The Stereoisomerism of Addition Polymers. Part I. The Stereochemistry of Addition and Configurations of Maximum Order.
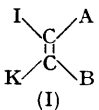
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Configurations for linear polymers which contain asymmetric carbon atoms have been deduced from a consideration of the steric factors in olefinic addition.

Diastereoisomeric forms arising from mutual chain termination are described.

The experimental data relevant to the method of derivation, and to polymer configurations, are discussed.

THE possibility of optical isomerism, including diastereoisomerism, in addition polymers containing asymmetric carbon atoms has been recognised for a considerable time (Marvel, Frank, and Prill, *J. Amer. Chem. Soc.*, 1943, **65**, 1647; Huggins, *ibid.*, 1944, **66**, 1991; Marvel and Overberger, *ibid.*, 1946, **68**, 2106), and more recently Frisch, Schuerch, and Szwarc (*J. Polymer Sci.*, 1953, **11**, 559) have presented a mathematical treatment of the possibility of continued partial asymmetric synthesis during addition polymerisation.

A method for the derivation of chain configurations, based on the control of the stepwise addition of monomer molecules by three steric factors, is now put forward. The chain configurations which are possible in the general case of polymerisation of a fully substituted ethylene are deduced, and from these, by simplification, those for less substituted ethylenes [Section (1)]. In Section (2), data in the literature concerning the stereochemistry of addition and configurations of polymers are discussed in relation to the configurations derived as above.

(1) *Derivation of Configurations of Maximum Order.*—Polymerisation of the olefin (I) is considered to be initiated by the formation of an intermediate (II) which has substantial steric stability; the initiating radical or ion, R, is bonded to both the carbon atoms of the original double bond, and the structure $\overset{C}{\underset{R}{\diagdown}}\overset{C}{\diagup}$ is perpendicular to the plane occupied by the groups I, A, K, B. The evidence for such structures is summarised in Section (2). A similar intermediate is formed during the addition of each successive molecule of monomer, when R becomes the tail carbon atom of the penultimate monomer unit. Head-to-tail ($>$CKB to $>$CIA) polymerisation, only, has been considered.

The experimental evidence [Section (2)] indicates that addition, whether ionic or free-radical, is normally *trans*; however, for completeness, configurations derived by *cis*-addition have been included. It has been assumed that, in any individual polymerisation, reaction is either *trans* at every step or *cis* at every step.

In addition to the possibility of *trans*- or of *cis*-reaction, two alternative steric courses are possible for the reaction of a second molecule of monomer with the radical or ion derived from the first. This may proceed by either of the two modes of presentation represented in (IV) and (V) for *trans*-, and in (VI) and (VII) for *cis*-addition. At the time of reaction the two molecules are in close contact and overlap to a substantial extent; the distances between the groups I, A, K, B, on the second and those on the first molecule are not the same for the two modes of presentation; the net interaction of these groups will, in general, differ for the two modes, and reaction will proceed more readily by one than by the other. (Reactions by the two modes of presentation become equally probable only when an axially symmetrical olefin, $CA_2\!:\!CB_2$, is undergoing polymerisation.) For any individual polymerisation it has been assumed that, at each step, a monomer molecule takes up the same presentation to the monomer unit which comprises the end of the growing chain. The presentation shown in (IV) and (VI) is referred to as mode [1] and that shown in (V) and (VII) as mode [1'].

Finally, in the Fischer projection formulæ of the polymeric chains derived from (IV)—(VII), the first group B lies to the right. Initial attack by the radical or ion R at the other side of the olefin molecule is equally probable, and the adduct so formed (III) gives rise to a series of polymeric chains enantiomeric with those derived from (IV)—(VII). The two series of chains are designated *D* and *L* respectively.
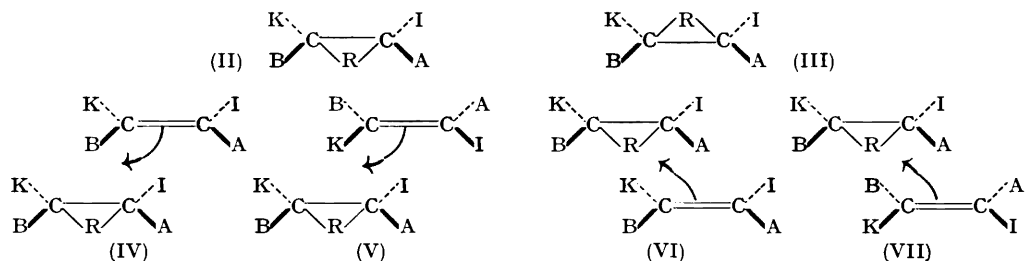
There are thus three stereochemical factors, *trans-* or *cis*-addition, presentation, configuration of initiation, which directly affect the configuration of a chain formed by addition polymerisation. Each presents two alternatives, and eight configurations are possible to a polyethylenic chain derived from the monomer (I). These configurations are represented by the Fischer formulæ (1—8), which arise as follows :

