

## Cyclic Polymer Dynamics

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### Abstract

*A number of works are dedicated to the investigation of the effects of the excluded volume interactions on the dynamics of cyclic polymers in good solvents using the Yu-Fujita model. Unfortunately, this latter does not satisfy the circularity condition. To overcome this problem, use is made of the Bensafi-Benmouna model which describes quite well their thermodynamic and structural properties in good solvents. This paper deals with the dynamic scattering properties of both cyclic homopolymers and copolymers in good solvents. These properties, such as the relaxation frequencies and the diffusion coefficient, are briefly discussed and the implications of the excluded volume interactions on such properties are emphasized more. Finally, cyclic chains dynamic properties are compared to those of their linear counterparts, in order to comprehend the effects of the cyclization of linear polymers under good solvent conditions.*

**Keywords:** cyclic polymer, dynamic diffusion, Rouse model, Zimm model, relaxation frequency, diffusion coefficient.

### 1. Introduction

The study of polymers with non-linear structures and, particularly, of those with cyclic architecture, is not much developed as that of linear chains. Indeed, that of cyclic polymers plays a crucial role in the field of theoretical developments related to the macromolecular behaviour. Translational symmetry and the lack of end groups in ring chains yield important simplifications in some treatments, making problem easier to treat than in linear chains. Nevertheless, the deficiencies present in the old experimental techniques (synthesis and characterization) for these rings suppressed in part the practical interest of the theoretical approaches, which could even be considered just as mathematical exercises and scarce applications. Recently, this situation has considerably changed. The improvement of experimental techniques allows nowadays both synthesis and accurate characterization of different classes of ring polymers [1]. This fact makes necessary a further theoretical development to try to explain the reactions that lead to the creation of cyclic structures and the equilibrium and dynamic behaviour of ring polymers, both with well-differentiated characteristics when compared to those corresponding to linear chains with the same molecular weight.

The most analytical expressions derived for the calculation of dynamic properties of flexible cyclic chains are based on the Rouse-Zimm bead-spring model, which included an equilibrium pre-averaging of hydrodynamic interactions [2].

Even later, developments suitable for more general models [3] and refinements over the Gaussian chain mode have maintained this approximation.

The dynamics of a flexible polymer chain in solution constitutes a non completely solved theoretical problem. The most popular description of the low frequency dynamics is provided by the Rouse-Zimm Theory [4]. In fact, the latter is based on a series of approximations, and the validity of the pre-averaging of hydrodynamic interactions is still an open question. In the same context, more rigorous treatments, based on the generalized Kirkwood Theory, can only be approached by means of perturbation techniques [4] or Renormalization-Group theory [5].

The static and dynamic properties of cyclic polymers in solution present some differences, in comparison with the case of linear chains [4,6-12]. These discrepancies originate, in particular, from their thermodynamic behaviour, conformational characteristics and evolution in time. Examples of these facts are the shift in theta temperature observed in dilute solutions of ring polymers in various solvents, such as cyclohexane, deuteriated cyclohexane and trans-decalin. The diffusion coefficient is larger for a cyclic polymer; this indicates that rings diffuse faster than their linear counterparts [12]. These properties were investigated recently for ring homopolymers and copolymers in solvent conditions close to the theta temperature, where the system is not perturbed by the excluded volume interactions.

Contrary to Benmouna et al. [13] who studied some dynamic properties of cyclic polymers in good solvents

using the Yu-Fujita Model, this paper is intended to extend such an investigation to the case of similar polymeric systems placed in similar solvent conditions. To this end, use is made of some model recently proposed by Bensafi and coworkers [14] in order to investigate the dynamical scattering relaxation properties.

It is worthwhile to recall that, among the quantities that allow the understanding of this dynamical behaviour and are accessible by quasi-elastic scattering techniques, the first cumulant,  $\Omega_r(Q)$ , of the intermediate scattering function,  $S_r(Q)$ , plays a crucial role. Here,  $Q$  denotes the wave-vector amplitude. The interesting feature lies in the fact that one does not need the entire form of the latter function to get useful information on the dynamics of these systems, and the initial decay rate  $\tau$ ,  $\Omega_r^{-1}(Q)$ , is quite sufficient for our purpose.

Over the last three decades, the structural properties of polymeric systems have been the subject of a great deal attention from theoretical and experimental points of view. In particular, considerable effort has been made in order to understand better such properties, especially static and dynamic behaviours both in solution and in the bulk state [13]. However, the investigations carried out on various polymeric systems of different architectures, reveal that the properties of ring polymers in solution present some discrepancies as compared with the case of their linear counterparts [4,6,10,14]. These deviations originate, particularly, from their thermodynamic behaviour, conformational characteristics, connectivity of cyclic chains, and time evolution of their correlation functions [15]. The present work aims to compare the effects of the excluded volume on dynamic properties of linear and ring homopolymers and copolymers.

This paper is organized as follows. In Sec. 2, we review the theoretical formalism enabling us to comprehend the dynamic scattering properties of systems under investigation, such as the relaxation frequencies and the diffusion coefficient, and discuss our main results, by emphasizing the impact of the solvent quality, hydrodynamic interactions and architecture effects on the dynamic properties. Some concluding remarks are drawn in the last section.

