

Fractionation and Determination of Molecular Characteristics of Elastomers. I. Neoprene W

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Synopsis

In this study of Neoprene W, it has been possible to show that this elastomer possesses a fairly wide distribution of molecular weights and presents some degree of branching. The relationship $[\eta] = 2.90 \times 10^{-3} \bar{M}_w^{0.74}$ has been established between the limiting viscosity number and the weight-average molecular weight. In addition, a study of the degradation of Neoprene W by mastication has shown that the behavior of this rubber is rather different from that of other elastomers. If the mastication has been carried out on relatively large amounts of rubber, the relationship $[\eta] = 1.25 \times \bar{M}_w^{0.28}$ may be used to determine the weight-average molecular weight from viscosity measurements. Different molecular characteristics of Neoprene W in tetrahydrofuran and in methyl ethyl ketone are also given.

A knowledge of molecular characteristics (molecular weights, mean-square end-to-end distances of chains, virial coefficients, etc.) and of distribution curves for high polymers is of particular importance since they have a certain bearing on their physical, chemical, and technological properties. Until now, saturated polymers have been extensively studied, while unsaturated polymers (and hence the majority of elastomers) have received relatively little attention, mainly because of their tendency to undergo oxidation, which renders determinations difficult. Moreover, published results show a significant degree of dispersion. It was with the object of completing and correlating previous studies that we undertook the determination of molecular characteristics of various types of commercial elastomers (natural rubber, polychloroprenes, polybutadienes, butadiene-styrene and butadiene-acrylonitrile copolymers, etc.). The first part of this study is concerned with the polychloroprenes, or neoprenes. Attempts have been made to obtain distribution curves and to determine certain molecular characteristics, and then to deduce from them a relationship between the weight-average molecular weight and the limiting viscosity number which could be used in the routine determination of molecular weights by viscometry. The influence of mastication on the molecular weight of neoprene was also investigated.

EXPERIMENTAL

Type of Neoprene Used

Neoprene W, a non-sulfur-modified type of polychloroprene was chosen for the following three reasons: (1) it is a commonly used, general-purpose rubber; (2) it is relatively stable on storage; (3) till now, only a limited number of physicochemical studies have been made (Table I).

TABLE I

Type of neoprene	Method	Solvent	Constants of the equation $[\eta] = KM^\alpha$		Number of fractions	References
			$K \times 10^2$	α		
GN	Osmometry and viscometry	Benzene, thiophene-free	1.46	0.73	17	1
GN	Osmometry and viscometry	Benzene, thiophene-free	1.26	0.75	6	1
GN	Osmometry and viscometry	Toluene	2.73	2/3	11	2
CG	Osmometry and viscometry	Benzene, thiophene-free	0.202	0.89	13	3
W	Osmometry and viscometry	Benzene, thiophene-free	1.55	0.71	11	4
GRT	Osmometry and viscometry	Toluene	2.445	0.696	—	5
WRT	Osmometry and viscometry	Toluene	5.074	0.61	—	5
Svitpren K	Osmometry and viscometry	Benzene	0.312	0.877	18	6

To prevent any variation in the polymer during the study, a stock of Neoprene W was set aside away from light and heat. Also, in order to reduce the risk of premature crosslinking the samples were not submitted to prior purification by total precipitation, but were simply washed several times with methyl ethyl ketone (MEK) to remove talc and visible contaminants.

Solvent

Methyl ethyl ketone was finally chosen after a series of preliminary experiments with various solvents. Solutions of neoprene in this solvent do, in fact, exhibit a high value of the specific refractive increment, which makes it possible to work with relatively low concentrations when using the light-scattering method, as in the present instance.

The solvents used were distilled under nitrogen and kept in the dark in special containers in which they could be kept in an inert atmosphere.⁷

Preparation of Solutions

Solutions were prepared by introducing sufficient neoprene into the methyl ethyl ketone to obtain a solution of a concentration in the region of 10^{-2} g./ml. After 36 hr., solution was completed by mechanical agitation for 3 hr. In order to check oxidation of the neoprene, 0.05% of an anti-oxidant (2,6-di-*tert*-butyl-4-methylphenol or Ionol) was added to the solutions. When a gel fraction appeared in the solution, it was removed prior to further operations by filtration through a No. 1 sintered glass filter.

Method of Fractionation

The determination of distribution curves for a polymer necessitates prior separation into several fractions which should be as little polydisperse as possible. Fractional precipitation was the method adopted in the case of Neoprene W. This is achieved by adding a given amount of methanol at constant temperature and with vigorous agitation to a solution of neoprene in methyl ethyl ketone until a turbidity is produced. The temperature is then raised to 30°C. to clarify the solution. The temperature is then allowed to drop again slowly to 25°C. When the precipitate has settled, which may take from 24 to 48 hr., it is removed by suction, and this fraction is allowed to settle in order to recover the supernatant liquor which is then returned to the fractionation vessel. Normally, when this method of fractionation is employed, the coacervates are dried under vacuum at ambient temperature to constant weight. However, in the case of unsaturated polymers, this method is a frequent cause of crosslinking which renders the fractions insoluble. This is particularly so when the fraction has a high average molecular weight.

