

HYDROPHOBICALLY ASSOCIATING POLYMERS AS RHEOLOGY MODIFIERS

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POLYMÈRES HYDROPHOBIQUEMENT ASSOCIATIFS
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Les polymères hydrophobiquement associatifs solubles dans l'eau sont essentiellement des chaînes de polymères hydrophiles contenant un petit nombre de groupements fortement hydrophobes répartis ou situés sur certains sites privilégiés des chaînes. En milieux aqueux, les unités hydrophobes tendent à s'associer de manière à réduire leur exposition à l'eau, conduisant à des réticulations de jonctions hydrophobes intra et intermoléculaires réversibles, même à de très faibles concentrations en polymères.

De tels réseaux temporaires influencent fortement les propriétés rhéologiques linéaires et non linéaires des solutions et font de tels polymères des candidats comme modificateurs de rhéologie dans des formulations à base d'eau telles que les fluides de forage. Dans cet article, nous étudions les principales propriétés rhéologiques de polymères hydrophobiquement associatifs solubles dans l'eau, l'influence de la présence d'un agent tensio-actif sur leurs propriétés rhéologiques et la rhéologie des solutions contenant un mélange de polymères hydrosolubles associatifs et non associatifs.

HYDROPHOBICALLY ASSOCIATING POLYMERS
AS RHEOLOGY MODIFIERS

Hydrophobically associating water-soluble polymers are essentially hydrophilic polymer chains containing a small number of strongly hydrophobic groups, distributed or located at some privileged sites on the chains. In aqueous media, hydrophobic units tend to associate in order to minimize their exposure to water, leading to reversible intra- and intermolecular hydrophobic junction networks, at even very low polymer concentrations.

Such temporary networks influence strongly the linear and non-linear rheological properties of the solutions and make such polymers candidates as rheology modifiers in aqueous-based formulations such as drilling fluids. In this paper, we present the main rheological characteristics of hydrophobically associating water-soluble polymers, the influence of the presence of a surfactant on their rheological properties and the rheology of solutions containing a mixture of associating and non-associating water-soluble polymers.

POLÍMEROS HIDROFÓBICAMENTE COMBINADOS
COMO MODIFICADORES DE REOLOGÍA

Los polímeros hidrofóbicamente combinados, solubles en el agua, constituyen principalmente las cadenas de polímeros hidrófilos que contienen un pequeño número de agrupaciones fuertemente

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hidrófobas distribuidas o situadas en ciertos emplazamientos preferentes de las cadenas. En medio acuoso, las unidades hidrófobas tienden a combinarse con objeto de reducir su exposición en el agua, conduciendo así a reticulaciones de enlaces hidrófobos intra e intermoleculares reversibles, incluso cuando se trata de muy reducidas concentraciones de polímeros.

Las redes temporales semejantes influyen ampliamente en cuanto a las propiedades reológicas lineales y no lineales de las soluciones y hacen que este género de polímeros sean candidatos como modificadores de reología en las formulaciones a base de agua, como así ocurre en los fluidos de perforación. Se estudian en este artículo las principales propiedades reológicas de polímeros hidrofóbicamente combinados solubles en el agua, la influencia de la presencia de un agente tensioactivo sobre sus propiedades reológicas y la reología de las soluciones que contiene una mezcla de polímeros hidrosolubles combinados y no combinados.

INTRODUCTION

Hydrophobically modified associating polymers consist of water-soluble polymer backbone to which few small hydrophobic groups are attached. They are of great interest in many industrial applications where they are used as rheology modifiers and controllers [1]. The particular linear and nonlinear rheological properties of such polymers are due to the fact that they can undergo reversible intra- and/or intermolecular weak associations in order to minimize water-hydrophobe contacts. The resulting microstructure and rheological behaviors depend on molecular characteristics such as number, length, position on the chain and nature of hydrophobic substituents but also on parameters such as temperature, concentration and solvent conditions.

Mainly two types of hydrophobically associating polymers are considered in the paper, both studied in our Laboratory:

- polymers which contain pendant hydrophobic side chains;
- polymers with hydrophobic terminal groups.

We try to give some characteristic linear and nonlinear rheological features of the two types of hydrophobically associating polymers studied, not to give a classification but rather to present the variety of shear flow behaviors observed, their possible interpretations in terms of microstructure and eventually to raise some present issues in the rheology of such polymeric systems. The influence of surfactant addition, nearly always present in industrial formulations, on the rheological properties is also investigated. At last, the rheological effects due to the presence of solid particles, encountered in many applications, are briefly discussed.

1 LINEAR BEHAVIORS

1.1 Zero-shear viscosity

Most hydrophobically modified polymers in water solutions exhibit a Newtonian behavior at low shear rates. The zero-shear viscosity is significantly higher than that of the nonmodified precursor above some concentration (near the overlap concentration); this thickening effect is ascribed to the existence of a temporary reversible hydrophobic interaction network [2].

Increasing the concentration to get a pronounced thickening effect may have a limit; indeed, above a

certain concentration, a phase separation may occur, as shown both theoretically and experimentally. The system phase then separates into two distinct regions: one very poor and the other one very rich in hydrophobic substituents. This phenomenon may be important in applications because commercial hydrophobic associating polymers always contain nonmodified macromolecules. From this point of view, the study of mixed solutions of hydrophobically modified and similar unmodified polymers is of major importance [3].

