334. *Branched-chain Super-esters.*

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Branched-chain super-ester molecules have been synthesised by the following method. Linear polyethylene adipate polymers were prepared by conventional methods using an excess of ethylene glycol to produce terminal hydroxyl groups. This was confirmed by estimating chemically the number of end-groups and measuring osmotically the number of polymer molecules present in a given sample. These linear polymers were then degraded to a small extent and allowed to react with pentaerythritol, dipentaerythritol, and trishydroxymethyl-propane in limited amounts. By end-group determinations and osmotic-pressure experiments it was shown that branched-chain molecules had been produced. The viscometric behaviour of solutions of these molecules was determined.

PART I.

MOST of the investigations into the synthesis and structure of high polymers have been concerned with linear molecules or with three-dimensional networks. Very little work has been attempted with branched-chain molecules. Such molecules are of interest for many reasons. In the early stages of the production of three-dimensional molecules they must have a transitory existence. Similarly, in the later stages of vinyl polymerisations the process of transfer to the polymer will give rise to branched molecules provided that termination of polymerisation only involves disproportionation between polymer radicals. There is therefore the problem of devising synthetic methods in both systems to isolate such structures, if possible unmixed with linear or three-dimensional molecules. Interest also attaches to the thermo-dynamics and the hydrodynamical behaviour of solutions of branched-chain molecules, for there is relatively little guidance from theory as to the behaviour to be expected. Conversely, such knowledge may yield some information about the extent of branching in polymers whose structure cannot easily be determined, for example, when end-group analysis is impracticable.
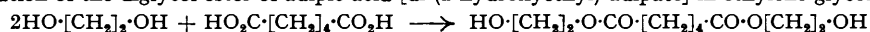
This paper is concerned with the problem of synthesis. The ideal way in which to synthesise a branched-chain polymer is to start with a linear polymer to which suitable reactive groups are attached. Another series of linear molecules containing only one terminal reactive group capable of reacting with the backbone is prepared and the two are brought together under suitable conditions. This approach was attempted in the following way but was unsuccessful. The backbone was polyvinyl alcohol of known molecular weight. A monofunctional polymer was made by polymerising styrene in presence of carbon tetrachloride so that each polystyrene molecule possessed a CCl_3 end-group. Unfortunately, it proved impossible to convert any appreciable fraction of CCl_3 groups into CO_2H. This method was therefore abandoned.

The other scheme of rather less flexibility consisted in using a super-ester with suitable terminal groups and condensing such a molecule with a polyhydric alcohol or polybasic acid. After some trials the system finally used was that of polyethylene adipate with terminal hydroxyl groups, with the polyhydric alcohols, pentaerythritol, dipentaerythritol, and trishydroxymethylpropane (2 : 2-bishydroxymethylbutan-1-ol). The problem in such systems is to achieve incorporation of the polyhydric alcohol without the formation of any appreciable amount of insoluble three-dimensional polymer. The advantage of this kind of system is that at the end of each branch in the molecule there is a hydroxyl group whose concentration can be determined by standard methods.
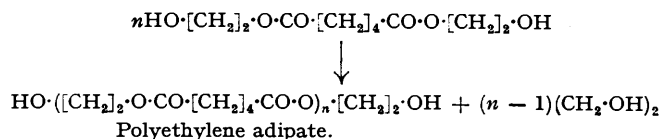
EXPERIMENTAL.

Preparation of the Parent Polymer.—On account of (a) the availability of monomers in a relatively pure state and (b) the viscosity of the resultant polymer, polyethylene adipate (obtained by the inter-condensation of adipic acid and ethylene glycol) was selected as the most suitable polymer from which synthesis of branched-chain polymers could be initiated. As absolute purity of the final product was essential, both reactants were purified before interaction, the adipic acid by recrystallisation (with use of charcoal) from ethyl alcohol, and the ethylene glycol by refluxing over lead monoxide followed by distillation of the fraction of b. p. 196—197°. No catalyst was used in the reaction, as the introduction of toluene-*p*-sulphonic acid, the usual catalyst employed, might have led to errors in physical measurements subsequently made on the linear and branched polymers.

The method of polyesterification chosen was that originally devised by Carothers, in which ester interchange was employed to produce high molecular weight polyesters from a reaction mixture in which the glycol was in stoicheiometric excess of the dibasic acid used (Carothers and Dorough, *J. Amer. Chem. Soc.*, 1930, **52**, 711; Carothers, *Chem. Reviews*, 1931, **8**, 353). Essentially, the method consists in refluxing a mixture containing a 3 : 1 molar mixture of ethylene glycol and adipic acid for 24 hours in a stream of oxygen-free gas, preferably nitrogen at atmospheric pressure. The mixture then consists of a solution of the diglycol ester of adipic acid [di-(2-hydroxyethyl) adipate] in ethylene glycol :

$$2HO \cdot [CH_2]_2 \cdot OH + HO_2C \cdot [CH_2]_4 \cdot CO_2H \longrightarrow HO \cdot [CH_2]_2 \cdot O \cdot CO \cdot [CH_2]_4 \cdot CO \cdot O[CH_2]_2 \cdot OH$$

In the second part of the process, the nitrogen stream is passed through drying towers of sulphuric acid and calcium chloride to ensure the greatest degree of condensation and to obviate any hydrolytic degradation of the polyester formed. The pressure of the dry oxygen-free nitrogen is then reduced to 0·1—0·25 mm. of mercury by means of a Speedivac pump regulated by a gas leak, and under the influence of heat and agitation excess of ethylene glycol is removed from the solution, followed by a further quantity of ethylene glycol eliminated as a by-product as the condensation reaction proceeds :

$$n\text{HO·}[CH_2]_2\text{·O·CO·}[CH_2]_4\text{·CO·O·}[CH_2]_2\text{·OH}$$

$$\downarrow$$

$$\text{HO·}([CH_2]_2\text{·O·CO·}[CH_2]_4\text{·CO·O})_n\text{·}[CH_2]_2\text{·OH} + (n-1)(CH_2\text{·OH})_2$$

Polyethylene adipate.

