be an acid in the sulfur dioxide system just as it is an acid in the water system.

Hägg[17] has explained the ease of oxidation of sulfur dioxide up to sulfur trioxide as being due to the electron pair on the sulfur.   Thus

$$:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{S}}:\overset{..}{\underset{..}{O}}: + :\overset{..}{\underset{..}{O}}: = :\overset{..}{\underset{..}{O}}:\overset{\overset{..}{O}}{\underset{..}{S}}:\overset{..}{\underset{..}{O}}:$$
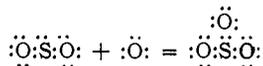
Thus, we could write the one to one addition compound with boron trifluoride

$$\begin{array}{cc} :\overset{..}{\underset{..}{O}}: & :\overset{..}{\underset{.}{F}}: \\ & S:B:F: \\ :\overset{..}{\underset{..}{O}}: & :\overset{..}{\underset{.}{F}}: \end{array}$$
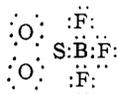
The fact that hydrogen sulfide formed the compound $H_2S \cdot BF_3$,[2] where only the sulfur can be the donor, would permit this latter mechanism.

Regardless of which structural formula represents sulfur dioxide, it is possible to account for

(17) Hägg, Z. physik. Chem., B18, 199 (1932).

the addition compound between the given structure and boron trifluoride.

Summary

In the present investigation it has been found that hydrogen chloride and methyl chloride give eutectics and no compounds with boron trifluoride, showing that, at least in these two compounds, chlorine does not act as a donor to boron trifluoride, thus refuting the existence of the reported compound $BF_3 \cdot 3HCl$.

It has been found further that nitrous oxide also will form no compound with boron trifluoride although it has been reported that nitric oxide does.   Sulfur dioxide, just as the other parent solvents, water and ammonia, forms a one to one compound with boron trifluoride and two eutectics.

Random Reorganization of Molecular Weight Distribution in Linear Condensation Polymers[1]

BY PAUL J. FLORY

In a recent publication[2] concerned with the viscosities of molten polyesters, it was observed that the viscosity of a mixture of two polyesters decreases when heated. This decrease was attributed tentatively to a change in the distribution of molecular species in the mixture, brought about by the occurrence of ester interchange between terminal hydroxyl groups and ester groups of the polymer chains

...—ORO—COR'CO—ORO—...

+ H—ORO—COR'CO—...

↓

...—ORO—COR'CO   + H—ORO—...

ORO—COR'CO—...
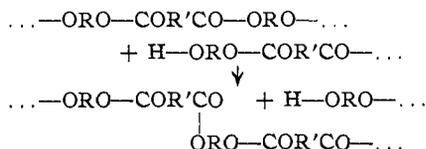
where —ORO— and —COR'CO— represent, respectively, the glycol and the dibasic acid residues of a linear polyester formed through polycondensation of a glycol and a dibasic acid. As the result of such an interchange process, an x-mer may react with a y-mer to yield a (y + z)-mer and an (x − z)-mer. There is no net change in the number of molecules; hence, the number

(1) A portion of this work has been discussed briefly by H. Mark and R. Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, 1941, p. 147.

(2) P. J. Flory, THIS JOURNAL, 62, 1057 (1940).

average molecular weight will be unaffected by reorganization processes of this sort. On the other hand, the distribution of species may be altered, and changes in distribution will produce corresponding changes in the weight average molecular weight. Since the viscosity of the molten polyester, composed of a mixture of polymeric species, depends directly on the weight average molecular weight,[2] the viscosity will be sensitive to changes in distribution caused by ester interchange, and these changes can be observed conveniently through viscosity measurements.

Investigations of rates of formation of polyesters and of their degradation[3] by monomeric alcohols have shown that the rate constant for alcoholysis, though somewhat smaller, is similar in magnitude to that for esterification under the same conditions. The two reactions are similarly affected by catalysts and temperature. After polyesterification has proceeded to the point where the average molecular weight is large, the free carboxyls are so overwhelmingly outnumbered by ester groups that the rate of reaction of the free hydroxyls with ester groups will exceed their rate

(3) P. J. Flory, ibid., 62, 2255, 2261 (1940).

of reaction with acid groups, despite the superiority of the esterification velocity constant. Thus, it is conceivable that ester interchange might exert a profound effect on the distribution of species obtained in the course of a polyesterification process.

