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Chain Stoppers in Reversible Supramolecular Polymer Solutions Studied by Static and Dynamic Light Scattering and Osmometry

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ABSTRACT: The effect of the addition of chain stoppers to solutions of hydrogen-bonded reversible supramolecular polymers was studied by vapor pressure osmometry and static and dynamic light scattering. Vapor pressure osmometry showed that within the range of concentrations studied the average degree of polymerization is independent of the overall monomer concentration and roughly inversely proportional to the mole fraction of chain stoppers, in agreement with theoretical predictions. The correlation length as measured by static light scattering has a maximum at the overlap concentration in solutions without chain stoppers. In the presence of a fixed fraction of chain stoppers, the results coincide with those without chain stoppers at low and high concentrations, but there is a plateau in the correlation length at intermediate concentrations. From the data, information about the association constant and the persistence length of the chains is obtained. The effectiveness of the chain stopper is discussed, and the results from osmometry and static light scattering are compared. Dynamic light scattering was used to measure the time autocorrelation function. From the characteristic decay time, the hydrodynamic correlation length was calculated. For solutions above the overlap concentration, the distribution of decay times showed a second peak at longer times. It is not yet fully understood what the mechanism behind this slow mode is.

1. Introduction

Supramolecular polymers are chains of monomers, held together by noncovalent, reversible interactions such as metal−ligand complexation or hydrogen bonding.[1−6] There is a dynamic equilibrium between bonded and free monomers, and the breaking and re-formation of the supramolecular bonds often occurs on experimental time scales, in which case the term *reversible* supramolecular polymers is appropriate. As a consequence of this equilibrium, the (average) length of the supramolecular polymer chains depends on the monomer concentration and also on parameters such as temperature and the choice of solvent. These parameters can thus be used to adjust the chain length in situ and therewith also the solution or material properties. For example, the rheological properties of supramolecular polymer systems can be varied easily and reversibly over a very wide range compared to classical covalent polymers.[7−9] This may be useful in industrial processes where high chain lengths and cross-link densities are often required to obtain the desired material properties, but the resulting high viscosities hamper processing. The strong concentration dependence of the viscosity may also be useful in other processes, such as polymerization-induced phase separation.[10] Another potential application is the synthesis of "smart" or self-healing materials which respond to changes in environmental conditions such as temperature or pH.[11,12]

It was shown that the incorporation of two complementary hydrogen-bonding motifs in a single monomer is a successful method for the formation of supramolecular polymers. Especially arrays of multiple hydrogen-bonding sites in apolar organic solvents display high association constants.[13−16] These bifunctional monomers can associate with each other into linear supramolecular chains. If the monomers contain more than two binding groups, branched chains and cross-linked networks can be formed. During synthesis and purification, one of the essential tasks is to avoid the presence of monofunctional monomers (monomers which have only one binding group), which are often called "chain stoppers". If a monofunctional monomer binds to a supramolecular polymer, it adds a nonfunctional or "dead" end to the chain, and the chain cannot grow further—hence the term "chain stoppers". The presence of chain stoppers thus decreases the average chain length. Even very small amounts of chain stoppers can have a large effect on solution and material properties.[13,16] However, chain stoppers can also be added deliberately in order to control the length of the chains and the properties of the system.[17,18] One of the advantages of using chain stoppers to adjust the chain length is that the average chain length may be varied independently of other parameters such as the (overall) monomer concentration and temperature, which is otherwise impossible for supramolecular polymers. On the other hand, the chains retain the possibility to break and recombine, which leads to unique properties, especially in the dynamics of supramolecular polymer solutions.

In some respects, supramolecular polymers are similar to wormlike micelles, which are also long, noncovalent aggregates of small molecules with a concentration- and temperature-dependent length.[19−22] Therefore, many of the theories and experimental techniques used for wormlike micelles can also be applied to supramolecular polymers. However, there are also important differences between the two. For example, the concept of monofunctional chain stoppers is only applicable to self-assembling systems based on very specific interactions. The formation of wormlike micelles is governed by less specific interactions between the surfactants and the solvent molecules. Therefore, despite the massive amount of literature on wormlike micelles, there are not much experimental data on chain stoppers and their effect on supramolecular polymer solutions.

It was shown previously that the bifunctional monomer 2,4-bis(2-ethylhexylureido)toluene (EHUT, Figure 1) forms long, rigid supramolecular chains in apolar organic solvents by the cooperative formation of four hydrogen bonds per monomer.[23] This was studied by IR spectroscopy, small-angle neutron scattering, light scattering and viscosity measurements,[24,25] and

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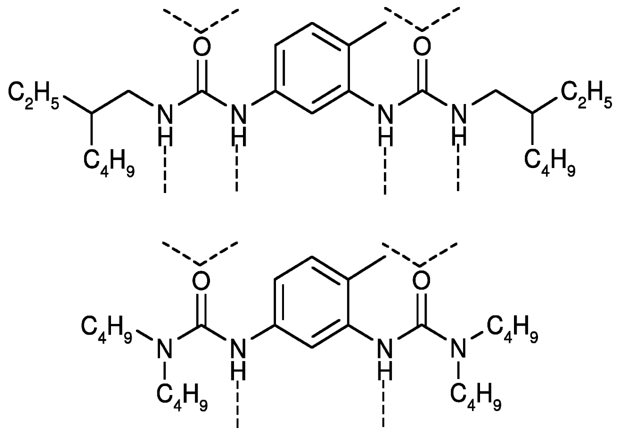

Figure 1. Bifunctional monomer EHUT (top) and monofunctional chain stopper DBUT (bottom). Possible hydrogen bonds are represented by dashed lines.

isothermal titration calorimetry.[26] The linear rheology of EHUT solutions was studied by rheometry and dynamic light scattering of probe particles.[27] From the linear density of the chains, obtained from the neutron scattering data, the effective monomer length was calculated to be 0.18 nm, which suggests the presence of two or three monomers per axial repetition unit. Additional experiments led to the conclusion that EHUT can form both thin and thick fibers, depending on the experimental conditions.[28]

An alkylated derivative of EHUT, 2,4-bis(dibutylureido)-toluene (DBUT), which could be used as a chain stopper for EHUT, was designed and synthesized.[18] Conveniently, EHUT and DBUT have the same molar mass (432 g/mol). As can be seen from Figure 1, DBUT is strictly speaking not a monofunctional chain stopper, since it may still form two hydrogen bonds with EHUT with its secondary amine groups. However, DBUT was shown to be the most effective of a number of chain stoppers in reducing the viscosity of EHUT solutions and was therefore selected for further experiments. The cooperativity in the simultaneous formation of four hydrogen bonds between two EHUT molecules probably strongly disfavors the formation of only two with DBUT, which explains the high effectiveness of DBUT as a chain stopper. The use of chain stoppers as a tool to tune the chain length was demonstrated previously in a study on the linear viscoelasticity of EHUT solutions.[17] By using chain stoppers, the effects of chain length and monomer concentration could be separated, which was previously impossible. It was also shown that experiments with chain stoppers can be used to obtain more information about the system without chain stoppers.[18]

In the present paper, the effect of the addition of chain stopper DBUT on static and dynamic properties of EHUT solutions is investigated in more detail. The average degree of polymerization at high stopper fractions is measured by vapor pressure osmometry (VPO), which gives new insight into the action of the chain stoppers. This technique has previously been used to study supramolecular polymers,[29,30] but we are not aware of any reports in which it is used to study the effect of chain stoppers on supramolecular polymer solutions. Static light scattering (SLS) is used to study the dependence of the correlation length on the amount of stoppers in dilute and semidilute solutions. Osmometry and SLS both yield information about the average chain length and the effectiveness of the stopper, and the results of both techniques are compared. The hydrodynamic correlation length is measured by dynamic light scattering (DLS), and the concentration dependences of the static and hydrodynamic correlation length are compared. Furthermore, a slow relaxation mode is observed in the DLS data of semidilute solutions. To our knowledge, this is the first time that a combined light scattering study of this kind was done on a supramolecular polymer system.

2. Theoretical Background

2.1. Average Chain Length. In supramolecular polymer solutions, formation and breaking of bonds between monomers occur simultaneously and continuously:

$$2 \text{ free binding groups} \rightleftarrows 1 \text{ bond}$$

A chain of N monomers has $N - 1$ bonds and 2 free binding groups at its ends. Consider a solution with monomer concentration c and number-average degree of polymerization $\langle N\rangle$. The average concentration of bonds in this solution is equal to $(c/\langle N\rangle)(\langle N\rangle - 1)$, and the average concentration of end groups is $2c/\langle N\rangle$. The association constant K is assumed to be equal for all monomers, e.g., independent of the degree of polymerization of the chain to which a monomer belongs. K can be written as

$$K = \frac{[\text{bonds}]}{[\text{free binding groups}]^2} = \frac{\langle N\rangle(\langle N\rangle - 1)}{4c} \qquad (1)$$

which can be rewritten to give an expression for $\langle N\rangle$:

$$\langle N\rangle = \frac{1+ \sqrt{1 + 16Kc}}{2} \approx 2\sqrt{Kc} \qquad (2)$$

where the approximation is justified if $Kc \gg 1$.

