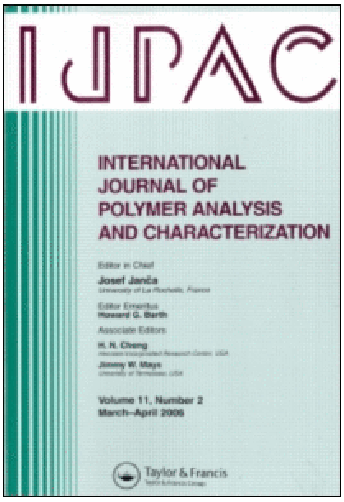

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Simulation of GPC-Distribution Coefficients of Linear and Star-Shaped Molecules in Spherical Pores: Comparison of Simulation and Experiment

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Simulation of GPC-Distribution Coefficients of Linear and Star-Shaped Molecules in Spherical Pores: Comparison of Simulation and Experiment

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Computer simulations of star-branched and linear polymers in spherical pores were performed in order to estimate their GPC-distribution coefficients. Based on these simulations, correction factors can be estimated, that allow correcting for the underestimation of the molecular weight of branched polymers if evaluated using a calibration curve based on linear standards.

The results of the computer simulations were compared with experimental results of GPC-light scattering experiments of star polymers having of defined arm-numbers and arm-molecular weights. Good qualitative and quantitative agreement was found between experimental and simulated correction factors.

The simulations were used additionally to elucidate the structure of coupling peaks in ATRP with multifunctional initiators. The elution volumes of these peaks were in good agreement with an expected dumbbell topology that would arise from arm-arm coupling of different stars.

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Keywords:

INTRODUCTION

The use of gel permeation chromatography (GPC) for the determination of the molecular weights and molecular weight distribution of branched polymers is hampered since standards for branched polymers are not available. The use of molecular weight sensitive detectors is required in order to get reasonable molecular weights[1–5]. However, the high price of such instruments prevents the use of such instrumentation in many laboratories. Thus, it would be helpful if the elution volume of a branched polymer relative to the linear molecule could be predicted from theory or simulation.

In order to do so one of the authors performed computer simulations of star-shaped and linear polymers in spherical pores in order to predict the correction factors necessary to correct the calibration curve of the linear polymer for the change in the size of the molecule due to branching[6]. These artificial calibration curves have been compared with experimental data on GPC-elution behavior of star-shaped polymers[7].

EXPERIMENTAL SECTION

Simulation

For the calculation of the distribution coefficients, polymer chains were modeled as self-avoiding walks (SAW) on a diamond lattice in order to determine the accessible fraction of the pore volume. For the simulation of the distribution coefficient of a particular conformation, the center of gravity, S, was placed in the center of the pore having radius R_P. An arbitrary direction was chosen, and the displacement vector, r, at which the chain intersects with the wall of the sphere, was calculated (Figure 1). A volume $V_{dir} = 4/3\pi r^3$ was assigned to the particular direction, and the volume was averaged over different directions. The distribution coefficient for this particular conformation was finally obtained as the ratio of the averaged accessible and the total pore volume. The distribution coefficient of the particular configuration was calculated as the average over all SAWs of that configuration.

Other quantities of interest that have been calculated are the mean squared radius *of gyration*, R_g, and the hydrodynamic radius in the non-draining limit, R_h.

Further details of the algorithm can be found elsewhere[6].

