:1 complexation, may be occurring. In addition, the accuracy of our uv studies is somewhat limited due to the poor solubility of anthracene, thus limiting the concentration range for the $K\epsilon$ determination. More studies are obviously necessary to fully characterize the complexing properties of this novel polymeric acceptor.

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Kink Bands in Modification II of Poly(vinylidene fluoride)

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Streaks along lines of constant ξ were found on the fiber diagram of modification II of poly(vinylidene fluoride), which could be obtained by annealing the oriented sample after attaching the ends to a metal holder. In this note, it is suggested that these streaks can be caused by the kink bands in the crystallite.

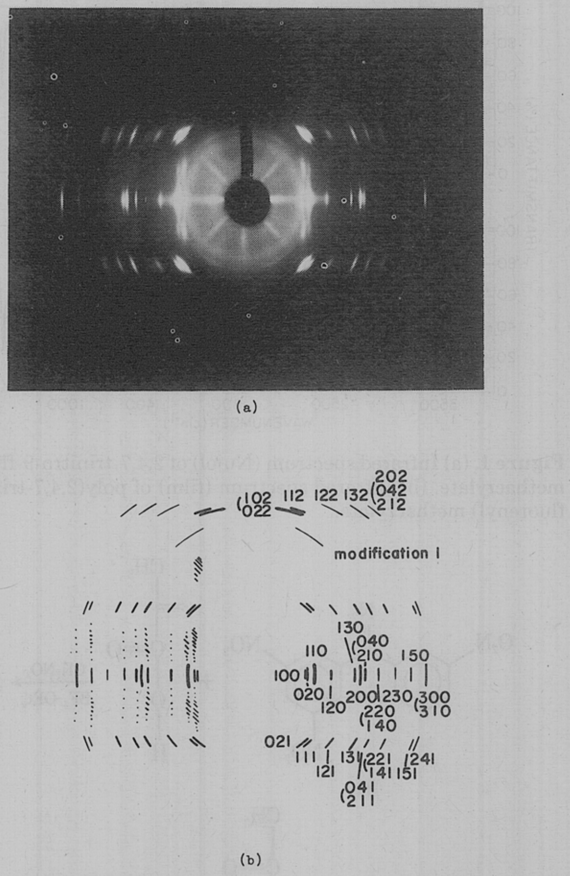

Figure 1. (a) Fiber photograph of modification II which gives the streaks and (b) its schematic representation.

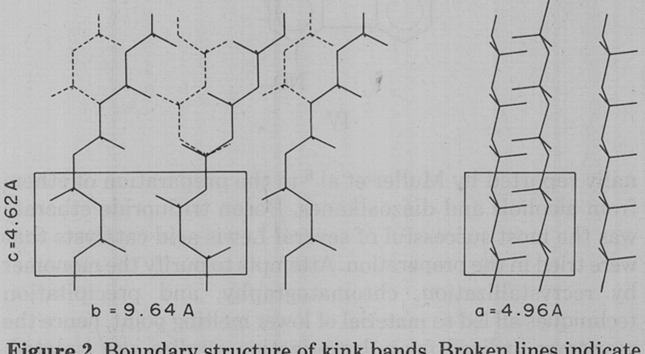

Figure 2. Boundary structure of kink bands. Broken lines indicate the structure of modification II. In the *b* projection, kink bands and modification II have the same structure.

A sample giving the streaks can usually be obtained by annealing an oriented sample of modification II at about 150 °C for about 24 h after fixing the ends on a metal holder. The oriented modification II was prepared by stretching a molten sample of KF-1100 (Kureha Chemical Industry Co., Ltd) at room temperature. Streaks have not yet been obtained from samples of Kynar 450 (Pennsalt Chemical Co., Ltd.).

As seen in the fiber photograph (Figure 1), the steaks have the following features: (1) they extend from Bragg reflections of modification II along lines of the constant ξ, (2) they are not observed in the $(h0\zeta)$, for example, (10ζ) and (20ζ), and the streak in the (02ζ) is the most intense, and (3) their intensity maxima are between layer lines of modification II. Feature (1) suggests that the disorder has the same periodicity as modification 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 . . . $\mathrm{TGT\overline{G}TTTTTGT\overline{G}}$ . . . . 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.

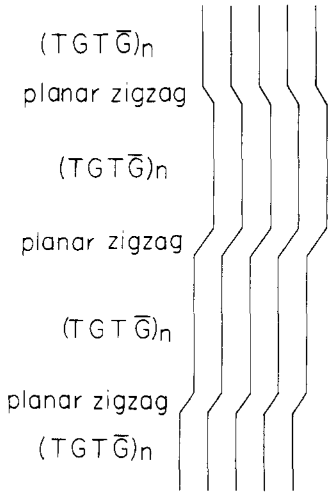

Figure 3. Kink bands in modification II of poly(vinylidene fluoride) in the *a* projection.

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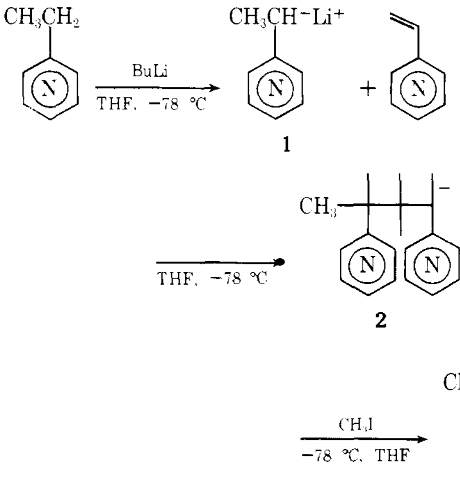
Communications to the Editor

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