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Structure and Dynamics of Networks in Mixtures of Hydrophobically Modified Telechelic Multiarm Polymers and Oil in Water **Microemulsions**

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Supporting Information

ABSTRACT: The structural and dynamical properties of oil-in-water (O/ W) microemulsions (MEs) modified with telechelic polymers of different functionality (e.g., number of hydrophobically modified arms, f) were studied by means of dynamic light scattering (DLS), small-angle neutron scattering (SANS), and high frequency rheology measurements as a function of the polymer architecture and the amount of added polymer. For this purpose, we employed tailor-made hydrophobically end-capped poly(N,N-dimethylacrylamide) star polymers of a variable number of endcaps, f, of different alkyl chain lengths, synthesized by the reversible addition-fragmentation chain transfer method. The addition of the different end-capped polymers to an uncharged ME of O/W droplets leads to a large enhancement of the viscosity of the systems. SANS experiments show that the O/W ME droplets are not changed upon the addition of the polymer, and its presence only changes the interdroplet



interactions. The viscosity increases largely upon addition of a polymer, and this enhancement depends pronouncedly on the alkyl length of the hydrophobic sticker as it controls the residence time in a ME droplet. Similarly, the high frequency modulus G_0 depends on the amount of added polymer but not on the sticker length. G_0 was found to be directly proportional to f-1. The onset of network formation is shifted to a lower number of stickers per ME droplet with increasing f, and the network formation becomes more effective. Thus, the dynamics of network formation are controlled by the polymer architecture. The effect on the dynamics seen by DLS is even more pronounced. Upon increasing the polymer concentration, slower relaxation modes appear that become especially pronounced with increasing number of arms. The relaxation dynamics are correlated to the rheological relaxation, and both are controlled by the polymer architecture.

INTRODUCTION

Microemulsions are, in general, isotropic, thermodynamically stable mixtures of oil and water stabilized by the presence of a surfactant. Their structure can be oil-in-water (O/W) or waterin-oil (W/O) droplets but also bicontinuous microemulsions (MEs) are known, $^{1-4}$ and it is controlled by the bending energy of the amphiphilic film.^{5,6} MEs are generally low-viscous liquids. However, for a variety of situations their technical applicability is limited by this low viscosity. Therefore, control of the viscosity of MEs is a highly interesting and important topic. There are various options for increasing the viscosity of MEs, which often are based on the addition of polymers. One option is the addition of conventional polymeric thickeners, thereby leading to a viscosity increase of the solvent. This alternative is problematic as, depending on the type of polymer chosen, one may have interactions with the ME and its stability.⁷ Another possibility is to cross-link the oil droplets by bridging amphiphilic polymers. The interconnection of droplets

leads to a substantial increase in viscosity once an effective percolation concentration of droplets and polymer have occurred.8,9

Telechelic associative polymers have received considerable attention because of their wide range of applications as rheological modifiers of aqueous systems. They are used either simply in water¹⁰ or together with surfactants, which often leads to a substantial enhancement of the viscosity.¹¹⁻¹⁴ Up to now almost all investigations have been restricted to doubly endcapped hydrophilic polymers (i.e., bifunctional bridging polymers). The most common case are hydrophobic ethoxylated urethane (HEUR) associative thickeners,¹⁵ which are widely applied and for which the viscosity was found to increase with a power law with an increasing length of the

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Table 1. Polymer Parameters

polymer	п	$M_{\rm n}{}^a$ (KDa)	$M_{\rm w}^{\ a}$ (KDa)	PDI ^a	$M_w^{\ b}$	R _{ee} (2 arms) (nm)	$r (wt\%)^c$
$(C_4 PDMA)_3$	493	147	169	1.15	219	28.4	0.152
$(C_{12}PDMA)_2$	293	59	61	1.05	73	21.9	0.38
$(C_{12}PDMA)_3$	221	67	69	1.04	86	19.2	0.49
$(C_{12}PDMA)_4$	229	92	97	1.05	120	19.4	0.48
$(C_{18}PDMA)_3$	330	nd	nd	nd	109	24.0	0.32

^{*a*}Molar mass as weight (M_w) and number (M_n) average as determined by MALLS-GPC. DMA units per arm (n) as calculated from M_n and polydispersity index (PDI) and end-to-end distance of 2 arms (R_{ee}) calculated as $\langle R_{ee}^2 \rangle = C_{\infty} 2nl^2 (C_{\infty} = 9.1)$.³². ^{*b*}Weight average molar mass, M_{w} , obtained from SANS in *d*8-THF as reported in reference 29. ^cNumber of stickers per droplet, *r*, per 1 wt % of the polymer.



Figure 1. Schematic representation of ME networks with end-capped star polymers with 2, 3, and 4 arms.

hydrophobic sticker¹⁶ (i.e., where apparently the activation energy required to pull out a sticker from the interconnected aggregates determines the viscosity). A rather high polydispersity of the contained aggregates has been deduced from fluorescence studies,¹⁷ and dynamic light scattering (DLS) measurements have shown a multimodal relaxation process once the concentration required for network formation is surpassed.¹¹

In particular, the admixing of doubly hydrophobically endcapped polyethylene oxide (PEO) to MEs has been studied intensely with respect to the formation of transient networks. In terms of the phase behavior, they exhibit an extended monophasic region with a fluid sol region at low droplet and polymer concentrations and a viscoelastic region at higher droplet, and polymer concentrations separated by a percolation line and a two-phase region.¹⁸ The phase separation has a purely entropic origin since the increase in polymer configurations overcomes the entropy loss due to the phase separation and the formation of a dense phase.¹⁹ The structural characterization of these systems by means of small-angle neutron scattering (SANS)^{8,20,21} confirmed that the admixture of telechelic polymer does not lead to a change of the droplet size, and they exhibit a net attractive interaction in the sol phase and a net repulsive interaction in the gel phase. The gel phase shows viscoelastic behavior with only one characteristic relaxation process.^{9,22} The relaxation time of the network depends on the length of the hydrophobic end-group. However, DLS experiments showed a rather complex behavior with various relaxation times.^{23,24} For the case of employing C_{12} or C_{18} hydrophobic stickers, it was observed that the rheological relaxation time increases by more than 3 orders of magnitude when switching from C_{12} to C_{18} , and at the same time the relaxation observed in DLS becomes much slower and requires an additional relaxation mode for the description.^{20,24} Such systems have also been analyzed theoretically with respect to the probability of the polymer for forming loops or bridges,

where it has been concluded that this depends largely on the ratio between the polymer end-to-end separation and the average droplet–droplet distance.²⁵

Recent investigations on 3-arm-end-capped polymers showed a preference for intra-association instead of interassociation in agreement with theory.²⁶ Networks of chemically cross-linked 4-arm PEG show less heterogeneities in the microstructure, leading to networks with enhanced mechanical properties.²⁷ We recently reported^{28,29} the synthesis of multiarmed-endcapped polymers, which in aqueous solution form networks of interconnected hydrophobic domains of the polymer, resulting in substantially enhanced viscosities. Furthermore, the elastic modulus increases with increasing number of arms.

