Analysis

Study of the Structure of Block Copolymer-Homopolymer Blends Using Small Angle Neutron Scattering

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SUMMARY

The structure of "dilute solid solutions" of poly(styrene-b-buta-diene) diblock copolymers within a matrix of polybutadiene has been studied using small angle neutron scattering. Experimental curves exhibit several intensity maxima which are characteristic of the scattering function of spherical particles with a low polydispersity. The scattering particles result from the association of several polystyrene blocks which form the core of micelles. The influence of the molecular characteristics of copolymer and matrix on the size of polystyrene particles has been examined.

INTRODUCTION

In recent years, there has been an increase in the interest for copolymer-homopolymer systems. In particular, an important experimental and theoretical work has been made in the case of blends comprising a block copolymer and the parent homopolymers (1).

As a part of our research program dealing with polymer compatibi-lity, we have undertaken the study of the morphology and thermodynamics of binary and ternary copolymer-homopolymer blends. One of the aspects we have developped focuses on the characterization of "dilute solid solutions" of a diblock copolymer within one of the parent homopolymers.

In the present note, are given the preliminary results we have obtained concerning the study of polystyrene-polybutadiene (PS-PB) block copolymers embedded in a matrix of polybutadiene, using small angle neutron scattering (SANS).

EXPERIMENTAL

The SANS study was performed on deuterated polystyrene-protonated polybutadiene copolymers embedded in a matrix of protonated polybuta-diene. The good contrast between deuterated polystyrene and polybutadiene chains allows the study of the polystyrene part of the blends.

Homopolymer and copolymer samples were synthesized via anionic polymerization. The narrow molecular weight distribution of polymers has been checked by GPC. Their molecular weights measured by light scattering and chemical composition determined by UV spectroscopy are listed in Tables 1 and 2.

Tab.1 : Molecular weight (M_w) of homopolybutadiene (PB) matrix

Ref.	M_w
M1	1600
M3	3300
M6	6500

Tab. 2 : Molecular characteristics of diblock polystyrene-polybutadiene (PS-PB) copolymers

Ref.	deuterated PS block		PB block	
	M_w	%	M_w	%
A	14 000	32.4	29 000	67.6
B	14 000	48.4	15 000	51.6
C	14 000	66.7	7 000	33.3
S	23 000	16.8	114 000	83.2
D	23 000	33.2	46 000	66.8

The blends were prepared as follows : the copolymer and the homopolymer were dissolved in benzene which is a good solvent for both components ; then the solvent was removed under vacuum using a rotating evaporator ; further vacuum drying was carried out at room temperature for at least 3 days. The mixtures obtained are transparent and homogeneous. The copolymer concentration in blends is ranging from 0.5 to 10% by weight. We have checked that the structure of the blends is reproducible : blends of the same composition but prepared from benzene solutions with different concentrations lead to identical SANS results.

SANS experiments were carried out at room temperature on the instrument D17 at the Institute Laue Langevin (ILL), Grenoble. The momentum transfers range from 5.10^{-2} to 1.3 nm^{-1}. Scattered intensity patterns were obtained from raw data using standard ILL procedure (2) A model fitting approach has been used to analyse the data. In this calcu-lation, the smearing arising from instrumental effects (wavelength distribution, angular divergence of the incident beam, finite resolution of the detector) has been taken into account by introducing a phenomenolo-gical instrument resolution function having a Gaussian form (3). Moreover, a particle size distribution function for the scattering particles has been considered. This distribution has been approximated by a zeroth order log normal function (4). In these preliminary fitting treatments, the interparticle scattering contribution and the thickness of the interface have been neglected. The convoluted model intensity has been compared with the measured intensity and the parameters varied to obtain the best agreement (5).

RESULTS AND DISCUSSION

A typical scattering pattern is shown in Fig. 1. The scattering curve exhibits a central maximum and a set of subsidiary smeared maxima and minima which can be interpreted in terms of the scattering function of particles with a low polydispersity.

