

CONFIGURATIONAL SEQUENCE STUDIES BY N.M.R. AND THE MECHANISM OF VINYL POLYMERIZATION

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INTRODUCTION

Many theoretical models have been proposed for the propagation steps in the polymerization of vinyl monomers. For the most part it has not been possible either to accept or to reject these proposals because of the absence of any experimental method for proving them to be either right or wrong. Much light would be shed on this problem if it were possible to do the following:

(i) To determine with some precision the stereochemical configuration of the polymer chains, as normally understood, i.e., the configurations at the α -carbon atoms. This should be done not merely in terms of the overall proportions of isotactic and syndiotactic placements of monomer units, but in terms of sequences of monomer configurations of 3, 4, and 5 units and perhaps even longer; ideally, of whole chains.

(ii) To determine the *direction of addition* of the active chain end to the double bond of the monomer during propagation, i.e., whether the double bond opens up in an apparently *cis* or *trans* manner. As we shall see, this is equivalent to determining the configurations at the β -carbon atoms.

High resolution n.m.r. spectroscopy is particularly well suited for providing information on both these questions. This paper will be concerned with showing in general and by particular example how this can be done. It will be shown that, by the intrinsic nature of n.m.r. and by the fundamental symmetry properties of vinyl polymer chains, these two types of information are strongly interrelated.

It should be stated at the outset that the studies to be reported do not deal primarily with the live polymerizing system itself, as do most studies of chemical mechanism. Although care has been taken to provide well-defined polymerizing systems, the main concern is the finished product—the dead polymer chain—and the main task is to deduce from the information recorded in it something concerning the process by which it was formed.

POLYMER STEREOCHEMISTRY AND N.M.R.

It may be useful to review briefly some of the basic principles of the determination of polymer stereochemistry by n.m.r. In n.m.r. spectra of polymethyl methacrylate (*Figure 1*) one can distinguish three species of α -methyl groups: those on monomer units flanked on both sides by units of

the same configuration, forming an *isotactic triad* (the central unit designated as an *i* unit); those on monomer units having units of opposite configuration on both sides, forming a *syndiotactic triad* (central *s* unit); and those on monomer units having a unit of the same configuration on one side and of opposite configuration on the other side, forming a *heterotactic triad* (central *h* unit). The *i*, *h*, and *s* α -methyl triad resonances in the polymethyl methacrylate spectrum appear at 8.67 τ , 8.79 τ , and 8.90 τ , respectively.

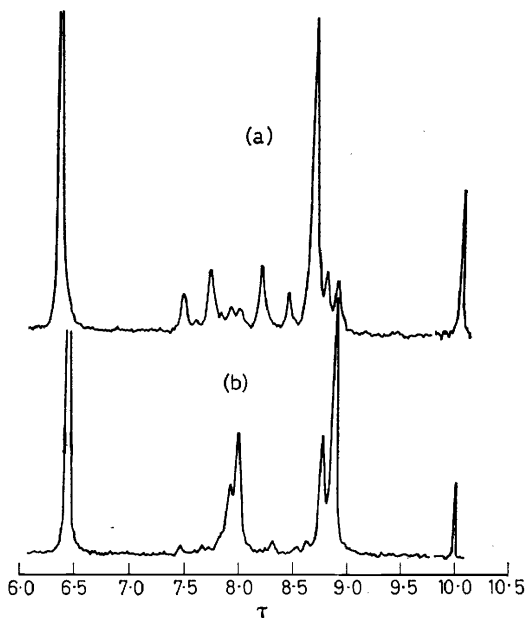


Figure 1. N.M.R. spectra of 15% solutions in chlorobenzene of polymethyl methacrylate prepared with (a) an anionic initiator and (b) a free radical initiator.

In a syndiotactic chain, the protons in each methylene group (termed *racemic* or *r*, by analogy with related small molecules) have the same average environment and therefore appear as a single chemical shift. In an isotactic chain, the protons of each methylene group (termed *meso* or *m*) do not experience the same average environment and have differing chemical shifts; in the absence of coupling to α -protons, a *meso* methylene group appears as an AB quartet. These observations are paralleled by numerous similar findings on analogous small molecules, and are of particular significance, as they furnish an absolute measure of the polymer's predominant configuration¹. Molecules or groups (including monomer sequences in polymer chains) having methylene groups, or more generally CM_2 groups where M is any observable nucleus or group, in which the M groups are differentiated, are termed *geminally heterosteric*; molecules in which they are equivalent (aside from fortuitous equivalence) are termed *geminally homosteric*, a terminology proposed by Professor Murray Goodman. In Figure 1, the predominantly isotactic polymer (a), shows a quartet for the methylene protons (centred at 7.90 τ), while the predominantly syndiotactic polymer shows a

CONFIGURATIONAL SEQUENCE STUDIES BY N.M.R.

narrow resonance in this position which is clearly not a quartet. The splitting observable in this "singlet" is not expected from the analysis so far given and would not be shown by a purely syndiotactic polymer. We shall return to this point shortly.

A considerable number of vinyl polymers have now been observed and at least partially interpreted in these terms, and the data have proved useful. However, *dyad* and *triad* information provide only a rather limited picture of polymer chain configuration. As experimental discrimination increases, through improved techniques and advances in instrumental design, finer structure becomes observable. With respect to α -substituents one may expect to resolve *pentads* of monomer units, their resonances appearing as fine structure on the isotactic, heterotactic and syndiotactic peaks. Similarly, in the methylene region of the spectrum, one may expect to resolve *tetrad* resonances, appearing as fine structure on the *meso* and *racemic* dyad resonances. In *Figure 2* are shown projections illustrating the configurations of the six possible tetrads, which will exhibit a total of ten different chemical shifts.