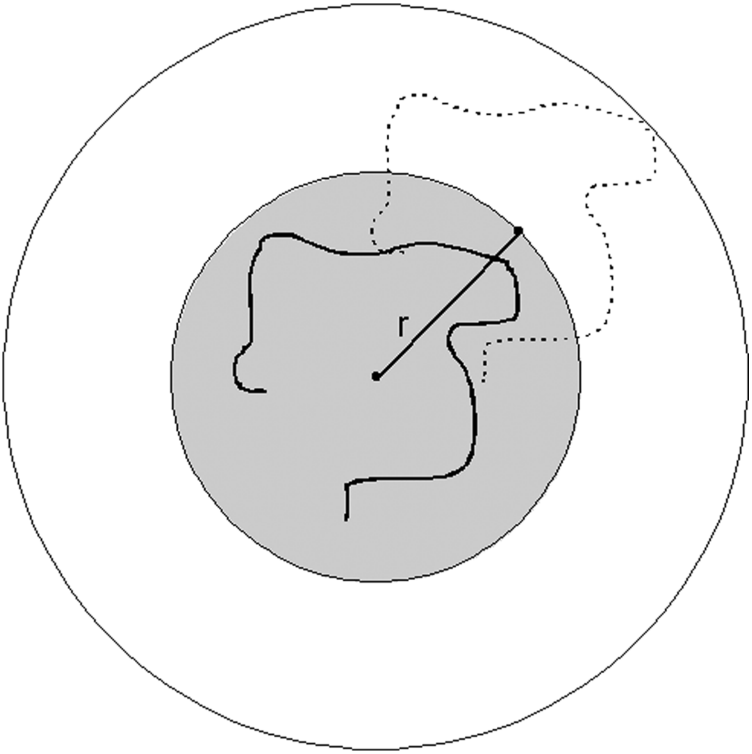


FIGURE 1 Determination of the distribution coefficient. The shift distance, *r*, at which the molecule intersects with the pore walls defines a volume. The average volume with respect to all directions divided by the total pore volume yields the distribution coefficient, *K*, of the particular conformation.

Synthesis

Star polymers, heterogeneous with respect to the number of arms, have been obtained by coupling narrow distributed living polystyrene (PS) anions with either a short poly(methyl methacrylate) (PMMA) molecule or using divinylbenzene (DVB) as coupling agent. These polymers were chromatographically separated into fractions; homogenous with respect to the number of arms, using a shallow acetonitrile/tetrahydrofuran (THF) gradient[7]. Samples prepared using well-defined terminating agents were obtained from PSS Standards Service (Germany) and Prof. A. Hirao[8,9], Tokyo Institute of Technology, Japan. PS and PMMA stars with more defined number of arms were synthesized

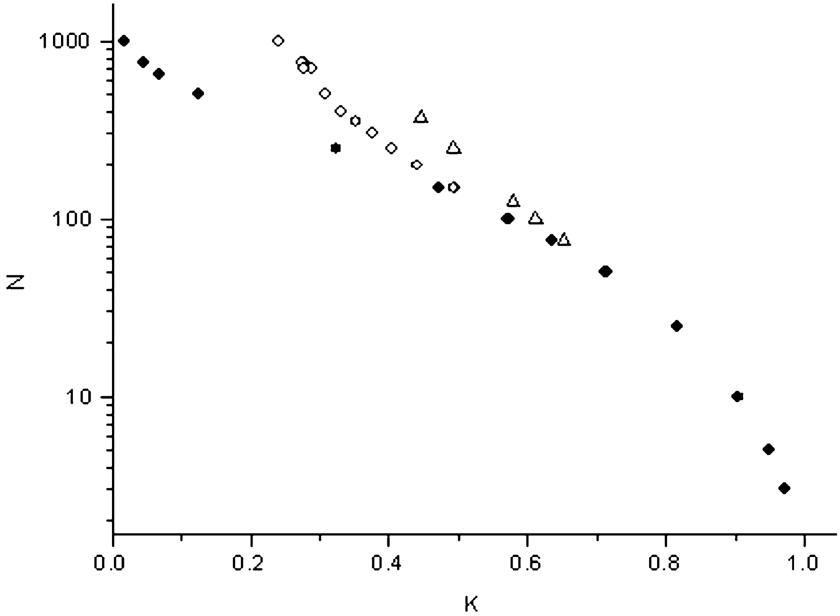


FIGURE 2 Comparison of calibration curves for linear and star-shaped polymers in spherical pores ($R_P = 75$); ●: linear chains, ○: stars $N_{arm} = 50$, △: stars 250 $N_{arm} = 25$.

by atom transfer radical polymerization (ATRP) using initiators with defined functionality[10].

Characterization

GPC analysis was performed in THF at a flow rate of 1 mL/min using a GPC equipped with Waters 510 pump, TSP AS100 autosampler, Waters 486 UV detector operated at 254 nm, Wyatt Technologies DAWN EOS light-scattering, detector, and Waters 410 RI-detector. A set of three columns (PL-Gel mixed B, mixed C, and mixed D, 30 × 0.8 cm each) was used. More detailed information can be found in Radke et al.[7].

RESULTS AND DISCUSSION

Figure 2 shows the simulated calibration curves of linear and star polymers. It is clear that strong deviations exist between the calibration curve of the star and the calibration curve for the linear polymers. Since

GPC separation is based on molecular size and not on molecular weight it was checked which size parameter might be universal. The ease in calculation of the mean-squared radius of gyration as compared to the hydrodynamic radius led to the frequent use of R_g for similar calculations. However, a plot of the distribution coefficient of the different structures as a function of the root-mean-squared radius of gyration shows a clear discrepancy for the curves of different structures (Figure 3). Often the authors relate to the original article by Casassa[11] and claim the ratio R_g/R_P to be the factor determining GPC elution behavior of polymers. However, Casassa's statement was in the context of linear polymers but never in this general form. In the same article he clearly showed that for star polymers the ratio R_g/R_P is not a universal parameter. Full agreement in this respect therefore is found between Casassa's calculations based on the Gaussian chain approximation and the simulations presented in this article.