The formation of a supramolecular polymer by reversible association of bifunctional monomers is in some respects analogous to the formation of a covalent polymer by condensation polymerization. The monomers of a (linear) condensation polymer are also bifunctional, and bonds between monomers are reversible, as they can be hydrolyzed by the liberated condensation product (often water). A theoretical treatment of condensation polymerization was already given in the 1930s.[31,32] The basic assumption is that there is a probability p that a binding group is part of a bond, which is again independent of the degree of polymerization of the chain to which the bond belongs. This leads to an exponential chain length distribution with a number-average degree of polymerization given by

$$\langle N\rangle = \frac{1}{1 - p} \qquad (3)$$

and a degree of polydispersity of $1 + p$. The concentration of bonds in a solution is pc, and the concentration of free binding groups equals $2c(1 - p)$. Substituting these relations in the first equality in eq 1 leads to

$$K = \frac{p}{4c(1 - p)^2} \Rightarrow p \approx 1 - \frac{1}{\sqrt{4Kc}} \qquad (4)$$

where the approximate equality applies for p close to unity. Substituting this in eq 3 leads to the expression for $\langle N\rangle$ derived in eq 2. Thus, using the probability p to analyze the association process is equivalent to describing it in terms of K and c.

When a bifunctional monomer binds to an existing chain, a new functional end group is formed. In contrast, when a monofunctional monomer binds to a chain, the new chain end cannot bind another monomer and is therefore "dead". In other words, monofunctional monomers act as chain stoppers. Note

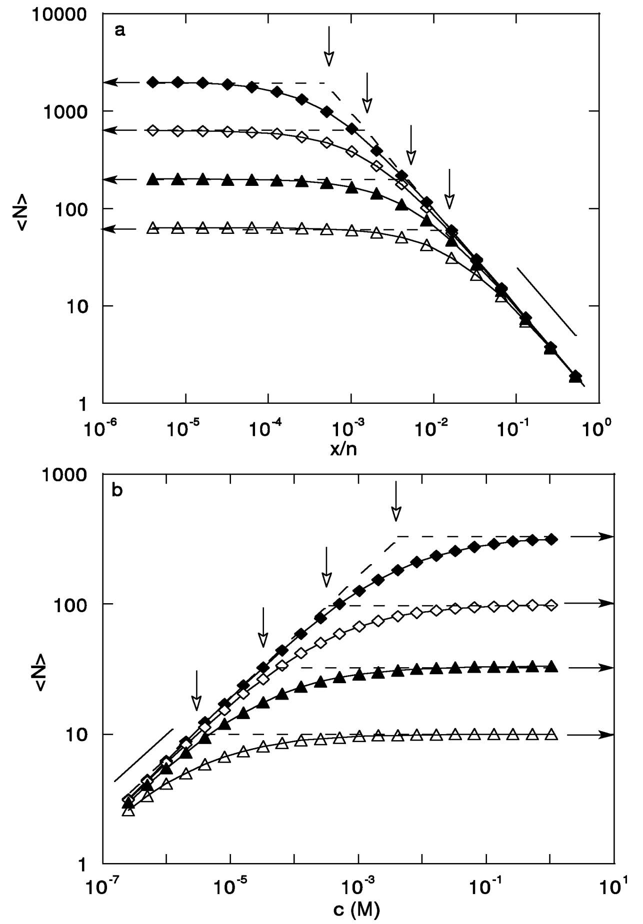

Figure 2. $\langle N\rangle$ calculated with eq 5 with $K = 10^7$ M^{-1}. (a) $\langle N\rangle$ as a function of the normalized stopper fraction x/n for 10^{-1} (◆), 10^{-2} (◇), 10^{-3} (▲), and 10^{-4} M (△) solutions. The line next to the curves indicates $\langle N\rangle \sim 1/x$. Open arrows indicate $(x/n)'$, and solid arrows indicate $\langle N(0)\rangle$. (b) $\langle N\rangle$ as a function of the concentration of bifunctional monomers at normalized stopper fractions x/n of 0.003 (◆), 0.01 (◇), 0.03 (▲), and 0.1 (△). The line next to the curves indicates $\langle N\rangle \sim c^{0.5}$. Open arrows indicate c', and solid arrows indicate n/x.

that the concept of chain stoppers also applies to condensation polymerization, where monofunctional monomers also decrease the average chain length (and therefore increase the number of chains at a given monomer concentration) by forming nonfunctional chain ends. In a simple approach, the addition of every n chain stoppers to a solution leads to the formation of one new chain. When a concentration k of chain stoppers is added to a solution, which makes up a fraction $x = k/(c + k)$ of all monomers, the concentration of chains is increased by $k/n = cx/n(1 - x)$. The number-average degree of polymerization in the presence of a fraction x of chain stoppers is decreased and is given by

$$\langle N(x)\rangle = \frac{n\langle N(0)\rangle}{n(1 - x) + x\langle N(0)\rangle} \approx n/x \tag{5}$$

where $\langle N(0)\rangle$ is the number-average number of monomers per chain without any chain stoppers as given by eq 2. The approximation of $\langle N(x)\rangle$ to n/x is justified for sufficiently high values of $\langle N(0)\rangle$ and x, when the term $n(1 - x)$ in the denominator can be neglected. This condition applies if the number of “dead” chain ends is much larger than the number of functional ones. Then, only the stopper fraction determines the average length of the chains, independent of monomer concentration and association constant (which determine $\langle N(0)\rangle$).

In Figure 2, the effect of the addition of chain stoppers as calculated with eq 5 is shown. Figure 2a shows that at low values for x/n the effect of the stoppers is negligible. Only a small minority of the chains contain chain stoppers; the number of dead chain ends is small compared to the number of functional ones and $\langle N\rangle \approx \langle N(0)\rangle$. When the number of dead chain ends becomes of the same order of magnitude as the number of functional ones (x/n of the order of $1/\langle N(0)\rangle$), $\langle N\rangle$ starts to decrease significantly. At even higher stopper fractions, the number of dead chain ends is much larger than the number of functional ones, and $\langle N\rangle$ no longer depends on $\langle N(0)\rangle$ but is fully determined by x and proportional to $1/x$, as indicated by the line with slope -1 next to the curves. This is the regime where the approximation in eq 5 is justified. Figure 2b shows that at low monomer concentrations the average chain length is not determined by the amount of stoppers. $\langle N\rangle$ is proportional to $c^{0.5}$ as indicated with the solid line with slope 0.5, the same dependence as without chain stoppers (eq 2). In this concentration range, $\langle N(0)\rangle$ is still small compared to n/x, and most chains do not contain chain stoppers. When the monomer concentration is increased, the slope starts to level off, and eventually $\langle N\rangle$ reaches a plateau at a value n/x, when virtually all chain ends are occupied by chain stoppers. In this range of concentrations, the average chain length is again independent of the monomer concentration and only determined by the stopper fraction.

A critical concentration c' beyond which $\langle N\rangle$ becomes independent of c at a given stopper fraction x/n can be estimated by calculating the concentration where the plateau value n/x and the line $2\sqrt{Kc}$ describing the chain growth without chain stoppers intersect (represented by the open arrows in Figure 2b):

$$2\sqrt{Kc'} = \frac{n}{x} \Rightarrow c' = \frac{1}{4K}\left(\frac{n}{x}\right)^2 \tag{6}$$

The same equation can be used to calculate a critical stopper fraction $(x/n)'$ for a given monomer concentration (represented by the open arrows in Figure 2a). From these figures, it can be seen that in order to be able to vary c and $\langle N\rangle$ independently in a controlled way both c and x have to exceed their critical value, which are mutually dependent. This criterion can be written as

$$(x\sqrt{c})' \gg \frac{n}{2\sqrt{K}} \tag{7}$$

When this condition is satisfied, the addition of chain stoppers thus offers the possibility to study the chain length and concentration dependence of supramolecular polymer solutions independently, which is otherwise impossible for supramolecular polymers without changing other parameters like temperature or solvent.

