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Local Polarity and Microviscosity of the Interior of Dendritic Polyethylene Amphiphiles

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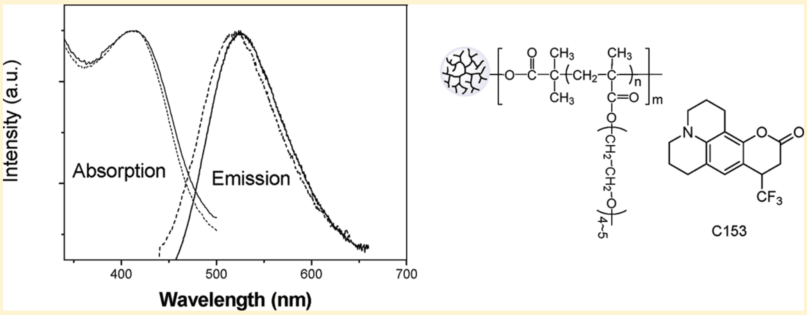
ABSTRACT:



From the temperature dependent steady-state and time-resolved fluorescence studies of coumarin 153 (C153) in dendritic polyethylene (DPE)−poly(oligo(ethylene gylcol) methacrylate) (POEGMA) unimolecular micelles, the polarity and microviscosity of the microenvironments of DPE−POEGMA were obtained. The analysis of the steady-state emission suggested that C153 sensed a more polar microenvironment in dendrimer polyethylene (dPE)−POEGMA than that in hyperbranched polyethylene (hPE)−POEGMA. It is found that the microviscosity around C153 in DPE−POEGMA micelle could be predicted from the measured reorientational time, which was observed to decrease with increasing temperature, and that local friction experienced by C153 in dPE−POEGMA decreases faster than in hPE−POEGMA with the increase of temperature, although both have similar local friction ranges.

INTRODUCTION

Dendritic polymeric amphiphiles have attracted a great deal of attention in past years due to their versatile applications including nanoreactors, drug delivery, sensor design, and green chemistry.[1] A detailed understanding of the microenvironment of dendritic polymeric amphiphile solutions is essential for optimizing chemical and physical processes on the nanometer scale, because modest changes in the polarity and local friction of microenvironment could lead to variable diffusion rates and reaction rates.[2]

As a well-characterized solvatochromic fluorescence probe, coumarin-153 (C153) has been shown to be an excellent probe of solvation dynamics[3] and local friction for microenvironment and has been used for probing complex environments of polymeric micelles,[4] such as poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) triblock copolymers,[5] and poly(*N*-decylacrylamide)-*block*-poly(*N*,*N*-diethylacrylamide) copolymers,[6] and amphiphilic scorpion-like and star-like macromolecules.[7] Moreover, polarity of the dendritic interior of biaryl-based amphiphilic dendrons with a charge-neutral penta(ethylene glycol) as the hydrophilic part and a decyl chain as the hydrophobic part was investigated using dye-based microenvironment studies.[8] However, the detailed understanding of the microenvironment of dendritic polymeric amphiphiles is little explored.

The dendritic polyethylene amphiphiles are especially attractive due to their completely hydrophobic core with branching topology structure, their globular shape in aqueous solution with molecular dimensions right in the nanometer range, and their many potential applications including controlled drug delivery and release, phase transfer, and molecular nanocarriers. On the basis of the unique chain walking polymerization mechanism,[9] the obtained dendritic polyethylene hydrophobic core possesses the complete carbon−carbon backbone construction and the special characteristics in branching topology structure, being different from those prepared by the typical condensation polymerization.[10] Compared with the conventional block copolymer micelles, the dendritic polyethylene amphiphiles possess much higher structural stability and exhibit the unimolecular micelle behaviors in aqueous solution.[11] Thus, it is necessary to study the nature of the microenvironments in dendritic polyethylene amphiphiles, but few attempts have been made. Considering that the investigation in this aspect would provide useful information about local polarity and microviscosity of dendritic polyethylene amphiphiles for comparison, we chose two types of

