

Shear-induced gelation of associative polyelectrolytes

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ABSTRACT

Copolymer of *N,N*-dimethylacrylamide (DMA) and acrylic acid (AA) was functionalized with pendant alkyl groups. Their dynamic mechanical properties in aqueous solution were investigated using continuous shear and oscillatory shear. Shear flow showed an abrupt divergence of the viscosity at a critical shear stress (σ_c). Oscillatory shear showed, with increasing applied stress, slight shear thinning followed by strong shear thickening above σ_c . The effect of the polymer concentration and the oscillation frequency (ω) was investigated. The behaviour at all concentrations and frequencies was fully determined by the product of the oscillation frequency and the terminal relaxation time (τ) of the systems at rest. Master curves of the data determined at different concentrations and frequencies were obtained if the reduced shear modulus was plotted versus the reduced applied stress at constant $\omega\tau$. The effect of shear increased with decreasing value of $\omega\tau$. At low frequencies the storage shear modulus crossed the loss modulus with increasing shear. A model is proposed for this phenomenon of shear-induced gelation.

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1. Introduction

Associative polymers consist of solvophilic backbone chains with solvophobic functional groups either attached to or incorporated within the chain. In solution the functional groups associate into multiplets, which leads to polymer aggregation and above a critical concentration to the formation of a transient network [1]. The number of groups per multiplet depends not only on the length of the backbone and the functional groups, but also on the solvent quality and may depend on the temperature, adjuvant etc. If the attraction is very strong the association can lead to macroscopic phase separation [2–5].

The linear viscoelastic properties of transient gels formed by associative polymers have been studied in detail. In the case of so-called telechelic polymers that contain functional groups only at the two extremities of the chains, it was found that the gel could be well modelled as a rubber elastic network in which the multiplets act as crosslinks [5–10]. The shear modulus at high frequencies is determined by the chain concentration and the relaxation is characterized by a single relaxation process with a relaxation time equal to the life time of the functional groups in the multiplets. When the polymer backbone contains randomly distributed pendant functional groups, the relaxation is characterized by a broad distribution of relaxation times as the escape of a single

group from a multiplet is not sufficient to fully relax the stress on the chain [11–13].

The non-linear viscoelastic properties have been studied in less detail. In general, weak shear thickening is observed in flow experiments with increasing flow rate before strong shear thinning at higher rates [14,15]. The shear thickening is thought to be caused by an increase of the number of multiplets shared by different chains acting as crosslinks [16,17] and/or non-Gaussian stretching of the chains [18], while the subsequent shear thinning is thought to be caused by a decrease of the life time of the crosslinks [19].

For a few systems shear thickening was found to be so strong that one may speak of shear-induced gelation, i.e. the system stopped flowing altogether. This uncommon phenomenon was first alluded to for ionomer solutions [20], but has received very little attention so far. Recently it has been investigated in detail for two different associative polymers [21,22]. In both cases the chain backbone was a copolymer displaying polyelectrolyte characteristics, either based on *N*-isopropylacrylamide (NIPAM) or *N,N*-dimethylacrylamide (DMA)/Acrylic Acid (AA), and the functional groups were pendant alkyl groups. Both systems showed shear-induced gelation at a critical shear rate $\dot{\gamma}_c$ that increased strongly with decreasing polymer concentration.

For functionalized DMA/AA [21] copolymers, $\dot{\gamma}_c$ was found to increase with decreasing chain length, increasing grafting density and length of the functional groups, and decreasing charge density. For pNIPAM [22] with 10% of the segments

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functionalized $\hat{\gamma}_c$ was found to increase with increasing temperature. pNIPAM is a thermo-sensitive polymer with a lower critical solution temperature (LCST). However, for a less densely functionalized pNIPAM (5%) shear-induced gelation only occurred close to the LCST, while at lower temperatures weak shear thickening was found similar to that generally observed for associative polymers.

In previous studies only continuous shear flow was used to investigate shear-induced gelation. It was concluded that shear-induced gelation was caused by the increase of inter-molecular association leading to the formation of a system spanning network. However, the molecular origin of the strong shear-induced gelation effect could not be further investigated because of a strong Weissenberg effect which causes climbing of the shear-induced gels out of the Couette cell and additional possible wall slip. Here we report on a further investigation of the shear-induced gelation of functionalized DMA/AA copolymers using both oscillatory shear and continuous flow measurements. Use of oscillatory shear allowed us to show that shear-induced gelation is caused by a strongly increased terminal relaxation time. We will suggest a molecular mechanism that can explain the increase of the life time.

2. Materials and methods

2.1. Sample preparation

N,N-dimethylacrylamide was purchased from Aldrich. Dicyclohexylcarbodiimide (DCCI), *N*-methyl-2-pyrrolidone, acrylic acid and *n*-dodecylamine were provided by Acros.

