

# Linear viscoelastic behavior of densely grafted poly(chloroethyl vinyl ether)-*g*-polystyrene combs in the melt

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(Received 20 March 2002; final revision received 27 March 2003)

## Synopsis

We have measured the linear viscoelastic behavior in the melt of two densely grafted poly(chloroethyl vinyl ether)-*g*-polystyrene comb polymers. Both samples have a backbone of approximately 800 ethyl vinyl ether monomers and the fractions of grafted backbone monomers are 98% and 10%, respectively. The viscoelastic behavior shows remarkable features. The comb polymer with the highest grafting density shows a power law behavior over five orders of magnitude in frequency. The power law can be understood through a “Rouse-like” motion of the entire chains with an apparent friction coefficient coming from the fast Rouse dynamics of the short grafts. Alternatively, the same behavior can be described as the signature of a “fluctuating” physical gel. The less densely grafted comb polymer has a more complex behavior. © 2003 The Society of Rheology. [DOI: 10.1122/1.1579688]

## I. INTRODUCTION

There is a fast growing body of rheological characterization and modeling studies on complex macromolecular architectures in the melt. Over the years, numerous studies have described the behavior of model branched polymers. A selection of recent papers includes those of Lohse *et al.* (2000, 2002), Archer and Varshney (1998), and Gell *et al.* (1997) on stars, Daniels *et al.* (2001) on combs, and Houli *et al.* (2002) on dumbbells. Modeling advances have mainly focused on simple model architectures although more complex ones are at last being tackled [McLeish and Milner (1999); Larson (2001)]. Although the viscoelastic properties of combs have been studied for quite some time [Yurasova *et al.* (1994); Roovers and Toporowski (1987); Roovers and Graessley (1981)], there has been a renewed interest in recent times for *densely grafted* polymer combs [Miros and Vlassopoulos (2003); Vlassopoulos *et al.* (2000, 2002); Tsukahara *et al.* (2001), and references therein; Namba *et al.* (2001)]. When there is one graft per backbone monomer, the polymers are usually referred to as “polymacromonomers” (technically, polymacromonomers are obtained by polymerizing monomers with polymeric side

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chains). When the backbone is short with respect to the grafts, the polymer is called a “multiarm star,” otherwise it is usually named a “bottlebrush.” Because of dense grafting, bottlebrushes and multiarm stars have unique properties in solution: for short backbones, they behave like densely packed spheres and intrinsic viscosity is essentially independent of total molecular weight. As backbone length increases, intrinsic viscosity resumes the usual scaling with molecular weight (similar to linear polymers) but at a much lower viscosity level [Wintermantel *et al.* (1996); Schappacher *et al.* (1999)]. Their viscoelastic properties have been studied in a few recent papers [Miros and Vlassopoulos (2003); Tsukahara *et al.* (2001); Namba *et al.* (2001); Vlassopoulos *et al.* (2000, 2002)]. Dynamic moduli are dominated over a large frequency range by the dynamics of the side arms, in particular, by their entanglement or absence of it. In the first instance, star-like relaxations are observed while otherwise, the relaxation is mostly Rouse like. The objective of this paper is to provide a viscoelastic characterization in the melt of two densely grafted poly(chloroethyl vinyl ether)-*g*-polystyrene combs differing in grafting density but having the same backbone length. The polymers have been obtained by a “grafting to the backbone” strategy [Schappacher *et al.* (1999)], which allows to vary the grafting density while keeping the backbone length identical and polydispersity to a minimum. When compared to previous studies of densely grafted polymers, this system has either a much longer backbone [compared to Miros and Vlassopoulos (2003); Houli *et al.* (2002); Vlassopoulos *et al.* (2000)], or a much higher grafting density [e.g., compared to Roovers and Toporowski (1987), for instance]. The work of Tsukahara *et al.* (2001) describes polymacromonomers of similar backbone and arm lengths to our systems but of different chemistry.

## II. EXPERIMENT

### A. Samples

Two linear poly(chloroethyl vinyl ether)-*g*-polystyrene densely grafted combs have been synthesized as reported in [Schappacher *et al.* (1999)] by reaction of a polystyryl lithium solution with a poly(chloroethyl vinyl ether). They will be referred to as COMB10 and COMB98. Both samples have a backbone of approximately 800 ethyl vinyl ether monomers. The grafting density is 98% for COMB98 and 10% for COMB10 which amounts to 780 and 80 grafts per chain, respectively. The weight average molecular weight of the polystyrene grafts is 5000 for COMB10 and 4320 for COMB98. The polydispersity of the functional backbone and graft precursors is below 1.1. The same holds true for the densely grafted copolymers after fractionation from a minor fraction of unreacted and dimerized polystyrene.