It is the purpose of this paper to examine, both theoretically and experimentally, the consequences of interchange processes such as may occur in various linear condensation polymers. It will be shown that ester interchange, or any other analogous process in other polymers, provides a route to the most probable distribution of species. This happens to be the same distribution normally obtained by polycondensation without the occurrence of interchange.

Theoretical

The Equilibrium Distribution.—From a consideration of the kinetics of condensation polymerization, it has been shown that the molecular size distribution in linear condensation polymers containing equal numbers of the two co-reacting functional groups (e. g., OH and COOH) is given by

$$N_x = Np^x - {}^1(1 - p) \qquad (1)$$

where N_x is the number of molecules composed of x monomer units, N is the total number of molecules and p is the extent of reaction, i. e., the fraction of the functional groups which have condensed. Rate of reaction measurements[5] show the reactivity of a terminal functional group to be independent of the size of the molecule. Hence, the probability that any particular functional group has reacted is equal to the extent of reaction p. Equation (1) follows directly from statistical considerations.

In deriving (1) from this point of view it is assumed that once a given pair of functional groups condense, they remain forever united. If an interchange process such as ester interchange occurs, the ultimate distribution will be determined by the equilibria between the various polymer species, not by the rates of their initial formation through condensation. If the free energy of formation of a linkage between an x-mer and a y-mer is independent of x and y, then after equilibrium has been established through interchange, the probability that a particular functional group constitutes a part of an inter-unit linkage remains equal to the degree of conversion

(4) P. J. Flory, THIS JOURNAL, **58**, 1877 (1936).
(5) P. J. Flory, *ibid.*, **61**, 3334 (1939).

p, and the distribution (1) should obtain as before.[6]

The distribution (1) for the "equilibrated" linear polyester can be derived in a manner analogous to the derivation of the Maxwell–Boltzmann energy distribution law. We consider a polymer wherein interchange may occur freely, but in which the net degree of advancement of the inter-unit condensation process is fixed. Here

$$\sum_{x=1}^{\infty} N_x = N \qquad (2)$$

$$\sum_{x=1}^{\infty} xN_x = n_0 \qquad (3)$$

where n_0 is the total number of units and

$$N = n_0 (1 - p) \qquad (4)$$

Both n_0 and N are constant under the conditions. Equations (2) and (3) are analogous, respectively, to the conditions of conservation of matter and of energy in the Maxwell–Boltzmann derivation.[7] Here we define a micro state as one in which the size x of each molecule is specified. A macro state is defined merely by the numbers of molecules of the various sizes, i. e., by N_1, N_2, N_3, etc. For a given macro state there are

$$W = N!/\Pi N_x! \qquad (5)$$

micro states. Solution of (5) for the maximum value of W consistent with (2) and (3) by the usual variational method yields (1) for the most probable macro state. Thus, under the assumption that the thermodynamic stability of a given inter-unit bond is independent of the size of the molecule and of its position along the chain, the equilibrium distribution ultimately attained by interchange processes is identical with that obtained by random synthesis. The difference in entropy between a mole of a heterogeneous polymer and a mole of the single species of molecular weight equal to the number average molecular weight for the heterogeneous polymer is given by the entropy of mixing expression

$$\Delta S_h = -R\Sigma(N_x/N)\ln(N_x/N) \qquad (6)$$

which may be called the molar entropy of hetero-

(6) "Equilibration" of the distribution of species in a polyester containing a small amount of water, which impedes further increase in p, could take place through simultaneous hydrolysis and esterification as well as by ester interchange. In this connection, see G. V. Schulz, *Z. physik. Chem.*, **A182**, 127 (1938).

(7) F. T. Wall, THIS JOURNAL, **62**, 803 (1940), has applied this method to the derivation of the distribution of sequences of like units in random vinyl copolymers. In as much as no interchange subsequent to formation of the polymer chains may occur in this case, it is not immediately obvious that the "most probable" state will be obtained.

