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Theoretical Investigation of Star Diblock Copolymer Systems Using the Random Phase Approximation

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ABSTRACT

The study of star A–B diblock copolymers has garnered growing attention due to their unique physicochemical properties, which are strongly governed by incompatibility effects between their constituent blocks. Unlike their linear counterparts, star-shaped architectures exhibit distinct behaviors in micellization and phase separation, making them attractive for advanced materials design. While linear diblock copolymers have been the subject of extensive theoretical and experimental investigations, systems with more complex topologies such as star polymers remain relatively underexplored from a theoretical standpoint. In this work, we investigate the static scattering of mixtures composed of star diblock copolymers and homopolymers. Specifically, we analyze the scattering behavior of star A-B diblocks copolymers in the melt state, mixed with homopolymers, and in solution using the Random Phase Approximation. In this approximation, the absolute intensity measured by small-angle neutron scattering is determined only by the structure factors of the core or corona part of the star polymer, which depends on the type of homopolymer in the mixture. The angular variations of the structure factors $S_{BB}(Q)$ and $S_{AA}(Q)$, accessible by neutron scattering when homopolymers A and B are added to the star diblock copolymers, are graphically illustrated for various values of physicochemical parameters. The results reveal the appearance of a correlation peak for all considered parameter values and a more or less significant dependence of the scattered intensity at the thermodynamic limit. These findings are in qualitative agreement with the experimental observations reported by Adhikari et al., underscoring the critical role of homopolymers in determining phase behavior.

Keywords: diblock copolymer, homopolymer, star polymer, phase separation, neutron scattering, structure factor.

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The data supporting the findings of this study are included in the manuscript.

Conflicts of interest

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Author contributions

Hayat BENAHMED performed the theoretical modeling and calculations. Hayat BENAHMED and Khadidja LABDELLI contributed to the analysis of the results and the manuscript writing.

1. Introduction

With the recent advances in polymerization techniques, the field of polymeric materials has undergone a significant transformation over the past three decades. These technological breakthroughs have made it possible to access a wide range of innovative materials based on block copolymers. Block copolymers constitute a particularly promising class of materials due to their ability to combine distinct physicochemical properties within a single macromolecular architecture. To impart new functionalities to a polymeric material, one might consider blending homopolymers, each contributing specific properties. However, most homopolymers with differing physicochemical characteristics are inherently immiscible. As a result, their direct mixture typically leads to phase separation, often yielding heterogeneous materials with inferior properties compared to the individual homopolymers. One of the most effective strategies to circumvent this limitation is the synthesis of block copolymers, wherein two different homopolymer chains are covalently linked. This covalent linkage compels the blocks to remain in close proximity, thereby suppressing macrophase separation and confining phase segregation to the nanometric scale. Ideally, such block copolymers give rise to materials that are heterogeneous at the nanoscale while remaining homogeneous on the macroscopic level, thereby enabling a synergistic combination of the properties of the constituent homopolymers [1].

This nanoscale organization is precisely what endows block copolymers with unique properties, which have been exploited in various industrial applications for many years. More recently, over the past decade, the rapid development of nanotechnologies has renewed interest in these materials. In particular, the ability of block copolymers to self-assemble into well-defined nanostructures is now regarded as a powerful strategy for fabricating new nanofunctional materials. Notable examples include photonic crystals and high-density information storage media [2].

At the same time, research on polymer blends continues to expand and remains highly attractive, particularly due to its potential to reconcile performance requirements with industrial-scale production costs. The ever-growing consumer demand is driving the development of new generations of multiphase polymeric materials. Consequently, an increasing number of complex products are being discarded, most of which end up in landfills or are subjected to incineration or polymerization for energy recovery or chemical valorization. In this context, the urgency of implementing effective recycling strategies becomes evident, not only to recover valuable resources but also to reduce the environmental footprint associated with polymer waste [3].

From a theoretical standpoint, polymers with complex architectures exhibit physical properties that differ significantly from their linear counterparts, primarily due to the presence of branching points that restrict the conformational freedom of the chains within the system [4, 5]. The behavior of branched polymers, such as star polymers, has been investigated extensively, both theoretically, through the development of scaling laws [6, 7], and experimentally, where these theoretical predictions have been validated [8, 9]. A key feature distinguishing branched polymers from linear ones is the enhanced stretching of their chain segments, particularly in solution at comparable concentrations. This stretching arises from strong intramolecular repulsive interactions, which become increasingly pronounced with higher degrees of branching. These interactions are primarily a consequence of the elevated local monomer density near the branching points. The star polymer, which consists of multiple linear chains (arms) connected to a central core, represents the simplest architectural model of branched polymers, as it contains only a single branching point [10].

Star diblock copolymers have garnered considerable attention across a wide range of industrial sectors, including aerospace, electronics, automotive, textiles, and optics. This growing interest stems from their remarkable practical properties, such as ease of processing, low density, and relatively low production cost. One of the key challenges for researchers, both experimentalists and theorists, is to develop new polymeric systems or optimize existing ones to meet evolving technological requirements and environmental constraints.

In this context, the investigation of the structural properties, phase transitions, and thermodynamic stability of polymer blends proves to be essential for the design of advanced materials with tailored physicochemical characteristics. Over the past few decades, star diblock copolymers have attracted sustained attention from both theoretical and experimental perspectives. A number of theoretical models have been proposed to describe their scattering behavior, phase separation phenomena, and viscometric properties, whether in solution or in the melt state [11].

It is important to emphasize that star polymers belong to the broader class of branched polymers, which also includes graft polymers, dendrimers, and hyperbranched polymers. Unlike dendrimers and hyperbranched architectures, which are characterized by multiple levels of branching and secondary arms, star polymers possess a single, central branching point. They are composed of several linear polymer arms, typically three or more, radiating from a multifunctional core [12, 13].

A variety of theoretical models have been developed by researchers with the dual objective of, on the one hand, gaining fundamental insights into the behavior of such complex macromolecular architectures and, on the other hand, predicting their response under specific physicochemical conditions. The steady progress in computational technologies, including the development of advanced programming languages, high-performance processors, and numerical algorithms, has significantly enhanced the capacity of modeling as a scientific tool. In polymer science,

in particular, modeling has emerged as an essential complement to experimental techniques. Although it does not supplant experimentation, it allows for a deeper understanding of macroscopic and microscopic behavior and facilitates the prediction of key physicochemical, optical, and thermodynamic properties.
In this study, the random phase approximation (RPA) has been employed to investigate the static scattering and phase behavior of star A-B diblock copolymers in three distinct environments: in the melt state, in blends with homopolymers, and in solution. Following a general introduction outlining the scientific relevance of star diblock copolymers and the motivations behind the present work, the second section provides the theoretical framework used to analyze their static scattering properties. The third section is dedicated to the application of this theoretical formalism, with a particular focus on the influence of several key physicochemical parameters, such as the degree of polymerization, volume fraction, composition, number of arms, and interaction parameters, on the scattering behavior of the system. The results are presented successively for star diblock copolymers in the melt, in mixtures with homopolymers, and in the presence of a solvent. Finally, the fourth section summarizes the main conclusions drawn from this work, emphasizing the structural features and phase behavior that can be modulated by adjusting the system's parameters.

2. Static scattering properties of star diblock copolymers

The Random Phase Approximation (RPA) enables the analytical calculation of the scattered intensity in a multicomponent system subjected to a flux of neutron, X-ray, or light photons. This leads to a general matrix formulation that expresses the static structure matrix of the interacting system in terms of that of an ideal non-interacting system and the excluded volume matrix.

$$\boldsymbol{S}^{-\boldsymbol{1}}(Q)=\boldsymbol{S}_{\boldsymbol{0}}^{-\boldsymbol{1}}(Q)+\boldsymbol{V} \tag{1}$$

where the quantities $\boldsymbol{S}(Q)$, $\boldsymbol{S_0}(Q)$ and $\boldsymbol{V}$ denote the total static structure matrix, the bare (non-interacting) structure function matrix, and the thermodynamic interaction matrix (also referred to as the excluded volume matrix), respectively. The amplitude of the scattering wave vector Q is defined by the following relation:

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

with n, λ and θ representing the refractive index of the medium, the wavelength of the incident radiation, and the scattering angle, respectively.
In small-angle neutron scattering (SANS) experiments, the measured absolute intensity $I(Q)$ is given by the following expression:

$$I(Q)=\boldsymbol{D}^{T}\boldsymbol{S}(Q)\boldsymbol{D} \tag{3}$$

where the quantity $\boldsymbol{D}$ denotes a column vector whose elements correspond to the coherent scattering length contrast factors in the case of neutron scattering, $\boldsymbol{D}^{T}$ is its transpose (a row vector), and $\boldsymbol{S}(Q)$ represents the total structure matrix whose elements are the partial structure factors $S_{ij}(Q)$ [14]:

$$\boldsymbol{S}(Q)=\begin{bmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{bmatrix} \tag{4}$$

Considering the objective of this study, it is appropriate to derive and present, in what follows, the expressions of the structural matrix elements for star diblock copolymers in the melt state, in order to analyze their behavior in solution and their interaction with homopolymers (see Fig. 1).

