veniently prepared by the acetylation of phosphoric acid with ketene in ethereal solution, and is recovered as disilver acetyl phosphate. Similar acetylation of dibenzyl hydrogen phosphate yields acetyl dibenzyl phosphate.

2. Acetyl dihydrogen phosphate will acetylate ammonia and aniline under various conditions. No evidence of phosphorylating reactions could be obtained.

NEW YORK, N. Y. RECEIVED JANUARY 13, 1948

[CONTRIBUTION NO. 239 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

The Structure of Neoprene. I. The Molecular Weight Distribution of Neoprene Type GN

BY W. E. MOCHEL, J. B. NICHOLS AND C. J. MIGHTON

It has been recognized that synthetic high polymers in general are non-homogenous, particularly in respect to molecular weight. Therefore, the molecular weight of a particular polymer cannot be characterized accurately by a single value and there is required a knowledge of the distribution of molecular weights. Any single molecular weight value for a heterogeneous polymer must perforce be an average value and will differ appreciably with the method of averaging. Although it has been shown recently that the tensile strength of some polymers, *e. g.*, cellulose acetate, depends explicitly on the number average molecular weight regardless of the distribution of molecular weights,[1] other properties of high polymers such as plasticity,[2] are influenced markedly by the heterogeneity of molecular weights. The present investigation of the molecular weight distribution of neoprene (polychloroprene) is a part of an extensive study of the structures of these polymers.

There have appeared recently several new methods for determination of molecular weight distribution[3] but the standard method continues to be that of careful fractionation and examination of each fraction. This method also furnishes polymer samples of sufficient homogeneity that they can be used to calibrate the intrinsic viscosity–molecular weight relationship with an absolute method such as osmotic pressure. The two most common methods for fractionation of high polymers are: (1) precipitation by successive additions of a non-solvent to a solution of the polymer and (2) successive extractions of the polymer with solvent/non-solvent mixtures of increasing solvent concentration. It has been shown that neither method can give a really sharp separation of species[4] but the first method appears to be satisfactory for practical purposes if certain precautions are taken. Thus, it is advisable to use a reasonably dilute solution, precipitate at constant temperature and wash the precipitated fractions to remove low molecular weight material.

Experimental

Materials.—A sample of standard, commercial Neoprene Type GN of plasticity classification[5] P3 and age two months was selected for fractionation. Neoprene Type GN is a polychloroprene polymerized in aqueous emulsion in the presence of sulfur and is stabilized with tetraethyl thiuram disulfide.[6] (Neoprene Type GN is identical with GR-M currently manufactured at Louisville by the Office of Rubber Reserve, Reconstruction Finance Corporation.) To obtain the pure polychloroprene, essentially free from soap residues, stabilizers and adjuvants used in the polymerization, 55 g. of the finely-cut neoprene was dissolved in 500 ml. of thiophene-free, dry benzene, and 500 ml. of C. P. methanol was added slowly with stirring, to precipitate the polymer. Further addition of methanol to the clear, supernatant liquid produced no cloudiness. The polymer was washed twice with 100-ml. portions of methanol and dried at room temperature under vacuum. The dry polymer weighed 50.5 g. In these operations and all subsequent handling, the polymer, its solutions and the fractions were kept under an atmosphere of nitrogen.

The benzene–methanol mixture left after precipitation of the polymer was combined with the methanol wash liquors and evaporated to dryness under vacuum. The residue, consisting of 4.6 g. of dark brown, very viscous oil, was not investigated further.

Fractionation.—The purified polychloroprene prepared as described above (50.5 g.) was dissolved in 5 l. of thiophene-free, dry benzene and to the solution was added 0.5 g. of phenyl-α-naphthylamine to inhibit degradation of the polymer. After a sample (150 ml.) of the solution of whole polymer had been removed for test, fraction A was precipitated by the slow addition of methanol, with mechanical stirring, until the solution became hazy at 25°. It was then warmed gently until it became clear, at about 26–28°. Precipitation of the first fraction required 1200 ml. of methanol. The clear, warm solution was cooled slowly to 25° and maintained overnight at constant temperature, during which time the precipitated polymer settled out as a very viscous liquid containing the high molecular weight polymer in solution. The clear, supernatant solution was siphoned off and the fraction was washed twice with a benzene–methanol mixture of the same concentration as the mixture from which the fraction had precipitated. These washings were added to the main solution and the fraction

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[1] A. M. Sookne and M. Harris, *Ind. Eng. Chem.*, **37**, 478 (1945); P. J. Flory, THIS JOURNAL, **67**, 2048 (1945); *Ind. Eng. Chem.*, **38**, 417 (1946).