When we correlate the hydrodynamic radius and the distribution coefficient, however, a nearly perfect agreement of the calibration curves of different topologies is obtained (Figure 4). If the ratio of hydrodynamic

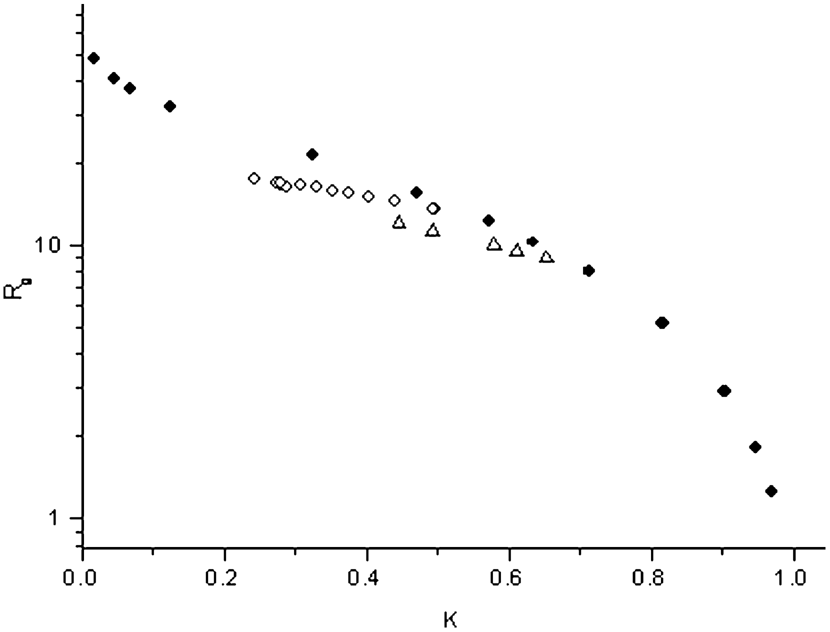


FIGURE 3 Comparison of the dependence of mean-squared radius of gyration on distribution coefficient for linear and star-shaped polymers in spherical pores ($R_P = 75$); ●: linear chains, ○: stars $N_{arm} = 50$, △: stars $N_{arm} = 25$.

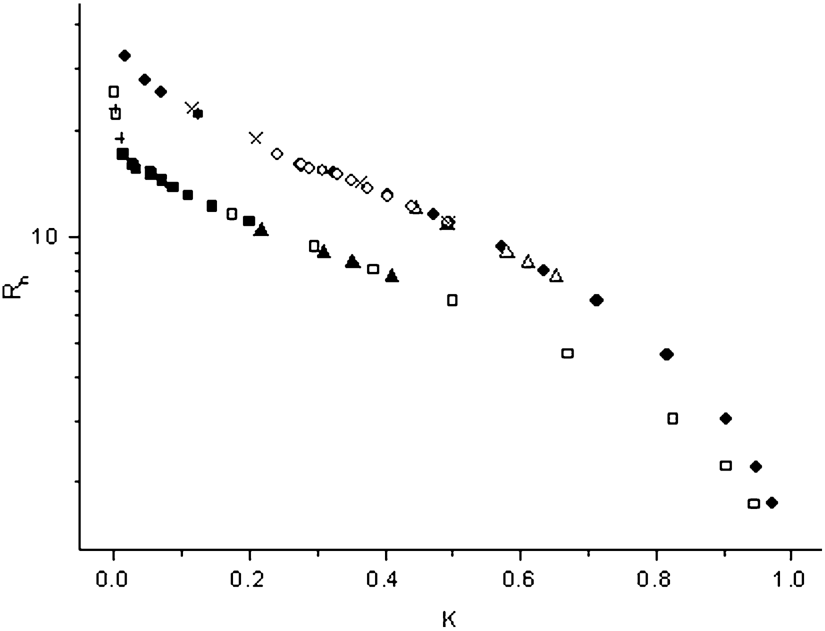


FIGURE 4 Comparison of the dependence of hydrodynamic radius on distribution coefficient for linear and star-shaped polymers in spherical pores of different sizes. $R_P = 75$; ●: linear chains, ○: stars $N_{arm} = 50$, △: stars $N_{arm} = 25$. $R_P = 40$, ■: linear chains, ▽: stars $N_{arm} = 50$, □: stars $N_{arm} =$ 25.

to pore radius is a universal parameter determining GPC elution volume, then the normalized plot R_h/R_P should be independent on pore size. Figure 5 shows such a normalized plot. For $R_h/R_P < 0.1$, slight deviations exist. Two explanations are possible. First, for $R_P = 40$ and $R_h/R_P < 0.1$ the corresponding degrees of polymerization are lower than 20. If the degree of polymerization is low, the equations used for the calculation of the hydrodynamic radius might not be adequate, since these equations are based on Gaussian subchains. A different explanation is as follows. When comparing different pore sizes at the same hydrodynamic volume, we change the ratio of segment length to pore radius R_P. Therefore, the deviations might be explained by changes of chain stiffness. However, despite the simplicity of the simulations of the hydrodynamic ratio, the simulations are useful to give a good qualitative picture.

