CALCULATION OF POLYMER MOLECULAR WEIGHT DISTRIBUTION

1. INTRODUCTION

TA Instruments' Rheology Advantage molecular weight distribution software was developed in collaboration with Prof. Dr. J. Hönerkamp and Dr. C. Friedrich of the University of Freiburg. For a full treatment of the theoretical background, users are referred to their work [1, 2, 3].

The molecules in a simple compound such as water or benzene all have the same molar mass (molecular weight): 18 g mol^{-1} in the case of water, 78 g mol^{-1} in the case of benzene. Most polymers, however, consist of a mixture of molecules of various molecular weights. Although the average molecular weight, M_n, of these molecules can normally be determined relatively easily, this is not usually enough to allow the physical properties of the polymer to be accurately predicted. These properties depend not just on M_n, but in an intimate way on the distribution of molecular weights, *w(M)* or mwd. For example, the shapes of *w(M)* for two polymers may be very different, despite them having the same average molecular weight. The two polymers will then show different physical properties; they will have different softening points, solubilities and processabilities, for example.

It is therefore important, in many situations, that the full distribution of molecular weights of the polymer molecules should be known. Usually size-exclusion chromatography, SEC, is used for its determination. The polymer is dissolved and passed under pressure through a chromatography column. The larger molecules pass through the column relatively quickly, the smaller ones are retained for longer. Some form of detector quantifies the amount of material coming off the column at any time, and *w(M)* is thereby obtained. Useful though this technique is, it does have its disadvantages. For one thing, some important polymers such as polyalkanes and poly(tetrafluoroethylene) can only be dissolved in solvents that are expensive or difficult to handle. For another, SEC is rather insensitive to very high molecular weights species, which greatly affect polymer processability.

For the last few years, polymer rheologists have therefore been working to establish a method of obtaining *w(M)* for polymer melts from rheological measurements. Rheological instrumentation has developed to the point where low cost reliable rheometers are available to most polymer laboratories, and the required measurements can be made without difficulty. A standard technique is low amplitude oscillation, in which the sample is subjected to a small, sinusoidally oscillating mechanical stimulus, and the response is monitored. The complex modulus, *G*(ω)*, which has both magnitude and phase, and depends on the frequency of the applied oscillation, can then be

calculated. $G^*(\omega)$, the in- and out-of-phase components of which, $G'(\omega)$ and $G''(\omega)$ respectively, are usually reported, is the starting point for the derivation of $w(M)$.

The first step in the transformation from $G^*(\omega)$ to $w(M)$ is the computation of the linear relaxation spectrum, $H(\tau)$. This function can be appreciated from its relationship to the linear relaxation modulus, $G(t)$ [4]. If a small strain, that is a deformation, is applied instantaneously to a sample, then there will be a resulting stress; a stress being a force acting over an area. This stress will relax, that is decay over time, and the relaxation modulus is the stress divided by the strain, so it too decreases with time. Relaxation is due to various processes taking place within the sample, principally the motion of the whole or parts of the polymer molecules. Each relaxation process, or "mode" contributes a strength and timescale to the overall relaxation effect, and $H(\tau)$ represents the strength of relaxation at each timescale.

$H(\tau)$ can be calculated using Rheology Advantage Data Analysis module, enhanced continuous relaxation spectrum model (see Rheology Advantage help system). Calculation of $H(\tau)$ from either $G^*(\omega)$ or $G(t)$ is not straightforward, but once this has been done, $H(\tau)$ can be used to generate $w(M)$. There are two main types of mode which contribute to $H(\tau)$ over standard timescales. At short timescales, commensurate with high frequencies, Rouse modes dominate. These are due to the motions of segments of each polymer molecule. At longer timescales, or lower frequencies, motions of whole molecules give rise to reptation modes. The Rouse modes are only weakly dependent on $w(M)$, and they must be subtracted from the spectrum. The part of the spectrum due to reptation modes is then used to provide $w(M)$.

An additional feature of Rheology Advantage is that the operation can be performed in the reverse direction, that $H(\tau)$ can be calculated from $w(M)$. The input data can either be generated from within Rheology Advantage, or copied from elsewhere.

