

Rheology of a reversible supramolecular polymer studied by comparison of the effects of temperature and chain stoppers

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The rheology of a reversible supramolecular polymer is studied by comparing the effects of an increase in temperature and the addition of chain stoppers. The dependence of the zero-shear viscosity and the terminal relaxation time on temperature is exponential, and the activation energy for viscous flow can be calculated. Above a critical stopper fraction, power laws describe the stopper dependence of the viscosity and relaxation time. A simple model for the effect of the addition of chain stoppers on the average degree of polymerization adequately describes the results. A comparison of flow curves at several temperatures and stopper fractions reveals considerable differences between solutions with the same zero-shear viscosity. These are mainly associated with differences in the terminal relaxation time. A mechanism of shear-induced alignment and subsequent elongation of chains is proposed, with which the experimental results are consistent. © 2007 American Institute of Physics. [DOI: 10.1063/1.2409296]

I. INTRODUCTION

For ages, scientists have used biological systems as a source of inspiration for the development of new structures and materials. One of the defining processes in biology is the ability to respond to changes in external conditions such as temperature, light, pH, or the presence of certain chemicals. Much recent scientific effort is aimed at the incorporation of this responsiveness in synthetic polymeric materials.¹⁻⁵ On a fundamental level, this may increase our understanding of complex biological systems. In terms of practical applications, the synthesis of so-called intelligent or self-healing materials is a promising perspective.

To react adequately and sensitively to a change in conditions, a responsive polymer must be able to quickly and reversibly change its properties. A relatively new class of polymers, with inherently highly dynamic properties, is “reversible supramolecular” polymers.^{6,7} In contrast to “normal” polymers, the monomers of a supramolecular polymer are not connected by covalent chemical bonds, but by weaker, reversible interactions such as hydrogen bonds, metal-ligand complexation or π - π interactions. Supramolecular polymers reproduce many of the characteristics associated with the macromolecular nature of covalent polymers. For example, they form viscous solutions or gels at sufficiently high concentrations. But the reversibility of the bonds also leads to important differences between supramolecular and covalent polymers. For example, the equilibrium chain length (distribution) of a supramolecular polymer is not fixed, but it depends on conditions such as the overall monomer concentration, temperature, and solvent. Furthermore, supramolecular polymers have interesting dynamical properties, owing to the continuous breaking and reformation of bonds. The ability to adapt their chain length makes supramolecular polymers promising candidates for applications in responsive materials.⁸⁻¹¹ Such applications require that the

equilibration (caused by the breaking and reformation of bonds) be sufficiently fast, so a change in conditions is translated into a measurable change in the material properties within a practically relevant time. For systems which satisfy both criteria (noncovalent bonds between monomers and sufficiently fast equilibration) the term “reversible supramolecular polymers” is used.

In many respects, supramolecular polymers are similar to the surfactant aggregates known as wormlike micelles.¹² These are also long, thin structures of small molecules, held together by noncovalent interactions. Wormlike micelles also have a temperature- and concentration-dependent length and a continuous exchange of monomers. They are used in a variety of applications, mainly based on their ability to (reversibly) alter the rheological properties of liquids.¹³ Despite the similarities, there are also fundamental differences between wormlike micelles and reversible supramolecular polymers. For example, wormlike micelles only exist within a certain range of conditions (surfactant and salt concentrations, temperature, etc.), whereas supramolecular polymers display polymeric properties in dilute and concentrated solutions as well as in the bulk.¹⁴ Furthermore, the interactions between the monomers in supramolecular polymers are much more specific than in wormlike micelles which enables a better control over the structure of the chains. For example, cross-linkers or chain stoppers (*vide infra*) can be added to adjust the chain architecture. Furthermore, directionality can be introduced in supramolecular polymer chains, which is predicted to strongly affect the interfacial behavior of supramolecular polymers.^{15,16}

Generally, the monomers of a supramolecular polymer contain two binding groups (bifunctional monomers), enabling them to associate into linear chains.^{7,14} The presence of monomers with three or more binding groups leads to branching and network formation. On the other hand, mono-

mers with only one binding group stop the growth of the chain to which they bind; they form a nonfunctional or “dead” chain end. These monofunctional monomers are therefore also called “chain stoppers,” and they decrease the average degree of polymerization.

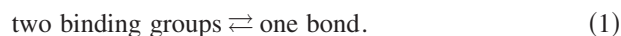
Many types of noncovalent interactions can be used to form supramolecular polymers. In aqueous environment, mixing of bisligands with chelating metal ions has proven to be a successful approach.^{17,18} Attempts to make water-soluble supramolecular polymers without metal ions include the use of π - π interactions.¹⁹ DNA base pairing,²⁰ and several types of host-guest interactions.^{21,22} In apolar organic solvents, (multiple) hydrogen bonds can be used to create supramolecular polymers.^{23,24} An example of a supramolecular polymer, based on the cooperative formation of four hydrogen bonds between consecutive monomers, is bisurea (2,4-bis(2-ethylhexylureido)toluene) (EHUT).^{25,26} This molecule forms long, semiflexible supramolecular chains in several apolar organic solvents, and has a very rich and complex rheological behavior.²⁷ Previously, it was demonstrated that 2,4-bis(dibutylureido)toluene (DBUT) can be used as a monofunctional chain stopper for EHUT, and the effect of the chain stopper on static properties of EHUT solutions was reported.^{28,29} It was also shown that chain stoppers can be used to investigate separately the effect of monomer concentration and degree of polymerization on linear rheology, which is normally impossible for supramolecular polymers.³⁰

In the present paper, two ways of adjusting the average degree of polymerization of EHUT solutions are compared: (1) increasing temperature and (2) addition of chain stoppers. The fact that chain stoppers form dead chain ends sets them apart from the other parameters which affect the average degree of polymerization (such as temperature). The addition of chain stoppers may therefore affect the solution properties in a different way than an increase in temperature. For example, it was recently suggested that there is a strong coupling between the shear-induced alignment of chains and chain growth in EHUT solutions due to their high persistence length.²⁷ This coupling could be weakened by the presence of dead chain ends, which prevent chains from associating with each other. The effect of chain stoppers and temperature on the linear rheology is investigated in Sec. IV A and flow curves at several temperatures and stopper concentrations are compared in Sec. IV B.

