Melt Rheology of Arborescent Graft Polystyrenes

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ABSTRACT: Arborescent graft or comb-burst polymers are highly branched, high molecular weight polymers that are constructed from linear polymer chains by a cascade grafting process. The arborescent graft polystyrenes studied here were prepared by a "graft on graft" synthetic strategy employing anionically prepared branches, which led to well-defined branched polymers with controlled branch lengths and low polydispersities. The dynamic mechanical behavior of these arborescent graft polystyrenes in the melt was studied as a function of branch length and grafting generation. Terminal relaxation times and zero-shear viscosities of the lower-generation arborescent graft polymers increase progressively with the molecular weight of the branches. Even in the case of the highly branched molecules, all samples demonstrated viscous flow behavior at small shear rates. The frequency dependence of the dynamic moduli changed with increasing number of grafting generations showing the features of a cross-linking polymer at the gel point. The most highly branched arborescent graft polymers display a frequency dependence similar to those of cross-linked networks and microgels.

Introduction

Polymer properties are strongly influenced by variables such as molecular weight, molecular weight distribution, and the degree of branching. In the last few decades, detailed rheological studies on well-defined branched polymers have provided insight into the effects of branching on viscoelastic properties. Branched polymers with controlled architectures and low polydispersities have proved to be essential in these studies. Several classes of branched polymers can be distinguished. When end-reactive polymer chains are linked together to a small molecule which serves as a multifunctional quencher, star polymers result.[1] A comblike polymer[2] is produced when chains are grafted onto a polymer backbone containing an array of reactive sites. Highly branched monodisperse polymers, called star-burst dendrimers,[3] are obtained in a step by step approach when monomers with at least two protected functional groups are linked together in a first step, followed by repetitive deprotection and addition of new protected monomer. High selectivity of the different reaction steps yields branching in a geometrical way. Star-burst dendrimers possess a spherical architecture and have the ability to enclose small molecules[4] which challenges fundamental studies on the use of these materials as microreactors and agents for the controlled release of drugs. An alternative approach to dendrimers is based on the convergent combination of AB_n functional monomers.[5]

A recent development in the synthesis of highly branched polymers are the arborescent graft or comb-burst polymers.[6−8] Instead of using small molecules as building blocks like in the case of dendrimers, polymeric chains were used to build novel macromolecular architectures. Starting with a linear chain and grafting it with polymeric side chains, a classical comb polymer was obtained. By development of new reactive sites along the side chains of this comb polymer, it was possible to branch these chains further. The use of this "graft on graft" strategy led to ultra high molecular weight polymers with a compact, spherical topology. So far, the spherical topology of the higher generations of these arborescent graft polymers was characterized by means of light scattering and intrinsic viscosity measurements.[9,10] For the higher generations, scanning force micrographs of thin films of the arborescent graft copolymers confirmed a compact globular shape with defined interfaces between individual molecules.[11] The melt properties of these materials are as yet unexplored. The present work has been directed towards the characterization of the viscoelastic properties of a series of well-defined arborescent graft polystyrenes whose preparation has been reported before.[6]

Experimental Section

Three series of arborescent graft polymers were prepared,[6] built from polystyrene chains with a molecular weight either of 5000 (S5-*G*), 10000 (S10-*G*) or 20000 (S20-*G*). The following procedure was used: partial chloromethylation of anionically prepared polystyrene with chloromethyl methyl ether and

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Table 1. Characteristics of the Arborescent Graft Polystyrenes

sample	$\langle M_w \rangle$[a]	$\langle r_g \rangle$ (nm)[a]	η_0 (Pa·s)	log $\tau_{G''max}$ (s)[b]	log $\tau_{n,1}$ (s)[c]	log $\tau_{m,1}$ (s)[d]
S5-0	8.0×10^4	11	$10^{2.81}$	−3.0		−2.65
S5-1	1.01×10^6	15	$10^{3.74}$	−3.0	−3.52	−1.00
S5-2	5.11×10^6	17	$10^{7.66}$ [e]	−3.0		
S5-3	2.85×10^7	31				
S10-0	1.56×10^5	11	$10^{3.14}$	−2.5		−2.37
S10-1	1.86×10^6	13	$10^{4.00}$	−2.5	−2.50	−0.37
S10-2	1.57×10^7	27	$10^{6.48}$ [e]	−2.5		
S20-0	3.89×10^5	14	$10^{3.74}$	−1.5	−1.60	−0.89
S20-1	6.80×10^6	14	$10^{4.65}$	−1.5	−1.62	0.60
S20-2	5.48×10^7	56	$10^{6.18}$ [e]	−1.5		

