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Solution-free methods for the determination of the molecular mass distribution of polymers

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Abstract. The known methods for the assessment of the molecular mass distribution of bulk polymers are considered. These are based on the analysis of the melt flow curves, the frequency dependence of the relaxation modulus, the shape of the free induction decay curve (pulse nuclear magnetic resonance spectroscopy) and the temperature dependence of compliance in the region of the rubbery elasticity plateau (thermomechanical analysis). The bibliography includes 121 references.

I. Introduction

The molecular mass (MM) and molecular mass distribution (MMD) are important structural characteristics which determine many physical properties of polymers.

Various methods are used for the determination of MM; however, only a few of them can be applied to assess MMD. Gel permeation chromatography (GPC)[1] is the most popular, since it is simple, fast in operation, reliable and relatively cheap. Other methods, in particular, those based on fractionation of a polymer, are time-consuming. All methods are based on analysis of the properties of dilute solutions. Therefore, MMD of many insoluble polymers cannot be assessed at all. This holds for, *e.g.*, polymer networks, where it is desired to know the size distribution of linear chain segments between cross-link points. On the other hand, a method based on destruction of polymers has been developed.[2] However, this method has found no practical use since it is laborious and requires preliminary establishment of the destruction mechanism, which itself is a rather complicated problem.

Attempts at using the relaxation properties of bulk polymers for the determination of MMD are also known. To this end, studies aimed at finding the relation between MMD and the relaxation time spectrum of a polymer were carried out. In this review, the results of such studies carried out over the last three decades are analysed.

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Several short reviews devoted to the studies on the assessment of MMD based on the analysis of the relaxation properties of polymers have been published.[3 – 10] However, the authors dwelled, as a rule, on one particular approach without comparing different methods of attacking the problem.

II. The direct problem

To find the MMD function from relaxation data, one should know the dependence of the relaxation properties of polymers on their MMD. This problem has rather long been posed;[11 – 17] however, no unambiguous solution has been found so far. Because of this, mixing rules of the contributions of polymer fractions to the relaxation properties are widely used. Theoretical prerequisites to the use of this approach can be found mainly in the reptation theory.[14, 17, 18] For instance, it is suggested that the time dependence of the relaxation modulus, $G(t)$, be described by the following expression[18]

$$G(t) = G_0\,\varphi(t)\,\mu(t),$$

where G_0 is the modulus of elasticity in the region of the rubbery elasticity plateau; φ(t) is the function which takes into account the tube renewal, $\mu(t)$ is the probability that motion of an arbitrarily chosen segment of a polymer chain is confined to a deformed tube. For a monodisperse system,

$$\mu(t) = \frac{8}{\pi^2}\sum_{p=1,3,\ldots} p^{-2}\exp\left(-\frac{p^2 t}{\lambda}\right) \equiv \mu_1\left(\frac{t}{\lambda}\right),$$

where p is the summation index (an odd number), t is the current time, λ is the maximum relaxation time for the Doi – Edwards model.[17] For a binary polymer blend, a linear mixing rule of the weight fractions w_i of each component is valid

$$\mu(t) = w_1 m\left(\frac{t}{\lambda_1}\right) + w_2 m\left(\frac{t}{\lambda_2}\right).$$

An analogous linear mixing rule has been used in other studies.[19 – 21]

A more complex $G(t)$ dependence based on the double reptation model has been proposed [22 – 25]

$$G(t) = \left[\sum_i w_i G_i^{1/2}(t)\right]^2.$$

Maier *et al.*[26] suggested a generalised empirical formula for calculating the time dependence of the relaxation modulus

$$G(t) = G_0\left[\int_{\ln M_e}^{\infty} F^{1/\beta}(t,M)w(M)\mathrm{d}\ln M\right]^{\beta}. \quad (1)$$

Here, $F(t,M)$ is the function which describes the relaxation behaviour of a polymer fraction with MM = M, t is the current time, β is the parameter characterising the mixing rule and M_e is the MM of a chain segment between entanglements.

The results obtained using different theoretical models were compared with the experimental data on the relaxation behaviour of binary polystyrene blends.[26] It was shown that dependence (1) fits the experimental data best with $\beta = 3.84$ virtually irrespective of the form of the function $F(t,M)$. In addition to the above-mentioned theoretical models,[18,22–25] the step[27] and exponential[28] functions and an empirical function containing a finite number (up to 25) of exponential terms with an empirical relaxation time spectrum (the so-called BSW spectrum)[29] were also considered. The last-mentioned function was found from the relaxation data for monodisperse specimens. It was found that none of the models considered described adequately the relaxation curves of both polymer blends and even monodisperse polymeric systems. This is consistent with the conclusions reported in a recent study[30] in which the results of calculations using the Doi–Edwards model were compared with the experimental results obtained for monodisperse polystyrene specimens.

