[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, THE CHEMSTRAND CORPORATION]

Branching in Polyacrylonitrile[1]

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Intrinsic viscosity molecular weight data have been obtained for low molecular weight fractions of a polyacrylonitrile–polyvinyl acetate copolymer containing less than 10% vinyl acetate. The data are more consistent with the Cleland and Stockmayer molecular weight equation for polyacrylonitrile than with other published equations. However, higher molecular weight fractions of polyacrylonitrile above $(\eta) = 3.0$ dl./g. do not follow the Cleland–Stockmayer equation. Light scattering and osmometry experiments show that polyacrylonitrile and the copolymer are broad in molecular weight distribution. This appears to be due to the presence of micro-gel in both cases rather than associated clusters. The micro-gel can only be separated from the soluble polymer by ultracentrifugation of very dilute solutions. High molecular weight fractions still curve away from the intrinsic viscosity molecular weight equation after the micro-gel has been removed which indicates that the polymer is branched.

Introduction

Of the values listed by Onyon[2] for the intrinsic viscosity molecular weight law for PAN, probably only three equations are of sufficient worth to be of practical use, those of Cleland and Stockmayer,[3] Bisschops[4] and Onyon,[2] which are listed as equations 1, 2 and 3, respectively.

$$(\eta) = 2.33 \times 10^{-4} M_w^{0.75} \qquad (1)$$

$$= 1.66 \times 10^{-4} M_w^{0.81} \qquad (2)$$

$$= 3.92 \times 10^{-4} M_n^{0.75} \qquad (3)$$

The Cleland–Stockmayer and Bisschops equations are based on weight average measurements: Stockmayer and Cleland's on especially prepared whole polymers determined by light scattering and Bisschops' on fractionated polymer determined by sedimentation–diffusion. Onyon's equation was also determined on especially prepared whole polymers but by, osmometry. There is a large discrepancy between the two weight average molecular weight equations. Since Stockmayer and Cleland's polymers were prepared by polymerization in solution to low conversion, the weight to number average molecular weight ratio of these polymers should be equal to 2.0. Onyon prepared similar polymers and measured the number average molecular weights by osmometry and found that they coincided with Stockmayer's data when adjusted for the effect of polydispersity.

It would be desirable to establish which of these equations, the Cleland–Stockmayer–Onyon or the Bisschops is more nearly correct. With this object, several preparations of polyacrylonitrile and polyacrylonitrile–polyvinyl acetate copolymer were fractionated in order to establish an intrinsic viscosity molecular weight equation. Since the vinyl acetate content of fractions of the copolymer did not vary with molecular weight (except for a small random scatter about the vinyl acetate content of the whole polymer due to the method of determination), it is believed that the small percentage of vinyl acetate in the copolymer, less than 10%, does not materially affect the dependence of molecular weight upon the intrinsic viscosity and the content of vinyl acetate makes the polymer easier to handle. The micro-gel fraction, recovered by ultracentrifugation, also had the same content of vinyl acetate.

Experimental

Polymers.—Copolymers of polyacrylonitrile and polyvinyl acetate were prepared by polymerization in aqueous suspension with persulfate–bisulfate initiator. Pure polyacrylonitrile was prepared either by aqueous suspension or by recipes of Cleland and Stockmayer.[3] Portions of these polymers were then fractionated and subjected to measurement. The vinyl acetate content was determined by an empirical relation between the infrared spectrum and percentage vinyl acetate.

Fractionation.—Ten grams of polymer was dissolved in 700 ml. of N,N-dimethylformamide (DMF) to which was added dropwise a 2:1 mixture of *n*-hexane and ether. At about 33% non-solvent a precipitate formed. Since the fractionation system would not redissolve the precipitate upon heating and a colloidal non-settling mixture occurred upon attempts to refractionate, only crude fractions could be obtained.

