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Hydrophobically Modified Polymers Rheology and Molecular Associations

Leif Karlson



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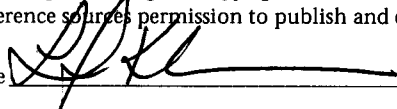
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Title and subtitle Hydrophobically Modified Polymers. Rheology and Molecular Associations		
Abstract Structure- property relationships and thickening mechanism in aqueous solution of two hydrophobically modified polymers (HM-P) with different architecture have been investigated. The two polymers, hydrophobically modified ethyl hydroxyethyl cellulose (HM-EHEC) and hydrophobically modified polyethylene glycol (HM-PEG), are commonly used as associative thickeners in the paint industry. The strength of the hydrophobic associations in an aqueous solution of a HM-P is very much influenced by the structure of the HM-P. Longer hydrophobic groups give stronger association and longer relaxation times resulting in a more elastic consistency to the solution. The thickening mechanisms of HM-EHEC and HM-PEG were studied by addition of cyclodextrin (CD). In an aqueous solution a CD molecule can form a complex with a hydrophobic molecule or part of a molecule provided that the hydrophobic group fits into the cavity of the cyclodextrin molecule. CD binds primarily to hydrophobic side- or end-groups of the polymer and not to hydrophobic segments of the polymer backbone. The addition of CD provides unique information about the thickening mechanism that can not be achieved by the addition of other substances that disconnect all types of hydrophobic associations, for example surfactants at high concentration. A remarkable observation is that in a HM-PEG solution of an intermediate concentration it is enough to terminate only a small fraction of the total amount of associative linkages to reduce the viscosity almost to the same level as for a solution of an unmodified PEG.		
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Contents

List of Papers	2
Chapter 1 Introduction	3
1.1 Hydrophobically modified polymers in paint	5
1.2 References Chapter 1	11
Chapter 2 Hydrophobically modified polymers	13
2.1 Structure and synthesis of hydrophobically modified polymers	14
2.1.1 HEUR thickeners	14
2.1.2 HM-EHEC	15
2.1.3 Comb HEUR thickeners	18
2.2 Hydrophobically modified polymers in aqueous solution	19
2.2.1 HM-PEG in aqueous solution	23
2.2.2 HM-EHEC in aqueous solution	26
2.2.3 Interaction between HM-Polymers and surfactants	28
2.2.4 Clouding	30
2.2.4.1 Cloud point of HM-PEG	32
2.2.4.2 Cloud point of HM-EHEC	33
2.3 References Chapter 2	34
Chapter 3 Inhibition of hydrophobic associations as a tool to study cross-linking mechanisms	37
3.1 Inhibition of hydrophobic interactions by changing solvent quality	38
3.2 Inhibition of hydrophobic interactions by addition of surfactant	40
3.3 Inhibition of hydrophobic interactions by addition of cyclodextrin	41
3.3.1 Structure and properties of cyclodextrin	42
3.3.2 Formation of inclusion complex between lipophilic guest molecules and cyclodextrin	43
3.3.3 Cyclodextrin and HM-Polymers	45
3.3.3.1 Cyclodextrin and HM-EHEC	46
3.3.3.2 Cyclodextrin and HM-PEG	49
3.4 References Chapter 3	55
Main conclusions	57
Popular summary (in Swedish)	58
Acknowledgements	61
List of commercially available hydrophobically modified polymers	62

List of Papers

- I **Rheology of an aqueous solution of an end-capped poly(ethylene glycol) polymer at high concentration**
Karlson, L.; Nilsson, S.; Thuresson, K. *Colloid Polym. Sci.* **1999**, *277*, 798-804.
- II **Clouding of a cationic hydrophobically associating comb polymer**
Thuresson, K.; Karlson, L.; Lindman, B. *Colloid and Surfaces A: Physicochem. Engin. Aspects* **2001**, *201*, 9-15
- III **Phase behavior and rheology in water and in model paint formulations thickened with HM-EHEC: influence of the chemical structure and the distribution of hydrophobic tails**
Karlson, L.; Joabsson, F.; Thuresson, K. *Carbohydrate Polymers* **2000**, *41*, 25-35.
- IV **A rheological investigation of the complex formation between hydrophobically modified ethyl (hydroxy ethyl) cellulose and cyclodextrin**
Karlson, L.; Thuresson, K.; Lindman, B. *Carbohydrate Polymers* **2002**, *50*, 219-226.
- V **Cyclodextrins in HM-PEG Solutions. Inhibition of Rheologically Active Polymer-Polymer Associations**
Karlson, L.; Thuresson, K.; Lindman, B. *Submitted*
- VI **Complex formed in the system hydrophobically modified polyethylene glycol / methylated α -cyclodextrin / water. An NMR diffusometry study**
Karlson, L.; Malmberg, C.; Thuresson, K.; Söderman O. *Submitted*

Chapter 1

Introduction

Aqueous solutions thickened with polymers are common in our daily life. Shampoo, for instance, is a water-based solution of surfactants that should have high viscosity, since a low viscosity would mean that it would flow between the fingers when you poured it out of the bottle. In cooking there are many examples of how water-soluble polymers are used for thickening. Starch from potatoes or corn can be used for thickening of a sauce and gelatin gives the jelly consistency to many desserts. Polymers are also used as thickener in many low fat products. Some pharmaceutical formulations are water-based systems that gain their flowing properties from polymers.

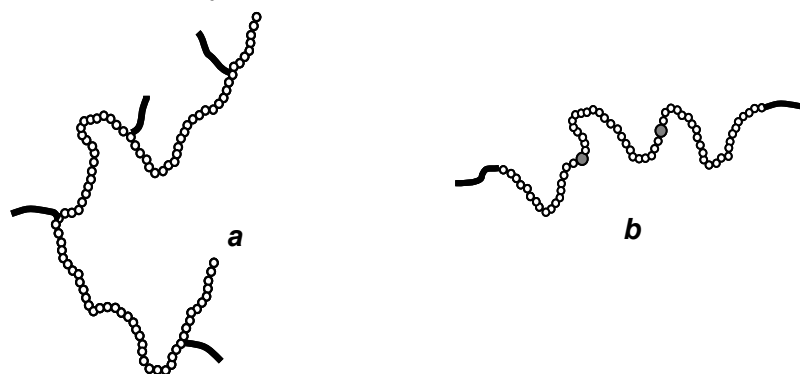
Water-borne paint is another example of an aqueous system that has to be thickened to behave in the way we want. In fact the use of Hydrophobically Modified Polymers (HM-P) in paint is the basis for this thesis and has therefore got a separate section (section 1.1 below).

The aim of this thesis is to provide useful knowledge for the development of new hydrophobically modified polymers with improved properties primarily for the paint application. In order to fulfill this goal the first part of the work is dealing with how hydrophobic modification influences the properties of the polymers in solution (Paper I, II, and III). In the second part of the thesis the thickening mechanisms of HM-polymers in aqueous systems have been investigated (Paper IV, V and VI).

The discussion in this thesis is based upon two types of HM-polymers, Hydrophobically Modified Ethyl Hydroxyethyl Cellulose (HM-EHEC) and Hydrophobically Modified Ethoxylated Urethane (HEUR). HM-EHEC is an example of a HM-polymer with a water-soluble backbone, and hydrophobic groups attached along the backbone (Figure 1.1.a). HM-EHEC has a relatively high molecular

weight (m_w) and the thickening mechanism of HM-EHEC may include contributions both from chain entanglement and associations between different hydrophobic parts of the molecule.

Figure 1.1. Schematic illustration of the structure of **a** HM-EHEC and **b** HEUR. White necklace represents hydrophilic monomers and the bold lines represent hydrophobic groups.



Hydrophobically modified Ethoxylated Urethane (HEUR) polymers have a water-soluble backbone with relatively low m_w and hydrophobic groups attached at both ends of the backbone (Figure 1.1.b). In a solution of a HEUR polymer the thickening effect relies mainly on hydrophobic associations and entanglements are expected to be of very small importance.

One way to obtain information about the thickening mechanisms of HM-polymers in aqueous systems is to synthesize both the HM-polymer as well as the unmodified version of the same polymer and study the difference in solution behavior. This has been the subject of numerous studies.¹⁻⁷

Another way to study the thickening mechanism is by addition of a third component capable of selectively inhibiting one or more of the mechanisms that contribute to the thickening effect. For instance it is well known that, depending on the concentration, addition of surfactant can either increase or decrease viscosity of a solution of a HM-polymer.^{1,8-23} At high surfactant concentrations associations between hydrophobic parts of the polymer chains are disrupted. However, this method is unselective and is expected to inhibit all types of hydrophobic interactions (including both interactions from polymer hydrophobic tails as well as from hydrophobic patches of the main chain). A much more selective method to disrupt only some types of hydrophobic interactions is offered by addition of

cyclodextrins, a group of cyclic substances with a hydrophobic cavity in an otherwise hydrophilic molecule.^{24,25} In an aqueous environment the hydrophobic cavity of the cyclodextrin can host a hydrophobic molecule or a hydrophobic part of a molecule provided that it fits into the geometry of the cavity. A hydrophobic group of a HM-polymer that has formed a complex with a cyclodextrin molecule does not take part in the thickening mechanism.²⁶⁻²⁸ In this way it is possible to distinguish between the contributions to the hydrophobic associations by different parts of the HM-polymer.

1.1 Hydrophobically modified polymers in paint

This section will summarize some properties that are important for the paint industry and that can be controlled by the choice of thickener. A water borne paint consists of several ingredients and an example of a simple recipe for a water borne paint can be found in Table 1.1. Even though the thickener constitutes less than 1 % of the paint it is a very important ingredient since it influences many of the paint properties.

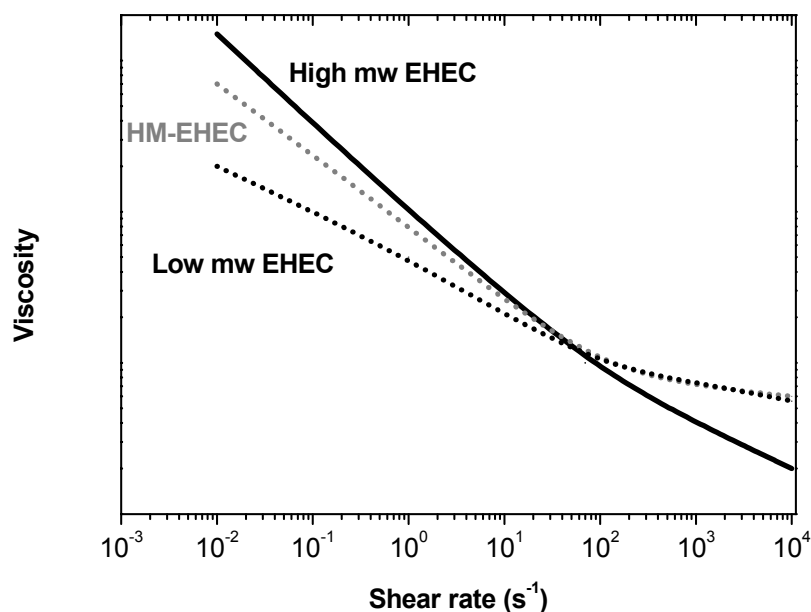


Figure 1.2. Schematic viscosity profile for three model paints formulated with 0.45 %w/w high mw EHEC, 0.9 %w/w low mw EHEC, or 0.45 %w/w HM-EHEC respectively

Table 1.1. Example of a simple recipe for a water borne paint

Ingredient	(wt%)
Water	242
Thickener	1
Defoamer	5
Dispersing Agent	6
Preservative	1
Filler	110
Pigment	180
Binder (Latex)	455



Figure 1.3. Example of a panel from a leveling test. In this test the surface should be as smooth as possible.

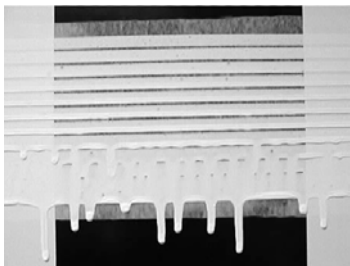


Figure 1.4. Example of a panel from a sagging test. In this test the thickness of the paint film gradually increases from the top line to the bottom line. The sagging is measured as the film thickness where the paint starts to sag.

Normally water borne paint is formulated aiming at a certain Stomer viscosity. The Stomer viscosity corresponds to the viscosity at a shear rate ($10 - 100 \text{ s}^{-1}$) similar to the shear rate when stirring the paint in the can, or when pouring the paint. A correct Stomer viscosity is also important when loading the brush since a too low viscosity means that the paint will drip off the brush. The Stomer viscosity is adjusted by the amount of the polymer. For this reason the polymer concentration may vary widely and depends on the thickening efficiency of the polymer. Conventional thickeners, with a high molecular weight, (m_w) normally have a high thickening efficiency and give the required Stomer viscosity with a small addition of the thickener. However at the same time they give a strongly shear thinning behavior (Figure 1.2). This means that the low shear viscosity ($<2 \text{ s}^{-1}$) is high whereas the high shear viscosity ($>10^4 \text{ s}^{-1}$) is low. Many important paint properties are influenced by the shear profile. The low shear viscosity ($<2 \text{ s}^{-1}$) is important since it influences the sedimentation of particles in the can. It also influences the flow properties in the paint film after application of the paint. The leveling is improved by a decreased low shear viscosity (Figure 1.3) but on the other hand the newly applied paint film will start to sag on a vertical surface if the low shear viscosity is too low (Figure 1.4). The high shear viscosity influences the thickness of the paint film during roller application, since the shear rate in the thin layer between the surface and the roller is high ($>10^4 \text{ s}^{-1}$). Increased high shear viscosity means that the applied paint film is thicker resulting in better hiding properties (Figure 1.5) and thereby reducing the number of coats required. The main advantage of a conventional high molecular weight thickener is the low concentration that is needed and thereby they become cost effective. However, the strong shear thinning behavior that results in bad leveling and bad hiding power is a problem.

A less pronounced shear thinning viscosity profile can be obtained by using a thickener with a lower m_w and compared to the high m_w thickeners the leveling and the hiding power are improved. A disadvantage with this approach is that in order to achieve a required

Stormer viscosity a much higher polymer concentration is required, which generates a higher cost.

In general hydrophobically modified polymers combine high thickening efficiency with a less marked shear thinning viscosity profile. By varying the length of the hydrophobic groups and molecular weight of the polymer the viscosity / shear profile can be controlled. The associative thickeners have a strong thickening effect and give the required Stormer viscosity already at low addition levels. Actually in most cases their thickening efficiency is comparable to what is achieved with non-associative thickeners with a high mw . Both high shear and low shear viscosities are influenced. Compared to the type of conventional thickeners with high mw the HM-P:s have a much less shear thinning profile (Figure 1.2).

In the paint industry, HM-P:s are often referred to as associative thickeners. Here hydrophobically modified cellulose derivatives (HM-HEC and HM-EHEC), HEURs and HM-acrylates are the most commonly used associative thickeners. There are also important differences within the group of associative thickeners (Figure 1.6). The HEUR thickeners together with low mw HM-acrylates give the lowest tendency to shear thinning. They have the lowest low shear viscosity and they retain a virtually constant viscosity up to high shear rates where the viscosity suddenly drops off. HM-HEC, HM-EHEC and high mw HM-acrylates show rheology profiles that are in-between the HEUR thickeners and the non-associative thickeners. The less shear-thinning behavior of the associative thickeners results in improved hiding power and leveling properties.

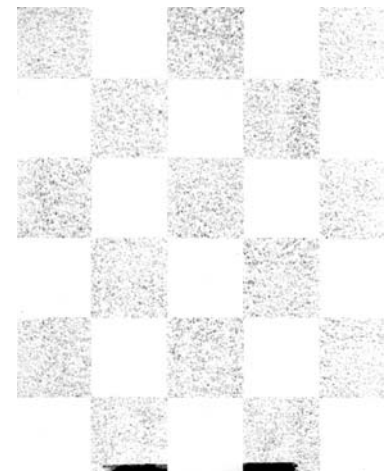


Figure 1.5. Result from a hiding power test

Figure 1.6. Viscosity, η , (filled symbols) and complex viscosity, η^* , (open symbols) as a function of shear rate for three different HM-polymers

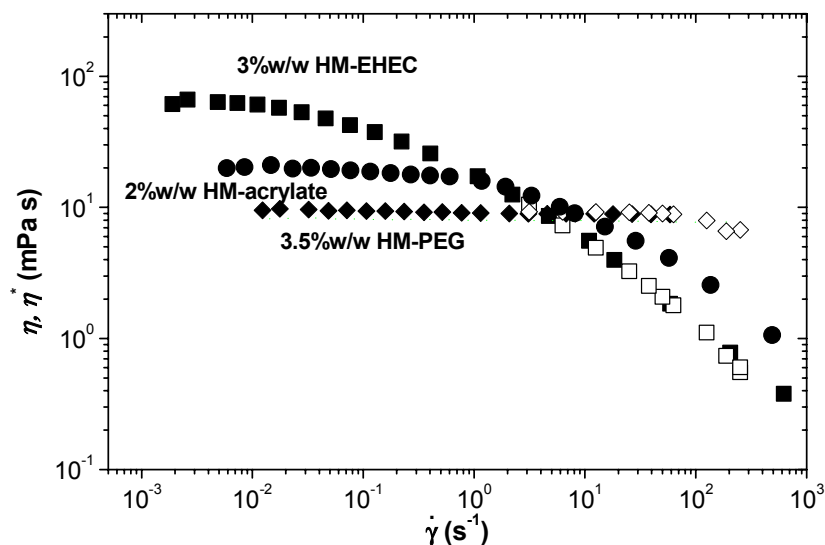


Figure 1.7. Results of spatter tests with two paints thickened with HM-polymer (upper) and conventional thickener (lower).