[2] R. L. Zapp and F. P. Baldwin, *ibid.*, **38**, 948 (1946).

[3] D. R. Morey and J. W. Tamblyn, *J. Appl. Phys.*, **16**, 419 (1945); R. F. Boyer and R. D. Heidenreich, *ibid.*, **16**, 621 (1945); P. M. Doty, B. H. Zimm and H. Mark, *J. Chem. Phys.*, **13**, 159 (1945); L. H. Cragg and H. Hammerschlag, *Chem. Rev.*, **39**, 79 (1946); D. R. Morey and J. W. Tamblyn, *J. Phys. Colloid Chem.*, **51**, 721 (1947).

[4] G. Gee, *Trans. Faraday Soc.*, **38**, 276 (1942); P. J. Flory, *J. Chem. Phys.*, **12**, 425 (1944); R. L. Scott, *ibid.*, **13**, 178 (1945); D. R. Morey and J. W. Tamblyn, *J. Phys. Chem.*, **50**, 12 (1946).

[5] P3 corresponds to a Williams plasticity range of 116–121; see A. M. Neal and P. Ottenhoff, *Ind. Eng. Chem.*, **36**, 653 (1944), this corresponds approximately to Mooney 2.

[6] A. M. Collins, U. S. Patent 2,264,173.

was dissolved immediately in 200 ml. of thiophene-free, dry benzene. A benzene/methanol azeotrope was distilled from this solution at 30° under vacuum until about 100 ml. had been removed; then another 100 ml. of benzene was added and the distillation was continued until the refractive index of the distillate checked that of pure benzene. The remaining solution of the fraction in pure benzene was used for subsequent measurements.

The above-described procedure was followed for the preparation of the first three fractions since it had been found that evaporation of these fractions to dryness resulted in the formation of small amounts of gel.[7] Remaining fractions were coagulated with methanol after being washed and were then evaporated to dryness under vacuum at room temperature. After approximately half of the polymer had been fractionated a single washing of each fraction was considered sufficient. Eventually, when 28 g. of the neoprene had been precipitated it was necessary to concentrate the solution to about 1% solids again before proceeding with the final fractionations. This was done at 25–30° under vacuum with a slow stream of nitrogen through a fine capillary tube. Finally, when no more material could be precipitated, the remaining solution was evaporated to dryness.

An attempt to improve the homogeneity of neoprene fractions further by solution and reprecipitation gave meaningless results, presumably because of degradative changes occurring during the longer time required for the additional operations. Consequently the neoprene fractions described here were not reprecipitated. Repeated measurements on the whole polymer gave good checks on intrinsic viscosity and osmotic pressure. To diminish the effects of degradative changes, the fractions were dissolved and their molecular weights measured within a few days after preparation.

A total of 17 fractions was obtained from the purified polychloroprene. The dried fractions were dissolved in thiophene-free, dry benzene to make solutions containing 1 g. of polymer and 0.0050 g. of phenyl-α-naphthylamine per 100 ml. of solution. Solids content of each solution was accurately determined by evaporation to dryness at 70° of a 25.00-ml. aliquot (measured at 25.0°) and the remaining solution was used for the determination of number average molecular weight and intrinsic viscosity. To obtain a check on the results a rough fractionation was carried out analogously to get 6 different fractions which would approach the above in homogeneity.

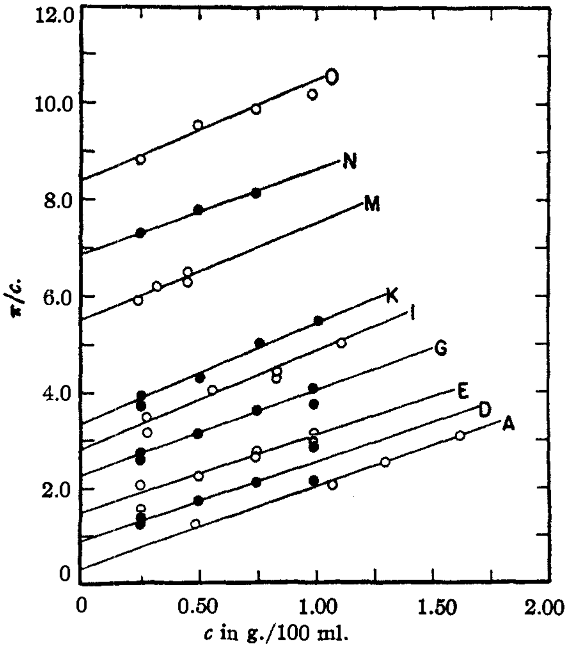

Fig. 1.—π/c vs. c curves for representative Neoprene Type GN fractions.