Osmometry.—Osmotic molecular weights were determined in High Speed Osmometers supplied by J. V. Stabin, Brooklyn, New York. Type 300 gel cellophane from the Film Division of American Viscose Corporation was conditioned first to 5% aq. NaOH then to DMF by Yanko's method.[5]

Light Scattering.—Weight average molecular weights were determined with a Brice Phoenix Photometer[6] in DMF and 436 mμ incident light in a cylindrical cell. Brice, Nutting and Halwer's[7] method was used to correct for the green fluorescence. A Hermans and Levinson[8] slit system was used before the photomultiplier tube. Zimm[9] plots were obtained for all high molecular weight material and the molecular weights were determined by both the Zimm and dissymmetry[10] methods. Solutions were clarified by centrifuging at 20,000 × *g*. Some of the later samples were first ultracentrifuged[11] at 144,000 × *g*, for 3 hr., dried, redissolved and then centrifuged at 20,000 × *g*. The instrument was calibrated by the internal opal glass standard. The calibration checked to within 5% of the values determined by Cornell Standard Polystyrene and by Ludox.

Results

Table I contains the molecular weights as determined by osmometry and by light scattering together with the intrinsic viscosity at 25° all measured in N,N-dimethylformamide. The sample numbers are followed by a letter which defines the type of polymer measured. In order to obtain sufficient quantity of polymer for measurement, sometimes several fractions with the same intrinsic

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[1] Presented at the 133rd National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

[2] P. F. Onyon, *J. Polymer Sci.*, **22**, 13 (1956).

[3] R. L. Cleland and W. H. Stockmayer, *ibid.*, **17**, 473 (1955).

[4] J. Bisschops, *ibid.*, **17**, 81 (1955).

[5] J. A. Yanko, *ibid.*, **19**, 437 (1956).

[6] Phoenix Precision Instrument Co., Phil., Pa.

[7] B. A. Brice, G. C. Nutting and M. Halwer, THIS JOURNAL, **75**, 824 (1952).

[8] J. J. Hermans and S. Levinson, *J. Opt. Soc. Am.*, **41**, 460 (1951).

[9] B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

[10] P. Doty and R. F. Steiner, *ibid.*, **18**, 1211 (1950).

[11] "Spinco" Model L Preparative Ultracentrifuge, Spinco Division, Beckman Instruments, Inc., Palo Alto, California.

viscosity were combined before determining the molecular weight. Samples 7 and 11 are homopolymers of polyacrylonitrile. The latter was prepared by recipe No. 4 of Cleland and Stockmayer.[3]

Intrinsic Viscosity Molecular Weight Equation.—The intrinsic viscosity of the fractions is plotted against the weight average molecular weight in Fig. 1. The Cleland–Stockmayer[3] and the Bisschops[4] equations are drawn as full lines. The higher molecular weights, above (η) = 3.0 dl./g., show distinct curvature away from the Cleland–Stockmayer line. Furthermore, these higher molecular weights also show distorted Zimm plots of the form described by Muus and Billmeyer[12] and by Moore.[13] However, below 3.0 dl./g., the data give reasonably good checks with the Cleland–Stockmayer equation and not with the Bisschops equation. The homopolymer, sample 11, prepared by recipe 4 of Cleland and Stockmayer also fell on the Cleland–Stockmayer line as it should. However, since higher molecular weight fractions of the homopolymer also show distortions of the Zimm plot and curvature away from the equation for fractions, the Cleland–Stockmayer equation, $(\eta) = 2.33 \times 10^{-4} M^{0.75}$, may not be applicable to polyacrylonitrile in general much above (η) = 3.0.

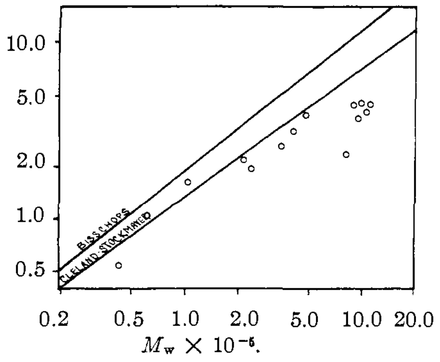

Fig. 1.—Intrinsic viscosity–molecular weight plot for fractions.

