

A Proposed Method for Estimating Polymer Molecular Weight Distribution Without Fractionation

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INTRODUCTION

The molecular weight distribution of a polymer is known to have important effects on rheological behavior and physical and mechanical properties. However, these relationships have not been extensively explored because accurate experimental determination of molecular weight distribution is, at best, difficult and time-consuming. F. Bueche and Harding¹ are the first to have achieved the goal of deducing the distribution of a (crosslinkable) polymer without experimental fractionation. Proceeding from the statistical relationship²

$$w_s = \sum_{y=1}^{\infty} w_y [1 - \rho(1 - w_s)]^y \quad (1)$$

between the weight fraction of sol w_s , in a partially crosslinked system of crosslink density ρ , and the weight fractions w_y of primary y -mer molecules, they developed a method of calculating the w_y values from experimental values of w_s and ρ . This is an important advance because it circumvents the laborious task and the uncertainties of fractionation, but it is still not so simple as one might wish. The Bueche-Harding method requires considerable experimental data on sol-gel ratio versus crosslink density, a separate determination of an average molecular weight to serve as a kind of "normalizing factor," and some five hours of computations. It also requires either data on the kinetics of crosslinking or else the assumption that the kinetics are at least approximately of first order. Their success, nevertheless, has inspired the present attempt to develop a simpler method. This is proposed below and it is admittedly in a form very likely capable of refinement. Present data for testing its accuracy are quite limited, and until more experimental information becomes available one should regard it as an estimation method, its chief usefulness at present being restricted perhaps to comparative studies on a given polymer system.

DERIVATION OF DISTRIBUTION PARAMETERS

We assume that the molecular weight distribution conforms to Tung's empirical function. On inserting the latter into eq. (1) one can solve the resulting expression explicitly for the distribution parameters. The differential form of the function can be written:

$$w_y = abM_0^{b-1}y^{b-1} \exp \{ -aM_0^b y^b \} \quad (2)$$

where $y = M/M_0$ is the degree of polymerization, and a and b are important empirical parameters. Tung³ has shown that eq. (2) fits quite well his fractionation data for several different polyethylenes, as well as published data for nylon 66, polymethyl methacrylate, and polystyrene. It also fits data for other polystyrene samples and for polyethylene terephthalate.^{4,5} With the possible exception of some (but not all) polyethylenes reported by Tung, eq. (2) is therefore applicable to a variety of chemically different polymers synthesized by different methods. The goodness of fit is not surprising, because the mathematical form of eq. (2) approximates some less empirical functions proposed by others. Green⁴ has tested this point by comparing eq. (2) with the functions of Schulz,⁶ Wesslau,⁷ and Beasley.⁸ He has shown, with data for five different polymers, that the Tung function gives results which are practically identical with those from the Schulz binomial distribution, but the results from the Wesslau and Beasley functions not only differ from those of Tung and Schulz, but also from each other. The simplicity and rather wide applicability of the Tung function, and its close agreement with that of Schulz, therefore make it a reasonable choice for the present treatment. As a further advantage, its two parameters are simply related^{3,4} to the various average molecular weights and to the polydispersity by the equations:

$$\bar{M}_n = a^{-\beta}/\Gamma(1-\beta) \quad (3)$$

where $\beta = 1/b$

$$\bar{M}_w = a^{-\beta} \Gamma(1+\beta) \quad (4)$$

$$\bar{M}_v = a^{-\alpha\beta} \Gamma(1+\alpha\beta) \quad (5)$$

$$\bar{M}_w/\bar{M}_n = \Gamma(1+\beta)\Gamma(1-\beta) \quad (6)$$

In these equations Γ is the gamma function, and α in eq. (5) is the exponent in the viscosity equation $[\eta] = K\bar{M}_v^\alpha$. The maximum in the differential distribution curve is located by

$$M_{\max} = [(b-1)/ab]^\beta \quad (7)$$

On substituting eq. (2) into eq. (1) and letting $aM_0^b y^b = x$, we obtain

$$w_s = a^{1/b} bM_0^{b-(1/b)} \sum_{y=1}^{\infty} x^{1-(1/b)} [1 - \rho(1 - w_s)]^{(x/aM_0^b)^{1/b}} \exp\{-x\} \quad (8)$$