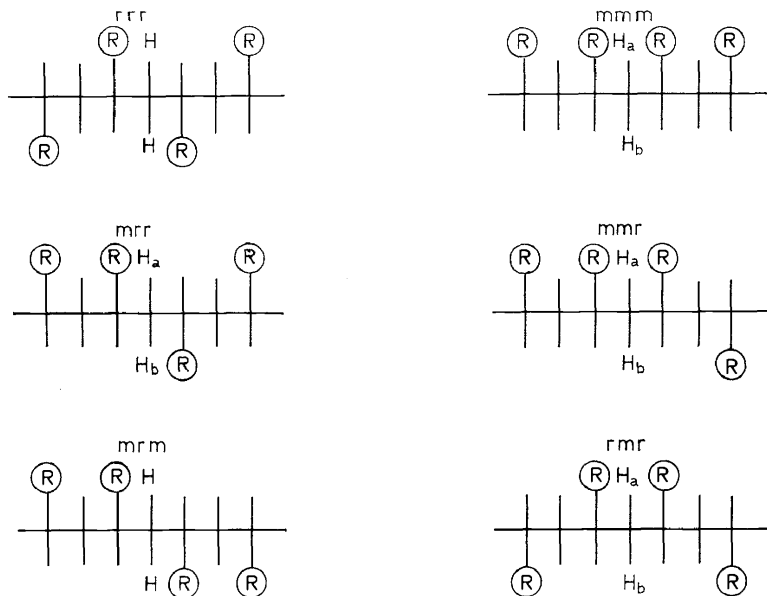


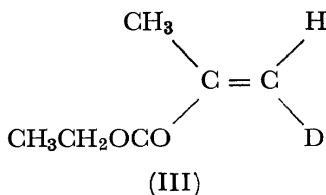
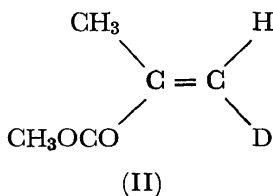
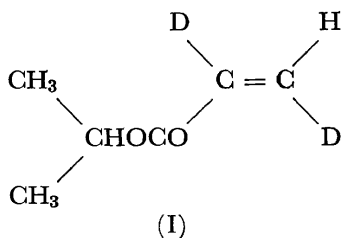
Figure 2. Monomer tetrad configurations for vinyl polymer chains, viewed along plane of planar zigzag.

Calculation shows that there are ten possible *pentads*, 20 possible *hexads*, 36 possible *heptads*, and so on, so that the complexity multiplies rapidly². Yoshino and Komiyama have recently shown that all six of the predicted tetrads can be seen in the spectrum of poly- α,β -dideuterovinyl chloride³. In *Figure 1a*, the racemic methylene resonance (approximately at the centre of the predominant *meso* quartet) can be seen to be split into three peaks. Similarly, the weak *meso* quartet in the predominantly syndiotactic polymer (*Figure 1b*) is shifted upfield. This clearly represents chemical shift differences between tetrads.

In this paper, it will be shown how the increasingly detailed information concerning polymer chain configuration which is now becoming available can be applied to gain information concerning the way in which the chain was formed. By labelling the methylene group in the vinyl monomer, we can determine the configurations at the β -carbon atoms and from this the direction of addition to the double bond. By observation and assignment of tetrad resonances we can say considerably more concerning the statistics of the propagation process than is possible from knowledge only of dyads and triads.

DIRECTION OF ADDITION TO THE DOUBLE BOND IN VINYL POLYMERIZATION

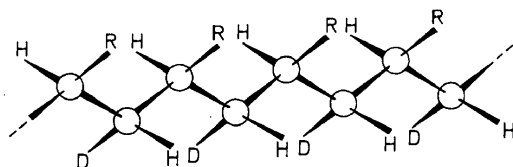
This work has dealt with the following three monomers:



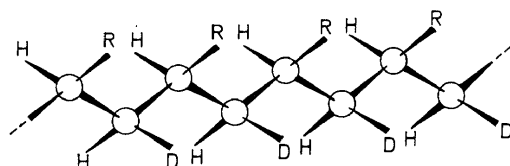
Work was initiated with the dideutero isopropyl acrylate (I)⁴, and more recently⁵ has dealt mainly with the methacrylates, of which (III) has been chiefly employed because of greater ease of synthesis. In the polymer n.m.r. spectra, principal attention centres on the β -proton spectrum, with the side-chain resonances providing important supporting information concerning triad sequence frequencies. These monomers are all of what may be termed the *cis* type, meaning that the β -deuterium label is *cis* to the ester group. Having substituents at both α and β carbons, such monomers can, upon polymerization, yield three types of stereospecific polymer:

CONFIGURATIONAL SEQUENCE STUDIES BY N.M.R.

erythrodiisotactic, *threodiisotactic*, and *syndiotactic*. Figure 3 is a reminder of the meaning of *erythro* and *threo* with regard to polymer chains of this type. This terminology is extended somewhat by also calling the β -proton of the *erythro* chain the "erythro proton" and the β -proton of the *threo* chain the "threo proton". Note that the *erythro* proton is on the same side of the planar



Erythrodiisotactic



Threodiisotactic

Figure 3. Erythrodiisotactic and threodiisotactic vinyl polymer chains. For methacrylate chains, R represents an ester group and the α -H is replaced by CH_3 .

zigzag as the ester group R. It is very easy to show that, in terms of simple ball-and-stick concepts, the steric relationships summarized in Figure 4 will hold⁶. At this stage we will take *cis* and *trans* double bond addition to have their usual meanings. The *erythro* proton results from *cis* addition, and the *threo* proton from *trans* addition. In Figure 5 ((d), (e), and (f)) are shown spectra of polyisopropyl- α -*cis*- β -dideuteroacrylate prepared in toluene solution at -78° with phenylmagnesium bromide as initiator. (Spectra

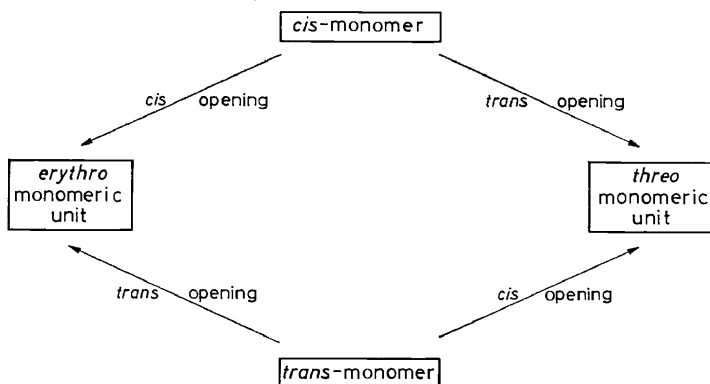


Figure 4. The formation of erythrodiisotactic and threodiisotactic polymer chains.

