

232. *The Stereoisomerism of Addition Polymers. Part II.* Configurations of Maximum Order from Alternating Copolymerisation. The Requirements for Optical Activity in Polymers.*

By C. L. ARCUS.

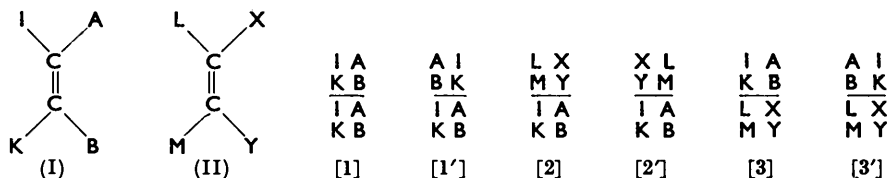
Configurations for linear alternating copolymers containing asymmetric carbon atoms have been deduced from a consideration of steric factors in initiation, propagation, and termination.

The steric effects of the use of optically active monomers in polymerisation are discussed, together with the conditions for the formation of a polymer having an optically active main chain.

THE configuration of a growing ethylenic-addition chain molecule, derived from a single monomer, has been shown in Part I to be dependent on three factors: (a) the geometrical type of addition; in any individual polymerisation it is assumed that reaction is either *trans* at every step or *cis* at every step; (b) the attack by the initiating radical or ion, which may be at either side of the monomer molecule; the enantiomeric adducts so formed lead to enantiomeric chains, designated *D* and *L*; (c) the mode of presentation of the monomer to the chain-end; for all types of monomer, except those which are axially symmetrical, there are two alternative modes, represented in formulæ (IV—VII) of Part I. The operation of these factors in alternating copolymerisation is now considered, and configurations for alternating copolymers are derived. Complete alternation in copolymerisation implies that both monomer reactivity ratios approach zero, and, whereas the assessment of the stereoisomerism of copolymers formed where these ratios are larger numbers probably requires statistical methods, configurations of maximum order for alternating copolymers can be derived relatively simply.

Relevant experimental results have become available in two recent reports,^{1,2} discussed in Section (2) below, on copolymerisations involving optically active monomers.

(1) *Configurations of Alternating Copolymers.*—The alternation of two monomers necessitates taking into account the presentation of each to the other. The two possible



modes of presentation for the polymerisation of the monomer (I), which are illustrated in Part I, may be written as [1] and [1'], the lower unit representing the growing chain end and the upper the next monomer molecule to be added. When a second monomer, (II), is copolymerised, the two possible modes of presentation of (II) to (I) are as shown in [2] and [2'], and those of (I) to (II) as in [3] and [3']. The modes [2], [2'], and [3], [3'], must be considered to be, in principle, independent, since the interactions of groups I, A, with M, Y, will mainly govern the former, while the interactions of L, X, with K, B, will be the most important for the latter. When common groups are present, this situation may be modified (below).

The configuration of the copolymer chain is therefore governed by four factors: *trans*- or *cis*-addition; configuration of initiation; the mode of presentation of (II) to (I), and

* Part I, *J.*, 1955, 2801.

¹ Overberger and Palmer, *J. Amer. Chem. Soc.*, 1956, **78**, 666.

² Beredjick and Schuerch, *ibid.*, p. 2646.