## 2. General formalism

### 2.1 Relaxation frequency

Among the dynamic properties that play a capital role in the study of the dynamics of polymeric systems, the first cumulant,  $\Omega_i(Q)$ , is the most important. This quantity, easily accessible by quasi-elastic light scattering techniques, represents the relaxation frequency of the intermediate dynamic scattering function,  $S_i(Q, t)$ , whose temporal evolution obeys the exponential decay

$$S_i(Q, t) = S_i(Q)e^{-\Omega_i(Q)t} \tag{1}$$

Where  $i = l, r$  (the subscripts l and r are for *linear* polymers and their *cyclic* counterparts). While the static structure factor,  $S_i(Q)$ , expresses as

$$S_i(Q) = \phi_i Z_i P_i(Q), \quad i = l, r \tag{2}$$

The form factor,  $P_i(Q)$ , describing the internal configuration of the polymer, is generally given by

$$P_i(Q) = \frac{2}{Z_i^2} \int_0^{Z_i} (Z_i - z) e^{-\frac{Q^2}{6} \langle r_z^2 \rangle_i} dz \tag{3}$$

where the amplitude of the scattering wave-vector  $Q$  is defined by

$$Q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{4}$$

where  $n$ ,  $\lambda$  and  $\theta$  denote the refraction index of the medium, the wavelength of the incident beam and the scattering angle, respectively. There, the quantity  $\langle r_z^2 \rangle_i$  representing the mean quadratic distance between two points separated by  $z$  monomers, along the polymer chain  $i$ , is given, in the case of swollen cyclic chain portion, by [14]

$$\langle r_z^2 \rangle_i = z^{\varepsilon+1} \left(1 - \frac{z}{Z}\right)^{1+\varepsilon} a^2 \tag{5}$$

with a the monomer size. In what follows, we shall assume that, regardless of their architecture, ring and linear polymers are characterized by the same length, molecular weight and volume fraction, that is  $Z_r = Z_l \equiv Z$  and  $\phi_r = \phi_l \equiv \phi$ . Recently, the properties, evoked above, were the subject of active studies, for cyclic homopolymers as well as for copolymers in theta solvent, where such systems are not perturbed by the excluded volume interactions [4,10,11,15,16].

The aim of this paper is to examine separately dynamic scattering properties of cyclic homopolymers and diblock copolymers in good solvent, using the model expressed by Eq. (5).

The computation of the form factor, based on the substitution of Eq. (5) into Eq. (2), leads to the expression

$$P_r(Q) = \frac{2}{1+\varepsilon} \int_0^1 x^{-1+1/(1+\varepsilon)} (1 - x^{1/(1+\varepsilon)}) e^{-u_\varepsilon x (1 - x^{1/(1+\varepsilon)})^{1+\varepsilon}} dx \tag{6}$$

with the notations

$$u_\varepsilon = Z^{1+\varepsilon} a^2 Q^2 / 6 \tag{6a}$$

$$x = \frac{z}{Z} \tag{6b}$$

In the case where the swelling parameter  $\varepsilon$  is zero (i.e. in theta solvent), we recover the well-known Casassa function [9]

$$P_r(Q) = \frac{2}{\sqrt{u}} e^{-u/4} \int_0^{\sqrt{u}/2} e^{t^2} dt, \quad u = Z a^2 Q^2 / 6 \tag{7}$$

It is worthwhile to note, furthermore, that this function has been confirmed experimentally by small-angle neutrons scattering measurements carried out by Hadziioannou et al. [11] on dilute solutions of cyclic polystyrene in cyclohexane.

In the case of linear chains in the presence of excluded volume, the form factor is given by the relation

$$P_i(Q) = \frac{2}{1+\varepsilon} \int_0^1 x^{-1+1/(1+\varepsilon)} (1 - x^{1/(1+\varepsilon)}) e^{-u\varepsilon x} dx \quad (8)$$

In theta solvent, this equation reduces to the Debye function [17]

$$P_i(Q) = \frac{2}{u^2} (e^{-u} + u - 1), u = Za^2 Q^2/6 \quad (9)$$

We note that, when  $\varepsilon = 0.2$  (in good solvent), the integrals (6) and (8) can be solved numerically.

On the other hand, in terms of the static structure factor,  $S_i(Q)$ , and the generalized mobility,  $M_i(Q)$ , the relaxation frequency,  $\Omega_i(Q)$ , is defined by the classical relation

$$\underline{\underline{\Omega}}(Q) = Q^2 K_B T \frac{\underline{\underline{M}}(Q)}{\underline{\underline{S}}(Q)} \quad (10)$$

Where  $T$  is the absolute temperature and  $K_B$  is the Boltzmann's constant.

In order to express the generalized mobility within the framework of the Zimm model [12] that takes into account the hydrodynamic interactions, it is possible to use the hydrodynamic model [18]. Nevertheless, these interactions can be modelled by the Oseen classic tensor [4],  $T(R)$ , that writes, as a function of real space coordinates, as follows

$$T(R) = \frac{1}{8\pi\eta_0 R} \left( I + \frac{R \otimes R}{R^2} \right) \quad (11)$$

Where  $\eta_0$ ,  $l$  and  $R$  stand for the solvent viscosity, the unit tensor and the distance between two monomers present in the solution, respectively, while the symbol  $\otimes$  means the tensorial product.

In reciprocal space, the Oseen tensor writes

$$T(K) = \frac{1}{\eta_0 K^2} \left( I - \frac{K \cdot K}{K^2} \right) \quad (12)$$

with  $k$  the three-dimensional wave-vector.

In particular, the component of the Oseen tensor, along the direction of the wave-vector, is given by

$$\langle T(r_{ij}) \rangle = \frac{1}{\eta_0 \pi \sqrt{6\pi} |r_{ij}|} \quad (13)$$

where  $|r_{ij}|$  is the distance that separates two monomers  $i$  and  $j$  along the chain.

