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Anions as efficient chain stoppers for hydrogen bonded supramolecular polymers

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Abstract: The chain length of hydrogen-bonded supramolecular polymers, and thus their rheological properties, can be controlled by the presence of so-called chain stoppers: those monofunctional monomers are able to interact with the monomers and to break the polymer chains. In this paper we show that the use of anions, strong hydrogen bond competitors, instead of precisely designed complementary units is a very simple approach to tune the rheology of hydrogen-bonded supramolecular polymers. Bisurea-based supramolecular polymer EHUT has been shown previously to self-assemble through hydrogen bonding into high molecular weight structures. All the anions tested were able to break EHUT chains, resulting in a dramatic drop of the viscosity of the solutions, and were found to be more efficient than the previously described organic stopper DBUT. A careful study of the

rheological properties of EHUT solutions in the presence of TBAH_2PO_4 showed that the presence of this anion does not modify the nature of the EHUT supramolecular assembly. For a molar fraction of stopper of only 10^{-5} , the viscosity of EHUT solutions decreases by a factor of ten, due to the formation of shorter supramolecular assemblies.

1. Introduction

Supramolecular polymers are linear chains of low molar mass monomers held together by reversible and highly directional non-covalent interactions.¹⁻³ Because of their macromolecular architecture, they can display polymer-like rheological or mechanical properties. The fact that non-covalent interactions are involved means that there is a constant dynamic equilibrium between monomer and polymer formation. We are particularly interested in hydrogen-bond mediated assemblies, as this interaction is highly selective, directional, and with controlled affinity due to the specifically designed hydrogen bond donor and acceptor functionalities.

The chain length of a supramolecular polymer depends on the strength of the association between the monomers, which is highly dependent on their concentration, the temperature, the solvent, i.e., environmental factors, but also on the presence of additives. Chain-stoppers are monofunctional monomers able to interact with the monomers and thus to break the polymer chains. They can be introduced in order to reduce the length of the supramolecular polymer^{4,5} (and thus reduce the viscosity of the solution), but also in order to block the concentration dependence of the supramolecular polymers.⁶⁻⁸ Chain stoppers can also be exploited to decorate the chain-ends in a dynamic fashion, with particular functional groups or labels.^{9,10} The effectiveness of these applications directly depends on the efficiency of the chain-stopper: the interaction between chain-stopper and monomer has to be at least as strong as the interaction between monomers. Consequently, all chain stoppers for hydrogen-bonded supramolecular polymers which are described in the literature are organic compounds bearing an associating unit with the same hydrogen bonded pattern as the monomer.³ Instead of using

precisely designed complementary units, another approach would involve the use of ionic compounds, which are known to be strong hydrogen bond competitors. Surprisingly, such an approach of using simple ionic species instead of carefully designed chain stoppers has never been evaluated before. Their easy availability, solubility in several solvents, and diversity should make ions promising and simple additives for the modulation of supramolecular polymer properties. To test this idea, bisurea-based supramolecular polymer EHUT (Figure 1, insert) has been chosen. This system has been shown previously to self-assemble through hydrogen bonding into high molecular weight structures.¹¹⁻¹³ Ureas are very well known to bind anions (by hydrogen bonding with the N-H groups), and have been used for the detection of many anionic species.¹⁴⁻¹⁶ Moreover, the use of ureidopyrimidinone hydrogen-bonded supramolecular assembly as fluoride anions sensor was reported.¹⁷ The disruption of H-bonding in a gel containing urea or oxalamide moieties was also studied in the presence of various anions.¹⁸⁻²³ We thus thought that anions would be able to reversibly cap chain-ends of supramolecular polymers based on bis-urea monomers.

In this paper we report the influence of several anions on the viscosity of EHUT solutions. The first part of this study is a screening of the efficiency of several ions. The second part is a more careful rheological characterization of the most efficient chain stopper.

2. Experimental Section

The synthesis of EHUT¹³ and DBUT⁶ was previously reported. Solvents and anionic species were used as received. The tetrabutylammonium salts were obtained from the following suppliers: fluoride (trihydrate, 99%, Acros), chloride (97%, Fluka), bromide (99%, Fluka), iodide (98%, Aldrich), dihydrogenphosphate (99%, Fluka), hydrogensulfate (97%, Fluka), hexafluorophosphate (99%, Fluka). Hygroscopic salts were stored under argon atmosphere. Solutions were prepared under stirring at room temperature, at least 1 day prior to use.

