Synthesis, Temperature Gradient Interaction Chromatography, and Rheology of Entangled Styrene Comb Polymers

Pierre Chambon,[†] Christine M. Fernyhough,[†] Kyuhyun Im,[‡] Taihyun Chang,[‡] Chinmay Das,[§] John Embery,[§] Tom C. B. McLeish,[§] and Daniel J. Read*[,||]

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom; Department of Chemistry and Center for Integrated Molecular Systems, Pohang University of Science and Technology, Pohang 790-784, South Korea; School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, United Kingdom; and Department of Applied Mathematics, University of Leeds, Leeds LS2 9JT, United Kingdom

Received March 18, 2008; Revised Manuscript Received May 6, 2008

ABSTRACT: We present the synthesis of polystyrene combs via an improved procedure, which allows the average number of arms to be small (3−5) but well controlled. It is shown that temperature gradient interaction chromatography (TGIC) proves to be a highly effective method for the analysis of these combs, providing directly the distribution of the number of arms on the synthesized comb molecules. We use this arm-number distribution to model the linear rheology of an entangled melt of such combs, via our previously published algorithm [Das et al. *J. Rheol.* 2006, *50*, 207−234], and demonstrate that this compares favorably with the measured linear rheology. A comparison is also made with the predicted rheology for two alternative assumptions about the distribution of arms on the comb, (i) where it is assumed that the addition of arms is an ideal random process and (ii) where there is a fixed number of arms per comb. These predictions also agree well with the experimental results, thus supporting the validity of simpler analytical approaches based on constant arm number, at least for the arm-number distribution considered here.

1. Introduction

For the past two decades, the study of well-characterized, monodisperse polymer melts of fixed chain architecture has been of central importance in the development of our understanding of the linear rheology of entangled polymer melts.[1] Carefully synthesized stars (both regular[2] and asymmetric[3]), H-polymers,[4] pom-poms,[5] combs,[6–16] and (most recently) Cayley trees[17] have provided a testing ground for theoretical developments in the tube model of entangled polymers. Of these, the combs are, in one specific detail, different from the rest. Although melts of all the other architectures inevitably contain impurities, by the very nature of the synthesis route used to make them combs contain an inherent distribution in the number and placement of arms along their backbone. It is, in principle, possible to make perfectly regular combs via a step-by-step synthesis, but this has so far been deemed prohibitively time-consuming and may yet result in a different set of impurities through side reactions (for example, May's "centipedes" by condensation reactions render broad polydispersity[18]).

How, then, should one model the linear rheology of a comb melt? Analytical models have been proposed[16,19,20] in which the number of arms is assumed to be a fixed quantity set at the average value for the melt. These models fit the experimental rheology well, but it is not clear whether the fitting parameters are actually dependent on the assumption of fixed arm number: would a more detailed model which included a distribution in arm number give an equivalently good fit but with different parameters? Recently, some of us developed a computational algorithm,[21] based on earlier work by Larson,[22] which is able to predict the linear rheology of an arbitrary distribution of branched polymers on the basis of the tube model. This algorithm uses, as input, a numerically specified (and potentially large) ensemble of branched polymer architectures and so can address a set of combs with a known distribution in the number of arms, placed at different positions along the backbone. This, however, generates a secondary question: what distribution of arm number and placement should one use? Assumptions can be made about (for example) random placement of arms along the backbones during the reaction (purely random placement gives a Poisson distribution for number of arms). However, it is not certain that this assumption is correct, and there remains the unknown of what happens during purification of the material. All such polymers are fractionated to remove unreacted arms and backbones, but this process may also affect the distribution of the combs themselves. It would be advantageous to measure the actual distribution of comb architectures present in the melt.

Size exclusion chromatography (SEC) is not an adequate characterization method to address this problem. Comb polymers with different numbers of side arms have similar hydrodynamic radii and so are not well separated. Fortunately, temperature gradient interaction chromatography (TGIC) provides a viable separation route because IC retention is almost independent of architecture for long chain branching and is determined by MW.[23–25] Furthermore, IC shows a far better resolution than SEC, which suffers from serious band broadening.[26,27]

In this paper, we present a novel procedure for the synthesis of polystyrene combs with a small, but well controlled, average number of side arms. We shall present their characterization by SEC and TGIC and in particular demonstrate that the latter provides an effective method for characterization by separation according to number of arms (giving the arm-number distribution of the synthesis product). We use this distribution to predict the linear rheology of the combs, comparing against the experimental rheology of the synthesis product. We also compare the measured arm distribution against the assumption of random addition of arms and investigate the effect of this assumption (and the assumption of fixed arm number) on the linear rheology prediction. We restrict ourselves to linear rheology in this article, since models of nonlinear rheology are

* To whom correspondence should be addressed.
[†] University of Sheffield.
[‡] Pohang University of Science and Technology.
[§] School of Physics and Astronomy, University of Leeds.
[||] Department of Applied Mathematics, University of Leeds.