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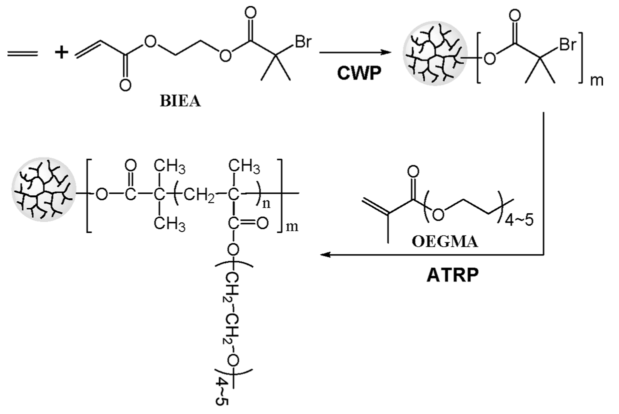
Scheme 1. Synthesis of the Dendritic Polyethylene Amphiphiles (DPE−POEGMA)



dendritic systems with different branching topology of polyethylene core, which were changed from dendrimer to hyperbranched architectures by varying ethylene pressure (P_E) of chain walking polymerization (CWP) conditions from 0.1 to 1 atm.[9c]

Here, we examine dendritic polyethylene (DPE)−poly(oligo(ethylene gylcol) methacrylate) (POEGMA) with core−shell architecture, which have been used previously by our group to study their temperature-sensitive phase transition behaviors.[11] The steady-state fluorescence emission and reorientation time constant measurements were employed to study the local environments in aqueous DPE−POEGMA solutions, using C153 as the fluorescence probe.

EXPERIMENTAL SECTION

Sample Preparation. DPE−POEGMA were synthesized by a tandem polymerization methodology, chain walking polymerization (CWP) followed by atom transfer radical polymerization (ATRP), as reported in the literature.[9c,11] The resultant dendritic product was purified by dialysis against methanol (molecular weight cutoff (MWCO) of dialysis bag used: 14 000).

Characterization. Steady-state fluorescence emission spectra of C153 in DPE−POEGMA aqueous solutions were measured with a Shimadzu RF-5301 PC fluorescence spectrophotometer. The reorientational dynamics for C153 in DPE−POEGMA were acquired using the time-correlated single photon counting (TCSPC) method on a laboratory-built instrument. For the present setup, the instrument response function (IRF) was ~60 ps (the full width at half-maximum, fwhm). Samples were measured with 420 nm excitation and 524 nm emission for dPE−POEGMA and at 519 nm for hPE−POEGMA. Sample temperatures were controlled to ±0.1 °C using a DBS PELTIER 1 × 1 accessory thermoelectric temperature controller with 10 min thermal equilibration times. The concentration of the sample in the aqueous solution was 1 mg/mL. The viscosities measured for all DPE−POEGMA aqueous solutions were close to that of pure water because the solutions are dilute. The concentration of coumarin dye was kept much lower than the micelle concentration, only in the range of 1−5 μM. With the above experimental conditions, the possibility of more than one probe molecule occupying a single micelle can be ignored. Such a situation is important to avoid the effect of any dye−dye interaction on the observed rotational relaxation dynamics results.[5c]

Time-resolved decay of polarization anisotropy $r(t)$ was calculated from fluorescence decays recorded in parallel and perpendicular directions with respect to the excitation polarization as follows

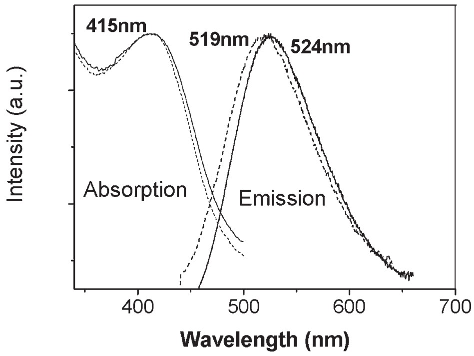


Figure 1. Absorption (left) and emission (right) spectra of C153 in dPE−POEGMA3 (solid) and hPE−POEGMA3 (dash) aqueous solutions at room temperature.

$$r(t) = (I_{VV}(t) - GI_{VH}(t))/(I_{VV}(t) + 2GI_{VH}(t)) \qquad (1)$$

where G is an instrumental correction factor and the subscripts VV and VH denote vertical excitation and vertical and horizontal emission polarizations, respectively. The orientation time-correlation function is given by $r(t)$

$$r(t) = \sum_{i=1}^{n} r_i \exp\left(-\frac{t}{\theta_{i,\mathrm{rot}}}\right) \qquad (2)$$

where r_i and $\theta_{i,\mathrm{rot}}$ are the individual amplitudes and reorientational time constants for the ith anisotropy decay, respectively.[12,13]

