

Modeling of the molar mass distribution of six-arm star-branched poly- ϵ -caprolactam using size-exclusion chromatography

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Received 30 December 2002; received in revised form 3 March 2003; accepted 27 May 2003

Abstract

This paper presents a modeling-based approach to the prediction of the molar mass distribution of the various species in a star-branched polycondensation mixture. The interpretation of experimental SEC data of the mixture of linear, cyclic and star-branched molecules is not straightforward, because of the different sizes of those molecules (having the same molecular mass). Therefore we have opted to use SEC analysis with only a concentration detector and fit the experimental data to the theoretical mass distribution, corrected for the volume of the various molecules. This allows the relative fraction and the distribution of the various species in the mixture (linear, cyclic and star-branched) to be determined. To demonstrate this, the six-arm star-branched poly- ϵ -caprolactam based on the six-functional coupling molecule, hexa(6-caproic acid) melamine has been analyzed. Five polymer mixtures with different initial concentration of coupling molecule have been synthesized. As the initial concentration of coupling molecule increased, we found that the weight fraction of star-branched molecules increased, while the weight fraction of linear and cyclic molecules decreased. We also found that the weight-average molar mass and the arm length decrease as the initial fraction of the coupling molecule increases.

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Keywords: Mass distribution; Polymers; Poly(ϵ -caprolactam); Polycondensates, star-branched; Star-branched polycondensates

1. Introduction

Size-exclusion chromatography (SEC) analysis is a well-known and powerful method to analyze the molar mass distribution of linear polymers. The parameter that determines retention in SEC analysis is the hydrodynamic volume of the macromolecular coil. The method can also be used for nonlinear polymers. Using only a concentration detector, however, a problem arises when a polymerization re-

action results in species with different volume-to-mass ratios, as calibration can only be done with one molecular species. Interpretation of the experimental data is therefore not straightforward. However, if molecular size and type of molar mass distribution are known a priori, it is possible to analyze the mixture with SEC.

This paper deals with star-branched polycondensates, particularly the six-arm star-branched poly- ϵ -caprolactam. This polymer is formed by reaction of caprolactam with a six-functional coupling molecule, hexa(6-caproic acid) melamine (HCAM), henceforth referred to as **R**. Star-branched polycaprolactam was

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first synthesized by Schaeffgen and Flory [1]. The reaction mixture yields three types of molecules: those without a coupling molecule, which are either linear or cyclic; and those with a coupling molecule, which are six-arm star-branched. The SEC analysis of branched polymers has been published [2,3] and that of the mixture of linear and cyclic polycondensates has been reported by Niehaus and Jackson [4]. To a large extent we follow their approach. We deviate from it, however, by explicitly using the a priori theoretical molar mass distribution, which is subsequently transformed into a “linear equivalent” mass distribution by incorporating the molecular size of the species and the solvent properties. We are then able to fit the parameters of the theoretical molar mass distribution with the experimental SEC data. We are particularly interested in star-branched polymers with more than two arms, which are non-linear. The general approach, however, can be applied to any well-defined mixture of polymers and oligomers.

2. General approach

The (weight) molar mass distribution of any mixture of n species may be represented by:

$$w(x) = \sum_{i=1}^n \phi_i w_i(x) \quad (1)$$

where $w(x)$ is the total mass distribution within the mixture of all the different species, x is the number of monomer units, $w_i(x)$ is the molar mass distribution of species i , and ϕ_i is the weight fraction of species i . Normalization dictates that:

$$\sum_{i=1}^n \phi_i = 1 \quad (2)$$

and

$$\int_0^{\infty} w_i(x) dx = 1 \quad \text{or} \quad \sum_{x=1}^{\infty} w_i(x) = 1, \quad (3)$$

$i = 1, 2, \dots, n$

For the six-arm star-branched polymer mixture we then have $n=3$ species: linear molecules containing no **R** group for $i=1$, star-branched molecules containing an **R** group for $i=2$, and cyclic oligomers for

$i=3$. Using the theoretical mass distributions and the weight fractions, we are able to determine the molar mass distribution for the mixture. This situation is presented graphically in Fig. 1. On the left side of the graph we have the cyclic oligomers, the fraction of which decreases rapidly with increasing molar mass. At medium molar mass we find the bell-shaped fraction for the linear molecules and at higher molar mass we find another bell-shaped curve representing the star-branched molecules.