geneity. For the most probable distribution, substitution of (1) in (6) gives

$$\Delta S_h = R[\ln(p/1 - p) - (\ln p)/(1 - p)] \quad (7)$$

which also can be obtained directly from the Boltzmann relation $S = k \ln W$, where W is taken to be $W_{max.}$ in (5). For a high molecular weight polymer p is near unity and

$$\Delta S_h \cong R[1 - \ln (1 - p)] \quad (7.1)$$

or

$$\Delta S_h \cong R[1 + \ln (\overline{DP}_n)] \quad (7.2)$$

since the number average degree of polymerization is given by

$$\overline{DP}_n = 1/(1 - p) \quad (8)$$

For the entropy of heterogeneity per mole of *structural units*, we have

$$\Delta S_h' = \Delta S_h/\overline{DP}_n \quad (9)$$

These equations express the maximum entropy of heterogeneity, or entropy of mixing, for a given degree of polymerization. Any distribution other than (1) will yield a lower entropy of heterogeneity. The entropy per mole of *polymer* molecules ΔS_h increases without limit as p approaches unity and $\overline{DP}_n$ approaches infinity; the entropy per mole of *structural units* $\Delta S_h'$, after reaching a maximum at a very low degree of polymerization, decreases asymptotically toward zero as $\overline{DP}_n$ increases.

Reorganization in Mixtures.—Since direct synthesis by polycondensation gives at once an equilibrium distribution, in order to observe the effects of interchange it is first of all necessary to obtain some other distribution. A product of greater homogeneity could be obtained by fractional precipitation. When subjected to interchange conditions, its distribution should broaden into the most probable one. An alternative method has been used here. Mixtures of greater heterogeneity have been obtained by mixing two normal products of synthesis, one of low and the other of high average molecular weight. The ensuing homogenization toward the most probable distribution was followed by means of viscosity measurements on the molten mixture.

The viscosity of the melt depends on the weight average chain length $\overline{Z}_w$ according to the relationship[2]

$$\log \eta = A + C \overline{Z}_w^{1/2} \quad (10)$$

where A and C are constants, and the weight average chain length is defined by

$$\overline{Z}_w = \Sigma w_x Z_x \quad (11)$$

where w_x is the weight fraction of x-mer. Whereas the number average chain length

$$\overline{Z}_n = \Sigma (N_x/N) Z_x \quad (12)$$

is unaffected by interchange, a transformation in the distribution will produce changes in the weight average chain length $\overline{Z}_w$, which may be calculated from viscosities using (10).

The decamethylene adipate polyesters which have been used are of two types. In the one case, the polymers possessed carboxyl and hydroxyl groups in equivalent quantities; in the other, an excess of glycol was used and the reaction was carried to completion, yielding a product having hydroxyl end-groups exclusively. For polymers of the former type

$$w_x = xp^{x-1}(1 - p)^2 \quad (13)$$

which can be derived from (1),[2,4] and

$$\overline{Z}_n = z/(1 - p) \quad (14)$$

$$\overline{Z}_w = z(1 + p)/(1 - p) \quad (15)[4]$$

$$= 2 \overline{Z}_n - z \quad (16)[2]$$

where z is the mean number of chain atoms per unit. ($z = 9$ for polydecamethylene adipate.) For the mixture composed of weight fractions f_1 and f_2 of polymers characterized by p_1 and p_2, respectively, the averages for the initial mixture are

$$\overline{Z}_n' = \overline{Z}_{n,1} \overline{Z}_{n,2}/(f_1 \overline{Z}_{n,2} + f_2 \overline{Z}_{n,1}) \quad (17)$$

$$= z/(1 - p') \quad (17.1)$$

where $\quad p' = f_1 p_1 + f_2 p_2$

$$\overline{Z}_w' = f_1 \overline{Z}_{w,1} + f_2 \overline{Z}_{w,2} \quad (18)$$

After equilibration through ester interchange (in the absence of either further esterification or of hydrolysis) $\overline{Z}_n'$ remains unchanged, but $\overline{Z}_w'$ becomes

$$\overline{Z}_w'' = z(1 + p')/(1 - p') = 2\overline{Z}_n' - z \quad (19)$$

Under the conditions of the experiments reported below, esterification occurs simultaneously with ester interchange, though at a slower rate. Consequently, p' increases slowly during the experiments. Nevertheless, the weight average chain length ultimately should reach a value given by (19), wherein p' is time dependent.