However, so far multiarmed (multifunctional) polymers have hardly been studied with respect to their ability to bridge MEs and their effects on the rheological properties despite the fact that the topology and functionality of the bridging polymer should have a substantial effect on the structures and, in particular, on the dynamics of the networks formed and similarly on their rheological behavior. Accordingly, such an extension of experimental studies on polymers with more complex architecture is undertaken here. In this study, we were interested in the effect that end-capped star polymers of low functionality (f = 2-4) have on the formation of ME networks, where the linear polymer (f = 2) serves as a reference. The polymers employed are given in Table 1. As depicted in Figure 1, such networks look generically similar, but they differ in the way the polymer bridges the droplets. While for a linear telechelic the move of one sticker leads to a break of the bridging, this is increasingly less the case with an increasing number of stickers. In addition, the number of bridges scales with $f^*(f-1)/2$.

As a model ME, we chose the well-known system of tetradecyldimethyl amine oxide (TDMAO) with decane as the oil phase.³⁰ This system is known to form low-viscous MEs containing small spherical and rather monodisperse droplets.³¹

In our experiments, we varied systematically the concentration of the added polymer, the length of the hydrophobic sticker, and most importantly, the functionality, as given by the number of arms. By combining the results from SANS, rheology, and DLS, our aim was to derive systematic correlations between the architecture and amount of added polymer and the structural, dynamical, and rheological properties of the ME/polymer mixtures.

EXPERIMENTAL SECTION

Materials. Tetradecyl dimethyl amine oxide (TDMAO, $C_{14}H_{29}N(CH_3)_2O$) was a gift from Huntsman (Empigen OH 25, 24–26%). The solutions were freeze-dried until the amount of water reached a value of 2.5 wt %, as determined by Karl Fischer titration. This water content was accounted for when preparing the TDMAO solutions. *N*-decane (\geq 98%) was obtained from Sigma Aldrich and used as supplied. The samples were prepared by taking the required amount of stock solution of 200 mM of a surfactant. The appropriate amounts of oil and water were added to establish the final composition of the ME with 100 mM TDMAO/35 mM decane/water.

The polymers were synthesized using reversible addition– fragmentation chain transfer (RAFT) polymerization. All details concerning synthesis and characterization of the polymers are given elsewhere.²⁹ The polymers are based on hydrophilic poly(N,Ndimethylacrylamide) (PDMA) blocks with n units and 2, 3, and 4 arms, with an aliphatic end chain of 4, 12, or 18 carbon units, respectively (see Figure 2). Table 1 gives the molecular weight as



hydrophobically end-capped hydrophilic poly(DMA) (C_xPDMA)_y; x = 4,12,18; y = 2,3,4

Figure 2. Structure of the end-capped star polymers.

weight (M_w) , and number (M_n) average as well as the polydispersity index (PDI = M_w/M_n) as determined in reference 29 by GPC-MALLS for all polymers employed in this study. The molecular weight of the (C₁₈PDMA)₃ could not be determined because the polymer aggregates in aqueous eluent. Table 1 also contains the molecular weight determined by SANS in d_8 -THF.²⁹ In the case of (C₁₈PDMA)₃, the latter value was used to calculate the number of polymers in solution.

The polymer containing MEs was prepared by mixing weighted amounts of MEs with varying amounts of polymer and mixing with a vortex mixer while heating (~ 60 °C) to ensure complete homogenization.

The number of stickers per droplet, *r*, is the ratio between the number density of stickers, n_{Sv} and the number density of droplets, $n_d = \phi/V_p = 3\phi/4\pi R^3$, assuming all end stickers to be located within the ME droplets.

$$r = n_{\rm St}/n_{\rm d} \tag{1}$$

with R being the radius obtained by SANS (2.4 nm).

The average distance between the ME droplets can be calculated assuming a cubic packing of the spheres, $d = (4\pi R^3/3\phi)^{3/2}$, for the given concentration and for their radius of 2.4 nm. This yields a value of d = 13.2 nm for our system of 100 mM TDMAO and 35 mM

decane (which has a volume fraction of 0.0357). This distance is somewhat shorter than the end-to-end distance, R_{eer} of the bridging polymers (see Table 1), which means that the polymers should be able to bridge the droplets effectively²⁵ and thereby would even have a tendency to be "squeezed together" by the presence of the droplets. The end-to-end distance of the two arms (listed in Table 1) was calculated as $< R_{ee}^{2} >^{1/2} = (C_{\infty} 2nl^{2})^{1/2}$, where *l* is the length of a *N*,*N'*-dimethylacrylamide monomer (0.23 nm), and $C_{\infty} = 9.1$ for PDMA in water.³²

Methods. Small angle neutron scattering (SANS) was performed at the spectrometer PAXY of the Laboratoire Léon Brillouin (LLB, CEA-CNRS, Saclay, France) with a neutron wavelength of 5 Å and sample-to-detector distances of 1.145 and 5.045 m. The covered range of the magnitude of the scattering vectors was 0.08 < q < 3.3 nm⁻¹. For some samples, an additional configuration at 5.045 m and 15 Å was measured going down to 0.04 nm⁻¹. The SANS data were treated according to standard procedures for absolute scaling, radial averaging, detector efficiency, and background subtraction. Water was used as an incoherent scatterer to calibrate the detector efficiency, and the attenuated direct beam was used to determine the absolute scaling.³ The data reduction and radial average was done with the software BerSANS³⁴ in order to obtain the absolute scattered intensity as a function of the magnitude, q, of the scattering vector: $q = 4\pi/\lambda sin(\theta/\theta)$ 2), where θ is the scattering angle. The solvent was D₂O, in order to reduce the incoherent background and increase the contrast. Sapphire cells with a 1 mm beam path were used for very viscous samples and Quartz Hellma cells (110-QS) of 1 or 2 mm thickness for the low viscous samples.

