Synthesis, Characterization and Rheological Properties, as a Function of Temperature, of Three Associative Polymers with Different Microstructure Obtained by Solution Polymerization

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Summary

In this work a study of the synthesis and characterization of several associative water-soluble polymer families, consisting of acrylamide (AM), N-isopropylacrylamide (NIPAM) and N,N-dihexylacrylamide (DHAM) is presented. Three different polymer structures: telechelic (with hydrophobic groups at the chain ends), multisticker (with hydrophobic groups along the polymer chain) and combined (with hydrophobic groups along the chain as well as at the chain ends) were prepared via free radical solution polymerization, using a hydrophobic initiator derived from 4,4´-azobis(4-cyanopentanoic acid) (ACVA) containing linear chains of 12 carbon atoms (C_{12}). The viscoelastic properties of these different families of associative polymers were investigated using steady-flow experiments in aqueous solution. The structures as a function of surfactant (sodium dodecylsulfate, SDS) concentration and temperature were investigated. It was observed that the viscosity remains fairly constant up to a certain temperature ("breaking point") and then decreases with increasing temperature. The breaking point occurs at 40°C in the case of the telechelic polymers, at 50°C for the multisticker polymers and at 60°C for the combined polymers.

Introduction

One of the most significant advances in water-soluble polymers in the last three decades has been its modification with hydrophobic parts [1,2]. Many papers dealing with water-soluble polymers with a moderate content of hydrophobic groups have been published [3,4]. These polymers play a very important role as aqueous thickeners that can be used in a variety of applications, e.g. controlled drug delivery [5,6], enzymes and cell immobilization [7,8], separation processes [9], etc. The basic structure of the associative hydrophobic polymers is essentially a hydrophilic long-chain backbone, with a small number of hydrophobic groups. These groups can be localized either randomly along the chain (multisticker polymers) [4,10], at the chain

ends (telechelic polymers) [11,12] or along the chain as well as at the chain ends (combined polymer) [13,14], combining the characteristics of both, the multisticker and the telechelic.

Temperature is an external parameter that may have adverse effects when the water-soluble polymers are used. At certain temperature, the viscosity of these polymers generally decreases, which can be an important disadvantage for some applications, such as oil recovery from subterranean oil-bearing formations [15] or in aqueous industrial applications where high temperatures are used and control of viscosity is required. There are other types of polymers that increase its viscosity when the temperature is increased; these polymers are based upon the switch properties of polymers, which are characterized by a lower critical solution temperature (LCST). The concept and design of these so-called thermoassociative, thermothickening or thermostimulated copolymers have been described by Hourdet et al. [16,17]. They have shown that, in aqueous solutions, such graft copolymers can produce a strong increase in viscosity with temperature, which can reach several orders of magnitude. Thus, it has been found that polymers with good thickening properties at room temperature drastically decrease when the temperature is increased. Also, polymers with good thickening properties at high temperatures become not so good at room temperature. From this point of view, the optimum would be a polymer that produces good thickening properties at room temperature as well as at high temperature ($\leq 60°C$).

In this study we discuss the synthesis and characterization of three different families of water-soluble polymers with different microstructure (telechelic, multisticker, and combined polymers) prepared by solution polymerization. This polymerization process has been studied early in our laboratory [18-20]. In addition we present a detailed study of the viscoelasticity of these polymers as a function of temperature. The studied polymers were prepared with acrylamide (AM), N-isopropylacrylamide (NIPAM) and N,N-dihexylacrylamide (DHAM) plus a hydrophobic initiator derived from 4,4´-azobis(4-cyanopentanoic acid) (ACVA) which consists of a long linear chain of 12 carbon atoms.

Experimental

Materials. Acrylamide (AM), 1,4-dioxane, N-isopropylacrylamide, chloroform d_6, deuterium oxide and tetrahydrofuran (THF) were acquired from Aldrich, and N,N-dihexylamine, SDS, 1-dodecanol, 4,4´-azobis(4-cyanopentanoic acid) ACVA and acryloyl chloride, were from Fluka. All chemicals were reagent grade.

Synthesis of the hydrophobic initiator. The hydrophobic initiator was prepared through a reaction between ACVA and 1-dodecanol ($C_{12}H_{25}OH$), according to the procedure previously described [19,20]. The yield on the hydrophobic initiator was 75 %.

