

CHARACTERIZATION OF COMB-SHAPED POLYMERS USING GPC-MULTI-DETECTION METHODS

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Introduction

Polymers with non-linear topologies have been subject of interest for a long time. However, a lack of suitable methods exists for the determination of the extent of branching in unknown polymers. Most approaches to determine the extent of branching are related to the size reduction of branched molecules relative to linear analogues of same molecular weight. The drawback is that technical polymers exhibit broad molecular weight distributions, but theories relating experimentally accessible quantities to branching are mostly applicable to monodisperse polymers¹. GPC with light scattering and/or viscosity detection is therefore assumed to be the method of choice. After separation into nearly monodisperse fractions, molecular weights and size-related properties (e.g. radius of gyration R_g , or intrinsic viscosity, $[\eta]$) can be obtained. Using these informations it might be possible to relate the contraction factors $g = \langle R_{g,br}^2 \rangle / \langle R_{g,l}^2 \rangle$ and $g' = [\eta]_{br} / [\eta]_l$ (the index *br* denotes the branched, the index *l* the linear molecule of same molecular weight) of nearly monodisperse fraction to theory and thus to degree of branching.

In order to test the suitability of GPC-LS or GPC-viscometry we have synthesized comb-shaped polymers which by incorporation of a UV-label into the side chains allow for independent characterization of the amount of side chains with each elution slice. Knowing the number and the molecular weights of side chains and branched polymer, it is possible to compare the theoretically expected g_0 and g_0' values with those found using GPC-LS/ GPC-viscometry (g , g').

Finally it is possible to compare the results obtained using GPC-LS/ GPC-viscometry on broad samples with literature data on narrow distributed model combs.

Experimental

Synthesis: Comb-shaped poly(p-methylstyrene)s were synthesized by grafting phenanthrene-labeled poly(p-methylstyrene)anions onto partially brominated linear poly(p-methylstyrene)s. The incorporation of the phenanthrene group into the side chains was achieved by reacting living poly(p-methylstyrene)anions with 1-phenanthryl-1-phenyl-ethylene prior to the coupling reaction.

Characterization: GPC analyses were performed in THF at 0.5-1ml/min using 5 μ PSS SDV columns (10³, 10⁵, 10⁶ Å, 30 · 0.8 cm each). Applied Biosystems S1000 UV diode array and Bischoff 8110 RI detectors were used. A Viskotek H502 B and/or a Wyatt Technology DAWN-F multi-angle light scattering detector could be added. Data acquisition was performed using PSS WinGPC and Wyatt Technology Winastra software. The injected amounts and flow rates were adjusted depending on molecular weights and polydispersities of the samples.

Simulation: Computer simulations were performed using an algorithm that creates non-reversal random walks on a tetrahedral lattice, which in a subsequent routine were transformed into self-avoiding walks using a random mixture of reptation and pivot algorithms². After expansion to self-avoiding walks, data were sampled until a steady average was reached for R_g^2 . Typically, a number of about 5*N* conformations was needed for one average (*N* = number of segments within the chain). 100 of such averages were sampled and batch averaged for each structure to obtain the final average of the property of interest.

Results and Discussion

The slope and curvature of the Mark-Houwink plot is often used to detect branching in polymers. By GPC-LS/viscometry we found that the Mark-Houwink exponents for combs do not differ much from those of linear polymers, in contrast to the Mark-Houwink plots of randomly branched polymers. Thus, comb polymers cannot be identified as branched polymers only by their Mark-Houwink exponents. As expected, increasing the fraction of material in the side chains results in lowering the intrinsic viscosity of the polymer. Similar behavior

is found for the exponent of the relationship $\langle R_g^2 \rangle^{1/2} \propto M^{a_s}$. The results are summarized in Table 1.