2.1. Static scattering of star A-B diblock copolymers in the melt state

In the case of star A-B diblock copolymers in the melt state (i.e., absence of both homopolymers and solvent) with f identical arms, it is necessary to derive the structure factors associated with each component (see Fig. 1 (a)). Each arm is composed of two distinct polymer blocks, A and B, connected at their junction point. The quantity $\boldsymbol{S_0}$ is a square matrix of order 2:

$$\boldsymbol{S_0}(Q)=\begin{bmatrix} S_{0AA} & S_{0AB} \\ S_{0BA} & S_{0BB} \end{bmatrix} \tag{5}$$

where the structure factor of block A is given by:

$$S_{0AA}(Q)=f\ \phi_A Z_A P_{AA}(Q) \tag{6}$$

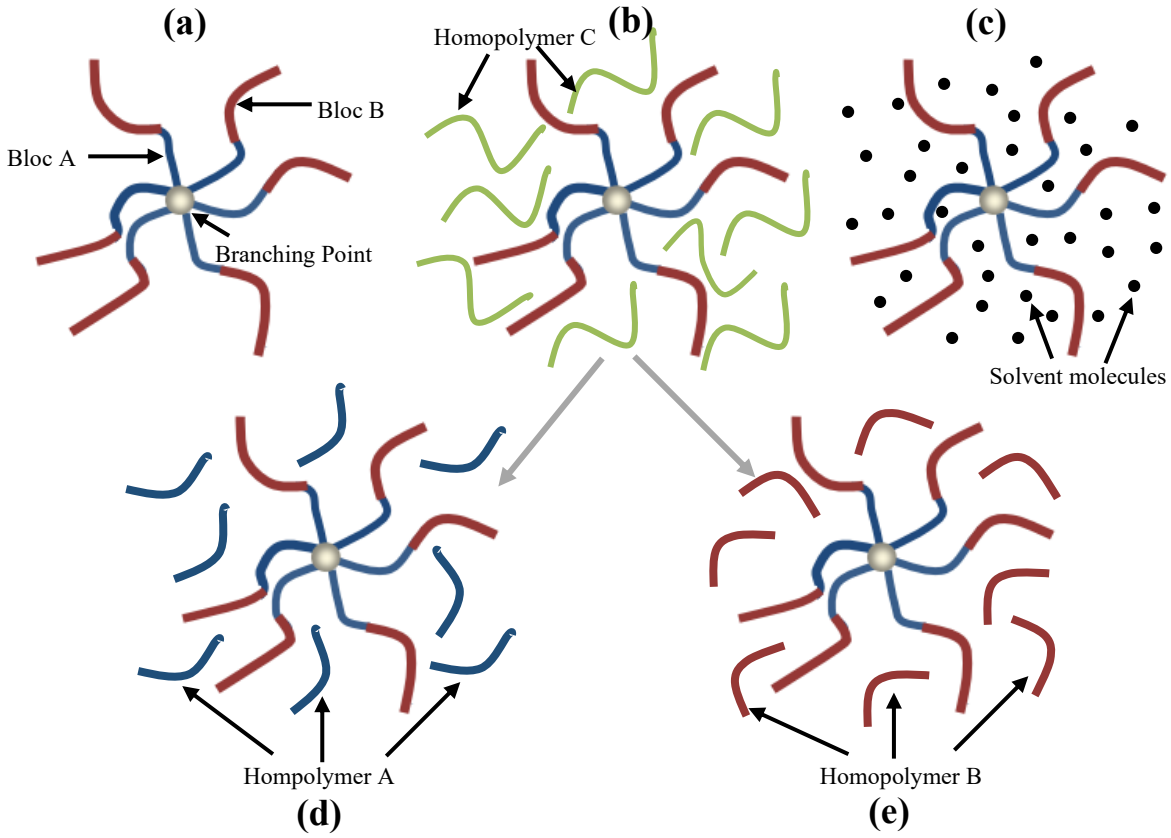


Fig. 1 Schematic representation of: (a) a star polymer composed of A-B diblock copolymers arms in the melt state; (b) a mixture of star A-B diblock copolymer with a homopolymer C; (c) a star A-B diblock copolymers in the presence of a solvent; (d) a mixture of star A-B diblock copolymer with a homopolymer A and (e) a mixture of a star A-B diblock copolymer with homopolymer B

In this expression, the quantities f, ϕ_A, Z_A and $P_{AA}(Q)$ denote, respectively, the number of arms, the volume fraction of component A, its degree of polymerization, and its form factor, which is given by the following relation:

$$P_{AA}(Q)=\frac{1}{f}\left(P_{A_1A_1}+(f-1)P_{A_1A_2}\right) \tag{7a}$$

with

$$P_{A_1A_1}=\frac{1}{Z_A}\left[1+\frac{2U_A}{1-U_A}\left(1-\frac{1}{Z_A}\frac{1-U_A^{Z_A}}{1-U_A}\right)\right] \tag{7b}$$

and

$$P_{A_1A_2}=\frac{U_A}{Z_A^2}\left(\frac{1-U_A^{Z_A}}{1-U_A}\right)^2 \tag{7c}$$

where the quantity U_A is given by:

$$U_A=e^{-\frac{Q^2a^2}{6}} \tag{7d}$$

where a denotes the statistical segment length of block A.

Similarly, the non-interacting structure factor of polymer B can be expressed as follows:

$$S_{0BB}(Q)=f\ \phi_B Z_B P_{BB}(Q) \tag{8}$$

where ϕ_B, Z_B and $P_{BB}(Q)$ represent, respectively, the volume fraction of component B, its degree of polymerization, and its form factor, which is given by:

$$P_{BB}(Q)=\frac{1}{f}\left(P_{B_1B_1}+(f-1)U_B^{2Z_A}P_{B_1B_2}\right) \tag{9a}$$

with

$$P_{B_1B_1}=\frac{1}{Z_B}\left[1+\frac{2U_B}{1-U_B}\left(1-\frac{1}{Z_B}\frac{1-U_B^{Z_B}}{1-U_B}\right)\right] \tag{9b}$$

and

$$P_{B_1B_2}=\frac{U_B}{Z_B^2}\left(\frac{1-U_B^{Z_B}}{1-U_B}\right)^2 \tag{9c}$$

where

$$U_B=e^{-\frac{Q^2b^2}{6}} \tag{9d}$$

where b is the statistical segment length of sequence B.

For the single arm of the A-B diblock copolymer, the non-interacting structure factor $S_{0AB}(Q)$ can be given by:

$$S_{0AB}(Q)=\sqrt{f\ \phi_A Z_A f\ \phi_B Z_B}\,P_{AB}(Q) \tag{10a}$$

with

$$P_{AB}(Q)=\frac{1}{f}\left[1+(f-1)U_A^{Z_A}\right]P_{A_1B_1} \tag{10b}$$

and

$$P_{A_1B_1}=\frac{\sqrt{U_AU_B}}{Z_AZ_B}\frac{\left[1-U_A^{Z_A}\right]\left[1-U_B^{Z_B}\right]}{(1-U_A)(1-U_B)} \tag{10c}$$

It is important to note that, for polymer blends composed exclusively of star diblock copolymers, i.e. in the melt state (in the absence of homopolymers and solvent), the RPA expression for the partial structure factors $S_{ij}(Q)$ becomes more complex. Nevertheless, it can be explicitly derived using matrix formalism, by treating one of the blocks as the background component. The partial structure factor $S_{AA}(Q)$ is then given by the following expression [15, 16]:

$$S_{AA}(Q)=\frac{S_{0AA}(Q)S_{0BB}(Q)-S_{0AB}(Q)S_{0BA}(Q)}{S_{0AA}(Q)+S_{0BB}(Q)+2S_{0AB}(Q)-2\chi(S_{0AA}(Q)S_{0BB}(Q)-S_{0AB}(Q)S_{0BA}(Q))} \tag{11}$$

where χ is the Flory-Huggins interaction parameter, which characterizes the interactions between the various components and governs the phase behavior of the system.

In small-angle neutron scattering (SANS) experiments, the measured absolute intensity $I(Q)$ is proportional to the quantity defined by equation (11).

$$I(q)\propto S_{AA}(Q) \tag{12}$$

2.2. Mixtures of star A-B diblock copolymers/ homopolymer C

The physical system under investigation consists of a blend of star A-B diblock copolymers with a homopolymer C. Each star polymer is assumed to be composed of identical arms, each representing an A–B diblock copolymer. In this multicomponent system, three chemically distinct constituents are present (see Fig 1 (b)). However, owing to the incompressibility condition, the mixture can effectively be treated as a two component system. One of the components is selected as the reference (background) component. In this work, homopolymer C is designated as the background. As a result, all matrices in equation (4) reduce to square matrices of order 2. The objective is to determine the static structure matrix $\boldsymbol{S}(Q)$ for this binary mixture. The excluded volume interaction matrix is defined as follows:

$$\boldsymbol{V} = \frac{1}{S_{0CC}} \boldsymbol{E}\ \boldsymbol{E}^T + \begin{bmatrix} v_{AA} & v_{AB} \\ v_{BA} & v_{BB} \end{bmatrix} \tag{13}$$

where $\boldsymbol{E}$ is a column vector whose elements are all equal to 1, and $\boldsymbol{E}^T$ denotes its transpose. The non-interacting structure factor S_{0CC} is given by the following expression:

$$S_{0CC}(Q) = \phi_C Z_C P_{CC}(Q) \tag{14}$$

where the quantities ϕ_C, Z_C and $P_{CC}(Q)$ respectively represent the volume fraction of homopolymer C, its degree of polymerization, and its form factor. It is further assumed that the latter can be described by the classical Debye function, as given by following equation, provided that the homopolymer C chains are modeled as linear Gaussian chains with a statistical segment length c:

$$P_{CC}(Q) = \frac{2}{U_C^2}\left(e^{-U_C} + U_C - 1\right) \tag{15a}$$

with

$$U_C = Q^2 \frac{Z_C\ c^2}{6} \tag{15b}$$

While the quantities v_{ij} are defined according to the following relationship:

$$v_{ij} = \chi_{ij} - \chi_{ic} - \chi_{jc} \tag{16}$$

The matrix elements can therefore be simplified as follows:

$$v_{AA} = \chi_{AA} - \chi_{AC} - \chi_{AC} = -2\chi_{AC} \tag{17a}$$

$$v_{BB} = \chi_{BB} - \chi_{BC} - \chi_{BC} = -2\chi_{BC} \tag{17b}$$

Due to symmetry considerations, we can write:

$$v_{AB} = v_{BA} = \chi_{AB} - \chi_{AC} - \chi_{BC} \tag{17c}$$

By employing the small-angle neutron scattering (SANS) technique [17], equation (2), which gives the experimentally measured absolute intensity $I(Q)$ as a function of the scattering length densities a', b', and c' of polymer chains A, B, and C, respectively, can be rewritten as follows:

$$I(q) = \begin{bmatrix} (a'-c') \\ (b'-c') \end{bmatrix}^T \begin{bmatrix} S_{AA} & S_{AB} \\ S_{AB} & S_{BB} \end{bmatrix} \begin{bmatrix} (a'-c') \\ (b'-c') \end{bmatrix} \tag{18a}$$

more precisely:

$$I(Q) = (a'-c')^2 S_{AA}(Q) + 2(a'-c')(b'-c') S_{AB}(Q) + (b'-c')^2 S_{BB}(Q) \tag{18b}$$