The polymer synthesis is described in Ref. [21]. In brief, first, a copolymer of DMA and AA (named DMA/AA in the following) is synthesized by free radical polymerisation of both monomers using a redox initiation. The number (Mn) and weight (Mw) averaged molecular weights of this precursor are characterized by Size Exclusion Chromatography (Mn = 1.0×10^6 g/mol, Mw = 3.2×10^6 g/mol) using NaNO₃ 0.1 M as the eluent. The AA content is determined by ¹³C NMR and by potentiometric measurements yielding 19 ± 1 mol% and 18 ± 1 mol%, respectively. The copolymer is statistical as discussed in Ref. [21].

In second step, almost 50% of the AA units of the precursor polymer are hydrophobically modified with dodecyl side-chains using DCCI as a coupling agent. The remaining AA units are then neutralized with an excess of NaOH and the polymer is dialysed against water and freeze dried. The extent of hydrophobic modification is measured with ¹H and ¹³C NMR, and potentiometric measurements yielding, respectively, 8.8 ± 0.2 mol%, 9.7 ± 0.5 mol% and 8.2 ± 0.5 mol%. The chemical formula of functionalized DMA/AA is given in Chart 1.

Solutions of polymer are prepared in ultrapure water (MilliQ) and left for several weeks to reach thermodynamic equilibrium. The hydrodynamic radius (Rh) of the aggregates formed in water has been measured by dynamic light scattering after extrapolation of the results to zero concentration.

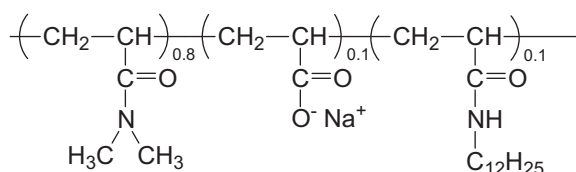


Chart 1. Chemical formula of the functionalized DMA/AA copolymers.

2.2. Rheology

Dynamic mechanical measurements and large amplitude oscillatory shear experiments were done with stress controlled rheometers ARG2 (TA instruments) and RS100 (Haake) using cone and plate geometries (angle 1° and diameter 60 or 2° and 35 mm). Flow measurements were done with an ARES rheometer (TA instruments) using a Couette geometry (inner radius = 16.5 mm) with a gap of 0.25 mm. Measurements were done at 20 °C unless otherwise specified. The viscosity was determined while increasing the shear rate using a measurement time of 5 s after an equilibration time of 20 s.

3. Results

3.1. Linear rheology

Before discussing shear-induced gelation we will briefly show the results in the linear viscoelastic regime for the sample used in this study, which was earlier investigated in more detail by Cadix et al. [21]. The frequency dependence of the storage (G') and loss (G'') shear moduli in the linear response regime is shown in Fig. 1a for polymer solutions at different concentrations. At high concentrations ($C > 10$ g/L) one can clearly see the viscoelastic response of transient networks that is characterized by an elastic response at high frequencies and a viscous response at low frequencies. With decreasing concentration the high frequency modulus decreased and the transition to liquid-like behaviour ($G' \propto \omega^2$, $G'' \propto \omega$) shifted to higher frequencies.

The data obtained at different concentrations can be superimposed by horizontal and vertical shifts resulting in a master curve, see Fig. 1b. The relaxation of the shear modulus is characterized by a very broad distribution of relaxation times, as is generally observed for randomly functionalized associative polymers. Both the elastic modulus (G_0) and the terminal relaxation time (τ) increased strongly with increasing concentration as was already reported by Cadix et al. [21].

The effect of temperature was studied between 5 and 30 °C for $C = 20$ g/L and showed that relaxation was faster with increasing temperature, but that the variation of G_0 was very small. The data could be superimposed using horizontal shift factors (a_T) that showed Arrhenius temperature dependence: $a_T \propto \exp(-E_a/RT)$ with an activation energy of $E_a = 120$ kJ/mol (results not shown).

3.2. Oscillatory shear

At higher applied stresses the experimental values of G' and G'' were no longer independent of the stress. Fig. 2 shows an example of G' and G'' measured at $f = 0.01$ Hz as a function of the imposed maximum shear stress (σ) for a solution at $C = 20$ g/L. Up to about $\sigma = 2$ Pa, G' and G'' are constant with $G' \ll G''$. With increasing stress G' and G'' decrease to $\sigma \approx 10$ Pa and then both increase strongly at higher stresses. The initial decrease and subsequent increase is much stronger for G' than G'' , and G' crosses G'' at $\sigma \approx 200$ Pa.

The dependence of G' and G'' on the imposed stress means that the strain response may no longer be purely sinusoidal. Examples of the strain (γ) during an oscillation cycle are included in Fig. 2 for different values of σ . Repeated oscillations were identical, which means that at each stress the system reached a steady state within the investigated frequency range. For $\sigma < 30$ Pa, the deviation from a purely sinusoidal response was negligible even though G' and G'' depended on σ . At larger stresses, small deviations from a purely sinusoidal response could be seen. It should be mentioned that the contribution of the third harmonic was less than 1% in all cases.