Osmotic Pressures.—The number average molecular weights in benzene solution were measured by means of static type osmometers using gel cellophane membranes (regenerated cellulose that has not been dried). The osmometers used were similar to those described by Schulz and by Wagner[8] and the membrane preparation was the same as that of Wagner.

For each sample, duplicate determinations were made at each of four different concentrations. To minimize the error due to thermometer effect, especially with the benzene solutions employed, the temperature was regulated within ±0.01°. The capillary correction for benzene was measured and since the correction for most solutions in organic solvents does not differ much from that of the pure solvent, separate measurements were not made for each individual solution. The measurements for each sample were plotted as π/c *vs.* c and extrapolated to zero concentration assuming a straight line relationship

$$\frac{\pi}{c} = \frac{RT}{M_n} + Bc$$

which appeared to fit within experimental error in the range of concentrations employed, *i. e.*, 0.25–1.50 g. per 100 ml. Representative curves are given in Fig. 1.

Intrinsic Viscosity.—Viscosities were measured in benzene solution using an Ubbelohde suspended level viscometer[9] modified by substitution of a 50-ml. reservoir for the usual 5–10 ml. bulb. Since the operation of the suspended level viscometer, unlike that of the Ostwald types, is not affected by the volume of liquid in the viscometer, it was possible to make carefully weighed additions of a 1–2% solution of polymer to solvent in the viscometer. Thus the viscosity at various concentrations could be measured without having to clean and refill the viscometer before each determination. The viscometer dimensions were such that the kinetic energy error was only 0.4% in the kinematic viscosity of benzene, having an efflux time of 116.4 seconds, and no correction was applied.

The dry, thiophene-free benzene used as solvent was measured at 25.0° in calibrated pipets and the efflux times were determined at the same temperature with a maximum fluctuation of ±0.02°. The efflux times were checked within ±0.2 second. Normally four additions of the polymer solution were made, keeping the relative viscosity between 1.15 and 1.4.

The concentration of the polymer by weight in the master solution was calculated using 1.23 as the specific gravity of polychloroprene[10] and 0.8735 as the specific gravity of benzene at 25°. The concentration of each solution measured was calculated in g. per 100 ml. and used to determine reduced viscosity, η_{sp}/c. Using a differencing technique[11] the four sets of η_{sp}/c *vs.* c values were fitted to the best straight line for the equation developed by Huggins and others[12]

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \qquad (1)$$

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(7) A similar observation was made in the case of natural rubber by G. F. Bloomfield and E. H. Farmer, *Trans. Inst. Rubber Ind.*, **16**, 69 (1940); G. Gee and L. R. G. Treloar, *ibid.*, **16**, 184 (1940).

(8) G. V. Schulz, *Z. physik. Chem.*, **A176**, 317 (1936); R. H. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **16**, 520 (1944).

(9) L. Ubbelohde, *ibid.*, **9**, 85 (1937); G. B. Taylor, This Journal, **69**, 635 (1947).

(10) L. A. Wood, N. Bekkedahl and F. L. Roth, *Ind. Eng. Chem.*, **34**, 1291 (1942).

(11) J. H. Awbery, *Phys. Soc. Proc.*, **41**, 384 (1929).

(12) M. L. Huggins, This Journal, **64**, 2716 (1942); G. V. Schulz and F. Blaschke, *J. prakt. Chem.*, **158**, 130 (1941).

The intrinsic viscosity was thus obtained as the limiting reduced viscosity and simultaneously the constant *k'* was evaluated. The experimental results are shown graphically in Fig. 2.

