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The Structure of Neoprene. III.[1] The Molecular Weight Distribution of Neoprene Type CG

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Neoprene Type CG and Neoprene Type GN are polychloroprenes made in essentially identical emulsion systems at 10 and 40°, respectively. They are both sulfur-modified polymers plasticized with tetraethylthiuram disulfide, but they differ markedly in physical properties, particularly with respect to rate of crystallization.[2] The polymer made at 10°, Neoprene Type CG, on standing at 25° hardens by crystallization in a few hours compared to days required for comparable changes in Neoprene Type GN. Furthermore,[2] Neoprene Type CG has greater plasticity than Neoprene Type GN and its vulcanizates show higher tensile strengths at 25 and 70°. These differences in physical properties have become well known since the introduction of Neoprene Type CG in 1941. It was of particular interest therefore in this study of the structure of neoprene to compare these polymers to obtain information about the structural features responsible for the differences in their properties.

Among the first constants desired in the characterization of any high polymer are the average molecular weight and the molecular weight distribution. That information is available for Neoprene Type GN[3] and the corresponding values are now reported for Neoprene Type CG. The same experimental methods, involving fractional precipitation from dilute benzene solution under controlled temperature conditions, and viscometric and osmometric examination of each fraction, were employed.[3] It is recognized that the fractionation method has certain deficiencies[4] but no clearly satisfactory substitute for general use has appeared.

Experimental

Materials.—A sample (55 g.) of standard, commercial Neoprene Type CG, approximately two months old, was cut into small pieces and dissolved in 500 ml. of thiophene-free, dry benzene. The polychloroprene was precipitated completely with methanol, washed twice with methanol and redissolved immediately in 500 ml. of benzene. After the addition of 0.5 g. of phenyl-α-naphthylamine the solution was diluted to 5 l. and a sample removed for determination of the constants of the original polymer. From the concentration of polymer in this solution it was calculated that 48.8 g. of purified polymer, free from soap residues and other contaminants, had been recovered for the fractionation.

Fractionation.—The fractionation was carried out by fractional precipitation from the approximately 1% solution in benzene, using methanol as the precipitant. Each sample was precipitated at 25° as described previously.[3] The first three fractions were not isolated as dry polymers since it was found that they became cross-linked and insoluble on drying.

Measurements.—Number average molecular weights in benzene solution were measured by means of static type osometers. For each sample, duplicate determinations made at each of four different concentrations were plotted as π/c *vs.* c and extrapolated to zero concentration, assuming a straight line relationship. Representative curves are given in Fig. 1.

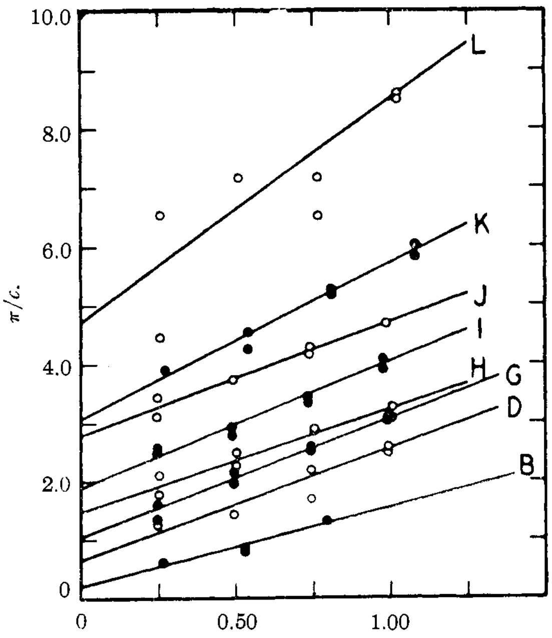

Fig. 1.—π/c *vs.* c curves for representative Neoprene Type CG fractions.

