

# SOME CONFORMATIONAL ASPECTS OF POLYMERS OBTAINED THROUGH THE ALTERNATING INTRA-INTERMOLECULAR MECHANISM

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It has recently become well-established<sup>1, 2</sup> that certain diolefinic monomers, predominantly 1,5- and 1,6-dienes, can undergo chain propagation by alternating intramolecular-intermolecular steps to produce high polymers containing cyclic recurring units. More than fifty publications (see reviews by Marvel<sup>1</sup> and Butler<sup>2</sup>) have appeared reporting on a wide variety of monomers and initiator systems and confirming the original proposal<sup>3</sup> that such polymers propagate by the proposed mechanism. Although polymers have been produced by this mechanism through initiation by all known types of initiators<sup>4</sup>, very little attention has been given to the possibilities of obtaining stereoregular polymers by this means of polymer propagation. It is the purpose of this paper to review the limited literature reports on this subject, to discuss the various possibilities of stereoregular polymers resulting from this means of propagation, and to offer an explanation for some of the observations.

The stereochemistry of polymers has become an important subject of investigation by research workers in the high polymer field. This interest resulted from the dramatic discovery by Ziegler<sup>5</sup> that ethylene could be polymerized to an essentially linear polymer by use of combinations of alkylaluminum compounds and transition metal halides, and the spectacular discovery by Natta<sup>6</sup> that  $\alpha$ -olefins, such as propylene, but-1-ene and styrene, could undergo polymerization in contact with the Ziegler-type catalysts to produce crystallizable polymers which are sterically different from those previously obtained from these monomers. Subsequent work by Natta and his co-workers<sup>7</sup> has led to the elucidation of polymer structure, as well as to refinements in experimental techniques leading to the control of polymerization and isolation of the various isomeric polymers. The terms "isotactic", "syndiotactic" and "atactic" were used by Natta and co-workers<sup>8</sup> to describe the various isomeric polymers obtained. The isotactic structure is that structure in which the  $\alpha$ -carbon substituents, *e.g.* the phenyl groups in polystyrene, are either all above or all below the plane of the backbone chain when the chain is brought into the conformation of a straight planar zig-zag so that all carbon atoms of the backbone are arranged in a horizontal plane. The syndiotactic structure is that in which the  $\alpha$ -carbon substituents alternate above and below the plane of the backbone chain, while the atactic structure is that in which the substituents are arranged in an irregular random manner about the backbone chain. The

isotactic and syndiotactic structures are capable of crystallizing<sup>6</sup>, while the atactic structure gives an amorphous, non-crystallizable polymer. Through use of X-ray diffraction studies, Natta and Corradini<sup>9</sup> have established some general rules regarding the conformation and mode of packing of macromolecular chains in crystals.

Prior to the discovery of stereospecific polymerization processes, only a relatively small number of crystalline synthetic hydrocarbon polymers were known, although the importance of stereo-isomerism as a determining factor of the ability of polymers to crystallize had long been recognized<sup>10, 11</sup>. Those polymers, obtained by polyaddition, have a marked tendency to crystallize. They were generally derived from monomers such as ethylene or some vinylidene monomers, which contain at least two planes of symmetry in the molecule, although some notable exceptions have been reported. Monomers with small, polar substituents, such as hydroxyl<sup>12</sup>, chloride<sup>13</sup>, cyanide or fluoride groups appear to produce polymers in which parallel long chains are capable of arranging themselves in a lattice-type structure even though the substituents are randomly arranged. A "pseudo" second plane of symmetry may be considered to be present due to the small size of the substituent which permits an orderly arrangement of polymer molecules.

Regarding the conformation and mode of packing of macromolecular chains in crystals, it has been established<sup>9</sup> that the monomeric units must occupy equivalent positions with respect to the axis of the chain, and that crystallizable polymers must have a type of regularity which will enable them to assume the helix- or glide-plane conformation.

The voluminous nature of the literature resulting from worldwide interest in stereoregular polymers has resulted in an excellent summary of this field covering developments until March, 1959<sup>14</sup>.

A number of research papers<sup>15, 16</sup> reporting on the mechanism of Ziegler-type catalyzed addition polymerizations have shown, without serious doubt, that stereoregular control is established through specific orientation of the monomer on fixed catalyst ions, and that propagation occurs by incoming preoriented and activated monomer molecules replacing or pushing the first monomer molecule away. In this, as well as in other related polymerizations<sup>17-19</sup>, the stereoregularity is believed to be imparted to the polymer by the directing influence of the initiating complex. Fox and co-workers<sup>18</sup> reported that a crystallizable form of poly(methyl methacrylate) was obtained by anionic polymerization, initiated by organolithium compounds in hydrocarbons at  $-60^{\circ}$ . Although this initiating system is homogeneous rather than heterogeneous as is the case with the Ziegler-type catalysts, evidence has been presented by Stavely and co-workers<sup>20</sup>, and by Hsieh and Tobolsky<sup>21</sup>, that under these conditions chain-propagation involves an ion pair rather than free ions and that the lithium counter-ion is apparently intimately involved in the transition state.

Although Huggins<sup>10</sup> originally suggested, in 1944, that all vinyl polymers are capable of stereo-isomerism, and that this isomerism can explain the varying behaviour of polymers prepared under different conditions, this concept was given little further consideration, except in a few isolated cases<sup>11-13, 22-24</sup>, until Natta's observation concerning the stereochemistry of polymers prepared by use of the Ziegler-type catalyst had its full impact.