For polyesters prepared from r moles of dibasic acid per mole of glycol, the reaction being carried to completion[3,4]

$$w_x = [(zx + \alpha)r^{(x-1)/2}(1 - r)^2]/[z(1 + r) + \alpha(1 - r)] \quad (20)$$

and

$$\overline{Z}_n = z(1 + r)/(1 - r) + \alpha \quad (21)$$

where α is an "end-group correction" which may be taken equal to three in the present instance.[3]

From statistical considerations analogous to those used in the derivation of (1) and (15)[2,3]

$$\bar{Z}_w = 2z(1 + r)/(1 - r) = 2(\bar{Z}_n - \alpha) \quad (22)$$

For the mixture of two such polymers, $\bar{Z}'_n$ is given by (17). In this case further esterification is not possible, and equilibration of the mixture through ester interchange yields

$$\bar{Z}_w'' = 2(\bar{Z}_n' - 3) \quad (23)$$

Experimental Results

The methods used for the preparation of the polyesters and for the measurement of their viscosities in the molten state have been described previously.[2,3] Polymers A and B were prepared by heating excess quantities of decamethylene glycol with adipic acid at 109° in the presence of about 0.1% by weight of p-toluenesulfonic acid until the viscosity showed no further change, indicating complete esterification of the adipic acid. In the preparation of Polymer A the mixture was heated sixty hours; for Polymer B twenty-five hours was sufficient for substantially complete esterification.

Data pertaining to these polymers are given in the second and third columns of Table I. The reactants were of high purity,[2] and the quantities used were carefully weighed. At the low temperature of reaction the amounts of glycol removed with effluent water vapor formed in the esterification were negligible. For these reasons the values of r given in the first row of Table I are believed to be accurately representative of the final products. The number average chain lengths given


Fig. 1.—Size distribution (weight fraction $vs.$ number of units) for the initial polymers A and B (curves 1 and 2, respectively), for the mixture composed of 42.4% of A and 57.6% of B (curve 3), and for the calculated equilibrium distribution for the mixture (curve 4).

in the second row have been calculated directly from r. Computation of the weight average chain lengths from r (third row of Table I) involves acceptance of the size distribution relationship (20). The constants which have been used in equation (10), $i. e.$

$$\log \eta = -1.435 + 0.1144 \, \bar{Z}_w^{1/2} \quad (10')$$

for the calculation of the viscosities given in the fourth row of the table have been established at 109° for decamethylene adipate polymers having hydroxyl and carboxyl end-groups in equal numbers.[2] The discrepancies between observed and calculated viscosities for the two polymers are doubtless due to minor dependence of the viscosity relationship on the end-groups.[8]

TABLE I

	Polymer A	Polymer B	Calcd. for mixture[a]	
			Initial	Equilibrium
Molar ratio r of acid to glycol	0.955	0.855	0.896	0.896
$\bar{Z}_n$ calcd. from r using (21)	394	118	168	168
$\bar{Z}_w$ calcd. from r using (22)	782	230	464[b]	330
η at 109°, calcd. from $\bar{Z}_w$ using (10')	58.2	2.00	10.7	4.40
η at 109°, poises (obs.)	51.9	1.78		4.15
$\bar{Z}_w$ calcd. from η (obs.) using (10')	758	217		322

[a] The mixture composed of 42.4 weight per cent. of Polymer A and 57.6% of Polymer B. [b] Calculated for the initial mixture prior to interchange using (18).

The distributions of species calculated from (20) for Polymers A and B are shown by curves 1 and 2 in Fig. 1. A mixture consisting of 42.4% by weight of A and 57.6% of Polymer B was employed in the interchange experiment. The distribution curve for the initial mixture, computed by multiplying ordinate values of curve 1 by 0.424 and those of curve 2 by 0.576 and taking the sum, is represented by the broken curve 3. Computed initial values of r, $\bar{Z}_n'$, $\bar{Z}_w'$ and η are given in Table I. Inasmuch as there is no possibility for an increase in the number of inter-unit bonds in the mixture, $\bar{Z}_n'$ must remain fixed during interchange. According to the theory presented above, the distribution of species should be transformed by interchange to the most probable distribution (20), r having the value given in Table I. This distribution is shown by curve 4 in Fig. 1.

(8) See pp. 2256, 2259 of ref. 3.

The weight average chain length for the final distribution 4 is considerably less than that for the initial distribution 3; the calculated viscosities differ correspondingly (see Table I).

