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Abstract

We report upon the characterization of the steady-state shear stresses and first normal stress differences as a function of shear rate using mechanical rheometry (both with a standard cone and plate and with a cone partitioned plate) and optical rheometry (with a flow-birefringence setup) of an entangled solution of asymmetric exact combs. The combs are polybutadienes (1,4-addition) consisting of an H-skeleton with an additional off-center branch on the backbone. We chose to investigate a solution in order to obtain reliable nonlinear shear data in overlapping dynamic regions with the two different techniques. The transient measurements obtained by cone partitioned plate indicated the appearance of overshoots in both the shear stress and the first normal stress difference during start-up shear flow. Interestingly, the overshoots in the start-up normal stress difference started to occur only at rates above the inverse stretch time of the backbone, when the stretch time of the backbone was estimated in analogy with linear chains including the effects of dynamic dilution of the branches but neglecting the effects of branch point friction, in excellent agreement with the situation for linear polymers. Flow-birefringence measurements were performed in a Couette geometry, and the extracted steady-state shear and first normal stress differences were found to agree well with the mechanical data, but were limited to relatively low rates below the inverse stretch time of the backbone. Finally, the steady-state properties were found to be in good agreement with model predictions based on a nonlinear multimode tube model developed for linear polymers when the branches are treated as solvent. © 2016 The Society of Rheology. [<http://dx.doi.org/10.1122/1.4944993>]

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I. INTRODUCTION

The effects of polymer branching on the deformation behavior in concentrated solutions and in the molten state are a topic of great technological importance. Although much progress has been made in the understanding of the effects of branching on the rheological properties, especially on the linear viscoelasticity, the exact nature of the nonlinear deformation behavior remains elusive [1–4]. Hence, there remains an interest in the nonlinear flow behavior of even the structurally most simple model polymers. Four related reasons can be quoted as to why their nonlinear rheology remains ill-understood. (i) Polymers are known to be problematic in strong, nonlinear flows in the sense that they have the tendency to display instabilities, i.e., not deform homogeneously [5]. Instabilities in flowing polymers are receiving more and more attention in recent years [6–10]. Controversies between the experimental findings of different groups have in fact been reported [7,10]. It has been shown that the effects of slight differences between the flow fields due to, e.g., alignment issues of the flow geometries play a key role for the occurrence of instabilities [7] and this could potentially explain the discrepancies between different studies. The issue remains however open and the current lack of understanding of the experimental conditions for homogeneous flow or shear banding [6–10] leave the issue of experimental and theoretical analysis of polymeric response in strong nonlinear flows wide open [8,9,11]. (ii) The syntheses of model polymers are mainly performed by anionic polymerization high-vacuum techniques resulting in well-defined molecular structures, which however come in very small quantities (typically <1 g) [12–14]. When theoretical models are being evaluated, such well-defined architecturally complex structures are indispensable, even though some disparity in molecular structure is unavoidable albeit not always problematic, and advanced characterization is often called for [15,16]. The low sample quantities call for the need to use appropriate (or modify existing) characterization methods, e.g., specifically for rheometry one cannot use a capillary rheometer as a characterization tool. (iii) The detailed understanding of the behavior of well-characterized model samples is the key to the elucidation of the underlying physics of polymer deformation [1–3]. Although some constitutive molecular models for branched polymers [4,17] are able to predict polymer flow in complex flow situations, a good agreement with experiments can often only be achieved by fitting multimode versions of the model to the data [18]. The different modes in these multimode models are assumed to act independently and, in this way, it is hard to provide exact physical meaning to the values of the various parameters. (iv) Based on experiments with (primarily) linear entangled polymers, it is established that in order to fully assess a constitutive model, it is important to examine the polymeric response in several different flow histories such as repeated shear, rate switch, and flow reversal [2,3,19,20]. Recent investigations on nonlinear flows suggest that a number of observed phenomena, such as arrested wall slip [10], metastable shear banding [21–23], and yielding in start-up extensional flow [24], require explanations. On the other hand, the tube model in its current, most advanced formulation for the nonlinear deformation of linear

polymers, known as the GLaMM model [25] has been shown to capture the macroscopic observations for start-up shear flow rather well [26]. The need to provide explanations and the debate about the adequacy or not of the tube model and the possible need for alternative theoretical frameworks has prompted the use of simulations at different levels of coarse graining as an independent means to assess nonlinear rheology of entangled linear polymers [27–31]. Consequently, given points (i)–(iv) above, it is natural to ask how entangled model branched polymers with inherent dynamic dilution and increased friction of the branch points will behave in shear flow [32]. This challenge must be addressed systematically, i.e., by gradually varying the complexity of the polymer architecture from linear to branched with different levels of branching.

In this work, we report upon an investigation of the linear viscoelasticity and the nonlinear shear flow behavior of a model exact comb polymer solution, signifying that the polymer has the overall structure of a comb and the position of the branches on the backbone is exactly known. We choose to study a solution as the aim of the work is to capture both the nonlinear shear stress as well as the first normal stress difference as a function of shear rate both mechanically with a rheometer and optically using flow birefringence in combination with the stress-optical rule. In the molten state, especially for a high modulus polymer like polybutadiene (PBD), flow instabilities and other practical problems would prevent one from obtaining reliable data at sufficiently high rates, hence a solution is the obvious choice. In Sec. II, we first discuss the synthetic and molecular details of the model branched polymer. We further discuss the employed methods in some detail. The linear viscoelasticity and the transient and steady-state nonlinear shear flow were studied by mechanical rheometry. We further employed flow birefringency to study the steady-state nonlinear shear flow behavior. Section II is concluded with a discussion of the two different tube-modeling approaches, one specific to describe the linear viscoelasticity for branched polymers and another specific to describe the nonlinear flow behavior of linear polymers. Subsequently, in Sec. III, we systematically discuss the experimental results starting from the linear viscoelasticity of the solution and the melt including the modeling approach for the linear viscoelasticity. We further report upon the qualitative features of transient start-up shear flow behavior of the shear stress and the normal stress difference. Subsequently, we discuss and compare the steady-state shear stress and first normal stress difference as a function of shear rate, as obtained mechanically and optically. Finally, we show that both nonlinear stresses can be quantitatively described with a tube model developed for linear polymers when treating the branches as dynamic solvent, as already qualitatively observed in [33,34].

