Synthesis and Stereochemical Characterization of Isotactic Poly(3-methyl-2-vinylpyridine)

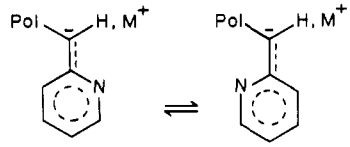
Ishrat M. Khan and Thieo E. Hogen-Esch*

Center for Macromolecular Science and Engineering and Department of Chemistry, University of Florida, Gainesville, Florida 32611. *Received December 29, 1986*

ABSTRACT: The oligomers prepared by initiation of 3-methyl-2-vinylpyridine by the lithium salt of 2-ethyl-3-methylpyridine and terminated with CH_3I or $^{13}CH_3I$ were separated by HPLC and analyzed by ^1H and ^{13}C NMR and by GC. The methylation stereochemistry changes from predominantly racemic (75%) for the dimer to predominantly meso (70–80%) for the trimer and higher oligomers. The stereochemistry of vinyl addition is predominantly meso (87–92%) for all degrees of polymerization. The stereochemistry of the polymer (P3M2VP) was analyzed by using the C_2 and $C_{3'}$ carbon spectra of the P3M2VP prepared by anionic and radical (AIBN) initiation and by a comparison of the stereochemistry of the chain end and the chain of anionic P3M2VP. The anionic P3M2VP is predominantly isotactic (~80%). The substantially larger isotactic content of P3M2VP compared to that of poly(2-vinylpyridine) prepared under identical conditions is consistent with the presence of a helical chain conformation resulting from an interaction of the 3'-methyl with the penultimate pyridine ring.

Introduction

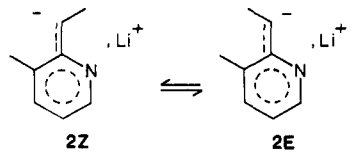
We have in recent years reported on the stereochemistry of oligomers and polymers of 2- and 4-vinylpyridines.[1-7] The studies on the oligoemrization processes have provided a significant understanding of some of the factors controlling the stereoregulation process in 2-vinylpyridine. Furthermore, we have carried out ^1H and ^{13}C NMR studies on the carbanion intermediates of the living polymer of 2-vinylpyridine.[8-10] Studies on the Li salts of dimer, trimer, and tetramer models of living oligo-2-vinylpyridine have demonstrated the existence of *E* and *Z* geometric isomers 1, the *E*/*Z* ratio being about one. The studies also show



1E 1Z

that the *E* and *Z* geometric isomers do not interconvert on the polymerization time scale but may be interconverted upon addition of the monomer, depending on the transition-state monomer conformation (Scheme I). The *E*/*Z* ratio of one in the Li/THF system indicates that both modes (s-cis and s-trans) of monomer presentation occur with approximately equal probability. This would mean that two distinct carbanion intermediates are simultaneously propagating in the polymerization process, somewhat analogous to a two-state Coleman–Fox mechanism.[11]

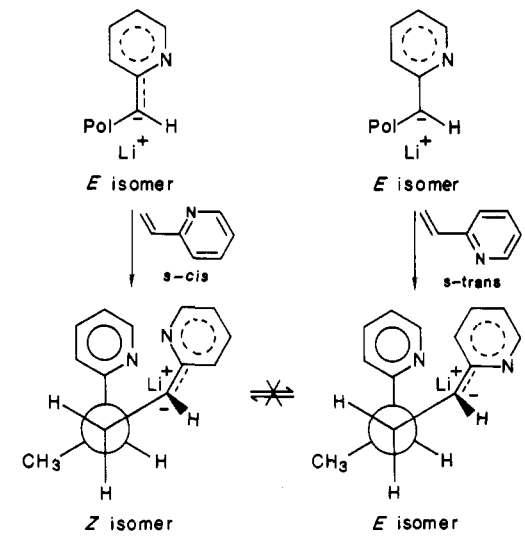
Examination of Scheme I raises the possibility of manipulating the mode of monomer presentation to the growing polymer chain end. Quite possibly, the placement of a substituent at the 3-position in 2-vinylpyridine may favor the s-cis addition over the s-trans addition to the propagating chain end because of steric constraints. A monomer of this type would be 3-methyl-2-vinylpyridine (3M2VP).[12] The simplest model of the corresponding carbanion intermediate of poly(3-methyl-2-vinylpyridine) is (2-ethyl-3-methylpyridyl)lithium (2) capable of existing as *E* and *Z* isomers (eq 1). Proton and ^{13}C NMR studies



2Z 2E (1)

of this model[10] show the presence of the *Z* isomer only and therefore demonstrate the dramatic effect of a substituent

Scheme I

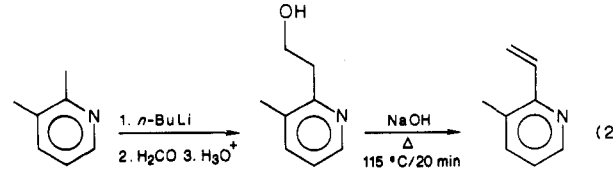


in the 3-position. Unlike 2-vinylpyridine, monomer addition in this case is expected to occur in s-cis fashion to produce a *Z* carbanion intermediate. This may profoundly affect the stereochemistry of polymerization.

