nmr is often not examining the total polymer. He found that the solubility of PVC decreased as the crystallinity of PVC increased and, consequently, a fraction of the polymer was not contributing to the proton nmr spectrum. At this point, we do not know what effect regions of crystallinity might have on the ^{13}C nmr spectra of PVC obtained at 130°. As has been suggested for *trans*-1,4-polyisoprene at 45°,[5] the presence of crystalline regions may result in a loss in signal intensity and broadening of the lines.

Carbon-13 nmr analysis of PVC for tacticity has an advantage over either 220- or 100-MHz proton nmr analyses in that there are no peak overlap effects in the decoupled methine resonances. Consequently, tacticity can be measured by measuring individual, isolated methine carbon peaks.

A Nuclear Magnetic Resonance Analysis of the Steric Course of Propagation of Vinyl Methyl Ether

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ABSTRACT: Stereospecifically deuterated cis and trans isomers of vinyl methyl ether have been polymerized under several conditions with various initiators. Some observations on initiation are recorded. It was found that only minor differences resulted in the proportion of erythro- and threo-meso protons produced within the isotactic sequence when a few different initiators and solvents were used. The presence of both erythro- and threo-meso protons defines the isotactic polymerization process as occurring by both syndiotactic-like and isotactic-like presentation of the monomer to the polymer cation. Polymers prepared with BF_3 and various etherates are more stereoregular at both the α and β positions than polymers prepared with PF_5 catalyst under the same conditions. From our proposed assignment of the downfield and upfield meso tetrad resonances to threo- and erythro-meso configurations, respectively, we suggest that isotactic-like approach of monomer is slightly preferred. Definition of the transition state is handicapped by a lack of knowledge of the nature of the ionic species, but some mechanistic interpretations are presented.

The homogeneous stereospecific polymerization of vinyl methyl ether has been of great interest since Schildknecht and coworkers first described the preparation of crystalline polymer by boron trifluoride etherate catalysis at low temperature.[1] Early studies directed at obtaining information concerning the distribution of configurational sequences in the polymer were hampered by the lack of any quantitative experimental technique.[2–4] However, since Bovey and Tiers first demonstrated that nuclear magnetic resonance could be used as a sensitive probe for the determination of polymer tacticity and homotactic sequence length,[5] many studies of the steric structure of poly(vinyl methyl ether) by this technique have been reported.[4,6–11]

Following Schildknecht's initial preparation of stereoregular poly(vinyl methyl ether), many workers have investigated various aspects of the synthesis of this stereoregular polymer and several mechanisms have been proposed to account for its formation. These involve formation of cyclic intermediates,[12] coordination of growing chain end with counterion and monomer,[13,14] and various steric and penultimate effects.[15,16] However, because of the large number of variables which must be explained, many of these mechanistic proposals do not have widespread applicability. Furthermore, only one proposal attempts to distinguish between possible cis or trans opening of the olefin bond of vinyl ethers,[16] even though this information should be basic in postulating a transition state.[16a] Although both cis and trans opening of the monomer double bonds have been reported for a variety of polymerization systems, it has been found that cis opening is the more common occurrence in homogeneous cationic polymerization. Natta, *et al.*, showed that cis opening of the olefin bond occurs for *trans*-isobutyl propenyl ether[17] as well as for *cis*- and *trans*-β-chlorovinyl ethers[18] when polymerized with homogeneous cationic catalysts. The same conclusion was reached by Ohsumi,[19,20] *et al.*, for the homogeneous polymerization of *trans*-methyl propenyl ether with boron trifluoride etherate.

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(16a) NOTE ADDED IN PROOF. K. Matsuzaki and K. Sakota, *Makromol. Chem.*, in press, present an investigation similar to this.

(17) G. Natta, M. Peraldo, M. Farina, and G. Bressan, *Makromol. Chem.*, **55**, 139 (1962).

