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Size exclusion chromatography of step-growth polymers with cyclic species: theoretical model and data analysis methods

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Abstract

The measurement of the molecular weight averages and the molecular weight distribution (MWD) of many step-growth polymers is complicated due to the presence of cyclic oligomers formed during polymerization. If size exclusion chromatography (SEC) is used to determine the MWD, the cyclic oligomers are generally only partly resolved from the linear polymer, and hence distort the measured linear MWD. Further, the cyclic oligomers require a different calibration curve from the linear species and hence, in general, their molecular weights are not accurately measured. In order to clarify the effect of cyclic species on the measured MWD, a model of the SEC separation of step-growth polymers with cyclic species was developed. In this article, this model is described and used to illustrate aspects of the characterization of these polymers using both conventional SEC and multi-detector SEC. The results from the model are used to develop methods for estimating the MWD of the linear polymer and to determine the weight fraction of cyclic species. The results of the model are compared with experimental data for nylon 6, nylon 6,6 and poly(ethylene terephthalate). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Size exclusion chromatography; Molecular weight average; Cyclic oligomers

1. Introduction

Many step-growth polymers of industrial importance, such as polyesters and polyamides, contain significant fractions of cyclic oligomers at equilibrium. The cyclic molecules form when one end of the polymer molecule is able to react with the other end. In this case, the polymer molecular weight distribution (MWD) is the sum of the distribution of linear species and that of cyclic species. The linear species still retain a most probable distribution, but the cyclic species have a very different distribution. The proportion of cyclic to linear molecules at a given molecular weight depends on the relative probability of the cyclic reaction of the ends, compared to the reaction of one or the other of the ends with another molecule. This is given by the molar cyclization equilibrium constant K_x. The first theoretical treatment of ring formation in polymers was given by Jacobson and Stockmayer [1,2] and applies to cyclic oligomers formed from linear species of sufficient length and flexibility to follow Gaussian statistics. The theory predicts that the number fraction distribution of cyclic polymers decreases rapidly with increasing molecular weight. This is a result of the decreased probability of one end of a given chain reacting with the other end, rather than with another molecule, as the chain length increases. The decrease in number fraction with increasing molecular weight is much more rapid than the corresponding decrease in the number-fraction of linear polymers formed, and the cyclic polymers are limited to relatively low molecular weights. When the weight-fraction distribution is considered, the cyclic polymer distribution still decreases rapidly and monotonically, in contrast to the linear polymer MWD which has the familiar broad single peak distribution. The theory was refined by Flory and coworkers [3–7] using rotational isomeric models to calculate the fraction of the possible conformations which could cyclize, and then taking into account the directional requirements of chain ends involved in cyclization.

The presence of both linear and cyclic species causes a number of difficulties in characterizing the MWD by size exclusion chromatography (SEC). Firstly, the linear and cyclic distributions overlap in molecular weight range and cannot be completely separated by SEC. Only the MWD of the mixture (or some fraction of the joint distribution) can be determined. Secondly, the cyclic polymers have a smaller average size than the corresponding linear polymer with the same degree of polymerization. As a result, the SEC

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calibration curve relating the molecular weight to the elution volume for the cyclic species is different from the calibration curve for the linear species. The true calibration curve would consist of a weighted average of the linear and cyclic calibration curves depending on the fraction of each species present at a given elution volume. In practice, such an approach is not feasible. The smaller size of the cyclic species does, however, work to the advantage of the separation of cyclic and linear species. The cyclic species elute at higher elution volumes than they would if they had the same size, for the same degree of polymerization, as the linear species, and hence are partially separated from the linear MWD.

If a molecular-weight-sensitive detector, such as a light scattering photometer or a viscometer, is used in conjunction with the chromatograph, the molecular weight of the cyclic as well as the linear species can be measured accurately (assuming that the detectors are sufficiently sensitive, and, in the case of the viscometer, the universal calibration holds for the cyclic species), but the imperfect resolution of the two species still cause problems.

In this article, the results of a model of the SEC separation of polymers containing cyclic species are presented and compared with the experimental SEC data. Theoretical MWDs are first calculated, and then the response of the chromatographic detectors to these distribution is calculated. The results are used to elucidate the significance of the errors in molecular weight determination measured by conventional single-detector SEC and SEC-light scattering. A method for estimating the MWDs of both the cyclic and the linear species, and the weight fraction of cyclic oligomers, is presented. This article is part of a series that uses computer simulation of chromatograms to study issues related to SEC characterization of polymers, and builds upon previously presented results [8–12].

2. Theory

2.1. Theoretical description of polymer molecular weight polymer distribution with cyclics

2.1.1. Cyclic molecular weight distribution

The thermodynamic equilibria between cyclic and linear molecules in a polymeric system may be represented by

$$M_y \Leftrightarrow M_x + M_{y-x}, \tag{1}$$

where M_y and M_{y-x} represent linear molecules of degree of polymerization y and $(y - x)$, and M_x represents the cyclic molecule. The population of cyclics can be expressed in terms of the molar cyclization equilibrium constant K_x for the individual x-meric cyclic molecules

$$K_x = \frac{[M_{y-x}][M_x]}{[M_y]}. \tag{2}$$

For a most probable distribution, the ratio of concentration of y-mers to $(y-x)$-mers is p^x, where p is the extent of reaction, i.e. the fraction of all functional groups that have condensed. In a distribution containing cyclic species, the extent of reaction, p, is replaced by p', a revised extent of reaction, which is corrected for the fact that some of the monomer has reacted into cyclics rather than linear polymer, defined by