(a) and (b) refer to the non-deuterated polymer.) The two peaks at 7.86τ and 8.32τ correspond to the *erythro* and *threo* protons, respectively. This assignment was first conjectured by us on the basis of known facts concerning nuclear shielding in analogous small molecules⁴, and was then proved in a very elegant model compound study by Yoshino and coworkers⁷. The polymer appears to be quite highly isotactic, as indicated by the virtual

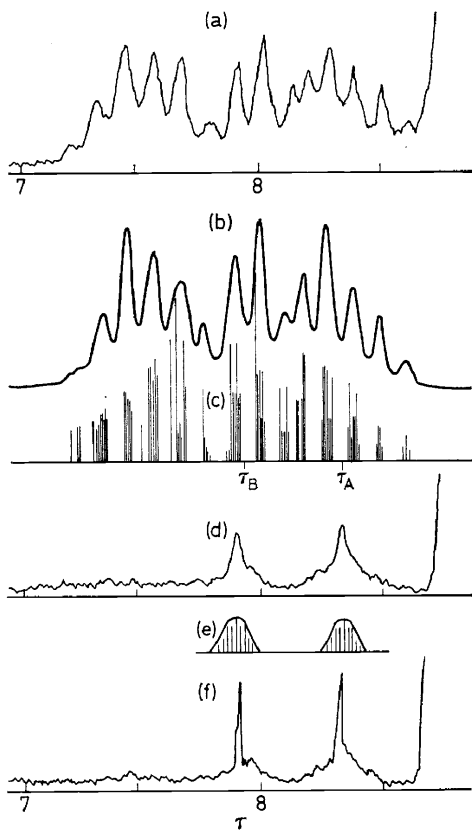


Figure 5. Spectra of isotactic poly-isopropyl- α,β -*cis*- d_2 -acrylate (14% in chlorobenzene at 150° ; spectra (a), (b), and (c) correspond to the non-deuterated polymer; spectrum (d): not decoupled; spectrum (f): deuterium irradiated; spectrum (e): calculated from D—H couplings.

absence of any peak at *c.* 8.20τ , where the racemic (i.e., syndiotactic) methylene resonance would be expected. Spectrum (e) is the calculated spectrum for the normally expected deuterium couplings. It can be seen that quadrupolar relaxation of the deuterium nucleus, particularly effective in slow-moving polymer chains, has partly decoupled the deuteriums from the protons; in spectrum (f), decoupling has been made complete by double irradiation. The lines are now sharp.

From the mechanistic viewpoint, the surprising thing about this spectrum

CONFIGURATIONAL SEQUENCE STUDIES BY N.M.R.

is the nearly equal intensity of the peaks. We expected addition to be either *cis* or *trans*, but not both. Further insight, or perhaps further confusion, was gained by varying the concentration of diethyl ether. Although the Grignard reagent was dried in vacuum, a small amount of ether remained in the polymerizing system producing the polymer shown in *Figure 5*. When this was rigorously removed by baking the initiator in vacuum, there was produced a polymer giving the spectrum shown as (c) in *Figure 6* (spectrum (b) is the same as in *Figure 5*). Now, *cis* addition is strongly preferred. When ether is added in 10:1 mole ratio to the Grignard, the polymer produced shows a very strong *threo* peak (*Figure 6*, spectrum (a)) and has been produced almost exclusively by *trans* addition. All polymers are isotactic. Thus, by varying the ether content in the system, one can control the β -configuration without affecting the α -configuration.

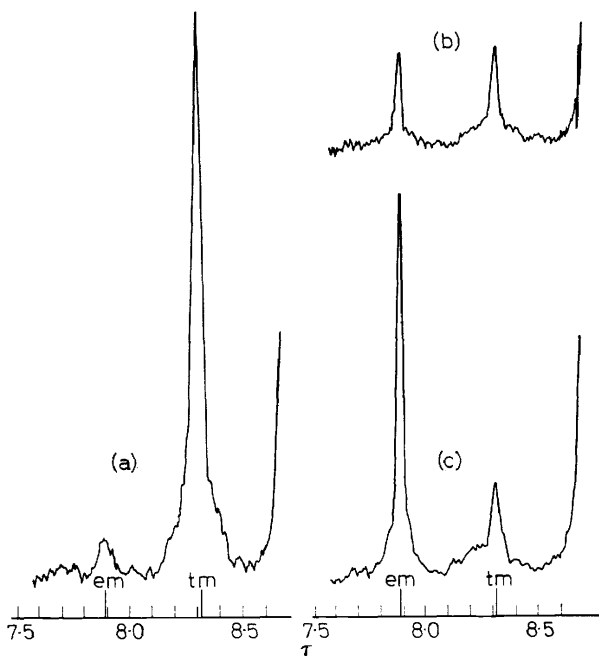


Figure 6. β -Methylene proton spectra of polyisopropyl- α,β -*cis*- d_2 -acrylate prepared with phenyl magnesium bromide and (a) a large molar excess of ether; (b) partial ether removal; (c) rigorous ether removal.

With metal alkyl initiators, in particular 9-fluorenyllithium, related but apparently opposite effects are observed. Preliminary work with isopropyl acrylate showed that increasing amounts of tetrahydrofuran caused *cis* addition to be increasingly preferred. More extensive work has shown that this behaviour is true also for methacrylates. In *Figure 7* are shown the β -proton spectra of *cis*- β -deutero ethyl methacrylate polymers prepared in toluene at -78° with increasing amounts of tetrahydrofuran. The mole ratio of tetrahydrofuran to initiator is indicated for each spectrum in the

figure title. Increasing proportions of tetrahydrofuran cause the β -configuration to shift from *threo* to *erythro*. At very high ether content, the α -configuration is also affected, and the polymer becomes predominantly syndiotactic, as shown by the growth of the racemic resonance around 8τ .