Viscosities were measured in benzene solution using an Ubbelohde suspended-level viscometer which had been modified by the substitution of a 50-ml. reservoir for the usual 5–10-ml. bulb. Dilutions were made directly in the viscometer and the viscosity measured at four different concentra-

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[1] Part II, Mochel and Peterson, THIS JOURNAL, **71**, 1426 (1949).

[2] Walker and Mochel, *Proc. Inter. Rubber Tech. Conf.*, London, 1948, Preprint No. 11.

[3] Mochel, Nichols and Mighton, THIS JOURNAL, **70**, 2185 (1948).

[4] *Cf.* Bamford and Dewar, *Proc. Roy. Soc. (London)*, **A192**, 329 (1948).

tions. The intrinsic viscosity and k' constants were then calculated by plotting reduced viscosity η_{sp}/c vs. c and applying the straight line equation, $\eta_{sp}/c = [\eta] + k' [\eta]^2 c$, developed by Huggins and others.[5] The experimental values are shown in Fig. 2. These procedures are described in greater detail in a previous publication.[3]

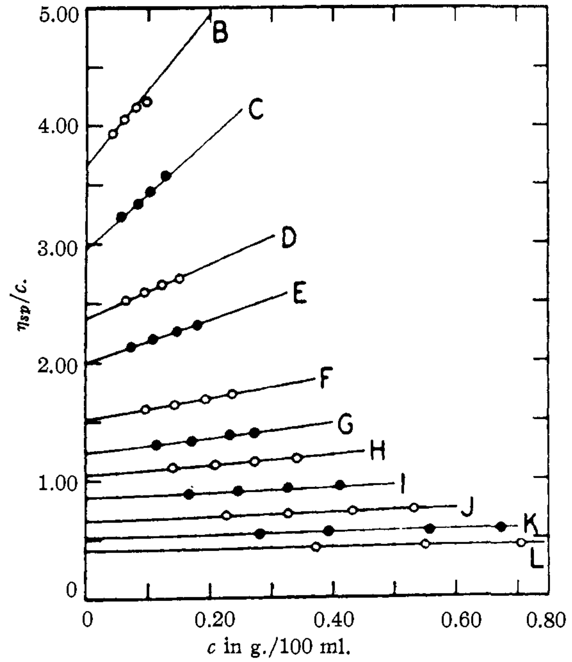

Fig. 2.—η_{sp}/c vs. c curves for Neoprene Type CG fractions.

Results and Discussions

The purified Neoprene Type CG was divided into 13 fractions having the properties given in Table I. The total weight of fractions isolated from the 48.8 g. of purified polymer used was 45.3 g. (93% recovery). It was assumed that the 7% loss that occurred had been uniformly distributed over all fractions and therefore the total weight of the isolated fractions was used in calculating that proportion of the whole each fraction constituted.

Fraction A, after precipitation, could not be redissolved in benzene even though the greatest care had been taken to avoid contact with air. Repetition of the experiment led to the same results, indicating that fraction A was probably inherently insoluble or very nearly so. The original whole polymer had been examined for gel content but was found to be completely soluble in benzene when tumbled with benzene and yielded only 0.6% gel when examined by a milder technique using the Baker cell.[6] However, a small amount of "microgel"[6] might well precipitate as a first fraction and carry down with it a small amount of soluble polymer in associated form, giving an insoluble product.

Table I

Neoprene Type CG Fractions

Fraction	Weight, g.	%[a]	$\overline{M}n$	B[b]	[η]	k'
Whole	(48.8)		168,000	2.02	1.56	0.60
A	3.00	6.6	gel	..	..	..
B	1.26	2.8	1,450,000 (?)	1.37	3.67	.47
C	1.86	4.1	579,000	1.67	2.96	.54
D	10.14	22.4	445,000	1.94	2.37	.41
E	2.04	4.5	362,000	1.86	2.00	.44
F	4.59	10.1	276,000	1.78	1.52	.37
G	4.60	10.2	276,000	2.07	1.23	.41
H	3.55	7.8	195,000	1.75	1.05	.38
I	4.16	9.2	153,000	2.10	0.86	.29
J	3.42	7.6	104,000	1.87	0.66	.35
K	2.60	5.7	93,400	2.62	.52	.31
L	2.10	4.6	61,400	3.75	.40	.33
Res.	2.0	4.4	....	..	..	..
	45.32					

[a] Per cent. of total isolated in fractions. [b] Slope term of osmotic pressure equation.