RESULTS AND DISCUSSION

As shown in Scheme 1, DPE−POEGMA with the hydrophobic core DPE and the hydrophilic shell POEGMA were synthesized by Cu(I)-mediated ATRP of OEGMA, using DPE terminated by the bromine group as macroinitiators.[9c] Two dendritic macroinitiators bearing multiple initiation sites bromine group were prepared at the same comonomer (BIEA) feed concentration but at the variable ethylene pressure: dendrimer macroinitiator with a number averaged molecular weight (M_n, measured by size exclusion chromatography using a multiangle light scattering detector (SEC-MALS)) of 31 500 g/mol, 4.5 mol % incorporated BIEA comonomer, and 37 initiation sites, and hyperbranched macroinitiator with a M_n of 55 900 g/mol, 2.8 mol % incorporated BIEA, and 45 initiation sites, as well as both with branching numbers of ~120 branches per 1000 carbons, determined by the ^{1}H NMR spectra.[11]

The branching topology of polyethylene core were changed from dendrimer to hyperbranched architectures by varying ethylene pressure (P_E) of CWP conditions from 0.1 atm to 1 atm, i.e., from dendrimer polyethylene (namely dPE) to hyperbranched polyethylene (hPE).[14] Despite the highly hydrophobicity of dendritic polyethylene cores,[15] the peripheral PEGylation around the dendritic polyethylene core makes DPE−POEGMA soluble in water at room temperature, and the extent of PEGylation is varied by changing ATRP time. These provided the possibility to investigate the effect of different structural parameter for core and shell on the microenvironment of DPE−POEGMA micelle.

Absorption and Steady-State Emission Spectra. Figure 1 displays the absorption and steady-state emission spectra of the C153 dye in DPE−POEGMA aqueous solutions at 25 °C. C153

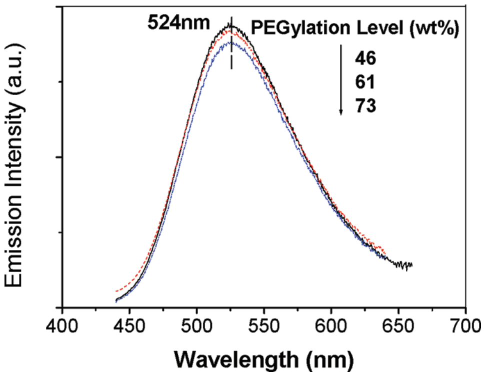


Figure 2. Steady-state fluorescence emission spectra of C153 in dPE−POEGMA with the different PEGylation levels at room temperature.

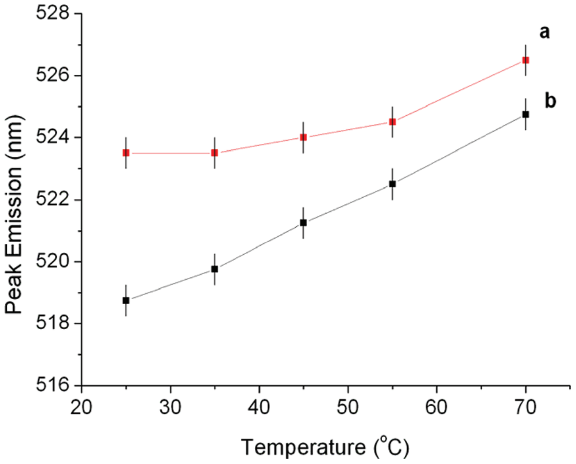


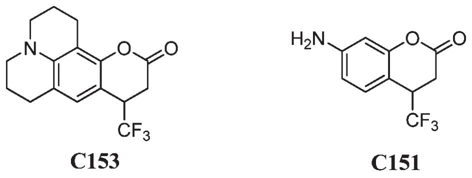
Figure 3. Temperature dependence of steady-state emission peak wavelength of C153 in dPE−POEGMA3 (a) and hPE−POEGMA3 (b) aqueous solutions.

exhibits an emission maximum at 524 nm in dPE−POEGMA and 519 nm in hPE−POEGMA at 25 °C, respectively. The emission wavelength of C153 is a sensitive reminder of the polarity of its local environment.[16,17] Because absorption spectra of C153 are less sensitive to the polarity changes, no significant shift is observed in the absorption spectra of the C153 dye in DPE−POEGMA micelle in comparison to that in emission spectra.

