The Stereochemical Configuration of Vinyl Polymers and Its Observation by Nuclear Magnetic Resonance

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It is well known that the stereochemical configuration of vinyl polymer chains is intimately related to their physical properties, particularly their crystallizability, their softening or melting temperatures, and their mechanical behavior. During the past decade, polymer chemistry has undergone a major revolution, initiated by Ziegler's development of metal halide–metal alkyl initiators for ethylene polymerization and greatly extended by Natta and his colleagues in Milan, who showed how similar catalysts can be used to produce polymers of *controlled stereochemistry* from a wide variety of vinyl and diene monomers.[1,2]

The advent of methods of preparing polymers of controlled stereochemistry has brought with it the need to determine what the stereochemistry actually is, so that one may correlate physical properties with structure. Very highly stereoregular polymers can usually be made to crystallize and then X-ray diffraction can be employed. This has been the chief method of the Natta school. Most polymers, however, do not crystallize, and even for some that do the X-ray data are ambiguous. For such polymers other methods of investigation must be found. High-resolution nmr spectroscopy appears to be by far the most effective now known. In this article we shall examine the fundamental basis of the study of polymer stereochemistry by nmr and then show how, by suitable labeling and statistical treatment, one may use stereochemical information to elucidate the mechanism of chain formation.

The Observation of Molecular Symmetry by Nuclear Magnetic Resonance

It is convenient to begin with a consideration of small molecules which are related in structure to vinyl polymers. Nmr is a very powerful method for providing information concerning the symmetry of molecules of uncertain structure or stereochemical configuration. The observation of molecular symmetry, or lack of symmetry, depends upon the fact that otherwise similar nuclei which occupy geometrically nonequivalent sites will, in general, be magnetically nonequivalent as well,[3]
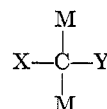
and will exhibit different chemical shifts and different couplings to neighboring nuclei. Environmental differences of this sort which are too subtle to detect by other means are often obvious in the nmr spectrum.

Important symmetry problems from the viewpoint of polymer structure are presented by molecules of the type

$$X—\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{C}}—Y$$

where X is a group which has a plane or axis of symmetry, such as phenyl, methyl, halogen, etc., and Y is a group having *in itself* no element of symmetry. M is any observable atom or group, such as hydrogen, fluorine, phenyl, methyl, trifluoromethyl, etc. In such a molecule, the groups M will be nonequivalent. The molecule is not necessarily asymmetric as a whole, however, for Y may, for example, be

$$—\underset{\underset{Q}{|}}{\overset{\overset{P}{|}}{C}}—\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{C}}—X$$
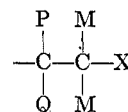
in which case the molecule has a plane of symmetry.

$$X—\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{C}}—\underset{\underset{Q}{|}}{\overset{\overset{P}{|}}{C}}—\underset{\underset{M}{|}}{\overset{\overset{M}{|}}{C}}—X$$

Such a molecule nevertheless satisfies the requirements for steric differentiation of the geminal M groups in each pair. To simplify the ensuing discussion, we shall refer to all such CM_2 groups in which the M groups are equivalent as *homosteric*, and to those in which the M groups are nonequivalent as *heterosteric*.[4]

Let us consider some specific examples which are relevant to polymers.

(a) Y Is an Asymmetric Carbon Atom, $CR_1R_2R_3$. For each optical isomer (not ordinarily distinguishable by nmr), there are three staggered conformers (Figure 1), and in each the environments of M_a and M_b are nonequivalent. Most of the observed differentiation between M_a and M_b probably arises from an energetic preference for one of the conformers,[5] but it can be

(1) G. Natta, *Chem. Ind.* (Milan), **46**, 397 (1964) (Nobel Prize Address).

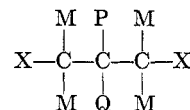(2) K. Ziegler, *Angew. Chem.*, **76**, 545 (1964) (Nobel Prize Address).

(3) We do not necessarily use the term "magnetically nonequivalent" here in the sense often employed by the nmr spectroscopist, *i.e.*, to refer to the nuclei of any group which are equivalent among themselves geometrically, and therefore have the same chemical shift, but are unequally coupled to the nuclei of another group. Thus in *cis*- or *trans*-HFC=CHF the protons and fluorine nuclei each constitute a group of nonequivalent nuclei, whereas in CH_2F_2 the members of each group are magnetically equivalent. In our discussion, some nuclei will be called equivalent which would be termed nonequivalent in this more rigorous usage.

(4) The author is indebted to Professor Murray Goodman for the suggestion of this terminology (*cf.* M. Goodman in "Topics in Stereochemistry," Vol. II, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, p 73). Mislow and Raban (K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. I, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, p 1) have offered the terms "enantiotopic" and "diastereotopic" to describe homosteric and heterosteric groups, respectively.

(5) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2916 (1962), and references cited therein.
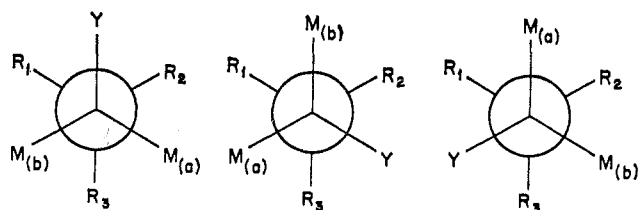
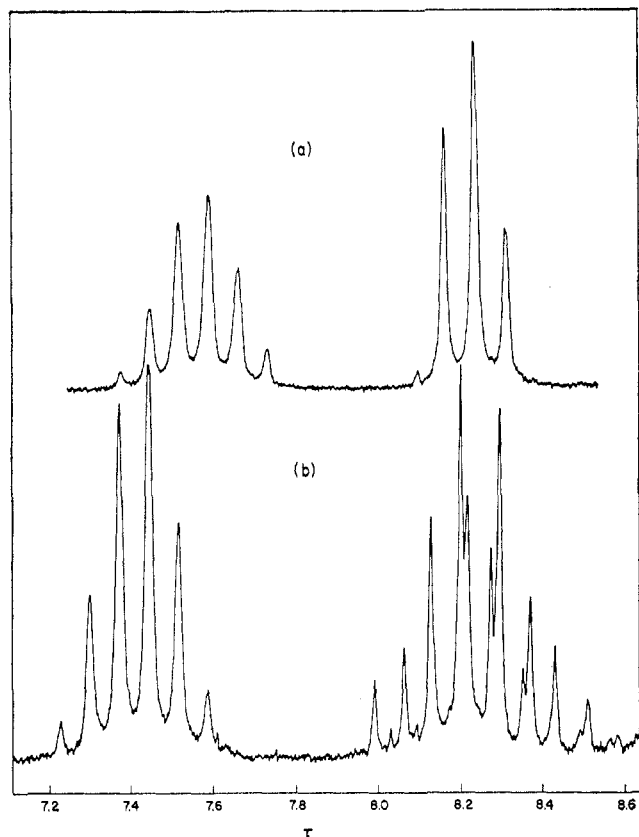Figure 1. Staggered conformers of substituted ethane ($X-CM_2-CR_1R_2R_3$).

Figure 2. The 100-MHz spectra of (a) racemic and (b) *meso*-2,4-diphenylpentane, 10% (v/v) in chlorobenzene at 35°.

readily shown by elementary symmetry considerations that in principle some degree of nonequivalence must persist even if all three were equally populated and in rapid equilibration with each other.[6] A great many examples of this type are now known, far too numerous to attempt to list here.