10.1021/ma800599m CCC: $40.75
Published on Web 07/03/2008

Table 1. Weight-Average Molecular Weight (M_w), Number-Average Molecular Weight (M_n), Polydispersity Index (PDI), and Average Number of Side Arms n_{arm} for Polystyrene Combs (PSC2 and PSC3) and Polystyrene Linear Polymers (PSL250 and PSL500)[a]

	backbone		arm		comb		
	M_w/M_n ($\times 10^3$)	PDI	M_w/M_n ($\times 10^3$)	PDI	M_w/M_n ($\times 10^3$)	PDI	av n_{arm}
PSC2	185/176	1.05	64/63	1.02	460/420	1.1	3.9 (3.9)
PSC3	200/190	1.05	85/83	1.02	595/540	1.1	4.2 (4.0)
PSL250	262/252	1.04					
PSL500	523/459	1.14					

[a] For the comb molecules, n_{arm} is estimated from number-averaged molecular weights. The value in parentheses is the average from the TGIC analysis.

not yet sufficiently advanced to make a quantitative prediction, dependent on the distribution of arm number.

2. Experimental Section

Comb Synthesis. Styrene (Aldrich) and deuterated d_8-styrene (CK gas) were initially dried over CaH_2 and then distilled from dibutylmagnesium prior to use. Benzene (Aldrich) was distilled from *n*-BuLi, to which a little styrene was added, an orange color indicating that the solvent was dry and oxygen-free. THF (Fisher) was first dried over CaH_2 and then distilled from sodium benzophenone prior to use. *sec*-BuLi (Aldrich) was distilled over a short-path using a coldfinger and diluted with dry cyclohexane, and the molarity of the resulting solution was determined by titrating a known volume against standard HCl using phenolphthalein as an indicator. Dimethoxymethane, thionyl chloride, and zinc(II) chloride (Aldrich) were used as received.

Anionic polymerization of styrene was performed using high-vacuum techniques,[28] reagents being transferred into a reactor via break-seals. *sec*-Butyllithium was used as the initiator and benzene as the solvent. The reactions were performed at room temperature overnight. Degassed methanol was used to terminate the reactions.

Chloromethylation reactions (performed with great caution in a well-ventilated fume hood) were performed using the method of Wright et al.,[29] whereby chloromethyl methyl ether was formed by the in situ reaction of dimethoxymethane and thionyl chloride in the presence of a Lewis acid catalyst (zinc(II) chloride). In a typical preparation PS (10 g, 190 000 g/mol) was dissolved in dimethoxymethane (50 cm^3) and the flask sealed under nitrogen. The solution was cooled to 0 °C and thionyl chloride added (18.5 cm^3, 0.25 mol); the solution was stirred at room temperature, and then the catalyst (0.4 mmol) was injected into the solution at 0 °C and then placed in a water bath at 30 °C. After 2.5 h the polymer was precipitated in methanol, redissolved in dichloromethane, precipitated once more, and then dried under vacuum.

The chloromethylated polystyrene was charged to a large ampule fitted with a greaseless stopcock, then freeze-dried from benzene, dissolved in THF (<5% w/v), and attached to a reactor. Polystyryllithium (PSLi) was synthesized in the reactor as described above. Benzene was removed from the living polystyrene by distillation and replaced with dry THF. A 3-fold molar excess of 1,1-diphenylethylene (DPE) was added to the PSLi, instantly turning the solution deep red. The temperature was lowered to −78 °C, and the chloromethylated backbone rapidly mixed with the PSLi branches. After the rapid disappearance of the characteristic red color of the DPE-end-capped PSLi, the temperature was raised to −50 °C and the solution stirred for 3 h. A 3× excess of diphenylhexyllithium was then injected into the reactor in order to react with any remaining chloromethyl groups. The temperature was allowed to slowly rise to room temperature and left stirring overnight. The product was collected after precipitation into methanol and dried under vacuum. In order to remove small amounts of residual linear polystyrene, fractionation was performed by the addition of 60−80 petroleum ether to a 1% solution of polymer in toluene.

In a typical reaction (e.g., PSC3) 15 g of backbone material was added to 27 g of polystyryllithium branches. The resulting polymer was fractionated, and similar fractions (according to SEC traces) were then combined. In this way, of order 20 g of comb material presenting the same average number of branches was gathered. Other fractions were retained separately with a view to possible further fractionation/purification processes.

NMR Characterization. ^{1}H NMR spectroscopy was performed in $CDCl_3$ at 30 °C using a Bruker AC250 MHz spectrometer. The number of chloromethylated styrene units was calculated using the peak integrals of the CH_2 protons adjacent to the chlorine at 4.5 ppm with the CH_2−CH protons of the PS backbone resonating between 0.7 and 2.5 ppm and/or the five aromatic protons located between 6 and 7.5 ppm.

SEC Analysis. For SEC analysis, two mixed bed columns (Polymer Laboratories., PLgel Mixed-C, 300 × 7.5 mm) were used at a column temperature of 40 °C. SEC chromatograms were recorded with a multiple detector (Viscotek TDA 300), light scattering (LS) detection at two scattering angles 7° and 90°, and refractive index (RI) detection at a wavelength of 670 nm. THF (Samchun, HPLC grade) was the eluent at a flow rate of 0.8 mL/min. Polymer samples were dissolved in THF at a concentration of ∼0.5 mg/mL, and the injection volume was 100 μL. The SEC characterization results of backbone and arm precursor materials are summarized in Table 1.