II. MATERIALS AND METHODS

A. Asymmetric exact comb synthesis, molecular characterization, and sample preparation

The synthesis of the asymmetric exact comb with five identical branches (as specified in Fig. 1) was reported in

FIG. 1. Molecular structure of the investigated asymmetric exact comb PBD. The numbers indicate weight-average molar masses of different segments. “K” refers to kg/mol.

detail in [14]. The term exact comb is chosen to indicate that the polymer has the overall structure of a comb and that the position of the branches on the backbone are exactly known in contrast with random-branched combs for which the positions of the branches on the backbone are random. Note that, in this work, we identified the backbone as the part of the molecule shown in black in Fig. 1 ($87\text{ K} + 48\text{ K}$), while the grey segments are called branches (all segments of 10 K). This is in principle different from the classical situation as usually for combs the backbone-ends are included in the definition of the backbone (i.e., $10\text{ K} + 87\text{ K} + 48\text{ K} + 10\text{ K}$). The specific comb is asymmetric in the sense that the middle branch point is not located in the middle of the backbone, but it has about $1/3$ of the backbone on one side and $2/3$ on the other. Briefly, the synthetic methodology involves the selective replacement of the three chlorines of trichloromethylsilane with two different 3-arm star $\{(10\text{ K})_2 87\text{ K}$ and $(10\text{ K})_2 48\text{ K}\}$ and linear (10 K) chains, using appropriate coupling chemistry. The total weight-average molar mass M_w , as measured by low-angle laser light scattering (LALLS) in cyclohexane at 25°C , was reported to be 186.5 kg/mol and the polydispersity index ($\text{PDI} = M_w/M_n$, with M_n the number average molar mass) of the exact comb was found to be 1.08 , as determined by size-exclusion chromatography (SEC) in CHCl_3 at 25°C [14]. The microstructure of the exact comb, determined by ^1H NMR in CDCl_3 at 25°C , was 87% – 90% $1,4$ and 13% – 10% $1,2$. The molecular structure and characteristics are specified in Fig. 1. For this type of exact comb samples, slight architectural dispersity is possible, i.e., the sample may not be 100% the target structure from Fig. 1 but may contain a number of side products, as shown in [15,16] for similar exact combs. Here, we discard the possible effects of side products on the viscoelasticity and shear flow behavior as we are aiming to find the main effects of controlled branching on the nonlinear flow behavior and for a study of this type, slight effects of architectural dispersity can be reasonably expected to be small for the exact combs, in agreement with [15,16]. The glass transition temperature T_g of the exact comb, as measured by differential scanning calorimetry (PL-DSC, TA-instruments, USA), was found to be -90°C (heating/cooling rate was 5°C/min).

A solution of $20\text{ vol. \%}$ of the polymer in the nearly athermal solvent squalene (Sigma-Aldrich) was prepared using the co-solvent tetrahydrofuran (THF) (Sigma-Aldrich). After dissolution of the polymer, the volatile co-solvent THF was removed by evaporation under vacuum at room temperature for several days. The solution also contains a tiny amount of antioxidant (2,6-di-*tert*-butyl-*p*-cresol, Sigma-Aldrich) to reduce the risk of degradation. Both the melt and

the solution were always stored in the freezer and vacuum dried overnight before use to remove any possible moisture.

B. Linear viscoelasticity

In order to characterize the polymer at hand in both the molten state and in solution and determine, in particular, the characteristic relaxation times, small-strain-amplitude oscillatory shear measurements were performed with an ARES-2KFRTN1 strain-controlled rheometer equipped with a force rebalance transducer (TA Instruments, USA). As flow geometries, parallel plates made of invar (a nickel-iron alloy with low thermal expansion coefficient) with the diameters of 8 and 25 mm were used. Temperature control was achieved with an accuracy of $\pm 0.1^\circ\text{C}$ by use of an air/nitrogen convection oven. A liquid nitrogen Dewar was used for measurements at temperatures below ambient. The sample was simply positioned on the bottom plate using a spatula and then compressed with the rheometer. After a stabilization time, the sample was trimmed with a spatula and slightly further compressed to a final height around 1 mm . Dynamic rheological measurements were carried out in the temperature range from -90 to 20°C . The thermal expansion of the plates was always taken into account when changing temperature by making the appropriate changes in gap spacing. At each temperature, dynamic time sweep and strain sweep experiments were conducted to ensure thermal equilibrium of the sample and to determine the linear viscoelastic region. Finally, the time-temperature superposition principle was used in order to combine frequency sweep experiments at different temperatures and to create the master curves (see Sec. III A).

For the melt, the terminal flow regime could not be reached at temperatures where the polymer is stable, i.e., where the polymer does not degrade due to oxidation. To extend the master curves to lower frequencies, and hence reach terminal relaxation, long-time, small-stress creep measurements were performed with the stress-controlled Physica MCR 301 (Anton Paar, Austria) equipped with a Peltier system combined with a nitrogen-fed convection hood. We utilized a parallel plate geometry with a diameter of 8 mm , and we performed measurements at 90°C . The linearity of the creep compliance results was ensured by performing several experiments with different stresses. The occurrence of polymer degradation/crosslinking was excluded by comparing the molar mass distribution determined by SEC before and after the creep test. The conversion of the resulting long-time creep compliance data $J(t)$ to the elastic G' and loss G'' moduli as a function of angular frequency ω is known to be problematic. We converted the data following the approximate method reported in [35]. Finally, the data are shifted toward the reference temperature using the shift factors obtained from the construction of the master curves based on the small-amplitude oscillatory data alone.

C. Nonlinear shear rheology studied with a rotational rheometer

The nonlinear shear flow behavior of the solution was measured with the ARES-rheometer equipped with a

stainless steel regular cone and plate (25 mm diameter, 0.04 rad cone angle) and also with a cone partitioned plate (CPP). The CPP allows one to perform reliable nonlinear shear measurements unaffected by edge fracture on rotational rheometers up to relatively high rates compared to the regular cone and plate. Our home-made CPP was inspired by earlier works [36–39], and a detailed discussion can be found in [40]. For the specific set of experiments under consideration, the cone angle was 0.1 rad and the diameter of the active plate was 8 mm.