(b) $X = Y = CR_1R_2R_3$, *i.e.*, the molecule has two similar asymmetric centers
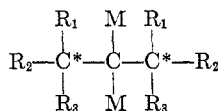

If X and Y are of the same handedness we have either the *d* or *l* diastereoisomer; the racemic mixture of *d* and *l* will usually be indistinguishable from either alone by nmr. The enantiomers are dissymmetric, but the CM_2 group is homosteric in each. If X and Y are

(6) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

of opposite handedness, we have the *meso* diastereoisomer, which of course has a plane of symmetry, but in which the CM_2 group is heterosteric. Molecules of this type are clearly very closely related to vinyl polymers. The most carefully studied examples are racemic and *meso* 2,4-disubstituted pentanes. Tiers and Bovey[7] showed that the fluorine nuclei of the central CF_2 group of *meso*-$CF_2ClCFClCF_2CFClCF_2Cl$ have differing chemical shifts and couplings, while those of the racemic isomer are identical. A great many molecules of this type have since been studied in many laboratories. The spectra of *meso* and racemic 2,4-diphenylpentanes (Figure 2), analogs of polystyrene, may serve as an example.[8] Analysis of these spectra by computer simulation shows that the methylene group protons differ by 0.21 ppm in chemical shift in the *meso* isomer, but are equivalent in the racemic isomer; this conclusion is qualitatively evident from the greater complexity of the CH_2 portion of the spectrum, centered at *ca.* τ 8.2, in Figure 2b. In both spectra, the sextuplet at lower field is that of the methine protons. (The aromatic and methyl resonances are omitted.)

Such studies have been extended to the 2,4,6-trisubstituted heptanes, for which there are three diastereoisomers, one of which is a racemic pair. They are, as we shall see, closely related to isotactic, syndiotactic, and hetereotactic triads of monomer units in polymer chains
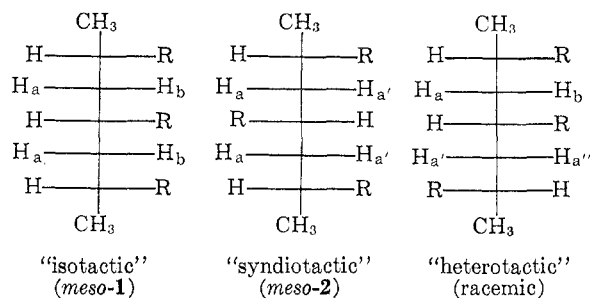
and are so named. All the methylene groups are heterosteric. The *meso* isomers each have two like heterosteric methylene groups; the racemic isomer has two unlike heterosteric methylene groups, so that all four of its methylene protons are nonequivalent. One might expect that the nonequivalence of the a' and a'' protons would be small, while that of the a and b protons might be quite large; this expectation appears to be borne out.[9-13]

It has been assumed in the foregoing discussion that the molecules may exist in any or all of their possible conformations and that the rate of interconversion of conformations is rapid on the nmr time scale. For

(7) G. V. D. Tiers and F. A. Bovey, *J. Polymer Sci.*, *Part A*, **1**, 833 (1963).
(8) F. A. Bovey, F. P. Hood, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).
(9) T. Shimanouchi, M. Tasumi, and Y. Abe, *Makromol. Chem.*, **86**, 43 (1965).
(10) Y. Abe, M. Tasumi, T. Shimanouchi, S. Satoh, and R. Chujo, *J. Polymer Sci.*, *Part A-1*, **4**, 1413 (1966).
(11) D. Doskocilova, J. Stokr, B. Schneider, H. Pivcova, M. Kolinshy, J. Petranek, and D. Lim, *ibid.*, *Part C-1*, **6**, 215 (1967).
(12) M. Murano and R. Yamadera, *ibid.*, *Part B*, **5**, 483 (1967).
(13) H. Pivcova, M. Kolinsky, D. Lim, and B. Schneider, Preprints, IUPAC Macromolecular Symposium, Brussels, 1967.
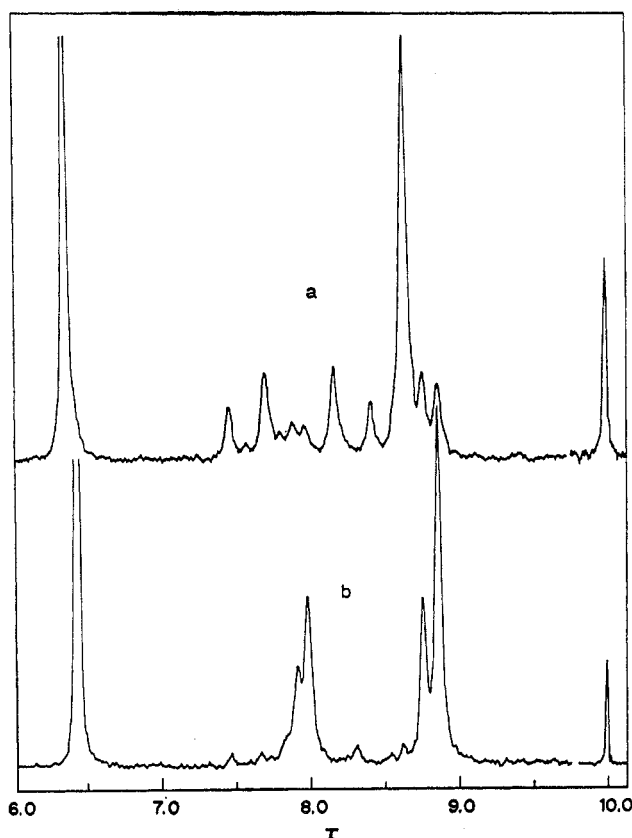
Figure 3. The 60-MHz spectra of 15% (w/v) solutions in chlorobenzene of polymethyl methacrylate prepared with (a) an anionic initiator (phenylmagnesium bromide) and (b) a freeradical initiator. The ester methyl resonance appears near τ 6.5, the β-methylene protons appear near τ 8.0, and the α-methyl protons give three peaks between τ 8.5 and 9.0. (The tetramethylsilane reference appears at τ 10.00.)

large molecules (including polymers), as for simple ethanic rotors, the existence of heterostericity or homostericity does not in principle depend upon any particular conformer being energetically preferred, nor upon there being a slow equilibration of the conformers.

Polymer Spectra. Poly(methyl methacrylate). It is now well recognized that these symmetry considerations can be extended to the long chains of polymers. In a way, very long chains simplify matters. If the degree of polymerization exceeds about 100, so that end effects can be neglected, then for a purely syndiotactic chain H_a and $H_{a'}$ can be considered strictly equivalent. Figure 3 shows the 60-MHz spectra of (a) predominantly isotactic and (b) predominantly syndiotactic poly(methyl methacrylate) in chlorobenzene solution at 150°. The methylene resonance of b is approximately the expected singlet, although somewhat broadened and complicated by the residual isotactic resonance and by additional effects with which we shall deal shortly. The methylene resonance in a is predominantly the expected AB quartet ($J = -14.9$ cps), with additional structure due to syndiotactic sequences. *The nature of these multiplets is an absolute measure of the polymer's predominant configuration, and it would not be necessary to have recourse to X-ray diffraction, even if it were possible.*

The spectrum of the α substituents does not in itself provide an absolute indication of configuration but must be correlated with the β-methylene resonance or some other absolute measurement. If this is done, the α-substituent spectrum may give more detailed configurational information than the β-methylene spectrum. The chemical shifts of α substituents commonly vary appreciably with the relative configurations of the nearest neighboring monomer units, but this is not always the case. For example, the α-methyl group resonance in poly(methyl methacrylate) is markedly dependent on configuration (Figure 3), whereas the ester methyl resonance is not. When such discrimination is possible one can observe three species of α substituents in a polymer which is not stereochemically pure: those on the central monomer units of *isotactic, syndiotactic*, and *heterotactic* triads of monomer units. The definitions of these correspond to the configurations shown above for the 2,4,6-trisubstituted heptanes. The simplest notations for these triad sequences are i, s, and h, respectively.[14] A more general notation is given below.[15] In Figure 3, the i, s, and h α-methyl resonances appear at τ 8.67, 8.90, and 8.79 in both spectra, their relative intensities of course varying greatly and affording a measure of the average configuration of the chains.

