Properties of Polymers as Functions of Conversion. II. Intrinsic Viscosities[1]

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When a polymerization reaction is carried out, the products obtained at different stages of conversion will generally exhibit different properties. Thus, for example, the average intrinsic viscosity of the polymer may be low at low conversions and then become higher at later conversions. Such a behavior, however, does not mean that the polymer molecules necessarily change with time; instead the changes observed often mean that the new polymer increments are appreciably different from those which formed earlier. Of course, it is also possible for completed polymer molecules to react further in some polymerization systems, so the over-all effects observed can be a combination of several possibilities.

In an earlier publication,[4] equations were derived with which "increment" properties of a polymer could be calculated from average or cumulative properties if the latter were known as functions of the conversion. The equations depend to some extent upon the manner in which the particular property of interest forms its average for a heterogeneous system. Thus some properties average by weight whereas others average by number of molecules. In the case of intrinsic viscosity, which averages by weight, the formula is relatively simple providing the independent variable (conversion) is measured in terms of the weight of polymer formed.

Partial Conversion Properties

For discussing the nature of a polymerization reaction, we now find it convenient to define what shall be known as "partial conversion properties." The concept involved is in rough analogy to that of partial molar quantities which has proved so very useful in thermodynamics. The notions to be set forth here may well be valid for many systems not involving polymers, but the examples by means of which these ideas will be developed will be high polymer systems. The partial conversion properties are defined as the *apparent* properties of the polymer increments forming at different conversions in the polymerization process. They can be calculated by means of formulas derived earlier.[4]

At this time it will be important to distinguish between three different concepts, namely: (a) average or cumulative properties, (b) partial

conversion properties, and (c) true increment properties. The average or cumulative properties are precisely those which one measures on all the polymer which has formed up to a given conversion. From a knowledge of such properties it is possible to calculate the partial conversion properties. The true increment properties would be the properties of the *new* polymer corresponding to a given increment of conversion. As will be shown later it becomes very difficult and sometimes impossible to determine a true increment property because the over-all changes observed sometimes intimately involve old polymer interacting with the new material being formed. To distinguish between the three classes mentioned above we shall henceforth put a double bar over the symbol for a partial conversion property, a single bar over that of the average or cumulative property, and no bar over the symbol for the true increment property.[4a] Actually, we shall have little occasion to think of the true increment property as such but will confine our thoughts primarily to the other two.

The formula by which one calculates the partial conversion intrinsic viscosity is[4]

$$\overline{\overline{[\eta]}} = \overline{[\eta]} + W\frac{d\overline{[\eta]}}{dW}$$

where $\overline{[\eta]}$ is the average intrinsic viscosity of the polymer, W is the weight conversion, and $\overline{\overline{[\eta]}}$ is the partial conversion value. As noted earlier, as long as a given portion of polymer once formed does not undergo further changes, $\overline{\overline{[\eta]}}$ will also represent the true increment intrinsic viscosity of the polymer.

Experimental.

Intrinsic viscosity data have been determined for a number of polymers including polybutadiene and copolymers of butadiene with styrene, with acrylonitrile, with 2,5-dichlorostyrene, and with 2-vinylpyridine. Numerous other combinations have also been investigated, but only the typical examples enumerated above will be reported here. Since the cumulative data must be of high accuracy to give significant partial conversion values, the polymerizations and measurements were carried out with special care not ordinarily required in polymerization work.

The polymerizations were conducted at $50 \pm 0.5°$ in 32-oz. beverage bottles which were rotated end-over-end 20 times per minute. Samples of latex were withdrawn

from the reactor by means of hypodermic syringes[5] which were inserted and removed through self-sealing bottle caps. Before each withdrawal a small amount of β-naphthol dissolved in ethanol was introduced into the syringe to shortstop the latex as soon as it entered the syringe.

Conversions were determined by measurement of total solids. Two 5-g. portions of latex were ejected into tared aluminum foil dishes and the material dried in an oven. The conversions were calculated by using the formula

$$\text{Per cent. conversion} = \frac{\dfrac{571.1d}{w} - 11.6}{200} \times 100$$

where

d = weight of dried polymer and non-volatile material (corrected by subtracting 0.01 g. to allow for β-naphthol and phenyl-β-naphthylamine present in the aluminum dish).

w = weight of wet latex.

571.1 = total weight of charge.

11.6 = weight of non-volatile material in total charge.

200 = weight of total monomers.

The equation reduces to the final simple form

Per cent. conversion = $(286\ d/w) - 5.8$

In preparing samples for the determination of gel content and intrinsic viscosity, the latex was coagulated by ejecting about 5 g. with mechanical stirring into 50-ml. portions of ethanol containing 0.2 g. of phenyl-β-naphthylamine. Since the system was stirred rapidly and the latex added dropwise, small crumbs of polymer were formed which were easy to wash and dry. The polymer was washed four times with distilled water and finally with a solution similar to the coagulating medium in order to leave a film of antioxidant on the rubber.