Figure 2 shows steady-state emission spectra of the C153 dye in DPE−POEGMA with varied PEGylation level at 25 °C. It is observed that the difference in the level of PEGylation with the same core does not result in different emission peak wavelength, suggesting little effect of the level of PEGylation on the local polarity of C153 dye.

Temperature dependence of the steady-state emission peak wavelength of C153 probe in dPE−POEGMA and hPE−POEGMA micelles were presented in Figure 3. It is shown that the emission peak of C153 shifts to the red with increasing temperature, indicating some slight increase in polarity for the probe microenvironment of both micelles at higher temperature. This rise in polarity of the microenvironment around C153 is related to the enhanced dehydration of PEG for DPE−POEGMA and the variable behavior of the water molecules present in the micellar phase at elevated temperature. The emission spectrum of C153 dye is sensitive to the proximity as well as the electric field of polar water molecules that affect the local solvation polarity around the probe.[18] Although the core is composed of hydrophobic, aliphatic carbons, water is likely present in or near the interior of the micelle. It is expected that the water molecules in the micelle can exist either in the hydrogen bonded forms with the oxoethylene groups (thermodynamically bound) or just as the mechanically trapped water.[19] And there will be an enhancement in the conversion from the thermodynamically bound to the mechanically trapped water molecules in the micelle at elevated temperatures, resulting in the rise in polarity of the microenvironment around C153 in the DPE−POEGMA micelle with temperature.

Scheme 2. Molecular Structures of Coumarin 153 (C153) and Coumarin 151 (C151)



For the comparison of C153, a relatively hydrophilic coumarin 151 (C151) dye is also used as the fluorescence probe for observation of the difference of local polarity in DPE−POEGMA micelle. The structures of C153 and C151 are shown in Scheme 2.

Because C153 and C151 is only sparingly soluble in water,[20] it is expected that it will preferably reside in the micellar phase. The same emission peak (493 nm) is observed for the C151 dye in both dPE−POEGMA and hPE−POEGMA at room temperature, indicating the same polarity microenvironment around C151 in both the micelles with varied PEGylation level. Moreover, no change for the emission peak wavelength of the C151 dye in DPE−POEGMA aqueous solution with varied temperatures is observed, indicating similar polarities for the microenvironments in both dPE−POEGMA and hPE−POEGMA micelles at different temperatures studied. The fact that the C153 and C151 dyes show somewhat different features in relation to the micropolarity in dPE−POEGMA versus hPE−POEGMA micelles is probably due to the differences in the solubilization sites of the probes in the micelles. The C153 and C151 probes are expected to be somewhat different in their hydrophobicity.[5c] Therefore, C151 can show some hydrophilic character and thus will prefer to reside more toward the micellar surface in comparison to the site of locations of the C153 dye in the micelles. Accordingly, it is possible that the C151 probe recognizes nearly similar environments in both dPE−POEGMA and hPE−POEGMA micelles but C153 recognizes a somewhat different environment in the two micelles.

The emission peak of C153 at room temperature is at 450 nm in a nonpolar *n*-heptane medium, and at 567 nm in a polar solvent such as ethylene glycol, respectively.[16,18] It indicates that C153 in the DPE−POEGMA unimolecular micelle remains in a region where the polarity is lower than that of ethylene glycol but higher than that of *n*-heptane, and that the microenvironment of hPE−POEGMA is more hydrophobic than that of dPE−POEGMA. According to our measurements, the emission peak of C153 is shown to shift from 548 nm in a polar, water-like environment to 542 nm in a polar water−PEG to 532 nm in a