Following this work, a number of papers have appeared containing evidence to support Huggins' prediction<sup>10</sup> that a preponderance of segments of chains either with isotactic or with syndiotactic configuration may arise even in homogeneous free radical polymerization if the free energy of activation for an isotactic placement is different from that for a syndiotactic placement. The papers by Fox and co-workers<sup>18, 25</sup> include the first published evidence which clearly demonstrated that homogeneous free radical polymerization of vinyl monomers to chains containing asymmetric atoms is stereospecific to an extent dependent on the temperature and on other environmental factors. These papers reported several crystallizable forms of poly(methyl methacrylate) which resulted from stereospecific polymerization effected by apparently homogeneous free radical and anionic initiating systems. Those polymers obtained by free radical polymerizations conducted at low temperatures and those obtained from anionic polymerization in highly-solvated media, such as those initiated by 9-fluorenyllithium in 1,2-dimethoxyethane at  $-60^\circ$  were quite similar in their properties and have since been identified<sup>26, 27</sup> as the predominantly syndiotactic poly(methyl methacrylate). While predominantly isotactic polymers were obtained by anionic initiators in hydrocarbons, a different type of polymer was obtained when polymerization was carried out using 9-fluorenyllithium as initiator at  $-70^\circ$  in toluene containing small amounts of dioxan. An isotactic-syndiotactic block copolymer structure has been suggested for this polymer<sup>18</sup>. The results of this study also showed that the infra-red absorption spectra and the glass temperature of the amorphous material vary with the stereoregularity of the chain structure.

Coleman<sup>28</sup> and Hughes<sup>29</sup> have independently carried out mathematical analyses for the general conditions of polymerization which produce polymers containing asymmetric carbon atoms in the principal polymer chain when such polymers are prepared in media which allow the polymer stereosequence to be determined by random processes. It has been pointed out by Coleman<sup>28</sup> that the propagation rate constant,  $k_\alpha$ , is equal to the sum of the two individual rate constants for isotactic and syndiotactic placements,  $k_\alpha$  and  $k_\beta$ , respectively, and that the over-all kinetics of polymerization at a given temperature are not affected by resolution of the propagating process into two competing reactions. It was further pointed out by both Coleman<sup>28</sup> and Fox and co-workers<sup>25</sup> that, if the activation energies corresponding to  $k_\alpha$  and  $k_\beta$  are different, then  $k_\alpha$  will no longer show the usual exponential dependence on the reciprocal of the temperature.

A series of papers by Fordham and co-workers<sup>30-32</sup> have dealt with both theoretical and practical aspects of stereoregular polymerization in which the directing influence considered is that of the free end of the propagating species rather than that of the initiating complex<sup>6</sup>. These papers have shown that only small differences in the free energies of activation of the isotactic and syndiotactic propagations are required for relatively significant changes in polymer structure, particularly at low temperatures. For example, the  $k_s/k_i$  ratio, which gives the ratio of syndiotactic to isotactic units in the polymer, was calculated, from the absolute reaction rate equations, to be  $> 10$  at  $-100^\circ$  for assumed values of  $\Delta S^*$  and  $\Delta H^*$  of  $-1$  e.u. and  $-1$  kcal/mole respectively. For assumed values of 0 e.u.

and  $-2$  kcal/mole respectively for  $\Delta S^*$  and  $\Delta H^*$ , the calculated  $k_s/k_i$  ratio is approximately 50 at  $0^\circ$  and approximately 25 at  $100^\circ$ . It has also been shown that both the relative amounts of the two configurations in the polymer and the distribution of individual sequence lengths bear a simple relationship to the two propagation constants. On consideration of rotational isomerism and the influence of both steric and electrostatic factors on the free energy difference between the *gauche*- and *trans*-conformations of certain selected well-known simple compounds, it was concluded that steric and electrostatic factors at the free end of the growing polymer chain can influence the structure in polymers. The energy of bond angle deformation was also taken into account; with respect to each of the three energy components, the syndiotactic configuration in poly(vinyl chloride) is the preferred structure by a net difference in total potential energy of 1.4–1.9 kcal/mole<sup>30</sup>.

Fordham, McCain and Alexander<sup>31</sup> have studied the effect of monomer structure on the polymerization of vinyl esters. It was concluded, from an X-ray examination, and from the solubility of the poly(vinyl alcohols) obtained by hydrolysis of poly(vinyl acetate), poly(vinyl chloroacetate), poly(vinyl dichloroacetate), poly(vinyl trichloroacetate) and poly(vinyl trifluoroacetate), that the degree of regularity increased in the order of increasing dissociation constants of the respective acids. These results suggest that, in the stereoregulated polymerization of vinyl esters, the electrostatic factor is more important than the steric factor. The chain-repeat distance indicates that the regular sequences of the poly(vinyl trifluoroacetate) have a syndiotactic configuration, thus confirming experimentally the prediction<sup>30</sup> that configuration along a polymer chain can be influenced by monomer structure.

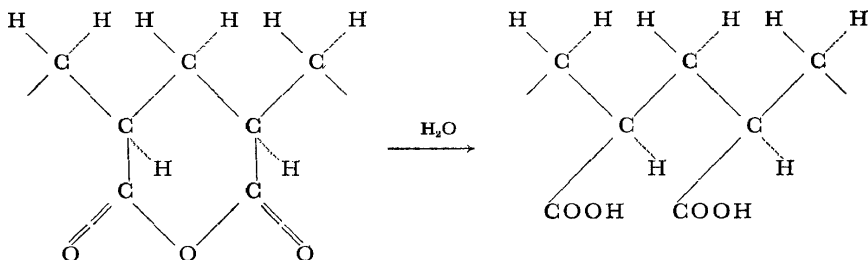
Fordham, Burleigh and Sturm<sup>32</sup> have studied the effect of temperature on the polymerization of vinyl chloride in order to test the prediction, arising from the theoretical treatment<sup>30</sup>, that syndiotactic propagation should be slightly favoured energetically over isotactic propagation in the free species. This prediction was confirmed experimentally by use of X-ray and infra-red investigations of poly(vinyl chloride) prepared at various temperatures. By consideration of the chain-repeat distance, the regular sequences in the polymer chain were indicated to have the syndiotactic configuration. Infra-red evidence, which indicated that syndiotacticity increased with decreasing temperature, was also presented. By use of certain simplifying assumptions, the activation energy difference between isotactic and syndiotactic propagation was estimated to be of the order of 0.5 kcal/mole, which is in the range of 25–33 per cent of the calculated potential energy difference of 1.5–2 kcal/mole between isotactic and syndiotactic placements in poly(vinyl chloride).