Viscometry

Measurements of EHUT solutions in chloroform were performed at $25 \pm 0.1^\circ\text{C}$ with a Cannon-Manning semi-microcapillary viscometer. The measurements were repeated 3 times. Measurements of EHUT solutions in toluene were performed at $25 \pm 0.1^\circ\text{C}$ with an automatic Anton-Paar AMVn viscometer (capillary internal diameter 1.8 mm ; ball diameter 1.5 mm). The measurements were performed with an angle of 20° , and repeated 6 times. Measurements of EHUT solutions in trimethylbenzene (TMB) could not be performed, as most of the anionic species were not soluble in this solvent even in the presence of EHUT.

Rheology

Tert-butylbenzene (TBB) was preferred to toluene because it is less volatile, and thus avoids problems of evaporation during the experiments. Dodecane, which was used in previous studies,^{24,25} could not be used either because of the insolubility of the anions in this solvent. Measurements were performed on a stress-controlled rheometer Haake RS 600 equipped with cone and plate geometry (diameter, 35 mm; angle, 2 deg.), at 20°C . The protocol for each sample was the following: first, the sample was submitted to a stress sweep at 1 Hz in order to determine the viscoelastic regime, before reaching the non-linear regime the stress sweep was stopped in order to preserve the sample. The stress sweep was followed by a frequency sweep covering a pulsation (ω) range from 0.001 to 100 rad/s. The loss (G'') and elastic (G') moduli were always measured in the linear viscoelastic regime. The experiment was performed at different EHUT concentrations (2 to 11 $\text{g}\cdot\text{L}^{-1}$, i.e., 4.6 to 25.5 mM). The presence of water in the TBB was shown to modify the relaxation time of the system. However, the presence of water has no influence on the value of G_0 (see Supporting Information). As the presence of water in the different anion containing samples was difficult to avoid, the differences observed for τ_c and η_0 were difficult to control, and we were only able to discuss the concentration dependence of G_0 .

3. Results and discussion

Efficiency of several anions as chain-stoppers

Since EHUT is capable of assembling in two distinct high molecular weight structures, respectively thin filaments and tubes,²⁵⁻²⁷ depending on the experimental conditions, we explored the influence of anions on both structures. Chloroform has been previously reported to favor the thin filament structure of EHUT aggregates, while the tubular structure is predominant in toluene.²⁶ Tetrabutylammonium was chosen as counter-cation of the different anions in order to improve the solubility of the salts in organic solvents. The potential chain stoppers have been tested by measuring the drop in viscosity of EHUT solutions after addition of 10 mol. % of stopper. Chosen anions were compared to DBUT (Figure 1, insert), which was previously reported to be a chain-stopper of EHUT.⁶ Some anions (nitrate and tetraphenylborate) could not be tested in toluene because of their low solubility, even in the presence of EHUT. Most of the others could be solubilized only after addition of EHUT, which evidences their interaction with the bis-urea moieties.

All the anions are efficient chain-stoppers, as they all dramatically reduce the viscosity of EHUT solutions (Figure 1). Moreover, they are all more efficient than the organic stopper DBUT. In chloroform, we found the following scale for the different anions:



In toluene, the ranking is very similar: $\text{F}^- \sim \text{HSO}_4^- > \text{H}_2\text{PO}_4^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{PF}_6^- > \text{DBUT}$

In both solvents the most efficient anions are H_2PO_4^- and F^- , which can be explained by their significant Brønsted and Lewis basicities, respectively, and thus their strong interactions with urea N-H moieties. The efficiency of the different anions as chain-stoppers is globally in good agreement with their basicity scale.^{28,29} These experiments show that anions can be used

as efficient and versatile chain stoppers for EHUT supramolecular polymer, either in its thin filament or tube structure.