When the polymer concentration increases, the solvent viscosity  $\eta_0$  should be replaced by a generalized one,  $\eta(k)$ , which writes, in reciprocal space, as

$$\eta(k) = \eta_0 \left( 1 + \frac{1}{\xi_h^2 k^2} \right) \quad (14)$$

where  $\xi_h$  is the hydrodynamic screening length.

It is easy to show that, in the presence of strong hydrodynamic interactions, i.e. for quite large values of the product  $\xi_h K$ ,  $\eta(k)$  coincides with  $\eta_0$  and the viscosity  $\eta(k)$  is more important as long as this product remains small. For finite values of the product  $\xi_h K$ , however, the hydrodynamic interactions are partially screened.

The computation of the generalized mobility  $M_i(Q)$  based on the pre-averaged version of the Oseen tensor (see Eq. (10)) and the model expressed by Eq. (5), leads to the following result

$$M_i(Q) = \frac{\Phi}{\zeta} + \sqrt{\frac{2}{3\pi}} \int_0^Z (Z-z) \frac{e^{-Q^2 (r_z^2)^{1/6}}}{\sqrt{(r_z^2)_i}} dz \quad (15)$$

where the quantity  $\zeta$  represents the friction coefficient of one monomer, assumed to be the same for the two polymeric species. In this equality, the first term in the right-hand side corresponds to the Rouse contribution, whereas the second one refers to that of Zimm model of hydrodynamic interactions.

In the case of cyclic polymers in good solvent, the combination of Eqs. (2), (5), (10), (15) and those expressing the form factors, leads to the renormalized relaxation frequency

$$\frac{\Omega_r(Q)}{Q^2} = \frac{K_B T}{Z \zeta P_r(Q)} + \frac{k_B T Q}{(1+\varepsilon) \eta_0 3\pi \sqrt{\pi u_\varepsilon} P_r(Q)} \int_0^1 x^{-1+1/(1+\varepsilon)} (1 - x^{1/(1+\varepsilon)}) \frac{e^{-u_\varepsilon x (1-x^{1/(1+\varepsilon)})^{1+\varepsilon}}}{\sqrt{x(1-x^{1/(1+\varepsilon)})^{1+\varepsilon}}} dx \quad (16)$$

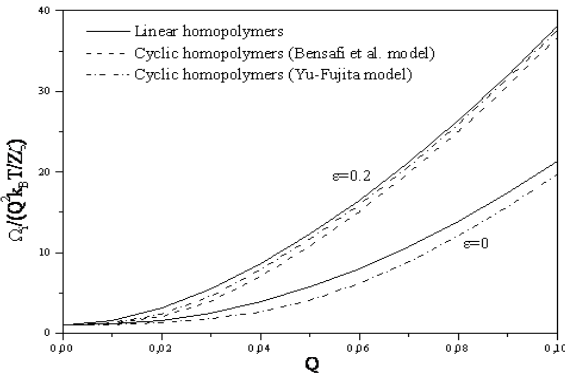
In the case of its linear homologous placed in similar solvent conditions, we obtain

$$\frac{\Omega_l(Q)}{Q^2} = \frac{K_B T}{Z \zeta P_l(Q)} + \frac{k_B T Q}{(1+\varepsilon) \eta_0 3\pi \sqrt{\pi u_\varepsilon} P_r(Q)} \int_0^1 x^{-1+1/(1+\varepsilon)} (1 - x^{1/(1+\varepsilon)}) \frac{e^{-u_\varepsilon x}}{\sqrt{x}} dx \quad (17)$$

To illustrate the angular dependence of the normalized relaxation frequency, we depict in Fig.1 the variations of the quantity  $\Omega_i(Q)/K_B T Q^2 Z^{-1} \zeta^{-1}$ , upon the wave-vector amplitude  $Q$ , in the Rouse limit, for linear and cyclic homopolymers placed under theta and good solvents conditions.

This figure clearly shows the effects of the excluded volume on the dynamics of linear homopolymers and their cyclic counterparts, in the absence of hydrodynamic interactions. In the case of cyclic homopolymers in good solvent, in addition to the Yu-Fujita model [13] that

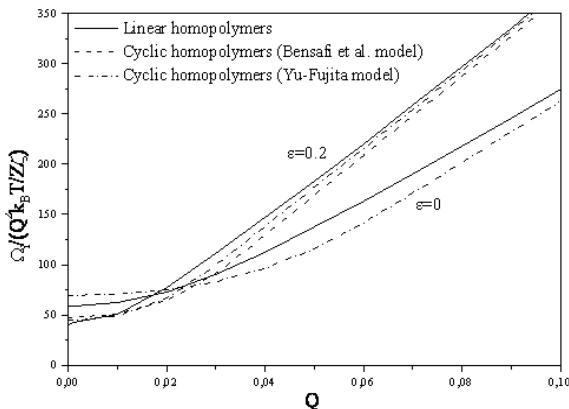
describes successfully the dynamics of a cyclic copolymer single chain, we have applied some recent model [14].



**Fig.1** Variations of the quantity,  $Z\zeta\Omega_i(Q)/Q^2K_B T$ , as a function of  $Q$ , in the Rouse limit, for linear and cyclic homopolymers under theta ( $\varepsilon = 0$ ) and good ( $\varepsilon = 0.2$ ) solvents conditions.

In this limit and under the two solvent conditions, we remark, on the other hand, that the dynamics of cyclic polymers is slower than that of their linear homologous. Fig.1 indicates that, in the Rouse limit and for values of the wave-vector such that  $Q < 0.05$  (expressed in  $a^{-1}$  unit,  $a$  being the monomer size), the results obtained using the Yu-Fujita model, are slightly different from those reported in the case of linear chains in good solvent, whereas, for  $Q > 0.05$ , they superpose. Contrary to this model that overestimates the relaxation of cyclic chains, results from Ref. [14] seem to be more reasonable.