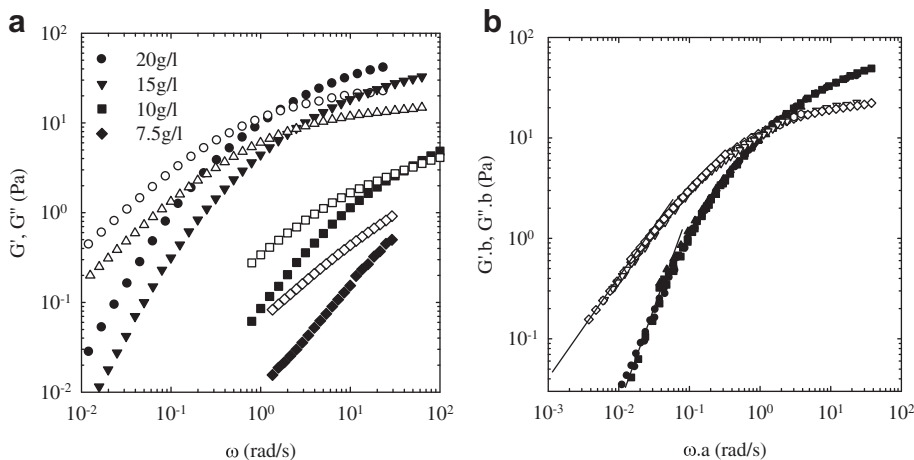


Fig. 1. (a) Frequency dependence of G' (filled symbols) and G'' (open symbols) for solutions of functionalized DMA/AA copolymers at different concentrations indicated in the figure. (b). Master curve obtained after vertical and horizontal shifts of the data shown in (a). The data obtained for 15 g/L are taken as reference. The solid lines through the filled and open symbols have slopes 1 and 2, respectively.

Measurements at other frequencies and concentrations also showed only small deviations. Nevertheless, the physical meaning of the results presented in this paper is not affected by the small non-linearities, which justifies the use of the dynamic moduli G' and G'' .

The dependence of G' and G'' on σ was studied as a function of the polymer concentration between 5 and 20 g/L and the oscillation frequency (f) between 10^{-3} and 1 Hz. At $C=20$ g/L, the polymer solution is predominantly viscous at low frequencies and elastic at higher frequencies. For this system we can study the effect of increasing the applied stress both at frequencies where in the linear response regime the system cannot relax the stress during an oscillation cycle ($\omega.\tau > 1$) and at frequencies where the system can fully relax ($\omega.\tau < 1$).

Fig. 3 compares the dependence of G' and G'' on σ at different frequencies. At $f=1$ Hz the linear response is mainly elastic ($G' > G''$) and increasing the stress leads to a modest increase of both G' and G'' above 50 Pa. At $f=0.1$ Hz and lower frequencies, the linear response is mainly viscous ($G' < G''$). In this case G' and to a lesser extent G'' decrease first with increasing σ followed by an increase at higher stresses. The minimum was very shallow at 0.1 Hz, but became more pronounced with decreasing frequency

whereas the subsequent increase became steeper. At all frequencies G' increased more steeply than G'' leading to crossing of G' and G'' at $\sigma = 150$ Pa for $f=0.1$ Hz and at a slightly higher stress for $f=0.01$ Hz. The minimum was situated at a stress of about 20 Pa that was only weakly dependent on the frequency.

The dependence of G' and G'' on σ at different polymer concentrations for a given frequency is shown in **Fig. 4** for $f=1$ Hz. The magnitude of the initial shear thinning and the subsequent shear thickening increased with decreasing polymer concentration. At all concentrations G' increased more strongly with increasing σ than G'' and they crossed at low polymer concentrations where $G' < G''$ in the linear regime.

It appears that both shear thinning and shear thickening are determined by the product of the angular oscillation frequency ($\omega = 2\pi f$) and the terminal relaxation time in the linear regime (τ), considered as the reciprocal of the crossing frequency of the moduli. The relaxation time increased with increasing polymer concentration, which caused the concentration dependence shown in **Fig. 4**. Notice that the same value of $\omega.\tau$ can be obtained at different concentrations by varying the frequency. This is illustrated in **Fig. 5** where we have plotted for 3 concentrations G' normalized

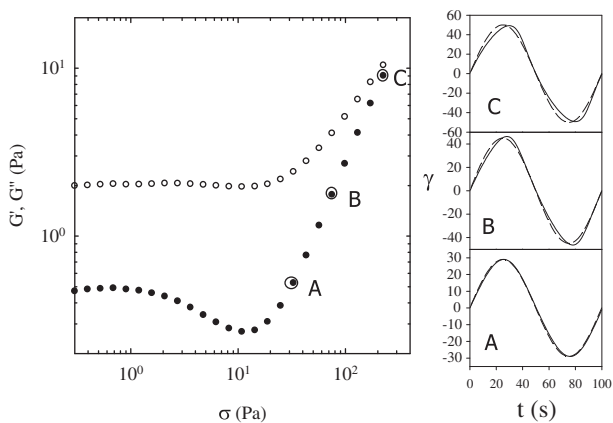


Fig. 2. Dependence of G' (filled symbols) and G'' (open symbols) on σ at $f=0.01$ Hz for a solution at 20 g/L. The deformation during an oscillation cycle is shown in the right panel for different σ as indicated in the main figure. The dashed lines represent a purely sinusoidal response.