One important advantage of HM-polymers is that the spatter from the roller when the paint is rolled on a wall or a ceiling is drastically reduced when the paint is thickened with a HM-polymer compared to when a conventional thickener is used (Figure 1.7). Improved gloss is another important parameter that is influenced by the use of an associative thickener compared to when non-associative ones are used. In light of this the associative thickeners seem to be a good choice.

It has, however, to be recognized that with the associative thickeners the properties of the paint may change quite dramatically. The major problem for associative thickeners is their sensitivity to variations in coating composition. Changes in type of latex, surfactant or co-solvent concentration, or addition of colorants, can have a pronounced effect on paint viscosity. This is due to the thickening mechanism of the associative thickeners that to a large extent is dependent on associations between the hydrophobic groups on the thickener, since these also associate with other ingredients in the paint. The associations are very sensitive to variations in paint composition. For example the monomer compositions of latex particles, type of surfactant, and the surfactant concentration all have a large impact on the paint viscosity. The non-associative thickeners rely mainly on chain entanglements which are much less influenced by changes in paint composition.

As will be discussed in section 2.2.3 the addition of surfactants can either increase or decrease the viscosity of the associative thickener solution depending on the surfactant concentration in the solution and what type of surfactant is used. One problem is that the surfactant content and the type of surfactants included in the paint are often unknown, even to the paint producer. A large fraction of the surfactant content in the paint originates from the synthesis of the latex, and details behind the commercial production of latex are well-hidden secrets. During the production of paint more surfactant is often added as a wetting agent for the pigment or to improve the stability of the paint. Normally the surfactant concentration in the paint is on a level above where the viscosity maximum occurs, as exemplified in Figure 1.8. Additional surfactant therefore causes a reduction of the viscosity. Paints formulated with HEUR thickeners are in general the most sensitive to addition of surfactant since associations of hydrophobic groups are the only effective thickening mechanism for the HEUR thickeners in the concentration range used in paint formulations. Hydrophobically modified acrylates and cellulose derivatives are less sensitive since they obtain a considerable part of their thickening power from chain entanglements.

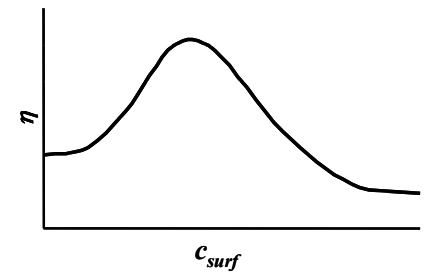


Figure 1.8. Schematic illustration of the viscosity, η , of a HM-polymer solution as a function of surfactant concentration, c_{surf} .

Colorants used for tinting the paint contain high amounts of surfactant. The additions of colorants can have a strong impact on viscosity. In the worst case a paint can lose as much Stormer viscosity as 30 to 40 KU (30 to 40%) when tinted to a deep-tone color.

Color acceptance is another parameter of great importance to the paint industry. A tinted paint can show variations in shade depending on the magnitude of the shear during the application of the paint. Bad color acceptance appears as brush-marks, which make the surface look striped, when the paint is applied with varying shear force from the paintbrush. In the paint industry the color acceptance is evaluated in a 'rub-out test' in which one part of the surface of the painted chart is rubbed while another part is untouched (Figure 1.9). The color acceptance is judged by means of differences in shade between the two parts (Figure 1.10). The color acceptance problem becomes

more pronounced when hydrophobic pigments are used. The color acceptance has been attributed to phase separation caused by the polymer but the problem is not fully understood.

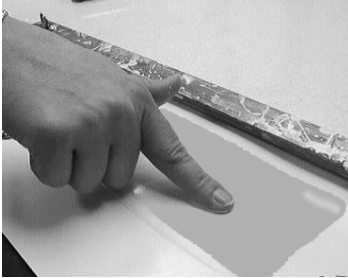
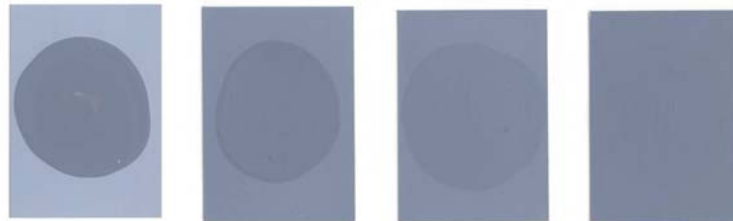


Figure 1.9. The "rub-out-test" for color acceptance

When formulated in paints the associative thickeners are often used in combinations, both with other associative thickeners and / or non-associative thickeners. One example is when a HEUR thickener is added to a paint thickened with a high mw non-associative thickener to increase the high-shear viscosity.²⁹ But formulating a paint with several different thickeners can be full of uncertainties since mixtures of polymers often phase separate. The phenomenon with phase separation is even more pronounced if one of the polymers is hydrophobically modified and the other is not.³⁰ This is probably the cause of some of the flocculation problems that occur when associative thickeners are tested in paint formulations that contain more than one thickener.

Figure 1.10. Results of color acceptance test. For a good result the paint should be as little affected as possible by the "rub-out test". The far right panel shows a good result whereas the far left panel shows a relatively poor result.



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Chapter 2

Hydrophobically modified polymers

Hydrophobically modified water-soluble polymers (HM-P) are polymers with hydrophobic groups chemically attached to a hydrophilic polymer backbone. They are often also referred to as associative polymers or associative thickeners. The first studies on HM-P were made by Strauss and coworkers more than 50 years ago. They are described in a review article.¹ The work was done with hydrophobically modified polyelectrolytes. The idea behind the studies was that since soap molecules associate to form micelles in aqueous solution also surfactants chemically grafted to a water soluble polymer would form micelles. That indeed was what they found. In addition they found that the “polysoaps” gave unique solubilizing effects and a surprisingly large increase of the viscosity to an aqueous solution. These two effects of HM-P are widely utilized.

The largest application for HM-P is as rheology modifier in water borne paint. Landoll and his coworkers described the first associative thickeners for water borne paint in the eighties.²⁻⁴ They worked with hydrophobically modified (hydroxyethyl) cellulose (HM-HEC) which is a nonionic cellulose ether. Hydrophobically modified ethyl hydroxyethyl cellulose (HM-EHEC), hydrophobically modified ethoxylated urethanes (HEUR) and hydrophobically modified polyacrylates (HM-PA) are other examples of associative thickeners that have been developed for the paint application. The hydrophobically modified cellulose derivatives are, still after 20 years, the largest class of associative thickeners for water borne paint.

2.1 Structure and synthesis of hydrophobically modified polymers

Depending on how the hydrophobic groups are situated in the molecule HM-polymers can be divided into two categories. The first has the hydrophobic groups attached at the ends of the polymer backbone and they are referred to as hydrophobically end-capped polymers (Figure 1.1.b). The second category has the hydrophobic groups grafted along the polymer backbone. These are called comb like HM-polymers (Figure 1.1.a).

2.1.1 HEUR thickeners

Hydrophobically modified ethoxylated urethanes (HEURs) are examples of end-capped water-soluble polymers. They consist of a hydrophilic polyethylene glycol (PEG) segment in the middle with hydrophobic groups attached at both ends. Compared to other polymers used as thickeners the molecular weight (m_w) of a HEUR thickener is normally relatively low, 15,000 to 50,000.⁵ Often the molecular weight distribution of a commercially available HEUR is broad due to the synthesis procedure used for the manufacture of the polymer. Polyethylene glycol of low molecular weight, e.g. 6000, is reacted with a slight excess of diisocyanate. The resulting polymer chains with isocyanate groups at both ends are then reacted to a long chain alcohol (Figure 2.1.a).⁵ A way to synthesize a HEUR with a more narrow distribution is offered by the reaction of an alcohol ethoxylate to diisocyanate (Figure 2.1.b). The HEUR-polymer from this process has a polydispersity index (weight average molecular weight (M_w) / number average molecular weight (M_n)) of about 1.1. This type of HEUR has been used in the present studies and is referred to as “Triblock” or HM-PEG. It should be mentioned that even though the present polymers have a low polydispersity index, model HEUR thickeners with even lower polydispersity index ($M_w/M_n = 1.01$) have been synthesized.⁶ Here the starting material was PEG, with narrow molecular weight distribution, which was reacted to alkyl p-toluene sulphonate at both ends.

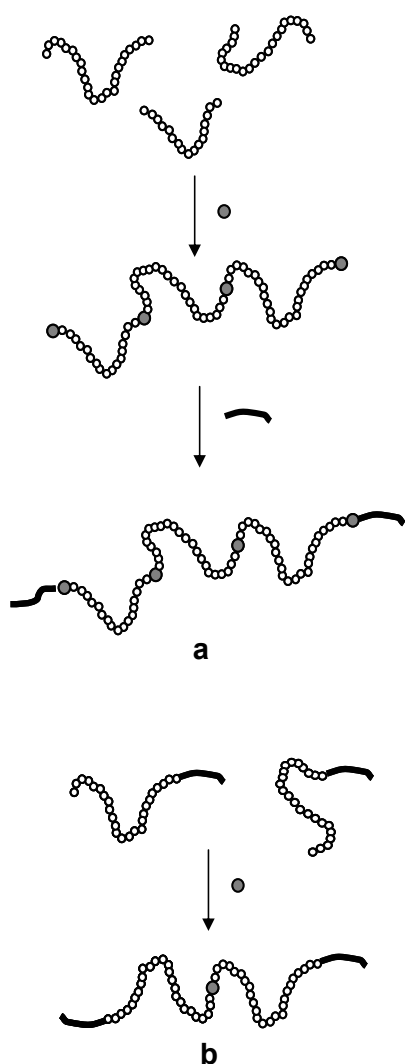


Figure 2.1. Schematic picture of the synthesis of HEUR-polymers. The necklaces represent polyethylene glycol chains. Bold lines represent hydrophobic end groups and filled balls represent diisocyanate groups or diurethane linkages.

2.1.2 Hydrophobically modified EHEC

The base for ethyl hydroxyethyl cellulose (EHEC) and for hydrophobically modified EHEC (HM-EHEC) is cellulose, one of the most common natural polymers. Cellulose is a polysaccharide built up from 1,4-anhydroglucose units (AHG). The cellulose molecules in native cellulose form large crystalline regions, and therefore cellulose is insoluble in water. To make cellulose soluble it has to be modified to split up the crystalline packing. The process for making cellulose derivatives starts with an alkalization step. The alkalization has two purposes. Firstly by introducing charges into the molecules, the cellulose swells. This makes individual cellulose chains available for the chemical reaction. Secondly it also acts as catalyzation for the modification reactions. During the synthesis of EHEC the alkalized cellulose is modified by a reaction with ethylene oxide and then with ethyl chloride. Both reaction steps are performed at elevated temperature. Since both ethylene oxide and ethyl chloride are volatile compounds a pressurized reaction vessel is required.

Each AHG has three hydroxyl groups available for reaction. The reaction of one ethylene oxide molecule to one of the hydroxyl groups on an AHG results in a new hydroxyl group that is also reactive (Figure 2.2). The newly formed hydroxyl group has a reactivity comparable to that of the hydroxyl groups on the AHG which means that besides the reaction of the hydroxyl groups on the AHG there is also a chain growth reaction going on. The outcome is that short oligo (ethylene oxide) chains are formed.⁷ The molar substitution of ethylene oxide (MS_{EO}) is the average total number of ethylene oxide groups per AHG (Figure 2.3). For practical reasons the upper limit for MS_{EO} is about 2.5 to 3 since the efficiency of the reaction decreases dramatically above that level due to side reactions. Up to this point about 70 % of the ethylene oxide reacts with cellulose to form ether groups. The remainder forms glycols by reaction with water, or ethers of glycols by reaction with ethyl chloride.⁷

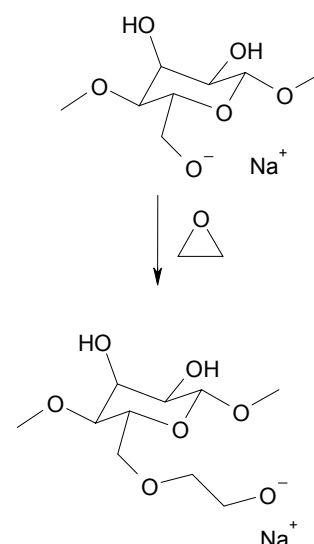



Figure 2.2. The reaction of ethylene oxide to alkalized cellulose.

Figure 2.3. Possible structure element of an

EHEC molecule.

 represents a hydroxyethyl group. Ethyl groups are represented by bold lines.

In this example

$$MS_{EO} = (4+3+0+2+1)/5 = 2$$

$$DS_{ethyl} = (2+2+0+1+1)/5 = 0.8$$

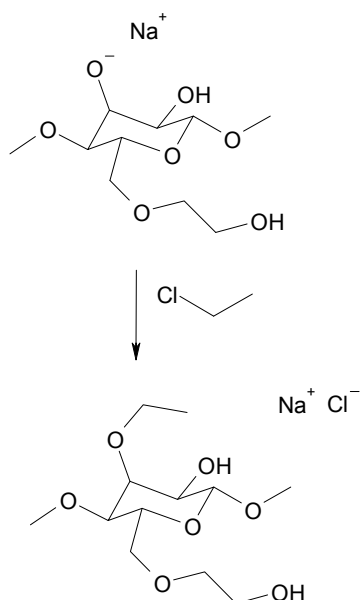
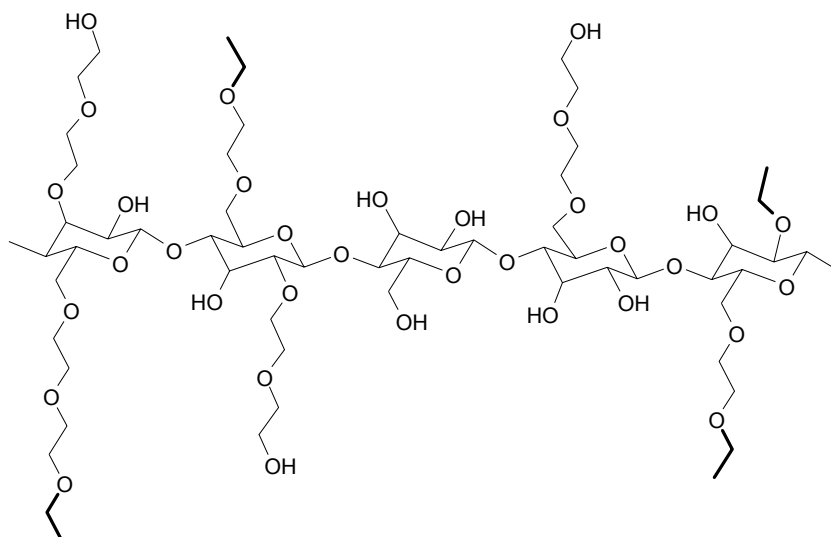


Figure 2.4. The reaction of ethyl chloride to alkalized hydroxyethyl cellulose.

In contrast to the reaction with ethylene oxide where new hydroxyl groups form, the ethyl chloride reaction consumes sodium hydroxide and the hydroxyl group that has reacted to an ethyl chloride is terminated for further reaction (Figure 2.4). The number of hydroxyl groups per AHG that has reacted is expressed as degree of substitution (DS) and the figure ranges from 0 to 3. Practically the upper limit for DS_{ethyl} is about 1 since the water solubility of the final EHEC polymer decreases dramatically with increasing DS_{ethyl} .⁸ Of course the reaction does not give a perfectly homogeneous substituent-distribution over all AHGs. It is likely that the synthesis process for EHEC gives an uneven distribution of the hydroxyethyl and ethyl substituents. Therefore the numbers of DS_{ethyl} and MS_{EO} are average values. Segments of anhydroglucose units that have a high degree of ethyl substituents are slightly hydrophobic. In water solution the ethyl groups can give rise to hydrophobic interactions provided that they are situated in long sequences. This is an origin of the backbone associations and the reason why the unmodified EHEC is surface active and shows an associative behavior.^{9,10} The situation is similar for other short hydrophobic groups (C_6 or shorter) where an anhydroglucose unit bearing hydrophobic groups can be seen as a hydrophobic monomer unit of a copolymer. The cellulose backbone is relatively stiff and the associations from the short hydrophobic groups are too weak to force the polymer backbone to bend into a loop where the hydrophobic groups could intra-aggregate. Instead the result is inter-associations between hydrophobic segments on

different polymer chains, which can be detected as increased solution viscosity.^{3,11,12} If the polymer concentration or the flexibility of the polymer backbone changes the situation may be different.