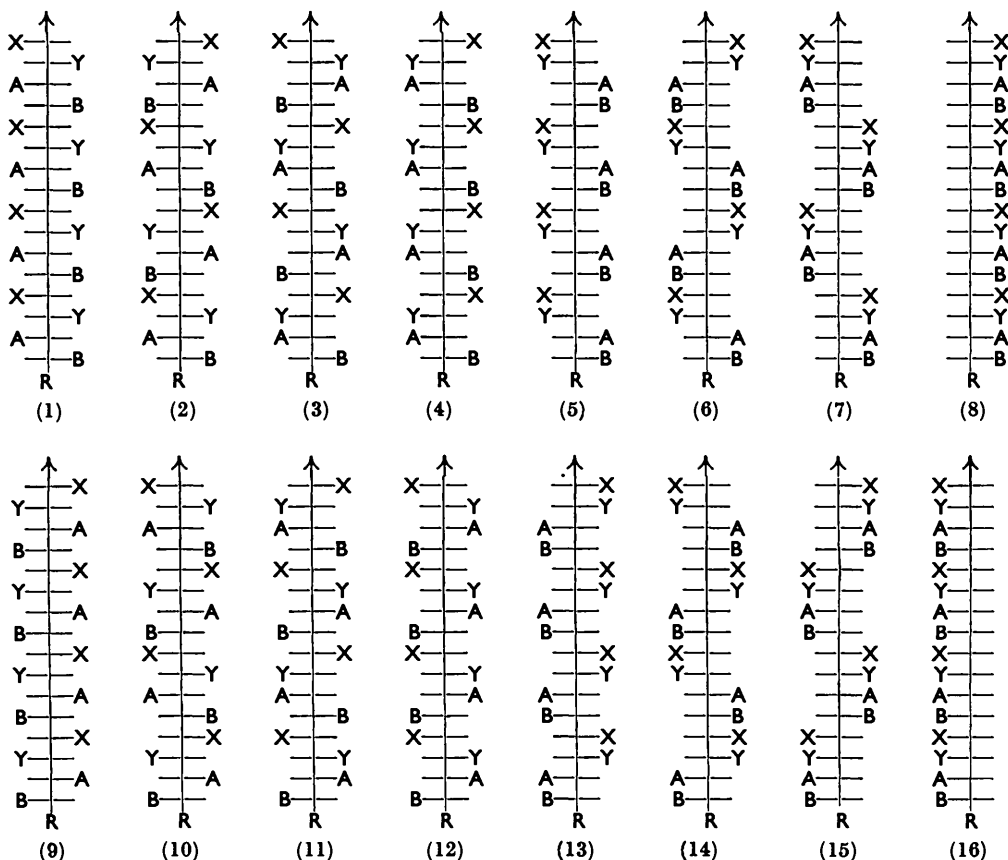
that of (I) to (II). Each presents two alternatives, and sixteen configurations, represented in Fischer formulæ (1—16), arise as follows:

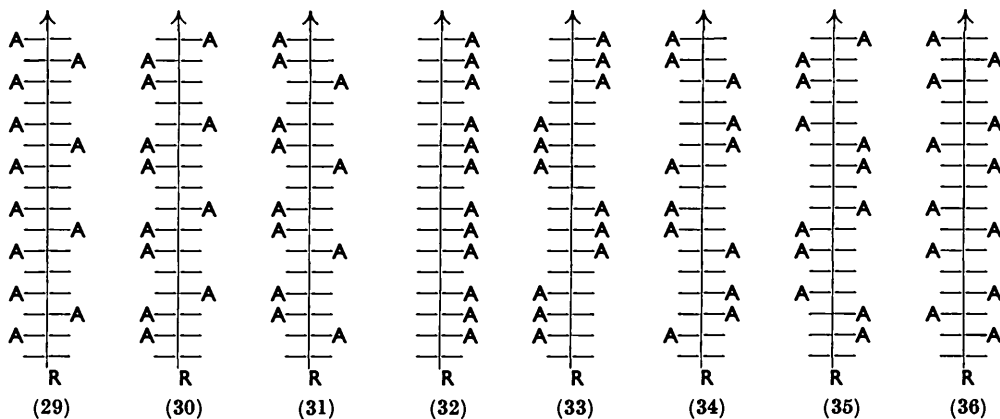
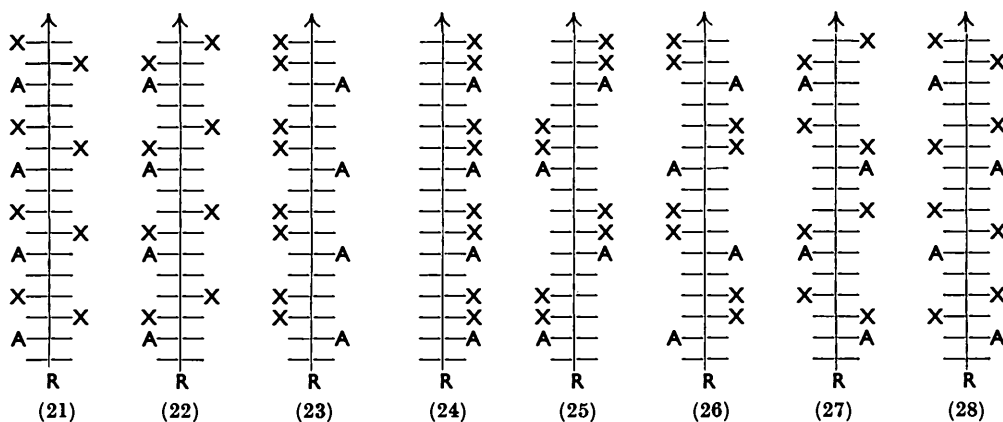
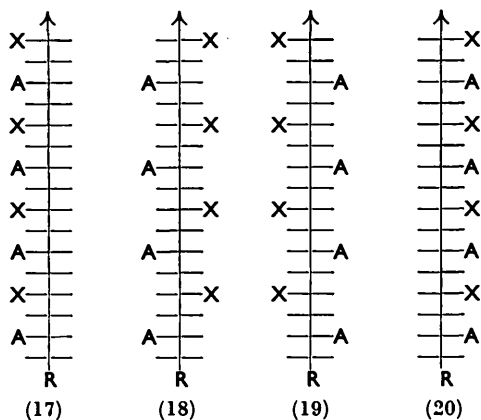
Addition	Presentation of (II) to (I)	Presentation of (I) to (II)	D-Initiation	L-Initiation
<i>trans</i>	[2]	[3]	(1)	(9)
<i>trans</i>	[2]	[3]	(2)	(10)
<i>trans</i>	[2']	[3]	(3)	(11)
<i>trans</i>	[2']	[3]	(4)	(12)
<i>cis</i>	[2]	[3]	(5)	(13)
<i>cis</i>	[2]	[3]	(6)	(14)
<i>cis</i>	[2']	[3]	(7)	(15)
<i>cis</i>	[2']	[3]	(8)	(16)