[a] Obtained from static light scattering measurements[9] in toluene. [b] Relaxation times associated with motion of the branches, estimated from a maximum in the G'' curves.[17] [c] Calculated relaxation times associated with motion of the branches. [d] Calculated terminal relaxation times. [e] Obtained from a steady-stress creep experiment.

$SnCl_4$ in CCl_4 afforded a core chain with about 15 chloromethyl groups, onto which anionically prepared living polystyrene could be grafted. The resulting comb polymer ($G = 0$) was again chloromethylated, now for stoichiometric reasons predominantly in the side chains. Grafting these side chains of the comb with living polystyrene gave a branched comb polymer, called generation $G = 1$. Repeating the chloromethylation-anionic grafting cycles produced the more highly branched polymers of $G = 2$. The polymers were purified by means of precipitation and, after drying under vacuum, obtained as white powders. SEC measurements gave evidence of the low polydispersity of the samples. Apparent polydispersities increased slightly upon branching and were found to be in the order of $\langle M_w/M_n \rangle = 1.1$ for $G = 0$ to 1.3 for $G = 2$. The molecular weight and radius of gyration of the arborescent graft polystyrenes were obtained from static light scattering measurements in toluene at 25 °C.[9,10] The results are given in Table 1 and show that these polymers are compact, high molecular weight molecules.

The polystyrene powders were pressed into clear, bubblefree disks at 140 °C. Dynamic moduli were obtained on the melts with a Rheometrics Dynamic Spectrometer RDS II, a strain-controlled instrument. A plate-plate geometry was used, the plate radius was 12.5 mm, and the plate separation was between 1.1 and 1.3 mm. Measurements were made every 10 °C from 190 to 130 °C in the frequency range 500−0.01 rad/s, under a N_2 atmosphere. Sample degradation was not observed under these conditions. Repeat measurements on new disks were performed for all arborescent graft polystyrenes. Plates with different diameters (20−25 mm) and varying sample heights (0.9−1.2 mm) were employed in order to assure linearity. The master moduli−frequency curves were constructed by superimposing phase angle data[12] obtained at the various temperatures to the data at the reference temperature (170 °C), using experimental shift factors along the frequency axis. The thermal variation of the shift factors log a_T could be described by a Vogel equation and appears to be independent of branch length and branching generation and equal to relations found for linear polystyrenes.[1,2,13,14] Zero-shear viscosities of the high molecular weight S5-2, S10-2 and S20-2 arborescent graft polystyrenes could not be measured with the RDS II instrument, but they could be approximated by means of a steady-stress creep experiment on a stress-controlled Rheometrics DSR instrument. Stress was varied between 800−2000 Pa (S5-2) or 150−800 Pa (S10-2 and S20-2), at 170 °C. While a constant stress σ was applied, the strain rate $\dot{\gamma}$ was monitored until it became constant, and the viscosity was determined. If the viscosity ($\sigma/\dot{\gamma}$)[12] was plotted against strain rate and extrapolated it to zero $\dot{\gamma}$, an indication of the zero-shear viscosity could be obtained.