HPLC Analysis. For the normal phase temperature gradient interaction chromatography (NP-TGIC) analysis, a silica column (Nucleosil, 7 μm, 500 Å pore, 250 × 2.1 mm) and a mixed eluent (57/43, v/v) of *n*-hexane (Samchun, HPLC grade) and THF (Samchun, HPLC grade) were used. Injection samples were dissolved in a small volume of the eluent. The temperature of the column was controlled by circulating fluid from a programmable bath/circulator (ThermoHaake, C25P) through a homemade column jacket. NP-TGIC chromatograms were recorded with a light scattering/refractive index (LS/RI) detector (Wyatt MiniDawn/Shodex RI-101) for online determination of the absolute molecular weight of polymers.

Rheology Measurements. The samples were dried under vacuum for 2 days at 95 °C in order to completely remove all residual methanol. The linear oscillatory rheology on the polystyrene combs and two linear samples (properties shown in Table 1) were carried out on a Rheometrics dynamic analyzer (RDA2) using 10 mm parallel plates. The temperatures employed for the analysis range was from 130 to 230 °C, using a frequency range from 100 to 0.1 rad/s at each temperature. The reference temperature was 170 °C for the purposes of time−temperature superposition, which for practical purposes appeared to work within experimental error. The peak strain applied to the samples varied with temperature from 1% at 130 °C to 3% and 5% respectively for PSC2 and PSC3 at 230 °C. These strains were well within the linear response regime.

3. Results and Discussion: Synthesis and Characterization

Several methods for the synthesis of well-defined polystyrene combs have been previously reported.[6–13] Nevertheless, it remains a challenge to limit the number of arms present on such a comb via the usual generic method of functionalizing the backbone and then substituting the functional group with a polymer chain. In previous experiments it was found that some control could be exerted over the number of chloromethyl groups on a polystyrene chain, through the regulation of the concentration of reagents, the reaction time, and temperature. However, if one wishes to synthesize a comb with a small but *specific* number of arms, it is difficult to do this by limiting the extent

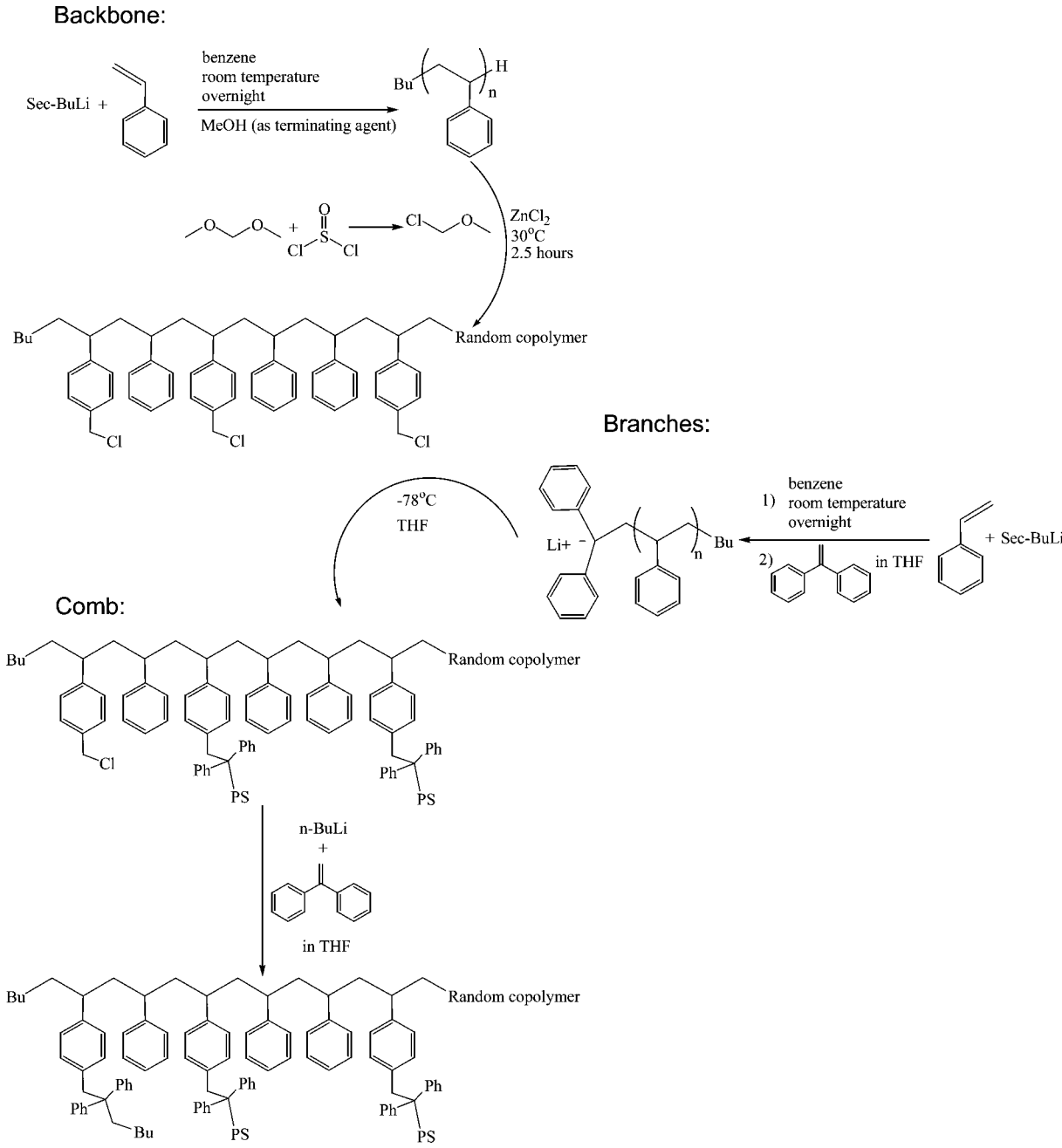

Figure 1. Reaction scheme for comb synthesis.