The second term within the brackets is much less than one, because $(1 - w_s)$ is always less than one in a crosslinked system and the crosslink density even in a fairly highly crosslinked network is usually of the order of 10^{-2} or less. We can therefore expand the quantity in brackets and drop higher terms. Substituting this approximation into eq. (8) and changing the summation to an integral with zero lower limit, we obtain

$$w_s = a^{1/b} bM_0^{b-(1/b)} \left\{ \int_0^\infty x^{1-(1/b)} e^{-x} dx - [\rho(1 - w_s)/(aM_0^b)^{1/b}] \int_0^\infty x e^{-x} dx \right\} \quad (9)$$

The first integral is finite if b is not less than 0.5. (This would apparently exclude one sample of polyethylene for which Tung reported $b = 0.386$; all other b values reported in the literature are larger than 0.5, and are mostly in the range of 1.5–2.5.) Integration of eq. (9) yields the final result

$$w_s = \frac{a^{1/b} bM_0^{b-(1/b)} \{ \Gamma[2 - (1/b)] - [\rho/(aM_0^b)^{1/b}] \}}{1 - bM_0^{b-(1/b)-1} \rho} \quad (10)$$

This equation relates the weight fraction of sol to the crosslink density and to the molecular weight distribution parameters.

APPLICATION OF EQUATION (10)

Distribution data reported in the literature are usually for "original" polymers, whereas the present method, or that of Bueche and Harding, will reflect any changes which may have occurred in the milling or processing of a vulcanizable mixture. The distribution in the latter condition is frequently

the more important; for example, it is the distribution that will govern vulcanizate properties. The "rheological distribution" governing processing will be some sort of time average of the original and final distributions, and will generally depend on a complexity of mechanical and chemical factors.

In order to determine a and b from eq. (10), one requires values of w_s and ρ for only two different states of crosslinking. One of these states should be low enough to yield an appreciable sol fraction (say, 5 or 10%) in order to minimize errors in the computed parameters. However, it should not be excessively low, for reasons to be explained later. If the two states of crosslinking are represented by subscripts 1 and 2, it is easily shown from eq. (10) that

$$bM_0^{b-(1/b)-1} = \frac{(w_{s1} - w_{s2})}{(\rho_2 - \rho_1) + (w_{s1}\rho_1 - w_{s2}\rho_2)} \quad (11)$$

The two sets of experimental values of w_s and ρ (suitably corrected as explained below) are substituted into eq. (11), along with the known molecular weight M_0 of the monomer unit, and the value of b is easily computed by trial and error. The value of a then follows from eq. (10), which can now be expressed in the more convenient form

$$a^{1/b} = \frac{w_s + bM_0^{b-(1/b)-1} \rho(1 - w_s)}{bM_0^{b-(1/b)} \Gamma[2 - (1/b)]} \quad (12)$$

The various average molecular weights, the polydispersity, and the maximum in the distribution curve are then simply computed from eqs. (3) to (7). If one of the average molecular weights happens to be known from other measurements, comparison with the corresponding calculated value can, of course, be made to check the accuracy of the method for the particular system under consideration.

ESTIMATION OF "TRUE" CROSSLINK DENSITY

Corresponding values of w_s and ρ can be determined from a single swelling experiment, and the expected precision in w_s should ordinarily be within a few per cent. If the polymer system contains an appreciable amount of nonpolymeric contaminants such as soaps or other extractable ingredients, a correction will, of course, be required. Pertinent information is usually available from analytical data or from the conditions of polymerization or compounding. Some typical computations with eqs. (11) and (12) show that the values of a and b are relatively insensitive to the normal precision in

w_s , and b is relatively insensitive to that in ρ . However, since in actual computations the two terms in the numerator of eq. (12) are more or less equal in magnitude, a given error in ρ will lead to a comparable error in a , if b is of the order of 2. Therefore, even though ρ can be measured from swelling experiments within a precision of about 5% or less, provided that fairly good values of the polymer-solvent interaction constant are available, one still has to be concerned with its accuracy.