### B. Rheological measurements

Dry polymer powders from synthesis have been mixed with 3000 ppm Irganox 1010 for thermal stabilization and compression-molded at 180 °C in a Fontijne press for 1 min only, in order to minimize thermal degradation. Molded disks have been used as such for rheological characterization.

Dynamic storage and loss moduli  $G'(\omega)$  and  $G''(\omega)$ , have been measured with the help of a strain-controlled rheometer (ARES from Rheometric Scientific) in the dynamic mode with a parallel-plate configuration (25 mm plates) at temperatures of 140 and 160 °C. The angular frequency interval was  $10^2$ – $10^2$  rad/s, with a strain amplitude of 10%. It belongs, for all samples studied, to the linear viscoelastic regime, located with the help of a previous strain sweep test. All measurements have been performed under nitrogen atmosphere. Because of the limited thermal stability of the samples, measurements at

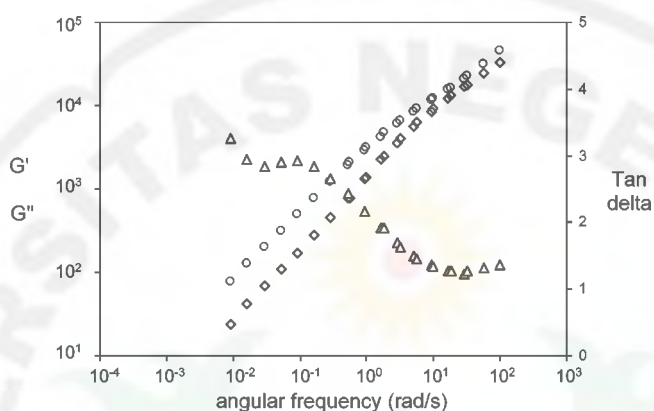


FIG. 1. Storage modulus (diamonds), loss modulus (circles), and tan delta (triangles) for COMB 10.

higher temperature could not be performed accurately. At lower temperature, the viscosity of the samples was too high.

Master curves (reference temperature of 140 °C) have been obtained by applying the time–temperature superposition principle. Because of the limited temperature range measured, the master curves are only indicative.

### III. RESULTS AND DISCUSSION

The master curves for COMB10 and COMB98 are reported in Figs. 1 and 2.

The time–temperature superposition principle seems to apply, as is virtually always the case for model polymer architectures. However, keeping in mind that we could only measure two temperatures, the test is not really conclusive. Therefore, no analysis of the shift factors is attempted.

It is immediately visible from dynamic moduli, that we could not access the terminal flow regime for either sample in the experimental frequency window. This terminal flow should indeed be apparent from the well known  $G' \propto \omega^2$  and  $G'' \propto \omega$  scalings.

The most spectacular result is obtained for COMB98 since a power law behavior is observed over the entire angular frequency range, i.e., five orders of magnitude, and probably more. Similar power laws have been observed previously for less densely

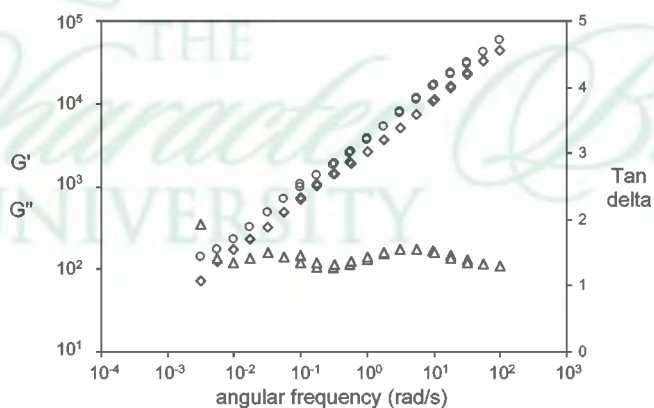


FIG. 2. Storage modulus (diamonds), loss modulus (circles), and tan delta (triangles) for COMB 98.