II. THEORETICAL BACKGROUND

A. Supramolecular polymers and chain stoppers

The equilibrium between breaking and reformation of bonds in a supramolecular polymer can be written as follows:



This equilibrium is very similar to that used in Flory's mean-field theory of condensation polymerization.^{31,32} The latter is also an equilibrium reaction (during the polymerization step) between bifunctional monomers, as the released condensation product can reversibly hydrolyze bonds between monomers. Flory's equation for the average degree of polymeriza-

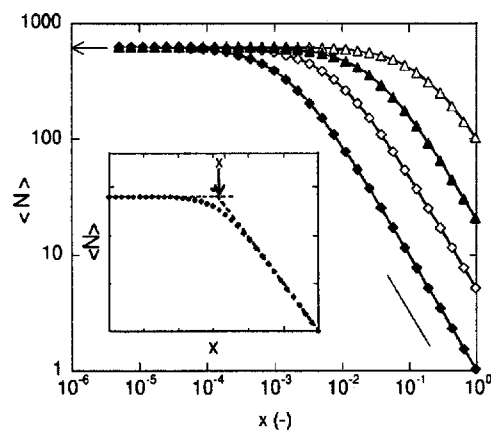


FIG. 1. Average degree of polymerization as a function of stopper fraction, calculated with Eq. (3) using $c=10^{-2}M$ and $K=10^7M^{-1}$ with $n=1$ (\blacklozenge), 5 (\diamond), 20 (\blacktriangle), and 100 (\triangle). The arrow indicates $\langle N(0) \rangle$; the line next to the curves has slope 1 and indicates $\langle N(x) \rangle \sim 1/x$. Inset: graphical representation of the determination of the critical stopper fraction x' , which can be calculated with Eq. (4).

tion $\langle N \rangle$ as a function of the overall concentration c of bifunctional monomers can thus also be applied here:

$$\langle N \rangle = 2\sqrt{Kc} \sim \exp\left(\frac{E_b}{2k_B T}\right)\sqrt{c}, \quad (2)$$

where K is the association constant of the equilibrium and $E_b \sim k_B T \ln(4K)$ is the effective bonding free energy (also called the end-cap or scission energy), the net free energy needed to cleave a bond. If the association constant is independent of the length of the chain to which a monomer binds (isodesmic association), the chain length distribution at thermodynamic equilibrium is exponential.^{29,32}

If the solution contains a concentration c of bifunctional monomers and a concentration k of monofunctional chain stoppers, the stopper fraction x is defined as $x=k/(c+k)$. We assume that for every n chain stoppers added to the solution, one extra chain is formed. Under this assumption, $\langle N \rangle$ as a function of x can be calculated.²⁹ Since the number of chains increases upon the addition of chain stoppers, the average degree of polymerization must decrease:

$$\langle N(x) \rangle = \frac{n\langle N(0) \rangle}{n(1-x) + x\langle N(0) \rangle} \approx \frac{n}{x}, \quad (3)$$

where $\langle N(0) \rangle$ is the average degree of polymerization without any chain stoppers, as given by Eq. (2). Figure 1 shows $\langle N(x) \rangle$ for several values of n .

At very low stopper fractions, $\langle N \rangle$ is hardly affected by x and $\langle N(x) \rangle \approx \langle N(0) \rangle$. On the other hand, at very high x (depending on $\langle N(0) \rangle$ and n), the first term in the denominator of Eq. (3) may be neglected, which leads to the approximation $\langle N(x) \rangle \approx n/x$. In this regime, virtually all chains are terminated by chain stoppers, and $\langle N \rangle$ is proportional to $1/x$ and independent of $\langle N(0) \rangle$, and thus of the overall monomer concentration. The intersection of the limiting behavior at low and high x yields a critical stopper fraction x' (see also the inset of Fig. 1) above which $\langle N(x) \rangle$ becomes independent of $\langle N(0) \rangle$ and is only determined by x and n . It can be calculated by equating n/x' to $\langle N(0) \rangle$, leading to

$$x' = \frac{n}{\langle N(0) \rangle} = \frac{n}{2\sqrt{cK}}. \quad (4)$$

The parameter n indicates the effectiveness of the chain stopper.²⁹ If one extra chain is formed for every stopper molecule added ($n=1$), the stopper has a maximum efficiency. If many stopper molecules are needed to form one new chain ($n \gg 1$), the stopper is not very effective. The effectiveness of a chain stopper can thus be defined as $1/n$ and can range from 0 ($n=\infty$, no stopper effect) to 1 ($n=1$, perfect stopper).

