Polymer 51 (2010) 2345–2350

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Effect of molecular architecture on the self-diffusion of polymers in aqueous systems: A comparison of linear, star, and dendritic poly(ethylene glycol)s

Y.J. Wang, H. Therien-Aubin, W.E. Baille, J.T. Luo, X.X. Zhu*

Département de Chimie, Université de Montréal, C. P. 6128, Succursale Centre-ville, Montréal, QC H3C 3J7, Canada

A R T I C L E I N F O

Article history:
Received 14 November 2009
Received in revised form
17 March 2010
Accepted 25 March 2010
Available online 31 March 2010

Keywords:
Star polymers
Diffusion
NMR spectroscopy

ABSTRACT

Star polymers with a hydrophobic cholane core and four poly(ethylene glycol) (PEG) arms, CA(EG$_n$)$_4$, have been synthesized by anionic polymerization. Pulsed-gradient spin-echo NMR spectroscopy was used to study the diffusion behavior of the star polymers, ranging from 1000 to 10,000 g/mol, in aqueous solutions and gels of poly(vinyl alcohol) (PVA) at 23 °C. The star polymers have a lower self-diffusion coefficient than linear PEGs at equivalent hydrodynamic radius. In water alone, the star polymers and their linear homologues have a similar diffusion behavior in the dilute regime, as demonstrated by the similar concentration dependence of the self-diffusion coefficients. In the semidilute regime, the star polymers tend to aggregate due to their amphiphilic properties, resulting in lower self-diffusion coefficients than those of linear PEGs. ^{1}H NMR T_1 measurements at 10–70 °C revealed that the PEG arms of the star polymers are more mobile than the core, suggesting the star polymers in solution have a conformation similar to that of poly(propylene imine) dendrimers.

1. Introduction

The study of diffusion is of fundamental importance in describing macromolecular solution dynamics. The determination of diffusion coefficients of macromolecules in solutions or gels of polymer matrices is also important for applications such as controlled delivery of drugs, gel electrophoresis, permeation through membranes, plasticizers in plastic materials, and encapsulation of drugs and fragrances [1–4]. The diffusion behavior of a variety of oligomers and polymers, including linear poly(ethylene glycol) (PEG) [5–8], dendrimer [9,10], hyperbranched [11–13], and star polymers [14–16] have been studied. The understanding of the dependence of the transport behaviors of the diffusants on their size and shape may help in the design of polymer systems with predictable properties [17,18]. The shape of a macromolecule may have a pronounced effect on its diffusion coefficient. For example, the rodlike protein tropomyosin (aspect ratio $R = 26$) and globular protein myoglobin (aspect ratio $R = 1.6$) exhibited similar behavior in agarose gels but markedly different diffusion in carrageenan gel [19], since agarose gel has a mesh size about 6 times of that of carrageenan gel, in which the diffusion of stiff tropomyosin was hindered more significantly. In aqueous solutions of poly(vinyl alcohol) (PVA), a cyclic poly(ethylene oxide) (PEO) of a lower molecular weight ($M_n = 6000$) was found to have almost the same self-diffusion coefficients as linear PEO of a higher molecular weight ($M_n = 10{,}000$) [20].

Star polymers have attracted significant research interests due to their compact structures and unique physical properties [21–23]. Pulsed-gradient spin-echo (PGSE) NMR experiments have revealed that the molecular mobility of star-branched polyisoprenes in C_6F_5Cl and CCl_4 solutions depends largely on the weight fraction of the polymer, and only weakly on the number of the arms [14]. Similarly, no marked difference was observed between linear and three-armed polystyrenes and polybutadienes ($M_n = 3000$–$1{,}000{,}000$) in CCl_4 solution from dilute to semidilute regime [15]. Although considerable research concerning the shape effect on both the static and dynamic parameters of polymer solutions has been conducted, very few general conclusions can be drawn. The factor of molecular shape is more difficult to address than the molecular size and the accumulation of results helps in the elucidation of such effects. We have previously compared the self-diffusion of linear PEGs and poly(propylene imine) dendrimers bearing triethylenoxy methyl ether as end groups (PPI(TEG)$_n$) [9]. In this work, we used star polymers CA(EG$_n$)$_4$, newly made by attaching four PEG chains to a cholane core (Fig. 1) by anionic polymerization [24] and studied their diffusion behaviors using the PGSE NMR technique. The star polymers with bile acid cores were characterized in a previous study [24]. All three series of polymers, star polymers CA(EG$_n$)$_4$, linear PEGs, and poly(propylene imine) dendrimers, share the same repeat unit, ethylene glycol, while the cores of the star polymers (cholic acid) and

---

* Corresponding author. Tel.: +1 514 340 5172; fax: +1 514 340 5290.
E-mail address: julian.zhu@umontreal.ca (X.X. Zhu).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.03.047

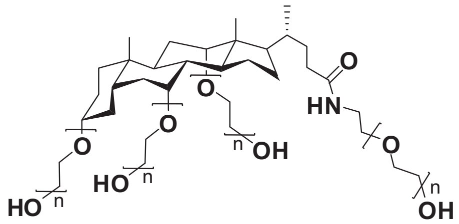

Fig. 1. The chemical structure of the star polymers used in this study. They are prepared by anionic polymerization of ethylene oxide on a core of cholic acid [24]. Four PEG chains are attached and the chain length $n = 4$, 6, 10, 17, 31, 39, and 54.

dendrimers (poly(propylene imine)) add structural variants for the comparative studies. The self-diffusion coefficient measurements were performed in either binary solutions of the diffusants or ternary systems of PVA-water-diffusant.