As a result the anionic polymerization of 3-methyl-2-vinylpyridine and stereochemical characterization of poly(3-methyl-2-vinylpyridine) (P3M2VP) is of interest.

Experimental Section

Monomer Synthesis. The monomer was synthesized according to equation 2.



(2)

To a THF solution of *n*-BuLi (9.8×10^{-2} mol) under high vacuum was added 8.7×10^{-2} mol of 2,3-lutidine at room temperature. The orange color of the carbanion was immediately perceptible. The reaction was allowed to proceed for 1 h with constant degassing and then cooled to −78 °C.

The formaldehyde was added by decomposing paraformaldehyde with a heat gun and distilling it into the carbanion solution, until the color disappeared. After protonation (CH_3OH) and removal of the THF, the residue was dissolved in 100 mL of deionized water of pH 9 and the solution was extracted three

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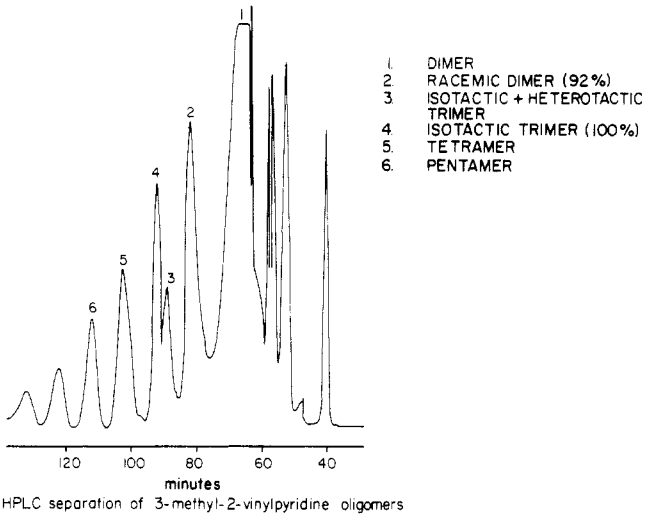


Figure 1. HPLC chromatogram of oligomers of 3-methyl-2-vinylpyridine (3M2VP).

times with ether. After drying and removal of the ether, the 2-(3-methyl-2-pyridyl)ethanol was collected by vacuum distillation. Yield was 40%. ^{1}H NMR: 2.30 (s, 3 H), 2.95 (t, 2 H), 3.87 (t, 2 H); 7.05 (q, 1 H), 7.50 (d, 1 H), 8.28 ppm (d, 1 H).

The dehydration reaction was carried out by adding 0.30 g of powdered NaOH and a trace amount of *tert*-butylcatechol to 1.87 g of the alcohol and refluxing the mixture for 20 min at 115 °C.[12] The crude reaction product mixture was dissolved in 30 mL of water (pH 9) and extracted three times with ether. After removal of the ether, the product was collected by vacuum distillation. The yield was 50%. ^{1}H NMR: 2.22 (s, 3 H), 5.50 (q, 1 H), 6.30 (q, 1 H), 6.93 (q, 1 H), 7.18 (q, 1 H), 7.58 (d, 1 H), 8.40 ppm (d, 1 H).

Prior to oligomerization or polymerization the monomer was purified by distillation once over CaH_2 and once over a potassium mirror on the high vacuum line.

Oligomerization and Polymerization of 3-Methyl-2-vinylpyridine. All oligomerization and polymerization reactions were carried out by using high vacuum (10^{-5}–10^{-6} mmHg) breakseal techniques.[3] Oligomers and polymers were prepared according to eq 3, by slow distillation of monomer onto the rapidly stirred initiator solution, followed by termination by ^{13}C-enriched (97–99%) CH_3I. The oligomers were worked up by first removing the THF, dispersing the residue in deionized water (pH ~9), and extracting with diethyl ether. The oligomer product mixture was separated by preparative liquid chromatography. Poly(3-methyl-2-vinylpyridine) was precipitated by slowly adding a concentrated THF solution into hexanes. Poly(3-methyl-2-vinylpyridine) was also synthesized by using AIBN as the initiator in benzene at 60 °C.

Chromatography. An "Altex" Model 332 programmable gradient system, fitted with a constant wavelength UV detector (254 nm), was used for all preparative separations. The columns used were Lobar (E Merck) with 40–63 Li Chro-prep Si60 silica gel. Solvent gradient elution was carried out with hexane (A) and 4:1 CH_2Cl_2–CH_3OH mixture (B), starting at 10% B to 60% B over a period of 120–300 min, depending on the sample. For best separation a flow rate of 5 mL/min was used. For stereoisomer separations about 100–200 mg of the sample was used.

A temperature programmable Hewlett-Packard Model 5880A instrument equipped with a flame ionization detector was used for all gas chromatographic analyses. The columns used were either a 25- or a 50-m SE-54 silicone gum (Hewlett-Packard) with a temperature limit of 350 °C. Helium was used as the carrier gas.