Scanning force micrographs were recorded as described before.[11]

Results and Discussion

Figure 1 depicts a schematic drawing of the structure and formation of the arborescent graft polystyrenes. Grafting has been performed by chloromethylation and subsequent nucleophilic substitution of poly(styryllithium).[6] Careful optimization of the reaction conditions guaranteeing high conversion and elimination of side reactions provided the basis for obtaining narrow molecular weight distributions and the exclusion of cross-linking. A high number of grafts per chain of the subgeneration yield nearly exclusive grafting on the branches of the last generation, which represents over 90% of the total molar mass. In addition, a fast growth in the molecular weight is achieved. For the denotation, we use a code starting with an S for Styrene, followed by a number giving the molecular weight $\times 10^3$ of the graft arms. The last digit gives the generation of grafting addition starting with 0 for the simple comb molecule. Thus, S10-2 denotes a polystyrene consisting of primary chains of 10000 Da which have been linked together in three subsequent grafting steps. With 15 grafts per primary chain this yields an expected molecular weight of 3.6×10^7 with 3600 branching points per molecule. This value is by a factor of 2 larger than the experimentally measured $\langle M_w \rangle$ (Table 1). Incomplete branching in the higher generations has been observed before,[6] but in general the agreement is rather satisfying.

The chemical coupling of defined numbers of polystyrene chains with a narrow size distribution ensures formation of branched molecules with very uniform size. This has been confirmed by size exclusion chromatography. Uniform size is also demonstrated rather clearly by scanning force microscopy (SFM) of solution cast films. Figure 2 gives a SF micrograph of a thin film of sample S05-3, demonstrating the uniform globular shape of the molecules.[11] The film, which consisted of two layers, was prepared by spin casting a 1 wt % solution of the polymer in toluene on a freshly cleaved piece of mica. From the cross sectional profile in Figure 2, the thickness of the top polymer layer was determined to be 30 ± 5 nm which corresponds to the molecular diameter in the solvent free state.[11]

Dynamic mechanical measurements in the melt were undertaken with the highly branched arborescent graft polystyrenes in order to study the influence of parameters as generation, branch length and branching density on their rheological properties. Three different regions can generally be distinguished in moduli−frequency curves of un-cross-linked high molecular weight polymers.[13] The high-frequency region of the spectrum ($\omega > 10^3$ rad/s) is attributed to coupled motions of small segments of polymer chains (transition zone to the glassy state). An intermediary region (plateau zone) is associated with motion of larger parts of the polymer chains restricted by entanglements. The length of the intermediary zone increases with molecular weight. The low-frequency region of the spectrum is associated with motion of the molecules as a whole. This relaxation is most successfully described by reptation and the tube model.[14] The dynamic mechanical spectra of anionically prepared low molecular weight polystyrene ($\langle M_w \rangle = 2.0 \times 10^4$) and a polystyrene sample prepared by radical polymerization ($\langle M_w \rangle = 2.7 \times 10^5$) are shown in Figure 3.

The rheological behavior of long-chain branched polymers differs markedly from that of linear polymers.

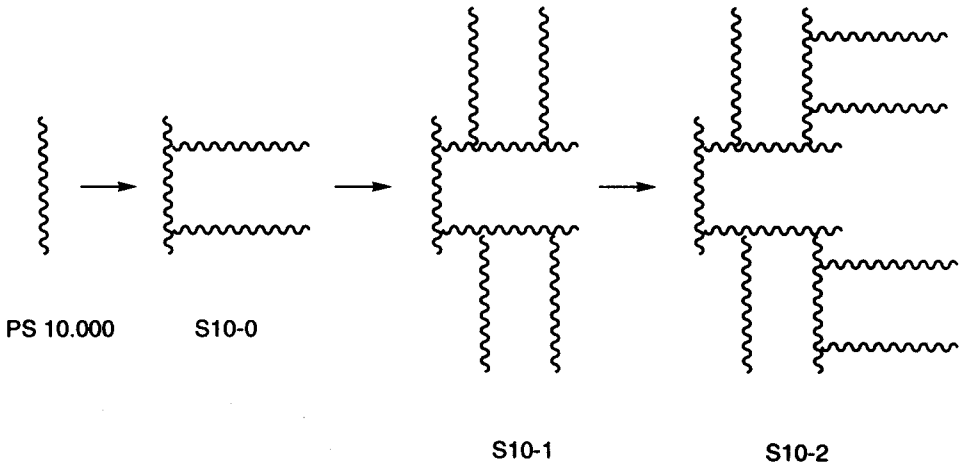

Figure 1. Formation of arborescent graft polystyrene in sequential chloromethylation−anionic grafting cycles.

