

MICROPHASE SEPARATION IN INTERPENETRATING CYCLIC POLYMER NETWORKS: STATIC AND KINETICS STUDIES

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Abstract- *The physical system we consider here is an interpenetrating polymer network made of two chemically incompatible cyclic polymers A and B, linked each to other by topological trapping. When the system is cooled down, below some critical temperature, the system undergoes a microphase separation. The latter results from a competition between the usual macrophase separation and the fact that the cyclic polymer chains are connected. Using an extended de Gennes theory, we first compute the static structure factor allowing the study of the static critical properties of such a transition. We show that this structure factor exhibits a maximum at some finite value of the wave-vector, q_c^* , of which the inverse, $\xi_c^* = q_c^{*-1}$, measures the size of microdomains. Second, we complete the study by kinetics of this microphase separation when the temperature of the system is lowered from an initial value towards a final one very close to the spinodal point. This kinetics is investigated through the relaxation rate, $\tau_c(q)$, that can be interpreted as the necessary time to form microdomains of size q^{-1} , where q is the module of the wave-vector q . In particular, we find that, at small scales compared to the mesh size ξ_c^* , that is for $q^{-1} \ll \xi_c^*$, the characteristic frequency, $\Omega_c(q) = \tau_c^{-1}(q)$, behaves according to: $\Omega_c(q) \sim q^6$, with a known amplitude. The obtained results must be compared to those relatively to the well-studied crosslinked polymer blends composed of connected linear chains. The main conclusion is that, the closed topology of connected polymer chains induces a drastic change of the critical behavior in comparison with the crosslinked systems.*

Keywords- Cyclic polymer network; microphase separation; phase separation kinetics.

I. INTRODUCTION

The subject of cyclic polymers effectively began with a pioneered paper by Jacob and Wollman [1], published in 1958. The authors confirmed that the genetic map of bacterial chromosomes of Escherichia coli showed circularity. Thereafter, one has put in evidence the existence of circular DNA [2, 3], which has received its final confirmation from electron microscopy of ϕ X174 DNA [4]. The discovery of large cyclic molecules in natural biological systems is described in Ref. [5] as well as in a more recent book by Semlyen [6].

The interest in studying cyclic polymers originates from both applied and fundamental reasons. In particular, they have quite different properties in comparison to their linear homologous of the same molecular-weight, due to their circular topology. From a theoretical point of view, cyclic macromolecules provide a good model of polymers that are free from end effects that present a serious challenge for the study of linear macromolecules.

The cyclic macromolecules have attracted much attention from a theoretical and experimental point of view [6 – 11]. Among these, we can quote circular DNA, cyclodextrine, cyclic copolyolefines or cyclic polycarbonates. Since the four last decades, it is recognized that the DNA molecule

produces in nature as long cyclic chains [6]. Due to the capital role of the DNA macromolecules in the organization of the living cells, the knowledge of their conformational properties in solution or in the absence of solvent is crucial for the comprehension of recent discoveries in genetics. On the other hand, the cyclodextrine has been the subject of extended investigations [6], because of its potential applications in high technology used in pharmaceutical industry, cosmetics and agriculture. Furthermore, the cyclic copolyolefines are characterized by their important properties (high glass transition temperature, excellent transparency, low density, great thermicity and chemical resistances, high optic performance, etc.). Finally, the cyclic polycarbonates are used for the enzyme immobilization, and in the polymer-based lithium batteries sector [6, 12].

This work is devoted to the investigation of the microphase separation (MPS) in an interpenetrating polymer network (IPN) composed of two cyclic polymers A and B, of different chemical nature. This system is formed as follows. One starts from unlike long linear chains with chemically active extremities in a reaction bath. Each chain reacts with itself and forms a closed macromolecule. At the end of reaction, one gets an IPN constructed with a topological trapping of circular chains of different kinds.