For greater clarity the groups I, K, L, M, have been omitted from (1—16), and, in the derived configurations, hydrogen has likewise been omitted.

On inspection of the chains (1—16) from their points of initiation, it is apparent that there are eight pairs of enantiomers, each pair diastereoisomeric with the others. When sections of these chains, of indefinite length and remote from end-groups, are considered, it is apparent that none possesses a plane of symmetry, but that (2) and (10) are identical, as are (3) and (11), (6) and (14), (7) and (15).

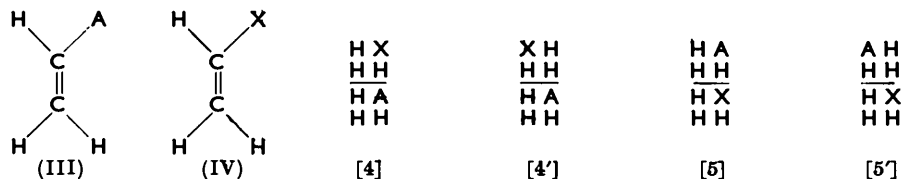
Configurations for copolymers of less-substituted ethylenic monomers have been derived by simplification of (1—16). It has been necessary to take into account the tendency of groups, on the chain-end and the approaching monomer, to associate or to repel; however, the forces on which these tendencies depend, *e.g.*, electrostatic, steric, and resonance interactions, and hydrogen bonding, of which the applicability will vary with the nature of the monomer, are not discussed.





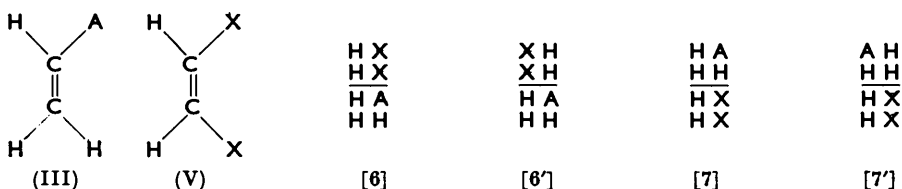
Copolymerisation of $\text{CH}_2\text{:CHA}$ and $\text{CH}_2\text{:CHX}$. Monomers (I) and (II) are replaced by (III) and (IV), and [2], [2'], [3], [3'], become [4], [4'], [5], [5']. However, if [4], in which X is relatively close to A, is appropriate for the presentation of (IV) to (III), then [5], not [5'], is probable for the presentation of (III) to (IV); similarly, if [4'], in which X and A are relatively remote, is appropriate, then [5'], not [5], is probable; *i.e.*, the application of the general case is to be limited in that [2] is here coupled with [3], and [2'] with [3']. The configurations derived from (1), (4), (5), (8), (9), (12), (13), (16), are, therefore, more probable than those derived from the remaining forms; these configurations lead to only