2. THEORY

2.1 Generalised mixing rule

To effect the transformation of $H(\tau)$ into $w(M)$, an approximation formula based on the double reptation rule is used. The basic equation is the (generalized) mixing rule:

$$G_{rept}(t) = G_N \left(\int_{Me}^{\infty} F(M,t)^{1/\beta} w(M) \frac{dM}{M} \right)^{\beta} \tag{1}$$

Where G_N is the plateau modulus, and $M_e \approx M_c/2$ is the entanglement molecular weight (M_c is the critical molecular weight). $F(M, t)$ denotes the relaxation kernel function, which describes the relaxation behaviour of a molecular weight fraction with a molecular weight of M, and β is a parameter which characterizes the mixing behaviour [1] . Several forms of relaxation kernel have appeared in the scientific literature; an evaluation has been made by Maier *et al.* [1]. That used by Rheology Advantage essentially decays exponentially. The subscript *rept* of the stress relaxation $G(t)$ indicates that only the contributions of the reptation dynamics of the whole polymer chain are considered, the dynamics of the chain segments (Rouse modes), which are only weakly dependent on $w(M)$, are not considered.

2.2 Definition of the relaxation spectrum, *H(τ)*

The linear relaxation model provides the following relation between $H(\tau)$ and the relaxation spectrum $G(t)$ [4]:

$$G(t) = \int_{-\infty}^{\infty} H(\tau) \exp(-t/\tau) d \ln \tau \tag{2}$$

where τ is the relaxation time and t is the experimental time. For $G_{rept}(t)$, this definition is modified to:

$$G_{rept}(t) = \int_{-\infty}^{\infty} H_{rept}(\tau) \exp(-t/\tau) d \ln \tau \tag{3}$$

where $H_{rept}(\tau)$ is that part of the relaxation spectrum to which only the reptation dynamics contribute. The contributions from the Rouse modes must therefore be subtracted from $H(\tau)$ before the conversion to $w(M)$ is made.

2.3 Scaling relation between *M* and τ.

The well known scaling relationship:

$$\tau = k_\tau M^\alpha \tag{4}$$

is used to relate the molecular weight *M* in Equation (1) to the relaxation time, τ, in Equation (2). Since values of k_τ are not usually available, the corresponding parameter k_η, defined by the relationship:

$$\eta_0 = k_\eta M^\alpha \tag{5}$$

where η_0 is the zero shear viscosity, and the relationship between k_τ and k_η is given by:

$$k_\tau = k_\eta / G_N \tag{6}$$

2.4 Summary

The combination of Equations 1 and 3 with 4 and 6 gives an analytical approximation for the relationship between *w(M)* and $H_{rept}(\tau)$. Rheology Advantage uses this relationship to generate *w(M)*.

2.5 Input material parameters

The material parameters required for the transformation of $H(\tau)$ to *w(M)* may be entered manually by the user, or in some cases calculated by Rheology Advantage or copied from the polymer library. They are:

M_e entanglement molecular weight: values for many polymers are available in the scientific literature, and for the commonest polymers are provided in the Rheology Advantage polymer library.

k_η prefactor in Equation 5 (denoted K_{eta} in Rheology Advantage): values for many polymers are available in the scientific literature, and for the commonest polymers are provided in the Rheology Advantage polymer library (where the subscript is omitted). Note that k_η is temperature dependent, and the values provided in the polymer library were obtained at the reference temperature quoted. If the data available for *G*(ω)*, and therefore $H(\tau)$, were obtained at a temperature other than that used to determine k_η, then the value of k_η needs to be adjusted accordingly. Rheology Advantage will perform this operation automatically, using either the Arrhenius or Williams Landel Ferry (WLF) models. Further information on these models and their use is provided in the Rheology Advantage help system. Some values for the required parameters are provided in the polymer library.

G_N plateau modulus: Rheology Advantage allows this to be calculated from $H(\tau)$ using:

$$G_N = \int_{\tau_e}^{\infty} \frac{H(\tau)}{\tau} d\tau \qquad (7)$$

where the entanglement relaxation time, τ_e is obtained by insertion of M_e into Equation 4. It may also be calculated from the material properties using the expression $G_N = \rho RT/M_e$ where T is the experimental thermodynamic temperature in kelvin, R is the universal gas constant $(8.314 \text{ J mol}^{-1} \text{ K}^{-1})$ and ρ is the sample density at the experimental temperature.