grafted comb macromolecules [Roovers and Graessley (1981); Hempenius *et al.* (1998)] but over two to three orders of magnitudes only. Houli *et al.* (2002) recently observed a similarly wide power law for a dumbbell polymer with a comparatively shorter backbone (approximately 100 monomer units) and very short grafts (polybutadiene with 1200 Mw). Tsukahara *et al.* (2001) observed a Rouse-like regime over four orders of magnitude for PMMA-*g*-PS polycromonomers with a long backbone and grafts below the molecular weight for entanglements. The power law exponent is 0.6 for both  $G'$  and  $G''$  and as a consequence  $\tan \delta$  is a constant:

$$G' \propto G'' \propto \omega^{0.6}, \quad (1)$$

$$G''/G' = \tan \delta = 1.43. \quad (2)$$

Interpretation of this behavior is not straightforward. Two readings are possible, which are not mutually exclusive.

First, one is tempted to associate a power law with an exponent close to 0.5 to Rouse-like motions [Ferry (1980)] because the molecular weight of the PS grafts is well below molecular weight for entanglements, usually taken around 18 500 [Ferry (1980); Leonardi *et al.* (2000)]. Houli *et al.* (2002) explain their dumbbell result in this way. The classical treatment of Rouse dynamics for unentangled [Ferry (1980)] melts yields an exact exponent of 0.5:

$$G'_{\text{Rouse}} = G''_{\text{Rouse}} \propto \omega^{0.5}, \quad (3)$$

$$G''_{\text{Rouse}}/G'_{\text{Rouse}} = \tan \delta = 1. \quad (4)$$

Real melts, including PS are known to depart slightly from this ideal behavior, with exponents higher than 0.5 and  $G''$  above  $G'$  [Ferry (1980); Onogi *et al.* (1970)]. The hypothesized Rouse motions probed by our measurements can however not be the classical Rouse modes of the short PS grafts. Their frequency is indeed at least two orders of magnitude above the measured range [Hempenius *et al.* (1998); Onogi *et al.* (1970)] and the Rouse time of COMB98 has to be well *below*  $10^{-2}$  rad/s since no hint of a transition to either a terminal flow regime or a “reptation” regime is observed [Ferry (1980)]. Moreover, the classical Rouse regime is usually limited to a single order of magnitude in frequency. Therefore a “Rouse-like” interpretation of the observed power law has to deal with motions of the entire backbone. Solution characterization [Schappacher *et al.* (1999)] has shown that the densely grafted combs studied here behave in solution as perturbed coils, i.e., they show some flexibility despite the high grafting level. Presumably, the few remaining ungrafted backbone units provide the required flexibility in agreement with Monte Carlo simulations [Saariaho *et al.* (1999)]. It is, therefore, possible to consider Rouse motions of the entire backbone as the origin of the power law. The fast Rouse motions of the grafts must provide an “apparent” friction coefficient between the bottlebrush molecules since the grafts of neighboring chains interpenetrate. A similar “apparent” friction coefficient idea has been used by McLeish *et al.* to model viscoelasticity of so-called “POM-POM” molecules, i.e., a linear backbones between two multiple star ends [McLeish and Milner (1999)]. Local Rouse motions of the backbone are only possible through cooperative motions of the grafts. Consequently, there is a vanishing probability that very long backbone sections will move on a certain time scale. The apparent coefficient of friction has to be huge, considering the very large number of interactions between grafts of neighboring chains. Since the Rouse time is proportional to the friction coefficient  $\zeta$  [Ferry (1980)], it should be located at very low frequencies, well

below the observed experimental range. Houli *et al.* (2002) do observe the onset of the terminal regime but the backbone of the dumbbell in their study is much shorter than in our case (100 units vs 800).

A second possible model for the power law is provided by the gel theory proposed by Winter and Chambon [Chambon and Winter (1985); Winter and Chambon (1986)]. Whereas this theory has been developed for chemical networks, its extension seems possible to purely physical “fluctuating” networks. Recently, Garcia-Franco *et al.* have used the theory to explain gel-like behavior of lightly branched polyethylene [Garcia-Franco *et al.* (2001)] in a limited frequency range. They interpret the power law as a result of the time-scale separation between fast motions of the arms and slow motions of the backbones of tree-like chains. In our case also, we have a (huge) time-scale separation between dynamics of the grafts, below milliseconds and dynamics of the backbone, in any case well above 100 s. Even more relevant, is the work by Fourmaux-Demange *et al.* (1998), who have interpreted a similar power law observed for flexible combs with mesogenic side groups as a result of dynamic interactions between the rigid-rod grafts. In our case, the fast Rouse motions of the grafts can provide a similar dynamic interaction through monomer friction. The gel theory of Winter and Chambon is based on the assumption that the network has a fractal nature and hence fractal dimension [Muthukumar and Winter (1986)]. The Rouse interactions are a consequence of Brownian motions. Their fluctuating and stochastic nature can undoubtedly provide a rationale to consider a fluctuating network of fractal dimension.