Different species can have a different molecular size for the same molar mass. It is well known that the molecular size of cyclic and star-branched molecules is smaller than that of linear molecules of equal molar mass. For star-branched molecules the size is also dependent on the mass of the individual arms.

In order to be able to compare the different species with the SEC analysis that has been calibrated on the basis of a linear polymer, we transform molar mass into “linear equivalent” molar mass (Fig. 2). This results in the curves for both the cyclic and star-branched species shifting to the left, giving less overlap between the cyclic and the linear molecules but more overlap between the star-branched and the linear molecules. We have also superimposed a Gaussian distribution in order to correct for band

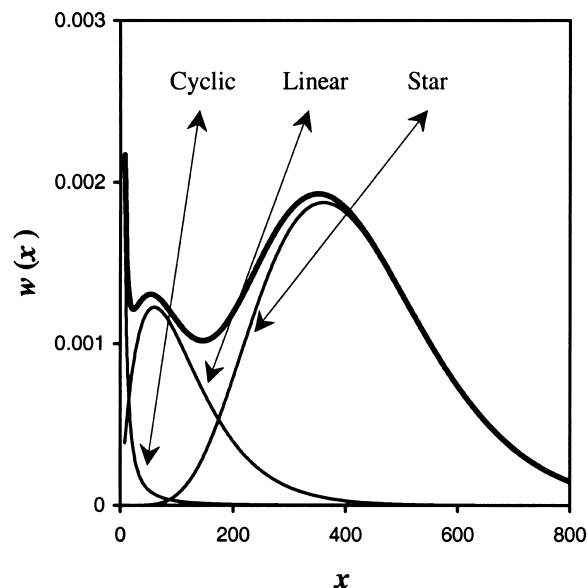


Fig. 1. Typical molar mass distribution of a star-branched polycondensate mixture.

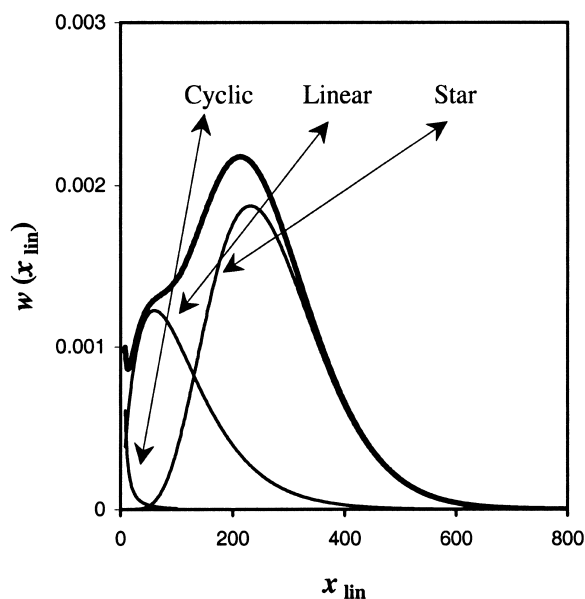


Fig. 2. Molar mass distribution of a star-branched polycondensate mixture in linear equivalent units.

broadening of the SEC analysis. The effect of this is minor as compared to the stochastic nature of the size of star-branched molecules with the same mass.

SEC results are typically presented on a logarithmic scale. However, this representation loses vital information at lower masses and therefore we have opted for a linear representation to do our fitting procedure of minimizing the quadratic differences between experimental data and theoretical molar mass distribution.

3. Molar mass distribution

The form of the molar mass distributions for the three different species in the star-branched polycondensate mixture is known. For linear polycondensates we use the continuous form of the Flory distribution [5]:

$$w_1(x) = \frac{x}{\beta^2} \exp(-x/\beta), \quad x \geq 0 \quad (4)$$

where β is the number average molar mass and x is the number of monomer units. The molar mass distribution of 100% star-branched polymer is given

by the independent addition of f Flory distributions [5]:

$$w_2(x) = \frac{x^f}{f! \beta^{f+1}} \exp(-x/\beta), \quad x \geq 0 \quad (5)$$

Compared to the linear molecule we need only to include one more parameter, f —the number of arms—which is known from the \mathbf{R} used in the reaction mixture. β represents the number-average mass of one arm.