Empirical mixing rules found mainly in the studies on the analysis of relaxation properties of binary blends of monodisperse polymers are applied to the relaxation time spectrum $H(\lambda)$ (λ is the relaxation time), which is defined as follows:

$$G(t) = \int_{\lambda_{\min}}^{\lambda_{\max}} H(\lambda)\exp\left(-\frac{t}{\lambda}\right)\mathrm{d}\lambda\,.$$

The simplest relation proposed by Ninomiya[31] has the form

$$H(\lambda) = \sum_{i=1}^{N} w_i H_i\left(\frac{\lambda}{A_i}\right),$$

where $H_i(\lambda)$ is the relaxation time spectrum of a monodisperse polymer; A_i is the time shift factor due to intermolecular interaction between polymers (such an interaction facilitates the relaxation of the components with higher MM and hampers the relaxation of the components with lower MM). Attempts at taking into account these interactions by deriving generalised formulae lead to sophisticated expressions[32–34]

$$H(\lambda) = \sum_{i=1}^{N}\sum_{j=1}^{N} w_i w_j H_{ij}\left(\frac{\lambda}{A_{ij}}\right),$$

$$H(\lambda) = \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N} w_i w_j w_k H_{ijk}\left(\frac{\lambda}{A_{ijk}}\right),$$

which seem to be hardly applicable in practice.

No simpler is yet another relationship[35,36]

$$H(\lambda) = \sum_{i=1}^{N} B_i H_i\left(\frac{\lambda_i}{A_i}\right), \quad (2)$$

where $B_i = w_i^2 + w_i\sum_{j=i+1}^{N} a_{ij}w_j$ is the form factor,[37,38] which is a function of MM, and $H_i\left(\frac{\lambda_i}{A_i}\right)$ is the BSW spectrum, namely,[29]

$$H(\lambda_i) = n\left(\frac{\lambda_i}{\lambda_{\max}}\right)^n h\left(1-\frac{\lambda_i}{\lambda_{\max}}\right),$$

n is a constant ($n < 1$) and h is the Heaviside step function.

Table 1. Characteristics of components and parameters A_i and B_i of Eqn (2) for a binary polystyrene blend.[39]

M_1	M_2	w_2 [a]	B_2	A_1	A_2
38900	427000	0.00	0.000	1.00	–
38900	427000	0.01	0.003	1.06	0.030
38900	427000	0.03	0.005	1.17	0.045
38900	427000	0.05	0.007	1.50	0.060
38900	427000	0.10	0.020	1.78	0.070
38900	427000	0.20	0.050	2.89	0.110
38900	427000	0.40	0.170	3.89	0.230
38900	427000	1.00	1.000		1.000
23400	2810000	0.01	0.00100	0.90	0.00023
38900	2810000	0.01	0.00080	1.10	0.00100
72400	2810000	0.01	0.00055	1.00	0.00650
124000	2810000	0.01	0.00040	1.20	0.04000

[a] $w_1 + w_2 = 1$.

As an example, Table 1 lists the values of the parameters of Eqn (2) taken from Ref. 39. As can be seen, the parameters A_i and B_i depend on the composition and MM of the polymer blend and on the ratio of MM of the blend components. It was also found that all these characteristics affect the values of the maximum relaxation time of each component. This can be exemplified in the data of a study on the relaxation of polymer chains by infrared dichroism[40] (Table 2).

Table 2. Maximum chain relaxation time (s) in a binary blend of deuterated and hydrogenated polyisoprene.[40]

Content of a high-molecular-mass component (vol. %)	λ_L (for H + L blend)	λ_M (for L + M blend)	λ_H (for M + H blend)
10	20	2.8	50
20	60	3.5	70
30	120	4.5	130
50	150	6.4	160
75	180	6.7	186
100	210	7.0	210

Note. H, M and L denote the blend components with high (370×10^3), medium (125×10^3) and low (53×10^3) molecular mass, respectively.

No general rule exists which would allow passage from the relaxation properties of monodisperse polymers to those of polydisperse polymers. This is largely due to the lack of a theory which can give an adequate description of the dynamic behaviour of polymeric systems.[41] Currently, there is no unique solution of the direct problem of obtaining a relaxation time spectrum based on a particular model or the relaxation properties of a known blend of monodisperse fractions. Obviously, this severely hampers the solution of the inverse problem, consisting of finding the MMD of a polydisperse polymer from its relaxation characteristics.

III. Relations between rheological properties and molecular mass distribution of polymers

Much attention has been paid to the studies on the relations between MMD and viscosity (η) of polymer melts and concentrated solutions.[12,42] Most often, this problem was solved by relating the viscosity to the number-average ($\bar{M}_n$), or weight-average ($\bar{M}_w$), or a high-level-average MM ($\bar{M}_z$), or even to their combination (*e.g.*, $\bar{M}_n\bar{M}_z/\bar{M}_w$).

These approaches have not been supported by any theoretical concepts. Attempts to represent the relation between viscosity and MMD in the form

$$\eta \propto \left(\sum_i M_i^{\alpha}\right)^{1/\alpha},$$

where α characterises the dependence of viscosity on the MM of a monodisperse polymer,

$$\eta \propto M^{\alpha}$$

are equally unjustified.

