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Dynamics of Charged Ring Polymers under Gel Confinement

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Electronic Supplementary Information

Abstract Ring polymers are ubiquitous in various fields including biomaterials, drug release and gene therapy. All of these applications involve the dynamics and diffusion process of ring polymers in a confined environment. By using dynamic light scattering (DLS), we discovered a dynamical transition for charged ring polymers with increasing ring concentration in the gel matrix from a diffusive state to a non-diffusive topological frustrated state with a more compact conformation. When the ring polymer size is smaller than the mesh size of the gel matrix, the rings are diffusive at low concentration of 5 g/L. The ring diffusion coefficient in the gel matrix is an order of magnitude smaller than that of rings in solution, obeying the Ogston's model. At high ring concentration of 40 g/L, the collective dynamical behavior of the charged rings exhibits a topologically frustrated non-diffusive state, which may originate from the inter-ring threading with the external confinement from the gel matrix. Based on our previous theoretical work, we also conjectured that in such a non-diffusive state, the ring polymers might adopt a more compact conformation with the overall size exponent ν=1/3.

Keywords Charged ring polymer; Dynamics under confinement; Non-diffusive topologically frustrated dynamics; Dynamic light scattering; Collective diffusion coefficient

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INTRODUCTION

The static and dynamic properties of ring polymers are one of the remaining challenges in polymer science.[1] Unlike linear polymers, ring polymers do not have free terminal segments or ends, they possess a closed contour, which leads to markedly different relaxation and diffusion mechanisms from linear chains. For example, both simulations and experiments have shown that concentrated ring polymers display unique features that are not easily reconciled with the reptation theory of linear polymers.[2–6] For the melt of linear chains, the excluded volume effects are screened and the chain conformation is Gaussian, which is characterized by the size exponent ν=0.5 ($R_g \sim N^{\nu}$, where R_g and N are denoted by the radius of gyration and the number of segment).[7] However, this result is not suitable for the ring polymer melts. Both theoretical and experimental studies show that ring polymers adopt a more compact conformation and diffuse faster than their linear peers.[8–11] Unentangled ring polymers with $N<N_e$ (N_e is denoted by the number of segments per entanglement strand) are almost ideal in melts with size exponent ν=0.5. However, the conformation of longer rings with $N>N_e$ are more compact.[12] Molecular dynamics simulation results show that with the increase of chain length in ring melt, the size exponent ν smoothly changes from Gaussian (ν=0.5) to crumpled globules (ν=1/3) *via* an intermediate regime with ν=2/5.[11] Combined with the simulation results, Iwamoto *et al*. studied the conformation of polystyrene rings in bulk by using small angle neutron scattering, they found that for ring polymers $R_g \sim N^{0.5}$ when $N/N_e \leq 1$ and $R_g \sim N^{0.33}$ when $N/N_e \geq 15$.[13] In such a case, although rings have overall globular conformation (ν=1/3), the entropic barrier to form apparently large open loops is so small that they are frequently observed.[4] Therefore, they still display significant mutual interpenetrations.

In addition to the difference of static conformation between ring and linear polymers, ring and linear polymers also exhibit markedly different dynamical behaviours due to the closed contour. Müller *et al*.'s simulation results show that the self-diffusion coefficient D_N is the same for linear chains and rings in dilute regime. While in the bulk melt, the rings are always faster than their linear counterpart of same mass. In addition, the chain stiffness will significantly affect the dependence of self-diffusion coefficient on the ring size ($D_N \propto N^{-1.22}$ for flexible chains and $D_N \propto N^{-1.68}$ for semi-flexible chains, where N denotes the degree of polymerization).[11] It should be noticed that their results are only applicable to the situation when the degree of polymerization is smaller than the entanglement crossover of linear chains. While the simulation results from Brown, S. and Szamel, G. show that when $N \approx 12.5N_c$, where N_c denotes the chain segment number of

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the entanglement crossover for linear chains, the rings still diffuse faster than their linear counterpart of the same mass in their bulk melts.[14]

In this work, we report the first experimental evidence for the dynamics of charged ring polymers under gel confinement by using dynamic light scattering (DLS) in 0.1 mol/L NaCl. We found a collective dynamical transition of charged ring polymers from the diffusive state to the non-diffusive topological frustrated state with the increase of the ring polymer concentration. From the experimental results and the analysis based on our former theoretical work, we conjecture that the ring polymers may adopt a more compact conformation when they are in the non-diffusive topological frustrated state under strong confinement.

