

Molecular Weight Distributions from Gel-Sol Ratios

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INTRODUCTION

It has become increasingly clear during the past few years that the physical properties of rubbers and plastics are strongly dependent upon the molecular weight distribution of the constituent macromolecules. For this reason, among others, considerable research effort has been expended in determining the MWD (molecular weight distribution) of various polymers. Unfortunately, the methods presently available for measuring MWD are tedious and very time consuming.

It is the purpose of this report to present a rather simple and convenient method for determining the MWD in high polymers. The method is applicable to those materials which can be crosslinked either by irradiation or vulcanization. It will be shown that the simplest form of the method gives good results where it has been applied, i.e., to synthetic rubber and natural rubber. A second approximation method will also be presented and tested on known sharp distributions.

FIRST APPROXIMATION THEORY

The present method is based upon the partition of polymer molecules between gel and sol in a partially crosslinked system. Theoretical descriptions of this situation have been developed by Flory¹ and Charlesby.² Both results may be reduced to the following relation:

$$W = (1/d) \sum_i n_i M_i (1 - e^{-\nu W M_i / d}) \quad (1)$$

In this equation it is assumed that the original polymer sample, which had unit volume and density d , consisted of a series of molecular weight species. The weight of material in the i th species is $n_i M_i$. If ν is the number of crosslinked units in the sample, then the weight fraction of gel, W , is given by eq. (1). This relation could be used as it stands to determine the MWD from a knowledge of gel-sol ratios at various values of ν . However, because of the complicated nature of

eq. (1), this turns out to be impractical. A much more useful procedure is outlined below.

An examination of eq. (1) shows that at a fixed value of ν , the terms in the summation which apply to low molecular weights are approximately $\nu W n_i M_i^2 / d$, while at high M_i the terms are just $n_i M_i$. A transition region exists where neither of these values is appropriate. However, we will show in a later section that for the present purposes one incurs only small errors if one writes

$$W = (1/d) \sum_i n_i M_i \psi_i \quad (2)$$

where $\psi_i = 1$ if $\nu W M_i / d \geq \lambda$

and $\psi_i = \nu W M_i / d$ if $\nu W M_i / d < \lambda$

The quantity λ will be so chosen as to preserve the experimental value for \bar{M}_w , the weight-average molecular weight. It will be seen that λ acts merely as a scale factor when plotting the MWD. Its proper value is easily found provided \bar{M}_w is known.

APPLICATION OF THE METHOD

Procedure

Suppose a graph has been obtained showing how W varies as a function of ν for some particular type of material. The data of such a plot can be analyzed by use of eq. (2) to obtain the MWD of the polymer. To do this, assume that the original sample consists of a convenient number of fractions, N . Assume further that the highest molecular weight fraction, M_n , contains negligible material. Choose a point on the W vs. ν curve at a very small value of W , and call its coordinates W_1, ν_1 .

One may now write eq. (2) as

$$W_1 = (1/d) \left[\sum_{i=N}^2 n_i M_i \psi_{i1} \right] + n_1 M_1 \psi_{11} / d + 0 \quad (a)$$

where M_1/λ is chosen large enough so that ψ_{11} is just unity, i.e.,

$$M_1/\lambda = d/\nu_1 W_1$$

Taking a second point (ν_2, W_2) at a slightly larger value of W , one can write

$$W_2 = (1/d) \left[\sum_{i=N}^2 n_i M_i \psi_{i2} \right] + n_1 M_1 \psi_{12}/d + 0 \quad (b)$$

where ψ_{12} is certainly unity because of the choice of M_1/λ . The term in ψ_{22} will be seen from what follows to be still sufficiently small that $\psi_{i2} = (\nu_2 W_2/\nu_1 W_1) \psi_{i1}$ when $i \geq 2$.

If one now multiplies eq. (a) by $(\nu_2 W_2/\nu_1 W_1)$ and subtracts eq. (b) from eq. (a) the result will be (since the bracketed terms now cancel)

$$W_1(\nu_2 W_2/\nu_1 W_1) - W_2 = (n_1 M_1/d) [(\nu_2 W_2/\nu_1 W_1) - 1]$$

One can easily solve this expression for $n_1 M_1/d$, the fraction of material having a molecular weight M_1 .