Equations (2) and (3) only give the average degree of polymerization. They contain no information about the distribution of chain lengths. Both with and without chain stoppers, bonds between monomers are continuously broken and formed. Thus, also in the presence of chain stoppers, the chain length distribution is still determined by thermodynamic equilibrium. In other words, the average degree of polymerization is decreased by the addition of chain stoppers, but the chain length distribution is not quenched and remains exponential. Note that Eqs. (2) and (3) were derived assuming a homogenous solution in equilibrium. However, different regions in the system may have different average chain lengths, for example, in a two-phase system.³³ Also, the presence of external fields (such as shear) may affect the average chain length and the chain length distribution.²⁷

B. Linear rheology

The dynamics of supramolecular polymers are usually considered within the theoretical framework developed by Cates and Candau for wormlike micelles.^{12,34} This theory is based on the reptation model for entangled covalent polymers,^{35,36} to which the kinetics of breaking and reformation of chains are added. In the reptation model, a chain is considered to be trapped in a “tube,” consisting of neighboring chains. Stress relaxation can only occur by curvilinear diffusion of the chain out of its original tube (reptation), which occurs on a characteristic time scale τ_{rep} . For monodisperse chains, this leads to a single exponential decay of the stress σ , with relaxation time $\tau_0 = \tau_{\text{rep}}$. For polydisperse systems, on the other hand, every chain length has its own reptation time, and the stress relaxation becomes strongly nonexponential.

When the reptation model is applied to wormlike micelles or supramolecular polymers, which are by definition polydisperse, it is important how fast a chain breaks and recombines relative to the reptation time. If the characteristic time scale on which a supramolecular chain breaks (τ_{break}) is much shorter than the reptation time, the chains will break and recombine many times before they have reptated out of their original tube. On the time scale of reptation, the chains lose the information about their initial length. The stress relaxation will therefore still be a single exponential, but with a different relaxation time τ_0 , which contains contributions from τ_{break} and τ_{rep} , depending on the flexibility of the chains.^{30,37} On the other hand, if τ_{break} is much slower than τ_{rep} , the chains do (on average) not break during the time they need to reptate out of their tube. In this case, the solu-

tion effectively contains a polydisperse mixture of nonbreakable chains and the same result as for polydisperse covalent polymers is obtained.

At time scales much longer than τ_{break} , corresponding to low shear rates, supramolecular polymer solutions thus display remarkably simple viscoelasticity, due to the frequent breaking and recombination of chains. The rheology can be described by the Maxwell model, in which a viscoelastic material is characterized by its zero-shear viscosity η_0 and its terminal relaxation time τ_0 . When a shear rate $\dot{\gamma}$ is applied at $t=0$, the stress increases monotonically to its steady-state value according to

$$\sigma(t) = \eta_0 \dot{\gamma} (1 - e^{-t/\tau_0}). \quad (5)$$

On the other hand, if the shear is stopped at $t=0$ after the steady-state stress has been reached, the stress decay is given by

$$\sigma(t) = \eta_0 \dot{\gamma} e^{-t/\tau_0}. \quad (6)$$

Thus, the zero-shear viscosity and the terminal relaxation time can be obtained from the transient stress response upon start-up or cessation of steady shear if the Maxwell model is obeyed. Within this model, there is a very simple relation between η_0 , τ_0 , and the elastic plateau modulus G_0 :

$$\eta_0 = \tau_0 G_0. \quad (7)$$

1. Dependence on $\langle N \rangle$

According to the model of Cates and Candau,^{12,34} the zero-shear viscosity and the terminal relaxation time depend on the overall monomer concentration and the average degree of polymerization according to power laws:

$$\eta_0 \sim \langle N \rangle^\alpha c^\beta, \quad (8)$$

$$\tau_0 \sim \langle N \rangle^\gamma c^\delta. \quad (9)$$

The values of the exponents depend on the flexibility of the chains and on the ratio of the breaking and reptation (or for rodlike chains the angular reorientation) time. Limiting values for flexible and rodlike chains in the fast- and slow-breaking limits were previously calculated.^{30,37} Note that without taking special measures, the separate exponents α to δ cannot be measured by measuring η_0 and τ_0 as a function of the overall monomer concentration, since $\langle N \rangle$ and c both change if the concentration is varied [Eq. (2)]. It was previously shown that the separate scaling exponents can be measured by using chain stoppers.³⁰

2. Temperature dependence

Viscous flow can be considered as a thermally activated diffusion process. This was originally derived for simple liquids,³⁸ but it is applied much more generally.^{39,40} Like other processes with an activation energy barrier, the temperature dependence of the viscosity can be described by an Arrhenius-type expression with an activation energy E_η , which contains contributions from the breaking of bonds and the reptation of chains. Moreover, the viscosity is proportional to $\langle N \rangle^\alpha$ [Eq. (8)], and for supramolecular polymers,

$\langle N \rangle$ also depends on temperature, as given by Eq. (2). This leads to an overall temperature dependence for the viscosity, given by

$$\begin{aligned}\eta_0 &\sim \langle N \rangle^\alpha \exp\left(\frac{E_\eta}{k_B T}\right) \\ &\sim \exp\left(\frac{\alpha E_b}{k_B T}\right) \exp\left(\frac{E_\eta}{k_B T}\right) \\ &= \exp\left(\frac{\alpha E_b + E_\eta}{k_B T}\right).\end{aligned}\quad (10)$$

The same line of argument can be applied to the terminal relaxation time. The temperature dependence of τ_0 is characterized by an Arrhenius-type equation with activation energy E_τ and the temperature dependence of $\langle N \rangle$ is included by combining Eqs. (2) and (9):

$$\begin{aligned}\tau_0 &\sim \langle N \rangle^\gamma \exp\left(\frac{E_\tau}{k_B T}\right) \\ &\sim \exp\left(\frac{\gamma E_b}{k_B T}\right) \exp\left(\frac{E_\tau}{k_B T}\right) \\ &= \exp\left(\frac{\gamma E_b + E_\tau}{k_B T}\right).\end{aligned}\quad (11)$$

Since both the viscosity and the relaxation time are determined by the typical breaking and reptation times of a chain and its flexibility, the overall temperature dependence exponents are expected to be equal,⁴¹ leading to the expression $\alpha E_b + E_\eta = \gamma E_b + E_\tau$

III. EXPERIMENT

A. Solutions

The syntheses of EHUT and DBUT were described elsewhere.^{25,28} Samples were prepared by dissolving EHUT and DBUT in dodecane while stirring for at least one night at $\pm 50^\circ\text{C}$. Solutions of 5.0 g/l EHUT were prepared with stopper fractions x ranging from 0 to 0.10. Experiments were done with solutions containing varying amounts of chain stoppers at a fixed temperature ($0 \leq x \leq 0.10$, $T = 20^\circ\text{C}$) and with solutions without chain stoppers at varying temperatures ($20 < T < 70^\circ\text{C}$, $x = 0$).