It was found that it is the case for neoprene and a special method of recovering the various fractions was devised.

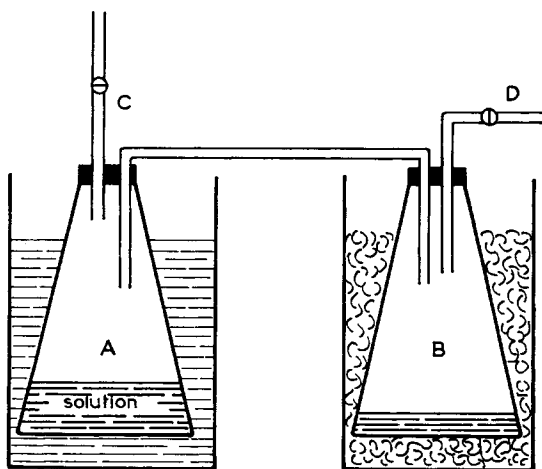


Fig. 1. Apparatus for the final preparation of the fractions.

The apparatus shown in Figure 1 was used. The coacervate is placed in vessel A and the apparatus is evacuated (with a water pump). Tap D* is then closed, and vessels A and B are placed respectively in water at 30°C. and in a cooling bath. The methanol/MEK azeotrope distils from A into B. Before evaporation is complete, pure methyl ethyl ketone is added to vessel A and the operation is repeated until the whole of the methanol disappears, which is indicated by measuring the refractive index of the distillate collected in vessel B.

Finally, the amount of rubber in each fraction is determined and also the final concentration of the solution. This solution is then used, after suitable dilution, for light scattering and viscosity measurements.

Viscometry

Viscometers of the Ubbelohde suspended level type⁸ with capillaries 0.4 mm. in diameter have been used. Kinetic energy and turbulence corrections were checked to ensure that they were negligible as compared with errors due to concentration or flow time.

Determinations were carried out at a temperature of $25 \pm 0.1^\circ\text{C}$. and concentrations were expressed in grams/milliliter.

The limiting viscosity numbers were obtained by extrapolation to zero concentration of the following functions:

$$(\eta - \eta_0)/\eta_0 C = f(C) \quad (1)$$

and

$$\ln(\eta/\eta_0)/C = f'(C) \quad (2)$$

η being the viscosity of a solution of concentration C and η_0 the viscosity of the pure solvent. These functions are generally linear for concentrations of less than 10^{-2} g./ml. When the two straight lines do not intersect on the ordinate axis, the arithmetic mean of the results was taken as the value of the limiting viscosity number.

Light Scattering

Light scattering was the method used to determine absolute molecular characteristics. In this way,⁹ apart from the weight-average molecular weight \bar{M}_w , it is possible to determine various molecular characteristics of a given polymer-solvent system, such as radii of gyration, virial coefficients, mean-square end-to-end distances of chains.

The equipment used was a Wippler and Scheibling light-scattering photogoniometer.¹⁰ The specific refractive increment dn/dc of Neoprene W in methyl ethyl ketone and in tetrahydrofuran (which was used in a number of experiments) are 0.152 and 0.138 ml./g., respectively for a wavelength of $\lambda = 5460 \text{ \AA}$.

* It has been found by experience that if tap D is not closed, i.e., if vacuum is continuously applied, the refractive index of the distillate always remains below that of the methyl ethyl ketone, because a small amount of water condenses in vessel B.

The vertical component of the light was measured, in each experiment, at eleven different angles between 30° and 150° and for four dilutions. Zimm's method¹¹ was used to interpret the results.

Before examination, the solutions were centrifuged for 1 hr. at 22,000*g* in a Phywe refrigerated centrifuge.

However, since the first light-scattering measurements carried out on unfractionated Neoprene W which had simply been centrifuged gave abnormally high values* of the weight-average molecular weight ($\bar{M}_w = 2.2 \times 10^6$), it was necessary to filter them before centrifuging by means of the technique proposed by Allen and Bristow.¹² This consists of filtering the solutions through progressively finer sintered glass filters (Pyrex Nos. 2 to 4) and then through a sintered stainless steel disk whose average pore diameter is 1 μ .

Since the amount of neoprene removed by filtration is less than 5% and since the limiting viscosity number of the solution remains constant, it may be concluded that this method of removing the crosslinked particles leaves the specimen virtually unchanged and the value obtained for the weight-average molecular weight ($\bar{M}_w = 501,000$) of the sample as a whole may be considered satisfactory. This method was therefore systematically used for all solutions.

