Synthesis, characterization and rheological properties of telechelic polyelectrolytes

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Abstract Rheological properties of hydrophobic associative telechelic polyelectrolytes obtained by -high solid content-solution polymerization have been studied as a function of polymer concentration. Associative polyelectrolytes of ionized methacrylic acid-co- ethyl acrylate, hydrophobically modified with linear hydrophobic initiators containing 16 (ACVA16), and 18 (ACVA18) carbon atoms, were synthesized; their rheological properties in solution were studied. It was found that concentration regimes vary according to the size of the hydrophobic group. According to this, polyelectrolyte T-18 exhibits intermolecular interactions at lower concentration than polyelectrolyte T-16. Rheological measurements lead to propose a relationship between hydrophobic chain length and polymer concentration. These polyelectrolytes were shown to exhibit different rheological properties on aqueous solutions due to a synergistic effect between hydrophobic attractive interactions and coil expansion phenomena.

Keywords: telechelic polymer, polyelectrolytes, rheology, associative polymer, solution polymerization

1. INTRODUCTION

In recent years, associative polymers have been subject of considerable scientific interest due to their great thickening properties in aqueous solution, entailing a great potential for industrial applications. These polymeric structures are formed by a long hydrophilic backbone which incorporates a small amount of hydrophobic groups (~1 mol%) either at the end or along the main chain. In aqueous solution, and above a certain concentration, these polymers can form intra and intermolecular associations, creating tridimensional transient networks, which are responsible of the remarkable increase in the viscosity.

Associative polymers can be classified according to the position of the hydrophobic group in relation with the hydrophilic backbone as: telechelic,(Alami et al., 1996, Maechling-Strasser et al., 1992, Tsitsilianis et al., 2010, Rao et al., 1995)in which the hydrophobic groups are located at terminal positions; multisticker, (Maechling-Strasser et al., 1992, Amis et al., 1986, Jiménez-Regalado et al., 1999, Jiménez-Regalado et al., 2000) with hydrophobic blocks randomly distributed along the hydrophilic chain; and combined, (Jiménez-Regalado et al., 2004, Lara-Cisneros et al., 2007, Lara-Cisneros et al., 2007, Rico-Valverdeetal., 2009) displaying characteristics of both the former and the latter.

Associative thickeners are particularly important in paint and coating industries as a small amount of polymer (ca 2 wt%) allows to improve the control of rheological properties by increasing the low shear viscosity, preventing pigment settling during storage, and instilling a suitable pseudoplastic and thixotropic behavior for proper application at high shear rates. Research about associative polymers is vast, with comprehensive studies on H.E.U.R. (Hydrophobically Modified Ethoxylated Uretane) (Cathébras et al., 1998, May et al., 1996) and H.A.S.E. (Hydrophobically modified Alcali Soluble Emulsion) polymers (Maestro 2002, Kumacheva et al., 1997). Since the latter are polyelectrolytes, they offer a significant improvement on the control of the viscosity of the solution, as a consequence of the formation of intra and intermolecular associations and electrostatic expansion of polymeric coils. However, as they are synthesized by emulsion polymerization, only multisticker polymers can be obtained, which prevents to make a comparison between the different microstructures and their thickening properties. In recent years, Jiménez-Regalado et al. (Jiménez-Regalado et al., 2004, Jiménez-Regalado et al., 2004, González-Coronel et al., 2009) have studied the solution polymerization technique that enables the synthesis of acrylamide derivatives with the three microstructures. Previous studies show that such microstructures can be obtained by solution polymerization using monomers commonly used in the H.A.S.E. polymers synthesis and, at the same time, it allows a high solids content (Velazquez-Garcia et al., 2014).
Another factor that affects the rheological and thickening properties of associative polymers is the hydrophobic chain length. Tirtaatmadja et al. (Tirtaatmadja et al., 1997) studied the effect of the variation of this parameter on the viscoelastic properties of H.A.S.E. polymers using hydrophobic monomers with an alkyl chain from C12 to C20. They found that an increase in the hydrophobic chain length increases both the shear viscosity and the hydrophobic associations. Tam et al. (Tam et al., 1998) studied the effect of the space between the hydrophilic backbone and hydrophobic groups. Varying the degree of ethoxylation, 2.5, 10 and 40 mol, in the hydrophobic macromonomer, they found that the best thickening effect was obtained with the polymer with 10 mol of ethylene oxide. Moreover, Abdala et al. (Abdala et al., 2004) found that the concentration of hydrophobic macromonomer has an important impact on the viscosity of the system. Using concentrations of hydrophobic monomer from 0.3 to 1.9 mol%, they observed that higher viscosities were obtained with an intermediate concentration (1 mol%). This effect was attributed to an increase in the number of intermolecular associations as the number of hydrophobes per chain increases, while at higher macromonomer concentration (1.9 mol%) more intramolecular association is favored, which results in lower viscosities compared to those of intermediate macromonomer concentrations.