For a given supramolecular polymer system, equations may be derived which take into account more details and specific features of the monomers and chain stoppers. For example, for supramolecular polymers based on the well-known ureidopyrimidinone unit, it is known that the chain stoppers can bind to both ends of the chain and can also bind to each other to form stopper dimers. An expression for $\langle N(x)\rangle$ which takes into account these elements was derived.[13] For sufficiently high stopper fractions, the result of this expression is equal to that of eq 5 with $n = 2$. For EHUT, it is known that the association process is cooperative.[23] The formation of dimers has a lower association constant (K_2) than the formation of higher oligomers or polymers (K_n).[25,26] However, under conditions where the number of free monomers is small ($\langle N(0)\rangle \gg 1$), dimer formation can be neglected. In that case, a single effective association constant $K = K_n^2/K_2$ describes the association accurately, and this K can be used for further calculations. In conclusion, for a specific system expressions for $\langle N(x)\rangle$ may be derived which take into account more details than eq 5. Nevertheless, eq 5 is a very general equation describing the effect of adding chain stoppers to a supramolecular polymer solution which is useful under the appropriate conditions.

2.2. Static Light Scattering. With static light scattering (SLS), the time-averaged scattered intensity is measured at a number of scattering angles, corresponding to different magnitudes of the scattering vector q, given by $(4\pi n_0/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident light, n_0 is the solvent refractive index, and θ is the scattering angle. From the q dependence of the intensity, information about the characteristic length scales in the sample can be derived. The segment density correlation length in the solution can be found using the Ornstein−Zernike equation for the structure factor:[33]

$$I(q) \sim \frac{1}{1 + q^2\xi^2} \tag{8}$$

In dilute solutions, the polymer chains do not interact, and the correlation length gives information about the (average) size of the individual molecules. The q dependence of the scattered intensity is given by

$$I(q) \sim \frac{1}{1 + \frac{1}{3}q^2\langle R_g^{\ 2}\rangle_z} \tag{9}$$

where $\langle R_g^{\ 2}\rangle_z$ denotes the z-average of the squared radius of gyration. Thus, for dilute solutions the segment density correlation length ξ from eq 8 can be identified as $\sqrt{\langle R_g^{\ 2}\rangle_z/3}$.

For a mixture of rigid supramolecular rods with an exponential chain length distribution it can be derived that $\langle R_g^2\rangle_z = \langle L\rangle_w^2/4$, where $\langle L\rangle_w$ denotes the weight-average length of the rods.[34] If the association constant is high ($p \approx 1$), the polydispersity index $M_w/M_n = 2$ (see section 2.1). For rods, the contour length is proportional to the molecular weight (or the degree of polymerization), so the ratio of 2 also holds for the contour lengths: $\langle L\rangle_w = 2\langle L\rangle$, with $\langle L\rangle$ the number-average contour length. Thus, it follows that in dilute solutions of supramolecular rods ξ can be identified as $\langle L\rangle/\sqrt{3}$. If the effective monomer length (the chain length per monomer, denoted as l_m) is known, the degree of polymerization $\langle N\rangle$ can be calculated from the relation $\langle L\rangle = l_m\langle N\rangle$.

For a flexible chain in a Θ solvent, the radius of gyration of a chain scales with the degree of polymerization as $R_g \sim \langle N\rangle^{0.5}$, whereas in a good solvent the exponent is 0.6.[35] For a rodlike chain, $R_g \sim \langle N\rangle$, independent of solvent quality. For supramolecular polymers, $\langle N\rangle \sim c^{0.5}$ (eq 2). In dilute solutions, it is therefore predicted that ξ increases with c according to a power law with an exponent between 0.25 (ideal flexible chains) and 0.5 (rodlike chains). If the solution is more concentrated and chains start to overlap (beyond the overlap concentration c^*), the polymers form a transient network and the correlation length no longer contains information about the size of the individual chains, but it reflects the mesh size ξ_m of the network. The mesh size decreases with increasing polymer concentration, and it only depends on the total volume fraction of polymer in the system and not on $\langle N\rangle$. For flexible chains in the semidilute concentration regime, scaling theory predicts $\xi \sim c^{-0.75}$.[35] At even higher concentrations (marginal regime) and in solutions of less flexible chains, where excluded-volume interactions are weaker, an exponent -0.5 is predicted.

Summarizing, theory predicts for supramolecular polymer solutions that ξ increases with c at low concentrations due to the increasing degree of polymerization, passes a maximum at c^*, and decreases again in the semidilute and more concentrated regimes due to the decreasing mesh size. The scaling exponents contain information about the flexibility of the chains, solvent quality, and concentration regime.

2.2.1. Crossover Region. A crossover between a length scale ξ_0 in dilute solution and ξ_m in the semidilute regime can generally be described by an expression of the form $\xi^{-\nu} = \xi_0^{-\nu} + \xi_m^{-\nu}$. An equation of this form was previously derived in calculations of the depletion layer thickness in monodisperse solutions of covalent flexible polymers in a mean-field approach.[36] In this case, the dilute length scale ξ_0 equals the radius of gyration of the polymers. Later, a very similar expression was derived in self-consistent-field calculations for flexible supramolecular polymers in a mean-field approximation.[37] In this analysis, polydispersity was taken into account, and ξ_0 was found to be equal to the radius of gyration of a chain of number-average length $\langle N\rangle$. The value of the exponent ν determines the width of the crossover region. In both cases, the exponent ν was found to be 2, but for other systems different values of ν may apply. As mentioned above, the length scale as measured by SLS for rigid rods with an exponential chain length distribution below the overlap concentration is $\langle L\rangle/\sqrt{3}$, and this may be substituted for ξ_0, leading to the following expression for ξ:

$$\frac{1}{\xi^\nu} = \frac{3^{\nu/2}}{\langle L\rangle^\nu} + \frac{1}{\xi_m^{\ \nu}} \tag{10}$$

2.3. Dynamic Light Scattering. Dynamic light scattering (DLS) measures temporal fluctuations of the scattered intensity arising from motion of the scatterers.[33] From the scattered intensity as a function of time, the intensity correlation function $g^{(2)}(\tau)$ is calculated for a number of time intervals τ:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} \tag{11}$$

The intensity correlation function is related to the normalized field correlation function $g^{(1)}(\tau)$ by the Siegert equation[33]

$$g^{(2)}(\tau) = 1 + A[g^{(1)}(\tau)]^2 \tag{12}$$

where A is a constant of order unity depending on the geometry of the experimental setup.

De Gennes developed a scaling theory for semidilute polymer solutions using a transient gel model.[35] According to this theory, $g^{(1)}(\tau)$ is an exponentially decreasing function with a single decay rate constant Γ, which is determined by the scattering vector q and the so-called gel diffusion coefficient D_g, according to

$$g^{(1)}(\tau) = e^{-\Gamma\tau} = e^{-q^2 D_g \tau} \tag{13}$$

D_g is given by

$$D_g = D_c\frac{M_g + M_o}{M_o} \tag{14}$$

where M_g is the gel modulus (the elastic or Young's modulus of the transient gel), M_o the osmotic modulus, defined as $c(\mathrm{d}\Pi/\mathrm{d}c)$, and D_c the collective diffusion coefficient, which is in turn related to the hydrodynamic correlation length ξ_H by the Stokes−Einstein equation[33]

$$D_c = \frac{k_B T}{6\pi\eta_0\xi_H} \tag{15}$$

where η_0 is the solvent viscosity. For polymers in a good solvent, $M_o \gg M_g$ and D_c is effectively equal to D_g. Experimentally, a distribution of decay rate constants Γ is generally measured, each with its own weight w, so $g^{(1)}(\tau)$ is given by

$$g^{(1)}(\tau) = \int_0^\infty w(\Gamma)e^{-\Gamma\tau}\, d\Gamma \tag{16}$$

Mostly, the value of Γ at the peak of the distribution is taken as "the" decay rate constant and used for further calculations.

In dilute solutions, when the polymers do not interact, the collective diffusion coefficient reflects the motion of a single chain, and ξ_H corresponds to the (average) hydrodynamic radius of the polymer. In the semidilute and more concentrated regimes, the hydrodynamic correlation length corresponds to the hydrodynamic mesh size of the transient network, the average distance between entanglement points. With SLS, the average mesh size of the transient polymer network is measured, whereas DLS measures the average diffusion coefficient of the meshes. From this diffusion coefficient and the viscosity of the solvent, the size of the mesh can be calculated with eq 15. The hydrodynamic correlation length ξ_H measured by DLS is thus not equal to the static correlation length ξ, but it is of the same order of magnitude and it scales in the same way with concentration.