In addition to the excluded volume, we have taken into account the effects of hydrodynamic interactions on linear and cyclic homopolymers dynamics. In Fig.2, we represent the variations of the renormalized relaxation frequency,  $\Omega_i(Q)/K_B T Q^2 Z^{-1} \zeta^{-1}$ , upon the wave-vector amplitude  $Q$ , in the Zimm limit, for the polymeric systems evoked above in theta and good solvents conditions.



**Fig.2** Variations of the quantity,  $Z\zeta\Omega_i(Q)/Q^2K_B T$ , as a function of  $Q$ , in the Zimm limit, for linear and cyclic homopolymers under theta ( $\varepsilon = 0$ ) and good ( $\varepsilon = 0.2$ ) solvents conditions.

This figure reveals that, in the small  $Q$ -range, the diffusion from cyclic homopolymers is faster as compared to that of their linear homologous. For  $Q > 0.01$  (theta solvent) and  $Q > 0.02$  (good solvent), this tendency is reversed. Therefore, whatever is the quality of the solvent, this diffusion behaviour for any specie is reversed.

In the small  $Q$ -limit, one can access directly to the diffusion coefficient of a single chain that expresses according to

$$D_{0i} = \lim_{Q \rightarrow 0} \frac{\Omega_i(Q)}{Q^2} = \frac{K_B T}{Z\zeta} + \frac{K_B T}{6\pi\eta_0 R_{hi}} \tag{18}$$

where the hydrodynamic radius  $R_{hi}$  is given by

$$\frac{1}{R_{hi}} = 2 \sqrt{\frac{6}{\pi}} \frac{1}{Z^{1+\varepsilon_i}} I_i, \quad (i = l, r) \tag{19}$$

In the case of cyclic chains, the integral  $I_i$  reads

$$I_r = \int_0^1 \frac{1-x}{\sqrt{x^{1+\varepsilon}(1-x)^{1+\varepsilon}}} dx \tag{19a}$$

While for their linear counterparts, we obtain

$$I_l = \int_0^1 \frac{1-x}{x^{1+\varepsilon}} dx \tag{19b}$$

The calculation of the gyration radius of a cyclic polymer in a good solvent, based on the model expressed by Eq. (5), yields the following result

$$R_{gr}^2 = Z^{1+\varepsilon} a^2 \int_0^1 x^{1+\varepsilon} (1-x)^{2+\varepsilon} dx \tag{20}$$

In theta solvent ( $\varepsilon = 0$ ), we get

$$R_{gr}^2 = 0.083 Z a^2 \tag{20a}$$

Whereas for ( $\varepsilon = 0.2$ ), the numerical solving of this integral provides the corresponding expression in the good solvent conditions

$$R_{gr}^2 = 0.06 Z^{1.2} a^2 \tag{20b}$$

Furthermore, combining Eqs. (19), (19a) and (20) yields the following relation between the gyration and hydrodynamic radii

$$R_{gr}^2 = \frac{36I_r^2}{\pi^2} \left[ \int_0^1 x^{1+\varepsilon} (1-x)^{2+\varepsilon} dx \right] R_{hr}^2 \tag{21}$$

For the corresponding linear chains [20], the gyration radius is given by

$$R_{gl}^2 = \frac{Z^{1+\varepsilon} a^2}{(2+\varepsilon)(3+\varepsilon)} \tag{22}$$

When ( $\varepsilon = 0$ ) (theta solvent), we obtain

$$R_{gl}^2 \approx 0.166 Z a^2 \quad (22a)$$

While for ( $\varepsilon = 0.2$ ) (good solvent), the result is

$$R_{gl}^2 \approx 0.142 Z^{1.2} a^2 \quad (22b)$$

It is interesting to point out that, whatever is the quality of the solvent with respect to linear chains or their cyclic homologous, the gyration radius naturally increases with increasing polymerization degree  $Z$ . However, the dimensions of linear chains remain always larger than those of the corresponding cyclic chains.

Concerning the mean quadratic radius of gyration of a cyclic polymer in good solvent,  $R_{gr}^2$ , it is related to that of its linear counterpart (of the same polymerization degree) by

$$R_{gr}^2 = \left[ (2 + \varepsilon)(3 + \varepsilon) \left( \int_0^1 x^{1+\varepsilon} (1-x)^{2+\varepsilon} dx \right) \right] R_{gl}^2 \quad (23)$$

from which, we extract the following result

$$R_{gr}^2 = 0.50 R_{gl}^2 \quad (23a)$$

for theta solvents ( $\varepsilon = 0$ ), and

$$R_{gr}^2 \approx 0.42 R_{gl}^2 \quad (23b)$$

for good solvents ( $\varepsilon = 0.2$ ). These results clearly show that the cyclic chains are less compact than their linear homologous in both good and theta solvents.

Putting  $\varepsilon = 0$  (theta solvent) and  $\varepsilon = 0.2$  (good solvent) into Eq. (21) yields the respective values 0.797 and 0.570 of the ratio  $R_{hr}/R_{gr}$ . For linear chains, this ratio has the respective values 0.665 and 0.537.

