Differential scanning calorimetry analysis of these two polymers indicated decomposition temperatures of 385 and 305 °C, respectively.

In a second study, films of the mixed substituent polymer and the homopolymer were sealed in evacuated ampules and placed for 12 h in an oven maintained at 300 °C. After being cooled to 25 °C, the film prepared from the phenyl trifluoroethoxyphosphazene had darkened in color and was now only partially soluble in THF. The GPC average molecular weight of the soluble portion showed a broadening toward the low molecular weight region. However, a significant quantity of the material still had a molecular weight in excess of 1×10^6. By contrast, the film cast from poly[bis(trifluoroethoxy)phosphazene] had been converted to an insoluble solid and a soluble oil. The soluble species had a molecular weight of less than 1×10^4.

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Oligomerization Stereochemistry of Vinyl Monomers. 7. Diastereomeric Ion Pairs as Intermediates in the Stereoregular Anionic Oligomerization of 2-Vinylpyridines. A proposed Mechanism

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ABSTRACT: Oligomers of 2-vinylpyridine have been prepared by addition of 2-vinylpyridine to THF solutions of alkali salts of 2-ethylpyridine followed by termination with CH_3I. With Li and Na as counterions, these oligomers were highly (>95%) isotactic as determined with ^1H and ^{13}C NMR. With K and larger counterions, the formation of dimers is not stereoselective. Epimerization of these types of compounds yields statistically expected mixtures of stereoisomers. Thus stereoselection appears kinetically controlled. Dimerization of 4-vinylpyridine or addition of 4-vinylpyridine to lithio-2-ethylpyridine followed by methylation is not stereoselective. The results particularly with the Li and Na salts indicate that the stereochemistry of methylation and 2-vinylpyridine addition is identical. A mechanism is proposed taking the chirality of the ion pair itself into account. For the Li and Na salts of the living oligomers, the cation appears to be coordinated with the nitrogen lone pair of the penultimate 2-pyridine unit. In such a case, one of the two possible diastereomeric ion pairs is expected to be favored, and this is most likely the reason for the observed stereoselectivity. Electrophilic attack is apparently occurring in a "syn" fashion.

There has been an increased interest in recent years in the synthesis of oligomers of vinyl monomers such as styrene,[2] methyl acrylate,[3] vinyl chloride,[4] as well as dienes.[5] Such investigations have been mostly useful in the elucidation of polymer configuration and conformation. Recently the stereochemistry of vinyl oligomerization itself has been reported.[6-9] We now wish to give a more complete account of our investigations on the stereochemistry of anionic oligomerization of 2- and 4-vinylpyridines and to present a more detailed analysis of the results of this work.

In order to obtain a better understanding of the mechanism of stereoregular anionic polymerization of monomers such as alkyl methacrylates, acrylates, 2-vinylpyridines, and similar monomers, it seemed that a careful study of models such as 1 is indispensable. In anions of this type, only one asymmetric center is present, and a comparison of the stereochemistry of anions 1 and their higher molecular weight homologues should facilitate a resolution

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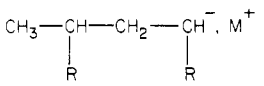


1

of the difficult problem of participation in the polymerization of penultimate, antipenultimate, and prior monomer segments of the propagating chain.

Models of type 1, moreover, lend themselves in principle for investigations of the stereochemistry of other reactions such as protonation or alkylation. Thus the stereochemistry of vinyl additions of this type may be compared to that of other reactions, and such comparisons may shed additional light on the nature of the polymerization stereoregularity. Furthermore, it appeared that stereochemical assignments in ^1H and ^{13}C NMR spectra of low molecular weight products **5–10** would suffer to a lesser extent from the uncertainties that are often inherent in the interpretation of the spectra of high molecular weight polymers.

Vinylpyridines were selected initially as the monomers for several reasons. First, the Grignard or dialkylmagnesium initiated polymerization of 2-vinylpyridine has been shown to be stereoregular in contrast to that of 4-vinylpyridine.[11] Second, the propagating poly(2-vinylpyridine) anion and anions like it are quite stable. For instance, lithio-2-ethylpyridine may be easily and cleanly prepared by reaction of 2-ethylpyridine with *n*-BuLi or alkali α-methylstyrene dianion salts in THF in contrast to, for instance, the corresponding ester substituted carbanions.[12] Third, the 2-pyridyl substituted carbanion salts have been studied in some detail, particularly with regard to ion pairing,[13,14] so that the role of this factor in the oligomerization stereochemistry may be examined.

Experimental Section

The 2- and 4-ethylpyridines (Aldrich) were stirred over CaH_2 overnight and vacuum distilled (~50 °C (30–35 mm)). The distillate is degassed on the vacuum line and stirred over fresh CaH_2 for several hours followed by room temperature distillation into an ampule equipped with break-seals cooled to −78 °C. After distillation, the ampule is sealed off. The ethylpyridines were further purified by distillation into ampules on the vacuum line from their conjugate carbanions (generated by addition of the ethylpyridines onto dried 1,1,4,4-tetraphenylbutane anion salts) followed by sealing of the ampule.

Monomers. The 2- and 4-vinylpyridines (Aldrich) were stirred over CaH_2 overnight followed by vacuum distillation over fresh CaH_2 into break-seal equipped ampules which are sealed. Vinylpyridines purified in this way are sufficiently pure for oligomerization studies.

2-(2-Pyridyl)propene. A solution of 25.2 g of 2-bromopyridine in 50 mL of diethyl ether was added over a 3-min period to an equivalent amount of *n*-BuLi (1.6 M in hexane) in 300 mL of dry ether at −18 °C. To this red solution of 2-pyridyllithium was added over a period of 10 min a slight excess (~5%) of dry acetone in ether. The solution was kept below −20 °C throughout. After hydrolysis with an ice-cold solution of ammonium chloride, the ether layer was extracted with 10% HCl. The acid extract was neutralized and extracted with diethyl ether. The solution was dried over Na_2SO_4. Vacuum distillation (bp 65–66 °C (4mmHg)) gave 17 g (~80%) of 2-(2-pyridyl)propanol, mp 58–60 °C. The alcohol (17 g) was dehydrated in 50 mL of concentrated H_2SO_4 at 110 °C for about 1.5 h. The mixture was slowly poured into ice water and an excess of aqueous ammonia was added. The organic base was extracted with ether. After the solution was washed with water and dried over Na_2SO_4, the solvent was evaporated and the residue was vacuum distilled to give 6.0 g of 2-(2-pyridyl)propene in 40% yield; bp 54–55 °C (5mmHg). The product was identified by NMR.

For polymerization studies, further purification is necessary. This consisted of distillation on the vacuum line of the monomers onto sodium or potassium mirrors followed by stirring for 1 h. At this stage a thin polymer film is often formed on the metal surface. The monomer is then distilled onto a second metal film followed by stirring and is finally distilled onto an ampule equipped with a break-seal cooled at −78 °C which is sealed and stored in the freezer.