$$p' = 1 - \left(\frac{1-p}{1-W_{\text{cyclics}}}\right), \tag{3}$$

where W_{cyclics} is the weight fraction of rings in the system. Eq. (2) can then be rewritten as

$$K_x = \frac{[M_x]}{p'^x}. \tag{4}$$

The theory of Jacobson and Stockmayer determines the concentration of cyclic species from the calculated probability that the end-to-end vector of a chain of x monomeric units is zero. The chains are assumed to be long enough, and of sufficient flexibility to obey Gaussian statistics. The molar cyclization constant is given by

$$K_x = \left(\frac{3}{2\pi\langle r_x^2\rangle}\right)^{3/2} \frac{1}{N_A \sigma_{Rx}}, \tag{5}$$

where $\langle r_x^2\rangle$ is the mean-square end-to-end distance of the chain and σ_{Rx} is a symmetry number corresponding to the number of skeletal bonds per monomer in the ring that can open in the reverse reaction in Eq. (1) multiplied by the degree of polymerization. For polymers made from a single bifunctional monomer (A–B) $\sigma_{Rx} = x$, for a copolymer of two bifunctional monomers (A–A and B–B) $\sigma_{Rx} = 2x$.

The molar concentration of cyclic species at a given degree of polymerization, thus, depends on the mean-square end-to-end distance which, in a Gaussian chain, depends on the effective bond lengths. Substituting Eq. (5) into Eq. (4) gives

$$[M]_x = \left(\frac{3}{2\pi\langle r_x^2\rangle}\right)^{3/2} \frac{(p')^x}{N_A \sigma_{Rx}}. \tag{6}$$

Rewriting in terms of the experimentally observable ratio of the mean-square radius to the molecular weight $\langle r^2\rangle/M$, which is molecular weight independent, gives

$$[M_x] = \left(\frac{3}{2\pi}\frac{M_x}{\langle r_x^2\rangle}\right)^{3/2} \frac{(p')^x}{N_A \sigma_{Rx} M_x^{3/2}}. \tag{7}$$

The weight fraction of cyclic species at degree of polymerization x formed at concentration c, for the case where $\sigma_{Rx} = x$, is then given by

$$W(x)_{\text{cyclics}} = \left(\frac{3}{2\pi m_0}\frac{M_x}{\langle r_x^2\rangle}\right)^{3/2} \frac{m_0 (p')^x}{c N_A x^{3/2}}, \tag{8}$$

where m_0 is the molecular weight of the monomeric unit. From Eq. (8) it can be seen that the Stockmayer–Jacobson model predicts that the weight concentration of cyclic species decreases with increasing molecular weight to the

−3/2 power. In addition, the weight fraction of the cyclic species at a given molecular weight and a given extent of reaction can be calculated from the unperturbed dimensions of the linear chain.

2.1.2. Linear molecular weight distribution

The linear MWD is still given by the most probable distribution. The only difference is that the sum of the weight, or number, fractions of the linear species is less than one because a fraction of the chains are in the cyclic distribution. The weight fraction of linear chains can thus be written as

$$W(x)_{\text{linear}} = (1 - W_{\text{cyclics}})(1 - p')^2 x p'^{(x-1)}. \quad (9)$$

The weight fraction distribution of the linear chains is a broad distribution with a peak at the number-average molecular weight, whereas the weight fraction distribution of the cyclic chains decreases exponentially with increasing molecular weight from a peak at the lowest degree of polymerization where cyclization is possible.

3. Methodology

The SEC data are calculated using the following procedure. First, the MWDs are calculated from Eqs. (8) and (9) depending upon the extent of polymerization and the unperturbed dimensions. The elution volume of each species is then determined. The elution profile of each species is broadened by a Gaussian band spreading function, then the detector responses are calculated at each elution volume depending on the concentration, average molecular weight, and average intrinsic viscosity of each elution volume increment.

The universal calibration curve relating the molecular weight, M, and intrinsic viscosity, $[\eta]$, to elution volume, V, is of the form

$$M(V)[\eta](V) = U_1 e^{-U_2 V}, \quad (10)$$

where in this study $\log_e(U_1) = 28$ and $U_2 = 1.0$, which approximates to a calibration curve for two 30 cm × 8 mm inner diameter columns. Thus, the elution volume of a polymer molecule of a given molecular weight and intrinsic viscosity is given by

$$V = \frac{-1}{U_2} \log_e\left(\frac{M[\eta]}{U_1}\right). \quad (11)$$

The intrinsic viscosity at each molecular weight is calculated from the unperturbed dimensions of the polymer chain and the expansion coefficient α_η using the two-parameter theory [13,14]

$$[\eta] = \alpha_\eta^3 \Phi \left(\frac{\langle r^2 \rangle}{M}\right)^{3/2} M^{1/2}, \quad (12)$$

where Φ is the Flory viscosity constant taken as 2.36×10^{23}. The expansion coefficient is defined as the ratio of the intrinsic viscosity under given conditions to the intrinsic viscosity in the unperturbed state

$$\alpha_\eta^3 = \frac{[\eta]}{[\eta]_0} \quad (13)$$

and can be expressed in terms of the excluded volume parameter z as [15]

$$\alpha_\eta^3 = (1 + 1.9z)^{3/5}, \quad (14)$$

where the excluded volume parameter is defined in terms of the interaction parameter B as

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \left(\frac{\langle r^2 \rangle}{M}\right)^{-3/2} B M^{1/2}. \quad (15)$$

A value of $B = 1 \times 10^{-18}$ is used for all the data shown in this article. Literature values of $\langle r^2 \rangle / M$ for polyamides were used to generate the model data. Eq. (12) can also be described by the empirical Mark–Houwink–Sakurada (MHS) equation

$$[\eta] = K M^a, \quad (16)$$

where K and M are constants for a given polymer-solvent solution at fixed temperature. The value of B considered in Eq. (15) gives a value of 0.70 for the exponent a in Eq. (16) at degrees of polymerization greater than about 10.