From the method of preparation, it is evident that a large proportion of the polyester molecules so formed will possess two terminal hydroxyl groups per molecule.

Condensation is continued usually for 8—12 hours, after which ethylene glycol vapour ceases to be removed and condensation is complete under the conditions of experiment. The molecular weights obtained by this procedure range from 8000 to 10,000 approximately, and the polymers possess the property of " cold-drawing," which may be adopted as a simple test of the extent of condensation.

Molecular-weight Determination.—(a) *Chemical method* [Private communication from Imperial Chemical Industries Limited (Dyestuffs Division)]. Molecular weights of polyesters prepared by the method outlined above can be determined by measurement of the number of alcoholic and acidic end-groups present in a given weight of polyester, and, from the knowledge that such polymers can, from the mechanism of condensation, possess two end-groups only, the molecular weight may be calculated.

The alcoholic end-groups are determined by the standard acetylation procedure and are expressed as the " acetyl value " of the polymer (mg. of potassium hydroxide per g. of polymer).

The acidic end-groups are determined by titrating approximately 8 g. of the polyester in neutral alcohol with standard caustic alkali and are expressed as the " acid value " of the polymer (mg. of potassium hydroxide per g. of polymer).

If S is the sum of the acetyl and acid values obtained for the polymer, the amount of hydroxyl group per g. of polymer is given by $17S/56$ and, since polyester molecules contain two end groups only, the weight of polymer containing the equivalent of two hydroxyl groups gives a measure of the molecular weight of the polymer.

Chemical methods of molecular-weight determination are, of necessity, number average values, *i.e.*, $\Sigma M_x N_x / \Sigma N_x$, where M_x is the molecular weight of an x-mer and N_x is the total number of x-mers. Any variations which introduce structural changes or an increase in the number of hydroxyl groups will alter the apparent molecular weight obtained.

(b) *Osmotic method.* The instrument used to measure osmotic pressures was closely similar to that described by Fuoss and Mead (*J. Physical Chem.*, 1943, **47**, 59). The cells, instead of being fashioned from two stainless-steel plates, were cut from δ-bronze forgings with valves of stainless steel, and the screw joints in the side-arms and capillary tubes had lead-foil washers. To lessen the volume of solution and therefore external temperature effects, the capillary tubes of 1-mm. diameter were sealed directly to the metal in the glass-to-metal seals.

Temperature was maintained constant within less than $\pm 0·01°$ by immersion in a thermostat controlled by a toluene–mercury regulator and " Thyratron " relay. In place of the partly denitrated nitrocellulose films used by Fuoss and Mead (*loc. cit.*) as the semi-permeable membrane of the osmometer, a disc of bacterial cellulose (Masson, Menzies, Cruickshank, and Melville, *Nature*, 1946, **157**, 74) was used in measurements by the dynamic method, while non-moisture-proof Cellophane was used for a static method to obtain molecular weights lower than those obtainable by the dynamic method.

When using the dynamic method, it was found that in dealing with polyester solutions, membranes re-swelled in alcohol–water mixtures containing 0—40% alcohol were of little use even with a membrane of 4-mm. wet thickness, for with all such membranes a considerable drift was apparent in the graphs of osmotic pressure against time. To obviate this, the thickest membranes (5—6 mm. in the swollen state) were used and by re-swelling these in 60 : 40 alcohol–water a membrane with a lower molecular weight limit of 25,000 could be obtained, while a membrane re-swelled in 70 : 30 alcohol–water gave a corresponding limit of 20,000. Mixtures of higher alcohol content could be used to obtain membranes with an even lower limit, but the time intervals required to obtain a good osmotic pressure–time curve became excessive and equally good results could be obtained statically with little increase in the time of experiment.

In the actual experiments, dilute solutions containing 0·5—1·0 g. of polymer per 100 g. of solution were used initially and a pair of matched curves was obtained, from which the osmotic pressure (π) appropriate to that concentration (c) was obtained. The solution was then diluted repeatedly, an osmotic pressure corresponding to each dilution being obtained (Masson, unpublished). A graph of π/c against c was extrapolated to zero concentration to give a value for $[\pi/c]_0$ which was then substituted in the equation

$$[\pi/c]_0 = 10,330 \times 0·0821 T/M$$

where 10,330 is the conversion factor from l.-atm. per °c. 100 c.c. to cm. of water per °c., T is the absolute temperature, and M the molecular weight of the solute. π/c was measured in g. of solute per 100 g. of solution, and the above constants apply irrespective of the solvent used.

For measurements on polymers of molecular weight $<20,000$, a " static " membrane was prepared from non-moisture-proof Cellophane, according to the method used by Carter and Record (*J.*, 1939, 660). The membrane of approximately 0·04-cm. dry thickness was prepared in the following stages : (a) Immersion for 1 hour in 60 : 40 ethanol–water to remove glycerol present as plasticiser.