Another typical problem that complicates the study of the nonlinear flow of highly elastic samples is the problem of instrument compliance due to the finite intrinsic stiffness of the devices. Compliance problems are known to be more problematic for the accuracy of normal force as compared to torque measurements, and they are especially important for transient experiments [41]. Focussing on the axial compliance, in a cone and plate geometry, the first normal stress differences that arise during nonlinear flow tend to push the tools apart. This results in a squeeze flow relaxing on a time scale t_a [41,42]

$$t_a = \frac{6\pi R\eta}{K_A \alpha^3},$$

with R , the sample radius (here, taken to be the radius of the complete sample of 7.2 mm, although this is an overestimate as the active element is only 4 mm), η , the viscosity (taken as the value of the steady viscosity at the relevant shear rate at -20°C , see Sec. III), K_A , the axial stiffness of the rheometer (for the ARES, $K_A = 2.4 \text{ N}/\mu\text{m}$, as measured by compressing the plates together with different forces and monitoring the displacement), and α , the cone angle (here 0.1 rad). In the zero-shear limit (using the zero-shear viscosity η_0 of 4000 Pa s at -20°C , see Sec. III), the response time is $t_a = 0.2 \text{ s}$. At a rate of 100 s^{-1} [which corresponds with the highest shifted rate of 1240 s^{-1} (at 20°C), see further], the response time t_a reduces to 0.009 s or a strain of 0.9 due to the low steady-state viscosity of 160 Pa s. In addition to the compliance, the startup time of the motor can be an issue as measurements were performed at very high rates given our interest in the steady-state properties and not necessarily the transients. Using a standard Brookfield silicon oil of 100 Pa s, we obtained startup times of the motor of about 0.01 s by monitoring the rotation speed of the motor directly using a data acquisition card connected to a LABVIEW program (National Instruments, USA) while performing step rate experiments from 0 to 10 s^{-1} and from 0 to 100 s^{-1} in a regular cone and plate geometry with a diameter of 25 mm and a cone angle of 0.1 rad at $T = 25^\circ\text{C}$. The measured start-up time of 0.01 s was (nearly) independent of shear rate. For a shear rate of 100 s^{-1} , this leads to a start-up strain of the motor of about 1. The above discussions of compliance and start-up time of the motor both indicate that the stress peaks in the transient experiments at higher shear rates will be shifted to higher strains though neither the steady-state values nor the shape of the curves and their qualitative features are expected to be affected.

Finally, we investigated the nonlinear shear flow behavior of the solution at very high shear rates (see Secs. III B and III C). To ensure that possible effects of viscous heating are

negligible, we calculated the Brinkman number for the case of cone-and-plate flow [43] $Br = (\eta R^2 \Omega^2)/(k_0(T + 273.2))$ (with η , the viscosity of the sample at the relevant shear rate, k_0 , the thermal conductivity of the sample, R , the radius of the sample, and Ω , the rotation rate of geometry) for the highest investigated shear rate. With values of $\eta = 70 \text{ Pa s}$, $\Omega = 31.6 \text{ rad/s}$, $R = 7.2 \text{ mm}$, $T = -20^\circ\text{C}$, and $k_0 = 0.2 \text{ W/(m K)}$ (the value for k_0 for PBD [44]), we find a value of 0.07 for the Brinkman number, which is well below 1, suggesting that viscous heating is not important.

D. Flow-birefringence and Stress-optical rule

Rheo-optical experiments were carried out using a phase-modulated flow-birefringence apparatus similar to the one described in [45,46]. A schematic of the optical train is shown in Fig. 2 with the indicated angular rotation of each optical element relative to the flow direction. A Couette flow cell was used to shear the solution. The Couette cell has inner and outer cylinder radii of 15.01 and 15.24 mm, respectively, with the inner cylinder being free to rotate. The inner cylinder of the shear cell is made of a steel core with an aluminum shell. The top and bottom of the inner cylinder are beveled at 3.5° in order to minimize secondary flows. The outer cylinder was made from acrylic to aid in visualizing air bubbles. The shear cell has a height of 23.27 mm. The shear rate was calculated using the narrow-gap approximation [43]. Couette shear cells are known to be more prone to instabilities and slip as compared to cone and plate geometries due to the inherent inhomogeneous nature of the flow field [5,47,48]. To ensure the validity of the narrow-gap approximation and to assess the inhomogeneity, we calculated the maximal variation of the shear rate over the gap using the derivation for the flow-field of a power-law fluid in a Couette cell following [43]. The power-law exponent was obtained by fitting the experimental

FIG. 2. Schematic of the flow-birefringence setup with the orientation χ and retardance δ of the elements.

nonlinear shear stress data with the power-law model at the relevant shear rates. Somewhat arbitrarily, we made the conservative choice to discard all data where the maximal variation of the shear rate over the gap was more than 5% from the mean value, thereby limiting the accessible shear rate to about 40 s^{-1} for our solution of exact combs. The gap-to-height ratio of 102 is sufficiently large to allow one to neglect end effects. Temperature control is achieved via an attached temperature bath.

The light from a HeNe laser (Melles-Griot, USA) passes through a linear polarizer oriented at 90° and then through a photoelastic modulator (Hinds PEM-80, USA) with the slow axis oriented at 45° . The phase shift or retardance along the slow axis varies in sinusoidal fashion by $\delta_m = A \sin(\omega t)$. The PEM modulates the birefringence of the light which causes the retardance between the two directions to modulate. The value of A is fixed at 2.4045 during calibration. Details of the calibration and alignment of the optical train can be found in [49]. The polarization of the laser beam is now modulated at $\omega/2\pi$ (42.09 kHz) and passes through a quarter wave retarder oriented at 0° . The light then passes through the flow cell along a path that is parallel to the axis of rotation of the inner cylinder. The polymer sample modulates the light with an unknown orientation angle χ and retardance δ . The light then passes through another quarter wave plate at 0° and then a polarizer oriented at -45° . A photodiode (Newport 818-SL, USA) is used to detect the light intensity. The intensity of the light at the detector can be related to the χ and δ properties of the sample following [50]. The birefringence can be calculated from the retardance δ using the standard relationship $\Delta n' = \lambda \delta / 2\pi h$ with $\lambda = 632.8 \text{ nm}$ being the wavelength of the laser light and h being the height of the Couette shear cell. Without further details, for our setup, the unknown orientation angle and retardance of the polymer sample, χ and δ , respectively, can be found from [49]