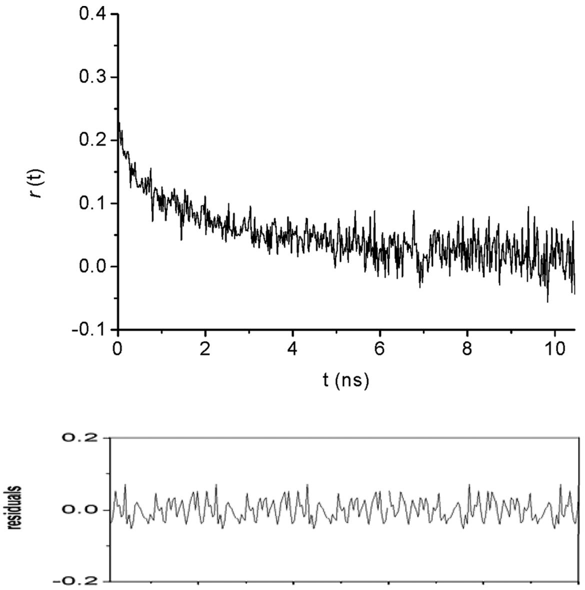


Figure 4. Fluorescence anisotropy decay of C153 in hPE−POEGMA3 aqueous solution.

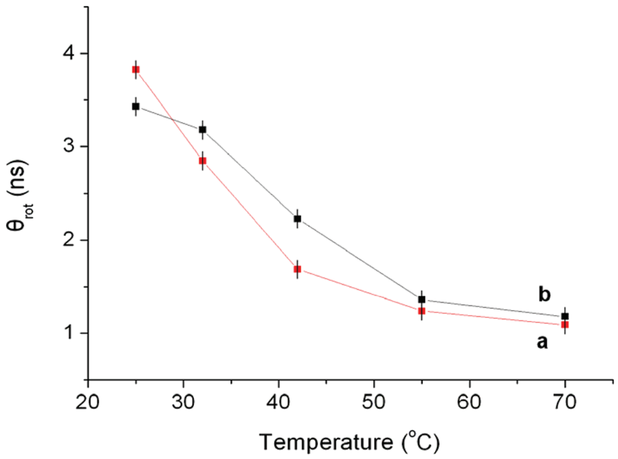


Figure 5. Temperature dependence of reorientation time constants, θ_{rot}'s, for C153 in dPE−POEGMA3 (a) and hPE−POEGMA3 (b) aqueous solutions.

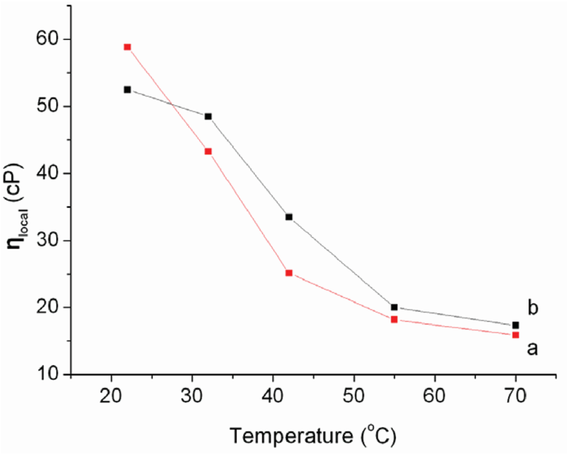


Figure 6. Temperature dependence of microviscosity for C153 in aqueous solutions of dPE−POEGMA3 (a) and hPE−POEGMA3 (b). The error bar for each data point is ±0.05.

pure PEG environment, which indicates the microenvironment around C153 in the DPE−POEGMA micelle is different from that in a polar water−PEG and even a pure PEG environment.

Reorientational Dynamics. Figure 4 shows the fluorescence anisotropy decay of C153 in hPE−POEGMA3 aqueous solution. The fluorescence depolarization anisotropies of C153 in DPE−POEGMA were obtained (eq 1) and best fit to the single-exponential equation given in eq 2. It is found that the difference in the level of PEGylation with the same core has little effect on the reorientation time constant of C153. Probe dissolved in the micellar core is expected to show single-exponential fluorescence anisotropy decay.[21] The exact location of C153 in micelles is yet to be in question. Hence, it is difficult to fathom exactly the location site of C153 dye in the DPE−POEGMA micelles.

The reorientation time constant θ_{rot} for C153 in DPE−POEGMA aqueous solution at different temperatures is displayed in Figure 5. The decrease in the reorientation time constant of C153 with increasing temperature could be observed, possibly due to the increase of the mechanicially trapped water molecules in the DPE−POEGMA micelles at higher temperatures. As the response of these water molecules is comparatively faster than that of the bound water molecules, it leads to a faster rotational relaxation dynamics in the DPE−POEGMA micelles. It is shown that the reorientation time constant θ_{rot} ranges from about 3.83 to 1.09 ns for dPE−POEGMA3 and from about 3.43 to 1.18 ns for hPE−POEGMA3 in the temperature range 25−70 °C, respectively. The reorientation time constants θ_{rot} for C153 in DPE−POEGMA solution are found to be similar, suggesting the similar motion of the C153 dye inside DPE−POEGMA micelles.