Concerning the intrinsic viscosity, it can be expressed, in terms of hydrodynamic and gyration radii, as

$$[\eta]_i = \frac{R_{hi} R_{gi}^2}{Z} \quad (24)$$

Substituting Eqs. (19) and (21) into the above equality gives, for  $\varepsilon = 0$  and  $\varepsilon = 0.2$ , the results

$$[\eta]_r \approx 0.020 Z^{0.5} \quad (24a)$$

and

$$[\eta]_r \approx 0.014 Z^{0.6} \quad (24b)$$

For comparison, the numerical prefactors in the above scaling laws, corresponding to the case of linear chains, increase to 0.04 and 0.03, respectively. These values show that the intrinsic viscosity is essentially two times more important than that of cyclic counterparts, whatever is the solvent quality.

Starting from these results, we can deduce the effects of the chain swelling, due to excluded volume

interactions and to the circularity condition imposed to chain ends, on the size and viscosity of cyclic polymers in good solvent.

It is convenient to remind that, in the intermediate values of the wave-vector amplitude  $Q$ , the form factor is approximately equal to

$$P_r(Q) = \frac{\Gamma(Q)}{2\sigma u_\varepsilon^Q} \quad (25)$$

with

$$\sigma = \frac{1+\varepsilon}{4} \quad (25a)$$

where  $\Gamma$  denotes the Euler Gamma function.

In this  $Q$ -range, the asymptotic limit of the first cumulant,  $\Omega_r(Q)$ , is very useful and can be readily deduced from Eq. (11) as follows

$$\Omega_r(Q) = 0.083 \frac{K_B T}{a^2 \zeta} (Qa)^4 + 0.053 \frac{K_B T}{\eta_0} Q^3 \quad (26a)$$

for  $\varepsilon = 0$  (theta solvent), and

$$\Omega_r(Q) = 0.019 \frac{K_B T}{a^2 \zeta} (Qa)^{3.66} + 0.071 \frac{K_B T}{\eta_0} Q^3 \quad (26b)$$

for  $\varepsilon = 0.2$  (good solvent).

These results are similar to those obtained for linear chains, and then, the internal dynamics of cyclic chains are not affected by the circularity condition. However, by neglecting the pre-averaged approximation of the Oseen tensor, the first cumulant is given by

$$\frac{\Omega_r(Q)}{Q^2} = \frac{K_B T}{Z \zeta P_r(Q)} + \frac{Q K_B T}{4\pi \eta_0 \sqrt{\pi} P_r(Q)} \int_0^1 (1-x) F[y(x)] dx \quad (27)$$

where the function  $F$  is defined by

$$F[y] = y^{-2} \left[ -y^{-1} + (2 + y^2) e^{-u_\varepsilon^2} \int_0^y e^{t^2} dt \right] \quad (28a)$$

With

$$y(x) = u_\varepsilon x^{1+\varepsilon} (1-x)^{1+\varepsilon} \quad (28b)$$

We note that, only the contribution of Zimm is found to be modified. Indeed, in this  $Q$ -range, the values of hydrodynamic radius and intrinsic viscosity, reported above, are not affected. On the other hand, the numerical coefficients, appearing in hydrodynamic terms of Eq. (28), become 0.071 and 0.079 [21], respectively.

## 2.2. Concentration effects on dynamics of cyclic polymers in solution

These effects can be introduced through the molecular interactions appearing in the static structure factor

$$S_r(Q) = \frac{\phi Z P_r(Q)}{1 + \nu \phi Z P_r(Q)} \quad (29)$$

where  $\phi$  represents the monomer volume fraction, and  $v$  refers to the excluded volume parameter. The latter can be expressed, in terms of the polymer-solvent interaction parameter  $\chi_0 = \chi_{PS}$ , according to the relation [22]

$$v = v_s \left( \frac{1}{\phi_s} - 2\chi_0 \right) \quad (30)$$

where  $v_s$  and  $\phi_s$  are the volume of the solvent molecules (volume occupied by one site in Flory lattice) and their volume fraction, respectively.

For a mixture of two polymers, the difference in their chemical nature can be described through the Flory interaction parameter  $\chi$ . In this case, the structure factor of such a polymeric system is well expressed in numerous works [10,21,23].

On the other hand, within the framework of the hydrodynamic model, the pre-averaged approximation seems to be reliable, and the viscosity  $\eta_0$  that appears in the Fourier transform of the Oseen tensor (see Eq. 12), should be replaced by the effective viscosity,  $\eta(K)$ , defined in Eq. (14).

Taking into account these arguments, expression (16) of the first cumulant  $\Omega_r(Q)$  then becomes

$$\frac{\Omega_r(Q)}{Q^2} = \frac{K_B T}{\zeta S_r(Q)} + \frac{Q K_B T}{(2\pi)^2 \eta_0} \int_0^\infty G\left(\frac{k}{Q}, Q \xi_h\right) \frac{S_r(k)}{S_r(Q)} dk \quad (31)$$

With

$$G(u, v) = u^2 \left[ \frac{u^2 + 1 + v^2}{4u} \log \frac{(u+1)^2 + v^2}{(1-u)^2 + v^2} - 1 \right] \quad (31a)$$

where  $\xi_h$  is the hydrodynamic screening length that can be experimentally adjusted, and it naturally depends on concentration.

