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Rheology of Small Spherical Polystyrene Microgels: A Direct Proof for a New Transport Mechanism in Bulk Polymers besides Reptation

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ABSTRACT: A recently developed synthetic technique, the polymerization in microemulsions, gives access to a new type of model polymer, spherical microgels or "rubbery nanospheres". These polymer molecules are narrowly distributed and have sizes in the range of 5 nm $< R <$ 50 nm. In this paper, we report the examination of the viscoelastic behavior of these microgels in the bulk above their glass transition. Opposite to all expectations, these microgels show viscous flow up to molecular weights of $M_w = 2 \times 10^6$ or related hard-sphere radii of $R = 9$ nm, and the zero-shear viscosity is remarkably lower than the one of linear chains of the same molecular weight. Similarily surprising, it is shown that frequency dependence of the mechanical response looks like the well-known Zimm- or reptation-type response, although a Zimm- or reptation-like mobility can be strictly excluded by the spherical architecture of the molecules. These results support the existence of a strong, secondary type of polymer mobility besides reptation which is more cooperative in its nature than a single-chain mobility. This mobility should play an important role in all bulk polymer systems and might explain the rather high transport rates and deviations from reptation reported in many polymer systems with higher complexity.

1. Introduction

The mechanistic understanding of the dynamics of polymers in the bulk is still one of the central questions in polymer physics. It is already 23 years ago when "reptation"[1] or the "tube model"[2,3] was given as the famous answer, and a large number of groups coming from various places confirm the concept of a snakelike motion inside a geometrical constrained environment with several experimental techniques.

Reptation and the tube model was originally developed to explain the typical dynamic-mechanical response of linear polymers of high molecular weight (see, for instance, ref 4) which is classically separated into a glassy zone, a transition zone, a plateau region, and a terminal zone (in the order of decreasing frequencies; see ref 5). This relaxation curve is not only qualitatively explained by the tube model but it also results in a quantitative explanation of the plateau modulus as well as it predicts nearly the correct scaling relation between zero-shear viscosity and polymer molecular weight, $\eta_0 \sim M^3$, instead of the experimental result $\eta_0 \sim M^{3.4}$ (for a good review related to the problem of quantitative descriptions with reptation, see ref 6).

More recently, dynamic neutron scattering experiments reveal a transition of the dynamics of entangled polymer melts between a more local, Rouse-like relaxation and a "constrained" behavior at longer distances.[7−9] Unequivocally, these experiments prove the existence of an intermediate microscopic length in polymer melts where the dynamics severely changes. This constraining length is on the order of 3.5−7 nm, depending on the type of polymer, and might be assorted to the tube diameter. The values for the tube diameter depend on the temperature and increase for poly(ethylenepropylene) as much as 50%.[9]

Maybe the most striking evidence for reptation was given by diffusion experiments. In these experiments, it was possible to follow the diffusive mobility of linear chains in networks[10] or matrices of linear chains of high molecular weight.[11,12] Here, the famous $D \sim M^{-2}$ law as well as the invariance of the mobility against crosslinking was observed. It was also shown that self-diffusion is usually much faster than diffusion in a high molecular weight matrix where the dependence on the matrix molecular weight cannot be explained by simple reptation-based ideas.[11]

On the other hand, an increasing number of experiments on very different systems also shows that reptation cannot be the one-and-only answer for all problems in diffusion or transport in polymer melts, and we are able to mention just a small excerpt of the long list of experiments.

A very illustrative example is the bulk diffusion and viscosity of ring polymers where a curvilinear mobility should result in close to no mobility at all. A very extensive study of the viscoelastic behavior,[13] however, shows that the mobility of rings is unexpectedly high and about the same value as linear chains of about the same molecular weight. Diffusion experiments which are more valuable since the probe and matrix can be varied independently[14,15] exhibit a very complicated situation where the mobility sensitively depends on the matrix used; nevertheless, it can be stated that the mobility of rings is still much too high.

A similar chasm can be observed in the case of the rheology of star polymers. Starting from the first concepts of de Gennes,[16] it was postulated that the zero-shear viscosity as well as the diffusion coefficient should

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depend exponentially on the arm length and, depending on theory, in some way on the number of arms. About 30 main papers dealing with this subject have appeared (a good review was given by Pearson[17]), and most of them show an algebraic dependence on the arm length only, close to no dependence on the arm number, and a very low viscosity compared to linear chains. The more selective diffusion experiments show that star transport in cross-linked matrices really occurs according to arm retraction,[18-20] but mobility is much higher in a matrix of the same type, e.g., stars in stars.[18] We have to underline the point that a 20-arm star of $M_w = 1 \times 10^6$ has about the same viscosity as a linear chain of $M_w =$ 100 000 which is an obvious contradiction to the original ideas.