Fox and co-workers<sup>18, 25</sup> have established that by the appropriate choice of initiator and conditions of polymerization, all of the stereoregular forms of poly(methyl metacrylate) can be obtained. The polymer obtained by free radical initiation at low temperature was indicated to be predominantly the syndiotactic isomer. A recent paper by Bovey and Tiers<sup>27</sup> reported the application of high-resolution nuclear spin resonance techniques in determining the stereochemical configuration and conformation of chains

SOME CONFORMATIONAL ASPECTS OF POLYMERS

of methyl methacrylate polymers. Measurement of the areas of the three  $\alpha$ -methyl proton peaks, shown by the polymers prepared with free radical and anionic initiators, indicated that these peaks could be attributed to: (a) isotactic sequences (*ddd* or *lll*); (b) syndiotactic sequences (*ldl* or *dld*); and (c) heterotactic sequences (*ldd*, *dll*, *ddl* or *lld*). This facilitated the establishment of the conformation and stereochemical configuration of the chains in this polymer. Previous reports<sup>18, 25</sup> showing that free radical initiated polymerization of methyl methacrylate results in predominantly syndiotactic polymers, and that anionic initiation results in predominantly isotactic polymers, were thus confirmed. Furthermore, it was pointed out in this paper that degrees of regularity, block sizes, *etc.*, appear to be determinable. These results also lend considerable support to the theoretical predictions and experimental confirmation of the predictions, published by Fordham and co-workers<sup>30-32</sup>, that syndiotactic propagation is energetically favoured over the isotactic propagation in free radical initiated polymerizations.

Crawshaw and Butler<sup>33</sup> reported that soluble linear poly(acrylic anhydrides) of high molecular weight could be obtained by polymerization of acrylic anhydride under a wide variety of conditions. A similar paper by Jones<sup>34</sup> appeared almost simultaneously. It was proposed by Crawshaw and Butler<sup>33</sup> that highly stereoregular poly(acrylic acid) could result from hydrolysis of the poly(acrylic anhydride), if, during the various propagation steps, the conformation of the methylene groups with reference to the respective rings was the same throughout the poly(acrylic anhydride) chains as follows:



The X-ray diffraction patterns of the polyacid derived from hydrolysis of poly(acrylic anhydride), when compared with that of normal poly(acrylic acid), showed a marked degree of crystallinity, as indicated by the size and sharpness of the peak in the X-ray pattern. In view of present knowledge of the relationship between crystallizability of polymers and stereoregularity, these results give a strong indication of the presence of considerable stereoregularity in the poly(acrylic anhydride) and the resultant poly(acrylic acid). Respective widths of the Bragg reflections at one-half of the maximum intensity were  $5^\circ$  for the poly(acrylic acid) derived from poly(acrylic anhydride),  $7^\circ$  for the normal poly(acrylic acid), and  $4^\circ$  for poly(methacrylic acid) prepared by hydrolysis of poly(methacrylic anhydride). Crystalline poly(acrylic acid), obtained by hydrolysis of crystalline

poly(*t*-butyl acrylate)<sup>36</sup>, has subsequently been described by Miller, Botty and Rauhut<sup>35</sup>. Crystalline poly(*t*-butyl acrylate) was prepared using lithium dispersion or *n*-butyllithium as initiators, and was converted to crystalline poly(methyl acrylate) by ester interchange. At present, these polymers do not appear to have been identified as to stereoregular form; however, on the basis of recent work by Fox and co-workers<sup>18, 25, 26</sup> and by Bovey<sup>27</sup>, it is highly probable that these crystalline polymers are predominantly the isotactic forms, as the polymers of methyl methacrylate, prepared by use of the same initiators, have been shown to be predominantly isotactic. Nuclear spin resonance data indicated that the poly(methyl methacrylate), which was obtained by use of phenyl magnesium chloride in toluene at 0° as initiator<sup>27</sup>, was 100 per cent isotactic. Grignard reagents as initiators for preparation of crystalline poly(methyl methacrylate) and crystalline poly(alkyl acrylates) had previously been reported by Miller and co-workers<sup>37</sup> and by Garrett and co-workers<sup>38</sup>.

The use of Ziegler-type catalysts to initiate polymerization in 1,5- and 1,6-dienes was first investigated by Marvel and Stille<sup>39</sup>, who reported that hexa-1,5-diene and hepta-1,6-diene resulted in polymers containing, respectively, five-membered and six-membered cyclic recurring units joined together at the 1,3-positions by methylene groups. No attempt was made to determine the stereochemical conformation of the polymers obtained, but it was reported that infra-red analysis indicated that from 5 to 8 per cent of the units did not cyclize, leaving pendant double-bonds. Although Ziegler-type catalysts might be expected to lead to one of the stereoregular isomers, the presence of the pendant alkenyl side-chains may well interfere with the crystallization process. More recently, however, Makowski and Shim<sup>40</sup> have carried out a systematic study of the preparation and properties of polyhexa-1,5-diene. The polymer was prepared with a number of modified alkyl-metal co-ordination catalysts. The polymer properties varied with the method of preparation and the catalyst modification, but every polymer was crystalline, had a melting-point above 100°, and a density greater than 1.0g/ml, and was very flexible. One specific polymer reported had a tensile strength of 5,400 p.s.i., a melting-point of 139°, and a density of 1.122g/ml. The polymer was very flexible with an apparent modulus of elasticity of 200,000 p.s.i. at - 50°.