The goal of the investigation was to predict the GPC-elution behavior of branched polymers relative to the linear analogs. Thus, we are not only interested in a qualitative but also in a quantitative agreement. In order to calculate the calibration curves of star polymers, we compared the

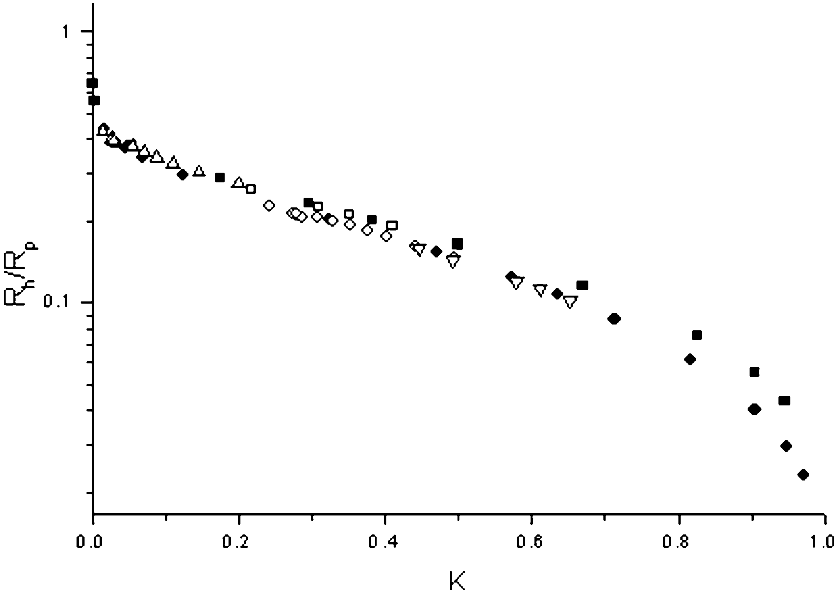


FIGURE 5 Normalized calibration curves for star-shaped and linear polymers in spherical pores of different sizes. $R_P = 75$; ●: linear chains, ○: stars $N_{arm} = 50$, △: 260 stars $N_{arm} = 25$. $R_P = 40$, ■: linear chains, ▽: stars $N_{arm} = 50$, □: stars $N_{arm} = 25$.

molecular weights of the branched polymer and the linear polymer having the same distribution coefficient. We define the ratio $\gamma = M/M_{lin}$ taken at the same distribution coefficient. These ratios are found to be nearly independent of pore size and selected arm length of the star. Figure 6 shows the dependence of the γ-ratios on the number of arms, f. The dependence of γ on arm number can be fitted to the following equation:

$$\gamma_{sim.} = 0.738 + 0.120 \cdot f - 8.67 \times 10^{-4} \cdot f^2 \qquad 20 \geq f \geq 3 \qquad (1)$$

Comparison of the simulated data, the fit according to Equation (1), and Casassa's[11] exact calculations for Gaussian chains shows good agreement (Figure 6), even though for Gaussian statistics, conditions with vanishing excluded volume should be appropriate, while the simulations are performed under good solvent conditions. In this respect, the present simulations show a behavior similar simulations of the branching ratios, $g = \langle R_g^2 \rangle_b / \langle R_g^2 \rangle_l$, where good agreement under good solvent conditions with exact calculations based on Gaussian statistics is found[12–14]. However, for other topologies the effect of the excluded volume cannot

