Experimental report

09/03/2021

Proposal: 6-04-282 **Council:** 10/2019

Title: CONCENTRATION FLUCTUATIONS AND BROADENING OF THE DYNAMICAL RESPONSE IN DYNAMICALLY ASYMMETRIC MIXTURES OF INDUSTRIAL INTEREST

Research area: Soft condensed matter

This proposal is a new proposal

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Local contacts: Lionel PORCAR

Samples: hSBR [C4H6-C8H8] / dPS [C8D8] blends

Instrument	Requested days	Allocated days	From	To
D22	3	1	07/09/2020	08/09/2020

Abstract:

Relating the dynamic response in dynamically asymmetric mixtures with concentration fluctuations is a fundamental issue, but can also be of utmost interest to elaborate predictive models for the behavior of the materials involved in the rubber industry.
In a previous work on blends of SBR with PS we have found that the size of the relevant region for the dielectric response, Rc, turns to be practically independent of temperature and composition, always of about 1nm. We want to check the universality of this important result by varying the properties of the high-Tg component (PS) of the mixture, in particular, changing its molecular weight. To do this we need to characterize by SANS the concentration fluctuations of the system and their temperature dependence.

CONCENTRATION FLUCTUATIONS AND BROADENING OF THE DYNAMICAL RESPONSE IN DYNAMICALLY ASYMMETRIC MIXTURES OF INDUSTRIAL INTEREST

Proposal 6-04-282. Experimental report

D22 - 07/09/2020 to 8/09/2020 - Local contact: Dr Lionel Porcar.

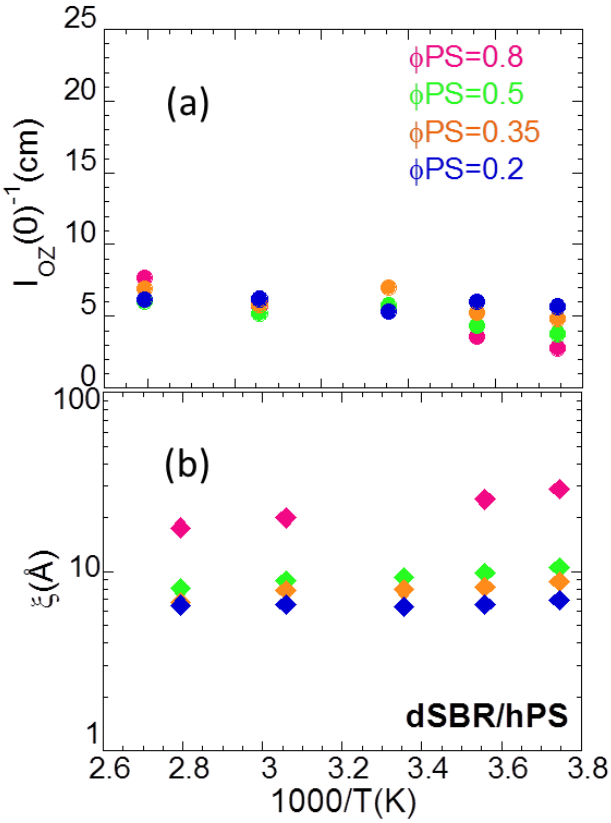
In mixtures, the self-concentration ingredient is believed to be the main reason for the dynamic asymmetry retained by the components, while fluctuation concentrations are thought to be behind the usually observed broad distribution of mobilities [1]. We want to characterize by SANS the concentration fluctuations and their temperature dependence in blends of SBR/PS with different compositions by varying the properties of the high-Tg component (PS) of the mixture. In previous work we have studied SBR/PS samples with PS of 1Kg/mol [2, 3].

SANS experiments on the instrument D22 were carried out at five different temperatures, at 267K, 282K, 298K, 327K and 360K. We used an incident wavelength (λ) of 6Å and three different configurations of sample-to-detector distances (2 m, 5.6 m and 17.6 m) to cover a Q-range of $0.003 \leq Q \leq 0.5$ Å^{-1}. The sample transmission was measured at the same wavelength and a distance 17.6 m. The background was measured under the same conditions and subtracted from measurements with labeled samples.