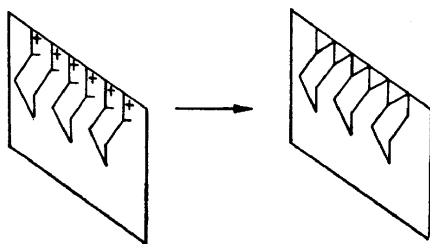
The fibre-repeat distance of polyhexa-1,5-diene, determined by X-ray diffraction methods, was found to be 4.80Å. The distance corresponds to a chain structure consisting of a linear zig-zag arrangement of 1-methylene-3-cyclopentyl groups. Four- and six-membered ring systems as recurring units in the polymer chain were ruled out on the basis of calculations on model systems, and on other considerations. The authors<sup>40</sup> pointed out that, although the fibre-repeat distance for a structure in which the methylene substituents in the 1,3-positions of the cyclopentane ring are placed *trans* on a *planar* ring is calculated to be 4.80Å, this system does not take into account all the known facts. *trans*-1,3-Dimethylcyclopentane is less stable than the corresponding *cis*-isomer by about 0.5 kcal/mole. This greater stability of the *cis*-isomer is believed to be the result of ring-puckering, which is known to occur in cyclopentane and its derivatives. In a system which accounts for all of the known facts about cyclopentane and polyhexa-1,5-

## SOME CONFORMATIONAL ASPECTS OF POLYMERS

diene, the methylene substituents would be *cis*- and have the C-2 atom of the ring puckered toward the methylene substituents to a perpendicular distance of  $0.25\text{\AA}$  above the plane of planar cyclopentane. In such a structure, the calculated fibre-repeat distance is  $4.85\text{\AA}$ . An examination of molecular models of the polymer shows that ring-puckering, as pointed out by the authors, results in an extension of an otherwise rather tightly-coiled molecule into a linear chain resembling that of polyethylene. The unexpected high density of  $1.122\text{g/ml}$  for polyhexa-1,5-diene was offered as additional evidence that the polymer contains carbocyclic rings, since no poly- $\alpha$ -olefins have such high densities. For example, polyhex-1-ene, the  $\alpha$ -olefin analogue of polyhexa-1,5-diene, is a low-density amorphous product.

Polyhexa-1,5-diene has a fairly high melting-point, excellent tensile properties, and high density, which indicate that the polymer would be a relatively rigid product. However, the polymer is, in fact, very flexible; this can be explained *via* the intra-intermolecular polymerization mechanism. Marvel and Stille<sup>39</sup> showed that from 5 to 8 per cent of the diene units enter the polymer chain through one double bond only, contributing some copolymer character to the polymer. A polyhexa-1,5-diene composed only of cyclized monomer units which have the same ring configurations would be expected to be highly crystalline, higher melting, more dense, and more rigid, since the carbocyclic rings would impart rigidity to the polymer chain. The presence of a small percentage of non-cyclized monomer units tends to disrupt the regularity, permitting the polymer to be somewhat less crystalline, lower melting, less dense and considerably more flexible.

Although the conformation of polyhepta-1,6-diene has not been established, the establishment of the all *cis*-conformation for the polyhexa-1,5-diene, the known tendency of the alkyl-metal co-ordination catalysts to exhibit strong stereochemical directive influences and certain known facts concerning the conformation of 1,3-substituted cyclohexane derivatives would lead to the prediction that the polymer would have the 1,3-diequatorial conformation. The following schematic representation supports this concept<sup>41</sup>:



The greater thermodynamic stability of the 1,3-diaxial over the corresponding diequatorial form is further evidence for the 1,3-diequatorial conformation. Allinger and Miller<sup>42</sup> have recently determined  $\Delta H$  for the 1,3-diaxial methyl-to-methyl interaction in cyclohexanes, and found a value of

3.70 kcal/mole. The 1,3-diequatorial conformation would be expected to be more stable by this quantity of energy. Although the Ziegler-type catalyst must not necessarily produce the most thermodynamically stable of a pair of isomers, an inspection of the above diagram, and consideration of the stereochemical directive influence of the catalyst surface, show that the configuration of the 1,3-carbon atoms of the cyclohexane must be the same, thus placing the respective methylenes between cyclohexane rings and the 2-methylene group of each cyclohexane ring in the same plane. The 4-methylene group of each ring could, of course, assume the boat conformation instead of the chair conformation, but, again, this conformation is thermodynamically unfavourable<sup>63</sup>.

The implications of some degree of stereospecificity during one or more of the propagation steps in free radical initiated polymerization of acrylic anhydride<sup>33</sup> were followed by contributions from Fox and co-workers<sup>18, 25, 26</sup> who showed that all the stereochemical forms of poly(methyl methacrylate) could be obtained by an appropriate selection of initiator, and from Bovey, Tiers and Filipovich<sup>44</sup> who made available an extremely useful method for determining the stereochemical configuration and conformation of polymer chains. These factors led Miller, Brey and Butler<sup>45</sup> to carry out a study of the stereochemical configuration of poly(methyl methacrylate) obtained by methylation of poly(methacrylic anhydride). The subsequent publication by Bovey and Tiers<sup>27</sup> made available a method which permits quantitative determination of isotactic, syndiotactic, and heterotactic sequences in poly(methyl methacrylate) chains. In this paper, the terms isotactic, syndiotactic, and heterotactic were redefined. Thus, an isotactic configuration is one in which the  $\alpha$ -methyl group is flanked on both sides by units of the same configuration, (*ddd*) or (*lll*). A heterotactic configuration is designated as one in which the central  $\alpha$ -methyl group is flanked on one side by a similar configuration and on the other by a dissimilar configuration, (*dll*), (*ddl*), (*lld*) or (*ldd*). The syndiotactic configuration is defined as one in which the central  $\alpha$ -methyl group is flanked on each side by monomer units of the opposite configurations, (*dld*) or (*ldl*). Nuclear spin

Table 1. Results of methacrylic anhydride polymerizations at 50 per cent monomer concentration in benzene

Sample number	Temperature (°C)	Initiator (AIBN) (wt %)	Time (h)	Conversion (%)
1*	1	1.0	19	78
2*	20	1.0	14.5	96
3*	30	1.0	7.3	68
4	30	1.0	22	33
5*	40	1.0	3	45
6	50	1.0	2	37
7	60	1.0	1.5	70
8	70	1.0	0.5	75
9	80	1.0	0.22	88
10	15	0.25†	2	46

\* Irradiated with ultra-violet lamp.