B. Rheology

Rheological measurements were done using a Paar Physica MCR 300 rheometer. This apparatus was used in controlled strain mode. We employed Couette geometries (with rotating inner cylinder) of different gap widths. No significant differences were observed for the different geometries. The temperature was controlled using a water bath. A solvent trap was used to minimize evaporation.

The steady-state stress was measured as a function of the applied shear rate, which was varied between 10^{-3} and 10^3 s^{-1} . These flow curves were recorded from high to low shear rate. Different shear histories were applied to the samples. These all lead to the same result, indicating that it is indeed the steady-state stress which is measured.

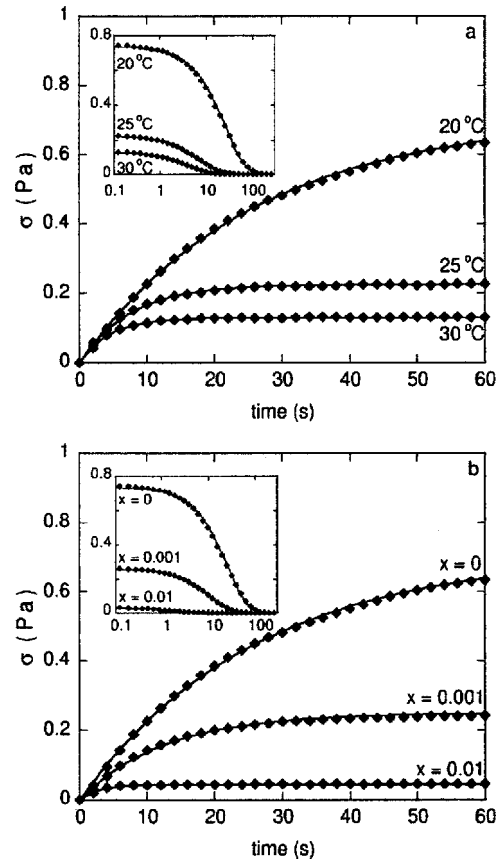


FIG. 2. Transient stress response of a 5.0 g/l EHUT solution upon start-up [main figures, lines are fits to Eq. (5)] or cessation [insets, lines are fits to Eq. (6)] of steady shear ($\dot{\gamma} = 0.002 \text{ s}^{-1}$ for all curves): (a) for several temperatures and (b) for several stopper fractions.

Transient stress responses were measured after the sample was left for at least 30 min to equilibrate. Shear flow was then started and the stress response was recorded as a function of time. After the steady-state stress had been reached, the shear was stopped and the relaxation of the stress was measured.

IV. RESULTS AND DISCUSSION

A. Linear rheology

The starting point for our experiments is a 5.0 g/l EHUT solution in dodecane at 20°C without added chain stoppers ($x = 0$). For this solution, the shear stress σ upon application of a steady shear rate of 0.002 s^{-1} is shown as a function of time in Figs. 2(a) and 2(b) (top curve). The line is a fit to Eq. (5) with $\eta_0 = 357 \text{ Pa s}$ and $\tau_0 = 27 \text{ s}$. After reaching the steady-state stress (which equals $\dot{\gamma}\eta_0 = 0.71 \text{ Pa}$), the shear was stopped instantaneously, and the decay of the shear stress was measured. The result is shown in the insets of Figs. 2(a) and 2(b) (top curve). The line is a fit to Eq. (6) with the same parameters as used for the start-up curve. From these results, it is clear that at this shear rate, the transient rheology is described very well by the Maxwell model. Since η_0 and τ_0 are known, G_0 (the elastic plateau modulus) can easily be calculated with Eq. (7): $G_0 = 13.2 \text{ Pa}$.

When the same experiment is done at a higher temperature [Fig. 2(a)], there is a strong decrease of the steady-state

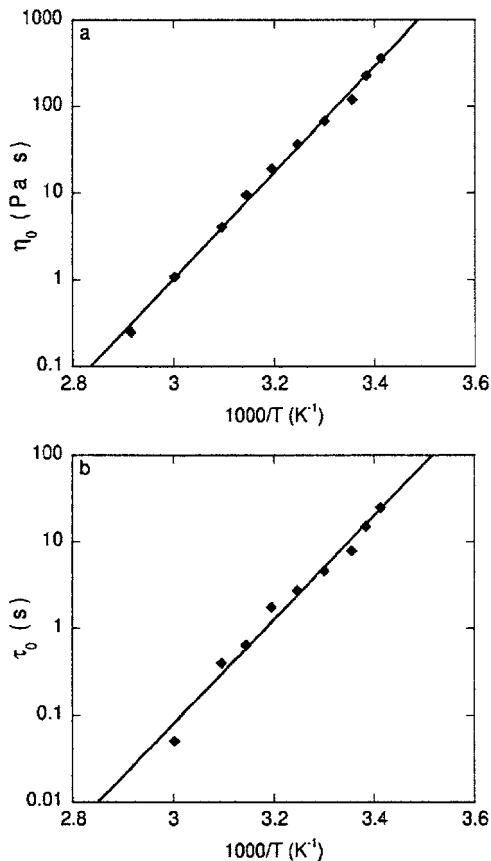


FIG. 3. Arrhenius plots showing the temperature dependence of the Maxwell parameters of a 5.0 g/l EHUT solution: (a) zero-shear viscosity; the line corresponds to $\eta_0 = 3.78 \times 10^{-19} \exp(1.41 \times 10^4/T)$. (b) Terminal relaxation time; the line corresponds to $\tau_0 = 6.93 \times 10^{-20} \exp(1.39 \times 10^4/T)$.