Preparation of 2,4-Di(2-pyridyl)pentane. An *n*-BuLi–hexane solution (19 mL, 1.6 M) is injected by syringe into a 200 cm^3 round-bottom polymerization flask under argon atmosphere. The hexane is removed by distillation on the vacuum line in the liquid nitrogen trap. THF (120 cm^3) is vacuum distilled into the flask kept at −78 °C followed by in vacuo distillation of 1.1 molar equiv of 2-ethylpyridine into the flask. The solution immediately turns red and is warmed to room temperature and stirred for about 0.5 h. The solution is cooled again to −78 °C and evacuated for 30 min to remove butane from the solution. 2-Vinylpyridine (3 mL) is now distilled over a 2-h period from a stirred 25 cm^3 round-bottom flask connected to the polymerization flask kept at −78 °C. After monomer addition, the anion is methylated by distillation on the vacuum line of methyl iodide or dimethyl sulfate kept over CaH_2. Upon disappearance of the red color of the carbanion, the solution is warmed to room temperature and evacuated to remove solvent and excess methyl iodide. The apparatus is then removed from the line and 120 mL of cold 10% aqueous HCl is added to the flask. The HCl solution is washed several times with diethyl ether. After neutralization with saturated Na_2CO_3 solution, the aqueous solution is extracted with 350 mL of diethyl ether. The organic layer is washed again with water and dried over anhydrous Na_2SO_4 overnight. After evaporation of the ether, the dimer is obtained by reduced pressure distillation (bp 106–108 °C/(0.25mmHg)). The yield is approximately 20–60%, decreasing with a faster rate of vinylpyridine addition. In such a case, polymer is the major byproduct.

Preparation of 1,3-Di(2-pyridyl)butane. This preparation is the same as that of the pentane dimer, the difference being the vacuum line distillation of methanol (or CH_3OD) into the flask cooled at −78° C. In this case the protonation is apparently not complete since a light red color persists. Upon warming the solution to room temperature, the red color disappears, but cooling to −78 °C produces a red color again. Apparently the protonation equilibrium is shifted to the carbanion side upon cooling. This is not unexpected.[15]

The existence of an equilibrium in the case of methanol protonation is confirmed by reaction of the anion with phenol. In this case, the proton donor is more acidic by about 6 pK units, and as expected the equilibrium lies completely on the product side.

The butane product is recovered in the same manner as the pentane dimer (bp 148–150 °C/(0.35mmHg)). The yield is 30–70%, depending on the rate of monomer addition.

Reactions of Pentane Anion 12. The lithium salt of 2-ethylpyridine is first generated in the manner described above. The monomer, 2-(2-pyridyl)propene (equimolar), is slowly distilled onto the carbanion salt kept at −78 °C. An excess of phenol dissolved in THF is then added from an ampule equipped with a break-seal. After the solution is warmed to room temperature, THF is removed by evacuation, followed by addition of 10% cold aqueous HCl. Isolation of the product is identical with that described above. The pentane dimer is distilled at reduced pressure (bp 100–111 °C (0.15mmHg)). The protonation of the pentane anion was also carried out by addition (or distillation) of CH_3OH. The stereochemistry of the reaction was virtually identical with the phenol protonation product (see Results).

The pentane anion was also generated by reaction of 1,1-diphenylhexyllithium with *meso*-1,3-di(2-pyridyl)pentane. In this case, after protonation, other products were isolated in addition to the pentane dimer. Attempts to generate the anion by reaction of **7** with *n*-BuLi failed.

Methylation was carried out in the same manner as the methylation of the butane anion. The product **13** was distilled at reduced pressure (bp 115–138 °C (1mmHg)).

Preparation of 1,3-Di(4-pyridyl)pentane (7a) and 1-(4-Pyridyl)-3-(2-pyridyl)pentane (7b). The synthesis of **7a** was carried out essentially in the same manner as that of **1** except that the 4-ethylpyridyllithium salt was generated by reaction of 1 equiv of 4-ethylpyridine with 1,1-diphenylhexyllithium that was in turn prepared by reaction of *n*-BuLi with 1,1-diphenylethylene. The

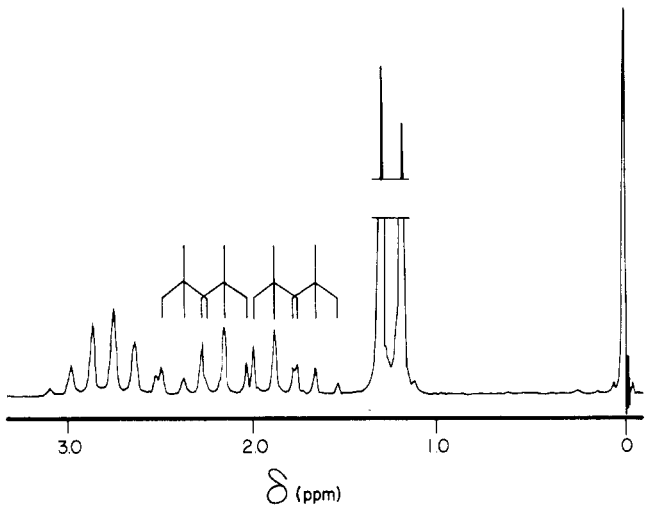


Figure 1. ^1H spectrum (60 MHz) of *meso*-2,4-di(2-pyridyl)pentane in CCl_4 at 35 °C

synthesis of **7b** was identical with that of **3**, the only difference being the use of 4-vinylpyridine in the monomer addition step. **7a** was isolated in 28% yield (bp 163–170 °C (0.25mmHg)), and **7b** was isolated in 58% yield (bp 115–120 °C (0.20mmHg)).

Preparation of 2-Vinylpyridine Trimers and Higher Oligomers. The synthesis of these oligomers is identical with that of the pentane dimer except that the monomer/carbanion ratio is increased according to the desired degree of oligomerization. After workup of the reaction mixture (see above), the oligomers were isolated by (50/50) ether/hexane elution from neutral alumina followed by diethyl ether and (50/50) diethyl ether/ethyl acetate. Fractions containing pure trimer and tetramer were obtained as well as a pentamer–hexamer mixture.

Epimerization Studies. Dimer, trimer, and tetramer were epimerized by addition of the vacuum-dried samples through break-seals to *t*-BuOK dissolved in Me_2SO (0.1 M). *t*-BuOK was dried under high vacuum for about 4 h. The Me_2SO was purified by high vacuum distillation from CaH_2 followed by addition to the sodium salt of the 1,1,4,4-tetraphenylbutane dianion ($Na_2^+D^-D^-$) and distillation into ampules.

After reaction of the samples in the *t*-BuOK/Me_2SO solution at room temperature for about 10 days, the reaction vessel was opened and diethyl ether was added (DEE/Me_2SO = 5/1 (v/v)). The ether solution is washed several times with water to remove the Me_2SO and dried over Na_2SO_4. After ether removal on a rotary evaporator, the residue is evacuated on the vacuum line for 4 h.

NMR Characterization of Oligomers. Oligomers were identified by 22.5 MHz ^{13}C and 60, 100, or 270 MHz ^1H NMR. The structures of the oligomers were identified by comparison of the relative proton absorptions of CH_3 end groups, methylene, methine, aromatic pyridine, and the 6-pyridine ring proton.

Results

Methylation. The methylation of salts of anion **3** was investigated first, since this process consists of a single reaction and leads to the conveniently identifiable meso or racemic product (eq 1). Upon addition of CH_3I to the

$$CH_3CH_2R \xrightarrow[-78\ ^\circ C/THF]{R^-M^+} \underset{\mathbf{2}}{CH_3CH^-R,M^+} \xrightarrow[-78\ ^\circ C/THF]{\rightleftharpoons R} \underset{\mathbf{3\text{-}6}}{CH_3[CHRCH_2]_nCH^-R,M^+} \xrightarrow[-78\ ^\circ C/THF]{CH_3I} \underset{\mathbf{7\text{-}10}}{CH_3[CHRCH_2]_nCHRCH_3} \quad (1)$$

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

Li salt of **3** at −78 °C in THF and workup of the product (see Experimental Section), pure 2,4-di(2-pyridyl)pentane (**7**) was obtained in about 60% yield. Proton NMR of the product in CCl_4 gave a first-order spectrum clearly showing the AB quartet of the nonequivalent methylene protons of this stereochemically pure (>99%) meso product (Figure 1). Chemical shifts and coupling constants are reported in Table I. The racemic isomer produced upon methylation of salts of larger or more extensively coordinated cations or generated by epimerization is conveniently distinguished by the different chemical shifts of the CH_3 absorption (Figure 2) (Table I).