Fraction B appeared to have a very high molecular weight but unfortunately the osmotic results for this fraction were scattered and a reliable molecular weight value was not obtained. Fraction D was larger than desirable for molecular weight distribution work; judging the amount of precipitant to add each time is one of the major problems of fractionation work. The molecular weight of fraction F or G is probably in error since it would not be expected that successive fractions would be identical. The number of fractions obtained was not as large as would be desired but it is believed that the general conclusions are valid. Reprecipitation of the fractions was not attempted since earlier work[3] had shown that the extra handling required for each fraction led to degradative changes which tended to nullify improvements in homogeneity.

The average molecular weight of whole Neoprene Type CG, 168,000, is considerably higher than that for Neoprene Type GN, 114,000, previously reported.[3] The calculated number average of the molecular weights of the individual fractions was 220,000, leaving out fraction A and the residue. This value is considerably higher than the measured value for the whole polymer due probably to the neglect of the residue. Assuming a reasonable molecular weight of 30,000 for the residue, the calculated number average would be 166,000. The molecular weight of fraction A would be high and would have little effect on the number average.

From the experimental values in Table I there is plotted the cumulative distribution curve of Fig. 3. From the smoothed curve there is calculated the differential molecular weight curve given in Fig. 4. Fifty per cent. of the Neoprene Type CG has a molecular weight above 250,000 compared to 165,000 for Neoprene Type GN. Also the maximum of the Type CG differential curve, *i. e.*, the

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[5] Huggins, This Journal, **64**, 2716 (1942); Schulz and Blaschke, *J. prakt. Chem.*, **158**, 130 (1941).

[6] Back, *Ind. Eng. Chem.*, **39**, 1339 (1947); Baker, *ibid.*, **41**, 511 (1949).

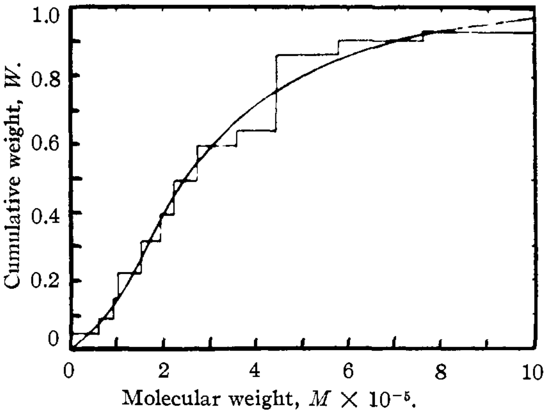

Fig. 3.—Integral molecular weight distribution for Neoprene Type CG.

most abundant species, is 160,000, compared to about 100,000 for Type GN. The molecular weight distribution curves for both polymers exhibit long extensions at the high molecular weight ends, believed to be due to the presence of soluble, branched and/or cross-linked material.[7] If the gelation of fraction A were due to cross-linking occurring after isolation, this extended tail on the molecular weight distribution curve should be decreased. However, it is believed, as stated before, that fraction A contained microgel and that the distribution curve as drawn is real.

A further difference between Neoprene Type CG and Type GN is that the maximum in the molecular weight distribution curve is not only at higher molecular weight for Type CG but the spread about this point is more uniform than in the case of Type GN. This uniformity is also shown by the lower value, $\beta = 1.12$, for the non-uniformity coefficient of Lansing and Kraemer[8] in contrast to the value, $\beta = 1.27$, reported for Neoprene Type GN[3] (Hevea rubber, $\beta = 0.70$). The logarithmic distribution curve calculated by the Lansing–Kraemer method is shown in Fig. 4 for comparison with the experimental curve. (For CG, $M_w/M_n = 316{,}000/168{,}000 = 1.88$, using the weight average molecular weight calculated from the fractions.)