The experimental results of this interchange experiment carried out at 109° are given in Table II. As has been observed previously in experiments on polyester mixtures, from fifteen to thirty minutes is required before complete mixing has occurred.[2] Interchange in the present instance is quite rapid due to the presence of an acid catalyst.[3] Hence, a valid extrapolation to the initial viscosity of the mixture prior to interchange is not possible from these data. The final viscosity is somewhat lower than that calculated from (10') for the most probable distribution (see Table I), but the discrepancy is of the order of that to be expected to result from the inaccuracy of (10') as applied to hydroxyl terminated polymers.[8]

TABLE II

Time, minutes	Viscosity, poises at 109°
29	6.85
62	5.80
103	5.06
156	4.72
200	4.52
281	4.38
345	4.33
420	4.27
535	4.17
840	4.15

Other interchange experiments have been carried out on decamethylene adipate polyesters having equivalent quantities of hydroxyl and carboxyl end-groups. These were prepared by heating equimolar quantities of the pure glycol and dibasic acid, in the absence of catalyst, until the desired degree of polymerization was reached. Glycol carried out of the reaction mixture with the slow stream of dry nitrogen, used to remove water, was carefully replaced in order to assure sufficiently precise balance between the two end-groups. Polymer C, prepared by heating the reactants at 202° for twenty-nine hours, had a viscosity at 109° of 164 poises. According to (10') and (16), $\overline{Z}_w = 1017$ and $\overline{Z}_n = 513$. For Polymer D, prepared by heating for two hours at 166°, $\eta_{109°} = 0.532$ poise; accordingly, $\overline{Z}_w = 103.0$ and $\overline{Z}_n = 56.0$. Neutral equivalents of the polymers were in close agreement with those calculated from these values of $\overline{Z}_n$, indicating satisfactory equivalence of the end-groups.

Table III presents a portion of the data for the interchange experiment performed on a mixture consisting of 40% of Polymer C with 60% of Polymer D. The mixture was heated at 109° in a dry nitrogen atmosphere.[9] The weight average chain lengths given in the third column have been computed, using equation (10'), from the measured viscosities given in the second column. Interchange is much slower than in the preceding experiment, due to the absence of an acid catalyst other than is furnished by the unreacted carboxyl end-groups. During the course of the experiment some inter-esterification continued to take place, as is shown by the neutral equivalents given in the fourth column. These were determined by titration of samples removed from the mixture. Values of $\overline{Z}_n$ calculated directly from the neutral equivalents, or number average molecular weights, are given in the fifth column. If interchange equilibrium were fully established, the weight average chain length should equal $2\,\overline{Z}'_n - 9$, according to the theory given above. These "equilibrium" values are presented in the sixth column. The corresponding viscosities calculated using (10') are given in the last column. The above theory requires that eventually the weight average chain lengths given in the third and sixth columns should coincide; or, the viscosities in the second and last columns should become identical.

TABLE III

INTERCHANGE BETWEEN MIXTURE CONSISTING OF 40 PARTS POLYMER C AND 60 PARTS POLYMER D (PARTIAL TABULATION ONLY)

Time, minutes	η poises, 109°	$\overline{Z}_w$	Neutral equivalent	$\overline{Z}_n'$	$\overline{Z}_w''$ (equil.)	η (equil.)
0	(11.0)[a]	(468.6)[a]		87.0	165.0	1.08
29	9.60	446.5				
68	7.85	414.8				
72			1392	87.5	166.0	1.09
109	6.38	383.3				
187	4.73	340.1				
315	3.54	300.8				
448	2.93	276.1				
625	2.53	258.4				
784	2.43	253.3	1599	101.2	193.4	1.43
947	2.40	251.7				
1125	2.42	252.7				
1270	2.44	253.6	1767	111.8	214.6	1.74

[a] Values computed for the initial mixture.

The data from this experiment are shown in full

(9) The experiments on mixtures of Polymers C and D are continuations of two of those reported previously[2] in connection with determinations of viscosities of polyester mixtures prior to interchange. It may be noted that the chain lengths of Polymers C and D differ slightly from those employed previously (Ref. 2, Table II, Series II). This discrepancy, which is of no real significance in either investigation, is due to inadvertent use, in the earlier tabulation, of constants in (10) which differ slightly from those used here.
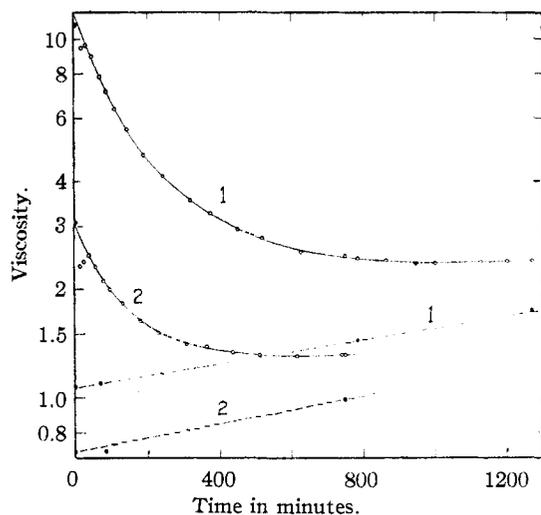
Fig. 2.—Experimental results for mixtures of Polymers C and D.

