[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & COMPANY (INC.), DU PONT EXPERIMENTAL STATION]

The Molecular Structure of Polyethylene. X. Optical Studies of Crosslinked Networks[1]

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Fawcett-type (commercial free radical) polyethylene frequently contains as a separate phase a small fraction of particles in the size range above one micron. The particles have been identified as crosslinked networks, mainly by phase contrast microscopy and small angle light scattering measurement. The particles retain their shape above the polymer melting point and exhibit little, if any, swelling. Their optical properties indicate a slightly higher density and a smaller thermal expansion coefficient than the molten polymer. For a particular polyethylene sample, the volume fraction of crosslinked networks is about 1.5%. The average diameter of the particles is about ten microns, corresponding to a "molecular weight" of about 10^{14}. However, inclusion of these "molecular weights" in the distribution for uncrosslinked molecules is inappropriate, since the contribution to the weight average molecular weight of more than 95% of the polymer would be overshadowed.

Introduction

The presence of crosslinked networks in the size range above one micron was detected in Fawcett-type polyethylene several years ago as a result of phase contrast microscope studies in this Laboratory. The effect of these structures on the light scattered from solutions of polyethylene was observed soon afterward and was discussed in Papers III[2] and VI[3] of this series. Other authors[4] have suggested that polyethylene may contain gel, microgel or highly ramified structures, on the basis of less direct evidence. Recently, spherical particles of diameter 500 Å. were reported in an electron microscope investigation of branched polyethylene.[5]

The present paper describes studies of covalently crosslinked networks in branched polyethylene by phase contrast microscopy, small angle light scattering and other molecular characterization techniques.

Experimental

Sample.—Polyethylene sample 10, used in this work, is a commercial high-pressure Fawcett-type branched polyethylene.[6] This sample was also described in Paper VI.[3] The results of both light scattering and ultracentrifuge experiments on sample 10 are similar to those for many Fawcett-type polyethylenes. This sample was selected for investigation because it contains a larger fraction of crosslinked networks with diameter in the ten micron range than most other polyethylenes.

Phase Contrast Microscopy.—Specimens for microscopy were prepared as shock cooled, melt-pressed films. Films used for quantitative investigation and photomicrography were pressed between cover glasses in a Model PA-6 "Preco" press (Pasadena Hydraulics, Inc., Pasadena, California) at 165° and 20,000 pounds gauge pressure. These films were between 14 and 41 μ thick. Thicker specimens were prepared for qualitative observations by hand pressing between a microslide and cover glass. Shock cooling was required to reduce spherulite size to prevent interference with the observation of crosslinked networks. Solvent-cast films were used occasionally.

Qualitative observations were made with a Bausch and Lomb Model BDA monocular microscope with phase contrast equipment, and a turret type Abbe condenser. Dark contrast phase plates were used. The light source was a ribbon filament lamp with a Corning 4010 green filter.

Phase contrast observations were made at elevated temperatures using a Kofler microheating stage (Arthur H. Thomas Co., No. 6887-A) modified[7] to permit the use of a Bausch and Lomb long working distance condenser close to the heated specimen. The phase contrast objective was cooled by means of a water jacket. The apparatus was used routinely at 150° and briefly at 180°.

Quantitative measurements were made on photomicrographs taken at room temperature with a 21X phase contrast objective. Magnification on the film was 220X. The volume fraction of crosslinked networks was determined by the Rosiwal method as the ratio of the sum of the particle intercepts on randomly selected straight lines to the total length of the lines.[8] The photomicrographs represented particle cross sections in a single plane, since the depth of field was small compared to the particle size. In this case, the intercept ratio gives directly the volume fraction. The average diameter ($\bar{d}$) of the crosslinked networks was derived as 3/2 times the average intercept.[9] The average cross section of a particle was obtained from the number and the area fraction, the latter being identical with the volume fraction.[8] The root-mean-square diameter $(\overline{d^2})^{1/2}$ was calculated as the diameter of the circle with 3/2 times the average cross section.[10]

Small Angle Light Scattering.—Light scattering studies in the angular range 0.2–50° were made with a photometer[11] having angular resolution better than 0.05°. Solutions of polyethylene in α-chloronaphthalene were observed at 125 ± 1° in an electrically heated sample chamber. The stainless steel sample cells with plane parallel glass windows were 1 cm. thick.