In addition to the decay rate constant associated with the collective diffusion coefficient, a second, slower decay time is often present in viscoelastic polymer solutions in the semidilute concentration regime. The two modes will from now on be denoted as the fast and the slow mode, respectively. A slow relaxation mode can be found in many different systems, and it can have several physical origins.[38,39] To determine which mechanism is relevant for a given system, it is useful to investigate the q dependence of the slow mode. For example, if the slow mode is caused by diffusion of large aggregates or domains, this would lead to a decay rate constant proportional to q^2, as for any diffusive mode (eq 13). Alternatively, it was proposed that concentration fluctuations in the polymer network are coupled to viscoelastic stress,[40−42] and this would lead to a slow mode with a q-independent decay rate.

3. Experimental Section

3.1. Materials. Cyclohexane (>99%) was obtained from Aldrich and used as received, unless stated otherwise. The syntheses of the self-associating monomer (EHUT)[23] and monofunctional chain stopper (DBUT)[18] are described elsewhere. The molar mass of both EHUT and DBUT is 432 g/mol. Solutions in cyclohexane were prepared by stirring at a slightly elevated temperature.

3.2. Osmometry. A Knauer vapor pressure osmometer was used to measure the osmotic pressure of solutions ranging in EHUT concentration from 4 to 17 g/L and in stopper fraction from 0.3 to 1 in cyclohexane at 30 °C. Solutions of naphthalene in cyclohexane were used as a calibration reference. The measured signal of EHUT solutions was converted to the number concentration of chains by comparison with this reference. No extrapolation to zero concentration was performed, and thus ideality (second virial coefficient $B_2 = 0$) was assumed. It was checked that this assumption was valid (see section 4.1). Note that extrapolating to zero concentration, a widely used procedure in polymer science, is generally useless for supramolecular polymers because of the concentration dependence of the average chain length.

3.3. Light Scattering. For light scattering measurements, cyclohexane (refractive index $n_0 = 1.426$) was filtered through a Teflon filter (pore size 0.45 μm) before preparing solutions. Measurements were done at room temperature using an argon ion laser with a wavelength of 514.5 nm. A pinhole detector was used with size 600 μm for SLS and 200 μm for DLS experiments. Solutions in cyclohexane were prepared with EHUT concentrations between 0.02 and 5 g/L and stopper fractions of 0 and 0.015.

Static Light Scattering. The scattered intensity of samples (I_{sample}) was measured at 5° intervals at scattering angles between 25° and 90° (corresponding to values of q between 7.5×10^6 and 2.5×10^7 m^{-1}). The scattered intensity of the pure solvent ($I_{solvent}$) was also measured. The reduced scattered intensity, denoted as $i(q)$, was used for further calculations:

$$i(q) = \frac{I_{sample}(q) - I_{solvent}(q)}{I_{solvent}(q)} \tag{17}$$

By using $i(q)$ instead of the absolute scattered intensity, both scattering from the solvent and the angular dependence of the scattering volume are taken into account and corrected for. From linear fits to plots of $1/i(q)$ as a function of q^2, ξ was calculated with eq 8.

Dynamic Light Scattering. The scattered intensity was measured at scattering angles of 60°, 90°, and 120°. To obtain correlation functions of sufficient quality, measuring times of 15 min per angle were used. The spectrum of decay rate constants was calculated from the correlation function using the CONTIN algorithm.[43]

4. Results and Discussion

Vapor pressure osmometry (section 4.1) can be used to obtain information about supramolecular polymer solutions within a certain range of monomer concentrations and stopper fractions, since it requires a minimum concentration of chains in order to have a measurable osmotic pressure. In practice, the method is therefore limited to high stopper fractions. Light scattering provides complementary information, since it requires a minimum concentration of objects with a certain minimum size. It can therefore be used to study conditions in which the chains are long (high concentrations, low stopper fractions). Thus, by using both techniques, a large range of monomer concentrations and stopper fractions can be covered. Static light scattering (section 4.2) provides information about the static correlation length in solutions. In section 4.3, the effectiveness of the chain stopper is discussed and the results from both techniques are compared. Dynamic light scattering experiments are described in section 4.4.

4.1. Vapor Pressure Osmometry. Osmometry experiments were limited to relatively high stopper fractions due to the detection limit of the apparatus ($\gtrsim$1 mM). Figure 3 shows the reciprocal normalized osmotic pressure (RTc/Π) of EHUT solutions with constant stopper fraction ($x = 0.30$) at various monomer concentrations. Assuming ideality (see below), this quantity equals $\langle N \rangle$. If there would be no chain stoppers present, $\langle N \rangle$ should increase by approximately a factor 2 within the concentration range used (assuming $\langle N \rangle \sim c^{0.5}$). The plot shows that $\langle N \rangle$ is constant within the experimental error. Therefore, we are in the regime where $\langle N \rangle$ is independent of c and only determined by x, and the approximation in eq 5 can be applied. The constancy of $\langle N \rangle$ also shows that nonideality of the solution can be neglected (if present, it is small compared to the experimental error) and that our method for determining the number concentration of chains from the osmotic pressure without extrapolating to zero concentration is valid. For a series of solutions with a constant EHUT concentration of 4.4 g/L varying in stopper fraction from 0.3 to 0.7, the osmotic pressure was also measured and converted to $\langle N \rangle$. The results are shown

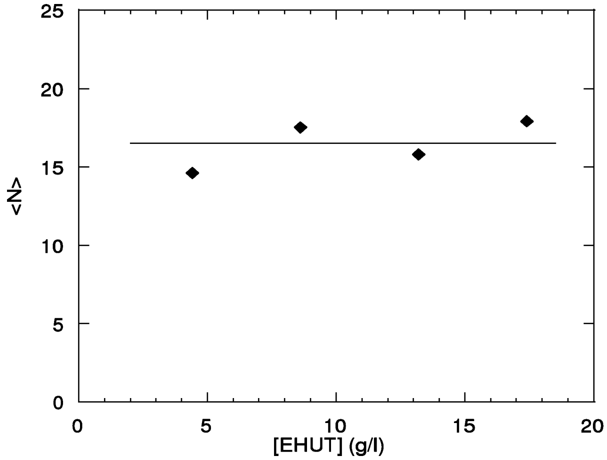

Figure 3. ⟨*N*⟩ as a function of EHUT concentration at a constant stopper fraction ($x = 0.30$). The horizontal line at ⟨*N*⟩ = 16.6 indicates the average value for the measured solutions.

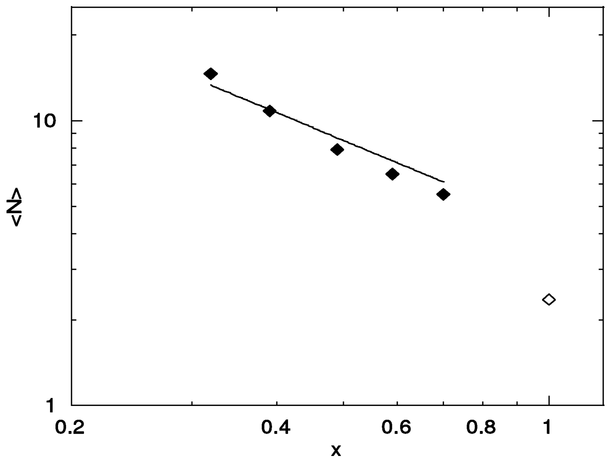

Figure 4. Number-average degree of polymerization ⟨*N*⟩ as a function of stopper fraction *x* for EHUT solutions of 4.4 g/L in cyclohexane (◆). The line corresponds to ⟨*N*⟩ = $4/x$. The open symbol shows ⟨*N*⟩ for a solution with only chain stoppers ($x = 1$).

by the solid symbols in Figure 4. The decrease of ⟨*N*⟩ with increasing *x* is described reasonably well by a power law with a slope of −1, indicated by the line which corresponds to ⟨*N*⟩ = $4/x$. Note that this is not a power law fit to the data; the line only serves to show that the data are broadly consistent with a power law with exponent −1. The approximate inverse proportionality with the stopper fraction shows that the conditions for applying the approximation in eq 5 are met. The proportionality constant indicates that on average approximately 4 stoppers have to be added to the solution to create one new chain ($n = 4$ in eq 5). This value for *n* means that DBUT is not a very efficient chain stopper. This is discussed in more detail in section 4.3.