Synthesis of the hydrophobic monomer. The hydrophobic monomer was prepared via a reaction of acryloyl chloride with N,N-dihexylamine, according to the procedure previously described by Valint et al. [21]. The yield on the hydrophobic monomer was 45 %.

Synthesis of the polymers. All polymers were prepared via solution polymerization using 1,4-dioxane as solvent. The initial monomer concentration (acrylamide, N-isopropylacrylamide and N,N-dihexylacrylamide) was maintained constant at 3 %

(wt/wt) based on the volume of 1,4-dioxane. The reaction temperature was fixed at 80°C and the initiator concentration was 0.07 mol% relative to the monomer feed. The terpolymerizations (multisticker and combined polymers) were carried out at 1 mol% of N,N-dihexylacrylamide relative to the total monomer feed. The telechelic polymer was prepared under identical conditions but without using N,N-dihexylacrylamide. The multisticker polymer was prepared under identical experimental condition using ACVA as initiator. A typical procedure during a solution polymerization experiment was as follows: the acrylamide 9.57 g, the N-isopropylacrylamide 5.0 g, the N,N-dihexylacrylamide 0.43 g and 468 g of 1,4-dioxane were added to a 600 mL reactor equipped with thermometer, condenser and mechanical stirrer. The mixture was maintained at room temperature and vigorously agitated and purged with nitrogen for 30 min. The mixture was then heated to 80°C under agitation. The hydrophobic initiator was then added to the mixture to start the reaction. Nitrogen bubbling was maintained during the polymerization. The reaction was run for about 1 h. The polymer obtained was insoluble in 1,4-dioxane. The polymer was recovered by filtration, washed with ether to remove traces of residual monomer and initiator, and finally filtered and dried under reduced pressure at 30°C for 48 h. The reactions are presented in Figure 1. For the rheological experiment of P(AM) in function of temperature a polymer with a weight-average molecular weight of ~ 40,000 g/mol was used. The polymer was synthesized in solution polymerization using water as solvent, a transfer agent (2-mercaptoethanol) and ACVA as initiator. The temperature was fixed at 50°C. This polymer was used because the molecular weight of the PAM (140,000 g/mol) obtained by solution polymerization using 1,4-dioxane, was very high in comparison with the synthesized copolymers (~46,000 g/mol).

Molecular Weight. The weight-average molecular weight, M_w, was determined by light scattering, using formamide as solvent. The refractive-index, measured at $\lambda = 633$ nm on a Brice-Phoenix differential refractometer in formamide, was 0.109 mL/g as previously described [22]. Size exclusion chromatography (SEC) characterization of these amphiphilic copolymers was not possible due to aggregation and adsorption phenomena, however, the homo-poly-acrylamide prepared under identical experimental conditions, but without the hydrophobe, showed a polydispersity index M_w/M_n, as determined by SEC, around 2.5. It was assumed then, that the polydispersities of the corresponding associative copolymers were the same as those of the homopolymers.

Characterization. The identification of the initiator, monomer and polymers was determined by ^{1}H NMR spectroscopy, using a 1 wt% sample solubilized in $CDCl_3$ (for monomer and initiator) and $DMSO/D_2O$ (85/15 wt/wt) (for polymers) at room temperature in a JEOL 300 MHz spectrometer.

Sample preparation. Stock aqueous solutions of pure polymers were first prepared at the desired concentration (15 wt%) in deionized water, and then stirred gently for 1 day. Appropriate amounts of SDS were directly added to a fraction of the stock polymer solutions to obtain stock polymer / surfactant solutions with the highest surfactant concentrations, C_{SDS} (typically $C_{SDS} \cong 12$ mM). Finally, the solutions were homogenized by stirring for 1 day. Solutions at lower surfactant concentrations were prepared by mixing the required weighted amounts of surfactant-free and surfactant containing stock polymer solutions, and the mixtures were allowed to equilibrate under mild stirring for one more day. In this study, the surfactant is used to increase the viscosity of solutions. Note that the aqueous solutions of the polymers investigated with or without surfactant, were in all cases, perfectly homogeneous and transparent at all the