four different configurations: (1), (16) \longrightarrow (17); (4), (13) \longrightarrow (18); (5), (12) \longrightarrow (19); (8), (9) \longrightarrow (20). Of these, (17) and (20), (18) and (19), are enantiomers. When non-terminal sections of the chains are compared, it is found that each has a plane of symmetry at every substituted carbon atom, and that (17) and (20) are identical, as are (18) and (19).



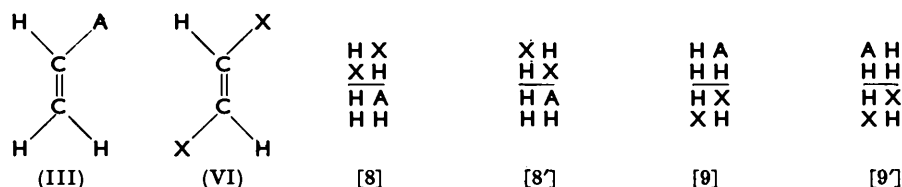
The copolymerisation of $\text{CH}_2\text{:CIA}$ and $\text{CH}_2\text{:CHX}$ involves a consideration of presentation similar to that above; the configurations derived from this copolymerisation are (17—20), except that the groups >CHA are replaced by >CIA .

Copolymerisation of $\text{CH}_2\text{:CHA}$ and cis- CHX:CHX . Monomers (I) and (II) are replaced by (III) and (V), and the presentations for this copolymerisation are given by [6], [6'], [7], [7']. From considerations similar to those above, [6] would be expected to be coupled



with [7], and [6'] with [7']. There arise four *D*- and four *L*-chain configurations, derived respectively from (1), (4), (5), (8), and (9), (12), (13), (16); the *D*-forms are represented in (21—24). Non-terminal sections of all these chains have no plane of symmetry, and sections of enantiomers are nowhere identical.

Copolymerisation of $\text{CH}_2\text{:CHA}$ and trans- CHX:CHX . Monomers (I) and (II) are replaced by (III) and (VI); the presentations are given by [8], [8'], [9], [9']. If, as in [8], the groups A and the lower X are relatively remote as the monomer molecule (VI) approaches the chain end, then [9'] is the more probable presentation for the addition of



(III). Conversely, if these groups are relatively close, as in [8'], then [9] is the more probable; *i.e.*, in the application of the general case, [2] is to be coupled with [3'], and [2'] with [3], whence forms (2), (3), (6), (7), and (10), (11), (14), (15), are applicable; they lead to four *D*- and four *L*-configurations, the *D*-forms being represented in (25—28). Non-terminal sections of these chains have no plane of symmetry, but sections of enantiomers are identical.

Configurations for the copolymerisation of $\text{CH}_2\text{:CIA}$ with *cis*- and with *trans*- CHX:CHX are (21—24) and (25—28), and enantiomers, except that the groups >CHA are replaced by >CIA .

Copolymerisation of $\text{CH}_2\text{:CHA}$ and cis- CHA:CHA . The derivation of the configurations is the same as that for the copolymerisation of $\text{CH}_2\text{:CHA}$ and *cis*- CHX:CHX , except that (V) is replaced by (VII); four *D*- and four *L*-configurations arise, of which the *D*-forms are represented in (29—32). Non-terminal sections of the chains possess the following

symmetry properties: (29) and (32), each of which is identical with its enantiomer, have a plane of symmetry at every CH_2 -group and at the mid CHA -group in the sets of three; (30) and (31) are not identical with the corresponding enantiomers, and have no plane of symmetry. However, such sections of (30) and the enantiomer of (31) are identical, and *vice versa*.