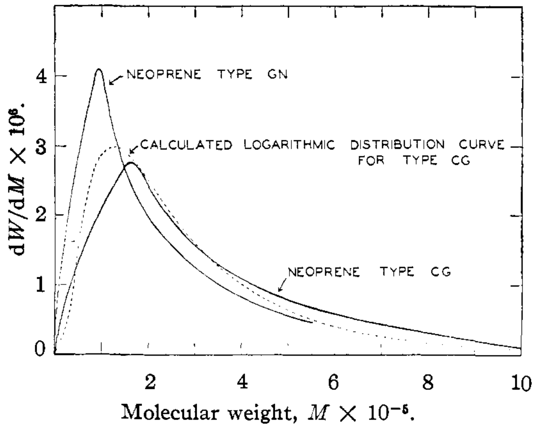

Fig. 4.—Differential molecular weight distribution curves for Neoprene Type CG and Neoprene Type GN. The logarithmic distribution curve (Type CG, calc.) was calculated by the method of Lansing and Kraemer.

From Table I it will be noted that the k' constants of the viscosity equations for the fractions of Neoprene Type CG are smaller than the value obtained for the whole polymer, in contrast to the results for Neoprene Type GN, where the fractions exhibited k' values as large or larger than that for the whole polymer.[3] It is believed that the reason for this difference in the case of Neoprene Type CG is that the whole polymer was not completely soluble but contained some microgel. Presumably, k' for fraction A would have been very high had it been possible to measure it. The k' constants for fractions B and C appeared to be slightly higher than average but the difference is not highly significant statistically because of the wide variations in k' constants for the other fractions. Assuming that this difference is real, it appears that fractions A, B and C, which constitute 13.5% of the total, are branched or cross-linked appreciably more than the rest of the polymer. Comparable fractions in Neoprene Type GN made up 25.2% of the total. These figures, however, should not be construed to be the actual percentages of branched or cross-linked material in either polymer. No evidence of micro gel was detected in GN, perhaps because of the lower molecular weight of the latter polymer. It will be noted that B, the osmotic slope term, is lower for fractions B and C than for the remainder. This can be due either to poorer solutions or to higher molecular weights and our evidence cannot distinguish between the two effects. B also shows a definite upward trend with decreasing molecular weight.[9] The k' values for fractions of Neoprene Type CG showed a significant correlation with the intrinsic viscosities (correlation coefficient = 0.787) even when the high values for fractions B and C were omitted. No such correlation was found for Neoprene Type GN.

A straight line relationship between number average molecular weights and intrinsic viscosities for fraction C to L, inclusive, is shown in Fig. 5. The equation for this line is $\log M = 5.2529 + 1.119 \log [\eta]$ or $M = 1.79 \times 10^5 [\eta]^{1.12}$. This may be rearranged into the more usual form $[\eta] = KM^a$ where K is 2.02×10^{-6} and a is 0.89. Agreement of most of the fractions with this relationship is seen to be very good; only B was in serious error and the osmotic value for B was dependent upon only four points in poor agreement. The significance of the high value for the exponent a is not fully understood. Note that the values of K and a for Neoprene Type GN are, respectively, 1.46×10^{-4} and 0.73 when calculated similarly.

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[7] Valyi, Janssen and Mark, *J. Phys. Chem.*, **49**, 461 (1945).

[8] Lansing and Kraemer, THIS JOURNAL, **57**, 1369 (1935).

[9] *Cf.* Doty and Mark, *Ind. Eng. Chem.*, **38**, 682 (1946).

Statistical analysis has shown that there is less than one chance in a thousand that the exponents for Neoprene Type CG and Type GN are different because of experimental error alone.