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The IPNs constitute new materials, which find considerable applications. As examples, we can cite crosslinked epoxy adhesives that show a great resistance to acids, bases and many solvents, and exhibits high glass transition temperature and thermal resistance, crosslinked mixtures of bacterial and seaweed polysaccharides gellan and agarose [13], novel IPNs made of polypropylene / poly(n-butyl acrylate) [14], or polysiloxane IPNs used as electronic device encapsulants [15].

The physical system we are interested in is a mixture made of two kinds of linear polymer chains A and B terminated each by two chemically active groups. We assume that the chemical reactions between these groups occurs in the one-phase region, that is at high temperature. Once these chemical reactions are stopped, one gets an IPN made of unlike cyclic chains. The obtained gel is different from a gel synthesized by controlled γ -irradiations of unlike linear chains [16], called crosslinked polymer blend (CPB). Then, the chemical reticulations process is replaced by a topological trapping. To simplify the study, we suppose that cyclic chains A are linked to cyclic chains B, and there are no links between cyclic chains of the same kind. Therefore, complications related to an eventual existence of links between chemically identical cyclic chains are not considered here.

When the system is cooled down, one assists to the appearance of microdomains alternatively rich in A and B-polymers. This is the so-called microphase separation, which results from a competition between the usual macrophase separation and the elasticity of the cyclic polymer network. The goal of this work is precisely a quantitative study of this phase transition that takes place within the considered cyclic IPN.

From a theoretical point of view, the first study of the MPS in CPBs was due to de Gennes [17], followed by several extended works [18 – 32]. The key idea of the author was an analogy between the crosslinked chains and a dielectric medium. The theoretical predictions of MPS was experimentally tested by Briber and Bauer [16] by small-angle neutron-scattering experiment on the PS-PVME mixture. But the de Gennes theory agrees with experiment in all wave-vectors range except in the zero-scattering-angle limit. More precisely, the theoretical structure factor vanishes at this limit, while the experimental one does not. This discrepancy between theory and experiment was solved in a series of published works [20 – 23, 25].

Our purpose is to extend these works to the static and kinetics studies of MPS within cyclic IPNs. As we shall see below, the presence of the closed topology induces substantial changes of the critical phase behavior of the considered IPN. The study of static properties of the MPS necessitates the knowledge of the static structure factor we determine exactly using the famous Random Phase Approximation (RPA) [33]. This structure factor presents a maximum at a finite value of the wave-vector, $q_C^* \sim a^{-1} N_e^{-1/2}$, of which the inverse measures the size of critical fluctuations (microdomains size), $\xi_C^* \sim a N_e^{1/2}$ (a being the monomer size and N_e the number of monomers between consecutive entanglement points). It is found that the latter is smaller than its homologous relatively to a CPB having the same rigidity constant. In the second part of this paper, we undertake the kinetics study of such a transition, when the temperature is changed from an initial value T_i towards a final one T_f very

close to the spinodal point. We note that the reptation motion of cyclic chains forming the IPN is frozen by the presence of entanglement points that play the role of permanent crosslinks for CPBs. Therefore, the only motion allowed to the connected cyclic chains is of Rouse type [33, 34]. Kinetics is studied through the relaxation rate, which is as a function of the wave-vector and temperature. The inverse of this relaxation rate is termed characteristic frequency. The latter we computed exactly is directly proportional to the inverse static structure factor. We show that this characteristic frequency is smaller than its homologous of a CPB. This tendency is a consequence of closed topology of chains. In addition, at small scales compared to the mesh size ξ_C^* , that is for $q^{-1} \ll \xi_C^*$, the characteristic frequency behaves as : $\Omega_C(q) \sim q^6$. Notice that this law is similar to that relatively to a CPB [19].

Indeed, at these scales, there is no distinction between entanglement points of the cyclic IPN and real crosslinks of a CPB.

The remainder of presentation proceeds as follows. In Sec. 2, we present the static study of the MPS within the framework of an extended de Gennes theory. Kinetics study of this MPS is the aim of Sec. 3. Some concluding remarks are drawn in the last section.