An attempt to find a physically substantiated method relating the rheological properties and MMD of a polymeric system has been undertaken.[43] This approach was based on the following assumptions: (i) the relaxation time spectrum is limited by the maximum relaxation time $\lambda_{max}(\dot\gamma)$, where $\dot\gamma$ is the shear rate; (ii) the maximum relaxation time is inversely proportional to the shear rate; (iii) the maximum relaxation time of a given polymer is affected by the presence in the blend of another polymer with a lower MM and (iv) the relaxation time spectrum of a given polymer is independent of the type of polydispersity of the polymer.†

Based on these assumptions, the following formula relating the MMD function to the viscosities of the polymer fractions was derived[43]

$$\sum_{i=m+1} w_i = \left[\left(\frac{\eta_{m+1}}{K}\right)^{1/3.4} - \left(\frac{\eta_m}{K}\right)^{1/3.4}\right](M_{m+1} - M_m)^{-1}, \quad (3)$$

where w_i is the weight fraction of a polymer fraction with MM = M_i, η_m is the viscosity of a polymer with MM = M_m, K is the coefficient in the equation relating the viscosity of a monodisperse polymer to its MM

$$\eta = KM^{3.4}.$$

Hence it follows that

$$w_m = \left(\frac{1}{K}\right)^{1/3.4}\left(\frac{\eta_m^{1/3.4} - \eta_{m-1}^{1/3.4}}{M_m - M_{m-1}} - \frac{\eta_{m+1}^{1/3.4} - \eta_m^{1/3.4}}{M_{m+1} - M_m}\right). \quad (3a)$$

Expression (3a) was used for analysing a number of binary blends and commercial polystyrene specimens.[44] It was shown that the polydispersity indices,

$$\gamma = \frac{\overline{M}_w}{\overline{M}_n},$$

determined by rheological methods are close to those found by GPC.

A physical substantiation of the rheological approach has been given by Malkin and Teishev[45–47] who used the phenomenon of flow separation in monodisperse polymers, discovered by Vinogradov,[48] as the basis for their consideration. Mathematically, this phenomenon can be described by the relation

$$\eta(\dot\gamma) = \begin{cases} \eta_0 \text{ for } \tau \leqslant \tau_s \\ \tau_s/\dot\gamma \text{ for } \tau > \tau_s. \end{cases}$$

Here η_0 is the highest Newtonian viscosity and τ_s is the stress at which flow separation occurs in the polymer.

Based on the known relationship,

$$\eta_0 = KM^{a},$$

Malkin and Teishev derived the formula[45, 46]

$$\eta(\dot\gamma) = \left[\int_0^{M(\dot\gamma)} (KM^a)^{1/a} f(M) dM + \left(\frac{\tau_s}{\dot\gamma}\right)^{1/a} \int_{M(\dot\gamma)}^{0} f(M) dM\right]^a, \quad (4)$$

where the integration limit is

$$M(\dot\gamma) = \left(\frac{\tau_s}{K\dot\gamma}\right)^{1/4},$$

and f(M) is the MM function.

Formula (4) can be used for unimodal MMD functions which include a small number of parameters (Malkin and Teishev[46] analysed the Bisley, lognormal and other two-parameter distribution functions). In this case, the melt flow curve is sufficiently sensitive to the parameters of the distribution function.

Gordon and Shaw[4] calculated the MMD function using another analytical expression for the flow curve, namely,

$$\eta(\dot\gamma) = \begin{cases} \eta_0 \text{ at } \tau \leqslant \tau_s \\ \dot\gamma^{-v} \text{ at } \tau > \tau_s, \end{cases}$$

where τ_s (and, correspondingly, $\dot\gamma_s$) defines the point of transition from Newtonian to a non-Newtonian flow and v is the exponent in the power law of the melt flow

$$\eta \propto \dot\gamma^{-v}.$$

The position of this point depends on the MM of the polymer.

The procedure for the calculation of the MMD function depends on which mixing rule for viscosities is used. Gordon and Shaw considered the following mixing rule:

$$\log\eta = w_1 \log\eta_1 + w_2 \log\eta_2.$$

Using this mixing rule, the relation between the integral MMD function F(M) and parameters of the melt flow curve has the form

$$F(M) = 1 + \frac{1}{v}\frac{d\ln\eta}{d\ln\dot\gamma}\Big|_{\dot\gamma = g(M)},$$

where the function $g(M)$ relates the shear rate to the MM of the polymer and the parameter v.

A more general mixing rule,

$$\eta^{1/a} = w_1\eta^{1/a} + w_2\eta^{1/a}$$

leads to the following formula,

$$F(M) = 1 + \frac{1}{v}\left(\frac{\eta}{\eta_0}\right)^{1/a}\left(\frac{\dot\gamma}{\dot\gamma_s}\right)^{v/a}\frac{d\ln\eta}{d\ln\dot\gamma}\Big|_{\dot\gamma = \dot\gamma_s m^{-a/v}},$$

where

$$m = \frac{M}{\overline{M}_w}.$$

An algorithm and software for calculations of the MMD function using the last two formulae have been published in a monograph.[4] It should be noted that the exponent a is not known with certainty. Recently,[49] it was shown that the parameter a depends on the shear rate (and frequency) in such a manner that its magnitude decreases from values in the range between 3 and 5, which is typical of low shear rates (the highest Newtonian viscosity), down to 0 for high shear rates (the lowest Newtonian viscosity). Moreover, it was empirically found that the parameter a depends also on MMD of the polymer as follows

$$a = \beta_0 + \beta_1\left(\frac{M_h}{M_l}\right), \quad (5)$$

where $\beta_0 = 3.39 \pm 0.37$, $\beta_1 = 0.03 \pm 0.04$, and M_h and M_l are the MM of the high-molecular and low-molecular mass components of a binary polymer blend, respectively. The values of the

† This assumption seems to be not universally true for systems with entanglements.

coefficients of equation (5) also vary to a certain degree depending on the type of the polymer.

With some grounds, it is believed [44,46] that the rheological approach can hardly be used for characterisation of an arbitrary MMD function; however, the authors of a monograph (Ref. 4) have a more optimistic view on these things.

