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New dendronized polymers from acrylate Behera amine and their ability to produce visco-elastic structured fluids when mixed with CTAT worm-like micelles

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ABSTRACT

Two new water soluble dendronized polymers (PLn) from acrylate Behera amine monomer of different molecular weights were successfully synthesized. The polymers were characterized by FTIR, NMR, GPC and DLS. Both GPC and DLS results indicated that these PLn have a remarkable tendency to form aggregates in solution that lead to apparent molecular weights that are much higher than their theoretical values, as well as large diameters in solution. However, the addition of any PLn to water did not cause any increase in viscosity up to concentrations of 1000 ppm.

The possible interactions of PLn with the cationic surfactant CTAT were explored by solution rheometry. A synergistic viscosity enhancement was found by adding small amounts of dendronized PLn polymers to a CTAT solution composed of entangled worm-like micelles. The highest association tendency with CTAT was found for PL1 at the maximum polymer concentration before phase separation (i.e., 100 ppm). The solution viscosity at low-shear rates could be increased by an order of magnitude upon addition of 100 ppm of PL1 to a 20 mM CTAT solution. For this mixture, the fluid obtained was highly structured and exhibited only shear thinning behavior from the smallest shear rates employed. These PL1/CTAT mixtures exhibited an improved elastic character (as determined by dynamic rheometry) that translated in a much longer value of the cross-over relaxation time and a pronounced thixotropic behavior which are indicative of a strong intermolecular interaction.

In the case of the polymer with a higher theoretical molecular weight, PL2, its association with CTAT leads to an extraordinary doubling of solution viscosity with just 0.25 ppm polymer addition to a 20 mM CTAT solution. However, such synergistic viscosity enhancement saturated at rather low concentrations (25 ppm) indicating an apparent lower solubility as compared to PL1, a fact that may be related to its higher molecular weight.

1. Introduction

The self-organization of a variety of molecular building blocks to construct well-defined architectures with appropriate functions is a key issue in the production of functional nanomaterials. There are numerous examples of building blocks from small molecules to high polymers [1–3].

Over the last years, dendrimers or dendrons have attracted great attention in the area of self-assembly due to their unique assembly characteristics [4–7].

Dendronized polymers are a novel class of branched polymers which carry dendrons at each repeating unit [8–11]. They are comprised of representatives which differ in dendron generation, nature of the backbone and branches and peripheral functional groups. Their unique structural characteristics [12] and promising applications [13,14] have triggered intense research activity. Normally, dendronized polymers are synthesized via the macromonomer route, although they can also be reached by the attach-to route or by combined approaches. In particular, the structural uniqueness of dendronized polymers with tightly packed dendron sequences provides an opportunity to construct unprecedented functional nanomaterials [15–17]. It is known that the key structural elements required for the self-assembly are amide branches or carboxyl functionality for hydrogen bonding, and alkyl tails to stabilize the assembled structures via van der Waals interactions [18]. For example, we previously reported the synthesis and rheology of an interesting structured fluid based on the self-assembly of amphiphilic dendrons and worm-like micelles [19].

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Two amphiphilic dendrons were synthesized by the combination of aliphatic chains and polar dendritic heads. The rheology of solutions of mixtures of each dendron with cetyltrimethylammonium p-toluenesulfonate (CTAT, a cationic surfactant) was characterized in simple shear flow. In the concentration range in which CTAT forms semidilute solutions of worm-like micelles, dendron addition produced a substantial synergy in zero-shear rate viscosity. Therefore, we reasoned that dendronized polymers with dendrons as side groups, which contain amide and carboxyl groups, might interact with CTAT in water, because the dendron units are positioned along the polymer chain so that they would have an opportunity to stack with CTAT to form self-assembled structures.

For this purpose, the aim of this work is to employ a dendronized polymer synthesized and specifically functionalized, for exploring the behavior and interactions with surfactants like CTAT and therefore to develop structured fluids that exhibit rheological synergy. The synthesis of a dendron with a polymerizable moiety as focal point, its radical polymerization and structural characterization are presented. The rheological behavior was investigated for mixtures of dendronized polymers and wormlike CTAT micelles. Samples were studied under dynamic and simple shear flow and results evidenced a positive synergistic interaction between them.

2. Experimental

2.1. Materials and equipment

The following chemicals were used as purchased: Behera amine (**1**, Frontier Scientific), dichloromethane (CH_2Cl_2, Anedra), triethylamine (TEA, Aldrich), sodium bicarbonate ($NaHCO_3$, Anedra), magnesium sulfate ($MgSO_4$, Cicarelli), formic acid (FA, 85% Cicarelli), ammonium persulphate (APS, Aldrich), tetramethylenetyhlendiamine (TEMED, Aldrich), methanol (MeOH, Cicarelli), diethyl ether (Et_2O, Taurus), sodium nitrate ($NaNO_3$, Cicarelli) and cetyltrimethylammonium p-toluenesulfonate (CTAT, Aldrich).

Fourier transform infrared spectra (FT-IR) were obtained on a Nicolet 5-SXC FT-IR spectrometer. A Bruker 500 MHz spectrometer was used for NMR characterization. A Waters 1525 Chromatograph with an automatic Waters 717 plus injector and Waters 2414 DRI detector was used for Gel Permeation Chromatography (GPC) characterization. Dynamic Light Scattering (DLS) studies were performed in a Malvern Nano Zeta Sizer ZEN 3600 at 173°. Electrospray mass spectrometer (ESI-TOF) spectrum were acquired on an Agilent 6210 system, consisting of an Agilent 1100 HPLC with a diode array detector and an ESI–MSD TOF by Agilent Technologies. Rheological measurements were conducted using a Reometrics Ares shear rheometer.

2.2. Synthesis of products

2.2.1. Synthesis of di-tert-butyl 4-acryloylamine-4-(2-tert-butoxycarbonylethyl)heptanoate *2*

To a stirred solution of Behera amine **1** (Scheme 1) (5.0 g, 12.03 mmol) and TEA (3.4 mL, 24.06 mmol) in CH_2Cl_2 (110 mL) at 0 °C, acryloyl chloride (previously synthesized) [20] (1.2 mL, 14.43 mmol) in CH_2Cl_2 (22 mL) was added dropwise over a period of 5 min. After stirring for 4 h at 25 °C, the reaction mixture was washed with $NaHCO_3$ and water. The organic phase was dried over $MgSO_4$, filtered and concentrated at vacuum to give a crude solid. Amide **2** (Scheme 1) was obtained (5.2 g, 92%) as a white solid.