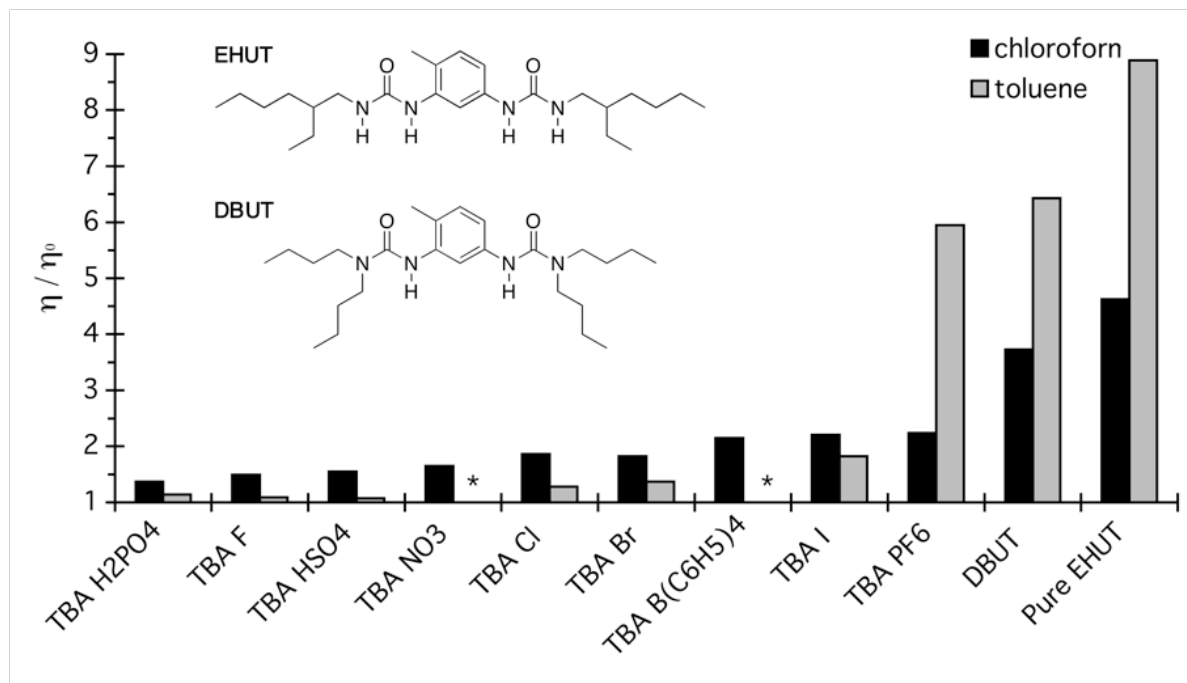


Figure 1: Relative viscosity of EHUT solutions in the presence of 10 % (mol/mol) of chain stopper (0.01M in chloroform (black) or toluene (grey), 25°C). Insert: structures of EHUT and DBUT. The stars indicate incomplete dissolution of the anion in the toluene solution, and therefore the absence of measurement.

Rheological properties of EHUT solutions in the presence of H₂PO₄⁻

We chose for the rheological experiments H₂PO₄⁻ as chain stopper, which was found to be one of the most efficient anions. EHUT presents a very rich and complex rheological behavior in several organic solvents.^{8,24,25,30} The solvent used for these studies was *tert*-butylbenzene (TBB). In this solvent EHUT self-assembles into tubes at concentrations above 1 mM, leading to viscoelastic solutions.²⁷ TBB was preferred to toluene because it is less volatile, and thus avoids problems of evaporation during the experiments.

First of all, the rheological behavior of EHUT without chain stopper was investigated. Figure S2 shows the storage modulus G' (the elastic component) and the loss modulus G'' (the

viscous component) as a function of the angular frequency ω for a solution of EHUT in TBB at 2 gL⁻¹ (4.6 mM). Our results confirm the viscoelastic nature of the EHUT solution in TBB, and are in good agreement with the previous observations in similar solvents (dodecane, cyclohexane). The analogy with the behavior of wormlike micelles has been previously described.^{8,24,30,31} At low frequencies, the mechanical response is dominated by the loss modulus, and the system displays a viscous behavior; in this region, the complex viscosity η^* is constant. Moreover, at low frequencies experimental data can be fitted with the Maxwell model. At a critical frequency ω_c , G' equals G'' , and the coordinates of the crossing point (G_c and ω_c) between the curves defines the plateau modulus $G_0 = 2G_c$ and the characteristic relaxation time $\tau_c = 2\pi / \omega_c$. At higher frequencies, the storage modulus is predominant and reaches a plateau value; deviations from the Maxwell model occurs for G'' . Previous studies in dodecane or cyclohexane showed that concentrated EHUT solutions present a Maxwellian behaviour at low frequency.^{8,24,30} If the breaking of the chains is fast compared to the reptation time, a single relaxation time governs the stress relaxation. At higher frequencies deviations from Maxwell behavior occur, because other relaxation mechanisms play a role. Moreover, it appeared that the plateau modulus G_0 , the zero-shear viscosity η_0 and the terminal relaxation time τ_c presented a concentration dependence in agreement with a scission/recombination process, and thus with the presence of ‘living’ polymer chains. For EHUT solutions, deviation from Maxwellian dynamics occurs at relatively low frequency compared to several fast-breaking wormlike micellar systems, which often remain Maxwellian at frequencies well beyond $1 / \tau_c$.^{32,33} This indicates that the breaking of the chains is not much faster than the reptation time, and that the system cannot be considered to be in the fast-breaking limit.