concentrations investigated. The critical micellar concentration (cmc) and aggregation number (N_{agg}) of the SDS at 25°C are $cmc_{SDS} = 8$ mM and $N_{agg,SDS} = 75$ [23].
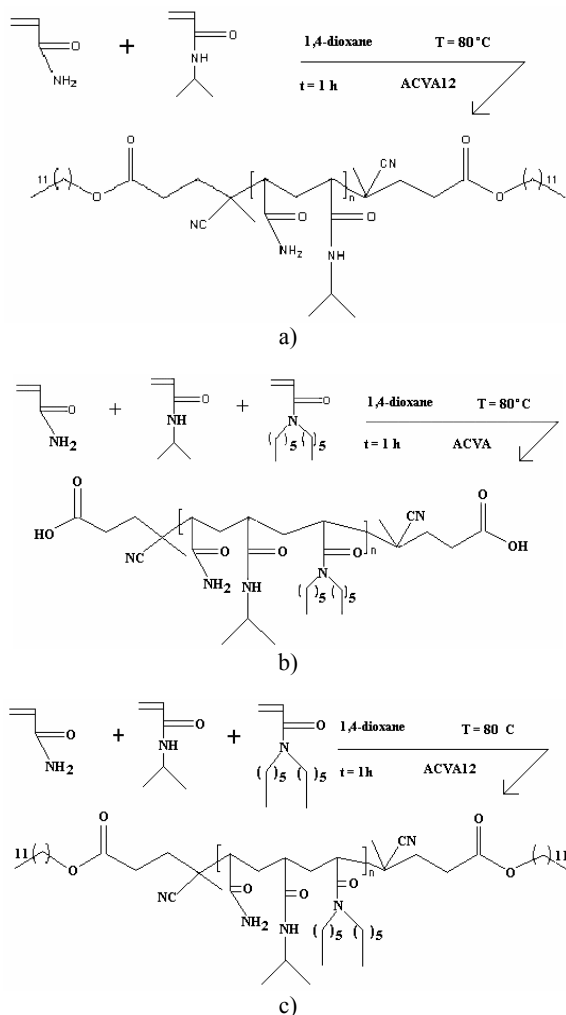

Figure 1. The synthesis of polymers a) Telechelic, b) Multisticker and c) Combined.

Rheological measurements. These experiments were performed in a Paar Physica UDS200 controlled rheometer equipped with a cone and plate geometry (angle 2° and diameter 50 mm) or double gap geometry, depending on the sample viscosity, at different temperatures (25, 30, 40 50 and 60°C). The viscoelastic properties of these different polymers were investigated using steady-flow experiments. The zero-shear viscosity (η_0) was obtained by extrapolation of the apparent viscosity.

The sample code of the copolymers refers to the hydrophilic monomers, hydrophobic monomer and the hydrophobic initiator, for example, P(AM-co-NIPAM-co-DHAM)C_{12} stands for a poly(acrylamide-co-N-isopropylacrylamide-co-dihexylacryl-

amide) obtained using the hydrophobically modified initiator with a 12 carbon atoms chain (C_{12}). The characteristics of the samples investigated are given in Table 1.

Table 1. Polymer characteristics

Polymer	AM^b Mol %	$NIPAM^b$ Mol %	$DHAM^b$ Mol %	Conversion (wt %)	M_w (g/mol)
PAM	100	-	-	75.3	140,000
PAM^a	100	-	-	95	38,700
P(AM-co-NIPAM)C_{12}	69.2	30.8	-	71.89	47,000
P(AM-co-NIPAM-co-DHAM)	72.4	27.35	0.25	72.5	46,000
P(AM-co-NIPAM-co-DHAM)C_{12}	68.7	31.0	0.3	94.1	45,000

[a] Obtained with a transfer agent (2-mercaptoethanol).
[b] Monomer content in the final polymer.