By reacting aliphatic groups to the EHEC polymer a hydrophobically modified EHEC is obtained (Figure 2.5). The HM-EHEC obtained in this way is an example of a comb like HM-P. It has hydrophobic groups grafted along the water-soluble EHEC backbone. Only a small amount of hydrophobic groups are required to totally change the properties of the polymer.^{3,11} In our study less than 1% of the glucose units of the EHEC backbone have hydrophobic groups attached and this was enough to substantially change the solution properties as compared to those of the corresponding unmodified EHEC.

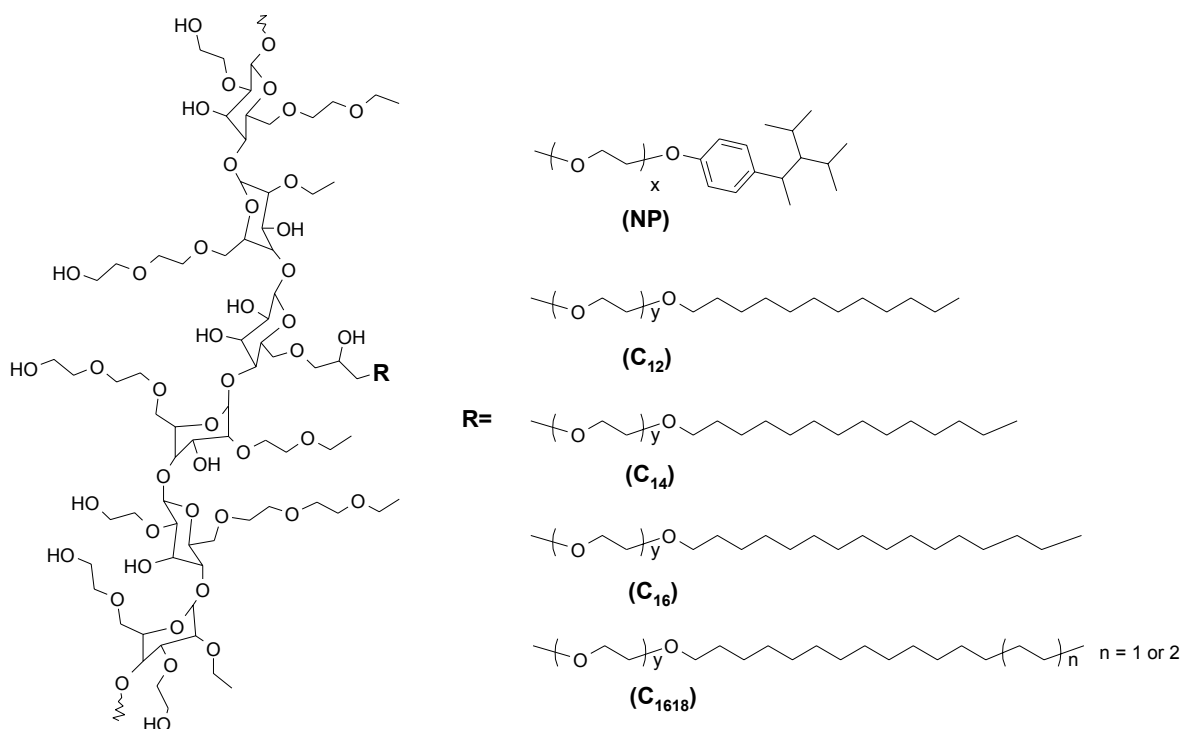


Figure 2.5. Possible structure segment of the HM-EHEC:s studied in paper III.

R=(NP) for HM-(NP)-EHEC, R=(C₁₂) for HM-(C₁₂)-EHEC, R=(C₁₄) for HM-(C₁₄)-EHEC, R=(C₁₆) for HM-(C₁₆)-EHEC, and R= a blend of (C₁₆) and (C₁₈) for HM-(C₁₆₁₈)-EHEC

In paper III we have investigated the effect of various chain lengths of the hydrophobic groups. Alkyl groups varying from C₁₂ to C₁₆ or a blend of C₁₆ and C₁₈ or nonylphenol have been used. The HM-EHEC polymers that were obtained with these hydrophobic groups are referred to as HM-(C₁₂)-EHEC, HM-(C₁₄)-EHEC, HM-(C₁₆)-EHEC, HM-(C₁₆₋₁₈)-EHEC and HM-(NP)-EHEC, respectively.

The values of MS_{EO} , DS_{ethyl} , and $MS_{hydrophobe}$ for the HM-EHEC:s included in this study are presented in table 2.1.2

Table 2.1.2. The substitution degrees of ethylene oxide (MS_{EO}), ethyl (DS_{ethyl}), and hydrophobic tails ($MS_{hydrophobe}$) of each of the polymer samples given as average numbers of substituents per repeating glucose unit. Independent repeated determinations render an uncertainty in the numerical values of about 5%. The abbreviations given in the 'Hydrophobic group' column refers to the unmodified parent EHEC (0), HM-EHEC modified with, nonylphenol groups (NP), C₁₂ groups (C₁₂), C₁₄ groups (C₁₄), C₁₆ groups (C₁₆), and with C₁₆ – C₁₈ groups (C₁₆₁₈). The values for concentration of hydrophobic groups in the solution, $c_{hydrophobe}$, are calculated for 1% w/w solutions.

Hydrophobic group	MS_{EO}	DS_{ethyl}	$MS_{hydrophobe}$	mw/AHG (g/mol)	$c_{hydrophobe}$ (mmolal)
0	2.1	0.8	0	277.0	0
NP	2.1	0.8	0.008	279.7	0.28
C ₁₂	2.1	0.8	0.0086	279.9	
C ₁₄	2.1	0.8	0.0082	280.0	0.29
C ₁₆	2.1	0.8	0.0081	280.1	
C ₁₆₁₈	2.1	0.8	0.009	280.9	

2.1.3 Comb HEUR

The comb-like HEUR polymers have some interesting properties but they have not yet received much attention. This may be because they are complicated to synthesize in a well-characterized way.⁵ One possible route to synthesize them is offered by reacting ethoxylated monoalkylamines (EMAA) to a diisocyanate (Figure 2.6). It is a step growth reaction and by changing the reaction conditions the molecular weight of the polymer is varied. The molecule consists of a number of EMMA-units, each bearing one hydrophobic group and one amine function. This means that the polymer at low pH has a

positive net charge, located close to each hydrophobic group. Two comb HEUR:s with this structure were studied in Paper II.

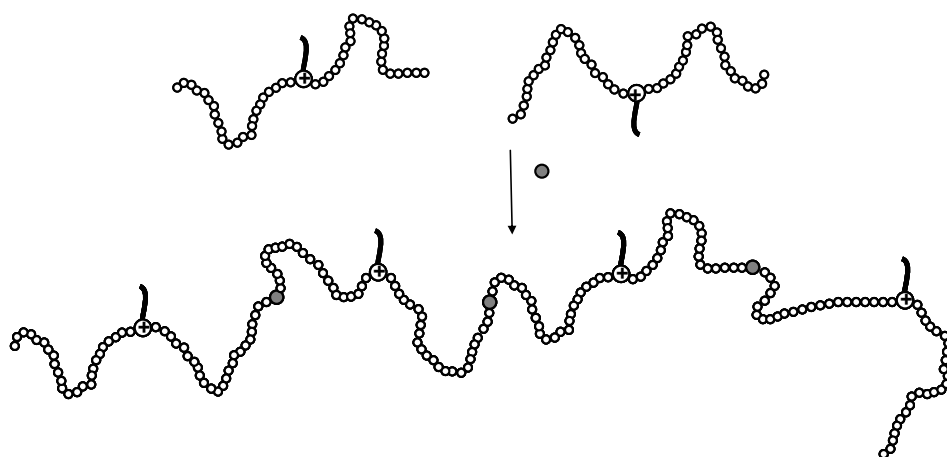


Figure 2.6. Schematic illustration of the synthesis process for comb HEUR polymers. White necklace represents a sequence of hydrophilic monomers and the bold lines represent the hydrophobic groups. Filled balls represent diisocyanate monomers and balls with a plus sign represent protonated amino groups.

Their alkyl group is in both cases a C₁₂ chain, while the length of the polyethylene oxide spacer between the alkyl groups has been varied. The polyethylene oxide chains on the alkylamine contain on average 51 or 74 units, respectively. The M_w was estimated at about 25 000 for both of the polymers, indicating that they on average consist of roughly four units. The way they have been produced suggests that they should have a wide distribution in molecular weight and it was found that M_w/M_n was about 2.2 for both these polymers.

2.2 Hydrophobically modified polymers in aqueous solution

The behavior of the polymer molecules in solution depends to a large extent on the polymer concentration, c . To describe how the behavior of a HM-P varies with the polymer concentration it is easier to start the discussion on the behavior of the unmodified parent polymer. The polymer concentration interval can be divided into three different regimes, the dilute, the semidilute and the concentrated regime (Figure 2.7).¹³ In the dilute regime c is low and the mean centrum to centrum distance between the polymer coils is larger than the mean radius of a single polymer coil denoted as the radius of gyration, R_g .

The individual polymer chains are expected to move independently of each other in the solution.

Figure 2.7. Polymer concentration intervals dilute solution ($c < c^*$), semidilute solution ($c > c^*$) and concentrated solution ($c \gg c^*$)

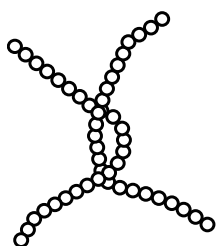
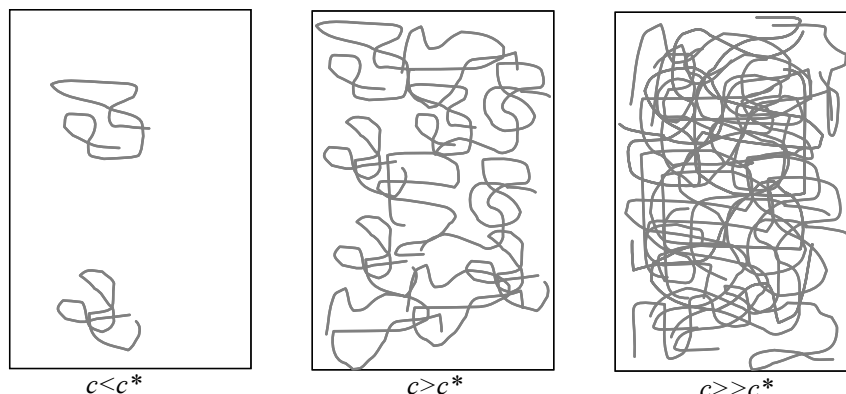


Figure 2.8. Entanglements of polymer molecules.

In the semidilute regime R_g is larger than the mean distance between the coils. Since the total volume of all polymer coils exceeds the volume of the solution the polymer coils are forced to overlap and the concentration where this occurs is often referred to as the overlap concentration and is denoted c^* . The chain of one polymer molecule will entangle with other polymer molecules (Figure 2.8). The result is entanglements of the polymer chains and the formation of a transient polymer network which can be detected as a dramatic increase in the viscosity of the polymer solution. The overlap concentration can roughly be estimated as the reciprocal of the intrinsic viscosity, $c^* \approx 1/[\eta]$, and is for most polymers in the region 0.1 to 10 %w/w. The importance of the entanglements to the dynamics increases with increasing polymer concentration. The chemical structure of the polymer is very important for the coil size and thereby for the behavior of the polymer in solution. An increased mw results in larger coils and more chain entanglements, which can be seen as increased viscosity.¹³ The coil size is also influenced by the chemical composition of the backbone. A polyethylene glycol based polymer is more flexible than a polymer with a cellulose origin and has therefore a smaller coil size.¹⁴ The repulsion between the ionic groups makes the polymer backbone of a polyelectrolyte stiff. The electrostatic repulsion is strongly influenced by the ionic strength in the solution. The fact that the viscosity of a polyacrylate solution decreases when

salt is added can be explained by reduced coil sizes due to increased flexibility of the polymer chains.^{11,15}

In the concentrated region the system consists of highly entangled polymer chains. The behavior of the polymer molecules is more similar to that in a polymer melt than to the behavior in the polymer network in the semidilute solution.

Describing the behavior of hydrophobically modified polymers it is important to notice that according to the properties of the unmodified analogue the HM-P molecule also has the possibility to associate with other HM-P molecules. The association of the hydrophobic groups is very similar to self-association of surfactants. To minimize the contact between water and hydrophobic groups the hydrophobic groups associate to each other and form a water-poor domain, which is the interior of a micelle. The surface of the micelle is covered by the hydrophilic polymer backbone. In aqueous solution the hydrophobic groups of a hydrophobically modified polymer associate with each other resulting in physical bonds holding different parts of the polymer chains together (Figure 2.9). In a snapshot picture it can be described as a cross-linked gel but in contrast to covalent bonds the physical bonds are reversible. They break and reform continuously. A hydrophobic group on one polymer molecule can either take part of an intra-molecular association, i.e. it interacts with another hydrophobic group on the same polymer chain, or interacts with a hydrophobic group on another polymer molecule (inter-molecular association) (Figure 2.10). At low concentrations the probability for interaction between different HM-polymer molecules is small. Intra-aggregation results in a reduced coil size.^{1,16-20} The intrinsic viscosity for a HM-P is therefore often lower than for the unmodified analogue of the same polymer. Upon increasing polymer concentration inter-molecular associations become more important and the three-dimensional network is formed. This gives rise to a dramatic increase of the solution viscosity. The onset concentration of inter-molecular association is often well below the overlap concentration, c^* , of the corresponding unmodified polymer with the same molecular weight.^{21,22}

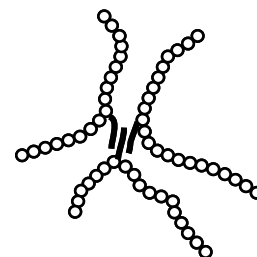


Figure 2.9. Associations of hydrophobic groups of HM-polymer molecules.

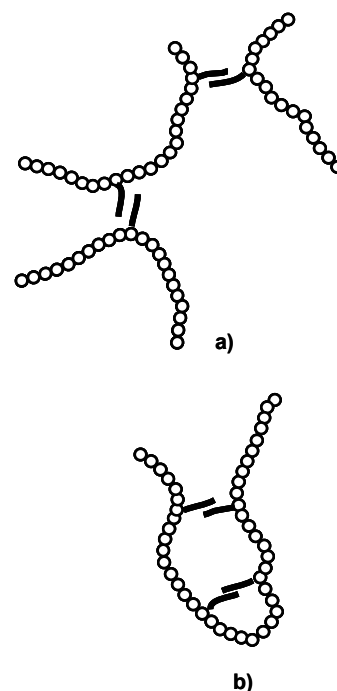


Figure 2.10. Illustrations of inter-molecular association (a) and intra-molecular associations (b).

The strength of the hydrophobic interactions between polymer chains is influenced by:

- the length of the hydrophobic groups
- the molar substitution of hydrophobic groups ($MS_{hydrophobe}$)
- the distribution of the hydrophobic groups along the polymer backbone.

Longer hydrophobic groups give an increased residence time of a hydrophobic group within the micelle and also increased lifetime of the aggregates of hydrophobic groups. This was illustrated by Sau et al, who found that if two identical polymers are substituted with different hydrophobic groups the polymer with the longer hydrophobic groups gives the highest viscosity to a water solution.⁴ The results in section 2.2.2 also illustrate this.

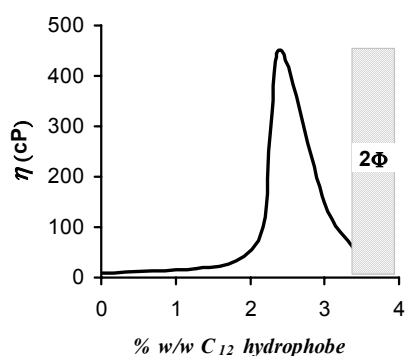


Figure 2.11. Brookfield viscosity of 2% w/w solution of HM-HEC substituted with 1,2-epoxydodecane as a function of degree of hydrophobic modification. Reproduced from ³

The influence of $MS_{hydrophobe}$ on the solution viscosity can be divided into three different regions: At low $MS_{hydrophobe}$ there is a positive correlation between $MS_{hydrophobe}$ and viscosity. This can be explained by an increased number of inter-connection points holding the polymer network together. Depending on the structure of the polymer backbone and the length of the hydrophobic groups there is a viscosity maximum somewhere typically in the range of 1 to 5 hydrophobic groups per 100 repeating units of the polymer backbone if a comb like polymer is investigated (Figure 2.11).³ The reason for the decrease is a conversion of intermolecular associations to intramolecular association and a gradual degradation of the polymer network.^{20,23} At even higher $MS_{hydrophobe}$ the HM-P becomes insoluble in water.