There are different expressions of the first cumulant. The simplest one, that is familiar in theories of coupled modes [24-26], writes

$$\frac{\Omega_r(Q)}{Q^2} = \frac{K_B T}{\zeta \xi_{0r}^2} \left[ \frac{R_{gr}^2}{\xi_{0r}^2} \right] \left[ 1 + Q^2 \xi_{0r}^2 \right] + \frac{K_B T}{6\pi\eta_0 \xi_{0r}} K(Q \xi_{0r}) \quad (32)$$

where the Kawasaki function [25],  $K(u)$ , is defined by

$$K(u) = u^2 \left( \frac{u^2 + 1}{2u} \log \left| \frac{1+u}{1-u} \right| - 1 \right) \quad (32a)$$

In Eq. (32), the quantity  $\xi_{0r}$  represents another correlation length, which can be related to the gyration radius by

$$\xi_{0r}^2 = \frac{R_{gr}^2}{1 + v\phi Z} \quad (33)$$

### 2.3. Application to cyclic diblock copolymer in good solvents

We note that the properties of linear copolymers systems are still the subject of investigations from a theoretical

and experimental point of view [27]. In what follows, we will present some results, related to dynamic properties of cyclic diblock copolymers chains, which are the subject of discussion. In the case of their linear homologous, if the monomers species have different cohesion energy densities, the system undergoes a phase separation. The end-to-end closure of both extremities of blocks A and B leads to the formation of a cyclic structure noted (A-B). Thereby, by contrast to the case of linear chains, spectacular changes appear in dynamic scattering properties of such systems [6].

For the sake of simplicity, we consider a symmetrical cyclic diblock copolymer. In other terms, both blocks have the same polymerization degree ( $Z_A = Z_B = Z/2$ ), the same gyration radius ( $R_{ga} = R_{gb} \equiv R_g$ ), the same volume excluded parameter ( $v_{AA} = v_{BB} \equiv v$ ), and present a slight compatibility introduced via the interaction parameter  $\chi_{AB} = v_{AB} - v \neq 0$ .

Taking into account these simplifying hypothesis and limiting the integration to  $Z/2$  monomers, we obtain the following expression for the form factor of a single diblock chain

$$P_{1/2r}(Q) = \frac{2}{1+\varepsilon} \int_0^1 x^{-1+1/(1+\varepsilon)} \left( 2 - x^{1/(1+\varepsilon)} \right) e^{-u_\varepsilon x^{(1-x^{1/(1+\varepsilon)})/2}} / 2^{1+\varepsilon} dx \quad (34)$$

We have used Eqs. (5) and (6a). In theta solvent ( $\varepsilon = 0$ ), analytic solving of this integral leads to the result

$$P_{1/2r}(Q) = \frac{1 - e^{-u/4}}{u/4} \quad (35)$$

where the quantity  $u$  is given

$$u = Q^2 R_{gl}^2 = Q^2 \frac{Za^2}{6} \quad (35a)$$

For  $\varepsilon = 0.2$ , however, the integral can be solved numerically.

For a linear diblock copolymer, the form factor expresses as

$$P_{1/2l}(Q) = \frac{2}{1+\varepsilon} \int_0^1 x^{-1+1/(1+\varepsilon)} \left( 2 - x^{1/(1+\varepsilon)} \right) e^{-u_\varepsilon x/2^{1+\varepsilon}} dx \quad (36)$$

In the case of ternary mixtures of two homopolymers or a diblock copolymer in solution, the first cumulant,  $\Omega(Q)$ , corresponds to a diagonal square matrix whose components are defined by the relationship [28]

$$\Gamma(Q) = K_B T Q^2 \frac{M(Q) + M'(Q)}{S(Q) + S'(Q)} \quad (37a)$$

$$\Gamma'(Q) = K_B T Q^2 \frac{M(Q) - M'(Q)}{S(Q) - S'(Q)} \quad (37b)$$

where the respective quantities  $M(Q)$  and  $M'(Q)$  denote the components of the generalized mobility matrix  $\underline{M}(Q)$ , whereas  $S(Q)$  and  $S'(Q)$  are those of the static structure matrix  $\underline{S}(Q)$ . In this case, we obtain

$$S(Q) = \frac{(\phi Z/4)\{P_{1/2r}(Q) + v\phi Z P_r(Q)[P_{1/2r}(Q) - P_r(Q)]\}}{\{1 + (v + \chi/2)\phi Z P_r(Q)\}\{1 - \chi\phi Z [P_{1/2r}(Q) - P_r(Q)]/2\}} \quad (38a)$$

$$S'(Q) = \frac{(\phi Z/4)\{2P_r(Q) - P_{1/2r}(Q) - (v + \chi)\phi Z P_r(Q)[P_{1/2r}(Q) - P_r(Q)]\}}{\{1 + (v + \chi/2)\phi Z P_r(Q)\}\{1 - \chi\phi Z [P_{1/2r}(Q) - P_r(Q)]/2\}} \quad (38b)$$

where the form factors of the total chain and of its half are defined in Eqs. (4a) and (28a), respectively. The mobility matrix components are defined by [4,12,24]

$$M(Q) = \frac{\phi}{2\zeta} + \frac{1}{(2\pi)^2\eta_0} \int_0^\infty F\left(\frac{k}{Q}\right) S(k) dk \quad (39a)$$

$$M'(Q) = \frac{1}{(2\pi)^2\eta_0} \int_0^\infty F\left(\frac{k}{Q}\right) S'(k) dk \quad (39b)$$

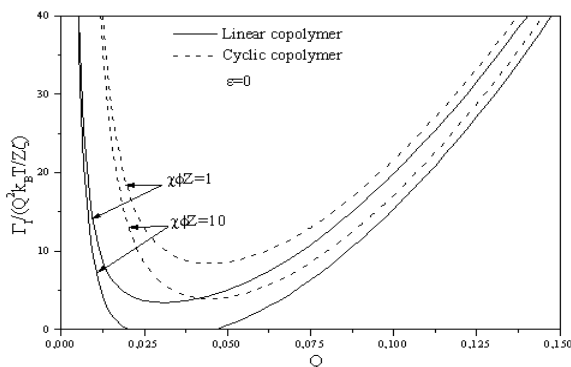
where the function  $F(x)$  is that defined in Eq. (32a).