Rheological experiments on block copolymers with spherical morphology show a mechanical behavior very similar to many-arm stars.[21] The replacement of a covalent star center by a spherical rubbery or glassy phase apparently does not alter the mechanical response.

But even the dynamics of linear polymers are, contrary to the apparent simplicity of the theory, far more complicated. For instance, it has been known for some years that the mode spectrum of linear polymer melts is not fully described by a Rouse- or a Zimm-type spectrum and the tube renewal time τ_R solely. Recently, Winter et al. showed that an additional mode spectrum in the intermediate time scale with algebraic characteristics is needed for the quantitative description of linear polystyrene and polybutadiene melts.[22] Fuller and Kornfield et al. showed with rheooptical experiments in a series of papers of high excellence[23-25] that the dynamics in binary blends (i.e., blends of two different, narrowly distributed linear polymers) has many features which cannot be explained by the standard theory. The smaller chain relaxation, for instance, becomes retarded by longer chains, whereas the longer chain mobility depends much stronger on the amount of smaller chains than predicted. Both results were explained by a new effect which was called "orientational coupling".[24,25]

Similar deviations are also observed in the case of model ionomers or interacting polymer molecules. For model ionomers with narrow molecular weight distributions, different charge densities and counterions, unexpectedly low zero-shear viscosities, and a broad relaxation time distribution have been observed.[26] Stadler and Fuller et al.[27] found for bidisperse polybutadiene melts wearing "sticker" molecules a relaxation dynamics which cannot be described by modified reptation concepts without assuming very high, "orientational coupling coefficients".

For an explanation of the experimental findings, more or less senseful extensions and supplements to the reptation model have been made, which might explain one experiment at a time. However, most of these theories miss the clarity and simplicity of the basic reptation concept and are, in our opinion, also less convincing.

These and some other arguments have already been reviewed in a thorough review of Lodge et al.[28] and discussed from a different viewpoint. We agree with these authors that the fundamental validity of the tube model remains controversial.

In 1988, we tried to establish a new model system which, in principle, should allow one to observe other mobility mechanisms than reptation: Self-cross-linking of monodisperse linear chains produces monodisperse microgels which exhibit a dynamic-mechanical behavior very different from that of their linear precursors.[29] The structure of these self-cross-linked polymers, however, remained unclear which disqualified them as a model.

It took us another 5 years to develop special techniques of the polymerization in microemulsions as a easy route for the synthesis of ultrafine polymer microgels with spherical shape and low polydispersity[30-32] (for a review, see ref 33). This technique now gives access to a new type of model polymer which might be described as "rubbery nanospheres". Rheological examinations on these systems offer some unique advantages which makes their data more valuable:

(1) These systems have, when highly cross-linked, no entanglements, since their network chains are too short (at least by the current definition of entanglements).

(2) They have a clear equilibrium geometry which is just slightly changed to some polyhedral morphology due to the dense packing.

(3) A clear size parameter is given by the radius of the particles.

In the following, we present a brief description of the viscoelasticity of these model polymer melts, thus giving the first clear proof for a second transport mechanism besides reptation.

2. Experimental Section

2.1. Polymer Synthesis. The technique of polymerization in microemulsions has recently been reviewed[33] and should for the present context just briefly be recapitulated. For the smaller particles in the range of $5 < R < 10$ nm, the metallosurfactant myristyldiethanolamine−copper is used,[32] whereas for all other systems, cetyltrimethylammonium chloride (CTAB) was taken as the surfactant.[31]

Typically, 10 g of freshly distilled styrene, the designated amount of cross-linker (0.38 g of *m*-diisopropenylbenzene for a cross-linking density of $^1/_{10}$ or one cross-link per 10 monomer units), and 150 mg of AIBN are mixed to form the oil phase. A solution of the calculated amount of surfactant (e.g., 20 g of CTAB (Aldrich) or myristyldiethanolamine−copper, synthesized according to ref 32) in deionized and degassed water is prepared separately (100 g altogether). Oil and water phases are mixed. Microemulsification occurs spontaneously in the case of the metallosurfactant, whereas for the CTAB system, vigorous stirring with a high-speed stirrer is helpful. After approach of equilibrium, the reaction mixtures are heated for 24 h at 60−70 °C. After this period, the conversions exceed 90%, as checked by the mass of the isolated polymer. A close-to-complete conversion must be guaranteed since unreacted pendant vinyl groups result in macroscopic gelling of the samples at elevated temperatures.