NMR Characterization. ^{1}H and ^{13}C NMR spectra were obtained on either a JEOL FX-100 instrument or Nicolet NT-300 NMR spectrometer. For ^{13}C NMR spectra a 45° flip angle was used. Also, the effect of relaxation time was determined by changing the pulse delay.

Results

In order to obtain information on the stereochemistry of poly(3-methyl-2-vinylpyridine), the stereochemistry of its oligomers is of interest (eq 3). The racemo dimer **4** and isotactic trimer **5** are easily separated (Figure 1). The products were identified by ^{1}H and ^{13}C NMR spectroscopy and capillary gas chromatography. The relative proportions of stereoisomers in the oligomers were found to be the same in both the crude reaction product and after purification by extraction with diethyl ether. This is in agreement with results obtained for oligomers of 2-vinylpyridine.[3]

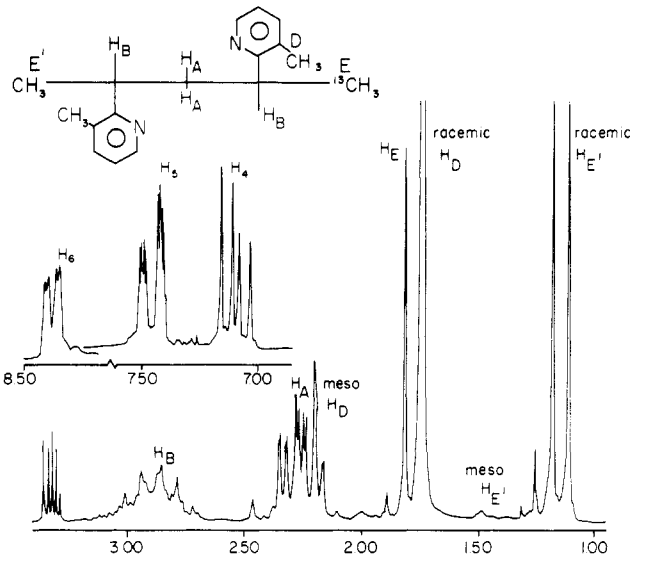
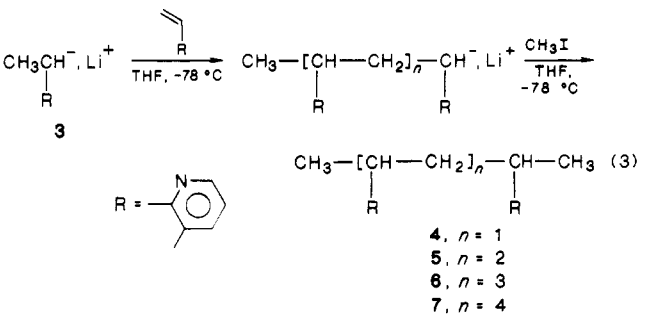


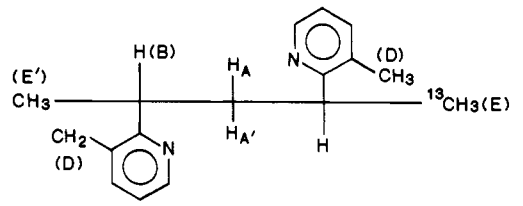
Figure 2. Proton NMR spectrum (100 MHz) of racemic dimer **4** in CD_3OD at 25 °C (upfield methyl doublet E^1 not shown).



Oligomer Stereochemistry. The 100-MHz ^{1}H NMR spectrum of the racemo isomer of dimer **4** obtained by liquid chromatography of the reaction product is shown in Figure 2. The methylene signal is a doublet of doublets. This is interpreted as due to two equivalent protons that exhibit two different couplings (J_{AB} and $J_{A'B}$) to the methine protons, as observed for *racemo*-2,4-diphenylpentane (**8**)[13] and *racemo*-2,4-bis(4-pyridyl)pentane (**9**).[14] The doublets in turn are split by the ^{13}C of the labeled methyl end group. The chemical shifts and coupling constants of the racemo dimer **4** are compared with **8**, **9**, and 2,4-dimethyl-2,4-bis(4-pyridyl)pentane (**10**[5]) in Table I. The two sets of peaks for H_E are due to one of the methyl groups being 99% enriched ($^1J_{HC}$ ~ 127 Hz). Capillary gas chromatographic analysis showed a 75/25 racemo/meso distribution of stereoisomers in dimer **4**. The same proportion of stereoisomers was found in the analogous system of 2-(3-methyl-2-pyridyl)-4-(2-pyridyl)pentane prepared by methylation of the corresponding lithium salt.[15]

The 300-MHz ^{1}H NMR spectrum of isotactic trimer **5**, isolated by preparative liquid chromatography, is shown in Figure 3. The methylene protons are nonequivalent

Table I
Chemical Shifts and Coupling Constants (Hz) for Racemo 2,4-Disubstituted Pentanes[a]



	solv	temp, °C	CH_3	H_A	$H_{A'}$	J_{AB}	$J_{A'B}$	ref
4	CD_3OD	25	1.15	2.31	2.31	7.5	6.5	this work
8	CCl_4	35	1.15	1.88	1.88	10.0	5.0	13
9	$CDCl_3$	25	1.17	1.89	1.89	7.8	7.5	14
10	CD_3OD	25	1.16	2.37	2.37			5

[a] Parts per million downfield from TMS.