in Fig. 2. The solid curve 1 represents the observed viscosities (second column of Table III), plotted on a log scale merely for convenience. The dashed curve represents the viscosities (last column of Table III) calculated for interchange equilibrium for the observed neutral equivalent. Similar results obtained at 109° using a mixture composed of 19.7% of Polymer C and 80.3% of Polymer D are represented by the solid and dashed curves 2 in Fig. 2. In each experiment the observed viscosity decreases to a minimum and then increases. During this latter stage the effect on the viscosity of the rate of change in distribution due to interchange is outweighed by the rate of interesterification. When interchange equilibrium has been established, the solid and dashed curves should coincide according to the theory presented herein. To the extent that they are asymptotic, this theory is confirmed.

Discussion

The similarity in rates of ester interchange and esterification assures simultaneous occurrence of interchange during the synthesis of a polyester by interesterification. The distributions of species in normal products of synthesis, such as those from which the mixtures were prepared, are determined to a large extent by interchange equilibria. It could be contended, therefore, that if it is permissible to assume, as has been done above, that the distributions in the initial polymers A, B, C and D are correctly represented by (1) and (13), or (20), these equations necessarily will apply to their mixtures after equilibration through interchange.

The above experimental results cannot be regarded as *explicit* experimental proof of adherence to (1), (13) and (20). They demonstrate convincingly, however, that the ultimate transformations of the size distributions in the mixtures are consistent with these equations. To this extent, these results confirm implicitly the correctness of the statistically calculated distributions. Previously they have received indirect substantiation from their applicability to the analysis of viscosities of polymer mixtures,[2] and to the degradation of polyesters by alcohols.[3]

The question may arise as to how one might synthesize a linear polyester having some other distribution. The conversion of cyclic esters to linear polyesters, investigated extensively by Carothers and co-workers,[10,11] is of particular interest in this connection. They have shown[10] that the conversion of the cyclic monomer to linear polymer is conditioned by the presence of small amounts of substances capable of providing functional groups to which the monomers may add successively. For example, in the case of a cyclic ester such as δ-valerolactone, a trace of water may yield the hydroxy acid, with which the lactone may then react as follows

$$\text{HORCOOH} \xrightarrow{+ \overset{\frown}{\text{ORCO}}} \text{HORCOORCOOH} \xrightarrow[\text{etc.} \quad (24)]{+ \overset{\frown}{\text{ORCO}}}$$

The addition of the lactone to the linear molecule of increasing length is an ester interchange,[12] which may be very rapid or negligibly slow, depending on the stability of the cyclic monomer, which in turn depends on the size of the ring.[10,11] Bezzi and co-workers[13] have found that lactide is similarly converted to a linear polymer of lactic acid and at a rate which depends directly on the amount (very small) of water added. On the basis of this observation they have discarded the Carothers mechanism (24) in favor of a process consisting of hydrolysis of the lactide followed by polymerization by interesterification. Actually their results do not contradict the much more plausible mechanism (24). Addition of water merely in-

(10) W. H. Carothers, G. L. Dorough and F. J. van Natta, THIS JOURNAL, **54**, 761 (1932).

(11) See also, W. H. Carothers, J. A. Arvin and G. L. Dorough, *ibid.*, **52**, 3292 (1930); W. H. Carothers, *Chem. Rev.*, **8**, 353 (1931); J. W. Hill and W. H. Carothers, THIS JOURNAL, **55**, 5031 (1933); F. J. van Natta, J. W. Hill and W. H. Carothers, *ibid.*, **56**, 455 (1934).

(12) Since esters generally interchange with alcohols much more readily than with acids, it is presumed that addition of lactone in (24) occurs predominantly at the hydroxyl end of the chain.