An aliquot of the latex is kept for characterization with dynamic light scattering and electron microscopy; the remainder is precipitated by addition of 200 mL of methanol. The surfactants are removed by a 3-fold reprecipitation. Here, the crude product is redissolved in 100 mL of THF and precipitated in methanol by dropwise addition of the microgel solutions. The resulting white powder is dried in a vacuum oven for 48 h at 50 °C. In the final products, no surfactant can be detected as checked by NMR and chloride analysis. The reproducibility of the polymerization procedure is demonstrated with samples MCU2.5a and MCU2.5b, the data of which are listed below.

2.2. Particle Size Characterization. The particle sizes and particle size distributions are determined by TFFF (thermal field flow fractionation) coupled with MALLS (multiangle laser light scattering) detection. The TFFF system used in this work was constructed and assembled in a way similar to those used in previously reported thermal FFF studies.[34] The system consists of two chrome-plated brass bars with highly polished faces clamped together over a sheet of Mylar in which the channel space had been cut. The channel

Table 1. Polymer Analytical Data of the Current Series of Microgels[a]

		dynamic light scattering		TFFF–MALLS		
sample	surfactant	r_H/nm	σ	M_w	M_w/M_n	SLS M_w
MCU3.0	MDEA-Cu $S = 3.0$	7.4	0.26	150 000	1.07	137 000
MCU2.5a	MDEA-Cu $S = 2.5$	8.1	0.24	187 000	1.14	182 000
MCU2.5b	MDEA-Cu $S = 2.0$	8.1	0.27	208 000	1.08	210 000
MCU2.0	MDEA-Cu $S = 2.0$	8.5	0.33	257 000	1.04	256 000
CTAB3.0	CTAB $S = 3.0$	12.6	0.30	1 030 000	1.10	980 000
CTAB2.5	CTAB $S = 2.5$	12.9	0.32	1 250 000	1.03	1 240 000
CTAB2.0	CTAB $S = 2.0$	14.1	0.26	1 980 000	1.04	2 050 000
CTAB1.0	CTAB $S = 1.0$	18.1	0.26			8.15×10^6
CTAB0.5	CTAB $S = 0.5$	27.8	0.28			39.2×10^6

[a] The column "surfactant" denotes the conditions of synthesis. r_H is the hydrodynamic radius of the microgels in the dispersed microlatex state determined with dynamic light scattering; σ represents the polydispersity of the dispersion, expressed as a Gaussian width. The weight average of the molecular weight, M_w, is determined with TFFF–MALLS as well as with static light scattering (SLS).

dimensions are 2.0 cm in width by 47.4 cm in tip-to-tip length. The Mylar spacers were of two thicknesses, creating channel widths w of 0.075 and 0.050 mm. The hot bar was heated by three 630-W electrical cartridge heaters controlled by the 902S temperature controller from Eurotherm. The cold bar has holes drilled through the entire length for cold-water flow. The temperature is checked 0.7 mm off the surface of both bars simultaneously at three different positions by Keithley Model 820 thermometers using a copper–constantan thermocouple. Measurements across the length of the channel showed a variation of less than 0.8 K. Polymer concentrations in the sample were typically 0.5 mg/mL; a ΔT value of 30 or 20 °C depending on the channel thickness was used throughout the study. Peak detection was obtained with a Knauer A 0298 refractive index monitor and a Knauer A 0293 UV–vis detector as well as a Wyatt Dawn F MALLS setup. All further details of the setup as well as its separation properties for complex and functionalized systems can be found in a separate publication.[35]

Dynamic light scattering was carried out using a Nicomp C370 particle sizer with the ability of multiangle detection. Only correlations with excellent contrast and correlation strengths above 0.6 were taken. In some special cases, the samples were also characterized with our standard setup consisting of an ALV ISP86 goniometer, an ALV5000 multi-τ correlator, and an ADLAS 325c laser, and the agreement is good. Using the software of the particle sizer, the correlation functions are fitted with a Gaussian distribution of relaxation times, thus resulting in a mean hydrodynamic radius r_H and the width of its Gaussian distribution, σ.