^{1}H NMR ($CDCl_3$) δ (ppm): 1.47 (27 H, s), 2.06 (6 H, t, J = 7.5 Hz), 2.28 (6 H, t, J = 7.5 Hz), 5.62 (1 H, dd, J = 12, 1.5 Hz), 6.05 (1 H, dd, J = 19.0, 10.0 Hz), 6.24 (1 H, dd, J = 18.0, 1.5 Hz), 6.26 (1 H, s) ^{13}C NMR ($CDCl_3$) δ (ppm): 28.0, 29.8, 30.1, 57.6, 80.7, 125.8, 131.7, 164.8, 173.0; IR (cm^{-1}): 3312 (N—H, amide), 3089 (C—H, vinyl) 1727 (C=O, ester), 1658 (C=O, amide), 1626 (C=C, vinyl); MS (ESI) m/z 492.2 [M+Na$^+$].

2.2.2. Synthesis of 4-acryloylamine-4-(carboxyethyl) heptanodioic acid *3*

Amide **2** (5.2 g, 11.08 mmol) was dissolved in 32 mL of FA and the mixture was stirred at 45 °C for 16 h. The product **3** (Scheme 1) (3.32 g, 99% yield) was obtained as a clear yellow solid after the solvent was evaporated under vacuum for 1 day at room temperature.

^{1}H NMR (D_2O) δ (ppm): 1.96 (6 H, t, J = 7.5 Hz), 2.27 (6 H, t, J = 7.5 Hz), 5.61 (1 H, dd, J = 12, 1.5 Hz), 6.04 (1 H, dd, J = 19.0, 10.0 Hz), 6.13 (1 H, dd, J = 18.0, 1.5 Hz); ^{13}C NMR (D_2O) δ (ppm): 28.0, 28.5, 57.4, 127.1, 130.4, 167.7, 177.8; IR (cm^{-1}): 3280 (N-H, amide), 3081 (C—H, vinyl), 1713 (C=O, acid), 1660 (C=O, amide), 1625 (C=C, vinyl), 911 (C—H, vinyl); MS (ESI) m/z 324.1 [M+Na$^+$].

2.2.3. Synthesis of polymers PLn

A typical procedure for the synthesis of the polymers, for example PL1 (Scheme 1) is described next: 120 mg of **3** and 12 mg of APS (13.6% mol) were dissolved in 0.8 mL of distilled water and stirred for 15 min; the mixture was purged with N_2 and then the polymerization was started by addition of 120 µL of TEMED solution (0.32 M). After stirring at 25 °C for 48 h, the solvent was evaporated; the polymer was dissolved in 2 mL of methanol and then precipitated with 2 mL of diethyl ether. Table 1 shows the experimental conditions used for the synthesis of two different molecular weights PLn. Solid brown colored polymers were obtained for the polymerization reactions. The conversion at 24 and 48 h was determined by ^{1}H RMN following the disappearance of vinyl bands of **3** by duplicate.

2.3. Characterization

2.3.1. FT-IR and ^{1}H NMR PLn

The PLn were characterized by Fourier Transformed Infrared Spectroscopy (FT-IR) and proton nuclear magnetic resonance (^{1}H NMR). For ^{1}H NMR conversion studies (Table 1), aliquots of 0.05 mL were extracted from the polymerization solutions at 24 and 48 h and dried at vacuum. Then, 0.1 mL of basic solution of benzoic acid (50 mg mL^{-1}) was added as internal standard and D_2O was added.

PL1 and PL2: ^{1}H NMR (D_2O) δ (ppm): 1.65 (2 H), 1.96 (6 H, t), 2.02 (1 H,), 2.27 (6 H, t); IR (cm^{-1}) 2500–3500 (OH, acid), 1713 (C=O, acid), 1660 (C=O, amide).

2.3.2. Gel permeation chromatography

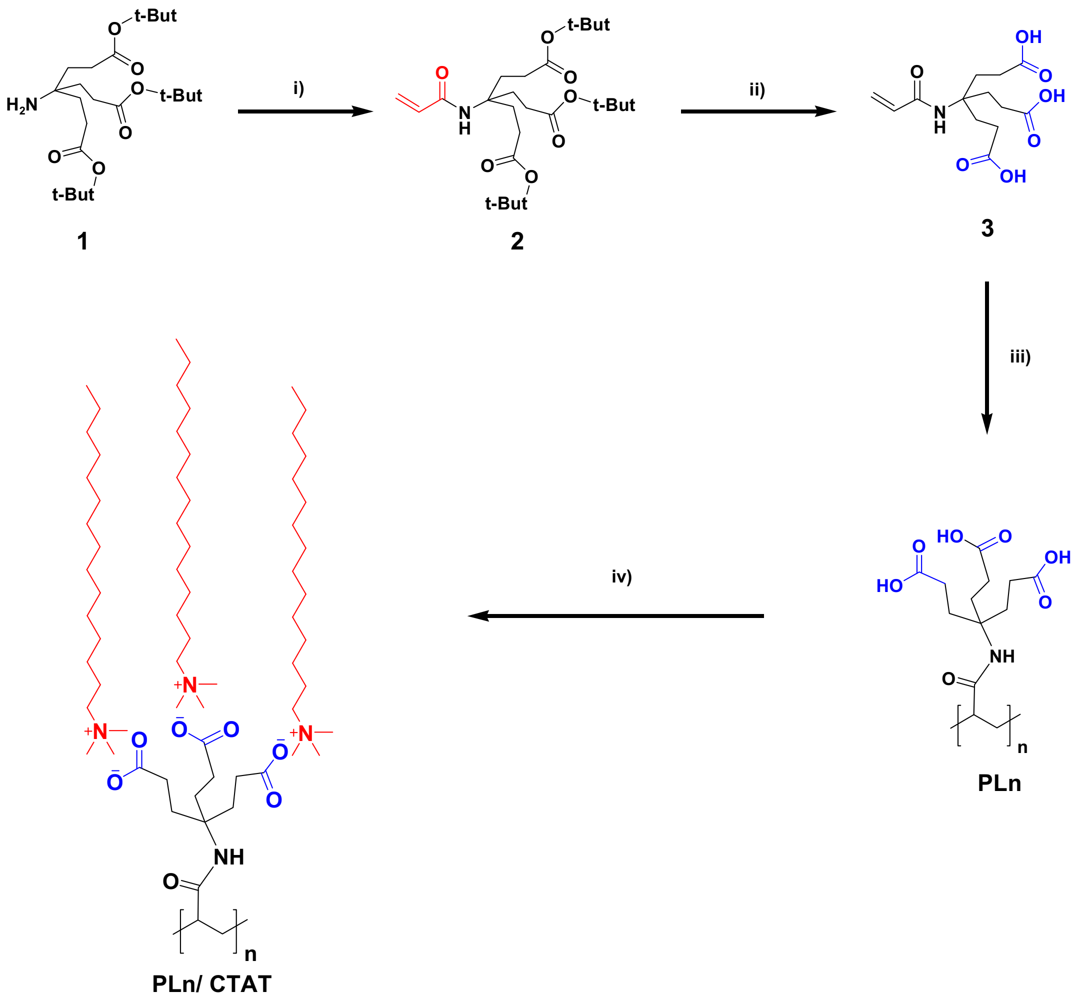
The polymers were easily dissolved in the mobile phase (phosphate buffer, 50 mM, pH = 7.00 + $NaNO_3$ 50 mM) to obtain polymer solutions (2 mg mL^{-1}). 100 µL of each sample was injected in the chromatograph by duplicate. The calibration curve was performed with 8 Pullulans Shodex Standards from M_n 5650 to 710,500 dissolved in the same mobile phase with a concentration of 1 mg mL^{-1}.