Table I
Methylation Stereochemistry of Anion **3**[f] as a Function of Cation and Solvent or Coordinating Agent

cation	solvent/coord agent	electrophile	T, °C	% meso
Li	THF	CH_3I	−78	>99
Li	THF	CH_3I	−30	98
Li	THF	CH_3I	0	95
Na	THF	CH_3I	−78	96
K	THF	CH_3I	−78	63
K	THF	CH_3I	0	65
Rb	THF	CH_3I	−78	57
Li	THF/pyridine[a]	CH_3I	−78	83
Li	THF/TG[b]	CH_3I	−78	93
Li	THF/12-crown-4[c]	CH_3I	−78	92
Li	toluene[d]	CH_3I	−78	>99
Li	toluene[g]	CH_3I	−78	60
Li	THF	CH_3SO_2F	−78	*e*
Li	THF	$(CH_3)_2SO_4$	−78	>99
Na	THF/18-crown-6[c]	CH_3I	−78	58

[a] 50% by volume. [b] Triglyme 20% excess over carbanion. [c] 20% excess of crown ether. [d] Trace of THF present. [e] Mixture of pentane and butane products. [f] About 0.2 M. [g] Ethyl carbanion salt prepared in toluene without the presence of THF.

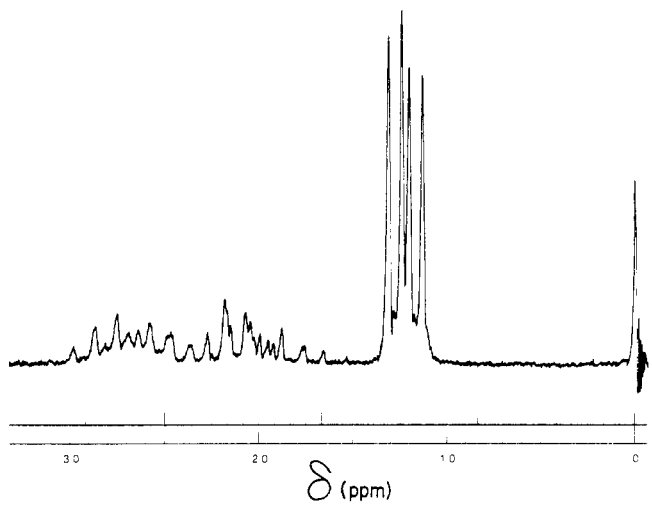
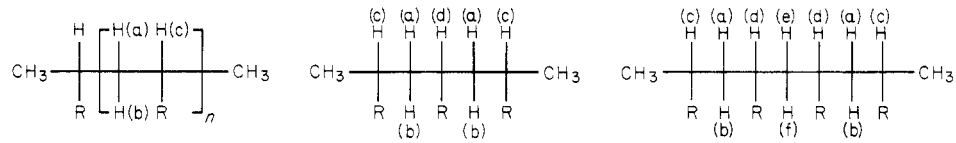


Figure 2. Epimerization product of *meso*-2,4-di(2-pyridyl)pentane with K-*t*-BuO/Me_2SO in CCl_4 at 35 °C.

The results of the stereochemistry of methylation according to eq 1 are shown in Table II. The effects of cation size and coordination are especially obvious. In THF there is a dramatic decrease in methylation stereoselectivity with increasing cation size, especially in going from Na to K to Rb salt. The effect of cation coordination is quite apparent in the methylation of the Li salt in the presence of 50% (volume) of pyridine. It is, however, interesting that a substantial concentration (~6 M) of pyridine is required for a relatively modest decrease in stereoselectivity. The effect of triglyme (2.2.2) and 12-crown-4 on the methylation stereoselectivity of the Li salt is very small. Apparently, either the coordination of the cation in the butane anion salt is a difficult process or the coordination of the cation will have to be very substantial

Table II
Chemical Shifts and Coupling Constants of Isotactic Oligomers and Polymers of 2-Vinylpyridine[a]



	(CH_2) (a, b) (e, f)	(CH) (c) (d)	(CH_3)	coupling constants, Hz J_{ab}	J_{ef}	$J_{ac/bc}$	$J_{ad/bd}$	$J_{ed/fd}$
dimer	(1.77, 2.25)	(2.80)	1.24	13.3		7.3/6.9		
trimer	(1.90, 2.17)	2.66, 2.66	1.17	13.5		7.9/8.3	5.7/6.3	
tetramer	(1.85, 2.15) (1.98, 2.11)	2.54, 2.66	1.12	13.3	13.5	8.5/9.5	5.3/6.0	6.8/8.0
polymer[b]	1.84, 2.14	2.63		13.3		6.6		
polymer[c]	1.84, 2.12	2.61		13.2		7.0		

[a] In CCl_4 except for the tetramer coupling constants that were obtained in benzene; chemical shifts in ppm. [b] K. Matsuzaki and T. Sugimoto, *J. Polym. Sci., Part A-2*, 5, 1320 (1967). [c] G. Weil and G. Hermann, *J. Polym. Sci., Part A-2*, 5, 1294 (1967).

before an effect on the stereochemistry is evident. The effect of 1 equiv of 18-crown-6 on the methylation of the Na salt is quite dramatic. The loss of stereoselectivity is essentially total. Replacing THF with solvents of lower polarity such as toluene does not seem to affect the stereoselectivity of the Li salt methylation. However, in this case small quantities of THF are certainly present since the carbanion solution was first prepared in THF followed by evaporation and distillation of toluene in the reaction flask. However, when the Li salt of **2** was prepared in toluene, the methylation stereoselectivity shows a dramatic decrease (Table II).

The question arises whether perhaps the overall stereochemistry is in whole or in part determined by the deprotonation or the vinyl addition steps. A comparison of methylation stereochemistry of the Li salts of **3** generated by the reaction of 2-ethylpyridine with *n*-BuLi or the Li salt of the α-methylstyrene tetramer followed by monomer addition indicates that the deprotonation step does not affect the stereochemistry. The preparation of **7** by the reaction of protonated **3** with the α-methylstyrene tetramer dianion Li salt followed by methylation yielded only meso product, indicating again the absence of a stereochemical role of the vinyl addition step.

Other possible factors that may influence methylation stereochemistry, such as temperature and leaving group ability, were shown to be relatively insignificant. It should, however, be pointed out that the variation of the leaving group ability is not great, and that chloride or bromide as leaving groups were not investigated.

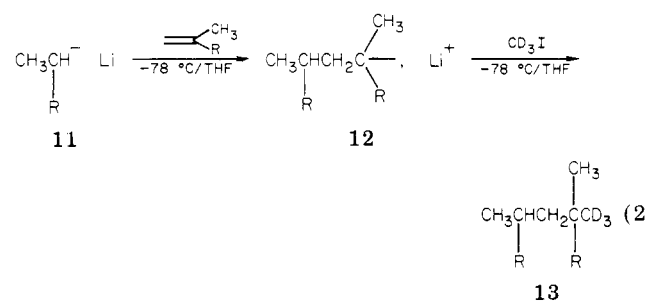
The methylation with CH_3SO_3F appears anomalous. In this case, a significant quantity of protonated product was isolated, so that it appears that partial proton transfer occurs from the relatively acidic protons of the methyl group.

The absence of significant temperature effects is interesting and correlates well with the observation that due to the tightness of such ion pairs, the structure of ion pairs of 2-pyridyl substituted carbanions does not vary significantly with temperature.[14] This, in turn, is consistent with the lack of effect of addition of relatively modest quantities of solvating agents such as glymes. Again it is obvious that the decrease in cation coordination expected at higher temperature is insufficient to substantially affect stereochemistry.