Table 1. Exponents of log R_g vs. log M and log $[\eta]$ vs. log M for Comb-shaped Poly(p-methylstyrene)s in THF. w_{SC} = weight fraction of side chains, I = percentage of branched backbone units

$M_{n,SC}$	I	w_{SC}	a_s	a_h
linear	0	0	0.57	0.73
3740	1,68	0,35	0,55	0,68
	0,69	0,18	0,53	0,69
	0,88	0,22	0,54	0,68
	0,47	0,13	0,53	0,68
11100	1,55	0,59	0,55	0,66
	0,61	0,36	0,50	0,67
	0,72	0,40	0,57	0,68
	0,38	0,26	0,55	0,66
15400	1,37	0,64	0,57	0,66
	0,58	0,43	0,52	0,66
	0,63	0,45	0,57	0,66
	0,35	0,31	0,59	0,68

The correlation between branching parameters and experimentally accessible quantities is mostly obtained from contraction factors, g . However, intrinsic viscosity and thus the contraction factor g' is much easier obtained experimentally. The relationship between g and g' is commonly written as $g' = g^e$ where $e = 3/2$ based on the Flory-Fox equation³. Knowing the weight fraction of the side chains (from the UV analysis of the label) and their molecular weight as well as the total molecular weight of the polymer from GPC-LS analysis, it is possible to calculate the theoretically expected contraction factors, g_0 , based on Gaussian chain statistics⁴ and to compare those with the ones obtained experimentally from GPC-LS or GPC-viscometry (using the Flory-Fox approximation).

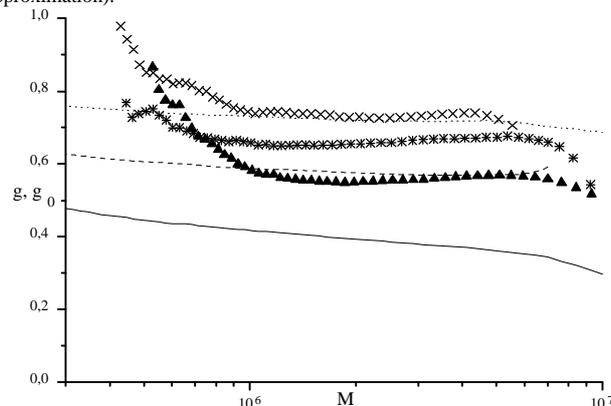


Figure 1: Experimentally found g (points), and theoretically predicted g_0 (lines), dependencies of contraction factors on molecular weight. Side chain molecular weight $M_n = 11100$, \times , \cdots : $\lambda = 0.38\%$; $*$, $---$: $\lambda = 0.72\%$; \blacktriangle , $---$: $\lambda = 1.55\%$ (λ = percentage of branched backbone units)

Fig. 1 shows the experimentally obtained g and the theoretically calculated g_0 values as a function of the molecular weight of the comb polymer. The contraction factors, g , as well as the expected ones, g_0 , do not vary much with molecular weight. This is a consequence of the homogenous distribution of side chains along the backbone. For a large number of side chains g_0 is expected to depend only on the weight fraction of material in the side chains⁴. Since from the UV analysis it is found, that the weight fraction of material stays relatively constant across the sample (i.e. there is a linear correlation between number of side chains and molecular weight), g_0 has to stay constant too. It becomes clear that the g values exceed the ones expected from Gaussian chain statistics. The

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same result is obtained for g values which have been calculated from experimentally obtained g' values based on the Flory-Fox equation.

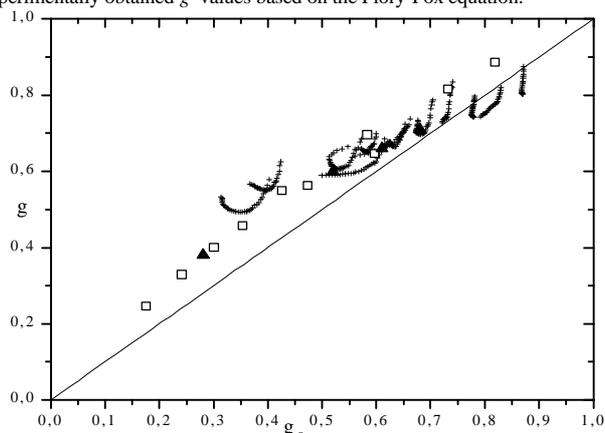


Figure 2. Comparison of experimentally obtained g vs. g_0 relationship with literature data⁵ (□) and simulated results (▲)

The effect of excluded volume on g was investigated using computer simulations⁷. These simulations were performed choosing a side chain length, N_{SC} , of 15 units. The spacing, s , between the side chains was kept constant and the molecular weight of the polymer, N , was increased by simultaneously increasing the length of the backbone and the number of side chains. As for the experimental data, g is found to exceed g_0 calculated on Gaussian chain statistics. g and g_0 approach limiting values for large molecular weights. The limiting values can be used to compare the dependence of g vs. g_0 found by experiment and simulation. Fig. 2 shows that the extrapolated values of the simulations yield a satisfactory agreement with experiment.