Sol–gel separations were carried out using a modified Baker and Mullen cell.[6] Forty-eight hours were allowed for equilibration, using benzene as the solvent. Intrinsic kinematic viscosity determinations were made on the polymer solutions with calibrated Fenske–Ostwald viscosimeters.

Discussion

The butadiene–styrene copolymers which have been investigated had initial monomer ratios of 40/60, 60/40, 75/25 ($i. e.$, GR-S), 90/10 and 100/0 by weight. The results on conversion studies $vs.$ time for these polymers are shown in Fig. 1. In Fig. 2 are given the conversion $vs.$ time curves for other copolymer systems, as well as the GR-S curve for comparison. It will be noted that in most instances the polymerization appears to follow zero-th order kinetics up to about 60% conversion. The curves for copolymers with high butadiene contents appear to deviate from zero-th order kinetics somewhat sooner.

The intrinsic viscosity data are given in Figs. 3–8. Viscosity curves are not given for the 60/40 and 90/10 butadiene–styrene copolymers, however, since they fall in line with the tendencies exhibited by the others. In each figure there is given the experimentally observed cumulative results as well as the calculated partial conversion values. The experimentally determined quantities are indicated by circles, whereas the calcu-

(5) R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *Ind. Eng. Chem.*, In press.

(6) W. O. Baker and J. W. Mullen, unpublished results. L. W. White, E. S. Ebers, G. E. Shriver and S. Breck, *Ind. Eng. Chem.*, **37**, 770 (1945).
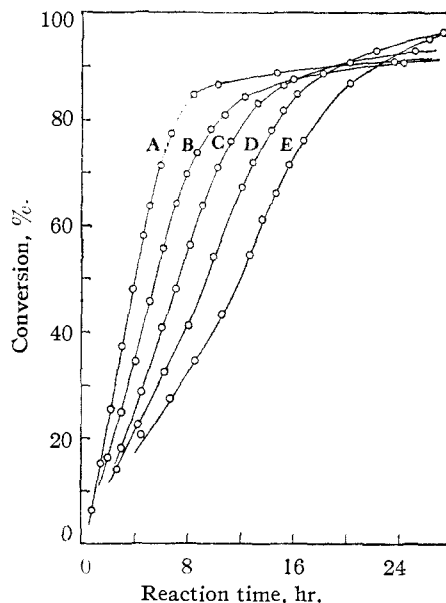
Fig. 1.—Conversion $vs.$ time curves for butadiene–styrene copolymers of different monomer ratios: A, B/S = 40/60; B, B/S = 60/40; C, B/S = 75/25; D, B/S = 90/10; E, B/S = 100–0.
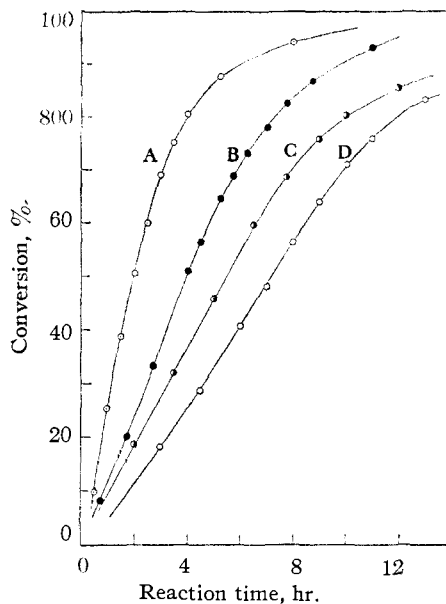

Fig. 2.—Conversion $vs.$ time curves for various copolymers: A, butadiene–acrylonitrile; B, butadiene-2-vinylpyridine; C, butadiene-2,5-dichlorostyrene; D, butadiene–styrene (GR-S).

lated partial conversion intrinsic viscosities are the smooth uninterrupted lines. Typical numerical data are given in Table I using the GR-S system as the example.

The graphs of average intrinsic viscosity $vs.$ conversion for the butadiene–styrene copolymers show several points of interest. The most striking and consistent feature is the large maximum ob-

TABLE I

GR-S (75/25 BUTADIENE/STYRENE)

Initial charge: 150.0 g. butadiene, 50.0 g. styrene, 0.5463 g. dodecylmercaptan, 350.0 g. of 3% solution of P. and G. SF flakes, 20.00 ml. of 3% solution of potassium persulfate.