Here we report the synthesis, characterization, and solution properties of hydrophobic associative telechelic polyelectrolytes containing methacrylic acid and ethyl acrylate obtained by solution polymerization. Specific features of the polymerization methods used, as well as the hydrophobic group length in relation to their thickening ability on aqueous solution were studied. The aqueous solution properties of the polyelectrolytes were studied on the steady and dynamic state.

2. EXPERIMENTAL

Materials. All reagents were analytical grade and were used as supplied by each company without further purification. Methacrylic acid (MAA), ethyl acrylate (EA), 1-hexadecanol, 1-octadecanol, ammonium hydroxide and deuterated solvents were purchased from Sigma-Aldrich. 4,4'-azobisis(cyanovaleric acid) (ACVA), N,N'-dicyclohexylcarbodiimide and 4-dimethylaminopyridine were obtained from Fluka. Tetrahydrofuran (THF) was supplied by Tedia. Methanol and acetone were purchased from J. T. Baker and hexane from Jalmex. Distilled and deionized water was obtained using an ionic exchange columns system of Cole-Parmer.

Synthesis of the hydrophobic initiators. The hydrophobic initiators were prepared through a reaction between ACVA and two different alcohols, 1-hexadecanol (ACVA16) and 1-octadecanol (ACVA18), according to the procedure previously described by Jiménez et al. (Jiménez-Regalado et al., 2004). The conversion attained in these reactions was 46.1 and 55% for ACVA16 and ACVA18 respectively.

Polyelectrolytes Synthesis. Polyelectrolytes synthesis was made considering different hydrophobic chain lengths, including the control reference polyelectrolyte without hydrophobic groups. All polyelectrolytes were obtained through solution polymerization using MAA and AE as the initial monomers. All polyelectrolytes were synthesized at a 70% in weight concentration in solids. The procedure is described as follows: in a 100 mL reactor, prepared with mechanical stirring and reflux, defined quantities of MAA, AE and ethanol were added. The reactor was degassed with nitrogen during 30 minutes. Temperature was increased to 70 °C, followed by the incorporation of initiator previously dissolved in ethanol. The polymerization time was set at 2 hours. After the reaction had ended, THF was added to dissolve the obtained polymer, which then was precipitated in hexane. Finally, the polymer was dried under vacuum at 50 °C during 24 hours. The quantities used in each synthesis reaction for the different polyelectrolytes are listed in Table 1.

Characterization. The composition of initiators and polyelectrolytes was determined by 1H-NMR spectroscopy, using 1 wt% solution in deuterated chloroform (CDCl3) for initiators and deuterated methanol (CD3OD) for polyelectrolytes at room temperature in a JEOL 300 MHz spectrometer.

Associative polyelectrolytes and control reference. For associative polyelectrolytes, the conversions were obtained by gravimetry, and molecular weights were characterized by size exclusion chromatography (SEC) in tetrahydrofuran using a polystyrene standard, are shown in Table 2. Figure 1 shows the 1H-NMR spectrum for telechelic polyelectrolyte T-18 displaying the disappearance of peaks of the C = C double bond of the monomer (5.8 - 6.5 ppm), indicating the copolymerization of monomers. Characteristic peaks of all monomers used are shown as well. It was not possible to find the shift corresponding the acid hydrogen (signal “a” in figure).
Table 1. Quantities used for the different polyelectrolytes.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reference</th>
<th>T-16</th>
<th>T-18</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACVA</td>
<td>0.9106</td>
<td>2.463</td>
<td>2.653</td>
</tr>
<tr>
<td>ACVA&lt;sub&gt;16&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACVA&lt;sub&gt;18&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAA</td>
<td>48.5768</td>
<td>48.5677</td>
<td>48.6185</td>
</tr>
<tr>
<td>EA</td>
<td>55.9232</td>
<td>56.45</td>
<td>56.43</td>
</tr>
<tr>
<td>Ethanol</td>
<td>45.013</td>
<td>44.99</td>
<td>44.97</td>
</tr>
</tbody>
</table>