In equilibrium the cyclic oligomer distribution is dependent on the distribution of linear molecules. The discrete version, based on Gaussian chains, is [6]:

$$w_3(x) = \frac{q^x}{Li_{3/2}[q] x^{3/2}} \quad x \in (1, 2, 3, \dots) \quad (6)$$

where the polylogarithm Li is defined as:

$$Li_p[q] = \sum_{k=1}^{\infty} \frac{q^k}{k^p} \quad (7)$$

and q is defined as:

$$q = \exp(-1/\beta) \quad (8)$$

4. Molecular size

In order to be able to transform the molar mass distribution into “linear equivalent” units, we need to establish the relation between the volume of a macromolecular coil (V) and the number of monomer units in the chain (x). From the general theory of long chain polymer solutions [7,8], we get the proportionality relation between the volume of a macromolecular coil and the mean square radius of the perturbed molecule ($\langle S^2 \rangle$):

$$V \propto \langle S^2 \rangle^{3/2} \quad (9)$$

The relation between the mean square radius of the perturbed and the unperturbed molecule is given by:

$$\langle S^2 \rangle = \alpha^2 \langle S^2 \rangle_0 \quad (10)$$

and more specifically for any molecule, it can be generalized as:

$$\langle S^2 \rangle = \alpha^2 g \langle S^2 \rangle_{0,\text{lin}} \quad (11)$$

where the mean square radius of the unperturbed molecule is represented by $\langle S^2 \rangle_0$ and the mean square radius of the unperturbed linear molecule by $\langle S^2 \rangle_{0,\text{lin}}$. α is the expansion factor; g is called the contraction factor, which is a constant for linear and cyclic molecules; but for star molecules it is stochastic, as each configuration of arms with equal molar mass of the molecule results in a different value for g . For stars with many arms ($f > 10$), we have to include an additional expansion factor coping for the increased segment density at the branch point [9,10].

In combination with the well-known proportional relation between the unperturbed mean square radius of the linear molecule and the number of monomer units (x), given by:

$$\langle S^2 \rangle_{0,\text{lin}} \propto x \quad (12)$$

we establish from Eqs. (9)–(12) the proportional relation between the volume of a macromolecular coil and the expansion factor, the contraction factor and the molar mass:

$$V \propto (\alpha \sqrt{gx})^3 \quad (13)$$

The expansion factor is dependent on the molar mass ([7], p. 407):

$$\alpha = \gamma x^c \quad (14)$$

where γ and c are constants and c is equal to $(2a-1)/6$, in which a is the constant in the Mark–Houwink–Sakurada formula. The parameter a is dependent on the polymer type, the type of solvent and the temperature, but is assumed to be independent of the molecule species.

Substituting Eq. (14) into Eq. (13) gives the following proportional relationship:

$$V \propto (\gamma \sqrt{g})^3 x^{a+1} \quad (15)$$

The parameters on the right hand side of the equation can be estimated for the various species using theoretical calculations and published experimental data.

5. Linear equivalent units

The parameter that determines the retention in

SEC analysis is the volume of the macromolecular coil. From Eq. (15) we can find the ratio between the volumes of any molecular species and a linear molecule:

$$\frac{V}{V_{\text{lin}}} = \left(\frac{\gamma \sqrt{g}}{\gamma_{\text{lin}}} \right)^3 \left(\frac{x}{x_{\text{lin}}} \right)^{a+1} \quad (16)$$

The subscript “lin” refers to a linear molecule. Without subscript the parameter refers to any molecule. With Eq. (16) we can establish the relationship between the molar mass in units of any species and the linear equivalent units, by evaluation of Eq. (16) under equal volume condition:

$$x = hx_{\text{lin}} | (V = V_{\text{lin}}) \quad (17)$$

with

$$h = \left(\frac{\gamma_{\text{lin}}}{\gamma \sqrt{g}} \right)^{3/(a+1)} \quad (18)$$