stress, due to the decreased viscosity of the solution. It can also be seen that the steady-state stress is reached much faster at higher temperatures, which indicates that τ_0 is also decreased. The stress relaxation curves (shown in the inset) give the same results for η_0 and τ_0 . A decrease in viscosity and relaxation time can also be achieved by adding chain stoppers to the solution [Fig. 2(b)]. The addition of 0.1% of chain stoppers ($x=0.001$) already causes a decrease of the viscosity of well over 50%.

Qualitatively, an increase in temperature thus has the same effect as the addition of chain stoppers to the solution. This is not surprising, as in both cases the average degree of polymerization of the supramolecular chains is decreased [Eqs. (2) and (3)]. It is more interesting to focus on quantitative differences in the dependence of the linear rheological parameters. In Sec. IV A 1, we describe the effect of temperature on η_0 and τ_0 in more detail, while the effect addition of chain stoppers is investigated in Sec. IV A 2.

1. Effect of temperature

When increasing the temperature from 20 to 70 °C, η_0 decreases dramatically by over almost four orders of magnitude [as shown by the Arrhenius plot, Fig. 3(a)]. Over this whole range of temperatures, the dependence is described by an exponential, as shown by the fitted line. From the slope of the fit, the activation energy $\alpha E_b + E_\eta$ can be calculated with Eq. (10). The result is an activation energy for viscous flow

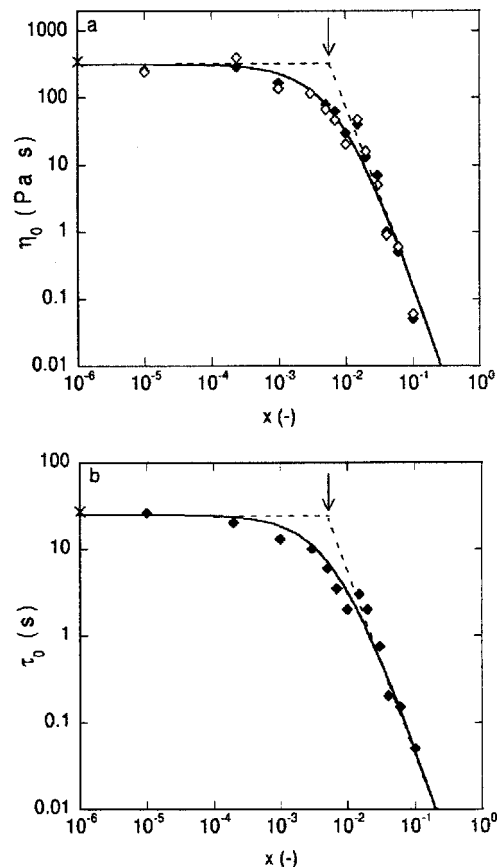


FIG. 4. Effect of stopper fraction on a 5.0 g/l EHUT solution. \times denotes η_0 and τ_0 of the solution at 20 °C and $x=0$. (a) Zero-shear viscosity, obtained from transients (\blacklozenge) and from the flow curves (\diamond). The solid line corresponds to $\eta_0 = 4 \times 10^{-8} \langle N(x) \rangle^{3.0}$, with $\langle N \rangle$ calculated with Eq. (3). The arrow denotes the critical stopper fraction x' . (b) Terminal relaxation time. The solid line corresponds to $\tau_0 = 4 \times 10^{-7} \langle N(x) \rangle^{2.3}$.

of 2×10^{-19} J, which is equivalent to approximately 150 kJ/mol or to $50k_B T$ at room temperature. Values of the same order of magnitude were found for wormlike micelles and other supramolecular polymers.^{7,12,42}

The temperature dependence of τ_0 is shown in Fig. 3(b). As can be seen, the terminal relaxation time also decreases exponentially with increasing temperature. The slope of the fitted line is virtually the same as for the viscosity, and the calculated activation energy is therefore also the same [Eq. (11)]: $\gamma E_b + E_\tau = 2 \times 10^{-19}$ J.

2. Effect of chain stoppers

The addition of chain stoppers can also decrease the viscosity by several orders of magnitude, as shown in Fig. 4(a). The results obtained from the transient stress response and from the flow curves (see Sec. IV B) are in good agreement. At very low $x (< 10^{-3})$, the effect on η_0 is small. At higher x , the viscosity starts to decrease significantly and at stopper fractions ≥ 0.01 , the viscosity can be described by a power law with a slope of -3.0 .