A strong consistency test for a “gel” power law comes from the strict relationship that has to be observed between the power exponent and  $\tan \delta$

$$\text{If } G' \propto G'' \propto \omega^n,$$

then

(5)

$$G''/G' = \tan \delta = \tan(n\pi/2).$$

The predicted  $\tan \delta$  value is 1.38, in excellent agreement with the observed value 1.43. The “fractal” dimension  $d_f$  of the gel “clusters” is also linked to the exponent of the power law [Muthukumar and Winter (1986); Mours and Winter (1996)]:

$$n = d_f/(2+d_f), \quad \text{or} \quad d_f = 2n/(1-n). \quad (6)$$

For  $n = 0,6$ , this leads to  $d_f = 3$ , lower than for a “tree” structure ( $d_f = 4$ ) but higher than for a threshold percolation cluster ( $d_f = 2.5$ ).

Based on our limited set of data, it is difficult to choose between the “Rouse-like” or the “gel-like” model. They may indeed be both valid.

The results for COMB10 can be interpreted from those of COMB98. There is a similar power law observable but it is limited to one experimental order of magnitude ( $10^1$ – $10^2$  rad/s on the master curve). The corresponding exponent is about 0.54 (with more uncertainty because of the limited frequency range), reasonably close to the 0.6 value measured for COMB98. Experimental  $\tan \delta$  is equal to 1.34 leading to a predicted exponent from the gel theory of about 0.59. Most probably, the high frequency range motions of COMB10 are similar to those observed (over the whole range) for COMB98. It is interesting to compare the  $G'$  and  $G''$  ratios for the two samples in the range defined by the 0.6 power law:

$$G'_{\text{COMB10}}/G'_{\text{COMB98}} = G''_{\text{COMB10}}/G''_{\text{COMB98}} = 0.75. \quad (7)$$

The Rouse model could provide some ground for interpretation of this ratio. If it is indeed linked to an “apparent” friction coefficient  $\zeta_{\text{app}}$  provided by the fast motions of the grafts, then  $\zeta_{\text{app}}$  should be proportional to the grafting density, at least in a naïve picture. This provides an estimation for the ratio between apparent friction coefficients of the two samples:

$$\zeta_{\text{app COMB10}}/\zeta_{\text{app COMB98}} = 10/98 = 0.102. \quad (8)$$

From Rouse theory we know that in the Rouse regime [Ferry (1980)]:

$$G' = G'' \propto \zeta_{\text{app}}^{1/2}. \quad (9)$$

Therefore, the ratio of dynamic moduli is predicted to be around 0.32. This is off by more than a factor 2 but the difference could be due to the dependence of the “classical” friction coefficient of the grafts versus molecular weight [Ferry (1980)]. Since molecular weight of the grafts for COMB98 is slightly lower than the corresponding one for COMB10 (4320 vs 5000), the discrepancy perhaps explainable that way. Therefore, the Rouse model is certainly not excluded by the comparison between dynamic moduli.

In the low frequency range (below 1 rad/s), there seems to be a transition to a more “fluid-like” behavior. This probably represents the transition to the terminal zone but it is interesting to notice that there still seems to be a power law in this region with an exponent of 0.8. The experimental  $\tan \delta$  value is 3, in perfect agreement with the gel prediction.

#### IV. CONCLUSIONS

We have observed that the linear viscoelastic behavior in the melt of poly(chloroethyl vinyl ether)-*g*-polystyrene combs shows some remarkable features. A densely grafted comb shows a power law behavior over five orders of magnitude in frequency. The power law can be understood through a “Rouse-like” motion of the entire chains with an apparent friction coefficient coming from the fast (true) Rouse dynamics of the short grafts. It can be argued that because of the very high grafting density, chains can never truly flow in the melt in the linear viscoelastic regime. Alternatively, the same behavior can be described as the signature of a “fluctuating” physical gel. The two interpretations are not mutually exclusive. A less densely grafted comb has a more complex behavior. At high frequencies, it exhibits the same power law as the first one but shows a transition toward a more fluid-like behavior at lower frequencies.

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