† Benzoin as photo-initiator; 10 per cent solution of monomer in *N*-dimethylformamide.



## SOME CONFORMATIONAL ASPECTS OF POLYMERS

resonance spectra of poly(methyl methacrylate) in chloroform solution at 90° showed three  $\alpha$ -methyl proton peaks. These were attributed to the three stereochemical configurations; the area described by each peak was found to be proportional to the number of isotactic, heterotactic and syndiotactic units present in the polymer chain.

Poly(methacrylic anhydride)<sup>45</sup> was prepared for these studies at 50 per cent monomer concentrations in benzene, using 1 per cent azobisisobutyronitrile (AIBN) as initiator. Samples were prepared at temperatures ranging from 1 to 80°. The samples prepared at the lower temperatures were irradiated with an ultra-violet source in order to get a reasonable rate of initiation. The results of the polymerizations are summarized in *Table 1*.

The poly(methacrylic anhydride) samples were hydrolysed to poly(methacrylic acid), and subsequently converted to poly(methyl methacrylate) by use of diazomethane.

A film of poly(methyl methacrylate) obtained from a sample of poly-anhydride prepared at 65° was cast from benzene solution and annealed at 90° for several days. A Laue diffraction pattern showed four distinct diffraction lines. A diffractometer trace showed broad diffuse peaks at 14–16° and 28–30°, and sharp peaks at 21·5° and 24·1°. These results indicated that the sample was approximately 50 per cent crystalline.

The nuclear magnetic resonance spectra were run on a Varian V-4302 high-resolution spectrometer, operating at 56·4 Mc/sec, at 90°, using chloroform as solvent. The results of the nuclear magnetic resonance measurements are shown in *Table 2*. Utilizing the relationships of the

*Table 2.* Fractions of poly(methyl methacrylate) in the three stereo-configurations as determined by nuclear magnetic resonance

Sample number	Polymerization temperature (°C)	Concentration (g/ml)	i (%)	h (%)	s (%)	$\alpha$ (based on i peak)
1	1	0.20	17.9	43.5	38.6	0.420
2	20	0.10	31.3	38.5	30.2	0.557
3	30	0.15	24.2	40.7	33.9	0.560
4	30	0.10	39.0	31.5	29.2	0.560
5	40	0.14	34.0	35.7	30.2	0.583
6	50	0.20	35.8	36.3	28.0	0.597
7	60	0.20	42.4	32.2	25.5	0.655
8	70	0.10	49.3	29.2	21.5	0.705
9	80	0.10	66.7	20.3	13.0	0.815
10	15	0.22	7	44	48	0.265

various probabilities in random chain growth as derived by Coleman<sup>28</sup> and subsequently by Bovey and Tiers<sup>27</sup>, the results of this study are plotted in *Figure 1*.

The probability that a growing chain will add a monomer unit to give the same configuration as that of the unit at the growing end of the chain was designated by  $\alpha$ . The assumptions were made that  $\alpha$  is controlled only by the configuration of the end-unit and not by the preceding one, and that the propagation is adequately described by a single value of  $\alpha$ . The probabilities,  $P$ , are:  $P_i = \alpha^2$ ,  $P_s = (1 - \alpha)^2$ , and  $P_h = 2(\alpha - \alpha^2)$ . Bovey

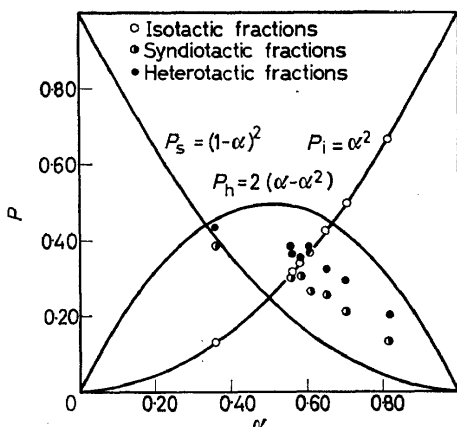


Figure 1. The probabilities of occurrence of isotactic, heterotactic and syndiotactic sequences of monomer units as a function of  $\alpha$ , the probability of isotactic placement of monomer units during propagation. The fraction of isotactic is placed on the isotactic line to determine the value of  $\alpha$

and Tiers<sup>27</sup> have compared the results of free radical polymerizations of methyl methacrylate to anionic polymerizations of the same monomer as described by Fox and co-workers<sup>18</sup>. The "atactic" poly(methyl methacrylate) or polymer prepared by free radical initiators at temperatures from 0–100° was shown to be predominantly syndiotactic. However, the poly(methyl methacrylate) samples prepared using anionic initiators did not fit the probability curves and were thus considered to be systems not described by a single probability value. This failure to fit the probability curves was attributed to the tendency of the metal ion to complex with both the solvent system and the growing chain.