Scattered intensities from solutions were corrected for solvent scattering. Other corrections[12] required by the geometry of the scattering cell were usually negligible. Small angle light scattering data were analyzed by plotting $\log I\theta^2$ against $\log \theta$ in a Sloan plot,[13] where I is the scattered intensity and θ is the angle of observation. A characteristic feature of a Sloan plot is a maximum in $I\theta^2$ at an angle depending on the size of the predominant scattering particles. The relation between particle diameter d in microns and angle θ pertinent to the crosslinked networks in

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[1] Presented at the 133rd National Meeting of the American Chemical Society, San Francisco, California, April 16, 1958. Papers I–IX of this series are published in THIS JOURNAL, **75**, 6110 (1953) and **79**, 5079 (1957).

[2] F. W. Billmeyer, Jr., *ibid.*, **75**, 6118 (1953).

[3] L. T. Muus and F. W. Billmeyer, Jr., *ibid.*, **79**, 5079 (1957).

[4] (a) W. O. Baker, W. P. Mason and J. H. Heiss, *J. Polymer Sci.*, **8**, 129 (1952); (b) L. D. Moore, *ibid.*, **20**, 137 (1956), (c) Q. A. Trementozzi, *ibid.*, **23**, 884 (1957); (d) T. Kobayashi, A. Chitale and H. P. Frank, *ibid.*, **24**, 156 (1957); (c) L. Nicolas, *Compt. rend.*, **244**, 80 (1957); *J. Polymer Sci.*, **29**, 191 (1958).

[5] L. D. Moore and V. G. Peck, presented at the 132nd National Meeting of the American Chemical Society, New York, September 11, 1957.

[6] E. W. Fawcett, R. O. Gibson and M. W. Perrin, U. S. Patent 2,153,553 (1939).

[7] We are indebted to Dr. H. K. Alber, Arthur H. Thomas Co., Philadelphia, Pa., for furnishing the modified heating stage.

[8] (a) A. Rosiwal, *Verh. Geol. Reichanstalt*, 143 (1898); (b) E. S. Larsen and F. S. Miller, *Am. Mineralogist*, **20**, 260 (1935); (c) E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1938, p. 447.

[9] The factor 3/2 is the ratio of the diameter to the mean length of the chords in a sphere.

[10] The factor 3/2 is the ratio of the maximum area to the mean area of the circles formed by intersecting a sphere with planes.

[11] W. H. Aughey and F. J. Baum, *J. Opt. Soc. Am.*, **44**, 833 (1954).

[12] R. S. Stein and J. J. Keane, *J. Polymer Sci.*, **17**, 21 (1955).

[13] (a) C. K. Sloan, *J. Phys. Chem.*, **59**, 834 (1955); (b) C. K. Sloan, C. H. Arrington and C. G. Wortz, papers presented at the 125th National Meeting of the American Chemical Society, Kansas City, Mo., April 1, 1954.