Table II
^1H Chemical Shifts (ppm) and Coupling Constants (Hz) of Methylene Groups for Isotactic 5, 11, and 12

	solv	temp, °C	H_A	H_B	J_{AB}	J_{BD}	J_{BC}	ref
5	CD_3OD	25	1.97	2.34	13.2	6.0	6.6	this work
12	$CDCl_3$	25	1.90	2.17	13.5	7.9	8.3	1
11	CCl_4	70	1.69	1.65	7.4	7.2		16

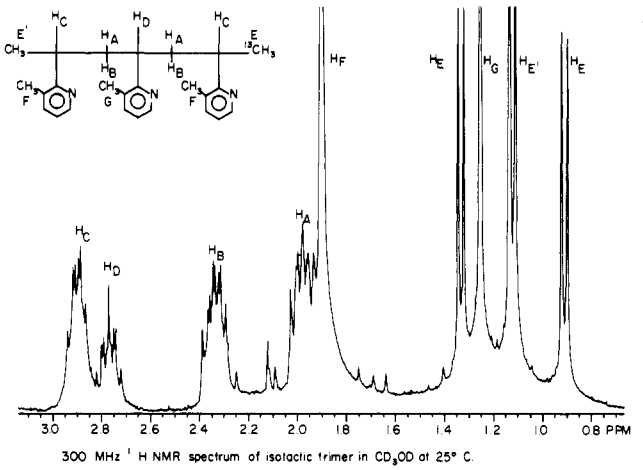


Figure 3. Proton NMR spectrum (300 MHz) of isotactic trimer **5** in CD_3OD at 25 °C.

(A and B protons) as observed for the isotactic isomers of 2,4,6-triphenylheptane (**11**)[16] and 2,4,-tris(2-pyridyl)heptane (**12**).[1] The splitting pattern of the methylene protons is consistent with that of the isotactic isomer of **5**. The results are compared in Table II.

The splitting pattern is slightly complicated by the coupling of one of the methylene protons with the ^{13}C-labeled methyl group (three-bond coupling constant, $^3J_{HC} \sim 4$ Hz). Capillary gas chromatography of the trimer product shows the presence of three stereoisomers. The GC peaks integrate as *mm* (62.6%), *mr* and *rm* (30.5%), and *rr* (6.9%). The isotactic and heterotactic isomer assignments are confirmed by ^1H and ^{13}C NMR spectroscopy.

Chain-End Stereochemistry. In order to determine the stereochemistry of poly(3-methyl-2-vinylpyridine) the chain end stereochemistry of the oligomers and the polymer is important.[17] Scheme II shows that the stereochemistry of methylation is given by the meso (racemic) content f_m (f_r) of the last dyad (eq 4). The stereochemistry of the penultimate dyad provides information on the distribution of the fraction X_m and X_r of the active sites

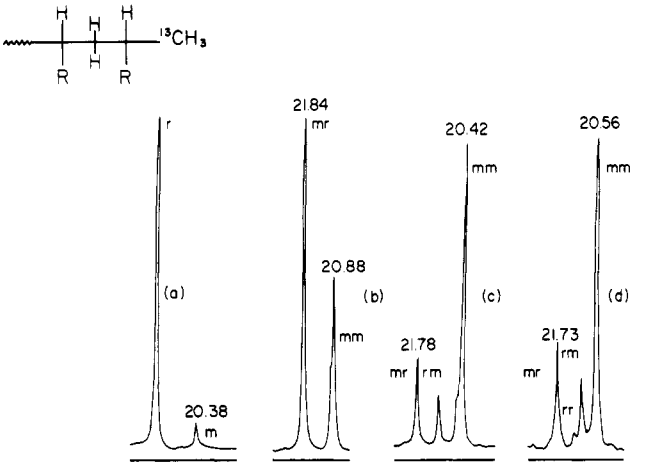
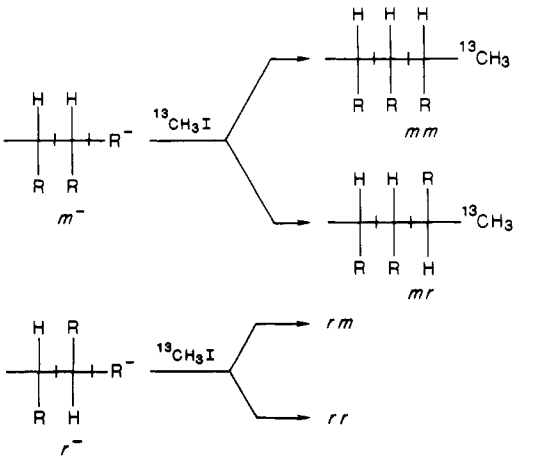


Figure 4. Carbon-13 (25 MHz) NMR spectra (CD_3OD at 25 °C) of oligomers 4–7 terminated with $^{13}CH_3I$: (a) dimer; (b) trimer; (c) tetramer; (d) pentamer.