For the cyclic species the intrinsic viscosity, and thus, the hydrodynamic volume, is taken to be 3/5 of the value for the corresponding linear polymer [15]. Universal calibration is considered to apply to the cyclic species as well as the linear species Eq. (11). The value of α_η is assumed to be equal for the linear and cyclic species with the same degree of polymerization [16–18].

The elution volume data are divided in steps of 1/60 ml for convenience. This corresponds to a data point every second at a flowrate of 1 ml/min. As a result, more than one polymer species may be present at a given elution volume, especially at higher molecular weights where the resolution is worse. This results in a distribution of molecular weights at a given elution volume, and this polydispersity is calculated for each data point.

The MWD described by Eqs. (8) and (9) is a discrete distribution corresponding to perfect resolution of each n-mer. In SEC the individual polymeric species are not resolved due to band broadening, and typically a continuous MWD is measured. To model this, Gaussian band broadening is added to the discrete MWD. The concentration profile of each molecular species at elution volume point, V_i, with concentration, c_i, is broadened by a Gaussian function with standard deviation, σ, so that it has a shape given by

$$c(V) = \frac{c_i}{\sigma\sqrt{2\pi}} e^{-(V - V_i)^2 / 2\sigma^2}. \quad (17)$$

The sum of these Gaussian profiles for each species in the MWD forms the concentration profile of the chromatogram. Every elution volume now contains a distribution of

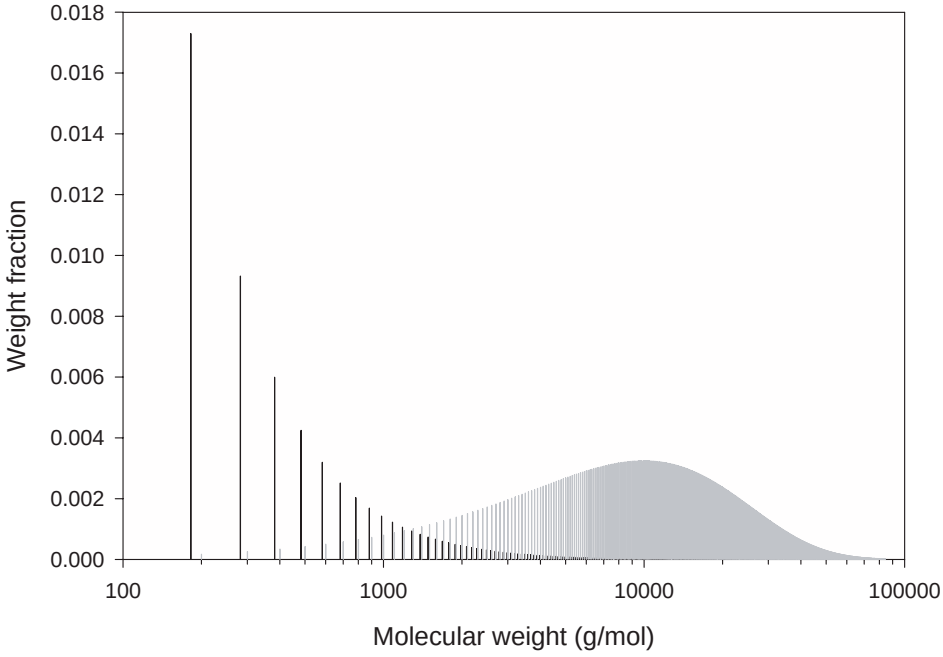

Fig. 1. Weight-fraction MWD for a step-growth polymer MWD including cyclic species (A–B type monomer) showing linear (gray lines) and cyclic (black lines) distributions.

molecular weights and the number, weight and *z*-averages at each volume are calculated. A value of $\sigma = 0.2$ ml is used for the band broadening which is typical for a set of two high resolution mixed bed SEC columns. The slight molecular weight dependence of σ is considered to be negligible for the purposes of the model.

The zero-angle light scattering intensity at each elution volume, $I(V)$, is calculated from

$$I_{\theta=0}(V) = M_w(V)\, c(V). \tag{18}$$

The concentration dependence of $I_{\theta=0}/c$, and thus the effect of the second virial coefficient, is considered negligible for the purposes of this model. Similarly, the molecular weight dependence of the specific refractive index increment d*n*/d*c* (which affects the scattered light intensity), and any possible difference in d*n*/d*c* between linear and cyclic species, is not considered [19]. The specific viscosity, η_{sp}, as a function of volume is calculated from.

$$\eta_{sp}(V) = [\eta](V)\, c(V), \tag{19}$$

where the intrinsic viscosity $[\eta]$ is calculated from Eq. (12). The effect of the Huggins constant, and the concentration dependence of the reduced viscosity, η_{sp}/c, is considered negligible for the purposes of this model.

4. Experimental

The size exclusion chromatograph consisted of an Alliance pump (Waters Associates, Milford, MA), the columns used were two Shodex HFIP-806 M linear columns with 10 m particles of crosslinked polystyrene-divinylbenzene packing (Showa Denko Corp., available from Waters Associates) and the mobile phase was hexafluoroisopropanol (E.I. du Pont de Nemours, Wilmington, DE) with 10 mM sodium trifluoroacetate (Aldrich Chemical Company, Milwaukee, WI) at 35°C. The detectors were a Model 410 refractometer (Waters Associates), Viscotek T-60 A combination right-angle light scattering and viscosity detector (Viscotek Corporation, Houston, TX). Data were collected and analyzed using TriSEC software version 3.0 (Viscotek Corporation). The nylon 6, nylon 6,6 and poly(ethylene) terephthalate samples were commercial samples manufactured by DuPont.