In Table I, the designations of monomer dyad and triad sequences are indicated. The *meso* dyad is designated m and the racemic dyad r. This system of nomenclature can be extended to sequences of any length. Thus, an isotactic triad is mm, a heterotactic triad mr, and a syndiotactic triad rr. Let us now assume that the probability of generating a *meso* sequence when a new monomer unit is formed at the end of a growing chain can be denoted by a single parameter, which we shall call P_m[16] (this probability has been previously designated as α[17] and as σ[14]). In these terms, the generation of the chain is then a Bernoulli-trial process. In making this assumption, we need not be concerned with the details of the monomer addition step but must assume that the probability of forming an m or r sequence is independent of the stereo-

(14) F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).

(15) The designation of the configuration of a vinyl monomer unit in a polymer chain as d or l, although not uncommon, is open to the objection that it suggests distinctions which are not experimentally observable, since vinyl polymers ordinarily show no optical activity, the α-carbon atoms being pseudo-asymmetric. A more serious objection to this notation is that it conflicts with the conventional use of the same notation to describe analogous small molecules. Thus, a methylene group in an isotactic chain can be regarded as the center unit in a *meso* dyad of monomer units having the same configuration, and such a dyad might be designated dd (or ll), but in the analogous small molecule, the 2,4-disubstituted pentane, the two asymmetric carbon atoms are of opposite configuration and are conventionally designated d and l. Similarly, for racemic dyads in syndiotactic chains, the monomer units are regarded by the polymer chemist as being of opposite configuration, whereas in the analogous pentane they have the same configuration. It is urged that the d and l notation be confined to small molecules and to polymers having true asymmetri ccenters (rather than pseudo-asymmetric), such as polypeptides, polypropylene oxide, and vinyl polymers with asymmetric side chains.

(16) H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.* **45**, 1565 (1966).

(17) B. P. Coleman, *J. Polymer Sci.*, **31**, 155 (1958).

Table I

	Designation	Projection	Bernoullian probability		Designation	Projection	Bernoullian probability
	— α Substituent —				— β-CM₂ —		
Triad	Isotactic, mm (i)		P_m^2	Dyad	meso, m		P_m
	Heterotactic, mr (h)		$2P_m(1-P_m)$		Racemic, r		$(1-P_m)$
	Syndiotactic, rr (s)		$(1-P_m)^2$	Tetrad	mmm		P_m^3
Pentad	mmmm (isotactic)		P_m^4		mmr		$2P_m^2(1-P_m)$
	mmmr		$2P_m^3(1-P_m)$		rmr		$P_m(1-P_m)^2$
	rmmr		$P_m^2(1-P_m)^2$		mrm		$P_m^2(1-P_m)$
	mmrm		$2P_m^3(1-P_m)$		rrm		$2P_m(1-P_m)^2$
	mmrr		$2P_m^2(1-P_m)^2$		rrr		$(1-P_m)^3$
	rmrm (heterotactic)		$2P_m^2(1-P_m)^2$				
	rmrr		$2P_m(1-P_m)^3$				
	mrrm		$P_m^2(1-P_m)^2$				
	rrrm		$2P_m(1-P_m)^3$				
	rrrr (syndiotactic)		$(1-P_m)^4$				

chemical configuration of the chain already formed. It follows of course that the probability of forming an r sequence is $1 - P_m$. A triad sequence involves two monomer additions; the probabilities of mm, mr, and rr are (see column 4 of Table I) P_m^2, $2P_m(1 - P_m)$, and $(1 - P_m)^2$, respectively. A plot of these relations is shown in Figure 4. It will be noted that the proportion of mr units rises to a maximum at $P_m = 0.5$, corresponding to random propagation. For a random polymer, the proportion $mm:mr:rr$ will be $1:2:1$. (A similar plot of dyad frequencies vs. P_m would obviously be two straight lines with slopes of $+1$ and -1

for m and r, respectively.) For any given polymer, if Bernoullian, the mm, mr, and rr sequence frequencies, as estimated from the relative areas of the appropriate peaks (α-methyl peaks for methyl methacrylate polymers), should lie on a single vertical line in Figure 4, corresponding to a single value of P_m. If this is not the case, then the polymer's configurational sequence deviates from Bernoullian. The polymer whose spectrum is shown in Figure 2b obeys these simple statistics within experimental error, P_m being 0.20 ± 0.01. Analysis of the spectrum in Figure 2a shows that this polymer does *not* obey Bernoullian statistics. As indicated in the caption to Figure 4, methyl methacrylate polymers produced by free-radical initiators usually follow Bernoullian statistics within experimental error, while those produced using anionic initiators do not.

The Observation of Longer Configurational Sequences

A large number of vinyl and related polymer systems, too long to list here, have now been studied by nmr in many laboratories, including this one, and their spectra have been usefully interpreted in the way just described. A little later we shall describe the spectra of two other vinyl polymers and their interpretation. Before doing so, however, we must consider the observation of sequences longer than dyads and triads, for this has become possible through improved techniques and advances in instrumental design, particularly with increasing strength of the magnetic field of the spectrometer. With respect to β-methylene groups (or, more generally, β-CM₂ groups) one may expect to resolve *tetrad* sequences of monomer units, appearing as a fine structure on the m and r resonances. As
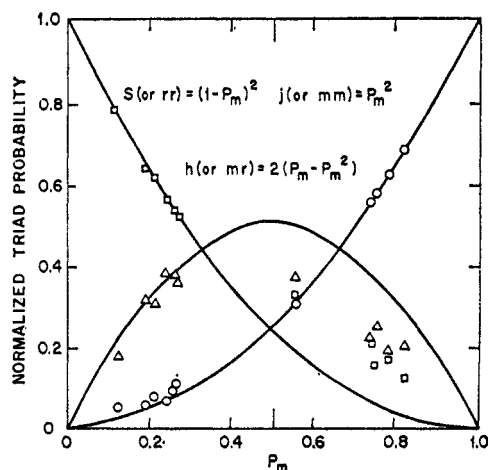
Figure 4. The probabilities of isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads as a function of P_m, the probability of m (isotactic) placement during propagation. The points on the left-hand side are for methyl methacrylate polymers prepared with free-radical initiators and those on the right-hand side are for methyl methacrylate polymers prepared with various anionic initiators. (More detailed information is given in ref 14.)

indicated in Table I, the m resonance should be resolved into three tetrad resonances, all heterosteric, giving six different chemical shifts. The r resonance should be split into two homosteric resonances and one heterosteric resonance, giving a total of ten observable β-CM$_2$ chemical shifts in a polymer which is not too highly stereoregular. One may also expect the α-substituent resonance to be resolved into ten peaks, corresponding to ten different *pentad* configurational sequences. If the polymer has been generated by a Bernoulli-trial propagation, the sequence frequencies will be as shown in columns 4 and 8 of Table I. These relationships are plotted for tetrad sequences in Figure 5 and for pentad sequences in Figure 6. Since m and r are conjugate terms in these relationships, the frequency plots are symmetrical, as indicated in the legends to these figures: three curves serve for six tetrad species and four curves for ten pentad species, as there are four pairs of sequences of which the members of each pair have the same probability.