It is now convenient to choose M_2/λ such that ψ_{22} is just unity, i.e., $M_2/\lambda = d/\nu_2 W_2$. Then we can rewrite eq. (b):

$$W_2 = (1/d) \left[\sum_{i=N}^3 n_i M_i \psi_{i2} \right] + n_2 M_2/d + n_1 M_1/d \quad (a')$$

The quantity $n_1 M_1/d$ is already known from the previous step. Choose a third point on the W vs. ν curve and write the following for it:

$$W_3 = (1/d) \left[\sum_{i=N}^3 n_i M_i \psi_{i3} \right] + n_2 M_2/d + n_1 M_1/d \quad (b')$$

One can now solve directly for $n_2 M_2/d$ by multiplying eq. (a') by $(\nu_3 W_3/\nu_2 W_2)$ and subtracting eq. (b') from eq. (a') as was done with eqs. (b) and (a). After this is done one writes:

$$W_3 = (1/d) \left[\sum_{i=N}^4 n_i M_i \psi_{i3} \right] + n_3 M_3/d + n_2 M_2/d + n_1 M_1/d \quad (a'')$$

After choosing a new point on the curve (W_4, ν_4) one can write an equation similar to (b) and (b') and repeat the procedure so as to find $n_3 M_3/d$.

This process is repeated time after time until the maximum value of W , usually unity, is reached, at which time $\sum n_i M_i$ should equal d . For each

solution, the weight of material having molecular weight M_p is given by:

$$(n_p M_p)_0 = \left[d(RW_p - W_{p+1}) - (R-1) \sum_{i=p-1}^1 n_i M_i \right] \times (R-1)^{-1} \quad (3)$$

where $R = (\nu_{p+1} W_{p+1})(\nu_p W_p)^{-1}$, and $\sum_{i=p-1}^1 n_i M_i$ is taken from the earlier solutions. The zero subscript on $(n_p M_p)_0$ is used here to distinguish this solution from a corresponding solution in a later part of this paper.

It is obvious that the number of fractions into which one splits the sample is arbitrary. The closer together one selects the points on the W vs. ν curve, the closer together will lie the fractions.

Finally, the value of λ is found from the fact that the fractions must give the proper value for \bar{M}_w . That is to say,

$$\bar{M}_w = \lambda \sum n_i M_i (M_i/\lambda) / \sum n_i M_i \quad (4)$$

This general method of computation has been applied to data for vulcanized synthetic rubber gum stock in which crosslinks are produced by reacting sulfur in a rather complex system. At high degrees of vulcanization one can compute the effective value of ν, ν_e , from swelling data. The value for ν is then found from the relation

$$\nu = \nu_e + 2/\bar{M}_n \quad (5)$$

Fortunately it turns out that the computed MWD is not very sensitive to the exact value one used for \bar{M}_n in eq. (5). Our method for choosing λ compensates somewhat for inaccuracies in \bar{M}_n and so, in general, any reasonable value for \bar{M}_n will not greatly change the distribution. Since the computed MWD allows one to evaluate \bar{M}_n , a more accurate value may then be substituted in eq. (5) if greater accuracy is required.

Measurements of swelling in benzene were used to determine ν_e . In practice it was found that the equilibration could be speeded considerably if the samples were heated to about 60°C. A typical procedure was to swell the samples for 20 hr. at 60°C. and then to equilibrate them at room temperature for 5 hr. before measuring the swollen weight. The value of ν_e was found in the usual way, μ -values of 0.37 for GR-S and 0.44 for natural rubber being used.