*Copolymerisation of $\text{CH}_2\text{:CHA}$ and *trans*- CHA:CHA .* The configurations are derived as for the copolymerisation of $\text{CH}_2\text{:CHA}$ with *trans*- CHX:CHX , except that (VI) is replaced by (VIII); four *D*- and four *L*-configurations arise, of which the *D*-forms are represented in (33—36). Non-terminal sections of these chains have the following symmetry properties: (33) and (36), each of which is identical with its enantiomer, have a plane of symmetry at every mid CHA -group in the sets of three; (34), (35), and their enantiomers, are all of one chain configuration which, however, has no plane of symmetry.

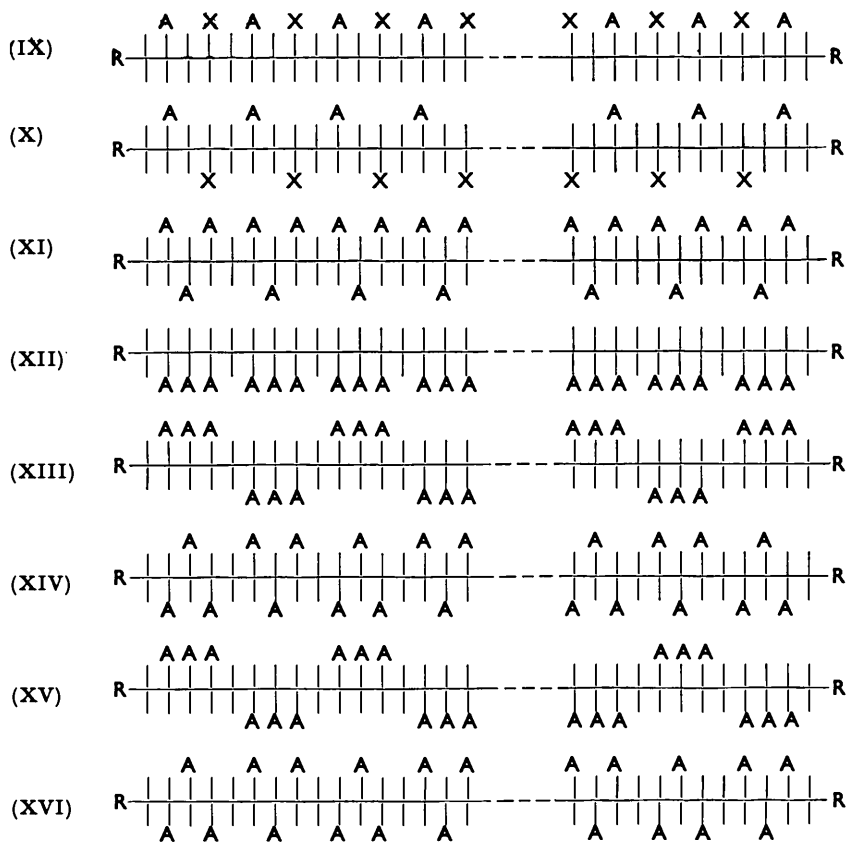
Termination and stereoisomerism. Formation of meso-type chain molecules in copolymerisation. With respect to their steric effects, mechanisms of termination fall into two classes (Part I): the simple terminations, which yield a molecule comprised of one of the chains, above, together with a relatively small terminating group, and mutual chain termination. The symmetry properties of simply terminated molecules are substantially those of non-terminal portions of the chains, which have been described above.

It has been shown (Part I) that in certain instances mutual chain termination results in the formation of *meso*-type chain molecules. By a *meso*-type of chain molecule is meant one in which (if irregularities at the point of juncture are ignored) the same "pattern" is apparent throughout the chain, and there are numerous "local" planes of symmetry. Examples are (XIV) and (XV) of Part I, and (IX—XVI) below. Such molecules arise by mutual termination in systems containing enantiomeric growing chains which themselves possess planes of symmetry; the act of termination produces a tail-to-tail unit which is, usually, a steric irregularity, and combination between two chains of like initiation (both *D* or both *L*) gives rise to an uncompensated unit at one end of the completed chain; when chains of unlike initiation combine, the chain ends are symmetrically disposed. If the chain configuration alternates, with identical sequences of groups to right and to left along the axis of the Fischer projection formula, then all mutual terminations give *meso*-type molecules; if such alternation is not present, then only (*D* + *L*) terminations yield these molecules. Of the possible mutual terminations, (*D* + *D*), (*L* + *L*), (*D* + *L*), the first two are enantiomerically related and must occur with equal frequency, but the last is in a diastereoisomeric relationship to the other two, and its frequency is not necessarily given by the random collision ratio of 1 : 1 : 2.