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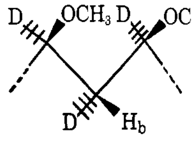
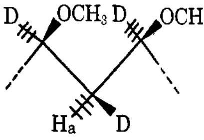
We have found that methoxyacetylene can be deuterated in a highly stereospecific fashion to yield the corresponding cis and trans α,β-dideuterated vinyl methyl ethers.[21] The high-resolution nmr spectrum of deuterated poly(vinyl methyl ether) provides a means for identifying the relative proportion of all possible stereochemical sequences up to four monomer units in length.[22] In addition, the spectrum provides an absolute measure of β tacticity as well as α tacticity. Thus, if one considers the cationic polymerization of α,β-dideuterated monomers, it is clear that the direction of approach of the β carbon of the monomer to the propagating polymer cation will determine the configuration of the β carbon introduced in the polymer. The present article is an interpretation of the propagation process in the homogeneous cationic polymerization of vinyl methyl ether.

Results and Discussion

In our initial work, stereospecifically deuterated cis and trans isomers of vinyl methyl ether were polymerized homogeneously at low temperature with $BF_3\cdot OEt_2$ and PF_5 catalysts.[22] The methylene resonance of the resulting polymers could be interpreted in terms of tetrad fine structure since the complications of geminal and vicinal proton couplings were not present in the deuterated polymers. The assignment of tetrads for poly(vinyl methyl ether) is that described in a previous communication.[22] At the present time it has not been established by empirical methods whether the downfield or upfield meso tetrads correspond to erythro- or threo-meso configurations in poly(vinyl methyl ether). However, it appears very probable, on the basis of bond anisotropy, that the upfield meso tetrads correspond to the eyrthro-meso configuration for which the β proton (H_b) is on the same side of the backbone plane as the methoxyl groups, when an isotactic sequence is depicted in a planar zigzag conformation. The downfield meso tetrads probably correspond to the threo-meso configuration for which H_a is on the opposite side of the backbone zigzag plane to the adjacent methoxyls. This conclusion is based on the known diamagnetic anisotropy associated with the C–O bond, and evidence for these assignments is provided in the Appendix.

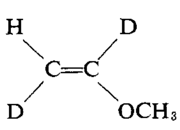


H_b (erythro-meso)

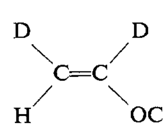


H_a (threo-meso)

The polymers were prepared from monomers I and II, respectively. As indicated in Table I, polymerization of the cis and trans monomers with PF_5 gives both downfield and upfield meso resonances in nearly equivalent amounts. From simple stereochemical relationships this process could be interpreted as meaning that both cis and trans opening of the double bond occurs with equal probability.[17] However, it has been cautioned that cis or trans opening of a monomer bond has no precise meaning in terms of the structure of the transition state for vinyl polymerizations as it has for four-centered additions to alkenes.[23,24] Consequently, we will interpret the results of this study in terms of the *mode of presentation* of the β carbon of the monomer to the polymer chain end. Accordingly, the results of Table I indicate that roughly equal numbers of isotactic-like and syndiotactic-like approaches of monomer to polymer chain end eventually appear in meso placements when either cis or trans monomer is polymerized with PF_5 catalyst. This conclusion is absolute, for it would be correct even if the assignment of chemical shifts to threo and erythro protons were reversed. Although the racemic content of polymers a–f is quite substantial, it is not possible to determine the mode of monomer approach resulting in a racemic placement from the nmr spectrum since the racemic methylene protons are, of course, in essentially identical magnetic environments.



I, vinyl-α,*cis*-β-d_2 methyl ether



II, vinyl-α,*trans*-β-d_2 methyl ether

TABLE I
NMR DATA OF POLYMERS PREPARED WITH PF_5 IN VARIOUS SOLVENTS AT −60°

Polymer	a	b	c	d	e	f
Monomer	I[a]	II[b]	I	I	I	I
Solvent	Toluene	Toluene	CH_3Cl	Me_2O	Hexane	TBB[c]
m	71	69	68	66	61	66
r	29	32	32	33	38	34
t_m	41	29	39	41	30	39
e_m	30	40	29	25	32	27
$t_{m/m}$	57	42	57	62	50	59
$e_{m/m}$	42	57	43	38	52	41
rr	9	11	6	13	14	12
mr	43	41	53	47	46	43
mm	48	48	41	40	40	44
μ (m)	3.2	3.3	2.5	2.7	2.4	3.0
μ (r)	1.2	1.6	1.2	1.5	1.4	1.6

[a] I = vinyl-α,*cis*-β-d_2 methyl ether. [b] II = vinyl-α,*trans*-β-d_2 methyl ether. [c] *tert*-Butylbenzene.