It should be emphasized that analyzing the static scattering properties of such a polymeric system requires prior knowledge of the various interaction parameters χ_{ij}. In the following, we consider two specific cases of mixtures involving star diblock copolymers and homopolymers. In the first case, the homopolymer C is assumed to be chemically identical to the inner blocks of the star copolymer (i.e., C=A); in the second case, it is considered identical to the outer blocks of the star copolymer (i.e., C=B). These two configurations lead to substantial simplifications in the governing equations of the system.

2.2.1. Mixtures of star A-B diblock copolymer/ homopolymer A

This case corresponds to replacing homopolymer C by homopolymer A, i.e. C=A, which means that the homopolymer mixed with the star A-B diblock copolymers has the same nature and length as the inner branches of the star (See Fig. 1 (d)). Under these conditions, this polymeric system leads to significant simplifications of the main equations, since its description only requires knowledge of the interaction parameter χ_{AB}; in fact, we obtain:

$$\boldsymbol{V} = \frac{1}{S_{0CC}} \boldsymbol{E}\ \boldsymbol{E}^T + \begin{bmatrix} 0 & 0 \\ 0 & -2\chi_{BA} \end{bmatrix} \tag{19}$$

Under these conditions, equation (1) then takes the following form:

$$\boldsymbol{S}^{-1}(Q)=\boldsymbol{S}_{\boldsymbol{0}}^{-1}(Q)+\begin{bmatrix}\frac{1}{S_{0CC}} & \frac{1}{S_{0CC}}\\ \frac{1}{S_{0CC}} & \frac{1}{S_{0CC}}-2\chi_{BA}\end{bmatrix} \tag{20}$$

It should be noted, however, that the Flory-Huggins interaction parameter, $\chi_{BA} = \chi_{AB} = \chi$ characterizes the interactions between polymer chains of species A and B.

Moreover, the inverse of the bare structure matrix $\boldsymbol{S}_{\boldsymbol{0}}^{-1}(Q)$ is given by:

$$\boldsymbol{S}_{\boldsymbol{0}}^{-1}(Q)=\begin{bmatrix}\frac{S_{0BB}}{\delta} & -\frac{S_{0AB}}{\delta}\\ -\frac{S_{0AB}}{\delta} & \frac{S_{0AA}}{\delta}\end{bmatrix} \tag{21a}$$

with

$$\delta=S_{0AA}(Q)S_{0BB}(Q)-S_{0AB}^{2}(Q) \tag{21b}$$

Consequently, for the polymeric system described above, in which species A and C share the same scattering length density (i.e., $c'=a'$), the expression simplifies to the following result:

$$I(Q)=(b'-a')^{2}S_{BB}(Q) \tag{22}$$

Based on these simplifying assumptions and starting from equation (20), we obtain the following expression:

$$S_{BB}(Q)=\frac{S_{0BB}(Q)S_{0CC}(Q)+\delta}{S_{0AA}(Q)+S_{0BB}(Q)+2S_{0AB}(Q)+S_{0CC}(Q)-2\chi\left[S_{0BB}(Q)S_{0CC}(Q)+\delta\right]} \tag{23}$$

This result demonstrates that the addition of a homopolymer A to a star A-B diblock copolymer system allows for the selective observation of the scattering signal from the B block, i.e., the corona of the star polymer. This condition holds true when small-angle neutron scattering (SANS) is employed.

2.2.2. Mixtures of star A-B diblock copolymer/ homopolymer B

This case corresponds to a mixture of star A-B diblock copolymers with homopolymers that are chemically identical and equal in length to the B bloc (see Fig. 1(e)). As in the previous case, our objective is to determine the partial structure factor, which is directly proportional to the intensity measured experimentally via small-angle neutron scattering (SANS). This quantity can be readily obtained by setting C=B in the above equations:

$$\boldsymbol{V}=\frac{1}{S_{0CC}}\boldsymbol{E}\ \ \boldsymbol{E}^{T}+\begin{bmatrix}-2\chi_{BA} & 0\\ 0 & 0\end{bmatrix} \tag{24}$$

Substituting equation (24) into equation (1) yields the following expression:

$$\boldsymbol{S}^{-1}(Q)=\boldsymbol{S}_{\boldsymbol{0}}^{-1}(Q)+\begin{bmatrix}\frac{1}{S_{0CC}}-2\chi_{BA} & \frac{1}{S_{0CC}}\\ \frac{1}{S_{0CC}} & \frac{1}{S_{0CC}}\end{bmatrix} \tag{25}$$

In the case of a binary mixture composed star A-B diblock copolymers and a homopolymer B, the scattering intensity can be readily deduced from equation (18b), given that polymer chains C and B share the same scattering length density:

$$I(Q)=(a'-b')^{2}S_{AA}(Q) \tag{26}$$

The inverse of the total structure matrix, as given in equation (25), provides direct access to the partial structure factor $S_{AA}(Q)$, which can be expressed as follows:

$$S_{AA}(Q)=\frac{S_{0AA}(Q)S_{0CC}(Q)+\delta}{S_{0AA}(Q)+S_{0BB}(Q)+2S_{0AB}(Q)+S_{0CC}(Q)-2\chi\left[S_{0BB}(Q)S_{0CC}(Q)+\delta\right]} \tag{27}$$

It is worth noting that this result allows us to recover the expression of the partial structure factor previously derived in equation (11), corresponding to star A-B diblock copolymers in the melt state, by setting Z_C=0 and ϕ_C=0 (i.e., in the absence of homopolymer C) in equation (27).

2.2.3. Mixtures of star A-B diblock copolymer/ solvent

As in the case of mixtures involving star A-B diblock copolymers and homopolymer C, it is also meaningful to investigate the structural behavior of the same star polymer in the presence of a good solvent. Based on the previous results, we now present the explicit expressions of the partial structure factors $S_{ij}(Q)$), which can be directly probed by neutron scattering experiments, by substituting the homopolymer C with a solvent (see Fig. 1(c)).

It should be noted that the solvent is treated as a molecule with degree of polymerization $Z_S=1$ and a form factor $P_{SS}(Q)$=1:

$$S_{0SS}(Q)=\phi_S Z_S P_{SS}(Q)=\phi_S = 1-\phi \tag{28}$$

where ϕ_S and ϕ represent the volume fractions of the solvent and the overall solution, respectively.
To determine the generalized interaction parameters, it is important to recall that, in the case of star diblock copolymer solutions, the elements of the excluded volume matrix denoted v_{AA}, v_{BB} and v_{AB} are obtained by substituting the subscript C with S in equations (17) as follows:

$$v_{AA} = \chi_{AA} - \chi_{AS} - \chi_{AS} = -2\chi_{AS} \tag{29a}$$

$$v_{BB} = \chi_{BB} - \chi_{BS} - \chi_{BS} = -2\chi_{BS} \tag{29b}$$

$$v_{AB} = \chi_{AB} - \chi_{AS} - \chi_{BS} \tag{29c}$$

Furthermore, it is assumed that the solvent quality is identical for both blocks A and B, i.e., $\chi_{AS}=\chi_{BS}=\chi_{PS}$. Under this assumption, we obtain:

$$v_{AA} = v_{BB} = -2\chi_{PS} \tag{30a}$$

$$v_{AB} = \chi_{AB} - 2\chi_{PS} = \chi - 2\chi_{PS} \tag{30b}$$

This latter simplification implies that the excluded volume parameters satisfy the following conditions:

$$\boldsymbol{V} = \frac{1}{\phi_S}\boldsymbol{E}\ \ \boldsymbol{E}^T + \begin{bmatrix} -2\chi_{PS} & \chi-2\chi_{PS} \\ \chi-2\chi_{PS} & -2\chi_{PS} \end{bmatrix} \tag{31}$$

By substituting equation (31) into equation (1), the following expression is obtained:

$$\boldsymbol{S}^{-1}(Q) = \boldsymbol{S_0}^{-1}(Q) + \begin{bmatrix} \frac{1}{\phi_S} - 2\chi_{PS} & \frac{1}{\phi_S} + \chi - 2\chi_{PS} \\ \frac{1}{\phi_S} + \chi - 2\chi_{PS} & \frac{1}{\phi_S} - 2\chi_{PS} \end{bmatrix} \tag{32a}$$