The experimental data over the whole range of x may be compared to our model describing the effect of chain stoppers by substituting Eq. (3) in Eq. (8). The concentration of bifunctional monomers does not change during our experiments, and neglecting the c dependence leads to

$\eta_0 \sim \langle N(x) \rangle^\alpha$. At high x , it is expected that $\langle N(x) \rangle \sim 1/x$, and thus $\eta_0 \sim \langle N(x) \rangle^\alpha \sim x^{-\alpha}$. The value of α thus follows from the power-law fit to the experimental data at high x : $\alpha=3.0$. This value is somewhat larger than that obtained previously for EHUT/DBUT solutions in cyclohexane (2.7),³⁰ but the difference can be explained by the scatter in the experimental data. Equation (3) contains two adjustable parameters: $\langle N(0) \rangle$ and n . $\langle N(0) \rangle$ is given by Eq. (2) and contains the known concentration of bifunctional monomers and the association constant K . By changing K , the plateau at low x (denoted by the horizontal dashed line) is shifted vertically, so K can be used to fit the data at low x [denoted by the horizontal dashed line in Fig. 4(a)]. The parameter n indicates the effectiveness of the chain stopper and can be used to fit the power-law part of the data [denoted by the dashed line at high x in Fig. 4(a)]. The curve shown in Fig. 4(a) was calculated using $K=8.6 \times 10^7 M^{-1}$ [$=2 \times 10^5$ l/g, using that the molar mass of EHUT is 432 g (Ref. 25)] and $n=17$.

By calculating the intersection of the horizontal plateau at low x and the power-law dependence at high x , we obtain the critical stopper fraction x' [denoted by the arrow in Fig. 4(a)], above which $\langle N \rangle$ becomes independent of $\langle N(0) \rangle$ (and thus of c) and inversely proportional to x . The value obtained from the viscosity data is $x'=8 \times 10^{-3}$.

The terminal relaxation time as a function of x is shown in Fig. 4(b). The same analysis as above can be applied to these data, which can be fitted to Eq. (9). The scaling exponent γ is found to be 2.3, which is the same value as obtained for EHUT/DBUT solutions in cyclohexane.³⁰ The curve shown in the plot was calculated with $K=1.3 \times 10^8 M^{-1}$ ($=3 \times 10^5$ l/g) and $n=17$. The critical stopper fraction is calculated as $x'=7 \times 10^{-3}$. Both results agree within the experimental error with the result obtained from the viscosity data.

We may compare our values of K and n to independent estimates of these parameters. From light scattering and calorimetry experiments, values of K for EHUT in several solvents were obtained. Values (at room temperature) vary from $1 \times 10^5 M^{-1}$ in chloroform¹⁹ to $4 \times 10^9 M^{-1}$ in cyclohexane,²⁹ which shows that the association constant is very sensitive to the polarity of the solvent. This is not surprising, as the polarity of the solvent strongly affects the strength of the hydrogen bonds between the monomers. Unfortunately, no data for dodecane are available. Compared to the existing data, an association constant of the order of $10^8 M^{-1}$ in dodecane at 20 °C is a reasonable value. The value of n was estimated from osmometry and light scattering experiments on EHUT/DBUT solutions in cyclohexane.²⁹ It was found that n as calculated from osmometry data ($n=4$) was much lower than the result obtained from light scattering ($n=17$). This was explained by the fact that with light scattering, only objects above a certain size are measured, whereas osmometry is also sensitive to very short chains. Short chains will also have a small contribution to the solution viscosity, so it is reasonable that the value of n as obtained from light scattering also shows a good agreement with the experimental viscosity data of Fig. 4(a).

It must be noted that Eqs. (3), (8), and (9) contain many adjustable or experimentally obtained parameters (numerical prefactors, K and n and the scaling exponents α and γ).

Nevertheless, the results demonstrate that our simple model describing the dependence of η_0 and τ_0 on the stopper fraction can be used to describe the experimental data using reasonable values of K , n , α , and γ , consistent with those obtained in previous experiments.

In Sec. IV A 1, it was found that the overall temperature dependence exponents of η_0 and τ_0 are the same; both lead to an activation energy of 2×10^{-19} J. We may substitute the experimentally determined values of α and γ in Eqs. (10) and (11): $3.0E_b + E_\eta = 2.3E_b + E_\tau = 2 \times 10^{-19}$. Without an independent measure of one of the energies, the others cannot be calculated from the present data. The activation energies E_η and E_τ and the bonding energy E_b are often hard to access experimentally, due to the complex interplay between relaxation, breaking and reptation times, chain length and flexibility, and temperature on rheological parameters.^{37,43}

B. Flow curves

Solutions of supramolecular polymers and wormlike micelles are well known for their rich nonlinear rheological behavior. Among the observed phenomena are flow instabilities, which can lead to phase separation. Such instabilities were first observed and classified by Schmitt *et al.*^{44,45} EHUT too has a complex nonlinear rheology, as can be seen from the flow curves (steady-state shear stress as a function of applied shear rate) in Figs. 5(a) and 5(b). The symbol \blacklozenge denotes a 5.0 g/l EHUT solution at 20 °C and $x=0$. In a recent paper, six regimes were identified in the flow curve of EHUT solutions.²⁷ At very low shear rates, the solution behaves as Newtonian: the slope of the curve is unity. All experiments described in Sec. IV A were done in this Newtonian regime. At $\dot{\gamma} \approx 0.01$ s⁻¹, there is a sudden change of the slope, and the stress even seems to pass a maximum. In this regime, “shear banding” occurs: the separation of the solution into regions with different shear rates. The presence of shear bands was confirmed by heterodyne light scattering. At higher shear rates, two more shear banding transitions are observed, which are associated with a shear-induced phase transition.