II. CRITICAL PROPERTIES OF MPS

Start from an IPN made of two kinds of cyclic polymers A and B of different chemical nature. We denote by N_e the mean number of monomers between consecutive entanglement points. Of course, we have $N_e < N$, where N denotes the common polymerization degree of linked cyclic polymer chains. We assume that the IPN is formed in the one-phase region, that is at high temperature. When the system is cooled down, below some critical temperature, appear microdomains alternatively rich in A and B-species. This is a MPS that originates from a competition between the usual macrophase separation and the elasticity of the gel.

As we will see below, the size of microdomains, ξ_C^* , scales as $\xi_C^* \sim a$, where a is the monomer size.

The critical properties of the MPS can be studied through the knowledge of the structure factor. The latter can be determined using the RPA method, and takes the following form [17]

$$S_C^{-1}(q) = [S_0^{-1}(q)]_C + C_G/q^2 \quad (1)$$

with

$$[S_0^{-1}(q)]_C = 2\chi_0 P_c^{-1}(q) - 2\chi, \quad (1a)$$

which is nothing else but the inverse structure factor of a mixture made of free cyclic polymers A and B. Here,

$$q = 4 \frac{\pi}{\lambda} \sin \frac{\theta}{2} \quad (1b)$$

denotes the module of the wave-vector (or wavenumber), with λ the wavelength of the incident radiation and θ the scattering-angle. There, χ stands for the Flory interaction parameter that is inversely proportional to the absolute temperature T [33, 35], and $\chi_0 = 2/N$ its critical value when the cyclic polymer mixture is uncrosslinked. There, the quantity $P_c(q)$ is the form factor of an ideal cyclic chain

$$P_c(q) = g_c(q), \quad (2)$$

with the Casassa function [36]

$$g_c(q) = \frac{2}{\sqrt{u}} e^{-\frac{u}{4}} - \int_0^{\frac{\sqrt{u}}{2}} e^{t^2} dt \quad (2a)$$

We have used the notation: $u = 3q^2 R_L^2/d$, where $R_L^2 = a^2 N/6$ is the squared gyration radius of an ideal linear chain, and d the space dimensionality. The integral in Eq. (2a) defines the degenerated hyper geometric function [37]

$$g_c(u) = \Phi\left(1; \frac{3}{2}; \frac{-u}{4}\right) \quad (2b)$$

Notice that the dependence on topology is entirely contained in the form factor (2). Of course, the latter is different from that of a free linear chain, $P_L(q)$, defined by the usual Debye function [33, 38, 39]

$$P_L(q) = g_D(u), \quad (3)$$

with

$$g_D(u) = \frac{1}{u^2} (e^{-u} + u - 1) \quad (3a)$$

We state that

$$P_c(q) > P_L(q) \quad (4)$$

in all wave-vectors range. The above inequality is true at least in the Guinier regime [40], that is

$$P_c(q) = 1 - \frac{u}{6}, \quad u \ll 1, \quad (5a)$$

$$P_L(q) = 1 - \frac{u}{3}, \quad u \ll 1, \quad (5b)$$

in formula (1), C_G accounts for the rigidity constant of the cyclic polymer network.

Following de Gennes [17], the latter scales as

$$C_G \approx \frac{1}{a^2 N^2 e}, \quad (6)$$

where a is the monomer size. Let us discuss now the structure factor $S_c(q)$ defined in Eq. (1).

Firstly, it depends on topology through the bare structure factor, relation (1a).

Secondly, due to inequality (4), this structure factor is greater than its homologous, $S_L(q)$, relatively to a CPB made of connected unlike linear chains, that is $S_c(q) > S_L(q)$, for all values of the wavenumber q . This comparison is made when the polymerization degree N , the Flory interaction parameter χ and the rigidity constant are the same for the two systems. For the CPBs, the number N_e plays the role of the number of monomers between consecutive crosslinks. Such an inequality traduces the known fact that cyclic polymers scatter better than the linear ones.