$$\delta = \arcsin\left(\sqrt{R_1^2 + R_2^2}\right) \quad \text{and} \quad \chi = \arctan\left(\frac{-R_2}{R_1}\right),$$

with $R_1 = -I_\omega / (\sqrt{2} I_{dc} J_1)$ and $R_2 = I_{2\omega} / (\sqrt{2} I_{dc} J_2)$. I_ω and $I_{2\omega}$ are measured using lock-in amplifiers (Stanford Research Systems SR830, Perkin-Elmer Model 7265, USA) tuned to the harmonics of the PEM frequency ω . I_{dc} is measured by passing the signal from the detector through a photodiode amplifier (Joseph Rolfe Associates Model 9312, USA). In theory, J_1 and J_2 , should have the values 0.52 and 0.43 at $J_0(2.4048)=0$ but they were determined experimentally by rotating a calibration optic in the setup without sample to correct for misalignments or nonidealities of the components [45,46].

Finally, the measured optical properties are related to mechanical stresses following the semiempirical stress-optical rule [50,51], which states that the anisotropic parts of the refractive index tensor are linearly related to the stress tensor via the stress-optical coefficient C . Following this rule, the steady-state shear stress σ and first normal stress difference N_1 in simple shear flow can be calculated as

$$\sigma = \frac{\Delta n'}{2C} \sin(2\chi) \quad \text{and} \quad N_1 = \frac{\Delta n'}{C} \cos(2\chi).$$

The value of the stress-optical coefficient C is obtained by comparing the shear stress from mechanical experiments with the unscaled shear stress calculated from optical experiments over a wide range of (low) shear rates. The experimentally determined value of C for the PBD comb was found to be $C = 2.2 \times 10^{-9} \text{ m}^2/\text{N}$, in good agreement with the literature [49,50]. In shear flow, the stress-optical rule was found to be valid for polymer melts and solutions but the accessible range of shear rates was generally relatively small and limited to low rates [19,51–55]. Hence, we can only state with certainty that the rule is valid at low shear rates when the chains remain unstretched. Theoretically, it is in fact expected that the rule starts to fail gradually at higher rates (above the inverse Rouse time) when the chains stretch [56].

E. Tube-based modeling

We attempted to model the linear viscoelastic data with the so-called Branch-on-Branch (BoB) model [57]. It is a tube model specially developed for branched polymers, and it is based on the “hierarchical relaxation principle” [58]. Models based on this principle have been found to successfully describe the relaxation behavior of a large variety of model architecturally complex polymers [15,16,57,59–62]. For combs, the idea is that the branches relax at high frequencies while the backbone remains frozen after which (at longer times) the backbone can relax while the branches act as a dynamic solvent and the branch points as points of high friction.

For the nonlinear shear flow data instead, we attempted to describe the steady-state shear viscosity and first normal stress difference with a model for linear polymers which is justified based on an earlier work where we found that combs with relatively short branches behave essentially like linear polymers in nonlinear shear flow with some small quantitative differences [33,34]. Strong qualitative as well as quantitative differences in the nonlinear shear flow behavior only became apparent when the branches were “long” and comprise more than about 70% of the total molecular structure [63]. The exact comb structure under consideration here falls in the same category as the combs in [33] and hence modeling with a model for linear polymers is justified, although it would be unreasonable to expect quantitative accuracy. A nonlinear single-mode constitutive model that includes all of the features of the molecular theory for entangled, linear, monodisperse polymers based on the tube idea, i.e., the orientation of the tube due to the flow at rates higher than the inverse terminal relaxation time, and, at rates above the inverse Rouse time of the chain, the stretch of the chain within the tube, was developed by Marrucci and Ianniruberto in [56], henceforth referred to as the “M-I model.” The relaxation of stress proceeds via the very fast relaxation of stretch (Rouse process) combined with other factors at longer times such as reptation and thermal and convective constraint release (CCR). Contour-length fluctuations cannot be described, as the model is single mode. Qualitatively, the model displayed all the key features: A shear-thinning steady shear viscosity, overshoots in stress and first normal stress

difference in start-up shear flow, and strain hardening in extensional flow. We adopted a multimode version of this model, following [64] and further included a spectrum of Rouse relaxation times to account for chain stretching. The model simply consists of a linear superposition of different single-mode models. Given the molecular structure of the comb investigated, i.e., small branches and large backbone (Fig. 1), this model is considered as a good first approximation especially for nonlinear shear flow. Analysis with a physically more meaningful molecular model is deferred to future modeling work. The procedure to obtain the predictions is to first determine the Rouse time of an entanglement segment τ_e following [65] (values and further details are provided in Sec. III D). Then, the linear viscoelastic data are fitted with a number of Maxwell modes in the regular way over the frequency range of interest to extract the discrete relaxation spectrum. This fit results in a number of “disengagement” times $\tau_{0,i}$. The corresponding set of entanglement densities $Z(i)$ for each mode i are calculated, assuming validity of the formula of Doi [66] (taking contour-length fluctuations into account): $\tau_{0,i} = 3\tau_e Z(i)^3 (1 - (1.47/\sqrt{Z(i)}))^2$ for each individual mode. From the entanglement densities, a set of Rouse times can be calculated as $\kappa \cdot \tau_e \cdot Z(i)^2$ with κ an adjustable parameter of order unity that provides a way to change and assess the importance of stretching in the model. A unit value for κ corresponds to the classical Rouse model for chain stretch. Finally, the remaining parameters in the model are the plateau modulus G_N^0 (determined as discussed in Sec. III D, treating the branches as solvent) and the CCR parameter β which is of order unity [56,64,67].