2.3. Dynamic-Mechanical Shear Experiments. The dried microgel samples are taken as a powder and compression molded at 150 °C to optically clear or slightly opaque disks with diameters of 13 mm and thicknesses of up to 2 mm, thus fitting the geometry of a plate/plate rheometer. This treatment and the following measurements do not change the original size distribution, as checked by dynamic light scattering after redissolution. This temperature stability in the mechanical experiment is just given when unreacted vinyl groups are excluded by reaction engineering.

A Rheometrics RMS 800 apparatus is used in an oscillating low-amplitude mode in a frequency range between 10^{-2} and 10^2 rad/s with an amplitude of 2%. It is checked that our measurements are within the linear regime which, depending on particle size, goes up to 20–50% strain. The measurements are controlled by a FRT2000 frequency response analyzer which also records the complex torque. A stream of dry nitrogen is blown over the sample in order to avoid thermal-oxidative damage during the measurements performed at 110–190 °C. After heating the sample to maximum temperature, the measurement at 150 °C is repeated to check for alterations. Only measurements are presented where no changes are observed. Master curves are constructed using the temperature–frequency superposition principle and the WLF equation. The WLF parameters differ slightly from sample to sample and remarkably from linear polystyrene. For the examined temperature range, "universal values" of $C_1 \sim 6$ and $C_2 \sim 105$ can be given.

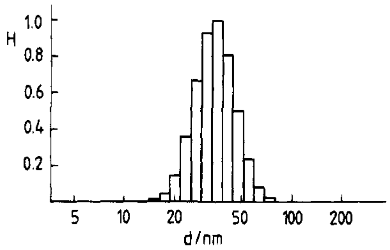

Figure 1. Particle size distribution of the CTAB0.5 microlatex, resulting from characterization with dynamic light scattering.

3. Results and Discussion

It was already mentioned that the synthesis of small spherical microgels, the systems with the most interesting physical behavior, was performed with a new synthetic process, the polymerization in microemulsion. Table 1 recapitulates the properties of the complete set of samples which are used for the present examination together with the type and amount of surfactant which was applied for their synthesis.

The hydrodynamic radius r_H and the polydispersity expressed as a fitted Gaussian width σ are data obtained for the microlatex dispersions, i.e., from the polymer microgels with the surfactant layers. These data are useful to estimate the polydispersity of the particles. These polydispersities can be regarded as upper limits, since it is known all particle interactions only broaden the apparent molecular weight distribution. The Gaussian widths can also be translated to the more common polydispersity indices M_w/M_n by mathematical standard procedures[36] and are generally below $M_w/M_n < 1.05$. Figure 1 shows, for a more illustrative point of view, which might be needed for the effects discussed below, a typical size distribution of the microlatex dispersion CTAB0.5 as obtained from the dynamic light scattering experiment.

In the case of the smaller microgels, it was also possible to characterize the purified microgels in THF solution by TFFF–MALLS coupling which allows the absolute determination of molecular weight distributions of complex or highly functionalized particles.[35] Figure 2 presents as a typical result of TFFF–MALLS the molecular weight distribution of MCU2.5b. With TFFF–MALLS, we are unable to characterize the complete molecular weight distribution since accurate light scattering measurements at the base of the peak are impossible. A data evaluation with RI and UV detection only, using a calibration curve gauged with light scattering, leads to the second set of data points in Figure 2 and a more precise polydispersity value.

These characterization results of TFFF–MALLS are also included in Table 1. Due to the separation char-

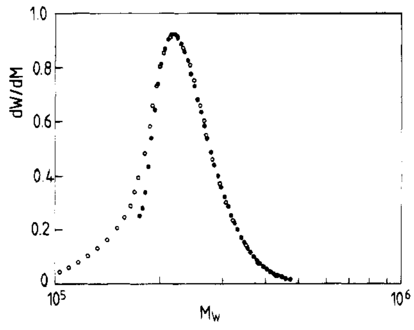

Figure 2. Molecular weight distribution of MCU2.5b, resulting from the TFFF–MALLS experiment. Filled circles: absolute determination with MALLS. Open circles: data evalution with calibration curve.