The osmotic pressure of two solutions of only chain stoppers ([DBUT] = 1 and 2 g/L, $x = 1$) was also measured, and the osmotic pressure of both solutions was lower than expected on the basis of their concentrations, approximately by a factor 2 (the open symbol in Figure 4). This strongly suggests that DBUT is capable of forming dimers or small oligomers, leading to a decreased osmotic pressure compared to a purely monomeric solution. In DBUT, two of the hydrogen bond donating NH groups which are present in EHUT are alkylated (see Figure 1). However, the two remaining secondary amines in DBUT may still form hydrogen bonds with the carbonyl oxygens of other DBUT molecules. Recently, isothermal titration calorimetry experiments confirmed that DBUT is indeed capable of self-association.[44]

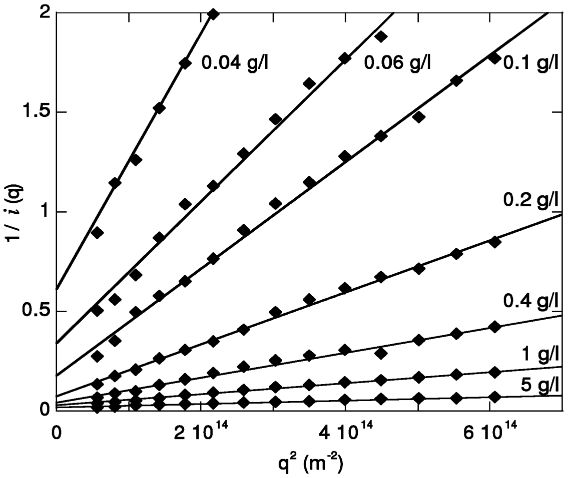

Figure 5. Reciprocal reduced scattered intensity as a function of q^2 for EHUT solutions of various concentrations, all with $x = 0.015$. The lines are linear fits to the data.

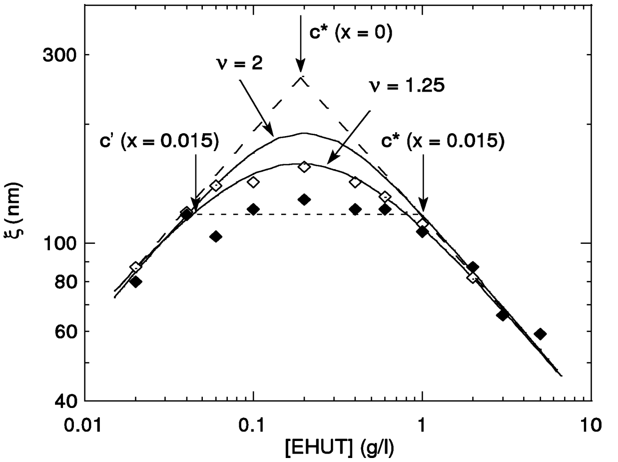

Figure 6. Static correlation length in EHUT solutions in cyclohexane without chain stoppers (◇) and with a stopper fraction $x = 0.015$ (◆). Arrows indicate the overlap concentrations with and without chain stoppers ($c^*(x)$ and $c^*(0)$, respectively) and the critical concentration $c'(x)$. The dashed lines below and above $c^*(0)$ indicate $\xi = 600c^{0.5}$ and $\xi = 120c^{-0.5}$, respectively. The solid lines represent a fit of the experimental data to eq 10 with $\nu = 2$ and $\nu = 1.25$, respectively. The dotted line indicates the plateau at 120 nm.

4.2. Static Light Scattering. Results of the static light scattering experiments are shown in Figure 5. From a linear fit to the experimental data, the correlation length was calculated using eq 8. The linearity of the plots confirms that eq 8 applies to our system for all concentrations used, both below and above the overlap concentration. Figure 6 shows the correlation length ξ for solutions of EHUT in cyclohexane both with and without chain stoppers.

4.2.1. Solutions with Chain Stoppers. At low concentrations, the correlation length is found to increase with increasing monomer concentration. Since in dilute solutions ξ reflects the size of the individual chains, the increase can be attributed to the growth of the chains. As mentioned in section 2.2, ξ can be identified as $\langle L\rangle/\sqrt{3}$. The data can be described reasonably well with the power law $\xi = 600c^{0.5}$ (see Figure 6), where *c* is given in g/L and ξ in nm. The exponent 0.5 indicates the presence of rodlike chains (see section 2.2). The proportionality constant 600 contains information about the association constant. Using an effective monomer length l_m of 0.18 nm,[24] ⟨*N*⟩ can be calculated from ξ, and the relation becomes $\langle N\rangle = 5.8 \times 10^3 c^{0.5}$, again with c in g/L. According to eq 2, the proportionality constant is now equal to $2\sqrt{K}$, and K can be calculated to be 8×10^6 L/g or 4×10^9 M^{-1}, using the molar mass of EHUT. Values for the association constant of EHUT in toluene and chloroform were measured previously by isothermal titration calorimetry, where K was found to be 2×10^6 M^{-1} in toluene at 40 °C and 1×10^5 M^{-1} in chloroform at room temperature.[26] The present results are in line with these findings, since both an increase in temperature and in solvent polarity will result in a decrease of the association constant. A number of assumptions and estimations have been made in the foregoing derivation, so the value of K is not very accurate. However, the analysis yields the order of magnitude of the association constant of EHUT in cyclohexane at room temperature. The association constant can also be estimated from the overlap concentration c^*, which was determined from viscosity measurements to be approximately 0.1 g/L without chain stoppers.[27] It is assumed that the chains are rigid rods with an average contour length $\langle L\rangle = l_m\langle N\rangle$, where $\langle N\rangle$ is given by eq 2, and that the chains occupy a volume equal to a sphere with a diameter equal to the rod contour length. As an estimate for the overlap concentration, the concentration at which these spheres fill the total volume of the system can be used. If c^* is known, K can be calculated:

$$K = \frac{3}{2\pi N_{av} {l_m}^3 (c^*)^2} \tag{18}$$

with N_{av} Avogadro's number. Using this expression and an overlap concentration of 0.1 g/L, K is calculated to be 6×10^6 L/g (3×10^9 M^{-1}), in good agreement with the present result from light scattering. This agreement confirms that the chains can be considered rodlike, at least up to their (average) length at the overlap concentration.

From concentrations above 0.06 g/L, deviations from the power law behavior are observed. This may be caused by the fact that the chains reach a length where they become longer than their persistence length and are no longer rigid rods. We may therefore estimate a lower limit for the persistence length of EHUT chains in cyclohexane from the onset of deviation from rodlike scaling. This occurs at a correlation length of approximately 150 nm, corresponding to a contour length of 250 nm (again using $\xi = \langle L\rangle/\sqrt{3}$). The latter value is a lower limit for the persistence length, since the deviation from the theoretical concentration dependence for dilute rods can also be caused by the crossover to the semidilute regime, in which case the chains can still be rigid at longer length scales. The correlation length reaches a maximum at approximately 0.2 g/L, which can be identified as the overlap concentration without chain stoppers. This is indicated as $c^*(0)$ in Figure 6 and can be calculated more precisely from the intersection of the linear extrapolations below and above the overlap concentration, which indeed occurs at 0.2 g/L. This result is in reasonable agreement with the value of 0.1 g/L from viscosimetry, especially since relatively few data points were measured close to c^* in the viscosity measurements.[27] When the concentration is increased further, the correlation length decreases, reflecting the decreasing mesh size in the polymer network. The concentration dependence of ξ is again consistent with a power law, this time with exponent -0.5 (see Figure 6). This scaling exponent was also found previously for the same system.[27] This exponent is expected for chains for which the persistence length is equal to or longer than the mesh size, so the chains are rigid rods on the length scale ξ_m. This power law scaling is a good description for concentrations higher than approximately 0.8 g/L, where $\xi \approx 150$ nm, which again leads to a lower limit for the persistence length of approximately 250 nm.

The correlation length is consistent with power laws at concentrations far below and above c^*. Equation 10 can be used to describe the crossover between these regimes. With the scaling relations for rigid rods ($\langle L\rangle \sim c^{0.5}$ and $\xi_m \sim c^{-0.5}$) and the exponent $\nu = 2$ (which was found in theoretical work for other systems[36,37]), the equation fits the experimental data far away from $c^*(0)$, but at concentrations around $c^*(0)$, the experimental ξ is systematically lower than the calculated value (see Figure 6). This may be explained by the possibility mentioned above that the chains may be semiflexible around c^*, while they are rodlike at lower concentrations and rigid at the length scale of the mesh size at higher concentrations. This would affect the shape of the curve around c^*, but it is not taken into account in eq 10, in which the scaling exponents for rodlike chains are used for the whole concentration range. As an alternative explanation, the exponent $\nu = 2$ was derived for flexible chains in a mean-field approximation, whereas EHUT chains are certainly not fully flexible. It is possible that for semiflexible chains a different value of ν applies. Therefore, ν was used as a fitting parameter, and the best results were obtained with $\nu = 1.25$, in which case the data are described well over the whole concentration range measured (see Figure 6). A lower value of ν corresponds to a wider crossover region. It is reasonable that the crossover is less sharp for polydisperse rigid chains compared to flexible ones. When the longest chains in a polydisperse solution start to overlap, the short ones are still in the dilute regime. The difference in size between long and short chains is larger for rods ($\langle R_g\rangle \sim \langle N\rangle$) than for coils ($\langle R_g\rangle \sim \langle N\rangle^{0.5}$), which could explain the wider crossover region. Furthermore, excluded-volume interactions are stronger for coils than for rods, which may also lead to a more gradual crossover between dilute and semidilute regime for rods. It is therefore reasonable that the value of ν obtained from the present experiments is lower than 2.