DLS was performed at 25 °C using a setup consisting of an ALV/ LSE-5004 correlator, an ALV CGS-3 goniometer, and a He–Ne Laser with a wavelength of 632.8 nm. Cylindrical sample cells were placed in an index matching toluene vat. Intensity autocorrelation functions were recorded under different angles between 50° and 130°. In the case of Gaussian scatterers and ergodic systems, the intensity autocorrelation function $g^{(2)}(t)$ measured in a homodyne experiment is related to the field autocorrelation function $|g^{(1)}(t)|$ by the Siegert relation³⁵

$$g^{(2)}(t) = 1 + B |g^{(1)}(t)|^2$$
(2)

where B is an instrumental constant that reflects the deviations from the ideal correlation that should have an ideal value of 0.33 in this setup.

Oscillatory rheology measurements were carried out using a Bohlin Gemini 150 rheometer especially equipped with a high-frequency extension with a piezo rotary vibrator,³⁶ which allows the measurement range to be extended by 2 orders of magnitude to higher frequencies. A plate–plate geometry of aluminum was used with a diameter of 40 mm. This setup then allows for measurements from 10 to 2000 Hz. This overlaps nicely with the conventional setup in which frequencies of 0.001-20 Hz are covered. The gap size was 0.1 mm and the deformation 0.1.

For viscosity measurements of low-viscous samples, a calibrated micro-Oswald capillary viscosimeter (Schott) type Ic was used.

SANS Models. The scattered intensity for the polymer containing ME droplets was given by the expression derived by Fuchs et al.³⁷ for polymer-colloid mixtures:

$$I(q) = n_{\rm s} V_{\rm s}^2 \Delta \rho_{\rm s}^2 P_{\rm s}(q) S_{\rm ss}(q) + n_{\rm p} V_{\rm p}^2 \Delta \rho_{\rm c}^2 S_{\rm pp}(q) + I_{\rm inc}$$
(3)

The total scattering intensity I(Q) is expressed in terms of the droplet and polymer segment scattering lengths, $\Delta \rho_s$ and $\Delta \rho_p$, their volumes, V_s and V_p , their number densities, n_s and n_p , and the normalized form factor accounting for the shape and size of the oil droplets, $P_s(q)$. $S_{ss}(q)$ is the structure factor accounting for interactions between the droplets, and I_{inc} accounts for the incoherent scattering. Cross-terms taking into account the correlations between the droplets and the polymer were neglected here. The decoupling of P(q) and S(q) is valid only strictly for monodisperse systems but commonly employed as well for polydisperse systems.³⁸ For $P_s(q)$, the model of an homogeneous sphere was employed

$$P_{s}(q) = n_{s} \int \log \operatorname{Norm}(R) \left(3 \frac{\sin qR - qR \cos qR}{(qR)^{3}} \right)^{2}$$
(4)

with the spherical particles having a log-normal size distribution of radii:

$$\log \operatorname{Norm}(R) = n_{\rm s} / R \sigma (2\pi)^{1/2} \exp\{-[\ln(R) - \sigma]^2 / 2\sigma^2\}$$
(5)

The PDI of this distribution is identical to the variance, σ . The values of $\Delta \rho$ are the difference of the scattering length density of the aggregates and the average scattering length density of the sample, which depends on the sample composition (described in more detail in the Supporting Information).

 $S_{\rm pp}(q)$ is the structure factor of the polymer segments, and there is no explicit polymer form factor. The scattering can be modeled according to a correlation term³⁹

$$n_{\rm p}V_{\rm p}^{2}\Delta\rho_{\rm c}^{2}S_{\rm pp}(q) = \frac{\alpha}{q\xi}\Gamma(\mu)\frac{\sin[\mu\,\arctan(q\xi)]}{(1-q^{2}\xi^{2})^{\mu/2}}$$
(6)

where $\Gamma(\mu)$ is the gamma function with argument $\mu = 1/\nu - 1$ with ν being the excluded volume parameter from the Flory mean field theory with a value of $\nu = 3/5$, as typical for polymers swollen in good solvents. The parameter α is the forward scattering, and ξ is the correlation length of the polymer network.

For the long-range repulsion, we employed a S(q) based on a potential U(r) of a hard sphere with a Yukawa tail⁴⁰

$$\frac{U(R)}{k_{\rm B}T} = \begin{cases} \infty & \text{for } 0 < R < R_{\rm HS} \\ U_0 \exp[-z(R - R_{\rm HS})]/r & \text{for } R > R_{\rm HS} \end{cases}$$
(7)

where $R_{\rm HS}$ is the hard sphere radius. For $R > R_{\rm HS}$, a Yukawa potential was chosen as it has been proven to successfully describe the longrange repulsion, for instance in electrostatically repulsive colloids⁴¹ or soft colloids such as star polymers.⁴² The radius and the volume fraction of the hard sphere in this model are constrained to be defined by those of the sphere form factor. The parameter U_0 is the potential energy at the particle surface and z its range. The direct correlation function, C(r), is obtained by solving the Ornstein–Zernike equation which has an analytical solution for the mean spherical approximation (MSA).⁴⁰ The Fourier-transformed correlation function, C(q), solved for macro-ion solutions was taken⁴³ and the structure factor is

$$S(q) = \frac{1}{1 + n_{\rm s} C(q)}$$
(8)

where n_s is the number density of the oil droplets.

RESULTS AND DISCUSSION

Phase Behavior. As a first step, the macroscopic phase behavior of the MEs composed of 100 mM TDMAO/35 mM decane was studied as a function of the amounts of the different added polymers (Table 1). All the mixtures of ME and polymer up to 8 wt % are homogeneous, transparent, and stable, but they differ substantially with respect to their viscosity. Higher concentrations of polymer were not explored. Samples with a C_4 -end-capped polymer are liquidlike, with a C_{12} polymer are viscous, and with a C_{18} polymer are very viscous (honeylike). In general, an increase in the polymer concentration leads to a pronounced increase of the systems viscosities. Of course, we were then interested in quantifying these observations and as a first step turned to determining the mesoscopic structure in these mixed polymer/ME systems.

Structure of the Microemulsion/Polymer Systems Using SANS. Comprehensive mesoscopic structural information is required for a better understanding of the formed ME/ polymer mixtures. For this reason, SANS measurements were performed for samples with MEs (TDMAO 100 mM/decane $35 \text{ mM/D}_2\text{O}$) and the telechelic star polymer added, where the length of the sticker, the concentration of polymer, and the number of arms were varied.