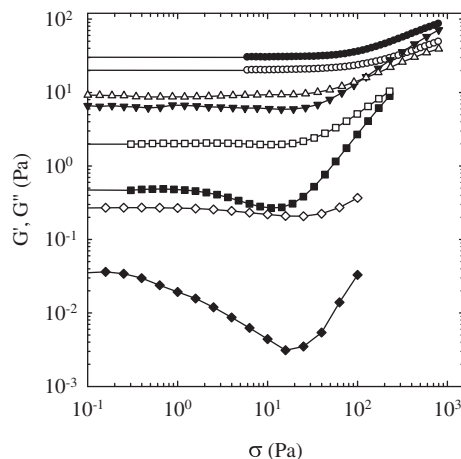


Fig. 3. Dependence of G' (closed symbols) and G'' (open symbols) on σ at different frequencies for a solution at 20 g/L. From top to bottom $f=1$ Hz, 10^{-1} Hz, 10^{-2} Hz and 10^{-3} Hz.

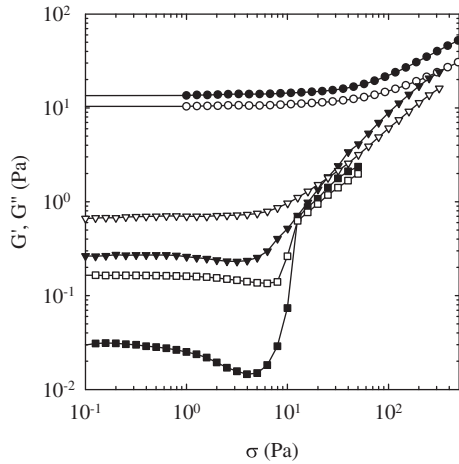


Fig. 4. Dependence of G' (closed symbols) and G'' (open symbols) on σ at different polymer concentrations for $f = 1$ Hz. From top to bottom $C = 15, 9$ and 5 g/L.

by the low shear value (G'_0) as a function of σ normalized by the critical value σ_c where shear hardening sets in. When G' showed a minimum, the onset of shear hardening could be defined unambiguously as the value of the stress at the minimum (σ_c). When G' did not have a minimum, σ_c was obtained by taking the intersection of the dependences of G' at low and high stresses. The frequencies were chosen such that $\omega \cdot \tau$ was about 0.3 (Fig. 5a) or about 0.03 (Fig. 5b).

Remarkably, for any given value of $\omega \cdot \tau$ master curves are obtained in this representation. This observation is one of the major results of the present study and is an important step towards the elucidation of the process of shear-induced gelation, see below. Shear thinning and subsequent shear thickening became more important with decreasing $\omega \cdot \tau$, i.e. either with decreasing oscillation frequency or with decreasing concentration. For small values of $\omega \cdot \tau$, shear thickening was very strong.

Fig. 6 shows the dependence on σ of the maximum deformation during an oscillation, which is, of course, a direct consequence of the variation of G' and G'' . Strong shear thickening caused stagnation or even a decrease of γ_{max} with increasing σ which is clearly seen at low concentrations ($\omega \cdot \tau \ll 1$). For $\omega \cdot \tau > 1$, where the effect of shear thickening was weaker, γ_{max} continued to increase with increasing stress.

The maximum shear rate during an oscillation cycle is equal to $\omega \cdot \gamma_{max}$ and the critical shear rate $\dot{\gamma}_c$ was defined as $\omega \cdot \gamma_{max}$ at σ_c .