5. Results and discussion

5.1. Theoretical chromatograms

A typical calculated weight-fraction MWD based on the theoretical model containing both linear and cyclic species is shown in Fig. 1. The extent of reaction for this MWD is $p = 0.99$, and the monomer molecular weight is 100 g/mol. The cyclic species have molecular weights of $(100n-18)$, where n is the degree of polymerization. The different shapes of the cyclic and linear distributions can be clearly seen. The most abundant species, both by weight and by number-fraction, are the lowest molecular weight cyclic species, however, the distribution rapidly falls off with increasing molecular weight. The weight-fraction of cyclics is negligible above 5000 g/mol. The cyclic species make up 11.4% of the total distribution by weight. The linear MWD has the familiar broad shape of the Flory distribution with a

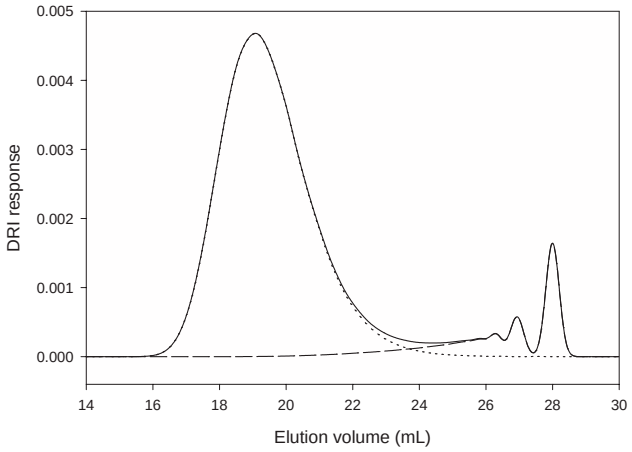

Fig. 2. Refractometer chromatogram for a step-growth polymer MWD including cyclic species (A–B type monomer). The chromatograms for the separate linear (···) and cyclic (– – –) MWDs are also shown.

peak value at the number-average molecular weight of about 20 000 g/mol. The molecular weights range from the monomer up to about 200 000 g/mol.

Fig. 2 shows the predicted SEC concentration chromatogram for the MWD shown in Fig. 1. The value of the unperturbed dimensions used to calculate the hydrodynamic radius is $(\langle r^2\rangle/M)^{1/2} = 0.087$ nm, which is typical for polyamides [20]. This value is used to calculate the number of cyclic species, as well as the intrinsic viscosity, and thus the elution volume, of both the cyclic and the linear polymers. The symmetry number σ_{Rx} is 1*x* corresponding to cyclic species made up from a single A–B type monomer such as nylon 6. The band broadening is $\sigma = 0.2$ ml. The dashed lines in Fig. 2 indicate the separate profiles of the linear and the cyclic species. The cyclic species elute later than the linear species due to their low molecular weight and also due to their smaller relative size. The cyclic monomer can be seen as a distinct resolved peak at 28 ml and the cyclic dimer, tri-mer and tetra-mer as partially resolved peaks. However, the two distributions are not separated completely and overlap over a wide molecular weight range. The species eluting before about 22 ml are almost entirely linear, and those eluting after 25 ml are almost all cyclic. In the region 22–25 ml, a mixture of cyclic and linear species elute. Close to the point where the two distributions cross, there is a minimum in the concentration detector response at around 24.4 ml. This is the first minimum after the main linear polymer peak.

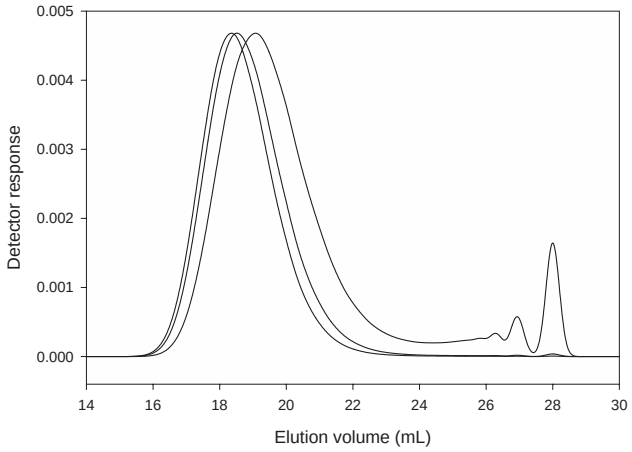

Fig. 3. Chromatograms from the light scattering and viscosity detectors, as well as the refractometer for the MWD in Fig. 1. From left to right the chromatogram peaks are LS, viscometer, DRI. The light scattering and viscosity detector chromatograms are normalized to the same height as the refractometer chromatogram. There is no volume difference between the three detectors in the model.

Fig. 3 shows the signals from the light scattering detector and the viscometer as well as the concentration detector for the same distribution. The cyclic species are barely detected by the other two detectors because of their low molecular weight, and correspondingly low intrinsic viscosity.

The calculated weight-average molecular weight as a function of elution volume is shown in Fig. 4. This is the weight-average molecular weight that would be measured at each elution volume by SEC-LS. The change in the molecular weight curve from linear polymer to cyclics can be seen as a shift occurring between 23 and 24 ml corresponding to molecular weights of 1000–2000 g/mol. The molecular weight curve also shows that the final peak is pure cyclic monomer with a molecular weight of 100 g/mol.

