Artifacts in Light Scattering Experiments Using Opaque Scattering Screens on the Example of Spinodal Decomposition

Volker Abetz

Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Postfach 3980, 55099 Mainz, Germany

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Introduction. It is known that the nature of scattering screens as they are sometimes used in light scattering setups may influence the scattering pattern. This was shown for example by comparing the particle scattering patterns of monodisperse spheres as obtained by a Marata and a volume scattering screen.[1,2] It was found using the experimental setup described in ref 3 that at small scattering vectors q, i.e., $q < 2\ \mu m^{-1}$, a Marata screen yields scattering patterns which agree with the theoretical scattering pattern well. This limiting scattering vector was found in experiments using a laser wavelength of 633 nm and corresponds to a scattering angle of ca. 11°. Also volume scattering screens yield good results in this q-range, though the extrema are smeared out a little more as compared to the Marata screen. Such smearing can be tolerated when no sharp features in the scattering pattern are observed. However, while the data obtained with a volume scattering screen and the theoretical scattering pattern agree with each other still well at larger q-vectors ($q > 2\ \mu m^{-1}$), the intensity drops drastically in the case of the Marata screen and almost no intensity is observed at $q > 7\ \mu m^{-1}$, although scattering intensity exists in that region. This is due to the strongly anisotropic scattering characteristics of the Marata scattering screen, which scatters most of the incident light in the direction of the incident light, while the volume scattering screen distributes the incident light homogeneously in all directions. From this it follows that the relative intensity distribution of an angular-dependent light source (a scattering sample for example) is only correctly transformed into a direct image of the scattering pattern when a volume scattering screen is used, while in the case of the Marata scattering screen, this image depends on the angular position of the camera. This is schematically shown in Figure 1.

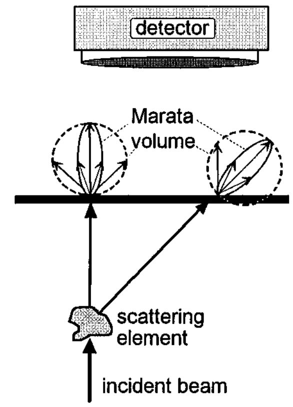

Figure 1. Scheme of scattering characteristics of a Marata and a volume scattering screen in a light scattering setup. The spheres and ellipses indicate the angular distribution of light intensity scattered by the different opaque screens.

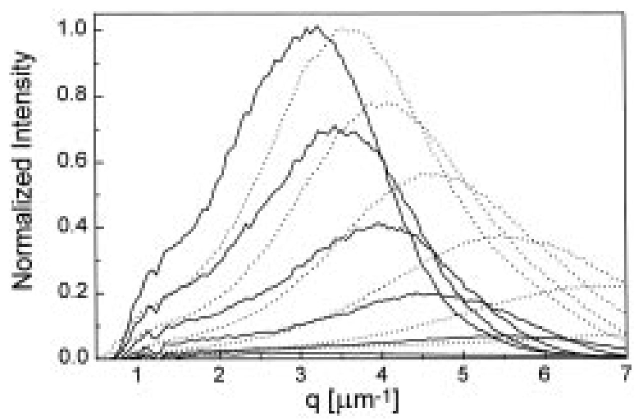

Figure 2. Light scattering intensity as a function of scattering vector at various times after a temperature jump from the single-phase region into the spinodal region (130 → 150 °C): 40, 60, 80, 100, 120, 140 min (from bottom to top). Volume scattering screen, dotted lines; Marata scattering screen, solid lines. Data are normalized to the highest peak in each data set, respectively.

Results and Discussion. Recently, results on spinodal decomposition of a polymer blend as obtained by the same small-angle light scattering setup using a Marata scattering screen were published in this journal.[3] During the early stages of spinodal decomposition, an almost temperature-independent position of the scattering maximum was found. As a consequence of this, the segmental interaction parameter would be apparently independent of temperature. This finding was associated with the rather small thickness of the samples and compared with other results.[4,5] Considering the strong damping behavior of the Marata scattering screen at larger q-vectors, it is obvious that a scattering maximum during a spinodal decomposition experiment can only appear at scattering vectors smaller than $8\ \mu m^{-1}$ and one never will find a scattering curve with an increasing intensity toward larger scattering vectors in the range of 7−8 μm^{-1}, i.e., curves with a maximum just beyond the experimental q-range.

In ref 3 it was further claimed that the interface thickness should increase with time during the later stages of spinodal decomposition, although usually a sharpening of the interface is observed due to the increasing concentration gradient between the different phases. The interface thickness was gained by a modified Porod plot, i.e., $\ln(I(q)\,q^4)$, versus q^2, where $I(q)$ is the scattering intensity at a scattering vector q. Although it was mentioned in the experimental part of ref 3 that the shape of scattering patterns is reliable only up to a scattering vector of $q = 3.5\ \mu m^{-1}$, the analysis of the modified Porod plot (ref 3, Figure 12) was obviously done in a scattering vector range above that critical value.