We have tried to determine which model of particles could correspond to the experimental curves. Considering that PS and PB chains are incompatible, the matrix of PB can be considered as a "non-solvent" for the PS part of the copolymer and as a "good solvent" for the PB blocks. Therefore, the system may be compared with the case of block copolymers in solution in a selective solvent for one block. It is well known that, in the latter case, there is formation of spherical micelles (6), the core of the micelle being made up from the association of
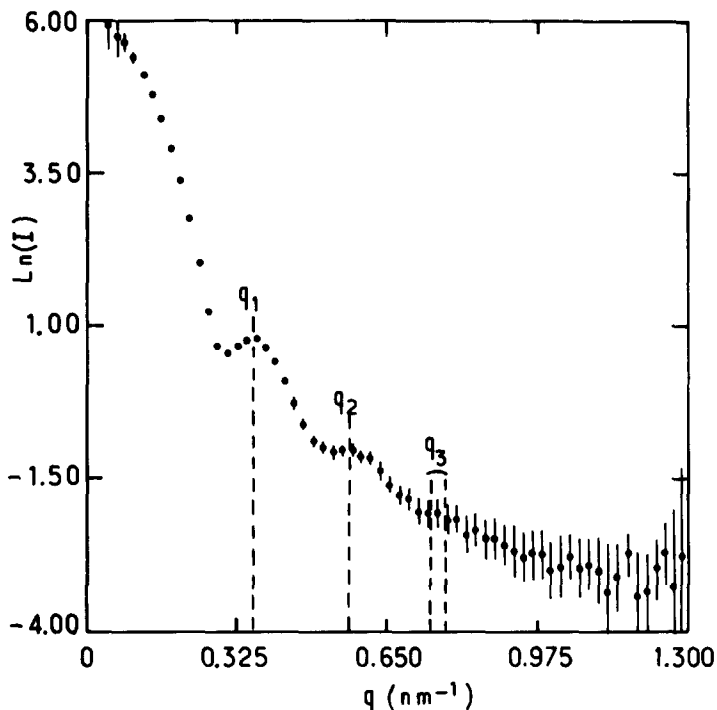
Fig. 1 :
Scattering curve (scattered intensity in logarithmic scale versus q) for sample 6D2 (copolymer D at 2% in matrix M6)

several insoluble blocks. Then, in the case of "dilute solid solutions" of poly(styrene-b-butadiene) copolymers within homopolybutadiene, we believe that the same type of structure arises. More precisely the "insoluble" collapsed PS blocks should be gathered in the core of the micelle and surrounded by a shell of PB blocks which insure the compatibility with the PB matrix (fig. 2). For this reason, a spherical model for the scattering particles (PS chains) is the more relevant.

Fig. 2 :
Sketch of the particle resulting from the association of several copolymer molecules (copolymer micelle)

▬▬ polystyrene blocks of the copolymer
▬ ▬ ▬ polybutadiene blocks of the copolymer
▬▬▬ homopolybutadiene
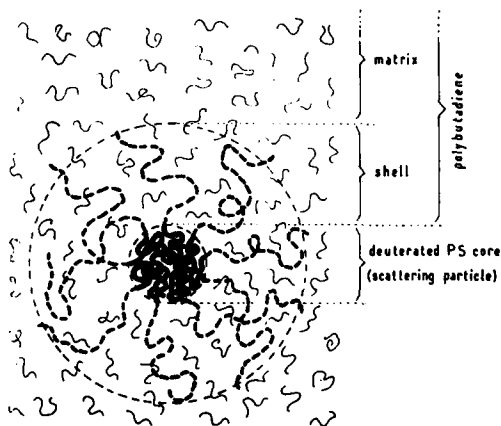
This assumption is confirmed by the fact that the relative positions of the maxima of the experimental curves agree with those of the scattering function of uniform spheres of radius R. Thus, from

Tab.3 : Values of the radius of the scattering spheres calculated from the position of the different maxima (example : sample 6D2, cf. Fig. 1)

Order	$(q \cdot R)_{max}$ (theoretical)	q_{max} (experimental)	R (nm) (calculated)
0	0		
1	5.765	0.360	16.0
2	9.095	0.567	16.0
3	12.32	$\sim$0.74–0.78	$\sim$15.8–16.6

theoretical values of $(qR)_{max}$ (7) and experimental values of q, we can deduce roughly the radius of spheres. For example, for the system given in Table 3, identical values of R are obtained from the position of the first three subsidiary maxima. On the other hand, the dimensions of spheres are much higher than those of the individual PS chains measured in the bulk (Rg=4.35nm), which confirms the micellar model.