Fig. 5 shows the MHS plot of calculated intrinsic viscosity against calculated weight-average molecular weight. This is the plot that would be obtained when the intrinsic viscosity is measured directly by the viscometer and the molecular weight by the light scattering detector. The change from predominantly linear to predominantly cyclic species can be clearly seen as a shift in the MHS curve, which occurs between molecular weights of 1000 and 2000 g/mol.

There is also a slight change in the slope of the MHS curve. Above 3000 g/mol the data gives a MHS exponent of 0.70, Eq. (16), and below 1000 g/mol the slope is 0.59. However, this is due to the increased excluded volume

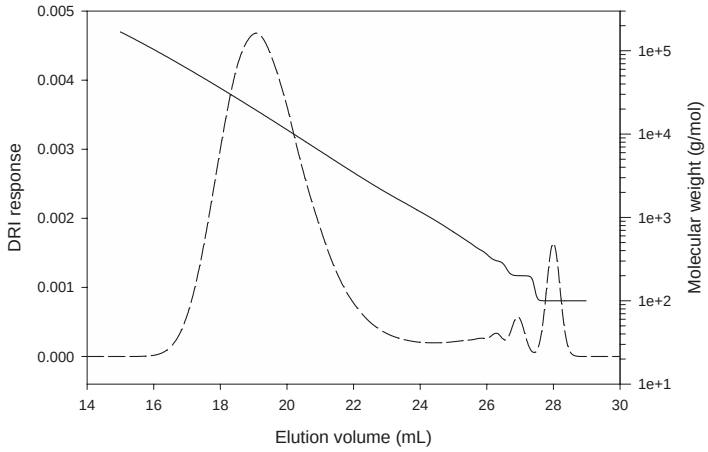

Fig. 4. The true weight-average molecular weight as a function of elution volume for the MWD from Fig. 1. The refractometer chromatogram (– – –) is also shown.

interaction at higher molecular weights, modeled by the approximation in Eq. (14), rather than the difference between cyclic and linear species. The model of intrinsic viscosity used gives the same MHS exponent for the cyclic and the linear species of the same molecular weight, however the prefactor K is shifted to a lower value.

The concentration detector chromatogram for the same MWD, but formed from two co-monomers is shown in Fig. 6. This corresponds to a symmetry number σ_{Rx} of $2x$. In the case of the polymerization of two bifunctional monomers of the form A–A and B–B, cyclic species can only form for even numbers of monomers. The unperturbed dimensions and the cyclization coefficient are the same as in Fig. 2. The cyclic species make up 5.7% of the distribution by weight. The di-mer (27 ml), tetra-mer and hexa-mer are partially resolved. However, the prominent cyclic monomer peak at 28 ml is no longer allowed, and the total weight fraction of cyclic species is much smaller. As in Fig. 2, there is a minimum in the chromatogram around 24.5 ml.

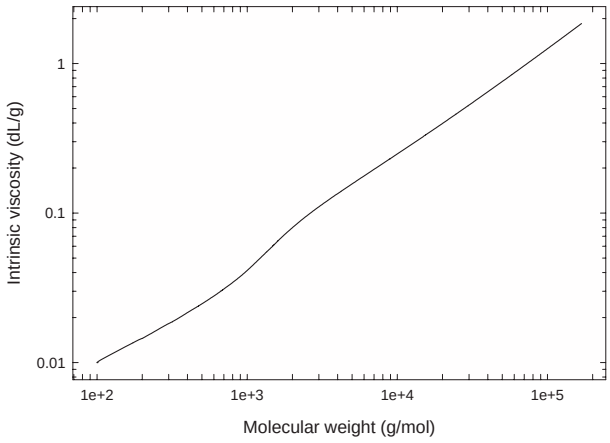

Fig. 5. The MHS plot of intrinsic viscosity against molecular weight for the MWD in Fig. 1.

5.2. Experimental chromatograms

Fig. 7 shows the experimental concentration chromatogram for a sample of nylon 6,6 with weight-average molecular weight of 35 000 g/mol. This corresponds to the copolymer shown in Fig. 6. The overall shape of the chromatogram is very similar to the theoretical model: the cyclic dimer and tetra-mer are clearly visible in both chromatograms, although the amount of cyclics present in the experimental chromatogram is less than in the theoretical chromatogram. The separation of the cyclic peaks from the main polymer peak is comparable. The minimum in the chromatogram between the mostly cyclic species and the mostly linear species is also present in the experimental chromatogram. Note that the experimental calibration curve is not the same as the calibration curve used in the theoretical model, hence the elution volumes of the two chromatograms are not identical.

Fig. 8 shows the experimental concentration chromatogram for a sample of nylon 6 with weight-average

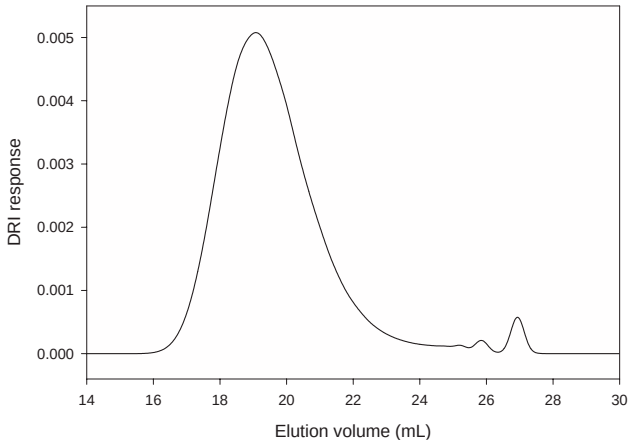

Fig. 6. Refractometer chromatogram for a step-growth polymer MWD including cyclic species made from two bifunctional monomers (A–A and B–B type monomers).