Based on the elements of the excluded volume matrix $\boldsymbol{V}$ and the non-interacting structure factor $\boldsymbol{S_0}^{-1}(Q)$, the following expression can be written:

$$\boldsymbol{S}^{-1}(Q) = \begin{bmatrix} \frac{S_{0BB}}{\delta} + v_{AA} & -\frac{S_{0AB}}{\delta} + v_{AB} \\ -\frac{S_{0AB}}{\delta} + v_{BA} & \frac{S_{0AA}}{\delta} + v_{BB} \end{bmatrix} \tag{32b}$$

The inverse of the total structure matrix $\boldsymbol{S}(Q)$ provides direct access to the partial structure factors $S_{ij}(Q)$, which can be expressed as follows:

$$S_{AA}(Q) = \frac{S_{0AA}(Q) + v_{BB}\delta}{\left(v_{AA}^2 - v_{AB}^2\right)\delta + v_{AA}\left[S_{0AA}(Q) + S_{0BB}(Q)\right] + 2v_{AB}S_{0AB}(Q) + 1} \tag{33}$$

$$S_{BB}(Q) = \frac{S_{0BB}(Q) + v_{AA}\delta}{\left(v_{AA}^2 - v_{AB}^2\right)\delta + v_{AA}\left[S_{0AA}(Q) + S_{0BB}(Q)\right] + 2v_{AB}S_{0AB}(Q) + 1} \tag{34}$$

$$S_{AB}(Q)=\frac{S_{0AB}(Q)-v_{AB}\delta}{\left(v_{AA}^2-v_{AB}^2\right)\delta+v_{AA}[S_{0AA}(Q)+S_{0BB}(Q)]+2v_{AB}S_{0AB}(Q)+1} \tag{35}$$

For such a solution, the expression for the scattering intensity is obtained by replacing the scattering length density c' with s'. Accordingly, equation (18b) becomes:

$$I(Q)=(a'-s')^2\,S_{AA}(Q)+2(a'-s')(b'-s')S_{AB}(Q)+(b'-s')^2\,S_{BB}(Q) \tag{36}$$

It is important to note that the quantity $S_{BB}(Q)$ is directly proportional to the scattered intensity when the scattering lengths densities of species A and S are equal, i.e., $a'=s'$ (in the case of neutron scattering). Similarly, $S_{AA}(Q)$ becomes directly accessible when the scattering lengths densities of species B and S are equal, i.e., $b'=s'$.

In the following, we undertake a detailed analysis of mixtures comprising star A-B diblock copolymers and homopolymers. The main objective is to investigate the impact of adding homopolymers; either identical to the inner A or outer B blocks of the star diblock copolymers; on the phase behavior of the system. The emergence of a correlation peak and a non-zero value of the scattering function in the thermodynamic limit are indicative of the mixture's capacity to influence or modify the morphology of the system.

3. Results and discussion

To clearly illustrate the influence of the total degree of polymerization Z, as well as the overall volume fraction ϕ, on the static scattering behavior of the system described above, it is necessary to express the degrees of polymerization and volume fractions of blocks A and B as functions of composition parameter x, as follows:

$$\phi_A=x\phi\ ,\ \ \phi_B=(1-x)\phi\ \ and\ \ Z_A=xZ\ ,\ \ Z_B=(1-x)Z \tag{37}$$

3.1. Effect of the degree of polymerization *Z*

In the following section, we examine in greater detail the effects of the degree of polymerization Z, the number of arms f, the composition x, the volume fraction ϕ, and the interaction parameter χ between blocks A and B on the structural properties of star diblock copolymer; both in the melt state, in solution, and in mixtures with homopolymers A and B.

To clearly illustrate the influence of the total polymerization degree Z on the scattering behavior of star polymers composed by f arms of A-B diblock copolymers, the results can be straightforwardly derived from the previously established equations by substituting the quantities ϕ_A, ϕ_B, Z_A, and Z_B with their respective expressions provided in equation (37), which need not be restated here.

It is worth emphasizing that the partial structure factor $S_{AA}(Q)$ exhibits strong sensitive to the polymerization degree Z, an aspect that warrants graphical representation. Accordingly, Fig. 2(a) displays the variations of $S_{AA}(Q)$ as a function of the wave vector Q, for various values of Z. The analysis of this figure reveals that the peak amplitude diminishes progressively as Z decreases, accompanied by a slight shift of the peak position toward higher Q values. This trend suggests an enhanced propensity for microphase separation as the incompatibility between blocks A and B increases. In the thermodynamic limit ($Q\rightarrow 0$), the scattered intensity approaches zero for all values of Z, i.e., $S_{AA}(Q=0)\approx 0$, while at high Q, the function asymptotically tends toward zero, $S_{AA}(Q\rightarrow\infty)\rightarrow 0$.

In the second part of this section, we focus on examining the impact of solvent quality on the static scattering properties of star diblock copolymer solutions. As previously discussed, the homopolymer C was replaced by a solvent S, which led to substantial simplifications in the analytical expressions for the partial structure factors $S_{ij}(Q)$.

To enable meaningful comparison with the melt state, we have analyzed the dependence of $S_{AA}(Q)$ on various physicochemical parameters. Figure 2(b) shows the behavior of $S_{AA}(Q)$ as a function of Q for several values of the degree of polymerization Z in solution. The overall qualitative trend is consistent with that observed in the melt state. However, two main differences are notable: (1) the scattered intensity exhibits a higher amplitude in the presence of a good solvent (with $\chi_{PS}=0.4$), and (2) the structure factor at the thermodynamic limit remains finite and non-zero, i.e., $S_{AA}(0)=1.40\neq 0$. It is also important to highlight that, in this thermodynamic limit, the value of $S_{AA}(Q)$ becomes independent of the total polymerization degree Z.

In order to investigate the influence of the total degree of polymerization Z and the overall volume fraction ϕ in a mixture composed of star A-B diblock copolymers and homopolymer C, it becomes necessary to introduce a second composition variable, denoted y, due to the ternary nature of the system, which involves three components with respective volume fractions ϕ_A, ϕ_B, and ϕ_C.

Assuming that the total volume fraction satisfies $\phi_A+\phi_B+\phi_C=\phi$, and defining y as the volume fraction of component C relative to the mixture, the individual volume fractions can be expressed as: $\phi_C=y\phi$,

$\phi_A = x(1-y)\phi$ and $\phi_B = (1-x)(1-y)\phi$, where x is the internal composition parameter of the A-B diblock copolymer.

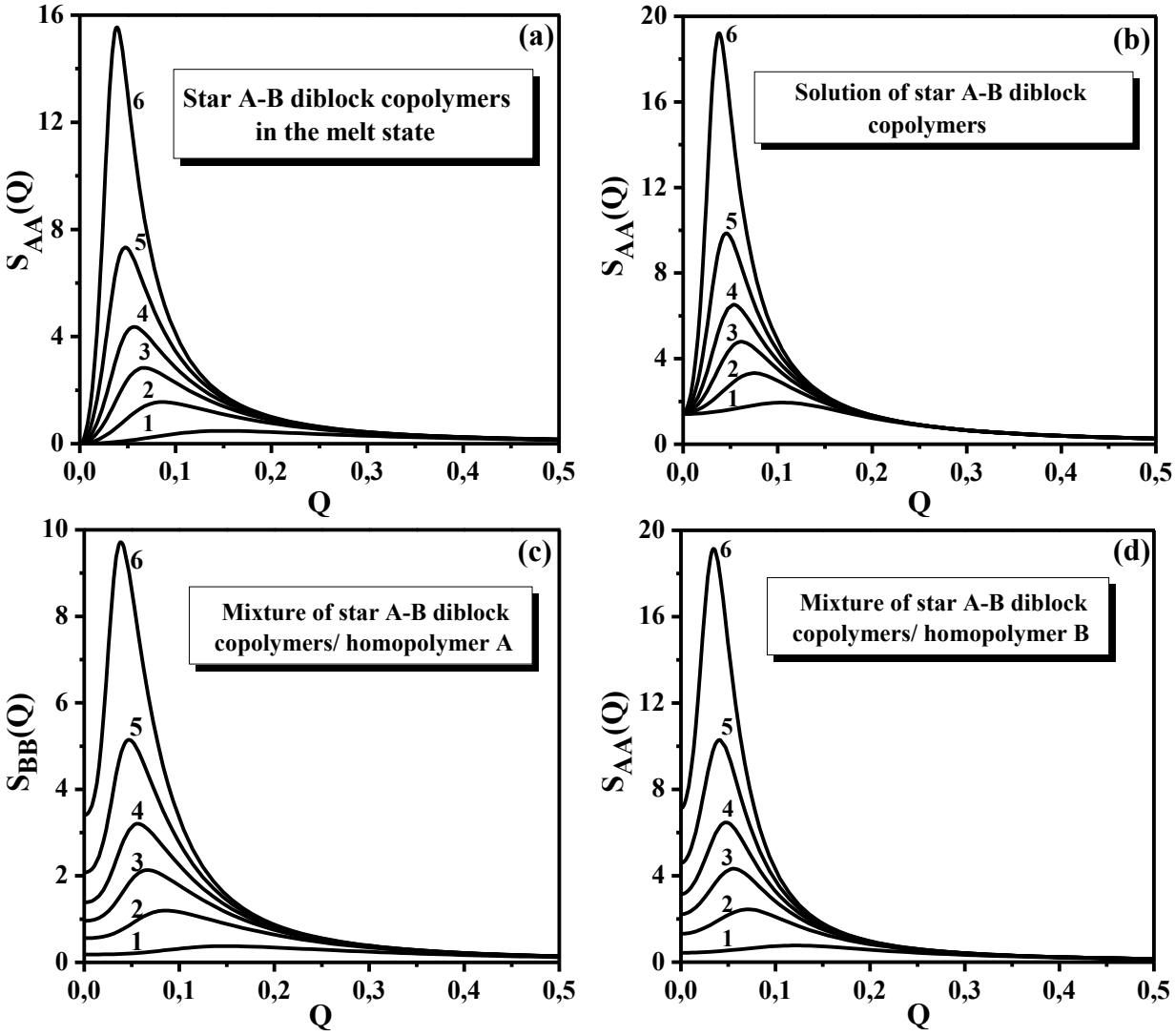


Fig. 2 *Variations of the partial structure factors $S_{AA}(Q)$ and $S_{BB}(Q)$ as functions of the wave vector Q, for different polymeric environments: star A-B diblock copolymers in the melt state (a), in solution (b), a mixture of star A-B diblock copolymers with homopolymer A (c), with homopolymer B (d). The different curves, shown from bottom to top, correspond to increasing values of the total degree of polymerization: Z=100, 300, 500, 700, 1000 and 1500. The numerical parameters used for plotting are: ϕ=0.1, χ=0.04, χ_{PS}=0.4, x=0.7, y=0.3, f=5, a=3.5 and b=2*