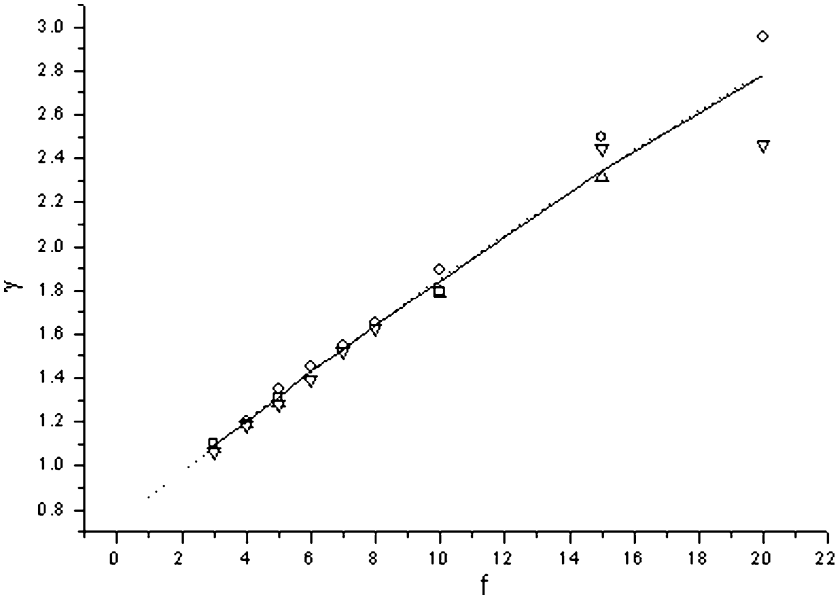


FIGURE 6 Dependence of simulated γ-values on arm number, f, for star polymers of different arm length in pores of different size. $R_P = 75$, ○: stars $N_{arm} = 50$, △: stars $N_{arm} = 25$. $R_P = 40$, ▽: stars $N_{arm} = 50$, □: stars $N_{arm} = 25$. The solid line corresponds to γ-values obtained by calculating calibration curves based on the calculations of Casassa, while the dotted line shows the fitting function according to Equation (1) .

be neglected. Recent simulations the distribution coefficient of comb-polymers show deviations between SAWs and RWs[15]. The deviations between the simulated branching ratios, *g*, of Gaussian chains and self-avoiding walks have also been found by Lipson[17,18] and Radke[19].

In order to compare the simulated γ-ratios with the experimental data, a variety of star polymers were synthesized and investigated by conventional and GPC-light scattering. The molecular weights at the peak maximum obtained from light scattering and conventional calibration were used to calculate γ-ratios as a function of the number of arms. Polystyrene stars of different sources as well as PMMA stars were investigated. Knowing the molecular weight of the star arms and assuming a certain number of arms, we used the simulated γ-ratios to calculate the molecular weight of the linear polymer having identical elution volume. The use of the standard calibration curve then allows assigning the elution volume to the star polymer. The qualitative picture obtained for the calibration curve of stars and linear polymers are very similar to the simulations (Figure 7). It becomes clear that for stars having high molecular weight arms the calculated and true calibration curves agree within approximately 0.1 mL. Thus, the accuracy of the calculated elution volume is better that 1%. The series with arm molecular weights of 5000 g/mol shows a somewhat larger discrepancy between simulation and experiment. However, the error in elution volume still is only about 3%.

Although the error in elution volume is small, it can result in significant errors in molecular weight. Figure 8 therefore shows the ratios $\gamma_{exp.}/\gamma_{sim.}$ which give the error in the molecular weight of the stars if evaluated using a simulated calibration curve. For the majority of the data points the error is less than 10–15%, while the error associated with the use of a standard calibration curves increases to a values of about 50–60% for 10 arms. A closer inspection of the data points falling outside the 15% region reveals that these data points are those having arm molecular weights less than 6000 g/mole or correspond to stars of functionality 3 and 4. The error in the absolute determination of

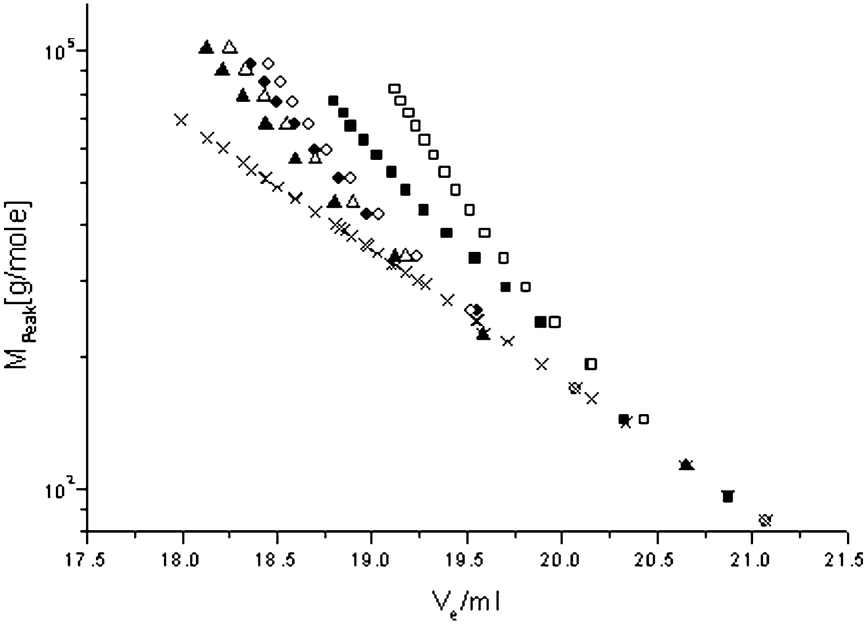


FIGURE 7 True (solid symbols) and simulation based (open symbols) calibration curves for star polymers with an arm molecular weight of $M_{peak,arm} = 4800$, (■□), 8500 (○●), and 11300 (▲△) g/mole in comparison to a calibration curve 270 constructed with linear standards (×).