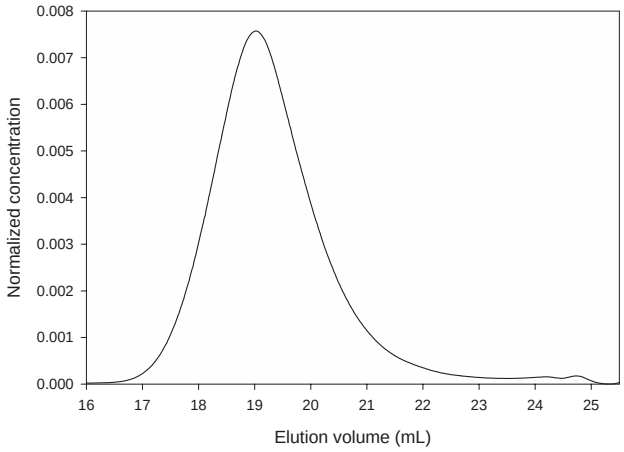

Fig. 7. Experimental concentration-detector chromatogram for nylon 6,6 polymer sample. (See text for details.)

molecular weight of about 30 000 g/mol. Again, the peak shape is very similar to the theoretical chromatogram for the homopolymer shown in Fig. 2, though there are fewer cyclics in the experimental chromatogram. The separation of the main peak from the cyclic peaks is comparable and the minimum between the two is present. The lower concentration of cyclic species in nylon polymers compared to that predicted by the Jacobson and Stockmayer theory has been observed in studies of the equilibration molar cyclization constants in the melt [21,22]. The theoretical treatment of cyclics of Flory, Mutter and Suter, which takes into account the correlation between the directions of terminal bonds, predicts a lower concentration and gives better agreement with the experimental results [4–7].

The concentration chromatogram for poly(ethylene terephthalate) is shown in Fig. 9. This chromatogram should be comparable to the copolymer chromatogram in Fig. 6, however, the cyclic conformation is not possible for the di-mer and tetra-mer because of steric hindrances. The first cyclic species is the hexa-mer which is present at a higher

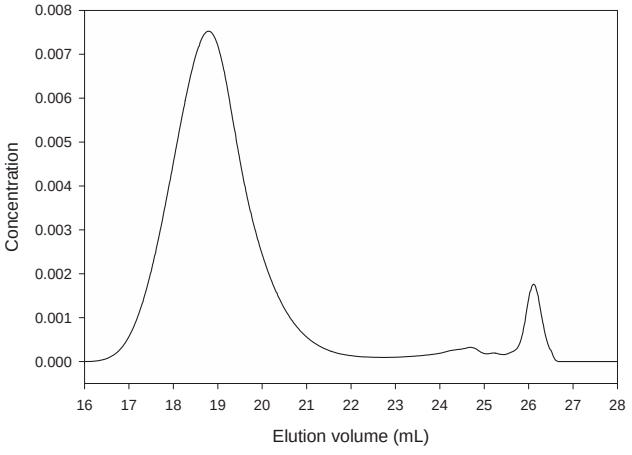

Fig. 8. Experimental concentration-detector chromatogram for nylon 6 polymer sample. (See text for details.)

concentration than predicted (the hexa-mer in the model is generally referred to as the cyclic tri-mer when the monomeric unit is considered to contain both the constituent monomers). This discrepancy between the theoretical model and experimental data has also been observed in studies of experimental cyclization equilibrium constants in the melt [23]. Nonetheless, the other features of the chromatogram, the separation of cyclic and linear peaks and the minimum between them, are in agreement with the model.

5.3. Calibration curve and band-broadening correction

Before proceeding to analyze the theoretical cyclic MWDs, we need to define the calibration and band broadening correction procedures used to analyze the model data. For the conventional SEC analysis, a broad MWD standard was used for calibration and band broadening correction. A broad MWD chromatogram was generated with the same linear MWD as the chromatograms to be analyzed, but without the cyclic species. This chromatogram was used to generate a linear calibration curve which will yield the correct M_n and M_w values (the linear calibration curve search method) [24]. The slope of the broad standard calibration curve is slightly less than the slope of the true calibration curve, used to generate the model data, due to band broadening. This method has the advantage of simplicity and automatically incorporates a correction for band broadening.

For the SEC-LS analysis, an effective interdetector volume shift was used to correct the band broadening. A number of workers have noted the relationship between band broadening and the interdetector volume in multidetector SEC [8,25–27]. When multiple detectors are used with SEC, the volume difference between the different detector cells must be corrected before the data are analyzed so that the measured values correspond to the same fraction of the eluting chromatogram. When molecular-weight-sensitive detectors are used with SEC, the width of the calculated MWD can be changed by altering the size of the volume correction used to compensate for the dead volume between the detector cells. This means that, rather than using a complex band broadening correction, approximately the same result can be achieved by manipulation of the interdetector volume. This “effective detector volume” corrects both the dead volume between detectors and the band broadening [25]. This method has recently been shown to provide accurate results for polymers with the most probable MWD [28].