Similarly to the previous analysis, we investigated the influence of the polymerization degree Z on the scattering behavior of star A-B diblock copolymers in the presence of added homopolymer A. It is important to note that the polymerization degrees Z_A and Z_B of the diblock copolymer are related to the total polymerization degree Z and the composition x through the relation (38). In contrast, the degree of polymerization of the homopolymer C is simply given by $Z_C = Z_A$. For this type of mixture, the relevant structure factor measurable by small-angle neutron scattering is $S_{BB}(Q)$, whose variation as a function of the wave vector Q is presented in Fig. 2(c) for several values of Z. The examination of this figure reveals a marked increase in the amplitude of the scattering peak located at Q_{max} as the polymerization degree increases. Simultaneously, the peak position undergoes a slight shift toward lower Q values. Moreover, in the thermodynamic limit ($Q \to 0$), the scattering function $S_{BB}(Q=0)$ remains finite and grows significantly with increasing Z. This behavior reflects a reinforcement of the tendency toward microphase separation, resulting from the enhanced incompatibility between blocks A and B. In addition, macrophase separation is accompanied by a rise in the low-Q scattering intensity, i.e., an increase in $S_{BB}(Q=0)$. Depending on the specific nature of the blend (whether miscible, immiscible, or partially miscible) various

morphologies may emerge, ranging from microphase-separated structures to macrophase-separated domains, or even coexisting phases exhibiting both types of separation.
At this stage, we have reproduced a similar analysis to that adapted previously and attempted to identify the new characteristics due to the presence of another homopolymer B instead of that A. This comparison was made under the assumption that the degree of polymerization of the homopolymer C is equal to $Z_C = Z_B$.

In Fig. 2(d), we present the angular dependence of the structure factor $S_{AA}(Q)$ for a mixture of star A-B diblock copolymers with homopolymer B, considering various values of the polymerization degree *Z*. The analysis of this figure reveals a qualitatively similar behavior to that observed in the case of mixtures containing homopolymer A. The main distinction lies in the higher amplitude of the scattering function $S_{AA}(Q)$ when homopolymer B is introduced. For such a system, a range of morphologies may arise, depending on the miscibility between the components. In particular, the tendencies toward both macrophase and microphase separation are reflected by a noticeable increase in the low-Q scattering function $S_{AA}(0)$. This increase becomes more pronounced as the incompatibility between blocks A and B intensifies, underscoring the significant role of inter-block interactions in driving the structural organization of the mixture.

3.2. Effect of the number of arms *f*

The angular dependence of the structure factor $S_{AA}(Q)$ is illustrated in Fig. 3(a) for various values of the number of arms *f*. The analysis of this figure shows that as the quantity *f* increases, the scattered intensity becomes more significant, and a peak clearly appears for all the considered values of *f*, especially in the domain of low Q values. It is worth noting, on one hand, that unlike other physicochemical parameters where the peak tends to disappear as one of these parameters increases or decreases, the influence of the number of branches f has shown that this maximum even exists for a minimum value of *f*, i.e., $f=3$. On the other hand, a small difference is observed between the various curves corresponding to the considered number of branches, indicating a less significant effect.
To investigate the influence of the number of arms *f* and the presence of a good solvent on the behavior of star A-B diblock copolymers, the angular dependence of the structure factor $S_{AA}(Q)$ was plotted for various values of *f*, as shown in Fig. 3(b). The analysis of this figure reveals that the differences between the melt state and the solution of star diblock copolymers are relatively minor, except for two notable aspects: the significantly higher amplitude of the scattering peaks and the nonzero value of the zero-angle scattering function in the presence of the solvent. These observations are expected, as the addition of a good solvent leads to the swelling of the polymer chains, thereby enhancing the contrast and the intensity of the scattered signal. This, in turn, provides a more detailed insight into the microstructural organization of the system driven by self-assembly phenomena.
The variations of the partial structure factor $S_{BB}(Q)$ as a function of the wave vector Q are presented in Fig. 3(c) for different values of the number of arms *f*. The analysis shows that $S_{BB}(Q)$ exhibits a relatively weak dependence on *f*, particularly in the wave vector range $0.017\ \text{Å}^{-1} \leq Q \leq 0.038\ \text{Å}^{-1}$. Additionally, the zero-angle structure factor $S_{BB}(0)$ displays only a minor sensitivity to changes in the number of arms. This behavior is consistent with expectations, as the incorporation of homopolymer chains into the star A-B diblock copolymer system alters the phase behavior of the blend, thereby diminishing the influence of the architectural parameter *f*. Furthermore, the analysis reveals that the position of the scattering peak remains nearly unchanged with increasing *f*, while the amplitude $S_{BB}(Q_{\max})$ significantly decreases before the structure factor reaches an asymptotic regime at high values of Q.
The angular variations of the partial structure factor $S_{AA}(Q)$ are shown in Fig. 3(d) for a blend of star A-B diblock copolymers with homopolymer B, considering different values of the branching number *f*. In contrast to the previously studied mixture, Fig. 3(d) reveals that the zero-angle scattering factor $S_{AA}(0)$ exhibits only a very weak dependence on the branching number *f*. However, the scattered intensity remains significant across all examined values of *f*, indicating that the addition of homopolymer B induces a strong scattering response that is relatively insensitive to the architecture of the star copolymers within the explored parameter range.

3.3. Effect of the composition *x*

In this section, we examine the influence of block composition x, which represents the relative length of the A block within the A-B diblock chains, on the behavior of the partial structure factor $S_{AA}(Q)$ as a function of the wave vector Q. The variations are illustrated in Fig. 4(a) for a polymer melt consisting of star A-B diblock copolymers with *f* identical arms. The figure reveals that, the maximum tends to disappear as the composition x increases and it slightly shifted towards lower values of Q. For compositions in the range $1/2<x<1$, the decay of the curves is practically regular, reflecting a behavior more typical of homopolymer-like chains. In contrast, for $x \leq 1/2$, the copolymer effect systematically appears, and the peak becomes more pronounced as the composition x becomes less significant. Furthermore, at the thermodynamic limit, a similar behavior is observed for all values of x, where the scattering function at zero angle, $S_{AA}(Q=0)$, is zero, suggesting an absence of long-range correlations. In the high-Q region, the scattering function rapidly decreases and approaches zero more sharply as the asymmetry between the A and B blocks increases.