EXPERIMENTAL

The synthetic details, experimental section and complementary data are presented in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

The dynamics of ring polymers under gel confinement was monitored by DLS. DLS can measure the scattered light intensity-intensity correlation function $g_2(q,t)$, which can be converted to the electric field-field correlation function $g_1(q,t)$ by Siegert relation:[15]

$$g_2(q,t) - 1 = <I(0)\, I(t)> / <I>^2 - 1 = a|g_1(q,t)|^2 \quad (1)$$

where a is the instrument coherent factor, t denotes the decay time, $I(t)$ represents the scattered light intensity at decay time t. $q = (4\pi n/\lambda)\sin(\theta/2)$ denotes the scattering wave vector with scattering angle θ, wavelength of the incident light λ and refractive index of the medium n. $g_1(q,t)$ can be represented as a sum or integral over a distribution of relaxation rates Γ by

$$g_1(q,t) = \int_0^\infty G(\Gamma)\, e^{-\Gamma t} d\Gamma \quad (2)$$

$G(\Gamma)$ is normalized so that $\int_0^\infty G(\Gamma)\, e^{-\Gamma t} d\Gamma = 1$. For a diffusive mode, the characteristic relaxation rate Γ is proportional to q^2, $\Gamma = Dq^2$. From the slope of Γ-q^2, the diffusion coefficient D can be obtained. For polymer solutions, the hydrodynamic radius R_h can be obtained from Stokes–Einstein relation $R_h = k_B T/6\pi\eta D$, where $k_B T$ is Boltzmann constant times the absolute temperature, η represents the solvent viscosity.[16] For gels, the electric field correlation function $g_1(q,t)$ is related with the correlation of the gel strands displacement U_q as

$$g_1(q,t) \sim <U_q(0)\, U_q(t)> = <U_q(0)>^2 e^{-\Gamma t} \quad (3)$$

From $\Gamma = D_{gel} q^2$ we can obtain the gel diffusion coefficient D_{gel}, which can be expressed as $D_{gel} = M/f$, where M is the longitudinal modulus and f is the friction coefficient between the polymers and solvent.[17,18] Therefore, the gel diffusion coefficient D_{gel} essentially represents the gel elasticity.

The Tetra-PEG gel matrix has a nearly monodispersed gel mesh size since the gel was synthesized by two types of four-armed PEG macromonomers with an equal arm length cross-linked through their end groups.[19,20] For Tetra-PEG gel matrix, the mesh size can be considered as the end-to-end distance h of two adjacent centers of the macromonomers (Fig. 1a). Assuming that the gel strands obey Gaussian chain statistics, the end-to-end distance h is:

$$h = \sqrt{N} L \quad (4)$$

where L denotes Kuhn length and N is the number of Kuhn segment. So the gel mesh size can be estimated as 11.6 nm (see detail in ESI). The normalized correlation function $g_1(q,t)$ at scattering angle 30° for the Tetra-PEG gel matrix alone with 0.1 mol/L NaCl is shown in Fig. 1(b). $g_1(q,t)$ of the gel matrix can be well fitted by one exponential decay. The blue triangles in Fig. 1(b) are the residuals between the fitting curve (red line) and the raw data (black square), indicating that the fitting quality is quite high. This result is consistent with the fitting result by using CONTIN fitting method.[15,21] As shown in Fig. 1(c), the corresponding relaxation time distribution obtained from CONTIN fitting method is monodispersed (Fig. 1c), indicating that the gel network is homogeneous. Moreover, as shown in Fig. 1(d), the relaxation rates Γ obtained at different scattering angle are proportional to q^2, and from the slope of Γ-q^2 the gel diffusion coefficient D_{gel}=(3.16±0.04)×10^{-7} cm^2/s can be obtained, representing the gel elasticity. The gel diffusion coefficient D_{gel} is also related to the dynamic correlation length of concentration fluctuations of the gel network.[2,3] So D_{gel} can be converted to the dynamic correlation length $\xi_{dynamic}$ by using the relation of $\xi_{dynamic} = k_B T/6\pi\eta D_{gel}$ = (7.8 ± 0.2) nm. The dynamic correlation length $\xi_{dynamic}$ = (7.8 ± 0.2) nm can be used to estimate the averaged mesh size of the gel network, and it is roughly close to the calculated value of the mesh size.

The ring polymer is positively charged cyclic poly(2-(dimethylamino)ethyl acrylate) (c-PDMA). The size exclusion chromatography (SEC) results (Fig. S2 in ESI) show that the molecule weight is M_w=28.9 kDa, and the ring polymer is monodispersed (polydispersity index PDI=1.08). DLS measurements are also conducted to estimate the size of the ring polymers. In order to screen the electrostatic interactions of the charged rings, all the DLS measurements were conducted in 0.1 mol/L NaCl solutions. The correlation function and the corresponding fitting results of 1 g/L c-PDMA ring polymer show that it is monodispersed (Figs. 2a–2c) with the diffusion coefficient $D_{c\text{-}PDMA}$=(5.16±0.03)×10^{-7} cm^2/s. Based on the Stokes–Einstein relation, the diffusion coefficient can be converted to the hydrodynamic radius R_h = 4.4 nm. The radius of gyration R_g can be obtained by Guinier plot $I_s(q) = I_s(0)\exp(-q^2R_g^2/3)$. From the slope of ln I_s-q^2 plot, R_g = (5.5±0.2) nm can be obtained and the overlap concentration c^* of rings in solution is c^* =68.9 g/L.[22] The shape factor R_g/R_h is 1.25, indicating they are ring polymers with Gaussian statics.[23] Here the size of ring polymer R_g =5.5 nm is smaller than the estimated gel mesh size.