Figure 2 shows the Cleland–Stockmayer equation along with data from some whole polymers. The data is well scattered within a small coördinate space area. It appears inadvisable to apply the equation to whole polymers, because of the deviations from the equation for high molecular weight fractions of these same polymers. The observed scatter may be due to different amounts of branching in the polymers.

Molecular Weight Distribution.—The distribution of molecular weights can be estimated from the knowledge of the weight and number average molecular weights. The actual distribution, however, can be obtained from these data only if a distribution function is known or can be assumed. No attempt will be made here to indicate the actual distributions of these polymers because, as will be seen below, all of these polymers apparently contain branched and gelled material. For this reason, integral distribution curves based upon the intrinsic viscosity of the various fractions cannot give the correct distributions for the higher molecular weights. However, the breadth of the distribution is such that the weight to number average ratios are in the range of 2.0 to 10.7. The first fraction of sample 2 had a weight to number average ratio of 23, as determined by the dissymmetry method. Except for sample 11H, polymerized in solution to low conversion and having M_w/M_n ratio of 2.4, the other samples, all of which have conversions of 70 to 95%, show much higher weight to number average ratios. As will be seen below, the broadness of the molecular

TABLE I

COMPARISON OF MOLECULAR WEIGHTS AND INTRINSIC VISCOSITY. BRACKETED MOLECULAR WEIGHTS SHOWED DISTORTION IN THE ZIMM PLOT

Sample[a]	$M_w \times 10^{-5}$ Zimm	$M_w \times 10^{-5}$ Dissym.	$M_n \times 10^{-5}$ Osm.	(η) at 25°	(z)
1	4.40	4.35	0.408	2.77	1.84
1F1	(9.80)	9.58	0.944	...	2.15
1F1[b]	8.80	8.65	...	4.45	2.30
2	2.44	2.38	0.258	2.48	1.27
2F1	(27.0)	27.8	1.21	4.61	3.95
2F2	9.81	8.16	...	4.55	1.98
2F4	10.62	9.47	...	4.13	1.42
3	2.12	2.12	0.353	2.11	1.18
4	2.67	2.73	0.326	2.39	1.36
4F3	4.65	5.28	...	3.89	1.67
5	2.28	2.29	0.371	2.39	1.30
6	(55.6–129)	?	...	8.1	5.40
6[b]	14.5	15.5	...	7.06	3.80
6F3	?	?	...	8.93	6.04
9	2.79	2.77	0.262	2.40	1.42
9F1	(3.98)	3.88	...	3.20	1.50
10	1.29	1.30	...	1.65	1.19
10F1	(2.32)	2.36	...	1.96	1.23
11H	2.49	2.38	0.991	2.48	1.48
11HF1	?	4.51	1.38	2.60	2.16
12F	...	0.42	...	0.56	1.0
13F	...	0.62	...	1.06	1.0
14F	0.90	1.03	...	1.63	1.05
15F	1.66	2.16	...	2.20	1.14
16F	2.72	2.90	...	2.81	1.19
17F	(9.48)	11.10	...	3.82	2.36
7H	(4.65)	2.15	...	2.16	1.25
7HF1	(7.95)	8.39	...	2.41	2.74
8F1	(11.00)	10.07	...	4.54	2.38

[a] F, fraction; H, homopolymer of acrylonitrile. [b] After ultracentrifugation.

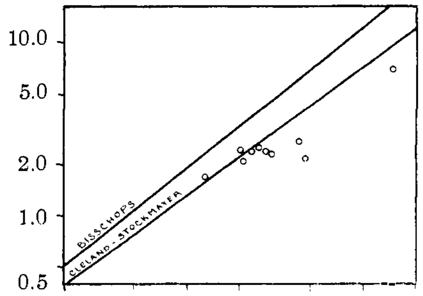

Fig. 2.—Intrinsic viscosity–molecular weight plot for whole polymers.

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(12) L. T. Muus and F. W. Billmeyer, Jr., THIS JOURNAL, **79**, 5079 (1957).