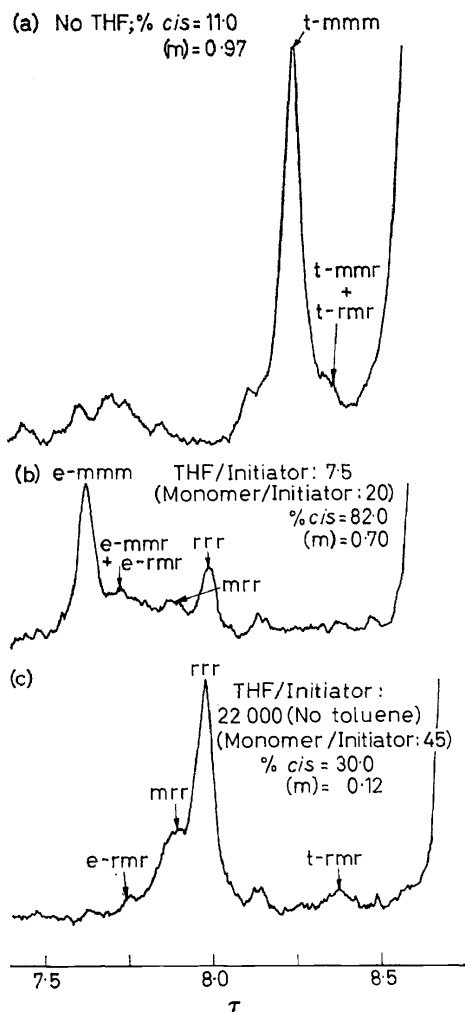


Figure 7. Effect of tetrahydrofuran on polymerization of *cis*- d_1 -ethyl methacrylate in toluene at -78° with 9-fluorenyllithium initiator: (a) no tetrahydrofuran; (b) tetrahydrofuran: initiator ratio 7.5; (c) tetrahydrofuran: initiator ratio 22000 (no toluene).

For polymers, such as shown in (d) and (f) in Figure 5, in which both *erythro* and *threo* methylenes are clearly present, an interesting question arises: are these sequences distributed at random or do they occur in long runs, perhaps even as entire *erythro* and entire *threo* chains? To study this question,

Yoshino and Kuno⁸ have carried out a most ingenious experiment. Using isopropyl *trans*- β -monodeutero acrylate, i.e., still having an α -proton, it was shown from the coupling patterns in the polymer spectra that virtually all the *threo* units have *threo* units as neighbours and all the *erythro* units have *erythro* units as neighbours. Thus, they must be produced in long runs. Perhaps there are certain catalyst sites that turn out only *threo* chains and others that turn out only *erythro* chains. Or perhaps a given site changes its properties periodically. If this is the case, it must do so at a rate slow compared to the propagation rate. We shall return later to the mechanistic implications of these findings.

CONFIGURATIONAL SEQUENCES

Now let us turn from the question of the direction of double bond addition to the interpretation of the tetrad fine structure in the methylene spectrum in terms of configurational sequence statistics and the mechanism of polymerization. A few general remarks are in order. In the first place, as already pointed out, we are limited so far to dyad, triad, and tetrad information. Now, there are certain *necessary relations* among the frequencies of occurrence of these sequences, which must hold regardless of any possible mechanism because they reflect basic statistical facts. Because they are independent of mechanism, these relationships are very useful in checking the validity of spectral assignments, but of course on the other hand they can give no possible information concerning mechanism. Some of the more helpful are shown in *Table 1*. For a more complete description, see reference 2. In this table, we indicate experimentally observable quantities. In a given chain one cannot distinguish the sequences *m**m**r* and *r**m**m* nor the sequences *r**m**r* and *m**r**r*, i.e., we cannot tell the direction of a sequence. By (*m**m**r*) we mean the sum of *m**m**r* and *r**m**m* and by (*m**r**r*) the sum of *m**r**r* and *r**m**r*.

For consistency, only the *m* and *r* terminology is used in *Table 1*. It should be recognized that *mm* = *i*, *mr* = *h*, and *rr* = *s*.

Table 1. N.M.R. observables and necessary relations

	$(m) + (r) = 1$
	$(mm) + (mr) + (rr) = 1$
Dyad-triad:	$(m) = (mm) + \frac{1}{2}(mr)$
	$(r) = (rr) + \frac{1}{2}(mr)$
Triad-tetrad:	$(mm) = (mmm) + \frac{1}{3}(mnr)$
	$(mr) = (mnr) + 2(rmr) + (mrr) + 2(mrm)$
	$(rr) = (rrr) + \frac{1}{3}(mrr)$
Tetrad-tetrad:	$(mnr) + 2(rmr) = 2(mrm) + (mrr)$
	Sum of all tetrads = 1

It should be noted from *Table 1* that of the six tetrad probabilities, only four (*not* five) are independent for any chain, so that the tetrad statistics are completely known if four tetrad resonances can be distinguished and measured. Unfortunately, at the present stage of experimental development,

this is seldom possible, at least for the acrylate and methacrylate polymers discussed here.

The sequence statistics most commonly considered are (a) the Bernoulli-trial and (b) the 1st-order Markov. Perhaps it is generally understood what each of these types of sequences implies concerning the mechanism producing it, but nevertheless it may be well to consider these types of distributions briefly here, because one sometimes finds statements in the literature concerning them that are inconsistent or misleading. In *Figure 8* is shown at the