Mastication of Samples

In the second part of this work, the variations in molecular weight of Neoprene W during mastication were determined. Mastication was carried out cold with a Troester mill. The nip between the rolls was kept constant during the experiments and samples were taken at different times during mastication. The weight of the samples was negligible as compared with the total amount of neoprene used (about 2000 g.) and, as a result, degradation of the samples was practically identical throughout mastication.

RESULTS AND DISCUSSION

Progressive degradation during the course of mastication gives polymer fractions of varying and regularly decreasing molecular weight. Such fractions of decreasing molecular weight may also be obtained by fractionation.

However, a fundamental difference exists between these two processes. The first yields samples in which the degree of heterogeneity remains important. On the other hand, the second preserves the integrity of the molecules and simply tends to separate the molecules corresponding to different degrees of polymerization. However, even these latter fractions also exhibit a certain heterogeneity.

* These were probably due to the presence in the solutions of highly crosslinked spherical particles which are known to cause considerable irregularities in light-scattering measurements.¹³

Distribution Curves of Neoprene W

Two fractionations of Neoprene W were carried out; however, the results of the first experiment were rejected for the plotting of the distribution curves, since a loss of 14.3% was recorded during fractionation, probably due to the several handling operations carried out on the fractions and the formation of irrecoverable deposits on the walls of the flask. The results of the second experiment on 48 g. of Neoprene W are shown in Table II.

TABLE II

Fraction	Fraction weight, g.	w_i , %	Cumulative weight fraction W	$\bar{M}_w \times 10^{-5}$	$\log \bar{M}_w$	$[\eta]$, ml./g.	$\log [\eta]$
φ_1	2.00	6.51	96.75	11.22	6.049	88	1.944
φ_2	0.88						
φ_3	7.44	16.83	85.07	10.84	6.035	80	1.903
φ_4	4.50	10.18	71.57	9.12	5.960	74.5	1.872
φ_5	5.60	12.67	60.15	7.94	5.900	68	1.832
φ_6	5.50	12.44	47.59	7.24	5.860	63	1.800
φ_7	3.02	6.83	37.96	6.02	5.780	56	1.748
φ_8	5.98	13.53	27.77	4.78	5.679	43	1.633
φ_9	1.28	2.90	19.56	4.36	5.639	39.5	1.596
φ_{10}	1.00	4.54	15.84	3.33	5.525	36	1.556
φ_{11}	1.01						
φ_{12}	6.00	13.57	6.79	2.04	5.310	25	1.398
	44.21						
Whole sample				5.01	5.700	48	1.681

It should be noted that it was found necessary to concentrate the mother solution during fractionation, because, when the concentration of neoprene drops below approximately 0.5%, the addition of methanol produces only a turbidity.

It was for this reason that the solution was distilled at 30°C. under partial vacuum in a gentle stream of nitrogen. When the volume had been reduced to one-half, addition of nonsolvent was again begun and it was possible to collect the final fractions.

The results in Table II show that in this case, too, it was impossible to collect the whole of the rubber taken into solution because of the formation of an irrecoverable deposit on the walls of the flask. The loss was 7.9%, and in order to construct the distribution curve it was necessary to assume that this loss was distributed throughout the whole of the fractions.

Since it was impossible to do viscosity and light-scattering determinations on fractions φ_1 , φ_2 , φ_{10} , and φ_{11} because they were so small, they were taken in pairs.

Since the values of \bar{M}_w and $[\eta]$ decreased regularly in passing from fraction φ_1 to fraction φ_{12} , it appears that fractionation of the sample of neo-

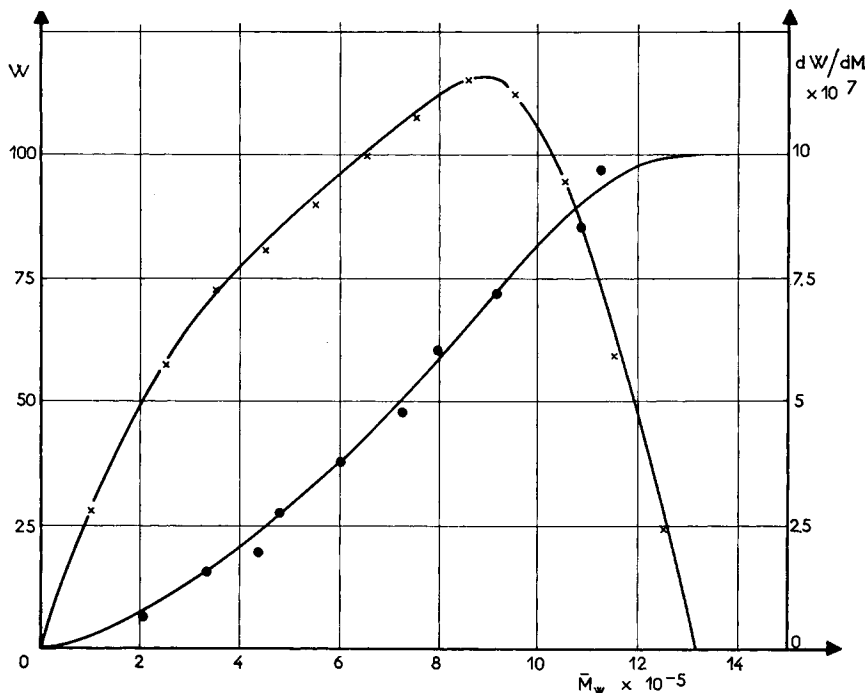


Fig. 2. Integral (●) and differential (×) weight distribution curves for Neoprene type W.

prene in question had been correctly carried out. It is therefore possible to use these results to plot the distribution curve.

