Radioactive isotopes, Sr,^{89} with a half-life of fifty-five days, and Ba^{133}, half-life of thirty-nine hours, were used as tracers.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymer Properties as Functions of Conversion[1]

BY FREDERICK T. WALL

When a polymerization reaction is carried out by a batch process, the product obtained will generally exhibit considerable heterogeneity. This heterogeneity is a direct consequence of the fact that the conditions under which the polymerization takes place are constantly changing as the reaction proceeds. Only for a process in which the reaction environment is kept constant can one expect a product possessing a high degree of homogeneity.

In this connection it should be noted that mechanical continuity of polymerization does not necessarily give rise to constancy of reaction conditions.[2] For example, if a batch or a series of batches are moved through a number of reactors (or through a reaction pipe) while polymerization takes place, mechanical continuity can be realized without attaining uniform reaction environment. To attain uniform conditions it would be necessary to have a steady introduction of raw materials into the reactor accompanied by a steady withdrawal of final product. Such a state of affairs would be difficult, if not impossible, to attain for many polymerization systems, especially those occurring in emulsion.

Recognizing that most polymerizations involve marked variations in the conditions of reaction, it naturally becomes of interest to learn something about the nature of the polymer which forms at each instant during the conversion. For this reason experiments are frequently carried out involving the measurement of various properties at different stages of conversion. Properties most frequently investigated with this idea in mind are the intrinsic viscosity, molecular weight and, in the case of copolymers, composition of the product. Although such measurements constitute a necessary step in the right direction, they do not go far enough, since they do not describe the character of the polymer formed at any given instant. This is true because the measurements are almost invariably carried out on all of the polymer formed up to the conversion of interest; hence the measurements represent over-all average values and not increment values. There will now be derived some equations by means of which such "average" data can be analyzed to obtain the properties of polymer increments.

Weight Average Properties as Functions of Weight Conversion.—Let us first consider a property which for a heterogeneous system averages by weight. Examples of such properties are weight average molecular weight, intrinsic viscosity (but not viscosity average molecular weight, except approximately),[3] weight per cent. of a given monomer in a copolymer, etc. If g represents such a property for any given increment and if W is the weight conversion, then by definition the average value of the property corresponding to a particular conversion will be given by

$$\bar{g} = \frac{\int_0^W g\mathrm{d}W}{\int_0^W \mathrm{d}W} = \frac{\int_0^W g\mathrm{d}W}{W} \tag{1}$$

Rearranging (1) there is obtained

$$\int_0^W g\mathrm{d}W = \bar{g}W \tag{2}$$

Differentiating (2) with respect to W, one obtains

$$g = \frac{\mathrm{d}}{\mathrm{d}W}(\bar{g}W) \tag{3a}$$

$$= \bar{g} + W\frac{\mathrm{d}\bar{g}}{\mathrm{d}W} \tag{3b}$$

It follows from equations (3) that if one knows $\bar{g}$ as a function of W, it becomes possible to obtain increment values. Equation (3a) suggests plotting $\bar{g}W$ *vs.* W and taking slopes; equation (3b) requires plotting $\bar{g}$ *vs.* W, taking slopes and then carrying out the indicated calculations. These methods are somewhat suggestive of those involved in determining partial molar quantities. Siggia, Hohenstein and Mark[4] have made use of this concept in connection with intrinsic viscosity.

Number Average Properties as Functions of Weight Conversion.—Let us now consider properties which form averages by numbers of molecules or moles. The most important example of such a property is the ordinary (or number average) molecular weight. Letting M equal the molecular weight and N the number of moles of polymer corresponding to a weight conversion W, we have by definition

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[1] The work reported in this paper was done in connection with the government research program on synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation (first reported in September, 1944).

[2] K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944).

[3] P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

[4] S. Siggia, W. P. Hohenstein and H. Mark, *India Rubber World*, **111**, 436 (1945).

$$\overline{M} = \frac{\int_0^N M\,\mathrm{d}N}{\int_0^N \mathrm{d}N} = \frac{\int_0^W \mathrm{d}W}{\int_0^W \frac{\mathrm{d}W}{M}} \tag{4}$$

Rearranging (4) it is seen that

$$\int_0^W \frac{\mathrm{d}W}{M} = \frac{W}{\overline{M}} \tag{5}$$

Differentiating with respect to W there is obtained.

$$\frac{1}{M} = \frac{\overline{M} - W\frac{\mathrm{d}\overline{M}}{\mathrm{d}W}}{\overline{M}^2} \tag{6}$$

or

$$M = \frac{\overline{M}^2}{\overline{M} - W\frac{\mathrm{d}\overline{M}}{\mathrm{d}W}} \tag{7}$$

Equation (7) can be used to calculate number average molecular weights of polymer increments when the over-all average ($\overline{M}$) is known as a function of conversion.