of a catalytic reaction.[14] The synthesis of combs with less than 10 arms per chain was found to be prohibitively difficult using this route. Additionally, the fewer the number of chloromethyl groups present on a long polystyrene chain, the more inaccurate becomes the calculation (from NMR integrals) of the number of chloromethyl groups. This is particularly an issue if routine analysis with a 250 MHz machine is employed (although greater accuracy would be expected if 500 MHz or even 800 MHz was used).

An alternative strategy is described in the Experimental Section. For these reactions, the estimated number of chloromethyl groups per backbone was 20 and 30 for PSC2 and PSC3, respectively. In order to attain a comb with <5 arms per chain, it proved to be judicious to add a limited number of arms to a backbone chain having an excess of functional groups as described in the Experimental Section: thus, the stoichiometric ratio of backbone:arms ultimately controlled the final number of arms. A reaction scheme is shown in Figure 1. The addition of diphenylhexyllithium to remove the excess functional groups was performed so that only C−C and C−H/C−D bonds were present in the final product as confirmed by NMR analysis; the rheology of the samples requires elevated temperatures, and the stability of the product with regards to decomposition and cross-linking has to be a prime consideration.

This general strategy for the comb synthesis was based on previous work regarding polybutadiene combs[15] whereby a small number of functional groups were introduced onto a polybutadiene backbone via a platinum-catalyzed hydrosilylation reaction. A limited number of polybutadienyllithium branches were then added, the few remaining functional groups being reacted with *n*-butyllithium in order to ensure that the final product was stable. A series of combs having a similar number of arms were thus produced, the only variation between samples being the arm length. The solution properties and the rheological properties of these materials could then be related to their molecular parameters.[15,16]

For the polystyrene combs studied here the main difference between the two samples is the level of deuteration; i.e., one comb was fully hydrogenous (PSC2) and one had deuterated arms and a hydrogenous backbone (PSC3: the deuteration is for a future neutron scattering study but of no specific relevance to the results in this article). It can be seen from the SEC results in Table 1 that for both the samples only an average of around 4 arms are present per comb molecule (this average is calculated from the number-average molecular weights of comb, arms, and backbone). The average backbone molecular weight for the two polymers differs by less than 8% and is of the order of 190 000 g/mol. The arm length of PSC3 is ~21 000 g/mol greater than for PSC2; this is equivalent to about 1.5 entanglements. It is important to note that for both samples the arms will be lightly entangled and that the backbone is lightly entangled between branch points.

Using the method described above, addition of arms to the backbone is a random process, and as such there will be a distribution in the number of arms per molecule and also variations in the position of the branch points. In SEC analyses, the polymer molecules are separated by the chain size in the eluent. The chain size not only is a function of molecular weight but also depends on the chain architecture. Therefore, SEC cannot separate branched polymers according to molecular weight if the branched polymer is structurally heterogeneous. As a result, SEC is not able to provide information on the distribution of the number of arms per backbone, but only its average. Although one can, making assumptions about the reaction statistics, derive a plausible distribution, it would be useful to test these assumptions by making a direct measurement. In contrast to SEC, IC retention is almost independent of architecture for long chain branching and is determined by molecular weight; therefore, for the comb polymers in this study with uniform backbone and arm lengths but with a distribution in the number of arms, IC is a better method to separate them in terms of the number of arms.

Figure 2 displays two TGIC chromatograms of the comb-shaped PS samples recorded by LS and RI detector. The IC elution sequence is opposite to the SEC separation. The column temperature was varied by a few linear ramps during the elution as shown in the upper abscissa of the plot. For both PCS2 and PCS3, the first peaks appearing near 3 min are the injection solvent peaks, and these show no light scattering signal intensity. Prior to the elution of comb polymers, three small peaks are eluted. They are byproducts of the comb synthesis such as unreacted arms, unreacted backbone, and coupled arms and backbone. Comb polymers start to elute after the byproduct. The molecular weight (MW) determined by LS/RI detection is also plotted in Figure 2. The MW values increases stepwise, reflecting that the comb polymers have a "quantized" distribution in MW. The MW increment of the adjacent two peaks is identical to the arm MW and the MW of each peak matches well with the MW of the corresponding PS combs, i.e., MW of backbone + MW of arm × the number of arms. For example, the peak appearing near 25 min (MW = 455K) of PSC3 is expected to contain the combs with three arms: 200K + (85K × 3) = 455K. Therefore, it is confirmed that TGIC successfully resolved the comb polymers according to the number of arms.