(*b*) Immersion for a further 4 hours in a bath of the same composition with 1% of ammonia added to remove fatty acids. (*c*) Immersion overnight in a bath of 60 : 40 ethanol–water, by which the permeability of the membrane was determined. Alteration of the composition of this bath alters the permeability accordingly. (*d*) Displacement of the absorbed water by alcohol, followed by displacement of the alcohol by the solvent to be used experimentally, in this case chloroform, the bath being changed repeatedly until all the alcohol had been removed.

In the manner described above for the dynamic method, a π/c–c curve can again be drawn to find $[\pi/c]_0$, the limiting value of π/c at zero concentration.

As this method of obtaining osmotic pressures and molecular weights entails protracted experimental work, one reading for π/c was taken at a concentration giving an osmotic pressure of approximately 1 cm. of polymer solution. At lower molecular weights, the difference between the value of the molecular weight given by this reading and that given by the actual value of $[\pi/c]_0$ is very small and is within experimental error. In this way, the time of experiment can be greatly reduced.

The Synthesis of Branched-chain Polymers.—It is well known that, when an organic compound which possesses more than two functional groups is co-condensed in appreciable proportions with monomers which by themselves are capable of linear-molecule formation only, the resulting product is a gel which is totally, or largely, insoluble in all solvents. As this is the direct result of condensation in three dimensions, as opposed to two dimensions in the case of a linear polycondensed molecule, it was thought that under chosen conditions an intermediate stage in the condensation should occur at which branched molecules were present. Branching must, of course, be a necessary preliminary to cross-linking, but under normal conditions the gelation reaction takes place so suddenly that little progress has been made in determining the structure of intermediate products.

In order to carry out an investigation on the alteration of the physical properties occasioned by the introduction of a polyfunctional reactant into the condensation process, a series of condensations was carried out in the apparatus shown in Fig. 1, in which successively greater percentages of pentaerythritol, $C(CH_2 \cdot OH)_4$, were added to a sample of polyethylene adipate which had been polymerised to its fullest extent under the conditions of experiment. After addition of the pentaerythritol the reaction mixture was heated by means of a vapour-bath of ethylene glycol for two hours, during which the polyester depolymerised slightly, allowing the pentaerythritol to dissolve and react with the polymer. Condensation was then carried out as before, exhaustively for at least eight hours, during which a quantity of the original pentaerythritol volatilised out of the melt.

FIG. 1.

A series of five polymers was prepared in this way, containing initially 1·0, 1·5, 1·8, 1·9, and 2·0% of pentaerythritol, the last being a gel.

It was evident, therefore, that under the conditions of the experiment a critical percentage of pentaerythritol could be added below which gelation would not take place. The copolymers so formed were soluble in the usual solvents with slightly greater difficulty than was linear polyethylene adipate, probably owing to an increase in viscosity.

Molecular-weight determinations were carried out on all these polymers, except that containing 1% of pentaerythritol, by means of dynamic osmometry giving π/c–c curves. The copolymer containing 1% of pentaerythritol gave " drifting " in the dynamic osmometer, and the value was therefore obtained statically. The results are given in the following table.

| Polymer.	$[\pi/c]_0$.	Mol. wt.
Ethylene adipate + 1·0% of P.E.	14·60	17,000
,, ,, 1·5% of P.E.	10·00	25,000
,, ,, 1·8% of P.E.	6·70	37,000
,, ,, 1·9% of P.E.	5·25	47,500

P.E. = pentaerythritol.

The value given by the copolymer containing 1·9% of pentaerythritol approximates to a four-fold increase in molecular weight compared with polyethylene adipate prepared under identical conditions. The acetyl and acid values of the 1·9% copolymer and of linear polyethylene adipate disclosed a doubling of the number of end groups per molecule, *i.e.*, four in place of two. With smaller quantities of pentaerythritol it is evident that the polymers will consist of linear together with branched-chain molecules.

From these details, it would appear that the pentaerythritol has acted as a nucleus for growth in four directions, each of the arms being of approximately equivalent length. In addition, any attempt to increase the percentage of added pentaerythritol results in gelation. It therefore appears that immediately before gelation the molecules are, on the average, essentially cruciform in shape.

In order to confirm this theory, it was necessary to prepare a series of such copolymers of penta-

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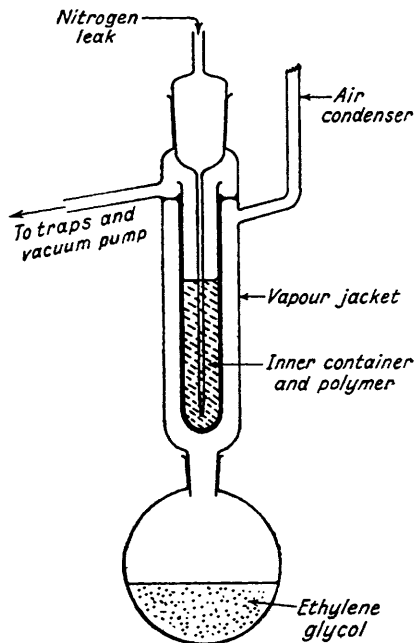
erythritol with linear polyethylene adipate, of differing molecular weights. Only in this way can the various physical properties of such polymers be typified and characterised.

When sufficient polyfunctional compound is added in the copolymerisation reaction to result eventually in the production of a gel, it should be possible, if the above theory is correct, to terminate the condensation process immediately before the gel point and to obtain thereby molecules whose average structure is completely branched in four directions. Again, with the addition of progressively larger percentages of polyfunctional compound, the molecular weights of these molecules so formed should be correspondingly reduced since branching will occur earlier in the condensation reaction (see Table I). The depolymerisation and recondensation procedure used was as previously described, the reaction being interrupted immediately before the gel point. This procedure is largely a matter of experience in recognising the signs of the onset of gelation during which the melt passes from a finite to an infinite viscosity.