(13) L. D. Moore, Jr., *J. Polymer Sci.*, **20**, 137 (1956).

weight distributions probably is due to the particulate matter found to be in the solutions.

Evidence of Branching and Micro-gel.—As stated above, the Zimm plot distortions became more and more pronounced as the molecular weight increased. Sample 6 with an intrinsic viscosity of 8.1 was run to see if a distorted plot also resulted (Fig. 3). This sample had an intrinsic dissymmetry of somewhere between 4.8 and 5.4 which, according to the theory presented below, is beyond the acceptable range. Further, the $c = 0$ line seemed to extrapolate to a value below zero, an impossibility. The polymer then was fractionated in the expectation of removing any gelled material that might be present in the first fraction. The first two fractions were discarded, and the third fraction was run. Here again the $c = 0$ line extrapolated to less than zero, the slopes of the constant angle lines varied with the angle, and the dissymmetry was 6.0, above the value predicted by theory for an infinite molecular weight coil, 5.8. It was now apparent that the molecular weight samples which gave distorted Zimm plots were in error, and that high molecular weight values could not be determined for PAN and its copolymers. It is believed that the varying slope of the constant angle lines, the large dissymmetry and the dipping downwards of the $c = 0$ line are all caused by the presence of micro-gel.

There are generally three causes for the dipping downwards of the $c = 0$ line: dust, some other type of particulate matter, and a bad light scattering cell. Dust, an ever present problem, is probably not causing the distortion because undistorted Zimm plots are obtained for lower molecular weights. A bad light scattering cell will cause severe deflections at small angles. In order to be sure that the above effects were not affecting the results, a sample fraction of polyisobutylene[14] with a determined weight average molecular weight by dissymmetry of 1.7×10^6 was studied in toluene. The refractive index of toluene is 1.50 while that of DMF is 1.44 so any cell error occurring in the PAN-DMF systems should also appear in the polyisobutylene–toluene scattering curves. The molecular weight of the sample checked very nicely with the reported value. The undistorted Zimm plots obtained in this case exclude dust and cell reflections as the cause of the distorted Zimm plots. The only alternate conclusion is that the solution contains some type of particulate matter which arises from the polymer. The work of Muus and Billmeyer[12] shows that the Zimm plot distortions can be due to micro-gel.

If particulate material is present in the clarified solution, the size of these particles must be such as to be beyond the limits of the usual equations for light scattering. Actually if the scattering particles are spheres, any size can be handled by the Mie theory. The usual equation for light scattering

$$Hc/\tau = 1/MP(\theta) + 2Bc + \ldots \qquad (4)$$

is a simplification of the Mie theory in the size range encountered. The mathematics of the Mie theory are so involved that the theory cannot be extended reasonably to handle coils and rods. However, it is known that rods and coils follow the light scattering theory up to larger sizes than do spheres. Equation 2 cannot handle spheres with a dissymmetry greater than 1.5.[15]

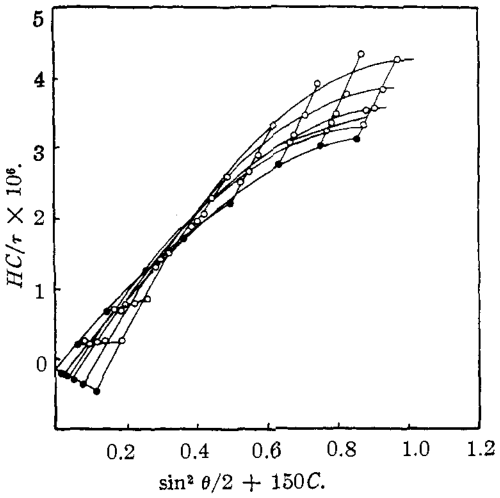

Fig. 3.—Zimm plot for sample 6.