As indicated for polymers a and b, the expected interchange between threo and erythro intensities was readily observed when the cis and trans monomers were polymerized with PF_5 in toluene. Thus, for polymer a, prepared from cis monomer, the t_m/m ratio is 57 (e_m/m = 42), while for polymer b, pre-

TABLE II
NMR DATA OF POLYMERS PREPARED WITH BF_2 AND VARIOUS ETHERATES IN TOLUENE AT −60°

Polymer	g	h	i	j	k
Monomer	I[a]	I	I	II[b]	I
Initiator	BF_3	$BF_3\cdot OMe_2$	$BF_3\cdot OEt_2$	$BF_3\cdot OEt_2$	$BF_3\cdot$ THF
m	75	73	72	70	76
r	25	27	28	30	24
t_m	49	46	45	27	45
e_m	26	27	26	43	31
$t_{m/m}$	65	63	62	38	60
$e_{m/m}$	35	37	36	62	40
rr	5	3	10	9	3
mr	35	41	35	41	36
mm	60	56	55	56	60
μ (m)	4.4	3.7	4.2	4.1	4.3
μ (r)	1.3	1.1	1.6	1.5	1.2

[a] I = vinyl-α,*cis*-β-d_2 methyl ether. [b] II = vinyl-α,*trans*-β-d_2 methyl ether.

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(21) J. R. Dombroski and C. Schuerch, *Macromolecules*, **3**, 257 (1970).

(22) J. R. Dombroski, A. Sarko, and C. Schuerch, *ibid.*, **4**, 93 (1971).

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pared from the trans monomer, the proportions are reversed. It is thus obvious that the same mechanism leading to threo- and erythro-meso placements is operating for both monomers when polymerized under identical conditions.

Although the sequence length $\mu_{(m)}$ of meso placements for polymers a–f is on the average slightly longer than that of the racemic placements $\mu_{(r)}$, the meso sequences are interrupted frequently by racemic placements which appear primarily in the high heterotactic triad values of Table I.

Table II shows the nmr data of polymers prepared with BF_3 and various BF_3 etherates in toluene at $-60°$. Although it has long been known that different etherates of borontrifluoride influence the rate of vinyl ether polymerization,[25] no studies have been reported concerning the effect of different etherates on stereoregularity. As shown in Table II, the polymers prepared with BF_3 and various etherates show nearly the same tacticities on both the α and β positions. However, compared with PF_5, the BF_3 system gives a slightly higher proportion of downfield meso protons (threo) with monomer I and also higher proportion of upfield meso protons (erythro) with monomer II. Thus, for the BF_3 system, isotactic-like approach of the monomer is slightly favored, if our assignment is correct.

For a complete interpretation of the mechanism of vinyl methyl ether polymerization, it is necessary to know not only the structure of monomer and polymer, but also the nature of the active propagating species. Unfortunately, little is known concerning the nature of Lewis acid catalysts in solution or the nature of the cationic propagating species.[26] However, reasonable mechanistic assumptions may be made in view of the added knowledge of the β-carbon stereochemistry.

The model of the propagating site which we prefer resembles that of Kunitake and Aso,[16] and with them we assume that in nonpolar solvents the gegenion is closely associated with the propagating cation. If there are no attractive forces acting between gegenion and ether functions, the gegenion should be located at the side of the carbonium ion away from the penultimate unit, as shown in Figure 1. One would also expect that the methoxyl group at the terminal and penultimate units would be as far apart from each other as possible in order to minimize dipole interactions and steric crowding.

If the terminal and penultimate methoxyls are in fact as placed, on opposite sides of the plane defined by the penultimate substituted carbon and the two carbons of the terminal chain unit, then approach of the monomer to the cation must necessarily be from the backside, opposite to the gegenion, in order to convert the terminal unit into a fixed meso configuration.