Table 2. Gravimetric conversions and molecular weight for the synthetized polyelectrolytes.

<table>
<thead>
<tr>
<th>Conversion</th>
<th>Mn (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>86.2 %</td>
</tr>
<tr>
<td>T-16</td>
<td>96.5 %</td>
</tr>
<tr>
<td>T-18</td>
<td>95.2 %</td>
</tr>
</tbody>
</table>

Figure 1. <sup>1</sup>H-NMR spectrum of T-18 polyelectrolyte.

**Rheological Study.** The rheological study was performed on an Anton Paar Physical MCR-501 rheometer coupled to a Julabo F-25 heating bath. The cone-plate geometry (50 mm 2°) was used. The study was made under steady shear and dynamic state at a temperature of 25±0.04 °C and an interval of shear rate measurements from 0.01 to 1000 s<sup>-1</sup> and frequency from 0.1 to 50 rad/s.

**Samples preparation for rheological study.** Polymer solutions were prepared by directly dissolving 1, 1.5 and 2 wt% of polymer in deionized distilled water. All of the polymer solutions were neutralized with a small amount of 30% ammonium hydroxide until the solutions were homogeneous (pH ~9) after that, samples were let to stand for 24 hours.
3. RESULTS AND DISCUSSIONS

Concentration regimes. The importance of a study showing different concentrations schemes for associative polymers lies in the imperative knowledge of the concentration needed to achieve a given thickening behavior, as the polymer concentration in the solution is directly related to the hydrophobic interactions established in the system. It is known that if the concentration of polymer C is lower than the critical aggregation concentration (C*) then hydrophobic interactions only occur within the same molecule, favoring intramolecular interactions, but if the polymer concentration is increased until C>C*, more intermolecular interactions are favored, improving the thickening power. (Williams 2007).

Note: In the case of associative polymers, the critical aggregation concentration is represented as Cη (this value is determined when the viscosity of the associative polymer exceeds that of the reference polymer), the concentration of entanglement as Cε and concentrated regime range as Cc.

Before further analysis of the results, it is useful to recall the main features of the rheological behavior of unmodified polymers. When discussing the dynamical properties of solutions of linear polymer chains, it is possible to distinguish four concentrations regimens. (de Genne 1979, Graessley 1980, Colby et al., 1994).

(i) The dilute regime C<C* for which the zero-shear viscosity is of the order of that of the solvent.

(ii) The semidilute unentangled regime C*<C<Cε. In this regime, the viscoelasticity of the solution is controlled by the Rouse dynamic and the viscosity increases moderately. Note that the ratio of Cε/C* is generally of the order of 5 – 10.

(iii) The semidilute entangled regime Cε<C<C**. The reptation model describes the viscosity properties in this regime and the viscosity follows a power law of the polymer concentration with an exponent close to 4. The plateau modulus is proportional to the density of entanglements.

(iv) The concentrated regime starts beyond C**; the reptation model still holds but the scaling behavior becomes different.

Figure 2 shows the variation of the steady-state viscosity (η) as a function of shear rate (γ) for the telechelic polyelectrolyte T-18 at different concentrations in aqueous solution. In the dilute regime (C ≤ 1 wt%), the viscosity is almost constant, that is, there is no detectable variation of η with γ. Upon further increasing the concentration (C ≥ 2 wt%), the viscosity increases drastically and the sample exhibits a stronger shear thinning behavior.