2.3.3. Dynamic light scattering

Solutions of the polymers were prepared in phosphate buffer pH = 7.40, (7 mg mL^{-1}) and filtered in cellulose filters of 0.2 µm. Then each sample was measured by triplicate at 25 °C.

2.4. Rheological measurements

Rheological measurements were conducted at 25 °C, above the Krafft point of CTAT (22.5 °C) using a shear rheometer equipped with double wall couette geometry. Frequency sweep experiments



Scheme 1. Synthesis of monomer, PLn and PLn interactions with CTAT. Reagents and conditions: (i) acryloyl chloride, TEA, CH_2Cl_2, 0–25 °C, 4 h (92% yield); (ii) FA 85 %, 45 °C, 16 h (99% yield); (iii) APS/TEMED, distilled water, 25 °C, 48 h (90–100% yield); (iv) CTAT, water, 25 °C, 24 h.

Table 1
Experimental reaction conditions used in the synthesis of the PLn.

Product[a]	3 (M)	APS (M)	APS/3 (%)	Conversion (%)		M_n, g/mol theory[b]	M_n, g/mol (PDI)[c]	Size (nm)[d]
				24 h	48 h			
PL 1	0.52	0.071	13.6	75	100	2211	255,000 (2.26)	19.5
PL 2	1.04	0.071	6.8	85	95	4423	188,000 (2.16)	9.3

[a] Radical polymerization performed in 0.8 mL of distilled water at 25 °C.
[b] ([**3**]/[APS]) × molecular weight of **3.**
[c] Measured by GPC using Pullulans Shodex Standard for calibration, PDI are polydispersity indexes.
[d] Diameter measured by DLS (see Fig. 3).

were performed at a constant strain of 30% (chosen to be within the linear viscoelastic range) over a wide range of oscillation frequencies. Concentrated stock solutions of dendronized polymer PLn and surfactant were prepared by adding the required amount of solid material in distilled and deionized water at 25 °C and maintained with constant stirring during 24 h. PLn solutions were heated to 50 °C in order to facilitate dissolution, afterwards, the temperature was lowered to 25 °C. Solutions of PLn/CTAT were prepared by mixing appropriated volumes of each stock solution and then gentle magnetic stirring was applied until complete dissolution. The prepared solutions were kept at rest for more than 24 h before conducting the rheological measurements in order to reach thermodynamic equilibrium. For PLn/CTAT mixtures, the CTAT concentration was fixed at 20 mM and the PLn concentration was varied from 5 to 100 ppm for dendronized polymer PL1. PL2 was studied in the range of 0.25–100 ppm. Concentrations larger than 100 ppm lead to liquid–liquid phase separation.

3. Results and discussion

3.1. Synthesis and characterization

The experimental conditions for the preparation of the PLn dendronized polymers are summarized in Scheme 1. Firstly, dendron **2** was synthesized with a 92% yield through the introduction of the acrylic moiety at the focal point of the Behera amine dendron by coupling the focal amine group of **1** with acryloyl chloride. Then, the acid hydrolysis of *tert*-butyl peripheral groups rendered dendron **3** with a 99% of yield.

The polymerization of monomeric dendron **3** was carried out using different initiator/monomer (APS/**3**) ratios in water and TEMED as activator**.** The structural characterization of the monomers was performed by FTIR, NMR and ESI-TOF (results not shown). The polymerization reaction of dendron **3** was corroborated by FTIR and ^{1}H NMR. As an example, Fig. 1 shows the ^{1}H NMR spectra for dendron **3** and PL1. As expected, the characteristic vinyl bands between 5.5 and 6.5 ppm present in the ^{1}H NMR spectrum of dendron 3 are not present in the spectrum of PL1. The disappearance of this monomer band was used to monitor polymerization conversion. In addition, the disappearing of the bands at 911 and 3082 cm^{-1} in the FTIR spectra of the polymers was also observed. In general, the polymerization conversion after 48 h was high but different for the PLn products depending on the monomer/ initiator ratio. As expected, monomer conversion increased as the APS/**3** ratio increases (Table 1).

As an example, Fig. 2 shows GPC chromatograms for the duplicate determination of M_n values of PL1. In general, the GPC curves for all the polymers were broad as expected for radical polymerization, however they were monomodal. Table 1 shows the theoretical and the experimental M_n values (calculated using pullulans as standards for calibration) determined by GPC analysis for the different PLn. Evidently, there is a substantial difference between the theoretical and the experimentally determined values of M_n. While the theoretical values are between 2200 and 4400 g/mol, the measured values are between 188 and 255 kg/mol. Clearly, the much higher M_n values determined by GPC suggest that these dendronized polymers are forming self-associations in solution. This result gives an idea of the intermolecular associating capacity of the polymers which are probably related to their dendronized moieties.

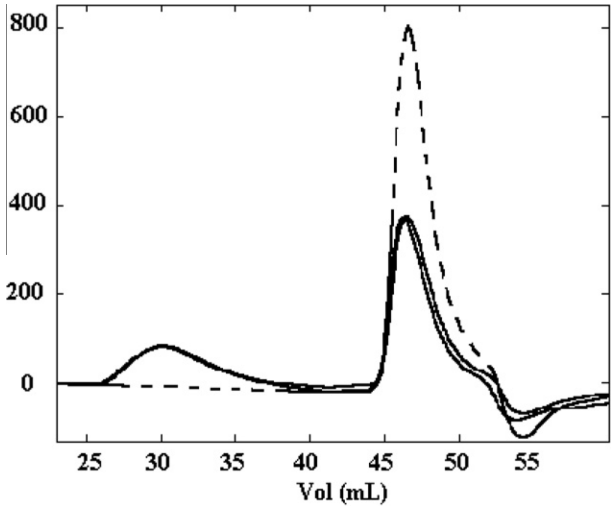


Fig. 2. GPC chromatograms for PL1. Mobile phase (- -) and PL1 (duplicate) (–).

DLS studies of PLn solutions (7 mg mL^{-1} in buffer phosphate pH = 7.4) showed a size distribution by volume whose maxima are located at the following approximate diameters 19.5 and 9.3 nm for PL1 and PL2 respectively (see Fig. 3). These values are also larger than expected and are also another evidence for intermolecular aggregation.