To demonstrate the problems arising from different scattering screens, Figure 2 shows scattering patterns of a blend from 50 wt % perdeuterated polystyrene and 50 wt % of poly(cyclohexyl acrylate[39 mol %]-*stat*-butyl methacrylate[61 mol %]) after a temperature jump into the spinodal region (from 130 to 150 °C), as obtained by using a Marata and a volume scattering screen with the same setup as in ref 3. The characterization of the polymers is given in Table 1. The thickness of the sample used here was similar to that of the samples studied in ref 3, and the sample was placed on a thin glass plate. Measurements at equal times after the temperature jump are compared with each other. While in the data obtained with the Marata scattering screen a maximum appears within the experimental q-range,

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Table 1. Characteristic Data of the Polymers

polymer	M_w (kg/mol)	M_n (kg/mol)	M_w/M_n
P(CHA$_{0.39}$-*stat*-BMA$_{0.61}$)	415[a]	192[b]	1.88[c]
PS-d_8	99[d]	92[d]	1.07[d]

[a] Light scattering (THF). [b] Membrane osmometry (toluene). [c] Gel permeation chromatography (THF, PMMA standard). [d] Gel permeation chromatography (THF, PS standard).

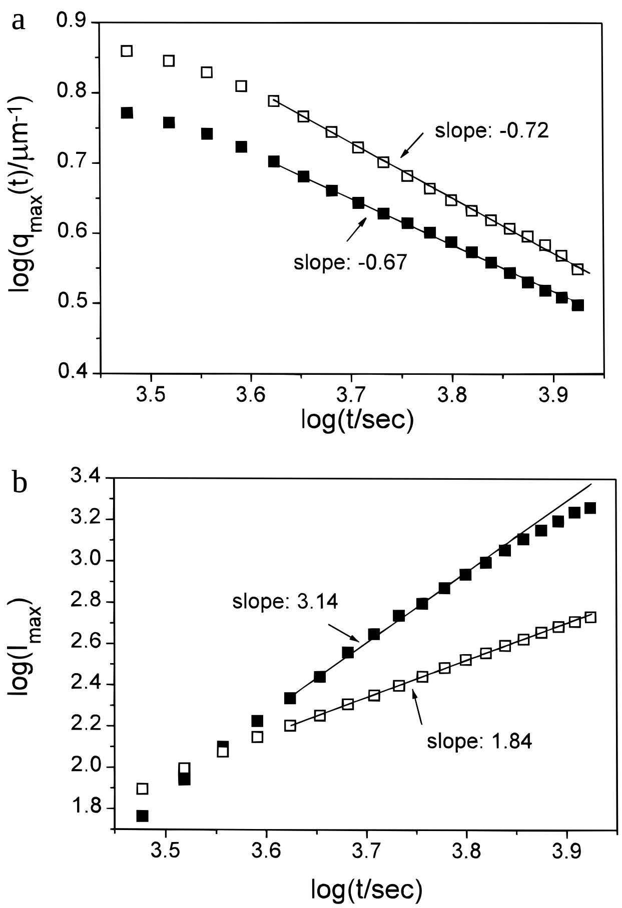

Figure 3. (a) Maximum position as a function of time for the experiment shown in Figure 2: Marata scattering screen (■); volume scattering screen (□). (b) Maximum intensity as a function of time for the experiment shown in Figure 2: Marata scattering screen (■); volume scattering screen (□).

the data obtained with the volume scattering screen clearly indicate a maximum outside the q-range covered by the experimental setup at the beginning of spinodal decomposition. Also the shape and the relative increase of the scattering curves are different for the two scattering screens. This is also shown in Figure 3a for the position of the scattering maximum, $q_{max}(t)$, and in Figure 3b for the maximum scattering intensity, $I_{max}(t)$, as functions of time in a double-logarithmic presentation. Such plots are used to determine the scaling exponents characterizing the later stages of spinodal decomposition. The scaling laws are as follows:[6−8]

$$q_{max}(t) \propto t^{-\alpha} \tag{1}$$

$$I_{max}(t) \propto t^{d\alpha} \tag{2}$$

with d being the dimension of the system. For intermediate stages, d is larger than the dimensionality of the system, while for late stages of spinodal decomposition d becomes identical with the dimensionality of the system. For the example shown in Figure 3a,b an intermediate stage of spinodal decomposition is found in the case of the Marata scattering screen ($d = 4.7$), while in the case of the volume scattering screen probably a late-stage behavior is determined with $d = 2.6$. This latter value indicates a dimensionality of the system between 2 and 3; i.e., the height of the thin sample becomes comparable to the domain size of the phases.

Conclusions. The use of Marata scattering screens to monitor light scattering patterns leads to erroneous results if the shape of scattering curves is discussed at scattering angles larger than ca. 11°. Structural features like Bragg peaks defining the periodicity length in the sample or the interface width of multiphase systems should not be determined with such a setup. Also the relative change of scattering intensities and Bragg peak positions with time in transient experiments is dependent on the kind of scattering screen. Comparisons of theoretical curves with measurements on monodisperse spheres indicate that volume scattering screens give better results.

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