The synthesis of HM-P is often performed in a two-phase system where one phase is an aqueous solution of the polymer backbone and the other phase consists of the hydrophobic reagent. This gives rise to a HM-P with a more or less blocky distribution of the hydrophobic groups along the polymer backbone. Depending on the type of hydrophobic groups and the length of the hydrophobic segments the more blocky structure can favor the formation either of

intra-associations or inter-associations (Figure 2.10). Provided that the hydrophobic associations are strong they can force the polymer backbone to adopt conformations that give rise to intra-molecular associations. Selb et al have shown that for HM-P with C₁₆-alkyl groups the viscosity of the polymer with the blocky structure can be several times less than that of the corresponding polymer with a more random distribution of the hydrophobic groups (compare to the right part of the diagram in Figure 2.11).^{23,24} This is in contrast to what is described in section 2.1.2 for short hydrophobic groups.

Hydrophobically modified ionic polymers like HM-PA are strongly influenced by the salt content in the solution. As mentioned above increasing salt concentration reduces the repulsion between ionic groups on the polymer backbone. At the same time the addition of salt makes the solvent more polar which promotes the hydrophobic associations (Figure 2.12). At low salt concentrations the increased interchain cross-linking predominates leading to a viscosity increase. At higher ionic strength the electrostatic effects prevail and a reduction in the viscosity occurs (Figure 2.12).^{15,25}

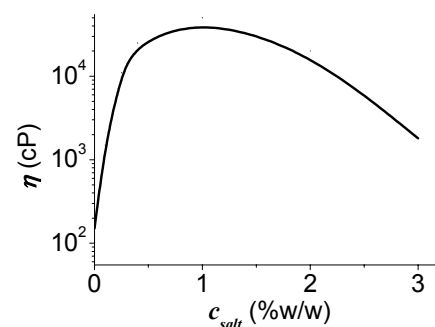


Figure 2.12. Viscosity as a function of NaCl concentration for 2% w/w solution of HM-polyacrylate substituted with C₁₈ hydrophobic groups (3% of the repeating units covered). Reproduced from¹¹

2.2.1 HM-PEG in aqueous solution

The commonly accepted mechanism for the association of the HEUR thickeners is somewhat different from the one for the comb like polymers described in the previous section (Figure 2.13).^{6,26-28} At very dilute conditions the HM-polymer molecules exist as free molecules (unimers) or as oligomers with low aggregation numbers.²⁷ With increasing polymer concentration the polymer molecules start to form small micelle-like structures with the hydrophobic parts of the thickener looping back into the micelle, forming flower-like structures. The onset of micelle formation generally occurs already at polymer concentrations far below the overlap concentration of the unmodified analogue of the polymer (c^*). The formation of micelles becomes more cooperative with increasing length of the hydrophobic groups.²⁸ The unfavorable entropy caused

by bending the hydrophilic backbone into a loop conformation opposes the micelle formation. Consequently the formation of flower micelles is favored by longer hydrophobic groups and by increased length of the PEO-spacer as can be seen as a decrease of the concentration where aggregation starts to occur. Fluorescence quenching techniques have been used to determine the average number of hydrophobic groups per micelle (N_R) on a variety of HEUR polymers.^{28,29,30,31} It was found that flower micelles are very uniform in size and contain in the range of 20 to 30 hydrophobic groups per micelle. Over a wide concentration range N_R is independent of the polymer concentration. N_R for HEUR polymers is considerably lower compared to the aggregation number for related surfactants forming spherical micelles, which is typically 60 to 80.¹³ This can probably be explained by the fact that the polymer backbones of HM-PEG are large head groups which limits the number of hydrophobic groups that can participate in the same micelle.

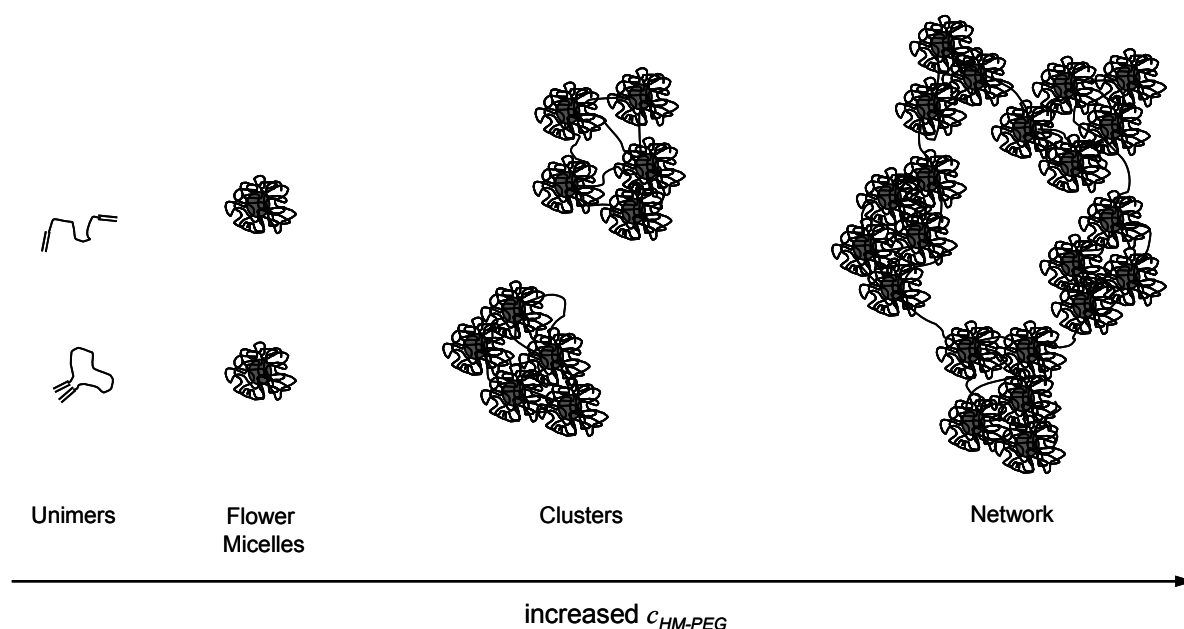


Figure 2.13. Schematic representation of the self-aggregation of HM-PEG as function of increasing c_{HM-PEG}

With increasing polymer concentration the average distance between the flower micelles becomes smaller and larger aggregates are formed. The flower micelles can be seen as building blocks for the formation of larger aggregates. Transient bridges consisting of HM-polymer molecules with one hydrophobic group in one micelle and the other end in a neighboring micelle are formed resulting in clusters of micelles. The driving force for this cross-linking is the lowering in free energy achieved by allowing some of the thickener molecules to attain more flexible conformations of the hydrophilic backbones with no strict need for looping back. In the case of long hydrophobic groups the aggregation into clusters starts at a concentration far below close packing of micelles. For the situation where the attraction forces are weaker (shorter hydrophobic groups) the aggregation starts at higher concentrations, but still below the concentration for close packing of micelles. Semenov et al predicted that these systems at concentrations below close-packed micelles would phase separate into one phase containing closely packed micelles and one phase impoverished in polymer.²² However, in our studies on aqueous solutions of HM-PEG with C_{16-18} hydrophobic groups (the structure is described in paper I) no macroscopic phase separation occurred at room temperature. Instead a microscopic phase separation has been suggested with polymer rich microdomains (clusters) in a diluted bulk phase.^{6,27,28} Contrary to the micelles, which have rather well defined aggregation numbers, it is reasonable that the clusters appear in a wide range of sizes and that the average cluster-size increases with increasing HM-PEG concentration.^{6,27,32} The polymer concentration inside the clusters differs from the average concentration in the solution. One indication for the solution being inhomogeneous is given by the phase behavior of triblock solutions which is further described in section 2.2.4.1.

Upon increasing polymer concentrations the distances between different clusters become smaller which gives the possibility for the polymer chains to more frequently connect micelles located in different clusters and a three-dimensional network that extends over macroscopic distances is formed. This can be detected as a dramatic increase of the solution viscosity. It occurs at a polymer concentration

where the solution is still likely to be very inhomogeneous with large concentration fluctuations. Due to the large concentration fluctuations the polymers that connect micelles located in different clusters and have to span polymer depleted regions are likely to be rare. In contrast the inter-micellar links within the clusters are much more numerous. All the physical bonds are temporary and the clusters continuously break and reform. Therefore the HM-P:s that are involved in forming bridges between the clusters at one moment can change to be an intra-micellar link at the next moment .

2.2.2 HM-EHEC in aqueous solution

In paper III we found that the hydrophobic group chain length had a dramatic effect on the low shear viscosity of aqueous solutions of HM-EHEC. The C₁₂-group only has a minor effect on the viscosity, and experiments with shorter hydrophobic groups (not presented) have shown that the hydrophobic groups should have at least 12 carbon atoms to have any noticeable effect on the viscosity. By increasing the length of the hydrophobic chains from C₁₂ to C₁₆ the viscosity increased two orders of magnitude (Figure 2.14). This is in good agreement with results from earlier studies.^{4,25,26} This effect is ascribed to the residence time of the hydrophobic chains in the “polymer micelles”, which increases for longer hydrophobic groups and results in slower motions of the polymer molecules and thereby a higher viscosity.^{26,33}

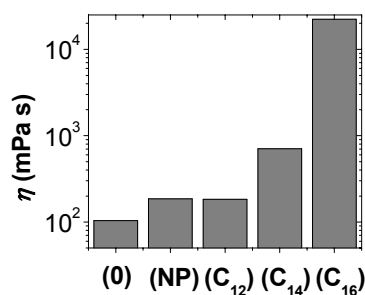


Figure 2.14. Viscosity of 1% w/w solutions of HM-EHEC with varying length of the hydrophobic groups. (0) represents unmodified EHEC

For grafted HM-P with low $MS_{hydrophobe}$, like HM-HEC and HM-EHEC, the average number of hydrophobic groups per micelle (N_R) is low. The low aggregation number is likely to result from the polymer chain being a very large head group. The relatively stiff backbone from cellulose ether prevents formation of loops and the consequence is that only a small number of hydrophobic groups can take part in the formation of each micelle. N_R for HM(NP)-EHEC and HM-HEC micelles have been determined to be about five to ten^{9,33} compared to 60 to 80 for surfactants forming spherical micelles¹³ and 20 to 30 for the more flexible HEUR thickeners. The consequence is that

rather poor micellar structures are formed with a high degree of contact between water and hydrophobic groups.

From what has been discussed above, it follows that there are at least three types of interpolymer crosslinks, that contribute to the formation of the three dimensional network of a HM-EHEC solution (Figure 2.15). Apart from chain entanglements and associations between hydrophobic side groups also associations of hydrophobic segments of the polymer backbone play an important role. The hydrophobic segments on the EHEC and HM-EHEC backbones have been ascribed to patches with high substitution density of ethyl groups, described in section 2.1.2.³⁴ Earlier when different HM-EHEC batches have been compared it has been assumed that since all studied HM-EHEC:s were synthesized according to the same process the substitution pattern should be similar and that the interactions of hydrophobic backbone segments contribute almost equally for all HM-EHEC:s. To give a clearer picture of the contribution from the different types of crosslinks it would be helpful to have methods to study the contributions separated from each other. This will be discussed in chapter 3.

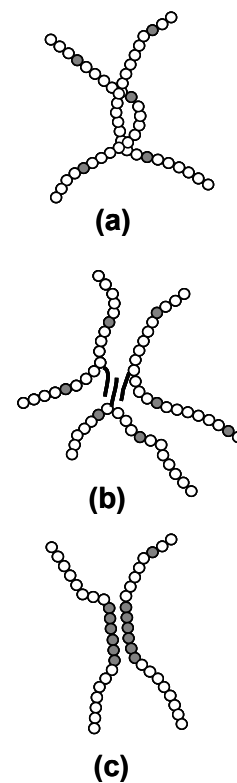
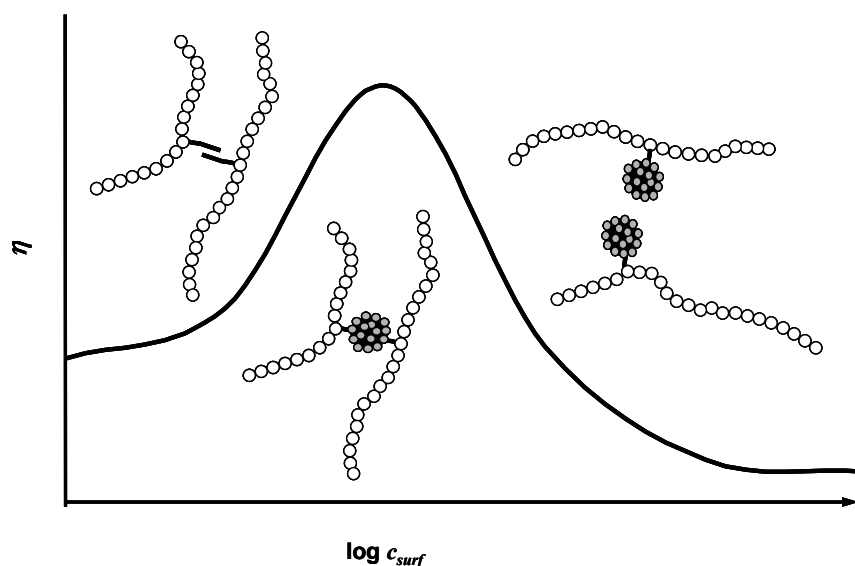


Figure 2.15. Interpolymeric cross-links in HM-EHEC solutions. **(a)** chain entanglements, **(b)** associations between hydrophobic side-chains and **(c)** associations between hydrophobic segments of the polymer backbone.

2.2.3 Interaction between hydrophobically modified polymers and surfactants

Figure 2.16. Schematic illustration of the influence of surfactant concentration on the viscosity of solutions of HM-polymers.



Hydrophobically modified polymers in aqueous solution interact strongly with surfactants leading to the formation of mixed micelles. At concentrations of HM-P corresponding to the semidilute regime of the unmodified parent polymer it is found that the viscosity passes via a pronounced maximum when the surfactant concentration is gradually increased (Figure 2.16).^{17,18,35-40} The degree of interaction is determined both by the structure of the surfactant and the nature of the polymer. As described in section 2.2.1 and 2.2.2 the micellar structures of HM-P normally have low aggregation numbers compared to surfactant micelles and the consequence is a quite large degree of contact between water and the hydrophobic groups. At low surfactant concentrations, already far below the *cmc* of the surfactant, the surfactant molecules are incorporated in the existing micelles from the HM-P. Incorporation of surfactant molecules into the micelles reduces the water hydrocarbon contact. This increases the activation energy for detachment of a hydrophobic group from the micelle thereby increasing the residence time of the hydrophobic groups within the micelles thus leading to stronger associations.^{9,40} The viscosity in an aqueous solution of a HM-P depends on the number of interconnecting links in the network and on the relaxation time. A

changed viscosity can be the result of a variation of either of these parameters, or both. For the end-modified polymers an increased number of active links has been observed^{29,41} while for hydrophobically modified cellulose ethers the effect of increased viscosity upon addition of surfactant is suggested to be caused mainly by increased relaxation times.^{9,33,42} Besides the increased viscosity the stronger association can also be detected as a dramatic shift to lower T_{Cp} (compare section 2.2.4.2).

At surfactant concentrations above the viscosity maximum the number of micelles in the solution increases. This results in an increased ratio between micelles and hydrophobic groups of the polymer. In this process the decreased viscosity is a consequence of the physical network losing some of its connectivity. At high surfactant concentrations where the number of micelles exceeds the number of polymer hydrophobic groups in the system there is only one polymer hydrophobic group in each micelle. At this stage the viscosity is independent of the surfactant concentration and has a value that is even lower than for the HM-P solution before addition of surfactant. How strong the effect is depends on the structure of the surfactant. Normally nonionic polymers interact more strongly with anionic surfactants than with nonionic or cationic surfactants. In line with this it has been found that anionic surfactants give the most pronounced viscosity increase and also the largest reduction of the viscosity at excess surfactant.³⁴

Hydrophobically modified polyelectrolytes, for instance HM-PA, interact strongly with oppositely charged surfactants. The interaction is caused by a combination of electrostatic attraction and hydrophobic forces. The strength of the hydrophobic associations increases with increasing length of the hydrophobic groups on the polyelectrolyte. With long hydrophobic groups the hydrophobic interactions can be strong enough to overcome the electrostatic repulsion between the polymer backbone and surfactants of the same charge resulting in a net attraction.^{36,43}

2.2.4 Clouding

For most substances the solubility increases with increasing temperature. This is not the case for EHEC and HEUR thickeners. They both belong to a family of polyethylene oxide containing substances that have a reversed relationship between solubility and temperature.⁴⁴ The solubility of these substances decreases with increasing temperature. At temperatures above a critical value a water solution containing any of these polymers phase separates into one polymer rich phase and one phase depleted in polymer. The phase separation can be detected by the scattering of light resulting in a cloudy appearance of the solution. The temperature where the solution first becomes hazy is referred to as the cloud point temperature, T_{Cp} . The process is reversible and decreasing the temperature below T_{Cp} results in a one-phase situation and a transparent solution. Many attempts to explain the reversed solubility phenomenon have been done. One reasonable explanation builds on conformational changes of the polymer molecules with changing temperature. The polyethylene oxide chain has a large number of possible conformations. The conformation with the lowest free energy in a polar environment (conformation **A** in Figure 2.17) has a low statistical weight. At low temperature the low energy conformation will dominate. Conformation **A** has a large dipole moment. With increasing temperature other conformations with higher energy but also with higher statistical weight will be more and more important. The higher energy conformations have a lower dipole moment and conformation **B** in Figure 2.17, for instance, has virtually no dipole moment. The consequence is that the polyethylene oxide chain becomes less and less polar with increasing temperature. This gives an increasing tendency to phase separation since water-polymer interactions become less favorable with increasing temperature.^{44,45}

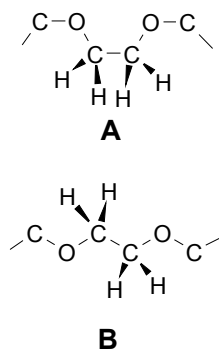


Figure 2.17. Different conformations of an ethylene oxide group. Conformation **A** has low energy and is more polar compared to conformation **B**.