For linear and cyclic molecules h is a scalar. For star-branched molecules with Flory distributed arms g is a stochastic variable [11] and consequently h is a stochastic variable too. For $f > 4$ and relevant values of a , the density function of h can be approximated by a Gaussian distribution with parameters $\mu_{h_{\text{star}}}$ and $\sigma_{h_{\text{star}}}$. Substitution of Eq. (17) (including the stochastic nature of h for stars) into the Eqs. (4)–(6) and then combining the result with Eq. (1) gives us the molar mass distribution in linear equivalent units:

$$w(x_{\text{lin}}) = \frac{\phi_1 x_{\text{lin}}}{\beta^2} \exp\left(\frac{-x_{\text{lin}}}{\beta}\right) + \frac{\phi_2 x_{\text{lin}}^f \mu'_{f+1}}{f! \beta^{f+1}} \exp\left(\frac{\sigma_{h_{\text{star}}}^2 x_{\text{lin}}^2}{2\beta^2} - \frac{\mu_{h_{\text{star}}} x_{\text{lin}}}{\beta}\right) + \frac{(1 - \phi_1 - \phi_2) q^{h_{\text{cyclic}} x_{\text{lin}}}}{Li_{3/2}[q] h_{\text{cyclic}}^{1/2} x_{\text{lin}}^{3/2}} \quad (19)$$

with

$$\mu'_f = \int_{-\infty}^{\infty} \frac{h_{\text{star}}^f}{\sigma_{h_{\text{star}}} \sqrt{2\pi}} \times \exp\left(\frac{-\left(h_{\text{star}} - \left[\mu_{h_{\text{star}}} - \frac{\sigma_{h_{\text{star}}}^2 x_{\text{lin}}}{\beta}\right]\right)^2}{2\sigma_{h_{\text{star}}}^2}\right) dh_{\text{star}} \quad (20)$$

which is the f th moment of the a Gaussian dis-

tribution with parameters $\mu_{h_{\text{star}}} - \sigma_{h_{\text{star}}}^2 x_{\text{lin}}/\beta$ and $\sigma_{h_{\text{star}}}$. The subscript “star” refers to a star-branched molecule and “cyclic” refers to a cyclic oligomer. Eq. (20) can be solved exactly and after some mathematics we arrive at ([12], p. 62):

$$\mu'_f = \sum_{k=0}^{\lfloor f/2 \rfloor} \binom{f}{2k} \frac{(2k)! \sigma_{h_{\text{star}}}^{2k} (\beta \mu_{h_{\text{star}}} - \sigma_{h_{\text{star}}}^2 x_{\text{lin}})^{f-2k}}{2^k k! \beta^{f-2k}} \quad (21)$$

in which $\lfloor \dots \rfloor$ represents the greatest integer less than or equal to the value of the expression between the brackets.

Band-broadening effects typically occur in chromatographic processes [13]. To correct for it we superimposed a Gaussian diffusion with constant variance of 0.7.

Eq. (19) represents a molar mass distribution of a mixture of three molecular species with only three parameters that need to be estimated: the weight fraction of the linear species (ϕ_1), the weight fraction of the star-branched species (ϕ_2) and the number-average arm length (β). The other parameters can be estimated from theoretical calculations (see Section 7).

6. Experimental

6.1. Synthesis

The star-branched mixture has been synthesized by combining 99 g of ϵ -caprolactam, 1 g of 6-amino caproic acid, 2 g of demineralized water and a variable amount of hexa(6-caproic acid) melamine (HCAM) in a 5-cm wide polymerization tube. The molar ratio of HCAM to caprolactam is referred to as α_f . The ratio ranged from 0.00111 to 0.0045. A magnetic stirrer bar was added to the polymerization tube, which was subsequently fitted with a condenser. The tube was flushed three times with nitrogen, under 20 mbar vacuum. Whilst under nitrogen, the tube was placed in an aluminum heater block at atmospheric pressure and heated from 20 to 265 °C over a period of 3 h, after which it was kept at this temperature for 11 h. The resulting polymer was cooled in liquid nitrogen, crushed and ground to a maximum grain size of 3 mm. The granulate was

washed for 2 h with an 8-fold excess of boiling water. After decanting, the washing step was repeated two more times. The polymer was then dried in a vacuum oven for 24 h at 60 °C and 200 mbar under a small nitrogen flow. Chemicals: Caprolactam (DSM, AP grade) was stored under nitrogen at 40 °C. 6-Amino caproic acid (Acros, 99+%) was used as received. HCAM was obtained by the stepwise reaction of di(6-caproic acid) amine with cyanuric acid chloride in water with sodium hydroxide as a base. Acidification of the reaction mixture gave the product in near quantitative yield [14]. The purity as determined by HPLC was 95%.