2. Experimental

2.1. Materials

PVA (MW = 89,000 – 98,000, 99% hydrolyzed) and deuterium oxide (D_2O) were purchased from Sigma–Aldrich (Milwaukee, WI). All chemicals were used as received. The star polymers (Fig. 1) were synthesized as reported previously [24]. The molecular weights of the star polymers measured by size exclusion chromatography (SEC), MALDI-TOF mass spectrometry, and NMR spectroscopy [24] are listed in Table 1 and all results show very low polydispersity indices (PDI = 1.02 – 1.05). The molecular weight were obtained both by SEC coupled with a refractive index detector (SEC-RI) calibrated with linear homologues and by SEC with a light scattering detector (SEC-LS). Both detection methods provided similar results, while the absolute molecular weights measured by SEC-LS are systematically 1.1 times of the values obtained by SEC-RI. It should be noted, however, that linear PEGs were used as the standards for SEC-RI. The molecular weights listed in the report are those obtained by SEC-RI unless otherwise specified. The refractive index increment, dn/dc, was measured with a series of 8 solution samples in the concentration range of 0.2–3.0 mg/mL for each polymer, using a refractive index detector from Wyatt. The molecular weights were determined by SEC equipped with a differential refractometer (Optilab) and a multiangle light scattering detector (DAWN EOS, wavelength 690 nm) in *N*,*N*-dimethylformamide (DMF) at a flow rate of 0.5 mL/min at 25 °C with a set of styragel columns (a TSK-gel α-M, particle size 13 μm, exclusion limit 1×10^7 Da for polystyrene in DMF, and a TSK-gel α-3000, particle size 7 μm, exclusion limit 1×10^5 Da for polystyrene in DMF) (Tosoh Biosep). Samples were filtered through 0.2 μm membrane filters before injection (volume 100 μL). In the NMR studies, the ratio of the peak intensity of CH_2 of the PEG segment (3.6 ppm) to that of the CH_3 of the cholane core (0.6 ppm) is used for the calculation of molecular weight.

Table 1
The molecular weights of the star polymers $CA(EG_n)_4$ determined by SEC, MALDI-TOF mass spectrometry, and ^1H NMR spectroscopy.

Samples[a]	SEC		MALDI-TOF		^1H NMR
	M_n (g/mol)	PDI	M_n (g/mol)	PDI	M_n (g/mol)
$CA(EG_4)_4$	1110	1.04	1360	1.03	1410
$CA(EG_6)_4$	1510	1.04	1810	1.03	2180
$CA(EG_{10})_4$	2190	1.04	2430	1.03	3140
$CA(EG_{17})_4$	3500	1.03	4230	1.03	5490
$CA(EG_{31})_4$	5870	1.05	5980	1.03	8600
$CA(EG_{39})_4$	7320	1.03	6860	1.02	11340
$CA(EG_{54})_4$	9890	1.05			15450

[a] The degrees of polymerization (n) are calculated from M_n by SEC.

2.2. Sample preparation

Samples for self-diffusion measurements were prepared following a method described previously [6,9]. A D_2O solution containing 1 wt.% of a diffusing probe (in this case the star polymers) was added to poly(vinyl alcohol) (PVA) weighed in a 5-mm-o.d. NMR tube. The concentrations of the star polymers are much lower than their critical aggregation concentrations (CACs) determined by surface tension measurements [24]. The final concentrations of the matrix, PVA, ranged from 0 to 0.25 g mL^{-1}, at an increment of 0.05 g mL^{-1}. Molal concentration (mole of solute per 1000 g of solvent) is used in this work because of its convenience in the preparation of samples. Note that for dilute solutions, the concentration in molality is close to that in molarity. The samples were sealed and heated at 110 °C for 24 h.

2.3. NMR measurements of self-diffusion coefficients

The stimulated echo pulse sequence developed by Tanner (STE: 90-t_1-90-t_2-90-t_1-echo) was used to measure the self-diffusion coefficients (D) of the star polymers [25]. Measurements were performed at 23 °C on a Bruker AV400 NMR spectrometer operating at a frequency of 400.27 MHz for protons. The self-diffusion coefficients (D) were obtained from the following relationship [26–28]

$$A = A_0 e^{-\gamma^2\delta^2 G^2 D(\Delta-\delta/3)} \qquad (1)$$

where A_0 and A are the NMR signals in the absence and in the presence of the gradient pulses of strength G, respectively, γ the gyromagnetic ratio of ^1H, δ the duration of the applied gradient pulses, and Δ the time interval between the two gradient pulses.