The dynamics of 5 g/L ring polymers confined in the gel matrix was monitored by DLS. A typical example of the normalized electric field correlation function $g_1(q,t)$ at a scattering angle of 30° is shown in Fig. 3(a) and can be best fitted by two exponential decays as

$$g_1(t) = a_1 e^{-\Gamma_1 t} + (1-a_1)\, e^{-\Gamma_2 t} \quad (5)$$

The quality of the fit is illustrated in terms of the fitting residuals (blue triangles) between the fitting curve (red curve) and the raw data (black square) in Fig. 3(a). The fitting results

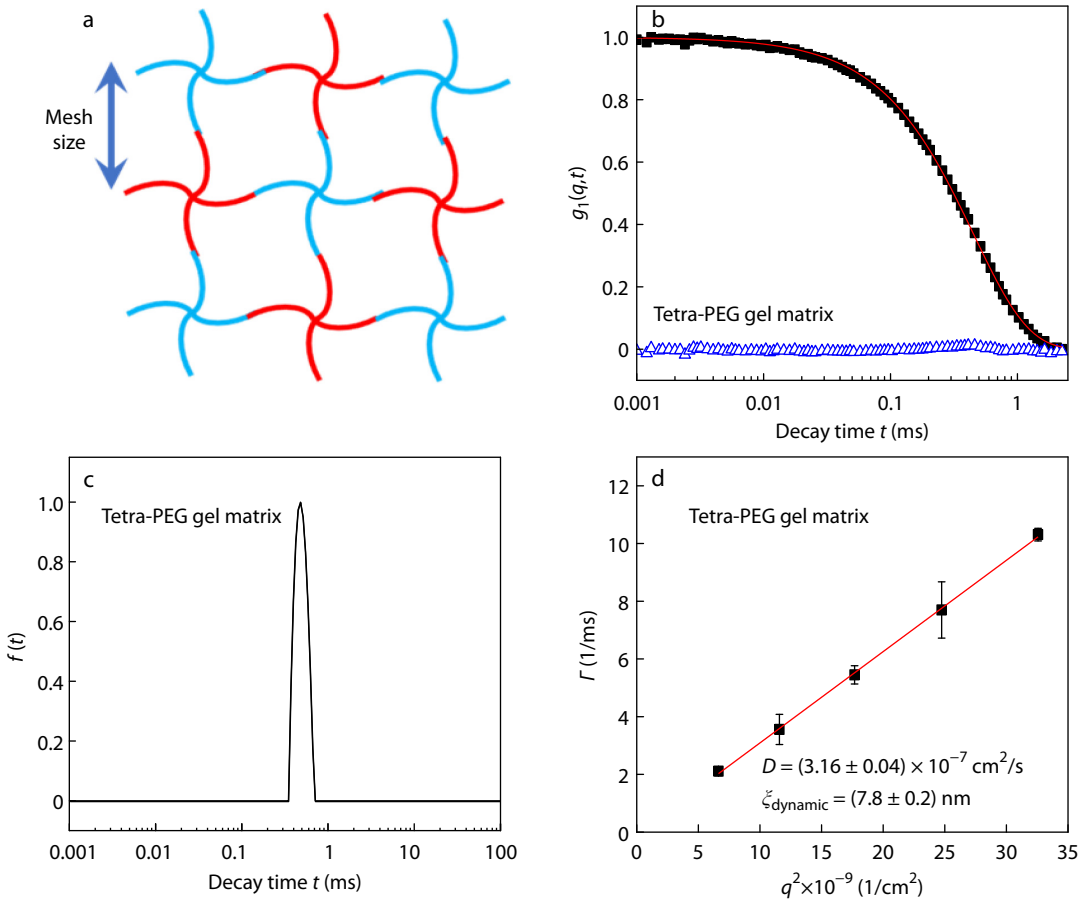

Fig. 1 Characterization of the Tetra-PEG host gel by DLS, the samples are with 0.1 mol/L NaCl. (a) Schematic illustration of the Tetra-PEG gel with uniform mesh size synthesized by two types of four-armed PEG macromonomers (two colours) with an equal arm length cross-linked through their end groups. (b) Normalized field correlation function $g_1(q,t)$ at a scattering angle of 30° for Tetra-PEG gel matrix. The blue triangles are the residuals between the fitting curve (red line) and the raw data (black square). (c) Corresponding decay time distribution function $f(t)$ for Tetra-PEG gel matrix at a scattering angle of 30°. (d) q^2 dependence of the relaxation rates Γ for the Tetra-PEG gel matrix. The dynamic correlation length of 7.8 nm can be obtained from D_{gel}.

show that the characteristic decay time for the two dynamical modes are t_1=0.35 ms, t_2=2.27 ms (see equation above Fig. 3a), so that the relaxation rates of the two dynamical modes are $\Gamma_1=1/t_1$=2.86 ms^{-1} and $\Gamma_2=1/t_2$=0.44 ms^{-1}. Besides, a_1=0.89 is the fraction of the first mode, and $(1-a_1)$=0.11 is the fraction of the second mode (Fig. 3a).