It has also been observed that both solvents and temperature affect the type and degree of stereo-control in polymerization systems. A decrease

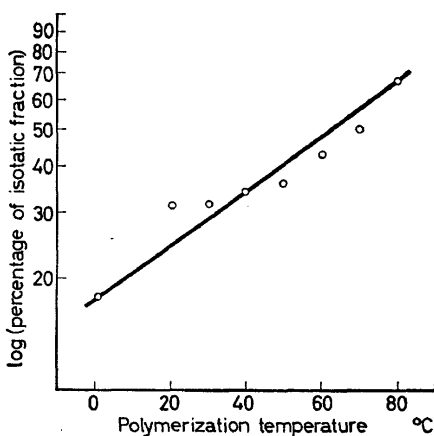
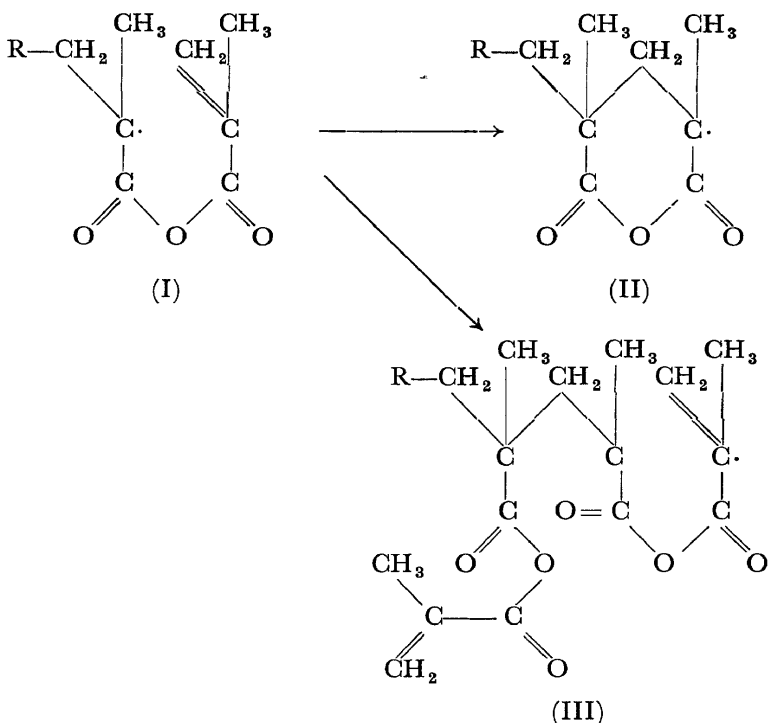
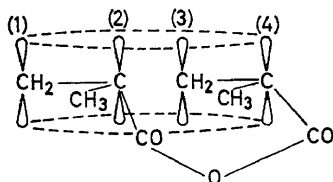


Figure 2. Plot of the logarithm of the percentage of isotactic fraction in the poly(methyl methacrylate) samples versus the temperature of polymerization





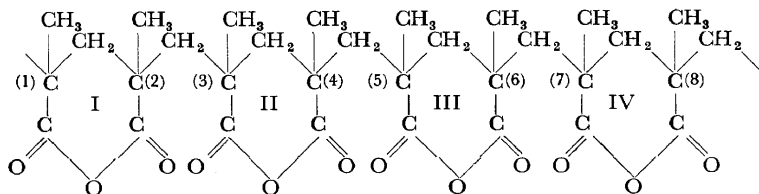
neighbouring monomer molecules does not occur until after ring-closure has occurred. Further consideration of the over-all propagation will be based on the assumption that methacrylic anhydride propagates as a bi-functional monomer rather than as a tetrafunctional monomer. The ring-closure reaction can be pictured as following a concerted mechanism controlled by  $\pi$ -orbital overlap between the  $\pi$ -electrons:



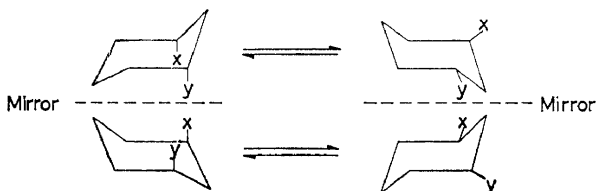
which transfers the unpaired electron to position (4) above without requiring the methylene group to move into position and make contact with the intermediate free radical. Such a proposal has been made by Butler<sup>2</sup>, and experimental evidence to support this proposal has been obtained by Miller<sup>49</sup> and Brooks<sup>50</sup>. The stereochemistry of the polyanhydride will then be dependent upon the conformation of the methylene groups with respect to the cyclic anhydride units. It follows that the stereochemistry of the resultant poly(methyl methacrylate) will be dependent upon the same factors provided hydrolysis and methylation are accomplished without

SOME CONFORMATIONAL ASPECTS OF POLYMERS

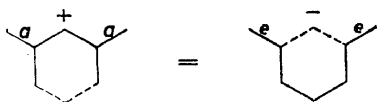
racemization. The possible conformations and the stereochemical configuration of the resultant poly(methyl methacrylate) is shown below for four poly(methacrylic anhydride) units:



The two isotactic forms are mirror images of each other since the 1,3-diaxial chair conformations are interconvertable with the 1,3-diequatorial chair conformations as shown:



It follows, then, that the conformation of a given ring may be designated as  $(e - e)$  or  $(a + a)$  with  $(-)$  having reference to a ring methylene behind the plane and  $(+)$  referring to a ring methylene in front of the plane:



All rings are assumed to be in the most stable chair form, although the anhydride portion of each ring probably approaches planarity. Since the end groups in high polymers are not considered to exhibit a significant influence on the asymmetry of the chain, it follows that only one type of propagation can lead to an isotactic polymer, namely,  $(e - e)$  (or  $(a + a)$ ), since  $(e + e)$  (or  $(a - a)$ ) would differ only by placing the end groups on opposite ends of the respective chains. It also follows by similar reasoning that only one type of propagation can lead to a syndiotactic polymer, namely,  $(e - a)$  (or  $(a + e)$ ), since  $(e + a)$  (or  $(a - e)$ ) would differ only by placing the end groups on the opposite ends of the chains. Further inspection of Table 3 will show that two types of propagation can result in a different type of stereochemical sequence which can be referred to as a regular alternation of pairs of isotactic substituents<sup>51</sup>. Such sequences have been designated "duosyndiotactic" by Spencer<sup>52</sup> and "syndioduotactic" by Hwa<sup>53</sup>. Such duosyndiotactic sequences can result from propagations which lead to  $(e - e)$ ,  $(a - a)$  (or  $(a + a)$ ,  $(e + e)$ ) conformations of the methylenes with the respective rings, or from propagations

which lead to  $(e - a)$ ,  $(a - e)$  (or  $(e + a)$ ,  $(a + e)$ ) conformations. It should be noted that the above  $(e - e)$ ,  $(a - a)$  propagation is more sterically favoured, but would yield the same duosyndiotactic polymer. It follows that the other propagation sequence which could lead to the duosyndiotactic configuration,  $(e - a)$ ,  $(a - e)$ , could proceed as  $(e - a)$ ,  $(e + a)$  or  $(a + e)$ ,  $(a - e)$ , all resulting in the same conformation. It should be pointed out that the two types of propagation leading to duosyndiotactic sequences, while distinctly different in character, would lead to polymers differing by only one pseudoasymmetric centre at the end of such a sequence.

An inspection of the results of Miller, Brey and Butler<sup>45</sup> shows that propagations leading to isotactic configurations,  $(ddd)$  or  $(lll)$ , decrease with temperature, and that both heterotactic,  $(dll)$ ,  $(ddl)$ ,  $(lld)$ , or  $(ldd)$ , and syndiotactic configurations,  $(dld)$  or  $(ldl)$  increase with decreasing temperature; heterotactic configurations usually predominate over syndiotactic configurations. All samples failed to fit the probability curves derived by Coleman<sup>28</sup> and Bovey and Tiers<sup>27</sup> and shown in *Figure 1*. These results suggest that, at lower temperatures, the more thermodynamically stable of the possible conformations will predominate. Such factors as electronic interactions between groups and steric factors as discussed by Fordham<sup>30</sup> should be permitted to approach their respective maximum effects upon the conformation of the polymer chain with decreasing temperature, as has been shown to be the case with free radical initiated polymerization of poly(vinyl trifluoroacetate)<sup>32</sup>, poly(vinyl chloride)<sup>31</sup>, and poly(methyl methacrylate)<sup>18, 25</sup>.

Consideration of the structure of the various propagating free radical intermediates suggests that one of these may be more stable than another and predominate at lower temperatures. The previous assumption that ring-closure is a type of very rapid concerted process will continue to be adhered to; however, it should be pointed out that ring-closure could occur to produce  $(e - e)$  conformations while the next ring-closure may

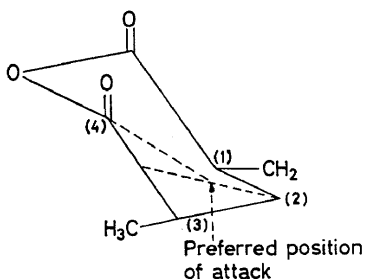
*Table 3.* Possible conformations of poly(methacrylic anhydride) and the stereochemical configuration of the resultant poly(methyl methacrylate):  $a$  = axial conformation;  $e$  = equatorial conformation;  $d$  = dextrorotatory configuration;  $l$  = levorotatory configuration

Ring I		Ring II		Ring III		Ring IV		Stereoregular form
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
(A) $\begin{cases} e(d) \\ a(l) \end{cases}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	Isotactic Isotactic
(B) $\begin{cases} e(d) \\ a(l) \end{cases}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	Syndiotactic Syndiotactic
(C) $\begin{cases} e(d) \\ a(l) \end{cases}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	$\begin{pmatrix} a(l) \\ e(d) \end{pmatrix}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	$\begin{pmatrix} a(l) \\ e(d) \end{pmatrix}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	Duosyndiotactic Duosyndiotactic
(D) $\begin{cases} e(d) \\ a(l) \end{cases}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	$\begin{pmatrix} a(l) \\ e(d) \end{pmatrix}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	$\begin{pmatrix} e(d) \\ a(l) \end{pmatrix}$	$\begin{pmatrix} (l)a \\ (d)e \end{pmatrix}$	$\begin{pmatrix} a(l) \\ e(d) \end{pmatrix}$	$\begin{pmatrix} (d)e \\ (l)a \end{pmatrix}$	Duosyndiotactic Duosyndiotactic

## SOME CONFORMATIONAL ASPECTS OF POLYMERS

result in formation of ( $e + e$ ) conformations. In other words, the generally recognized more stable diequatorial conformation can result in both rings but still result in a (*dlld*) configuration in the resulting poly(methyl methacrylate).

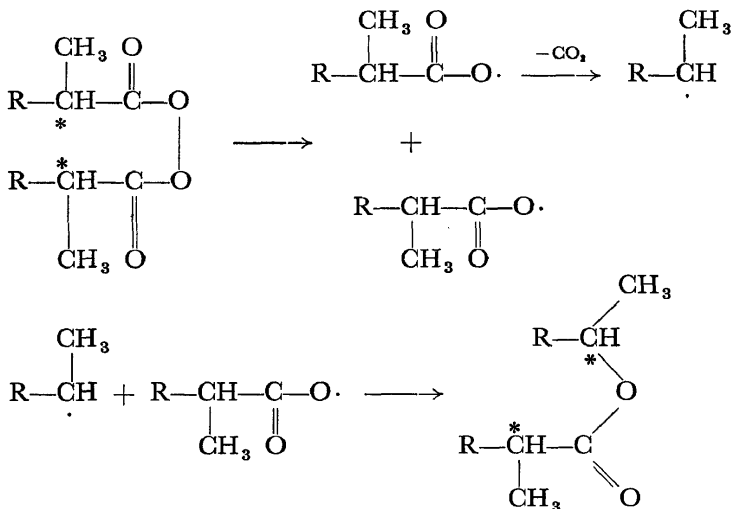
Free radical carbon intermediates, free carbonium ions, and even certain free carbanions are unable to retain optical asymmetry<sup>54</sup>, and are believed either to be planar to oscillate rapidly between two possible tetrahedral configurations. However, an inspection of the processes (*B*) in *Table 3* which can lead to syndiotactic polymers require that one of the steps result in an axial conformation. Also, processes (*D*) in *Table 3* which lead to duosyndiotactic polymers require that one of the steps result in an axial conformation. The free radical formed following the ring-closure could account for the preferred formation of an axial conformation at low temperatures during the intermolecular propagation step. Even though the free radical has a marked tendency to assume planarity, complete planarity at this position would place considerable strain on the remaining bonds in the otherwise chair conformation of the cyclic structure. In such a structure:



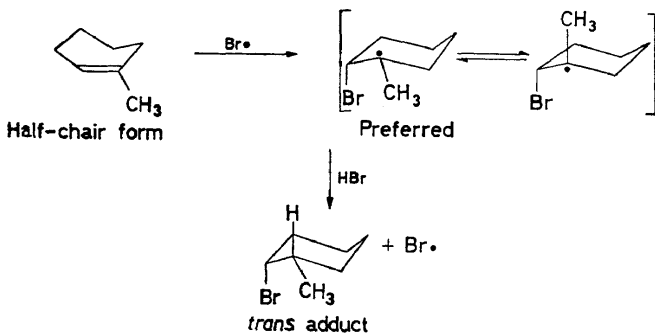
the methyl group at position (3) would assume a position very closely approximating to the equatorial conformation. If carbon atom (3) assumes a planar configuration, it must be in a common plane with carbon atoms (2), (4) and the methyl group. The extent to which carbon atom (3) is unable to assume complete planarity, a situation which would be most pronounced at low energies (and consequently at low temperatures, since additional energy would be required to increase the strain on the other bonds of the ring) is directly proportional to the extent to which the methyl group approaches the normal equatorial conformation when this carbon atom exists in the free radical state. It follows then that the activation energy for an equatorial propagation is higher than that for an axial propagation. An additional quantity of energy would be required to move the methyl group from an equatorial conformation to an axial conformation, making the equatorial propagation even less favoured.

In support of this retention of some pyramidal character, it is of interest that optically active diacyl peroxides, having asymmetric  $\alpha$ -carbon atoms,

decompose to esters in which the  $\alpha$ -carbon atoms, both in the alkyl and acyl sections retain their configurations<sup>55</sup>:



Further support for this argument is found in free-radical-initiated addition of hydrogen bromide to substituted cyclohexene. Addition to 1-methylcyclohexene gives *cis*-1-bromo-2-methylcyclohexane in which the incoming hydrogen and bromine atoms lie *trans* to each other<sup>56</sup>:



This has been explained on the basis of initial attack by the bromine atom at the least sterically-hindered position followed by the preferred intermediate cyclohexyl free radical attacking hydrogen bromide to give the *trans*-product. An analogous situation exists in the propagating methacrylic anhydride. If a *trans*-addition occurs, considering the ring-closure to be concerted, the resulting propagating functional groups would be arranged 1,3-*trans* which is equivalent to *ea* or *ae*. If the preferred intermediate cyclohexyl free radical propagates, the second conformation is required to





A rather careful examination of molecular models confirmed that the model of the poly(methacrylic anhydride) constructed with  $(e + e)$ ,  $(e + e)$ ,  $(e + e)$ ,  $(e + e)$ , or  $(a - a)$ ,  $(a - a)$ ,  $(a - a)$ ,  $(a - a)$ , conformations is the most difficult to construct, has the least flexibility, and also has the greatest amount of overlap and interaction between similar groups. It should be noted that the all-axial model cannot be constructed; however, since  $(a - a)$  is the same as  $(e + e)$ , all conformations could assume the preferred equatorial arrangement. Poly(methacrylic anhydrides) leading to isotactic poly(methyl methacrylate) are required to have the two methyl groups of the ring diaxial or diequatorial, but always *cis*, which also requires that the two methylene groups always be *cis* to each other but having the opposite conformation to the methyl groups. Models show that the structures leading to the other two stereoregular forms can be constructed with approximately equal ease, that there is more flexibility in the chain leading to the duosyndiotactic structure, and that identical groups in the chain are quite far apart in both so that overlap and interactions are at a minimum. Inspection of the models shows that propagations which can lead to syndiotactic or duosyndiotactic polymers, namely  $(e - a)$  and  $(e + a)$ , appear to occur equally readily.

It can be concluded from the limited number of examples cited in this paper that the alternating intra-intermolecular propagation mechanism can lead to some stereocontrol and that this stereocontrol, depending upon the initiator system, appears to parallel that which has been observed by others in studying polymerization of conventional monomers.

## Summary

Polymers obtained through the alternating intra-intermolecular mechanism offer a number of possibilities from the following viewpoints:

- (a) the conformations of the rings produced during the propagation process;
- (b) the conformation of the methylene linking groups between rings; and
- (c) the conformation of the products formed by ring-opening of certain polymers obtained through this mechanism.

It has been shown previously in free-radical-initiated vinyl polymerizations that the configurations of successive units are dependent upon a number of factors. Among the most important of these factors are the effects of kinetic and equilibrium considerations on the incoming placements, although both solvent and temperature effects have been observed. A qualitative treatment of these effects on the micro-structure of polymers obtained by way of the intra-intermolecular mechanism is made, and the experimental methods of the determination of conformations is discussed. Experimental results on the micro-structure of poly(methyl methacrylate) derived from poly(methacrylic anhydride) are presented; the poly(methacrylic anhydride) was obtained by free radical initiated polymerization of methacrylic anhydride *via* the intra-intermolecular mechanism.

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G. B. BUTLER

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