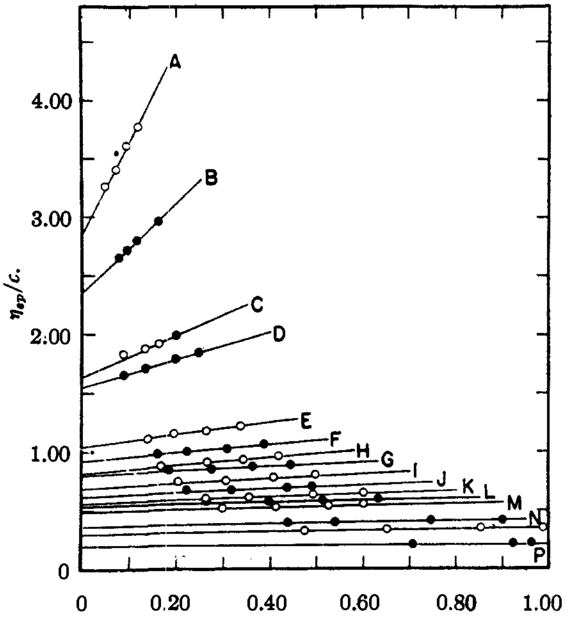

Fig. 2.—η_{sp}/c *vs.* *c* curves for Neoprene Type GN fractions.

Results and Discussion

The purified polychloroprene was divided into 17 fractions, the last one of which gave such erratic osmotic measurements that its molecular weight could not be calculated. The total weight of fractions isolated from the 49.0 g. of polymer fractionated (50.5 g. minus 1.5 g. for a sample of whole polymer) was 46.48 g. There was thus a loss of 2.52 g. of polymer during the fractionation. On the assumption that this loss had been uniformly distributed over all fractions, the total weight of the isolated fractions was used in calculating what per cent. of the whole each fraction constituted. The results obtained are given in Table I.

TABLE I

FRACTIONATION OF NEOPRENE TYPE GN

Fraction	Weight, g.	%[a]	$\overline{M}_n$	B[c]	$[\eta]$	k'
Whole	(49.0)	(100)	114,000	2.14	1.07	0.43
A	3.02[b]	6.5	959,000	1.71	2.88	.92
B	4.56[b]	9.8	488,000	1.68	2.38	.65
C	4.13[b]	8.9	387,000	1.36	1.65	.62
D	6.33	13.6	322,000	1.61	1.56	.48
E	4.71	10.1	190,000	1.55	1.05	.44
F	3.69	7.9	152,000	1.73	0.93	.37
G	2.56	5.5	127,000	1.70	.80	.30
H	1.92	4.1	121,000	1.90	.82	.47
I	1.65	3.6	103,000	2.05	.69	.44
J	2.27	4.9	100,000	2.29	.62	.45
K	1.65	3.6	86,400	2.05	.56	.43
L	1.75	3 8	83,000	1.80	.54	.30
M	0.70	1.5	52,000	1.95	.49	.38
N	1.78	3.8	42,000	1.76	.36	.48
O	2.64	5.7	34,500	2.10	.30	.47
P	2.10	4.5	20,500	2.31	.20	.40
Q	1.02	2.2	...	..	.04(?)	..

[a] Per cent. of the total isolated in the fractions. [b] Calculated weight; see procedure. [c] Slope term of the osmotic pressure relationship.

Note in Table I that although the number average molecular weight of the *whole* polymer was 114,000 there was present a broad range of molecular species, from 959,000 to less than 20,500 molecular weight. This range, of course would be widened by any degradation which occurred in the period of almost four weeks which elapsed between the precipitation of fraction A and isolation of the final fraction. However, the calculated number average of the molecular weights of the individual fractions was 105,000 compared with 114,000 for the original polymer indicating that degradation had not been extensive.

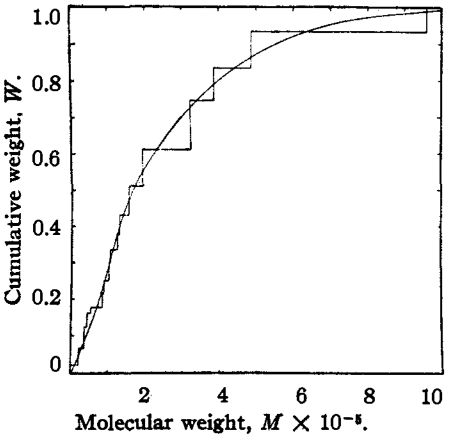

Fig. 3.—Integral molecular weight distribution for Neoprene Type GN.