The first mode is diffusive since Γ_1 is proportional to q^2, and from the slope of Γ_1/q^2 the diffusion coefficient D_1 = (3.93±0.10)×10^{-7} cm^2/s can be obtained (Fig. 3b). Since D_1 value is very close to the value of gel diffusion coefficient D_{gel} = (3.16±0.04)×10^{-7} cm^2/s for the gel alone (Fig. 1d), so the first mode with D_1=(3.93±0.10)×10^{-7} cm^2/s is the gel mode representing the gel elasticity. Therefore, the dynamics of the ring polymers will come into the second mode. The second mode is also diffusive with the corresponding diffusion coefficient D_2=(6.48±0.17)×10^{-8} cm^2/s (Fig. 3c), which is an order of magnitude smaller than the diffusion coefficient of ring polymer in solutions (Fig. 2c). Besides, the size of guest ring polymers (R_g=5.5 nm) is smaller than the averaged mesh size of the host gel, so the dynamics of 5 g/L ring polymers in the gel matrix obeys the Ogston's model.[24]

When the charged ring polymer concentration increases to 40 g/L in the confined gel matrix, they exhibit entirely different dynamics. Fig. 4(a) is a typical example of the correlation function $g_1(q,t)$ at scattering angle 30° for 40 g/L ring polymers in the gel matrix, now it can be best fitted by one exponential decay and one stretched exponential decay expressed as

$$g_1(t) = a_1 e^{-\Gamma_1 t} + (1-a_1)\, e^{-(\Gamma_2 t)^{\beta}} \quad (6)$$

where the characteristic decay time for the two dynamical modes are t_1=0.20 ms, t_2=57.45 ms (see equation above Fig.4a), so that the relaxation rates of the two dynamical modes are $\Gamma_1=1/t_1$=5.0 ms^{-1} and $\Gamma_2=1/t_2$=0.017 ms^{-1}, and a_1=0.42 is the fraction of the first exponential decay, $(1-a_1)$ = 0.58 is the fraction of the second stretched exponential decay, β=0.5 is the stretched exponent. The first exponential decay is the gel mode with $D_{gel}=D_1$= (6.78±0.15)×10^{-7} cm^2/s, which is in the same order of magnitude of D_{gel} for the gel alone (Fig. 4b). Yet D_{gel} values increase with the increase of the guest ring polymer concentration in the host gels.[25] When the ring polymer concentration increases to 40 g/L, the D_{gel} value is already double the D_{gel} value for the gel alone (Fig. 1d). While the second mode of the stretched exponential decay represent the dynamics of the

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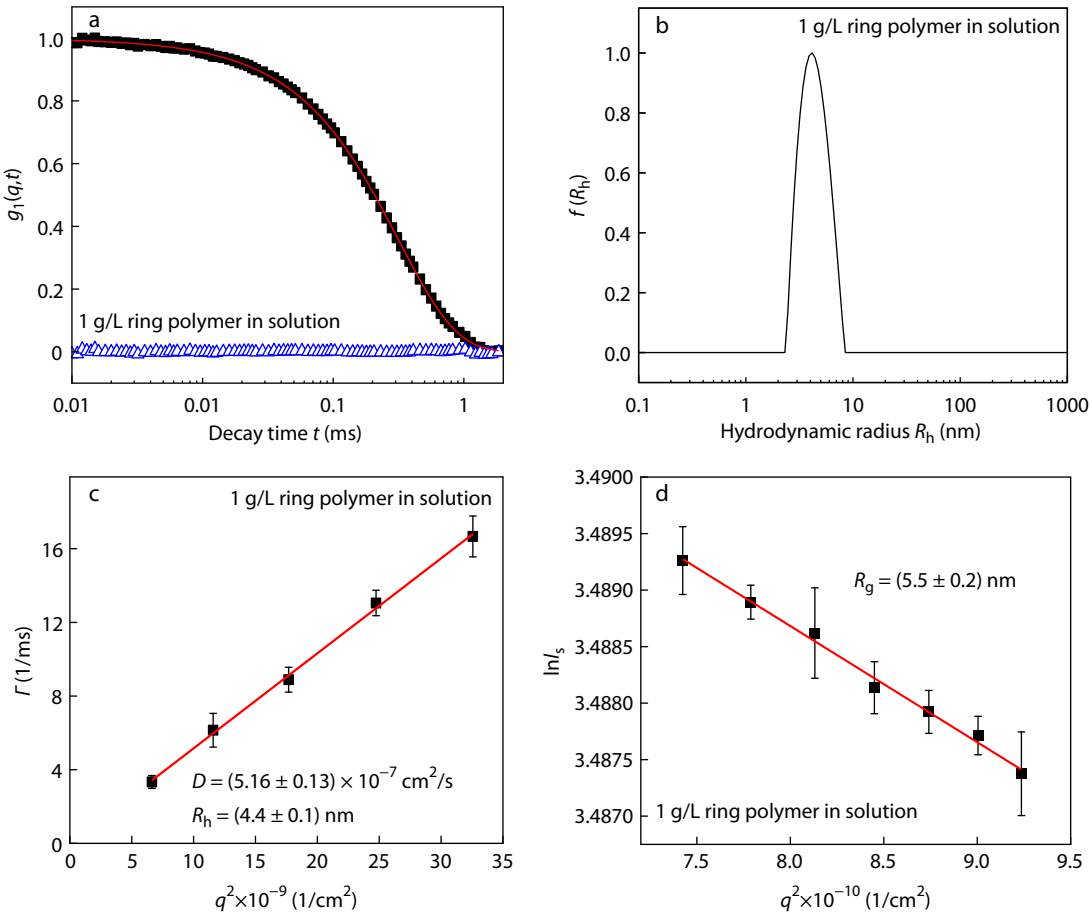