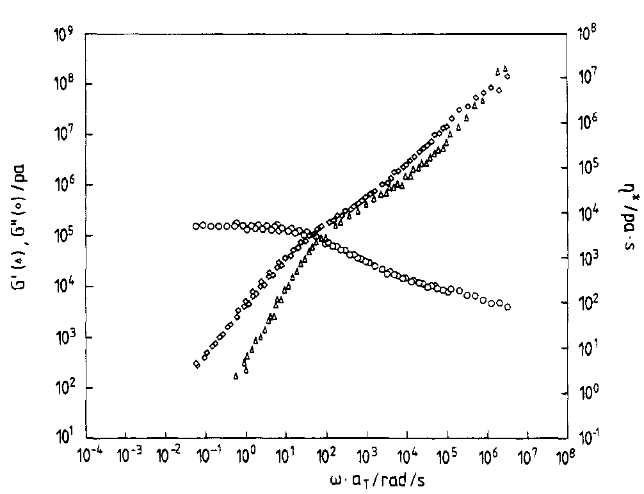

Figure 3. Storage modulus G' (△), loss modulus G'' (◇), and dynamic viscosity η^* (○) of sample MCU2.5a in dependence of the shear frequency ω, as obtained from the time–temperature superposition. The reference temperature is 443 K.

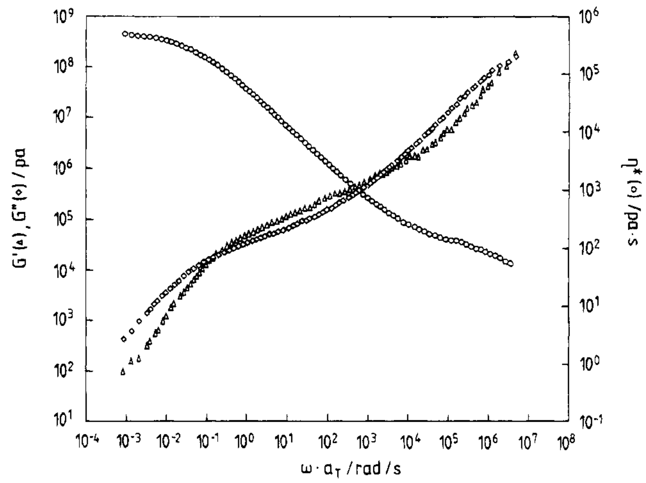

Figure 4. Storage modulus G' (△), loss modulus G'' (◇), and dynamic viscosity η^* (○) of sample CTAB3.0 in dependence of the shear frequency ω, as obtained from the time–temperature superposition. The reference temperature is 443 K.

acteristics of thermal field flow fractionation (which offers just a separation being algebraic in molecular weight; see refs 34 35), we were unable to characterize the complete set of samples under the applied separation conditions.

For all microgels, static light scattering with a standard setup to determine M_w was performed. With this technique, no polydispersity analysis is possible.

In all cases, we are sure about the compact architecture and the cross-linking densities of our microgels, since they have been the object of many polymer analytical experiments such as small-angle neutron scattering (SANS) or viscometry in solution,[30,31] the presentation of which is omitted in this paper. For the present context, it is just important to note that SANS had established that the present microgels are compact, nonfractal objects with sharp interfaces, as proven by the fulfillment of the Porod law. Due to the small size of the present microgels, we choose a cross-linking density of ${}^1/_{10}$ (or on the average 10 monomer units of styrene between two cross-links) for the complete sample set which suppresses the influence of the number of fluctuations of the cross-linking density. In addition, the average length of dangling ends is automatically adjusted to be of the same size as the cross-links; their number can be estimated from the ratio of network chain length to kinetic chain length of the polymerization process and is comparably low (1 dangling chain per 40 network chains at maximum). The coexistence of linear chains in this limit of the cross-linking density also is strictly excluded.

Figure 3 shows the dynamic-mechanical master curves of the storage modulus G', the loss modulus G'', and the complex viscosity of sample MCU2.5a, a microgel with $M_w = 187\,000$. We obtain a spectrum which looks very similar to the one of an unentangled polymer chain in the melt. At high frequencies, related to the response of smaller polymer subunits, we obtain a Zimm-type spectrum, characterized by $G' \sim G'' \sim \omega^{0.7}$. Below $\omega = 20\ \mathrm{s}^{-1}$, standard Newtonian behavior is obtained. It is obvious that highly cross-linked spheres cannot perform Zimm-type relaxation modes, but their spectra are looking exactly the same.