6.2. SEC analysis

The SEC experiments were performed on a Agilent chromatograph (HP 1090) equipped with a differential refractometer (HP 1047A) and a differential viscometer (Viscotek H502B). Four Nucleosil-70H (Machery Nagel) were applied. The mobile phase was hexafluoroisopropanol with 0.1 wt% potassium trifluoroacetate (Aldrich) and the flow-rate was 0.4 ml/min. Minor flow-rate fluctuations were corrected. The SEC apparatus, columns and detectors were operated at 25 °C. Data were collected and analyzed using Tri SEC version 2.7 (Viscotek). The conventional calibration method was used employing linear nylon 4,6 (Stanyl) samples that we synthesized specifically for that purpose. Samples were dried for 16 h under vacuum before dissolution in the solvent under nitrogen atmosphere.

7. Values of h for the six-arm star-branched mixture

In order to compare the “theoretical” molar mass distribution of Eq. (19) with the experimental SEC data, we have to establish the values for the parameter h , which can be determined from g , γ and a by use of Eq. (18). For linear molecules we have $g_{\text{lin}} = 1$ by definition, for cyclic species $g_{\text{cyclic}} = 0.5$ [15] and for Flory distributed star-branched polymers we have deduced that $g_{\text{star}} = 6f/(f+1)/(f+2)$ [11]. The ratio happens to be exactly the same as that for a uniformly distributed star-branched polymer [16].

The ratio χ_{lin}/γ can be estimated from the excluded volume theory. Cyclic species, because of the

restrictions enforced by the ring structure, have a higher segment density in the center and therefore expand more as compared to the linear molecule, due to chain and solvent interactions. The ratio $\alpha_{\text{cyclic}}^2/\alpha_{\text{lin}}^2$ is 1.09 in good solvent condition [17] (excluded volume = 0.5), so that $\gamma_{\text{lin}}/\gamma_{\text{cyclic}} = 0.958$.

For star-branched polymers there are two opposing effects: the segment density near the core is higher, which enhances the overall expansion. On the other hand the star structure provides a topological constraint at the branch point opposing such expansion [18]. The net effect is that the expansion factor is slightly larger than the expansion factor of linear molecules with equal excluded volume. For regular six-arm star molecules the ratio $\alpha_{\text{star}}^2/\alpha_{\text{lin}}^2$ increases asymptotically to a value of 1.03; at an excluded volume of 0.5, $\alpha_{\text{star}}^2/\alpha_{\text{lin}}^2$ is only 1.014 [18]. Assuming that this last value is also representative for polydisperse stars and is realistic for a good solvent, we estimate that $\gamma_{\text{lin}}/\gamma_{\text{star}} = 0.993$.

A value of 0.65 has been reported for a for the polyamide 6/HFIP(0.05 M CF_3COONa) at 20 °C [19] and a value of 0.63 for the polyamide 6,6/HFIP(0.1 M CF_3COONa) at 25 °C [20]. At low masses (below 1000 g/mol) the reported value of a is 0.59 and above 300 g/mol a becomes 0.7 for the polyamide/HFIP(0.01 M CF_3COONa) at 35 °C [4]. For polyamide/HFIP(0.01 M CF_3COOK) at 25 °C we find values for a in the range of 0.68–0.74 in SEC/DV (see for details Section 6). Because of this wide range of a , we have opted to use $a = 0.7$ for all masses and to include a sensitivity analysis in Section 10. For $a = 0.7$ we get $h_{\text{lin}} = 1$ for linear molecules, $h_{\text{cyclic}} = 1.71$ for cyclic molecules and for

star-branched molecules with f arms, a Gaussian distribution of h_{star} with parameters $\mu_{h_{\text{star}}} = (\gamma_{\text{lin}}/\gamma_{\text{star}})^{3/(a+1)}(-0.3856a + 1.7725) = 1.48$ and $\sigma_{h_{\text{star}}} = (\gamma_{\text{lin}}/\gamma_{\text{star}})^{3/(a+1)}(-0.1815a + 0.331) = 0.2$.