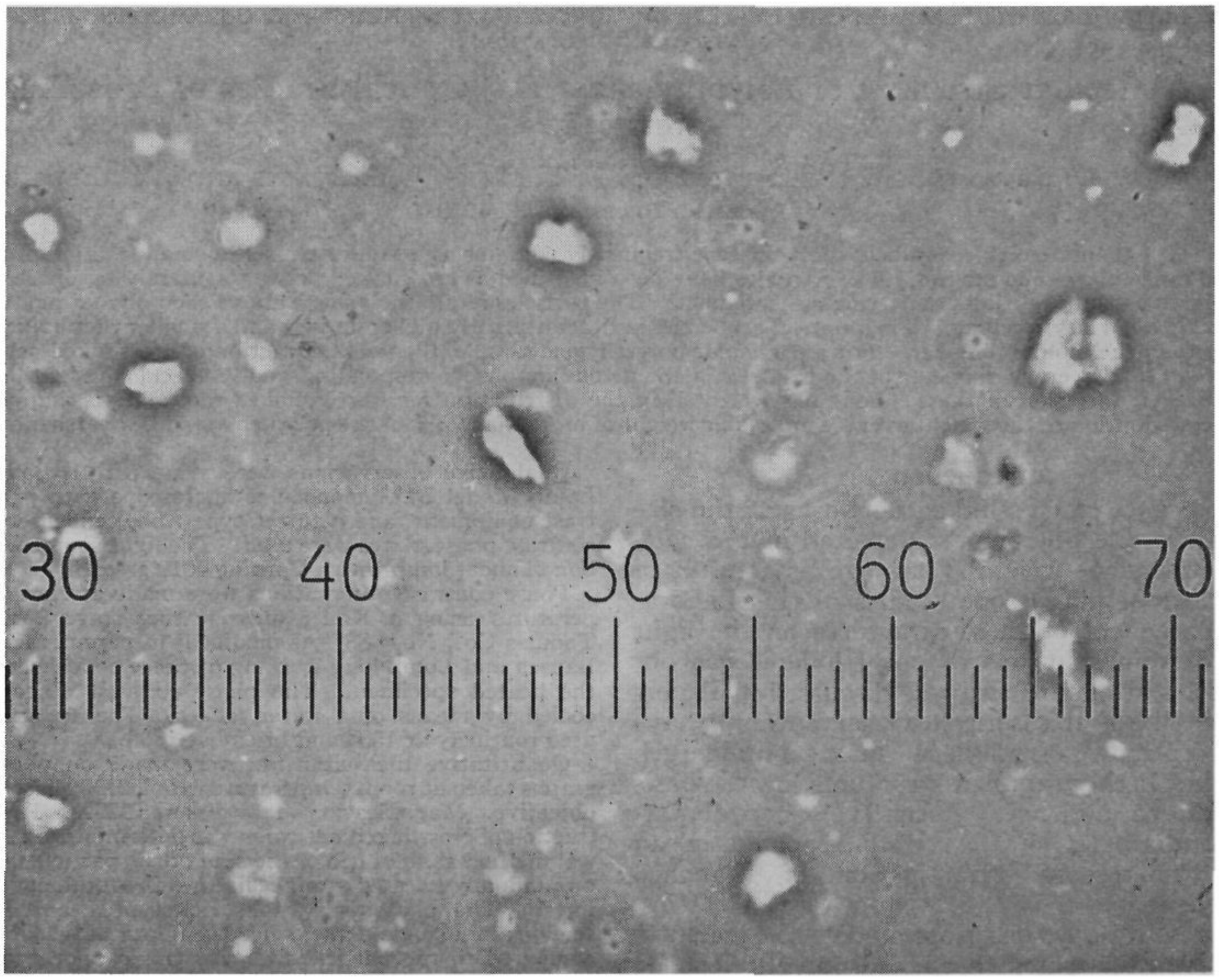

Fig. 1.—Photomicrograph of crosslinked networks in polyethylene sample 10; dark phase contrast microscopy; one scale division = 5.1 microns.

polyethylene is $d = 18.4/\theta$, derived from classical diffraction theory.[14]

Ultracentrifugation.—High temperature ultracentrifugation of sample 10 was performed by the techniques of Paper VI[3] to obtain the crosslinked networks relatively free from other polymeric material. The crosslinked networks were precipitated by centrifuging a 2% solution in n-decane at 110° for 6 hr. at an average acceleration of 35,000 times that of gravity. These conditions were less severe than those used in Paper VI.[3] The supernatant liquid was poured off and the residue was redispersed in α-chloronaphthalene at 125°. To avoid difficulty in redispersion, the residue was not completely dried.