Since the $P(\theta)$ equation for polydisperse coils[10] is in such a simple form

$$P(\theta)\text{ (polydisperse)} = 2/(2 + u) \qquad (6)$$

where

$$u = \frac{8\pi^2}{3}\left(\frac{nR}{\lambda}\right)^2 \sin^2 \theta/2 \qquad (7)$$

it is easy with the aid of the equation for dissymmetry

$$z = P(45)/P(135) \qquad (8)$$

to derive an equation relating (nR/λ) and z. Thus

$$(nR/\lambda)\text{ (Polydisperse)} = \frac{2(z - 1)}{K(135) - zK(45)} \qquad (9)$$

and $K(\theta) = 26.319 \sin^2 \theta/2$. Now, when $z = K(135)/K(45) = 5.831$ the value of (nR/λ) is equal to infinity. It can be shown that $(nR/\lambda) = \infty$ for $z = 5.831$ with the equation for monodisperse coils. In other words, the radius of the polymer molecule is infinite and therefore insoluble. Since eq. 7 approaches infinity so rapidly in the range of 5.0–5.831 and (nR/λ) is greater than 1.5, the theory is probably not applicable. Above $z = 3.8$, the sizes of the molecules are approaching and surpassing the wave length of light in solution. Thus, light scattering measurements with dissymmetries greater than 3.8 probably should be treated by another theory. Granted the latter assumption, the extent of applicability of light scattering is in the range of $0 \leqslant nR/\lambda \leqslant 0.80$ for coils. Doty and Edsall[15] have made the restriction that $0 \leqslant nR/\lambda \leqslant 0.26$ for spheres. Sample 6 exceeds the permissible values in both equations.

A one-tenth per cent. solution of sample 6 was sedimented in an analytical ultracentrifuge[16] at

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[14] Kindly supplied by Dr. Hershall Markowitz of the Mellon Institute, Pittsburgh, Pa.

[15] P. Doty and J. T. Edsall, "Advances in Protein Chemistry," Vol. VI, Academic Press, Inc., New York, N. Y., 151, p. 88.

[16] The author wishes to express his thanks to F. W. Billmeyer, Jr., for suggesting the use of an ultracentrifuge and to Dr. Ward Pigman for use of the University of Alabama Medical School's ultracentrifuges.

TABLE II

COMPARISON OF SAMPLES BEFORE AND AFTER ULTRACENTRIFUGATION

Sample	% Whole	Untreated M_w[a]	Untreated (η)[b]	Ultracentrifuged M_w	Ultracentrifuged (η)[b]
1	100	440,000	(2.49)		
1F1	16.0			865,000	(4.57)
1F1	16.4	(958,000)	(4.56)		
6	100	(indeterminate)	8.1	1,450,000	7.06
11H	100	202,000	2.48	201,000	
11HF1	25.0	(552,000)	2.78	345,000	2.63

[a] Values in parentheses show distorted Zimm plots. [b] Values in parentheses measured at 35.4°, others at 25.0°.

30,000 r.p.m. Visual viewing of the schlieren pattern showed that a mass of polymeric material had settled to the bottom of the sector cell within five minutes. A solution of sample 1F1 was ultracentrifuged in a preparative ultracentrifuge at 39,000 r.p.m. for 30 minutes and the reclaimed polymer was subjected to a light scattering run. Except for a small difference in slope at 30°, which may be caused by a trace of gel or dust, the Zimm plot is not distorted. This may be compared with the Zimm plot for *another* first fraction of the same polymer as in Fig. 5. Note that this figure is not strictly a "before and after" plot because the first fractions of two separate fractionations of this same polymer are used for the "before" and the "after." Solutions of samples 6 and 11HF1 were ultracentrifuged for three hours at 40,000 r.p.m. Figure 4 shows the same copolymer as Fig. 3 except that the Zimm plot is now undistorted, and reasonable results are obtained. Zimm plots were made on sample 11H as the whole polymer, and as the first fraction, which comprises one-fourth of the whole polymer. The whole polymer Zimm plot does not appear to be distorted, but the first fraction Zimm plot is distorted. The distortion is removed and the molecular weight lower after ultracentrifugation. Sample 7H was polymerized in aqueous medium to high conversion and shows Zimm plot distortion in both the whole polymer and in the top fraction, which comprised one-fifth of the original polymer. The properties of the polymers before and after ultracentrifugation are shown in Table II.