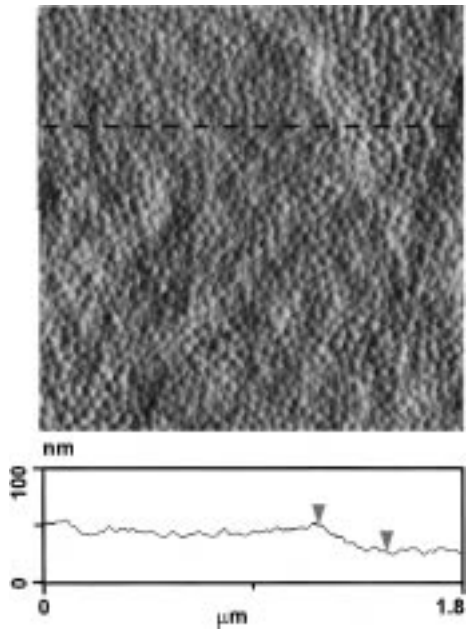

Figure 2. Tapping scanning force micrograph of a bilayer film of S5-3 polymers. Each sphere corresponds to one arborescent graft polystyrene molecule having a diameter of 50 nm. The molecules were vertically compressed during adsorption and solvent evaporation resulting in a monolayer thickness of 30 ± 5 nm. The cross-sectional profile was drawn along the dotted line in the micrograph. The arrows indicate the difference in thickness between the top layer and the sublayer.

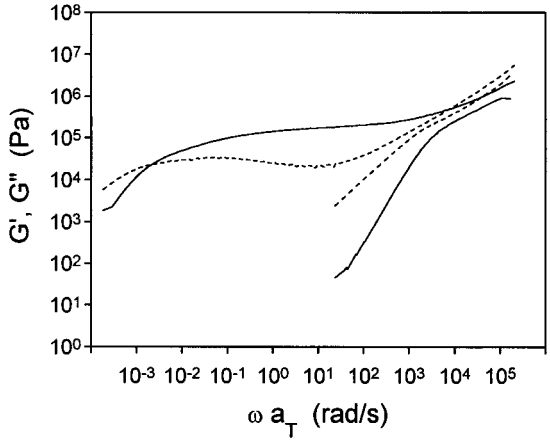

Figure 3. Dynamic moduli−frequency curves of low molecular weight polystyrene ($\langle M_w \rangle = 2.0 \times 10^4$, $\langle M_w/M_n \rangle = 1.05$) and radically polymerized polystyrene ($\langle M_w \rangle = 2.7 \times 10^5$) at 170 °C: (—), G'; (- -), G''.

Especially in the case of highly branched polymers, relaxation by simple reptation mechanism is unlikely,[15−18] whereas path breathing[15] or constraint release[17,18] has been proposed as a model mechanism for molecular relaxation of star- and comb-branched molecules.

The arborescent graft polystyrenes of the first generation (Sx−0; x = 5, 10, 20) are low molecular weight combs. S5-0 and S10-0 have backbones and branches well below the polystyrene entanglement molecular weight[2] ($M_e = 1.8 \times 10^4$). The moduli−frequency curves of the combs (Figures 4a−6a) strongly resemble those of linear low molecular weight polystyrenes. Plateau regions which give evidence of entanglements are not observed for S5−0 and S10−0 because of the low molecular weights. An inflexion in G' observed in the case of S20-0 indicates entanglement coupling. In the low-frequency region, normal limiting behavior is found: G' and G'' have slopes of +2 and +1, respectively.