The general problem for any property that averages by number of molecules will now be treated. If h is such a quantity, then

$$\bar{h} = \frac{\int_0^W h\frac{\mathrm{d}W}{M}}{\int_0^W \frac{\mathrm{d}W}{M}} \tag{8}$$

Combining (8) with (5) there is obtained

$$\int_0^W \frac{h}{M}\,\mathrm{d}W = \frac{\bar{h}W}{\overline{M}} \tag{9}$$

Differentiating (9) with respect to W and combining the result with (7), one finds that

$$h = \bar{h} + \frac{\overline{M}W\frac{\mathrm{d}\bar{h}}{\mathrm{d}W}}{\overline{M} - W\frac{\mathrm{d}\overline{M}}{\mathrm{d}W}} \tag{10}$$

It will be noted that before (10) can be used to calculate increment values of h, it is necessary to know both $\bar{h}$ and $\overline{M}$ as functions of conversion.

Number Average Properties as Functions of Moles Polymer Conversion.—If $\bar{h}$, the number average value of some property, is known as a function of N, the conversion expressed in moles of polymer, then an equation different from (10) but similar to (3) will be obtained. For by definition

$$\bar{h} = \frac{\int_0^N h\,\mathrm{d}N}{\int_0^N \mathrm{d}N} = \frac{\int_0^N h\,\mathrm{d}N}{N} \tag{11}$$

Manipulating (11) in a manner similar to that employed in connection with equations (1) and (2), there is obtained

$$h = \frac{\mathrm{d}}{\mathrm{d}N}(\bar{h}N) \tag{12a}$$

$$= \bar{h} + N\frac{\mathrm{d}\bar{h}}{\mathrm{d}N} \tag{12b}$$

The use of equations (12) is obvious from previous considerations.

Weight Average Properties as Functions of Moles Polymer Conversion.—A weight average property given in terms of moles conversion gives rise to a somewhat more complicated increment formula. The derivation, however, parallels the previous derivations, for if g represents such a property, then

$$\bar{g} = \frac{\int_0^N gM\,\mathrm{d}N}{\int_0^N M\,\mathrm{d}N} = \frac{\int_0^N gM\,\mathrm{d}N}{\overline{M}N} \tag{13}$$

where $\overline{M}$ is the *number* average molecular weight. Multiplying through by $\overline{M}N$ and differentiating, it is seen that

$$gM = \bar{g}\overline{M} + \bar{g}N\frac{\mathrm{d}\overline{M}}{\mathrm{d}N} + \overline{M}N\frac{\mathrm{d}\bar{g}}{\mathrm{d}N} \tag{14}$$

But from equation (12) it follows that

$$M = \overline{M} + N\frac{\mathrm{d}\overline{M}}{\mathrm{d}N} \tag{15}$$

Hence from (14) combined with (15) one obtains

$$g = \bar{g} + \frac{N\overline{M}\frac{\mathrm{d}\bar{g}}{\mathrm{d}N}}{\overline{M} + N\frac{\mathrm{d}\overline{M}}{\mathrm{d}N}} \tag{16}$$

Equation (16) probably will not find frequent application. Like equation (10) its use requires more knowledge than just the relationship between the conversion and the average of the particular property under consideration.

Discussion

Of the several equations just derived, (3) and (7) will probably be found most useful. Equation (3) can be used not only in connection with intrinsic viscosity but also to analyze composition of copolymers. It thus provides a means of checking the theories of copolymerization recently developed by various authors.[5] The use of equation (3) does not depend upon the validity of any particular copolymerization theory, and hence can be applied as a direct test as soon as sufficient data are available.

There is, however, one important assumption involved in the foregoing derivations which should be made clear. It is assumed, once a polymer increment has been formed, that increment does not change in character as more polymer forms. This assumption is a very reasonable one as far as composition is concerned, but it may not be valid with respect to some other properties.

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(5) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); F. T. Wall, *ibid.*, **66**, 2050 (1944).