It was suggested²⁷ that the first shear banding transition (where the maximum in the flow curve occurs) is caused by a strong coupling between the shear flow and the alignment of EHUT chains, owing to their large persistence length.^{26,29} Alignment of chains in the flow direction may facilitate their association into longer chains. The elongated chains would have a stronger tendency to align, and this would provide a positive feedback mechanism which could explain the extreme shear thinning which can eventually lead to shear banding. A possible way to test this hypothesis is by comparing the effect on the flow curve of increasing temperature and the addition of chain stoppers. An increase in temperature decreases the association constant [Eq. (2)] and shifts the equilibrium between breaking and formation of bonds [Eq. (1)] towards the side of “free binding groups,” thus decreasing $\langle N \rangle$. Chain stoppers, on the other hand, do not affect K . They reduce $\langle N \rangle$ by blocking chain ends, thus pre-

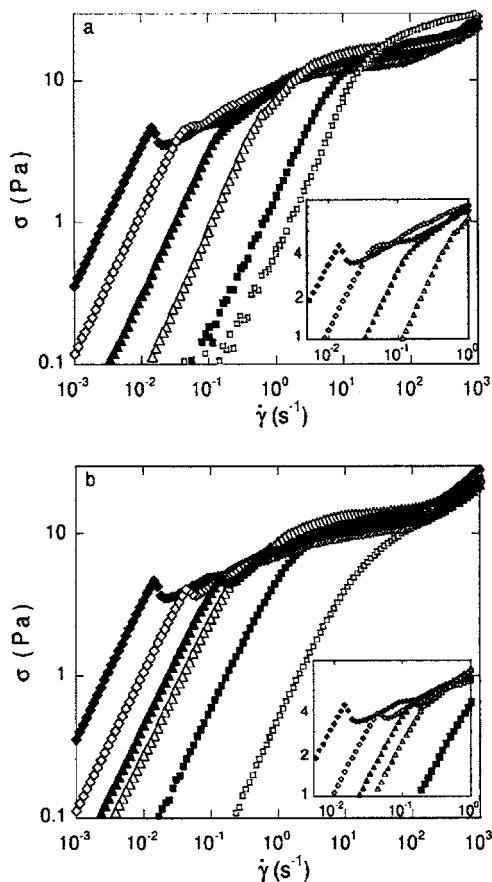


FIG. 5. (a) Flow curves of a 5.0 g/l EHUT solution at 20 (\blacklozenge), 30 (\diamond), 40 (\blacktriangle), 50 (\triangle), 60 (\blacksquare), and 70 $^{\circ}\text{C}$ (\square). Inset: magnification of the area where the maximum in the flow curve occurs. (b) Flow curves of a 5.0 g/l EHUT solution at 20 $^{\circ}\text{C}$ with stopper fractions $x=0$ (\blacklozenge), 0.005 (\diamond), 0.007 (\blacktriangle), 0.015 (\triangle), 0.030 (\blacksquare), and 0.060 (\square). Inset: magnification of the area where the maximum in the flow curve occurs.

venting the addition of more monomers. Blocked chain ends would interfere with the proposed coupling between chain alignment and growth.

Flow curves at several temperatures are shown in Fig. 5(a). With increasing temperature, the steady-state stress at a given shear rate in the Newtonian regime decreases strongly, which reflects the decreased solution viscosity. Furthermore, the maximum in the flow curve rapidly becomes less pronounced with increasing temperature. At 30 $^{\circ}\text{C}$ it is hardly visible anymore, and at higher temperatures, the stress is a monotonously increasing function of the applied shear rate. At shear rates beyond the stress maximum, there is not much difference between the flow curves at different temperatures. Figure 5(b) shows that the dependence of the flow curve on the stopper fraction is similar to that of temperature: the viscosity decreases, the maximum becomes less pronounced, and beyond the stress maximum the flow curves are almost independent of the stopper fraction. It is noticeable that the maximum disappears at $x \approx 0.01$, close to the critical stopper fraction x' (Sec. IV A 2). This observation is consistent with the proposed coupling between shear flow and the alignment and subsequent elongation of chains. Above x' , most chains are terminated by chain stoppers. This would severely hinder

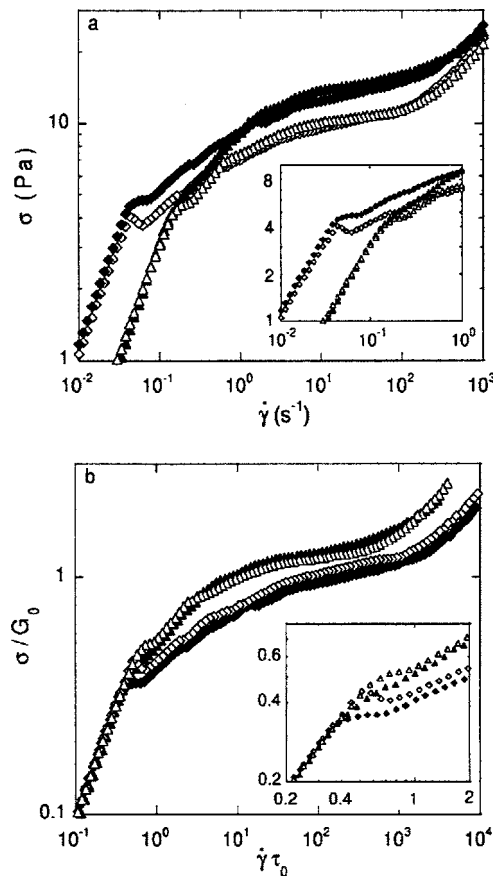


FIG. 6. (a) Flow curves of solutions with the same zero-shear viscosity, as obtained by either an increased temperature or the addition of chain stoppers. Pair I: S_{T1} (\blacklozenge) and S_{x1} (\diamond); pair II: S_{T2} (\blacktriangle) and S_{x2} (\triangle). The inset shows a magnification of the area of the force curve where the maximum occurs. (b) Same data with the shear rate normalized by τ_0 and the shear stress by G_0 .

the association and elongation of shear-aligned chains, and thus prevent the flow instability and shear banding from occurring.