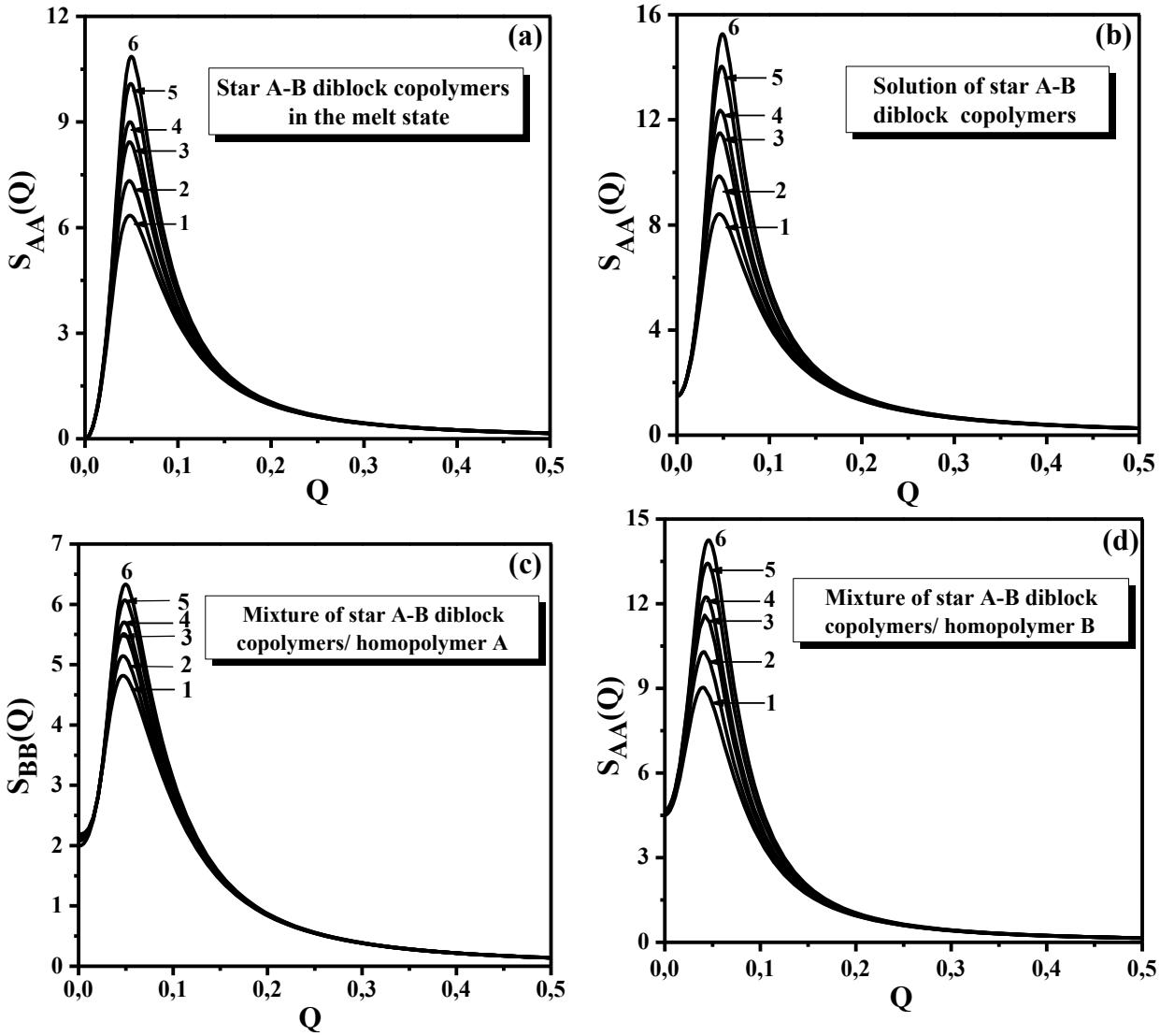


Fig. 3 *Variations of the partial structure factors $S_{AA}(Q)$ and $S_{BB}(Q)$ as functions of the wave vector Q, for different polymeric environments: star A-B diblock copolymers in the melt state (a), in solution (b), a mixture of star A-B diblock copolymers with homopolymer A (c), with homopolymer B (d). The different curves, shown from bottom to top, correspond to increasing values of the number of arms: f=3, 5, 8, 10, 15 and 20. The numerical parameters used for plotting are: ϕ=0.1, χ=0.04, χ_{PS}=0.4, x=0.7, y=0.3, Z=1000, a=3.5 and b=2*

For a star polymer consisting of f branches of A-B diblock copolymers immersed in a good solvent, investigated the effect of block composition x on the scattering behavior of the system. Figure 4(b) presents the angular dependence of the structure factor $S_{AA}(Q)$ for different values of x. As anticipated, consistent with the behavior observed in the melt state illustrated in Fig. 4(a), the partial structure factor $S_{AA}(Q)$ exhibits a strong sensitivity to the composition x, further amplified by the presence of the good solvent. It is important to emphasize that, in the thermodynamic limit ($Q\rightarrow 0$), the scattering function shows a reduced dependence on the composition x. In particular, for values of $x \leq 0.1$, corresponding to very short A-blocks, the structure factor $S_{AA}(Q)$ becomes almost independent of x, reflecting the limited contribution of block A to the overall scattering signal under these conditions.

Figure 4(c) presents the angular dependence of the partial structure factor $S_{BB}(Q)$ for a mixture of star A-B diblock copolymers and homopolymer A, for various values of the composition x. The results reveal a marked sensitivity of $S_{BB}(Q)$ to this parameter. The amplitude of the scattering peak increases with the length of block A, up to a value of $x > 0.5$, corresponding to a nearly symmetric architecture, beyond which the behavior becomes more complex. Furthermore, the zero-angle structure factor $S_{BB}(0)$ exhibits a strong dependence on the composition x, indicating a pronounced tendency towards macrophase separation between the star copolymer and the homopolymer A. A slight shift of the scattering peak towards lower Q-values is also observed with increasing x, reflecting changes in the characteristic domain sizes.

Figure 4(d) displays the scattering behavior of a mixture of star A-B diblock copolymers and homopolymer B for various values of the composition x. The analysis reveals that the amplitude of the correlation peaks increases with x up to x=0.5, corresponding to a symmetrical copolymer architecture, where the phenomenon becomes controversial. It should be noted that we could not plot the curves corresponding to x=0.05 and x=0.1, as we did in the previous mixture represented by Fig. 4(c). The curves obtained for these two values showed an asymptotic behavior of the diffusion function at Q_{max} (i.e., $S_{AA}(Q_{max})\rightarrow-\infty$). Therefore, we started representing the angular evolution of the quantity $S_{AA}(Q)$ from the smallest value of x, i.e., x=0.25, which exhibited a different behavior compared to all the other considered values of x. Indeed, the analysis of this figure reveals that the scattered intensity for x=0.25 gradually decreases, passes through a minimum, then undergoes a substantial increase, reaching a maximum before adapting an asymptotic form in the domain of large scattering angles.

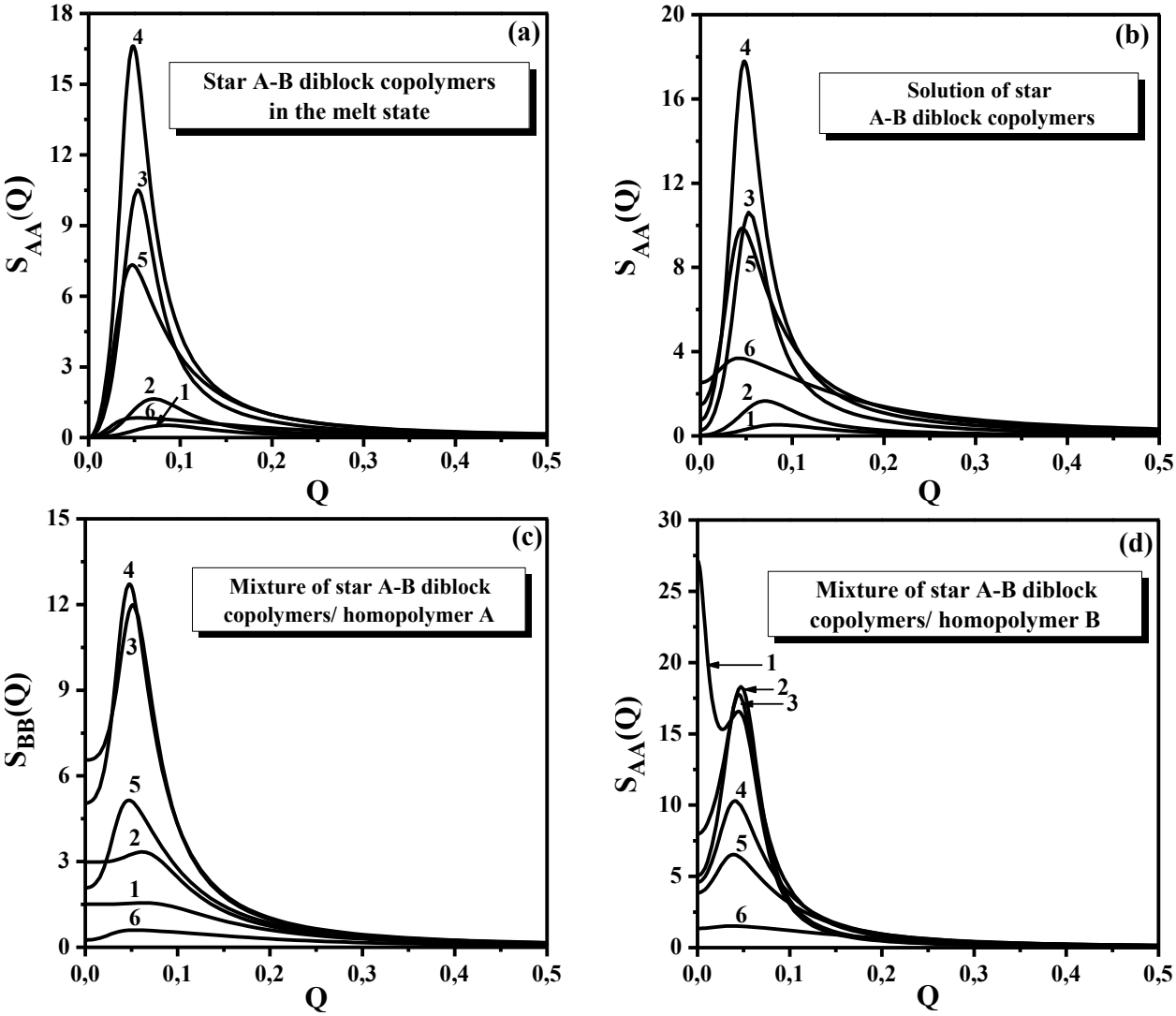


Fig. 4 *Variations of the partial structure factors $S_{AA}(Q)$ and $S_{BB}(Q)$ as functions of the wave vector Q, for different polymeric environments: star A-B diblock copolymers in the melt state (a), in solution (b), a mixture of star A-B diblock copolymers with homopolymer A (c), with homopolymer B (d). The different curves, shown from bottom to top, correspond to increasing values of the composition: x=0.05, 0.1, 0.3, 0.5, 0.7 and 0.9 (Fig. 4d: x=0.25, 0.3, 0.5, 0.7, 0.8 and 0.95). The numerical parameters used for plotting are: ϕ=0.1, χ=0.04, χ_{PS}=0.4, Z=1000, y=0.3, f=5, a=3.5 and b=2*

3.4. Effect of the concentration ϕ

To illustrate the influence of the concentration ϕ on the scattered behavior, Fig. 5(a) presents the angular dependence of the structure factor $S_{AA}(Q)$ for a star melt composed by f arms of A-B diblock copolymers. The curves exhibit qualitatively similar behavior across all values of ϕ. In particular, the structure factor vanishes at

the thermodynamic limit, i.e., $S_{AA}(0)=0$, and displays a well-defined peak whose amplitude increases with concentration, while the peak position Q_{max} remains essentially constant. At high scattering vectors Q, the structure factor decays asymptotically to zero.