Phase behavior studies give the possibility to study the influence of other substances on the interaction between the polymer chains. Addition of a third water soluble component can have a large impact on the T_{Cp} .⁴⁵ For instance most salts decrease the T_{Cp} (salting out) but some salts with large anions, e.g. I^- and SCN^- , have the opposite

effect (Figure 2.18). The addition of a salt that does not interact with the polymer molecules results in a more polar environment and thereby stronger hydrophobic interactions and increased tendency for phase separation. On the contrary the large polarizable anions I^- and SNC^- interact with the unpolar parts of the polymer molecules resulting in an increased entropic penalty of phase separation.

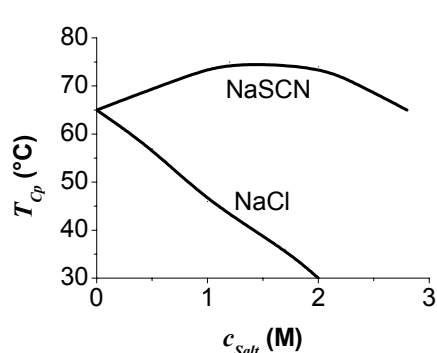


Figure 2.18. T_{Cp} as a function of salt concentration for 0.9% w/w solution of EHEC. Reproduced from⁴⁵

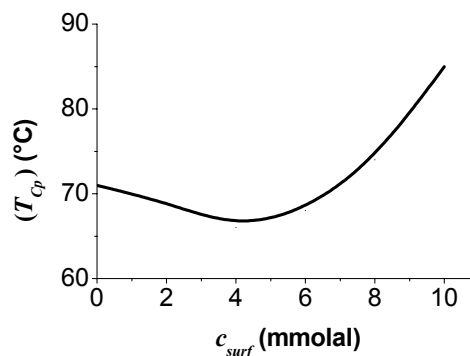


Figure 2.19. T_{Cp} as a function of sodium dodecyl sulphate concentration for 0.9% w/w solution of EHEC. Reproduced from⁴⁵

Surfactants are another type of substance that strongly influences the phase separation temperature. Depending on the surfactant concentration, c_{surf} , and type of surfactant, addition of surfactants can either increase or decrease the T_{Cp} . Upon progressively increasing the surfactant concentration, c_{surf} , of the ionic surfactant $C_{12}SO_4Na$ (SDS), T_{Cp} is found to decrease initially (Figure 2.19). At slightly higher c_{surf} the T_{Cp} passes through a minimum and at even higher c_{surf} T_{Cp} increases. The trend is similar for addition of other micelle forming surfactants provided that the surfactant molecules associate with the polymer. If there is no association between polymer and surfactant the result can be a segregative phase separation with the polymer enriched in one phase and the surfactant in the other phase.

Since T_{Cp} is strongly influenced by added surfactants it is also likely that other surface-active ingredients have a large impact on the phase separation temperature. It is therefore not sufficient to measure the T_{Cp} in water to predict the phase separation temperature for a

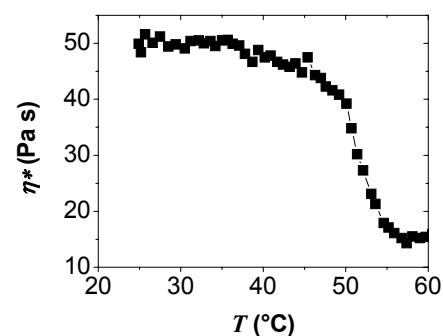


Figure 2.20. Complex viscosity as a function of temperature for a model paint thickened with EHEC. The phase separation can be detected as a step decrease in viscosity.

paint. Since the paint is a dispersion of particles rather than a clear solution it is not possible to use the normal cloud point measurements to detect the phase separation. As illustrated in Figure 2.20 the phase separation can instead be determined as a dramatic viscosity decrease when the temperature is increased.

2.2.4.1 Cloud point of HM-PEG

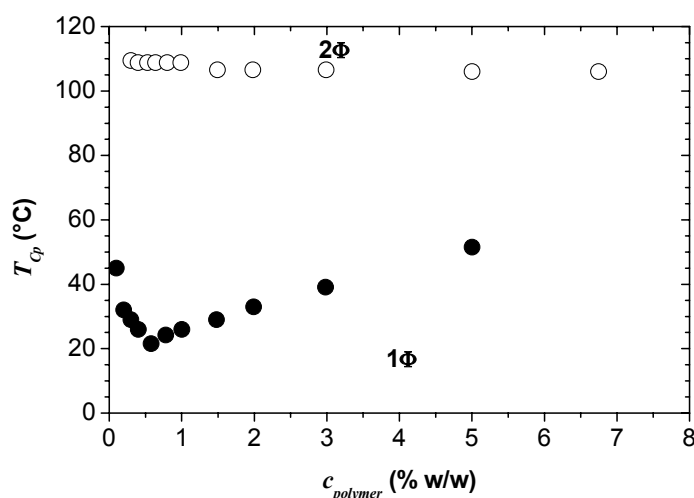


Figure 2.21. T_{Cp} as a function of polymer concentration for $C_{1618}-(EO)_{140}$ polymer (open circles) and for $C_{1618}-(EO)_{140}$ -IPDU- $(EO)_{140}$ - C_{1618} polymer (filled circles).

HM-PEG with hydrophobic groups at both end show a dramatic drop in the T_{Cp} compared to unmodified PEG or PEG that is only modified at one end (Figure 2.21).^{6,30,46} T_{Cp} also strongly depends on the polymer concentration and the cloud point curve as a function of polymer concentration passes via a minimum. The effect of T_{Cp} depression by introducing hydrophobic groups to the polymer structure is very strong and cannot be explained only by the small shift in hydrophobic/hydrophilic balance between the polymers. It is more likely that it depends on the strength of the hydrophobic associations holding the polymer network together and restricting the swelling of the polymer matrix. The formation of one concentrated phase in equilibrium with one phase depleted in polymer requires the hydrophobic associations to be strong enough to compensate for the entropic loss following the formation of the concentrated phase.

2.2.4.2 Cloud point of EHEC and HM-EHEC

For EHEC T_{Cp} is correlated to MS_{EO} and DS_{ethyl} , and T_{Cp} increases with increasing MS_{EO} and decreases with increasing DS_{ethyl} .⁸ The cloud point is dramatically influenced by the introduction of hydrophobic groups on the EHEC polymer. As an example T_{Cp} decreased by 15°C, from 65 to 50°C, when on average about one out of 120 glucose units of the unmodified EHEC (0) was grafted with nonyphenol groups (NP). On a typical HM-EHEC molecule this corresponds to five to ten hydrophobic groups. As can be seen in Figure 2.22 the shift in T_{Cp} is even stronger when the EHEC is modified with alkyl groups. The longer the alkyl chain, the more pronounced is the shift in T_{Cp} . The large difference in T_{Cp} between the polymers indicates that the strength of the hydrophobic association is much larger for longer hydrophobic groups. Also the effect on the solution viscosity of the polymers reveals large variations in the strength of the associations (compare section 2.2.2).⁴⁷

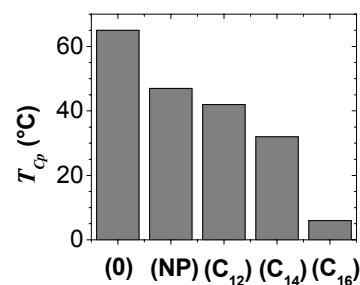


Figure 2.22. T_{Cp} of 1% w/w solutions of HM-EHEC with varying length of the hydrophobic groups. **(0)** represents unmodified EHEC

2.3 References Chapter 2

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Chapter 3

Inhibition of hydrophobic associations as a tool to study cross-linking mechanisms

Many studies have tried to investigate how the hydrophobic modification influences the solution properties of a polymer. Of course it is possible to get an idea of the strength of the associations of hydrophobic groups by synthesizing both the hydrophobically modified polymer and its unmodified analogue. This was the approach of many of the early studies.¹⁻⁵ However, if both polymers are synthesized in separate reactions it is possible that their structures differ by more than just the hydrophobic modification. Sometimes this problem can be circumvented by using the unmodified polymer as starting material in the synthesis. It is likely that with this approach the HM-P and the parent polymer differ in molecular weight since an additional reaction step often leads to a degradation of the polymer backbone. By decoupling the polymer network it is possible to gradually move in the direction of the unmodified system. The decoupling can be achieved by changing the solvent quality or by the addition of a third component (co-solute). Surfactants and cyclodextrins are examples of co-solutes that dramatically change the strength and number of the associations. Different information can be achieved by using the different methods. By changing the solvent quality or by the addition of an excess of surfactant all types of hydrophobic associations can be decoupled. It would therefore be desirable to have a method to specifically disconnect associations caused by hydrophobic side chains. The addition of cyclodextrin, on the other hand, offers the possibility to specifically decouple the associations originating from hydrophobic side chains. This is for example particularly useful for the evaluation of HM-EHEC since the associative interactions originate both from associations of hydrophobic segments of the polymer backbone and from associations of hydrophobic side groups. The different methods are discussed in more detail in the following sections.

3.1 Inhibition of hydrophobic interactions by changing solvent quality

Hydrophobically modified polymers have a much stronger tendency to associate in water than in other (less) polar solvents, e.g. alcohols and glycols.^{4,6} This is to be expected since the driving force for association is to minimize contact between the hydrophobic moieties of the HM-P and the solvent molecules and this becomes less important when the polarity of the solvent is reduced. It is also in agreement with what is found for self-assembly of surfactants.⁷ Upon gradual addition of a less polar solvent to an aqueous polymer solution the intermolecular hydrophobic associations are broken since it becomes less important to avoid the contact between the hydrophobic tails and the solvent. In Figure 3.1 the viscosity of 1 % w/w HM-(C₁₄)-EHEC and 1 % w/w HM-(NP)-EHEC solutions are given as a function of the concentration of diethylene glycol monobutylether (BDG), c_{BDG} , in the solvent. Since the viscosity of the solvent changes with changing ratio between BDG and water the viscosity is presented as the relative viscosity, $\eta_{rel} = \eta / \eta_{solvent}$, where $\eta_{solvent}$ in each point is the viscosity of the solvent at that specific BDG/water ratio.

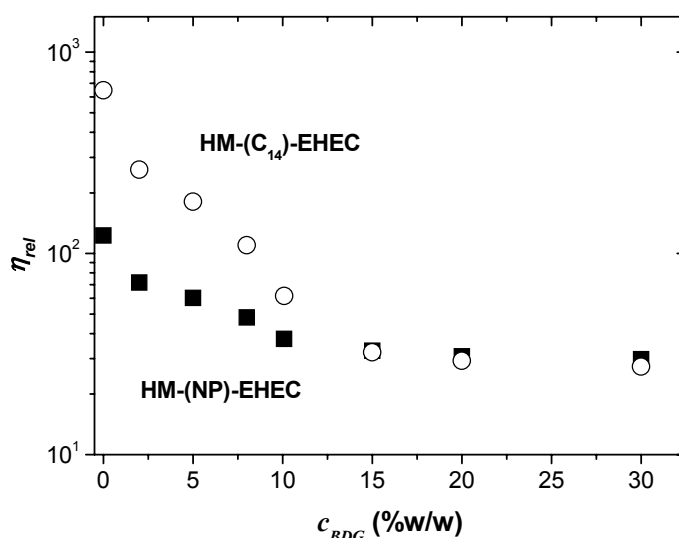


Figure 3.1. The influence of c_{BDG} on the viscosity of 1%w/w solutions of HM-EHEC.

A “saturation level” where η_{rel} is independent of c_{BDG} is reached at about 15 % w/w BDG. Above that BDG concentration the relative

viscosity of the polymer solution is constant. In paper III a BDG/water ratio of 20 / 80 was used, and in the following text viscosity measured in such a solution is referred to as η_{BDG} . The fact that both HM-(C₁₄)-EHEC and HM-(NP)-EHEC have a η_{BDG} that is almost the same as η_{BDG} for the corresponding unmodified EHEC indicates that the hydrophobic interactions from the hydrophobic modification are totally decoupled. A way to represent the influence by the hydrophobic interaction is Q_{BDG} which is the ratio between the value of the (Newtonian) viscosity in water η to that observed in water/BDG, η_{BDG} (equation (3.1)).

$$Q_{BDG} = \frac{\eta}{\eta_{BDG}} \quad (3.1)$$

Q_{BDG} can be regarded as a phenomenological measurement of the influence of hydrophobic associations on the viscosity in the aqueous solution. In this way different polymer samples (regarding chemical structure of the hydrophobic tails, modification degree, modification pattern etc.) can be ranked. With this method it is evident that the unmodified EHEC also has a contribution to the viscosity originating from hydrophobic interactions. This was observed as a small but significant Q_{BDG} of about 1.2 (Figure 3.2). Since this polymer has no hydrophobic grafts the origin of the interactions has to be sought elsewhere. As described in section 2.2.2 the uneven distribution of ethyl substituents results in hydrophobic segments along the backbone and it is likely that the blocky structure causes hydrophobic associations. The low Q_{BDG} of 1.2 indicates that the strength of these interactions is much weaker than those given by the hydrophobic grafts, provided that the length of the hydrophobic groups is C₁₂ or longer. Since all hydrophobic associations are disconnected and chain entanglements are the only remaining interpolymer cross-links in the solution, η_{BDG} can be used as a measure of the chain entanglement contribution to the viscosity.

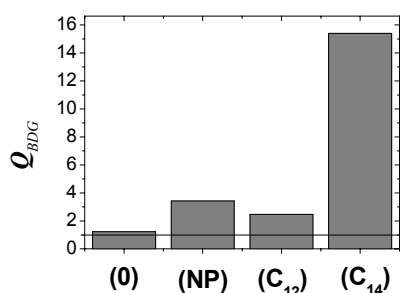


Figure 3.2. Q_{BDG} for HM-EHEC with different hydrophobic groups. From left to right; unmodified EHEC (0), HM-EHEC modified with nonylphenol groups (NP), with C₁₂ and C₁₄ groups.

Figure 3.2 shows the influence of the length of the hydrophobic tails on the solution viscosity and Q_{BDG} of some HM-EHEC:s. The strength of the association of the hydrophobic grafts is strongly dependent of the length of the hydrophobic groups as can be seen from the Q_{BDG} . The values of Q_{BDG} for HM-EHEC grafted with short hydrophobic groups (C₁₂ or NP) are 2.5 and 3.4 respectively whereas it increases dramatically for the longer hydrophobic groups (C₁₄).

With this method it is not possible to separate contributions to the viscosity from associative interactions of different origin, since it was found that the contribution from grafted hydrophobic groups as well as the contribution from a hydrophobic polymer backbone was affected by the addition of BDG.

3.2 Inhibition of hydrophobic interactions by addition of surfactant

In section 2.2.3 is described the influence of surfactant on the associative behavior of HM-polymers. At high concentration of surfactant the number of micelles exceeds the number of hydrophobic groups of the polymer which means that on average each micelle contains only one hydrophobic group from a HM-polymer, as illustrated in Figure 3.3. The result is that the hydrophobic associations between HM-polymers are decoupled and the polymer network is disconnected. This can be detected as a decreased solution viscosity and increased self-diffusion of the polymer molecules.^{4,8-23} The viscosity and self-diffusion in a solution of a HM-polymer at excess surfactant are expected to attain the same values as for a solution of the corresponding unmodified polymer (provided that the molecular weight is the same). This has for example been illustrated for HM-HEC and unmodified HEC.¹⁹

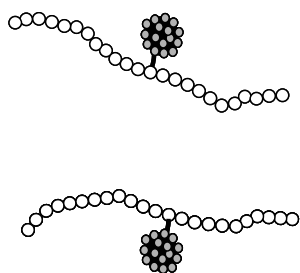


Figure 3.3. Schematic picture of HM-P at high c_{surf} where the associations between hydrophobic side chains are decoupled by surfactant.