Since, as we shall see, these sequences apparently represent the limits of resolution attainable at present, we shall not describe longer sequences in detail. However, it may be instructive to point out[16] that if $N(n)$ is the number of distinguishable n(ads), we have the values

n	2	3	4	5	6	7	8
$N(n)$	2	3	6	10	20	36	72

or, in general

$$N(n) = 2^{n-2} + 2^{m-1}$$

where $m = n/2$ if n is even and $m = (n - 1)/2$ if n is odd. It is evident that, regardless of the generating statistics, the number of possible types of sequences increases rapidly with their length (asymptotically as 2^{n-2} as $N \to \infty$) and that their discrimination beyond pentads, or hexads at most, will be very difficult.

The methylene spectrum of the predominantly syndiotactic polymethyl methacrylate (Figure 3b) shows a clear splitting (alluded to previously) into two peaks with a third weaker one as a shoulder on the low-field side. Similar resonances can be seen, in altered relative intensity, in the spectrum of the predominantly isotactic polymer (Figure 3a). It is also significant that, in the residual *meso* quartet in Figure 3a, the upfield doublet is at markedly higher field than the corresponding doublet in Figure 3b. These features clearly represent a discrimination of tetrad sequences.[18]

It is well known that, as the magnetic field (and observing radiofrequency field frequency) of the nmr spectrometer is increased, chemical shift differences, expressed on a gauss or frequency scale, increase proportionately but that spin–spin J couplings are unaffected. The result is improved discrimination and spectral simplification. The 100-MHz spectra of these polymers show an appreciable improvement over the 60-MHz results. A much more dramatic improvement
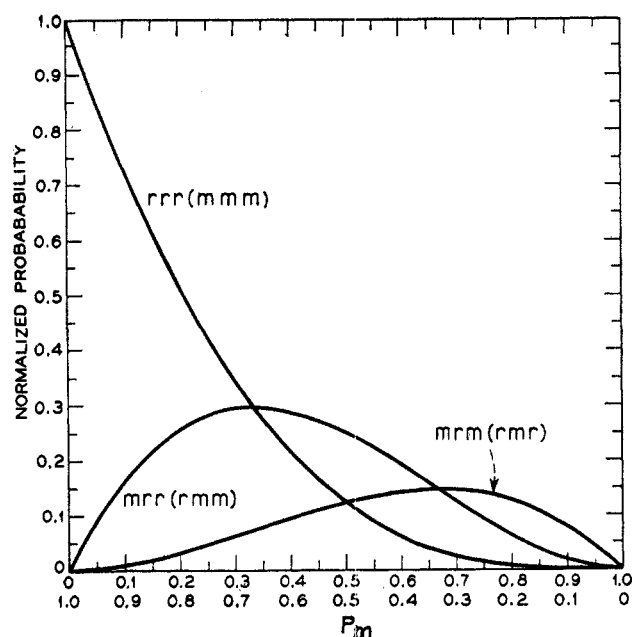

Figure 5. Tetrad sequence probabilities as a function of P_m. For rrr, mrr, and mrm the upper P_m scale is used; for mmm, rmm, and rmr the lower P_m scale is used.
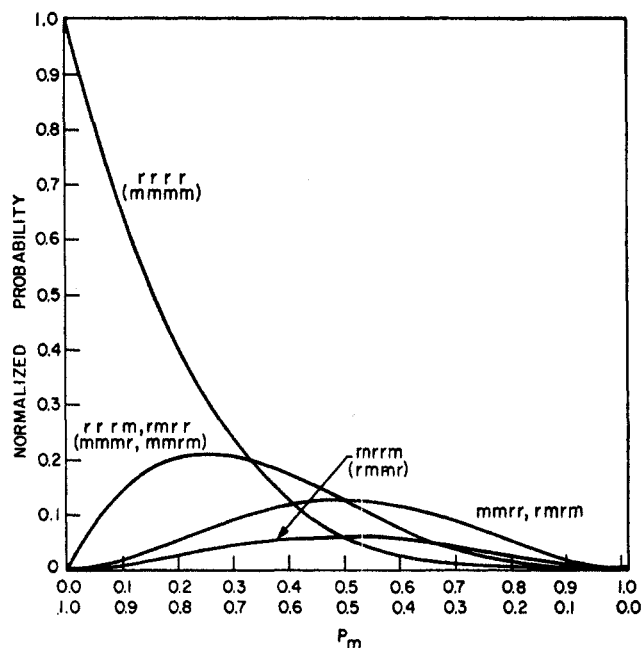

Figure 6. Pentad sequence probabilities as a function of P_m. The lower scale should be used for sequences in parentheses.

in discrimination, however, is achieved with a 220-MHz instrument employing a 51.7-kgauss superconducting solenoid.[19] The spectra in Figures 7a and 7b are for the same polymers as in Figure 3; they were observed by Dr. R. C. Ferguson (Du Pont) and are reproduced with his permission. Essentially similar spectra have now been observed in these laboratories.[20] In Figure 7a, the spectra of the α-methyl groups (τ ~8.6–9.9) and β-methylene protons (τ ~7.4–8.6) are

(18) F. A. Bovey, *Chem. Eng. News*, **43**, 98 (Aug 30, 1965).

(19) R. C. Ferguson and W. D. Phillips, *Science*, **157**, 257 (1967).
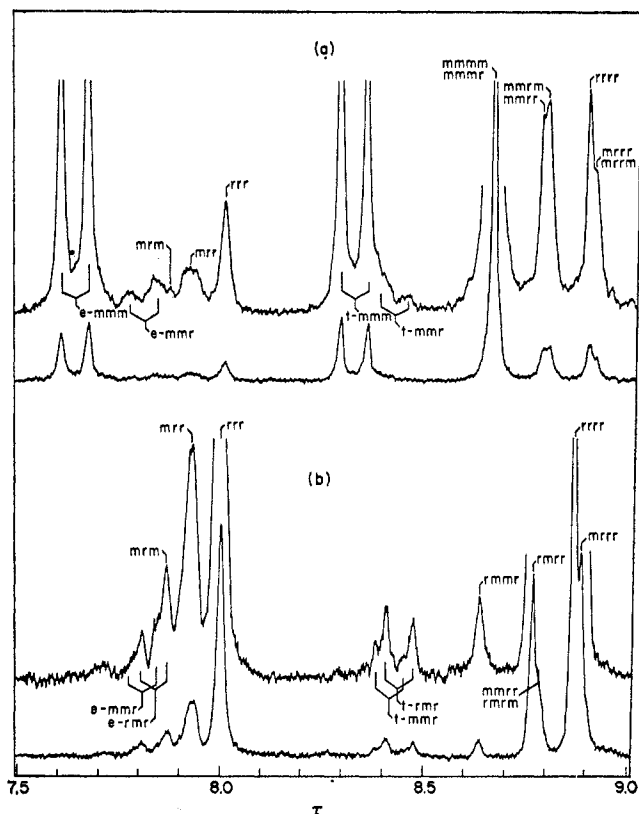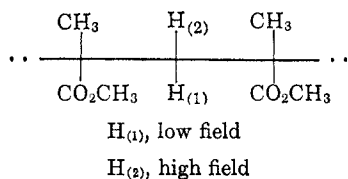(20) F. Heatley and F. A. Bovey, unpublished observations.