4.2.2. Solutions with Chain Stoppers. In these experiments, the stopper fraction x was kept constant at a value of 0.015, while the EHUT concentration varied between 0.02 and 5 g/L. At the lowest concentrations measured, the correlation lengths of the solutions with and without chain stoppers are approximately equal. The chain stoppers have a negligible effect on $\langle N\rangle$, which means that the number of functional chain ends is much larger than the number of dead ones. In other words, the chains are short and their number is so high that most of them are not terminated by chain stoppers.

Since the chain length increases with the square root of the monomer concentration, the number of chains also scales as $c^{0.5}$. The concentration of chain stoppers increases linearly with the total monomer concentration, so the number of chain stoppers increases relative to the number of chain ends if the overall EHUT concentration is increased at constant x. As a result, more chain ends will be formed by chain stoppers and the chain length is significantly decreased. At concentrations above approximately 0.04 g/L, the chain length becomes independent of c, leading to a plateau in ξ at approximately 120 nm (see Figure 6), similar to the plateaus in the theoretical Figure 2b. The fact that ξ is determined by x indicates that the number of dead chain ends is much larger than the number of functional ones, according to eq 5. The onset of the plateau at $c = 0.04$ g/L for $x = 0.015$ corresponds to the critical condition of eq 7. By substituting these values for c and x and assuming $K = 8 \times 10^6$ L/g (see section 4.2.1), the value of n can be calculated to be 17. The plateau region of the curve will be discussed in more detail below. Since the chains are shorter at a given monomer concentration in the presence of chain stoppers, the number of chains is higher (it is proportional to $\langle N\rangle^{-1}$). If we again assume that a chain occupies a volume equal to a sphere with a diameter equal to its contour length, the volume occupied by a single chain scales as $\langle N\rangle^3$. By combining these two scaling relations, it can be easily seen that the total volume occupied by the chains scales as $\langle N\rangle^2$; thus, chains with chain stoppers occupy less volume than chains without chain stoppers at a given monomer concentration. As a result, more chains (a higher monomer concentration) are needed to fill the whole volume with chains, and the overlap concentration in the presence of chain stoppers is increased. The correlation length above the overlap concentration is independent of chain length, so solutions with and without chain stoppers should give the same value for ξ. The overlap concentration $c^*(x)$ at a given stopper fraction can therefore be obtained by calculating the concentration at which the plateau level of ξ (120 nm for $x = 0.015$) in the dilute regime and the semidilute correlation length ξ_m ($120c^{-0.5}$) intersect (see Figure 6). From this, it follows that the overlap concentration at a stopper fraction of 0.015 equals 1 g/L. Figure 6 shows that indeed at higher concentrations than this the correlation lengths with and without stoppers are equal. The value of 1 g/L may thus be considered a reasonable estimate for c^* ($x = 0.015$).

Using the present results, the overlap concentration at other stopper fractions can be estimated. The plateau in ξ is a result of the fact that $\langle N\rangle$ becomes independent of c and is proportional to $1/x$ (see Figure 2b). Under these conditions, we can write for dilute rodlike chains $\xi_{\text{plateau}} = B/x$ (using that $\xi \sim \langle L\rangle \sim \langle N\rangle \sim 1/x$). The proportionality constant B can be calculated by substituting the present data ($x = 0.015$, $\xi_{\text{plateau}} = 120$ nm), leading to $B = 1.8$ nm. As explained above, the overlap concentration can be found by calculating the intersection of the plateau with the semidilute correlation length. Above the overlap concentration, the correlation length is independent of $\langle N\rangle$, and therefore also of stopper fraction, and was found to be equal to $120c^{-0.5}$ nm (if c is expressed in g/L). Equating this to $1.8/x$ leads to the expression $c^*(x) = (67x)^2$ (again in g/L). Note that this equation is based on experimental data, and it is affected by errors in the determination of the level of the plateau and the semidilute correlation length. It can therefore not be expected to give a very accurate prediction of $c^*(x)$, but it should give a reasonable estimate.

If eqs 8 and 9 apply and the chains are rigid rods, the plateau correlation length of 120 nm would correspond to a number-average contour length of approximately 200 nm. Equation 9 is valid for small values of q, that is if the probed length scale $2\pi/q$ is larger than ξ. With values of q and ξ from our experiments this assumption is reasonable. As was mentioned in the discussion of the overlap concentration, the persistence length is estimated to be at least 250 nm. The plateau in ξ occurs at 120 nm, so it is reasonable to assume that chains with the corresponding contour length of 200 nm are indeed rigid. The assumption that $p \approx 1$ is also reasonable, as can be seen when the estimated value of K of 4×10^9 M^{-1} is substituted in eq 4. Even at the lowest monomer concentrations, p is still very close to unity. In conclusion, eqs 8 and 9 should apply reasonably well to our experimental system under the experimental conditions used in the present paper.

4.3. Effectiveness of Chain Stoppers. A chain stopper with the highest possible effectiveness has an infinitely high association constant with the supramolecular polymer chains and can only associate to one side of the chain. Furthermore, the addition of a single chain stopper to a chain completely stops the chain from growing. In that case, the value of n (as defined in eq 5) equals 1. Generally, the effectiveness of a chain stopper can be reduced because of properties of the chains and properties of the chain stoppers.

The properties of the chains reduce the effectiveness for example if the stopper can bind to both sides of the chain (as is the case for the ureidopyrimidinone-based supramolecular polymers[13]). In that case the (minimum) value of n is 2. Thus, more stoppers have to be added to reach a given value of $\langle N\rangle$, and the chain stopper is less effective. For branched chains, the minimum value of n can even be much higher. The chain architecture also plays a role. If the chains have one monomer per axial repetition unit (the cross section of the chain consists of a single monomer), the addition of one stopper to a chain end completely stops the chain from growing at that end. However, if the cross section of the chain consists of more than one monomer (as was proposed for EHUT chains[24,28]), a higher number of chain stoppers may have to bind to the chain at the same position to completely stop it from growing. If the number of associated chain stoppers at a certain position in the chain is less than this number, the chain may still grow further, and the chain stoppers may only form a “defect” in the chain instead of stopping it. By this mechanism, chain stoppers can be incorporated in the chain, and this also reduces the effectiveness of the stopper. The stoppers themselves can also cause a decreased effectiveness. This is the case if they do not associate very strongly to the chains (in which case there will be free chain stoppers in solution) or if they form aggregates such as the proposed DBUT dimers mentioned in section 4.1. The combination of all these factors leads to an overall stopper effectiveness, which can be defined as $1/n$ and which can range from 1 ($n = 1$, ideal stopper) to 0 ($n = \infty$, no stopper effect).

A chain of 200 nm (the number average contour length corresponding to the plateau value of ξ of 120 nm) consists of approximately 1100 monomers (using $l_m = 0.18$ nm). In our experiments, a stopper fraction of 0.015 was used. To get chains of 1100 monomers at a stopper fraction of 0.015, the value of n should be 17. The same value was also obtained from the critical concentration of 0.04 g/L at $x = 0.015$ (see section 4.2.2). It is not surprising that the effectiveness derived from light scattering ($n = 17$; $1/n = 0.06$) is higher than that derived from osmometry ($n = 4$; $1/n = 0.25$). As mentioned in section 4.1, DBUT is probably capable of forming dimers or small oligomers. These aggregates are very small and do not contribute significantly to the scattered intensity in SLS experiments, but they do contribute to the osmotic pressure. Thus, light scattering only gives information about chains above a certain size, whereas osmometry also measures the shortest chains and DBUT oligomers. The chain length as measured by osmometry will therefore be smaller than with light scattering, and as a result, the calculated value of n will also be smaller. Since only a part of the chain length distribution is measured with light scattering, whereas osmometry measures all chains, the effectiveness as derived from osmometry (0.25) is probably a more reliable value for the overall effectiveness of DBUT.