(13) S. Bezzi, L. Ricoboni and C. Sullam, *Mem. accad. Italia, Classe sci. fis., mat. nat.*, **8**, 127 (1937); S. Bezzi and B. Angeli, *Gazz. chim. ital.*, **68**, 215 (1938).

creases the concentration of functional groups to which monomers may add, thereby increasing the over-all rate of conversion of monomer to polymer.

Successive addition of cyclic ester monomers to a fixed number of molecules bearing a suitable functional group (e. g., OH) as in (24) is strictly analogous to the polymerization of ethylene oxide,[14] for which the distribution of species is represented by Poisson's distribution function[15]

$$N_x = Ne^{-\nu}\nu^{x-1}/(x-1)! \qquad (25)$$

where

$$\nu = \overline{DP}_n - 1$$

The entropy of heterogeneity for this distribution, obtained by substituting equation (25) in (6) (see Appendix), is given to a close approximation when the degree of polymerization is large by

$$\Delta S_h = \frac{R}{2}[1 + \ln(2\pi\overline{DP}_n)] \qquad (26)$$

The distribution (25) covers a much narrower range than the equilibrium distribution. Correspondingly, its entropy of heterogeneity is less than for the equilibrium distribution as given by equation (7.2). Therefore, if interchange between polymer molecules occurs, the distribution (25) will be broadened toward the equilibrium distribution (1).

The actual distribution of species which will be obtained from the conversion of a cyclic monomer to linear polymer will depend on the extent to which polymer–polymer interchange accompanies the primary addition process (24). If the latter process, an ester interchange between a terminal functional group and a cyclic monomer, is much more rapid than interchange with ester groups of the polymer molecules, the comparatively sharp Poisson distribution (25) will be obtained. In the opposite situation, the more heterogeneous equilibrium distribution (1) should be found. In intermediate cases, distributions of intermediate heterogeneity will be produced.

Other condensation polymers, e. g., the polyamides and polyanhydrides investigated by Carothers and co-workers,[11] are subject to analogous interchange processes. These doubtless can be treated in complete analogy with the polyesters. The concept of a most probable distribution is equally applicable to three-dimensional condensation polymers, although the situation here becomes much more complex. The most probable distributions for equal stability of all possible inter-unit linkages have been treated by statistical methods in previous publications[16] on three-dimensional polymers.

Appendix

Entropy of Heterogeneity for a Poisson Distribution of Species.—Substituting equation (25) in (6)

$$\Delta S_h = Re^{-\nu}$$
$$\sum_{x=1}^{\infty} \left\{ \frac{\nu^{x-1}}{(x-1)!} [\nu - (x-1)\ln \nu + \ln (x-1)!] \right\}$$

Shifting the lower limit on the summation to $x = 0$ and replacing x by $x + 1$, and introducing Stirling's approximation for $\ln x!$

$$\Delta S_h = R\left[e^{-\nu} \sum_{x=0}^{\infty} \frac{\nu^x}{x!}\left(\nu - x + \frac{1}{2}\ln 2\pi\right) + \right.$$
$$\left. e^{-\nu} \sum_{x=0}^{\infty} \frac{\nu^x}{x!} x \ln (x/\nu) + \frac{e^{-\nu}}{2} \sum_{x=0}^{\infty} \frac{\nu^x}{x!}\ln x \right] \quad (27)$$

Since $\sum_{x=0}^{\infty} \frac{\nu^x}{x!} = e^\nu$, the first summation reduces readily to $\frac{R}{2} \ln (2\pi)$. The second and third terms may be evaluated by approximate methods valid when ν is large. Nearly all of the contributions to these sums come in the vicinity of $x = \nu$. Hence, in the case of the second term, we expand $\ln (x/\nu)$ about $(x/\nu) = 1$, giving

$$e^{-\nu} \sum_{x=0}^{\infty} \left\{\frac{\nu^x}{x!} x \left[\left(\frac{x}{\nu} - 1\right) - \frac{1}{2}\left(\frac{x}{\nu} - 1\right)^2 + \frac{1}{3}\left(\frac{x}{\nu} - 1\right)^3 - \cdots\right]\right\}$$

Summation over five terms of the series yields

$$1 - \frac{1}{2}(1 + 1/\nu) + \frac{1}{3}(4/\nu + 1/\nu^2) - \frac{1}{4}(3/\nu + 11/\nu^2 + 1/\nu^3) + \frac{1}{5}(25/\nu^2 + 26/\nu^3 + 1/\nu^4)$$