Fig. 2 Characterization of the guest ring polymer c-PDMA by using DLS, all the samples are with 0.1 mol/L NaCl. (a) Normalized field correlation function $g_1(q,t)$ at a scattering angle of 30° for 1 g/L c-PDMA solution. The blue triangles are the residuals between the fitting curve (red line) and the raw data (black square). (b) Hydrodynamic radius distribution function $f(R_h)$ for 1 g/L c-PDMA solution at a scattering angle of 30°. (c) q^2 dependence of the relaxation rates Γ for 1 g/L c-PDMA solution. From the slope the diffusion coefficient D can be obtained and also converted to the hydrodynamic radius R_h. (d) R_g of 1 g/L c-PDMA in 0.1 mol/L NaCl solution has been obtained by Guinier plot $I_s(q) = I_s(0)\exp(-q^2R_g^2/3)$. From the slope of ln I_s - q^2 plot, we get R_g=(5.5±0.2) nm can be obtained.

ring polymers, and this ring polymer mode is non-diffusive since their relaxation rates Γ_2 are not proportional to q^2 (Fig. 4c). Besides, the stretched exponent β values are independent of the scattering angles (or q^2) and the stretched exponent β is 0.5 averaged over all the scattering angles (Fig. 4d). It should be noted that the non-diffusive mode of 40 g/L guest ring polymers in the confined host gel monitored by dynamic light scattering is a collective dynamical behaviour of ring polymers.

To understand the possible physical mechanism of β=0.5 for the charged ring dynamics, we briefly introduce the relevant theories as below. For charged linear chains, when they are in the non-diffusive topologically frustrated dynamical state, their correlation function $g_1(q,t)$ is a stretched exponential decay expressed as[25,26]

$$g_1(t) = e^{-(\Gamma t)^{\beta}} \quad (7)$$

For polymer melts they obey Rouse segmental dynamics and for polymers in aqueous environment they follow Zimm segmental dynamics. Here for the charged rings in the aqueous hydrogels containing a large amount of water, the segmental dynamics of these charged ring polymers would follow Zimm dynamics. Thus, the corresponding stretched exponent β for Zimm segmental dynamics can be expressed as β = 1/(3ν + 1) (where ν is the size exponent).[25,26] Based on the averaged value of β=0.5, we can get the size exponent ν=1/3, which indicates that the ring polymers have overall more compact conformations when they are in the non-diffusive topologically frustrated dynamical state. In our previous work,[25] the topologically non-diffusive frustrated dynamics originate from the multiple entropic barriers created by the gel meshes under the condition of $R_g \gg \xi \gg l$. Here in this work, the dynamical transition from diffusive to non-diffusive state arises from the increase of the ring polymer concentrations under the condition of $R_g < \xi$. Such an observed topologically frustrated non-diffusive dynamical state may originate from the topological restrictions between ring polymers with the increase of ring polymer concentration, such as interpenetration between rings. In order to verify this, small angle neutron scattering measurements need to be done to measure the conformation of the labelled ring polymers, which is related to our future work.

For linear polymer chains at intermediate confinement, the long-lived metastable state of non-diffusive topologically frustrated dynamics is originated from the multiple entropic