III. EXPERIMENTAL RESULTS

A. Linear viscoelasticity

The experimental master curves for the elastic G' and loss G'' moduli as a function of angular frequency ω for the exact comb in the molten state and in solution are shown in Fig. 3(a) at a reference temperature of 20 °C. The black lines in Fig. 3(a) result from the conversion of the long-time creep compliance $J(t)$ data obtained at 90 °C to the storage and loss moduli and subsequent shifting to the reference temperature using the shift factors obtained from the construction of the master curves as described in Sec. II B. One can clearly observe the two step relaxation behavior typical for comb polymers for both the melt and the solution due to the hierarchy of modes discussed above. Figure 3(b) shows the horizontal a_T and vertical b_T shift factors as functions of temperature T as utilized in the construction of the master curves. The master curves were obtained using time-temperature superposition with 2D minimization (using the RSI Orchestrator software), and all data are shifted to 20 °C. The full lines in Fig. 3(b) are the fits of the horizontal shift factors with the Williams-Landel-Ferry (WLF) equation [68] $\log(a_T) = (-C_1 \cdot (T - T_{\text{REF}})) / (C_2 + T - T_{\text{REF}})$. With $T_{\text{REF}} = 20^\circ\text{C}$, we found $C_1 = 3.74$ and $C_2 = 162^\circ\text{C}$ for the melt and $C_1 = 3.69$ and $C_2 = 175^\circ\text{C}$ for the solution. The dashed grey line is the vertical shift factor calculated as [68]: $b_T = (\rho(T_{\text{REF}})(T_{\text{REF}} + 273.2)) / (\rho(T)(T + 273.2))$ taking into account the temperature dependence of the density. For

FIG. 3. (a) Master curves for the storage G' (filled symbols) and loss G'' (open symbols) moduli as a function of angular frequency ω for the comb melt (triangles) and solution (circles) at $T_{\text{ref}} = 20^\circ\text{C}$ and fits with the BoB-model (dark and light grey lines for the melt and solution, respectively). The black lines result from the conversion of the creep compliance data for the melt. (b) The horizontal a_T (circles) and vertical b_T (triangles) shift factors as a function of temperature T together with the WLF-fits (full lines) for the melt (in grey) and solution (in black). The dashed dark grey line indicates the calculated b_T following the density compensation method.

PBD, the temperature dependence of the density ρ (in g/cm^3) is extracted from [69] as $\rho(T) = 1.055 - 5.6 \cdot 10^{-4}(T + 273.2) + 5.33 \cdot 10^{-21}(T + 273.2)^2$. One can see that the experimental b_T 's follow the theoretical ones closely, thereby indicating that the data are of good quality, except for the solution at the lowest two temperatures where the vertical shift factors become somewhat erratic. This can be attributed to different thermal expansion coefficients for polymer and solvent (i.e., for a solution the scaling with the density of PBD is of course not strictly valid due to the presence of the solvent) and changes in solvent quality with temperature. In relation to this last point, we note that squalene has a melting temperature of -75°C and is hence expected to crystallize at the lowest temperatures. Nevertheless, the trend of the data is correct, and in particular, the terminal regime is well fitted. We did not attempt to further explore the issues at the lowest temperatures as our aim was indeed to investigate the nonlinear shear flow behavior of the solution at room temperature.

The solution is of main interest here, and hence, it is important to further discuss the quantities that can be extracted from the master curves. The zero-shear viscosity η_0 , the zero-shear recoverable compliance J_S^0 , and the longest relaxation time τ_0

were evaluated as discussed in [33] by fitting different models to the low frequency data. For the solution (at 20 °C), we found $\eta_0 = 362 \pm 9$ Pa s, $J_S^0 = (1.77 \pm 0.09) \times 10^{-4}$ Pa⁻¹, and $\tau_0 = \eta_0 J_S^0 = 0.064 \pm 0.003$ s. It is further of interest to compare the plateau moduli at low (1.6×10^4 Pa) and high frequencies (3.5×10^4 Pa). They were taken as the values of G' at the local minima of $\tan(\delta) = G''/G'$, and they are somewhat prone to error especially because the high frequency minimum is unclear. Following the hierarchical relaxation picture, in which the branches act as dynamic solvent at long times, one can take the ratio of the low-frequency over the high-frequency moduli thereby assessing the volume fraction of the backbone ϕ_{BB} in the structure. The ratio scales as $\phi_{BB}^{1+\alpha}$ with α being the dynamic dilution exponent. Its value is currently unsettled but thought to be either 1 or 1.3 [70,71]. Assuming $\alpha = 1$, as typically used in the BoB-model [4,57], we obtain a value for the volume fraction of the backbone ϕ_{BB} of 0.68 (with $\alpha = 1.3$, $\phi_{BB} = 0.71$). On the other hand, from the molecular structure in Fig. 1, one can write $\phi_{BB} = M_{\text{Backbone}} / (q \cdot M_{\text{Branch}} + M_{\text{Backbone}}) = 0.73$ (with q and M_{Branch} , the number and molar mass of the branches, and M_{Backbone} , the molar mass of the backbone), slightly higher but nevertheless in reasonable agreement with the value from the linear viscoelastic data of the solution. Note that, when we compare the high and low frequency moduli for the melt, we obtain the same values of 0.68 for ϕ_{BB} with $\alpha = 1$ (and 0.72 with $\alpha = 1.3$). Upon comparing the (high frequency) modulus of the pure melt (9.2×10^5 Pa) with the one of the solutions following the theta-solvent scaling for the moduli [3,72] $G_N^0(\phi)/G_N^0(1) = \phi^2$, we find a volume fraction of 0.20, identical to the targeted composition in the preparation of the solution (see Sec. II A). If we follow the good solvent scaling for the moduli instead, $G_N^0(\phi)/G_N^0(1) = \phi^{2.3}$, we obtain a volume fraction for the comb in solution of 0.24. A further comparison of the data shows that the high-frequency crossover between G' and G'' for the solution occurs at a lower frequency as compared to the melt. This is somewhat unusual but inline with the comments given in the previous paragraph: The melting temperature of squalene is around -75 °C, and hence, we do not expect a “simple plasticization” at these low temperatures.