Graft polymers of the second generation (Sx−1; x = 5, 10, 20) yielded moduli−frequency curves with two inflexions (Figures 4b−6b), one at intermediate times and one at long times, evidencing the existence of two different relaxation mechanisms. The inflexion at long times noticeably shifted to longer times when arm molecular weights increase. Normal limiting behavior is observed in the terminal region. In between an $\omega^{1/2}$ dependence (Rouse behavior) was observed covering a large frequency range. This behavior has also been observed for high molecular weight comb polystyrenes.[2]

Further branching to arborescent graft polystyrenes of the third generation (Sx−2; x = 5, 10, 20) has a large influence on the dynamic moduli (Figures 4c−6c). The storage modulus in the Sx−2 series is now equal to or larger than the loss modulus, as opposed to the earlier generations. Both G' and G'' are approximately proportional to $\omega^{1/2}$ over several decades. Such a behavior has been observed earlier in crosslinking polymer systems at the gel point,[19,20] *i.e.*, when the crosslinking reaction has proceeded to a critical extent in forming highly branched high molecular weight macromolecules.

The most highly branched arborescent graft polystyrene, the S5-3, shows a plateau in G' over a broad frequency range and a decreased G'' at intermediate and low frequencies (Figure 6d), features which are typical of a polymer network[21] and samples of microgel particles.[22,23]

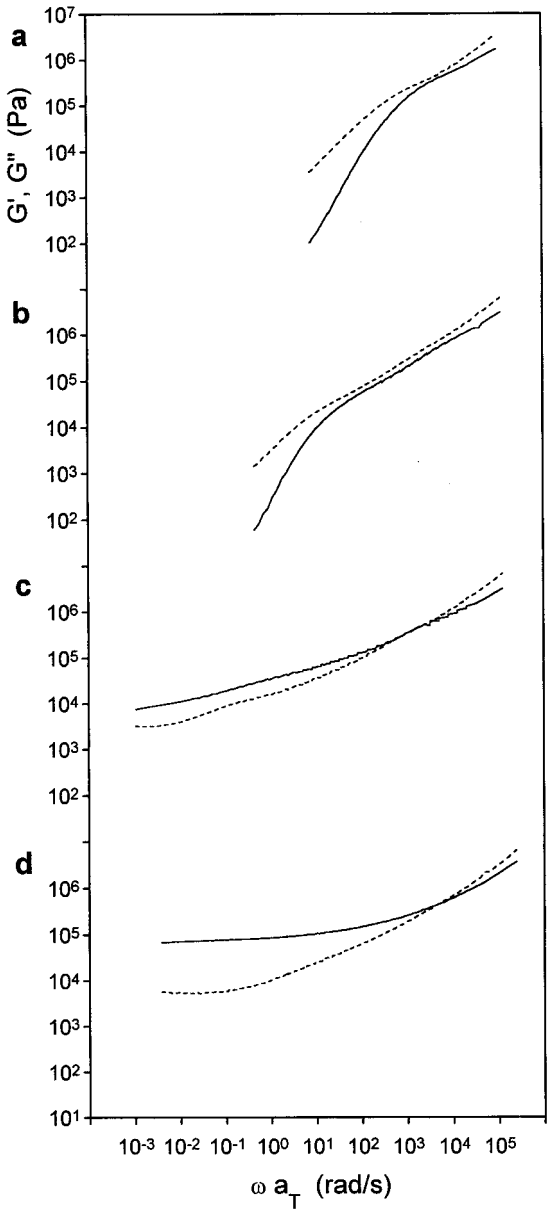

Figure 4. Dynamic moduli−frequency curves of S5 arborescent graft polystyrenes at 170 °C: (—), G'; (- -), G''. Key: a, S5-0; b, S5-1; c, S5-2; d, S5-3.

The dynamic moduli−frequency curves of a variety of branched polymers such as stars,[1] combs,[2] and star−combs,[18] show inflections which reveal the existence of different relaxation mechanisms. Usually, inflections at intermediate times are associated with motions of the branches, while inflections at longer times are associated with movement of the molecule as a whole. The time for the relaxation of the branches, the arm length equilibration time $\tau_{G''\max} = 1/\omega_{G''\max}$, can be estimated from the inflection in G'' and a step in G'.[17] The $\tau_{G''\max}$ of the Sx−0, Sx−1 and Sx−2 arborescent graft polystyrenes are given in Table 1. The moduli curves of the low molecular weight Sx−0 combs show only one inflection, but the presence of a closely spaced second relaxation cannot be ruled out. The inflections in the moduli curves of the Sx−1 polystyrenes indicate that two important, distinct relaxation mechanisms exist for these arborescent graft polymers.