Now, to get simplified analytic results, we replace $P_c(q)$ and $P_L(q)$ by their expansions (5a) and (5b). These approximative expressions are believed to be true in a wide-range of the wave-vector. In these conditions, we have the simpler form

$$S_c^{-1}(q) = 2(\chi_0 - \chi) + \chi_0 \frac{q^2 R_L^2}{3} + \frac{C_G}{q^2}, \quad (7)$$

for a cyclic IPN, and

$$S_L^{-1}(q) = 2(\chi_0 - \chi) + 2\chi_0 \frac{q^2 R_L^2}{3} + \frac{C_G}{q^2}, \quad (8)$$

for a linear one. We recall that $R_L^2 = a^2 N/6$ and $\chi_0 = 2/N$.

The structure factor defined in Eq. (7) exhibits a maximum at the finite value

$$q_c^* = \frac{\sqrt{3}}{a} N e^{-\frac{1}{2}} \quad (9a)$$

Therefore, a MPS occurs at $q \neq 0$. This value must be compared to its homologous relatively to a CPB

$$q_L^* = \frac{\sqrt{3}}{2^{\frac{1}{2}} a} N e^{-\frac{1}{2}} \quad (9b)$$

A comparison between relations (9a) and (9b) clearly shows that $q_c^* > q_L^*$. Consequently, the closed topology has as effect to shift the maximum q^* towards its higher values. To give more signification to this inequality, we consider the sizes of microdomains $\xi_c^* = q_c^{*-1}$ and $\xi_L^* = q_L^{*-1}$. Then, we have $\xi_c^* < \xi_L^*$. Consequently, the size of critical fluctuations is reduced by the presence of closed topology.

The structure factor at $q = q^*$ diverges at spinodal for

$$\chi_S^C = \frac{2}{N} + \frac{1}{3} \frac{1}{N e} \quad (10a)$$

We have used Eq. (9a) and definition $\chi_0 = 2/N$. This critical parameter must be compared to that of a CPB

$$\chi_S^L = \frac{2}{N} + \frac{\sqrt{2}}{3} \frac{1}{N e} \quad (10b)$$

These formulae indicate that $\chi_S^C < \chi_S^L$ this means that the MPS in cyclic IPN takes place at a temperature greater than that relatively to a CPB. The above inequality allows a comparison between the thermal compressibilities $S_c(q_c^*) \sim (\chi_0 - \chi_S^C)^{-1}$ and $S_L(q_L^*) \sim (\chi_0 - \chi_S^L)^{-1}$. The above inequality then implies that $S_L(q_L^*) > S_c(q_c^*)$. Indeed, this is compatible with the fact that the closed topology considerably reduces the thermal fluctuations of composition. In Fig. 1, we compare the structure factor, $S_c(q)$, as a function of the wavenumber q , to its homologous $S_L(q)$. These curves are drawn with parameters: $\chi_0 - \chi = 0.01$ and $N_e = 50$, and reflect the discussion made above.

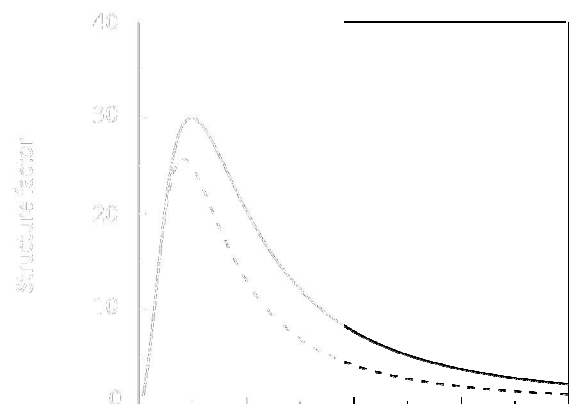


Fig. 1 The structure factor $S(q)$ versus the wavenumber q (expressed in a unit), for acyclic IPN (solid line) and a CPB (dashed line). These curves are drawn with parameters:

$$\chi_0 - \chi = 0.01 \text{ AND } N_e = 50.$$

III. KINETICS OF MPS

Now, assume that the cyclic IPN are out equilibrium. This can be produced, for instance, by a change of temperature for an initial value T_i to a final T_f very close to the spinodal point. Kinetics is studied through the relaxation rate, $\tau(q)$, which describes how the composition fluctuation relaxes in time. More precisely, within the framework of linearized theory [41], the Fourier transform of the fluctuation $\partial\varphi(r,t) = \varphi(r,t) - \bar{\varphi}$ ($\bar{\varphi} = \phi_A - \phi_B$) is the difference of compositions of unlike cyclic polymers and ϕ some mean value) is such that [41]

$$\partial\varphi(q,t) = \partial\varphi(q,0)e^{-\frac{t}{\tau(q)}} \quad (11)$$

with the relaxation rate [41]

$$\tau_c^{-1}(q) = q^2 \Lambda_c(q) S_c^{-1}(q), \quad (12)$$

where $\Lambda_c(q)$ is the Onsager transport coefficient, and $S_c(q)$ the static structure factor, relations (1) or (7). The inverse $\Omega_c(q) = \tau_c^{-1}(q)$ represents the characteristic frequency. Since the motion of the connected chains is local, the transport Onsager coefficient $\Lambda_c(q)$ must scale as its homologous, $\Lambda_L(q)$, of a CPB, that is [19]

$$\Lambda_c(q) \sim \Lambda_L(q) \sim q^{-2}, \quad (13)$$

provided that one explores regions of space of which the size is much smaller than the microdomains one $\xi^*(q^{-1}) \ll \xi_c^*$. Combining formulae (12) and (13) yields the characteristic frequency

$$\Omega_c(q) \sim \Omega_c^0 q^6, \quad q^{-1} \ll \xi_c^*, \quad (15)$$

with the prefactor

$$\Omega_c^0 = \frac{\chi_0 R_c^2}{3} = \frac{a^2}{9}. \quad (15a)$$

We have used the definitions: $R_c^2 = a^2 N/12$ and $\chi_0 = 2/N$. For a CPB, the corresponding prefactor is rather :

$$\Omega_L^0 = \frac{2\chi_0 R_L^2}{3} = \frac{2a^2}{9}.$$

We note that the scaling behavior (15) of the characteristic frequencies is very similar to that found by de Gennes [42] and Pincus [43], for binary polymer mixtures. The authors have shown that this sixth power behavior for frequency has as origin a combination of two contributions, which are related to a Rouse and a reptation motions. For the cyclic IPNs we consider here, however, the interpretation of the above scaling law should be different, since only local motions are possible, due to the permanent presence of entanglement points. The other contribution corresponding to slow modes that exists in uncrosslinked mixtures [33], is related for IPNs to a spinodal decomposition. More discussions about the above behavior, for CPBs, can be found in Ref. [27]. Come back to relation (14) and notice that this has as consequence

$$\Omega_c(q) \gg \Omega_L(q) \quad (16)$$

or

$$\tau_c(q) \gg \tau_L(q). \quad (17)$$

These inequalities remain valid in all wave-vectors range, due to the fact that $S_c^{-1}(q) \gg S_L^{-1}(q)$. Relation (14) first suggests that the characteristic frequencies depend, as it should be, on the topology nature of the considered gel. Second, the relaxation rate for the cyclic IPN is greater than that relative to a CPB having the same rigidity constant. But the interesting question to ask is a comparison between the relaxation rates at the maximum $\tau_c(q_c^*)$ and $\tau_L(q_L^*)$. These quantities can be interpreted as the necessary times to form microdomains of sizes ξ_c^* and ξ_L^* , respectively. Some algebra yields: $\tau_c(q_c^*) = \tau_L(q_L^*)/\sqrt{2}$. We have used Eqs. (9a), (9b), (15) and (15a). Thus, we have $\tau_c(q_c^*) \gg \tau_L(q_L^*)$. This is a natural result, since ξ_L^* is larger than ξ_c^* .

Finally, in Fig.2, we superpose the variations of the characteristic frequency upon the wavenumber q , for a cyclic IPN and a CPB. The curve relative to the first system is below that of the second one. In principle, this tendency remains the same at all temperature.