At the longest elution times in Figure 2, it is clear that some relatively high molecular weight material is present. It is likely that this includes some material in which coupling reactions have occurred between backbones. A relatively mild Lewis acid (zinc(II) chloride) was employed, and the reaction conditions were carefully chosen in order both to limit the extent of the reaction and to minimize side reactions, namely Friedel−Crafts alkylation, which can lead to such cross-linking and ultimately gelation. We cannot, however, eliminate such coupling reactions completely. On the basis of the TGIC and SEC traces, we estimate that as much as 10 wt % of the final product is due to coupled backbones.

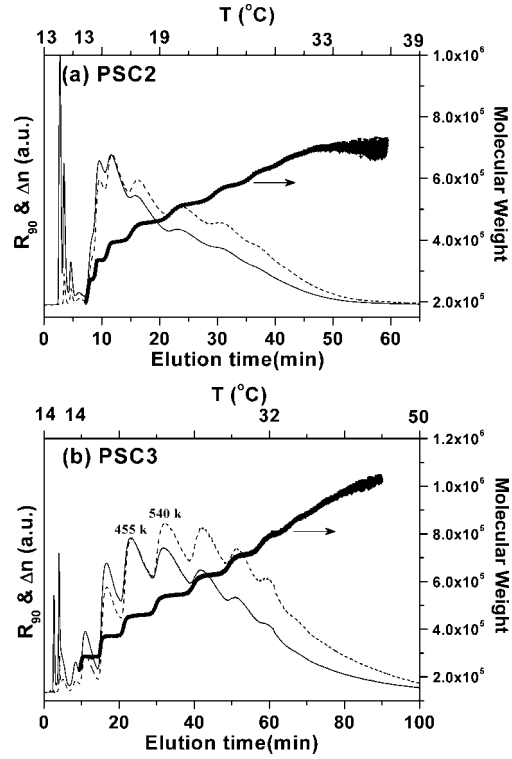

Figure 2. NP-TGIC chromatograms of PS combs (a) PSC2 and (b) PSC3 recorded by RI (solid curves) and LS (dashed curves) detectors. The molecular weight distribution curves were obtained from the LS detection and are shown in the plots. The temperature program is shown in the top abscissa. Column: Nucleosil, 500 Å pore, 7 μm particle, 250 × 2.1 mm i.d.; eluent: *n*-hexane/THF (57/43, v/v) at a flow rate of 0.3 mL/min.

Figure 3 displays cumulative MW distributions obtained from the analysis of the chromatograms shown in Figure 2. The histogram of number of arms can be made from this plot and is displayed in Figure 4. The average number of arms per comb may be calculated from this distribution and compared against the averages from SEC: the results are shown in Table 1. We find almost perfect agreement between SEC and the TGIC average for PSC2. The small discrepancy for PSC3 is within the bounds set by typical errors of molecular weight determination by SEC. We also show, in Figure 4, analytical predictions of the distribution of arm number based on the assumption of random arm addition (see below for further discussion).

4. Rheology Results and Modeling

To model the rheology of the polymers, we use a computational scheme[21,22,30] which faithfully represents the polydispersity in both the molar mass and the architecture. The scheme is based on the tube theory and its extensions for entangled polymer melts.[1,31] Briefly, this involves creating a numerical ensemble of the polymers at the segment level from consideration of the synthesis process. The short-time dynamics of these polymers are modeled by considering the motion of the Rouse beads forming the segments. Retraction of the free ends is handled by integrating the differential form for retraction in the tube potential, modified by dynamic dilution of the tube constraint and by the initial Rouse contribution of the free ends. Completely retracted side arms introduce localized drag points with the friction determined by the tube diameter at which the arm retracts completely for the first time. Compound arms,

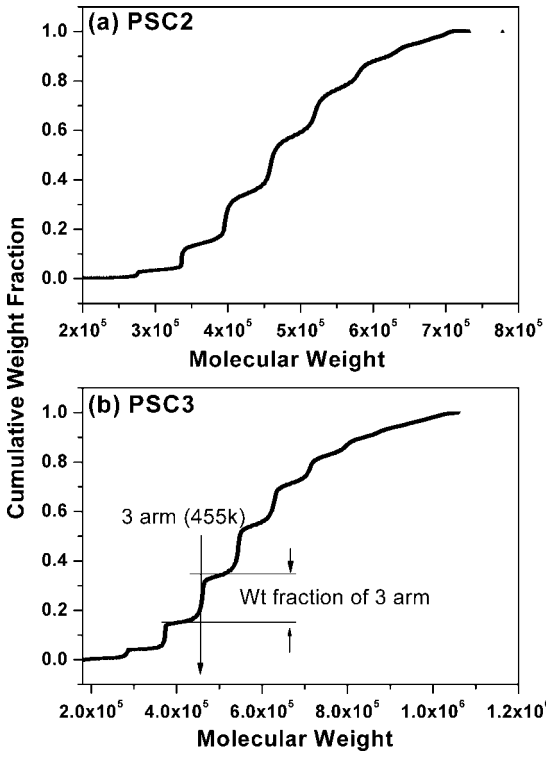

Figure 3. Cumulative weight fraction vs molar mass for PS combs (a) PSC2 and (b) PSC3.