The value of ρ (physical) obtained from a swelling measurement depends in part on polymer statistical theory, and has been shown by Moore and Watson⁹ to be, very roughly, about twice as large as the "true" value ρ (chemical) obtained from the chemical measurement of crosslinks in peroxide-cured natural rubber. The divergence depends on the crosslink density and, if the latter is not too small, we find from Moore and Watson's plots that

$$\rho(\text{chemical})/\rho(\text{physical}) = 0.811 - 17.1 \times 10^{-4}/\rho(\text{physical}) \quad (13)$$

The value below which eq. (13) becomes invalid is about $\rho(\text{physical}) = 21 \times 10^{-4}$. Below this value, chain entanglements and free-end corrections become dominant, as Moore and Watson have shown, and the relationship between the crosslink densities becomes a function of molecular weight. Since comparisons between ρ (chemical) and ρ (physical) are not known for systems other than peroxide-cured natural rubber, we must assume for the time being that the correction factor given by eq. (13) is applicable to other polymers. Only future experiments will show how valid this is; but since the divergence is due to the physical factors mentioned, the assumption may be temporarily admissible. The values thus corrected should, in any event, be better than the uncorrected ones.

RESULTS FOR PEROXIDE-CURED SBR

In most published papers containing crosslink density values for vulcanized polymers there has been little reason, unfortunately, for reporting the corresponding sol fraction values. Information for testing the present method is therefore meager. Kraus¹⁰ has published some data suitable for this purpose. Table 17 of his paper lists crosslink densities and "per cent extractables" for pure gum vulcanizates of cold SBR (Philprene 1500) which contained different concentrations of dicumyl peroxide and were cured for different lengths of time. The crosslink densities ν are reported in moles per c.c.

Assuming that his polymer contained butadiene and styrene units in the weight ratio of 75/25 and had a density of 0.93, one can convert the ν values to ρ values by dividing by 0.015. The latter, in turn, were corrected to ρ (chemical) by means of eq. (13). Kraus' values for "per cent extractable" also require correction for our purpose since, as he has pointed out,¹¹ synthetic SBR emulsion polymers contain some 5-7% of fatty acid and soap; these contaminants will be included with the extracted sol. Inspection of his data shows that the "per cent extractable" values level out at a minimum value of about 6.9% in the pure gum systems, in good agreement with the quoted contaminant level. We have accordingly corrected the extractables values by this amount in order to obtain values of w_s representative of the polymer sol fraction. As for M_0 , we have employed a number-average value of 61, based on the assumed ratio of butadiene to styrene units in the polymer. Table I contains the data selected for these calculations, together with the corrected values. From the data given in the last two columns of Table I we have calculated the distribution values shown in Table II.

The distribution characteristics of the Philprene 1500 on which Table II is based are not known.

TABLE I
Data for Peroxide-Cured Cold SBR (Based on Data by Kraus)

Di-cumyl peroxide, phr	Cure time at 307°F., min.	$\nu \times 10^4$, moles/c.c. (from swelling)	Extractables, % (from swells)	$\rho \times 10^3$ (from ν)	$\rho \times 10^3$ (corrected)	w_s (corrected)
0.5	15	0.13	24.2	0.867	—	0.173
	30	0.19	18.3	1.27	—	0.114
1.0	15	0.47	13.1	3.13	0.83	0.062
	45	0.71	9.9	4.73	2.12	0.030
2.0	15	0.78	9.3	5.20	2.51	0.024
	30	1.32	6.9	8.80	5.42	0.0

TABLE II
Calculated Distribution Values for Peroxide-Cured Cold SBR

Di-cumyl peroxide, phr	Tung parameters		Molecular weights $\times 10^{-4}$			Polydispersity \bar{M}_w/\bar{M}_n
	a	b	M_{\max}	\bar{M}_w	\bar{M}_n	
0.5	—	—	—	—	—	—
1.0	1.63×10^{-9}	2.084	1.20	1.46	0.966	1.51
2.0	1.48×10^{-7}	1.782	1.56	0.605	0.338	1.79

However, Bueche and Harding¹ have reported values of $\bar{M}_n = 31,000$ and $\bar{M}_w/\bar{M}_n = 7$ for a compounded sample of cold SBR. Although their values are higher than those listed in Table II the agreement is not too bad when one considers that they arrived at their values by neglecting the lowest 10% of the polymer. Furthermore, their sample, which was prepared with sulfur, probably experienced less degradation during processing than did the peroxide-containing Philprene sample. Booth and Beason¹² have reported values of $\bar{M}_n = 80,000$ and $\bar{M}_w/\bar{M}_n = 3.4$ for a sample of type 1500 SBR that had not been subjected to any compounding or processing. In view of the differences mentioned, the results in Table II are therefore regarded as reasonable. The polydispersity values in Table II appear to increase with increasing peroxide content. This result, if significant, is concordant with the view that chain scission by the peroxide may have occurred. Statistical analyses have shown¹³ that when random scission occurs, the original distribution broadens markedly during the initial stages, and not until an advanced state of scission has occurred does the polymer become more homogeneous as lower molecular weight species accumulate.