In principle, the association constants in the EHUT/DBUT system (EHUT−EHUT, DBUT−DBUT, and DBUT−EHUT) can be calculated from experimental data ($\langle N\rangle$ as a function of c and x) if the chain structure and architecture are also known. Unfortunately, this information is presently not available for the EHUT/DBUT system. EHUT certainly forms long, semi-flexible linear structures with a very high association constant.

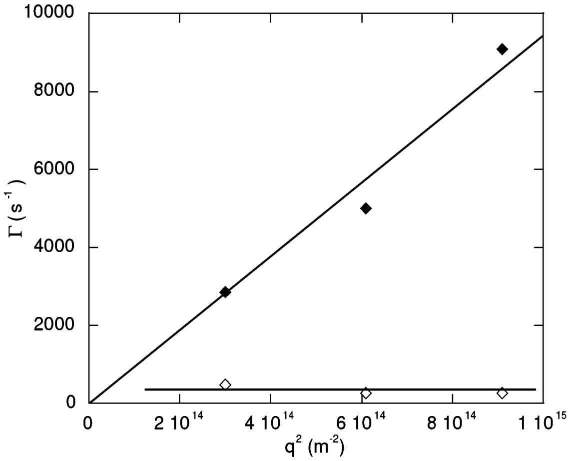

Figure 7. q^2 dependence of Γ_{fast} (◆) and Γ_{slow} (◇) for a 3 g/L EHUT solution with $x = 0.015$. Γ_{fast} is proportional to q^2, as indicated by the linear fit, which corresponds to $\Gamma_{fast} = 9.45 \times 10^{-12}q^2$. The horizontal line at $\Gamma_{slow} = 335$ s^{-1} shows that the slow mode does not depend significantly on q.

However, the exact structure of EHUT chains is still ambiguous, especially since there is evidence which shows that the chains can change their structure depending on the conditions.[28] It is possible that the association of DBUT to a chain also affects the chain structure. It remains to be studied how DBUT associates to the different chain structures. There are independent estimates for the EHUT−EHUT association constant[26] (see also section 4.2.1), but not yet for the DBUT−DBUT and EHUT−DBUT association. So far, only preliminary experiments have been carried out in which the formation of these bonds has been studied qualitatively.[44] From the foregoing, it is clear that much work has to be done before a complete picture of the association of EHUT/DBUT can be constructed.

4.4. Dynamic Light Scattering. At low concentrations, the distribution of decay rate constants obtained from a CONTIN analysis of the correlation function has a single peak which is related to the collective diffusion coefficient and the hydrodynamic correlation length, as explained in section 2.3. Above a certain concentration, a second peak, corresponding to a slow relaxation mode, appears at longer decay times. Typical correlation functions $g^{(1)}(\tau)$ at different scattering angles and the corresponding spectra of relaxation times can be found in the Supporting Information.

Without chain stoppers, the slow mode is present at all concentrations measured, except for the lowest one (0.2 g/L). In the solutions with chain stoppers, the second peak only appears at concentrations above 1 g/L. Both observations indicate that the slow mode is only present above the overlap concentration as measured by SLS (0.2 and 0.8 g/L without and with chain stoppers, respectively). The fact that the slow mode only appears above the overlap concentration suggests that it might have something to do with the formation of the transient polymer network. A typical result for the q^2 dependence of both modes is shown in Figure 7. Both modes will be discussed in more detail below.

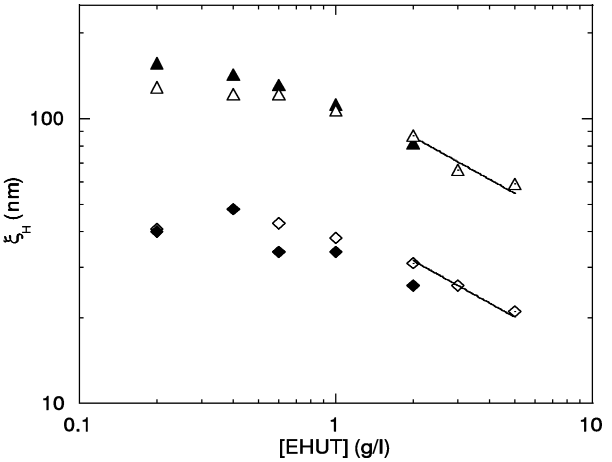

Figure 8. Hydrodynamic correlation length as a function of EHUT concentration for solutions without chain stoppers (◆) and for solutions with $x = 0.015$ (◇). The static correlation lengths for solutions without chain stoppers (▲) and with $x = 0.015$ (△) are replotted from Figure 6. The solid lines both have a slope −0.5 and indicate $\xi \sim c^{-0.5}$.

4.4.1. Fast Mode. The peak value of Γ in the "fast" peak (Γ_{fast}) is taken as the decay rate constant which is related to the collective diffusion coefficient. When the values of Γ_{fast} at different scattering angles are plotted as a function of q^2 (see Figure 7), it can be seen that Γ_{fast} is proportional to q^2, which shows that the fast mode is indeed diffusive. The slope of the fitted line corresponds to the gel diffusion coefficient D_g of eqs 13 and 14. Since cyclohexane is a good solvent for EHUT, $M_o \gg M_g$ and D_g equals the collective diffusion coefficient D_c (eq 14). Using this, the hydrodynamic correlation length ξ_H can be calculated with eq 15. The results of this procedure are shown in Figure 8, where the hydrodynamic correlation length is plotted as a function of EHUT concentration for solutions with and without chain stoppers. For comparison, the static correlation length ξ_m as measured with SLS is also shown. It can be seen that the quality of the data obtained from DLS is less good than the SLS data. This is probably mainly caused by the limited quality of the correlation functions due to the low scattered intensity and the limited number of decay rates used in the CONTIN analysis. Therefore, only qualitative conclusions will be drawn on the basis of the DLS results. Since there are no data below c^* for the solutions without chain stoppers (due to the low intensity of the scattered light), it is not possible to calculate the overlap concentration from the maximum in the correlation length as was done with SLS. However, it can be seen that as the concentration is decreased toward c^*, ξ_H levels off. At concentrations > c^*, ξ_H decreases, and the results can be fitted with a power law with exponent −0.5. This is the same scaling exponent as found with SLS. It can be seen from Figure 8 that the curves from SLS and DLS are more or less parallel over the whole range of concentrations measured. This shows that the hydrodynamic correlation length indeed depends on concentration in the same way as the static correlation length, but they are not equal. The difference between the values is approximately a factor of 3. Roughly the same factor was found for the ratio between the static and hydrodynamic radius of gyration for dilute solutions of monodisperse stiff chains.[45]

4.4.2. Slow Mode. As can be seen from Figure 7, the decay rate constant associated with the slow mode does not depend significantly on the scattering angle. Therefore, it can be concluded that the slow mode is not caused by the diffusive motion of large aggregates or domains, as this would lead to a relaxation time proportional to q^2. The average of the measured values at different q is taken as Γ_{slow}, and the reciprocal of this equals τ_{slow}. The concentration dependence of τ_{slow} is shown in Figure 9 for solutions with and without chain stoppers.

The fact that the slow mode only appears above the overlap concentration and that there is no significant q dependence suggest that it might be related to the viscoelastic relaxation time of the solutions, as mentioned in section 2.3. However, there is a large difference between the relaxation times obtained from the DLS measurements and from rheometry. The vis-

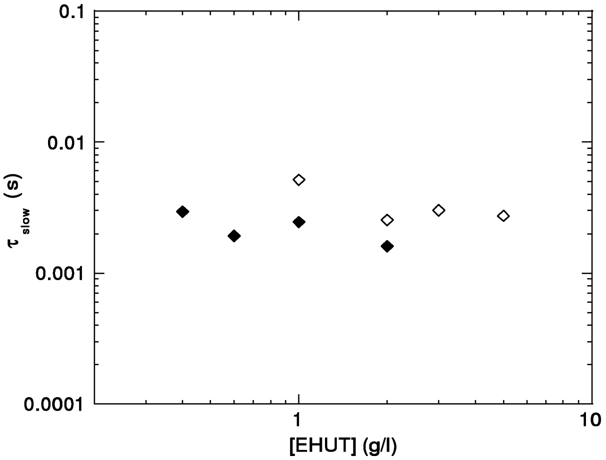

Figure 9. Decay time τ_{slow} of the slow mode as a function of EHUT concentration for solutions without chain stoppers (◆) and for solutions with $x = 0.015$ (◇).

coelastic relaxation time τ_0 (from rheometry) has a value of a few seconds,[17] whereas τ_{slow} (from DLS) of the same solution is only a few milliseconds (Figure 9). In experiments with other polymers and also with wormlike micelles, a much closer agreement between these values was reported.[46−49]

The large difference found in the present experiments could be related to the rigidity of the chains or to the fact that for EHUT several stress relaxation mechanisms (e.g., reptation and breaking of chains) occur on the same time scale.[17] But it is perhaps more realistic to assume that the slow decay time is not the result of coupling of concentration fluctuations to viscoelastic relaxation and is therefore not (directly) related to τ_0. More experiments are needed in order to find a conclusive answer.