Scheme II



$$f_m = mm + rm \quad (4a)$$
$$f_r = mr + rr = 1 - f_m \quad (4b)$$
$$X_m = mm + mr \quad (5a)$$
$$X_r = rm + rr \quad (5b)$$

Table III
^{13}C Methyl Chemical Shifts for Tetramers 5, 12, and 13[a]

	chemical shifts			
	mm	*rm*	*rr*	*mr*
6	20.42	21.13		21.78
13	20.30	20.85	21.60	22.30
14	20.40	20.85	22.60	23.00

[a] Parts per million downfield from TMS.

preceded by meso or racemic chain ends (m^- and r^- respectively) (eq 5).

The NMR spectra of the ^{13}C-labeled methyl end groups of **4**, **5**, **6** and **7** are shown in Figure 4. The end group assignments of **4** and **5** were made by isolation of the pure stereoisomers followed by ^{13}C NMR analysis. The tetramer **6** end group assignments are made by comparison with the isotactic and heterotactic trimer **5** and also with the aid of a chromatographed sample of tetramer that was 80% isotactic as determined by GC. The stereochemical assignments for **6** are in good agreement with the previous assignments for 2,4,6,8-tetrakis(2-pyridyl)nonane (**13**)[12] and 2,4,6,8-tetrakis(4-pyridyl)nonane (**14**)[14] and are compared in Table III. The methyl end group assignments of the pentamer **7** were made by comparison with the lower oligomers.

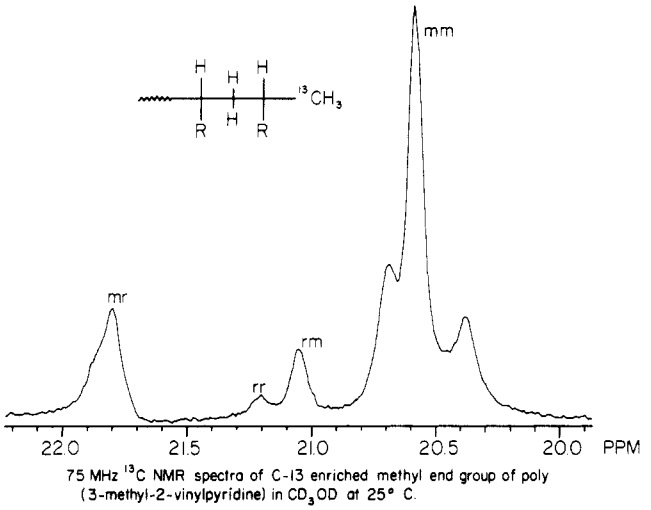


Figure 5. Carbon-13 NMR spectrum (75 MHz) of $^{13}CH_3$-terminated P3m2VP in CD_3OD at 25 °C.

Table IV
^{13}C NMR Chemical Shifts for the Methyl End Groups of 4, 5, 6, Poly(3-methyl-2-vinylpyridine) (P3M2VP), and Poly(2-vinylpyridine) (P-2VP) Determined in CD_3OD at 25 °C at 25 and 75 MHz

	chemical shifts			
	mm	*rm*	*rr*	*mr*
5	20.88			21.84
6	20.42	21.13		21.78
7	20.56	21.00	21.24	21.73
P3M2VP	20.60	21.05	21.20	21.72
P2VP	20.2	21.1	21.8	22.8

[a] Parts per million downfield from TMS.

Table V
Stereochemistry of Chain End, Methylation, and Last Vinyl Addition for 4, 5, 6, 7, and Poly(3-methyl-2-vinylpyridine)

					methylation stereoselectivity		stereochemistry last vinyl addition	
	mm	*mr*	*rr*	*rm*	f_m	f_r	X_m	X_r
4					0.25	0.75		
5	0.63	0.24	0.07	0.06	0.69	0.31	0.87	0.13
6	0.69	0.20	...	0.11	0.80	0.20	0.89	0.11
7	0.60	0.22	0.04	0.14	0.74	0.26	0.82	0.18
P3M2VP	0.76	0.16	0.02	0.06	0.82	0.18	0.92	0.08

The ^{13}C NMR assignments for the end group of poly(3-methyl-2-vinylpyridine) were made by comparison with the end group spectra of the oligomers and are shown in Figure 5. In Table IV, the ^{13}C NMR chemical shifts are listed for the methyl end groups of **5,6,7**,poly(3-methyl-2-vinylpyridine), and poly(2-vinylpyridine). The results are in good agreement with the corresponding spectra of poly(2-vinylpyridine).[17] The 75-MHz ^{13}C NMR spectrum for the end group of poly(3-methyl-2-vinylpyridine) shows a better triad stereochemical resolution. Definitive assignments of the higher *n*-ads are not clear at present. However, the triad information provides us with the stereochemistry of methylation (f_m and f_r) and the last vinyl addition (X_m and X_r). In Table V, the chain end stereochemistry of the methylation is given as well as that of the last vinyl addition for **4,5,6,7**, and poly(3-methyl-2-vinylpyridine).