The experiment was then performed at different concentrations (2 to 11 gL⁻¹, i.e., 4.6 to 25.5 mM) to determine the concentration dependence of G_0 . The power law obtained ($G_0 \sim$

$c^{1.8}$) for EHUT in TBB is similar to those previously reported for EHUT in dodecane ($G_0 \sim c^{2.26}$)²⁴ or in cyclohexane ($G_0 \sim c^{1.8}$)³⁴. These values were interpreted within the framework of the Cates model for living polymers as an indication that the chains are semiflexible.^{8,35}

We then investigated the effect of the addition of chain stopper. Figure 2 represents the storage modulus G' and the loss modulus G'' as a function of the angular frequency ω for solutions of EHUT in TBB at 10.8 gL^{-1} (25 mM) with increasing molar fractions of chain stopper ($x = 8.8 \cdot 10^{-6}$ to $8.8 \cdot 10^{-5}$).

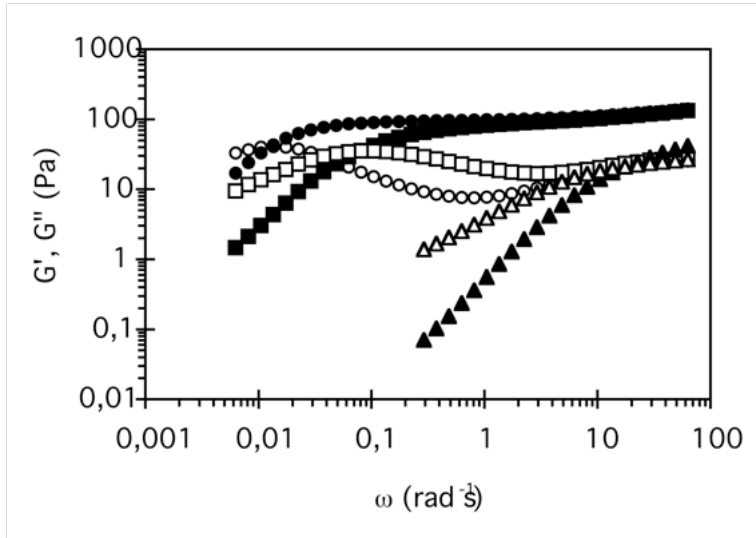


Figure 2: G' (full symbols) and G'' (open symbols) versus ω for solutions of EHUT in TBB at 10.8 gL^{-1} (25 mM) with various molar fractions of chain stopper TBAH_2PO_4 (pure EHUT, circles; $x = 8.8 \cdot 10^{-6}$, squares; $x = 8.8 \cdot 10^{-5}$, triangles). $T = 20^\circ \text{ C}$, $\sigma = 1 \text{ Pa}$.

The plateau modulus G_0 is constant when the molar fraction of stopper increases. In contrast, the critical frequency ω_c increases, which means that the characteristic relaxation time τ_c decreases. These observations show that the same kind of supramolecular structures remain in solution after the addition of the chain stopper, but the dynamic is accelerated. This result was confirmed by the study of the system in the non-linear regime. These experiments are not detailed here, but flow curves (i.e., steady-state shear stress σ as a function of applied

shear rate $\dot{\gamma}$) of EHUT solutions at 11 gL⁻¹ (25.5 mM) with various molar fractions of chain stopper can be found in Supporting Information. The behavior of EHUT solutions with increasing amounts of anionic stopper was found to be qualitatively similar to that already described for this system in the presence of DBUT organic stopper,³⁰ or when increasing the temperature.^{24,30}

On Figure 3 the viscosity of EHUT solutions in TBB with increasing amounts of chain stopper is plotted. The effect of the addition of H₂PO₄⁻ is visible for molar fractions as low as 10⁻⁵, which decreases the viscosity by a factor of ten. In comparison, the organic chain stopper DBUT was reported to have a critical molar fraction of 10⁻².³⁰ The anionic chain stopper H₂PO₄⁻ is then approximately a thousand times more efficient than DBUT. Such an effect on the viscosity of EHUT solutions is possible only if a significant fraction of polymer chain-ends are functionalized by the stopper. This means that the order of magnitude of the DP of the polymer chains was at least 10⁵ before the addition of stopper.³⁶ This value of DP is in good agreement with the value already reported for EHUT solutions in toluene, at the same temperature and concentration (DP = 4 · 10⁴).³⁷ TBB having a slightly lower polarity than toluene, the DP values of polymer chains in TBB are therefore expected to be larger than in toluene, but in the same range.