The times associated with the relaxations in the moduli−frequency curves of the Sx−0 and Sx−1 polystyrenes were obtained by using a generalized Maxwell model to fit the experimental curves of the dynamic viscosities $\eta'(\omega)$ and $\eta''(\omega)$:[24]

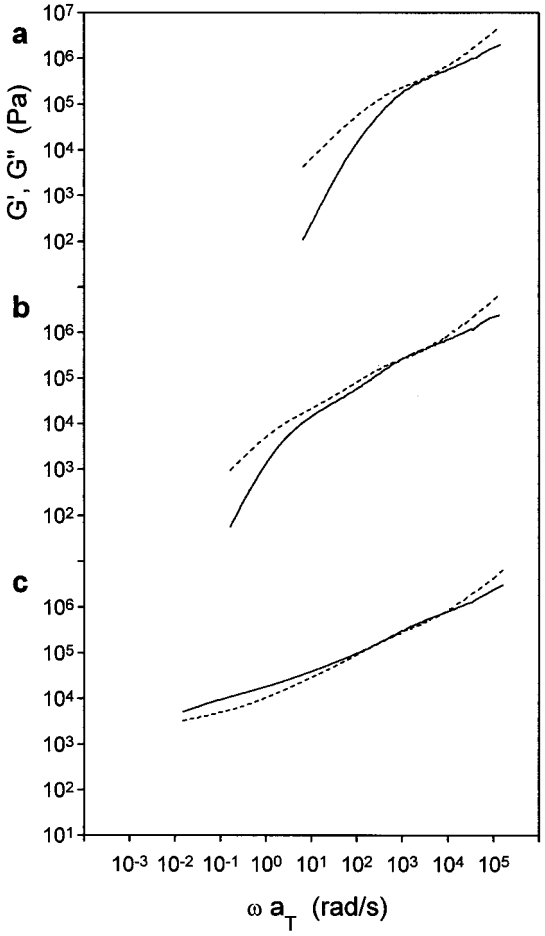

Figure 5. Dynamic moduli−frequency curves of S10 arborescent graft polystyrenes at 170 °C: (—), G'; (- -), G''. Key: a, S10-0; b, S10-1; C, S10-2.

$$\eta'(\omega) = \eta'_{\infty} + G_{\mathrm{m}} \sum_{i=1}^{N} \frac{\tau_{\mathrm{m},i}}{1+\omega^2 \tau_{\mathrm{m},i}^{\ 2}} + G_{\mathrm{n}} \sum_{j=1}^{N} \frac{\tau_{\mathrm{n},i}}{1+\omega^2 \tau_{\mathrm{n},j}^{\ 2}} \quad (1)$$

$$\eta''(\omega) = G_{\mathrm{m}} \sum_{i=1}^{N} \frac{\omega \tau_{\mathrm{m},i}^2}{1+\omega^2 \tau_{\mathrm{m},i}^2} + G_{\mathrm{n}} \sum_{j=1}^{N} \frac{\omega \tau_{\mathrm{n},j}^2}{1+\omega^2 \tau_{\mathrm{n},j}^2} \quad (2)$$

Two groups of times, long ($\tau_{\mathrm{m},i}$) and short ($\tau_{,\mathrm{n},j}$), together with their respective relaxation strengths (G_{m} and G_{n}) are entered in eqs 1 and 2. Assuming that both relaxation processes conform to Rouse dynamics, the relaxation times for these modes are expressed relative to the longest relaxation times[18,24] $\tau_{\mathrm{m},1}$ and $\tau_{\mathrm{n},1}$ as $\tau_{\mathrm{m},i} = \tau_{\mathrm{m},1}/i^2$ and $\tau_{\mathrm{n},j} = t_{\mathrm{n},1}/j^2$.