The interval Δ between the gradient pulses was fixed to 100 ms, the duration of the gradient pulse was set at 1 ms. The gradient strength was varied in 16 steps within a range from 0.1 to 10 T/m (the minimum and maximum varied depending on the system studied) to achieve an attenuation of at least 80% for the diffusants. The gradient was applied along the z axis. For selected samples, the self-diffusion coefficients were also measured in the x and y direction and the self-diffusion was found to be isotropic. The mean-squared displacement in one dimension can be estimated by $2D(\Delta - \delta/3)$. Since the typical self-diffusion coefficients are of the order of magnitude of 10^{-11} m^2/s, at $\Delta = 100$ ms the root-mean-squared displacements are substantially larger than the radius of gyration of either monomeric diffusants or their micellar aggregates. Therefore, the self-diffusion coefficients measured by PGSE NMR experiments reflect the center-of-mass diffusion. The model of Petit et al. [29] was used to fit the experimental data. The coefficients of determination (R^2) obtained were in the range of 0.989–0.999.

2.4. T_1 measurements

A standard inversion-recovery pulse sequence ($180°_x - \tau - 90°_x$ – ACQ) was used to determine the longitudinal relaxation time (T_1) of the characteristic groups of the diffusants. The T_1 measurements at variable temperatures (10–70 °C) were carried out on a Bruker AV400 NMR spectrometer. The T_1 measurements of the solutions with different concentrations were performed at 25 °C. A total of 16 increments of the recovery delay times (τ) between 0.01 and 4 s were used and 8 scans were accumulated for all measurements.

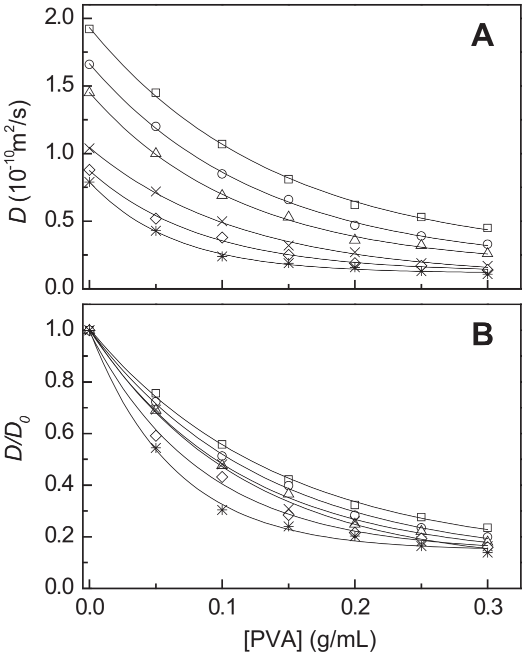

Fig. 2. Self-diffusion coefficients (A) and reduced self-diffusion coefficients (B) of the star polymers as a function of PVA concentration at 25 °C. CA(EG_4)$_4$, (□); CA(EG_6)$_4$, (○); CA(EG_{10})$_4$, (△); CA(EG_{17})$_4$, (×); CA(EG_{31})$_4$, (◇); CA(EG_{39})$_4$, (✳). The lines are fits to Eq. (2).

3. Results and discussion

3.1. Diffusion behaviors in PVA-water-diffusant tenary systems

Fig. 2 shows the effect of PVA concentration on the self-diffusion coefficients of the star polymers. Both the increase in viscosity and hydrodynamic interactions contribute to the substantial decrease in their diffusion coefficients with increasing PVA concentration. A higher PVA concentration generally means more obstructions for the diffusants [30]. The PVA network used in the study have a correlation length in the range of 0.4–3 nm [5], which is smaller than or similar as the hydrodynamic radius, R_H, of the probes (1.3–3.1 nm, as obtained from Stokes–Einstein relation) (Table 2). Although the star polymers show similar trend as linear PEGs [6] and poly(propylene imine) dendrimers [9], an increase in PVA concentration causes a larger decrease in the self-diffusion coefficient of the linear PEGs in comparison to the CA (PEG)$_4$ stars and the dendrimers of similar molecular weight.

The size of the diffusants has a clear effect on their self-diffusion coefficients in polymers [6,8–10,13,18]. The self-diffusion coefficients D are normalized with their values in pure water (D_0) and the results in Fig. 2B clearly show that the D/D_0 values decrease faster in the PVA concentration range of 0–0.15 g/mL with increasing MW of the star polymers. The change of diffusion coefficients is more significant for the molecules of higher molecular weight and larger size, which are expected to interact more extensively with the PVA matrix.

The experimental values of the self-diffusion coefficients as a function of PVA concentration can be fitted with the model of Petit et al. [29]

$$D = \frac{D_0}{1 + ac^{-\nu}} \tag{2}$$

where $a = D_0/(k\beta^2)$, ν and β are constants which are characteristic of the polymer-solvent system, k represents the jump frequency over the energy barriers, which is expected to depend on the temperature and on the size of the diffusant, and c is the polymer concentration. In this model, the polymer solution is treated as a statistical network.