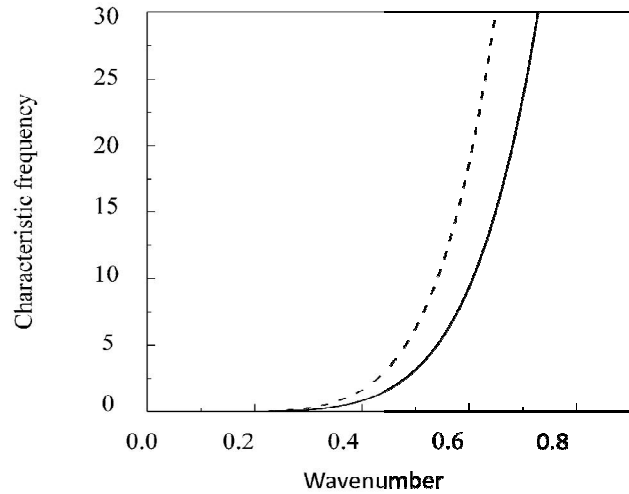


Fig. 2 Superposition of the variations of the characteristic frequency $\Omega(q)$ upon the wavenumber q , for a cyclic IPN (solid line) and a CPB (dashed line). The former and the second are expressed in arbitrary units.

IV. CONCLUSIONS

We recall that the purpose of the present work was static and kinetics studies of MPS in interpenetrating cyclic polymer networks. The main question was a comparison of theoretical properties of MPS from cyclic IPNs to those of CPBs. Using a generalized de Gennes theory, we first determined the exact form of the static structure factor, $S_c(q)$, as a function of the wave-vector q and the Flory interaction parameter χ . Of course, this structure factor crucially depends on topology of the gel. First, we found that this structure factor is greater than its homologous relatively to a CPB, $S_L(q)$, in all range of the wave-vector and whatever the value of temperature. This means that the cyclic polymers scatter better than the linear ones. Second, we have shown that the static structure

factor $S_c(q)$ exhibits a maximum at finite value, q_c^* , of the wavenumber. This is a signature of a MPS. This typical value was found to be greater than its homologous of a crosslinked polymer network, q_L^* . This indicates that the size of microdomains $\xi_c^* < \xi_L^*$ is reduced by the fact that the linked polymer chains are cyclic. The main conclusion is that, the critical fluctuations are very sensitive to topology of the considered gel. It was natural to complete the static study by an investigation of kinetics of MPS of a cyclic IPN, when its temperature is suddenly lowered from an initial value to a final one very close to the spinodal point. Between these values, the composition fluctuation varies in time, and we were interested in how it relaxes. The kinetics was studied through the relaxation rate, $\tau_c(q)$, of which the inverse $\Omega_c(q) = \tau_c^{-1}(q)$ defines the characteristic frequency. The latter was computed for all values of temperature and wave-vector. First, we stated that the kinetics is controlled by local motions or Rouse type, because unlike cyclic chains are linked each to other. The motions of chains at large scales (reptation motion) are then frozen. Second, our calculations revealed that, as it should be, the fact that the connected chains are closed increases the relaxation rate. This tendency is expected and can be attributed to a reduction of the critical fluctuations of composition by the presence of cyclic chains. Third, we demonstrated that, at scales smaller than the mesh size ξ_c^* , that is for $q^{-1} \ll \xi_c^*$, the characteristic frequency behaves according to : $\Omega_c(q) \sim q^6$. Notice that this sixth power law is similar to that of a CPB. As a matter of fact, at these scales, one cannot distinguish between a linear chain and a cyclic one. The only difference is that, the corresponding amplitude is topology-dependent.

In this work, we have avoided some complications, such as the effect of topological constraints [44]. Such a problem may be overcome when the polymer chains, before they are linked, are of high-molecular-weight. The topological (or circularity) constraints can induce a quantitative change of results, but to our opinion, the conclusions remain the same.

Finally, questions like effects of solvent and charges on the MPS of cyclic IPNs are under consideration.

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