The two frequencies  $\Gamma$  and  $\Gamma'$  characterize the dynamic behaviour of the system under consideration. The physical meaning of the former has been previously discussed in various studies [29-33]. In the case of a symmetrical diblock copolymer in solution, these both frequencies, denoted  $\Gamma_c$  and  $\Gamma_l$ , identify to the cooperative (total polymer concentration fluctuations) and interdiffusive (composition fluctuations) modes, respectively, and read

$$\Gamma_c(Q) = Q^2 \left(\frac{K_B T}{Z\zeta}\right) \frac{1}{P(Q)} + [1 + (v + \chi/2)\phi Z P(Q)] \times \left\{1 + \frac{Z}{(2\pi)^2} \left(\frac{\zeta}{\eta_0}\right) \int_0^\infty F\left(\frac{k}{Q}\right) \frac{P_r(k)}{1 + (v + \chi/2)\phi Z P_r(k)} dk\right\} \quad (40a)$$

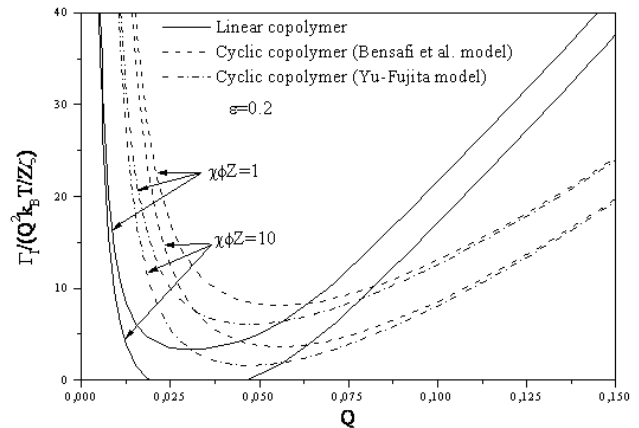
And

$$\Gamma_l(Q) = Q^2 \left(\frac{K_B T}{Z\zeta}\right) \frac{1}{P_r(Q)} \left[\frac{1}{P_{1/2r}(Q) - P_r(Q)} - \frac{\chi\phi Z}{2}\right] \times \left\{1 + \frac{Z}{(2\pi)^2} \left(\frac{\zeta}{\eta_0}\right) \int_0^\infty F\left(\frac{k}{Q}\right) \frac{P_{1/2r}(Q) - P_r(Q)}{1 - \chi\phi Z [P_{1/2r}(k) - P_r(k)]/2} dk\right\} \quad (40b)$$



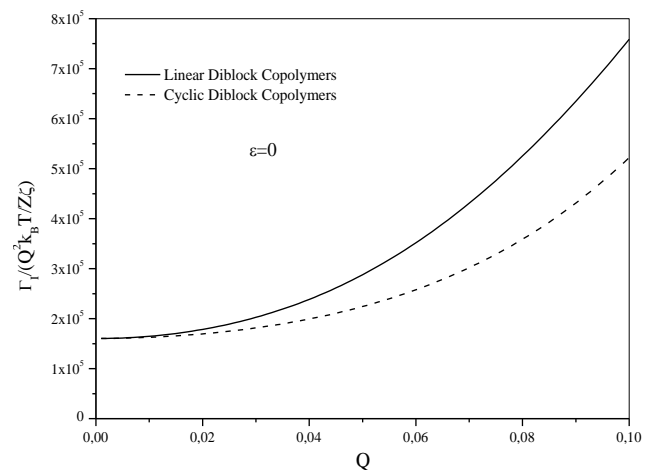
**Fig.3** Variations Variations of the normalized relaxation frequency  $Z\zeta\Gamma_l(Q)/Q^2 K_B T$ , upon the wavenumber  $Q$ , in the Rouse limit, for linear and cyclic symmetrical diblock copolymers under theta solvent conditions ( $\varepsilon = 0$ ) and for two values of the concentration  $\chi\phi Z = 1$  and 10.

In the Rouse limit, the angular variations of the latter quantity, in theta ( $\varepsilon = 0$ ) and good ( $\varepsilon = 0.2$ ) solvents, are depicted in Figs.3 and 4, for linear and cyclic diblock copolymers. Due to the fact that  $R_{gr} < R_{gl}$ , the observation, evoked above, is fully justified.

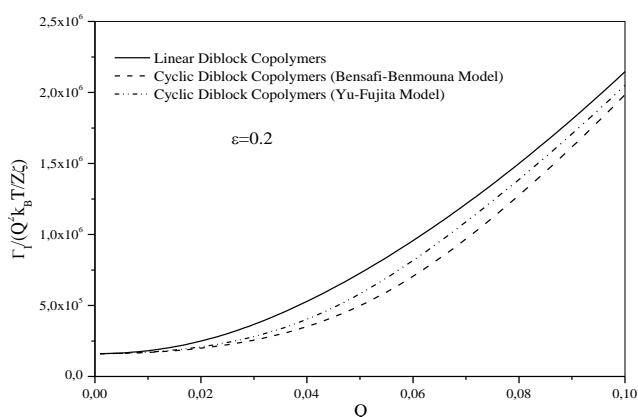


**Fig.4** Variations Variations of the normalized relaxation frequency  $Z\zeta\Gamma_l(Q)/Q^2 K_B T$ , upon the wavenumber  $Q$ , in the Rouse limit, for linear and cyclic symmetrical diblock copolymers under good solvent conditions ( $\varepsilon = 0.2$ ) and for two values of the concentration  $\chi\phi Z = 1$  and 10.