Polymer Stereochemistry. The C_2 region of poly(3-methyl-2-vinylpyridine) prepared at −78 °C in THF in the presence of Li ion is shown in Figure 6. The stereochemical assignments are made on the basis of a Bernoulli trial mechanism[18] using a P_m value (P_m = fraction of meso dyads of the chain) of 0.92 obtained from Table V. The isotactic pentads are quite close together as was also observed for polystyrene[19] and the polyvinylpyridines.[20] The *mm*-centered pentads are occurring downfield from the *mr*-centered pentads as was also observed for poly(2-vinylpyridine) and the chemical shift dispersity for these two pentads is also similar.

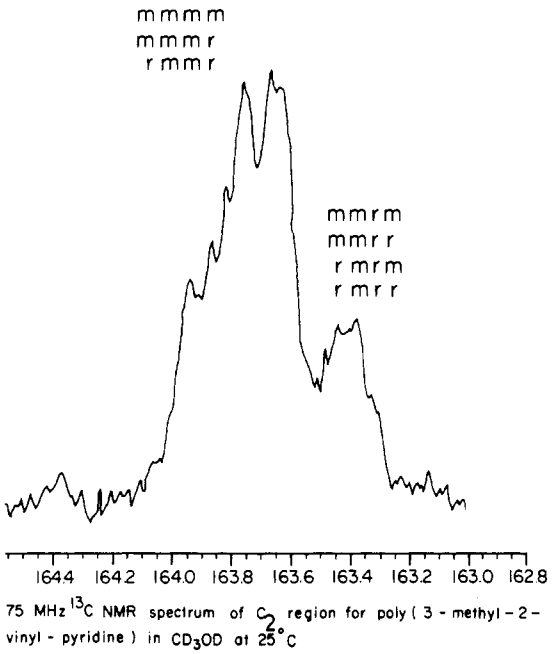


Figure 6. Carbon-13 NMR spectrum (75 MHz) of the C_2 region of poly(3-methyl-2-vinylpyridine) in CD_3OD at 25 °C.

Table VI
Tacticity of P3M2VP Prepared by Anionic and Radical Initiation

	P3M2VP (anionic)			P3M2VP (radical)		
	C_2	C_3	calcd[a]	C_2	$C_{3'}$	$C_2 + C_{3'}$
mmmm	0.82	0.76	0.72	0.43	0.78	0.43
rmmr			0.01			
mmmr		0.20	0.12			
mmrm	0.17		0.12			0.35
mmrr		0.03	0.01			
mrmr			0.01	0.57		
rmrr			0.00			
mrrm	0.01	0.01	0.01		0.22	0.22
mrrr			0.00			
rrrr			0.00			

[a] Calculated values by Bernoulli trial using P_m = 0.92.

These assignments can be supported by comparison with the spectrum obtained for poly(3-methyl-2-vinylpyridine) synthesized by using radical initiation (Table VI). The isotactic content of the radically (AIBN) initiated polymer is significantly lower than P3M2VP prepared by anionic polymerization. The *mr* and *rr* peaks overlap, however and their individual integration is not possible. Interestingly, the C_3' region, shown in Figure 7, shows a peak at 19.0 ppm for poly(3-methyl-2-vinylpyridine) obtained radically and not for the anionically initiated polymer. This peak is assigned to the *rr* triad and is easily integratable. The resulting triad distribution of the two polymers is shown in Table VI and is compared with the triad tacticities of poly(3-methyl-2-vinylpyridine) and poly(2-vinylpyridine) in Table VII. Substitution of the methyl group at the 3-position of the pyridine ring results in a significant increase in the isotactic content of poly(3-methyl-2-vinyl-

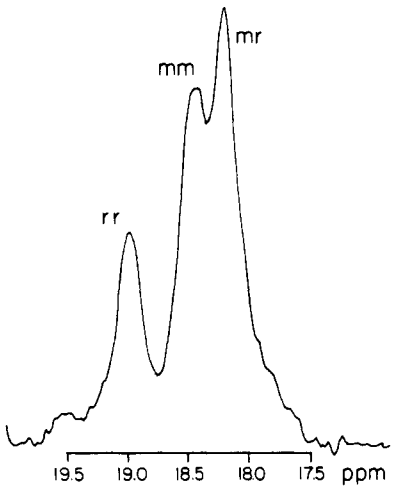


Figure 7. Carbon-13 NMR spectrum (25 MHz) of the $C_{3'}$ region of poly(3-methyl-2-vinylpyridine) in CD_3OD at 25 °C.

Table VII
Triad Tacticity of Poly(3-methyl-2-vinylpyridine) and Poly(2-vinylpyridine)

		solv/T	*mm*	*mr*	*rr*
poly(3M2VP)	anionic (Li^+)	THF/−78 °C	0.83	0.16	0.01
poly(3M2VP)	radical	benzene/60 °C	0.43	0.35	0.22
poly(2-VP)	anionic (Li^+)	THF/−78 °C	0.44	0.47	0.09
poly(2-VP)[a]	radical	toluene/60 °C	0.24	0.51	0.25

[a] See ref 21.

pyridine) over poly(2-vinylpyridine) prepared under anionic or radical conditions.