Let us now compare the flow curves of solutions with the same zero-shear viscosity, which is reached by either increasing temperature (at $x=0$) or by adding chain stoppers (at 20 $^{\circ}\text{C}$). The results for two such pairs of solutions are shown in Fig. 6. The parameters of these solutions are summarized in Table I.

Because they have nearly the same zero-shear viscosity, the flow curves of solutions S_{T1} and S_{x1} and those of S_{T2} and S_{x2} overlap in the Newtonian region. However, there are marked differences at higher shear rates. The flow curve of

TABLE I. Parameters of solutions S_{T1} and S_{x1} of pair 1 ($\eta_0 \approx 70$ Pa s), and solutions S_{T2} and S_{x2} of pair 2 ($\eta_0 \approx 30$ Pa s). Relaxation times were obtained from the transients at low shear rates, see Sec. IV A. Values of G_0 were calculated from η_0 and τ_0 with Eq. (7).

Solution	S_{T1}	S_{x1}	S_{T2}	S_{x2}
T ($^{\circ}\text{C}$)	30	20	40	20
x (-)	0	0.005	0	0.015
η_0 (Pa s)	71	67	31	34
τ_0 (s)	4.5	6.0	1.8	3.0
G_0 (Pa)	16	11	17	11

S_{x1} shows a distinct maximum, whereas that of S_{T1} only has a very weak maximum. The curve of solution S_{x2} does not have a maximum anymore, but there still is an inflection point. The slope of the flow curve of S_{T2} also decreases in this range of shear rates, but much less strong. At higher shear rates, the flow curves of S_{T1} and S_{x1} and those of S_{T2} and S_{x2} are more or less parallel.

Even though solutions belonging to the same pair have nearly the same zero-shear viscosity, their terminal relaxation time may be different, as shown in Table I. To investigate to what extent the differences between the flow curves are correlated with differences in τ_0 , the flow curves were plotted in a reduced dimensionless form, where the shear rate is multiplied by the terminal relaxation time and the stress is divided by the plateau modulus. The reduced flow curves are shown in Fig. 6(b). Now, the curves belonging to the same pair overlap over the whole range of reduced shear rates, except around the maximum (pair 1) or the inflection point (pair 2). As can be seen from Table I, solutions S_{T1} and S_{T2} have shorter relaxation times compared to S_{x1} and S_{x2} , respectively. As explained in Sec. II, τ_0 is determined by both the reptation time τ_{rep} and the breaking time τ_{break} of a chain. It is reasonable to assume that solutions with equal η_0 have the same chain length distribution and thus the same reptation time: $\tau_{\text{rep}}(T) = \tau_{\text{rep}}(x)$. The difference in relaxation time must thus be due to a difference in breaking time. Indeed, an increase in temperature enhances the exchange rate of monomers between chains,¹² whereas the addition of chain stoppers does not. Thus, $\tau_{\text{break}}(T) < \tau_{\text{break}}(x)$. The foregoing leads to the conclusion that τ_0 of a solution with a given amount of chain stoppers is longer than the relaxation time of a solution without chain stoppers with the same viscosity, reached by increasing temperature. In other words: $\tau_0(T) < \tau_0(x)$, in agreement with the experimental observations.

The reduced flow curves show that most of the difference between the temperature and the stopper curves can be explained by the difference in τ_0 , except for the area where the maximum in the flow curve occurs. This is also the range of shear rates where the first shear banding transition occurs. This is consistent with the hypothesis that this transition is somehow related to a coupling of chain alignment and growth, leading to a flow instability. At these shear rates, the curves of S_{x1} and S_{x2} show more pronounced features (maximum and inflection points) and higher reduced stresses than those of S_{T1} and S_{T2} , respectively. However, the present data do not allow detailed conclusions to be drawn about the molecular mechanism behind this flow behavior.

V. CONCLUDING REMARKS

In this paper, the rheology of solutions of a reversible supramolecular polymer is studied. This is done by comparing the effects of an increase in temperature and the addition of chain stoppers. Both methods decrease the average degree of polymerization, but in different ways. The systems under investigation were solutions in dodecane of hydrogen-bonded supramolecular polymer EHUT and chain stopper DBUT.

The linear rheology can be described by the Maxwell

model. The dependence of the zero-shear viscosity and the terminal relaxation time on temperature is exponential. From Arrhenius plots, the activation energy for viscous flow was calculated to be 2×10^{-19} J.

The effect of chain stoppers on rheology is relatively small at low stopper fractions. Above a critical stopper fraction, the viscosity and relaxation time decrease strongly, following power-law behavior with scaling exponents of -3.0 for the zero-shear viscosity and -2.3 for the terminal relaxation time. The results can be explained by a simple model describing the effect of the addition of chain stoppers on the average degree of polymerization, and are consistent with previous experimental results.

The flow curve of EHUT solutions is very complex; it has a maximum and shows extreme shear thinning. Flow curves at various temperatures and stopper fractions were measured. Both show the same trends: decreasing viscosity, diminishing and disappearance of the maximum, and overlap of flow curves at high shear rates. However, a direct comparison revealed considerable differences between pairs of flow curves with the same zero-shear viscosity (one curve obtained by increasing temperature, the other by adding chain stoppers). Reduced flow curves show that the differences are mostly associated with differences in the terminal relaxation time. The results are consistent with a mechanism of shear-induced alignment and subsequent elongation of chains.

The results presented in this paper demonstrate that the use of chain stoppers can be a valuable tool to increase our understanding of the dynamics of supramolecular polymers. Without being the final answer, they provide new insight into the microscopic mechanisms underlying the complex rheological behavior of supramolecular polymer solutions.

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