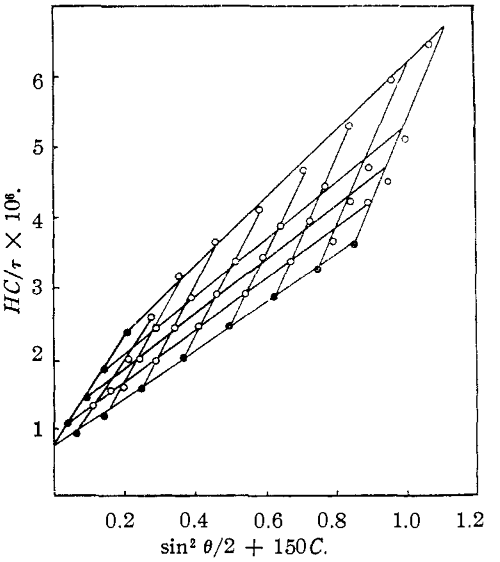

Fig. 4.—Zimm plot for sample 6 after ultracentrifugation.

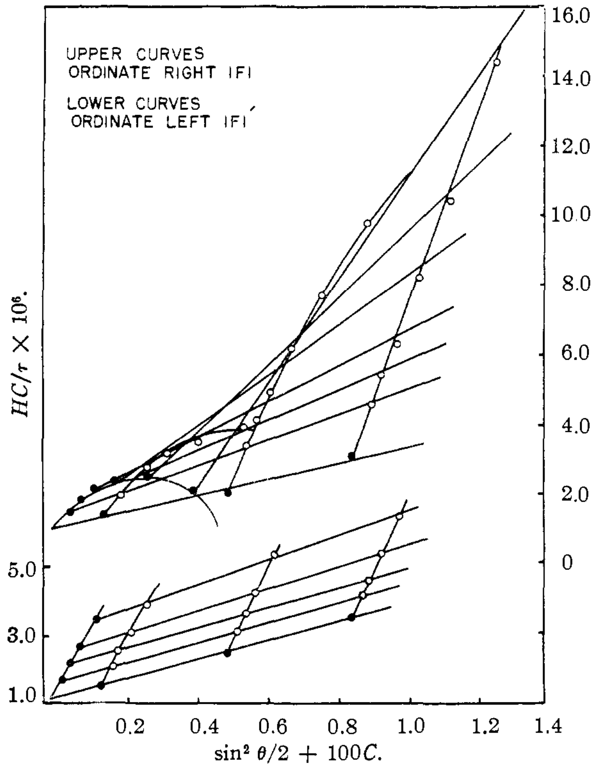

Fig. 5.—Zimm plot for sample 1 before and after ultracentrifugation.

It thus has been determined that some type of matter peculiar to the polymer is causing the Zimm plot distortions and this material may be removed by room temperature ultracentrifugation. The matter may be either micro-gel or an associated cluster of macromolecules of the type observed by Doty and Mishuck[17] and by Doty, Wagner and Singer[18] in dioxane solutions of polyvinyl chloride. In the case of polyvinyl chloride in dioxane, these authors observed an eightfold change in the weight average molecular weight over a range of 35°, which returned very slowly toward the original molecular weight upon cooling. They concluded from this that the particulate matter in their solutions was actually associated macromolecular clusters which at least partially dissolve at higher temperatures. In the present case comparable ob-

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[17] P. Doty and E. Mishuck, THIS JOURNAL, **69**, 1631 (1947).

[18] P. Doty, H. Wagner and S. Singer, *J. Phys. Chem.*, **51**, 32 (1947).

servations should permit one to decide whether the material which can be sedimented is truly insoluble, as micro-gel would be, or is undissolved associated material unconnected with the presence of branched and cross linked polymer.