At very low degrees of crosslinking one can no longer find ν from eq. (5). This is the result of

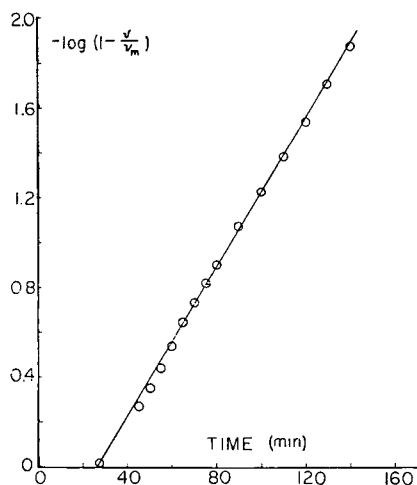


Fig. 1. Typical curve showing increase of crosslinking with time of vulcanization: data taken with hot GR-S.

two factors. First, swelling measurements are very inconvenient at low crosslinking values since the rubber swells so tremendously. Second, eq. (5) is valid only if a large weight fraction of the material remains in the gel. For this reason we have used a different method for obtaining ν at low crosslinkings.

There is considerable reason to believe that the crosslinking reaction is a first-order reaction.³ Assuming that this is true, one has

$$\nu = \nu_m(1 - e^{-kt})$$

In this relation ν_m is the maximum value reached by ν when the reaction has reached completion, k is a rate constant, and t is the time since the reaction started.

Taking logarithms, one has

$$\log [1/(1 - \nu/\nu_m)] = (\text{const.}) t \quad (6)$$

Therefore a plot of $\log [1/(1 - \nu/\nu_m)]$ vs. t should result in a straight line. Since several points on this line are available from the swelling data at high degrees of crosslinking, an accurate extrapolation to small values of ν is possible. In practice a straight line is found, but this straight line does not go through the origin. This is a result of a delay in the beginning of the vulcanization reaction, the duration of which varies from system to system.

The small- ν end of the straight line obtained from eq. (6) becomes extremely accurate when use is made of the fact that gel first forms when $\nu = d/\bar{M}_w$. We have found that accurate values for ν can be obtained by plotting the straight line of eq. (6) from the swelling values for ν_e

and the value of ν at the gel point. A typical plot of this nature is shown in Figure 1. In some cases the upper points in plots like Figure 1 will deviate markedly from a straight line because of a poor estimate for ν_m . Although the proper procedure in such cases is to make a new estimate for ν_m , it is usually true that a fair enough straight line results so that one can get reliable values at small ν without making a new plot. This is particularly true since once again the computed MWD is not very sensitive to the exact value of ν . We have found that even when the crosslinking reaction is not first order, the resultant curve obtained in such a plot is convenient for treating the data.

Viscosity-average molecular weights were measured in toluene in an Ubbelohde viscometer. No corrections were made for rate of shear. The viscosities were interpreted by use of the equation $[\eta] = KM^{0.67}$ where K was taken to be 5.2×10^{-4} and 5.0×10^{-4} for GR-S and natural rubber, respectively. The resultant values for \bar{M}_v were assumed identical to \bar{M}_w for the present purposes. This, of course, is not strictly true. However, since the absolute value of \bar{M}_w is not the object of the present study, this approximation will be of no concern. In this connection, it should be noted that for a normal distribution, \bar{M}_w and \bar{M}_v would differ by about 8%.

Results on Natural Rubber

The cumulative and differential molecular weight distributions found for hot and cold GR-S having \bar{M}_w of 185,000 and 200,000, respectively, are shown in Figures 2 and 3. These materials had

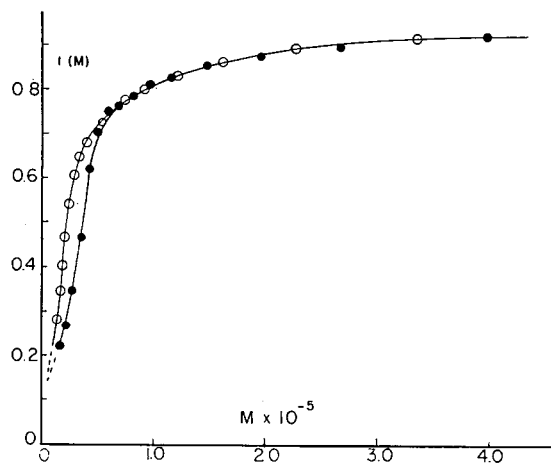


Fig. 2. Cumulative molecular weight distribution for two synthetic rubbers: (O) hot GR-S; (●) cold GR-S.