IV. Methods based on dynamic measurements

Attempts at using the frequency dependences of the real and imaginary parts of the relaxation modulus of elasticity for the determination of the MMD of polymers have long been undertaken. Ninomiya and Fujita seem to be the first who reported studies in this line of investigation as long ago as 1957.[50–52] This approach is based on theoretical or empirical relationships between the relaxation time spectrum and MM of polymers [12,13,53] (see also Section II).

In the simplest form, the theory of polymer dynamics was reported by Rouse who developed the well-known single-chain model which is basic to the studies by Ninomiya.[31,50–52,54,55] More recent investigations [56] were based on the Doi–Edwards model in which interchain interaction is considered as interweaving of polymer chains, or entanglements, which confine mainly lateral displacements of the polymer chains.

The results of studies carried out on monodisperse specimens of different polymers and their blends (for the most part, binary blends) [26,39,40,57–61] can be outlined as follows.

For polymers with narrow MMD, the log-log plots of the frequency dependence of the real part of the relaxation elasticity modulus, $G'(\omega)$, nearly coincide in the high-frequency region (the region of the rubbery elasticity plateau). Marked distinctions are observed in the region of low-frequency 'tails' where $G'(\omega)$ depends on ω as

$$G'(\omega) \propto \omega^2.$$

The 'tails' can be matched by using a shift factor proportional to MM raised to a certain power; it is commonly accepted [12,13,62,63] that the exponent value lies between 3.4 and 3.7.

The frequency dependences of the imaginary part of the relaxation modulus of elasticity, $G''(\omega)$, pass through a maximum. The position of the maximum depends on MM of a polymer in the same way as the low-frequency 'tails' of the $G'(\omega)$ and $G''(\omega)$ curves.

In binary polymer blends, the polymer fractions possess similar relaxation properties; however, no complete coincidence with the behaviour of monodisperse systems is achieved. That is, the low-frequency 'tails' are shifted towards higher frequencies for the component with the higher MM and towards lower frequencies for the component with the lower MM.

This phenomenon is associated with the interchain interaction (coupling effect, nematic interaction),[39,40,64–68] which also manifests itself as the orientation of low-molecular-mass chains (even oligomers) in the bulk of the oriented high-molecular-mass matrix.

It should be noted that this frequency shift should occur even in the absence of intermolecular interaction. Indeed, let the relaxation properties be determined by the only relaxation time, which is of course dependent on the MM of the high-molecular-mass fraction. Then, for $\omega \to 0$, the real part of the relaxation modulus of elasticity of a binary polymer blend takes the form

$$G'(\omega) = w_1 \frac{\omega^2\lambda_1^2}{1+\omega^2\lambda_1^2} + w_2 \frac{\omega^2\lambda_2^2}{1+\omega^2\lambda_2^2} \to \omega^2(w_1\lambda_1^2 + w_2\lambda_2^2).$$

Obviously, it is this effect that should be observed if $\lambda_1 > \lambda_2$, namely, a shift of the relaxation moduli of elasticity of the high-molecular-mass and low-molecular-mass fractions towards high and low frequencies, respectively. An analogous relationship is also valid for $G''(\omega)$, for $\omega \to 0$

$$G''(\omega) = w_1 \frac{\omega\lambda_1}{1+\omega^2\lambda_1^2} + w_2 \frac{\omega\lambda_2}{1+\omega^2\lambda_2^2} \to \omega(w_1\lambda_1 + w_2\lambda_2).$$

The aforesaid can be illustrated by the corresponding plots shown in Fig. 1. On the other hand, a direct mutual effect of the polymer fractions (see Table 2) cannot also be ruled out.

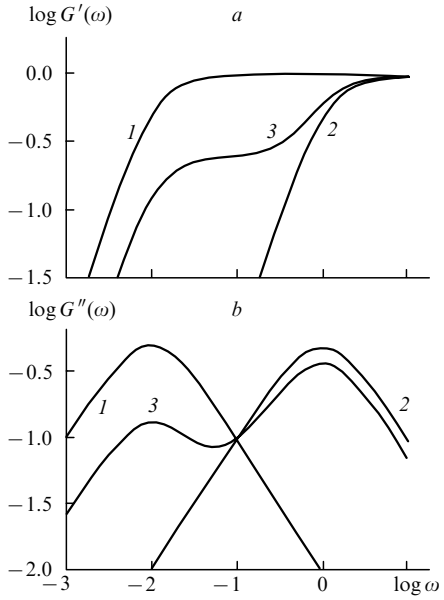


Figure 1. Frequency dependences of the real (*a*) and imaginary (*b*) parts of the relaxation modulus of elasticity for specimens with one relaxation time of 100 (*1*) and 1 arbitrary unit (*2*) and for their blend containing 25% of the first component (*3*).

A salient feature of the $G'(\omega)$ and $G''(\omega)$ curves of binary blends is that the height of the rubbery elasticity plateau (in the first case) and that of the peak (in the second case) depend on the relative concentration of components. Similarly to the $G(t)$ curve, a 'step' appears on the $G'(\omega)$ curves. The $G''(\omega)$ curves are characterised by two peaks and the peak height ratio depends on the ratio of the blend components.