It seems that choosing one group of relaxation times for S5-0 and S10-0 and two different groups of relaxation times to describe the dynamic mechanical behavior of S20-0 and the Sx−1 polymers is justified, since a very good agreement between experimental and calculated curves was obtained. The measured and calculated η' and η'' curves of polystyrene S10-1 are shown in Figure 7 as an example. The curves of the Sx−2 polystyrenes cannot be described by using two distinct groups of relaxation times. Multiple relaxations at intermediate

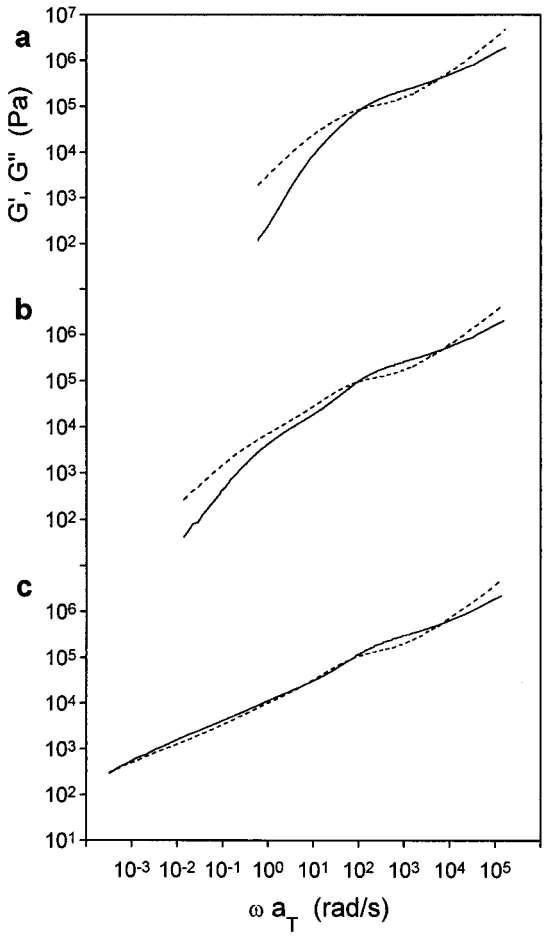

Figure 6. Dynamic moduli−frequency curves of S20 arborescent graft polystyrenes at 170 °C: (—), G', (- -), G''. Key: a, S20-0; b, S20-1; c, S20-2.

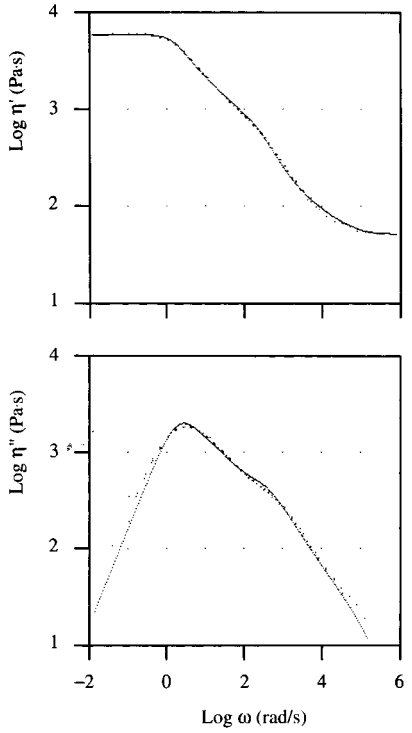

Figure 7. Measured and calculated (···) η' and η'' curves of the arborescent graft polystyrene S10-1.

and low frequencies occur in these complex, highly branched molecules.

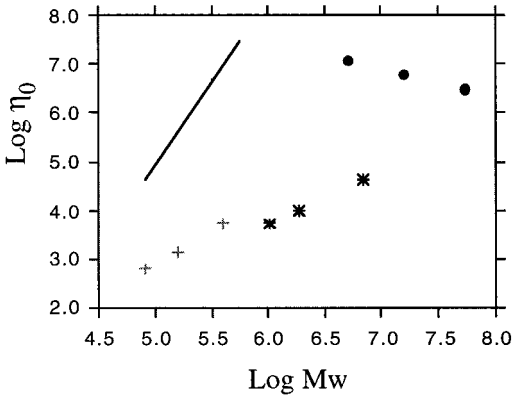

Figure 8. log η_0 (Pa·s) at 170 °C against log M_w: (+) Sx−0; (*) Sx−1; (●) Sx−2 (x = 5, 10, 20); (—) linear polystyrene.