Figure 3 shows scattering patterns of the pure ME and the system with 5 wt % of the 3-arm polymers with varying end-cap



Figure 3. SANS patterns of the aggregates of ME (\Box) , $(C_4PDMA)_3$ (O), $(C_{12}PDMA)_3$ (\triangle), and $(C_{18}PDMA)_3$ (\diamond) at a concentration of 5 wt % added polymer in D₂O at room temperature. The lines correspond to the fits with eq 3.

lengths (4, 12, and 18 carbon units). The pure ME shows the typical scattering pattern of sterically repulsive-interacting spherical aggregates. The polymer-containing samples show a much more pronounced correlation peak and a higher scattering intensity in the high q range. The latter is due to the scattering of the polymer chains and to an increased incoherent scattering due to the higher concentration of H atoms in the sample. In the intermediate q range, the scattering curves are basically superimposed. This indicates that the droplet structure of the ME remains unaltered by the polymer addition. The decreasing scattering intensity at low q and the corresponding evolution of a correlation peak arises from an increased repulsive interaction due to the presence of the polymer chains between the ME droplets. This leads to an effectively excluded volume between the droplets.

In addition, we studied the effect of the polymer concentration. Exemplarily, the scattering patterns of the pure ME and the ME with 2, 5, and 8 wt % of $(C_{12}PDMA)_3$ are shown in Figure 4a. As observed above, the scattered intensity increases at a high q due to the incoherent scattering and the scattering of the chains. Both contributions increase proportionally to the amount of polymer. Again, the size of the ME droplets, as indicated by the intermediate q range, is not affected. With increasing polymer concentration, the correlation peak becomes more pronounced. This indicates a higher repulsive interaction due to a larger amount of hydrophilic polymer chains between the droplets that are functioning like an effective excluded volume.

Finally, in order to elucidate the effect of the number of arms, the SANS patterns for 5 wt % solutions of $(C_{12}PDMA)_2$, $(C_{12}PDMA)_3$, and $(C_{12}PDMA)_4$ with similar molecular weight in ME are given. They show no significant difference at identical polymer concentrations (Figure 4b). This means that neither the droplet structure nor their interactions are affected by the number of arms of the polymer present.



Figure 4. SANS patterns of the aggregates of ME at room temperature (a) with an increasing content of added $(C_{12}PDMA)_3$ and (b) with $(C_{12}PDMA)_2$, $(C_{12}PDMA)_3$, and $(C_{12}PDMA)_4$ at a concentration of 5 wt % added in D₂O.

The fit of the curve of the pure ME, using the model described by eq 3 without the chain contribution, $P_s(q)$ (the second term in eq 2) yields a radius of 2.4 nm with a standard deviation of the log-normal distribution of 0.18. This value is higher than the previously reported one of $\sigma = 0.102$,³¹ because it also contains the experimental smearing.

The curves of the polymer-containing samples were fitted using eq 3. The radius of the droplets, R, and the standard

deviation of the log-normal distribution, σ , were kept constant according to the values obtained from the ME. The volume fraction was fixed according to the sample composition. The scattering length density difference was calculated as the difference of the scattering length of the droplets and the sample average scattering length density (see the Supporting Information). The hard sphere radius, $R_{\rm HS}$, and the hard sphere volume fraction, $\phi_{\rm HS}$, were chosen to be equal to the ME droplet radius and droplet volume fraction, respectively. In this way, the number density is kept constant and the number of parameters in decreased. R_{HS} might be slightly larger for the droplets, but this additional repulsion is included in the interaction potential. The prefactor of the chain scattering form factor, α , the blob size, ξ , and the structure factor parameters, U_0 and z, were fitted. All the parameters are listed in Table 2. This model fits our experimental data rather well and, accordingly, seems to be an accurate description of the structural situation.

As is expected, α is simply proportional to the amount of polymer contained (see Table S3 of the Supporting Information). The parameters, z and U_0 , are strongly coupled, but nonetheless, there seems to be some clear trends to be observed for the different systems. When the same concentration of $(C_{12}PDMA)_3$ and $(C_{18}PDMA)_3$ is added, U_0 and z are relatively similar. This is not surprising since both polymers have the same length, and the same number of chains are present in the sample. In the case of $(C_4PDMA)_3$, U_0 is substantially lower because the smaller anchoring of the short C₄ chain in the ME droplets is much weaker, and accordingly, it only leads to a much less pronounced repulsion. Therefore, we can state that the structure does not depend on the sticker length, if the sticker has a minimum length. This is in good agreement with previous results with C_{12} and C_{18} telechelic polymers, where the effective interaction between the droplets was found to be independent of the sticker length.²⁰ As long as the hydrophobic sticker is located most of the time within the ME droplets (which will be the case for C_{12} and C_{18}), the effective interaction will be independent of the sticker length and only be determined by the polymer chain bridging different droplets. This does not hold for the C₄ stickers, and thus the effective repulsion is less pronounced.

Moreover, we observe a pronounced increase of U_0 with increasing polymer concentration, which is in agreement with the intuitively expected proportionality of U_0 to the number of stickers per droplet, *r*. In order to quantify the interaction in a more stringent way, we calculated the dimensionless second virial coefficient as

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Table 2. SAINS Parameters of the Curves Presented in Figures 5 and 4	ŧ."

polymer	C (wt%)	ϕ	r	$I_{\rm inc}~({\rm cm}^{-1})$	$\alpha ~({\rm cm}^{-1})$	$\Delta ho~({ m cm}^{-2})$	$z~({ m nm}^{-1})$	$U_0 (k_{\rm B} { m T})$	B_2
-	0.0	0.032	0			6.43	0.106	0.03	4.11
$(C_4 PDMA)_3$	5.0	0.031	1.1	0.077	0.81	6.17	0.134	0.11	7.11
$(C_{18}PDMA)_3$	5.0	0.031	1.7	0.107	0.82	6.17	0.049	0.81	13.8
$(C_{12}PDMA)_3$	2.0	0.032	1.0	0.076	0.38	6.32	0.153	0.19	4.37
$(C_{12}PDMA)_3$	5.0	0.031	2.7	0.093	0.81	6.17	0.079	1.20	13.8
$(C_{12}PDMA)_3$	8.0	0.030	4.5	0.11	1.09	6.01	0.114	3.94	18.2

^{*a*}Polymer concentration, *C*, droplet volume fraction, ϕ , number of stickers per droplet, *r*, scattering length density contrast, $\Delta\rho$, and the parameters obtained from the fits using eq 2: incoherent background, I_{inc} (error: 0.9%), prefactor of the polymer chain correlation term, α (error: 3%), the range, *z* (error: 10%), and the strength, U_0 (error: 6%), of the repulsive interaction potential. The radius of the sphere, *R* (and hard sphere radius R_{HS}), was 2.37 nm (error: 0.2%), and the chain blob size, ξ , was 1.82 nm (error: 0.2%). The hard sphere volume fraction, ϕ_{HS} , was the same as the droplet volume fraction.