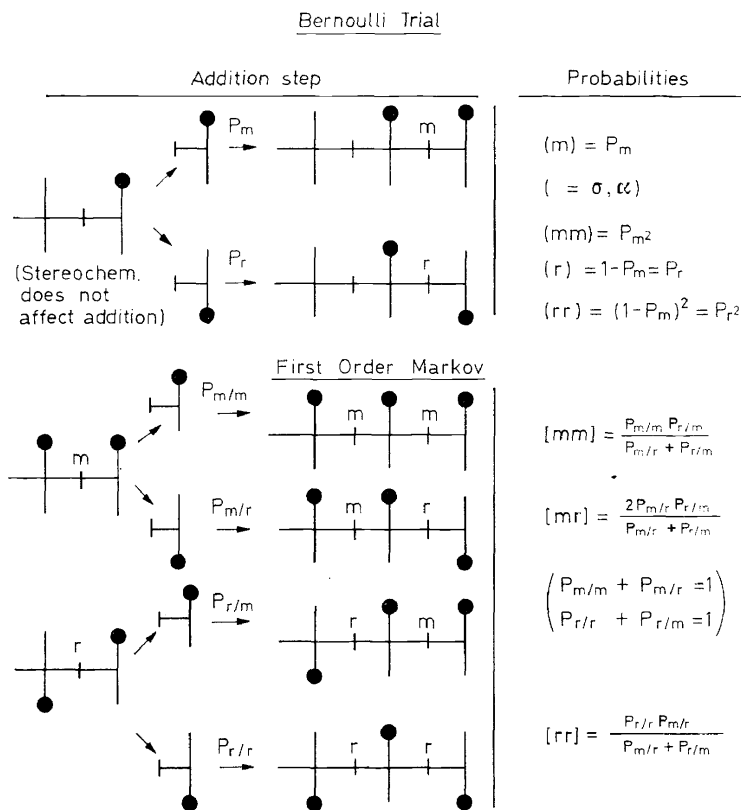


Figure 8. Bernoulli-trial and first-order Markov propagation steps and probabilities.

top the building up of a chain by Bernoulli-trial steps. The chain-end is not represented as having any particular stereochemistry, i.e., not only is it not *d* or *l* (a terminology to be avoided; see ref. 1) but it is also 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 here P_m , and has been called variously p , σ , and α elsewhere. It is often said of this mechanism that the addition "is influenced only by the end-unit of the growing chain"; such statements should not be understood to mean that it is influenced by the *stereochemistry* of the end of the growing chain — for it is not: *one* monomer chain unit considered alone has no

stereochemistry, but can of course exert a steric influence. Free radical polymerizations generally follow these simple statistics, although Reinmüller and Fox⁹ have very recently obtained evidence for deviations in methacrylate polymerizations at low temperature, and Tsuruta *et al.*¹⁰ have found similar deviations for methacrylates with bulky side-chains.

The 1st-order Markov sequence is generated by propagation steps in which the adding monomer *is* influenced by the stereochemistry of the growing chain end, which may be m or r. 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 here the probability that the monomer add in m-fashion to an r chain end, etc.) For the triad frequencies we have:

$$(mm) = \frac{P_{m/m} P_{r/m}}{P_{m/r} + P_{r/m}} \quad (1)$$

$$(mr) = \frac{2P_{m/r} P_{r/m}}{P_{m/r} + P_{r/m}} \quad (2)$$

$$(rr) = \frac{P_{r/r} P_{m/r}}{P_{m/r} + P_{r/m}} \quad (3)$$

We also have the relationships:

$$P_{m/m} + P_{m/r} = 1, \quad (4)$$

and

$$P_{r/r} + P_{r/m} = 1. \quad (5)$$

There are thus really only two independent probabilities, which we shall take as $P_{r/m}$ and $P_{m/r}$. The propagation may be characterized if we can determine values of these conditional probabilities. Of course, one can also easily imagine 2nd-order Markov processes, characterized by four conditional probabilities, and implying an influence of an additional chain unit — and still higher-order Markov propagation steps. One can also imagine non-Markov processes, one of which we shall discuss later.

Concerning the fitting of data to postulated mechanisms, we can say the following:

(i) From *dyad* information alone, i.e., (m) and (r), any mechanism can be *fitted* but none can be *tested*. By “tested”, we mean that a polymer can be shown to be consistent or inconsistent with a given model, at a given level of sequence discrimination. But there is always the possibility that examination with higher discrimination may reveal inconsistencies with the proposed model.

(ii) From *triad* information (which implies dyad as well), i.e., [mm], [mr], and [rr], a Bernoulli model can be *tested* and Markov models of any order can be *fitted*. In addition, certain non-Markov models can be *tested*, as we shall see.

(iii) From *tetrad* information, a 1st-order Markov model can be *tested*, and higher orders fitted. This is as far as we need to go with such statements at the present time.

From triad data, consistency with Bernoulli statistics may of course be tested by the familiar relationships:

$$(mm) = P_m^2 = (m)^2$$

$$(mr) = 2P_m(1 - P_m) = 2(m)[1 - (m)]$$

$$(rr) = (1 - P_m)^2 = [1 - (m)]^2$$

This is equivalent to fitting to the now familiar parabolic curves describing P_m (or σ) as functions of triad frequency; dyad data is useful for support, but is not necessary. A polymethyl methacrylate obeying these relationships is shown, together with the pertinent quantitative data, in *Figure 9*.

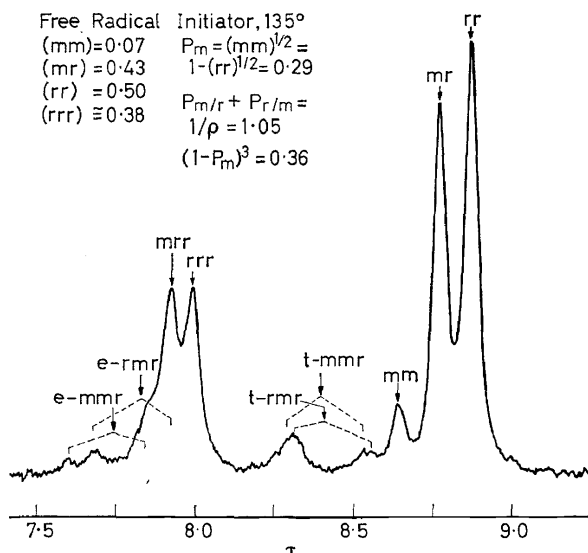


Figure 9. Polymethyl methacrylate prepared with free radical initiator at 135° (15% in chlorobenzene, 150°).

There is an important point in connection with such fitting to Bernoullian schemes that deserves emphasis. So far as passing the triad test is concerned, it is sufficient that the placement of the adding monomer unit be independent of whether the stereochemistry of the chain *end* is *m* or *r*; it can be influenced to an arbitrarily high degree by the stereochemistry of the next placement down, i.e., can be subject to a very strong *antepenultimate* effect, and still look Bernoullian. This would correspond to a 2nd-order Markov mechanism. If tetrad frequencies are known, a more rigorous test can be applied, since they must fit the curves shown in *Figure 10*, and correspond to a single value of σ or P_m ; these curves are the analogue of the parabolas expressing triad frequencies. In the present case, it is not possible to measure the tetrad intensities with much accuracy, but they are at least in qualitative accord with these curves for a P_m of 0.29.