![Figure 2. Steady-state viscosity η versus shear-rate for T-18 sample at various concentrations in water.](image-url)
For control reference polyelectrolyte the tests were performed conducting a sweep of polymer concentrations from 0.05 to 14 wt%. Figure 3 shows the variation of the log-log viscosity extrapolated to zero shear rates ($\eta_0$) as a function of polymer concentration (C). It is observed that the $C^*$ value is 0.3 wt%, while the value of $C_e$ is approximately 5 wt%. It is also observed that above $C_e$ (semidilute entangled regime) the values follow a straight line with a slope of about 4, which has also been observed by other researchers using other associative polymers. (9,16)

![Figure 3. Zero-shear viscosity ($\eta_0$) as a function of concentration (C) for the reference sample.](image1)

Figure 3. Zero-shear viscosity ($\eta_0$) as a function of concentration (C) for the reference sample.

Figure 4 shows the variation of log-log of $\eta_0$ versus C for telechelic polyelectrolytes with 16 and 18 carbons and the control reference polyelectrolyte. It is noted that the $C^*_\eta$ of T-16 appears in C=0.3 wt%, the same as the control reference polyelectrolyte, whereas $C^*_\eta$ for T-18 appears at C=0.8 wt%. This displacement of the dilute regime of T-18 may be due to strong intramolecular interactions of hydrophobic groups, which make the polymeric chains to remain ball shaped in a wider range of concentrations. In addition to that, it is observed that the concentration of the polyelectrolyte entanglement regime, $C_T$ for T-18 presents itself at lower concentration than the one for T-16, which indicates that an increase in the hydrophobic chain length increases the viscosity of the solution, due to the appearance of the semidilute entangled regime at lower concentration because of the intermolecular hydrophobic interactions which form three-dimensional networks. Finally, with concentrations above $C_T$ both polyelectrolytes exhibit linear behaviors with a slope close to 4.

![Figure 4. $\eta_0$ as a function of C for T-16 and T-18 polyelectrolytes.](image2)

Figure 4. $\eta_0$ as a function of C for T-16 and T-18 polyelectrolytes.
Figure 5 shows typical frequency dependences of the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$. At lower frequencies, the behavior of the complex shear modulus is Maxwellian, as ascertained by the variations of $G'(\omega)$ and $G''(\omega)$ versus $\omega$, that scale respectively like $\omega^2$ and $\omega$. The curves $G'(\omega)$ and $G'(\omega)$ cross each other at a frequency $\omega_{\text{cross}}$. The inverse of $\omega_{\text{cross}}$ is often taken as the characteristic time of the system. As a matter of fact, the comparison between the actual experimental variations of $G'(\omega)$ and $G'(\omega)$ and those calculated from the Maxwell model show deviations appearing already before the crossing frequency. The shape of the $G'(\omega)$ and $G'(\omega)$ curves at higher frequencies is indicative of the occurrence of fast modes superimposing on a slow relaxation process. Indeed, the current models describing the dynamics of associating polymers predict a multiple relaxation process (at least two characteristic times). It follows that the relaxation time determined from $\omega_{\text{cross}}$ is smaller than the longest relaxation time. The behavior reported in Figure 5 is quite general and is observed for most of the samples. In fact, the slope of the $G'(\omega)$ curves is equal to 1 for all the samples studied, whereas that of the $G'(\omega)$ curves was found to decrease from 2 down to 1.8 for samples with long relaxation times.

From the analysis of the data in the low frequency range, we have attempted to determine the longest relaxation time ($T_R$), and the plateau modulus ($G_0$), associated with this slowest process. These values are obtained from the following relationships:

$$ T_R = \lim_{\omega \to 0} \left( \frac{1}{\omega} \frac{G'}{G''} \right) $$

$$ G_0 = \frac{1}{T_R} \lim_{\omega \to 0} \left( \frac{G'}{\omega} \right) $$

Figure 5. Storage ($G'$) and loss ($G''$) modulus as a function of frequency for T-18 sample (C = 8 wt%). The lines are fitted to one-mode Maxwell model ($T_R = 0.037$ s and $G_0 = 96$ Pa).