Results and discussion

The ^{1}H NMR spectrum of the combined polymer P(AM-co-NIPAM-co-DHAM)C_{12} is presented in Figure 2. It is observed that the protons corresponding to the methyl group of the DHAM appear at 0.8 ppm, those of the ethyl groups present in the three monomers appear at 1.5 and 2.2 ppm. In addition, the protons that correspond to the ethyl groups directly bonded to the nitrogen atoms in the NIPAM appear at 3.55. The NMR does not show the signals of the hydrophobe initiator, which can be due to the small quantity of initiator used.
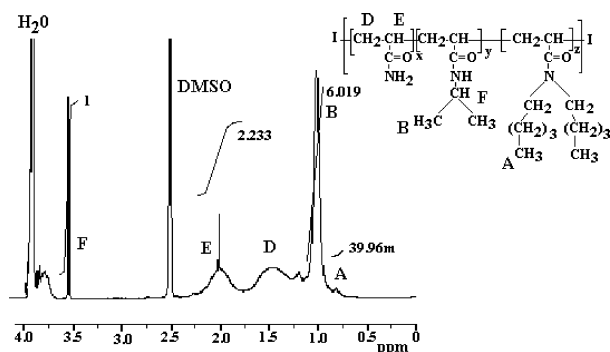

Figure 2. ^{1}H NMR spectrum of the combined polymer P(AM-co-NIPAM-DHAM)C_{12}.

Figure 3 shows the variation of η_0 as a function of temperature for different SDS concentrations for the homopolymer PAM of Mw ~ 40,000 g/mol.

It was observed that all samples of PAM presented practically the same viscosity independently of the SDS concentration. This can be explained because the polymer does not contain hydrophobic groups. The same behavior has been observed by other investigators [24]. With respect to the viscosity as a function of temperature, it was observed that viscosity decreased in the temperature interval studied.
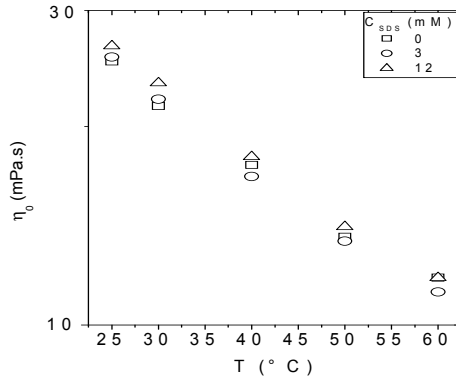
Figure 3. Viscosity η_0 as a function of temperature for different SDS concentrations for the homopolymer PAM of Mw ~ 40 000 g/mol.

Figure 4 shows the variation of the zero shear viscosity (η_0) as a function of the SDS concentration for the telechelic polymer P(AM-co-NIPAM)C_{12} at 25°C. A small increase in viscosity is observed when the SDS concentration increases from 0 to 3 mM, followed by a continuous decrease, up to an SDS concentration of 12 mM. This increase could be explained because the surfactant molecules tend to move and engage onto the hydrophobic parts of the polymer, which could cause three situations: a) the presence of the surfactant will cause an increase of hydrophobic attachments in the medium, b) the duration of the hydrophobic attachments will be increased, and c) the two previous situations occur at the same time. All three situations described above will increase the viscosity. If the surfactant concentration continues to increase, the viscosity reaches a maximum, and then decreases. This decrease could be explained considering that at high surfactant concentrations, micelles will begin to form and solubilize the hydrophobic parts, which will cause the rupture of the hydrophobic attachments and the decrease in viscosity [25]. It can also be observed that all the maxima occur at lower concentrations than the cmc of the surfactant (< 8 mM). This suggests that the surfactant begins to solubilize the hydrophobic parts
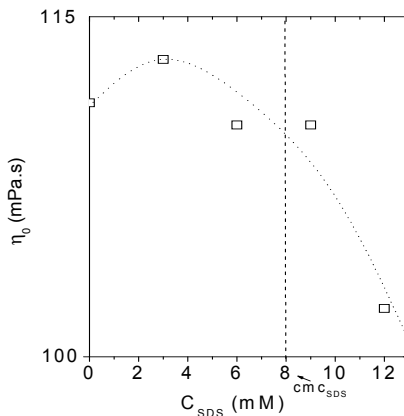

Figure 4. Viscosity (η_0) as a function of SDS concentration (C_{SDS}) for the telechelic polymer P(AM-co-NIPAM)C_{12}. T = 25°C.

before it begins to form micelles. This could be due to the small amount of hydrophobic groups in the medium.