RESULTS FOR CROSSLINKED POLYSTYRENE

It is immaterial to the present method whether the polymer is crosslinked by a vulcanization reaction or by synthesis. If a trace amount of a suitable polyfunctional comonomer is used in the synthesis, the distribution characteristics of the product might be considered to approximate those of the "pure" homopolymer prepared under the same synthesis conditions. Or alternatively, the homopolymer distribution features might be deduced by extrapolation from products containing several small, but different, comonomer concentrations. Boyer and Spencer¹⁴ have published extensive crosslinking and swelling data for slightly crosslinked polystyrene containing trace amounts of divinylbenzene as comonomer. We have computed ρ values from their values of M_c , but we were not able to correct these in accordance with eq. (13) because they are too small. We have estimated the corresponding values of w_s from their data on short- and long-time equilibrium swelling ratios. Table III contains these data and the calculated distribution values. The average molecular weights appear to be reasonable, although they may be high by a factor of perhaps two, because of the use of uncorrected ρ values. The polydispersity, which can be shown to be practically independent of this cor-

TABLE III
Distribution Values for Divinyl benzene Crosslinked Polystyrene (based on data by Boyer and Spencer)

DVB, wt.-%	$\rho \times 10^4$ (swelling)	w_s	Calculated distribution values
0.0333	4.59	0.120	$a = 2.28 \times 10^{-12}$
0.0462	7.89	0.059	$b = 2.358$
			$\bar{M}_w = 7.65 \times 10^4$
			$\bar{M}_n = 5.58 \times 10^4$
			$\bar{M}_w/\bar{M}_n = 1.4$

rection, agrees rather well with the value of 1.41 (for \bar{M}_w/\bar{M}_n) which Booth and Beason have recently determined from Guzman's fractionation data¹⁵ for a low-conversion polystyrene synthesized at room temperatures. It is interesting that the calculated value of b (2.358) agrees closely with that of 2.27 which Tung derived from Schulz and Dinglinger's fractionation data¹⁶ for a "pure" polystyrene. While agreement might be expected, since both values are based on the use of the same distribution function, the values nevertheless represent two rather different polymer samples. The agreement suggests that the presence of a trace of comonomer during synthesis influences a much more than b . However, since the Tung distribution is empirical, one can do little more than speculate about the possible fundamental significance of this observation.

CONCLUSION

The close agreement which Green has demonstrated between results from the Schulz binomial and the Tung distribution and the applicability of the latter to a variety of fractionation data for different polymers both seem to outweigh possible objection that the present method assumes a particular distribution function. Green's results suggest to us that the apparent exceptions found by Tung for some polyethylenes containing large amounts of low molecular species may possibly be attributed to fractionation inefficiency, rather than to the inadequacy of his function. The internal consistency or smoothness of data does not, of course, constitute proof of precise fractionation. In fact, one can safely say it is no easy matter to find complete fractionation data, of established precision, that can provide a critical test of a distribution function over the entire molecular weight domain.

In his study of polyethylenes, Tung suggested that his function tends to exaggerate the low molecular weight end of the distribution, in the sense that the \bar{M}_n values calculated from his parameters

were only about half as large as those obtained by summation of the experimental data for the fractions. His calculated and experimental values of \bar{M}_w , on the other hand, were in satisfactory agreement. One might be tempted to use this to reconcile the \bar{M}_n values of the SBR system in Table II with the higher values reported by others. However, this procedure would be indefensible because simply doubling the \bar{M}_n values would give polydispersity values of less than unity. It would therefore seem incorrect to generalize that the Tung function gives abnormally small \bar{M}_n values for all polymers, especially when there is some reason to believe that it is better than it seems, even for polyethylenes. Much more likely, the differences between the average molecular weights and the polydispersity of the peroxide-SBR system of Table II, and the corresponding quantities reported by Bueche and Harding for sulfur-SBR and by Booth and Beason for un compounded SBR, are real and are due to chemical and other factors already mentioned.