Molecular Light Scattering.—The techniques of Paper VI[3] were used for determination of molecular weight by light scattering in the angular range 25–120°.

Solution Viscosity.—The viscosity of the ultracentrifuge residue of sample 10 was measured in α-chloronaphthalene at 125° for four concentrations as described in Paper III.[2]

Infrared Analysis.—The residue from an ultracentrifugation of sample 10 was redispersed in xylene and washed repeatedly with methanol. After drying, the residue was cold-pressed into a thin film for infrared analysis by the methods described in Paper II.[15,16]

Results

Phase Contrast Microscopy.—Crosslinked networks in solvent-cast or melt-pressed polyethylene films are scarcely visible by ordinary microscopy because of low contrast. They are seen with some difficulty in polarized light between crossed nicols because their birefringence differs but slightly from that of the surrounding spherulites. By phase contrast microscopy, however, particles between 0.5 μ (practical limit of resolution) and *ca.* 20 μ in diameter are plainly seen (Fig. 1). They appear as clear jagged particles with sharply defined conchoidal fracture boundaries resembling those of crushed glass. With dark phase contrast equipment, the particles appear bright against the darker background of the polymer matrix. Their refractive index is about 0.01 to 0.02 less than that of the matrix at room temperature, as shown by the degree of contrast.

The particles were observed continuously by phase contrast microscopy as the temperature of the specimen was increased. The contrast decreased with increasing temperature and the particles disappeared close to the polymer melting point (110°). Near 120° the particles reappeared, still with sharp outlines and with the characteristic shapes seen at room temperature, but with low contrast which increased gradually as the temperature was raised to 180°. At temperatures above 120°, the particles appeared darker than the background; their refractive index was estimated to be a few thousandths of a unit greater at 180° than that of the polymer melt. Particles suspended in the melt were noted to be reversibly

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[14] The scattering from a large sphere is approximated by the Airy formula for diffraction from a circular disc or aperture: (a) G. Airy, *Camb. Phil. Trans.*, 283 (1834); (b) R. W. Wood, "Physical Optics," 2nd Ed., The Macmillan Co., New York, N. Y., 1919, p. 236; (c) H. C. van de Hulst, "Light Scattering by Small Particles," John Wiley and Sons, Inc., New York, N. Y., 1957.

[15] W. M. D. Bryant and R. C. Voter, THIS JOURNAL, **75**, 6116 (1953).

[16] We are indebted to H. B. Kessler for carrying out the infrared analyses.

deformable on application of slight pressure to the cover glass; greater pressure sometimes caused a particle to fracture into smaller pieces with sharp boundaries. Thus the material had the properties of a weak, readily torn rubber. Gradual cooling of the preparation led to a reversal of the change in contrast observed on heating. However, the slow cooling resulted in a coarser spherulitic texture of the matrix.

The volume fraction of crosslinked networks for sample 10 was measured from photomicrographs (Table I). The average value for the volume fraction of these particles (1.5%) is in good agreement with those estimated from ultracentrifugation and small angle light scattering data. The data for the volume fraction in Table I show no significant effect of sample thickness. Furthermore, no dependency is found between sample thickness and the number of crosslinked networks either per unit length or per unit area. The average particle diameter from the photomicrographs is in good agreement with that determined by small angle light scattering (Table I).