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$$B_2 = \frac{2\pi}{V} \int_0^\infty \left\{ 1 - \exp[-U(r)/k_{\rm B}T] \right\} r^2 dr$$
(9)

From the definition of B_2 , the excluded volume contribution is represented by $B_2 = 4$. If $B_2 < 4$ the interaction is attractive, and if $B_4 > 4$ the interaction is repulsive. The results are summarized in Table 2. The second virial coefficient, B_2 , for the ME is 4 (i.e., it behaves like a model hard-sphere system as it has been seen frequently before for nonionic MEs).^{4,9,31,44-47}

In general, the ME/polymer mixtures have values of B_2 higher than 4 (see Table 2), indicating that the net interaction between the droplets is repulsive. B_2 is proportional to the number of stickers per droplet, r, and apparently, each connecting chain has a similar contribution to the overall repulsion. The repulsion itself arises from the fact that the end-to-end distance of the polymers, which is also the average spacing between the hydrophobic stickers, is larger than the average spacing between the ME droplets. Accordingly, having two stickers in neighboring droplets leads to a repulsion between them. In contrast, if the polymer length is smaller than the interdroplet distance, the net interaction is expected to be attractive, leading to phase separation.^{18,48}

In summary, we find that the addition of the telechelic polymers has virtually no effect on the droplet structure of the MEs but mainly affects their interaction potential and thereby their structure factor, thus rendering the droplet interactions increasingly repulsive.

Rheology. In order to gain quantitative insight into the thickening behavior of the end-capped star polymers, we performed rheological measurements for the polymers of various architectures and different sticker lengths.

First, we considered the effect of the sticker length on the viscosity of ME-3-arm polymer mixtures. Figure 5a shows oscillatory measurements of samples with 5 wt % of $(C_{12}PDMA)_3$ and $(C_{18}PDMA)_3$. The curves show the typical behavior of a viscoelastic fluid with an increase of the storage modulus *G'* and the loss modulus *G''* with increasing frequency until at a certain frequency where *G'* reaches a plateau. The viscoelastic behavior can to a first approximation be described by the Maxwell model, described by eqs 10 and 11.

$$G' = G_0 \frac{\omega^2 \tau_{\rm R}^2}{1 + \omega^2 \tau_{\rm R}^2}$$
(10)

$$G'' = G_0 \frac{\omega \tau_{\rm R}}{1 + \omega^2 \tau_{\rm R}^{2}} \tag{11}$$

where G_0 is the shear modulus; τ_R is the characteristic time of the relaxation process, and the angular frequency is $\omega = 2\pi f$. This simple model describes the experimental data very well. Deviations at high frequency, especially in the case of G'', appear in such systems because in this frequency regime the links can be regarded as permanent, and the system behaves rather rubberlike yielding a higher G'' than predicted by the Maxwell model.⁹ The obtained values of G_0 and τ_R are collected in Table 3. The plateau modulus G_0 for C_{12} and C_{18} is on the same order of magnitude, and the slight difference can be attributed to the somewhat different number of stickers per droplet, r. The structure of the network is very similar as observed by SANS. However, the structural relaxation time differs markedly depending on the sticker length for C12 and C_{18} . The structural relaxation time is related to the lifetime of a network junction. Assuming that the lifetime is the residence time of the alkyl chain of a surfactant in a micelle, it is related to

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Figure 5. (a) Storage (*G'*) and loss modulus (*G''*) as a function of the frequency (f) for ME with (C_{12} PDMA)₃ and (C_{18} PDMA)₃ of a concentration of 5 wt % (solid lines are fits with eqs 10 and 11). (b) Effect of the end-cap chain length in terms of carbon units on the zero shear viscosity for a concentracion of 5 wt %. The dotted line represents the fit using $\eta_0 \sim \exp(E_a^*/k_BT)$.

the activation energy E_a for the exit of a sticker from the ME droplet by the Arrhenius law $\tau_0 \sim \exp(E_a/k_BT)$. For linear saturated chains, the activation energy is 1.1–1.2 k_BT per CH₂.⁴⁹ The relaxation time of the C₁₈ stickers is 300 times larger than for C₁₂, corresponding to an E_a of 1.0 k_BT per CH₂.

The zero shear viscosity is directly proportional to the structural relaxation time, $\eta_0 = \tau_R G_0$. Figure 5b shows the zeroshear viscosity, η_0 , for the samples containing 5 wt % of 3-arm polymers with different stickers. One observes a very pronounced viscosity increase, which rises exponentially with the number of methylene groups of the sticker in the form of η_0 ~ $\exp(E_a^*/k_BT)$, yielding a value of 1.0 k_BT per CH₂ group. Since the values of the plateau modulus G_0 are very similar, the viscosity variation is dominated by the variation in the relaxation time. This value is close to the 0.9 k_BT reported before¹⁶ for the viscosity of linear hydrophobically end-capped polymers. The somewhat higher viscosity values in our case suggest that the trithiocarbonate group adds hydrophobicity to the sticker.

In the next step, we consider the variation of the polymer concentration. The mixtures of telechelic star polymers and

Table 3. Rheological	Parameters for	r Different Sticke	r Lengths C	Obtained fr	rom the l	Fit with Ec	is 10 and	11"
0			0					

polymer	C (wt %)	r	η_0 (Pa)	G_0 (Pa)	$\tau_{\rm R}~({\rm ms})$	$D_{\rm eff} \left({\rm m}^2 { m s}^{-1} ight)$	$<\tau_{2}>$ (ms)	β_2
$(C_4 PDMA)_3$	5	0.76	2.95×10^{-3}			5.78 ×10 ⁻¹¹	1.02	0.66
$(C_{12}PDMA)_3$	5	2.5	17.1	1608	11.1	7.40 ×10 ⁻¹¹	64.7	0.31
$(C_{18}PDMA)_3$	5	1.6	3.09×10^{3}	1129	2.73×10^{3}	6.60 ×10 ⁻¹¹	4.36×10^{3}	0.68

^{*a*}Plateau modulus, G_0 , relaxation time, τ_{R_s} and zero shear viscosity. As the sample with (C₄PDMA)₃ was too fluid to be measured with the Gemini rheometer, the viscosity was measured with a capillary viscometer. In addition, effective diffusion coefficient, D_{eff} mean value of the second relaxation time, $\langle \tau_2 \rangle$, and stretching parameter, β_2 , as obtained from DLS.

MEs exhibit an increase on the viscosity upon increasing the concentration of the polymer, such that the relaxation time and the value of the plateau modulus become higher (Figure 6).