Fig.3 shows that, in theta solvent, the cyclic copolymers scatter more rapidly than their linear counterparts placed in the same conditions. On the other hand, as shown in Fig.4, the scattering behaviour of cyclic copolymers is reversed, for large values of  $Q$ . Regardless of the architecture of the two copolymers, the scattering behaviour is more slow as the concentration is increased. Finally, Figs.5 and 6 also confirm the predictions of the cyclic diblock copolymers model [14].



**Fig.5** Variations of the normalized relaxation frequency  $Z\zeta\Gamma_l(Q)/Q^2 K_B T$ , against the wavenumber  $Q$ , in the Zimm limit, for linear and cyclic symmetrical diblock copolymers under theta solvent conditions ( $\varepsilon = 0$ ) and for the concentration  $\chi\phi Z = 1$ .



**Fig.6** Variations of the normalized relaxation frequency  $Z\zeta\Gamma_1(Q)/Q^2K_B T$ , against the wavenumber  $Q$ , in the Zimm limit, for linear and cyclic symmetrical diblock copolymers under good solvent conditions ( $\varepsilon = 0.2$ ) and for the concentration  $\chi\phi Z = 1$ .

### 3. Concluding remarks

We recall that this paper has been devoted to a comparative analysis of dynamical scattering from linear and cyclic homopolymers and copolymers in solution (with theta or good solvents). To this end, use was made, first, of the Oseen tensor that gives a description of the long-range coupling between monomers in the solution, and second, of some recent model [14]. Within the framework of the latter, we gave a detailed description of the effects of the excluded volume on dynamic scattering properties. The choice of such a model can be justified by the fact that a comparison between theory and experiment is favourable. In addition, this same model is found to be relatively more appropriate to describe the effects of excluded volume on thermodynamic and structural properties of cyclic polymers in good solvents. In the light of the obtained results, it appears numerical discrepancies between linear and cyclic chains, especially, in the small  $Q$ -range. This tendency is natural, since the two systems are not of the same topology.

Furthermore, we recall that, in the small  $Q$ -limit, Yu-Fujita model overestimates the swelling effect of cyclic homopolymer (or copolymer) chains.

The present analysis revealed that, above the overlap concentration, hydrodynamic interactions are essentially screened out, and then, the Rouse model is sufficient for the description of the dynamic behaviour of the two kinds of systems. Also, we note that, in the Rouse limit, the angular evolution of the cooperative mode, for linear copolymers as well as for their cyclic homologous, does not present any specific characteristics of the dynamics that should allow to distinguish the cyclic chains from their linear homologous, excepted probably in the large  $Q$ -range, where the dynamics reflects the intramolecular form factors  $P_r(Q)$  and  $P_l(Q)$ . On the other hand, the interdiffusive mode, which plays a capital role in the dynamics of polymeric systems under investigation, is

illustrated in Figs.3 and 4, which represent the respective angular dependence of the corresponding normalized frequencies, for  $\chi\phi Z = 1$  and  $\chi\phi Z = 10$ , in both Rouse and Zimm limits.

Analysis of these two figures reveals that, in linear copolymers case, the characteristic frequency is practically zero at minimum  $Q = Q_m$ , in the two limits, for  $\chi\phi Z = 10$ , whereas it remains positive and quite raised for their cyclic homologous. In fact, for these latter, the normalized frequency corresponding to the interdiffusive mode, tends to 0 at  $\chi\phi Z \gg 10$  (i.e., for an interaction parameter whose value is approximately two times more important than that observed in the case of linear chains at the same concentration).

In addition, a meticulous examination of these two figures show that, in the case of a cyclic copolymer, the position of the minimum  $Q_m$ , in the Rouse and Zimm limits, is shifted towards the raised values of  $Q$ . These observations confirm the reliability of the predictions of a certain recent model [14]. On the other hand, they show that there are substantial differences between the dynamic behaviours of the two types of copolymers, which would be put in evidence or by elastic light scattering or by quasi-elastic light scattering.

Below overlap concentration, i.e. in diluted regime, the effects of hydrodynamic interactions become important and, hence, the cooperative and interdiffusive modes present important discrepancies between the linear copolymer and its cyclic homologous. For instance, it should be interesting to graphically illustrate, in another figure, the variations of  $Z\zeta\Omega_c(Q)/Q^2K_B T$ , as a function of  $Q$  for  $\chi\phi Z = 1$  and 10, for both systems. This figure should show that, in the small  $Q$ -range, the diffusion coefficients inequality  $D_{cr} > D_{cl}$  agrees with experimental observations [30]. On the other hand, near  $QR_g = 2$ , the scattering behaviour is reversed, and above the corresponding value of  $Q$ , dynamics of internal modes, which found to be more slow for cyclic copolymers, has not, up to now, still been observed experimentally.

It has been previously mentioned that, in the framework of the Rouse model, kinetics of the microphase separation takes place for an interaction parameter which is approximately twice in the case of a cyclic copolymer. In the presence of hydrodynamic interactions, the form of the representative curves of the function  $\Omega_r(Q)/Q^2 = f(Q)$  is drastically modified. We note that, when the hydrodynamic interactions are taken into account, one observes a deep minimum whose position  $Q_m$  is substantially shifted. These results clearly show that the validity range of the used formalism is larger than that of cyclic copolymers. For this reason, we have focussed our attention on this latter mode.

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