In order to improve the analysis of the data, we have tried to fit the experimental curves with the simulated curves using a homogeneous density sphere model according to the procedure described in the experimental section. A good correspondence (fig. 3) is obtained between experimental and theoretical curves for copolymer concentrations not exceeding 5% by weight. Then, from parameters used for obtaining the best fit, a mean particle radius $\bar{R}$ and the standard deviation of the size distribution (ranging from 11 to 16%) can be determined.
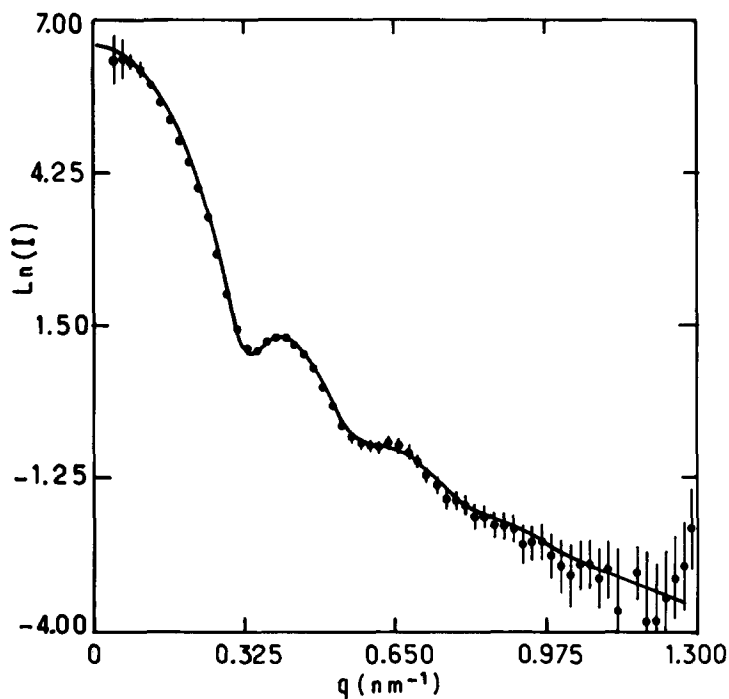

Fig. 3 :
Scattering curve for sample 6D5 (copolymer D at 5% in matrix M6)
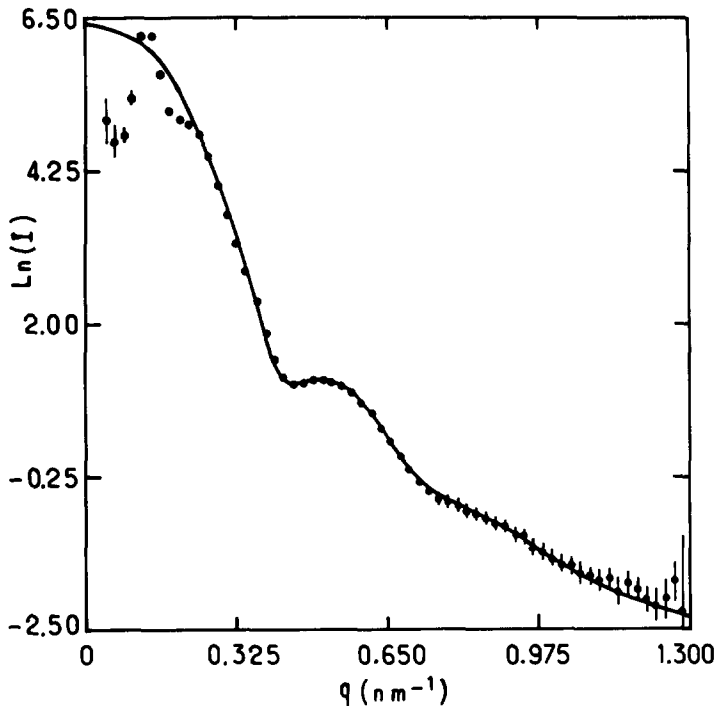• data points
— fit using model

Fig. 4 :
Scattering curve
for a system
with strong
interparticle
interferences.
(sample 1D10 :
copolymer D at
10% in matrix
M1)

• data points

—— fit using
model

For higher copolymer contents, an additional peak appears at low q values (fig. 4), which must be due to interparticle interferences. In this case, experimental data cannot be simply fitted using a single particle scattering function only.

The influence of different parameters on the radius of spheres $\overline{R}$ has been examined. The first conclusions of this study are as follows :

(i) For a given copolymer at a given concentration (Table 4) $\overline{R}$ increases with increasing the molecular weight of the matrix. This result can be explained as follows : the incompatibility between the matrix of PB and the PS chains increases with the molecular weight of the matrix. Consequently the degree of association of copolymer molecules increases as well $\overline{R}$. Moreover, the maxima are not as well defined when the

Tab. 4 : Influence of the molecular weight of the PB matrix on $\overline{R}$ (*)

matrix	Cop.D at 2%		Cop.D at 5%		Cop.B at 2%	
	sample	$\overline{R}$(nm)	sample	$\overline{R}$	sample	$\overline{R}$
M1	1D2	11.7	1D5	10.1	1B2	9.6
M3	3D2	14.3	3D5	11.5	3B2	11.5
M6	6D2	15.2	6D5	13.5	6B2	12.3