If we compare the results of GPC and DLS they are consistent with each other since the size of the aggregates obtained by DLS is proportional to the experimental M_n values (also to M_w since

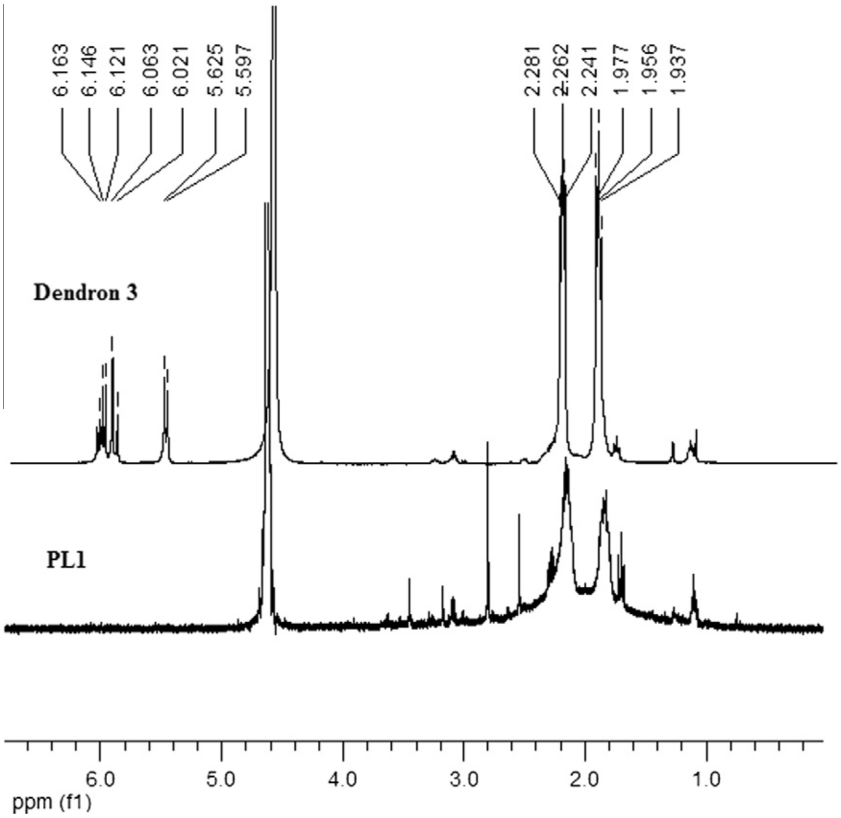


Fig. 1. Comparative ^{1}H RMN spectrum of dendron 3 and PL1 after 48 h of polymerization.

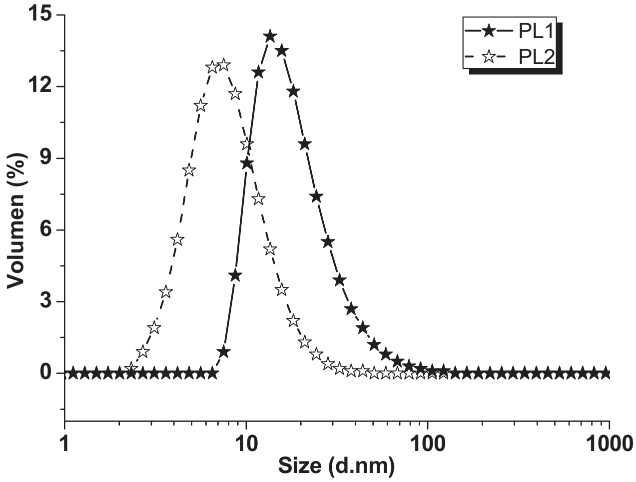


Fig. 3. Size distribution by volume of the polymers determined by DLS.

the polydispersity is close to 2.2 for all cases, see Table 1): PL1 (19.5 nm/255 kg/mol) > PL2 (9.3 nm/188 kg/mol). However, these trends do not relate with the theoretical M_n values of the individual PLn chains, hence their aggregation properties may be related to several factors other than just molecular size. Rheological results (shown below) also evidence the extraordinary ability of these polymers to form aggregates in aqueous solution with CTAT micelles.

3.2. Rheology

3.2.1. Simple shear behavior

The rheological behavior of CTAT aqueous solutions has been studied [21–32]. It is well-known that this cationic surfactant forms worm-like micelles in aqueous solution displaying strong viscoelastic behavior. At its critical micellar concentration (CMC) which has been reported to be of 0.26 mM at room temperature [23,24,26], it forms spherical micelles. As the surfactant concentration is increased and its critical rodlike concentration (CRC) is surpassed, a transition from spherical to rodlike micelles occurs [26]. The CRC value is reported to be 1.97 mM [26]. Beyond this CRC, the rodlike micelles turn increasingly flexible and can be described as worm-like micelles that grow in size and number, coexisting initially in a dilute regime, without micelle/micelle interactions. As the semi-dilute regime with respect to the worm-like micelles is reached, above $\varphi*$ (11 mM) [25], the micelles are fully entangled under static conditions and therefore exhibit relatively high zero-shear rate viscosities with slight shear thickening and pronounced shear thinning at high shear rates. The shear thickening behavior has been attributed to “shear induced structure” (SIS) formation. Increasing the concentration, for instance higher than 20 mM, entangled worm-like micelles persist under static conditions and solutions show pronounced shear thinning effect. These micellar aggregates have a high degree of association and may present several and interesting applications in different areas [21,22,26,33–38].

3.2.2. PL1/CTAT mixtures

Aqueous solutions of both PLn in water at concentrations lower or equal to 1000 ppm yielded one phase homogeneous solutions with identical viscosities to that of water. In this concentration regime, the PLn polymers are not able to induce any viscosity increase (results not shown except for one example in Fig. 4).

Mixtures of PLn/CTAT display limited solubility; hence, tests were performed to determine solubility windows at 25 °C. The CTAT concentration was kept constant at 20 mM (a concentration that ensures the presence of entangled worm-like micelles of CTAT) and PL1 was varied. In the case of PL1/CTAT mixtures, it was found that the maximum polymer concentration to achieve a stable single phase was 100 ppm at 25 °C. Above this concentration phase separation takes place.

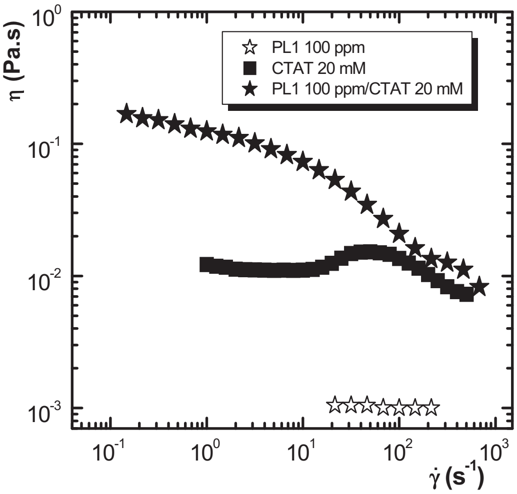


Fig. 4. Rheological behavior of aqueous solutions of PL1/CTAT mixtures in comparison with neat PL1 dendronized polymer solutions and CTAT solution (T = 25 °C).