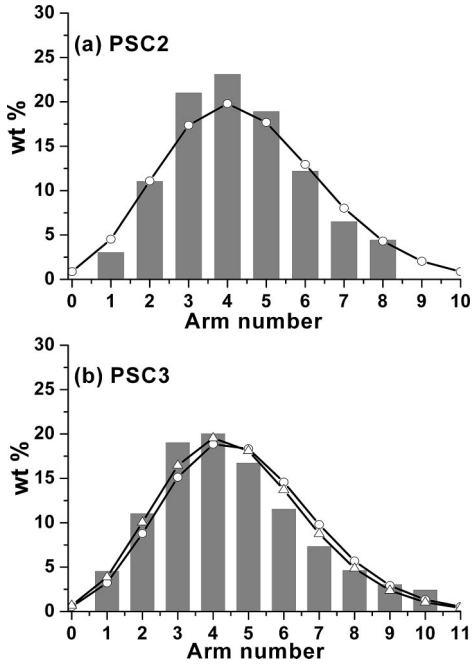

Figure 4. Distribution histogram of number of arms (a) PSC2 and (b) PSC3. The bar plots are results from the TGIC analysis, while circles are analytical estimates from the average number of arms using SEC results and assuming a random association reaction (the connecting line is a guide to the eye). For PSC3 we also show the analytical estimate using the average number of arms (4.0) from the TGIC analysis (triangles).

which have several such localized drag points and hence need the solution of a multidimensional Kramers' problem, are recast as retractions in an approximate one-dimensional potential, which takes care of the connection topology of the localized drag points. Relaxation continues until only an unrelaxed linear chain section remains (with no unrelaxed side arms). The effectively linear polymer continues to relax by arm retraction from both ends until the time at which reptation is feasible for the final relaxation. When the above-described relaxation mechanisms predict increase of the tube diameter faster than the rate permitted by Rouse relaxation, the effective orientational constraints responds more slowly by constraint release Rouse motion and the dynamic dilution formalism is appropriately modified. For details of the scheme, see refs 21 and 30.

This prescription has been used in the past for successfully modeling several model architectures, mildly branched metallocene catalyzed polyethylene,[21] and even the extreme example of branch-on-branch architecture of a series of resins which tends toward the limit of a gel as a function of the extent of reaction.[32] Once the topological connectivities are fully specified, the only parameters needed for a given chemistry are the usual entanglement molar mass, M_e, defining the diameter of the tube constraints and the Rouse time of segments between entanglements τ_e related to the microscopic friction. Two more chemistry-independent parameters are involved in the model: the dynamic dilation exponent, assumed to be 1 in this study, and a parameter p which specifies the size of hops in units of the tube diameter that the branch points take at the time scales of complete retraction. Following earlier studies,[21,32] we use $p^2 = 1/40$.

For this study, it is necessary to generate the numerical ensemble of representative comb polymers. These are built from linear polymer sections, for which we use chains with a log−normal distribution giving the same average molar mass and PDI as observed experimentally. For the present polystyrene combs, the TGIC peaks for the different arm fractions are sufficiently separated to calculate the weight fraction of the molecules with different number of arms (as shown in Figure 4). We use the TGIC results to specify the weight fractions in our numerical ensemble of combs with different numbers of arms. The TGIC results do not, however, allow determination of the arm positions along the backbone, so at fixed number of arms we generate a set of representative combs with arms placed randomly along the backbone. We also allow for the possibility of a coupling reaction between backbones; we generate the architecture for the coupled backbone material by linking together two combs at a randomly chosen point along each backbone.

Figure 5 shows the experimental rheological modulus (G' and G'') as a function of frequency, along with the predictions of the modeling, both with and without 10 wt % of the coupled backbone material. We use temperature $T = 170$ °C, density $\rho = 969$ kg/m^3, $M_e = 15\,300$ g/mol, and $\tau_e = 1.0 \times 10^{-3}$ s. We determine these parameters from a best fit to the rheology of the linear polymers; they are nevertheless consistent with those given in ref 33, which lists values for atactic and isotactic PS. We assume that the small fraction (of order 1%) of backbone monomers with substituted groups does not significantly affect the rheological parameters. For both the linear and comb molecules, the rheology predictions are in good agreement with the experimental results over the entire frequency range. Adding 10 wt % of coupled backbone material makes a small change to the terminal relaxation prediction, in fact improving the prediction for PSC2 but making the prediction for PSC3 slightly worse.

For this particular set of parameters of arm number and arm and backbone length, one cannot distinguish separate peaks in G'' for arm and backbone relaxation (in contrast to some other comb materials[16,17]). Nevertheless, comparison between the linear rheology of the comb and linear materials in Figure 5 indicates that the relaxation spectrum of the comb materials is significantly broader than that of their linear counterparts. In