Samples where the SBR is deuterated and the PS is protonated and samples where the SBR is protonated and PS is deuterated were prepared. Protonated and deuterated styrene-butadiene rubber (hSBR and dSBR) were synthesized by anionic polymerization by the Michelin Company. The protonated and deuterated polystyrene (hPS and dPS) were purchased from Polymer Source. Since the blend is immiscible for high-M_w PS, we have considered oligomers of M_w= 500 g/mol. Table 1 shows the molecular weights, glass transition temperatures T_gs as determined by differential scanning calorimetry (DSC) and densities of the pure components. Blends of different compositions (ϕ_{PS}=20, 35, 50, 80%) have been explored.

sample	M_n (g/mol)	PDI	T_g (K)	d (g/cm^3)
hSBR	69900	1.09	208	0.94
dPS	500	1.12	260	1.07
dSBR	38100	1.13	210	1.06
hPS	500	1.2	273	0.999

Table 1. Molecular weights, Polydispersities, Glass-Transition Temperatures and Densities of the Homopolymers.



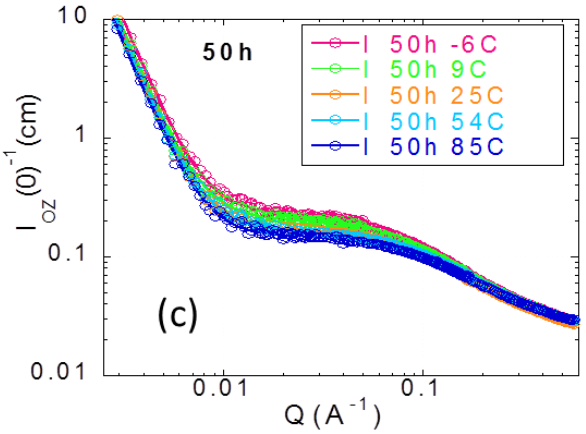


Figure 1. Inverse temperature dependence of the parameters characterizing the concentration fluctuations as deduced from SANS: inverse of amplitutde $I_{oz}(0)$ (a) and correlation lenght ξ (b), for the different compositions investigated of the system dSBR/hPS.
(c) SANS results on the sample ϕ_{PS}=0.5, described with Ornstein-Zernike law.

SANS experiments provided us information on thermally driven concentration fluctuations (TCFs). In Figure 1c are shown representative SANS results for the blend dSBR/hPS with ϕ_{PS}=0.5 at different temperatures. TFCs have been characterized using the Ornstein-Zernike (OZ) equation; to account for the total scattered intensity, a power law (describing the low-Q behavior) and a constant background were added:

$$I_{exp}(Q) = \frac{A}{Q^x} + \frac{I_{OZ}(0)}{1 + (Q\xi)^2} + BG$$

The inverse of the values obtained for the OZ amplitudes ($I_{OZ}(0)$) are represented in Figure 1a. In the explored range of compositions, the amplitude increases with PS concentration and for a given sample, it increases with decreasing temperatures. The correlation length ξ also slightly increases with decreasing temperature (see Figure 1b). Within the uncertainties, the correlation length ξ has similar value independently of the labeling (dSBR/hPS or hSBR/dPS); in the well mixed samples, its values are around 5-10 Å. These results will be analyzed together with dielectric spectroscopy results on the same samples. Following the unified approach developed in our previous work [4], we will be able to determine the relevant length scale of segmental relaxation also in these blends where the PS component is extremely small, and compare it with existing results in the literature.

1. Colmenero,J., Arbe, A. (2007) Soft Matter 3, 1474.

2. Gambino, T., Alegria, A., Arbe, A., Colmenero, J., Malicki, N., Dronet, S., Schnell, B., Lohstroh, W., Nemkovki, K. (2018) Macromolecules 51, 6692-6706.

3. Gambino, T., Alegria, A., Arbe, A., Colmenero, J., Malicki, N., Dronet, S. (2020) Polymer 187, 122051.

4. Gambino, T., Shafqat, N., Alegria, A., Malicki, N., Dronet, S., Radulescu, A., Nemokovski, K., Arbe, A., Colmenero, J. (2020) Macromolecules 53, 7150-7160.