However, data on the relation between the peak heights and the concentration of the blend components are contradictory. Different authors use different formulae. For instance, a linear dependence was suggested [69]

$$G(t) = w_1 G_1\left(\frac{t}{d_1}\right) + w_2 G_2\left(\frac{t}{d_2}\right);$$

the parameter d is associated with the coupling effect.

Other (mainly quadratic) types of mixing rules have also been suggested.[13,70–72] For instance, based on the concept that each polymer fraction can be characterised by a frequency corresponding to the MM of the fraction and that at lower frequencies the contribution of this fraction to the relaxation modulus can be neglected, a procedure was developed [26] for the determination of the MMD function taking into account a quadratic dependence of the real part of the relaxation modulus of elasticity on the concentration of the high-molecular-mass component. Each fraction makes a contribution

$$w_i = \left[\frac{G'(\omega_i)}{G_0}\right]^{1/2}.$$

Comparison of the results obtained using this procedure with those obtained by GPC showed [27] that for binary polymer blends the dynamic approach is less accurate than the rheological method based on the analysis of the melt flow curve.

The complex viscosity, $\eta^*(\omega)$, was also proposed[44,49] to be used for assessing the MMD function.

$$\eta^*(\omega) = \frac{\sqrt{[G'(\omega)]^2 + [G''(\omega)]^2}}{\omega}.$$

In the high-frequency region (for $\omega \to \infty$), the complex viscosity decreases nearly proportionally to ω^{-2}, whereas in the low-frequency region (for $\omega \to 0$) its takes the limiting value corresponding to the highest Newtonian viscosity. It is in the low-frequency region that the strongest dependence of $\eta^*(\omega)$ on MMD of a polymer melt is observed and the parameter a [see Eqns (4) and (5)] has the maximum value. Thus, the frequency dependence of viscosity is similar to the dependence of viscosity on the shear rate, which corresponds to the Cox–Merz rule.[12]

Comparison of different approaches to the solution of the problem of determining the MMD function allowed Tuminello and Cudre-Mauroux[44] to conclude that the best results can be obtained by analysing the frequency dependence of the complex viscosity; it was also found that analysis of the real part of the relaxation modulus of elasticity gives overestimated, whereas analysis of the imaginary part gives underestimated values.

Investigations on the relaxation of dielectric properties are widely used for studying the relaxation properties of polymers. The relation between dielectric properties and MMD has been analysed[73–77] taking *cis*-polyisoprene as an example. It was shown that in this case the dielectric loss function can be predicted with ease if the autocorrelation function of a single chain, the mixing rule and the MMD function are known. Difficulties arise when considering the inverse problem. An attempt has been undertaken[77] to find the MMD function from the dielectric relaxation data using the Tikhonov regularisation, which was previously used for calculating the relaxation time spectra.[78,79] This study was carried out assuming a linear mixing rule and that the MMD function is described by the Flory–Schulz equation

$$\mathrm{f}(M) \propto M^{\nu} \exp\left(-\frac{M}{\overline{M}_\mathrm{n}}\right).$$

Information on the width of MMD can be obtained from the analysis of the effective relaxation time[80] in the low-frequency region or, in other words, of the low-frequency 'tails' of the $G'(\omega)$ and $G''(\omega)$ curves. Indeed, assuming that the relaxation time of a monodisperse polymer depends on its MM,

$$\lambda = KM^a,$$

for $\omega \to 0$ we get

$$G'(\omega) \approx G_0\omega^2 \sum_i w_i\lambda_i^2 = G_0\omega^2K^2 \sum_i w_iM_i^{2a},$$

$$G''(\omega) \approx G_0\omega K \sum_i w_iM_i^a.$$

Hence

$$\langle\lambda\rangle_2 \equiv \frac{G'(\omega)}{G''(\omega)} = \omega K \frac{\sum_i w_iM_i^{2a}}{\sum_i w_iM_i^a} = \omega K\langle M^a\rangle_2,$$

$$\langle\lambda\rangle_1 \equiv \frac{G''(\omega)}{G_0} = \omega K \sum_i w_iM_i^a = \omega K\langle M^a\rangle_1.$$

The subscripts 2 and 1 on the mean values of λ and MM correspond to a greater degree of averaging in the former case and to a lesser one in the latter. The ratio of the mean values can serve as a measure of the width of MMD. This algorithm is analogous to that which is commonly accepted for assessing the width of MMD and uses the mass-average and number-average MM and their ratio as the polydispersity index; the difference is that in the latter case $a = 1$ (in the relaxation method, $a \approx 3-4$).

Of course, it should be kept in mind that even monodisperse polymers possess a relaxation time spectrum; as a rule, the higher the MM the broader the relaxation time spectrum.[29]

V. Spin-spin relaxation technique (pulse NMR spectroscopy)

Both rheological and relaxation approaches have been used for the analysis of the MMD of linear polymers. For polymer networks, a steady flow is impossible. However, analysis of stress relaxation data (especially, of the frequency dependences of the relaxation modulus) can be used for extracting information on the MMD of chains of a polymer network. This was done using the spin-spin relaxation technique (pulse NMR spectroscopy).[81–89]

At sufficiently high temperatures ($T > T_\mathrm{g} + 100$), the dependence of the free induction decay on time is given by the following expression

$$G(t) = \int_1^N \int_0^{\pi/2} \left\{\left[g(N,\theta,t)\mathrm{P}(N)\sin\theta\right]\mathrm{d}\theta\right\}\mathrm{d}N, \qquad (6)$$

where N is the number of segments (the chain length) and θ is the angle between the vector connecting the chain ends and the direction of external magnetic field.

$$g(N,\theta,t) \approx \exp\left[-\omega_\mathrm{l}^2(3\cos^2\theta - 1)^2t^2\frac{\ln N}{N^2}\right],$$

where ω_l is the second moment of the free induction decay curve, expressed in frequency units.