We may test for Bernoullian fitting in a slightly different, although

CONFIGURATIONAL SEQUENCE STUDIES BY N.M.R.

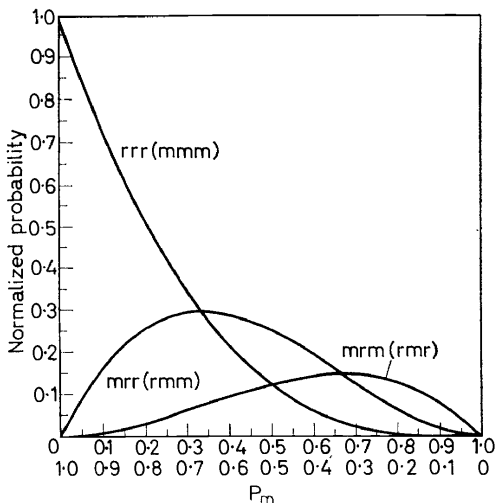


Figure 10. Tetrad probabilities for Bernoulli-trial vinyl polymer chains. For (rrr), (mrr), and (mmm), the upper P_m scale is used; for (mmm), (mrm), and (rmr) the lower scale is used.

really equivalent way, by calculating values of $P_{m/r}$ and $P_{r/m}$ from triad data, using the equations below:

$$P_{m/r} = \frac{[mr]}{2[mm] + [mr]} \quad (6)$$

$$P_{r/m} = \frac{[mr]}{2[rr] + [mr]} \quad (7)$$

These are readily obtained from Eqs. (1)–(5). It is easily shown that for Bernoullian propagation, $P_{m/r} + P_{r/m} = 1$. In the present case, $P_{m/r} + P_{r/m} = 1.05$, which means that the chain is Bernoullian within experimental error. Since only triad information is used, this test is subject to the limitation just mentioned. Even passing the tetrad test does not rule out mechanisms of higher order than 2nd-order Markov, as we have seen, but one usually accepts agreement at this point as indicating Bernoullian statistics, as it is generally considered undesirable to make such interpretations unnecessarily complicated. In a strict sense, however, one can *never* rule out mechanisms of a higher order than one is able to test.

In Figure 11, is shown the spectrum of a methyl *cis*- β - d_1 -methacrylate polymer, made in toluene solution at -78° with phenylmagnesium bromide initiator and a 9:1 mole ratio of ether to initiator. When the α -methyl triad intensities are used to calculate the 1st-order Markov probabilities, we obtain:

$$P_{m/r} = 0.31$$

$$P_{r/m} = 0.25,$$

the sum of which is 0.56 and indicates clearly a deviation from Bernoullian

F. A. BOVEY

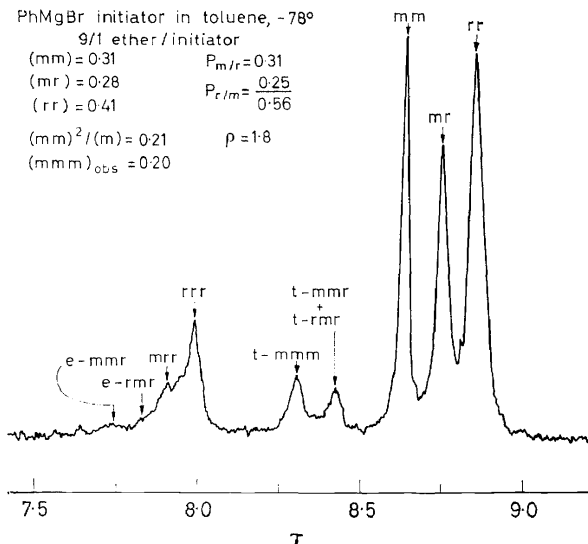


Figure 11. Poly-*cis*- β - d_1 -methyl methacrylate, prepared with phenylmagnesium bromide initiator in toluene, -78°; 9:1 molar ratio of diethyl ether to initiator. (15% in chlorobenzene, 150°).

statistics. To test consistency with a 1st-order Markov mechanism, we must use tetrad information, and the following relations:

$$(mmm) = \frac{(1 - P_{m/r})^2 P_{r/m}}{P_{m/r} + P_{r/m}} \left[= \frac{(mm)^2}{(m)} \right] \quad (8)$$

$$(mmr) = \frac{2P_{m/r} (1 - P_{m/r}) P_{r/m}}{P_{m/r} + P_{r/m}} \left[= \frac{(mm)(mr)}{(m)} \right] \quad (9)$$

$$(mrm) = \frac{P_{m/r} \times P_{r/m}^2}{P_{m/r} + P_{r/m}} \left[= \frac{(mr)^2}{4(r)} \right] \quad (10)$$

$$(mrr) = \frac{2P_{m/r} \times P_{r/m} (1 - P_{r/m})}{P_{m/r} + P_{r/m}} \left[= \frac{(mr)(rr)}{(m)} \right] \quad (11)$$

$$(rmr) = \frac{P_{m/r}^2 \times P_{r/m}}{P_{m/r} + P_{r/m}} \left[= \frac{(mr)^2}{4(m)} \right] \quad (12)$$

$$(rrr) = \frac{P_{m/r} (1 - P_{r/m})^2}{P_{m/r} + P_{r/m}} \left[= \frac{(rr)^2}{(r)} \right] \quad (13)$$

As we have seen, one ought to show that four of the left-hand relationships hold, but this is not always possible. The relationships in brackets hold for the Bernoullian case also, and hence do not constitute a test for 1st-order

Markov; they are useful in testing non-Markovian chains, as we shall see shortly. In the present case:

$$(\text{mm})^2/(\text{m}) = 0.21$$

$$(\text{mmm})_{\text{obs}} = 0.20$$

The polymer is thus 1st-order Markov within the probable experimental error. Another useful quantity is the *persistence ratio*, defined by Coleman and Fox^{11, 12} as:

$$\rho = 2[(\text{m})(\text{r})]/(\text{mr}),$$

which is equal to $1/(P_{\text{m/r}} + P_{\text{r/m}})$ for 1st-order Markov statistics. For this polymer, then:

$$\rho = 1/0.56 = 1.8$$

This quantity is unity for a Bernoullian polymer. In the present case, both the r and m sequences persist longer than for a Bernoullian polymer, i.e., the polymer tends toward the "block" type, a now well recognized species. It might be appropriate to summarize the four possible types of chains that can be described in 1st-order Markov terms; polymers resembling the last three can of course be produced by Bernoullian propagation, the limits being the three corresponding pure polymer types:

1.	"Block":	$P_{\text{m/r}} < 0.5$ $P_{\text{r/m}} < 0.5$
2.	Heterotactic-like:	$P_{\text{m/r}} > 0.5$ $P_{\text{r/m}} > 0.5$
3.	Isotactic-like:	$P_{\text{m/r}} < 0.5$ $P_{\text{r/m}} > 0.5$
4.	Syndiotactic-like:	$P_{\text{m/r}} > 0.5$ $P_{\text{r/m}} < 0.5$

Mechanistically, one can certainly plausibly account for the tendency of the *meso* stereochemistry to propagate itself, for one may easily imagine, as many authors have suggested, that in Grignard or in metal alkyl initiated polymerizations the counterion chelates with the incoming monomer and the chain-end in such a way as to favour m placements. It is not quite so easy to see why the r placement should tend to propagate itself, although again complexing can be imagined which would account for this. About 4 years ago, Coleman and Fox suggested an alternative mechanistic scheme which is physically appealing¹². They suggested that in polymerizing systems (usually initiated by metal alkyls) in which "runs" of m's and r's are produced, i.e., "block" chains, there may be two (or possibly more) states of the propagating chain-end, corresponding to chelation by counterion and the interruption of this chelation by solvation. The intervals between arrival and departure of the solvating species (usually an added ether) are imagined to be longer than that corresponding to an average propagation step, but not necessarily very much longer, since block lengths are often very short. To describe the statistical consequences of this mechanism, we may write modified forms of the relationships holding for simple Markov propagation².

It is sufficient for our purposes here to say that a , b , c , and x are related to the rate constants in the two-state mechanism (refs. 2 and 12 may be consulted for a fuller description).

$$\langle mm \rangle = \langle m \rangle^2 + ax \quad (14)$$

$$\langle mr \rangle = 2\langle m \rangle \langle r \rangle - 2ax \quad (15)$$

$$\langle rr \rangle = \langle r \rangle^2 + ax \quad (16)$$

$$\langle mmm \rangle = \frac{\langle mm \rangle^2 + abx^2}{\langle m \rangle} \quad (17)$$

$$\langle mmr \rangle = \frac{\langle mm \rangle \langle mr \rangle - 2abx^2}{\langle m \rangle} \quad (18)$$

$$\langle mrm \rangle = \frac{\langle mr \rangle^2 + 4acx^2}{4\langle r \rangle} \quad (19)$$

$$\langle mrr \rangle = \frac{\langle mr \rangle \langle rr \rangle - 2acx^2}{\langle r \rangle} \quad (20)$$

$$\langle rmr \rangle = \frac{\langle mr \rangle^2 + 4abx^2}{4\langle m \rangle} \quad (21)$$

$$\langle rrr \rangle = \frac{\langle rr \rangle^2 + acx^2}{\langle r \rangle} \quad (22)$$

Such a polymerizing system will *in general* generate chains which cannot be described by 1st-order Markov statistics or by Markov statistics of any finite order. Let us, however, imagine the particular case (which is a plausible one) that when the chain-end is in state 1 only one type of propagation, say isotactic, can occur, while in state 2 only syndiotactic propagation can occur. Under these conditions, b and c become zero, but a and x are still non-zero and positive. The extra terms in the tetrad relationships (Eqs. 17–22) become zero, so these revert to the bracketed relationships in Eqs. (8)–(13), i.e., to 1st-order Markov statistics. The extra terms in the dyad–triad relationships (Eqs. 14–16) remain, but the corresponding deviations from Bernoullian statistics cannot be told from those that would be expected for 1st-order Markov statistics. In other words, the resulting chain has a structure indistinguishable from that which would be generated on the assumption of a “penultimate” effect, but without assuming such an effect.

It might also be remarked that if the arrival and departure intervals of the solvating species become short compared to the propagation steps, the term, a , will become zero, and the polymer will become Bernoullian.

A polymer apparently conforming to the general two-site mechanism — or at least consistent with it — is illustrated in *Figure 12*. It was prepared with phenylmagnesium bromide in toluene at -78° . Both triad and tetrad

CONFIGURATIONAL SEQUENCE STUDIES BY N.M.R.

frequencies deviate from either Bernoullian or 1st-order Markov and are consistent with a two-state mechanism. What the two sites are or why the polymer differs in this respect from that shown in *Figure 11* is not clear at present. Coleman *et al.* have very recently reported other similarly prepared polymers showing such deviations¹³.

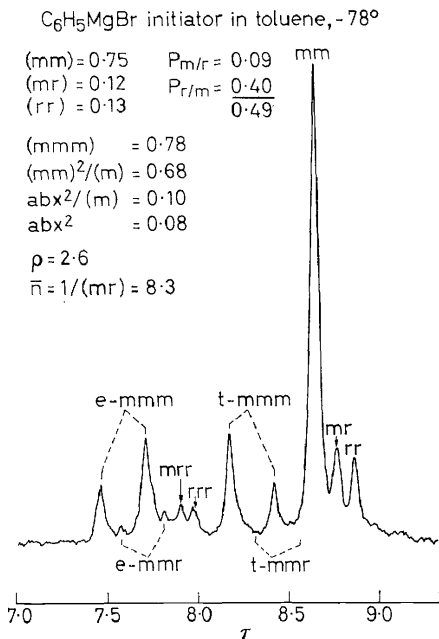


Figure 12. Polymethyl methacrylate prepared with phenylmagnesium bromide initiator in toluene, -78°; \bar{n} is the number-average "block" sequence length. (15% in chlorobenzene, 150°).