TABLE I

CROSSLINKED NETWORKS IN POLYETHYLENE SAMPLE 10

A. Phase contrast photomicrography

Sample thickness	Av. particle diameter, μ Intercept method ($\bar{d}$)	Area method $(\bar{d^2})^{1/2}$	Vol. fraction, %
14μ	9	8	1.4
28	8	8	1.4
41	8	9	1.7
Av.	8	8	1.5

B. Small angle light Scattering

Av particle diameter, μ. 10

C. Ultracentrifugation

Wt. fraction, %. . . . .*ca.* 1.8

Small Angle Light Scattering.—Figure 2 presents Sloan plots for solutions in α-chloronaphthalene of polyethylene sample 10, its ultracentrifuge residue and the polymer from the supernatant liquid. Solvent scattering was subtracted and the curves normalized to a solute concentration of 10 g./100 ml. assuming intensity of scattered light proportional to concentration at constant angle of observation.

The shape of the curve for the whole polymer is typical of that for many Fawcett-type polyethylenes. The maximum in $I\theta^2$ corresponds to the particle diameter 10 μ in good agreement with the results from phase contrast microscopy (Table I). Comparison with the theoretical scattering curve for 10 μ spheres, included in Fig. 2, suggests that the scattering material contains few particles larger than 20 μ in diameter but an appreciable amount of material at least as small as 0.5 μ.

The scattering curve for the whole polymer and that for the dispersion of crosslinked networks have almost the same shape (Fig. 2). Since, on an equal weight basis, the crosslinked networks scatter 50 times as much as the whole polymer, their weight concentration in the whole polymer is approximately 2%.

The Sloan plot of the polymer from the supernatant liquid suggests that a small fraction of the crosslinked networks was not removed in the ultracentrifugation, although the intensity of light scattered at 2° was reduced by a factor of 150 below that for the whole polymer. The molecular light scattering results support this view.

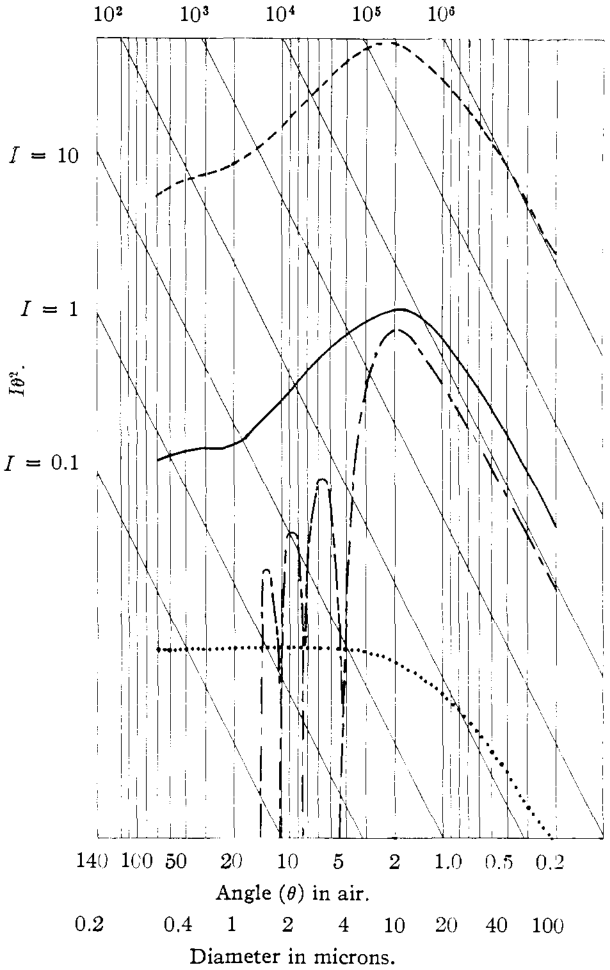

Fig. 2.—Sloan plots for solutions of whole polymer (———) and polymer for supernatant liquid (. . . . . .), and dispersion of ultracentrifuge residue (- - - -) of polyethylene sample 10: solute concentration 10 g./100 ml.; curve for monodisperse 10 μ diameter spheres (— — — -) shown for comparison.