An illustrative example of the striking synergistic effect observed after the addition of PL1 to a CTAT solution containing worm-like micelles is shown in Fig. 4. It is possible to compare the rheological behavior between a PL1/CTAT mixture, the pure polymer and the pure surfactant aqueous solution. At 20 mM, CTAT displays a relatively high shear rate viscosity with slight shear thickening followed by shear thinning at higher rates. The shear thickening has been attributed to the shear induced structuring process whereby the shear flow induces further interaction and worm-like micelle entanglements [27].

At low-shear rates, the 100 ppm PL1/CTAT mixture exhibits a shear viscosity that is about one order of magnitude higher than the 20 mM CTAT solution, though the viscosity of the 100 ppm PL1 solution is identical to water (water data not included for clarity purposes). Furthermore, the mixture PL1/CTAT becomes strongly shear thinning in almost the whole range of shear rate explored with a minor residual shear thickening at high shear rates. Fig. 5 shows the well-known rheological behavior of CTAT as a function of concentration (see for instance Müller et al. [27] and references therein). When the CTAT concentration is increased to 30 mM, the entanglement density between the worm-like chains is so high that the fluid achieves its maximum structuring level. In this case, shear flow can no longer induce the formation of any more transient structures and the solution turns shear thinning as the flow destroys the associations in between the surfactant molecules. Here, it is interesting to point out that the rheological behavior of the 100 ppm PL1/20 mM CTAT mixture (Fig. 4) is qualitatively similar to that of a more concentrated CTAT solution in the absence of PL1 (see Fig. 5, data for 30 mM CTAT). In other words, the mere addition of 100 ppm of PL1 can induce a strong interaction between the CTAT worm-like chains in view of its association capacity through the dendronized moieties (see Scheme 1).

Fig. 6 shows the effect of adding different amounts of PL1 to a 20 mM CTAT solution. In general, the low-shear viscosity increases with PL1 concentration (c_{PL1}). Three regimes were observed that will be described as follows:

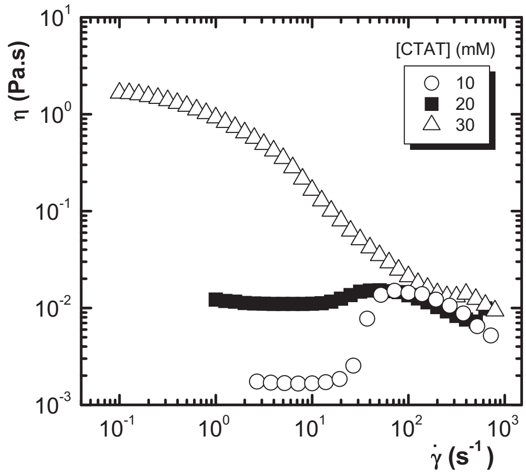


Fig. 5. Shear viscosity as a function of shear rate for CTAT aqueous solutions at the indicated concentrations (T = 25 °C).

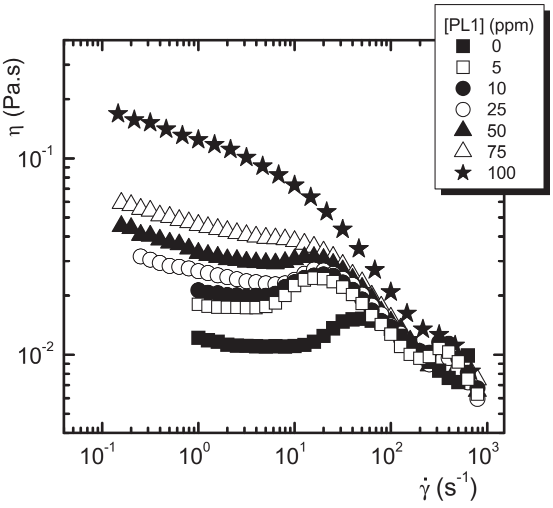


Fig. 6. Shear viscosity as a function of shear rate for PL1/CTAT aqueous solutions at T = 25 °C. [CTAT] = 20 mM. PL1 concentration is indicated in the legend.

(i) When $c_{PL1} \leqslant 10$ ppm, i.e., at low PL1 concentrations, the solutions exhibit a pseudo-Newtonian plateau at low-shear rates, followed by a shear thickening region at intermediate shear rates, and a shear thinning region at high shear rates. This behavior is reminiscent of that displayed by neat CTAT 20 mM solutions, except for the fact that the critical shear rate at which the shear thickening appears (the inverse of this critical shear rate should be proportional to the disentanglement time of the transient network induced by shear flow) is shifted to lower shear rate values. This fact indicates a clear increase in the disentanglement time of the CTAT wormlike micellar network induced by the presence of the associating PL1 molecules.

(ii) At intermediate PL1 concentrations ($c_{PL1} \geqslant 25$ ppm but lower than 75 ppm), mixtures of PL1/CTAT displayed a moderate shear thinning effect at low-shear rates (with higher shear rate viscosities), followed by a less pronounced shear thickening effect that finally leads to another more pronounced shear thinning effect, as shear destroys the structure of the fluid.

(iii) As concentration increases ($c_{PL1} > 75$ ppm), no shear thickening is observed as the structure of the fluid is saturated by intermolecular interactions. The disappearance of shear thickening in the case of neat CTAT has been associated with the saturation of the worm-like micelles entanglements or interactions [27]. In other words, the fluid already possesses a saturated structure that is composed of entangled CTAT micelles with a maximum degree of interpenetration or maximum entanglement density. As shear thickening has been attributed to SIS under flow, once the fluid possesses a saturated structure, even the lowest shear rates can only induced de-structuring or disentanglement. We speculate that a similar situation has been reached in our CTAT/PL1 mixtures when the PL1 concentration reaches 100 ppm and shear thickening disappears. It would seem that a saturated fluid structured has been reached where the intermolecular interactions between PL1 and CTAT have reached a maximum value probably limited by steric interactions (see Scheme 1). It should be remembered that at higher PL1 concentrations the solution undergoes phase separation.

Calderon et al. [19] reported a similar behavior for mixtures of amphiphilic dendrons with CTAT. They observed that dendron addition produced a substantial synergy in low-shear rate viscosity due to the attachment of dendron micelles to wormlike CTAT micelles in a similar manner to micellization of surfactants on polyelectrolytes. So, we believe that the synergistic viscosity produced by the addition of polymer PL1 to entangled wormlike micelle solutions is a consequence of specific interactions between the polymer chains and the CTAT worm-like micelles (see scheme 1).

3.2.3. Oscillatory shear behavior

PL1/CTAT mixtures presented significant changes in their dynamic rheological properties as compared to those of the neat 20 mM CTAT solution, which are a result of the structural and morphological evolution experienced by the worm-like micelles in solution.