In the time domain, the free induction decay has a long slowly descending component. The initial portion of this component contains information on MMD, while the length of its 'tail' is proportional to the average length of the chain segment between entanglements and inversely proportional to the current time t. Hence it follows that one can assess the MMD for those chains which are shorter than the length of the chain segment between entanglements (N_0). As was shown experimentally,[85] $N_0 \approx 10^5$ segments. It should be noted that no independent determination of the chain segment length was performed, which introduces an error into the results obtained. However, even assuming that the segment is a unit of the polymer chain, this method can be applied to those linear polymers for which MM is much higher than 10^6.

An essential result obtained in a series of studies[85–89] is that formula (6) can be used for assessing MMD of chain segments between entanglements in polymer networks. At $T > T_\mathrm{g} + 100$, intermolecular interaction has almost no effect on the relaxation of sufficiently long chains with the number of segments $N > 10$. Hence the curve of the free induction decay characterises the MMD of chain segments between entanglements. In this case, the integral of the function $G(t)$ can be represented in a linearised form

$$F(t) = \int_0^t t_1G(t_1)\mathrm{d}t_1 \approx -0.03\langle N^2\rangle + \langle N\rangle t\frac{\pi}{2\sqrt{3}}.$$

The coefficients of this equation define the polydispersity index of the chains of the polymer network, γ_n:

$$\gamma_\mathrm{n} = \frac{\overline{M}_\mathrm{nw}}{\overline{M}_\mathrm{nn}} = \frac{\langle N^2\rangle}{\langle N\rangle 2}$$

(the index n indicates that the chains of the polymer network are considered).

Thus, the analysis of the curve of the free induction decay makes it possible to assess MMD of both linear polymers and chain segments between entanglements of the polymer network.

The theoretical conclusions have been confirmed experimentally taking poly(tetrahydrofuran) with isocyanate end groups as an example.[90] In this case, the polymer network resulted from a trimerisation reaction,[91] which would ensure identical MMD for both the initial prepolymer and chain segments between entanglements. Comparison of the GPC data on MMD of poly(tetrahydrofuran) macromolecules with the results of NMR studies on MMD of the chains of the polymer network made it possible to

draw a conclusion that NMR spectroscopy can be effectively used in this case.

Pulse NMR spectroscopy was used for studying the MMD of the chains in different polymer networks depending on the conditions of the synthesis,[88] as well as the evolution of MMD during ageing [92] and at thermal [92,93] and mechanical [94] destruction.

Limitation on the use of NMR spectroscopy for assessing the MMD of the chains of polymer networks with low concentration of nodes is due to the fact that entanglements behave as chemical cross-link points, which leads to the anisotropy of the molecular motion of chain segments. This limitation is similar to that which appeared in the determination of the equilibrium modulus of elasticity of polymer networks: for networks with low node concentration, the number of nodes is equal to the sum of chemical (covalent) cross-link points and topological entanglements.[95–102]

In highly cross-linked polymer networks, the effective dipole-dipole interaction is determined not only by the interaction of protons in the same chain, as is theoretised; an appreciable contribution comes also from the interaction between protons of different chains. This imposes some limitations on the use of NMR spectroscopy. Finally, one should keep in mind that the model network considered here has a simple topology (chains linked by tri- or tetrafunctional cross-link points), whereas the real network contains 'tales', small rings, a sol fraction and other defects responsible for considerable uncertainty of the relaxation time spectra of a polymer.[95,103,104]

VI. Thermomechanical analysis

Usually, thermomechanical curves of polymers are analysed based on the concepts of the relaxation time spectrum and the temperature dependence of relaxation times.[12] It is this approach that has been used for the rationalisation of (i) the relation between the temperature dependence of the extent of the rubbery elasticity plateau and the MM of linear polymers discovered by Kargin and Slonimskii [105] and (ii) such an important relation as the Williams–Landel–Ferry formula.[13] It is the relaxation nature of deformation phenomena that is responsible for the fact that the shape of a thermomechanical curve is 'sensitive' to the polydispersity of a polymer.[106]

Recently,[107] a procedure for solving the direct problem, which implies theoretical determination of the flow point (temperature) of a linear polymer, T_f, under conditions of thermomechanical analysis (TMA) from the structure and MM of the polymer, has been proposed. However, the authors were rather sceptical of the possibility of using TMA for the determination of MMD of polymers.

On the other hand, such a possibility has been demonstrated.[108,109] Physical substantiation [110–113] of the approach used was based on the model of a network of physical links.[41,114]

In its most explicit form, the relaxation modulus (compliance or deformation at a given stress) can be related to the MMD of a polymer using the classical theory of rubbery elasticity of polymer networks and the temperature dependence of the concentration of physical nodes.[110] However, an analysis [112] showed that the concentration of nodes formed by weak intermolecular bonds cannot vary substantially in a rather narrow temperature range between the glass transition temperature and the flow point (for linear polymers) or the temperature at which the equilibrium modulus is attained for covalent polymer networks (the extent of the rubbery elasticity plateau). Much stronger is the temperature dependence of the lifetime of the nodes as well as the dependence of the relaxation of the polymer chain conformations on the temperature–time superposition. Irrespective of the details of the physical pattern of the phenomenon, the kinetic law can be to sufficient accuracy expressed by a step function.[110] Relaxation occurs in a narrow time range near the characteristic relaxation time, which depends on the MM of a polymer or a chain segment between entanglements of the polymer network.