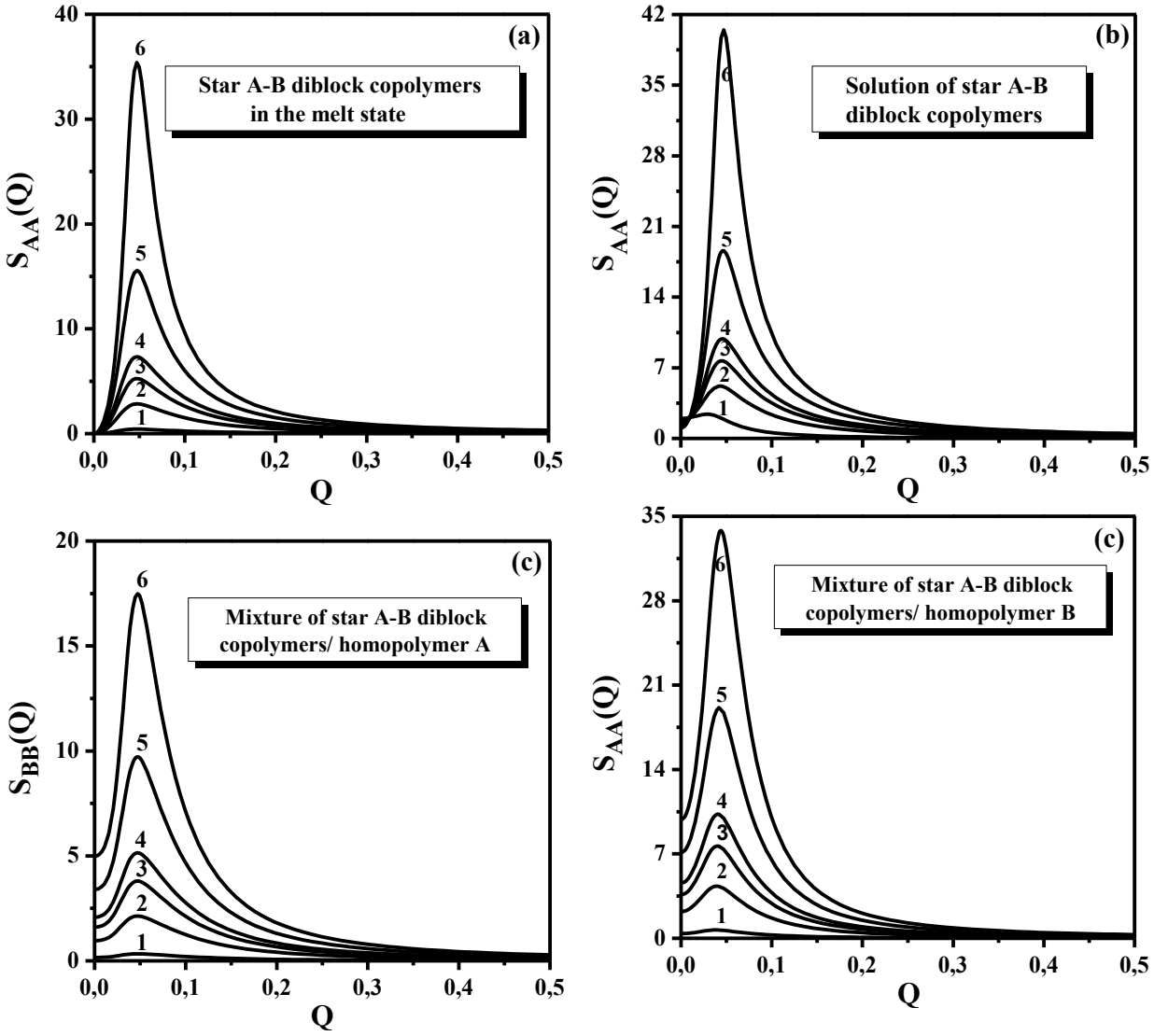


Fig. 5 *Variations of the partial structure factors $S_{AA}(Q)$ and $S_{BB}(Q)$ as functions of the wave vector Q, for different polymeric environments: star A-B diblock copolymers in the melt state (a), in solution (b), a mixture of star A-B diblock copolymers with homopolymer A (c), with homopolymer B (d). The different curves, shown from bottom to top, correspond to increasing values of the concentration: ϕ*=0.009, 0.05, 0.08, 0.1, 0.15 and 0.2. *The numerical parameters used for plotting are: Z=1000, χ=0.04, χ_{PS}*=0.4, *x=0.7, y=0.3, f=5, a=3.5 and b=2*

The analysis is extended to solutions of star A-B diblock copolymers in a good solvent. Figure 5(b) shows the corresponding angular dependence of $S_{AA}(Q)$ for several values of the volume fraction. A pronounced enhancement of the scattering intensity is observed as ϕ increases, indicating greater contrast and segmental correlations in denser solutions. However, it should be noted that as the concentration ϕ decreases, a scattering peak disappears and its position Q_{max} shifts slightly towards the small-angle domain. Notably, in the thermodynamic limit (i.e., Q=0) and for all values of ϕ, the quantity $S_{AA}(Q)$ remains finite and is not very sensitive to the concentration ϕ.
To investigate the effect of the concentration ϕ on the scattering behavior of the partial structure factor $S_{BB}(Q)$, its angular dependence was examined for various values of the volume fraction ϕ, while keeping the composition parameter fixed at y=0.3. Figure 5(c) indicates that the general trend of the scattering intensity remains similar across all considered concentration values. Nonetheless, as ϕ decreases, the characteristic scattering peak becomes less pronounced and eventually disappears, although the peak position Q_{max} remains nearly unchanged. It is also worth noting that, in the thermodynamic limit ($Q\rightarrow0$), the structure factor $S_{BB}(0)$ remains finite for all

concentrations. In the present analysis, with y = 0.3 fixed, the chosen volume fractions correspond to systems where the star diblock copolymer content is greater than that of the homopolymer A ($\phi_A + \phi_B \succ \phi_A$).

Similarly, Fig. 5(d) presents the angular evolution of the structure factor $S_{AA}(Q)$ for a mixture of star A-B diblock copolymers with homopolymer B, for various values of the volume fraction ϕ. The overall behavior is qualitatively analogous to that obtained in the case of mixtures containing homopolymer A (see Fig. 5(c)). The main difference lies in the amplitude of the scattering curves, which is noticeably higher in the presence of homopolymer B. This enhancement suggests stronger compositional fluctuations or increased incompatibility between the respective polymer components.

3.5. Effect of the Flory-Huggins interaction parameter χ

The angular dependence of the structure factor $S_{AA}(Q)$ is presented in Fig. 6(a) for various values of the Flory-Huggins interaction parameter χ. The analysis of this figure shows that an increase in χ results in a more pronounced scattering peak, with both its sharpness and amplitude increasing significantly. In particular, a marked enhancement in $S_{AA}(Q)$ is observed at small scattering vectors Q, along with the emergence of a maximum at a well-defined wave vector Q_{max}, which appears to be independent of the specific value of χ. Furthermore, it is noteworthy that, throughout the variation of the interaction parameter, the position of the peak remains essentially unchanged. In the thermodynamic limit ($Q \rightarrow 0$), the structure factor $S_{AA}(0)$ is found to be independent of the Flory–Huggins parameter χ ($S_{AA}(0)$=0).

As previously mentioned, the angular dependence of the structure factor $S_{AA}(Q)$ for solutions of star A-B diblock copolymers, shown in Fig. 6(b) for various values of the Flory-Huggins interaction parameter χ, exhibits, on the one hand, a strong sensitivity of the scattered intensity to variations in χ, and on the other hand, a weak dependence of the zero-angle scattering function. Notably, as $Q \rightarrow 0$, the quantity $S_{AA}(Q)$ tends toward a constant value, while the position of the correlation peak shifts slightly toward higher Q values as χ increases. These behaviors contrast with those observed in the melt state of star diblock copolymers, as illustrated in Fig. 6(a), where such dependencies are not apparent.

The variations of the structure factor $S_{BB}(Q)$ as a function of the wave vector Q are illustrated in Fig. 6(c) for different values of the Flory-Huggins interaction parameter χ. The analysis of this figure indicates that, as χ increases, the scattered intensity becomes more pronounced, and a clear peak emerges at low values of Q. It should be noted that, on the one hand, the zero-angle scattering function $S_{BB}(0)$ increases slightly with the interaction parameter, and on the other hand, the peak position remains unchanged regardless of the value of χ. Moreover, it is worth emphasizing that the tendency toward microphase separation is strengthened as the incompatibility between blocks A and B increases.

The dependence of the structure factor $S_{AA}(Q)$ on the wave vector Q is illustrated in Fig. 6(d) for various values of the Flory–Huggins interaction parameter χ. This figure exhibits a qualitatively similar behavior to that shown in Fig. 6(d), with the exception of the significantly higher amplitude of the scattered intensity $S_{AA}(Q)$ when compared to the case involving the addition of homopolymer A. The position of the scattering peak is slightly shifted towards higher values of the wave vector Q.

The study of the effect of various physicochemical parameters has revealed the existence of different morphologies, ranging from microphase separation in star A-B diblock copolymer melts to macrophase separation and the combination of both phenomena in mixtures of these with homopolymers, with a slight modification of their morphology in the presence of a solvent.