It is furthermore of interest to obtain an estimation for the stretch time of the backbone of the comb $\tau_{S,BB}$ for the solution as it is important to interpret the transient nonlinear shear data. First, we need to estimate the molar mass between entanglements M_e . It can be obtained from the high-frequency plateau modulus taking into account the effects of the solvent (and including the 4/5 prefactor) as [57,68] $G_N^0(\phi) = (4/5)(\phi \rho RT / M_e(\phi))$, with ρ , the density of PBD at 20 °C (890 kg/m^3 [69]), T , the temperature in Kelvin (293.2 K), R , the ideal gas constant [8.314 J/(mol K)], and ϕ , the volume fraction of the polymer in the solution (0.20), which yields a molar mass between entanglements for the solution M_e equal to 9.9 kg/mol . The number of entanglements of the backbone Z_{BB} can now be calculated and is equal to 13.6, while the number of entanglements of the branches in the solution is 1.0. Now treating the branches as dynamic solvent at long times, we can calculate the number of entanglements of the dynamically diluted backbone as $Z_{BB}^{DIL} = \phi_{BB}^\alpha Z_{BB}$ with the dynamic dilution exponent α equal to 1,

we obtain 9.9. One can estimate the comb $\tau_{S,BB}$ with reasonable accuracy using the approach outlined in [73] according to which the ratio of the longest relaxation time over the stretch time of the backbone of the comb can be approximated by the direct comparison with the analogue ratio for linear polymers as in $\tau_{0,lin}/\tau_{R,lin} = \tau_0/\tau_{S,BB}$. In this approach, one needs to compare linear chains with a number of entanglements Z equal to Z_{BB}^{DIL} thereby treating the branches as dynamic solvent. The ratio $\tau_{0,lin}/\tau_{R,lin}$ can be calculated following the earlier quoted formula of Doi [66] for the relation between the longest relaxation time for linear, monodisperse polymers with number of entanglements Z , and the relaxation time of an entanglement τ_e (taking contour-length fluctuations into account) $\tau_0 = 3\tau_e Z^3 (1 - (1.47/\sqrt{Z}))^2$ and the classical formula for the Rouse time $\tau_{R,lin} = \tau_e Z^2$. As we need to calculate the ratio of the two, τ_e cancels out and upon insertion of $Z_{BB}^{DIL} = 9.93$ for Z , we obtain the desired ratio which leads to a value for the stretch time for the backbone of the comb of $\tau_{S,BB} = 0.0075$ s. Note that an alternative formula for the longest relaxation time of linear, monodisperse polymers, namely, $\tau_{0,lin} = 3\tau_e Z^3 (1 - (2C_1/\sqrt{Z}) + (C_2/Z) + (C_3/Z^{1.5}))$ with Z , the number of entanglements and $C_1 = 1.69$, $C_2 = 4.17$, and $C_3 = -1.55$ was proposed in [74]. Using this formula leads to a value of 0.0072 s for $\tau_{S,BB}$, in good agreement with the previous value. Note that, in both approximations, possible effects of the increased friction of the branch points on the stretch time are not taken into account [34,75,76]. If anything, one can expect that the increased friction of the branch points renders the stretch time of the backbone somewhat higher [63,73].

We attempted to model the master curves of G' and G'' for both melt and solution with the BoB-model [57]. The resulting predictions are shown with light grey lines for the solution and dark grey lines for the melt in Fig. 3(a). For both the melt and the solution, we used the following parameters in the model: A dynamic dilution exponent $\alpha = 1$ as typically used in the BoB-model, a density ρ of 890 kg/m^3 , a temperature T of 293.2 K, a molar mass of the monomer M_0 of 0.0541 kg/mol , and a number of monomers between entanglements N_e of 32. This corresponds to a molar mass between entanglements $M_e = N_e M_0 = 1.7 \text{ kg/mol}$, in good agreement with the experimental data (when calculating the molar mass between entanglement from the plateau modulus). The structure of the comb in the simulations was identical to the one in Fig. 1, with each segment having a log-normal molar mass distribution with a chosen PDI of 1.1. Architectural dispersity as in [15,16] is not considered here. The final parameter for the model is the relaxation time of an entanglement segment τ_e . It was given a value of 1.0×10^{-6} s for the melt and 1.3×10^{-8} s for the solution. For the solution, we simulated the solvent as short linear, monodisperse polymers with a molar mass of 0.4 kg/mol , i.e., the molar mass of squalene, and the volume fraction of polymer ϕ was set to 0.2. As one can observe in Fig. 3(a), the prediction of the model for the melt is roughly feasible albeit slightly less broad than the experimental data while the prediction for the solution is significantly broader than the experimental data and a relatively good fit of the terminal regime could only be obtained by setting the τ_e about two decades “too low.” Hence, although the model describes the melt relatively well, clearly the model

does not describe the linear viscoelastic data of the solution as well as expected from earlier works [4,34,57]. We chose not to pursue this issue here. It is evident from both the fits with the BoB-model, the shift factors [in Fig. 3(b)], and the shift in the high-frequency modes upon addition of solvent [in Fig. 3(a)] that local solvent-polymer interactions need to be better understood. Seemingly, for the solution, especially the relaxation of the branches is significantly less broad than predicted by the model, which presumably relates to changes in the interactions between the solvent and the polymer at low temperatures.

B. Transient start-up shear flow in the CPP

The key interest in this work is in a full characterization of the steady-state shear flow behavior of the solution including both the shear stress σ and the first normal stress difference N_1 . Given this objective, we performed measurements with the CPP at very high shear rates, up to 316 s^{-1} . At these rates, compliance effects and effects of startup of the motor of the rheometer are known to influence the mechanical measurements rather drastically during the start-up transient, while not affecting the steady-state results as discussed in Sec. II C. In this section, we report upon the most complete data set on the transient start-up shear flow obtained at -20°C , keeping in mind these problems and limitations. Also note that the transient start-up shear flow behavior has been studied in the CPP for a variety of combs in the molten state in [33,63].