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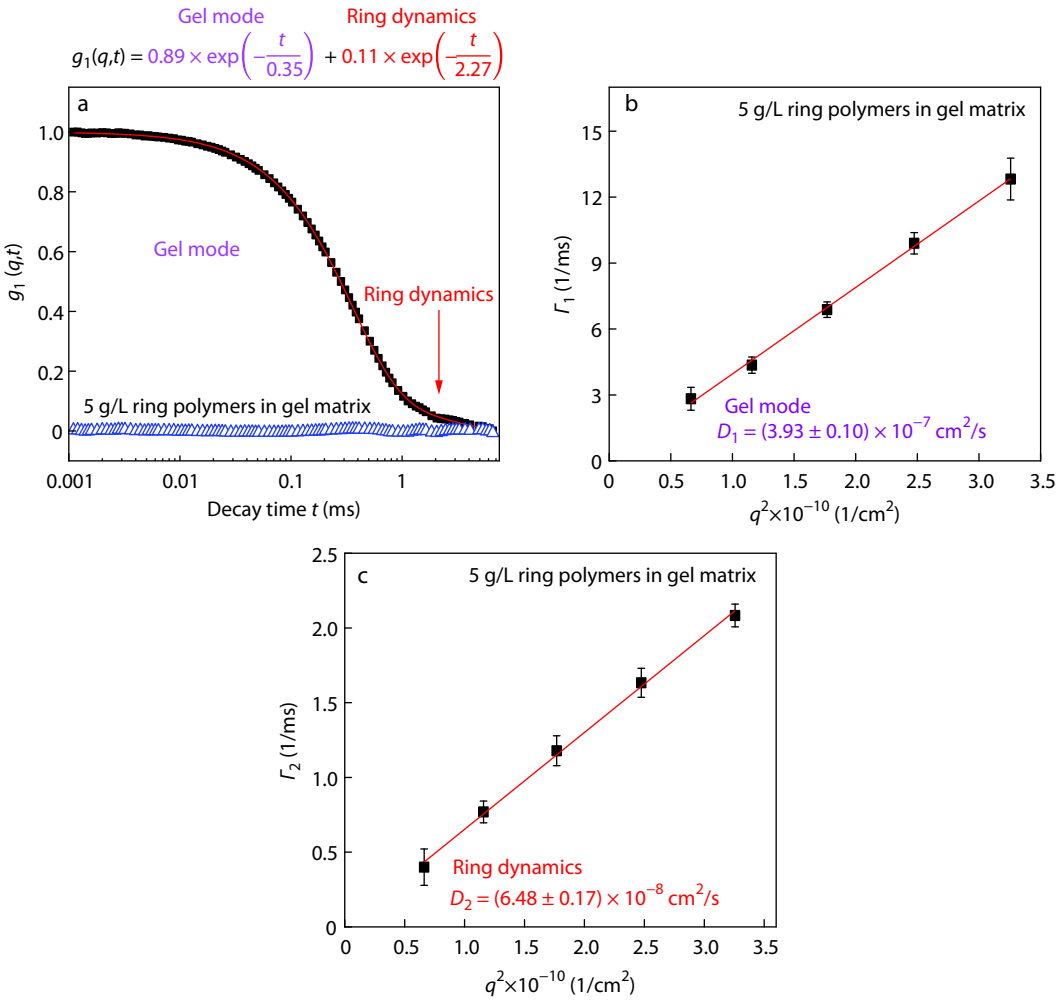

Fig. 3 Dynamics of 5 g/L ring polymers in the Tetra-PEG gel matrix with 0.1 mol/L NaCl. (a) Normalized field correlation function $g_1(q,t)$ at a scattering angle of 30°. The blue triangles are the residuals between the fitting curve (red curve) and the raw data (black square). (b, c) q^2 dependence of the relaxation rates Γ_1 and Γ_2 for the first mode (b) and the second mode (c).

barriers.[25–27] While for ring polymers, previous studies show that although they have overall globular conformation (ν=1/3), the entropic barrier to form apparently large open loops is so small that they are frequently observed and they still display significant mutual interpenetrations.[4] Here the ring polymers are charged and 0.1 mol/L NaCl may not be enough to fully screen the electrostatic interactions of such a high concentration of 40 g/L charged ring polymers. Therefore, these charged ring polymers are not as flexible as their neutral counterparts due to the electrostatic repulsion so that the entropic barriers to change the conformation is higher and the probability of their conformational change will be relatively lower. Besides, although the ring polymer concentration of 40 g/L is lower than the estimated overlap concentration c^* =68.9 g/L of ring polymers in solution, the gel matrix provides the external confinement for the collective dynamics of the charged ring polymers. Therefore, they exhibit the non-diffusive collective dynamical behavior monitored by dynamic light scattering. The self-diffusion of each individual ring can be studied by tracking the labelled ring polymers using spin echo neutron scattering or fluorescence microscopy, and this is related to the future work.

CONCLUSIONS

In summary, we have studied the dynamics of charged ring polymers in the gel matrix with mesh size larger than the ring polymer size. At low ring polymer concentration of 5 g/L, the rings are diffusive in the gel matrix and its diffusion coefficient is an order of magnitude smaller than that of rings in solutions, obeying the Ogston's model. At high polymer concentration of 40 g/L, we have discovered that they exhibit non-diffusive collective dynamical behaviour. With the reference of our previous work, we speculate the rings might be with the averaged size exponent ν=1/3, indicating they adopt an overall more compact conformation. Based on our experimental discovery, lots of puzzles still remain unknown and need to be solved in the future. For example, the critical concentration of rings for the dynamical transition from diffusive state to non-diffusive state need to be carefully determined. The conformation of each individual ring at both high and low ring polymer concentrations within the gels needs to be systematically studied by tracking labelled tracer rings using small angle neutron scattering. Besides, the self-diffusion and single ring dynamics at different polymer concentrations should also be systematically studied