Figure 7. The 220-MHz spectra of the same methyl methacrylate polymers appearing in Figure 3. (reproduced by permission of Dr. R. C. Ferguson).

run at two amplifications; in Figure 7b, the β-methylene protons only are so shown. The resolution of tetrad signals is much clearer in these spectra, and a partial resolution of pentad signals (splitting of the α-methyl triad peaks) is also achieved. The assignment of peaks (indicated directly on the spectra) is based largely on the assumption that the predominantly syndiotactic polymer is Bernoullian and on the comparison of observed intensities with the appropriate curves of Figures 5 and 6. In heterotactic methylene groups it is desirable to make a definite assignment of the two distinguishable protons, as we shall see in later discussion. This has been done for polyacrylate chains in a very elegant study of model compounds by Yoshino, et al.[21] If we can assume that the same relative chemical shifts hold for methacrylate chains as well, the assignment is

$$\cdots \underset{\text{CO}_2\text{CH}_3}{\overset{\text{CH}_3}{|}} \underset{\text{H}_{(1)}}{\overset{\text{H}_{(2)}}{|}} \underset{\text{CO}_2\text{CH}_3}{\overset{\text{CH}_3}{|}} \cdots$$

H$_{(1)}$, low field

H$_{(2)}$, high field

By an extension of the terminology used in describing small molecules having two dissimilar asymmetric carbons, H$_{(1)}$ is called the *erythro* proton and H$_{(2)}$ the *threo* proton. The basis of this terminology will be

(21) T. Yoshino, M. Shinomiya, and J. Komiyama, *J. Am. Chem. Soc.*, **87**, 387 (1965).

more evident when we discuss β-deuterium-labeled polymers.

Peak assignments, particularly in the spectra of clearly non-Bernoullian polymers, are also aided by certain necessary relationships among the frequencies of occurrence of sequences, which must hold regardless of the configurational statistics. These cannot be treated in detail here but are described in ref 16.

Sequence Statistics. Although free-radical addition polymerizations proceed (with rare exceptions) by a Bernoulli-trial process with regard to the configurational sequences, this is not the only kind of sequence statistics observed in polymer chains. As we have seen, anionic polymerizations, *i.e.*, those carried out using metal alkyls or Grignard reagents as initiators, are usually non-Bernoullian. The most commonly considered non-Bernoullian process is the first-order Markov process. In Figure 8 is shown (at the top) the building up of a polymer chain by Bernoulli-trial steps. The chain end is not represented as having any particular stereochemistry, *i.e.*, it is unimportant whether it is m or r. The process is thus like reaching *at random* into a large jar containing balls marked m or r; the proportion of m's in this jar is called P_m, as already defined.

The first-order Markov sequence, on the other hand, is generated by propagation steps in which the adding monomer *is* influenced by the stereochemistry of the chain end, as shown in the lower portion of Figure 8. We now have four probabilities characterizing the addition process: $P_{m/m}$, $P_{r/m}$, $P_{m/r}$, and $P_{r/r}$. (The designation $P_{r/m}$ means the probability that the monomer adds in m fashion to an r chain end, etc.) These, however, are related

$$P_{m/m} + P_{m/r} = 1 \tag{1}$$
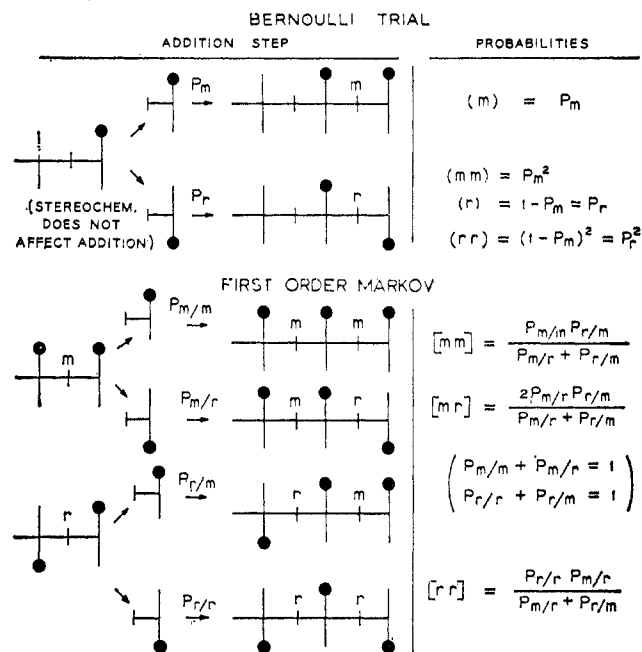
$$P_{r/r} + P_{r/m} = 1 \tag{2}$$

Figure 8. Schematic representation of Bernoulli-trial and first-order Markov propagation steps and sequence probabilities.

and so we actually need to consider only two independent probabilities, conveniently taken as $P_{r/m}$ and $P_{m/r}$. These can be determined from triad frequency data (but not from dyad data) and have been considered by a number of authors (summarized in ref 16). It is outside the scope of this article to consider in detail how this is done. For a Bernoulli-trial chain, $P_{r/m} + P_{m/r} = 1$.

It is also possible to imagine more complex mechanisms in which the configuration of the adding monomer unit is influenced by the configurations of the last *two* monomer units, corresponding to a second-order Markov process. The validity of such proposed mechanisms cannot be assessed from a knowledge of triad frequencies; one must have information concerning tetrad frequencies.[16] Higher order Markovian and also non-Markovian[22,23] mechanisms are also possible. These also can be tested if one has a sufficiently detailed knowledge of the configurational information stored in the chain.

Poly(vinyl chloride). The spectrum of poly(methyl methacrylate) is relatively simple because, although there is a strong geminal coupling of the protons of the *meso*-methylene groups, there is no observable coupling of the methylene and α-methyl protons. In polymers of monosubstituted monomers, such as vinyl chloride, the *vicinal* coupling of the α- and β-methylene protons produces a splitting of the observed resonances. On the simplest basis one would expect the α protons, being coupled to four neighboring β protons, to appear as a quintuplet and the β protons, coupled to two α protons, as a triplet. The observed spectrum (Figure 9, spectrum a) does indeed apparently show a pentuplet centered at τ 5.53 (in chlorobenzene solution) but shows a group of five peaks centered at τ ~7.9 for the methylene protons.[24-27] The methylene resonance is essentially two overlapping triplets centered at τ 7.78 and 7.96, corresponding to *meso* and racemic methylene groups, respectively.

This interpretation is confirmed by double resonance.[26] As is shown in Figure 9 (spectrum b), when the β protons are decoupled from the α protons two peaks are observed, separated by 0.20 ppm. A very similar spectrum is shown by the polymer of α-deuteriovinyl chloride[26] (spectrum d), ClDC=CH₂. The substitution of hydrogen by deuterium represents another means of spectral simplification, for the resonance of deuterium is very far removed from that of hydrogen; in addition, the H–D coupling has less than one-sixth the magnitude of the corresponding H–H coupling and produces no observable multiplicity in polymer spectra.