The position of the nitrogen atom in both ultimate and penultimate pyridine groups is of considerable interest. The corresponding methylation of the 1,3-di(4-pyridyl)-butane anion **3a** generated in a manner similar to that of the 2-pyridyl derivative is not stereoselective. In order to probe whether the loss of methylation stereoselectivity of this anion is due to the 4-pyridyl group in either or both positions, the methylation of 1-(4-pyridyl)-3-(2-pyridyl) anion **3b** prepared by the addition of 4-vinylpyridine to lithio-2-ethylpyridine was investigated. Again the two diastereomeric mixtures of enantiomers were formed in about equal quantities so that the 2-pyridyl group in the 1 and 3 positions is apparently essential for stereoselectivity (see Discussion).

An inspection of Table II would suggest that the stereochemical preference for the meso isomer is kinetic in nature. In order to evaluate the validity of this conclusion, the meso dimer, prepared by methylation of the Li salt, was epimerized in K-*t*-BuO/Me_2SO at 25 °C for about 10 days. After workup, approximately equal amounts of meso and racemic dimer were recoverd, indicating that the two diastereomers are about equal in stability (Figure 2). This result is in agreement with the finding of Flory and coworkers,[2] who reached a similar conclusion for the corresponding epimerization of 2,4-diphenylpentane. It appears, therefore, that the stereochemical preference observed in these systems is kinetically determined.

An additional question of interest is the stereochemical effect of the α-methyl group of the carbanion on the stereoselectivity of the methylation reaction. This was investigated by a CD_3I methylation of the pentane anion (eq 2).



11 12 13

The two geminal methyl groups in **13** are diastereotopic, and reaction of **12** with CH_3I indeed shows two absorptions of equal intensity at 1.16 and 1.26 ppm in addition to the doublet centered at 1.06 ppm corresponding to the single methyl group (Figure 3). The spectrum of **13**, however, clearly shows a single absorption at 1.26 ppm without any evidence of an absorption at 1.16 ppm (Figure 3). The methylation stereoselectivity of the pentane anion is thus very high (>95%).

Interestingly, the α-methyl group of the carbanion does not appear to exert a decisive influence on the methylation

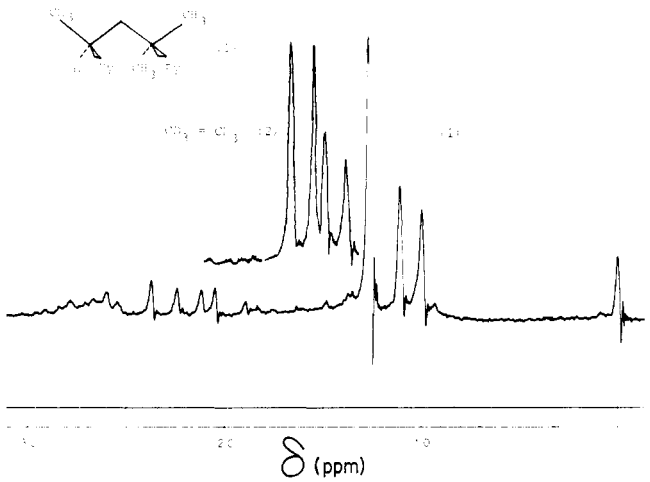


Figure 3. ^1H spectra (60 MHz) of the methylation products of 12 with CH_3I and CD_3I in CCl_4 at 35 °C.

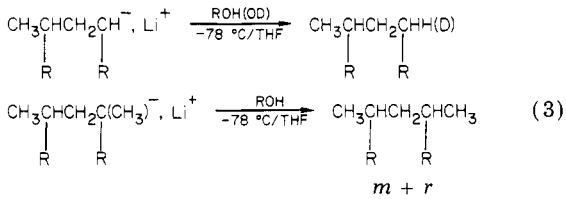
Table III
The Protonation Stereochemistry of Butane Anion 3 and Pentane Anion Lithium Salts 12 in THF at −78 °C, with $CH_3OH(OD)$ and Phenol

anion	ROH	% meso	stereoselectivity
12	CH_3OH	33	
12[a]	PhOH	37	
12[c]	*t*-BuOH	~50	
3	CH_3OD		67/33[b]

[a] Prepared by reaction of meso dimer 7 with 1,1-diphenylhexyllithium in THF at −78 °C. [b] Ratio of diastereotopic protons determined by using deuterium decoupling. [c] Refers to the epimerization experiment using K-*t*-BuO/Me_2SO.

stereoselectivity. At present we do not have an unequivocal stereochemical assignment of the two diastereotopic methyl groups. However, since both the butane and pentane anion Li salts are methylated with very high stereoselectivity, the reaction appears to proceed with identical stereochemistry (see Discussion).

Protonation. In order to further investigate the stereochemical behavior of the butane and pentane anions **3** and **12**, their protonation stereochemistry was briefly examined (eq 3). The pentane or butane anion Li salt



(3)

prepared as described above (Experimental Section) was reacted with CH_3OH (CH_3OD) or phenol by distillation of the alcohol into the flask containing the carbanion or by break-seal addition of a THF solution. The stereochemistry of the resulting pentane product is conveniently determined by 60 MHz NMR (Table III). The product was predominantly racemic (63–67%). A similar result was obtained when the pentane anion was obtained by deprotonation of the *meso*-pentane **7**, using 1,1-diphenylhexyllithium as the base. The stereochemistry of protonation in the butane anion case was examined using CH_3OD as the deuterating agent. The geminal hydrogens of the butane product are diastereotopic (2.61 and 2.69 ppm) so that the stereochemistry of deuteration could be examined. The deuterium decoupled ^1H spectrum shows

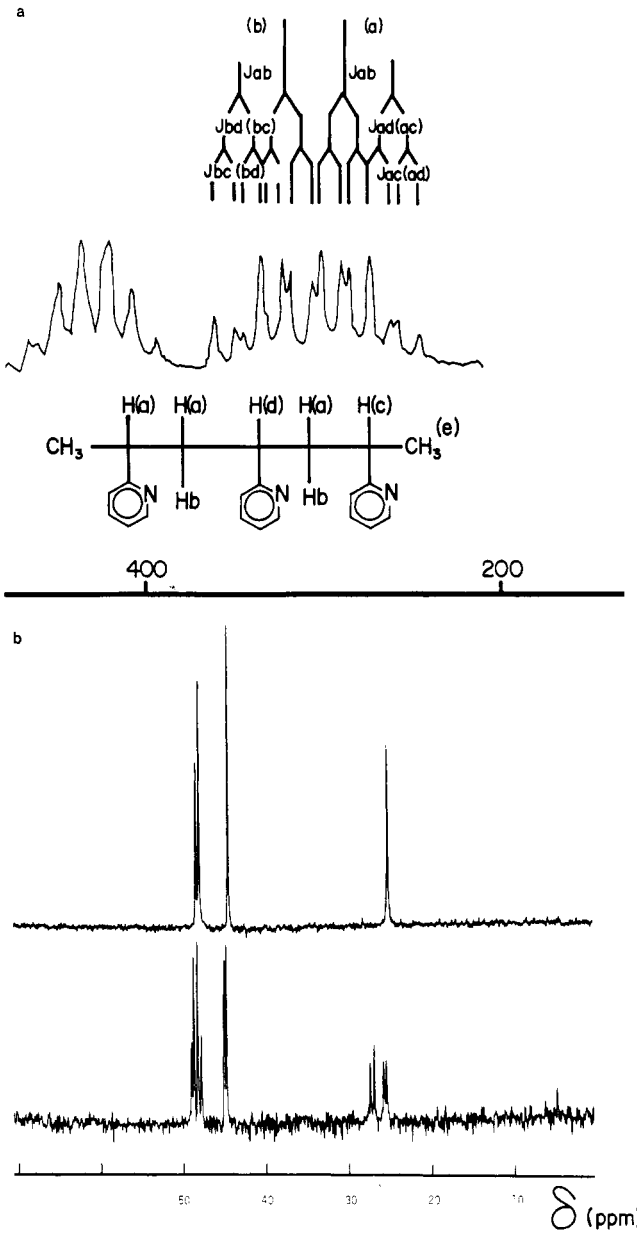


Figure 4. (a) ^1H spectrum (100 MHz) of the CH_2/CH portion of isotactic 8 in CCl_4 at 35 °C. (b) ^{13}C spectra (25.2 MHz) of CH_3, CH_2, and CH absorptions of epimerized 8 (lower) and isotactic 8 (upper).

two absorptions in a 67:33 ratio, the stronger absorption occurring upfield.