Although the meager data at hand leave some question as to the accuracy with which the present method can predict absolute values of the various average molecular weights, the key to the matter seems to be the ratio of the true to the physically measured crosslink density for polymers in general, rather than the particular distribution function employed here. Less uncertainty is attached to the polydispersity, since this is a function of only one parameter, b , which is quite insensitive even to large errors in ρ . The method may therefore be useful, even in its present state, for comparative studies in a given system. These might include, for example, the effects of synthesis or processing variables on distribution characteristics and product properties or the effects of stabilizers in aging or other degradative processes.

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Synopsis

A method is proposed for estimating rather simply and with relatively little experimental data the molecular weight distribution characteristics of any crosslinkable polymer which follows the Tung distribution function. This function is combined with a fundamental relationship from the statistical theory of sol-gel ratios in randomly crosslinked polymers, to yield a result which relates explicitly the sol-gel ratio, the crosslink density, and the molecular weight distribution parameters. These parameters give the various average molecular weights and the polydispersity by simple computation. The method has been tested with meager data available for a peroxide-cured SBR and a divinylbenzene-crosslinked polystyrene. Reasonably satisfactory results were obtained. A critical test of the absolute accuracy of the method requires experimental data not now available, and some refinements may eventually have to be made. However, the method should be useful, in its present state, for estimating distribution characteristics and, especially, for comparative studies within a given polymer system.

Résumé

On a proposé une méthode relativement simple et exigeant assez peu de données expérimentales, en vue d'évaluer la distribution moléculaire caractéristique d'un polymère pouvant être ponté suivant une fonction de distribution de Tung. Cette fonction combinée à la relation fondamentale de la théorie statistique des rapports sol-gel dans les polymères pontés au hasard, permet d'obtenir des résultats rendant compte explicitement du rapport sol-gel, de la densité de pontage et des paramètres de la distribution moléculaire. Ces paramètres donnent les divers poids moléculaires moyens et la polydispersité par simple compilation. La méthode a été testée à l'aide d'un petit nombre de données obtenues pour un polymère SBR ponté aux peroxydes et pour un polystyrène ponté par le divinylbenzène. Des résultats satisfaisants ont été obtenus. Un test critique d'exactitude absolu de la méthode exige des données expérimentales qu'il n'est pas possible d'obtenir actuellement. Quelques améliorations devront éventuellement être apportées. La méthode devrait cependant être utile, sous sa forme actuelle, pour estimer les caractéristiques de distribution et, de façon plus spéciale, pour des études comparatives limitées à un système polymérique défini.

Zusammenfassung

Eine Methode zu einer ziemlich einfachen und verhältnismässig wenige experimentelle Daten erfordernden Bestimmung der Molekulargewichtsverteilungskarakteristik von irgendwelchen vernetzbaren Polymeren, die die Verteilungs-

funktion von T folgen, wird angegeben. Diese Funktion wird mit einer grundlegenden Beziehung der Theorie des Sol-Gelverhältnisses bei statistisch vernetzten Polymeren kombiniert, wodurch eine explizite Verknüpfung des Sol-Gelverhältnisses, der Dichte der Vernetzungsstellen und der Parameter der Molekulargewichtsverteilung erhalten wird. Diese Parameter liefern durch einfache Rechnung die verschiedenen Molekulargewichtsmittel und die Polydispersität. Die Methode wurde mit den wenigen Daten getestet, die für ein peroxyd-vulkanisiertes SBR und ein divinylbenzolvernetztes Polystyrol zugänglich sind. Es

wurden annehmbar befriedigende Ergebnisse erhalten. Ein kritischer Test der absoluten Genauigkeit der Methode würde experimentelle Daten erfordern, die im Augenblick noch nicht vorhanden sind; vielleicht müssen dann noch gewisse Verfeinerungen angebracht werden. Es sollte jedoch auch schon in ihrem gegenwärtigen Zustand die Methode zur ungefähren Festlegung der Verteilungscharakteristik und besonders für vergleichende Studien in einem gegebenen Polymersystem nützlich sein.

Received April 22, 1960