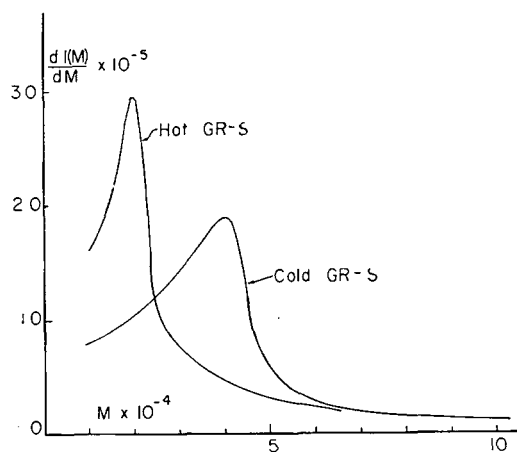


Fig. 3. Differential molecular weight distribution for two synthetic rubbers.

been compounded with sulfur, and the recipe is given in the appendix. It will be noted that we have not tried to subtract out the compounding and residual polymerization chemicals from the cumulative distribution. We estimate such extractables to be about 18% of the whole. Unfortunately, the recipes quoted for these rubbers did not give high enough crosslinking to insure that all of the rubber was retained in the gel. Consequently, the most that we can say is that approximately 14 and 12% of the original material in hot and cold GR-S, respectively, has $M < 10,000$. The cumulative curves below this value must therefore be considered only approximate.

The number-average molecular weights can be computed by the method outlined in the previous section. Considerable error may result because of the uncertainty at the low molecular weight end of the distribution. Neglecting the lowest 10% of the material, which we believe to be chiefly compounding ingredients, we found \bar{M}_n to be 31,000 and 24,000 for cold and hot GR-S, respectively.

It is clear from the data of Figures 2 and 3 that considerable difference exists between hot and cold GR-S at the lower end of the distribution. This is in line with accepted concepts regarding these rubbers. However, one should note that the distributions for the two rubbers are still very similar at high values of M . In fact, our data allowed us to extend the curves much further than shown in the figures, and we found that the amount of material having $M > 10^6$ is about 2% for both rubbers.

As a crucial test of the MWD method, a sample of hot GR-S was extracted with a 50-50 solution

of benzene and methyl alcohol. Most of the rubber was insoluble in this mixture, and the MWD of the insoluble material was run. It should and did exhibit a cutoff of molecular weights below about 15,000. The fact that the low molecular weight material was shown to be missing from the MWD is further confirmation of the validity of the method.

Results on Natural Rubber

The MWD for natural rubber smoked sheet which had been stored at room temperature for three years has also been run. In order to circumvent the uncertainties of milling, the material was crosslinked in the presence of benzoyl peroxide at 190°F. The benzoyl peroxide was added to the rubber in benzene solution and subsequently dried at low temperatures. Either because of the experimental errors or perhaps because the vulcanization reaction is not first order in this case, a good straight line was not obtained for the log plot. Fortunately, however, the value of \bar{M}_n is high for this polymer and, using the fact that ν at the gel point is d/\bar{M}_w , it was a simple matter to extrapolate to the lowest values of W on the W vs. ν curve.

The resulting distribution for natural rubber is shown in Figure 4. Although data are available at still higher values of M , the remainder of the curve is not exceptional. It turns out that fractions containing 3.6, 4.2, and 2.7% are found at M 's of 2.35, 5.2, and 28×10^6 , respectively.