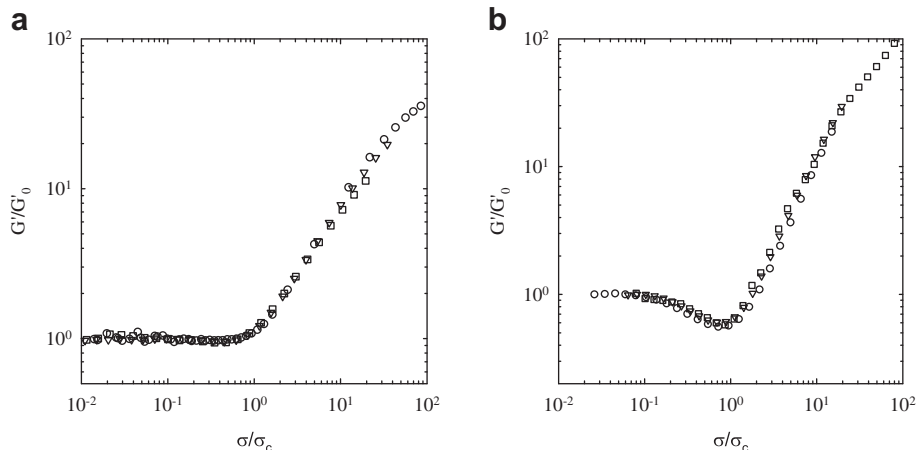


Fig. 5. Normalized storage shear modulus as a function of the normalized shear stress for different polymer concentrations. The frequencies were chosen such that $\omega \cdot \tau$ was approximately 0.3 (a) or 0.03 (b). $C = 10$ g/L (\circ), 15 g/L (∇) and 20 g/L (\square).

Fig. 7 shows σ_c and $\dot{\gamma}_c$ as a function of the polymer concentration at different frequencies. The dependence of σ_c and $\dot{\gamma}_c$ on the frequency was small considering that the latter was varied over 4 decades.

$\dot{\gamma}_c$ decreased with increasing concentration, while the concentration dependence of σ_c showed a minimum at $C \approx 9$ g/L. The deformation associated with the critical stress (noted γ_c in the following) can be measured. γ_c decreased with increasing frequency and concentration covering a wide range from about 5×10^4 at $f = 10^{-3}$ Hz and $C = 5$ g/L to about 3 at $f = 1$ Hz and $C = 20$ g/L.

3.3. Continuous shear flow

The viscosity as a function of the shear rate ($\dot{\gamma}$) is shown in Fig. 8 for solutions with different polymer concentrations between 3 and 20 g/L. A dramatic increase of η was observed at a critical shear rate $\dot{\gamma}_c$. At higher shear rates wall slip occurred. Similar results were already reported by Cadix et al. [21] who did continuous shear measurement on solutions of the same polymer with different molar masses. The increase of η occurred after a delay time that depends on the distance between $\dot{\gamma}$ and $\dot{\gamma}_c$, which means that the value of $\dot{\gamma}_c$ depends on the waiting time at each shear rate. However, the delay time decreased rapidly with increasing $\dot{\gamma}$ so that the uncertainty was small. For instance, at $C = 3$ g/L the increase occurred within 30 s at $\dot{\gamma} = 1000$ s $^{-1}$ and no increase occurred within one hour at $\dot{\gamma} = 900$ s $^{-1}$.

The concentration dependence of $\dot{\gamma}_c$ and the corresponding critical shear stress (σ_c) are compared to the values obtained by oscillation in Fig. 7. The concentration dependence is close to that observed in oscillatory shear. The close correspondence between the values of σ_c and $\dot{\gamma}_c$ obtained from continuous shear flow and oscillatory shear shows that the same phenomenon occurred in both experiments except perhaps at the highest frequencies. This is not surprising if one considers that in most oscillation measurements $\gamma_{max} \gg 1$ implying that also during oscillation the system flowed substantially.

4. Discussion

4.1. The equilibrium structure

The viscoelastic behaviour of DMA/AA solutions before functionalising was similar to that generally observed for polymer solutions [21]. The effect of entanglements on the viscosity started

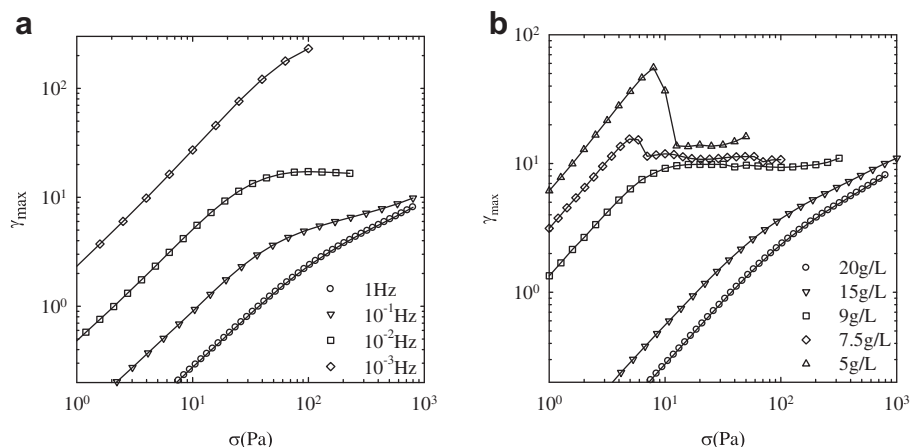


Fig. 6. Dependence of the maximum deformation on σ at different frequencies for $C = 20$ g/L (a) and for different concentrations at $f = 1$ Hz (b).

to become visible at about 10 g/L, but it was not important in the concentration range used in this study (up to 20 g/L).