Molecular Light Scattering.—A Zimm plot of the molecular light scattering data from the ultracentrifuge residue is shown in Fig. 3. This may be compared to the Zimm plot for the whole polymer given in Paper VI.[3] The curvature of both Zimm plots is associated with the residue containing the crosslinked networks.

In the angular range 25–45° data were obtained from both small angle and molecular light scattering experiments. After correction for cell geometry,[12] the small angle data for the whole polymer were joined smoothly to the molecular light scattering data. The resulting curve (Fig. 4) drops continuously with decreasing angle to about 0.5° ($\sin^2\theta/2 = 5 \times 10^{-5}$). At smaller angles (Fig. 5), the scattered intensity remains constant with angle so that extrapolation to zero angle is possible.

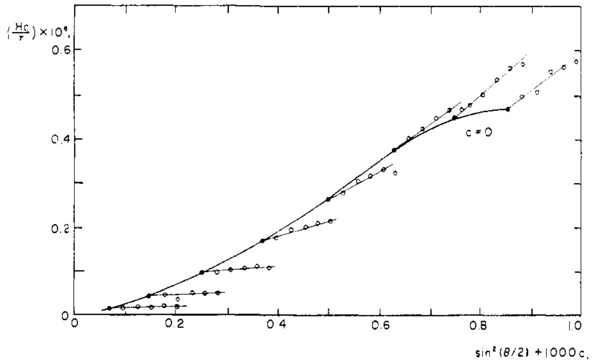

Fig. 3.—Zimm plot for the ultracentrifuge residue of polyethylene sample 10: angular range 25–120°.

The extrapolation corresponds to a "molecular weight" of about 10^{11}. When the observations were limited to molecular light scattering data in the angular range above 25°, an extrapolation to zero angle yielded a "molecular weight" of about 5×10^6 (Paper VI[3]). Combination of small angle and molecular light scattering data for the ultracentrifuge residue gave similar results. There is clearly no justification for calculating a weight average molecular weight by extrapolation of a curved Zimm plot to zero angle on the basis of data obtained only at large angles of observation.

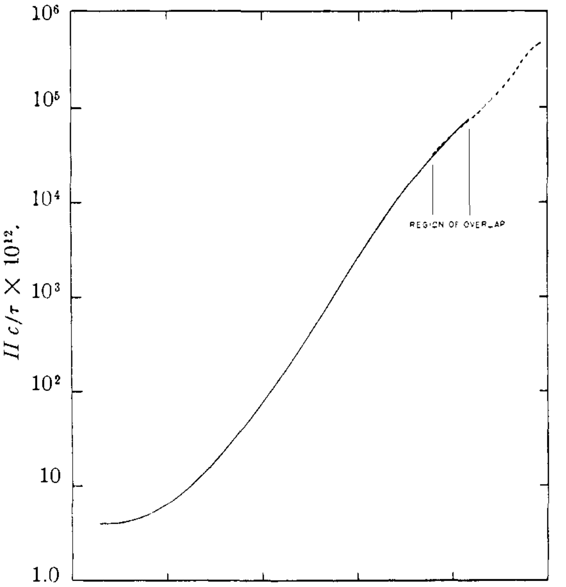

Fig. 4.—Reciprocal intensity of scattered light as a function of angle of observation for polyethylene sample 10; angular range 0.2–120°. Both axes are logarithmic. Solid line is derived from small angle, and dashed line from molecular light scattering measurements.

The Zimm plot for the polymer from the supernatant liquid in the present ultracentrifuge experiment was not linear with respect to the angular coördinate $\sin^2\theta/2$, in agreement with the small angle light scattering result. Linear Zimm plots were obtained, however, after ultracentrifugation under more severe conditions (Paper VI).[3]

Other Properties of the Ultracentrifuge Residue.—An accurate material balance was not obtained for the ultracentrifugation of sample 10, since it was preferred not to isolate the ultracentrifuge residue. The approximate weight fraction of the residue was 1.8% (Table I).