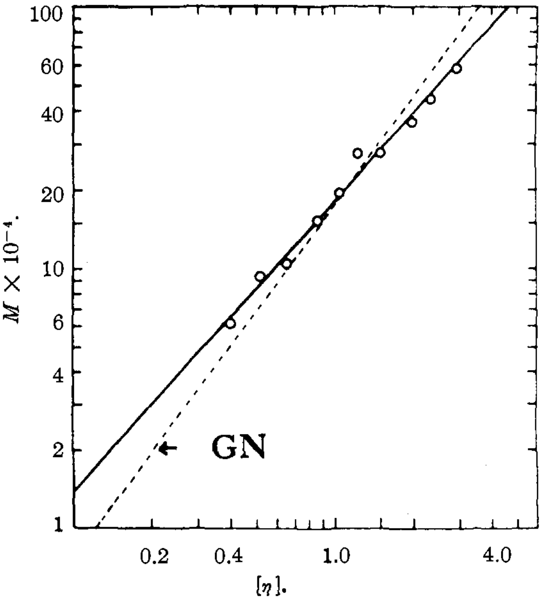

Fig. 5.—Log M_n *vs.* log $[\eta]$ for Neoprene Type CG fractions (GN, neoprene type GN).

The higher value of a for Neoprene Type CG than for Type GN would appear to indicate that the former polymer has less flexible molecules than has GN[10] or that the shielding effect is smaller,[11] due perhaps to greater intermolecular attraction. This exponent a was observed to *increase* with increasing polymerization temperature in the case of styrene,[12] a situation the opposite of that reported here for neoprene, and the results have been interpreted in terms of poorer symmetry, of a stereochemical type, in polystyrene made at high temperatures.[13] The change in a for neoprene may be reversed because of much greater interchain attractive forces, as evidenced by its tendency to crystallize. Certainly poorer symmetry would not be expected in Neoprene Type CG. An attempt to measure association of Neoprene Type CG in benzene solution by determination of intrinsic viscosities at 25 and 50° gave values whose ratio varied from 0.90 to 0.97. These are the same as observed for Type GN and as reported for polychloroprene of a different origin.[14] Whatever the explanation for the difference in values for a, it is evident that there must be a structural difference between Neoprene Type CG and Type GN, quite apart from the differences in molecular weight and molecular weight distribution.

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Summary

The low temperature polychloroprene rubber, Neoprene Type CG, has been fractionated by partial precipitation from dilute solution and the fractions examined both osmotically and viscometrically in benzene solutions. The molecular weight distribution curve for Neoprene Type CG based on osmotic pressure measurements shows a pronounced maximum at 160,000 molecular weight compared to 100,000 for Neoprene Type GN and the curve has a more uniform distribution about the maximum value. Neoprene Type CG whole polymer has a higher number average molecular weight than GN, 168,000 *vs.* 114,000.

Calibration of the intrinsic viscosity–molecular weight relationship by osmotic pressure measurements gave good agreement with the equation $[\eta] = KM^a$ where $K = 2.02 \times 10^{-5}$ and $a = 0.89$. The exponent a, which is generally considered to be related to the flexibility of the molecules in solution, indicates that the molecules of Neoprene Type CG are less flexible or have greater intermolecular attraction than those of GN. It is clear therefore that there is a structural difference between these two polymers in addition to the observed differences in average molecular weight and molecular distribution.

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[10] *Cf.* Huggins, *Ind. Eng. Chem.*, **35**, 980 (1943); Simha, *J. Chem. Phys.*, **13**, 188 (1945).

[11] Debye, *ibid.*, **14**, 636 (1946); Debye and Bueche, *ibid.*, **16**, 573 (1948).

[12] Alfrey, Bartovics and Mark, THIS JOURNAL, **65**, 2319 (1943). Values for k' of polystyrenes decreased as the polymerization temperature was raised; similarly k' of the neoprene made at 10° appears to be higher than that of the polymer made at 40°.

[13] Huggins, *ibid.*, **66**, 1991 (1944).

[14] Staudinger and Staudinger, *J. prakt. Chem.*, **162**, 148 (1943).