After functionalisation, pendant alkyl groups of the DMA/AA chains associated in aqueous solution in the form of multiplets that consist of a dense hydrophobic core containing the alkyl groups and a corona of hydrophilic chains. If the alkyl groups are randomly distributed along the chain it is difficult to determine the number of groups per multiplet (N_{ag}), but a combination of techniques indicated that multiplets with N_{ag} about 40 were formed in aqueous solution of polyacrylate randomly functionalized with a small fraction of dodecyl groups [23]. For the polymer studied here the molar mass between alkyl groups was on average 10^3 g/mol and $M_n \approx 10^6$ g/mol so that each chain contained about 25 multiplets if we assume that $N_{\text{ag}} \approx 40$. In reality, N_{ag} may be somewhat larger or smaller, but that does not matter for the interpretation of the experimental results given here as long as N_{ag} is not very small, which we consider highly unlikely. A schematic drawing of the functionalised polymer in aqueous solution is shown in Fig. 9.

At very low concentrations the multiplets were formed essentially by alkyl groups from the same polymer, which leads to contraction of the chains due to intra-chain association as predicted by Borisov and Halperin [24,25]. For the system studied here, the hydrodynamic radius R_h decreased from 66 nm before functionalisation to 44 nm after functionalisation. It follows that in the concentration range studied here the functionalized polymers were at most weakly overlapping and were not entangled.

With increasing concentration, chains have an increased probability to encounter each other so that alkyl groups of two different chains can form a single multiplet. Such multiplets act as crosslinks between different chains leading to aggregation. For strongly associating polymers, one expects phase separation into a highly concentrated and a dilute phase [26]. Phase separation was indeed observed after addition of salt, but not in the absence of added salt. Probably the ensuing large loss of translational entropy of the counterions inhibited phase separation in the latter case.

The number and size of the polymeric aggregates increased with increasing concentration until a transient network was formed above a critical percolation concentration. The transient gel was elastic at high frequencies and applying the standard theory of rubber elasticity of polymer gels, the elastic shear modulus (G_0) is equal to:

$$G_0 = RT\nu \quad (1)$$

with ν the molar concentration of elastically active chains, R the gas constant and T the absolute temperature. One can also express eq. (1) in terms of the molar mass between crosslinks (M_c): $G_0 = CRT/M_c$. Using the experimental values of G_0 , we find that M_c decreased from 5.6×10^6 g/mol at $C = 7$ g/L to 1.6×10^6 g/mol at $C = 20$ g/L. Comparison with the molar mass of the polymers ($M_n \approx 10^6$ g/mol) entails that the chains were only weakly crosslinked and that most of the multiplets were purely intra-chain, i.e. formed by alkyl groups belonging to a single chain.

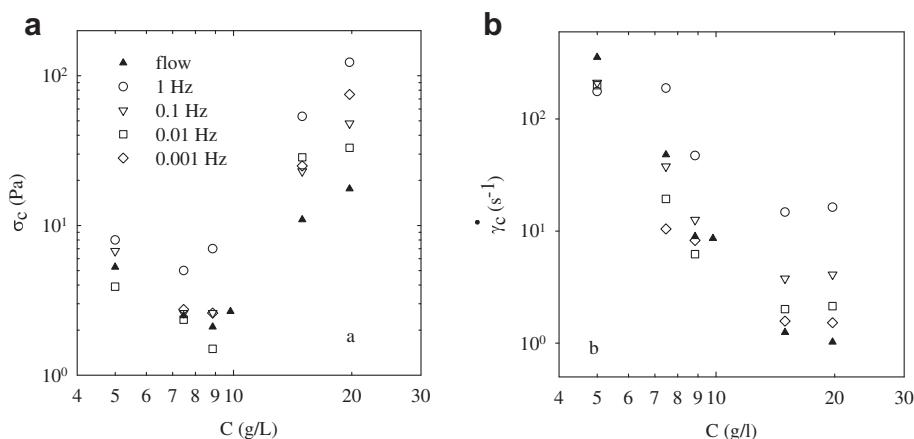


Fig. 7. Dependence of the critical stress (a) and the critical shear rate (b) on the polymer concentration during oscillatory shear at different frequencies (open symbols) and during continuous shear flow (filled symbols).

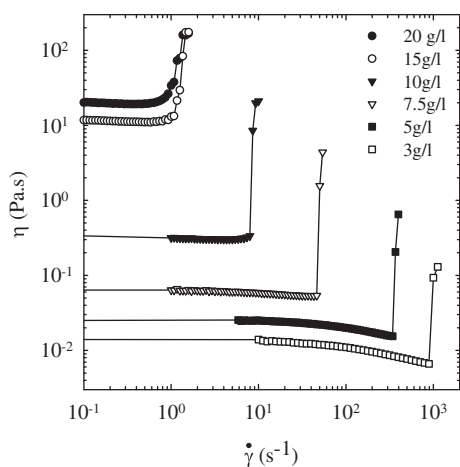


Fig. 8. Shear rate dependence of the viscosity at different polymer concentrations.