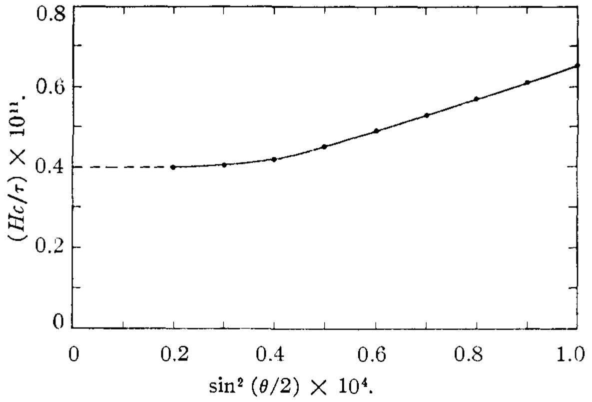

Fig. 5.—Zimm plot for polyethylene sample 10; angular range 2–1°.

The intrinsic viscosity of the ultracentrifuge residue was 0.89 dl./g. This value is far above that expected for insoluble crosslinked networks[17] and suggests that the ultracentrifuge residue also contains high molecular weight polymer. On the other hand, the intrinsic viscosity is much lower than that for a residue consisting exclusively of soluble high molecular weight species. Somewhat larger residues (about 4%) were obtained by ultracentrifugation under more severe conditions (Paper VI).[3]

The ultracentrifuge residue had essentially the same infrared absorption bands as the original polymer.

Discussion

The particles observed as a separate phase in Fawcett-type polyethylene are covalently crosslinked networks of polyethylene chains, since they have a combination of properties explicable only in terms of these structures. Properties characteristic of crosslinked networks are limited swelling, persistence of shape above the polymer melting point, a density slightly above that of the amorphous polymer, and a thermal expansion coefficient smaller than that of the amorphous polymer.[18]

Comparison of observed particle size in a film with that from small angle light scattering experiments for a suspension in α-chloronaphthalene shows little, if any, swelling (Table I). Hot stage phase microscopy demonstrates that the particles retain their shape far above the polymer melting point. Here the refractive index of the particles is higher and decreases more slowly with increasing temperature than that of the polymer melt. Par-

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(17) (a) A. Einstein, *Ann. Physik*, [4] **19**, 289 (1906); **34**, 591 (1911); (b) L. H. Cragg and J. A. Manson, *J. Polymer Sci.*, **9**, 265 (1952).

(18) (a) P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 521 (1943); (b) P. J. Flory, *Chem. Revs.*, **39**, 137 (1946); (c) A. I. Medalia, *J. Polymer Sci.*, **6**, 423 (1951); (d) T. G. Fox and S. Loshaek, *ibid.*, **15**, 371 (1955).

ticles and polymer matrix are similar in chemical composition, as evidenced by infrared analysis and close correspondence in refractive index. The particles, therefore, have a higher density and a smaller thermal expansion coefficient than the melt, since a small increase in refractive index is proportional to a small increase in density.[19]

The observed average diameter of the crosslinked networks is about 10 μ and corresponds to a "molecular weight" of about 10^{14} assuming them to be solid spheres with a density of 1 g./ml. A random coil with radius of gyration 5 μ would have molecular weight 3×10^9.[20] This estimate is low since crosslinking will have the effect of decreasing the particle radius below that of a random coil. In any case, the experiments demonstrate the inappropriateness of including the "molecular weights" of these particles in the distribution for the uncrosslinked polymer molecules, since the resulting weight average molecular weight reflects no contribution from the major part of the polymer.

The particles observed by phase contrast microscopy and small angle light scattering are much larger than those with diameter 500 Å. reported in a study of polyethylene by electron microscopy.[5]

The crosslinked networks are precipitated by ultracentrifugation in *n*-decane. The amount of precipitate is approximately the same as the volume fraction of crosslinked networks derived from phase contrast observations on films. However, viscosity measurement indicates that the ultracentrifuge residue contains other polymeric material in addition to the crosslinked networks, such as branched molecules of high molecular weight.