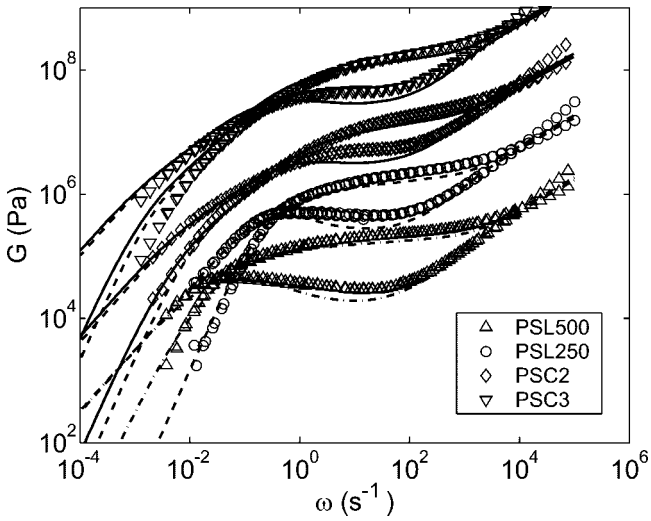

Figure 5. G' and G'' for PSL250, PSL500, PSC2, and PSC3. The lines are predictions from modeling. In the case of the combs, theoretical predictions are shown both with (solid line) and without (dashed line) 10 wt % of material with coupled backbones. Successive data sets are shifted vertically by factors of 10 for clarity.

particular, for the linear materials the crossover frequency for G' and G'' and the terminal frequency are not well separated, as would be expected for a material dominated by a single terminal time (the reptation time). For the comb materials the crossover frequency and the terminal frequency are separated by almost 2 decades; this is a result of the fact that a significant portion of the stress is carried by the arms, but the terminal time is given by reptation of the backbone (subject to the friction from the arms).

We additionally investigated an alternative method of generation of a numerical ensemble of combs. We assume that the attachment of the side arms on the backbone for the case of the comb polymers is an uncorrelated random event. This gives a Poisson distribution in number of arms on a given comb molecule, the only free parameter being the average number of arms which we can specify from the SEC results. We can directly compare the results of this assumption against those using the TGIC results for weight fraction as a function of arm number, as shown in Figure 4. As seen from the figure, the distribution is mostly identical for PSC3 (where we have shown distributions based on the average number of arms from both SEC and TGIC measurements), except at the extreme tails of the distribution. For PSC2, the distribution measured by TGIC is significantly sharper than the random attachment prediction. We may attribute the differences seen to the postsynthesis fractionation of the combs which, although designed primarily to remove unreacted impurities, is likely also to remove selectively some of the combs with either very few or very many arms. However, the differences between rheological predictions with arm distributions chosen either from TGIC or from a Poisson distribution were found to be negligible.

In addition to generating a numerical ensemble of combs using the above random-addition assumption, we also investigated generating combs with a fixed number of arms, set at the average. For this exercise we chose a hypothetical comb with the backbone and the arm length and polydispersity index same as in the case of PSC3, but the average number of arms is chosen to be an integer, 4, so that we can create polymers with a fixed number of arms. This assumption is the closest our rheology-prediction algorithm can approach the typical analytical methods present in the literature[16,19,20] for prediction of linear comb rheology. It is usually prohibitive, in such approaches, to consider a distribution in arm number, and it is useful to know

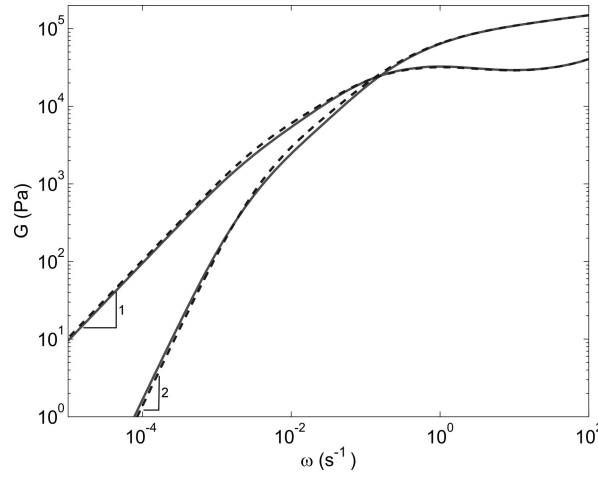

Figure 6. G' and G'' for a comb with backbone and arm molecular mass distribution same as PSC3, but the average number of arms being 4. The solid line is the result when a Poisson distribution of number of arms considered. The dashed line denotes the prediction from an ensemble in which all the combs have exactly 4 arms. The terminal slopes of 2 and 1 for G' and G'', respectively, are indicated.

to what extent this limitation affects the rheology prediction. Perhaps surprisingly, the answer is that it affects the rheology very little. Figure 6 shows the rheology predictions from both the approaches (arm number from Poisson distribution, fixed arm number). For the fixed number of arms, the elastic modulus is slightly higher at intermediate frequencies but decays slightly faster at low frequencies than the Poisson distribution case. As a result, the viscous modulus is slightly higher across low and intermediate frequencies for a fixed number of arms. It would appear that there is a degree of "motional narrowing" in (especially) the terminal relaxation of the predictions with a varying arm number: slow relaxation of combs with larger arm numbers is compensated for (and, due to constraint release, sped up by) fast relaxation of combs with smaller arm numbers. This observation is important, in that it supports the validity of simpler analytical approaches based on constant arm number, at least for the comb distribution considered here.