Increasing the molecular weight or the size results in another type of mechanical response which is shown in Figure 4. In this case, the average molecular weight of the nanospheres is $M_w = 1.03 \times 10^6$; the related size of a compact sphere $R = 7.3$ nm. Here, the typical response of a slightly polydisperse, entangled polymer melt is obtained. We can cut up the curve in a terminal, a plateau, and a transition zone, as is textbook knowledge for linear polymers. From the descend shape of the plateau, one would only deduce a broad distribution of relaxation times related to some polydispersity, but even the absolute height of the plateau is similar to the value of entangled, linear polystyrene ($G_n{}^0 = 2.0 \times 10^5$ Pa). In the case of this slightly larger microgel too, we can exclude the existence of a reptation-like mobility, the presence of a tube (as to the constraint for the transition zone), or even the existence of entanglements in the classical sense.[37] It is just that the mechanical curve of a microgel of $M_w = 1.03 \times 10^6$ looks like the response of a linear polystyrene chain of about $M_w = 150\,000$.

A further increase of microgel size leads to the expected results shown in Figure 5. This spectrum results from a particle with $R = 24$ nm but is typical for all larger microgel samples. We note that a similar response was already published in 1990 where the mechanical response of a microgel with $R = 55$ nm was presented.[30] Although optically transparent bulk materials are obtained by compression molding (an indication of viscous flow under pressure), no terminal zone or zero-shear viscosity can be determined which is due to the large size and the related molecular weight of 39.2×10^6. Therefore, a differentiation between a shear-induced flow with or without a yield stress (the existence of transport under quiescent conditions) can-

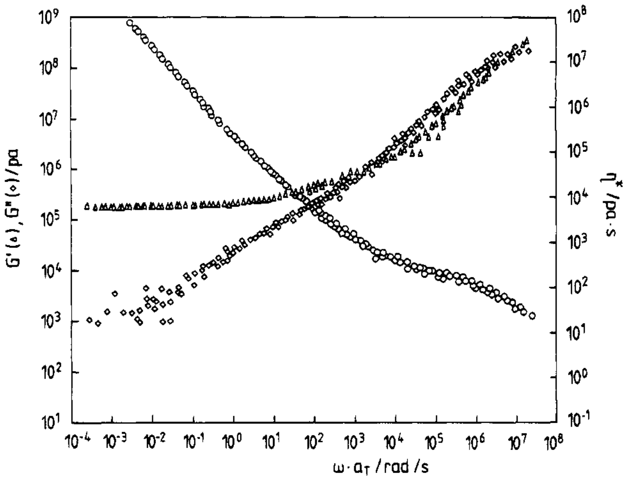

Figure 5. Storage modulus G' (△), loss modulus G'' (◇), and dynamic viscosity η^* (○) of sample CTAB0.5 in dependence of the shear frequency ω, as obtained from the time–temperature superposition. The reference temperature is 443 K.

not be performed but is surely a topic for the future. The plateau zone extends over a wide range of frequencies, and tan $\delta = G''/G'$ goes to values of 0.02 at low frequencies. At high frequencies, we still observe the transition zone with a Zimm-type spectrum. It is noteworthy mentioning that the transition zones of the examined spherical microgels are quite similar and that their behavior in this frequency region agrees well with the transition zone of entangled linear polystyrenes.[5]

In the limit of large sizes, spherical microgels rather behave like their macroscopic counterparts, networks (i.e., predominantly elastic). The only peculiarity which is left is the plateau height which is still about the value of $G_N{}^0$ of linear polymers but does not reflect the very high cross-linking density of $^1/_{10}$. This point was already marked in ref 30 but reappears in the present context in a new light since the low plateau value might be understood as the remainder of the cooperative mobility of the smaller microgels. A tentative explanation was already given in ref 30 (cooperativity) but a more conclusive picture is still missing. A value of tan δ = 0.02 also agrees with our earlier experiments and is typical for highly cross-linked polystyrene networks but, nevertheless, well below the value of ultrahigh molecular weight polystyrene.[22] This shows that linear polystyrenes in the plateau region still have some additional ways of dispersing energy (as demonstrated by Winter[22]), which obviously do not exist in the present large-sphere melts.