The small angle light scattering experiments show that no information about the weight average molecular weight of the polymer can be obtained from measurements in the angular range above 25° when crosslinked networks are present even in small amounts. The intensity of light scattered from the network particles outweighs by far that from the branched polymer molecules, especially at small angles. There is no obvious way of separating the simultaneous scattering of the two species.

Fawcett-type polyethylene is characterized by extensive long chain branching.[2,3] The long branches are formed by chain transfer to polymer in the polymerization process.[21] However, chain transfer alone can result neither in an infinite branched molecule nor in a crosslinked network.[22] An additional reaction, such as intermolecular or intramolecular recombination of pairs of branched radicals,[23] is required for the formation of crosslinked networks.

Acknowledgment.—The authors gratefully acknowledge the background provided by C. K. Sloan, C. H. Arrington, Jr., and W. H. Aughey in the respective fields of angular dependence light scattering technique, theoretical approximations and instrumentation. The pioneering work of E. J. Hennelly laid the foundations for the successful application of these methods to polyethylene.

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[19] (a) H. A. Lorentz, "Theory of Electrons," Teubner, Leipzig, 1909; (b) J. H. Gladstone and T. P. Dale, *Phil. Trans.*, **153**, 317 (1863); (c) J. F. Eyckman, *Rec. trav. chim.*, **14**, 177 (1895); (d) E. Jenckel, *Kolloid-Z.*, **120**, 160 (1951).

[20] J. T. Atkins, L. T. Muus, C. W. Smith and E. T. Pieski, THIS JOURNAL, **79**, 5089 (1957) (Paper IX).

[21] (a) P. J. Flory, THIS JOURNAL, **69**, 2893 (1947); (b) J. K. Beasley, *ibid.*, **75**, 6123 (1953) (Paper IV).

[22] P. J. Flory, *Ann. N. Y. Acad. Sci.*, **57**, 327 (1953).

[23] T. G. Fox and S. Gratch, *ibid.*, **57**, 367 (1953).

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 5205 FROM THE DIVISION OF APPLIED CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Electronic Structure and Reactivities of Monoölefins

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LCAO-MO method with the inclusion of overlap integrals between adjacent orbitals and with the assumption of hyperconjugation was applied to calculate the free valences, excitation energies, atom and bond localization energies, bond orders and electron densities of a number of monoölefinic hydrocarbons. These quantities were compared with the relative rate constants of addition reactions with methyl, ethyl and trichloromethyl radicals (radical reagents) and of oxygen atoms (^3P), peracetic acid, bromine and dibromocarbene (electrophilic reagents). For the reactions of the radical reagents the logarithms of relative rate constants were found to be roughly linearly related to the free valences and for the reactions of the electrophilic reagents good correlations were obtained with the excitation energies and the bond orders. In the former case a statistical factor of one-half was applied to the rate constants of symmetrical olefins.

Introduction

Attempts to correlate trends in chemical reactivity with various quantities which can be derived by the application of the molecular orbital theory have met with considerable success in spite of the crude approximations which have to be made in order that the calculations can be carried out. So far the same approach has been applied to olefins only to a relatively limited extent.

In the present paper the concept of hyperconjugation, originated by Mulliken and his co-workers,[2] is employed to calculate the free valences, excitation energies, atom and bond localization energies, bond orders and electron densities for a number of monoolefins. These quantities are compared with the literature values for the experimentally observed trends in the rates of addition to the olefinic double bonds of (a) methyl, ethyl and trichloromethyl radicals (radical reagents) and (b) bromine, bromocarbene, peracetic acid and ground state

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[1] National Research Council Postdoctorate Fellow, 1956–1958.

[2] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL **63**, 41 (1941).