Kunitake and Aso reasonably propose that the monomer would approach the cation in a syndiotactic sense to minimize nonbonded interactions with the cation methoxyl[27] group. However, this is not the case. With phosphorus pentafluoride as catalyst the two modes of approach of monomer are nearly equally favored, and there is only a moderate preference for one mode of approach when boron trifluoride is catalyst. Our assignments of threo- and erythro-meso chemical shifts indicate the preferred mode of approach with BF_3 to be isotactic, and it is difficult to find a suitable explanation of this modest preference.

Following bond formation, some reorganization of the propagating site and migration of the gegenion to the new carbonium ion is necessary. However, it appears unwise to attempt to define such speculation in much detail (*cf.* Figure 1).

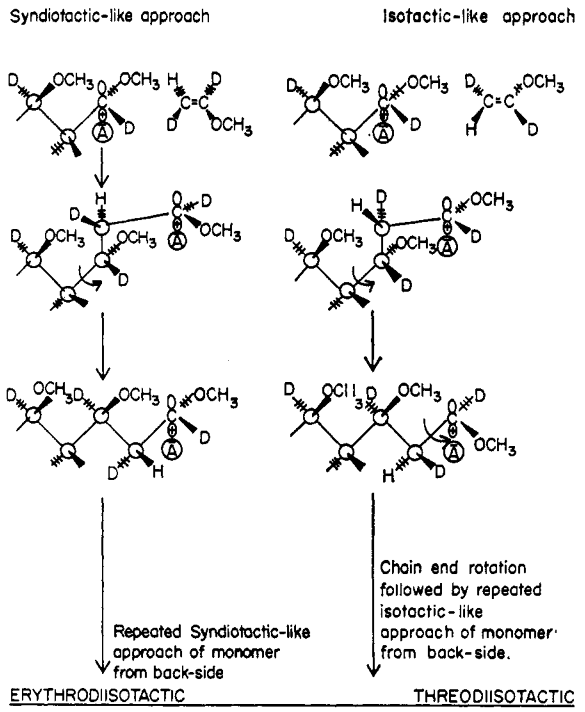

Figure 1. Mechanism for incorporation of erythro- and threo-meso placements in deuterated poly(vinyl methyl ether).

According to the proposed mechanism, racemic placements may be accounted for on the basis that a small fraction of monomer additions may occur by front-side attack. The probability of front-side attack is further enhanced in polar solvents, since the gegenion will be only weakly interacting with the growing cation. Accordingly, it is known that the racemic content of poly(vinyl methyl ether) increases as the polarity of solvent increases.[9]

Other mechanistic schemes were considered. These generally involved coordination of the penultimate and terminal methoxyl groups with the gegenion as a means of explaining the observed α-carbon isotacticity. Coordination of the negative gegenion with the methoxyl groups seems highly unlikely, however, and the schemes were discarded.

As seen from Table III, both BF_3- and PF_5-initiated polymer systems have triad sequence distributions which obey Bernoullian statistics within experimental error. The observed methoxyl triads were evaluated from the nmr spectra by means of a computer curve-resolution technique as previously described.[22] Consistency with the Bernoullian process at the triad level may be tested by comparing the observed triad values with those calculated for a Bernoullian structure.[28] This is equivalent to fitting to the familiar parabolic curves describing P_m as a function of triad frequency.[5] The use of tetrad frequencies permits a more rigorous test for Bernoullian statistics. In a manner analogous to the triad tests, the observed tetrad fractions are compared with those predicted for a Bernoullian structure.[28] The mmm and rrr tetrads are used here to test for a Bernoullian process; however, it is necessary to compare only one of the observed tetrad fractions with the corresponding calculated value to establish

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Table III

Comparison of Observed Triads and Tetrads with Those Predicted from Bernoullian and First-Order Markov Statistics