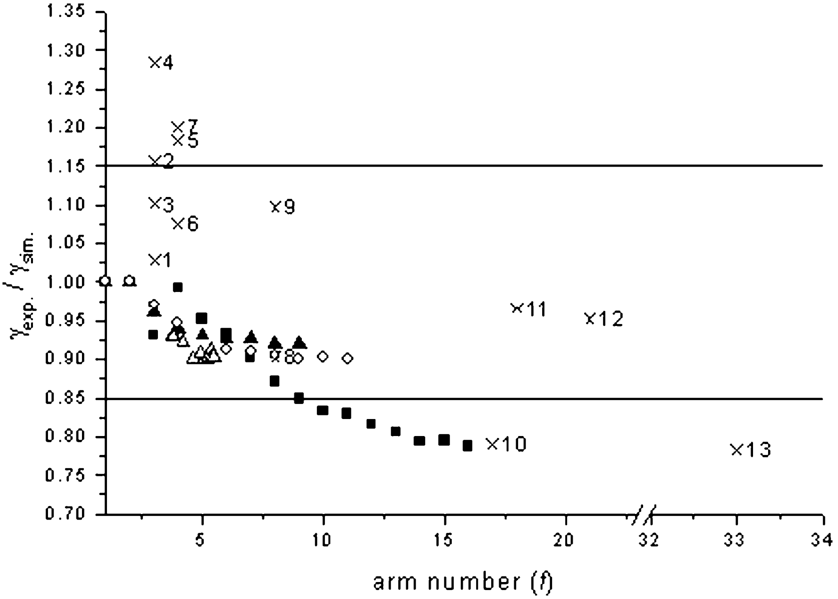


FIGURE 8 Ratios $\gamma_{exp.}/\gamma_{sim.}$ as function of the number of arms for all samples investigated (■: $M_{peak,arm} = 4500$ g/mole, ○: $M_{peak,arm} = 8500$ g/mole, ▲: $M_{peak,arm} = 11300$ g/mole, △: data taken from Lipson[17], × : others). Lines denote 15% errors. The numbers correspond to the entries in Table I.

molecular weights of polymers is in the order of 10–15%. Since for the stars with three and four arms the error associated with the use errors of a conventional calibration curve is in the order of 5–20%, the errors in molecular weight determination will easily cover the systematic errors associated with the use of the linear calibration curve. It is therefore reasonable to conclude that for sufficiently long arms the use of simulated calibration curves for star polymers is as accurate as the absolute determination of their molecular weights.

During the investigations of the star polymers by GPC we found shoulders at the high molecular side of the refractive index (RI) chromatograms (Figures 9 and 10). These shoulders show up even stronger in the LS traces. Similar observations have been described in literature[10,16]. For the three-arm star prepared by ATRP the light-scattering analysis yields a molecular weight of 28600 g/mol and $\gamma_{exp.} = 1.2$ for the peak maximum of the RI (Figure 9). For the peak maximum of the light-scattering signal we obtain a molecular weight of approximately 54000 g/mole and $\gamma_{exp.} = 1.12$. Thus, the molecular weight of the unknown second peak is about twice the molecular weight of the

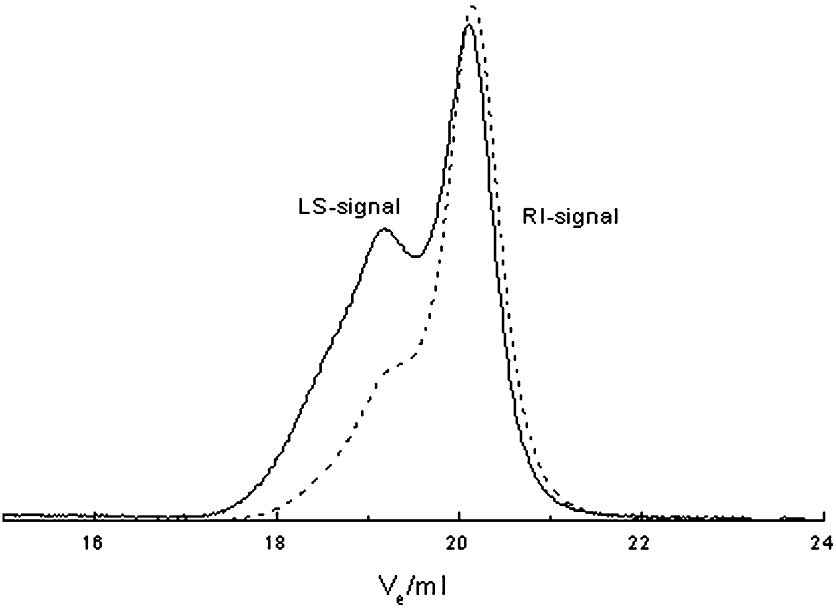


FIGURE 9 RI (dotted curve) and 90°LS trace (solid curve) for three-arm star polymer obtained by ATRP.