It is known that undissolved or precipitated PAN contains crystalline regions, and the polymer is with difficulty soluble at room temperature. In fact rapid solution only occurs at elevated temperatures. If the polymer in solution forms associated clusters, the molecular weight of these clusters should vary with temperature and should re-form when the temperature is lowered. Light scattering at elevated temperatures or ultracentrifugation at elevated temperatures are possible methods of distinguishing between micro-gel and micro-crystalline regions. The latter procedure is the easier of the two and requires the assumption that the disassociated material will not sediment at high temperatures and will re-form when the polymer is dried. Distorted Zimm plots should persist after this treatment if they result from the presence of microcrystalline aggregates. Sample 11HF1 was ultracentrifuged at 90°, dried, redissolved, and the molecular weight was determined by light scattering. A distorted Zimm plot did not occur. The weight average molecular weight of another top fraction of sample 11H ultracentrifuged at room temperature was 341,000 with $(\eta) = 2.68$. The comparable data for a separate portion of this fraction ultracentrifuged at 90° was 297,000 and 2.71. Therefore, it is concluded that the material that is causing the difficulties probably is micro-gel and not associated clusters.

Distorted Zimm plots have been observed for every high molecular weight sample run to date. These include both high conversion copolymers and the first fraction of both a low and a high conversion homopolymer.

Possible Mechanisms of Branch and Gel Formation.—Ham[19] and Cleland and Stockmayer[3] have determined the chain transfer constant to monomers for polyacrylonitrile in dilute solution and come to the conclusion that little or no branching should occur at higher conversion.

The copolymer, of course, contains less than 10% vinyl acetate based on polymer content. Polyvinyl acetate is known to be branched easily. In fact, extreme care must be taken in the polymerization of vinyl acetate if linear molecules are desired. Thus, some branching might be expected in the copolymer as a result of the presence of vinyl acetate. However, PAN also shows the same behavior and therefore must itself contain micro-gel and therefore also be branched.

It is thus evident that the estimates of the severity of branching based on the literature data on the chain transfer constant cannot be correct. Even the PAN sample, which was prepared at 9% conversion, shows evidence for the presence of micro-gel and therefore must be branched.

The method of formation of micro-gel in PAN is not known, but some speculations may be presented. A multifunctional unit with a functionality greater than three will cause cross linking if present in polymerization or if it is formed sometime during the polymerization process.

By this mechanism it is possible that polymerization may proceed through a nitrile group. Although this process may not be energetically favorable, only one nitrile group out of 700 need enter the reaction to cause cross linking. The mechanism of branch formation by chain transfer is generally considered not to lead to gelation unless assisted by an independently occurring intermolecular reaction.[20]

Acknowledgments.—The author wishes to express his appreciation to Dr. Thomas W. DeWitt for many helpful discussions concerning this work, to Mr. Robert F. Crafts for making the measurements, to Dr. Lloyd T. Jenkins for preparing the polyacrylonitrile samples and to the Chemstrand Corporation for permission to publish this work.

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[19] G. E. Ham, *J. Polymer Sci.*, **21**, 337 (1956).

[20] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Radiation Chemistry of Organic Compounds. III. Branched Chain Alkanes

BY H. A. DEWHURST

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The yields of gas and liquid products, in the presence and absence of iodine, have been determined for the radiolysis (800 kvp. electrons) of the hexane isomers and a selected group of other branched alkanes. Infrared determination of the unsaturation showed that the kind of double bond formed was related to the hydrocarbon structure. The product distributions determined by gas chromatography reflect a marked structural effect in the radiolysis processes showing a preference for reactions adjacent to the branch site. The non-equivalence of radical fragments as determined by iodine scavenger suggests that simple C–C bond fission does not occur.

Introduction

Relatively little attention has been given to the effect of branching on the radiolysis of saturated aliphatic hydrocarbons. Schoepfle and Fellows[1] examined the gas products from three isomeric octanes and found that increased methyl substitution increased the methane yield and decreased the hydrogen yield. Schuler and co-workers,[2]

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[1] C. S. Schoepfle and C. H. Fellows, *Ind. Eng. Chem.*, **23**, 1396 (1931).

[2] E. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research* **3**, 68 (1955).