Addition	Mode of presentation	*D*-Initiation	*L*-Initiation
trans	[1]	(1)	(5)
trans	[1′]	(2)	(6)
cis	[1]	(3)	(7)
cis	[1′]	(4)	(8)

Configurations for other polymerisations, of types more frequently encountered experimentally, have been derived (below) by simplification of (1—8). For greater clarity the groups I and K have been omitted in (1—8), they can in every instance be written in from the positions of A and B; in the derived configurations (9—20) hydrogen has likewise been omitted.

On inspection of the chains (1—8) from their points of initiation, it is apparent that there are four pairs of enantiomers, each pair diastereoisomeric with the others. If sections of these chains, of indefinite length and remote from the end-groups, are considered, configurations (1), (4), (5), (8) have a plane of symmetry at every carbon atom, and (2), (3), (6), (7) have no plane of symmetry. Further, comparison of such sections (without regard to the terminal sections of the chains) shows that (2), (3), (6), (7) are identical, as are (1) and (5), also (4) and (8). These identities become important if attempts are made to correlate *X*-ray crystallographic structures (which are essentially for such isolated chain-sections) with mechanisms of polymerisation.

Polymerisation of $CH_2{:}CHA$ (*and of* $CH_2{:}CIA$). Monomer (I) is replaced by (VIII); forms (1—8) lead to only four different configurations : (1), (8) ⟶ (9); (2), (7) ⟶ (10);
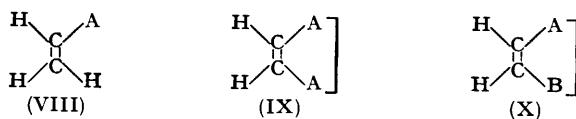
(3), (6) ⟶ (11); (4), (5) ⟶ (12); of these (9) and (12), (10) and (11) are enantiomers. When non-terminal sections of the chains are compared it is found that (9) and (12) possess a plane of symmetry at every carbon atom, and are identical, and that (10) and (11) have a plane of symmetry at every >CHA group, and are identical. The configurations derived from the polymerisation of $CH_2{:}CIA$ are (9—12), except that the groups >CHA are replaced by >CIA.

Polymerisation of a symmetrical cyclic olefin. The configurations (*e.g.*, for the linear

polymerisation of acenaphthylene) are derived by replacing (I) by (IX); forms (1—8) lead to four pairs of enantiomers of which the *D*-forms are represented in (13—16). On inspection of non-terminal sections of the chains, it is seen that : (13) and its enantiomer have no plane of symmetry and are not identical; (14) and its enantiomer have planes of

R (1) R (2) R (3) R (4) R (5) R (6) R (7) R (8)

R (9) R (10) R (11) R (12)

R (13) R (14) R (15) R (16) R (17) R (18) R (19) R (20)

symmetry between the rings, and are identical; (15) and its enantiomer have planes of symmetry across the centres of the rings, and are identical; (16) and its enantiomer have planes of symmetry across the centres of the rings and between the rings, and are identical.

Polymerisation of a non-symmetrical cyclic olefin. The configurations (*e.g.*, for the linear polymerisation of indene) are obtained by replacing (I) by (X); four pairs of enantiomers

are given of which the *D*-forms are represented in (17—20). Non-terminal sections of these chains possess no plane of symmetry, but such sections of (18) and its enantiomer are identical, as are those of (19) and its enantiomer, whereas those of (17) and enantiomer, and (20) and enantiomer, are not identical.

Effects of termination reactions on stereoisomerism. A number of mechanisms of termination lead to the formation of chain molecules whose structures are represented by the Fischer formulæ given above, together with relatively small terminating groups; these are referred to, below, as simple terminations. Such mechanisms are : reaction with an initiator radical or with an inhibitor; chain transfer with monomer or with solvent; loss of a proton in ionic polymerisation; the transfer of a hydrogen atom between two chains, yielding one saturated and one olefinic end-group. The symmetry properties of simply terminated molecules are substantially those assigned, above, to non-terminal portions of the chains.

Mutual chain termination results in the formation of molecules of several stereoisomeric types. Since, in the derivation of the configuration of maximum order for a given polymerisation, *trans*- or *cis*-addition and mode of presentation are regarded as constant, it is necessary only to consider mutual termination in a system containing enantiomeric chains. The lengths of chains (a, b) which combine will, in general, be different, and the resultant molecule (XI) approximates in structure to a molecule (XII) in which two sections of length b are united, together with a simply terminated molecule (XIII) of length $(a$—$b)$.