α exponent in Equation 4 (denoted Alpha in Rheology Advantage): values for many polymers are available in the scientific literature, and for the commonest polymers are provided in the Rheology Advantage polymer library. In most cases $\alpha \approx 3.4$, and it is suggested that this value should be used if no other information is available.

β mixing rule in Equation 1 (denoted Beta in Rheology Advantage): conventional values for β are 1 (the linear mixing rule), or 2 (the quadratic mixing rule). It is suggested that the default value of 2 should be used if no other information is available.

2.5 Elimination of the Rouse modes.

To effect the transformation of the relaxation spectrum $H(\tau)$ to the molecular weight distribution $w(m)$, only the strongly molecular weight dependent contributions from reptation dynamics are considered. The weakly molecular weight dependent contributions from Rouse modes must be eliminated, i.e:

$$H_{rept}(\tau) = H(\tau) - H_{Rouse}(\tau) \qquad (8)$$

Rheology Advantage can do this automatically. For that purpose the Rouse part of the spectrum is modeled by a simple power law:

$$H_{Rouse}(\tau) \propto \left(\frac{\tau}{\tau_e}\right)^s \exp[-(\tau/\tau_R)^{s_c}] \qquad (9)$$

where τ_e is the entanglement relaxation time, related to M_e through Equation 4. The input parameters are therefore:

Power law exponent: s in Equation 9. This is given by Rouse theory as −0.5 [5] and Zimm theory as −0.67 [6]. If no other information is available it is suggested that the default value of −0.5 is used.

Rouse time: τ_R in Equation 9. An expression for this may be derived [7]:

$$\tau_R = \frac{k_\eta}{G_N}(2M_e)^{\alpha-2}(M_n)^2 \tag{10}$$

Rheology Advantage uses this expression to obtain value for τ_R by iteration, the initial value for the iteration being obtained M_n generated from $H(\tau)$ without elimination of the Rouse modes.

Cut-off parameter: s_c in Equation 9. This governs the smoothness of the exponential cut-off at $\tau = \tau_R$. A sharp cut-off would be an oversimplification for polydisperse samples, for which since the Rouse contribution to $H(\tau)$ does not vanish abruptly at $\tau = \tau_R$. The larger the value of s_c, the sharper the cut-off, the limiting case of $s_c = \infty$ giving an absolutely sharp cut-off, corresponding to a perfectly monodisperse sample. For a wide range of real polymers, a value of between 1 and 2 has been found to be optimal. If no other information is available, it is suggested that the default value of 1.5 is used.

The effect of elimination of the Rouse modes can be checked by generating *w(M)* with and without elimination (see below).

2.6 Calculation of the moments of molecular weight

Rheology Advantage will calculate the first four moments of molecular weight from *w(M)*, i.e. the number average, M_n, weight average, M_w, z-average, M_z, and z + 1 average, M_{z+1}, and the polydispersity. For definitions of each of these, see standard polymer texts [8].

2.7 Calculation of *G(t)* from *w(M).*

The calculation described above can be performed in the reverse direction to provide *G(t)* from *w(M)*. This operation is mathematically more straightforward than the original operation; this allows the use of alternative kernel functions. Those available in Rheology Advantage are:

(i) *The Tuminello kernel:*

$$F(M, t) = 1 \text{ if } \tau < \tau_0(M) \tag{11}$$

Where τ_0 is the terminal relaxation time,

$$\text{else} \qquad F(M, t) = 0 \tag{12}$$

(ii) *The Single-exponential kernel:*

$$F(M, t) = exp(-t/\tau_0) \tag{13}$$

(iii) *The Doi kernel:*

$$F(M,t) = \frac{8}{\pi^2} \sum_{n \in odd}^{\infty} \frac{\exp[-tn^2 / \tau_0(M)]}{n^2}$$

(14)

(iv) *The Baumgaertal, Schausberger and Winter(BSW) kernel*

and (v) *The des Cloizeaux kernel*

For descriptions of these last two functions, see reference [1]. Note that the BSW kernel requires the steady state compliance, J_{ss}, to be known.