TABLE I.

Copolymer no.	Acetyl value.	Acid value.	Chemical mol. wt.	Osmotic mol. wt.
1	22·68	0·89	9,500	10,000
2	21·30	0·92	10,000	19,500
3	15·60	0·78	14,000	15,000
4	18·45	0·86	11,500	20,000
5	13·70	0·96	15,500	17,000
6	8·89	0·88	23,000	23,000
7 (E.A.* + 1·9% P.E.)	—	—	—	47,500

* E.A. = Polyethylene adipate; P.E. = pentaerythritol.

A series of six polymers was prepared in this fashion, and to this series was added the highest molecular weight polymer given by the last series of experiments which, in effect, gives seven similar polymers in all.

Osmotic and chemical molecular-weight determinations were again used as a basis of comparison, but, as distinct from the previous chemical molecular weight determinations in which the molecule was known to be dihydric, the present series were evaluated on the basis that each molecule was tetrahydric. The molecular weight (M) is given by $224 \times 1000/S$, where S is the sum of the acid and the acetyl values. The results are given in Table I.

It will be seen that the values for molecular weight given by the two methods show good agreement except for copolymers nos. 2 and 4 which will be discussed later. It appears that there is considerable justification for the theory that, immediately before gelation, all the molecules formed by copolymerisation of pentaerythritol possess on the average four end groups.

In order to discover whether other polyfunctional compounds could be made to undergo similar condensation reactions, linear polyethylene adipate was copolymerised first with dipentaerythritol, a dimer of pentaerythritol possessing six hydroxyl groups per molecule, and secondly with 1 : 1 : 1-tris-hydroxymethylpropane, having three hydroxyl groups; both these copolymers are capable, under given conditions, of giving rise to gelation.

The method of synthesis in the case of dipentaerythritol was identical with that used in the preparation of pentaerythritol copolymers, except for the precaution of adding a slightly greater percentage of dipentaerythritol to offset its greater volatility at ordinary pressures when raised to the temperature of experiment. Under reduced pressure, this volatility is even more marked.

A series of nine copolymers was prepared of which one showed no signs of gelling. Details of chemical and osmotic molecular weights were again obtained, as shown in the following table, the chemical

Polymer no.	Acetyl value.	Acid value.	Mol. wt. (chemical).	$[\pi/c]_{20°}$.	Mol. wt. (osmotic).
1	11·35	0·26	29,000	8·96	27,000
2	11·98	0·25	24,000	10·93	23,000
3	22·90	0·31	15,000	16·05	15,500
4	24·30	0·49	13,500	18·10	13,700
5	27·10	0·42	12,200	17·65	14,000
6	31·48	0·42	10,500	22·95	10,800
7	36·19	0·42	9,200	26·80	9,300
8	39·94	0·61	8,300	31·40	8,000

molecular weight being calculated on the basis of six hydroxyl groups per molecule. Again, agreement between chemical and osmotic molecular weights is very good and appears to justify the determination of chemical molecular weights on the basis of six hydroxyl groups per molecule. One point is noteworthy : although six hydroxyl groups are present per molecule, there is a definite threshold effect above which gelling occurs, and below which gelling does not take place. In the pentaerythritol series, it appeared that the introduction of a second nucleus was necessary for gelation, brought about by the increase in the number of hydroxyl groups per molecule and consequently in the opportunity for intramolecular condensation. In dipentaerythritol polymers, there are already six hydroxyl groups, but these apparently do not react intramolecularly until a second nucleus is introduced.

Copolymerisation of ethylene adipate with 1 : 1 : 1-trishydroxymethylpropane presented considerable difficulty in view of its great volatility under experimental conditions. Even at ordinary pressures, its vapour pressure was sufficiently high for a notable proportion of the compound originally added to distil out of the reaction mixture. To minimise this effect, modifications in experimental procedure were necessary.

The reaction was carried out initially for two hours at 100°, and then for two hours in a vapour-bath of ethylene glycol (197°), both at atmospheric pressure. This was followed by condensation at the

latter temperature. Even with this method of experimentation, the greater part of the trishydroxy-methylpropane was lost by volatilisation.

Eight copolymers were prepared, of which two gelled and another showed no signs of gelling. The remaining five polymers were subjected to the tests discussed above. As, in this case, the number of groups present per molecule was unknown, acid and acetyl values were measured, and molecular weights were determined by the static osmometer. From these quantities, the number of hydroxyl groups was calculated for each polymer molecule, as follows. It will be seen that the number of hydroxyl groups per

Polymer no.	Acetyl value.	Acid value.	$[\pi/c]_{20°}$.	Mol. wt. (osmotic).	No. of OH groups.
1	9·30	0·28	13·13	19,000	3·25
2	14·35	0·37	16·65	14,900	3·92
3	16·60	0·30	16·90	14,700	4·44
4	21·80	0·33	23·49	10,500	4·17
5	42·30	0·35	33·62	7,400	5·63

molecule varies considerably but is, on the average, close to four. Divergences in the cases of polymers nos. 1 and 5 may be ascribed to the experimental difficulties. For No. 1, it is highly probable that insufficient of the trifunctional compound was present to cause gelation, but owing to the considerably higher viscosities encountered it was difficult to decide whether the melt would gel. The discrepancy with No. 5 can be explained by the comparatively large amount of trishydroxymethylpropane added. Any unchanged functional compound would result in increased acetyl values, but in the osmotic experiments such small molecules can pass through the membrane and set up an equilibrium on both sides of it, while the polymer molecules exert their normal osmotic pressure.