Figure 5 shows the variation of η_0 as a function of temperature for different SDS concentrations for the telechelic polymer P(AM-co-NIPAM)C$_{12}$. It is observed that the samples without SDS, as well as the samples with 9 and 12 mM of SDS maintain a relatively constant viscosity (~105 mPa.s) up to 40°C. Thereafter, the viscosity decreases continually. The samples with 3 and 6 mM of SDS, present a similar behavior, but the onsets of the continuous decrease in viscosity occurs at 30°C. It is clearly noticed then, that the telechelic samples maintain a fairly constant viscosity up to 30 or at most up to 40°C.
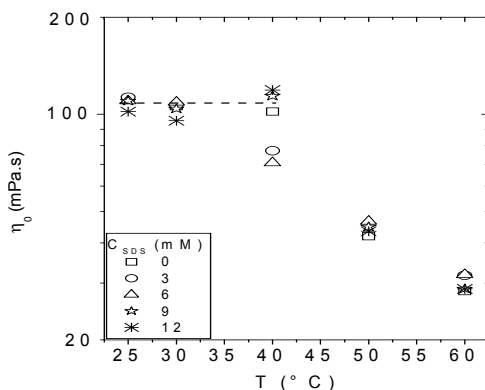

Figure 5. Viscosity (η_0) as a function of temperature for different SDS concentrations, for the telechelic polymer P(AM-co-NIPAM)C$_{12}$.

Figure 6 shows the variation of η_0 as a function of SDS concentration for the multisticker polymer P(AM-co-NIPAM-co-DHAM), at 25°C. In this case, it was observed that viscosity increases with increasing C$_{SDS}$, for the two polymers studied. Further, although there is not a clear maxima in zero shear viscosity, it is clearly seen that, after increasing, the viscosity tends to a constant "upper" value with increasing
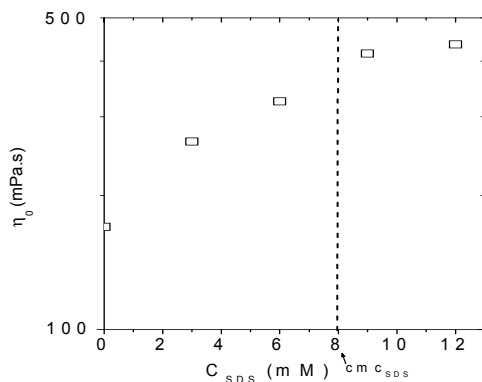

Figure 6. Viscosity (η_0) as a function of SDS concentration (C$_{SDS}$) for the multisticker polymer P(AM-co-NIPAM-co-DHAM). T = 25°C.

SDS concentration. It can be assumed then, that there is a maximum in viscosity which occurs above the higher SDS concentration studied.

It is observed also that all these maxima in η_0 occur at an SDS concentration above the cmc of the surfactant, which is 8 mM suggesting that the surfactant begins to form micelles without solubilizing the hydrophobic parts, which could be due to the great amount of hydrophobic groups in the medium.

Figure 7 shows the variation of η_0 as a function of temperature for different SDS concentrations for the multisticker polymer P(AM-co-NIPAM-co-DHAM). This polymer presents slightly higher viscosities in comparison with the telechelic polymer. It is observed that, in general, the viscosity remains approximately constant up to 50°C, at which point, the viscosity decreases markedly implying that the multisticker samples maintain a fairly constant viscosity up to 50°C. There are however, certain particular minor deviations. For example, the sample with an SDS concentration of 9 mM, shows a marked decrease in viscosity at 30°C, followed by an increase, and thereafter, follows the general decrease in viscosity with temperature. This behavior can be explained considering that as temperature increases up to 30°C, the polymer solubility increases and the viscosity decreases [26]. At 40°C, there appears a small increase in viscosity, which could be due to the phase separation that NIPAM presents at the microscopic level at this temperature. However, if the temperature is increased further, there occurs an increase in the viscosity of the solution due to an increase in the hydrophobic parts. But, as the temperature is increased further above 50°C, the viscosity of all polymers decreases markedly. It is important to note that, for the sample with an SDS concentration of 3mM, the decrease in viscosity up to 40°C is very little and remains practically constant up to 50°C (~220 mPa.s). The sample without SDS showed a similar behavior, but lower viscosity (~150 mPa.s).
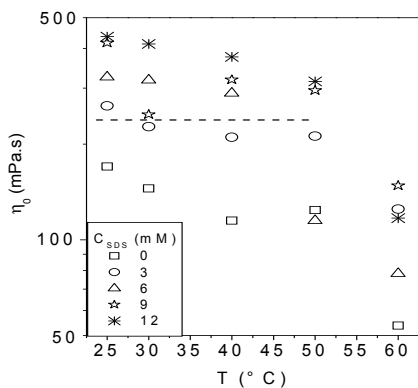

Figure 7. Viscosity (η_0) as a function of temperature for different SDS concentrations, for the multisticker polymer P(AM-co-NIPAM-co-DHAM).