From the complete series of microgels, we are able to estimate the molecular weight dependence of the zero-shear viscosity for these model systems. This is shown in Figure 6. A strong dependence of η_0 on M_w is observed. A force fit with a scaling relation results in something like $\eta_0 \sim M^{3.6}$ or $\eta_0 \sim R^{10.8}$. Doubtless, this fit is quite inaccurate due to the strong scatter of the data. The high dependence and the scatter are related since slightly different polydispersities or small errors in the size determination get reflected in large differences of the viscosity. For a more illustrative point of view, we note that a microgel with an average radius of 18 nm contains significant amounts of particles of 10 and 30 nm radius (as has been demonstrated in Figure 1), the mechanical influence of which is hardly estimated. For the required precision of the determination of the molecular weight dependence of the zero-shear viscosity of spherical microgels, rheological examinations on a wider sample set with comparable polydispersity values are required. We also have to look for possibilities to close the molecular weight gap between the two surfactant series by some modifications in the synthetic procedure. All these experiments are currently in progress.[38]

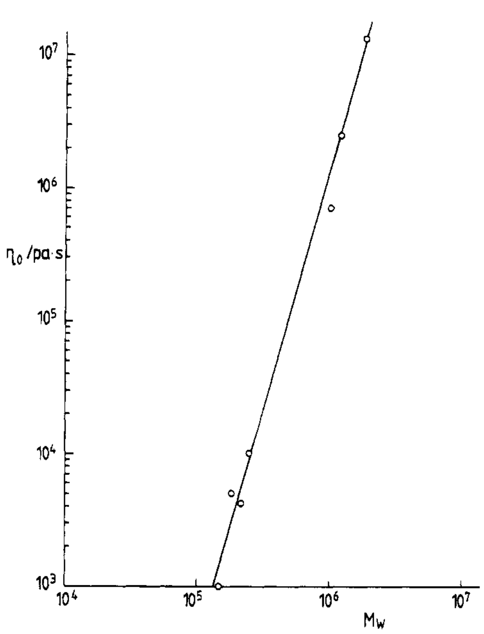

Figure 6. Zero-shear viscosity η_0 in dependence of M_w of the microgels for a reference temperature of 443 K. A force fit of the data with a scaling law results in $\eta_0 \sim M_w{}^{3.6}$.

Comparing the zero-shear viscosities of spherical microgels with those of linear polymers with similar molecular weight as taken from the literature,[13] we observe a very similar molecular weight dependence but a decreased viscosity for spheres by a factor of 200. In other words, spherical molecules of the same molecular weight flow more easily than linear chains. This observation is closely related to all old experiments on star-shaped polymers where mobility does not depend on arm number but on the size of a hydrodynamically equivalent sphere, only. Following these ideas, we might superimpose the data of linear chains, stars, spherical microgels, and other topologies such as rings and H-shaped polymers by comparing the zero-shear viscosities related to a certain length scale, a viscometric radius R_η, rather than their molecular weight dependencies. This comparison is shown in Figure 7; the viscosity data for linear polymers and rings are taken from refs 13 and 45, the data for stars from refs 46 and 47, and the data for the H's from ref 48. For the R_η values of linear chains, the viscometric radii in a Θ-solvent according to ref 49 were taken. Stars were shifted to this scale by taking the size of an equivalent linear chain with twice the arm length (as already delineated by Pearson[17] and Masuda[46]), rings were shifted by dividing the molecular weight with $\sqrt{2}$, and H's were shifted by dividing with $(5/3)^{1/2}$. For the microgels, the radii of equivalent hard spheres were calculated. Surprisingly, but also a little suggestive, this comparison of the behavior of all different topologies results at least in a qualitative agreement (the right order of magnitude as well as about the same scaling) of all data. Due to the large scatter of our data and the influence of slightly varying WLF parameters, a quantitative superposition of the microgel viscosities with the other topologies might not be expected.