Calculated on the basis of four hydroxyl groups per molecule, the comparison is as follows : Again

Polymer no.	1	2	3	4	5
Chemical mol. wt.	23,000	15,200	13,300	10,200	5,300
Osmotic mol. wt.	19,000	14,900	14,700	10,500	7,400

agreement appears to be close, two molecules of trishydroxymethylpropane being required to satisfy the experimental results.

PART II.

Branched-chain Polymers.—In view of the necessity for a greater understanding of the effects of shape and size of polymer molecules on their physical characteristics, particularly viscosity, all three series of copolymers were subjected to viscometry in chloroform solution by means of an Ostwald viscometer. In order to effect a strict comparison, the measurement taken was the limiting viscosity of the polymer, which is given by the expressions $[\eta_{sp.}/c]_{c \to 0}$ and $[(\log_e \eta/\eta_0)/c]_{c \to 0}$, where $\eta_{sp.}$ is the specific viscosity, η/η_0 the relative viscosity, and c the concentration in g. of polymer per 100 c.c. of solution (Staudinger and Fischer, *J. pr. Chem.*, 1940, **157**, 19 ; 1941, **157**, 58 ; Kraemer, *Ind. Eng. Chem.*, 1938, **30**, 1200). At zero concentration both expressions give the limiting viscosity, but the latter expression, the intrinsic viscosity, was chosen for use because it was more nearly directly proportional to concentration at low concentrations and therefore allowed easier extrapolation to zero concentration at which the intrinsic viscosity becomes the limiting viscosity. The limiting viscosity (designated [I.V.]₀ below) was obtained by determining the relation of the viscosity of a solution of the polymer at two concentrations to that of the pure solvent at 20°, plotting $(\log_e \eta/\eta_{sp.})/c$ against c, and extrapolating to zero concentration. The concentrations were of the order of 0·5 and 0·25 g. of polymer per 100 c.c. of solution, the second concentration being obtained by dilution. The results are shown in Table II.

TABLE II.

Polymer.	$[I.V.]_{0.25}$.	$[I.V.]_{0.50}$.	$[I.V.]_0$.	Mol. wt., osmotic.
Polyethylene adipate	0·304	0·296	0·312	10,000
,, + 1·0% P.E.	0·308	0·294	0·322	17,000
,, + 1·5% P.E.	0·327	0·312	0·342	25,000
,, + 1·8% P.E.	0·396	0·384	0·408	37,000
,, + 1·9% P.E.	0·448	0·439	0·457	47,500
,, + 2·0% P.E.	—	Gelled	—	—

P.E. = pentaerythritol.
(These polymers are identical with those described on p. 1615.)

When the limiting viscosity is plotted against the amount of pentaerythritol added, there is little increase in gradient up to 1·5% of added pentaerythritol, but additional amounts cause a very rapid increase in gradient. A plot of the limiting viscosity and molecular weight gives a curve whose gradient gradually increases with increasing molecular weight.

Copolymers of ethylene adipate with more pentaerythritol than is required to gel the melt on complete condensation gave another set of figures (Table III) whose limiting viscosity–molecular weight plot lay at a higher viscosity level than the polymers recorded in Table II.

As previously, the agreement between chemical and osmotic molecular weights was good, except in the cases of copolymers No. 2 and 4. These copolymers also show limiting viscosities which are out of all proportion to their molecular weights, and it is clear that the physical properties (*e.g.*, size and shape) of these copolymers have altered.

As shown before, the molecular weight can be determined chemically from the expression, $M = 56,000x/S$, where M is the molecular weight, x the number of hydroxyl groups per molecule, and S the

TABLE III.

Copolymer no.	[I.V.]$_{0 \cdot 25}$.	[I.V.]$_{0 \cdot 50}$.	[I.V.]$_{0}$.	Mol. wt., osmotic.
Ethylene adipate + excess of P.E., No. 1	0·345	0·333	0·356	10,000
,, ,, No. 2	0·542	0·539	0·545	19,500
,, ,, No. 3	0·374	0·368	0·379	15,500
,, ,, No. 4	0·661	0·657	0·665	20,000
,, ,, No. 5	0·388	0·378	0·399	17,000
,, ,, No. 6	0·446	0·444	0·448	23,000
,, ,, No. 7	0·448	0·439	0·457	47,500

(These polymers are identical with those in Table I.)

sum of the acetyl and acid values.   By substituting the osmotic molecular weight for M, and the sum of acetyl and acid values for S, x can be calculated for these polymers : it is 7·75 and 6·80 for copolymers Nos. 2 and 4, respectively, so that these copolymers in fact possess more hydroxyl groups than do those which show average figures.   This can be accounted for by the introduction of another pentaerythritol nucleus into some of the polymer molecules, which are therefore intermediate between the average polymer and the insoluble network.   This view is supported by the fact that these anomalous copolymers dissolve with considerably greater difficulty than the normal copolymer.