Four types of chain arise :

Type	Initiation of a	Initiation of b	(XI) (XII)	(XIII)
(i)	D	D	DD	D
(ii)	D	L	DL	D
(iii)	L	D	LD	L
(iv)	L	L	LL	L

The effects of mutual chain termination on the configurations of the complete polymer molecules derived from the monomers CH_2:CHA (also CH_2:CIA), and symmetrical and unsymmetrical cyclic olefins, may be evaluated by application of the types (i—iv) to the configurations (9—20).

Mutual termination gives rise to polymer molecules of all the types (i—iv) in systems containing the following pairs of chains : (13 + enantiomer), (17 + enantiomer), (18 + enantiomer), (19 + enantiomer), (20 + enantiomer). With the remaining configurations considerable simplification occurs, owing to the presence of planes of symmetry.

Of the molecules which are formed by mutual termination in a system containing enantiomeric chains (9) and (12), those derived from (i) and (iv) have no exceptional symmetry, but those which arise from (ii) and (iii) have a *meso*-structure which is highly symmetrical except for the presence of one tail-to-tail unit at the point of combination [for example, (XIV), derived from (ii)]. The system (16 + enantiomer) resembles (9 + 12). Mutual termination in a system containing enantiomeric chains (10) and (11) yields, for all types of combination (i—iv), a highly symmetrical *meso*-type of molecule. It is irregular only in that a tail-to-tail unit is present and, in the molecules derived from (i) and (iv), an uncompensated unit at one end of the molecule [for example, (XV), derived from (i)]. The systems (14 + enantiomer) and (15 + enantiomer) resemble (10 + 11).

Owing to the symmetry of the monomer, there is no structural irregularity at the point

of mutual termination in those systems (13—16 and enantiomers) which are derived from (IX). Half of the molecules formed from (14 + enantiomer) and (15 + enantiomer) are

(XIV) R—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—R
      A A A A A A A AA A A A A A

        A   A   A   A   A   A   A
(XV) R—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—|—R
      A   A   A   A   A   A   A

sterically regular at this point, in the remainder a steric irregularity occurs; the molecules which arise from (16 + enantiomer) by (ii) and (iii) are all sterically regular at the point of termination.

(2) *The Stereochemistry of Addition, and Recorded Polymer Configurations.*—It appears to be generally accepted that cationic intermediates of type (II) are formed during ionic addition to olefins; such a structure was originally proposed by Roberts and Kimball (*J. Amer. Chem. Soc.*, 1937, **59**, 947) for bromine addition. The cationic form of (II) is considered to be stabilised by resonance between (XVI) and (XVII). The subsequent

(XVI)   (XVII)

addition of a nucleophilic reagent to the complex cation is *trans* to the group R; McKenzie's results (*J.*, 1912, **101**, 1196) demonstrate *trans*-addition for the reaction of bromine with fumaric and maleic acids, and those of Winstein and Lucas (*J. Amer. Chem. Soc.*, 1939, **61**, 1576, 2845), on the conversion of *erythro-* and *threo-*3-bromobutan-2-ol into *meso-* and racemic 2 : 3-dibromobutane, respectively, require *trans*-addition to a complex cation of type (II). It is inferred, therefore, that cationic polymerisation proceeds by a series of *trans*-additions. In the initial step, R is (in the majority of examples) a hydrogen ion formed by reaction of the electrophilic reagent (boron trifluoride, titanium tetrachloride, stannic chloride) with the co-catalyst (water, trichloroacetic acid) [literature reviewed by Bawn (*Ann. Reports*, 1950, **47**, 36) and by Collinson, Dainton, and Ivin (*ibid.*, 1953, **50**, 62)]; examples of styrene polymerisation have been reported in which R is an alkyl cation (Plesch, *J.*, 1953, 1664). Thereafter, successive monomer molecules function as nucleophilic reagent and R becomes the tail carbon atom of the penultimate unit.

The free-radical addition of hydrogen bromide to 1-bromo- and 1-methyl-*cyclo*hexene has been shown by Goering, Abell, and Aycock (*J. Amer. Chem. Soc.*, 1952, **74**, 3588) to be *trans*. These authors propose a resonance-stabilised intermediate of type (II; R = Br). For olefinic polymerisation, where R is at first the initiator radical and thereafter the penultimate tail carbon atom, the contributing forms are (XVIII) and (XIX).