For telechelic polymers, stress relaxation of the fully formed transient gel is characterized by a single relaxation time that is equal to the time needed for an alkyl group to escape from a multiplet (τ_e) [6]. Generally, Arrhenius temperature dependence is observed with an activation energy that increases with

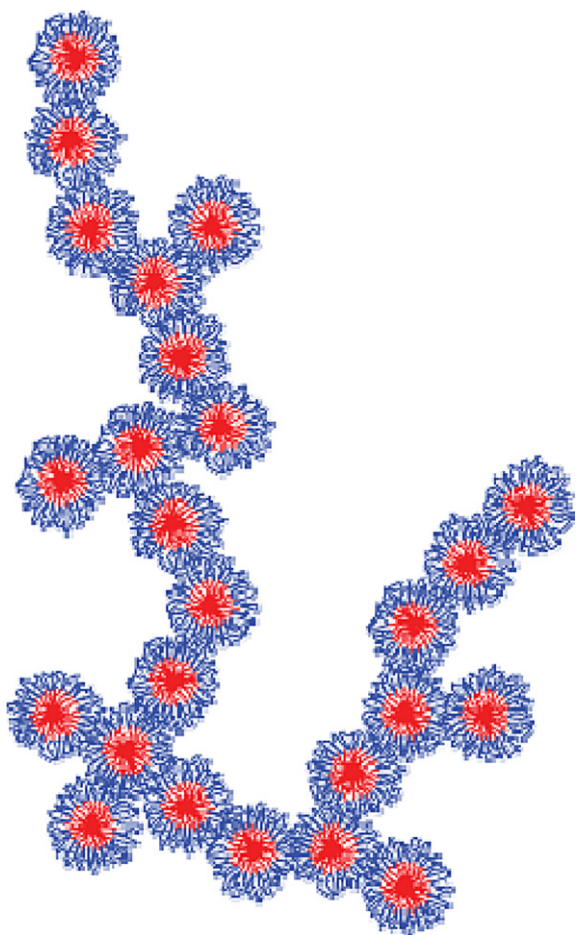


Fig. 9. Schematic drawing of a functionalised polymer showing the polymer backbone (blue) wrapped around the multiplets formed by the pendant alkyl groups (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

increasing alkyl length. For the system studied here we also found Arrhenius temperature dependence, and we presume that the stress relaxation is also determined by the escape time. However, in the present case, a crosslinking multiplet contains more than one covalently linked alkyl group of the polymer chains involved in the crosslink. Therefore in order to break the crosslink and thus to relax the stress several alkyl groups have to escape from the crosslink. In addition, the number of alkyl groups belonging to one chain in the multiplet varies from one crosslinking multiplet to another. As a consequence, the relaxation process is characterized by a broad distribution of relaxation times and the terminal relaxation time τ is much longer than τ_e . This situation is reminiscent of the description given by Semenov et al. [27].

4.2. Shear-induced gelation

As long as $\tau\dot{\gamma} \ll 1$ the shear rate had little influence on the viscosity. But with increasing $\dot{\gamma}$ the transiently aggregated chains were increasingly elongated by the flow, which decreases the friction and leads to shear thinning. Rheo-optical measurements [28] showed an increased birefringence (factor of 5) with respect to the parent unmodified polymer and a significantly lower orientation angle despite a lower viscosity.

The following mechanism has been proposed by several authors to explain shear thickening of associative polymer solutions [16,17]. When $\dot{\gamma}$ exceeds τ^{-1} the bridging chains become overstretched and multiplets (which might act as crosslinks in the semi-dilute regime) are increasingly broken by the flow. The disengaged alkyl groups will quickly diffuse into other multiplets, which in the flow are more likely to be shared with other polymers than at rest. This increases the number of multiplets acting as elastic crosslinks and therefore a larger stress is needed to maintain the flow. However, oscillatory measurements reported here cannot be explained by this mechanism.

An important result of the present study was the observation that the system showed the same behaviour as a function of the shear stress at a given value of $\omega\tau$ independent of the polymer concentration. This implies that it is not the density of the transient network that determines the effect of applied shear stress, but the terminal relaxation time of the network.

At high frequencies and high concentrations, the increase of G' with increasing σ was relatively weak. At these conditions $\omega\tau > 1$ and the elastic modulus of the transient network is observed. The weak increase of the elastic modulus (factors 3–4) with increasing shear stress implies that the number of elastically active chains is not increased much by shear. Shear-induced gelation can thus not be explained by a dramatic increase of the number of crosslinks.

A very strong increase of the shear moduli with increasing stress is observed for $\omega\tau < 1$ where we probe the viscous response of the transient network. This increase, in addition to the observation that G' becomes larger than G'' , can only be explained by an increase of the life time of the crosslinks. For shear-induced gelation to occur the life time has to increase by several orders of magnitude.