An interesting result is obtained upon plotting the ratio of the intrinsic viscosity of the comb polymer to that of the parent backbone polymer, $g'' = [\eta]_{br} / [\eta]_{bb}$ (bb = backbone), as a function of the ratio of side chain distance, s , over side chain length, $P_{n,SC}$ (Fig. 3). It is observed that the intrinsic viscosity of the comb-shaped polymer is nearly equal to that of the parent backbone. Only when the length of the side chains becomes larger than the spacing the relative viscosity increases significantly. In these cases the shape of the polymer resembles closer that of a star-shaped structure than of a comb.

The exponent e in the relation $g' = g^e$ takes a value of $3/2$ based on the Flory-Fox equation while Zimm and Kilb⁸ calculated $e = 1/2$ for star polymers and assumed this value to be universal for branched polymers. The use of GPC-

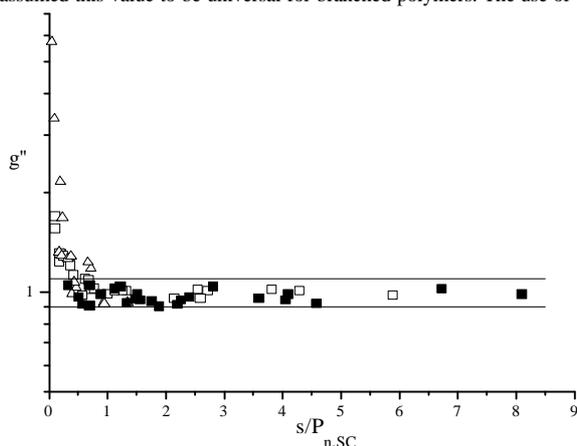


Figure 3: $g'' = [\eta]_{br} / [\eta]_{bb}$ (bb = backbone) as function of the ratio of side chain distance, s , to side chain length, $P_{n,SC}$. The lines correspond to a 10% deviation between the viscosity of comb polymer to parent backbone polymer. ■: this work, △, □: literature data.^{5,6}

LS and GPC-viscometry allows the determination of the parameter e from broad samples. It becomes clear from Fig. 4 that none of the proposed values for e yield satisfactory agreement with the data obtained. Instead a value of $e = 1$, i.e., $g' = g$, seems to be appropriate from our results, and agrees well with data taken from literature.

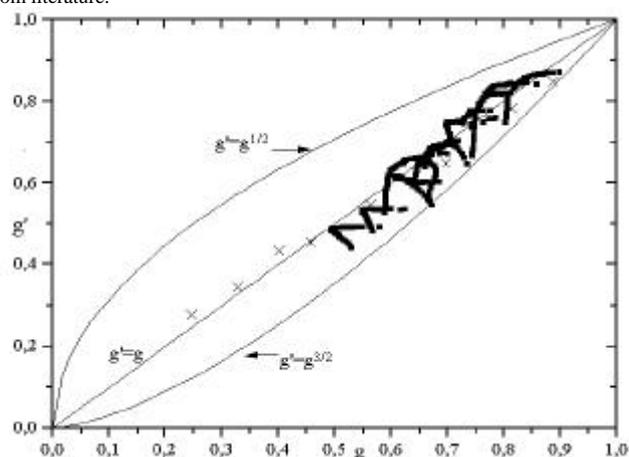


Figure 4. Dependence of g' on g for broad distributed poly(p-methylstyrene) combs. For comparison, data of Roovers⁵ (×) are shown, as well as the dependencies $g' = g^e$ for $e = 3/2, 1$ and $1/2$.

Conclusions

The use of GPC-LS or GPC-viscometry allows the determination of contraction factor as well as the parameter e in the relationship $g' = g^e$. Neither $e = 3/2$ nor $e = 1/2$ which are deduced from theoretical considerations yield satisfactory agreement with experiment. A value of $e = 1$ seems more appropriate. The deduction of the number of branches from experimentally obtained contraction factors gives no satisfactory results. The reason might be an inadequate description of the contraction factors in good solvents by existing theories which are based on Gaussian distribution functions. Computer simulations for self-avoiding walks seem to offer a better agreement. Finally, it is found that the intrinsic viscosity of comb-shaped polymers is merely given by that of the backbone as long as the distance between the side chains is not closer than about $1/2$ of the side chain length.

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