Discussion

Methylation. The sharp reversal in stereochemisry of methylation in going from dimer to trimer is in sharp contrast to that of the corresponding 2-vinylpyridine system and is to our knowledge unprecedented. In the latter case the stereochemistry of methylation of the Li and Na salts of the living oligomers–polymer is predominantly meso (>95%) and independent of the degree of polymerization. This has been explained by a strong intramolecular coordination of the pro-meso metal ion by the penultimate pyridine nitrogen. Such a coordination of metal ion in the present system is highly unlikely as a result of steric hindrance due to the penultimate 3′-methyl group as was demonstrated by the stereochemistry of methylation of 1-lithio-1-(2-pyridyl)-3-(3′-methyl-2-pyridyl)butane[15] that is virtually identical with that of dimer **4** (Table V). As a result the methylation stereochemistry is actually reversed, the racemic or racemic-like isomer being preferred (~75%). The contrasting meso-selective methylation of the trimer anion of 3M2VP therefore must be due to other factors. Inspection of CPK space-filling models of the oligomeric anions indicate a preference for a helical –tgtg– type conformation as a result of the interaction of the 3′-methyl with the penultimate pyridine ring.

The models also indicate that the pro-meso prochiral face of the carbanion is much less hindered than the pro-racemic face. As a result the large solvated lithium ion is expected to preferentially associate with this less encumbered face, and the cation-side methylation therefore results in a meso dyad.

Vinyl Addition. A similar rationale should apply in this case. Thus cation-side attack of the monomer on the helical propagating chain should lead to the formation of predominantly isotactic chains the degree of stereoselectivity being somewhat higher perhaps as a result of the somewhat more sterically demanding transition state compared to that for methylation. It can be seen from the models that the preferred s-cis monomer conformation should be readily incorporated as a *Z* anion whereas the *E* carbanion formed as a result of s-trans addition is expected to disrupt the helical conformation.

The large difference in stereochemistry between vinyl addition and methylation of dimer **4** remains puzzling but is not implausible since mesolike addition of s-cis monomer should give rise to the conformationally preferred helix. The greater isotactic content in the case of the radical polymerization of 3-methyl-2-vinylpyridine compared to that of 2-vinylpyridine lends some support for the proposed helical growth. However, in this case the polymerization was carred out at 60 °C. At 60 °C the monomer conformation is probably shifted toward the s-trans form contributing to the lesser stereoselectivity. Radical polymerization at low temperatures should help in clarifying this point.

Interestingly P3M2VP prepared by radical polymerization gives a persistence ratio, *p*, of 1.37 whereas that of the anionic polymer is 1.02.[21] Barring incorrect assignments of triads the former polymer is thus non-*Bernoullian* showing a tendency toward stereoblock characteristics.

The satisfactory correspondence of the stereochemistry of the chain end and that of the chain itself in the case of the anionically prepared polymer is of interest. Such a correspondence is further evidence for the occurrence of Bernoullian statistics.[17,22] A process of this type would be consistent with the participation of only one type of geometric isomer (*Z*) in the polymerization process. Thus the participation of both *E* and *Z* isomers, each propagating according to Bernoullian statistics, has been shown to lead in general to non-Bernoullian and non-Markoffian chains.[23] However, the occurrence of non-Bernoullian statistics for the polymer prepared by radical initiation is not well-understood. These problems are being studied further.

Conclusions

In contrast to 2-vinylpyridine the anionic polymerization of 3-methyl-2-vinylpyridine in the presence of Li ion gives rise to highly isotactic oligomers and polymers. The tacticity of the polymer is probably due to a helical polymer conformation caused by nonbonded interactions due to the 3′-methyl group. Whether such a helical conformation is stable enough to allow the preparation of optically active polymers resulting from macromolecular asymmetry as for instance in the case of poly(trityl methacrylate)[24,25] is not known.

Acknowledgment. Support from the National Science Foundation, DMR Polymers Program, is gratefully acknowledged. We also acknowledge the use of the Nicolet NT-300 spectrometer supported by the Instrument Program of the NSF Chemistry Division. We thank Dr. J. Lovy for many valuable discussions and "Reilly Tar" for a generous supply of 2,3-lutidine.

Registry No. **4**, 100550-02-5; **5**, 110027-15-1; **6**, 110027-16-2; **7**, 110027-17-3; P3M2VP, 110027-18-4; CH_2O, 50-00-0; 2,3-lutidine, 583-61-9; 2-(3-methyl-2-pyridyl)ethanol, 4723-26-6; 3-methyl-2-vinylpyridine, 22382-94-1.