In Fig. 3 is plotted the molecular weight of each fraction as a part of the whole polymer and from the smoothed curve there is calculated the differential molecular weight distribution given in Fig. 4. This illustrates very well the broad range of molecular weights and shows that the polymer species most abundant are those having molecular weights of about 100,000. The extension of the

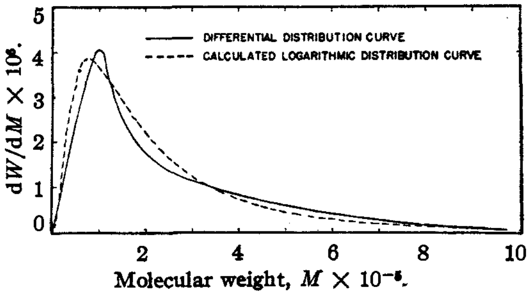

Fig. 4.—Differential molecular weight distribution for Neoprene Type GN.

neoprene distribution curve at the high molecular weight end suggests that there is present some soluble branched and/or cross-linked material, since it has been shown[13] that 10–100 p.p.m. of a cross-linking agent (diisopropenyldiphenyl) in polystyrene gave completely soluble polymers but altered the shape of the distribution curve and markedly increased the length of the high molecular weight end as the concentration of cross-linking agent was increased from 10 to 100 p.p.m.

Decreasing complexity of the fractions as the molecular weight decreases is indicated by the highly significant (probability of occurrence by chance alone is less than 1 in 100) decrease in k' of the viscosity equation (1) from 0.93 for fraction A to 0.406 as an average for fractions D to P. This constant is said to be a characteristic of any given solute–solvent system and is independent of molecular weight.[14] From studies in this laboratory it appears that k' is larger for complex molecules in a given homologous series than for simple, *i. e.*, linear ones. The greater-than-average values of k' for fractions A, B, and C indicate that approximately 25.2% of the neoprene is branched and/or cross-linked appreciably more than the major portion of the polymer. This corresponds to 5.4% of the molecules by number. The major portion of the polymer appears to be uniform in structure, at least within experimental error.

This increase of k' with polymer chain complexity is indicated also by the work of others. For example, Speiser and Whittenberger[15] showed that k' was higher (1.47) for the branched structure, amylopectin, than for the unbranched molecule, amylose (k' = 0.58). Also Morrison, Holmes and McIntosh[16] found that k' of solutions of polyvinyl acetate in bis-(2-chloroethyl) ether containing small amounts of ferric chloride increased as the viscosity increased and the solution gelled, indicating branching and cross-linking reactions, but in the presence of air the viscosity decreased, indicating chain scission, while k' remained constant. Furthermore, Spurlin, Martin and Tennent[17] demonstrated that k' is greatest for solutions where the solvents are poorest. Similarly, a given liquid would be a poorer solvent for cross-linked molecules than for linear molecules of the same species. The present investigation has shown that k' for polychloroprene solutions is not increased by heterogeneity of molecular species,[18] as was reported for polystyrene in toluene.[19] The whole polymer had a lower k' than several of the fractions and k' was not raised by mixing two fractions together, *e. g.*, two fractions having respective $[\eta]$ and k' values of 1.56–0.60 and 0.60–0.40, when mixed in approximately equal parts gave $[\eta]$ = 0.99 and k' = 0.43. Unfortunately the error in k', particularly at low intrinsic viscosity, is frequently quite large, depending in calculation as it does upon the square of the intrinsic viscosity.

The same change in complexity of the fractions is suggested by the change in the slope term B of the osmotic pressure relationship[20]

$$\frac{\pi}{c} = \frac{RT}{M_2} + Bc, \text{ where } B = \frac{RTd_1}{M_1d_2^2}(0.5 - \mu)$$

c is the solute concentration, M_1 and M_2 are the molecular weights and d_1 and d_2 the densities of the solvent and solute, respectively. The constant μ, which depends upon the entropy and heat of mixing for each solvent–solute combination, approaches the value 0.5 for poor solvents, causing B to approach zero. Thus the somewhat lower values of B for early fractions indicate poorer solutions as would be expected if there were present branched and/or cross-linked polymers, but it is recognized that the variations in B may be influenced also by the different molecular weights of the fractions.

The intrinsic viscosities of Neoprene Type GN fractions ranged from 2.88 to 0.20 as noted in Table I. The calculated weight average of the individual values was 1.18 which is not as close to the observed value, 1.07, for the whole polymer as would be desired. There is apparently an error in the value for fraction G or H since the viscosity would be expected to decrease in going from G to H. The discrepancies, however, are not large enough to nullify the general conclusions drawn in this paper.