The start-up shear stress σ^+ obtained at -20°C is shown as a function of strain γ in Fig. 4(a) for different shear rates. The curves are shifted to a temperature of 20°C using the shift factors from the linear data [Fig. 3(b)]. At low rates, below the inverse terminal relaxation time, the stress reaches its steady-state monotonically. At higher rates, the stress displays an overshoot before reaching a steady value. Initially, the peak-strain is slightly above 2 and independent of rate, while, at higher rates, the peak-strain shifts to larger values. This picture is qualitatively identical to the behavior of linear monodisperse polymers [39,40,77] and also in agreement with the earlier work on combs with short branches [33]. The simultaneously measured start-up apparent normal stress difference N_{APP}^+ is shown in Fig. 4(b) for different shear rates. (The two highest shear rates are not shown here as a clear steady-state could not be identified, which is also to some extent the case for the shifted rate of 1240 s^{-1} .) The apparent normal stress difference N_{APP} , as measured with the CPP, is not equal to the first normal stress difference N_1 as in a regular cone and plate [36,38]. This will be discussed in more detail in Sec. III C. Here, it suffices to say that, with some assumptions, the first normal stress difference can be calculated from the apparent one and that qualitatively, both with respect to the trend and the order of magnitude, N_1 and N_{APP} are identical. As can be observed in Fig. 4(b), the errors on the normal stress difference are rather large and the data are intrinsically of rather low quality. At least partially, this is an effect of small thermal fluctuations of $\pm 0.1^\circ\text{C}$ and the resulting density fluctuations which have been shown to affect the normal force measurements [36]. Furthermore, the problems with compliance are much more severe for the normal force than the torque [41]. These issues imply that the

FIG. 4. Startup shear stress σ^+ (a) and apparent normal stress difference N_{APP}^+ (b) as a function of strain γ for the comb solution. The data were obtained at -20°C and shifted to 20°C . The shifted rates are shown next to the curves in s^{-1} . Only selected rates are shown for clarity.

data for the transient first normal stress differences are rather qualitative in nature. The values for the steady-state first normal stress differences can however be reliably extracted (see also Sec. III C) as they are not affected by compliance and thermal fluctuations in the same way [36,41]. Hence, although we do not claim quantitative accuracy of the transient normal stress difference data, it remains of interest to discuss its qualitative features. Tube models developed for linear polymers predict a gradual monotonic increase of the first normal stress difference toward steady state as a function of time for shear rates below the inverse Rouse-stretch time of the chains [78]. At higher rates, around and above the inverse Rouse time of the linear chains, an overshoot develops on the first normal stress difference due to the stretching of the chains [78]. In Fig. 4(b), we can observe that an overshoot appears for the first time for the data at 120 s^{-1} . This value is in excellent agreement with the estimation of the stretch time of the backbone of the comb $\tau_{\text{S,BB}}$ of 0.0075 s as derived in Sec. III A.

The steady-state shear stresses σ and apparent normal stress differences N_{APP} , discussed in Sec. III C, were always obtained by averaging over the steady-state portions of the start-up curves in Figs. 4(a) and 4(b). The errors on the steady-state values are calculated as the standard deviations, and they are shown further on as error bars (usually they have about the same size as the symbols).

C. Steady-state shear flow

Different data sets for the steady-state shear stress σ as a function of shear rate $\dot{\gamma}$ are plotted in Fig. 5(a) at 20 °C. The open black squares are obtained with a regular cone and plate at 20 °C. This data set is limited to low rates as the sample was observed to fracture at higher rates upon entering the nonlinear regime. The black and light grey circles are from measurements with the CPP performed at 20 °C. The dark grey circles are the experimental points as obtained from the data in Fig. 4(a) (data obtained at –20 °C with the CPP and shifted to 20 °C). The overlap between the different data sets obtained with the regular cone and plate (open black squares) and the CPP (black, light and dark grey circles) indicates the excellent reproducibility of the data. The black line is a representation of the empirical Cox-Merz rule [79], i.e., $\eta(\dot{\gamma}) = \eta^*(\omega)|_{\omega=\dot{\gamma}}$, or in terms of stress, $\sigma(\dot{\gamma}) = G^*(\omega)|_{\omega=\dot{\gamma}}$ and has been obtained directly from the linear data in Fig. 3(a). It overlaps within experimental error with the before-mentioned circles except (perhaps) at the highest rates. Also in the earlier work on the nonlinear shear flow behavior in a

FIG. 5. Steady-state shear stress σ (a) and first normal stress difference N_1 (b) as a function of shear rate $\dot{\gamma}$ at 20 °C. The black, light, and dark grey circles represent three different sets of measurements performed with the CPP, the two former at 20 °C, the latter at –20 °C. The open black squares are mechanical data obtained with a regular cone and plate at 20 °C. The open black triangles represent the optical data obtained via flow birefringence in combination with the stress-optical rule. The black line in (a) represents the linear viscoelastic data $b_T \cdot G^*$ as a function of angular frequency.

CPP-geometry of model combs in the molten state, the Cox-Merz rule was found to be obeyed in all cases for combs with short branches, and we only found violations of the rule when the branching level became very high [33,63,80]. Note that the mechanical data as reported here for the exact comb solution are in all respects in agreement with the earlier work on combs with short branches (in terms of shear-thinning slope, obedience of the Cox-Merz rule, evolution of the peak-strains, and the relative heights of the overshoot) [33,80]. The open black triangles in Fig. 5(a) are the data obtained via flow birefringence by applying the stress-optical rule, as discussed in Sec. II D. The stress-optical data set is in excellent agreement with the mechanical data sets which provides further confidence to the data. Note that also the stress-optical data are limited to lower shear rates compared to the mechanical data due to the inhomogeneous nature of the flow field in the Couette geometry as discussed in Sec. II D. Here, we somewhat arbitrarily limited the shear rates in the Couette to $40 s^{-1}$. At this rate, the shear thinning slope for the solution is 0.5 and the corresponding maximal inhomogeneity, i.e., the maximal total variation of the shear rate over the gap as calculated using the expression for a power-law fluid (see Sec. II D), is 5% [43].

The apparent normal stress difference N_{APP} , as measured with the CPP, is not equal to the first normal stress difference N_1 but is given by [36,38,39] $N_{APP} = N_1 + 2(N_1 + 2N_2) \ln(R_{sample}/R_{plate})$, with N_1 and N_2 , the first and second normal stress differences, R_{plate} , the radius of the active plate of the CPP geometry (here 4 mm), and R_{sample} , the radius of the sample as loaded in the CPP (in this case, the radius of the sample is measured to be 7.2 mm using a caliper after opening the CPP-geometry. This measurement can be done with an accuracy of about 0.1 mm). By assuming a ratio of $N_2/N_1 = -0.2$ as found in [39] for linear, monodisperse polymers, one can calculate the first normal stress difference N_1 from the measured apparent normal stress N_{APP} with the CPP. The steady-state first normal stress difference N_1 calculated as just outlined with the necessary approximation for $N_2 = -0.2N_1$ is plotted as a function of shear rate $\dot{\gamma}$ in Fig. 5(b) at 20 °C. The dark grey circles are the experimental points as obtained from the data in Fig. 4(b). The open black triangles result from the flow-birefringence measurements via application of the stress-optical rule. We can clearly see that, for N_1 , the two techniques are complimentary, with the flow-birefringence technique rendering reliable values at low rates where the mechanical technique is not sensitive, while at high rates, the mechanical measurements are more reliable, while the stress-optical technique has problems with instabilities in the inhomogeneous flow field. Also note that the error on N_1 is significantly larger than the error on the shear stress.