If mechanical properties of a system are considered according to the Kelvin–Voigt model, the following formulae relating the function $\varphi(T)$ containing information on MMD to compliance (deformation) are valid:

for a linear polymer

$$\varphi(T) = \frac{J_T - J_0}{J_T}, \tag{7}$$

for a polymer network

$$\varphi(T) = \frac{J_T - J_0}{J_T} \frac{J_{eq}}{J_{eq} - J_0},$$

where J_T, J_{eq} and J_0 is the compliance at a given temperature, the equilibrium compliance (for a polymer network) and the compliance of a hypothetical polymer with infinite MM, respectively.

The function $\varphi(T)$ is in essence the integral MMD function expressed in terms of the flow point of a chain with a given MM rather than the MM of a polymer fraction:

$$\varphi(T) = \sum_{i=1}^{\infty} w_i \delta_i(t, T),$$

$$\delta_i(t, T) = \delta[t - \lambda_i(T)] = \begin{cases} 0 & \text{for } t < \lambda_i(T) \\ 1 & \text{for } t \geqslant \lambda_i(T), \end{cases}$$

$\lambda_i(T)$ is relaxation time of the chain conformation. The J_0 value characterises that part of the temperature dependence of the modulus of elasticity (compliance) which is unaffected by the MM and MMD of the polymer and serves as a basis for the calculations of the function $\varphi(T)$ [see Eqn (7)].

Schematically, the procedure for the determination of $\varphi(T)$ using the temperature dependence of deformation (compliance) of a linear polymer is shown in Fig. 2. From the rod displacement with respect to the dilatometric curve *1* one can determine the J_0 value (in rod displacement units, this is the value h_0 calculated as the difference between the corresponding points on curves *2* and *1*) and compliance J, which is proportional to h calculated as the difference between the corresponding points on curves *3* and *1*.

The main problem of TMA studies is to determine the relation between the temperature and MM, *i.e.*, to pass from the function $\varphi(T)$ to the integral MMD function $\varphi(M)$. Such a relation can be found after choosing a particular mixing rule. As in many cases considered above, it seems reasonable to assume that the relaxation time of a chain conformation with a given MM is independent

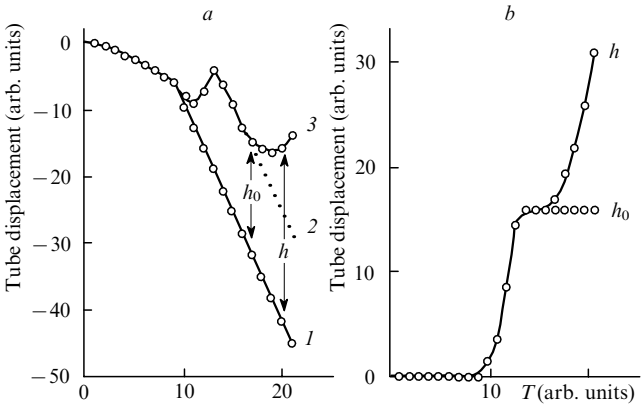


Figure 2. Rod displacement (h) curves obtained in TMA studies. Experimental curves (*a*) and difference between the rod displacement and dilatometric curves (*b*). Dilatometric curve (*1*), hypothetical curve for a polymer with infinite MM (*2*) and the real rod displacement curve (*3*).

of whether it is a monodisperse or a polydisperse polymer. As can be seen, this problem is common to all methods for the determination of the MMD function.

At first glance, if this condition is met, the problem seems to be simple. That is, one needs to find a relation between the extent of the rubbery elasticity plateau,

$$\Delta T = T_f - T_g$$

and MM. However, constructing this dependence faces some difficulties. The first problem is to determine the basic function, $J_0(T)$. This requires studying the temperature dependence of the deformation of model polymer specimens with narrow MMD and high MM in the region of the rubbery elasticity plateau. Here, it is encouraging that such a dependence is rather weak,[110, 113] so to a sufficient accuracy the function $J_0(T)$ can be considered constant.

Yet another problem is associated with the fact that the temperature range corresponding to passage from the rubbery elasticity plateau to the flow of a polymer is rather wide and depends on both the MM and MMD of the polymer. That is why several formulae for calculating the function $\Delta T(M)$ were derived, *e.g.*, the Kargin–Slonimskii formula [105] and a number of similar formulae,[109] *e.g.*:

for polar polymers

$$\log M = 1.6 + \frac{20\Delta T}{200 + \Delta T},$$

for non-polar polymers,

$$\log M = 2.0 + \frac{10\Delta T}{100 + \Delta T}.$$

In a recent study [113] of monodisperse specimens of poly(oxyethylene glycol) with low-molecular masses (1500–12000), a rather sharp transition from the rubbery elasticity plateau to the flow of a polymer was observed and a calibration curve was constructed in the form