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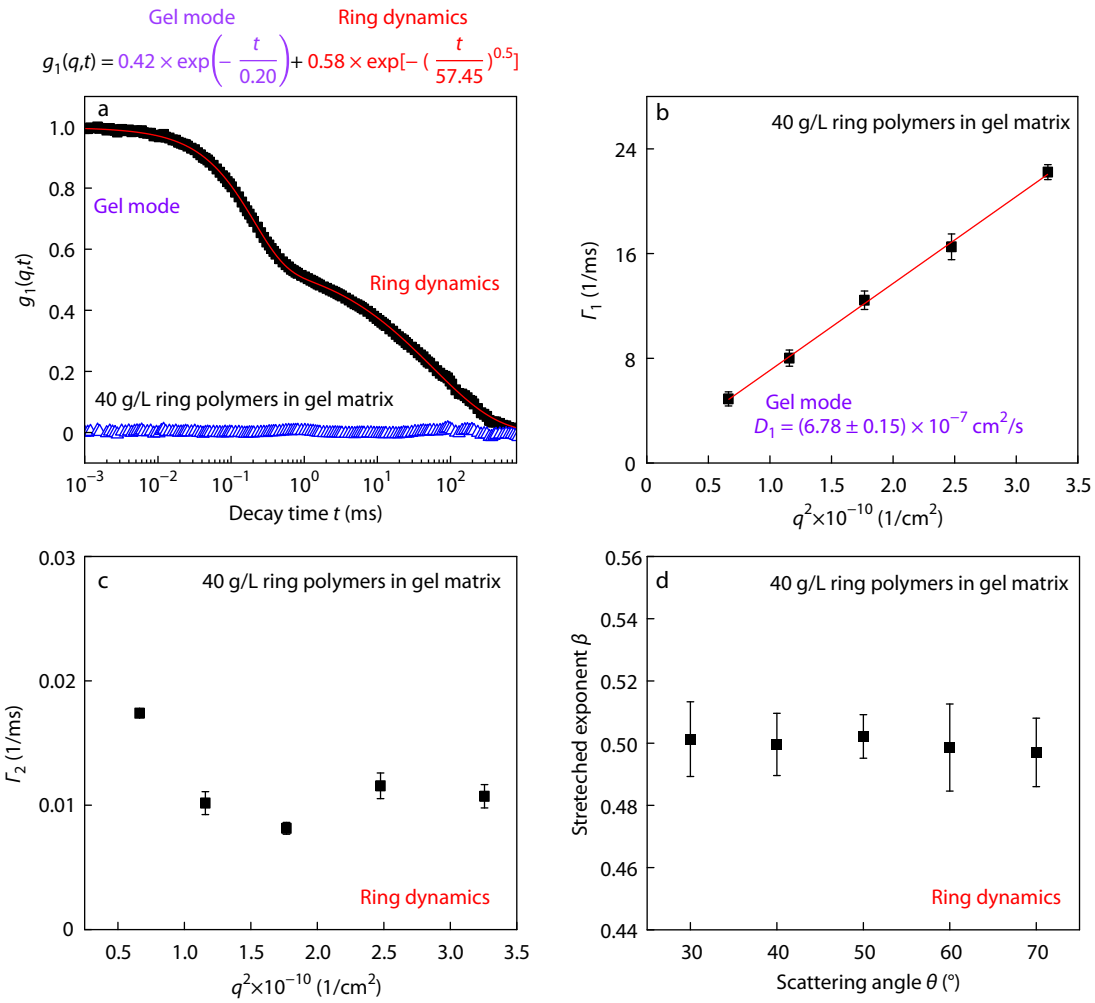

Fig. 4 Dynamics of 40 g/L charged ring polymers in Tetra-PEG gel matrix with 0.1 mol/L NaCl. (a) Normalized field correlation function $g_1(q,t)$ at a scattering angle of 30°. The blue triangles are the residuals between the fitting curve (red curve) and the raw data (black squares). (b, c) Fitting results of the relaxation rates Γ_1 and Γ_2 as a plot of q^2 at all scattering angles for the first and second modes, respectively. (d) Stretched exponent β as a plot of different scattering angles.

by using spin echo neutron scattering or fluorescence microscopy in the future.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-025-3291-0.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The author's contact information: jiadi11@iccas.ac.cn.

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REFERENCES

1 McLeish, T. Floored by the rings. *Nat. Mater.* **2008,** *7*(12), 933-935.
2 De Gennes, P. G. *Scaling concepts in polymer physics*. Cornell University Press, **1979**
3 Doi, M.; Edwards, S. F. *The theory of polymer dynamics*. Oxford University Press, **1988**.
4 Halverson, J. D.; Lee, W. B.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. Molecular dynamics simulation study of nonconcatenated ring polymers in a melt. I. Statics. *J. Chem. Phys.* **2011**, *134*, 204904.
5 Halverson, J. D.; Lee, W. B.; Grest, G. S.; Grosberg, A. Y.; Kremer, K.