FIG. 2.
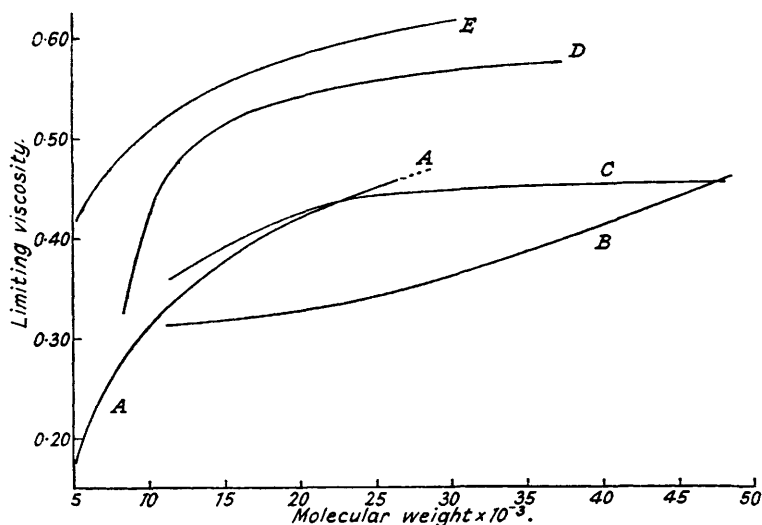
(A) *Polyethylene adipate*
(B)   ,,   + *pentaerythritol.*
(C)   ,,   + *pentaerythritol.*
(D)   ,,   + *dipentaerythritol.*
(E)   ,,   + 1 : 1 : 1-*trishydroxymethylpropane.*

By omitting those two polymers and plotting limiting viscosity–molecular weight curves, it was shown that, as a whole, the curve lies above the curve plotted from Table II, tending to meet it only at the extreme ends (Fig. 2).   It would appear that Table II gives values for copolymers in which cruciform molecules were in the process of being formed, or in fact, had been actually formed, but were diluted by the presence of linear polyethylene adipate present in the copolymer.   It is highly probable that, since condensation had been carried out to the limit, a mixture of such molecules is, in fact, present.

On carrying out the same type of work on the excess dipentaerythritol copolymers, it was found that the limiting viscosities lay at a much higher level for corresponding molecular weights :

Copolymer.	[I.V.]$_{0 \cdot 25}$.	[I.V.]$_{0 \cdot 5}$.	[I.V.]$_{0}$.	Mol. wt., osmotic.
Ethylene adipate + excess of D.P.E., No. 1	0·545	0·539	0·551	27,500
,, ,, No. 2	0·563	0·558	0·568	23,000
,, ,, No. 3	0·517	0·511	0·523	15,500
,, ,, No. 4	0·489	0·480	0·498	13,700
,, ,, No. 5	0·461	0·455	0·467	14,000
,, ,, No. 6	0·442	0·432	0·452	10,800
,, ,, No. 7	0·356	0·350	0·362	9,300
,, ,, No. 8	0·338	0·328	0·348	8,000

D.P. = dipentaerythritol.
(These polymers are identical with those on p. 1616.)

The curve for limiting viscosity–molecular weight lies, as before, at a higher viscosity level, with much steeper initial slope, but the same limiting effect is apparent at higher molecular weights, the viscosity showing little increase with increasing molecular weight (Fig. 2). That the viscosity has been increased for corresponding molecular weights when compared with the curve given by Table II can be accounted for by the greater tendency of a molecule with six arms originating in one nucleus to become spherical.

Similar treatment of the 1 : 1 : 1-trishydroxymethylpropane series of copolymers gave the following figures :

Copolymer.		$[I.V.]_{0\cdot25}$.	$[I.V.]_{0\cdot50}$.	$[I.V.]_0$.	Mol. wt., osmotic.
Ethylene adipate + excess of T.M.P.,	No. 1	0·571	0·556	0·586	19,000
,,	,, No. 2	0·540	0·525	0·555	14,900
,,	,, No. 3	0·520	0·511	0·529	14,700
,,	,, No. 4	0·504	0·496	0·512	10,500
,,	,, No. 5	0·463	0·457	0·469	7,400

T.M.P. = trishydroxymethylpropane.
(These polymers are identical with those on p. 1617.)

The plot of molecular height and limiting viscosity in this series of polymers is even higher than those of the previous copolymers and lies roughly parallel to the curve obtained from the data in Tables II and III, but is slightly less steep in the low-molecular-weight region.

DISCUSSION.

Any degree of branching in any polymer should be reflected in a lowering of the value of the branching coefficient α if the modified Staudinger equation (Huggins, *Ind. Eng. Chem.*, 1943, **35**, 980) :

$$[I.V.]_0 = KM^\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[I.V.]_0$ is the limiting viscosity, K is a constant, and M the molecular weight, and where the values of α lie between zero for spheroid particles and approximately unity for linear polymers. This equation may be evaluated simultaneously to give a value for α in terms of two values of $[I.V.]_0$ and the corresponding values of M for any one polymer. In the case of linear polyethylene adipate over the range $M = 5800$—9500, α is $0\cdot85$, while for the pentaerythritol copolymer over the range $M = 11,000$—$48,000$ it is $0\cdot17$, for the dipentaerythritol copolymer over the range $M = 10,000$—$30,000$ it is $0\cdot28$, and for the trishydroxymethylpropane copolymer for $M = 10,000$—$30,000$ it is $0\cdot16$. In all the copolymers (*i.e.*, excepting ethylene adipate alone), there was a tendency for the value of α to become very low at molecular weights higher than those cited.