Fig. 7 shows the rheological responses CTAT and PL1/CTAT mixtures under oscillatory shear. For the 20 mM CTAT solution we observed that the loss modulus G'' is higher than the elastic modulus G' until the crossover frequency ($\omega_c \approx 88.2$ rad/s) is reached and a pronounced dependence of both dynamic moduli with the oscillation frequency is clearly seen. This is the expected behavior of CTAT solutions at this concentration level and is consistent with

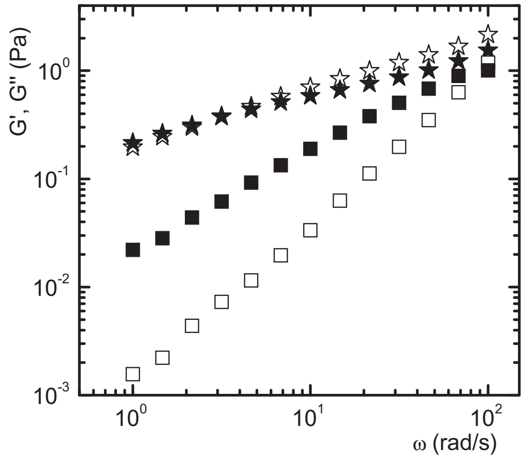


Fig. 7. G' (open symbols) and G'' (filled symbols) as a function of frequency for PL1/CTAT aqueous solutions in oscillatory shear flow. The CTAT concentration is fixed at 20 mM. The concentration of PL1 in the mixtures is: 0.0 ppm (squares) and 100 ppm (stars). T = 25 °C.

previous literature reports [19,30,32]. Addition of 100 ppm of the dendronized polymer PL1 (maximum concentration allowed before phase separation occurs) to the 20 mM CTAT solution shifted the crossover point between G' and G'' to lower frequencies (more than one order of magnitude in frequency shift) reaching a value of 3.3 rad/s. The end result is that the PL1/CTAT solution is much more elastic than the neat CTAT solution as evidenced by the predominance of G' over G'' in a wide frequency range.

Furthermore, the presence of PL1 causes an increase in both, the elastic and the viscous modulus G' and G'' respectively and this indicates a high degree of strong intermolecular entanglements, also consistent with the shear thinning behavior observed in Fig. 4. A weak frequency dependence of the moduli is also seen in these results giving further evidence of a weak gel-like behavior of these mixtures.

The inverse of the crossover frequency can be considered the longest mean relaxation time for the formation or breakup of the fluid microstructure. In Fig. 8 we can see how the crossover relaxation time increases with polymer concentration, giving further evidence that the presence of PL1 changes the dynamics of the association of the CTAT worm-like micelles in solution.

3.2.4. Thixotropy

Most liquids with microstructure can show thixotropy, because thixotropy only reflects the finite time taken to move from any state of microstructure to another and back again, whether from different states of flow or to or from rest [39]. One of the most frequently employed methods to measure thixotropy is the step shear rate experiment. During this experiment, a constant shear rate is applied over a period of time until no changes, in torque or viscosity, are observed which means that the system has reached a steady-state. Afterwards, a sudden change of the shear rate is imposed, usually to break the microstructure, and finally the experiment ends with a sudden change to the initial shear rate to verify the system recovery.

To study the breakdown of the microstructure of PL1/CTAT mixtures, an initial low-shear rate of 3 s^{-1} is applied to the sample at rest and the evolution of the viscosity is recorded as a function of time until steady-state is achieved. Then, the shear rate is immediately changed to a higher one, i.e., 250 s^{-1}, until the viscosity reaches a new equilibrium. To study the formation of the microstructure or the restructuring of the fluid, the shear rate is instantaneously decreased to the initial value (i.e., 3 s^{-1}) until equilibrium is reached again.

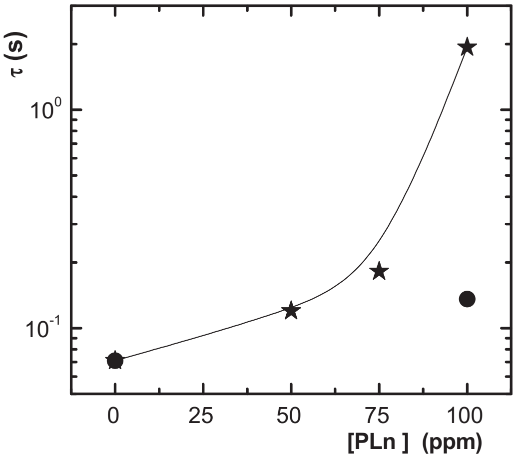


Fig. 8. Cross-over relaxation times as a function of PLn concentration for PLn/CTAT aqueous solutions: PL1/CTAT (stars), PL2/CTAT (circle). The CTAT concentration is fixed at 20 mM. T = 25 °C.

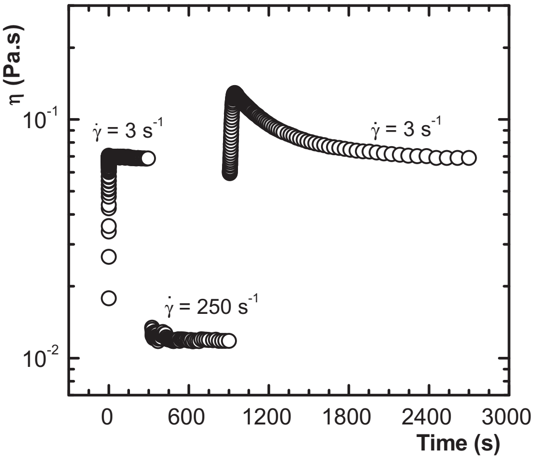


Fig. 9. Thixotropic behavior of 100 ppm PL1 with 20 mM CTAT aqueous solution. Initial shear rate 3 s^{-1}, then it was instantaneously increased to 250 s^{-1} and finally switched again to 3 s^{-1} (T = 25 °C).

As it can be seen in Fig. 9, at the initial and constant shear rate of 3 s^{-1} the fluid undergoes an instantaneous increase of viscosity and eventually reaches a constant value (i.e., during the first 300 s). When the shear rate is increased to 250 s^{-1} the viscosity drops due to the breakdown of the microstructure (shear thinning effect) and a new equilibrium is achieved. Finally, the change to the initial shear rate (3 s^{-1}) results in an overshoot viscosity but thereafter the viscosity decreases and ends up at the same value that was recorded in the initial stage of the test. The change of the viscosity with time (at constant shear rate) after this sudden decrease in shear rate provides the clearest indication of thixotropy and also gives further evidence that a restructuring process occurs though a much longer time is required to achieve similar viscosity values.

The same step shear rate test performed to the neat 20 mM CTAT solution yields a much lower thixotropy behavior (results not shown), because the solution is an order of magnitude less viscous and as indicated in Fig. 7 it also displayed much lower elasticity than the PL1/CTAT mixture.