The intrinsic viscosity is a measure of the viscosity average molecular weight, which approaches the weight average value fairly closely for most polymers, whereas the osmotic pressure determination measures the number average molecular weight. These relationships can be indicated as follows[21]

$$\text{number average: } \overline{M}_n = \frac{\Sigma NM}{\Sigma N}$$

$$\text{viscosity average: } \overline{M}_v = \left(\frac{\Sigma NM^{a+1}}{\Sigma NM}\right)^{1/a}$$

$$\text{weight average: } \overline{M}_w = \frac{\Sigma NM^2}{\Sigma NM}$$

Of course, if a polymer is homogeneous, *i. e.*, all molecules are of the same size, these averages all reduce to the same value. Consequently by assuming that the neoprene fractions were reasonably homogeneous it was possible to calibrate the

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(13) I. Valyi, A. G. Janssen and H. Mark, *J. Phys. Chem.*, **49**, 461 (1945). Addition of cross-linking agent does not necessarily result in the theoretical number of cross-links; see J. W. Breitenbach, *Experientia*, **3**, 239 (1947).

(14) M. L. Huggins, *Ind. Eng. Chem.*, **35**, 980 (1943); T. Alfrey, A. Bartovics, and H. Mark, This Journal, **65**, 2319 (1943); M. L. Huggins, *ibid.*, **66**, 1991 (1944).

(15) R. Speiser and R. T. Whittenberger, *J. Chem. Phys.*, **13**, 349 (1945).

(16) J. A. Morrison, J. M. Holmes and R. McIntosh, *Can. J. of Res.*, **24**, 179 (1946).

(17) H. M. Spurlin, A. F. Martin and H. G. Tennent, *J. Polymer Sci.*, **1**, 63 (1946).

(18) W. E. Davis, This Journal, **69**, 1453 (1947), reports similar results for cellulose nitrate.

(19) R. S. Spencer and R. F. Boyer, *Polymer Bull.*, **1**, 129 (1945).

(20) M. L. Huggins, This Journal, **64**, 1712 (1942); P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(21) P. J. Flory, This Journal, **65**, 380 (1943).

viscosity-molecular weight relationship against the osmotic pressure determinations. The only check on homogeneity of the neoprene fractions was obtained on a fraction from a later, similar, careful fractionation, where the osmotic molecular weights ($\overline{M}_n$) of 186,000 and 190,000 in duplicate determinations, were, within experimental error, the same as those ($\overline{M}_w$), 192,000 and 193,000, obtained by light scattering. The excellence of this agreement was probably fortuitous but the results demonstrate that the fraction was essentially homogeneous.

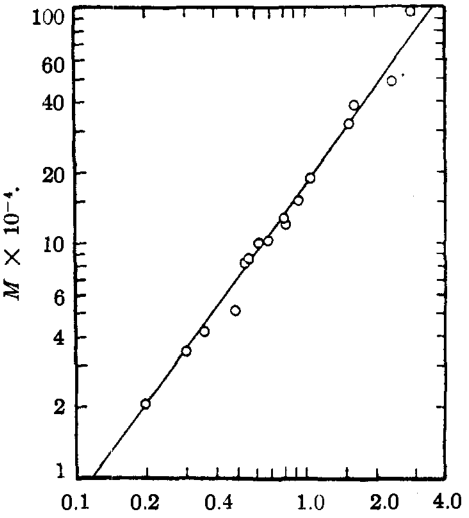

Fig. 5.—Log $\overline{M}_n$ *vs.* log [η] for Neoprene Type GN fractions.

The values of $\overline{M}_n$ and [η] for fractions A to P are plotted on a log–log scale in Fig. 5. The calculated best straight line is seen to account fairly well for the majority of the experimental points. The equation of this line is $\log M = 5.2466 + 1.367 \log [\eta]$ or $M = 1.76 \times 10^5 [\eta]^{1.37}$ which can be rearranged into the usual form: $[\eta] = KM^a$ where $K = 1.46 \times 10^{-4}$ and $a = 0.73$. A duplicate fractionation of only six fractions gave the equation $[\eta] = 1.26 \times 10^{-4} M^{0.75}$. This expression confirms the one above within experimental error but is less accurate because of the fewer fractions and consequent lower homogeneity of the fractions. It is of interest to note that the exponent "a" has a higher value than the 0.66 reported for GR-S[22] and the 0.67 reported for natural rubber,[23] indicating that polychloroprene chains are somewhat stiffer than those of GR-S or rubber.