1. Conclusions

The main objective of this work was to investigate the static scattering properties of star A-B diblock copolymers using the Random Phase Approximation (RPA). This theoretical framework enabled a detailed analysis of the influence of various physicochemical parameters on the scattering behavior of such polymeric systems, both in the melt state, in mixtures with homopolymers, and in solution.

In the first part of the study, we presented the general theoretical formalism based on RPA to describe the scattering response of multi-component systems subjected to neutron, X-ray, or light radiation. This approach led to a matrix formulation expressing the static structure matrix of an interacting system in terms of that of a non-interacting reference system and an excluded volume matrix. Within this framework, we analyzed the absolute scattering intensity I(Q) measurable by Small-Angle Neutron Scattering (SANS) for star copolymers and their blends.

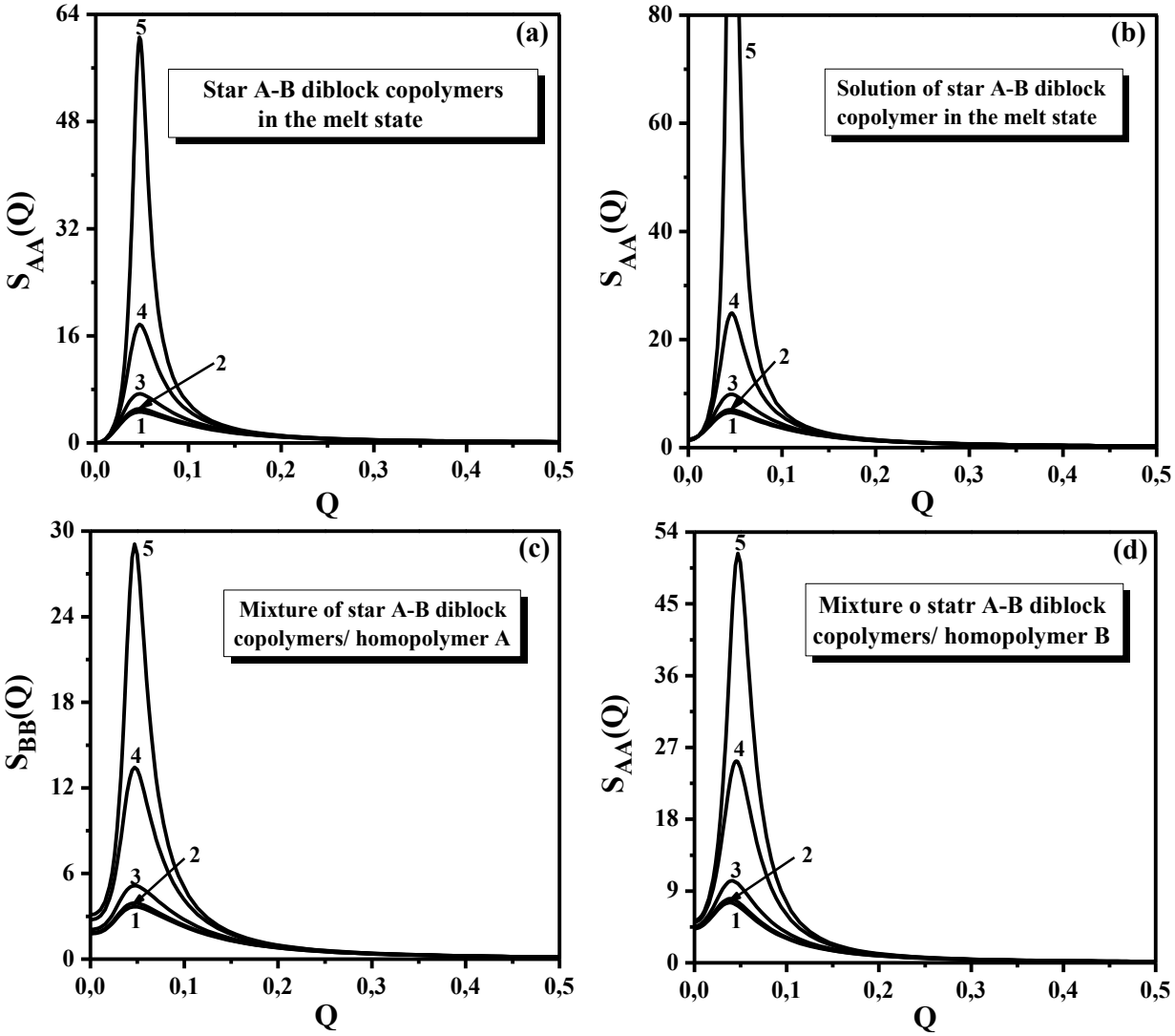


Fig. 6 *Variations of the partial structure factors $S_{AA}(Q)$ and $S_{BB}(Q)$ as functions of the wave vector Q, for different polymeric environments: star A-B diblock copolymers in the melt state (a), in solution (b), a mixture of star A-B diblock copolymers with homopolymer A (c), with homopolymer B (d). The different curves, shown from bottom to top, correspond to increasing values of the interaction parameter*: χ=0.0001, 0.01, 0.04, 0.08 and 0.1. *The numerical parameters used for plotting are: Z=1000,* ϕ=0.1, χ_{PS}=0.4, *x=0.7, y=0.3, f=5, a=3.5 and b=2*

Our findings showed that the observed scattering signal is primarily determined by the structure factors associated with the core or corona domains of the star polymer, depending on the nature of the added homopolymer. In this context, particular attention was given to contrast conditions, which play a crucial role in determining the accessible partial structure factors in experiments.

We then extended the theoretical treatment of star A-B diblock copolymers in the melt state to their mixtures with homopolymers C. Given that these homopolymers correspond to one of the constituent blocks (A or B) of the diblock copolymer, they can also be regarded as selective solvents. We therefore separately examined mixtures involving homopolymer A and homopolymer B. Lastly, we considered solutions of star A-B diblock copolymers formed by *f* arms in the presence of a good solvent. The results obtained in this case led to a substantial simplification of the general equations and allowed us to derive analytical expressions for the partial structure factors $S_{ij}(Q)$.

In the final part of this study, we applied the developed theoretical framework to star A-B diblock copolymers in the melt state, with the aim of investigating the influence of various physicochemical parameters on their phase behavior. For this purpose, we analyzed the variations of the partial structure factor $S_{AA}(Q)$ as a function of the wave vector Q, for several values of the selected parameters.

The analysis of the resulting scattering profiles revealed the presence of a correlation peak at a well-defined wave vector Q_{max}, located in the low-Q region. This observation indicates a tendency towards microphase separation, which arises from the incompatibility between the two blocks A and B. Moreover, in the thermodynamic limit (i.e., as $Q \rightarrow 0$), the scattering intensity was found to vanish, $S_{AA}(Q=0)\approx 0$, reflecting the absence of macrophase

separation between the two blocks. At large values of the wave vector (high Q), all the curves exhibited a similar asymptotic decay, confirming that $S_{AA}(Q\rightarrow\infty)\rightarrow 0$ as Q increases.
Subsequently, we turned our attention to two particular cases involving mixtures of star A-B diblock copolymers with homopolymers, focusing on the effect of incorporating a homopolymer that is either identical to the inner (A) or outer (B) block of the star copolymer. The analysis showed that the appearance of a well-defined scattering peak along with a non-zero value of the zero-angle structure factor, $S_{ij}(0) \neq 0$, revealed a modified phase behavior in these blends. These changes suggest that the addition of homopolymers can significantly alter the morphology of the system, either by reinforcing microphase separation or by introducing a degree of macrophase segregation, depending on the nature of the added homopolymer.
Using scattering techniques, particularly neutron scattering, several studies have demonstrated that the addition of homopolymers to star A-B diblock copolymers significantly modifies the phase behavior of the resulting mixtures. The experimental findings reported by Adhikari et al. [18–20], as well as by other researchers [21–22], highlight several key effects. First, the incorporation of homopolymers leads to substantial changes in the system's morphology. Second, the phase behavior of the blend is strongly influenced by the nature of the added homopolymer, specifically the block of the star copolymer with which it is chemically identical. Third, depending on the miscibility of the system, whether the components are fully miscible, immiscible, or partially miscible, a variety of morphologies have been observed, ranging from microphase separation to macrophase separation, or even a combination of both. These structural transitions have been shown to depend strongly on the molecular weight of the homopolymer [11, 23].
In accordance with these results, the angular dependence of the structure factors $S_{BB}(Q)$ and $S_{AA}(Q)$, which become experimentally accessible via neutron scattering when homopolymers A or B are introduced into star diblock copolymer systems, was plotted for various physicochemical parameters. Analysis of these plots revealed the emergence of a correlation peak at a well-defined wave vector Q_{max} across all tested conditions, as well as a varying low-Q scattering intensity in the thermodynamic limit ($Q\rightarrow 0$). These findings are in excellent agreement with the experimental results reported by Adhikari et al. [17–19], confirming that the phase behavior of the blends is strongly affected by the presence and nature of the added homopolymers.
To ensure a comprehensive analysis, we have also examined the case of star A-B diblock copolymer solutions. The angular evolution of the scattering function $S_{AA}(Q)$, plotted for various values of physicochemical parameters, reveals a behavior qualitatively similar to that observed in the melt state. However, two major differences are noteworthy. First, the peak amplitude is significantly enhanced in the presence of a good solvent. Second, the zero-angle scattering function, $S_{AA}(0)$, remains finite and exhibits only a weak dependence on the considered parameters. These findings suggest an increased propensity for microphase separation and a moderate alteration of the system's morphology compared to the melt state.

Acknowledgments

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