Figure 8 shows the variation of η_0 as a function of SDS concentration for the combined polymer P(AM-co-NIPAM-co-DHAM)C_{12}, at 25°C. These polymers present higher viscosities than the telechelic and multisticker polymers. As can be seen in Fig. 8, the combined polymers present a behavior similar to that of the multisticker polymer, in which the viscosity increases with C_{SDS}, but in this case, a maximum viscosity is not observed. As explained above, this could be due to the

great amount of hydrophobic groups in the medium (each molecule with hydrophobic groups at the chain ends as well as along the main chain).

Figure 9 shows the variation of η_0 as a function of temperature, for different SDS concentrations, for the combined polymer P(AM-co-NIPAM-co-DHAM)C$_{12}$. The same behavior observed with multisticker polymers, is observed in this case. In general, it can be noticed that the combined polymer samples maintain a fairly constant viscosity up to 50°C. There are however, certain particular deviations. For example, the samples with an SDS concentration of 9 and 12 mM, show a decrease in viscosity up to 40°C, followed by a plateau, and thereafter follow the general decrease in viscosity with temperature. In almost all cases the viscosity decreases up to 40°C (except in the samples with an SDS concentration of 9 and 12 mM, where viscosity decreases all along the temperature interval examined). It is important to note that for the samples with SDS concentration of 0 and 3 mM, the viscosity remains almost constant at all the studied temperatures, ~ 180 and ~ 250 mPa.s respectively, with the except at 40°C where a very small decrease in viscosity is observed.
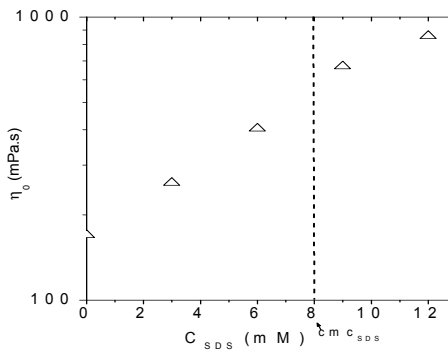

Figure 8. Viscosity (η_0) as a function of SDS concentration (C_{SDS}) for the combined polymers P(AM-co-NIPAM-co-DHAM)C$_{12}$. T = 25°C.
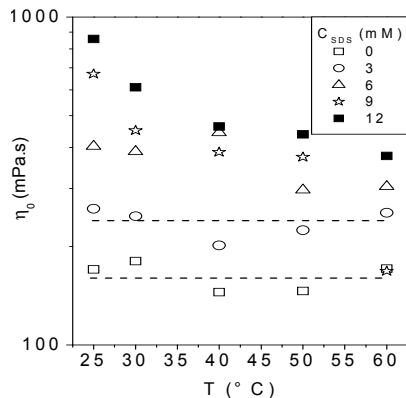

Figure 9. Viscosity (η_0) as a function of temperature for different SDS concentrations, for the combined polymer P(AM-co-NIPAM-co-DHAM).

Conclusions

Three different types of associative hydrosoluble polymers (telechelic, multisticker and combined polymers) were prepared by a free radical solution polymerization. ^{1}H NMR confirmed the presence of the monomers used in the final polymer. In the rheological study as a function of temperature, we concluded that in the case of the telechelic polymer, the samples with SDS concentrations of 0 mM were those that presented no variation of viscosity until a temperature of 40°C (~ 105 mPa.s) after this temperature, the viscosity decreases. For the multisticker polymer were 0 and 3 mM and these extended until 50°C (~ 150 and ~ 220 mPa.s respectively) and for the combined polymer were 0 and 3 mM and these extended until 60°C (~ 180 and ~ 250 mPa.s respectively). While the viscosity is low compared to other associative water-soluble polymers reported in the literature, the main contribution of this study has been the preparation of polymers in which its viscosity is not a function of temperature.

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