It is known for branched polymers such as stars and combs that their limiting properties depend strongly on arm molecular weight or the number of entanglements per arm.[17,18] In accordance with this, the terminal relaxation times $\tau_{m,1}$ of the Sx−0 and Sx−1 polystyrenes (Table 1) increase progressively with M_{arm}, even within the limited range of arm molecular weights used in the arborescent graft polystyrenes. Zero-shear viscosities η_0 of the Sx−0 and the Sx−1 polystyrenes were obtained directly from the limiting values of the η' curves, and show a similar progressive increase with arm molecular weight in the generations Sx−0 and Sx−1 as was found for $\tau_{m,1}$ (Table 1).

As limiting values were not reached in the case of the Sx−2 polystyrenes, their zero-shear viscosities had to be determined by means of a steady-stress creep experiment. In Figure 8, η_0 values of Sx−0, Sx−1, Sx−2, and linear polystyrene[1,13] are plotted against molecular weight. The increase in η_0 in the sequence S5-0, S10-0, S20-0, S5-1, S10-1, and S20-1 can be explained from an increase in the total molecular weight and arm length. It is of interest to note that η_0 for the samples Sx−0 and Sx−1 scales as M_w^1 instead of $M_w^{3.4}$ for linear flexible polymers above M_c. This important point illustrates the lack of entanglements in these structures. The Sx−2 series, however, shows a remarkable behavior, with η_0 decreasing in the order S5−2, S10-2, S20-2. In this generation, the influence of branching density appears to become dominant. Each chain, whether its M_w is 5000 or 20000, is always grafted with 15 side chains. Consequently, the arborescent graft polystyrenes built from short chains have the highest branching density which, in the case of the S5-2 polymer, is 4 times higher compared to S20-2.

While the lower-generation Sx−0 and Sx−1 series are regarded as flexible, branched polymers,[6,9] the Sx−2 polystyrenes are much more rigid, globular-shaped macromolecules as a result of steric crowding from the grafts.[11] In the latter series, relaxation by path breathing[15] or constraint release[17,18] will be hampered, especially in the case of the highly branched S5-2 and S5-3 samples. This hinders translational movement of the molecules by reptational type motion of the molecular segments and inhibits configurational renewal of the molecule as a whole, explaining the increase in η_0 in the sequence S20-2, S10-2, and S5-2.

Conclusion

The dynamic mechanical behavior of the highly branched, high molecular weight arborescent graft

polystyrenes was studied as a function of branch length and grafting generation. The arborescent graft polystyrenes show low zero-shear viscosities compared to linear polystyrenes of the same molecular weight. Terminal relaxation times and zero-shear viscosities of the low-generation arborescent graft polymers, however, increase progressively with arm molecular weight. In the higher-generation polymers, the terminal properties are strongly affected by the branching density. Zero shear viscosity η_0 scales as M_w^1 instead of $M_w^{3.4}$, evidencing the lack of entanglements for these branched structures. Increasing branching densities augment the structural rigidity of the molecules hindering configurational renewal. Thus flow or movement of the molecule as a whole is less facilitated and involves increasingly long relaxation time. At shorter times the hairy balls appear to be clasped and behave like a polymer network, similar to what was observed for microgels.[22,23]

On the basis of intrinsic viscosity and light scattering measurements on both arborescent graft polystyrenes[6,9] and arborescent graft polybutadienes,[8] the transformation from flexible branched polymers to rigid spherically shaped macromolecules was found to occur upon developing generation S$x-1$ into S$x-2$. It is interesting to note that this structural stiffening is accompanied by a distinct change in the dynamic moduli−frequency curves upon going from S$x-1$ to S$x-2$.

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