For this purpose, the method of Schulz and Dinglinger¹⁴ was employed:

$$W = (w_i + 1)/2 + \sum_1^i w_i \quad (3)$$

where W and w_i are, respectively, the cumulative weight fraction and the percentage of the fraction i .

The values of W are collected in column 4 of Table II and they were used to plot the integral and differential distribution curves (Fig. 2). They show firstly that 50% of Neoprene W consists of macromolecules of weights less than 725,000, and secondly that the most important part consists of macromolecules having a weight-average molecular weight in the region of 900,000. Moreover, the form of the differential curve indicates that Neoprene W possesses a fairly wide distribution.

If from the limiting viscosity numbers $[\eta_i]$ of each of the fractions the average limiting viscosity number of the whole sample is calculated, it is found that $[\bar{\eta}] = 58.5$ ml./g., whereas the experimental value is only 48 ml./g. It therefore appears that fractionation was imperfect and that the losses detected during this experiment affected in particular the low molecular weight fractions which clearly involves a displacement of the differential weight distribution curves towards higher values of the molecular weight.

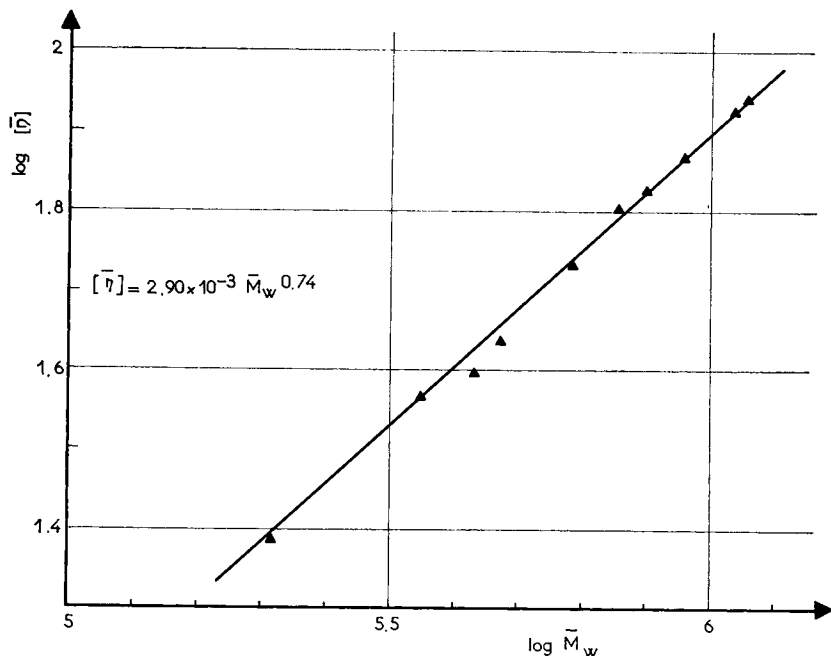


Fig. 3. Weight-average molecular weight-viscosity relationship for Neoprene type W.

As a result, it is impossible for us to determine to which type of distribution Neoprene W belongs, and further work will have to be carried out to find an answer to this question.

From the results shown in Table II it was also possible to determine the constants K and α in the Mark-Houwink equation $[\eta] = K\bar{M}^\alpha$. If $\log [\eta]$ is plotted as a function of $\log \bar{M}_w$ (Fig. 3), it is found that the experimental points lie very close to a line whose slope is 0.74. Calculation gives $K = 2.90 \times 10^{-3}$.

The Mark-Houwink equation for Neoprene W in methyl ethyl ketone is therefore:

$$[\eta] = 2.90 \times 10^{-3} \bar{M}_w^{0.74} \quad (4)$$

This value of α agrees very well with those usually found in the literature; in particular, on referring to Table I it will be seen that, for the same type of neoprene, Mochel and Nichols⁴ found $\alpha = 0.71$, which is perfectly compatible with our results if it is recalled that these authors used an osmotic method of absolute measurement and benzene as the solvent.

This value of α is slightly higher than that corresponding theoretically to a complete extension of perfectly linear chains. This divergence is probably due to a certain degree of rigidity of the polychloroprene chains in methyl ethyl ketone.