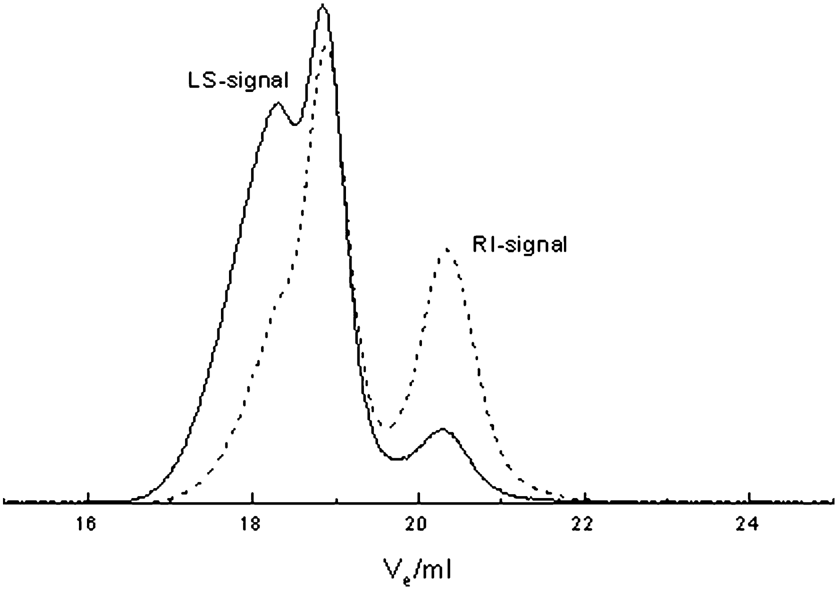
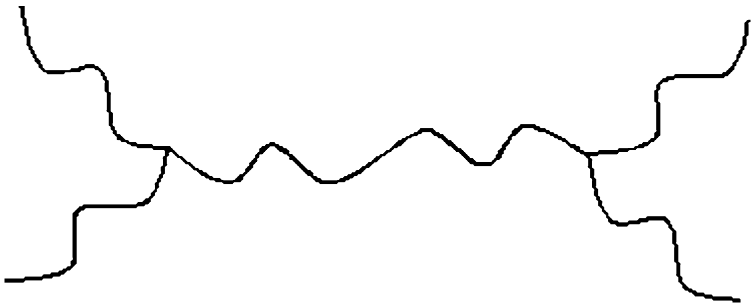


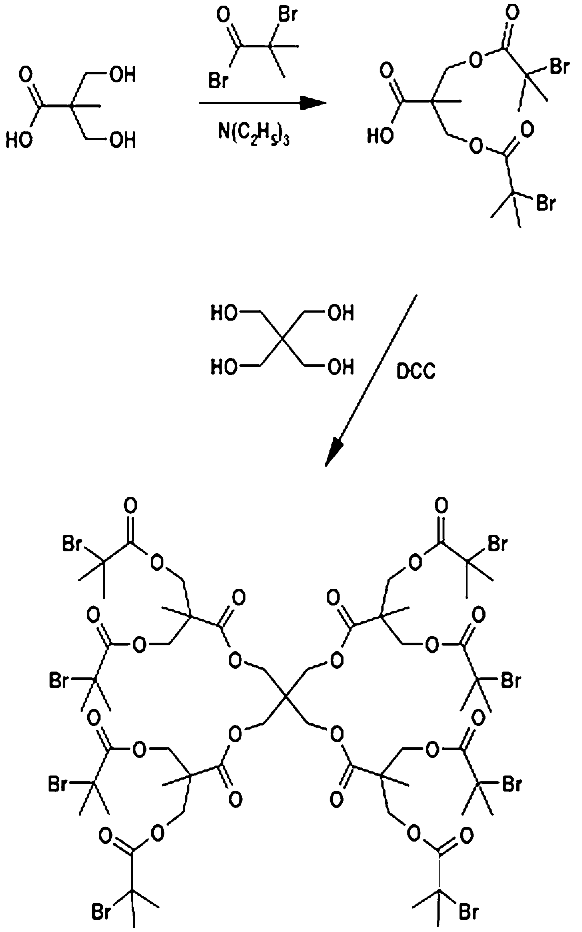
FIGURE 10 RI (dotted curve) and 90°LS trace (solid curve) for eight-arm star polymer obtained by ATRP.