Although the absolute stereochemistry of the protonation of 3 could not be determined, the stereochemistry of protonation of butane and pentane anions appears to be similar, and this is consistent with the observation that the α-methyl group of the carbanion does not appear to play an important role in these reactions (see above).

Addition of 2-Vinylpyridine. This was accomplished by slow (1–2 h) distillation of the monomer into the reaction flask, followed by methylation (eq 1). The trimer **8** was obtained by chromatography over neutral Al_2O_3. The 100 MHz ^1H spectrum of the product obtained by using lithio-2-ethylpyridine as the initiator is shown in Figure 4a and clearly indicates that the product is isotactic (>95%). A similar result was obtained with the Na salt (Table IV). The isolation of an isotactic product was not due to separation on the column, since epimerization of the isotactic trimer in K-*t*-BuO/Me_2SO followed by chromatographic isolation of the product yielded approx-

Table IV
Stereochemistry of Formation of 2,4,6-Tri(2-pyridyl)heptane as a Function of Cation and Cation Coordination

	I *mm*	H *mr(rm)*	S *rr*
Li, THF	>95	<5	<5
Na, THF	>95	<5	<5
Na, THF, Na, CE, THF[a]	~50	~50	
t-BuOK/Me_2SO[b]	~25	~55	~20

[a] 18-Crown-6 present during methylation. [b] Epimerization of isotactic trimer for about 2 weeks in *t*-BuOK/Me_2SO at 25 °C.

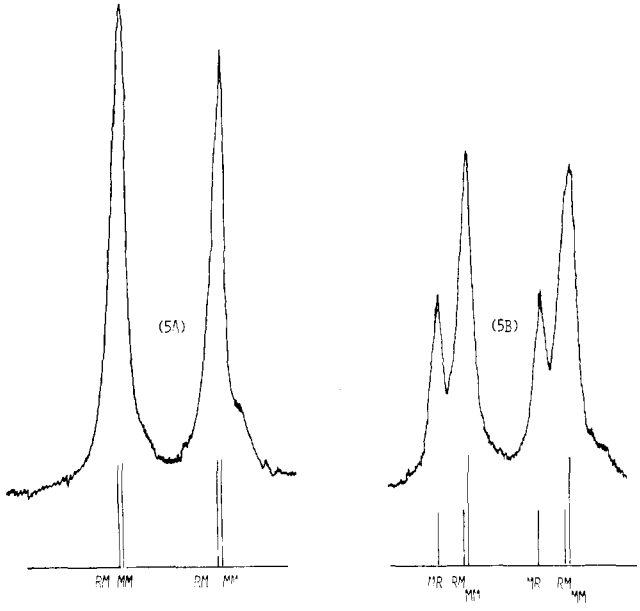
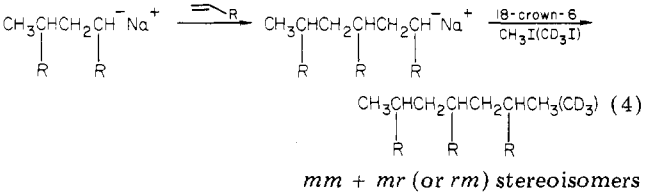


Figure 5. ^1H NMR spectrum (100 MHz) of the CH_3 portion of CH_3I and CD_3I terminated 4 prepared according to eq 3.

imately a 1:2:1 mixture of isotactic, heterotactic, and syndiotactic stereoisomers (see below). When the 2-vinylpyridine addition methylation sequence was carried out in the presence of 18-crown-6 with sodio-2-ethylpyridine as the initiator, isolation of a pure trimer proved difficult due to the presence of side products (see below). However, when the 18-crown-6 was added after the 2-vinylpyridine addition immediately prior to methylation, a mixture of two stereoisomers was isolated (eq 4). This



(4)

mm + *mr* (or *rm*) stereoisomers

was confirmed by comparison of the spectra of the CH_3I and CD_3I terminated products (Figure 5). The low field doublet is absent in the deuterated product. Since the vinyl addition step to the butane anion must give rise to a meso sequence, this doublet should correspond to the (*mr*) CH_3 group, while the (*rm*) and (*mm*) CH_3 absorptions have approximately the same chemical shift. This result is similar to that found during the methylation of the crown ether complex of the Na butane anion salt (see above). Thus the methylation of the hexane anion Na crown ether salt yields likewise a 50/50 mixture of meso and racemic sequences. Comparison with the 100 MHz proton spectrum of the *t*-BuOK/Me_2SO epimerized isotactic trimer (Figure 6) allows an unequivocal assignment

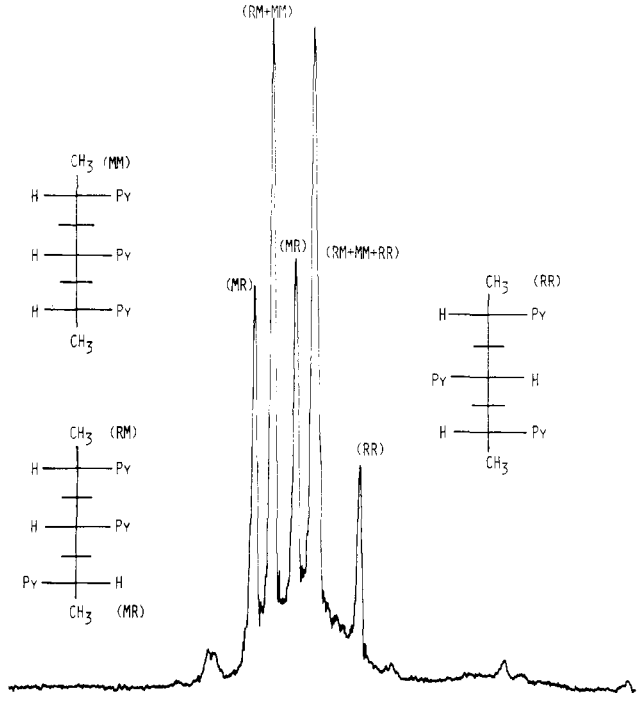


Figure 6. ^1H NMR spectrum (100 MHz) of the CH_3 portion of K-*t*-BuO/Me_2SO epimerized trimer 8.

of the four methyl doublets. Interestingly, the (*mr*) methyl doublet absorbs downfield from the (*mm*) signal whereas the (*rr*) doublet absorbs upfield. The approximately random distribution of stereoisomers indicates that the free energies of the three stereoisomers are close, so that, as exected, the Li and Na salts give a kinetically controlled product.

The ^1H chemical shifts of the CH_3 end groups are quite sensitive to the stereochemical configuration of the dimer and trimer model compounds. The same is true for the corresponding ^{13}C spectra (Figure 4b). Because of its greater simplicity, the $^{13}CH_3$ spectra should be of value in an elucidation of oligomer configuration, especially for the higher oligomers **10**, where the proton NMR signal of the methylene groups is complex.