If the polymer which is formed early in the reaction should undergo a change during later stages of conversion, anomalous results might be obtained. For example, the reciprocal of the instantaneous molecular weight, $1/M$, which is given by equation (6), is equal to dN/dW. If it should be found at some stage of the polymerization that dN/dW were negative, one would have a proof of cross-linking. Obviously a negative molecular weight would be meaningless, but a negative value for dN/dW would be very meaningful. Cross-linking and branching might also affect "increment" intrinsic viscosities in an unusual but significant manner. Compositional analyses, however, should be free from any such anomalous effects.

Summary

Equations are derived by means of which "average" polymer data known as functions of conversion can be analyzed to give the properties of polymer increments forming at different stages of conversion. Suggestions are given as to the types of data which can be so studied and to possible interpretations of anomalous results.

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[CONTRIBUTION FROM THE IPATIEFF HIGH-PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, AND UNIVERSAL OIL PRODUCTS CO.]

Studies in the Terpene Series. IV.[1] Method for the Determination of Rings in Bicyclic Dihydroterpenes. Isomerization of Pinane in the Presence of Dilute Aqueous Salt Solutions

BY V. N. IPATIEFF AND HERMAN PINES

The study of the structure of bicyclic dihydroterpenic hydrocarbons could be greatly facilitated if the relative size of the various rings could be established. This has now been achieved by treating the various dihydroterpenic hydrocarbons with dilute aqueous acid-acting salt solutions at elevated temperatures and pressures, using experimental conditions given in a previous paper of this series.[2] From the present study of the action of 1–2% aqueous magnesium chloride solution upon cyclofenchene, pinane, isobornylane and isocamphane, it has been shown that the most stable bicyclic hydrocarbons are those containing a five-membered within a six-membered ring; less stable are those having a four-membered ring and the most reactive are those having a three-membered ring.

It was found that the cyclopropane ring in *cyclofenchene* underwent scission when this hydrocarbon reacted with aqueous magnesium chloride solution at 280°. Bicyclic olefinic hydrocarbons were formed which on hydrogenation yielded dihydrodicyclic hydrocarbons. The hydrocarbons, according to their properties and analysis, had the formula $C_{10}H_{18}$ and contained at least one five-membered ring.

Isocamphane when heated with the same catalyst to 400° underwent partial dehydrogenation; no rupture of the rings occurred. The product of the reaction on hydrogenation at 50° formed the original isocamphane, m. p. 62°.

Isobornylane was heated at 425° for several hours but remained without change.

It was found that in *pinane* the cyclobutane ring underwent rupture when it was heated at 350°, under pressure in the presence of an equal volume of a 2% aqueous solution of magnesium chloride. Under these conditions, the pinane did not yield the expected methylisopropylcyclohexene but underwent, mostly, isomerization into an unsaturated hydrocarbon containing a five-membered ring consisting, probably, of 1-ethyl-2-isopropylcyclopentene. The product of the reaction was distilled on a 45-plate column and the distillation curve (Fig. 1) showed a plateau at 157° corresponding to the five-membered-ring hydrocarbon and a plateau at 165°. The preliminary investigation showed that the higher product consisted mainly of unreacted pinane admixed with unsaturated monocyclic hydrocarbons, the structure of which we intend to study.

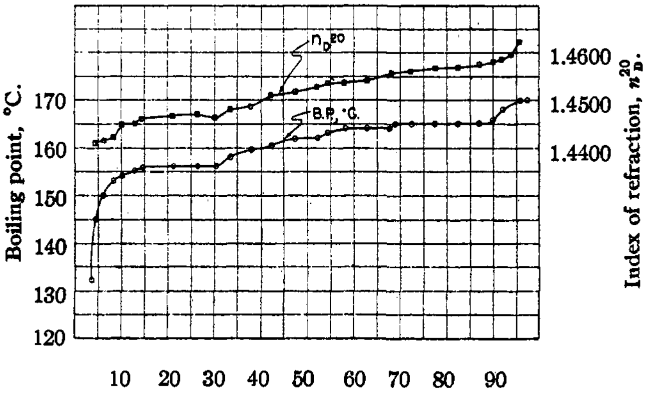

Fig. 1.

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[1] For paper III of this series see V. N. Ipatieff and H. Pines, THIS JOURNAL, 67, 1226 (1945).

[2] V. N. Ipatieff and H. Pines, *ibid.*, 66, 1120 (1944).