8. Fitting results

Six samples of six-arm star-branched polycaprolactam were analyzed. The samples featured different initial concentrations of the coupling molecule and therefore different molar mass distributions. We performed a least squares analysis using the method of the steepest descent of the Microsoft Excel Solver function by comparing Eq. (19) with the SEC concentration chromatogram data for the non-extracted polymer. In the fitting procedure we disregarded the first seven members of the SEC data, to minimize the interference of the ring tension with the Gaussian chain assumption for the cyclic molecules and to adjust for the fact that the polymer is washed. Only the values of ϕ_1 , ϕ_2 , β were estimated; the values for the other parameters are deduced in Section 7. Weight fractions and number-average arm length are given in Table 1. The root mean square error (RMSE) is given in Table 1 as well and indicates a very good fit. We found, however, that the analysis does not converge to realistic results for $\alpha_f < 0.001$, probably due to the flatness of the slope, which gives a shallow minimum with almost the same residual squares. The mass distributions of three selected samples are given in Fig. 3. For low α_f (sample 2h327) we find a broader distribution com-

Table 1
Estimated parameters of six-arm star-branched polycaprolactam

| Code | Initial molar fraction of \mathbf{R} (α_f) | Weight fraction of linear molecules (ϕ_1) | Weight fraction of star-branched molecules (ϕ_2) | Number-average arm length (β) | Root mean square error ($\times 10^4$) |
|-------|---|--|---|---------------------------------------|--|
| 2h327 | 0.00111 | 0.261 | 0.733 | 71.0 | 1.4 |
| 2h241 | 0.00167 | 0.198 | 0.791 | 62.7 | 2.0 |
| 2h326 | 0.00206 | 0.130 | 0.864 | 59.3 | 1.3 |
| 2h325 | 0.00242 | 0.126 | 0.862 | 55.0 | 2.5 |
| 2h240 | 0.00333 | 0.106 | 0.888 | 42.6 | 1.3 |
| 2h324 | 0.00450 | 0.067 | 0.929 | 35.8 | 0.9 |

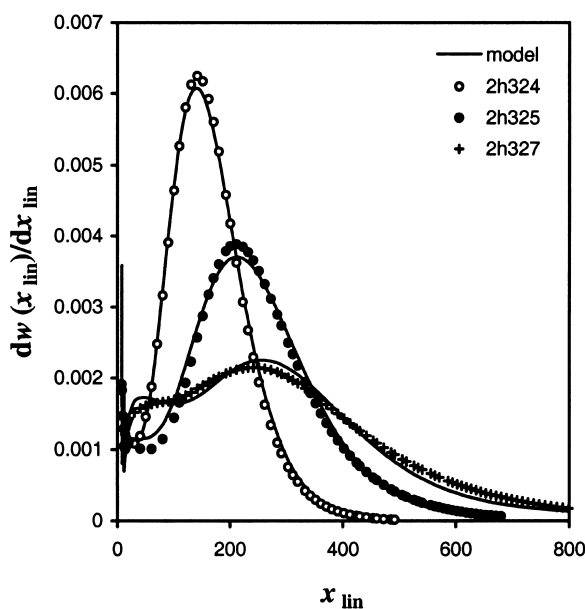


Fig. 3. Selected molar mass distributions of six-arm star-branched polycaprolactam (SEC analysis versus model).

pared to high α_f (sample 2h324). The higher the value of α_f , the higher the weight fraction of star molecules. For the linear and cyclic species the reverse is true (Fig. 4). β decreases with increasing α_f (Fig. 5), because of stoichiometric unbalance of the end groups. The solid lines in Figs. 4 and 5 represent best-fit lines.

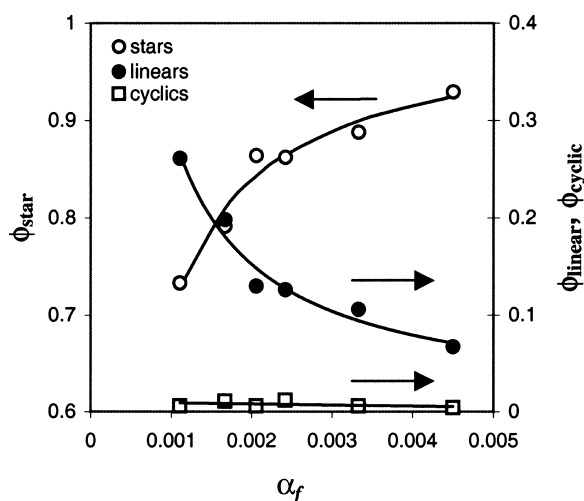


Fig. 4. Weight fractions versus initial molar ratio of \mathbf{R} (α_f).