3 OPERATION

The operation to generate *w(M)* for a typical polymer is described here. It is assumed that the user is familiar with the standard operation of TA Instruments Rheology Advantage software. The example data used here were obtained on a polystyrene sample with a nominal weight average molecular weight, M_w, of about 250 000, at 160°C.

Step 1 Open or generate a continuous relaxation spectrum file using Rheology Advantage Data Analysis module (for help in doing this, see the Rheology Advantage Data Analysis help system). This file will have a –cspx termination. The spectrum for the example polymer is shown below.
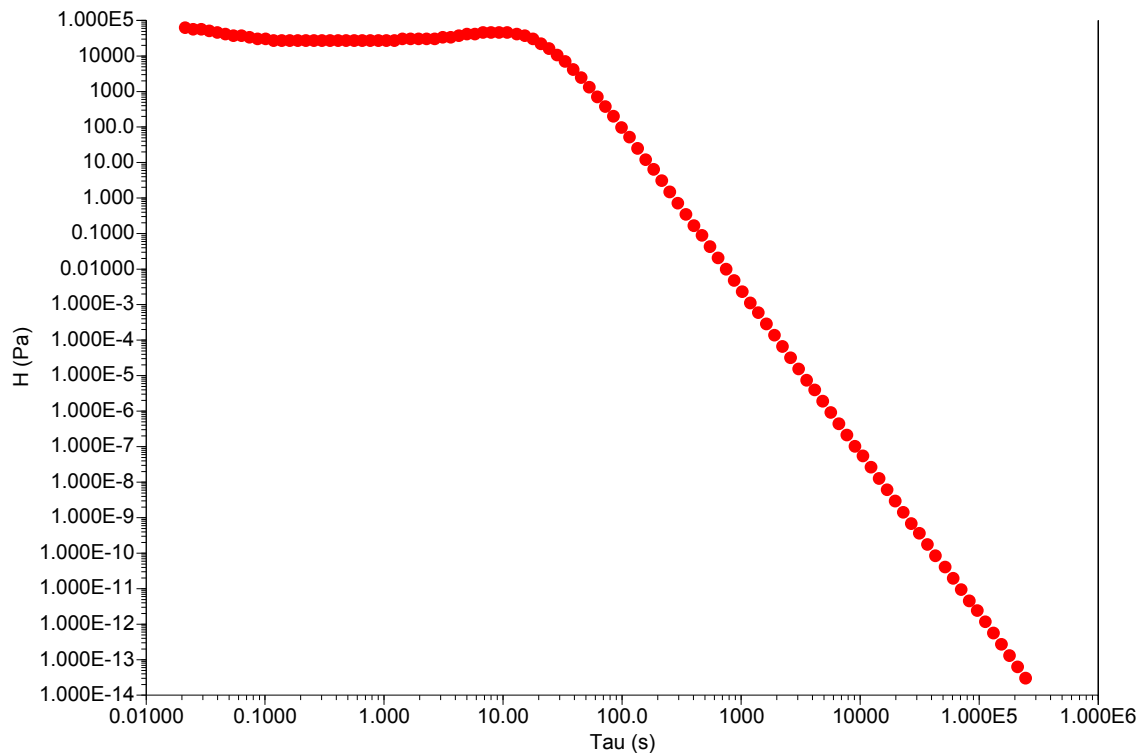
Step 2 Highlight the spectrum filename using the cursor, then on the **File** menu point to **Transformations** and click **Molecular weight distribution…**. This box will appear:

Enter the required values for each parameter. Values for common polymers are given in Rheology Advantage polymer library, to view which click **Polymer library**. The box below will appear (note that the values shown were taken from the references quoted, and may differ from those given by other sources). Values can be copied directly into the **Create molecular weight distribution file** box by clicking **Copy values**. To view the automatically calculated Rouse time, click the **Auto calc.** arrowed button. When the required values have been entered, click **OK**.