It is obvious from a comparison of Figures 2, 3, and 4 that tremendous differences exist between the molecular weight distributions in synthetic and natural rubber. It is difficult to

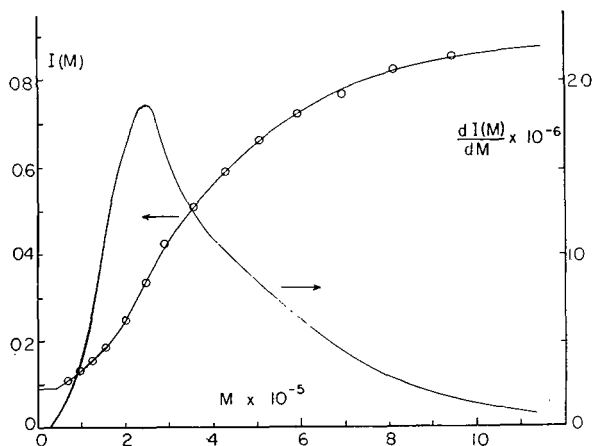


Fig. 4. Cumulative and differential molecular weight distribution for natural rubber.

characterize these differences in any simple way. In some respects the MWD for natural rubber is even wider than that for the synthetic rubbers. Not too much difference exists in the ratio of \bar{M}_w to \bar{M}_n . It is about 7 for synthetic rubber and $1.5 \times 10^6/3 \times 10^5$, or 5, for natural rubber. The chief difference is in the relative position of the distributions on the molecular weight scale. Whereas natural rubber contains negligible rubber with $M < 40,000$, more than half the synthetic rubber is of lower molecular weight. This fact certainly supports previous inferences concerning the causes of the poor dynamic properties of synthetic rubber.⁴

SECOND-ORDER APPROXIMATION

In order to see how the second approximation arises, it is necessary to write out eq. (2) in more detail. One has for the p th values of W and ν

$$dW_p = \sum_{i=N}^{p+3} (n_i M_i \psi_{ip}) + n_{p+2} M_{p+2} (1 - e^{-\nu_p W_p M_{p+2}/d}) + n_{p+1} M_{p+1} (1 - e^{-\nu_p W_p M_{p+1}/d}) + n_p M_p (1 - e^{-1}) + n_{p-1} M_{p-1} (1 - e^{-\nu_p W_p M_{p-1}/d}) + n_{p-2} M_{p-2} (1 - e^{-\nu_p W_p M_{p-2}/d}) + n_{p-3} M_{p-3} (1 - e^{-\nu_p W_p M_{p-3}/d}) + \sum_{i=p-4}^1 n_i M_i \psi_i \quad (7)$$

We now make the approximations $\psi_i = \nu_p W_p M_i/d$ for $i > p+3$ and $\psi_i = 1$ for $i < p-4$. Taking a new point with coordinates (ν_{p-1}, W_{p-1}) one can write a second equation similar to (7) and eliminate the terms in the first summation of eq. (7) by solving the two equations simultaneously. The end result is quite long and will not be written in detail here. However, if one chooses the points (ν, W) so as to make the ratio R (see eq. (3)) equal to a constant, the equation becomes particularly simple. Upon solving the equation so obtained for $n_p M_p$, one finds

$$n_p M_p = Q^{-1} \left\{ \left[d(RW_p - W_{p+1}) - (R-1) \sum_{i=p-1}^1 n_i M_i \right] - A_1 n_{p+2} M_{p+2} - A_2 n_{p+1} M_{p+1} + A_3 n_{p-1} M_{p-1} + A_4 n_{p-2} M_{p-2} + A_5 n_{p-3} M_{p-3} \right\} \quad (8)$$

where

$$R = \frac{\nu_{p+1} W_{p+1}}{\nu_p W_p} = \frac{M_p}{M_{p+1}}$$

$$Q \equiv (R-1) + e^{-R} - Re^{-1}$$

$$A_3 \equiv Re^{-R} - e^{-R^2}$$

$$A_1 \equiv (R-1) + e^{-1/R} - Re^{-1/R^2}$$

$$A_4 \equiv Re^{-R^2} - e^{-R^3}$$

$$A_2 \equiv (R-1) + e^{-1} - Re^{-1/R}$$

$$A_5 \equiv Re^{-R^3} - e^{-R^4}$$

We have approximated λ by unity to obtain the factor e^{-1} in this expression. Dropping terms after the brackets, one gets a first approximation:

$$n_p M_p = \left[d(RW_p - W_{p+1}) - (R-1) \sum_{i=p-1}^1 n_i M_i \right] \times [(R-1) + e^{-R} - Re^{-1}]^{-1}$$