Figure 6 shows the evolution of $T_R$ as a function of polymer concentration for the reference sample. It can be seen that as the polymer concentration increases, there is an almost linear increase in the relaxation time. This can be explained by the fact that as the polymer concentration increases, the mobility of the chains decreases and therefore the time for the hydrophobic groups to bind together increased.
Figure 6. Terminal time ($T_R$) as a function of $C$ for the reference sample.

Figure 7 shows the results of the behavior of the elastic modulus as a function of polymer concentration for the control reference sample. The behavior observed is the same as that of the previous figure (6), i.e. an increase in modulus with increasing concentration. The resultant behavior on the relaxation time evolution and the elastic modulus is attributed to the increase of the molar fraction of chain and the development of bonds between hydrophobic groups.

Figure 8 shows the evolution of the relaxation time ($T_R$) versus $C$ for T-16sample. It can be seen that at low polymer concentrations ($C \leq 10$ wt%), $T_R$ increases slightly, which may be explained, as previously mentioned, by the fact that at these concentrations the polymer can move without difficulty, even allowing the hydrophobic joints to break, with the consequence of moderate increases of $T_R$. Increasing the polymer concentration ($C \geq 12$ wt%), shows a more marked increase of $T_R$, possibly due to fact that, at these concentrations, the chains are too close together to move, which increases the time of attachment of the hydrophobic groups.
Figure 8. $T_R$ as a function of $C$ for the T-16 sample.

Figure 9 shows the results obtained in the behavior of $G_0$ against $C$ for the T-16 polyelectrolyte. There is a maximum in the curve at a concentration of 10 wt% followed by a decrease of $G_0$ as increases $C$. This could be explained as follows: as $C$ increases ($\leq 10$ wt%) the amount of hydrophobic groups increases as well, so there are more points of attachment and $G_0$ rises. At larger concentrations ($\geq 12$ wt%) $G_0$ decreases. This may be due the fact that, because of the higher polymer concentration, most of the hydrophobic groups are linked and new hydrophobic groups that are added fail to form cross links; thus, most of them form intra molecular bonds, which results in a decrease in $G_0$. It is important to note that these concentrations ($\geq 12\%$ by weight) are in the semi dilute entangled regime, where the associations are predominantly intermolecular, which favors an increase.

Figure 9. $G_0$ as a function of $C$ for the T-16 sample
The evolution of the relaxation time ($T_R$) as a function of C to T-18 sample is presented in the Figure 10. It can be observed that this sample exhibits the same behavior as the one observed in Figure 8, i.e. a moderate increase of $T_R$ at low C (≤ wt7%) with a more marked increasing of $T_R$ at a polymer concentration above 8 wt%. This behavior has already been explained above.

![Figure 10. $T_R$ as a function of C for the T-18 sample.](image)

Figure 11 shows the evolution of $G_0$ versus C of the T-18 sample. It can be seen that this sample exhibits the same behavior as the one observed in Figure 9, i.e. an increase in $G_0$ at polymer concentrations ≤ 8 wt% and a decrease in $G_0$ with polymer concentration higher than 10 wt%. This behavior has already been explained above.

![Figure 11. $G_0$ as a function of C for the T-18 sample.](image)
4. CONCLUSION

Three polyelectrolytes were obtained, one as control reference and two telechelic type with different lengths of the hydrophobic group, \( C_{16} \) and \( C_{18} \) (T-16 and T-18).

In the telechelic type polyelectrolytes the modified initiators ACVA\(_{16} \) and ACVA\(_{18} \) were used. The concentration regime of the polyelectrolytes were obtained performing rheological steady shear tests. It was found that these regimes vary according to the microstructure or the amount of hydrophobic groups in the chain. In relation to the rheological study in dynamic state of telechelic type polyelectrolytes, it was found that the relaxation time \( (T_R) \) at low polymer concentrations have a moderate increase up to a particular concentration, above which the increase in \( T_R \) is very marked. With respect to the elastic modulus \( (G_0) \) it was found that at low C, \( G_0 \) increases up to a maximum, after which \( G_0 \) decreases.

Acknowledgements

The authors would like to acknowledge the Consejo Nacional de Ciencia y Tecnología de México (CONACYT) for the financial support of this work through project number 105712. The authors also thank R. Mendoza-Carrizales and J.G. Tellez-Padilla for their help in the experimental characterization.

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