Polymer Library

Polymer	k (Pa.s)	alpha	Tref (K)	c1	c2 (K)	Ea (kJ/m...	Me (g/mol)
Polyethylene (HDPE)	3.400E-15	3.600	463.0			26.70	1250
Polyethylene (HDPE)	5.010E-14	3.420	433.0				1900
Polyethylene (LLDPE)	9.450E-16	3.670	493.0			30.00	1900
Polypropylene	4.100E-17	3.770	458.0			44.00	3500
Polypropylene (atactic)	2.840E-16	3.590	463.0			42.00	6520
Polypropylene (isotactic)	5.320E-17	3.600	463.0			42.00	6520
Polyisobutylene	4.120E-15	3.430	423.0	5.300	325.0	48.00	9400
Polystyrene	1.650E-12	3.380	423.0	6.350	100.0	59.00	17400
Poly(vinyl chloride)	9.020E-12	3.400	463.0	2.600	151.0	85.00	3100
Poly(vinyl acetate)	2.000E-15	3.400	473.0	3.990	226.0	67.00	12500
Poly(vinylidene fluoride)	5.560E-14	3.400	473.0				22700
Poly(tetrafluoro ethyle...	1.790E-13	2.940	370.0			63.00	5490
Poly(methyl methacryl...	4.000E-14	3.400	493.0	22.30	122.0	65.00	5000
Polybutadiene	3.790E-14	3.400	373.0	3.150	233.0	26.00	3000
Polyisoprene	9.470E-15	3.400	373.0	3.970	227.0	23.00	5000
Poly(ethylene oxide)	1.800E-13	3.400	343.0			27.00	1700
Poly(ethylene terepht...	1.800E-13	3.400	543.0			45.00	3000
Polyamide 6	5.990E-14	3.400	543.0			36.00	18000
Polyamide 12	3.500E-13	3.550	473.0				1500
Polycarbonate	5.990E-13	3.400	573.0			85.00	1500
Poly(dimethyl siloxane)	1.790E-16	3.400	393.0	1.350	312.0	15.00	15000
Poly(e-caprolactone)	2.000E-12	3.400	413.0			40.00	3000

Add Entry   Remove Entry   Restore Defaults   Copy values   Close

Step 3 When **OK** is clicked, a new file with termination –cspx-mwd will be created. This will appear in the file list. To display the data graphically, on the **View** menu click **Send data to graph**. The graph for the example polymer is shown below. Closed symbols are with elimination of the Rouse modes, open symbols are without.
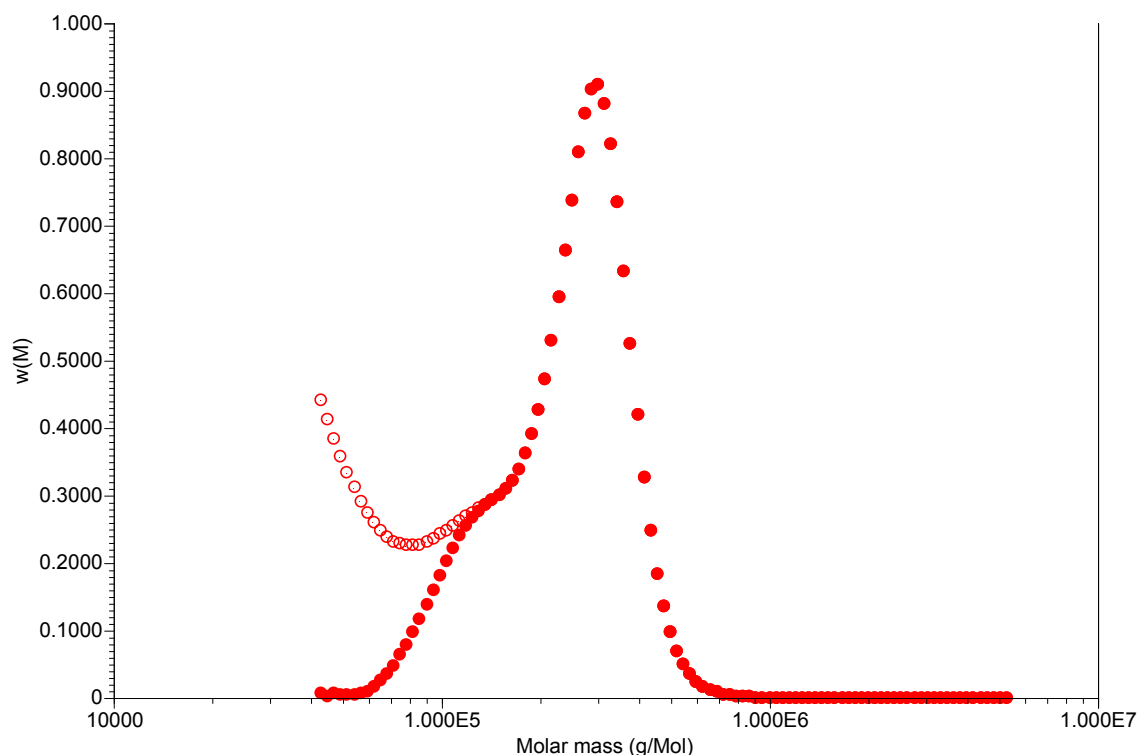
Note that the parameters used in the calculation of *w(M)* and *H(τ)* are stored with the file. To view these, on the **View** menu click **Notes**. Parameters are shown in the **Experiment notes** box. To scroll through the full list use the up and down arrow keys on the computer keyboard. The list for the above example is shown below. The first analysed file is that used to generate *w(M)*, the second is that used for *H(τ)*.