To a very close approximation when ν is large, the second term is given therefore by

$$\frac{1}{2}(1 + 1/6\nu) \cong \frac{1}{2}$$

The third term may be written

$$\frac{e^{-\nu}}{2} \sum_{x=0}^{\infty} \frac{\nu^x}{x!}[\ln(x/\nu) + \ln \nu]$$

Expanding $\ln (x/\nu)$ in series as above and summing each term, we obtain a power series in $1/\nu$ the first term of which is $-1/2\nu$. Hence, the contribution of the third term is

$$\frac{1}{2}[\ln \nu - 1/2 \nu + \cdots]$$

(14) H. Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932; S. Perry and H. Hibbert, THIS JOURNAL, **62**, 2599 (1940).

(15) P. J. Flory, THIS JOURNAL, **62**, 1561 (1940).

(16) P. J. Flory, ibid., **63**, 3083, 3091, 3096 (1941).

Combining the above values for the three terms in (27)

$$\Delta S_h = \frac{R}{2}[\ln(2\pi\nu) + 1 - 1/3\nu - \ldots] \qquad (28)$$

Equation (28) reduces to (26) when ν is replaced by $\overline{DP}_n$ and series terms of the order of $1/\nu$ or smaller are neglected.

Summary

The individual molecules of a linear polyester have only a temporary existence when heated to a suitable temperature, due to the occurrence of ester interchange between an ester group of one polymer molecule and the terminal functional group of another. While such processes have no effect on the number average degree of polymerization, they may modify the distribution of species.

Such considerations lead to the concept of an entropy of heterogeneity and of an equilibrium size distribution; the latter is identical with that obtained directly by random poly-condensation.

The transformation in the distribution of species in a mixture of polyesters has been observed by viscosity measurements. The results confirm the theoretical predictions.

The conversion of a cyclic ester (lactone) to a linear polyester should yield a much narrower distribution of species than is obtained by poly-condensation, but if ester interchange occurs between the polymer molecules subsequent to their initial formation, the distribution will be broadened.

Dipole Moments in the Vapor State and Resonance Effects in Some Substituted Benzenes

BY EVERETT C. HURDIS AND CHARLES P. SMYTH

The influence of resonance upon the dipole moment of a molecule containing a single polar group has been observed in both aromatic and unsaturated aliphatic molecules and the mutual effects of two polar groups in an aromatic molecule have been noted in a few cases, such as that of p-nitroaniline. In the case of two identical groups para to one another on the benzene ring, these mutual effects upon the dipole moments cancel each other and cannot, therefore, be detected, while in the ortho position, the mutual inductive effects of the two groups tend to obscure any effect of the resonance of one upon that of the other. It was hoped that, in spite of the smallness of the differences between the different carbon–halogen moments, accurate determinations in the vapor state of the moments of para-dihalogenated benzenes containing two different halogens might give quantitative evidence of the differences in resonance effects of the halogens. Unfortunately, the possibility of the presence of small quantities of the ortho-disubstituted benzenes as impurities in the samples of the para-compounds, which were too small for extensive purification, reduces the presumed accuracy of the results obtained for these compounds. Measurements upon iodo-benzene and confirmation of moment values al-

ready in the literature for chloro- and bromoben-zene were carried out to check the precision of the measurements and facilitate the interpretation of the results for the dihalogenated benzenes. Measurements were also made upon very pure samples of o-xylene and p-xylene with the object of observing possible small mutual induction or resonance effects of two adjacent methyl groups and of checking the group moment value to be assigned to a methyl group attached to a benzene ring.

Purification of Materials

Chlorobenzene.—Material from the Eastman Kodak Company was dried over calcium chloride and fractionally distilled; b. p. 130.5° (755 mm.).

Bromobenzene.—Material from the Eastman Kodak Company was dried over calcium chloride and fractionally distilled; b. p. 154.7° (753 mm.).

Iodobenzene, Sample I.—Material from the Paragon Testing Laboratories was fractionally distilled in a column of fourteen theoretical plates; b. p. 188.3° (762 mm.).

Iodobenzene, Sample II.—Iodobenzene was prepared by the method of "Organic Syntheses," Collective Volume I, p. 316, an all glass system being used. Fractionation gave 234 g. of material boiling between 188.2 and 188.5° (760 mm.). This was further distilled under low pressure, the main fraction (b. p. 98° at 37 mm.) being used for the measurements. The freezing point of this sample was measured by means of a platinum resistance thermometer