5.4. Baselines and peak integration limits

As the linear and cyclic species are not completely resolved, it is necessary to develop a method to divide the two parts of the chromatogram in order to get the linear MWD. Fig. 10 shows the baseline and the peak integration limit chosen to analyze the data. The baseline is drawn from before the chromatogram “A” to after the cyclic species

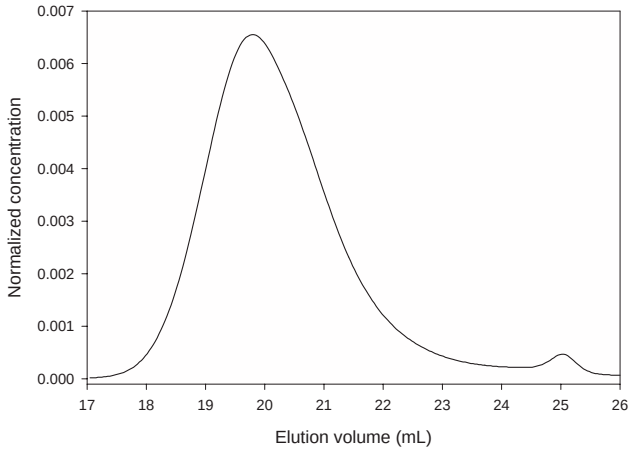

Fig. 9. Experimental concentration-detector chromatogram for poly(ethylene terephthalate) sample. (See text for details.)

"C". The peak is divided into two areas on either side of a vertical line drawn at the elution volume corresponding to the first minimum in the chromatogram at about 24.4 ml "B". This point was chosen as being a constant distinguishing feature in all the simulated chromatograms. Another possible baseline is also shown in the figure, going from the beginning of the peak "A" to the point in the chromatogram before the cyclic peaks elute "B". This possibility has been investigated previously by Martin and Balke for SEC analysis of poly(ethylene terephthalate) and was found to overestimate the average molecular weights by up to 8% [29]. This is because it selectively excludes part of the low molecular weight end of the chromatogram from the calculation of the MWD. This can be seen by comparing the baseline AB with the actual cyclic distribution shown in Fig. 2.

5.5. Results for theoretical data

The results of using this approach to separate the linear and the cyclic MWDs are shown in Tables 1 and 2. Table 1 shows the results for the distribution with A–B cyclics shown in Fig. 2. Table 2 shows the results for the distribution with A–A and B–B cyclics shown in Fig. 6. Both tables show the total MWD and the linear and cyclic MWDs calculated by both SEC and SEC-LS cutting off the distribution at the minimum in the chromatogram.

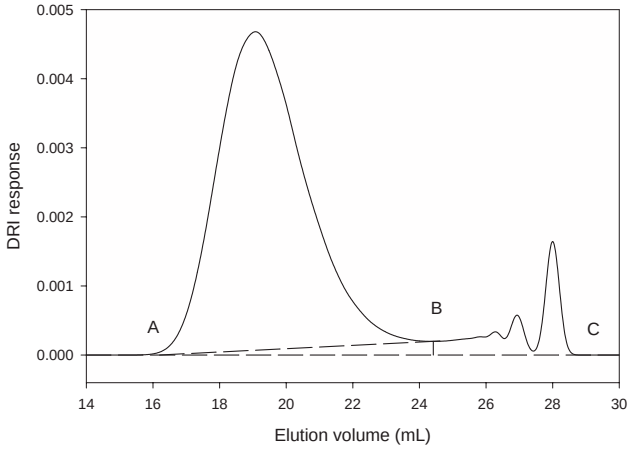

Fig. 10. Baselines (– – –) and peak split between linear and cyclic species used to analyze the data. (See text for details.)

Table 1
Molecular weight distributions for type AB polymer distribution with cyclic species

	Method	M_n	M_w	M_z	M_w/M_n	M_z/M_n
Total distribution	True	1340	17 700	29 700	13.2	1.68
	SEC	1100	17 600	29 700	16.0	1.69
	SEC-LS	1330	17 700	29 700	13.3	1.68
Linear distribution	True	10 000	19 900	29 850	1.99	1.50
	SEC	9 800	19 500	29 800	1.99	1.53
	SEC-LS	10 000	19 600	29 700	1.96	1.51
Cyclic distribution	True	170	710	5250	4.18	4.18
	SEC	120	200	350	1.67	1.75
	SEC-LS	150	260	450	1.73	1.73

All the methods studied are in good agreement with the molecular weight averages for the total MWD. The weight, and *z*-average molecular weight values were within 1% of the true values. The relative errors in the determination of the number-average molecular weight were large, but the absolute errors were small. The closest agreement was obtained by SEC-LS using the volume shift method of band broadening correction. The conventional SEC methods underestimate M_n because of the different calibration curve required for the cyclic species.

The linear MWD was calculated by ending the peak integration at the first minimum in the concentration detector chromatogram. This approach worked well for all the methods and the results were in good agreement with the true values. The errors in M_w and M_z were less than 2% and 1% respectively, and the errors in M_n were less than 5%. For the cyclic distribution, approximated by the section of the chromatogram after the first minimum, the errors were much higher. The number-average values were the closest, but the weight and *z*-average values were greatly underestimated because the long high molecular weight tail in the cyclic distribution is excluded from the calculation. The calculated weight fraction of cyclic species is in reasonable agreement with the theoretical values. For the A–A polymer, the weight fraction was 11.4% and the calculated amount was 10%. For the A–A and B–B polymer, the true amount was 5.7% and the calculated amount was 4.8%. Results from model distributions with higher (M_n = 20 000 g/mol) and lower (M_n = 500 g/mol) molecular weights gave comparable results.