Figure 6. Storage (G') and loss modulus (G") as a function of the frequency (f) for solutions of (C_{12} PDMA)₃ in ME (35 mM TDMAO/100 mM decane) for different polymer concentrations. The symbols correspond to the experimental data and the lines to the fit analysis with the Maxwell model (eqs 10 and 11).

The evolution of the plateau modulus G_0 with the number of stickers per droplet, *r*, for different number of stickers per polymer is illustrated in Figure 7. We note that the values of the plateau modulus differ largely for the three polymers at a given concentration, where SANS shows no differences on the local structure and only small changes in the interaction potential. From the percolation theory, ⁵⁰ one expects

$$G_0 = G_{00}(r - r_c)^a \tag{12}$$

where r_c is the percolation threshold, and *a* is predicted to be about 1.7.⁵⁰ The percolation threshold, r_c is 0.93, 0.8, and 0.6 for $(C_{12}PDMA)_2$, $(C_{12}PDMA)_3$, and $(C_{12}PDMA)_4$, respectively. This decrease may be explained by a decreasing probability of having a polymer not connecting different droplets but instead forming loops. The best results were found for a value of the exponent a = 1.2. This value differs somewhat from the one predicted by theory $(1.7)^{50}$ and found experimentally for MEs with bifunctional telechelic polymers $(1.4-1.6)^{.9,22,51}$ Hence, the curves follow the same power law, but they differ in the magnitude of the modulus, being larger with an increasing number of arms.

The inset of Figure 7 shows the relaxation times obtained from the fits of the rheological data using eq 10. Interestingly, all fall on top of each other (i.e., they are described by a master curve for the various systems studied). The relaxation process depends only on the sticker length and the effective



Figure 7. (a) Plateau modulus as a function of the number of stickers per droplet, *r*, for $(C_{12}PDMA)_2$ (\Box), $(C_{12}PDMA)_3$ (\bigcirc), and $(C_{12}PDMA)_4$ (\triangle) added to the ME. The lines are the fits to the power law, $G_0 \propto (r - r_c)^{1.2}$ (see Table 4). The inset shows the relaxation time, $\tau_{\rm R}$, as a function of *r*. The line corresponds to the equation $\tau = 8(r - 0.8)^{0.66}$. (b) Log–log representation of the plateau modulus as a function of $r-r_p$.

connectivity of the droplets. Experimentally, we find that $\tau_{\rm R}$ follows a power law of *r* with an exponent of 0.66, where this exponent describes the increase of connectivity due to the increasing number of bridges present. For a simple network model, G_0 is proportional to the number density, *n*, of rheologically active cross-linking points⁵²

$$G_0 \cong nk_{\rm B}T \tag{13}$$

where n can be approximated by the number density of polymer chains linking two droplets. For our multibridging polymers the number of links will be related to the number of arms, f_i by

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$$G_0 = n_{\rm p} f(f-1) k_{\rm B} T/2 \tag{14}$$

where n_p is the number density of polymer molecules. It should be noted that this expression should be valid once all the polymer molecules are actively bridging (i.e., well above the percolation threshold). As *r* is fn_p/n_d (n_d being the number density of ME droplets), we expect

$$G_0 = rn_{\rm d}(f - 1)k_{\rm B}T/2 \tag{15}$$

This means that the shear modulus is expected to increase linearly with the number of branching points of the polymer. Indeed, all the data could be reasonably well fitted by the expression $G_0/n_pk_BT = 0.3(f-1)(r-r_p)^{1.2}/r$ (see Figure 8). This



Figure 8. Reduced plateau modulus, G_0/n_pk_BT , as a function of the number of stickers per droplet, *r*, for $(C_{12}PDMA)_2$ (\Box), $(C_{12}PDMA)_3$ (\bigcirc), and $(C_{12}PDMA)_4$ (\triangle) added to the ME. n_p is the number density of linking polymers. The lines are $G_0/n_pk_BT = 0.4(f-1)(r-r_p)^{1.2}/r$.

expression is now different than eq 15 as it also well describes the region just above the percolation threshold. For that purpose, we have to consider the percolation threshold, r_p , and also describe the increase of the shear modulus, G_0 , by a power law but the scaling in terms of the dependence of the number of arms should remain the same (i.e., it should depend on f -1). For large values of r, this power law then should loose validity and approach the asymptotic limit given by eq 15, but for the experimental range of r values investigated here, we just described the whole data set by the power law dependence.

The reduced modulus, $G_0/n_pk_B\hat{T}$, n_p being the number density of linking polymers, should be 1 for an ideal elastic network. However, it is normally smaller due to network failures, such as dangling or backfolding arms or due to higher order links. The ratio is approaching unity (see Figure 8) with increasing *r*. This demonstrates that the portion of network

Table 4. Fit Parameters to the the Power Law, $G_0 = G_{00}(r - r_c)^{1.2}$, of the Plateau Modulus as a Function of the Number of Stickers Per Droplet, *r* for (C₁₂PDMA)₂, (C₁₂PDMA)₃, and (C₁₂PDMA)₄ Added to the ME

polymer	G_{00} (Pa)	r _p
$(C_{12}PDMA)_2$	480	0.93
$(C_{12}PDMA)_3$	600	0.80
$(C_{12}PDMA)_4$	786	0.64

failures is lower when increasing the number of arms from 2 to 4. Hence, the effectiveness of network forming increases with an increasing number of end-capped arms in a polymer.

Dynamic Light Scattering (DLS). The rheological results indicate rather complex dynamical properties of the multiarm polymer/ME system, that depend on concentration, sticker length, and number of arms. In order to gain further insight into these dynamical properties, comprehensive DLS measurements were performed.