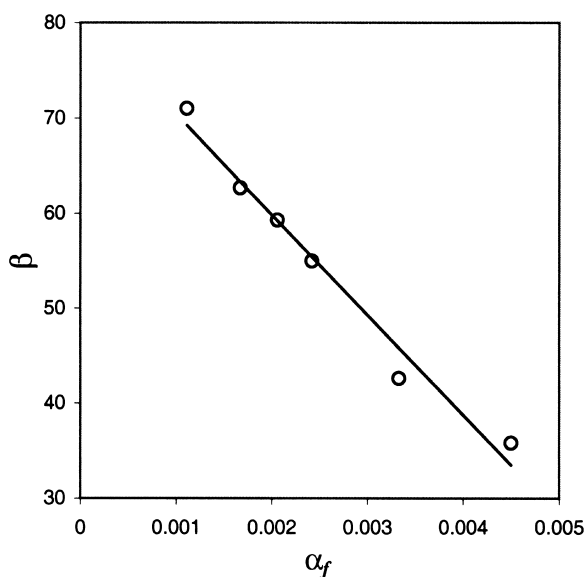


Fig. 5. Arm length (β) versus initial molar ratio of \mathbf{R} (α_f).

9. Derived results

From ϕ_1 , ϕ_2 , β we can derive the averages of the mass distribution and estimate the ratio of initial \mathbf{R} versus monomer. The weight average molar masses are calculated as 2β for linear, $(f+1)\beta$ for star-branched and $Li_{1/2}[q]/Li_{3/2}[q]$ for cyclic species. The weight average molar mass of the mixture is then equal to $2\phi_1\beta + (f+1)\phi_2\beta + (1-\phi_1-\phi_2)Li_{1/2}[q]/Li_{3/2}[q]$.

From the estimated parameters and the theoretical mass distribution we can calculate the number average molar mass for linear ($=\beta$), for star-branched ($=f\beta$) and for the cyclic species ($=Li_{3/2}[q]/Li_{5/2}[q]$). The number average molar mass of the mixture is then equal to $\phi_1\beta + f\phi_2\beta + (1-\phi_1-\phi_2)Li_{3/2}[q]/Li_{5/2}[q]$, with ϕ_1 and ϕ_2 being the number fraction of linear and star-branched species, respectively. The number fractions can be expressed in relation to the estimated parameters as $\varphi_1 = Af\phi_1/[f\beta + f(A-\beta)\phi_1 + (A-f\beta)\phi_2]$ and $\varphi_2 = A\phi_2/[f\beta + f(A-\beta)\phi_1 + (A-f\beta)\phi_2]$ with $A = Li_{3/2}[q]/Li_{5/2}[q]$.

Average molar masses (given in mass units) of the various species and the mixture are given in Table 2. The average molar mass follows the trend dictated by parameter β . The higher β , the higher the mass. The figures are given as if no extraction has taken

Table 2
Average molar mass of six-arm star-branched polycaprolactam mixture

| Code | Number-average | | | | Weight-average | | | |
|-------|----------------|--------|---------|---------|----------------|--------|---------|---------|
| | Linears | Stars | Cyclics | Mixture | Linears | Stars | Cyclics | Mixture |
| 2h327 | 8000 | 48 100 | 190 | 12 300 | 16 000 | 56 100 | 690 | 45 300 |
| 2h241 | 7100 | 42 500 | 190 | 9500 | 14 100 | 49 600 | 650 | 42 100 |
| 2h326 | 6700 | 40 200 | 190 | 14 100 | 13 400 | 46 900 | 630 | 42 300 |
| 2h325 | 6100 | 37 300 | 190 | 9200 | 12 400 | 43 500 | 610 | 39 000 |
| 2h240 | 4800 | 28 900 | 180 | 12 200 | 9600 | 33 700 | 540 | 31 000 |
| 2h324 | 4000 | 24 300 | 180 | 12 900 | 8100 | 28 300 | 500 | 26 800 |

place. The polydispersity for the mixture ranges from 4 to 2 for $\alpha_f = 0.00111$ and 0.0045, respectively. The weight-average masses are 7–12% higher compared to SEC analysis, where we do not take the molecular size of the different species into account.