By comparison of this expression with eq. (3), it is seen that our previously obtained first approximation values, $(n_i M_i)_0$ are related to the present $n_i M_i$ by the relation:

$$n_i M_i = (n_i M_i)_0 [1 + (e^{-R} - Re^{-1}) (R-1)^{-1}]^{-1} = \beta (n_i M_i)_0 \quad (9)$$

Substituting this expression in terms higher than p , one has

$$n_p M_p = Q^{-1} \left\{ d(RW_p - W_{p+1}) - \left[(R-1) \sum_{i=p-1}^1 n_i M_i \right] - A_1 \beta (n_{p+2} M_{p+2})_0 - A_2 \beta (n_{p+1} M_{p+1})_0 + A_3 n_{p-1} M_{p-1} + A_4 n_{p-2} M_{p-2} + A_5 n_{p-3} M_{p-3} \right\} \quad (10)$$

It is assumed that the values of $(n_i M_i)_0$ will have been obtained from the application of the first approximation method. The values of $n_i M_i$ still retained in eq. (10) will have been obtained by successive applications of eq. (10) starting with the largest value of M_i , namely M_1 .

In practice it is convenient to take R to be 1.413. This value was chosen because of the fact that $\log R = 0.150$. For this particular value of R eq. (10) becomes

$$n_p M_p = (7.30) \left\{ d(1.413W_p - W_{p+1}) - 0.413 \sum_{i=p-1}^1 (n_i M_i) - 0.149 (n_{p+2} M_{p+2})_0 - 0.258 (n_{p+1} M_{p+1})_0 + 0.208 n_{p-1} M_{p-1} + 0.132 n_{p-2} M_{p-2} + 0.066 n_{p-3} M_{p-3} \right\} \quad (11)$$

TECHNICAL CONSIDERATIONS

In applying eq. (10) to the experimental data it is convenient to plot the result of the first approximation in the form $I_0(M)$ vs. $\log(M/\lambda)$. It is then a simple matter to mark off on this curve values of (M/λ) which are in constant ratio to each other, this ratio being R . For example, in using eq. (11) one marks off points on the log scale which are separated by a distance of 0.150. The first approximation for the $(n_i M_i)_0$ for each of these molecular weights is obtained as the difference in the values of $I_0(M)$ at the points 0.075 on either side of the chosen value for $\log(M/\lambda)$. From this graph one can now construct a table relating M/λ and $(nM)_0$ for the chosen values of M/λ .

Similarly one can plot a graph of W vs. M/λ . This is possible since M/λ was computed in the first approximation procedure by use of the relationship $\nu_p M_p W_p / \lambda d = 1$, so that M/λ is uniquely related to a value of W . From this graph it is also possible to enter a value for W in the table mentioned above for each value of M/λ . This table will now contain the necessary data for the successive evaluation of a set of equations like eq. (11).

Starting with the highest value of M/λ , namely M_1/λ , one has the corresponding values W_1 and the first-order approximations to $n_i M_i$. Therefore the second approximation to $n_1 M_1$ can be found by substitution in eq. (11). After that is done, one is able to evaluate the similar equation for $n_2 M_2$, and so on.

If the experimental data are not too accurate one will sometimes find that certain values of $n_i M_i$ appear to be negative. When this occurs it means that the previous values for nM were too large, and the computation is trying to correct for this inaccuracy. In these cases it seems best to consider the negative fractions to have zero values for nM , and to continue the calculating process as usual.