Using the data of Table I the weight average and viscosity average molecular weights can be calculated by the above formulas

$$\overline{M}_w = 257{,}000$$
$$\overline{M}_v = 233{,}000$$

The ratio $\overline{M}_v/\overline{M}_w = 0.91$ indicates that the viscosity average approaches the weight average reasonably closely. From $\overline{M}_w/\overline{M}_n = 2.25$ the Lansing and Kraemer[24] non-uniformity coefficient was obtained: $\beta = 1.27$. This value shows that Neoprene Type GN is less homogeneous than sol natural rubber ($\beta = 0.7$)[25] but is more homogeneous than GR-S as indicated by $\beta = 1.60$, calculated from the data of French and Ewart.[22]

A comparison of distribution curves calculated from the non-uniformity coefficients by means of the logarithmic function of Lansing and Kraemer[24] is given in Fig. 6.[26] The neoprene molecular weight distribution curve is unlike that of sol natural rubber both in shape and in the molecular weights of the most abundant species, which undoubtedly accounts for some of the differences in physical properties of these rubbers. Natural rubber sol appears to have a somewhat narrower distribution of molecular weights and a more nearly symmetrical curve with a broad maximum at M = 2–300,000. Note, however, that natural rubber peptized with phenylhydrazine[26] exhibits a distribution curve which in shape is more like that of Neoprene Type GN although it does not extend to as high molecular weight as the latter. From the data available it would appear that the distribution curve for GR-S is similar to that of Neoprene Type GN in shape but that the peak occurs at somewhat lower molecular weight.

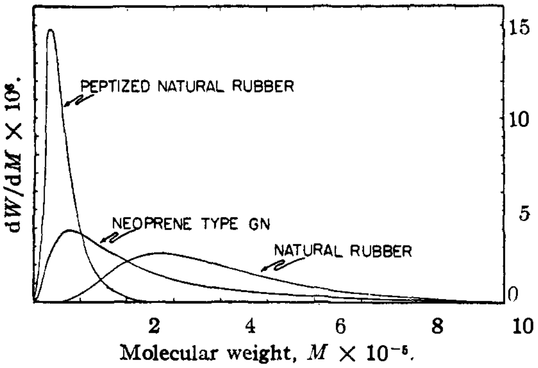

Fig. 6.—Comparison of molecular weight distribution curves for Neoprene Type GN, natural rubber sol and a peptized natural rubber.

It is to be noted that the experimental distribution curve for neoprene exhibits a positive skewness and is fairly well represented by the normal logarithmic distribution of Lansing and Kraemer

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[22] D. M. French and R. H. Ewart, *Anal. Chem.*, **19**, 165 (1947).

[23] W. C. Carter, R. L. Scott and M. Magat, This Journal, **68**, 1480 (1946).

[24] W. D. Lansing and E. O. Kraemer, *ibid.*, **57**, 1369 (1935).

[25] E. O. Kraemer and J. B. Nichols in T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Oxford Press, 1940, p. 353. A value of $\beta = 1.0$ is reported here for an early experimental sample of polychloroprene.

[26] Similarly calculated distribution curves based on ultracentrifuge measurements made in this laboratory for GR-S sol rubber, low viscosity (peptized) rubber and an early, experimental sample of neoprene before and after peptization have been published; E. O. Kraemer and J. B. Nichols, *ibid.*, p. 423; L. B. Sebrell, *Ind. Eng. Chem.*, **35**, 736 (1943).

(see Fig. 4). Attempts to apply a two parameter distribution function[27] of the Schulz type to these data have not given particularly consistent results. The Lansing–Kraemer logarithmic distribution is considered a better representation of the data for Neoprene Type GN within the experimental errors of fractionations and molecular weight determinations.

Acknowledgment.—The authors gratefully acknowledge the helpfulness of preliminary experiments on the fractionation of neoprene carried out in this laboratory by Dr. S. L. Scott, now of the Service Department of the du Pont Company. Acknowledgments likewise are made to Dr. F. T. Wall and Dr. H. Mark for many helpful discussions during the course of this research and to Miss B. L. Price for her assistance in the osmotic pressure measurements.