	Obsd			Calcd Bernoullian values			Obsd	Calcd Bernoullian values[a]	Obsd		Calcd Bernoullian values		First-order Markov values[a]	
Polymer	rr	mr	mm	rr	mr	mm	P_m	P_m	mmm	rrr	mmm	rrr	mmm	rrr
a	9	43	48	7	39	53	0.69	0.72	0.50	0.07	0.39	0.02	0.33	0.03
b	11	41	48	10	43	47	0.68	0.68	0.36	0.07	0.32	0.03	0.34	0.04
c	6	53	41	11	44	46	0.68	0.68	0.35	0.07	0.31	0.03	0.25	0.01
d	13	47	40	13	46	40	0.64	0.63	0.32	0.06	0.26	0.05	0.25	0.04
e	11	52	37	14	46	40	0.63	0.63	0.25	0.06	0.25	0.05	0.22	0.03
f	12	43	44	12	45	43	0.66	0.65	0.31	0.07	0.29	0.04	0.30	0.05
g	5	35	60	5	35	60	0.77	0.77	0.46	0.03	0.46	0.01	0.46	0.01
h	3	41	56	6	36	59	0.77	0.77	0.44	0.04	0.44	0.01	0.41	0.00
i	10	35	55	7	40	53	0.73	0.73	0.44	0.06	0.38	0.02	0.42	0.04
j	9	36	55	7	39	53	0.73	0.72	0.41	0.08	0.39	0.02	0.41	0.03
k	3	36	60	5	34	62	0.79	0.79	0.46	0.05	0.48	0.01	0.46	0.00

[a] See ref 28.

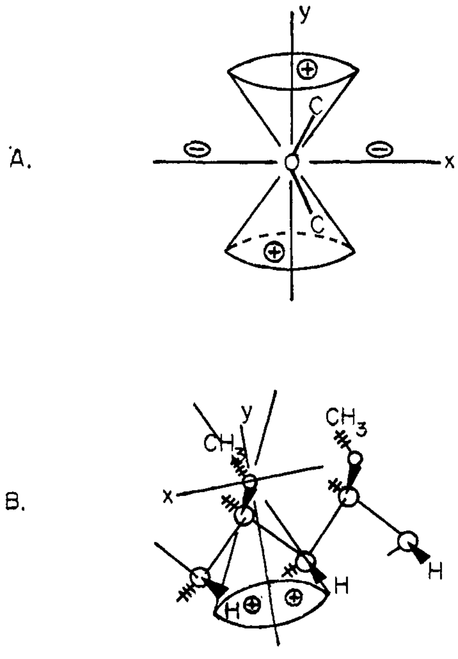

Figure 2. (A) Anisotropy associated with the oxygen–carbon bond. (B) Shielding of the erythro-meso proton by diamagnetic anisotropy associated with the α-methoxyl group.

consistency. As indicated in Table III, the fit at the tetrad level departs somewhat from Bernoullian, although agreement is still fairly good and at least as good as that for first-order Markovian statistics. This Bernoullian fit may put in doubt the necessity for the interpretations of Cram and Kopecky[12] and Bawn and Ledwith,[13,14] who propose that steric control is exercised by coordination of the carbonium ion with the mer unit preceding the penultimate one. Probably first-order Markovian statistics would be expected in such a mechanism.

Experimental Section

Materials. The preparation of stereospecifically and isotopically pure deuterated vinyl methyl ether monomers has been described previously.[21] Monomer was usually contained in a sealed, calibrated ampoule and dried over small pieces of calcium hydride for 24 hr. Further purification was performed by allowing the monomer to stand over a freshly prepared sodium mirror for at least 48 hr.

Solvents such as hexane, *tert*-butylbenzene, and dimethyl ether were initially dried over calcium hydride and finally over a sodium mirror before being used for polymerization. Methyl chloride, contained in a sealed glass ampoule, was dried over calcium hydride for several days.

Boron trifluoride was generated by pyrolysis of $Ca(BF_4)_2$. The preparation of $Ca(BF_4)_2$ was carried out using high-vacuum techniques according to the procedure of Bistline[29] and Coombes and Eley.[30] The boron trifluoride etherates of dimethyl ether and tetrahydrofuran were prepared according to the procedure of Brown and Adams.[31] The etherate complexes were distilled under vacuum and dried over calcium hydride[32] in sealed glass ampoules prior to being used for polymerization initiators.