5. Concluding Remarks

In supramolecular polymer solutions, the number-average degree of polymerization $\langle N \rangle$ is a function of the concentration c of bifunctional monomers: $\langle N \rangle \sim c^{0.5}$. The addition of a mole fraction x of monofunctional chain stoppers to the solution causes a decrease in $\langle N \rangle$. Within a certain range of concentrations and stopper fractions, $\langle N \rangle$ is expected to be proportional to $1/x$ and independent of c. For the system of bifunctional monomer EHUT and chain stopper DBUT in cyclohexane, vapor pressure osmometry and static and dynamic light scattering were performed on solutions with and without chain stoppers.

From osmotic pressure measurements, $\langle N \rangle$ is indeed found to be independent of monomer concentration and proportional to $1/x$ for the studied range of concentrations and stopper fractions. Results also indicate that DBUT forms small aggregates, thereby decreasing its effectiveness as a chain stopper.

The static correlation length in EHUT solutions without chain stoppers as measured with SLS has a maximum at the overlap concentration. From the overlap concentration and the scaling of the correlation length in dilute solutions, the association constant of EHUT in cyclohexane was estimated to be of the order of 10^9 M^{-1}, in agreement with results from previous experiments. The concentration dependence of the correlation length indicates that the persistence length of the chains is at least 250 nm. In the presence of a fixed fraction x of chain stoppers, there is a plateau in the correlation length above a certain monomer concentration, showing that the chain length is only determined by x and independent of monomer concentration under these conditions. Furthermore, the overlap concentration in the presence of chain stoppers is increased due to the decreased chain length.

Dynamic light scattering is used to measure the hydrodynamic correlation length. It scales in the same way as the static correlation length and is of the same order of magnitude, in agreement with theoretical predictions. For solutions above the overlap concentration, the distribution of decay times shows a second, slow mode. The behavior of the slow decay time shows qualitative agreement with the terminal viscoelastic relaxation time measured previously with rheometry, but the latter is substantially longer. It is unclear if the slow mode is related to viscoelasticity or which other physical process causes it.

Acknowledgment. L. Bouteiller is kindly thanked for generously donating samples of EHUT and DBUT.

Supporting Information Available: Correlation functions as measured by DLS for solutions below and above the overlap concentration and the corresponding spectra of relaxation times. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lehn, J.-M. In *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.
(2) Zimmerman, N.; Moore, J. S.; Zimmerman, S. C. *Chem. Ind.* **1998**, *15*, 604−610.
(3) Moore, J. S. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 4, 108−116.
(4) *Supramolecular Polymers*, 2nd ed.; Ciferri, A., Ed.; Marcel Dekker: New York, 2005.
(5) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.
(6) Bosman, A. W.; Brunsveld, L.; Folmer, B. J. B.; Sijbesma, R. P.; Meijer, E. W. *Macromol. Symp.* **2003**, *201*, 143−154.
(7) Lange, R. F. M.; van Gurp, M.; Meijer, E. W. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 3657−3670.
(8) Ten Cate, A. T.; Sijbesma, R. P. *Macromol. Rapid Commun.* **2002**, *23*, 1094−1112.
(9) Colombani, O.; Barioz, C.; Bouteiller, L.; Chanéac, C.; Fompérie, L.; Lortie, F.; Montès, H. *Macromolecules* **2005**, *38*, 1752−1759.
(10) Keizer, H. M.; Sijbesma, R. P.; Jansen, J. F. G. A.; Pasternack, G.; Meijer, E. W. *Macromolecules* **2003**, *36*, 5602−5606.
(11) Kiyonaka, S.; Sugiyasu, K.; Shinkai, S.; Hamachi, I. *J. Am. Chem. Soc.* **2002**, *124*, 10954−10955.
(12) Zhou, S.-L.; Matsumoto, S.; Tian, H.-D.; Yamane, H.; Ojida, A.; Kiyonaka, S.; Hamachi, I. *Chem.*—*Eur. J.* **2005**, *11*, 1130−1136.
(13) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.
(14) Sherrington, D. C.; Taskinen, K. A. *Chem. Soc. Rev.* **2001**, *30*, 83−93.
(15) Sijbesma, R. P.; Meijer, E. W. *Chem. Commun.* **2003**, 5−16.
(16) Armstrong, G.; Buggy, M. *J. Mater. Sci.* **2005**, *40*, 547−559.
(17) Knoben, W.; Besseling, N. A. M.; Bouteiller, L.; Cohen Stuart, M. A. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2390−2398.
(18) Lortie, F.; Boileau, S.; Bouteiller, L.; Chassenieux, C.; Lauprêtre, F. *Macromolecules* **2005**, *38*, 5283−5287.
(19) Cates, M. E.; Candau, S. J. *J. Phys.: Condens. Matter* **1990**, *2*, 6869−6892.
(20) Lequeux, F. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 341−344.
(21) Walker, L. M. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 451−456.
(22) Hassan, P. A.; Narayanan, J.; Manohar, C. *Curr. Sci. India* **2001**, *80*, 980−989.
(23) Boileau, S.; Bouteiller, L.; Lauprêtre, F.; Lortie, F. *New J. Chem.* **2000**, *24*, 845−848.
(24) Lortie, F.; Boileau, S.; Bouteiller, L.; Chassenieux, C.; Demé, B.; Ducouret, G.; Jalabert, M.; Lauprêtre, F.; Terech, P. *Langmuir* **2002**, *18*, 7218−7222.
(25) Simic, V.; Bouteiller, L.; Jalabert, M. *J. Am. Chem. Soc.* **2003**, *125*, 13148−13154.
(26) Arnaud, A.; Bouteiller, L. *Langmuir* **2004**, *20*, 6858−6863.
(27) Van der Gucht, J.; Besseling, N. A. M.; Knoben, W.; Bouteiller, L.; Cohen Stuart, M. A. *Phys. Rev. E* **2003**, *67*, 051106.
(28) Bouteiller, L.; Colombani, O.; Lortie, F.; Terech, P. *J. Am. Chem. Soc.* **2005**, *127*, 8893−8898.
(29) Miyauchi, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2005**, *127*, 2984−2989.

(30) Hasegawa, Y.; Miyauchi, M.; Takashima, Y.; Yamaguychi, H.; Harada, A. *Macromolecules* **2005**, *38*, 3724−3730.
(31) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *78*, 1877−1885.
(32) Flory, P. J. *Principles of Polymer Chemistry;* Cornell University Press: Ithaca, NY, 1964.
(33) *Light Scattering: Principles and Development*; Brown, W., Ed.; Clarendon Press: Oxford, 1996.
(34) Oberthür, R. C. *Makromol. Chem.* **1978**, *179*, 2693−2706.
(35) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(36) Fleer, G. J.; Skvortsov, A. M.; Tuinier, R. *Macromolecules* **2003**, *36*, 7857−7872.
(37) Van der Gucht, J.; Besseling, N. A. M.; Fleer; G. J. *Macromolecules* **2004**, *37*, 3026−3036.
(38) Buhler, E.; Rinaudo, M. *Macromolecules* **2000**, *33*, 2098−2106.
(39) Brown, W.; Nicolai, T. *Colloid Polym. Sci.* **1990**, *268*, 977−990.
(40) Brochard, F.; de Gennes; P. G. *Macromolecules* **1977**, *10*, 1157−1161.
(41) Semenov, A. N. *Physica A* **1990**, *166*, 263−287.
(42) Doi, M.; Onuki, A. *J. Phys. II* **1992**, *2*, 1631−1656.
(43) Provencher, S. W. *Makromol. Chem.* **1980**, *180*, 201−209.
(44) Bouteiller, L., personal communication.
(45) Burchard, W. *Makromol. Chem., Macromol. Symp.* **1988**, *18*, 1−35.
(46) Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760−1770.
(47) Koike, A.; Yamamura, T.; Nemoto, N. *Colloid Polym. Sci.* **1994**, *272*, 955−961.
(48) Nemoto, N.; Kuwahara, M.; Yao, M.-L.; Osaki, K. *Langmuir* **1995**, *11*, 30−36.
(49) Buhler, E.; Munch, J. P.; Candau, S. J. *J. Phys. II* **1995**, 765−787.

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