These values are not strictly comparable but show that definite structural changes have taken place within the polymer meolcule which have had the effect of reducing α to a considerably lower figure than that of the linear polymer. The limiting value of α is that postulated by Einstein for spherical particles (*Ann. Physik*, 1906, **19**, 289; 1911, **34**, 591), *viz.* :

$$[I.V.]_0 = 2\cdot5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which can be written in a form comparable with equation (1), *viz.* :

$$[I.V.]_0 = 2\cdot5M^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From this it can be seen that the more spherical a molecule becomes, the more the value of α tends to zero, and the more should the limiting value of the viscosity tend towards $2\cdot5$. From the above figures, the various copolymers appear to show a definite tendency towards the formation of spheroid molecules, although it is hardly to be expected that equation (3) would be obeyed, as such copolymer molecules are in fact open structures in which the arms assume a more or less extended shape depending on the solvent power of the medium used.

Again, with regard to the shape of the various copolymer molecules, it can be seen that a molecule possessing six arms emanating from one nucleus will have a greater tendency towards a spherical shape than one possessing only four. Thus it is to be expected that the dipentaerythritol copolymers will have a higher viscosity level than pentaerythritol copolymers. Again it is reasonable to expect that a molecule such as the trishydroxymethylpropane copolymers, where two nuclei are present, should exert less steric effects, and therefore less restriction on the mobility of the arms; it will consequently approximate more closely to a spherical particle in solution, and should therefore lie at a higher viscosity level than either of

the other copolymers. These relative viscosity levels, however, depend to a considerable extent on solubility, as can be seen from the following table for polymers dissolved in *o*-chlorophenol :

	$[I.V.]_{0.25}$	$[I.V.]_{0.50}$	$[I.V.]_0$	Mol. wt.
E.A. + T.M.P., No. 2	0·751	0·725	0·777	14,900
E.A. + D.P.E., No. 4	0·610	0·601	0·619	13,700
E.A. + P.E., No. 5	0·602	0·584	0·620	15,500

It will be seen that, in *o*-chlorophenol, the limiting viscosities are considerably higher. To find out the relative solubilities of these polymers in *o*-chlorophenol and chloroform, solutions (0·5 g./100 c.c. of solution) of one polymer (E.A. + T.M.P., No. 3) were treated with methyl alcohol, in which the polymer is insoluble, till turbidity appeared in the solution. For 10 c.c. of the *o*-chlorophenol solution 31·2 c.c. of methyl alcohol were required, and for the chloroform solution only

FIG. 3.
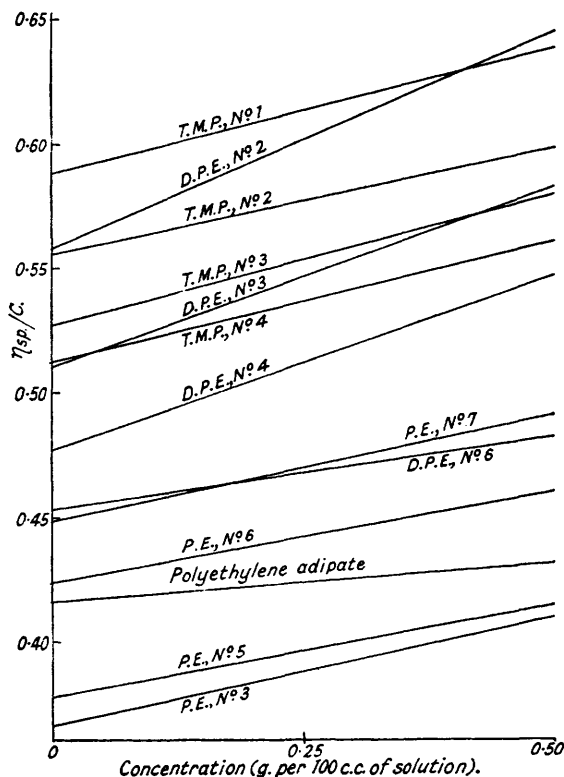
$P.E. = pentaerythritol.$ $D.P.E. = dipentaerythritol.$ $T.M.P. = trishydroxymethylpropane.$

15·0 c.c. The solubility in *o*-chlorophenol is therefore much greater than in chloroform. The increase in solubility is accompanied by an increase in viscosity (Alfrey, Bartovics, and Mark, *J. Amer. Chem. Soc.*, 1942, **64**, 1557). This is accounted for by the fact, that, since the viscosity has increased, the field in which the flexible arms of the molecule can move has also increased because of the greater penetrative power of the solvent towards the nucleus of the molecule. The arms therefore become more extended in a good solvent, resulting in an increase in viscosity.

To discover whether any such solubility effect could account for the varying viscosity levels of the copolymers, representative solutions (0·5 g./100 c.c. of solvent) of polymers (mol. wt. = about 10,000) were titrated with methyl alcohol to the turbidity point, with the following results :

Polymer.	Mol. wt.	MeOH, c.c.
E.A.	10,000	17·5
E.A. + P.E., No. 1	10,000	16·3
E.A. + D.P.E., No. 7	9,300	16·6
E.A. + T.M.P., No. 4	10,500	17·0

It will be seen that polyethylene adipate is the most soluble and that the copolymers show little difference. It is therefore unlikely that solubility effects can account for the variation in viscosity levels, which must therefore be entirely due to differences in structure.

Further interesting information is afforded by an investigation into the viscosities obtained for the various copolymers from the point of view of the Huggins equation, modified to allow of its use in polymer solutions by the introduction of the Huggins constant; this constant depends on the size, shape, and inter-attractive properties of solute and solvent molecules. The equation in its more general form is

$$\eta_{\text{sp.}}/c = [\eta](1 + K\eta_{\text{sp.}})$$

where $\eta_{\text{sp.}}$ is the specific viscosity, $[\eta]$ is the limiting viscosity, and K the Huggins constant, and holds at low concentrations (Huggins, *J. Physical Chem.*, 1938, **42**, 911; 1939, **43**, 439; *J. Amer. Chem. Soc.*, 1942, **64**, 2716).