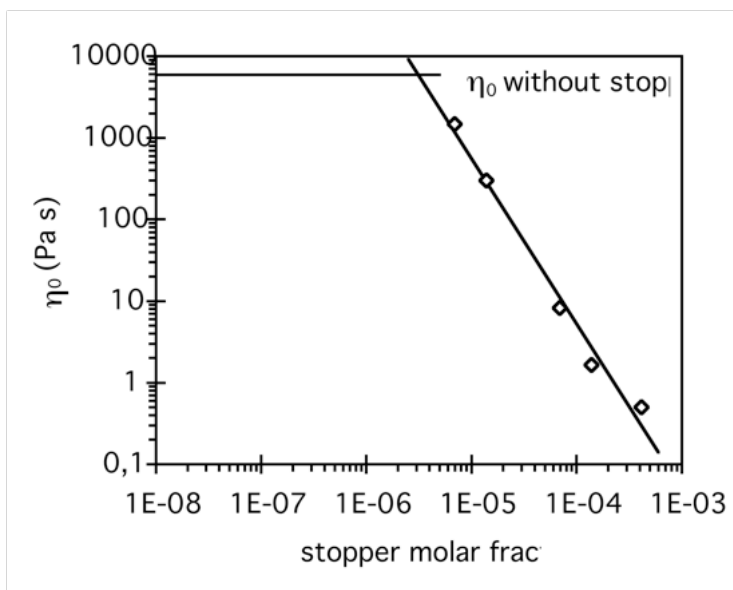


Figure 3: Zero shear viscosity (η_0) as a function of H_2PO_4^- chain stopper fraction for solutions of EHUT in TBB at 10.8 gL^{-1} (25 mM, 20°C).

Finally, the exponent for the concentration dependence of the plateau modulus was found to be identical ($G_0 \sim c^{1.8}$) for EHUT solutions without or in the presence of a definite molar fraction of chain-stopper H_2PO_4^- (with $x = 8.8 \cdot 10^{-6}$ and $x = 1.8 \cdot 10^{-5}$, Figure S3). These concentration-dependent experiments confirm that the addition of the anionic chain-stopper H_2PO_4^- does not modify the nature of the EHUT supramolecular assembly.

4. Conclusion

We showed in this study that anions could be used as efficient chain stoppers for bis-urea based supramolecular polymers. To our knowledge, the use of anions as chain-stoppers for supramolecular polymers has never been reported before. All the anions tested were able to break EHUT chains. H_2PO_4^- and F^- were found to be the best chain-stoppers for EHUT, either in its thin filament or tube structure. EHUT solutions with added anionic chain stoppers display a Maxwellian behavior, characteristic of a scission/recombination process, and thus of

the presence of ‘living’ polymer chains. The rheological behavior of EHUT solutions with increasing amounts of anionic stopper is qualitatively similar to that already described for this system in the presence of organic stopper.³⁰ Moreover, the presence of anions does not modify the nature of the EHUT supramolecular assembly. However, the phosphate anion is a thousand-fold more efficient than the previously described organic stopper DBUT, leading to a decrease in the viscosity of EHUT solutions by a factor of ten for a molar fraction of stopper of only 10^{-5} , due to the formation of shorter supramolecular assemblies. These results show that the use of simple ions is a viable route to control the rheology or functionalize the chain ends of hydrogen-bonded supramolecular polymers. This approach is potentially much simpler than the synthesis of specific organic chain stoppers.

Supporting Information Available: Additional rheology data, in particular the effect of water and flow curves of EHUT solutions with various molar fractions of chain stopper can be found in supplementary materials. This material is available free of charge via the internet at <http://pubs.acs.org>.

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36. The strong viscosity drop due to the addition of $2.5 \cdot 10^{-7}$ M of chain stopper means that the number of chains has been significantly increased. Moreover, the concentration of new chains formed by the addition of the chain stopper is at most equal to the concentration of added chain stopper (at least one chain stopper per chain). Then it means that the number of chains before addition of the chain stopper was not much larger than $2.5 \cdot 10^{-7}$ M, or in other words, that the DP was not much smaller than 10^6 .
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Table of Contents Graphic

Anions as efficient chain stoppers for hydrogen bonded supramolecular polymers

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