No.		Reaction time, hr.	% Conversion Found		Av.	% Solubility Found		Av.	$[\eta]$ Found		Av.	$\overline{\overline{[\eta]}}$
1	2	3	18.2	18.2	18.2	100	99	100	1.10	1.18	1.14	1.68
3	4	4.5	29.3	28.3	28.8	100	99	100	1.43	1.36	1.40	2.12
5	6	6	41.1	40.7	40.9	99	99	99	1.63	1.60	1.62	2.08
7	8	7	48.3	48.0	48.2	99	99	99	1.62	1.58	1.60	1.60
9	10	8	56.5	56.5	56.5	100	99	100	1.76	1.78	1.77	3.20
11	12	9	63.9	64.2	64.0	99	99	99	1.94	1.93	1.94	3.94
13	14	10	71.4	71.0	71.2	99	100	100	2.32	2.28	2.30	8.46
15	16	11	75.6	76.8	76.2	100	99	100	2.78	2.79	2.78	3.55
17	18	13	83.4	..	83.4	77	89	83	2.48	2.26	2.37	−2.50
19	20	15	..	86.9	86.9	88	91	90	2.29	2.28	2.28	−5.25
21	22	20	91.9	90.4	91.1	69	69	69	1.58	1.56	1.57	....
23	24	25	93.5	92.9	93.2	81	71	76	1.07	1.05	1.06	....

served in every case around 75% conversion. The pronounced rise in viscosity represents an increase in molecular weight due in part to cross-linking. Moderate cross-linking will give rise to soluble molecules of high molecular weight, and, accordingly, of high viscosity. As cross-linking continues, however, gelation occurs, thereby removing the large molecules of high viscosity from the solution. The gel point occurs in the neighborhood of the peak in the viscosity curve and the rapid falling-off of viscosity after that point is due in part to the removal of the large molecules from solution. (It will be remembered that intrinsic viscosities can be measured only on the sol portion of a polymer.) It is also possible that degradation begins to occur at the high conversions, which would also tend to lower the viscosity. Taylor and Tobolsky[7] have discussed in some detail the radical chain processes by which the effects described above can take place.

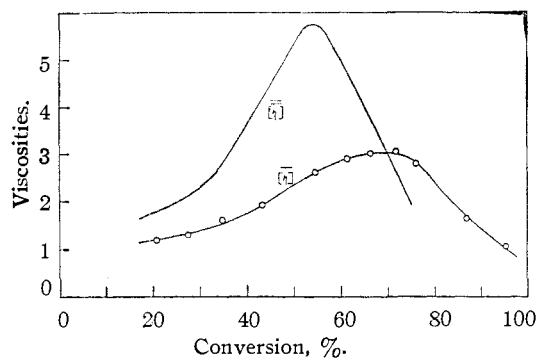Another effect to be noted is the pronounced change in the slope of the curves around 30%

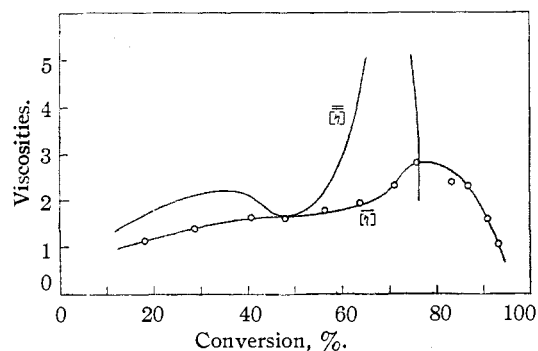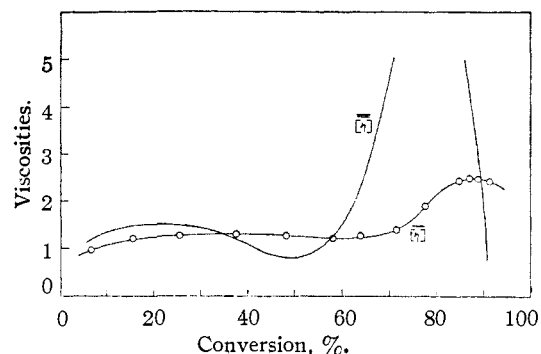Fig. 3.—Average and partial conversion intrinsic viscosities for polybutadiene.

Fig. 5.—Average and partial conversion intrinsic viscosities for 40/60 butadiene/styrene copolymer.