PRECISE TESTS

We will obtain a precise test of the method outlined above by applying it to two known molecular weight distributions. One of these is the distribution of a sharp fraction, characterized by $I(M) = 0$ for $M < \bar{M}_w$ and $I(M) = 1$ for $M \geq \bar{M}_w$. The other is the most probable distribution, for which

$$dI(M)/dM = (\bar{M}_w/2)^{-2} M e^{-2M/\bar{M}_w}$$

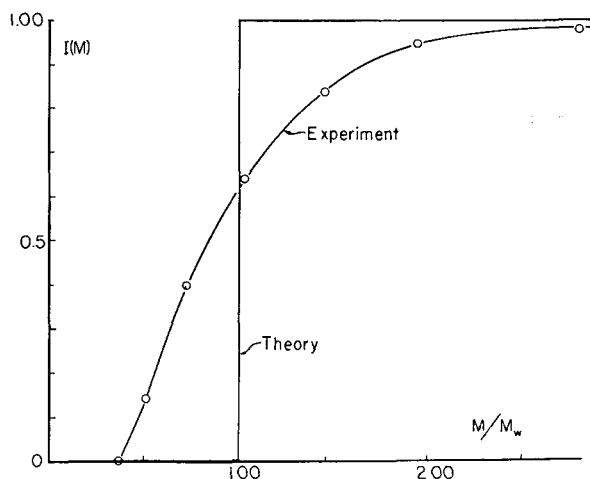


Fig. 5. Experimental determination of molecular weight distribution for a known sharp fraction.

It is a simple matter to substitute these distributions in eq. (2) and compute the gel fraction one should find for any degree of crosslinking. By this procedure we can generate the "experimental" data which we need in order to apply our MWD method. We may now use these data to try to compute the known MWD from which they arise.

The results of this computation are shown in Figures 5 and 6. It will be seen that in the case of the most probable distribution, the computed distribution agrees very closely with the exact curve, provided the second approximation is used. The values of \bar{M}_w/\bar{M}_n are 3.4 and 2.10 for the first and second approximations, respectively.

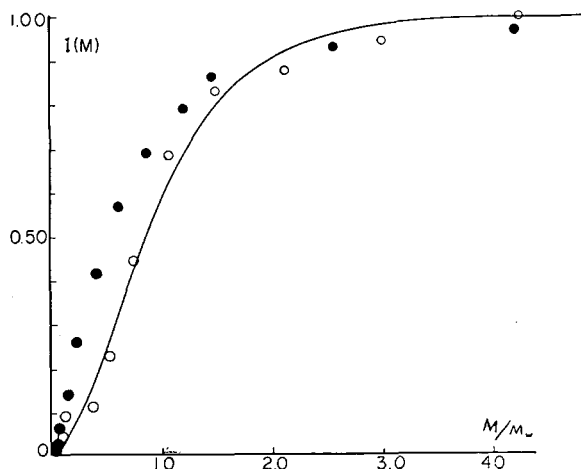


Fig. 6. Results of first approximation method and second approximation method applied to the "most probable" distribution: (—) theoretical; (●) first approximation method; (○) second approximation method.

The exact value is 2.00. No effort was made to maintain high accuracy in the computation since experimentally obtained data would be rather imprecise. Consequently, the small discrepancy between 2.10 and 2.00 is certainly understandable and is negligibly small for most purposes.

In the case of the sharp fraction, even the second approximation is still not too precise. One finds \bar{M}_w/\bar{M}_n to be 1.24, whereas it should be 1.00. However, if one recalls that even in the best types of fractionation techniques this ratio is seldom less than 1.10 and is usually closer to 1.20, it is clear that even in this extreme case the method is satisfactory for many uses.

Finally, we have applied the second approximation method to the previously reported data for hot GR-S. As expected for such a wide distribution, the second approximation does not change the results very much. Within experimental error, the curves for $I(M)$ are unchanged. In addition, in one typical example, the value for \bar{M}_w/\bar{M}_n was changed from 7.4 to 7.3 by applying the second approximation.

CONCLUSION

It is apparent that the determination of molecular weight distributions is possible from gel-sol ratios. The first approximation appears satisfactory for samples having \bar{M}_w/\bar{M}_n larger than about five. In the case of sharper distributions it is necessary to carry out the second approximation. This results in fairly reliable data even in the case of polymer fractions.

The reader may conclude that the procedure for computation as outlined here is complicated and laborious. It is true that the second approximation does increase the work by about a factor of two. However, it is our experience that after one has applied the method once or twice, a typical complete computation may be easily carried out in about five hours. Although the time and labor involved are far from negligible, it is clear that they are only a small part of what is necessary for a full-scale fractionation.