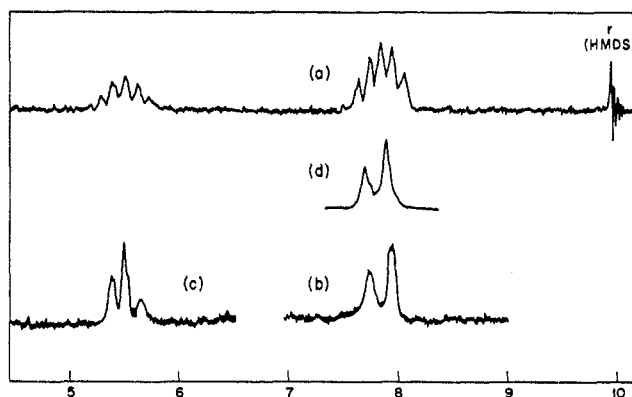When the CH₂ protons are irradiated, the α-proton resonance shows peaks at τ 5.48, 5.59, and 5.71 (Figure

Figure 9. Normal and decoupled spectra of polyvinyl chloride and poly(vinyl-α-d₁ chloride) (see text).

9, spectrum c); the dependence of the decoupled α-proton spectrum upon Δν has been employed[26] to demonstrate that these peaks correspond to syndiotactic, heterotactic, and isotactic triads, respectively, assuming the correctness of the above assignment of the β-proton resonances. The normal α-proton spectrum thus is actually three overlapping quintuplets.

Yoshino and Komiyama[28] have shown that the spectrum of poly(vinyl-α,cis-β-d₂ chloride) exhibits the ten different chemical shifts expected if one can discriminate all six of the β-methylene tetrad resonances. It is observed that the central β protons in all three of the *meso* tetrads are heterosteric, as expected (Table I), but the nonequivalence is substantial only for the *rmr* tetrad. The presence of geminal coupling, as in normal poly(vinyl chloride) or poly(vinyl-α-d₁ chloride), tends to concentrate intensity at the center of the band.

In these terms, the spectrum of polyvinyl chloride can be more fully interpreted. In Figure 10, curve a, the spectrum shown in Figure 9d is presented in greater detail. This polymer was prepared at 100°. It can be seen that it exhibits extra peaks, particularly one near τ 7.82, which are not explained by the earlier simpler interpretation.[24-26] Curve c shows calculated AB quartets (for heterosteric CH₂ groups) and singlets (for homosteric CH₂ groups) corresponding to the six methylene tetrads. The assignments of the chemical shifts are shown in this figure; these assignments are the same for three other polymers, prepared at 50, 0, and −78°. The observed and calculated spectra of the polymer prepared at −78° are also shown in Figure 10. The relative intensities of the calculated resonance lines are obtained from Figure 5—i.e., from Bernoullian statistics—choosing values of P_m which give the best match of experimental and calculated spectra at each temperature. The calculated spectra b and e in Figure 10 are obtained from a computer program which allows one to introduce any chosen line width (2.5 cps in these spectra) and to sum up the resulting spectra in any desired proportion. By visual inspection and matching of relative peak heights in calculated and

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(24) U. Johnsen, *ibid.*, **54**, S6 (1961).

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(26) F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).

(27) F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *J. Phys. Chem.*, **71**, 312 (1967).

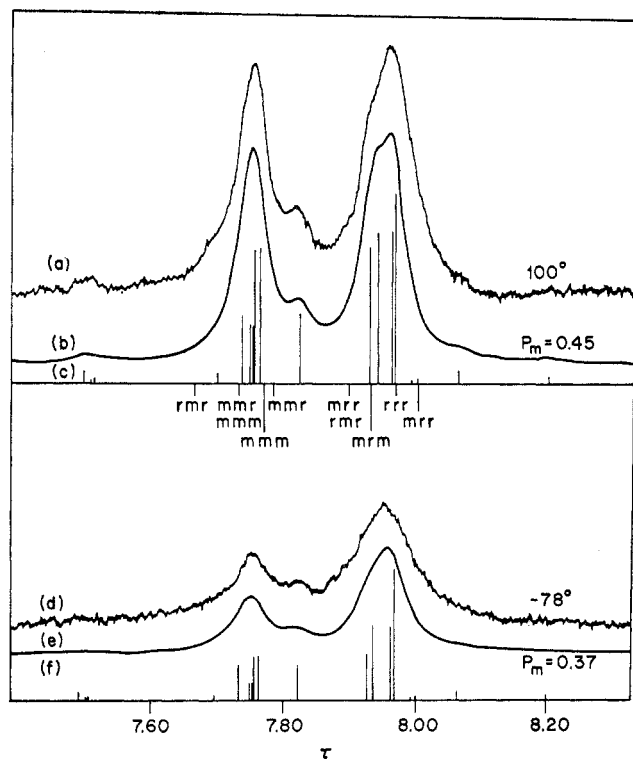(28) T. Yoshino and J. Komiyama, *J. Polymer Sci.*, Part B, **3**, 311 (1965).

Figure 10. Calculated and experimental spectra of poly(vinyl-α-d_1 chloride) prepared at 100 and $-78°$. Spectra a and d are the observed; c and f are calculated "stick" spectra; b and e are calculated spectra with an appropriate line width ($\sim$3 cps). Observed at 150° in chlorobenzene solution ($\sim$10% w/v).

Figure 11. Calculated and experimental 220-MHz spectra of isotactic polystyrene: a and d, observed spectra of α-CH and β-CH$_2$ protons, respectively, at 130° in 2.5% (w/v) o-dichlorobenzene solution; c and f, "stick" spectra calculated using six-spin dimer model (see text); b and e, calculated spectra with 4-cps line width. The calculated spectrum was obtained using the following parameters: τ_A 7.742, J_{AB} = 6.25 cps; τ_B 8.429, J_{AC} = 7.25 cps; τ_C 8.463, J_{BC} = -14.5 cps.

experimental spectra, the following values of P_m are deduced: $-78°$, 0.37; 0°, 0.43; 50°, 0.45; 100°, 0.46. From these data it can be seen that there is a measurable tendency for vinyl chloride to give more syndiotactic polymers at lower temperatures, but this appears insufficient to account for the alteration in properties observed for low-temperature polymers, particularly the enhanced crystallizability.[29]

Polystyrene. The earliest reported polymer spectra were of polystyrene,[30,31] which in carbon tetrachloride solution gave an aromatic resonance showing a separate peak for the *ortho* protons, upfield from the *meta–para* proton resonance, and a single broad peak for the aliphatic protons. More recent work[8] has shown that isotactic polystyrene can give a quite well-resolved spectrum if observed at elevated temperatures (up to 200°); from the measured vicinal couplings of the backbone protons and a comparison to the spectra of the 2,4-diphenylpentane model compounds (see Figure 2) it was concluded that isotactic polystyrene chains have a local left-handed 3_1 helical conformation the same as that which they are known to have in the crystalline state. However, in these spectra, obtained at 60 MHz, it was not possible to distinguish the two different chemical shifts of the heterosteric β-methylene groups,
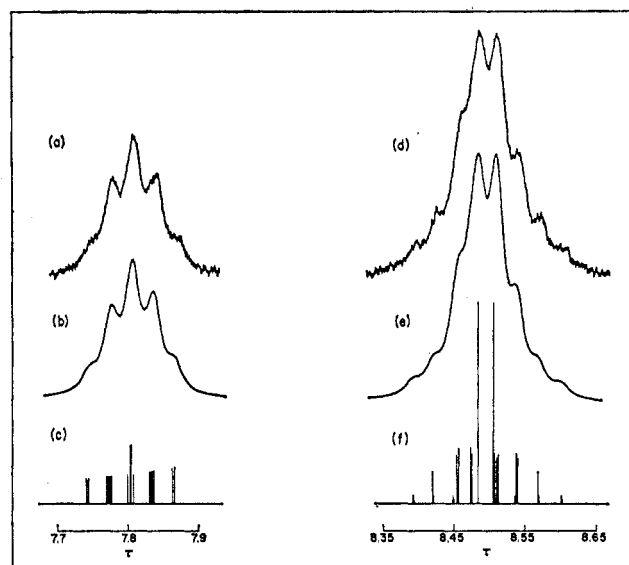
and so it could not be unequivocally demonstrated by nmr that the polymer was isotactic.