D. Tube-model predictions for the steady-state shear stress and first normal stress difference

The first stage of the implementation of the M-I model was the regression of the master curves of the dynamic moduli [Fig. 3(a)] to extract the discrete relaxation spectrum. Ten modes, distributed and equally spaced (on a log-scale) were fitted over a wide range of frequencies (1–1500 rad/s) to the

FIG. 6. Steady-state shear stress σ (a) and first normal stress difference N_1 (b) as a function of shear rate $\dot{\gamma}$ for the solution at 20 °C. The experimental data are as in Fig. 5. The thick black lines are the predictions from the M-I model.

dynamic moduli. The maximum frequency has been chosen in order to fit the dynamic moduli data in the range of frequencies, where the viscoelastic response is dominated by the backbone relaxation. Following the estimation of the Rouse time of the entanglement segment τ_e for PBD melts in [65], i.e., $\tau_e(20^\circ\text{C}) = 1.9 \times 10^{-7}$ s, one can estimate the value for the solution by following [72] to estimate the effects of dilution on the monomeric friction coefficient. In doing so, one arrives at a value of $0.85 \mu\text{s}$ for the τ_e of the solution, more than one decade above the too low value used in the BoB-model in Sec. III A to obtain quantitative agreement in the terminal regime. κ , the parameter that controls the importance of stretch in the model (see Sec. II E), has been used as a fitting parameter of order unity and it was found that a value of 2 led to a good description. The plateau modulus of the equivalent (diluted) linear polymer solution has been calculated assuming that the concentration of the comb polymer in the solution is 20 vol. %. Furthermore, we assume that the arms are always fully relaxed and act as a “dynamic” solvent following the hierarchical relaxation picture. As the fraction of backbone in the comb is 0.73 (see Sec. III A), the volume fraction of the equivalent (dynamically diluted) linear polymer solution is 15% ($0.73 \times 0.20 = 0.15$). As in Sec. III A,

the dynamic dilution exponent α used to calculate the dilution effect on G_N^0 has been set equal to 1. Finally, the value of the CCR-parameter β has been set equal to 1 which is a typical value used in the literature [55,56,64,67,81,82].

In Fig. 6(a), the modeling results for the steady-state shear stress are compared with the set of experimental results previously reported in Fig. 5(a) with the thick black line being the shear stress calculated from the model. In Fig. 6(b), the modeling results for the steady-state first normal stress difference are compared with the set of experimental results reported in Fig. 5(b). The M-I model correctly predicts a monotonic increase, with increasing shear rate, of steady shear stress and first normal stress difference due to CCR and chain stretching. As one can see, the predictions are in good agreement with the experimental data, with some deviations at the higher shear rates, suggesting that the nonlinear shear flow behavior of the particular comb with relatively short branches can be well described by assuming it to be a solution of linear polymers with the branches acting as dynamic solvent. Considering that the model has been developed for linear polymers, it is remarkable that besides the linear viscoelastic spectrum, just a single fitting parameter κ could be utilized to obtain a satisfactory description of the steady nonlinear shear properties and its value is consistently of order unity. It is also worth noting that the disengagement time corresponding to the terminal crossover frequency corresponds to an equivalent linear polymer with a molar mass approximately the double of the actual molar mass of the backbone of the comb. This can be rationalized by considering an extra contribution of the branches to the friction, which is not taken into account by M-I model, which might reduce the rate of stress relaxation by reptation.

IV. CONCLUSIONS

In this work, we reported upon the nonlinear shear flow behavior of a solution of model asymmetric exact comb PBDs. The steady-state shear stress and the first normal stress difference were obtained experimentally with mechanical measurements using a regular cone and plate and a CPP geometry and optically using flow birefringence in combination with the stress-optical rule. The steady-state shear stress followed the Cox-Merz rule and is in agreement with the earlier results on combs with short branches studied with the CPP [33]. In [33], the first normal stress differences were not reported due to severe compliance issues for polymer melts. On the other hand, the optical setup is not appropriate for the study of molten polymers. In this work, due to high amount of solvent in the sample, we did manage to collect the steady-state first normal stress differences with both techniques.

Although the transient start-up mechanical data as obtained with the CPP are only qualitative due to the high shear rates employed, we did discuss its qualitative features. More specifically, the transient first normal stress differences displayed an overshoot starting from rates around $100 s^{-1}$. For linear monodisperse polymers, tube models predict that the first normal stress difference reaches its steady value gradually and monotonically in time in startup shear flow at

rates below the inverse Rouse time of the chain, while overshoots only appear at rates above this value [78]. Hence, the rate where the overshoot starts to appear in the data of the exact comb solution is in remarkable good agreement with our simple estimation of the stretch time of the backbone (see Sec. III A). This indicates that the friction of the three branch points, which is neglected in our estimation of the stretch time, is not a primary concern for the stretching behavior.

Finally, due to the lack of an appropriate full molecular tube model for nonlinear shear flow of model branched polymers, we attempted to gain additional understanding from a modeling approach developed for linear polymers. This approach is motivated by our earlier work [33] where we found that comb polymers with short branches behave qualitatively essentially like linear polymers with some minor quantitative differences. The modeling approach was shown to fit well with the behavior of the comb solution when treating the branches as additional solvent. This is in agreement with our expectations and acts as further proof that branched polymer solutions with a “relatively small” number of “relatively short” branches behave in simple shear essentially like linear polymers when the branches are treated as additional solvent. The exact interpretation of “relatively small number” and relatively short is currently still unclear, but this nevertheless provides a clear picture for the nonlinear flow behavior of branched polymers.

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