First, we consider the variation of the concentration. Figure 9a depicts the change of $g^{(2)}(t)$ as a function of the amount of



Figure 9. Intensity autocorrelation function $g^{(2)}(t) - 1$ as a function of time for (a) $(C_{12}PDMA)_2$ and (b) $(C_{12}PDMA)_3$ for various concentrations of the polymer added to the O/W ME (data taken at a scattering angle of 90° and a temperature of 25 °C).

added $(C_{12}PDMA)_2$. As expected, the pure ME exhibits a single relaxation mode due to the diffusion of the droplets in the aqueous medium. The curve can be described by a single exponential function

$$|g^{1}(t)| = a_{1} \exp(-t/\tau_{1})$$
(16)

where the effective diffusion coefficient, $D_{\rm eff}$ is related to the fast relaxation time as

$$D_{\rm eff} = \frac{1}{\tau_1 q^2} \tag{17}$$

Thus, it can be related to the hydrodynamic radius, $R_{\rm H}$, through the Stokes–Einstein equation, $R_{\rm H} = k_{\rm B}T/6\pi\eta D$, where $k_{\rm B}$ is the Boltzmann constant; *T* is the temperature, and η is the viscosity of the solvent. The hydrodynamic radius, $R_{\rm H}$, of the ME droplets is 2.7 nm, which is in very good agreement with the radius obtained by SANS (2.4 nm). The somewhat higher value for $R_{\rm H}$ can be attributed to a hydration shell of the ME droplets of 0.3 nm, as similarly deduced before from the scattering experiments.^{31,53,54}

Upon addition of $(C_{12}PDMA)_2$ to the ME, the obtained correlation functions change little until a concentration of about 1 wt % is surpassed (Figure 9a). Only for concentrations above 2 wt %, does a second much slower relaxation mode clearly become visible, while for the highest concentrations of 6 and 8 wt %, a third relaxation mode is observed clearly. This was also seen before for end-capped PEO in aqueous solution.^{11,22} This becomes further evidenced when looking at the CONTIN evaluation⁵⁵ of these autocorrelation functions (Figure S5 of the Supporting Information), where for the higher concentrations slower modes are clearly indicated, while the relaxation is monomodal without and also for low polymer content. For the samples exhibiting a multimodal relaxation mechanism, this is also the concentration regime, where the samples become substantially more viscous.

The dynamic behavior also depends strongly on the number of arms of added telechelic polymer, as shown in Figure 9b. The appearance of the slower relaxation becomes much more pronounced upon addition of $(C_{12}PDMA)_3$ and occurs already for lower polymer concentration. This trend is continued for the addition of the 4-arm telechelic polymer $(C_{12}PDMA)_4$ (Figure S4 of the Supporting Information). The presence of these slower relaxation modes is also visible from the corresponding CONTIN analysis (see Figure S5 of the Supporting Information). In general, the slowest relaxation mode moves to increasingly longer times upon increasing the polymer concentration, while the intermediate mode becomes smaller.

Typically, a multimodal relaxation is observed for viscoelastic ME/polymer networks, which becomes increasingly pronounced with increasing elasticity and number of arms of the telechelic polymers. However, compared to the rheological changes, DLS is much more sensitive to the multifunctionality of the polymers. Apparently, the relaxation mechanisms observed by light scattering are very sensitive to the connectivity and the dynamic properties of the networks formed by bridging the ME droplets. In addition to the fast relaxation that corresponds to the diffusion process of the individual ME droplets, one observes an intermediate decay in the range of 10 ms and an additional slow and broad decay in the range of 1-100 s (i.e., in the range that is at the limit that can be explored by conventional DLS). These slower relaxation modes become more prominent with an increasing polymer concentration and with the number of arms, f.

The CONTIN analysis must be treated with caution as the distributions deduced often are too closely spaced to be reliable. Thus, we analyzed the autocorrelation functions in terms of a sum of normal or stretched exponential decays $g^{(1)}(t)$. Accordingly, the curves were fitted to a generalized Kohlrausch–Williams–Watt (KWW) equation^{56–58}

$$|g^{(1)}(t)| = a_1 e^{-t/\tau_1} + \sum a_i e^{-(t/\tau_i)^{\beta_i}}$$
(18)

A similar approach was applied before for describing the DLS data of an O/W ME bridged by a PEO distearate.²⁴ In addition to the conventional diffusion of the ME droplets (τ_1), this expression describes the additional relaxation modes of the viscoelastic network, by one- or two-stretched exponentials for the slower modes, respectively. The parameters a_i are the amplitudes for the respective relaxation modes with decay times, τ_i and β_i ($0 < \beta < 1$) is a measure of the width of the distribution of the relaxation times.⁵⁹ The more β differs from 1, the broader is the distribution of relaxation rates. In general, eq 18 allows for a quantitative description of the DLS data.

The slower relaxation processes can arise from different mechanisms which may be distinguished by the q dependence of the relaxation time, τ , which typically follows a power law $(1/\tau \sim q^a, \alpha \text{ being 2 for diffusive processes}).$

As already stated above, the fast relaxation is purely diffusive as shown by the q^{-2} dependence on its relaxation time (see Figure 10). In contrast, the intermediate relaxation time, τ_2 , shows almost no q dependence and therefore is apparently independent of size. For the case of viscoelastic polymer networks, such a q independent ($\alpha = 0$) relaxation has been reported before.^{60,61} In this case, the relaxation time is strongly



Figure 10. Intensity autocorrelation functions (a) $g^{(2)}(\tau)$ (taken at 90°) and (b) q dependence of the different relaxation times fitted using eq 18 for solutions of $(C_{12}PDMA)_2$, $(C_{12}PDMA)_3$, and $(C_{12}PDMA)_4$ at 5 wt % in ME solution at a scattering angle from 50° to 130° and a temperature of 25 °C.

correlated to the relaxation time of oscillatory shear experiments and thus was interpreted as the average lifetime of the network junctions.^{22,62} In our case, the relaxation time of the second relaxation mode, τ_2 , is in the same range as the rheological relaxation time (see Table 3) and remains constant with an increasing polymer concentration (see Tables S4–S6 of the Supporting Information). The stretching exponent, β_2 , is typically in the range of 0.35–0.8, becoming somewhat larger with an increasing polymer concentration (see Tables S4–S6 of the Supporting Information). Thus, the values of β_2 observed are similar to the value of 0.82 reported before for PEO distearate.²⁴

The slowest relaxation mode shows a rather unspecific q dependence. This is mainly attributed to the fact that for such long times, the limits of conventional DLS is reached, and consequently, the relaxation times obtained have rather large uncertainties. This applies similarly to β_3 which typically is in the range of 0.4–0.8, and increases somewhat when going from the 3-arm to the 4-arm polymer, thereby indicating that it has become a more well-defined relaxation process. The slowest relaxation mode could not be directly linked to structural features of the network. Most likely, it is associated with a kind of "breathing mode" of the network.