Still more recently,[32] isotactic polystyrene has been observed at 220 MHz. In Figure 11, spectra a and d are those of the backbone protons, observed in chlorobenzene solution at 150°. The multiplet centered at τ $\sim$7.74 is that of the α proton and that at τ $\sim$8.45 corresponds to β-methylene protons. Spectra b and e are a computer simulation of the observed spectrum, using a six-proton spin model, as suggested by Tincher[33,34] (spectra c and f are the same with zero line width). This calculation, also employed in an earlier study,[8] in effect
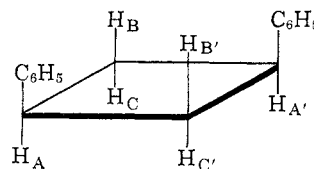
assumes that the polymer is a cyclic dimer, and that couplings through more than three bonds can be neglected. The computed spectrum was obtained using the parameters shown in the caption of Figure 11. The methylene portion of the spectrum cannot be matched by assuming that $\tau_B = \tau_C$ but only by assuming a difference of 0.034 ppm. The relative magnitudes of J_{AC} and J_{AB} make it probable, by comparison to spectra[21,35] of other isotactic polymers where the assignment is

(29) J. W. L. Fordham P. H. Burleigh, and C. L. Sturm, *J. Polymer Sci.*, **20**, 251 (1956).

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(32) F. Heatley and F. A. Bovey, *Macromolecules*, in press.

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(35) T. Yoshino, Y. Kikuchi, and J. Komiyama, *J. Phys. Chem.*, **70**, 1059 (1966).

known, that proton B is *threo* and proton C is *erythro*, but this is not entirely certain.

The Direction of Addition to the Double Bond. β-Carbon Stereochemistry

It was first demonstrated in 1958 by Fox and co-workers[36-38] that the anionic polymerization of methyl methacrylate at low temperature using metal alkyl initiators can give various crystallizable forms of the polymer, depending upon the composition of the polymerization solvent. Polymer prepared in the strongly solvating solvent ethylene glycol dimethyl ether was highly syndiotactic. Polymer prepared in toluene was highly isotactic. Polymer prepared in toluene containing small proportions of ethers contained both isotactic and syndiotactic "block" sequences. These observations have since been confirmed and extended to other acrylic monomers by a number of authors.

For a more complete understanding of the mechanism of these polymerizations, it is necessary to consider both the stereochemistry at the α carbon, as already discussed, and to consider the β-carbon stereochemistry in a different way from that of the previous discussion. The β-carbon stereochemistry is very important with respect to the mode of addition of the growing chain end to the double bond of the monomer. Natta, *et al.*,[39] and Peraldo and Farina[40] observed that the polarized infrared spectra of polymers of propylene-*cis*-1-d_1 and propylene-*trans*-1-d_1 are quite different. Miyazawa and Ideguchi[41] showed that propylene-*cis*-1-d_1 yields the *erythro*-diisotactic polymer and that propylene-

R H R H R
··· —|—|—|—|—| ···
H D H D H

erythro-diisotactic
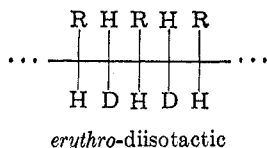
trans-1-d_1 yields the *threo*-diisotactic polymer. These

R D R D R
··· —|—|—|—|—| ···
H H H H H

threo-diisotactic
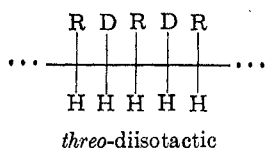
results were interpreted as indicating that, with the Ziegler–Natta catalyst employed, *cis* opening of the double bond occurs. The same conclusion was reached by Natta, *et al.*,[42] for the polymerization of *trans*-propenyl isobutyl ether and *cis*- and *trans*-β-chloro-

vinyl alkyl ethers.[43] It is very easy to see that, in terms of simple "ball-and-stick" concepts, the steric relationships shown below must hold for *meso* β-methylene units.[43]

cis monomer
/cis   trans\
erythro-diisotactic   *threo*-diisotactic
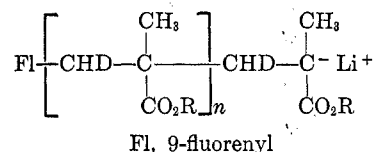\trans   cis/
trans monomer
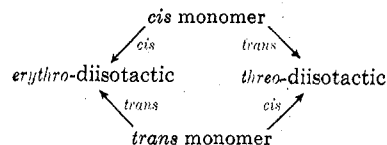
For racemic placements, there is no distinction between *erythro* and *threo* protons, at least for long stereoregular chains, and so only one syndiotactic polymer is possible, regardless of the mode of addition. (In the *mrr* tetrad, a distinction is possible in principle, but not actually observable even at 220 MHz; see Figure 7.)

Such studies have been extended to acrylate and methacrylate monomers.[44-49] In the work to be described here (which is only part of a larger study),[45] the monomer employed was

$$\begin{matrix} CH_3 \\ CH_3CH_2OOC \end{matrix} {>} C{=}C {<} \begin{matrix} H \\ D \end{matrix}$$
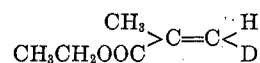
This monomer is "*cis*" in the sense employed above. The question asked is: will the remaining β proton end up *erythro* or *threo* in the polymer chain? The answer is that, when anionic initiators are employed, it depends on the solvent. In Figure 12 are shown the methylene proton spectra of polymers produced from this monomer in three different solvents at −78° using 9-fluorenyllithium as initiator. Spectrum a is that of the polymer obtained in toluene. This polymer is highly isotactic, as expected,[36-38] m being ∼0.90. The m protons are 88% *threo*, as indicated by the strong *threo-mm* tetrad peak. In this "living"[50,51] polymer system, viscosity,[45] spectroscopic,[52] and conductance[45,53] measurements indicate that *contact* ion pairs, not specifically solvated, are the chain carriers.

$$Fl{-}\left[CHD{-}\underset{\underset{CO_2R}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]_n{-}CHD{-}\underset{\underset{CO_2R}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}Li^+$$

Fl, 9-fluorenyl

Triad analysis indicates that the configurational statistics are Bernoullian.

In the presence of tetrahydrofuran at a 7.5 mol ratio to the 9-fluorenyllithium (the latter being 0.047 M)

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(37) B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, C. L. Levesque, A. Spell, J. D. Stroupe, and W. H. Watanabe, *J. Am. Chem. Soc.*, **81**, 1007 (1959).

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(42) G. Natta, M. Farina, and M. Peraldo, *Chim. Ind.* (Milan), **42**, 255 (1960).

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(50) M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

(51) M. Szwarc, *Nature*, **178**, 1168 (1956).

(52) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).