Analysed file: mwdexample-cspx
Alpha: 3.380
Me: 17400
Keta: 1.650E-12
Tref: 423.0
Shift model: Arrhenius
Ea: 59.00
Experiment temperature: 433.2
Shifted keta: 1.114E-12
Plateau modulus: Calculated from spectrum
Plateau modulus value: 2.344E5
Density: 1.000E-3
Beta: 2.000
Subtract Rouse modes: yes
Power law exponent: -0.5000
Cutoff parameter: 1.500
Auto calculate Rouse time: yes
Rouse time: 0.4036

Analysed file: mwdexample-o
Time range: Reciprocal plus e^(PI / 2)
Minimum time: 0.02079
Maximum time: 2.405E5

Spectrum points per decade: 15
Calculate Ge: no
Maximum time: 2.405E5
Spectrum points per decade: 15
Calculate Ge: no

Step 4: To view the data in tabular form, the calculated moments of molecular weight, and the polydispersity, highlight the molecular weight distribution filename and on the **View** menu click **Table**. For the example used here, M_n = 205 200 g mol^{-1}, M_w = 252 500 g mol^{-1}, M_z = 294 700 g mol^{-1} and M_{z+1} = 332 900 g mol^{-1}. The polydispersity = 1.231.

Step 5: To calculate *G(t)* from *H(τ)*, highlight the molecular weight distribution filename, then on the **File** menu point to **Transformations** then click **Stress relaxation…** This box will appear:

Enter the required values for the material properties, plateau modulus and mixing rule, and select the required kernel function. Note that **Target Data** refers to the stress relaxation file that is to be generated. The graph for the example polymer is shown below.
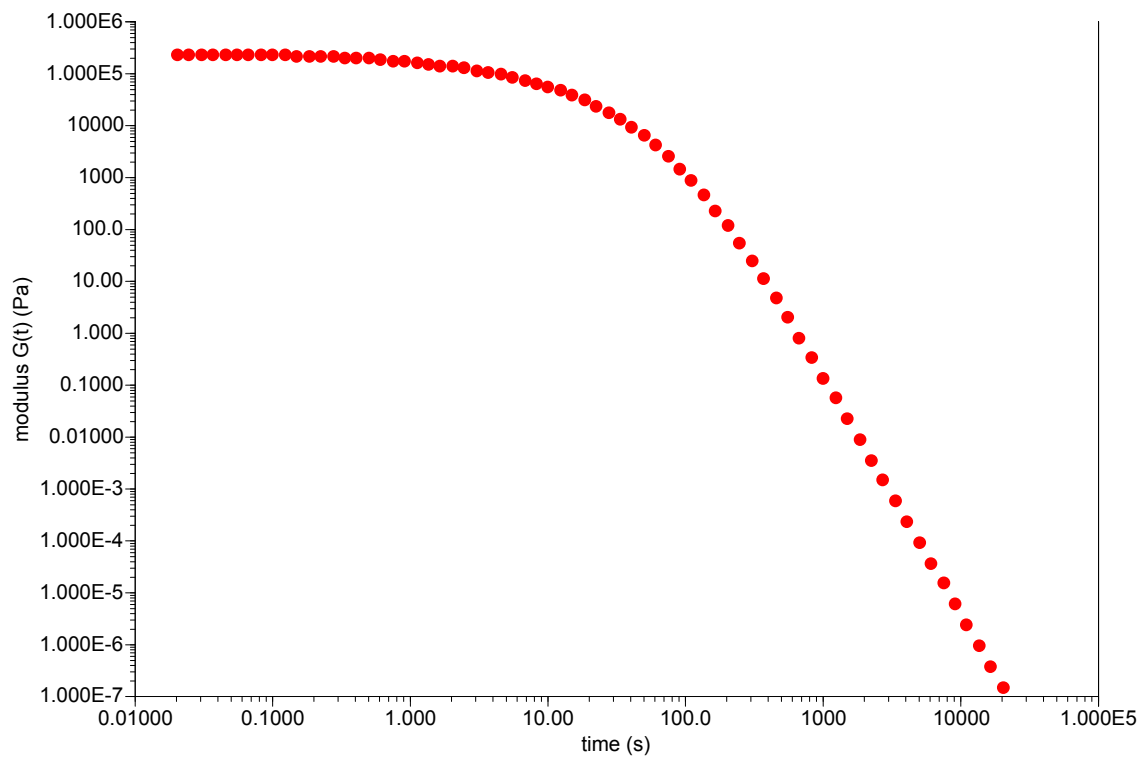
4 LIMITATIONS

4.1 Sample types

The theory described above was developed for amorphous, linear, homopolymers. The effects of crystallinity or long chain branching were not considered. It was assumed that the polymer was free from diluents, fillers, plasticisers, significant levels of residual initiator, and so on. The presence of any of these may substantially affect the results obtained. It is not known whether theory is applicable to copolymers or mixtures of polymers of different types.

4.2 Minimum molecular weight

To arrive at the molecular weight distribution, the theory makes use of the observation that polymer molecular motions are retarded by entanglements between molecules. These only occur when the molecular weight of the species involved exceeds the entanglement molecular weight, M_e, which depends on the polymer type. Species with molecular weights lower than M_e therefore cannot be detected. This may affect both the form of $w(M)$, and the values calculated for the moments of molecular weight (in practice, this restriction is not important for typical industrial polymers, in which most species have molecular weights considerably higher than M_e)

4.3 Molecular weight range

For the full molecular weight range to be accessible, the relaxation spectrum must run from the terminal region ($H(\tau) = 0$) through the transition region ($H(\tau)$ contains only Rouse and shorter timescale relaxation modes). Visual inspection will usually show whether these limits have been achieved. The relationship between relaxation time and molecular weight is given by Equation 4. It can be seen from this equation, that the molecular weight range depends on the range of τ in the relaxation spectrum, and the value of α. Specifically, if the ratio of the highest value of τ to the lowest value is R, then the ratio of the highest value of M to the lowest value of M will be $R^{1/\alpha}$, i.e. the α root of R. In the example presented above, the maximum value of τ is 240 500 s, and the minimum value is 0.02079 s, a ratio of 11 568 062 : 1. The value of α was 3.38, and the ratio of highest to lowest value of M is therefore $11\,568\,062^{1/3.38}$: 1 = 122.9 : 1 (the actual values were 5 215 000 g mol^{-1} and 42 410 g mol^{-1} respectively). Note that the relationship between M and τ given by Equation 4 also indicates the range of τ required for a given range of M. Since the value of α is usually $\approx$ 3.4, each decade of M will require approximately 3.5 decades of τ.

4.4 Data quality

The quality of the molecular weight distribution profile produced will depend strongly on the quality of the relaxation spectrum used to generate it. If the spectrum contains spurious peaks, these will be reflected in the $w(M)$ data. Such peaks can sometimes be removed by using the Rheology Advantage smoothing function.

REFERENCES

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