3.2.5. PL2/CTAT 20 mM mixtures

PL2 was also evaluated under simple shear flow. Interactions between PL2 at different concentrations and a 20 mM CTAT solution are shown in Fig. 10 by the changes experienced in the rheology of the solutions. Surprisingly, the addition of only 0.25 ppm of PL2, i.e., 0.003% of the total solute in the solution, increases the low-shear viscosity of neat CTAT solutions by a factor of two. Additionally, a reduction in the critical shear rate for shear thickening from 10.5 to 5.0 s^{-1}, for neat CTAT and PL2/CTAT, respectively was observed.

Nevertheless, as it will be shown in detail below, the maximum low-shear viscosity achieved at a limiting polymer concentration of 100 ppm (larger concentrations cause phase separation) are lower than those obtained with PL1/CTAT mixtures. Another important feature is that the shear thickening character of the fluid is never lost, a fact that indicates an intermediate level of structuring. The elasticity of the fluid was also found to be much lower for the PL2/CTAT mixtures than for PL1/CTAT mixtures. In fact, we only determined dynamic rheological properties for the PL2/CTAT mixture with 100 ppm PL2 (lower concentrations lead to behaviors resembling that of neat 20 mM CTAT solution). The changes of G' and G'' with frequency are shown in Fig. 11. The addition of 100 ppm of PL2 to a 20 mM CTAT solution only causes an slight increase in both, the elastic and the viscous modulus G' and G'' respectively. The cross-over relaxation time for this PL2/CTAT

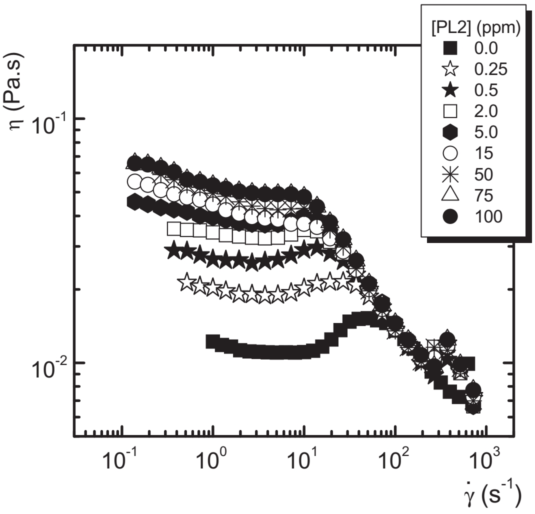


Fig. 10. Shear viscosity as a function of shear rate for PL2/CTAT aqueous solutions. The concentration of CTAT is fixed at 20 mM while that of PL2 is indicated in the legend ($T = 25$ °C).

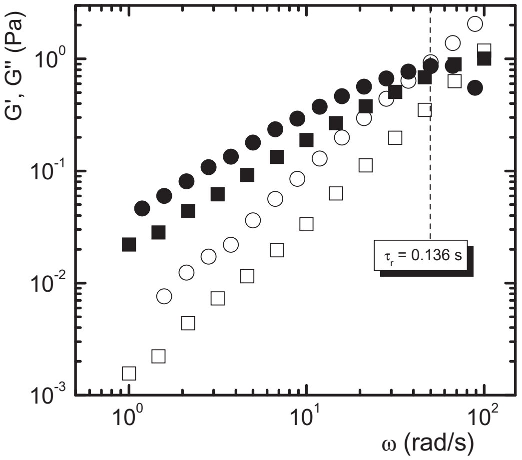


Fig. 11. G' (open symbols) and G'' (filled symbols) as a function of frequency for PL2/CTAT aqueous solutions in oscillatory shear flow. The CTAT concentration is fixed at 20 mM. The concentration of PL2 in the mixtures is: 0.0 ppm (squares) and 100 ppm (circles). $T = 25$ °C.

mixture was found to be one order of magnitude lower than that of PL1/CTAT mixture at identical concentrations, as shown in Fig. 8. Thixotropy tests also indicated a much faster achievement of the initial viscosity value after breakdown and recovery of the PL2/CTAT structure (i.e., lower thixotropic character) as compared to PL1/CTAT (results not shown).

In Fig. 12 a comparison between PLn/CTAT mixtures evaluated at a fixed polymer concentration of 100 ppm is shown (the maximum concentration at which a homogeneous solution can be prepared with both polymers). There is a definite synergistic interaction between both polymers and the worm-like CTAT micelles. The viscosity increases in the mixtures at low-shear rates, but the increase provided by the addition of PL2 is not as substantial as that obtained with the addition of PL1. Furthermore, the addition of PL1 to the 20 mM CTAT solution eliminates the shear thickening, since the solution become strongly shear thinning in almost the whole range of shear rate explored. This is an indication of the fully structured nature of the fluid where the entanglement density of the worm-like micelles reaches saturation.

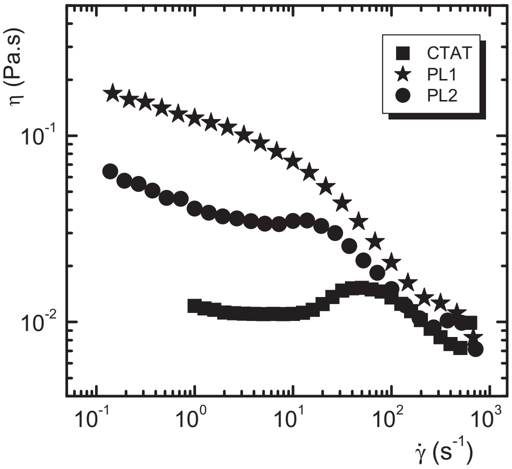


Fig. 12. Shear viscosity as a function of shear rate for PLn/CTAT aqueous solutions. The concentration of PLn is fixed at 100 ppm and that of CTAT at 20 mM ($T = 25$ °C).

The results indicate that in aqueous solution the aggregation of each polymer with itself and with CTAT is different, as observed by GPC and DLS. At the concentration of 100 ppm, the polymer with the lowest theoretical molecular weight but with the highest capacity to form aggregates (as indicated by GPC and DLS), i.e. PL1, seems to have a better ability to form aggregates with CTAT than PL2, a fact that leads to a substantial increase in viscosity and a change in the rheological profile. Taking into account the rheology of CTAT worm-like micelles (Fig. 5) it is clear that PL1 can lead to a more densely structured fluid upon mixing it with CTAT than PL2. The mixtures of PL2 and CTAT at the maximum polymer concentration of 100 ppm exhibit a rheological behavior typical of an intermediate state of structuring, where the fluid is still capable of exhibiting shear thickening.

A summary of the synergistic behavior displayed by the PLn/CTAT solutions can be found in Fig. 13, where the shear viscosity at the lowest shear rate employed ($\dot{\gamma} = 1\ s^{-1}$) is plotted as a function of PLn concentration (CTAT concentration is fixed at 20 mM).