(*) sample identification code : for example, 6D2=copolymer D at 2% in matrix M6.
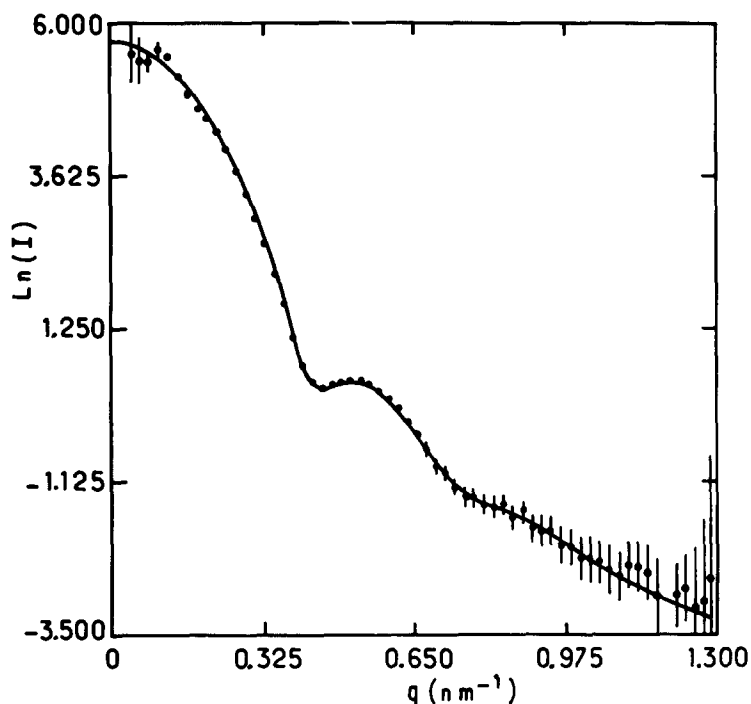
Fig. 5 :
Scattering
curve for sam-
ple 1D5 (co-
polymer D at
5% in matrix
M1).
To be compared
with Fig. 3
(same copoly-
mer in diffe-
rent matrix)

molecular weight of the matrix decreases (fig. 5), which indicates a higher size polydispersity. In fact, this smearing effect may also be attributed to a more diffuse interface.

(ii) With increasing copolymer concentration, an unexpected decrease of $\overline{R}$ is observed (Table 5). Such a behavior is perhaps due to the fact that both interparticle scattering contribution and thickness of interface have been neglected.

Tab. 5 : Influence of the copolymer concentration on $\overline{R}$ (example : Cop.D in matrix M1)

sample	% cop.	$\overline{R}$ (nm)
1D05	0.5	14.5-15
1D1	1	13.6
1D2	2	11.7
1D5	5	10.1
1D10	10	∿10.3

(iii) For copolymers with a same PS block, it appears (Table 6) that the higher the molecular weight of the PB block, the lower the radius of particles. This is interpreted by an expected increase in copolymer "solubility" within the matrix and by an increase of the mean lateral

packing area per chain (which limits the number of associated molecules), when the PB block is greater.

Tab. 6 : Influence of the PB content of the copolymer on $\bar{R}$

Copolymers			2% in matrix M3		2% in matrix M1	
Ref.	M_{PS}	%PB	sample	$\bar{R}$(nm)	sample	$\bar{R}$
A	14.000	67.6	3A2	10.5	1A2	8.5
B	"	51.6	3B2	11.5	1B2	9.6
S	23.000	83.2	3S2	12.0		
D	"	66.8	3D2	14.3		

(iv) For copolymers with an identical chemical composition (Table 7), $\bar{R}$ increases with the molecular weight of the copolymer) i.e. with the length of the PS chains.

Tab. 7 : Influence of the molecular weight of the copolymer on $\bar{R}$ (co-polymers : PS content/PB content $\sim$ 1/2)

copolymers		2% in matrix M1		2% in matrix M3	
Ref.	M_w	sample	$\bar{R}$(nm)	sample	$\bar{R}$
D	69.000	1D2	11.7	3D2	14.3
A	43.000	1A2	8.5	3A2	10.5

CONCLUSION

This work shows that the investigated copolymer-homopolymer blends, although macroscopically homogeneous , give rise to a microphase separation. Polystyrene microdomains are formed due to the micellar association of copolymer molecules. The variation of the dimensions of particules as a function of the molecular characteristics of polymers can be qualitatively related to the degree of compatibility between the two components of the blend. More detailed information about these systems is to be obtained from SANS fitting refinements in progress : (i) by taking into account the interparticle structure factor, (ii) by considering spheres with a diffuse boundary (iii) by using other types of particle size distribution.

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