The values obtained for the parameters, D_0, $k\beta^2$, and ν are listed in Table 2. The D_0 values obtained from fitting agree well with the experimental data, with a clear dependence on the molecular size of the diffusants. The parameter ν is dependent on the solvent and falls in the range of 0.50–0.70 for the ternary system, indicating water is a marginal solvent for PVA [29]. The parameter $k\beta^2$ decreases with increasing hydrodynamic radius of the diffusing star polymers (Table 2). Since β should remain constant for a given polymer-solvent system [29], the results indicate that an increase in the size of the diffusant (R_H) leads to a lower jump frequency k. Similar decreasing trend was obtained with the linear PEGs [6] and PPI(TEG)$_n$ dendrimers [9]. At a comparable R_H value, the $k\beta^2$ parameter varies according to the general order of

Table 2

Self-diffusion coefficients (D_0), Hydrodynamic Radii (R_H), and fitting parameters $k\beta^2$ and ν obtained for the star polymers CA(EG_n)$_4$ in PVA-water-diffusant ternary systems.

sample	M_n[a] (g/mol)	D_0 (10^{-10} m^2/s)		$D_{s,0}$ (10^{-10} m^2/s)	R_H (nm)[c]	ν[b]	$k\beta^2$ (10^{-11} m^2/s)[b]
		exp.	calcd.[b]				
Star polymers							
CA(EG_4)$_4$	1110	1.92	1.92		1.28	0.65	1.17
CA(EG_6)$_4$	1510	1.66	1.66	1.60	1.48	0.66	0.82
CA(EG_{10})$_4$	2190	1.45	1.45		1.69	0.65	0.65
CA(EG_{17})$_4$	3500	1.04	1.04		2.36	0.70	0.35
CA(EG_{31})$_4$	5870	0.88	0.88	0.85	2.79	0.58	0.40
CA(EG_{39})$_4$	7320	0.79	0.79	0.78	3.10	0.56	0.31
Linear polymers							
PEG-600	1100 (530)	1.86	1.87		1.32	0.58	1.20
PEG-1000	1220 (970)	1.66	1.66		1.48	0.49	1.20
PEG-1500	1600 (1460)	1.13	1.13		2.17	0.54	0.68
PEG-2000	1960 (2140)	1.07	1.02		2.29	0.53	0.53
PEG-4000	4050 (4430)	0.96	0.96		2.55	0.50	0.47
PEG-8000	9100 (8000)	0.64	0.65		3.83	0.60	0.10
Dendrimers							
PPI(TEG)$_8$	2000	1.64	1.64		1.49	0.59	0.79
PPI(TEG)$_{32}$	8600	0.91	0.91		2.69	0.68	0.16
PPI(TEG)$_{64}$	17000	0.70	0.69		3.50	0.69	0.10

[a] For CA(EG_n)$_4$, the M_n values were measured by SEC-RI in THF. For linear PEGs, the M_n values were measured by SEC in THF and in water (values in parentheses) [6,10]. For the dendrimers, the M_n values were measured by ^{1}H NMR spectroscopy [9].

[b] Obtained as a fitting parameter from Eq. (2).

[c] Calculated from Stokes–Einstein equation.

linear > star > dendrimer. This implies that the linear PEGs have a higher jump frequency than the diffusants in the other two series of comparable molecular size. When the R_H is larger than ca. 2 nm, the $k\beta^2$ values of both dendrimers and star polymers decrease more slowly since the movement of longer linear chains is hindered more substantially than the corresponding star-shaped polymers and dendrimers.

3.2. *Scaling relation between the hydrodynamic radius and the molecular weight of the diffusant in water-diffusant binary systems*

Logarithmic plots of R_H versus M for linear PEOs, CA(EG$_n$)$_4$ star polymers, and the dendrimers are shown in Fig. 3, with the slopes of the linear fitting being 0.57, 0.47, and 0.40, respectively. The star polymers essentially present a random coil conformation as some flexible linear polymers, whose scaling constant of the relation, $R_H \sim M^{\nu}$, falls in the range of 0.5–0.6 [15,31,32]. Globular proteins [33], star polymers [34,35], and dendrimers [36–39] normally have a scaling constant of 0.3–0.4 due to the globular shapes and the compact, space-filling nature. However, the scaling parameter of star polymers varies, and some star polymers such as 4–16-arm poly(ethylene oxide)s from carbosilane dendrimers have a scaling constant of 0.5 [40]. Linear PEOs have slightly lower hydrodynamic radii than the corresponding CA(EG$_n$)$_4$ star polymers at low molecular weight due to the presence of a large cholane core in the star polymers. When the molecular weight is further increasing, R_H of the star polymers increases at a lower rate because the linear PEOs have a more extended structure in solution [41]. Since the molecular weights of star polymers are usually underestimated using SEC-RI calibrated with linear homologues [42], SEC-LS was used to determine the absolute molecular weights of the star polymers. The comparison of the results obtained with both detectors shows that the absolute molecular weights measured by SEC-LS are 1.1 times of the values obtained by SEC-RI. Thus, the linear relation shown in Fig. 3 also holds if the absolute molecular weights of the star polymers are used. The density of dendrimers is higher than those of branched and linear polymers due to their dense intramolecular packing, thus R_H increases slowly with higher M_n, as shown by PPI(TEG)$_n$ dendrimers in Fig. 3. The observation agrees well with increasing molecular density of the dendrimers with higher generation numbers [9].