APPENDIX

The two synthetic rubbers used in this work were compounded according to the following recipe:

GR-S 1006 or 1500	100
Zinc oxide	3
Stearic acid	3
Anax	1
Santocure	1.25
Sulfur	2

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Synopsis

A method for determining molecular weight distributions is presented, based upon the partition of polymer molecules between gel and sol in a partly crosslinked system. It is assumed that the polymer sample consists of a series of molecular weight species, and analysis of previously developed theories covering this situation yields an expression which equates the weight fraction of gel to a summation involving the weight fraction of the material in each species and the number of crosslinked units in the sample. The data are presented in the form of a graph showing how the weight fraction of gel varies as a function of the number of crosslinked units in the sample. Data for the graph are obtained from swelling measurements made in the usual manner. The procedure is outlined for using the information from the graph to make a step-by-step evaluation of the fractional weight of each molecular weight species in the sample for as many fractions as may be arbitrarily chosen. Both a first approximation method and a more refined second approximation method are outlined. The procedure has been applied to samples of natural rubber, synthetic rubbers, and to two known molecular weight distributions.

Résumé

La détermination de la distribution des poids moléculaire est basée sur la répartition des molécules de polymère entre un gel et un sol dans un système partiellement ponté. On admet que l'échantillon de polymère consiste en une série d'espèces moléculaires, et les théories développées antérieurement sur cette situation sont analysées afin d'obtenir une expression qui exprime la fraction en poids du gel par une sommation de la fraction en poids du matériau dans chaque échantillon et du nombre d'unités pontées dans l'échantillon. Les résultats présentés sous forme de graphique montrent comment la fraction en poids du gel varie en fonction du nombre d'unités pontées dans l'échantillon. Les données du graphique ont été obtenues aux dépens de mesures de gonflement effectués de la manière usuelle. La méthode présentée indique le procédé d'utiliser les informations de ce graphique pour obtenir une évaluation progressive de la fraction en poids de chaque espèce moléculaire au sein de l'échantillon pour autant de fraction qu'on a choisi arbitrairement. On indique deux méthodes, l'un par première approximation, l'autre plus raffinée par seconde approximation. Le procédé a été appliqué à des échantillons de

caoutchouc naturel, de caoutchouc synthétique et a deux distributions de poids moléculaires connues au préalable.

Zusammenfassung

Das hier beschriebene Verfahren zur Bestimmung von Molekulargewichtsverteilungen beruht auf der Verteilung von Polymermolekeln zwischen Gel- und Solphase in einem teilweise vernetzten System. Es wird angenommen, dass die Polymerprobe aus einer Reihe von Molekulargewichtssorten besteht; früher entwickelte Theorien dieser Gegebenheit werden analysiert und diese Analyse führt zu einem Ausdruck, der den Gewichtsbruchteil des Gels einer Summierung gleichsetzt, die den Gewichtsbruchteil des Stoffes in jeder Sorte sowie die Anzahl der Vernetzungseinheiten in der Probe enthält. Die Ergebnisse werden in Form eines Dia-

gramms dargestellt, das die funktionelle Abhängigkeit des Gewichtsbruchteils an Gel von der Anzahl der Vernetzungseinheiten in der Probe zeigt. Die Angaben für das Diagramm werden durch Quellungsmessungen erhalten, die in der üblichen Weise ausgeführt werden. Die beschriebene Methode beinhaltet das Verfahren zum Gebrauch der aus dem Diagramm erhaltenen Information zur schrittweisen Ermittlung des Gewichts der Fraktion einer jeden Molekulargewichtssorte in der Probe und zwar für eine beliebig gewählte Anzahl von Fraktionen. Sowohl eine Methode erster Näherung als auch eine verfeinerte zweite Näherung werden beschrieben. Das Verfahren wurde auf Proben von Naturkautschuk, synthetischem Kautschuk und auf zwei bekannte Molekulargewichtsverteilungen angewendet.

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