As described in section 2.2.2 the hydrophobic associations of HM-EHEC consist of associations between hydrophobic side chains as well as interaction of hydrophobic segments of the polymer backbone. Thuresson et al have shown that not only HM-EHEC but

also unmodified EHEC is affected by the addition of surfactant.⁵ The suggested explanation is that the surfactant associates both to the hydrophobic segments of the main chain and to hydrophobic side chains. At excess surfactant the viscosity of solutions of the hydrophobically modified polymer and the unmodified parent polymer attains the same value. In analogy with the effect of addition of BDG, discussed above, the observation that the viscosity for a solution of the parent polymer is lower compared to when no surfactant is added indicates that the associations from hydrophobic segments of the backbone are decoupled by addition of surfactants. Surfactants cannot be used to selectively decouple any of the types of hydrophobic associations. Similarly to the solvent approach (section 3.1) it is therefore not possible to distinguish between the contribution from hydrophobic associations of the polymer backbone and the contribution from associations of hydrophobic side chains by this method.

3.3 Inhibition of hydrophobic interactions by cyclodextrin

Cyclodextrin (CD) is a cyclic molecule with a hydrophobic cavity (Figure 3.4 and 3.5). CD binds selectively to hydrophobic molecules or parts of molecules that fit into the cavity. In aqueous solutions of HM-polymers the CD molecules bind primarily to hydrophobic side- or end-groups and not to hydrophobic segments of the backbone. Therefore addition of CD provides a unique possibility to specifically decouple the association caused by hydrophobic groups grafted to the polymer backbone. The deactivation of hydrophobic associations by CD gives unique information about the association mechanisms of HM-polymers that cannot be achieved by deactivation at excess surfactant or by changed solvent quality.

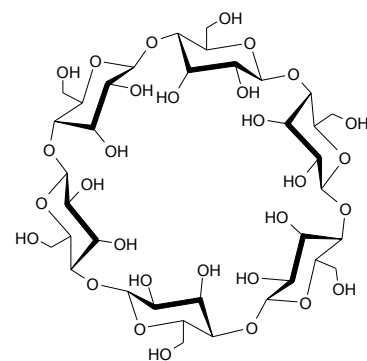


Figure 3.4. Chemical structure of α -cyclodextrin.

3.3.1 Structure and properties of cyclodextrin

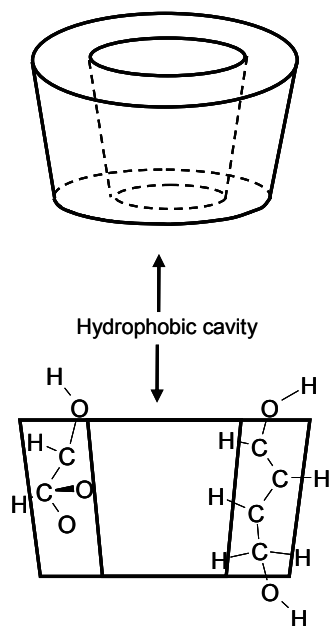


Figure 3.5. Schematic representation of the geometry of a cyclodextrin molecule.

Cyclodextrins (CD:s) are cyclic oligomers of α -D-glucose. Three different CD:s, denoted α -, β -, or γ - cyclodextrin, are naturally occurring and they consist of 6, 7 or 8 glucose units respectively.^{24,25} They are synthesized by enzymatic degradation of starch. Their chemical structure is very rigid and the three-dimensional shape can be described as a shallow truncated cone with a cavity in the center extending from one end to the other (Figure 3.5).^{24,25} The exterior of the cone is hydrophilic since all the hydroxyl groups of the AHGs are located there while the cavity has non-polar properties. The size of the cavity varies depending on whether it is α -, β -, or γ - cyclodextrin. Some useful physical properties of the different cyclodextrins are listed in table 3.1.

By substitution, the physical properties of the cyclodextrins can be changed. Substitution with methyl- (M-) or hydroxypropoxyl (HP-) groups has been used to increase the solubility of CD in organic solvents. As a natural consequence of the location of hydroxyl groups the substituents will be located on the rims of the molecule, resulting in an increase in the height of the torus. More surprising is that the diameter of the cavity is reduced by the derivatization.²⁶ The overall result of the derivatization is that the cavity volume increases. Acetyl (Ac-) is used to increase the solubility of β -cyclodextrin in water, which in its natural form has a quite poor aqueous solubility. Somewhat unexpected it is found that also "slightly hydrophobic" substituents like methyl and hydroxypropyl increase the water solubility (Table 3.2.). A reduced possibility to form crystalline structures is the most probable reason (compare with native cellulose that is insoluble while methyl cellulose and hydroxypropyl cellulose are soluble).²⁷

Table 3.1. Properties of α -, β -, and γ Cyclodextrin.

Cyclodextrin	Number of glucose units	Molecular weight	Cavity diameter (Å)	Torus height (Å)
α -	6	972	4.7 – 5.3	8
β -	7	1135	6.0 – 6.5	8
γ -	8	1297	7.5 – 8.3	
Per-O-methyl- α	6	1224	4.2	11
Per-O-methyl- β	7	1429	5.8	11

Data obtained from²⁶ and²⁴

Table 3.2. Solubility in water at 25°C for α -, β -, and γ cyclodextrin substituted with methyl (M-), hydroxypropyl (HP-), and acetyl- (Ac-) groups

Cyclodextrin	Degree of substitution	Solubility in water at 25°C (g/100ml)
α -	-	14 ^{a)}
β -	-	2 ^{a)}
γ -	-	23 ^{a)}
M- α -	1.8	388 ^{b)}
M- β -	1.8	300 ^{b)}
HP- β -	0.75	200 ^{b)}
Ac- β -	1	220 ^{b)}
M- γ -	1.8	330 ^{b)}
HP- γ -	0.6	180 ^{b)}

a) Data obtained from²⁴

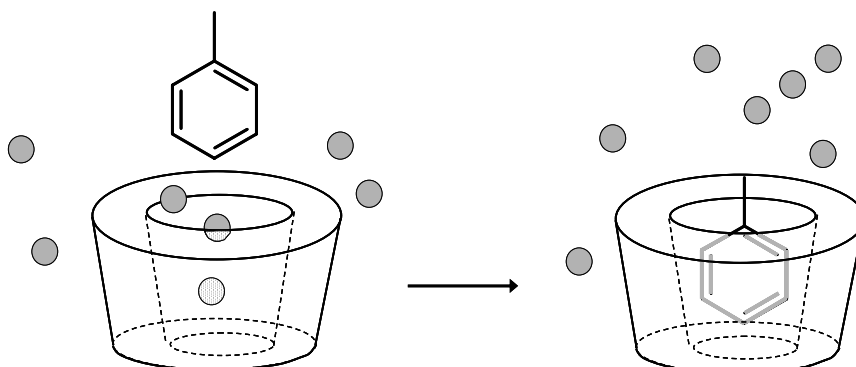
b) Data supplied by Dr Stephan Neuman, Wacker-Chemie GmbH, Germany

3.3.2 Formation of inclusion complex between lipophilic guest molecules and cyclodextrin

In an aqueous solution a less polar guest molecule readily substitutes the polar water molecules inside the cavity provided that the unpolar molecule has the correct dimensions to fit within the cavity (Figure 3.5). This hydrophobic attraction drives the formation of an inclusion complex. The complex formation has frequently been studied and surfactant/cyclodextrin systems especially have received a lot of attention. Various methods, e.g. calorimetry or surfactant selective electrodes, have been used to determine complex constants.²⁸⁻³⁴ The complex constants for the formation of an inclusion complex

between α -CD or β -CD and some commonly used surfactants are listed in Table 3.3.

Figure 3.5. Schematic representation of the inclusion of a lipophilic group into the cavity of a cyclodextrin molecule. The filled balls represent water molecules.



The changed shape of the cavity, as a result of the derivatization of the CD, influences the ability for the modified CD:s to form a complex with another substance. Therefore the complex constants for the modified CD:s differ from the constants from the corresponding unmodified CD:s.²⁶ An increased length of the cavity often results in a stronger tendency for complex formation. On the other hand a reduced cavity diameter from the derivatization results in a reduced ability to form complex with bulky hydrophobes e.g. aromatic groups.²⁶

The fact that lipophilic molecules can hide inside the cavity of an otherwise hydrophilic and water-soluble molecule has given cyclodextrins many technical applications. One obvious application is to enhance water solubility of poorly soluble substances but it has also been used to mask unpleasant odors and tastes and to reduce the vapour pressure of volatile organic compounds dissolved in water.²⁴

Table 3.3. Complex formation constant, K_1 (mM^{-1}), for α -CD and β -CD in combination with sodium dodecyl sulphate (SDS), sodium tetradecyl sulphate (STS), sodium hexadecyl sulphate (SHS), dodecyl trimethyl ammonium bromide (DTAB), tetradecyl trimethyl ammonium bromide (TTAB) and cetyl trimethyl ammonium bromide (CTAB).

Surfactant	K_1		Reference
	α -CD	β -CD	
DTAB		23.7	30
TTAB	61.0	39.8	30
CTAB	99.2	67.7	30
SDS		25.6	33
STS		48.2	33
SHS		53.3	33

3.3.3 Cyclodextrin and HM-P

The hydrophobic tails of an HM-polymer in an aqueous solution can form inclusion complexes with added cyclodextrin molecules. This leads to a disruption of the physical bonds holding the three dimensional polymer network together (Figure 3.6). This can be detected as a reduction in the viscosity of the polymer solution. This is similar to the effect of the addition of excess surfactant or by changes of the solvent quality to a less polar system as discussed in section 3.1 and 3.2. Eisenhart and Lau and their coworkers were the first to report the viscosity reducing effect by the addition of cyclodextrin in two patents.^{35,36} They used the inhibition of hydrophobic interactions to reduce the viscosity in highly concentrated solutions of associative thickeners. The reduced viscosity is desired during production and handling (pumping etc.) of the thickener or at other occasions when the polymer is present at high concentration and therefore gives very high viscosity. The complexation is reversible and by addition of e.g. a surfactant with higher affinity to the cyclodextrin the thickening effect can be regained.

In some later papers it has been reported that the degree of association in solutions of hydrophobically modified polymer can be

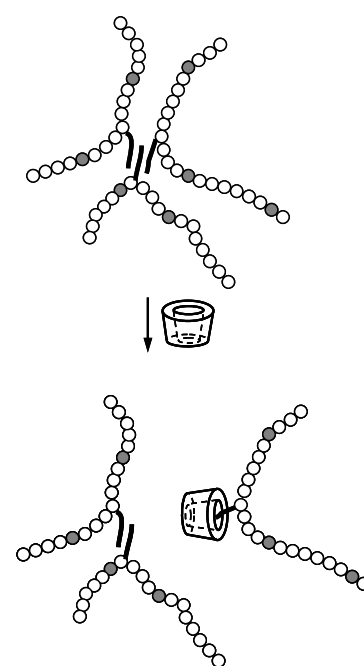


Figure 3.6. A schematic representation of the disruption of the polymer network following the complex formation between cyclodextrin and polymer hydrophobic tails.

controlled by addition of cyclodextrin.³⁷⁻³⁹ The viscosity is reduced with increasing CD concentration (c_{CD}) and levels off at a CD/HM-P ratio where all hydrophobic interactions are inhibited.^{37,38} At excess CD the HM-P molecules are expected to be unable to associate to each other. This can be used if the molecular weight of the HM-polymers should be determined by techniques such as light scattering methods or by gel permeation chromatography (GPC). Islam and coworkers have demonstrated how the use of cyclodextrins simplifies the determination of the molecular weight of a hydrophobically modified polyacrylate by preventing self-association.⁴⁰

3.3.3.1 Cyclodextrin and HM-EHEC

In paper IV we have studied the formation of an inclusion complex in aqueous solution between cyclodextrin and the hydrophobic groups grafted on EHEC. We found, in agreement with earlier studies^{37,38} that in the region where c_{CD} is low compared to the total concentration of polymer hydrophobic groups in the solution ($c_{hydrophobe}$), the viscosity decreases with increasing CD concentration in the solution (Figure 3.7). At $c_{CD} > c_{hydrophobe}$ the viscosity levels off and attains a constant value. Three different cyclodextrins, methyl- α -CD, β -CD and methyl- β -CD, were used in combination with two HM-EHEC samples with either nonyl phenyl (HM-(NP)-EHEC) or tetradecyl (HM-(C₁₄)-EHEC) hydrophobic groups. By representing the complex formation within a Langmuir adsorption model and assuming that 1:1 “nut and bolt” complexes are formed the concentration of “adsorption sites”, B , and the complex constant, K , can be determined. A detailed description of how equation (3.2) is derived is found in the appendix of paper IV.

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = 1 - \frac{\frac{B + c_{CD} + 1/K}{2} - \sqrt{\frac{(B + c_{CD} + 1/K)^2}{4} - Bc_{CD}}}{B} \quad (3.2)$$

The viscosity without CD is represented by η_0 and the viscosity at excess CD by η_∞ . From fitting equation (3.2) to our experimental data points ($(\eta - \eta_\infty)/(\eta_0 - \eta_\infty)$ vs. c_{CD}) with K and B as fitting parameters, B and K could be determined.

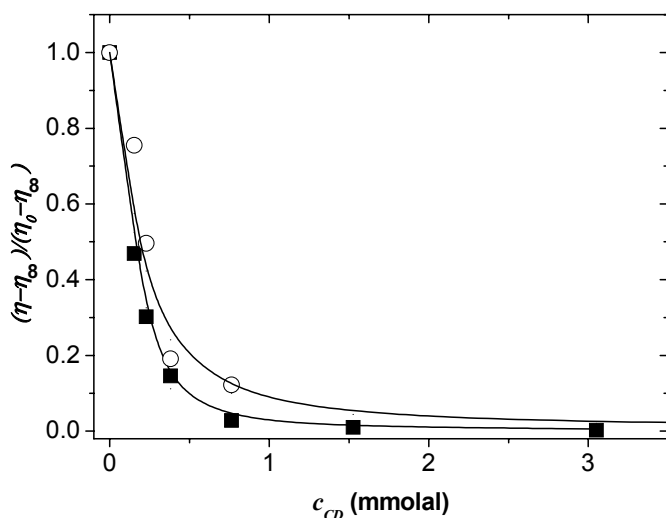


Figure 3.7. Relative viscosity as a function of the concentration of methylated- β -cyclodextrin, c_{CD} , of 1% w/w solutions of HM-EHEC. Open symbols represent HM-(NP)-EHEC and filled symbols represent HM-(C₁₄)-EHEC. The full lines represent a fit of Equation (3.2) to the data.

In table 3.4 it can be seen that the complex constant, K , is very much influenced both by the shape of the polymer hydrophobic group and the structure of the CD. For the HM-EHEC with C₁₄-hydrophobic groups the highest values of K are found for the methylated cyclodextrins. As described in chapter 3.3.1 methylation of a CD makes the cavity deeper and narrower. This indicates that the long and relatively thin C₁₄ hydrophobe fits better into the longer and more narrow cavity of a methylated cyclodextrin. The values of K are slightly lower but in the same range as those found for the complex formation between CD and surfactants containing C₁₄ alkyl groups (see table 3.3.). This is reasonable since the backbone of HM-EHEC is an extremely large and bulky head-group that is likely to oppose the complex formation.

Compared to the HM-(C₁₄)-EHEC the values of K are in general lower for the HM-(NP)-EHEC. On the other hand it seems that the more bulky nonyl phenol group fits best into the wider cavity of the β -CD as indicated by the highest K for β -CD in combination with HM-(NP)-EHEC.

Table 3.4. Complex formation constant, K , and concentration of “adsorption sites”, B , obtained by fitting Equation (3.2) to the experimental data. η_∞ is the viscosity at excess CD and η_0 is the viscosity when no CD is added.

HM-EHEC	CD	K (mmolal ⁻¹)	B (mmolal)	η_0 (mPa s)	η_∞ (mPa s)
NP	M- α	2.7	0.27	440	115
	β	22.6	0.25	440	105
	M- β	17.0	0.26	440	105
C ₁₄	M- α	44.0	0.32	1439	50
	β	11.2	0.31	1439	80
	M- β	66.0	0.30	1439	80
0	M- α	-	-	45	45

For HM-(C₁₄)-EHEC the concentration of binding sites, B , obtained from the model (table 3.4) almost perfectly matches the concentration of hydrophobic tails ($C_{hydrophobe} = 0.29$ mmolal) obtained from chemical analysis. This gives an indication that all hydrophobic groups are potentially important for the formation of the polymer network and that all hydrophobic tails can form a complex with CD. With NP the situation is different, and it can be concluded that the values of B are lower than the total concentration of hydrophobic groups for HM-(NP)-EHEC. Judging from the values of B and ($C_{hydrophobe} = 0.28$) 5 to 10% of the hydrophobic groups are not available for complex formation with CD. The nonylphenol used for the synthesis of HM-(NP)-EHEC is of technical quality that contains both mono- and di-nonyl phenol. In mono-nonyl phenol the nonyl group can be situated either in ortho position or para position on the phenol ring. It is possible that the 5 to 10% that is not available for complex formation consists of di-nonyl phenol and ortho-nonyl phenol. They have the most bulky structure and are therefore more difficult to fit into the cavity of CD.