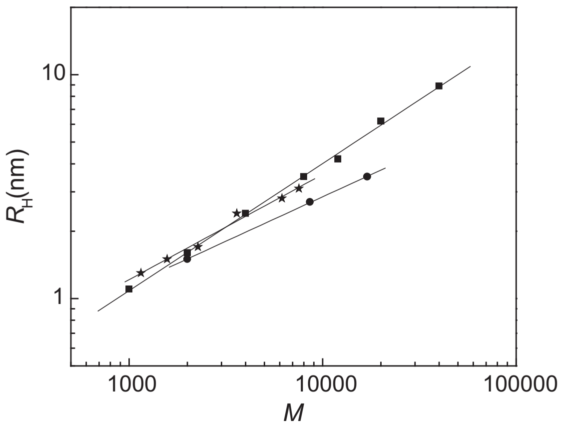

Fig. 3. Logarithmic plot of the hydrodynamic radius R_H as a function of molecular weight for linear PEOs (■, data from reference [43]), dendrimers (●, data from reference [9]), and the star polymers (★) in aqueous solutions at 23 °C. Good linear relations were observed with the coefficients of determination (R^2) of 0.9983, 0.9998, and 0.9855, respectively.

3.3. *Effect of diffusant concentration on the self-diffusion coefficient in water-diffusant binary systems*

For a better understanding of the system, the self-diffusion coefficients of the probes were measured in the absence of a polymer matrix, with representative results of selected samples (Table 3) shown in Fig. 4A. For the star polymers CA(EG$_n$)$_4$, the self-diffusion coefficient decreases significantly with increasing concentration of the diffusants in solution (Fig. 4A). The decrease is more significant for those with higher molecular weights. de Gennes' prediction of a scaling regime $D \propto c^{-1.75}$ in semidilute solution [44] is not apparent in the molecular weight range from CA(EG$_6$)$_4$ ($M_n = 1510$ g/mol) to CA(EG$_{54}$)$_4$ ($M_n = 9890$ g/mol). No c^* (overlap concentration) can be defined for the star polymer of low molecular weights, such as CA(EG$_6$)$_4$. The self-diffusion coefficient of CA(EG$_6$)$_4$ decreases only slightly with increasing concentration. Similarly, previous work of Callaghan and Pinder showed that no semidilute regime was observed in the case of low MW linear polystyrene (MW = 2000) in CCl_4 [32].

For comparison purposes, Fig. 4A also shows the literature data for linear PEOs [20]. The molecular weights and hydrodynamic radii of these polymers are summarized in Table 3. Diffusion coefficient measurements of two star polymers and two linear PEOs show similar decreasing trend within the concentration range of 0–40 millimolal. At very low concentrations (<5 millimolal), CA(EG$_{54}$)$_4$ ($M_n = 9890$) overlaps with linear PEO ($M_n = 6000$). At higher concentrations, the star-shaped diffusants showed slower diffusion than their linear homologues. Differences are expected between the star polymers and linear PEGs due to the presence of the hydrophobic core of the star polymers. Micelles can form in solutions above the CAC of the star polymers. According to surface tension measurements [24], the CAC of CA(EG$_{31}$)$_4$ is ca.19 millimolal and the value for CA(EG$_{54}$)$_4$ may be slightly higher than this number because it is overall a more hydrophilic molecule. A comparison between CA(EG$_{17}$)$_4$ and its *n*-alkyl poly(ethylene glycol) ether surfactant counterpart with similar molecular weight, C$_{17}$EG$_{84}$ (17 is the number of carbons in the alkyl chain and 84 the number of ethylene oxide units, with a CAC at 2.5 μM) [47], shows that CA(EG$_{17}$)$_4$ (with a CAC at 16 millimolal) starts to aggregate at a much higher concentration. Therefore, at a similar molecular weight, the star polymer is much less hydrophobic than such a linear amphiphilic polymer and does not aggregate as easily.

A scaling relationship between the self-diffusion coefficient at infinite dilution and the molecular weight for a given diffusant, $D_{s,0} \propto M^{-n}$, originally proposed by Flory [48], was observed for star polymers CA(EG$_n$)$_4$ dissolved in D_2O at 23 °C. The values of $D_{s,0}$ of CA(EG$_n$)$_4$ were determined from the initial linear region of a plot of D^{-1} versus c (Fig. 4B) by fitting to the first-order expression of

$$D^{-1} = D_{s,0}^{-1}\left(1 + k_f c + \ldots\right) \tag{3}$$

where k_f and similar higher order coefficients are independent of c [32]. Logarithmic plots of $D_{s,0}$ versus molecular weight (Fig. 4C)

Table 3
Molecular weights and hydrodynamic radii of the polymers shown in Fig. 4A.