first peak, indicating a coupling reaction. If, after consumption of the monomer, two living radicals combine at their growing arms, a dumbbell topology should result (Scheme 1). The distance between the two branch points is then twice the molecular weight of an arm. For such a structure we performed computer simulations similar to those for the stars. We obtained a value of $\gamma_{sim.} = 1.10$ for a branch point functionality of 3. The experimental value ($\gamma_{exp.} = 1.12$) therefore perfectly fits this picture.

A second example for side reactions occurring in ATRP is obvious from the chromatograms of an eight-arm star shown in Figure 10. Here three different species can be distinguished. The molecular weights of these species as determined by GPC-light scattering are 15000, 58800, and 111000 g/mole. Using the apparent molecular weights from the conventional calibration curve, the γ-ratios found are $\gamma_{exp.} = 1.06$, 1.53, and 1.90, respectively. A value of $\gamma_{sim.} = 1.64$ is expected for the eight-arm star. Thus, a value of $\gamma_{exp.} = 1.06$ is much too low for the expected structure. By comparison of the molecular weights of the first and second peak we realize that the molecular weight of the second peak is approximately four times the molecular weight of the first one. The synthesis of the octafunctional initiator includes a coupling reaction of bifunctional initiator moieties with a tetrafunctional linking agent (Scheme 2). It is therefore reasonable to assume, that due to insufficient cleanup of the final product, residues of the bifunctional initiator are responsible for the peak at the highest elution volume. The low value of the γ-ratios supports this assumption. The second peak has to be interpreted as the expected eight-arm star in good agreement with the γ-ratio found ($\gamma_{exp.} = 1.53$, $\gamma_{sim.} = 1.64$). The third peak has about twice the molecular weight of the star and might be attributed again to the dumbbell structure resulting from the coupling reaction of two eight-arm stars. Agains, a good agreement is found for experimental and expected and γ-ratios ($\gamma_{sim.} = 1.79$, $\gamma_{exp.} = 1.90$).



SCHEME 1 Dumbbell topology resulting from coupling of three-arm stars.



SCHEME 2 Synthesis of octafunctional initiator for ATRP.

CONCLUSION

Simple SAW simulations in spherical pores allow predicting the calibration curves of star-branched polymers relative to linear ones. The errors associated with the use of a simulated calibration curve are of the same magnitude as the errors associated with absolute methods for molecular weight characterization. The calculated ratios between the true and the apparent molecular weight can be used as a tool to prove assumptions about unknown structures occurring due to side reactions.

REFERENCES

[1] Haney, M. A. (1985). *J. Appl. Polym. Sci.* **30**, 3037.
[2] Haney, M. A. (1985). *J. Appl. Polym. Sci.* **30**, 3023.
[3] Haney, M. A. (1985). *Ame. Lab.*
[4] Wyatt, P. J. (1994). *Anal. Chim. Acta.* **677**, 21.
[5] Yau, W. W. (1990). *Chemtracts Macromol. Chem.* **1**, 1.
[6] Radke, W. (2001). *Macromol. Theory. Simul.* **10**, 668.
[7] Radke, W., J. Gerber, and G. Wittman. (2003). *Polymer* **44**, 519.
[8] Hirao, A. (2001). Paper presented at the International Symposium on Ionic Polymerization, Crete.
[9] Hirao, A., M. Hayashi, and N. Haraguchi. (2000). *Macromol. Rapid Commun.* **21**, 1171.
[10] Matyjaszewski, K., P. J. Miller, J. Pyun, G. Kickelbick, and S. Diamanti. (1999). *Macromolecules* **32**, 6526.
[11] Casassa, E. F. and Y. Tagami. (1969). *Macromolecules* **2**, 14.
[12] Zifferer, G. (1991). *Makromol. Chem.* **192**, 1555.
[13] Zifferer, G. (1990). *Makromol. Chem.* **191**, 2717.
[14] Zifferer, G. (1992). *Macromol. Simul.* **1**, 55.
[15] Radke, W. (submitted). *Macromolecules.*
[16] Angot, S., K. S. Muthy, D. Taton, and Y. Gnanou. (1998). *Macromolecules* **31**, 7218.
[17] Lipson, J. E. G. (1991). *Macromolecules* **24**, 1327.
[18] Lipson, J. E. G. (1993). *Macromolecules* **26**, 203.
[19] Radke, W. 1999. Ph.D.diss. Technische Universität Mainz.