Tetramer Formation

Addition of 3 equiv of 2-vinylpyridine to lithio-2-ethylpyridine at −70 °C in THF followed by methylation (CH_3I) and workup of the product produces a reasonable (25%) yield of tetramer along with some dimer, higher oligomers, and polymer. The 100 MHz spectrum (CCl_4) of the tetramer does not appear to give a first-order spectrum, but the 270 MHz ^1H spectrum lends itself to convenient analysis (Figure 7a). The spectrum indicates that the tetramer is predominantly (>90%) isotactic. One of the inner methylene protons is clearly separated from the outer methylene protons facilitating assignments **17**. Double irradiation experiments allow assignment of the downfield methine absorption as due to the two inner methine protons. The chemical shifts and coupling constants are shown in Table I.

Epimerization in K-*t*-BuO in Me_2SO yields a product, the ^1H NMR spectrum of which is quite complex. Eight CH_3 doublets corresponding to four symmetrical and two unsymmetrical tetramer stereoisomers are expected for such a product mixture. The ^{13}C spectrum of the epimerized product is shown in Figure 7b, along with that of the isotactic stereoisomer. Although no individual stereoisomers could be assigned, it is clear that substantial epimerization had occurred and that the $^{13}CH_3$ signal is

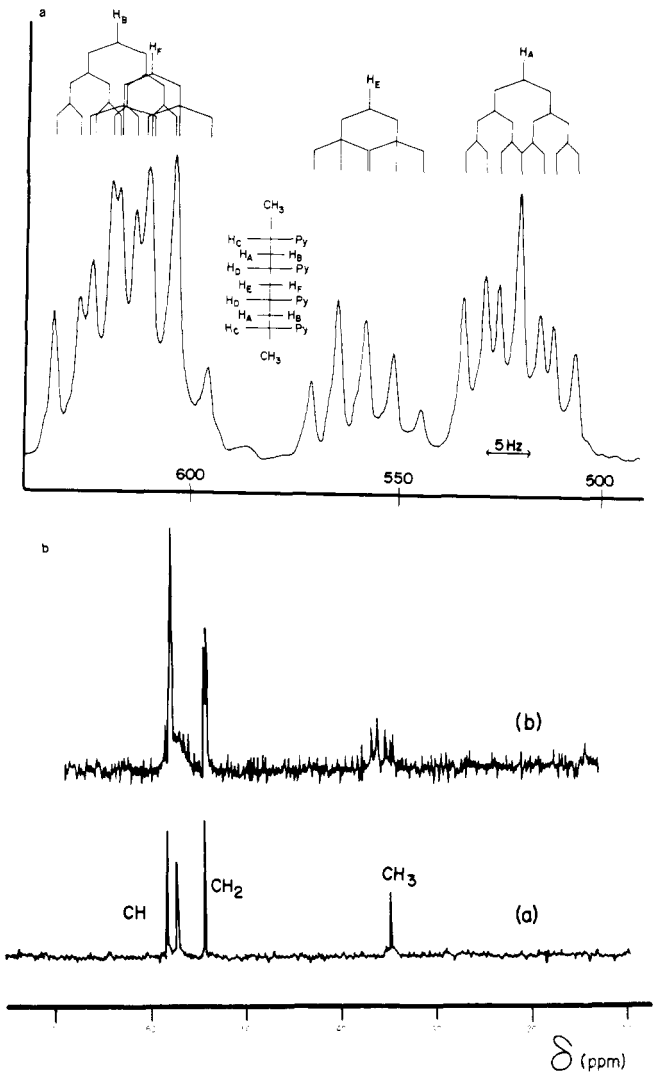


Figure 7. (a) Methylene portion of the ^1H 270 MHz spectrum of isotactic tetramer **9**. (b) ^{13}C spectra (25.2 MHz) of epimerized **9** (upper) and isotactic **9**.

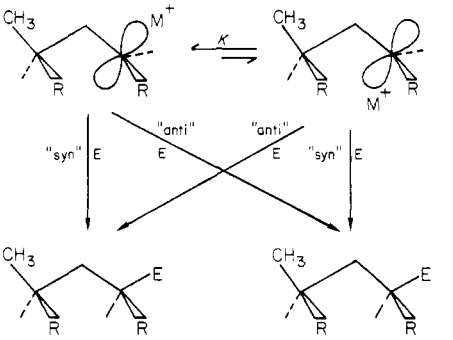
again very sensitive to chain configuration. Careful epimerization experiments aimed at identification of the $^{13}CH_3$ absorptions of the tetramer stereoisomers are currently in progress.

Summary of Experimental Results

On the basis of the work cited above, the following conclusions may be drawn: (1) The methylation of the 1,3-di(2-pyridyl)butane anion Li or Na salts in THF with CH_3I or $(CH_3)_2SO_4$ is highly stereoselective. This stereoselectivity decreases with increasing cation radius and increasing cation coordination. (2) The location of nitrogen in the 2-position in both ultimate and penultimate pyridine rings is essential for methylation stereoselectivity. (3) Methylation stereoselectivity of the butane, hexane, and octane anion lithium salts appears to be identical. No effect of antipenultimate or prior units is observed. (4) Methylation of the butane and pentane lithium salts appears to occur with the same stereochemistry, although the absolute stereochemistry in the latter case could not be ascertained. A similar conclusion appears to hold for the protonation of these salts. (5) For the systems studied so far, methylation and vinyl addition appear to occur with identical stereochemistry. Protonation appears to occur in a largely nonstereoselective manner. (6) Epimerization of meso dimer and isotactic trimer yields stereoisomers in statistically expected proportions. Thus at least for the systems studied so far the stereoselectivity appears to be kinetically, not thermodynamically, determined.

Discussion

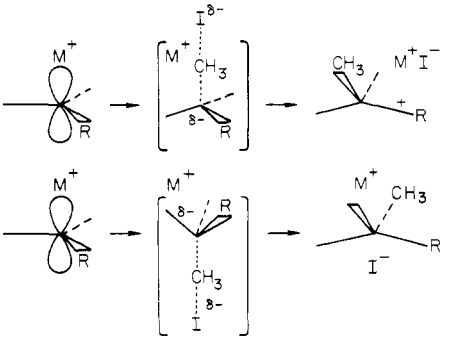
Explanations for the stereoregular anionic polymerization of methyl methacrylate in low polarity media with Li as the counterion have been offered by several authors.[18-21] These descriptions often involved coordination of the counterion with the penultimate ester group of the polymer chain and with the monomer prior to its induction into the chain. The present results clearly indicate an important role of the penultimate Lewis base site and the counterion in the anionic oligomerization of 2-vinylpyridine. However, the present results indicate that methylation and 2-vinylpyridine addition occur with identical stereochemistry. Since the cation coordinating abilities of CH_3I and 2-vinylpyridine are expected to differ widely, it is possible that it is the structure of the carbanion site itself that is of unique importance. In this substantially delocalized anion, the carbanion is essentially sp^2 hybridized and the cation is most likely located over the π cloud of this ambident type anion.[22,23] CNDO calculations on the uncoordinated ion pair indicate that such a position of the cation is substantially (~60 kcal) lower than an optimized nodal plane position in which the cation would be associated with the nitrogen σ electron pair. The ion pair of the 2-pyridyl-substituted carbanion is thus most likely chiral, and in the presence of a penultimate chiral center, for instance for **3**, two diastereomeric ion pairs **14** and **15** should exist that differ in carbanion configuration (eq 5).