When the molecular weight averages were calculated by SEC-LS using the baseline AB for the chromatogram shown in Fig. 2, the weight and *z*-average molecular weights were overestimated by 2%, but the number-average molecular

Table 2
Molecular weight distributions for AA and BB polymer distribution with cyclic species

	Method	M_n	M_w	M_z	M_w/M_n	M_w/M_n
Total distribution	True	4750	19 200	29 800	4.04	1.55
	SEC	4140	19 100	29 800	4.61	1.56
	SEC-LS	4760	19 200	29 800	4.03	1.55
Linear distribution	True	10 000	19 900	29 850	1.99	1.50
	SEC	9800	19 600	29 800	2.00	1.52
	SEC-LS	10 000	19 700	29 800	2.97	1.51
Cyclic distribution	True	330	1030	5630	3.12	5.47
	SEC	200	260	330	1.30	1.27
	SEC-LS	260	330	420	1.27	1.27

weight was overestimated by 16%, leading to a large error in the calculated polydispersity. Similar errors were found when this approach was used on other theoretical results and this baseline was not used in the analysis.

5.6. Results for experimental data

The PET sample shown in Fig. 9 was used to compare the theoretical results for conventional SEC analysis with experimental results. A purely linear broad MWD standard was prepared by extracting the cyclics from the experimental sample by precipitating the HFIP solution in tetrahydrofuran. The precipitate was considered to be purely a linear polymer. SEC-Visc-LS was used to determine the weight-average molecular weight of the linear polymer and this sample was then used to generate a broad MWD standard calibration curve, assuming a most probable distribution [30]. Fig. 11 shows the overlaid concentration chromatograms of the PET sample and the extracted polymer. The cyclic species are no longer visible in the extracted polymer and the distribution returns to the baseline at about 25 ml. The two later peaks are the residual THF and the sodium trifluoroacetate, respectively. Notice that the chromatogram for the linear extracted polymer extends under the cyclic hexa-mer peak for the standard polymer as predicted in Fig. 2.

Table 3
Molecular weight distributions for PET sample calculated by conventional SEC

	M_n	M_w	M_z	M_w/M_n	M_w/M_n
Total distribution	8950	44 800	67 800	5.01	1.51
Linear distribution	22 300	45 500	67 800	2.04	1.49
Extracted polymer	23 500	45 100	67 000	1.92	1.49

Table 3 shows the SEC results for the PET standard based on the broad standard calibration curve. The MWD of the whole sample has a polydispersity of 5, however when the chromatogram is truncated at the minimum in between the linear and cyclic peaks, the polydispersity is 2 and the molecular weight results are in good agreement with those obtained from the extracted linear calibration standard.

The SEC-LS results were compared with those obtained by SEC-Visc-RALLS on the nylon 6,6, nylon 6 and PET samples shown in Figs. 7–9. In SEC-Visc-RALLS, the molecular weight is measured directly at each elution volume using the 90° scattered light intensity. This initial estimate of molecular weight is then corrected for any angular asymmetry in the scattering using a size estimate

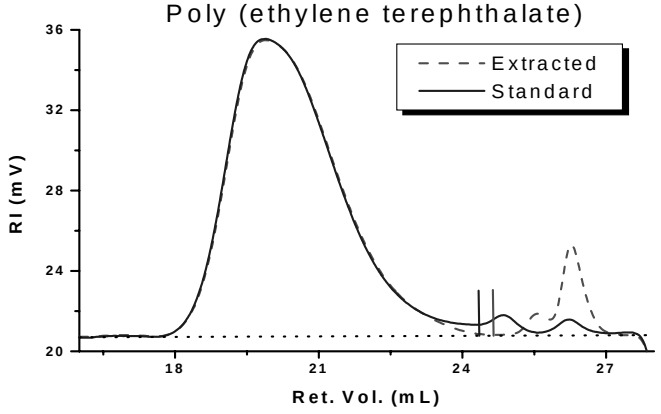

Fig. 11. Experimental refractometer chromatograms for the poly(ethylene terephthalate) sample (—) compared to the same sample with the cyclic species extracted (– – –). The vertical lines indicate the end of the peak integration, and the dotted line shows the baseline used for calculations.

Table 4
Molecular weight distributions of the whole polymer and the truncated chromatogram for the nylon 6,6, nylon 6, and PET samples

Polymer		M_n	M_w	M_z	M_w/M_n	M_z/M_n
Nylon 6,6	Total distribution	12 900	34 100	55 500	2.64	1.63
	Linear distribution	16 700	34 500	55 600	2.06	1.61
Nylon 6	Total distribution	11 900	29 100	44 000	2.44	1.51
	Linear distribution	16 200	29 800	44 200	1.84	1.48
PET	Total distribution	18 900	44 900	69 500	2.38	1.55
	Linear distribution	24 400	45 800	69 800	1.88	1.52

determined from the intrinsic viscosity at that elution volume. For relatively low molecular weight polymers, such as most step-growth polymers, this method gives results equivalent to SEC-LS [12,31]. Table 4 shows the molecular weight moments calculated for the whole distribution and for the truncated distribution. In all three cases, the truncated distribution gives results with a polydispersity M_w/M_n close to 2. The value of M_z/M_w is also close to the most probable distribution value of 1.5 for the PET and nylon 6 samples. In the sample of nylon 6,6 the value is higher, possibly due to small amounts of long chain branching at high molecular weights.

Finally, a practical difficulty with the approach described before should be noted. The noise in the LS signal at low molecular weights will lead to errors in calculating the cyclic molecular weights. A viscometer provides greater sensitivity to the low molecular weight species, however, such an approach would rely on the assumption that universal calibration applies to the cyclic species. The authors are unaware of any studies that have addressed this question.

6. Conclusions

A theoretical model of SEC of step-growth polymers with cyclic species was developed and found to describe the features of experimental chromatogram accurately. The model was used to develop a simple method to estimate the linear MWD of polymers containing cyclics, as well as the weight fraction of cyclic species present. The method was applied to experimental data and found to be in good agreement with the predicted results for the linear fraction of the MWD.

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