It is important to emphasize that the use of eq. (4) in determining the molecular weight of Neoprene W from viscosity measurements is strictly

possible only if operating conditions employed correspond as closely as possible to those used in establishing the equation (i.e. identical solvent and type of neoprene, preliminary fractionation, etc.).

Degradation of Neoprene W by Mastication

Mastication was carried out at ambient temperatures and atmosphere on an amount of Neoprene W (~ 2000 g.) such that successive amounts removed were small in proportion to the amount of rubber still to be masticated. Several samples were taken during mastication and were dissolved in methyl ethyl ketone. After filtration through sintered stainless steel disks, viscometric and light-scattering measurements were carried out in parallel on each of the solutions.

Table III shows the results of two successive series of experiments and curves A and B in Figure 4 show the variations in limiting viscosity number and of weight-average molecular weight as a function of mastication time.

It is immediately obvious that refining of the Neoprene W results in a sharp increase in the two parameters.

Kovacic and Andersen,^{16,17} in addition to other workers,^{18,19} having shown that during the polymerization of chloroprene, approximately 5% polymerizes into the 1,2 or 3,4 forms rather than the *trans*-1,4 form, it is plausible to assume that this increase in the molecular weight is due to the

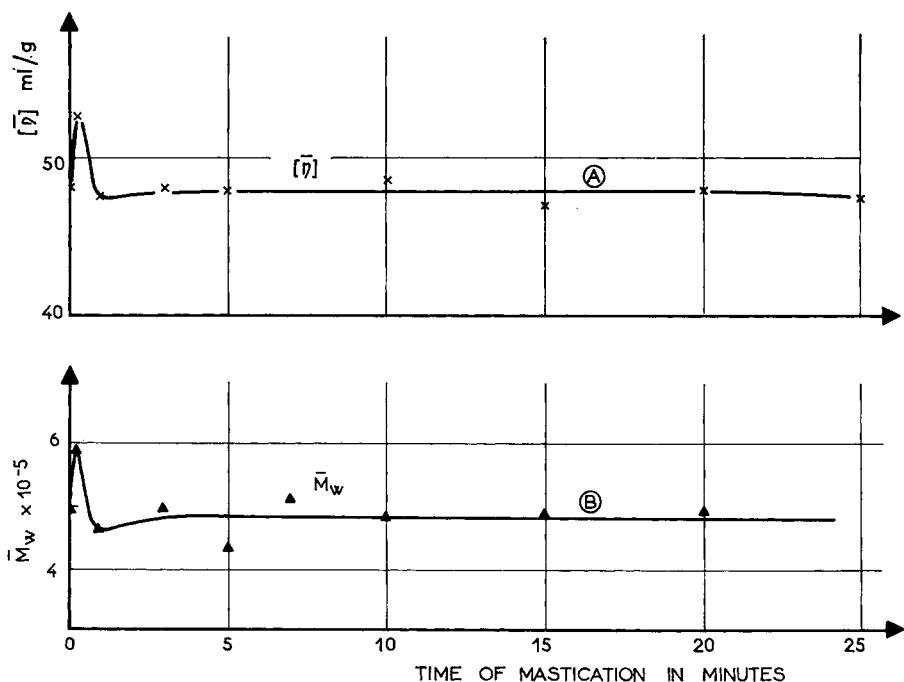


Fig. 4. Variations of the limiting viscosity number and the weight-average molecular weight for Neoprene W samples, in function of the time of mastication.

TABLE III

Mastication time, min.	[η], ml./g.			$\bar{M}_w \times 10^{-6}$			Mooney viscosity
	Expt. 1	Expt. 2	Mean	Expt. 1	Expt. 2	Mean	
0	48	48.5	48.25	5.0	4.80	4.90	5.690
Tight rolls	—	53	—	—	5.91	—	5.772
1	48	47.6	47.8	5.0	4.30	4.65	5.667
2	49	—	—	5.0	—	—	5.699
3	48	48.4	48.2	5.0	4.90	4.95	5.695
5	46	50	48	4.25	4.40	4.325	5.636
7	49	49.4	49.2	5.50	4.75	5.125	5.710
10	49	48.4	48.7	5.50	4.10	4.80	5.681
15	49	45.4	47.2	5.50	4.10-3.65	4.42	5.645
20	49	44.5-49.4	48	5.50	4.0	4.75	5.677
25	49	—	—	5.50	—	—	5.740
30	49	46.1	47.5	5.50	3.90	4.70	5.672
40	—	46.4	—	—	4.15	—	5.618
50	—	47	—	—	3.75	—	5.572

formation of intermolecular crosslinks between the linear neoprene chains, very probably by elimination of hydrochloric acid between two allyl bonds.²⁰

It should, moreover, be noted that analogous increases in limiting viscosity number and molecular weight had already been demonstrated by Seligman²¹ during the first hours of aging of a neoprene latex, and by Polacek⁶ on samples of Svitpren K aged naturally or artificially.