Procedures. The preparation, isolation, and spectral analysis of polymers initiated with phosphorus pentafluoride and boron trifluoride diethyl etherate in toluene at −60° have been previously described.[22] It was found that when monomer and solvent were scrupulously dried over a sodium mirror for several days and the BF_3 etherate was dried over calcium hydride, the system would not polymerize at the usual temperature of −78°,[7,8,33] even after several days. However, when the sealed polymerization ampoule was transferred to a bath at −60°, the monomer polymerized to a clear gel after several hours. Similarly, $BF_3 \cdot OMe_2$ and BF_3THF would not initiate polymerization of vinyl methyl ether or the deuterated analogs even at room temperature. However, when a trace of water was added (mole % initiator/mole % H_2O = 1) the polymerizations proceeded smoothly at −60°. These experiments were duplicated several times with reproducible results. These results should be considered in any interpretation of the mechanism of initiation.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Appendix

Pople[34] has calculated the diamagnetic anisotropy effect of the oxygen atom in ethers and concluded that its largest axis of polarizability corresponds to the y axis defined in Figure 2A, with the other two principal axes of polarizability being equal. The associated long-range shielding is described by the cones illustrated in Figure 2A. It seems likely, therefore, that the significant chemical shift difference ob-

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(30) J. D. Coombes and D. D. Eley, *J. Chem. Soc.*, 3700 (1957).

(31) H. C. Brown and R. M. Adams, *J. Amer. Chem. Soc.*, **64**, 2557 (1942).

(32) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 28 (1963).

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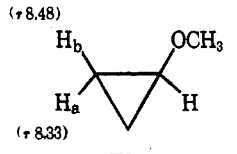
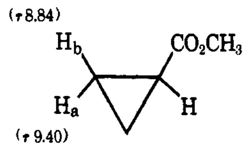
(34) J. A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).

served for the protons of a meso methylene group of poly(vinyl methyl ether) may be accounted for by the anisotropy of the C–O bond. Examination of molecular models of isotactic poly(vinyl methyl ether) in the planar zigzag conformation as well as in a variety of other probable conformations indicates that the shielding zone of diamagnetic anisotropy associated with the O–CH_3 bond readily intersects the adjacent erythro-meso protons (Figure 2B). A recent X-ray investigation[35] of the crystal structure of isotactic poly(vinyl methyl ether) indicates that the conformation of the methoxyl groups with respect to the main chain sites is essentially that illustrated in Figure 2B. Although the chain is depicted here in the planar zigzag conformation, the X-ray study reveals a helical conformation for the polymer.[35] However, examination of the molecular model of isotactic poly(vinyl methyl ether) constructed in the threefold helical conformation again shows that the shielding zone associated with the O–CH_3 bond readily intersects the erythro-meso proton. Consequently, the β-methylene protons of a meso dyad are nonequivalent and spin couple with each other and give rise to the expected AB[6,8] pair of doublets.

A similar assignment of threo and erythro methylene protons of isotactic polypropylene has recently been made by Heatley and Zambelli.[36] They assigned the downfield meso tetrads to the threo configuration and the upfield meso tetrads to the erythro configuration. It seems likely that anisotropic shielding by the C–CH_3 bond is responsible for the observed chemical shift difference for the meso β-methylene protons, and it has been suggested that long-range shielding by the C–C bond is similar to that of the C–O bond.[37] Ohsumi and coworkers[19,20] also made similar assignments for the respective β-methyl protons of poly(*cis*- and *trans*-methyl propenyl ethers). In contrast, the methylene protons of isotactic poly(methyl methacrylate) show the influence of an opposite shielding effect; *i.e.*, the erythro-meso resonance is downfield from the threo-meso absorption. Yoshino's[38] assignment of methylene protons of poly(methyl acrylate), based on a study of deuterated model compounds, demonstrates that the carbomethoxy group has a significant deshielding effect on the β-methylene protons situated on the same side of the planar backbone. A study of analogous small molecules clearly demonstrates the respective shielding and deshielding influences of methoxyl and carbomethoxy groups in close proximity to a proton. As indicated above,



III



IV

the methoxyl group (III)[39,40] shields proton b by 0.15 ppm relative to proton a, while the carbomethoxy group (IV)[41,42] exerts a deshielding effect on the corresponding b proton. While these models are not meant to represent polymer chain segments, they do, in fact, demonstrate the opposite anisotropy associated with these two functional groups. Furthermore, since isotactic poly(vinyl methyl ether)[35] and isotactic polyacrylate[43,44] chains are both known to have 3_1 helical conformations, it is probable that the same anisotropy difference exhibited by the methoxyl and carbomethoxy groups in III and IV may also be observed for the respective polymers.

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