As the contribution of the whole micelle rotation to the observed $r(t)$ decays seems to be quite negligible,[22] the changes in the rotational relaxation times are not directly related to the changes in the micellar size with temperature. We thus infer that the changes in the rotational relaxation times reflect the changes in the microviscosity inside the micellar region.

Microviscosity Inside DPE−POEGMA. The reorientation time constant obtained from C153 fluorescence anisotropy experiments could give information about the local friction or microviscosity of the fluorophore environment on the relevant molecular length scales, which is often poorly correlated to the bulk solution viscosity.[23] By using the molecular volume of C153,[24] one can estimate the effective local viscosity from the measured time constants for reorientation by considering the Stokes−Einstein−Debye equation for a model spherical rotor with stick boundary conditions. In this work we will simply consider the average rotational relaxation times directly to obtain a qualitative understanding of the changes in microviscosity in the micellar region with temperature. On the basis of the empirical equation $\langle\theta_{rot}\rangle_{polar} = (58.1 \pm 1.6)\eta^{0.96\pm0.03}$ of Horng et al.,[24] we could predict the effective microviscosity experienced by C153 from the measured reorientational time constant. The microviscosity of the environment probed by C153 in DPE−POEGMA solutions at different temperatures are shown in Figure 6. The result shows a gradual decrease of the microviscosity around C153 in DPE−POEGMA with the increase of temperature, consistent with the rotational dynamics becoming faster. The microviscosity around C153 in the temperature range 25−70 °C is found to vary from 59 to 16 cP in dPE−POEGMA3 and from 52 to 17 cP in hPE−POEGMA3 solution, respectively. The decrease in the reorientational time constant with temperature is possibly due to the inverse relation of viscosity with temperature.[25] Thus, even though the dehydration of the DPE−POEGMA micelle enhances with temperature,[11] the microviscosity around the probe in the micelle shows a decreasing trend with temperature. Moreover, it is noted that local friction experienced by C153 in dPE−POEGMA decreases faster than in hPE−POEGMA with the increase of temperature, although both have similar local friction ranges.

Comparison of the Microenvironment of DPE−POEGMA with Other Nonionic Micelles. It is interesting to compare the microenvironment of DPE−POEGMA micelles probed by C153 with other nonionic micelles such as P123, F127, TX-100, and Brij-35, because the same oxoethylene chains are involved in the formation of the corona region for all these micelles, in spite of the different molecular structure for DPE−POEGMA from other micelles. In normal micelles, like TX-100, TX-165, and BJ-35,[5c] the emission peak of C153 is at ∼536 nm, while the emission peak for the block copolymer micelles (P123 and F127) are expected to be 515 and 530 nm, respectively. Compared with the polarity for the above-mentioned normal micelles, the polarity of the interior of DPE−POEGMA micelles sensed by C153 is indicated to be much lower and the interiors have a lower degree of hydration than the Palisade layer of the neutral micelles like TX-100, TX-165, BJ-35, and even F127. The microviscosity of the DPE−POEGMA micelles is found to be similar to those of P123 and F127 micelles, which are higher than those of TX-100 and Brij-35 micelles.[21a]

CONCLUSION

In this work, the local polarity and microviscosity on the nanoscale were investigated in dendritic polyethylene amphiphile (DPE−POEGMA) aqueous solutions as a function of temperature by measuring the steady-state and time-resolved fluorescence spectroscopy of encapsulated C153. Because the solubilization sites of C151 and C153 probes can vary significantly, C151 is also used as the fluorescence probe for the comparison of C153 to study the local polarity in DPE−POEGMA. Analysis of the steady-state emission shows that C153 is in a less polar environment in hPE−POEGMA solution than in dPE−POEGMA, and that some increase in polarity for the probe microenvironment is observed with increasing temperatures. The local friction as reported by C153 in the interior of DPE−POEGMA decreases with increasing temperature, possibly related to the enhancement in the conversion from the thermodynamically bound to the mechanically trapped water molecules in the micelle at higher temperatures.

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