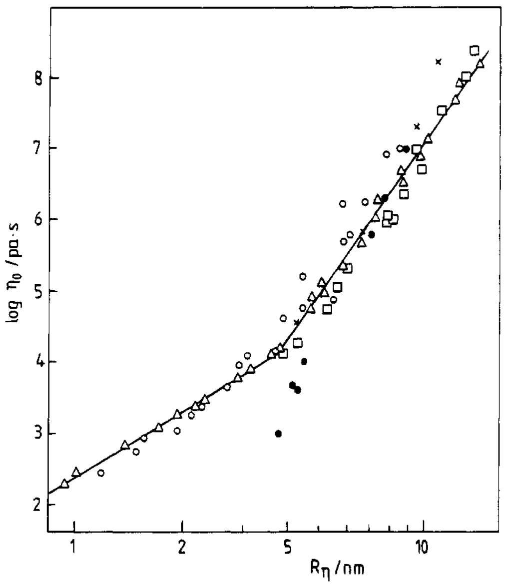

Figure 7. Comparison of the zero-shear viscosities η_0 of different polymer topologies (polystyrenes) for a reference temperature of 443 K: (△) linear polymers; (○) ring polymers; (□) 3-, 4-, and 6-arm star polymers; (×) H-shaped polymers; (●) spherical microgels. For all polymers, M_w is transferred to a viscometric radius R_η as delineated in the text.

Contrary to all the behavior of the other topologies, a systematic deviation of the smaller microgels to lower viscosities is observed. In the present data set, we do not detect any slope change in the region between the "unentangled" and the "entangled" regime (for microgels differentiated by the frequency dependencies of the mechanical response), analogous to the M_c of linear polymers. No explanations for this difference can be given; we only might speculate that the spherical approximation fails for the very small microgels due to the small number of cross-links involved.

It must be underlined that, as shown in Figure 7, the classical M_c of linear polymers is transferred to a R_η of about $R_\eta = 5$ nm. This size agrees well with the constraining length detected in dynamic neutron scattering (as mentioned above), which gives cross-evidence for the used master curve.

4. Conclusion and Outlook

We have shown that we can mimic a large number of characteristics of the rheology of linear polymers in the unentangled as well as in the entangled state by a model system consisting of narrowly distributed globular particles. Interestingly enough, we observe viscous flow for such microgels with radii of up to 10 nm, a mobility which can just be explained by cooperative movements rather than by a sum of single-chain mobilities, as classically performed for polymeric bulk systems.

The mechanical curves of small microgels consist of a terminal zone and a transition zone only. The transition zone is characterized by a $G' \sim G'' \sim \omega^{0.7}$ scaling, also characteristic for the Zimm model of hydrodynamically coupled chains. For larger particles, we observe the development of a plateau zone between the terminal and transition zones, as known for entangled polymer melts. In the limit of larger particles, we also obtain the correct magnitude of the plateau modulus for linear chains, although our particles possess a cross-linking density 1 order of magnitude larger than the classically calculated entanglement density.

Since spherical particles neither perform Zimm-type movements nor can reptate along a (not either existing) tube, we must conclude that a different mobility mechanism exists which results—qualitatively and for some characteristics even quantitatively—in a very similar type of mechanical response. Due to the simple architecture of microgels, the characterization of this movement as cooperative by nature is stringent: many coupled chains are moved at the same time.

One must also note that some modern descriptions of the bulk rheology of polymers exist where this cooperativity is a key feature for the understanding of the complex relaxation behavior. Ngai, for instance, describes with his "coupling model" the complex local relaxation dynamics of bulk polymers.[39,40] Schweizer developed a microscopic mode coupling theory which produces all essential features of the transition of Zimm- to tube-like dynamics without the assumption of a tube.[41-43] From an experimental point of view, the applicability of a mode coupling approach to the complex relaxation dynamics of a semiconcentrated model fluid consisting of spherical microgels has already been demonstrated.[44] Here, the relaxation behavior of the dynamic structure factor was determined with dynamic light scattering, and a concentration transition from an uncoupled free diffusion behavior toward a coupled, structurated dynamics with a marked terminal relaxation time was observed. This is already very close to the present experiments performed at much smaller microgels but in the bulk.

All these points give very strong evidence that reptation is not the only answer to the problems of polymer bulk dynamics.

The present examination certainly leaves a number of still open experimental questions and possibilities which are to be treated in the near future. For a more extensive examination of the rheology of these particles, a broader sample set with high uniformity is surely required, followed by a more precise characterization with a variety of rheological techniques.[38] It is also necessary to change the cross-linking density of the particles, which in fact results in a further increase of the mobility of the particles, as seen in preliminary experiments with particles with cross-linking densities of $^1/_{20}$ and $^1/_{40}$. A further decrease of the cross-linking density, however, has to result in an increase of the zero-shear viscosity again, since we expect a smooth transition toward the behavior of linear chains.

In addition, it is planned to perform bulk diffusion experiments of such microgels, since the combination of diffusion coefficient and viscosity allows the determination of further characteristics of this new transport mode.

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