The initial molar ratio between the coupling molecule **R** and the monomer (α_f) can be estimated from the three estimated parameters because of the dependence between linear and star-branched species [21]. Corrected for the fraction of cyclic molecules the estimated ratio is: $\alpha_{f,est.} = 2(1 - \phi_1 - \phi_2)/f(2\beta - 1)(1 - \phi_1) \approx (1 - \phi_1 - \phi_2)/f\beta(1 - \phi_1)$. The initial molar fraction seems to be slightly overestimated, particularly at lower values of α_f (Fig. 6). The solid line in this figure represents a best-fit line.

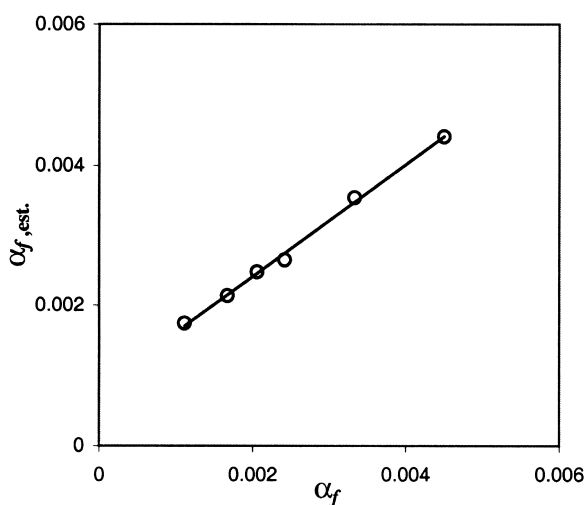


Fig. 6. Estimated ($\alpha_{f,est.}$) versus initial molar ratio of **R** (α_f).

10. Discussion

The comparison between a theoretical model and the experimental data improves with the use of a more realistic model and more accurate data. To arrive at the theoretical mass distribution we have used the molecular size of the various species compared to linear molecules at excluded volume of 0.5 from modern polymer solution theory. This relative molecular size is representative for a good solvent and is (slightly) dependent on molar mass. Although relative molecular size is far less dependent on molar mass than the actual molecular size, the analysis might be improved by assessing the solution properties of the system polycaprolactam/HFIP. Another inference is that star-branched polymers tend to stretch more at low arm length and less at higher arm length. The exact effect on the distribution, however, is not known.

Apparently the error made is the highest in the lower region of the chromatogram. This area is mostly occupied by cyclic molecules and therefore the uncertainty is greatest for the cyclic species. One of the reasons is that we have used the Jacobson and Stockmayer relation, which does not include the ring tension, and therefore the fraction of small cyclic molecules is not determined correctly. A powerful method has recently been developed that can analyze cyclics up to 50 monomer units [22,23]. Incorporating such an analysis will benefit the assessment of the molar mass distribution of the polycondensate mixture.

As the values that have been reported for the Mark–Houwink–Sakurada parameter *a* for equivalent polymer/solvent systems ranges from 0.63 to

0.74, we have assessed the sensitivity with respect to a . We found the weight fractions are only very slightly dependent on a and that β decreases by 0.16 monomer units for an increase of 0.01 of a . So from the minimum value (0.63) to the maximum value (0.74) the effect on β —and consequently on average molar mass—is 2.4%.

11. Conclusions

Conventional SEC analysis can be used to analyze the molar mass distribution of a mixture of a six-arm star-branched polycondensate. The mixture can be broken down into its molecular components (linear, cyclic and star-branched molecules) by use of the theoretical mass distribution, corrected by volume. With increasing initial concentration of coupling molecule we found an increasing weight fraction of star-branched molecules, while the linear and cyclic molecules decreased. Further, the weight-average molar mass and the arm length decrease as the initial fraction of the coupling molecule increases. With increasing initial concentration of coupling molecule we found an increasing weight fraction of star-branched molecules, while the linear and cyclic molecules decreased. Further the weight-average molar mass and the arm length decrease as the initial fraction of the coupling molecule increases.

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