(5)

It should be pointed out that the interconversion of the two ion pairs in such a case will have to occur by migration of the counterion from the top to bottom side of the carbanion plane, either by a dissociation–association pathway or by some other process such as a "conducted tour" pathway proposed by Cram.[24]

The stereochemistry of carbanion pairs of this type is expected to depend on several factors: (1) since the two ion pairs are diastereomeric, they differ at least in principle in free energy so that under certain conditions one or the other may predominate (see below); (2) the mode of electrophilic attack may occur "syn" or "anti" with respect to the metal ion (eq 6). We believe that in these systems



(6)

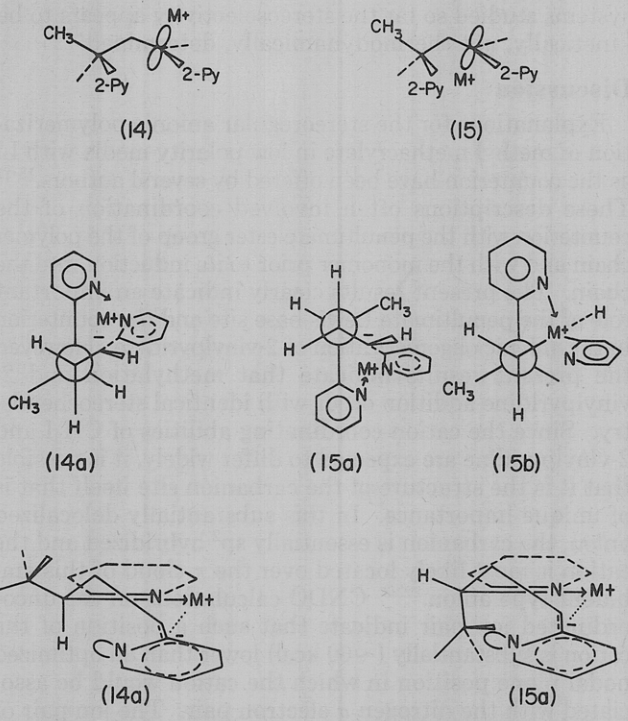


Figure 8. Stereochemical representations of diastereomeric ion pairs **14** and **15**.

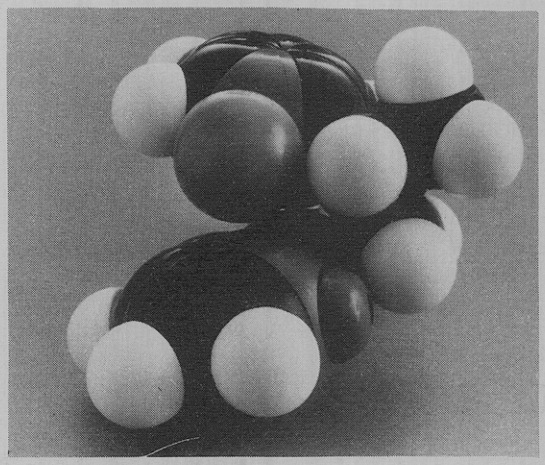


Figure 9. Space filling CPK model of **14**.

the "syn" approach is favored. The ion pair generated during the "anti" reaction mode would represent a "product separated" ion pair. In the case of the reaction with CH_3I, such an ion pair is expected to be quite unfavorable. For instance, conductance measurements on alkali iodide salts in THF indicate the virtual absence of solvent separated ion pairs.[25] Since product separated ion pairs are expected to be even less stable than solvent separated ion pairs, the transition state for the "anti" approach should be quite unfavorable compared to the "syn" reaction mode where a tight ion pair type transition state may be generated. Such a rationale has been used to describe the predominantly "syn" type carbanion protonation observed by Cram,[26] Szwarc,[27] and others[28] in low polarity media. It should be pointed out that barring great differences in reactivity between the two ion pairs, a highly stereoselective reaction can only take place if the constant K describing equilibrium between the two ion pairs is either $\gg 1$ or $\ll 1$ and that the mode of reaction is either predominantly syn or anti. In the case of the highly stereoselective reactions of the lithium or sodium salts of **3**, it would thus appear that ion pair **14** is preferred over **15** since a syn attack on **14** produces a meso sequence. What could be the reason for this preference? Several years ago, Szwarc and Sigwalt,[13] through careful conductance measurements on living polymers of 2-vinylpyridine and similar polymers having a penultimate styryl unit, independently showed that the Na^+ counterion is most likely coordinated with the nitrogen lone pair of the penultimate pyridine ring. Newman projections of model compounds of the two diastereomeric ion pairs possessing these features are shown in Figure 8 along with stereochemical representations of the cyclohexene type ring system formed by the M^+_ penultimate pyridine coordination. Ion pair **14a** is favored ($\sim$1 kcal) because of a butane gauche type nonbonded interaction in **15a**. **15b** shows an ion pair conformation which can be viewed as generated from **14a** by 180° rotation of the CH_2–CH–R bond followed by inversion of the carbanion pair. Such an ion pair seems less likely since the metal ion is further removed from the penultimate pyridine lone pair. A comparison of **14a** with **15a** points up the nonbonded CH_3-nitrogen lone pair interactions in **15a** where the CH_3 group has a pseudoaxial orientation in the cyclohexene type ring. Inspection of a space-filling CPK model of **14a** (Figure 9) also shows the severe steric crowding that would result from an inversion of configuration of the penultimate asymmetric center (equivalent to an inversion of the ion pair), for instance by H–CH_3 exchange. This model also predicts that solvation of the counterion by THF should be hindered for ion pair **15** due to nonbonded interactions with the CH_3 group. From the above, it is not improbable that the free energy of **14a** may be several kilocalories lower than that of **15a**. Even a relatively small difference in free energy, however, may have a substantial impact on the equilibrium between **14** and **15**. For instance, a free energy difference of only 3 kcal gives a ratio of **14**/**15** of about 150. Hence the very large stereoselectivities observed in these systems are not totally surprising. It should be pointed out that it is the stereochemistry of the active site itself, especially of the metal cation, that appears to be the key factor in the stereochemistry in these systems.

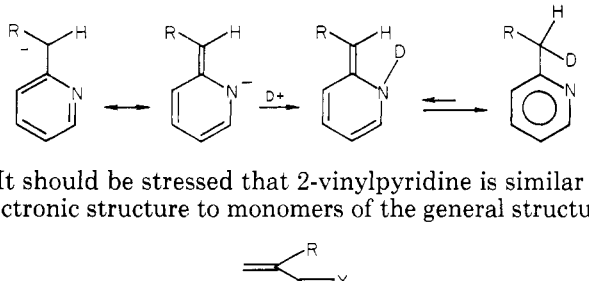
The mechanism proposed above appears consistent with all of the observed facts. The effects of cation size and coordination are in fact expected. The much less strongly coordinating K and Rb ions would not be complexed by penultimate pyridine as strongly as Li or Na and therefore the proportion of uncomplexed ion pairs (for which **14** and **15** should be essentially equal in free energy) is expected to increase. Hence the stereoselectivity drops. The same rationale holds for the effects of cation complexing agents such as 18-crown-6 that are expected to disrupt the intramolecular cation coordination. The proposed mechanism is also consistent with the observed identical stereochemistry of methylation and 2-vinylpyridine addition. Since it is the structure of the active site itself that determines the stereochemical behavior of the anion, the similarity between the two reactions is not unexpected. The stereoselectivity should not depend on the coordinative ability of the electrophile, and this is indeed observed.

The effects of structure (or lack thereof) on the stereochemistry are likewise accommodated by the proposed mechanism. The presence of a 4-pyridyl group in the penultimate position makes intramolecular cation coordination impossible. The lack of methylation stereoselectivity of the 1-(2-pyridyl)-3-(4-pyridyl)butane anion lithium salt is less obvious. The metal ion position is possibly changed, being closer to the negative nitrogen atom of the carbanion. Alternatively, the tighter ion pair of the 4-pyridyl-substituted carbanion[14] is less easily co-

ordinated by the penultimate 2-pyridyl group. Perhaps both factors play a role.