As Dvorak has shown,²⁰ these intermolecular bonds are probably rather weak, since a correlative drop in weight-average molecular weight and limiting viscosity number is observed, these then remaining constant even if mastication is continued for 40 or 50 min.

Since the molecular weight remains constant, it is reasonable to assume that the molecular rearrangements taking place during mastication offset the mechanochemical degradation usually observed with most elastomers.²²⁻²⁴ Furthermore, such rearrangements give rise to branched chains rather than to a three-dimensional network or particles of microgel,¹³ since the samples remain perfectly soluble and no anomalies have been detected in the light-scattering measurements.

Moreover, Mooney viscosity measurements on various samples confirm this theory, since the values obtained decrease regularly in passing from one sample to the next, and Peticolas²⁵ has shown that the presence of branching in a linear chain should result, for a same molecular weight, in a drop in the bulk viscosity.

Since, in addition, the limiting viscosity number of the individual samples remains virtually constant, it may be deduced that the existence of branching has a greater effect on the bulk viscosity than on the solution viscosity, which Peticolas had already suspected.

Relation between Weight-Average Molecular Weight and Limiting Viscosity Number during Degradation of Neoprene W. It is possible to establish, from the results shown in Table III a relationship between the limiting viscosity number and the weight-average molecular weight for samples of Neoprene W degraded by mastication. If one plots $\log[\bar{\eta}]$ as a function of $\log \bar{M}_w$, it will be seen that the experimental points lie on a straight line (Fig. 5) corresponding to the equation $[\bar{\eta}] = 1.25 \bar{M}_w^{0.28}$.

This formula may be used for determining the weight-average molecular weight of Neoprene W after mastication by carrying out simple limiting viscosity number determinations.

It is, however, necessary to point out that the field of application of this equation is fairly small; it should therefore only be used under experimental conditions approximately the same as those under which it was established.

Comparison of Degradation of Neoprene W with that of Other Elastomers. It was also considered of interest to compare the behavior of Neoprene W during mastication with that of other elastomers. For this purpose, plots were made on the same graph (Fig. 6) of the variations of limiting viscosity number as a function of Mooney viscosity for Neoprene W, natural rubber,²⁶ and a polybutadiene.²⁷ It is immediately obvious that the behavior of these three elastomers is quite distinct.

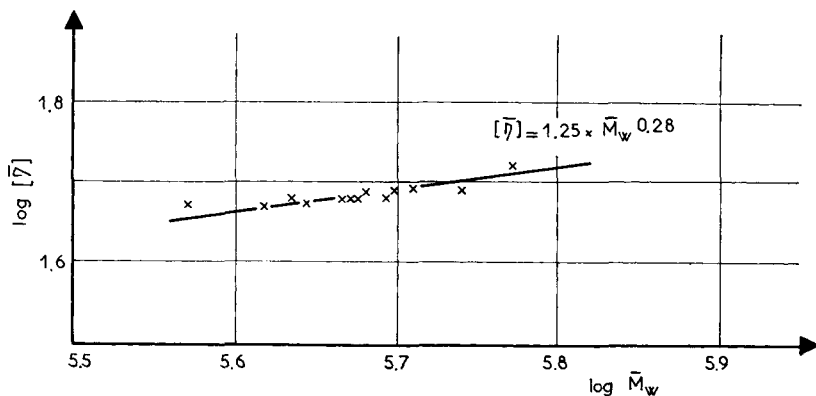


Fig. 5. Weight-average molecular weight–viscosity relationship for masticated Neoprene type W samples.

In the case of natural rubber, the limiting viscosity number decreases linearly as a function of the Mooney viscosity, corresponding thus to mechanochemical degradation of the polyisoprene chains during mastication.

On the contrary, in the case of polybutadiene, the solution and bulk viscosities remain absolutely constant for mastication times from 0 to 60 min.; consequently, during this period there is neither degradation nor modification (branching or crosslinking) of the polymer. Finally in the case of Neoprene W, whose limiting viscosity number remains constant while its Mooney viscosity diminishes regularly, mastication leads to molecular rearrangements (probably as the result of branching), but not to degradation.

Determination of other Molecular Characteristics of Neoprene W

In the course of this work other molecular parameters of Neoprene W were also determined (second virial coefficient, mean square end-to-end distance of chains, radius of gyration) in two different solvents, i.e., tetrahydrofuran and methyl ethyl ketone.