(If enantiomeric chains of exactly the same length combine, a molecule is formed which is *meso* in the classical meaning of the word, irrespective of the presence of planes of symmetry in the individual chains. However, this is an event of low probability, and such molecules will form only a small fraction of the whole product.)

No *meso*-type chain molecules are derived from the following configurations and their enantiomers, since they contain no planes of symmetry: (21—28), (30), (31), (34), (35), nor are such molecules given by combination between chains of like initiation in systems containing (17 + 20), (18 + 19), (29 + enantiomer), (32 + enantiomer). *Meso*-Type molecules are formed by combination of chains of unlike initiation in these last four systems, and in (33 + enantiomer) and (36 + enantiomer), in both of which *meso*-type molecules are also formed by combination of chains of like initiation. The molecules so formed are respectively exemplified in (IX—XVI). Since they are derived from the same two systems,

in the manner described, (XV) and (XVI) differ from (XVIII) and (XIX) only in possessing an uncompensated unit at one end of the molecule.



(2) *Polymerisation and Copolymerisation of Optically Active Monomers.*—Several investigations in this field have now been reported, and a comparison of the results with the configurations above, and of Part I, is made in the present Section. The experimental procedures all involve the polymerisation or copolymerisation of a monomer in which an ethylenic group is attached to an optically active group, followed by removal of the latter groups and measurement of the rotatory power of the remaining polymer or copolymer. These investigations present two aspects: the influence of the optically active groups on the course of the polymerisation, and the extent to which the polymer structure, after removal of these groups, is capable of existence in a dissymmetric, optically active form.

The effects of the use of an optically active monomer on the course of polymerisation are considered to be as follows: (a) When such a monomer is the first unit of a growing chain, then either *D*- or *L*-initiation occurs preferentially, since the adducts of the monomer and the initiating radical or ion [(II) and (III) of Part I] are no longer optical isomers, but diastereoisomers, and will differ in rate of formation. (b) In the derivation of chain configurations, it is considered that a monomer which possesses a plane of symmetry through the σ -bond system [*e.g.*, (I) or (II)] presents a certain side of the molecule to a growing *D*-chain end, or, with equal facility, the other side to a growing *L*-chain end. With a monomer which does not possess such a plane of symmetry this equality is absent: the transition states comprised of the monomer (of, *e.g.*, configuration *d*), and polymer main chains of configurations *D* and *L*, become diastereoisomeric, *d*-*D* and *d*-*L*, and the rates of reaction and hence of chain growth will, in general, be different. (c) A further

element of dissymmetry is contributed to the transition states by the incorporation, in the growing chains, of optically active side groups, which render the chains themselves no longer optically isomeric, but diastereoisomeric.

Thus the factors (a), (b), (c) so operate that two enantiomeric main chains are not initiated or propagated at equal rates. Further, it has been envisaged (Part I) that, at intervals, a monomer molecule may be added irregularly, either as regards *trans*- or *cis*-addition, or with regard to mode of presentation; when such dislocations occur in polymerisations involving optically active monomers, the dissymmetric factors, as in (b) and (c), will assist the propagation of one chain configuration rather than the other.

Thus the presence of optically active groups in the molecules of a monomer can potentially give rise to a polymer the main chain of which is optically active; whether the polymer or copolymer remaining after the removal of the optically active side groups is in fact optically active, or not, would be expected to depend on the absence or presence of planes of symmetry in the chains so formed.