5. Conclusion

This paper has presented the synthesis of polystyrene combs via an improved procedure which allows the average number of arms to be small (3−5) but well controlled. We have shown that temperature gradient interaction chromatography (TGIC) proves to be a highly effective method for the analysis of these combs, providing direct information on the distribution of the number of arms on the comb molecules. This information is useful for modeling the linear rheology of an entangled melt of such combs. We demonstrated that, armed with such information, a successful prediction of the linear rheology is obtained from our previously published algorithm.[21,30] We were also able to investigate the sensitivity of the predicted rheology to this distribution, concluding that, in the present case, the assumption of random addition of arms, or of a fixed number of arms per comb, would also yield a reasonable prediction. This latter observation supports the validity of simpler analytical approaches based on constant arm number,[16,19,20] at least for the comb distribution considered here.

Acknowledgment. The groups from Sheffield and Leeds gratefully acknowledge the financial support of EPSRC through the "Microscale Polymer Processing 2" project. T.C. acknowledges the financial support of KOSEF (NRL program).

References and Notes

(1) McLeish, T. C. B. *Adv. Phys.* **2002**, *51*, 1379–1527.
(2) Adams, C. H.; Hutchings, L. R.; Klein, P. G.; McLeish, T. C. B.; Richards, R. W. *Macromolecules* **1996**, *29*, 5717–5722.
(3) Frischknecht, A. L.; Milner, S. T.; Pryke, A.; Young, R. N.; Hawkins, R.; McLeish, T. C. B. *Macromolecules* **2002**, *35*, 4801–4820.
(4) McLeish, T. C. B.; Allgaier, J.; Bick, D. K.; Bishko, G.; Biswas, P.; Blackwell, R.; Blottiere, B.; Clarke, N.; Gibbs, B.; Groves, D. J.; Hakiki, A.; Heenan, R. K.; Johnson, J. M.; Kant, R.; Read, D. J.; Young, R. N. *Macromolecules* **1999**, *32*, 6734–6758.
(5) Nielsen, J. K.; Rasmussen, H. K.; Denberg, M.; Almdal, K.; Hassager, O. *Macromolecules* **2006**, *39*, 8844–8853.
(6) Deffieux, A.; Schappacher, M. *Macromolecules* **1999**, *32*, 1797.
(7) Roovers, J. E. L. *Polymer* **1975**, *16*, 827.
(8) Roovers, J. E. L. *Polymer* **1979**, *20*, 843.
(9) Ryu, S. W.; Hirao, A. *Macromolecules* **2000**, *33*, 4765–4771.
(10) Pannell, J. *Polymer* **1971**, *12*, 558–578.
(11) Candau, F.; Ranta, E. *Makromol. Chem.* **1971**, *149*, 41–50.
(12) Candau, F.; Rempp, P. *Makromol. Chem.* **1969**, *122*, 15–29.
(13) Gauthier, M.; Tichagwa, L.; Downey, J. S.; Gao, S. *Macromolecules* **1996**, *29*, 519–527.
(14) Fernyhough, C. M.; Young, R. N.; Ryan, A. J.; Hutchings, L. R. *Polymer* **2006**, *47*, 3455–3463.
(15) Fernyhough, C. M.; Young, R. N.; Poche, D.; Degroot, A. W.; Bosscher, F. *Macromolecules* **2001**, *34*, 7034–7041.
(16) Daniels, D. R.; McLeish, T. C. B.; Crosby, B. J.; Young, R. N.; Fernyhough, C. M. *Macromolecules* **2001**, *34*, 7025–7033.
(17) van Ruymbeke, E.; Orfanou, K.; Kapnistos, M.; Iatrou, H.; Pitsikalis, M.; Hadjichristidis, N.; Lohse, D. J.; Vlassopoulos, D. *Macromolecules* **2007**, *40*, 5941–5952.
(18) Iatrou, H.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 6697–6701.
(19) Inkson, N. J.; Graham, R. S.; McLeish, T. C. B.; Groves, D. J.; Fernyhough, C. M. *Macromolecules* **2006**, *39*, 4217–4227.
(20) Kapnistos, M.; Vlassopoulos, D.; Roovers, J.; Leal, L. G. *Macromolecules* **2005**, *38*, 7852–7862.
(21) Das, C.; Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B. *J. Rheol.* **2006**, *50*, 207–234.
(22) Larson, R. G. *Macromolecules* **2001**, *34*, 4556–4571.
(23) Lee, H. C.; Chang, T.; Harville, S.; Mays, J. W. *Macromolecules* **1998**, *31*, 690–694.
(24) Lee, H. C.; Lee, W.; Chang, T.; Yoon, J. S.; Frater, D. J.; Mays, J. W. *Macromolecules* **1998**, *31*, 4114–4119.
(25) Chang, T. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1591–1607.
(26) Lee, H. C.; Chang, T. *Polymer* **1996**, *37*, 5747–5749.
(27) Lee, W.; Lee, H.; Cha, J.; Chang, T.; Hanley, K. J.; Lodge, T. P. *Macromolecules* **2000**, *33*, 5111–5115.
(28) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211–3234.
(29) Wright, M. E.; Toplikar, E. G.; Svejda, S. A. *Macromolecules* **1991**, *24*, 5879–5880.
(30) http://sourceforge.net/projects/bob-rheology.
(31) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, 1986.
(32) Das, C.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B. *Phys. Rev. E* **2006**, *74*, 011404.
(33) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1023–1033.

MA800599M