Polymer	M_n (g/mol)		R_H (nm)
	SEC	NMR	
CA(EG$_6$)$_4$	1510	2180	1.5
CA(EG$_{31}$)$_4$	5870	8600	2.8
CA(EG$_{54}$)$_4$	9900	15460	4.1
Linear PEO-6k[a]	6000	6200	5.6
Linear PEO-10k[a]	10000	10600	7.1

[a] M_n and R_H values of the linear PEOs are from reference [20] and the same nomenclature is employed.

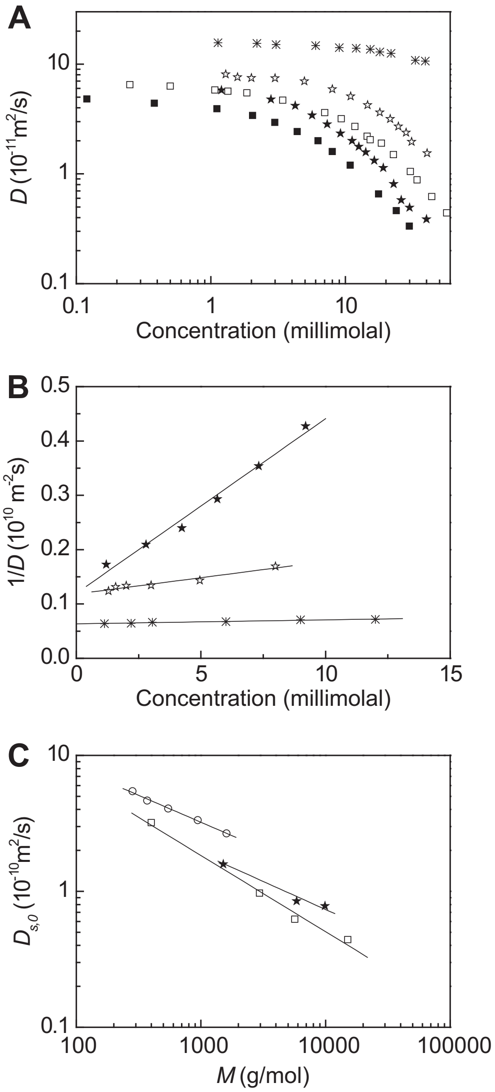

Fig. 4. (A) The dependence of self-diffusion coefficient D on the concentration of polymer diffusants in water: $CA(EG_6)_4$ (✳) ($M_n = 1510$), $CA(EG_{31})_4$ (☆) ($M_n = 5870$), CA $(EG_{54})_4$ (★) ($M_n = 9890$), linear PEO-6 k (□), linear PEO-10 k (■).Sample details are given in Table 3. Data of PEO-6 k and PEO-10 k are from reference [20]. (B) Variation of $1/D$ as a function of concentration of the star polymers. Sample details are given in Table 2. The lines are fits to Eq. (3) and the derived self-diffusion coefficient at infinite dilution ($D_{s,0}$) are shown in Table 2. (C) Variation of $D_{s,0}$ as a function of molecular weight of the star polymers in D_2O at 23 °C (★), linear PEGs in D_2O at 25 °C [45] (□), and linear PEGs in D_2O at 30 °C [46] (○). A scaling behavior $D_{s,0} \sim M^{-n}$ was observed with the scaling indices of 0.41 for the star polymers at 23 °C, and 0.60 and 0.43 for the linear PEGs at 25 and 30 °C, respectively.

show that the $CA(EG_n)_4$ series has a scaling exponent n of 0.41. The scaling exponent of the star polymers is very close to the value of low molecular weight linear PEGs (monomer to N-mer of 40) at 30 °C ($n = 0.43$) reported in a study by Shimada et al. [46]. The scaling factor obtained from another study by Blum et al. is 0.60 for linear PEGs in D_2O at 25 °C [45]. In this temperature range, the small differences in temperature would have little effect on the self-diffusion coefficients of the polymers. The difference may be explained by the different molecular weight range (dimer to N-mer of 14,000) covered in the work of Blum et al. [45] and the high polydispersity for PEGs with high molecular weight. Similar to the cases of the linear and star PEGs, a report regarding linear and 3-armed polybutadienes showed no qualitative difference in self-diffusion coefficient between the two systems [15].

3.4. The longitudinal relaxation times of the diffusants (T_1)

T_1 values provide additional information about the molecular dynamics of polymers in solution [49]. The ^{1}H NMR T_1 values of two polymers ($CA(EG_{31})_4$ and $CA(EG_{54})_4$) at different concentrations were measured at 23 °C. With increasing concentration of the star polymers, the T_1 value of methylene on the PEG chain decreases while that of the methyl group on the cholane core increases slightly (Fig. 5A). The changes of the T_1 values for the larger CA $(EG_{54})_4$ are more pronounced. The temperature dependence of T_1 was also studied in order to clarify the relation between the mobility of the PEG moieties and the concentration of $CA(EG_n)_4$. In the range of 10–70 °C, T_1 values of the methylene protons on the PEG segments of $CA(EG_{54})_4$ at selected concentrations increase significantly with an increase in temperature, while those of the methyl protons of the cholane core first decrease and then increase within this temperature range (Fig. 5B). In the Bloembergen-Purcell-Pound theory (BPP theory), T_1 shows a minimum along with the correlation time (τ_c, decreasing mobility) [50]. The results indicate that these PEG methylene protons lie in the fast motion regime (where T_1 increases with increasing mobility), while the cholane core is in the intermediate motion regime (where T_1 is close to the minimum in the plot of T_1 vs τ_c). This mobility difference between the core and PEG chains of star polymers $CA(EG_n)_4$ is similar to that observed for the core and the exterior of poly (propylene imine) dendrimers [51,52], which suggests that the star polymers behave similarly in solution as the dendrimers. Star