1.2 Linear viscoelasticity

The study of the linear viscoelastic properties of hydrophobically modified polymers allows an investigation of the nature, topology and resulting dynamics of the reversible hydrophobic association network. The linear viscoelastic behavior seems to depend much on the position of the hydrophobic groups on the chains.

For polymers with few randomly distributed hydrophobic groups, the model of Leibler *et al.* [4] has been experimentally validated and seems to give good results, at least qualitatively [2]: the dynamics on a long time scale is mainly governed by reptation-like motions slowed down by association/dissociation processes. The dynamics at short time scales is governed by the mean "lifetime" of a hydrophobic junction; it may be very difficult to measure this time using classical dynamic rheometry because of its low order of magnitude.

For polymers with hydrophobic groups located at each chain end, the linear viscoelastic behavior has been shown to be very well described by a Maxwell model, the relaxation time of which is the average duration of a reversible hydrophobic bond. The rheological data on such systems, at least in moderately concentrated regime, do not support the view that reptation dynamics prevails [5]. For unentangled associating polymers of that type, the theory by Tanaka and Edwards [6] is certainly the best one whereas the model by Cates [7] works when entanglement occurs to describe the linear viscoelastic properties.

2 NONLINEAR BEHAVIORS

2.1 Transient viscosity

Transient rheological measurements are certainly good techniques of investigation of associating

polymers because the association/dissociation process at work in flow conditions is essentially time-dependent.

For example, start-up shear measurements have been proved to be useful to give order of magnitude of characteristic time scales of hydrophobic associating polymers and to study association/dissociation processes in shear flow conditions [2].

Besides, for reversible networks, shear stress or shear rate sweep procedures must not be used and the steady shear viscosity has to be determined as the limit of the transient viscosity curve.

2.2 Nonlinear steady shear viscosity

First of all, the study of nonlinear rheological properties of associating polymers is of major importance from a practical point of view; indeed in most industrial applications where such polymers are used, the behavior is strongly nonlinear.

For polymers with few randomly distributed hydrophobic groups, a dramatic drop of viscosity at a certain shear stress has been observed. Such a strongly nonlinear behavior has been shown to correspond to the total breakage of the associating network at a shear rate equal to the mean dissociation rate of a hydrophobic group [2]. Thus, under high shear rates conditions, the viscosity of the hydrophobically modified polymer solution may be equal to the viscosity of the nonmodified polymer solution. To our knowledge, no rheological model exist to predict such a strongly nonlinear behavior in polymeric systems where an entanglement network and an associating reversible network superpose.

For polymers with hydrophobic groups located at each chain end, shear thickening is often observed [5]. This behavior is not thoroughly understood at the present time, even though it is predicted by some models, such as the transient network theory by Tanaka and Edwards [6].

3 INFLUENCE OF SURFACTANT

In many applications, hydrophobically modified associating polymer solutions contain surfactant molecules. The surfactant/associating polymer interactions depend mainly on the surfactant concentration; the resulting rheological effects are often very strong.

For polymers with few randomly distributed hydrophobic groups, up to a surfactant concentration (may be different of the critical micellar concentration), surfactant addition leads to a thickening effect due to a reinforcement of the temporary association network. This effect can be explained by a progressive increase of the number and/or strength of the intermolecular hydrophobic junctions.

Further levels of surfactant addition leads to a weakening and, for sufficiently high levels, to the disruption of the reversible network. This effect can be explained by the progressive envelopment of hydrophobic groups by surfactant micelles which then break the intermolecular associating junctions [8] and [9].

4 INFLUENCE OF THE PRESENCE OF SOLID PARTICLES

In industrial water based formulations, the associating polymers are often encountered in the presence of solid particles. The rheological properties of such systems depend much on the adsorption properties of hydrophobically associating macromolecules on solid surfaces. Adsorption properties have been shown to be influenced by the associative character of polymer: the existence of non-classical multiple layers through hydrophobic associations has been proposed as possible mechanism [10]. Much work remains to be done in that field to precise the adsorption mechanism.

Moreover, the presence of associating polymers has been proved to affect the linear and nonlinear rheological properties of suspensions. For example, an enhancement of the viscoelastic properties of the suspension may be obtained via strong interparticle interactions mediated by the reversible associating network [11]. The study of the rheological properties of such complex systems is, according to us, still at the beginning.

CONCLUSION

From both a theoretical and an experimental point of view, the linear viscoelastic properties of hydrophobic associating polymers are rather well described and understood. On the contrary, much work, both theoretical and experimental, is needed to be able to understand and predict correctly the strong nonlinear

rheological responses (shear-thinning and shear-thickening) of such systems.

Yet, the structures which are responsible for the rheological behaviours measured are not always well defined and more work is needed to relate the reversible network topology to the observed behaviours.

The field where a lot of progress are to be made is certainly that of suspensions in the presence of hydrophobically associating polymers. It is probably one of the most challenging topics in the next few years in the field of associating polymer rheology, at least for industrial applications.

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