The effective diffusion coefficient of the droplets was obtained from the q^2 dependence of τ_1 calculated with eq 17 (see Figure S4 of the Supporting Information) for $(C_{12}PDMA)_2$, $(C_{12}PDMA)_3$, and $(C_{12}PDMA)_4$ at each measured concentration. Comparing the diffusion constant with the diffusion in the neat ME, the fast relaxation may be assigned to collective diffusion of the ME droplets, as it has already been seen in previous investigations.²⁴ The relative effective diffusion D_{eff}/D_0 coefficient is depicted in Figure 11a (where D_0 is the diffusion coefficient of the polymer-free ME droplets). The ratio $D_{\rm eff}/D_0$ first decreases with the polymer concentration indicating attractive interactions. This can be explained by the formation of dimers, trimers, etc. of connected ME droplets for low content of the bridging polymer. As to be expected for such a scenario, this effect becomes more pronounced with an increasing number of arms because then the polymer is more effective in forming such small clusters of droplets. The subsequent rise of D_{eff} with increasing r is simply related to the increasing repulsive interaction between the droplets introduced by increasing concentrations of the polymer.

At the same time, the reduction of the amplitude, a_1 , of the fast relaxation mode (Figure 11b) upon addition of the polymer becomes more pronounced with an increasing number of arms, f (i.e., the slower modes become much more prominent). These slower relaxation modes have to be related to the formation of a more complex network with an increasing number of arms.

Finally, we consider the variation of the sticker length. The intensity correlation functions for ME without and with 5 wt % of 3-arm polymers added, which vary with respect to their end-cap length (4, 12, and 18 carbon units), are given in Figure 12. Again, the intermediate relaxation time is on the same order of magnitude as the structural relaxation time from rheology (see Table 3). Moreover, it gives an activation energy per CH₂ group (as derived from the dependence of the time constant on the chain length of the alkyl sticker) of $0.6k_{\rm B}T$ (for $\theta = 90^{\circ}$) similar to the value obtained from rheology experiments, corroborating the relation between this relaxation mode and the structural relaxation seen in rheology.



Figure 11. (a) Effective diffusion coefficient of the droplets and (b) amplitude of the fast relaxation mode for solutions of $(C_{12}PDMA)_{2}$, $(C_{12}PDMA)_{3}$, and $(C_{12}PDMA)_{4}$ in ME as a function of the number of stickers per polymer.



Figure 12. Intensity correlation function $g^{(2)}(t) - 1$ as a function of time for systems of $(C_4PDMA)_3$, $(C_{12}PDMA)_3$, and $(C_{18}PDMA)_3$ at 5 wt % in ME solution at a scattering angle of 90° and a temperature of 25 °C. The arrows indicate the position of the second relaxation mode.

In general, it can be stated that the DLS experiments show the most pronounced and complex effects of polymer addition on the properties of the MEs, especially with respect to its dependence on the number of arms but also to the length of the stickers. While the network formation is clearly visible in the rheological properties, it leads to very pronounced changes of the DLS curves and additional, slower relaxation modes are observed. Apart from the fast relaxation, which can be attributed to the diffusion of the ME droplets or clusters thereof, and the intermediate relaxation mode, which is directly related to the rheological relaxation of the network, also a third, still slower, relaxation mode is observed that cannot be connected to a simple structural relaxation process of the network. We suggest that this slowest relaxation is attributed to a breathing mode of the network, as indicated before for polymer networks.⁶³

CONCLUSIONS

We studied the structure and dynamics of droplet O/W MEs with admixed telechelic multiarm polymers, where the length of the hydrophobic alkyl sticker, the concentration of polymer, and, in particular, the number of arms were varied. Though all MEs become more viscous upon polymer addition, the detailed behavior depends strongly on the molecular architecture of the added polymer. An increase of the sticker length has an enormous impact on the rheology and on the dynamic properties due to a stronger affinity of the end-cap chain to the oil droplets. The viscosity of such systems scales with the relaxation time $\tau_{\rm R}$ (via $\eta_0 = G_0 \tau_{\rm R}$), which is determined by the exit time $\tau_{\rm exit}$ of an alkyl chain from a ME aggregate, the latter increasing exponentially with the alkyl chain length, $\tau_{\rm exit} \sim \exp[n(CH_2)]$.

At the same time, the structure of the ME droplets, as seen by SANS, is hardly affected by the addition of the polymer. Its presence only leads to an enhanced repulsive interaction, which is proportional to the polymer concentration and arises from the steric requirements of the hydrophilic polymer chain, irrespective of the number and the length of the stickers. This is a result of the fact that in our system the mean spacing between the ME droplets is smaller than the end-to-end distance of the polymer chains (the natural spacing of the stickers). Under these conditions, the formation of loops is much less likely than the formation of bridges. In contrast, the effect of polymer addition on the dynamic properties as observed by DLS and rheology is much more pronounced and complex. These mixtures become increasingly viscous with polymer addition, and the structural relaxation time of rheology depends strongly on the length of the hydrophobic sticker and the number, r, of polymer stickers per ME droplet, while we find a universal scaling of τ_R on r, independent of the number of arms.

The shear modulus, G_0 , depends only little on the sticker length, but mostly on the sticker concentration (i.e., the network structure is generically the same). In contrast, the rheological relaxation time does not depend on the number of arms but increases with increasing sticker number per droplet. The effect of the polymer architecture is more subtle; we find that the shear modulus is proportional to the number of arms, as that determines the number of bridges between the ME droplets. This might be the result of having less network failures when using polymers with higher functionalities, without affecting the fundamental morphology of the network formation significantly.

In DLS, a second and third relaxation mode appears upon polymer addition. These become much more pronounced with increasing concentration and depend strongly on the number of arms and the length of the sticker. For the linear compound (i.e., the classical two arm system) only a small slower relaxation mode is observed in addition to the droplet diffusion mode. In contrast, for the 3- and 4-arm polymers, the two slow modes become dominant. The intermediate mode corresponds to the rheological relaxation and is independent of q. The slowest mode is attributed to some larger scale domainlike relaxation or "breathing" of the network, whose origin is not really clear at this moment. In parallel with rheology, one finds that the structural relaxation time increases largely with increasing sticker length. In general, these differences may be attributed to the increasing immunity against network ruptures with an increasing number of arms.⁶

In summary, we show that the morphology of the polymers allows for control of the dynamic properties of the networks formed by them over a large range. Accordingly, both the relaxation times and the shear modulus can be varied over several orders of magnitude. This allows for the formation of MEs of relatively low viscosity up to effectively gelled ones with relaxation times from the millisecond to the hours range. Rheology and the dynamical behavior in general can be controlled via the polymer concentration and, in particular, by the number of arms (for G_0) and the length of the hydrophobic sticker (for τ_R). This means that the architecture of these newly synthesized telechelic polymers is suitable for tailoring the rheological and dynamical properties of ME over a large range, without affecting the basic ME droplet structure, which may be a key for many of their future applications.

ASSOCIATED CONTENT

S Supporting Information

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Notes

The authors declare no competing financial interest.

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