The values obtained for unfractionated Neoprene W are given in Table IV. From these the corresponding values of the Flory-Huggins interaction constants χ were deduced by using the Flory equation:

$$B = (RT/V_1\rho^2) (1/2 - \chi) \quad (5)$$

TABLE IV

	Second virial coefficient, cal.-ml./g. ²	χ	$r^2 \times 10^6$	r , A.
Tetrahydrofuran	0.41	0.42	3.3	1815
Methyl ethyl ketone	0.21	0.45	1	1000

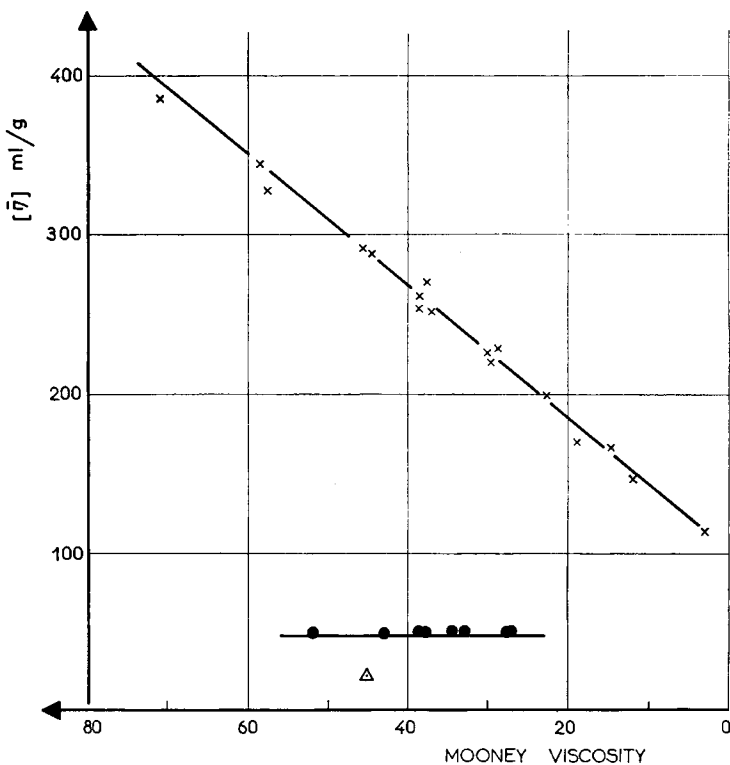


Fig. 6. Relationships between limiting viscosity number and Mooney viscosity for (x) natural rubber, (●) Neoprene W, and (Δ) polybutadiene Phillips 66. (The point Δ is the average value corresponding to 17 different samples having mastication times between 0 and 60 min.).

where V_1 is the partial molecular volume of the solvent and ρ is the density of Neoprene W.

From these it is possible to show that tetrahydrofuran is a better solvent for neoprene than methyl ethyl ketone. It would have been therefore logical to use it as solvent in this work, but it has a distinct tendency to produce peroxides which could give rise to crosslinking and furthermore, the specific refractive increment of Neoprene W in tetrahydrofuran is less than in methyl ethyl ketone. It was for this reason that the latter solvent was our final choice, even though its solvent power was slightly lower.

The values of the mean-square end-to-end distance of the chains given in Table IV complete these results, and in fact, show that the macromolecular chains of Neoprene W are more completely disentangled in tetrahydrofuran than in methyl ethyl ketone.

In addition, with the object of confirming the effectiveness of the preliminary fractionations carried out, the mean-square end-to-end distances of the chains were calculated for the six fractions obtained during the first fractionation of Neoprene W indicated above. The results in Table V

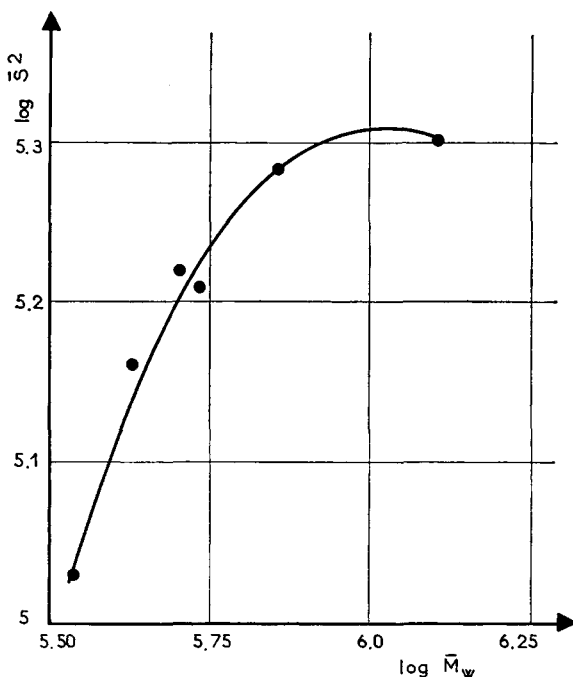
Fig. 7. Log \bar{S}^2 vs. log \bar{M}_w for Neoprene W.

TABLE V

Fraction	$\bar{M}_w \times 10^{-5}$	log \bar{M}_w	$r^2 \times 10^6$	r , A.	$\bar{S}^2 \times 10^{-6}$	log \bar{S}^2
F1	12.60	6.100	1.2	1090	0.20	5.301
F2	8.30	5.919	—	—	—	—
F3	7.10	5.851	1.15	1070	0.19	5.283
F4	5.40	5.732	0.98	990	0.16	5.209
F5	4.25	5.628	0.87	930	0.145	5.161
F6	3.50	5.540	0.65	802	0.11	5.029
Whole sample	5.01	5.700	1.0	1000	0.165	5.220

show, as was to be expected, that they vary regularly in the same direction as the weight-average molecular weight.