(XVIII)   (XIX)

The literature on the hydroxylation of olefins has little relevance to the stereochemistry of free-radical addition because in no instance are both the steric course and a free-radical mechanism established. Mugdan and Young (*J.*, 1949, 2996) have collected the recorded steric results for the hydroxylation of olefins by hydrogen peroxide in the presence of osmium tetroxide and pervanadic and pertungstic acid; neglecting doubtful cases, they find that catalysis by osmium tetroxide results in *cis*-addition of hydroxyl groups, and that addition in the presence of the per-acids is *trans*. These authors reject mechanisms of addition by hydroxyl radicals in favour of reaction *via* a cyclic osmic ester (Criegee, *Annalen*, 1936, **522**, 75) and, for the per-acids, either epoxide formation or ionic addition of the per-acid itself. Reaction *via* hydroxyl radicals does not appear to contribute extensively to oxidation by dilute alkaline permanganate (Kenyon and Symons, *J.*, 1953, 3580), whence steric results obtained with this reagent are probably not relevant to free-radical addition.

The polymer configurations which have been derived, above, are those of maximum

order; if, at intervals, a monomer molecule is added irregularly, either as regards *trans*- (or *cis*-) addition, or with regard to mode of presentation, then thereafter the chain will follow the configuration enantiomeric to the former section. The frequency with which irregularities occur probably varies with the monomer and the conditions of polymerisation; in particular, the mode of presentation would be expected to depend for uniformity directly on the strengths of the interactions between the substituents I, A, K, B, at the end of the growing chain and those attached to the monomer molecule.

A small number of chain configurations, determined by *X*-ray- or electron-diffraction methods, have been recorded for polymers containing asymmetric carbon atoms.

Fuller (*Chem. Reviews*, 1940, **26**, 164), from *X*-ray crystallographic analysis, has assigned to poly(vinyl chloride) a structure identical with (10) [or (11); isolated sections are identical].

From electron-diffraction patterns of multilayers of the polymers, Coumoulos (*Proc. Roy Soc.*, 1944, *A*, **182**, 166) has deduced structures identical with (10) [or (11)] for poly-(methyl and ethyl acrylate), five poly(alkyl methacrylates), and for poly(vinyl acetate).

Poly(vinyl acetate) (which has not been obtained crystalline) yields on hydrolysis poly(vinyl alcohol), which crystallises well in fibre form. From the most recent *X*-ray crystallographic analysis Bunn (*Nature*, 1948, **161**, 929) concludes that the hydroxyl groups are essentially randomly placed in left- and right-hand positions along the chain, and (personal communication) that regular sequences longer than 3 or 4 monomer units are rare. If hydrolysis proceeds by acyl–oxygen fission then the order in poly(vinyl alcohol) ought to be equal to that in poly(vinyl acetate). Coumoulos (above) has found the ordered structure (10) [or (11)] for the latter, and it is now suggested that the chain configuration is rendered irregular by the intervention of vicinal acetyl groups during hydrolysis, leading to alkyl–oxygen fission. The results of Winstein and his co-workers (summarised by Braude, *Ann. Reports*, 1949, **46**, 122) show vicinal intervention to be probable during the hydrolysis of such a structure as poly(vinyl acetate). For example, if the intermediate
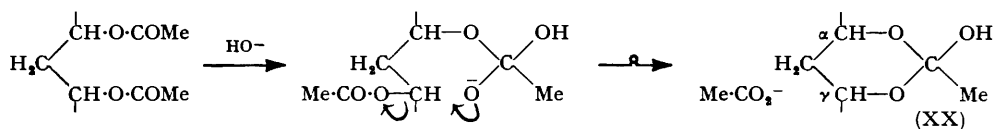
(XX) is formed as shown, then further hydrolysis by acyl–oxygen fission leads to (overall) inversion if at C_γ, but to retention if at C_α, while bimolecular attack by hydroxyl ion leads to inversion if at C_α, but to retention if at C_γ.

If it be assumed that poly(vinyl chloride) and the acetate, and the above poly-acrylates and -methacrylates, are formed by *trans*-addition, then in each instance reaction has proceeded with the presentation, [1'], in which like groups are at the maximum distance apart.

The present conclusions are summarised as follows.

The configuration of a growing ethylenic-addition chain-molecule is governed by three factors : (*a*) *trans*-, alternatively *cis*-, addition; (*b*) the mode of presentation of the monomer to the chain end; (*c*) the steric configuration of the attack by the initiating radical or ion. The recorded steric evidence implies *trans*-addition for both ionic and free-radical mechanisms. The regular operation of factors (*a*), (*b*), (*c*), leads to the formation of a limited number of orderly chain-configurations. Mutual termination of chains may yield molecules of more complex diastereoisomeric types, but can also lead to highly symmetrical *meso*-structures.