In the case of PL2/CTAT we observed significant changes in the viscosity at very low polymer concentrations. When 0.25 ppm is added (see insert in the same figure), a rapid increase in shear viscosity is observed as a consequence of the aggregates formed between PL2 and CTAT. However, the viscosity of PL2/CTAT solutions reaches a plateau with polymer concentration at 25 ppm. Notice that the relative increase in the viscosity is much more abrupt than the behavior exhibited by the PL1/CTAT mixtures at low polymer concentration. Moreover, for PL1/CTAT mixtures the synergistic increase in low-shear viscosity is relatively small at low polymer concentrations whereas it is more pronounced for PL1 concentrations higher than 75 ppm with an increase in viscosity of one order of magnitude with respect to the solution of neat CTAT.

The aggregation trend shown by the PLn in solution is not entirely clear. The results indicate that, under static conditions (i.e., DLS), PL1 has the largest capacity to self-aggregate as compared to PL2 (at the concentration employed to perform the DLS measurement); thus, forming bigger size particles in solution.

The results obtained by rheology indicate that even though both polymers lead to significant increases in viscosity when they are added to a 20 mM CTAT solution, the trend varies with polymer concentration. At concentrations below 75 ppm, adding small amounts of PL2 can lead to higher viscosities. Nevertheless, the PL2/CTAT fluids have a low-shear viscosity value that saturates above 25 ppm and the fluid never looses its shear thickening capacity (see Fig. 10). On the other hand, at 100 ppm, the PL1/CTAT

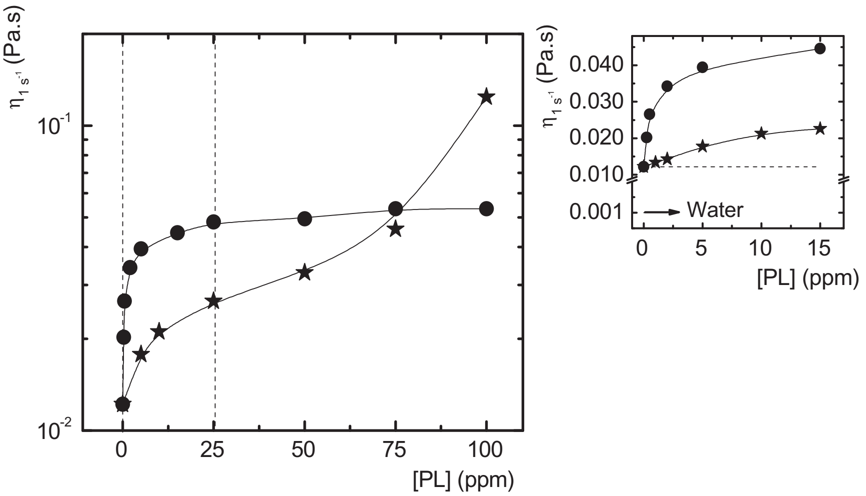


Fig. 13. Low shear rate viscosity ($\dot{\gamma} = 1\ s^{-1}$) as a function of dendritic polymer concentration for PLn/CTAT solutions: PL1/CTAT (stars), PL2/CTAT (circles). [CTAT] is fixed at 20 mM. The inset shows the viscosity increase at low PLn concentrations ($T = 25$ °C).

fluid is highly structured with the highest viscosity value obtained for PLn/20 mM CTAT mixtures, with an enhanced elastic character and longer relaxation time than PL2/CTAT mixtures of identical concentration.

When the PLn/CTAT mixtures are examined by rheology two important factors are changing as compared to the measurements performed by DLS. The first one is that PLn molecules will have the choice to interact with themselves or with CTAT worm-like micelles. The second one is that such interactions are probed under dynamic conditions (i.e., under the state of flow).

In view of the synergistic increases in viscosity obtained, it seems likely that the CTAT–PLn interactions are favored over the PLn–PLn interactions in aqueous solution.

Another possibility is that under dynamic conditions the PL1 aggregates could be disrupted more quickly by the shear forces than those of PL2, i.e., under shear PL1 could form smaller aggregates and a gradual viscosification is produced when interacting with CTAT worm-like micelles. At high polymer concentration, these smaller aggregates should have more chances of being entangled with the worm-like micelles. If we take into account that smaller particles have a larger surface area, PL1 presents a higher probability of interacting with the functional groups on the surfaces of CTAT micelles, a fact that might explain the higher viscosity observed at 100 ppm.

Also, slight differences in solubility could contribute to the results obtained here. PL1 can be considered more soluble than PL2 in the CTAT solution because of its theoretically lower Mn value. Then an early saturation of the viscosity with the increase in polymer concentration would be expected for the less soluble PL2 polymer.

The associating fluids formulated in this paper (i.e., CTAT and CTAT/PLn) exhibit a complex rheological behavior. One of their characteristics is a time dependence of the rheological response that has been demonstrated by: (a) the change in the critical shear rate for shear thickening (Fig. 6), (b) the change in the characteristic relaxation time of the network formed by the entangled worm-like micelles and PLn, as shown in the data presented in Fig. 8 and derived from oscillatory shear measurements and (c) the thixotropic behavior displayed by the CTAT/PLn solutions (Fig. 9). Another interesting characteristic is the fact that when the solution viscosity of the mixtures is high (at relatively high concentrations of PLn), the solutions do not exhibit a Newtonian plateau at low-shear rates (in fact we have avoided employing the term zero-shear solution viscosity and have used the term low-shear solution viscosity instead) but they are shear thinning.

4. Conclusions

New dendronized polymers were successfully synthesized by polymerization of Behera amine acrylated. GPC and DLS indicated that these PLn have a remarkable tendency to form agglomerates in solution that lead to apparent molecular weights that are much higher than their theoretical values, as well as diameters in solution. The polymer with the highest tendency to self-aggregate was PL1, the dendronized polymer with the lowest number average theoretical molecular weight. The addition of any PLn to water did not cause any increase in viscosity up to concentrations of 1000 ppm. On the contrary, a synergistic viscosity enhancement was found by adding small amounts of dendronized PLn polymers to a CTAT solution composed of entangled worm-like micelles. The highest association tendency with CTAT was also found for the polymer with the lowest theoretical molecular weight. The solution viscosity could be increased by an order of magnitude upon addition of 100 ppm of PL1 to a 20 mM CTAT solution. Under these conditions the fluid obtained was highly structured and exhibited only shear thinning behavior from the smallest shear rates employed. Additionally it displayed much larger values of both the loss and the storage moduli than the neat 20 mM CTAT solution and a much higher elastic character that translated in a much longer value of the cross-over relaxation time and a pronounced thixotropic behavior.

In the case of PL2, its association with CTAT leads to an extraordinary doubling of solution viscosity with just 0.25 ppm addition to a 20 mM CTAT solution. However, such synergistic viscosity enhancement saturated at rather low concentrations (25 ppm) indicating an apparent lower solubility as compared to PL1.

Acknowledgments

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