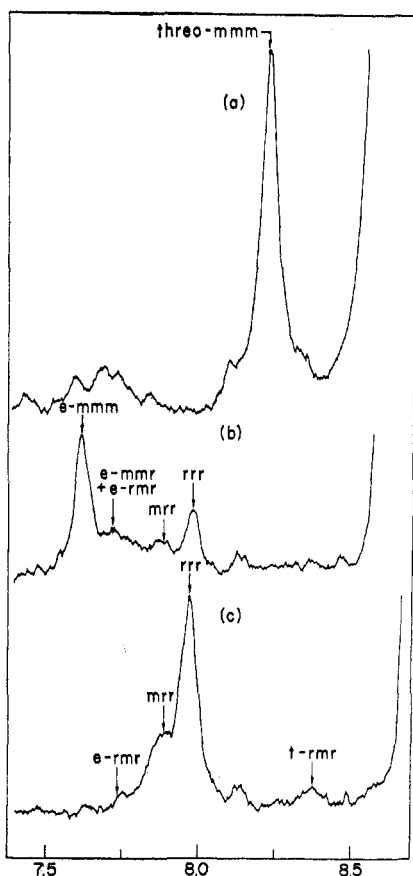(53) T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 318 (1966).

Figure 12. Effect of tetrahydrofuran (THF) on the polymerization of ethyl cis-d_1-methacrylate in toluene at $-78°$ with 9-fluorenyllithium: (a) no THF; (b) THF:initiator 7.5; (c) THF: initiator 2.2×10^4 (no toluene)

the polymer remains predominantly isotactic (m = 0.70) but the m protons are now 89% *erythro* (b in Figure 12). The polymer departs markedly from Bernoullian statistics, as shown by triad and tetrad analysis. When the polymerization is carried out in tetrahydrofuran alone (c in Figure 12) the polymer is highly syndiotactic, as shown by the strong rrr peak, m being now only 0.12. In tetrahydrofuran, as in toluene, the propagating species shows negligible conductance[45,53] and must likewise be ion pairs in which the ions are *solvated and separated by the solvent* but are not free to move independently.[52,53] Propagation by this species exhibits no steric control by the counterion, the configurational statistics being the same as for a polymer obtained using a free-radical initiator at this temperature.[54-56] Spectrum b indicates, however, that the mechanism is more complex than can be explained by only two species of chain carriers, for here the propagation proceeds predominantly by m placements, but these are *erythro* rather than *threo* as in spectrum a. Evidently a third species, termed *peripherally solvated*,[45] is predominant in the presence of a relatively low concentration of tetrahydrofuran.

It should be realized that the terms *cis* and *trans* do not have the same precise meanings in terms of transition-state structures when describing vinyl monomer propagation as they have for a simple four-center reaction. It is helpful to distinguish between the *true* mode of addition, *i.e.*, the actual direction in space along which the active chain end and monomer approach each other, and the *apparent* mode of addition, *i.e.*, the direction of addition as conventionally judged by the stereochemical configuration about the resulting bond. We shall assume that, primarily for steric reasons, the *true* mode of addition is always *trans*, as represented at the top of Figure 13. Then, in the formation of the next *meso* dyad, the *β-carbon configuration will depend on the mode of presentation or approach of the monomer to the growing chain end*. (If a *racemic* dyad is formed the β configuration of the dyad is of course indeterminate.) The growing chain end is assumed to be effectively planar but to have a definite and fixed stereochemical relationship to the next unit (not specifically represented in Figure 13), *i.e.*, the end of the chain is either m or r and remains so during placement of the next monomer unit. The α-carbon configuration may of course also be determined by the monomer approach mode. The monomer might approach in a syndiotactic-like or racemic manner, as in b, and add on in this fashion without further change, giving an r dyad, but in the presence of an effectively chelating counterion (represented as M^+) rotation of the newly formed chain end could occur, giving an *erythro-meso* placement. *Thus, the α-carbon configuration depends upon chain-end rotation as well as upon approach mode.* On the other hand, if the mode of approach is "isotactic-like," as in mode a in Figure 13, the *meso* protons in the resulting dyad will be *threo*.
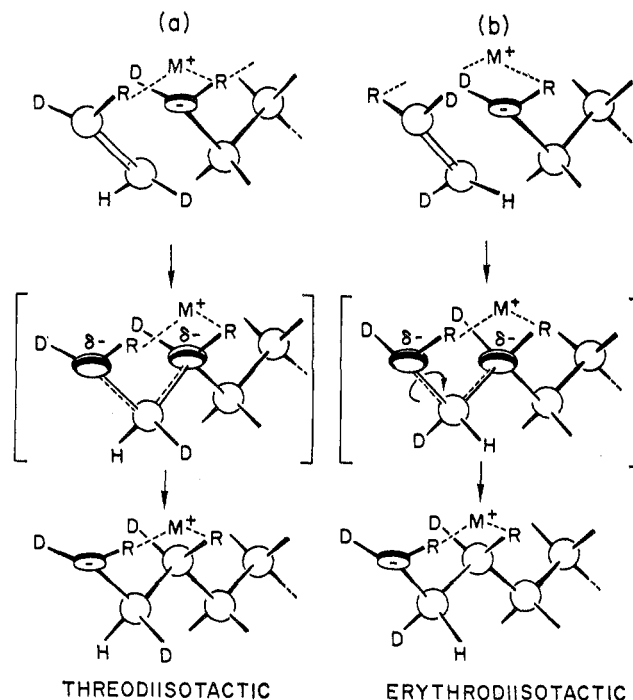

Figure 13. Monomer approach modes in isotactic placement.

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Figure 13 is actually of course a considerably over-simplified view of the view of the growing chain end, since it does not specifically represent the role of the tetrahydrofuran. It is believed that in hydrocarbon solvents the lithium counterion coordinates with the carbonyl oxygen atoms of the end and penultimate monomer units and with the carbonyl of the incoming monomer. In this way the counterion not only encourages rotation of the chain end in the event of syndiotactic-like approach, as discussed above, but also is able to guide the incoming monomer so as to make isotactic-like approach strongly preferred. In the absence of solvating molecules this guidance is ~90% effective; chain-end rotation is not necessary, and consequently the polymer is threo-diisotactic. As solvating molecules (tetrahydrofuran) are added, the monomer approach control function of the counterion begins to be seriously disturbed and eventually abolished, because in the peripherally solvated ion pair (b) the lithium is fully coordinated by tetrahydrofuran and the chain end carbonyl groups and does not coordinate with the monomer to be added. Syndiotactic-like approach, which is assumed to be inherently strongly preferred (as in free-radical propagation), becomes

possible. If this happens, chain-end rotation is still fairly effective and the polymer remains predominantly isotactic, but becomes largely or almost entirely erythro-diisotactic. Finally, at high tetrahydrofuran concentrations, all influence of the counterion ceases, and the polymer becomes predominantly syndiotactic. In the solvent-separated ion pair which now dominates, the coordination of the Li$^+$ is entirely with the tetrahydrofuran; Glusker, et al.,[57] find that four tetrahydrofuran molecules are associated with each living chain.

The chelated model of the growing chain end which we have described here is in some ways similar to earlier proposals of Goode, et al.,[58] Cram and Kopecky,[59] Cram,[60] and Bawn and Ledwith.[61] These models, however, do not provide an explanation for the behavior of the β-carbon configuration as a function of solvent composition.

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(58) W. E. Goode, F. H. Owens, and W. L. Meyers, J. Polymer Sci., 46, 317 (1960).
(59) D. J. Cram and K. R. Kopecky, J. Am. Chem. Soc., 81, 2748 (1959).
(60) D. J. Cram, J. Chem. Educ., 37, 317 (1960).
(61) C. E. H. Bawn and A. Ledwith, Quart. Rev. (London), 16, 361 (1962).