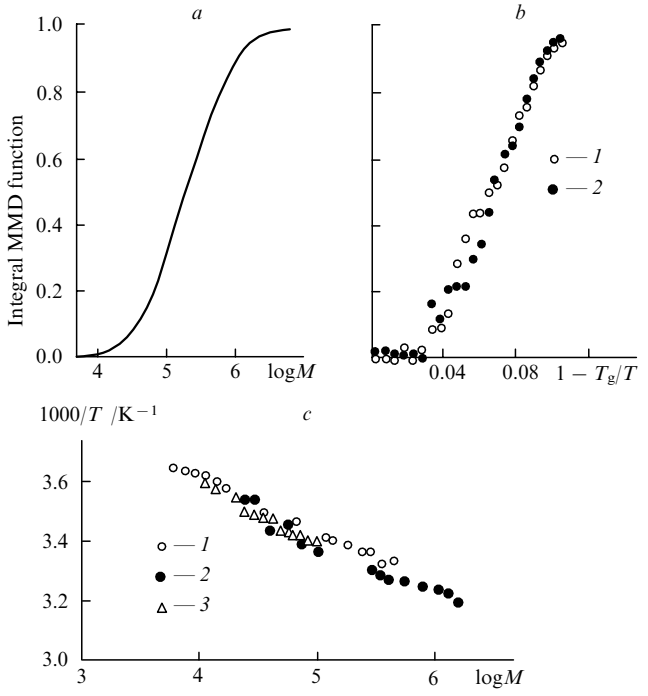


Figure 3. Integral MMD functions (*a*, *b*) and calibration curve (*c*) for amorphous polypropylene.[115]
Obtained from GPC (*a*) and TMA (*b*) studies. Rod load, g: 0.5 (*1*), 2.0 (*2*). 10^{-3} MM: 180 (*a*, *b*); *c*: 52 (*1*), 189 (*2*) and 330 (*3*).

$$\ln M = A + B\left(1 - \frac{T_g}{T}\right). \quad (8)$$

It was found that for a wide array of polymers $A \approx 3$ and $B \approx 17$.

A calibration procedure was proposed,[115] which refers to a polymer with an arbitrary MMD characterised by, *e.g.*, GPC. To this end, the integral curve $\varphi(M)$ is compared with the integral curve $\varphi(T)$ which can be constructed in the $\varphi(T) - T_g/T$ coordinates. By comparing the MM and T values corresponding to the same value of the integral fraction it is possible to find the relation between MM and temperature, *i.e.*, to construct a calibration curve for a wide range of MM using the data for one polymeric specimen.

The integral MMD curve of amorphous polypropylene is shown in Fig. 3 *a* and the dependence $\varphi(T)$ in the coordinates of Eqn (8) is shown in Fig. 3 *b*. The calibration curve (Fig. 3 *c*) was constructed by comparing the MM and T values. As can be seen, the results obtained for three samples of polymers with different MM give a versatile dependence of the type (8).

Thermomechanical analysis can be applied to different types of loading of polymeric specimens, among which penetration and tension are the most popular.[106, 113]

VII. Conclusion

Consideration of 'solution-free' approaches to the determination of MMD of polymers proposed by different authors shows that, in essence, there are no well-developed methods so far. First of all, this is due to the fact that the inverse problem, *viz.*, determination of the relaxation time spectrum and, hence, the MMD of a polymer from the relaxation data, belongs to the so-called ill-posed mathematical problems.[26, 47, 77–79, 116–118] Attempts at solving the problem require some *a priori* statements or experimental establishment of the relaxation time spectrum (or other property, *e.g.*, viscosity or the flow point) with the MM of a polymer. In essence, it is this point to which all the approaches discussed above come. Regularisation methods for solving ill-posed problems,[119] as applied to the problem of determining the relaxation time spectrum or, more particularly, the MMD of a polymer [77–79, 117, 118] are also based on certain assumptions (see, *e.g.*, Ref. 77).

Baumgarten *et al.*[29] derived the relaxation time spectrum (the so-called BSW spectrum) of monodisperse polystyrene specimens without any preliminary postulates by analysing the relaxation data using IRIS software (see Ref. 120). More recently, the BSW spectrum was used for the description of the relaxation properties of polybutadiene.[38, 39] Empirical constants characterising the BSW spectrum, as well as the relaxation time spectrum itself, have no theoretical substantiation and it is unclear to what extent the expansion of the function $G(t)$ in exponents is unique.

It is likely, the lack of a well-founded theory which takes into account mutual effects of polymers with different MM is the most serious obstacle to the development of a relevant relaxation method for the determination of MMD of polymers. Similarly to the Rouse and Doi–Edwards theories, such a theory would help to obtain an exact relation between the MM and the corresponding relaxation time. An empirical relation,

$$\lambda(M) \propto M^{\alpha},$$

where $\alpha \approx 3.4$ casts some doubt since there are strong reasons (see, e.g., Refs 30, 41, 80,121) to believe that $\alpha = 4$.

Thermomechanical analysis seems to be the most promising method. Probably, mutual effects of polymers are more pronounced in isothermal (rheological and frequency) experiments than in the studies on the temperature dependence of deformation parameters. The relaxation time spectrum uniquely characterises both the frequency and temperature dependences of the relaxation properties of a polymer. However, as was shown experimentally, the relation between the flow point and the MM of a polymer is

much more pronounced than the relation between the frequency (time) of this transition and MM.

Further development of 'solution-free' methods will open prospects for the determination of MMD of polymer blends and composite matrices. This may give an impetus to scientific research in this area.

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