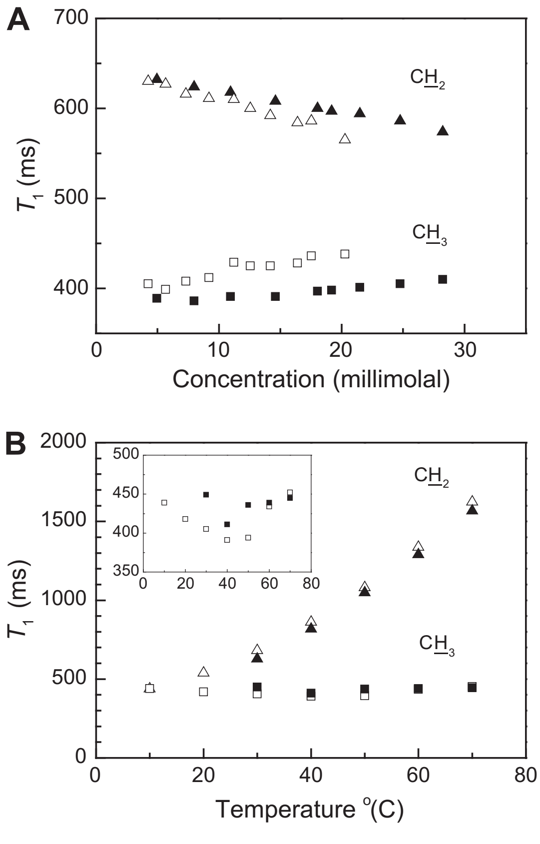

Fig. 5. The ^{1}H T_1 values for CH_2 of PEG chains (triangles) and CH_3 of the cholane core (squares) measured for the star polymers. (A) Effect of concentration for two polymers $CA(EG_{31})_4$ (closed symbols), $CA(EG_{54})_4$ (open symbols) at 25 °C; (B) Effect of temperature for $CA(EG_{54})_4$ at 1.2 (open symbols) and 19.1 millimolal (closed symbols). The inset shows the variation of the T_1 values of CH_3 of the cholane core near the minimum with a different scale. The error of the T_1 values is estimated to be ±10 ms by multiple experiments.

polymers CA(EG_n)$_4$ are amphiphilic and tend to form micelles in solution. However, no critical aggregation concentration or temperature was observed by NMR for such polymers. The micelles and the star polymers are in a dynamic process between free and aggregated states. The mobility reflected from the T_1 relaxation times is only an averaged observation.

4. Conclusion

In an effort to understand the effect of molecular shape and architecture of polymeric diffusants on the diffusion in polymer hydrogels, we have compared the diffusion behaviors of PEG-based macromolecules including linear and star-shaped polymers and dendrimers in aqueous solutions and PVA gels. The results show that the star polymers have an intermediate diffusion rate or jump frequency that is higher than the dendrimers but lower than linear polymers at comparable hydrodynamic radii. In the dilute regime of the binary system, star polymers have the similar diffusion behavior as linear PEGs. In the semidilute regime, a difference between the star polymers and their linear homologues is observed due to the presence of the hydrophobic core of the stars. For both 4-armed star polymers and linear PEGs, similar scaling relationships are found between the self-diffusion coefficient at infinite dilution and the molecular weight of the diffusants. The dependence of the ^{1}H T_1 values of the star polymers on temperature and concentration indicates that the cholic acid core of the star polymers is less mobile than the PEG arms. The understanding of the effect of molecular shape of the diffusants may help in designing molecules and biopolymers with predictable properties for applications such as drug delivery and tissue engineering.

Acknowledgements

The financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada and Canada Research Chair program is gratefully acknowledged. We thank Dr. Cédric Malveau for his help with PGSE NMR data analysis.