The apparent lack of stereochemical effect of displacing H by CH_3 in the α position of **3** is easily accommodated by the above mechanism. Intramolecular cation coordination is not hindered by the presence of a carbanion CH_3 group, and inspection of space filling models does not indicate the presence of other nonbonded interactions with this CH_3 group that are likely to affect the equilibrium between the diastereomeric ion pairs or their reactions. Experiments now in progress on the anionic oligomerization of 2-(2-pyridyl)propene with Li as counterion likewise indicate that the addition of this monomer, like the methylation, is highly stereoselective.

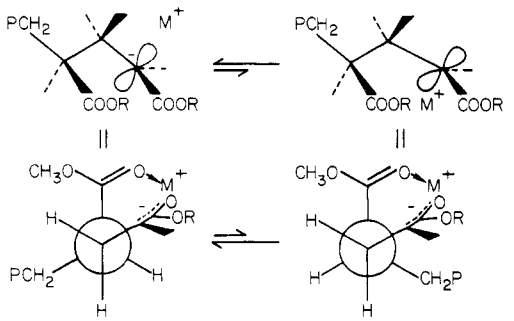
Interestingly, the similarity between methylation and 2-vinylpyridine addition does not extend to protonation. If protonation occurs at carbon, such a difference in stereochemistry would conflict with the proposed mechanism. Differences in protonation and methylation stereochemistry are not unusual.[30] In several instances, notably with ambident anions such as enolates, such differences are thought to be due to protonation of the heteroatom followed by tautomerization to the carbon acid. A similar protonation mechanism may well occur in the present case. The 2-pyridyl substituted anion is an ambident type anion because of extensive delocalization of negative charge onto nitrogen, thus giving this species nitranion character.[8,14] Protonation of nitrogen now generates an achiral enamine that rearranges to a mixture of stereoisomers of the more stable carbon acid:



It should be stressed that 2-vinylpyridine is similar in electronic structure to monomers of the general structure

where R = H or alkyl, X = O or N, and Y = C, O, or N. Therefore, monomers such as (meth)acrylates, (meth)acrylamides, vinyl ketones, and similar compounds may undergo anionic oligomerization or polymerization reactions subject to a similar reaction mechanism.

Thus, for instance, for the polymerization of acrylates, equilibrium (eq 7) is expected to lie to the left so that



(7)

under conditions where the intramolecular six-membered ring is formed, the formation of meso dyads is predicted. Such a prediction is in accordance with the general observations that for monomers of this type and in low polarity media, small cations tend to lead to isotactic polymers, and also with the fact that highly syndiotactic polymers (>90%) are seldom formed under anionic conditions. Undoubtedly the coordinating ability of the X group, along with factors such as cation size and coordinating power of the solvent, is expected to and is found to play an important role in the stereochemistry of anionic vinyl oligo- or polymerization. For instance, methyl, isopropyl, and *tert*-butyl acrylates have been dimerized in THF at −78 °C according to a reaction analogous to eq 1. In this case, however, the stereoselectivity was much less compared to that of the 2-vinylpyridine case, and this was attributed to the lesser coordinative ability of the ester carbonyl group compared to the 2-pyridyl nitrogen.[31]

Experiments designed to test the applicability of the proposed mechanism to the above monomers are currently in progress.

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Syntheses of Methyl Methacrylate–Stearyl Methacrylate Graft Copolymers and Characterization by Inverse Gas Chromatography

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ABSTRACT: Graft copolymers of well-defined structure and composition were prepared by radical copolymerization of methyl methacrylate and poly(stearyl methacrylate) macromonomers. The latter was prepared by polymerization of stearyl methacrylate (SMA) in the presence of thioglycolic acid as a transfer agent, followed by reaction with glycidyl methacrylate. The copolymerization involving the methacrylate monomer and macromonomer was azeotropic with $r_1 \approx r_2 \approx 1$, allowing a quantitative conversion to a graft copolymer of the desired composition. The gas chromatograph retention diagram of *n*-dodecane on the graft copolymers revealed that a microscopic phase inversion occurs around 20–30 wt % SMA, above which the poly(SMA) segments constitute a continuous phase. The random copolymers and the homopolymer blends showed different diagrams which were expected for a single-phase polymer with a lower T_g and for a completely phase-separated mixture, respectively.

Graft copolymers have found many important applications in the polymer industry. We have a particular interest in their use for surface modification purposes. Generally, the surface structure and properties of polymers are known to be of considerable importance in determining their applications for uses as coatings, adhesives, and dispersants and also for biomedical use of current interest. Among many surface modification techniques including chemical, UV, and plasma treatments, graft copolymers appear to be most promising in obtaining a structure–property relationship to obtain a design of a controlled surface structure for any particular use. This is expected because graft copolymers of controlled structure and composition can be relatively easily prepared in favorable cases and also because they offer possibilities for providing a wide range of properties depending on the amphipathic nature of the segments (polar–nonpolar, soft–hard, and hydrophilic–lyophilic), their surface activity, and also their ability to compatibilize polymer blends.

The present paper describes the preparation of stearyl methacrylate (SMA)–methyl methacrylate (MMA) graft copolymers as a simple model in approaching the above mentioned goal. The comb-type graft copolymers of well-controlled architecture and composition were prepared by radical copolymerization, using macromonomers according to the method described by Walbridge and Waite.[1] The surface properties and the morphology were characterized by use of the inverse gas chromatography[2] which has been successfully applied in the characterization of the surface of hydrophilized polyethylene[3] and the surface and bulk properties of styrene–tetrahydrofuran block copolymers[4] and random copolymers containing *p*-dodecylstyrene or fluorinated methacrylate.[5]

Experimental Section

Materials. Commercial MMA, glycidyl methacrylate, and thioglycolic acid were distilled under vacuum. SMA and azobis(isobutyronitrile) (AIBN) were recrystallized from ethanol and methanol, respectively. Benzene and xylene were distilled over sodium. Chloroform, used as a coating solvent for gas chromatography, was dried over calcium chloride and distilled. Methanol, ethanol, hydroquinone, *N,N*-dimethyllaurylamine, *n*-dodecane, and Chromosorb G (AW-DMCS treated, 60–80 mesh) were used as supplied commercially.

Graft Copolymers. SMA, AIBN, and thioglycolic acid (TGA) were weighed into an ampule and degrassed and sealed under vacuum. Polymerization at 60 °C gave a prepolymer having a carboxyl group terminal at the one end. The polymer was precipitated into ethanol, purified twice by reprecipitation from benzene into methanol or ethanol, then dried under vacuum. The carboxyl-group content was determined by titrating the polymer in tetrahydrofuran with 0.1 N aqueous potassium hydroxide, using phenolphthalein as an indicator.

The carboxyl group of the prepolymer was reacted with glycidyl methacrylate (50 mol % excess) at 140 °C in xylene with small amounts of hydroquinone and *N,N*-dimethyllaurylamine to yield the macromonomer having a methacryl group at one end. After the reaction had gone on for 4 h it was complete as confirmed by there being no titratable carboxyl group. The polymer was recovered by precipitation into methanol and reprecipitated from benzene into methanol.

The poly(SMA) (PSMA) macromonomer thus obtained was copolymerized with MMA in benzene with AIBN at 60 °C to give the comb-type graft copolymers with PSMA branches. The copolymerization was conducted in an ampule which was degassed by three freeze–thaw cycles and sealed under vacuum. The reaction was continued for 4 to 6 days to give a quantitative con-

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