Summary

Polychloroprene rubber, Neoprene Type GN, has been fractionated by partial precipitation from dilute solution in benzene and the fractions examined both osmotically and viscometrically in benzene solutions.

The molecular weight distribution curve for Neoprene Type GN based on osmotic pressure measurements shows a pronounced maximum at 100,000 but has a long extension to molecular weights of over one million, indicating the presence of branched or cross-linked material which is still soluble. The uniformity is somewhat less than that of sol natural rubber, while in shape the neoprene distribution curve resembles more closely that of a peptized natural rubber than fresh sol rubber.

Observed variations in the slopes of the π/c vs. c and the η_{sp}/c vs. c curves also indicate the presence in solution of complex, branched and/or cross-linked molecules.

Calibration of the intrinsic viscosity-molecular weight relationship by osmotic pressure measurements gave good agreement with the equation $[\eta] = KM^a$, where $K = 1.46 \times 10^{-4}$ and $a = 0.73$.

WILMINGTON, DELAWARE RECEIVED FEBRUARY 12, 1948

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[27] G. V. Schulz, *Z. physik. Chem.*, **B43**, 25 (1939); R. F. Boyer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 342 (1946); I. Jullander, *J. Polymer Sci.*, **2**, 329 (1947).

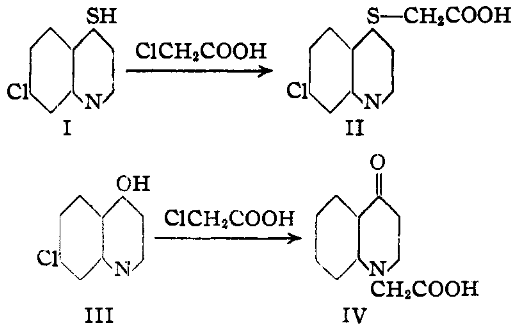
[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Basic Esters and Amides of 4-Quinolylmercaptoacetic Acid Derivatives

BY ALEXANDER R. SURREY

The present investigation was undertaken to synthesize 4-quinolyloxy-, 4-quinolylamino- and 4-quinolylmercaptoacetic acid derivatives to make them available for pharmacological study.

It was observed that, in alcohol solution, 4,7-dichloroquinoline[1] reacts with thiourea to yield a thiouronium salt which on treatment with sodium carbonate gives 7-chloro-4-quinolinethiol (I) and a small amount of 7,7′-dichloro-4,4′-diquinolyl sulfide. The thiol (I) reacts with chloroacetic acid to give (7-chloro-4-quinolyl)-mercaptoacetic acid (II). The fact that compound II was also obtained by the reaction of 4,7-dichloroquinoline with mercaptoacetic acid indicates that the structure of II must be correct.



The behavior of the thiol, I, with chloroacetic acid is strikingly different from that of the corresponding 4-hydroxyquinoline, III. The reaction of III with chloroacetic acid yields only the 4-keto-1(4)-quinolineacetic acid IV. Similarly, when ethyl chloroacetate was allowed to react with 4-amino-7-chloroquinoline, ethyl 7-chloro-4-imino-1(4)-quinolineacetate (V) was obtained. The formation of IV and V is not unexpected when one considers the known behavior of similar compounds on treatment with alkyl iodide.[2] Hydrolysis of V with 5% sodium hydroxide solution gives the quinolone IV. Both V and the ethyl ester prepared from IV are high melting solids, insoluble in the usual organic solvents. A comparison of the ultraviolet absorption spectra of IV with the mercaptoacetic acid, II, is shown in Fig. 1.[3]

Inasmuch as the 4-amino- and 4-hydroxyquinolines did not give the desired intermediates, the present work was confined mainly to the 4-quinolylmercaptoacetic acid derivatives. The acids (Table I) were prepared from the corresponding 4-chloroquinoline by treatment with mercaptoacetic acid. The basic esters were prepared by ester interchange. Accordingly, the appropriate methyl ester (Table I) was refluxed in Skellysolve

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[1] Surrey and Hammer, THIS JOURNAL, **68**, 113 (1946).

[2] F. W. Bergstrom, *Chem. Rev.*, **35**, 133, 135, 177 (1944).

[3] The absorption spectra were determined in these laboratories under the direction of Dr. G. W. Ewing, present address Union College, Schenectady, N. Y.