Three examples of polymerisation of optically active monomers $\text{CH}_2\text{:CHA}$ or $\text{CH}_2\text{:CIA}$, with subsequent removal of the active groups, have been recorded: Marvel and Overberger³ polymerised (+)-*sec*-butyl *p*-vinylbenzoate, hydrolysed the polymer, and obtained optically inactive poly(*p*-vinylbenzoic acid); Overberger and Palmer¹ polymerised (+)-*o*-(*sec*-butylthiomethyl)styrene, quantitatively removed sulphur (and therefore the *sec*-butyl groups) from the polymer by catalytic hydrogenation, and obtained an optically inactive polymer; Beredjick and Schuerch² polymerised (–)-1-phenylethyl methacrylate, removed the phenylethyl groups by reduction with phosphonium iodide, and obtained optically inactive poly(methacrylic acid). The configurations which have been deduced for the polymerisation of $\text{CH}_2\text{:CHA}$ (or $\text{CH}_2\text{:CIA}$), (9–12) of Part I, all contain numerous local planes of symmetry, in accord with the absence of optical activity in the final polymers above.

Overberger and Palmer¹ also copolymerised (+)-*o*-(*sec*-butylthiomethyl)styrene with methyl methacrylate, obtaining a copolymer which contained 0.43 mole-fraction of the former monomer; scission, as above, of the *sec*-butyl groups yielded an optically inactive copolymer. There is no evidence on the degree of alternation in this copolymer, but it is of interest to compare the configurations, (17–20) above, for the alternating copolymer which is most closely related. These configurations all contain numerous local planes of symmetry, whence they are incapable of existing in an optically active form, and it is possible that the structure of the above copolymer is sufficiently similar to be essentially symmetrical.

The preparation of a copolymer, the main chain of which was optically active, has been reported by Beredjick and Schuerch:² a partial asymmetric synthesis was effected by the copolymerisation of (–)-1-phenylethyl methacrylate with maleic anhydride, followed by removal of the phenylethyl groups by reduction with phosphonium iodide.

The reality of the asymmetric synthesis is to be accepted with some reserve, since the hydrogen content of the final copolymer (7.2%) is in 49% excess of the calculated value (4.85%). A partial asymmetric synthesis effected by hydrogenation has been reported,⁴ and it does not seem impossible that some structure in the copolymer may have been reduced asymmetrically before complete removal of the 1-phenylethyl groups. However, the asymmetric synthesis being accepted, the steric structure of the copolymer can, in part, be estimated.

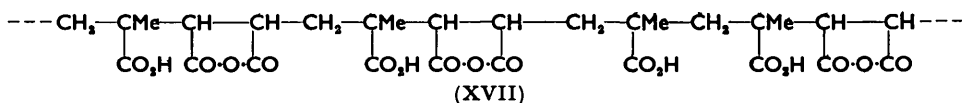
The (–)-1-phenylethyl methacrylate–maleic anhydride copolymer contained these units in ratio 1.5 : 1, whence the copolymer is not strictly alternating. The monomer reactivity ratios⁵ for the copolymerisation of methyl methacrylate (M_1) and maleic anhydride (M_2) are: $r_1 = 6.7$ and $r_2 = 0.02$. Probably, therefore, in the above copolymer,

³ Marvel and Overberger, *J. Amer. Chem. Soc.*, 1946, **68**, 2106.

⁴ Arcus and Smyth, *J.*, 1955, 34.

⁵ de Wilde and Smets, *J. Polymer Sci.*, 1950, **5**, 253.

a maleic anhydride unit is almost always followed by a methacrylate unit, but the converse does not necessarily hold, though steric hindrance between 1-phenylethyl groups might be expected to reduce r for 1-phenylethyl methacrylate below the value for methyl methacrylate. The structure of the reduced copolymer is exemplified in (XVII). Of the



chain configurations for alternating copolymerisation, forms (21—24), together with their *L*-enantiomers, are most closely related to (XVII). Pairs of groups X, in these configurations, represent the anhydride bridges, and groups A the carboxyl groups of the methacrylic acid units; the joining of pairs of groups X in a ring does not affect the configurations; also, were the anhydride rings hydrolysed to pairs of carboxyl groups, the carbon atoms bearing the carboxyl groups of the methacrylic acid units would remain distinguishable by the attached methyl groups. These configurations, which cover all the variations in mechanism which have been envisaged above, possess no planes of symmetry, and are therefore intrinsically capable of existing in optically active forms. If it be assumed that *trans*-addition occurs (Part I) and that the carbonyl groups of anhydride and ester tend to repel each other, leading to presentations [6'] and [7'], where A = CO·O·CHMePh, and the pairs of groups X = CO·O·CO, then configuration (22) or its enantiomer approximates most closely to this copolymer.

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