With rod-like molecules, *e.g.*, linear polyesters, interference between molecules would be expected to be low, so $\eta_{\text{sp.}}/c$ would also be low, while the introduction of branching would incline the molecule to a more spherical shape, with a resultant increase in mutual interference between molecules. It is therefore reasonable to expect that the slope of the curve obtained on plotting $\eta_{\text{sp.}}/c$ against c would increase with the introduction of a more spherical molecule built up by means of branches. Little work has been done to support this theory, but figures obtained for amylopectin and amylose appear to agree with these postulates (private communication from Imperial Chemical Industries Limited, Dyestuffs Division).

To test this theory, various copolymers from each series were evaluated for $\eta_{\text{sp.}}/c$ from the data used for evaluation of limiting viscosities. The figures were obtained as follows (the slope of the line to the concentration axis is given by tan θ) (Fig. 3) :

Polymer.	$\eta_{0\cdot25}/c$.	$\eta_{0\cdot5}/c$.	η_0/c.	tan θ.	Mol. wt.
E.A. + P.E., No. 3	0·388	0·410	0·366	0·22	14,000
,, No. 5	0·396	0·415	0·377	0·19	15,500
,, No. 6	0·442	0·461	0·423	0·19	23,000
,, No. 7	0·470	0·492	0·448	0·22	47,500
E.A. + D.P.E.,No. 2	0·602	0·647	0·557	0·45	42,000
,, No. 3	0·547	0·584	0·510	0·37	20,000
,, No. 4	0·512	0·547	0·477	0·35	13,700
,, No. 6	0·468	0·483	0·453	0·18	11,000
E.A. + T.M.P., No. 1	0·614	0·640	0·588	0·26	23,000
,, No. 2	0·578	0·660	0·556	0·22	15,200
,, No. 3	0·554	0·581	0·527	0·27	13,300
,, No. 4	0·537	0·562	0·512	0·25	10,200
Linear E.A.	0·424	0·432	0·416	0·08	20,000

From a consideration of these figures, information on the shape of the molecule may be obtained. Since K, the Huggins constant, and hence tan θ are shape factors, variations will reflect an alteration in the structural shape of the molecule, and, if the possibilities mentioned before are taken into consideration, linear molecules ought to show a low value of tan θ, and any tendency towards formation of spherical molecules should be shown by an increase in the value of tan θ. As shown above, linear polyethylene adipate has a value of 0·08, pentaerythritol copolymers have an average of 0·20, and trishydroxymethylpropane copolymers 0·25, whereas dipentaerythritol copolymers show a much greater increase, to 0·35.

As mentioned above, K (and hence tan θ) is essentially a shape factor bound up with the inherent shape of the molecule itself and of the effect of solvents on the shape which the molecule assumes in solution. Branching changes a molecule which is linear and possesses little or no mutual interference in dilute solution into a molecule which is more inclined to a spherical shape and, because of its extensible arms, has greater possibilities of mutual interference. The increase in the value of tan θ from 0·08 for linear polyethylene adipate to 0·20 for the pentaerythritol copolymer is thus explained. Since there is little difference in the solubilities of polyethylene adipate and its copolymers, solubility can have little bearing on tan θ.

The slight but definite difference in the value of tan θ for the trishydroxymethylpropane copolymer cannot be attributed to the variation in solubility, and must arise from structural considerations alone. Both this and the pentaerythritol copolymer contain, on the average, four hydroxyl groups per molecule, and it is evident that the molecules must differ considerably in structure. Only one pentaerythritol nucleus is required to give four end groups, but for trishydroxymethylpropane two such nuclei are necessary, so that the molecule must take up a " double-Y " shape, two arms extending from each end of the linear portion of the molecule.

The field covered by such a molecule in the " kinked " position will be larger for comparable molecular weights, although it may not attain a completely spherical shape. Since the field is larger, the mutual interference must be greater, the result being a small but definite increase in the value of the Huggins constant and consequently in tan θ.

From a consideration of the relative limiting viscosities at corresponding molecular weights, it can be seen that the trishydroxymethylpropane copolymer has a greater claim to being considered spherical since it tends more to the limiting value of 2·5 (as given by the Einstein equation), evaluated for rigid spheres in suspension and in such dilution that inter-attractive forces are negligible. A molecule with two pairs of extended arms originating at each end of a linear polymer chain has an even greater possibility for mutual interference than a polymer in which four arms extend from a central nucleus, and in addition possesses less steric effects within itself.

In considering the dipentaerythritol copolymer, one can visualise the reason for the increase in tan θ where six arms are present in place of four. Such a molecule would have a considerably greater opportunity for mutual interference, but at the same time must be severely restricted in the movements of its arms by steric forces which are bound to be present when six arms emanate from one nucleus. For this reason, the value of tan θ is considerably higher than for the other two polymers, but on account of steric factors this polymer is unable to form as spherical a field as the trishydroxymethylpropane copolymer.

From these observations, it will be seen that viscosity data, as applied to the Huggins equation incorporating the shape factor K, are helpful in determining the degree of branching in polymers of approximately similar structure, although structural differences in " isomeric " molecules will alter the values of K slightly. From the observations above, it would appear that there is no correlation between the value of the shape factor K (or tan θ) and the limiting viscosity.

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