Molecular dynamics simulation study of nonconcatenated ring polymers in a melt. II. Dynamics. *J. Chem. Phys.* **2011**, *134*, 204905.
6 Kapnistos, M.; Lang, M.; Vlassopoulos, D.; Pyckhout-Hintzen, W.; Richter, D.; Cho, D.; Chang, T.; Rubinstein, M. Unexpected power-law stress relaxation of entangled ring polymers. *Nat. Mater.* **2008**, *7*, 997–1002.
7 Khokhlov, A. R.; Grosberg, A. Y.; Pande, V. S. *Statistical Physics of Macromolecules*. Springer, **1994**.
8 Cates, M.; Deutsch, J. Conjectures on the statistics of ring polymers. *J. Phys.* **1986**, *47*, 2121–2128.
9 Suzuki, J.; Takano, A.; Deguchi, T.; Matsushita, Y. Dimension of ring polymers in bulk studied by Monte-Carlo simulation and self-consistent theory. *J. Chem. Phys.* **2009**, *131*, 144902.
10 Arrighi, V.; Gagliardi, S.; Dagger, A.; Semlyen, J.; Higgins, J.; Shenton, M. Conformation of cyclics and linear chain polymers in bulk by SANS. *Macromolecules* **2004**, *37*, 8057–8065.
11 Müller, M.; Wittmer, J.; Cates, M. Topological effects in ring polymers. II. Influence of persistence length. *Phys. Rev. E* **2000**, *61*, 4078.
12 Ge, T.; Panyukov, S.; Rubinstein, M. Self-similar conformations and dynamics in entangled melts and solutions of nonconcatenated ring polymers. *Macromolecules* **2016**, *49*, 708–722.
13 Iwamoto, T.; Doi, Y.; Kinoshita, K.; Ohta, Y.; Takano, A.; Takahashi, Y.; Nagao, M.; Matsushita, Y. Conformations of ring polystyrenes in bulk studied by SANS. *Macromolecules* **2018,** *51*, 1539-1548.
14 Brown, S.; Szamel, G. Computer simulation study of the structure and dynamics of ring polymers. *J. Chem. Phys.* **1998**, *109*, 6184–6192.
15 Han, C. C.; Akcasu, A. Z. *Scattering and dynamics of polymers: seeking order in disordered systems, C.* John Wiley & Sons, **2011**, pp. 36–78.
16 Hiemenz, P. C.; Lodge, T. P. *Polymer chemistry*; CRC Press, 2007. pp. 346–357
17 Xue, J. Z.; Pine, D.; Milner, S. T.; Wu, X. L.; Chaikin, P. Nonergodicity and light scattering from polymer gels. *Phys. Rev. A* **1992**, *46*, 6550.
18 Tanaka, T.; Hocker, L. O.; Benedek, G. B. Spectrum of light scattered from a viscoelastic gel. *J. Chem. Phys.* **1973**, *59*, 5151–5159.
19 Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U. i. Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. *Macromolecules* **2008**, *41*, 5379–5384.
20 Matsunaga, T.; Sakai, T.; Akagi, Y.; Chung, U. i.; Shibayama, M. SANS and SLS studies on Tetra-arm PEG gels in as-prepared and swollen states. *Macromolecules* **2009**, *42*, 6245–6252.
21 Provencher, S. W. CONTIN: a general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. *Comput. Phys. Commun.* **1982**, *27*, 229–242.
22 Cai, X.; Liang, C.; Liu, H.; Zhang, G. Conformation and structure of ring polymers in semidilute solutions: a molecular dynamics simulation study. *Polymer* **2022**, *253*, 124953.
23 Haydukivska, K.; Blavatska, V.; Paturej, J. Universal size ratios of Gaussian polymers with complex architecture: radius of gyration *vs* hydrodynamic radius. *Sci. Rep.* **2020**, *10*, 14127.
24 Ogston, A. G.; Preston, B. N.; Wells, J. D.; Snowden, J. M. On the transport of compact particles through solutions of chain-polymers. *Proc. R. Soc. A: Math. Phys. Eng. Sci.* **1973**, *333*, 297–316.
25 Jia, D.; Muthukumar, M. Topologically frustrated dynamics of crowded charged macromolecules in charged hydrogels. *Nat. Commun.* **2018**, *9*, 2248.
26 Jia, D.; Muthukumar, M. Electrostatically driven topological freezing of polymer diffusion at intermediate confinements. *Phys. Rev. Lett.* **2021**, *126*, 057802.
27 Jia, D.; Tsuji, Y.; Shibayama, M.; Muthukumar, M. Topologically frustrated dynamical state of polymers trapped in ideal uniform Tetra-PEG gels. *Macromolecules* **2023**, *56*, 9389–9397.

https://doi.org/10.1007/s10118-025-3291-0