SOME CONCLUSIONS

Now, finally, let us attempt to synthesize what we have found concerning the apparent direction of double bond addition and our conclusions concerning configurational sequences, and see if we can construct a rational mechanism that accounts for both. Another and equivalent way of stating this is to ask if we can account mechanistically for both the α -carbon and β -carbon configurations and configurational sequences. What I will say from this point refers, so far as the experimental findings are concerned, to the polymerization of ethyl and methyl methacrylates initiated by metal-alkyls—specifically 9-fluorenyllithium—in toluene solvent, with or without an ether present—specifically tetrahydrofuran. The conclusions are based on evidence from many more polymerization results⁵ than have been considered here. They are not completely applicable to other seemingly closely related systems, such as acrylates and methacrylates initiated by Grignard reagents¹⁴. (These latter show some puzzling features which are not at present completely understood, but may be related to the heterogeneous nature of the polymerization system.) It has been possible to draw

several conclusions of interest concerning the probable reacting species present under varying conditions of solvent and temperature, i.e., contact ion pairs, solvated ion pairs, and solvent-separated ion pairs. This is discussed in another publication⁵.

First, we must realize 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-centre 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 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. The α -carbon configuration may of course also be conditioned 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

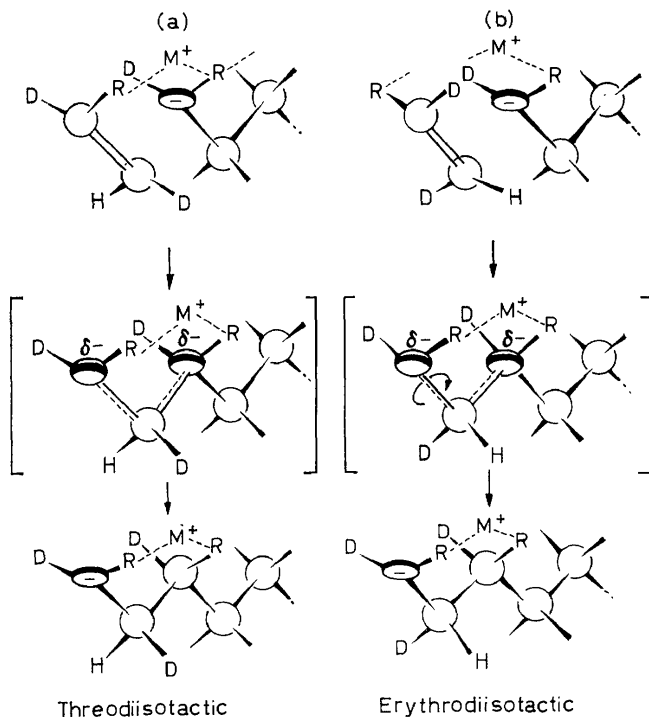


Figure 13. Monomer approach modes in isotactic placement.

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 approach mode. On the other hand, if the mode of approach is "isotactic-like," as in (a) in Figure 13, the *meso* protons in the resulting dyad will be *threo*. Thus, whether the addition is apparently *cis* or *trans* depends, according to this picture, on the mode of presentation of the monomer.

In hydrocarbon solvents, the chelating counterion may be imagined not only to encourage rotation of the chain-end, in the event of syndiotactic-like approach, but also to guide the incoming monomer in such a way that the isotactic-like mode of approach is preferred. In the absence of ether or other solvating molecules, isotactic-like approach guidance appears to be highly effective, and so no chain-end rotation is necessary; the polymer is *c.* 90 per cent *threodiiisotactic*, as we have seen earlier. As solvating species are added in increasing concentration, the monomer approach guidance function of the counterion begins to be seriously disturbed and eventually abolished. 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 *erythrodiisotactic*. Finally, at high tetrahydrofuran concentrations, all influence of the counterion ceases, and the polymer becomes predominantly syndiotactic. (The remaining *meso* sequences are apparently now both *erythro* and *threo*, for some reason not at present clear.)

It might be noted that the counterion chelation and guidance of the incoming monomer approach implies a 1st-order Markov propagation with respect to the β -carbon configuration if such chelation is to some degree dependent upon chain-end stereochemistry, or, more specifically upon the latter being *meso*; this does not seem unreasonable. One may also readily imagine chain-end rotation, following syndiotactic-like monomer approach, to be similarly correlated with chain-end stereochemistry. On the other hand, the assumption of a two-state mechanism does not imply such dependence upon chain-end propagation, but may be Bernoullian in each state and yet explain the observed facts in 9-fluorenyllithium-initiated methacrylate polymerization. Such two-state mechanisms have been so far considered only with respect to the α -carbon stereochemistry. The observation of Yoshino⁸ that *erythro-meso* and *threo-meso* placements can be produced in long runs in the same polymerizing system is likewise strongly suggestive of a two-state mechanism, and represents a type of evidence not available from unlabelled polymers.

ACKNOWLEDGEMENTS

It should be pointed out here that the initial stimulus for these mechanism studies came from a suggestion of Professor Conrad Schuerch about five years ago that the heterosteric character of a vinyl polymer *meso* methylene group should allow one to determine the direction of addition of deuterium-labelled monomers. The observation of longer sequences was an unexpected byproduct. The monomers and polymers have been prepared by Professor

Schuerch's students at Syracuse University, principally Dr. William Fowells. The observation and interpretation of n.m.r. spectra has been the responsibility of Mr. Perry Hood and myself at the Bell Laboratories and Dr. Fowells. Very closely parallel and quite independent work with deuterium-labelled monomers has been carried out in Japan by Dr. Yoshino and his colleagues at the Toyo Rayon Co., as indicated at various points in the text, and I am glad to say that for the most part our conclusions are in agreement. Still more recently, Reinmöller and Fox have reported at the 152nd American Chemical Society meeting in New York in September 1966 the measurement of tetrad resonances in *non*-deuterated methacrylate polymers and their interpretation in terms of configurational statistics and polymerization mechanism^{9,13}.

The discussion of configurational sequence statistics of course owes much to many previous authors who have considered these questions (see reference 2 and references contained therein). It is a pleasure to acknowledge here many stimulating and helpful conversation with Dr. H. L. Frisch, who is the co-author of a pioneering paper¹⁵ on this subject, published many years ago.

The polymer shown in *Figure 12* was prepared at the Rohm and Haas Laboratories (W. Goode) and was obtained through the courtesy of Dr. Y. Ishida.

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