One way in which such an increase of the life time could occur is that shear stretches the chains and allows multiplets of both chains next to a crosslinking multiplet to exchange alkyl groups and thereby to reinforce the crosslink. The life time of the junction between two chains increases tremendously if the junction zone contains more shared multiplets and if the fraction of alkyl groups from each chain is more equally distributed. By this mechanism, the life time is strongly increased without increasing strongly the crosslinks density. A schematic drawing of the junction zone at rest and during high shear is given in Fig. 10.

A consequence of the increased relaxation time is that at lower frequencies both G' and G'' increase with increasing stress, but the

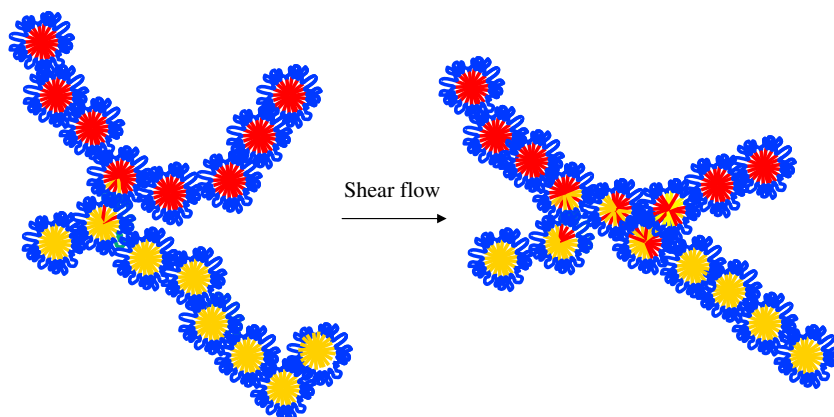


Fig. 10. Schematic drawing of two polymer chains at rest and under shear. The hydrophobic groups of the two different chains are represented in yellow and red. The hydrophilic groups of both chains are represented by blue lines. Each bead corresponds to a multiplet. Under shear, the chains align in the flow leading to reinforcement of already existing crosslinks by increased sharing of neighbouring multiplets schematized by the mixed colours. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

increase of G' is much stronger, than G'' which may lead eventually to crossing of G' and G'' . The observation that shear causes G' to cross G'' prompted us to use the expression shear-induced gelation.

The shear-induced gel relaxes back to its equilibrium state after cessation of the flow, but with a time scale that is much longer than the terminal relaxation time at rest. Indeed, Cadix et al. [21] found that relaxation of the shear-induced gel took about 40 s. This means that the system remained in the shear-induced gel state during an oscillation cycle, which could explain the relatively weak deviations from a sinusoidal response shown in Fig. 2. The lower is the frequency the more time the system has to react to the variation of the shear rate during an oscillation cycle. The form of the strain when it deviates from a sinus can be qualitatively explained as follows. Starting from $t = 0$ where the shear rate is highest, shear thickening causes the elastic modulus to increase. As a consequence the increase of γ becomes weaker than if no shear thickening had occurred indicated by the dashed line. When the shear rate becomes slow these additional crosslinks relax again to a limited extent so that γ decreases more steeply. This effect is of course stronger at low frequency. As a first approximation, the difference between the solid and the dashed line characterizes the variation of the shear moduli during a cycle. For all systems studied and for the investigated frequency range, the increase of the shear moduli for $\sigma > \sigma_c$ was much larger than its variation during a cycle.

The question remains why shear-induced gelation has so far only rarely been observed, while almost all associative polymers show modest shear thickening. In aqueous solutions it has only been observed when the chain was charged and at the same time contained groups with a strong tendency to associate. As mentioned above, charge may be necessary to avoid phase separation, so one reason that the phenomenon is rare could be that a strong association and yet solubility is needed. Another condition for clear observation of the effect is that in the linear regime the life time of the crosslinks needs to be relatively short so that the transient network flows easily. The life time will be short if only few functional groups have to escape from the multiplet in order to break the crosslink. At the same time the life time of the shear-induced crosslinks should be much longer so that spontaneous relaxation during the flow becomes less likely. It is clear that more experimental work will be needed in order to fully elucidate the phenomenon of shear-induced gelation.

5. Conclusion

Pendant dodecyl groups that are randomly incorporated in a polyelectrolyte chain associate into multiplets that can act as crosslinks between chains leading to aggregation. With increasing concentration the number and size of the polymeric aggregates increases and above a critical concentration a transient percolating network is formed, which causes a strong increase of the viscosity. The linear viscoelastic response of the transient network is characterized by a broad relaxation time distribution.

With increasing shear rate the systems show weak shear thinning followed by shear-induced gelation at a critical shear rate both during continuous shear and oscillatory shear, even at very low frequencies. The shear thinning and thickening behaviors were found to be fully determined by the product of the terminal relaxation time of the transient network at rest and the oscillation frequency. Shear-induced gelation was caused by the dramatic increase of the terminal relaxation time above a critical shear rate. This was attributed to a more intimate interconnection of two chains at the already existing crosslinks induced by shear. The increase of the number of crosslinks was less important.

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