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Liquid Crystalline Compounds and Polymers from Promesogens

James C. W. Chien,* Renmo Zhou, and C. Peter Lillya*

Department of Polymer Science and Engineering, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received February 24, 1987*

ABSTRACT: Alkyl 4-[(4-alkoxybenzoyl)oxy]benzoates (with C_1–C_{10} alkyl and alkoxy groups) are monotropic compounds which melt directly to isotropic liquids. Twin liquid crystalline compounds, TLCC's of [(alkoxybenzoyl)oxy]benzoic acid have been synthesized. The TLCC with methoxy end groups and trioxyethylene spacer is weakly mesogenic, but replacement of the methoxy with an *n*-butoxy end group results in a smectic mesophase. With the decamethylene spacer, the TLCC with a methoxy end group shows a nematic mesophase, whereas the compound with *n*-butoxy end groups exhibits both smectic and nematic mesophases. The latter has much higher ordered liquid crystalline states than the former. The polymeric TLCC's with *n*-butoxy end groups and $\bar{M}_n$ = 650 poly(THF) and $\bar{M}_n$ = 725 poly(propylene oxide) spacers display weak liquid crystalline order with only one mesophase transition. Decreasing the $\bar{M}_n$ of the poly(propylene oxide) spacer to 425 resulted in much stronger liquid crystalline order, exhibiting both smectic and nematic phases. It is suggested the microphase separation due to dissimilar solubility parameters can be an important contributing factor toward mesophase formation.

Introduction

Several types of twin liquid crystalline compounds (TLCC's) have been synthesized and characterized recently.[1-6] Most were prepared by coupling two mesogenic units with an aliphatic spacer, usually $(CH_2)_n$ (n = 2–12). The thermodynamic data show an even–odd effect for n. The purpose of this work is 2-fold. First, we demonstrate that coupling of two promesogenic (PM) units with either monodisperse $(CH_2)_n$ or $(CH_2CH_2O)_n$ spacers yielded TLCC's. Second, we show that twin liquid crystalline polymers (TLCP's) can be obtained by coupling the same PM cores with α,ω-dihydroxy-terminated poly(THF) and poly(propylene oxide) (poly(PPO)).

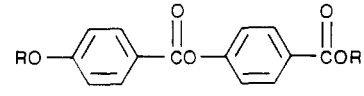
Experimental Section

Materials. 4-Methoxybenzoyl chloride, 4-butoxybenzoyl chloride, 4-hydroxybenzoic acid, ethanol, propanol, decanediol, and triethylene glycol were all obtained from Aldrich Chemical Company. 4-Methoxybenzoyl chloride was distilled at 117–118 °C/14 mm, 4-butoxybenzoyl chloride was distilled at 160 °C/8 mm, and 4-hydroxybenzoic acid was dried at 85 °C in vacuo for 1 h, mp 215–217 °C. Ethanol and propanol were refluxed with magnesium and distilled. Decanediol was vacuum dried at 60 °C for 5 h. Triethylene glycol was dried over anhydrous $MgSO_4$ and distilled at 137 °C/0.5 mm. α,ω-Dihydroxy-terminated poly(THF) (MW 650) and poly(PPO) (MW 425 and 725) were obtained from Polyscience, Inc.

4-[(4-Alkoxybenzoyl)oxy]benzoic acids were prepared by reaction of the appropriate 4-alkoxybenzyl chloride with 4-hydroxybenzoic acid in pyridine at 0 °C for 20 h. The products were precipitated with dilute aqueous HCl, washed to neutrality with distilled water, and recrystallized. The compounds have the literature thermotropic transitions: 4-[(4-methoxybenzoyl)-oxy]benzoic acid (T_{K-L} = 210 °C, T_{L-I} = 270 °C);[7] 4-(4-butoxybenzoxy)benzoic acid (T_{K-L} = 160 °C, T_{L-I} = 260 °C).[8]

4-[(4-Alkoxybenzoyl)oxy]benzyl chloride was obtained by refluxing the corresponding acid in an excess of purified thionyl chloride. After vacuum removal of all volatile substances, the products were used without further purification. Their melting points are in agreement with literature values: [(4-methoxybenzoyl)oxy]benzoyl chloride (T_m = 140 °C); [(4-butoxybenzoyl)oxy]benzoyl chloride (T_m = 78 °C).

Synthesis. Promesogens were prepared by reaction of 1 equiv of the appropriate 4-[(4-alkoxybenzoyl)oxy]benzoyl chloride dissolved in dry dioxane with 1.5 equiv of alcohol. The reaction mixture containing excess pyridine was refluxed overnight and then was poured into stirred distilled water. The precipitated product was washed in succession with 3% aqueous HCl, aqueous $NaHCO_3$, and water and was purified by preparative thin-layer chromatography on silica. Samples used for optical and thermal studies were homogeneous on thin-layer chromatography. These compounds exhibit intense infrared absorptions at 1730 and 1715 cm^{-1} for the aryl benzoate and alkyl benzoate carbonyls, respectively, and at least five bands in the C–O stretch region from 1000 to 1300 cm^{-1}. The structures of the four promesogens are



I

a, R = methyl, R' = *n*-propyl
b, R = *n*-butyl, R' = ethyl
c, R = *n*-butyl, R' = *n*-propyl
d, R = *n*-butyl, R' = *n*-decanyl

The procedure described above for promesogens was also used here with the α,ω-diols (decane-1,10-diol and triethylene glycol),

0024-9297/87/2220-2340$01.50/0