If it is now assumed, as a first approximation,* that the macromolecular chains of Neoprene W in methyl ethyl ketone are statistically in the form of an ideal coil, it is possible to calculate the mean-square radius of gyration \bar{S}^2 from the mean-square end-to-end distance of the chains by means of eq. (6):

$$\bar{S}^2 = r^2/6 \quad (6)$$

Now, it is theoretically possible to verify from values of the radius of gyration, whether or not a high polymer is entirely linear or partially

* This is only strictly true in the case of a θ solvent in which the intermolecular attraction and repulsion effects are exactly counterbalanced at the test temperature.

branched. Zimm and Stockmayer²⁸ have, in fact, shown that the mean square radius of gyration is related to the molecular weight by means of the equation:

$$\bar{S}^2 = KgM^{1/\epsilon}$$

where K and ϵ are constants and g is a function which depends on the linearity of the polymer. If the latter is completely linear, $g = 1$; if the opposite is the case, g is less than unity.

It is for this reason that $\log \bar{S}^2$ is given on Figure 7 as a function of $\log M$ for each of the fractions in Table V.

This figure shows that the experimental points lie not on a straight line but on a curve whose concavity downwards is increasingly accentuated as the molecular weight increases; as a matter of fact, it is logical that the longest chains also possess the highest degree of branching.

It may therefore be concluded that in all probability the macromolecular chains of Neoprene-W are not completely linear.

It would also have been of interest to check similarly if increased branching also occurred during mastication of neoprene as assumed in the second part of our investigations. Unfortunately, as the result of their polydispersity, the various samples masticated give very irregular Zimm plots, such that even the approximate determination of the mean-square end-to-end distance of the chains and of the radii of gyration would be of no value.

It was therefore impossible to verify the hypothesis in question.

CONCLUSION

This study, the first of a series aiming at analyzing the physicochemical properties of a number of commercial elastomers, has been devoted to Neoprene W.

It has shown that this elastomer is fairly polydisperse, that its weight-average molecular weight is in the neighborhood of 5×10^5 , and that it is branched. Furthermore, it appears that during mastication, the behavior of this rubber is somewhat different from that of other elastomers (natural rubber and polybutadiene).

It would therefore be of interest to study other types of neoprene to discover if this behavior is confined to Neoprene W. It is, in fact, known that type G neoprenes, as opposed to type W, are sulfur-modified, and it is possible that this modification produces certain changes in the polydispersity of the elastomer or in its behavior during mastication. It is proposed to verify this in a similar study to be carried out on Neoprene GN.

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Résumé

Dans cette étude relative au Néoprène W, il a été possible de montrer que cet élastomère possède une distribution de poids moléculaire assez large et présente un certain degré de ramification. La relation suivante, $[\eta] = 2.90 \times 10^{-3} \bar{M}_w^{0.74}$, entre le nombre viscosimétrique limite et la masse moléculaire moyenne en poids a pu être établi. De plus, on a trouvé que la dégradation de Neoprene W par malaxage diffère de celle des autre élastomères. Si on fait le malaxage sur de grandes quantités de Neoprene W, on peut employer la relation suivante $[\eta] = 1.25 \times \bar{M}_w^{0.28}$ pour délaminer la masse moléculaire moyenne en poids à partir des mesures de viscosités. On donne aussi les différentes caractéristiques moléculaires du néoprène W dissous dans le tétrahydrofurane et la méthyl-éthyl-cétone.

Zusammenfassung

In der vorliegenden Untersuchung über Neopren W konnte gezeigt werden, dass dieses Elastomere eine ziemlich breite Molekulargewichtsverteilung besitzt und einen gewissen Verzweigungsgrad aufweist. Zwischen der Viskositätszahl und dem Gewichtsmittel des Molekulargewichts wurde die Beziehung $[\eta] = 2.90 \times 10^{-3} \bar{M}_w^{0.74}$ hergestellt. Weiters zeigte eine Untersuchung des Abbaus von Neopren W durch Mastizierung, dass sich dieser Kautschuk in seinem Verhalten recht stark von anderen Elastomeren unterscheidet. Bei der Mastizierung verhältnismässig grosser Kautschukmengen kann die Beziehung $[\eta] = 1.25 \times \bar{M}_w^{0.28}$ zur Bestimmung des Gewichtsmittels des Molekulargewichts aus Viskositätsmessungen verwendet werden. Schliesslich werden verschiedene Molekülcharakteristika für Neopren W in Tetrahydrofuran und Methyl-äthylketon mitgeteilt.

Received January 18, 1965

Revised June 21, 1965

Prod. No. 1236