Considering the size of the hydrophobic segments of the backbone of HM-EHEC it is reasonable to assume that CD is not capable of decoupling the associations of such segments. The fact that the viscosity of a solution of the unmodified EHEC was not affected at all by addition of CD suggests this.

The viscosity at excess CD, η_∞ , also tells something about the ability of the CD to decouple the polymeric network. For M- α -CD the value of η_∞ is almost equal to the viscosity for a solution with the same polymer concentration of the unmodified EHEC (HM-(0)-EHEC) with the same molecular weight. This is an indication that all associations that stem from the grafted hydrophobic groups are disconnected. We note that η_∞ is higher than η_{BDG} (Figure 3.1) where also associations between hydrophobic segments are disconnected. For the other combinations η_∞ is somewhat higher than the viscosity of the unmodified polymer and especially for the HM-(NP)-EHEC this is obvious. The reason is that all polymer hydrophobic tails are not available for complex formation with CD in these cases. From the values of η_∞ and by using equation (3.2) the fraction of hydrophobes in the solution of HM-(NP)-EHEC that is not available for complex formation can be estimated to be about 16%, which is quite close to what was found above when B was compared to $C_{hydrophobe}$.

CD offers a selective way of decoupling the associations of hydrophobic side chains, provided that the hydrophobic side chains have a structure that fits into the cavity, but leaving the associations from hydrophobic patches of the backbone intact. The quotient, Q_{CD} , between η_∞ and η_0 (equation 3.3) can be used as a phenomenological measurement of the contribution to the viscosity caused by association between hydrophobic side chains.

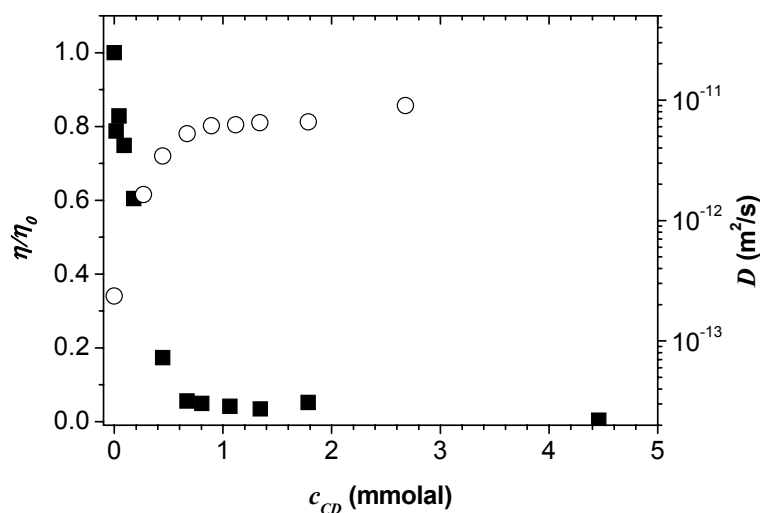
$$Q_{CD} = \frac{\eta_0}{\eta_\infty} \quad (3.3)$$

3.3.3.2 Cyclodextrin and HM-PEG

In analogy with the results for HM-EHEC the addition of cyclodextrin to an aqueous solution of HM-PEG results in a degradation of the polymer network as indicated by a reduction of the solution viscosity and an increased mean self-diffusion coefficient of HM-PEG (D_{HM-PEG}) (Figure 3.8). In papers V and VI we have studied the degradation of the polymer network in the HM-PEG system in the polymer

concentration range 3 to 10% w/w. We adopted the same model as we used for the HM-EHEC – CD system (equation 3.2).

Figure 3.8. Relative viscosity (filled symbols) and mean self-diffusion coefficient (open symbols) of a 3% w/w solution of HM-PEG as a function of the concentration of methylated- α -cyclodextrin, c_{CD} .



Low concentration of CD

Figure 3.9 shows that the viscosity decreases dramatically with the addition of methylated α -cyclodextrin (M- α -CD) to the HM-PEG solution. The change is most pronounced at small additions of CD, below 1 mmolal. In an attempt to determine the number of binding sites, B , in the same way as described for the CD /HM-EHEC system in section 3.3.4 equation (3.2) was fitted to the viscosity data points (η/η_0 vs. c_{CD}). The best representation of the experimental results was obtained for $B = 0.4$ mmolal which constitutes only 10% of the total number of hydrophobic groups. The results show that deactivation of the first few hydrophobic associations has a much stronger influence on the viscosity than would be expected if all associations were equally important for the viscosity. This is supported by the measurements of D_{HM-PEG} also included in Figure 3.9. The increase in D_{HM-PEG} is steep at $c_{CD} < 0.5$ mmolal and at higher concentrations it levels off. This shows that it is enough to terminate about 10% of the hydrophobic tails to change the viscosity and D_{HM-PEG} almost to the levels achieved at excess CD where the network is totally decoupled.

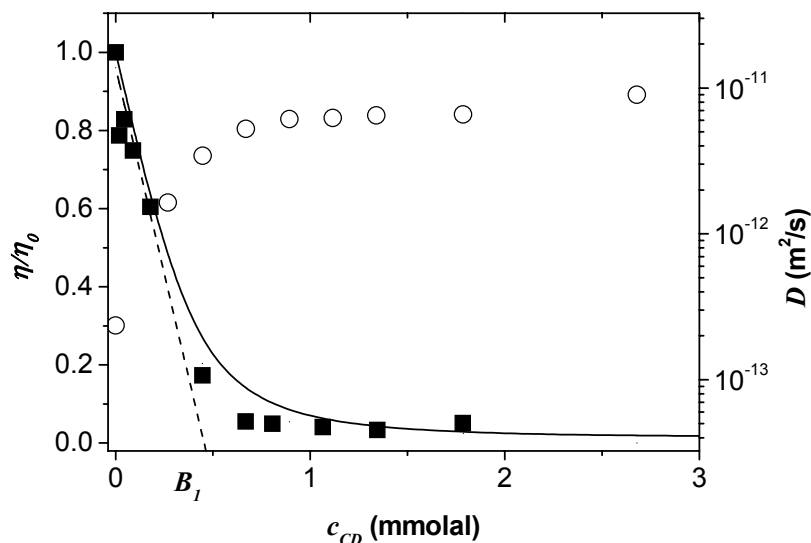


Figure 3.9. Relative viscosity, η/η_0 , (filled symbols) and mean self-diffusion coefficient, D_{HM-PEG} , (open symbols) as a function of the concentration of methylated- α -cyclodextrin, c_{CD} , for a 3% w/w solution of HM-PEG. The full line represents a fit of Equation (3.2) to the relative viscosity data. B_1 was obtained by extrapolation to $\eta/\eta_0=0$ from the behavior at low c_{CD}

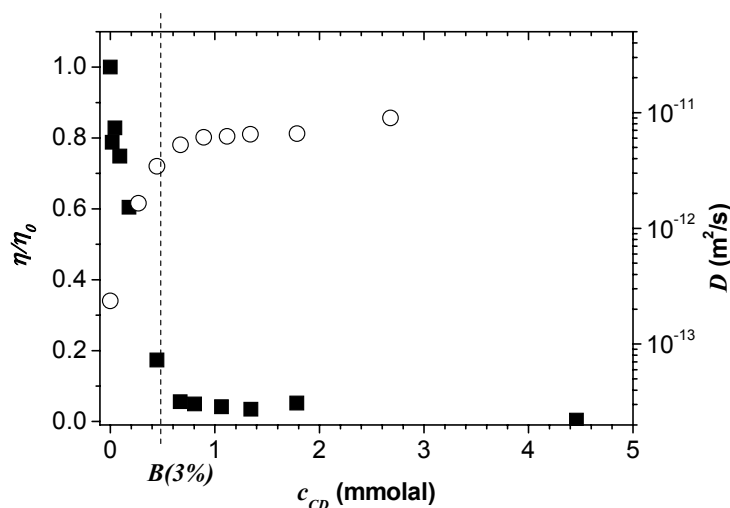
To explain this we must go back to the model of the network formation of HEUR thickeners in aqueous solution (section 2.2.1). 3% w/w HM-PEG is in the region where the HM-PEG is expected to be present in a percolated network built of clusters of flower micelles (Figure 2.13). At this HM-PEG concentration the solution is expected to be inhomogeneous with rather large concentration fluctuations where inter-micellar links inside the clusters are numerous while the polymers that connect micelles located in different clusters are rare. It is likely that the polymers that connect different clusters give a relatively more important contribution to connectivity of the network and therefore are more important to the viscosity and D_{HM-PEG} than the polymers involved in associations inside the clusters. The dramatic change in η/η_0 and D_{HM-PEG} can be understood if primarily hydrophobic associations responsible for connecting different clusters are deactivated at low c_{CD} .

Viscosity measurements show that B is virtually independent of the polymer concentration in the concentration range between 3 and 10 %w/w ($B = 0.45$ mmolal at 3% w/w, $B = 0.42$ mmolal at 5% w/w and $B = 0.53$ mmolal at 10% w/w). This indicates that the number of linkages between the clusters stays almost unchanged with increasing polymer concentration whereas the clusters grow in size. This has been suggested before by Alami et al.⁴¹

Intermediate concentrations of CD

At intermediate concentrations, where $B < c_{CD} < c_{hydrophobe}$, a new region appears, as can be seen in Figure 3.10. The changes in η/η_0 and in D_{HM-PEG} are much less dramatic in this region. The break-point between the two regions in the viscosity curve almost coincides with what is found from the self-diffusion measurements. It is reasonable that it is the size of the “decoupled” clusters that influences the viscosity of the solution and D_{HM-PEG} in this region indicating that the size of the clusters decreases with increasing concentration of CD. This indicates that it is the “inter-micellar” linkages inside the clusters that are disconnected leading to a degradation of the clusters into separate micelles and further into separate polymer molecules bearing a CD molecule at each end. The distribution in self-diffusion coefficients, σ , reflects the size distribution of the polymer aggregates.^{42,43} As can be seen in Figure 3.12, σ decreases with increasing c_{CD} . This also indicates that the clusters are degraded since the clusters are expected to have a broad distribution in sizes while the size of the micelles is rather uniform.

Figure 3.10. Relative viscosity, η/η_0 , (filled symbols) and mean self-diffusion coefficient, D_{HM-PEG} , (open symbols) as a function of the concentration of methylated- α -cyclodextrin, c_{CD} , for a 3%w/w solution of HM-PEG in the intermediate region of c_{CD} .



High concentration of CD

In the region $c_{CD} > c_{hydrophobe}$ both the viscosity and D_{HM-PEG} are expected to be independent of c_{CD} and to be on same level as that found in a solution containing the corresponding unmodified PEG with similar molecular weight. In fact this is what we found.

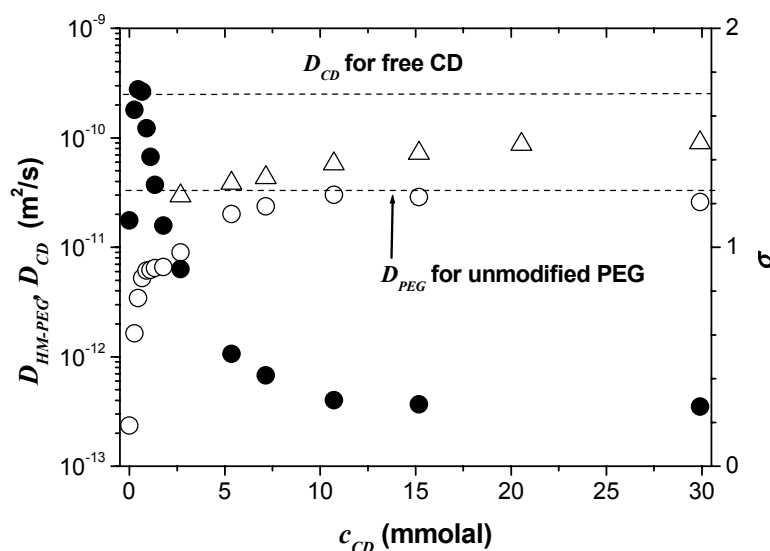


Figure 3.11. Mean self-diffusion coefficients for HM-PEG, D_{HM-PEG} ; (open circles) and for M- α -CD, D_{CD} , (triangles) and the distribution in D_{HM-PEG} , σ , (filled circles) as a function of CD concentration in 3%w/w solution of HM-PEG. The lower dashed line represents the mean self-diffusion coefficient for unmodified PEG (D_{PEG}) ($m_w=20000$ g/mol) in 1% w/w solution of PEG. The upper dashed line represents D_{CD} when no HM-PEG or PEG is present.

Since the self-diffusion at high c_{CD} does not attain a plateau value until c_{CD} is above twice B this indicates that more than one cyclodextrin molecule can bind to each hydrophobic group. Another explanation could be that the complex formation is not quantitative and free cyclodextrin is present in the solution in this region.

The self diffusion of M- α -CD (D_{CD}) has also been measured (Figure 3.11). D_{CD} changed moderately with c_{CD} and reached a plateau at about 10 to 15 mmolal. The value of D_{CD} at the plateau was low compared to D_{CD} in a solution of CD where no HM-PEG was present. Experiments where HM-PEG was substituted by unmodified PEG showed that interactions between the PEG chain and CD are of minor importance. This indicates that the reduction of D_{CD} at high c_{CD} is mainly caused by obstruction effects.

The fraction of CD that is bound to HM-PEG (P_b) can be determined by the use of equation 3.4 where $D_{CD,obs}$ is the observed self-diffusion

of CD at the actual c_{CD} and $D_{CD,free}$ is the self-diffusion of CD at excess CD.

$$D_{CD,obs} = P_b D_{HM-PEG} + (1 - P_b) D_{CD,free} \quad (3.4)$$

The fraction of bound CD decreases with increasing c_{CD} . A calculation at $c_{CD} = 10.7$ mmolal gave the result that the average number of bound CD per hydrophobic group (CD/hydrophobe) was 1.4 which supports that more than one CD molecule can bind to each hydrophobic group. In line with this Olson et al have shown by NMR-measurements that two or even more α -CD molecules can bind to a C_{12} -hydrophobic group attached to a PEG chain.⁴⁴

A model for the degradation of the HM-PEG network

From the results presented above a model for the degradation of the polymer network in the HM-PEG solution is suggested (Figure 3.12). In the region $c_{CD} < B$ the CD primarily breaks the linkages between different clusters. In the region $B < c_{CD} < c_{hydrophobe}$ where the change in viscosity is less pronounced the viscosity is mainly influenced by the size of the clusters. At high CD concentration, $c_{CD} > c_{hydrophobe}$, the HM-PEG appears mainly as small aggregates or as individual molecules with the hydrophobic groups hidden inside the interior of the CD molecules.

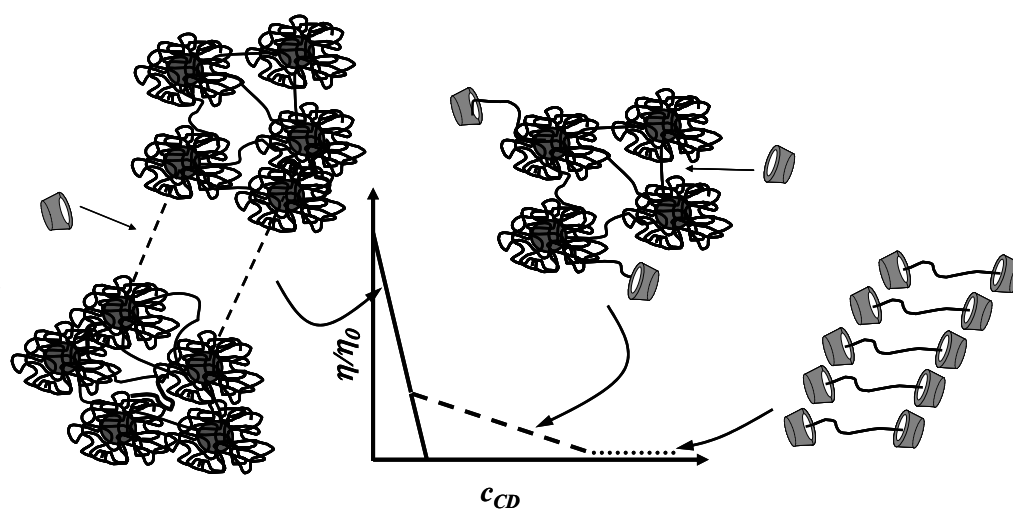


Figure 3.12. Schematic representation of the suggested model for the degradation of HM-PEG network with cyclodextrin

3.4 References Chapter 3

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Main conclusions

One intention of this thesis has been to support the development of improved associative thickeners for water borne paint and it is my opinion that novel information has been obtained.

It has been shown that the viscosity of HM-PEG solutions as a function of polymer concentration passes via a maximum. At concentrations above 50% w/w the viscosity decreases considerably. This was referred to a gradual transition from a state containing micelle-like structures to a more meltlike state (Paper I). This is important when the goal is to have high concentration of polymer while keeping the viscosity moderate, and may be utilized to minimize handling and transportation costs of the product.