References

[1] Hoare TR, Kohane DS. Polymer 2008;49:1993–2007.
[2] Fieber W, Herrmann A, Ouali L, Velazco MI, Kreutzer G, Klok HA, et al. Macromolecules 2007;40(15):5372–8.
[3] Gao P, Fagerness PE. Pharm Res 1995;12:955–64.
[4] Clericuzio M, Parker WO, Soprani M, Andrei M. Solid State Ionics 1995;82: 179–92.
[5] Petit J-M, Zhu XX, Macdonald PM. Macromolecules 1996;29:70–6.
[6] Masaro L, Zhu XX, Macdonald PM. Macromolecules 1998;31:3880–5.
[7] Masaro L, Ousalem M, Baille WE, Lessard D, Zhu XX. Macromolecules 1999;32: 4375–82.
[8] Masaro L, Zhu XX. Langmuir 1999;15:8356–60.
[9] Baille WE, Malveau C, Zhu XX, Kim YH, Ford WT. Macromolecules 2003;36:839–47.
[10] Thérien-Aubin H, Zhu XX, Moorefield CN, Kotta K, Newkome GR. Macromolecules 2007;40:3644–9.
[11] Kharchenko SB, Kannan RM, Cernohous JJ, Venkataramani S. Macromolecules 2003;36:399–406.
[12] Kharchenko SB, Kannan RM. Macromolecules 2003;36:407–15.
[13] Baille WE, Zhu XX, Fomine S. Macromolecules 2004;37:8569–76.
[14] von Meerwall E, Tomich DH, Hadjichristidis N, Fetters LJ. Macromolecules 1982;15:1157–63.
[15] von Meerwall E, Tomich DH, Grigsby J, Pennisi RW, Fetters LJ, Hadjichristidis N. Macromolecules 1983;16:1715–22.
[16] Furukawa T, Ishizu K, Yamane Y, Ando I. Polymer 2005;46:1893–8.
[17] Westrin BA, Axelsson A, Zacchi G. J Contr Release 1994;30:189–99.
[18] Michelman-Ribeiro A, Horkay F, Nossal R, Boukari H. Biomacromolecules 2007;8:1595–600.
[19] Gong JP, Hirota N, Kakugo A, Narita T, Osada Y. J Phys Chem B 2000;104: 9904–8.
[20] Griffiths PC, Stilbs P, Yu GE, Booth C. J Phys Chem 1995;99:16752–6.
[21] Gao H, Matyjaszewski K. Macromolecules 2006;39:7216–23.
[22] Breland LK, Storey RF. Polymer 2008;49:1154–63.
[23] Kennedy JP, Jacob S. Acc Chem Res 1998;31:835–41.
[24] Luo J, Giguère G, Zhu XX. Biomacromolecules 2009;10:900–6.
[25] Tanner JE. J Chem Phys 1970;52:2523–6.
[26] Callaghan PT, Trotter CM, Jolley KW. J Magn Reson 1980;37:247–59.
[27] Stilbs P. Prog Nucl Magn Reson Spectrosc 1987;19:1–45.
[28] Price WS. Concepts Magn Reson 1997;9:299–336.
[29] Petit J-M, Roux B, Zhu XX, Macdonald PM. Macromolecules 1996;29:6031–6.
[30] Favre E, Leonard M, Laurent A, Dellacherie E. Colloids Surf A 2001;194: 197–206.
[31] de Gennes PG. J Chem Phys 1971;55:572–9.
[32] Callaghan PT, Pinder DN. Macromolecules 1981;14:1334–40.
[33] Tanford C. Physical chemistry of macromolecules. New York: John Wiley & Sons; 1961.
[34] Huang H-M, Liu I-C, Tsiang RC-C. Polymer 2005;46:955–63.
[35] Trollsås M, Atthof B, Würsch A, Hedrick JL, Pople JA, Gast AP. Macromolecules 2000;33:6423–38.
[36] Scherrenberg R, Coussens B, van Vliet P, Edouard G, Brackman J, de Brabander E. Macromolecules 1998;31:456–61.
[37] Rietveld IB, Bedeaux D. Macromolecules 2000;33:7912–7.
[38] Wong S, Appelhans D, Voit B, Scheler U. Macromolecules 2001;34:678–80.
[39] Sagidullin AI, Muzafarov AM, Krykin MA, Ozerin AN, Skirda VD, Ignat'eva GM. Macromolecules 2002;35:9472–9.
[40] Comanita B, Noren B, Roovers J. Macromolecules 1999;32:1069–72.
[41] Devanand K, Selser JC. Macromolecules 1991;24:5943–7.
[42] Taromi FA, Grubisic-Gallota Z, Rempp P. Eur Polym J 1989;25:1183–7.
[43] Choudhury RP, Galvosas P, Schönhoff M. J Phys Chem B 2008;112:13245–51.
[44] de Gennes PG. Macromolecules 1976;9:587–93.
[45] Waggoner RA, Blum FD, Lang JC. Macromolecules 1995;28(8):2658–64.
[46] Shimada K, Kato H, Saito T, Matsuyama S, Kinugasa S. J Chem Phys 2005;122 (24):244914.
[47] Hakansson B, Hansson P, Regev O, Soderman O. Langmuir 1998;14:5730–9.
[48] Flory PJ. Principle of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[49] Mirau PA. A practical guide of understanding the NMR of polymers. Hoboken, New Jersey: John Wiley & Sons; 2005.
[50] Hatada K, Kitayama T. NMR spectroscopy of polymers. Berlin Heidelberg: Springer-Verlag; 2004.
[51] Chai M, Niu Y, Youngs WJ, Rinaldi PL. J Am Chem Soc 2001;123:4670–8.
[52] Malveau C, Baille WE, Zhu XX, Ford WT. J Polym Sci Part B Polym Phys 2003;41:2969–75.