Fig. 4.—Average and partial conversion intrinsic viscosities for 75/25 butadiene/styrene copolymer (GR-S).
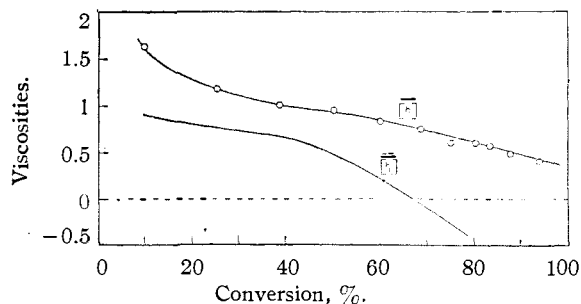

Fig. 6.—Average and partial conversion intrinsic viscosities for 75/25 butadiene/acrylonitrile copolymer.

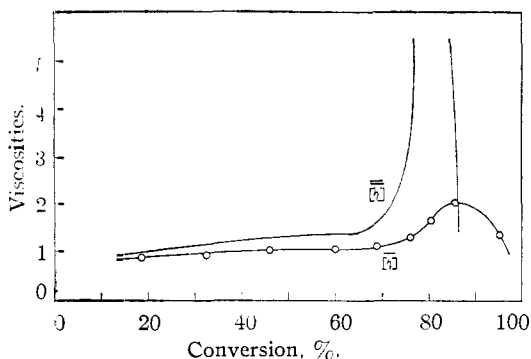(7) H. S. Taylor and A. V. Tobolsky, THIS JOURNAL, 67, 2063 (1945).

Fig. 7.—Average and partial conversion intrinsic viscosities for 75/25 butadiene/2,5-dichlorostyrene copolymer.

Fig. 8.—Average and partial conversion intrinsic viscosities for 75/25 butadiene-2-vinylpyridine copolymer.

conversion. With increasing styrene content the change in slope occurs at lower conversions and the effect increases until there is a definite minimum in the curve corresponding to the 40% butadiene copolymer. It will also be noted that the height of the larger peak increases and shifts to lower conversions as the ratio of butadiene in the charge is increased. This effect is explained by the increased probability of cross-linking as the butadiene content is increased.

The effects observed in the average intrinsic viscosities are much accentuated when one deals with the partial conversion properties. The partial conversion intrinsic viscosities go through a slight maximum during early conversions and through a very high maximum just before the gel point is reached. This high maximum may correspond to viscosities of 8 or 9 although the precise values cannot be determined with great accuracy. After they begin falling off, the partial conversion intrinsic viscosities drop to very low values and in fact become negative. Although a negative intrinsic viscosity is meaningless for an actual polymer, it does have meaning as far as the partial conversion property is concerned. This is true because the partial conversion properties reflect the effects of gelation and degradation as well as the character of the newly formed polymer.

Butadiene with 2-vinylpyridine and with 2,5-dichlorostyrene behaves in much the same way as it does with styrene. The copolymer with acrylonitrile, on the other hand, is markedly different. In this case the intrinsic viscosity steadily diminishes and the partial conversion viscosity falls off to zero in the neighborhood of 70% conversion and subsequently becomes negative. Since the solubility remains high, this behavior suggests the occurrence of chain scission by some degradative process.
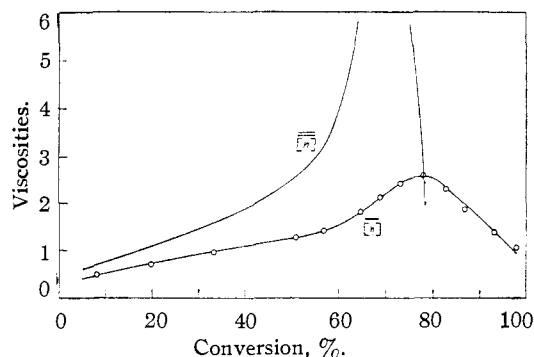
The partial conversion curves give much valuable information about the manner in which the polymerization proceeds. With the exception of the acrylonitrile copolymer, it appears that the polymer chains are fairly short at the beginning of the reaction and that they tend to increase with conversion as the effective modifier concentration decreases. At about 30–35% conversion there appears to be a resurgence of modifier action, thus reducing the chain lengths and causing the increment viscosity to decrease. The effects at higher conversions are clear from the graphs. The type of analysis described above has also been carried out by Siggia, Hohenstein and Mark[8] on polystyrene.

Summary

The concept of partial conversion properties of polymers is defined as an aid to understanding the different stages of a polymerization process. Partial conversion properties can be calculated from a knowledge of the average properties if the latter are known as functions of conversion.

Experimental data on the intrinsic viscosities and solubilities of various rubber-like polymers have been determined and the results interpreted from the partial conversion point of view. Polybutadiene and several copolymers with butadiene initially exhibit increasing viscosities with increasing conversion due in part to cross-linking reactions. At higher conversions the viscosity tends to fall off again because of gel formation and degradation. The copolymer of butadiene with acrylonitrile appears to behave differently for the viscosity starts out at its greatest value and steadily diminishes as the conversion is increased.

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