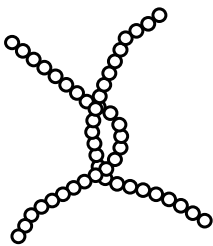
The dynamics, and the strength, of hydrophobic associations of hydrophobically modified polymers in aqueous solution are very much influenced by the length of the hydrophobic groups. Longer hydrophobic groups give, due to slower dynamics and increased relaxation times, an increased viscosity. When formulated in a paint a HM-polymer with long hydrophobic groups gives a more elastic consistency compared to when a HM-polymer with shorter hydrophobic groups is used. (Paper III)

In an aqueous solution a cyclodextrin (CD) molecule can form an inclusion complex with a hydrophobic group on a HM-polymer. This prevents the hydrophobic group from associating with other hydrophobic groups, and it leads to a degradation of the physically cross-linked polymer network. This can be detected as a reduction of the viscosity. At excess CD the viscosity attains the same value as for a solution of the unmodified polymer with the same molecular weight. This can be used to deduce the part of the total thickening effect that has its origin in associations of hydrophobic side chains (Paper IV). This observation has already been implemented in analysis methods for quality control in the production of HM-EHEC.

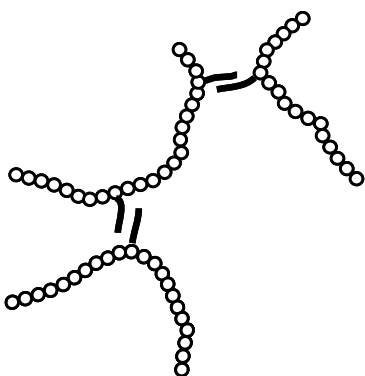
In a HM-PEG solution it is enough to terminate only a small fraction of the total amount of associative linkages to reduce the viscosity almost to the same level as that for a solution of an unmodified PEG. The results were confirmed by self-diffusion measurements. The changes in viscosity and self diffusion are for instance much more dramatic compared to what can be observed when surfactant is added. The suggested interpretation is that it is primarily hydrophobic associations involved in connecting different clusters of micelles that are disconnected (Paper V and VI). These results have supplied new information that can be useful for the understanding of the thickening mechanisms of HM-PEG, both in water solution and in more complicated systems like a paint.

Populärvetenskaplig sammanfattning

Tre begrepp som är viktiga för denna avhandling är viskositet, polymer och hydrofob grupp. Ett materials viskositet är ett mått på hur trögt eller hur lätt materialet flyter. Låg viskositet betyder att materialet flyter lätt medan hög viskositet betyder att det flyter trögt. En polymer är en stor molekyl, som bildas genom kemisk reaktion där små molekyler, monomerer, kopplas samman till en mycket större kedjemolekyl. Vissa polymerer är lösliga i vatten och kan användas som förtjockare för vattenbaserade system, d.v.s. att de höjer viskositeten hos vattenlösningen. Begreppet "hydrofob grupp" antyder att den inte tycker om vatten. (hydro- är ett förled som anger att något innehåller eller har samband med vatten och -fob kommer av pho'bos som på grekiska betyder 'fruktan', 'skräck'.) I själva verket är det så att det är vattenmolekylerna som hellre omger sig med andra vattenmolekyler än att komma i kontakt med den hydrofoba gruppen. För att minimera kontakten med vatten söker sig den hydrofoba gruppen till andra hydrofoba grupper i lösningen. Man säger att de hydrofoba grupperna associerar till varandra.



Figur 1. Schematisk bild av polymermolekyler som trasslar in sig i varandra



Figur 2. Schematisk bild av polymermolekyler med hydrofoba grupper som associerar till varandra.

En bra bild för att förstå hur förtjockningen med polymerer går till är en tallrik spagetti. Trådarna av spagetti trasslar in sig i varandra och det är svårt att röra runt med gaffeln. Polymermolekylerna i en lösning uppträder på samma sätt. De är långa trådar som trasslar in sig i varandra och hindrar varandra från att röra sig vilket resulterar i en förhöjd viskositet (Figur 1). Om man skär spagettin i mindre bitar går det lättare att röra omkring med gaffeln. På samma sätt är det med polymerlösningar. Korta polymermolekyler (låg molekylvikt) förtjockar mindre än långa polymermolekyler.

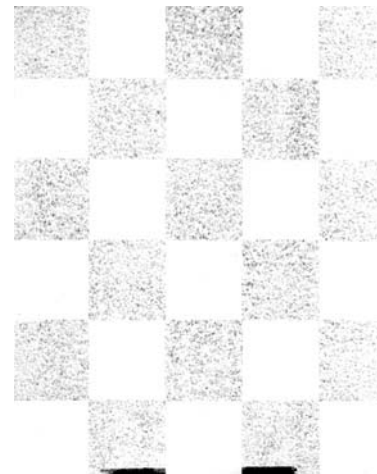
I en hydrofobmodifierad polymer (HM-polymer) har en liten mängd hydrofoba grupper reagerats fast längs polymerkedjan. De hydrofoba grupperna associerar till varandra och ger tvärbindingar mellan polymerkedjorna (Figur 2). Det betyder att alla polymerkedjorna hänger ihop i ett enda stort nätverk. Resultatet blir en avsevärd

förhöjning av viskositeten. Stora hydrofoba grupper ger starkare tvärbindingar än små grupper och därför högre viskositet. I liknelsen med spagetti kan man säga att de hydrofoba grupperna är som riven ost som klistrar ihop spagettin och gör det ännu svårare att röra runt.

Vattenlösningar förtjockade med polymerer är vanliga i vårt dagliga liv. Ett exempel är schampo, som är en vattenlösning som bör ha hög viskositet. Om den inte hade det skulle den rinna ut mellan fingrarna när den hölls ur flaskan och ner i handen. Andra exempel kan man hämta från matlagningen. Stärkelse från potatis eller majs, används för att reda (förtjocka) såser och gelatin används i många efterrätter för att ge dem dess konsistens.

Vattenbaserad målarfärg är ytterligare ett exempel på en vattenlösning som måste förtjockas för att den skall uppföra sig som vi vill. I en färg med för låg viskositet sjunker alla partiklar snabbt till botten på burken och när man målar kan man bara ta lite färg i penseln om inte färgen skall droppa. För att färgen skall få rätt viskositet tillsätts vattenlösliga polymerer.

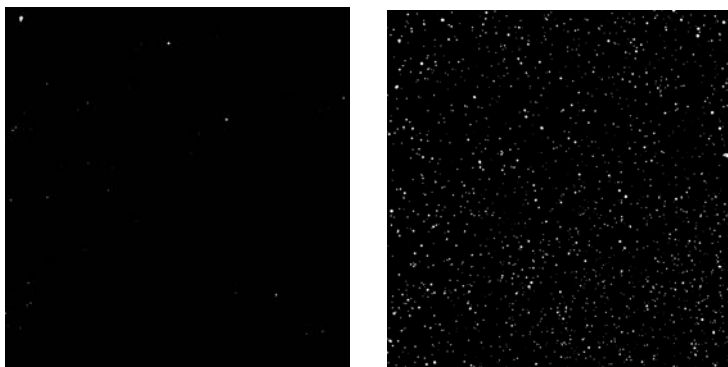
Polymerer med hög molekylvikt är effektiva förtjockare vilket betyder att bara lite polymer behöver tillsättas för att ge den önskade viskositeten. Nackdelen är att färg förtjockad med polymer med hög molekylvikt har dålig täckförmåga vilket betyder att man måste göra flera strykningar för att få bra täckning (Figur 3). Andra nackdelar är att färgen har dålig utflytning d.v.s. att den målade ytan får märken av penseldrag (Figur 4) och att den skvätter mycket när man rollar den på väggen eller i taket (Figur 5). Polymerer med lägre molekylvikt ger bättre färegenskaper men i gengäld måste mycket mer polymer tillsättas för att man skall få önskad viskositet.



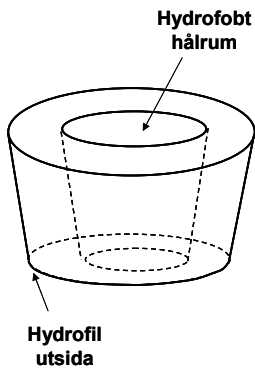
Figur 3. Färgen rollas på en svartvitrutig panel när täckförmågan skall bedömas.



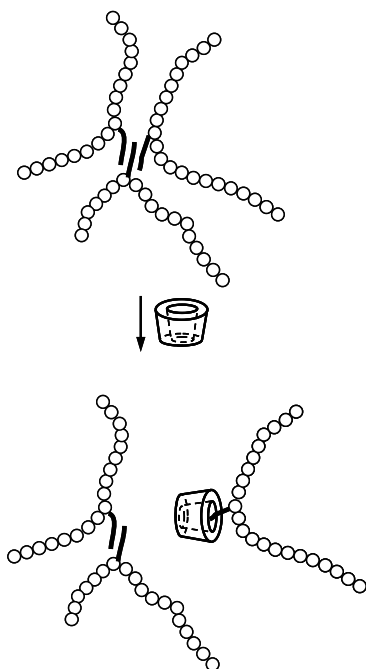
Figur 4. Panel från utflytningsförsök. Bra utflytning ger en jämn yta medan dålig utflytning ger en yta med tydliga linjer efter penseldrag.



Figur 5. När man skall avgöra hur mycket en färg skvätter rollas färgen på väggen. På ett svart papper som har placerats horisontellt en bit nedanför kan man avgöra hur mycket färgen har skvätt. Panelen till vänster är ett exempel på när en färg skvätter lite medan färgen som använts till panelen till höger skvätter mycket.



Figur 6. Schematisk bild av en cyclodextrinmolekyl



Figur 7. Schematisk bild av hur polymernätverket bryts ner av cyclodextrin.

När HM-polymerer används som förtjockare i färg ger de en kombination av de goda egenskaperna från polymerer med hög och låg molekylvikt. Samtidigt som de ger bra färegenskaper såsom bra täckförmåga, bra utflytning och lite skvätt ger de hög förtjockningseffekt d.v.s. lite polymer behöver tillsättas.

Hydrofobmodifierade polymerer förtjockar både genom intrassling av polymerkedjorna (spagetti) och genom associationer mellan hydrofoba grupper (smält ost). Arbetet i denna avhandling har gått ut på att försöka förklara hur förtjockningen går till och hur polymerens struktur påverkar dess egenskaper. Ett sätt att studera detta som jag har använt i det här arbetet är att tillsätta cyclodextrin till vattenlösningar av polymerer och se hur det påverkar lösningarnas viskositet. Cyclodextrinmolekylen liknar en mutter i formen (Figur 6). På utsidan är den hydrofil (tycker om vatten) medan hålet i mitten är hydrofob (tycker inte om vatten). En hydrofob grupp på polymeren kan gömma sig inuti hålrummet på en cyclodextrinmolekyl förutsatt att den inte är för stor för att få plats i hålet. Det finns olika cyclodextriner med olika storlek på hålrummet. Med rätt cyclodextrin får det bara plats en hydrofob grupp i varje cyclodextrinmolekyl och bara en cyclodextrin får plats på varje hydrofob grupp. En hydrofob grupp som har gömt sig inuti hålrummet i en cyclodextrinmolekyl kan inte längre delta i att bilda tvärbindingar. Resultatet blir att polymernätverket faller sönder och viskositeten sjunker. Eftersom varje cyclodextrinmolekyl tar hand om en hydrofob grupp kan man bryta tvärbindingarna i polymernätverket på ett mycket kontrollerat sätt och därmed få en detaljerad bild av hur förtjockningen går till.

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**Krister and I, in Krister's and Maria's living room, making the last adjustments before submitting one of the papers*

List of commercially available hydrophobically modified polymers used as associative thickeners in the paint industry.

More than 100 associative thickener products exist of which the majority is sold in very small volumes. This is not a complete list of all products but a selection of some of the most commercially important. The column Producer's comment contains information the producers use to characterize their products. All data are obtained from internet.

Product	Type	Producer's comment	Solvent	Producer
Acrysol TT 615	HASE ¹	high low shear visc/low high shear visc	water	R & H ¹⁰
Acrysol TT 935	HASE ¹	high low shear visc	water	R & H ¹⁰
Acrysol DR 1	HASE ¹	high low shear visc/low high shear visc	water	R & H ¹⁰
Acrysol DR 73	HASE ¹	high low shear visc/high high shear visc	water	R & H ¹⁰
Acrysol RM 5	HASE ¹	high low shear visc/low high shear visc	water	R & H ¹⁰
Acrysol RM 55	HASE ¹	high low shear visc/low high shear visc	water	R & H ¹⁰
Acrysol DR 72	HASE ¹	high low shear visc/ pseudoplastic	water	R & H ¹⁰
Acrysol RM825	HEUR ²	KU efficient	BDG/w ⁶	R & H ¹⁰
Acrysol SCT275	HEUR ²	KU efficient	BDG/w ⁶	R & H ¹⁰
Acrysol RM2020	HEUR ²	high low shear viscosity	water	R & H ¹⁰
Acrysol RM 8 W	HEUR ²	KU efficient	water	R & H ¹⁰
Acrysol RM 12 W	HEUR ²	high low shear visc/ pseudoplastic	water	R & H ¹⁰
Aquaflow NLS-200	HM-PE ⁴	low shear efficient	BDG/w ⁶	Aqualon
Aquaflow NLS-210	HM-PE ⁴	low shear efficient	BDG/w ⁶	Aqualon
Aquaflow NHS-300	HM-PE ⁴	high shear efficient	water	Aqualon
Bermocoll EHM200	HM-EHEC ³	250 – 600 mPa s (1% solution)	none	ANSC ¹¹
Bermodol HAC 2000	HASE ¹	high medium shear visc.	water	ANSC ¹¹
Bermodol HAC 2001	HASE ¹	newtonian	water	ANSC ¹¹
Bermodol PUR 2102	HEUR ²	high low shear visc.	BDG/w ⁶	ANSC ¹¹
Bermodol PUR 2110	HEUR ²	newtonian..	none	ANSC ¹¹
Bermodol PUR 2130	HEUR ²	newtonian.	water	ANSC ¹¹
Bermodol PUR 2150	HEUR ²	high low shear visc. surfactant	w/surf. ⁷	ANSC ¹¹
DSX 1514	HEUR ²	low structural viscosity	BTG/w ⁸	Cognis
DSX 1550	HEUR ²	structural viscosity	BDG/w ⁶	Cognis
DSX 2000	HM-PE ⁴	newtonian	BDG/w ²	Cognis
DSX 3000	HM-PE ⁴	newtonian	w	Cognis
DSX 3256	HEUR ²	pseudoplastic	w/diluent ⁹	Cognis
DSX 3290	HEUR ²	high low shear viscosity	w/diluent ⁹	Cognis
Natrosol Plus 100	HM-HEC ⁵	5 – 25 cP (1% solution)	none	Aqualon
Natrosol Plus 330	HM-HEC ⁵	150 – 500 cP (1% solution)	none	Aqualon

Product	Type	Comment	Solvent	Producer
Natrosol Plus 340	HM-HEC ⁵	750 – 1200 cP (1% solution)	none	Aqualon
Natrosol Plus 430	HM-HEC ⁵	5000 – 9000 cP (1% solution)	none	Aqualon
Rheolat 255	HEUR ²	antisetling	BDG/w ⁶	Elementis
Rheolat 278	HEUR ²	antisetling	BDG/w ⁶	Elementis
Rheolat 420	HASE ¹	antisetling	water	Elementis
Tafigel PUR 40	HEUR ²	pseudoplastic	BTG/w ⁸	Münzing ¹²
Tafigel PUR 45	HEUR ²	newtonian	BTG/w ⁸	Münzing ¹²
Tafigel PUR 50	HEUR ²	pseudoplastic	water	Münzing ¹²
Tafigel PUR 60	HEUR ²	strongly pseudoplastic	BTG/w ⁸	Münzing ¹²
Tafigel PUR 61	HEUR ²	strongly pseudoplastic	water	Münzing ¹²
Ucar Polyphobe 202	HASE ¹	highly associative	water	Dow
Ucar Polyphobe 203	HASE ¹	low associative nature	water	Dow
Ucar Polyphobe 205	HASE ¹	low high shear viscosity	water	Dow
Ucar Polyphobe 206	HASE ¹	high low shear viscosity	water	Dow

¹ Hydrophobically modified polyacrylate (Hydrophobically modified Alkali Swellable Emulsion)

² Hydrophobically modified urethanes

³ Hydrophobically modified ethyl hydroxyethyl cellulose

⁴ Hydrophobically modified polyether

⁵ Hydrophobically modified hydroxyethyl cellulose

⁶ mixtures of diethyleneglycol monobutylether and water

⁷ water with surfactant

⁸ mixture of triethyleneglycol monobutylether and water

⁹ water with viscosity reducing agent

¹⁰ Rohm & Haas

¹¹ Akzo Nobel Surface Chemistry

¹² Münzing Chemie