A TIME-RESOLVED LOW-ANGLE LIGHT SCATTERING APPARATUS. APPLICATION TO PHASE SEPARATION PROBLEMS IN POLYMER SYSTEMS

Čestmír KOŇÁK[1,]*, Jaroslav HOLOUBEK[2] and Petr ŠTĚPÁNEK[3]

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic; e-mail: [1] konak@imc.cas.cz, [2] holou@imc.cas.cz, [3] stepan@imc.cas.cz

A time-resolved small-angle light scattering apparatus equipped with azimuthal integration by means of a conical lens or software analysis of scattering patterns detected with a CCD camera was developed. Averaging allows a significant reduction of the signal-to-noise ratio of scattered light and makes this technique suitable for investigation of phase separation kinetics. Examples of applications to time evolution of phase separation in concentrated statistical copolymer solutions and dissolution of phase-separated domains in polymer blends are given.

Keywords: Time-resolved low-angle light scattering; Conical lens; CCD camera; Phase separation; Copolymers; Blends; Polymer solutions.

Immiscibility is common in polymer systems[1]. The process of phase separation is initiated when the temperature or pressure of a copolymer melt or solution is changed and the polymer sample enters the multiphase region. The early stage of the phase separation (*e.g.*, nucleation) is conveniently examined by scattering experiments measuring the time evolution of the structure factor $S(q,t)$, which is the spatial Fourier transform of the polymer concentration or density correlation function[2]. Here, $q = (4\pi n/\lambda) \sin (\theta/2)$ is the magnitude of the scattering vector, λ is the wavelength of the incident radiation and θ is the scattering angle. Typically, small-angle X-ray and neutron scattering probe the distance scales from 5 to 200 nm while small-angle light scattering (SALS) probes length scales[2] from 0.5 to 100 μm. Since the characteristic size of phase-separated domains approaches or exceeds the wavelength of visible light, small-angle light scattering measurements ($\theta < 40°$) are often of interest for the investigation of phase separation problems.

The SALS is often realised with a laser as a light source for illumination. Lasers provide many advantages such as high intensity, parallel beam, and monochromatic light. On the other hand, the high coherence of laser light used for illumination is accompanied by the speckle effect, which decreases the signal-to-noise ratio of the scattered light intensity[3] measured by point-like detectors. This problem starts to be very important if the speckle dynamics is comparable with measuring times of SALS. Such a situation is commonly observed in time-resolved measurements of phase separation dynamics in melts, concentrated solutions and solid samples. A variety of techniques have been developed to solve this problem, based mainly on the spatial averaging of light collected in a light scattering experiment[4,5]. We have used two procedures to perform the spatial averaging: (i) optical integration by means of a conical lens and (ii) software azimuthal integration of scattering patterns detected with a CCD camera using a specially developed program.

TIME-RESOLVED SMALL-ANGLE LIGHT SCATTERING APPARATUS

Optical Integration by Mean of a Conical Lens

Optical integration of the scattered light by means of a conical lens[6] is schematically demonstrated in Fig. 1a. Light beams emerging from the scattering volume at different scattering angles are focused on the optical axis at different distances from the front of the lens. Thus, a unique transformation of scattering angles to axial distances from the centre of the lens occurs. For a given scattering angle, light from the full range of azimuthal angles $(0–2\pi)$ is collected by the conical lens and focused at a single point. The light scattering intensity integrated over all azimuthal angles can be measured as a function of scattering angle by moving a suitable light detector (a photomultiplier or a photodiode) along the line of optical axis of the conical lens. The angular resolution of the conical lens is determined by the size of circular aperture in front of the light detector. There are, of course, some limitations of the optical system regarding the range of scattering angles given by the cone angle, β, diameter of the conical lens, d, the refractive index of the glass, n, and the scanning length of the detector, l_s. If we take the parameters of our equipment, $\beta = 27°$, $d = 10$ cm, $n = 1.508$ and $l_s = 50$ cm, then the accessible range of light scattering angles is from 0 to 16°. In order to increase the range of scattering angles, a spherical lens ($f = 5$ cm) was interposed between the scattering volume and the conical lens. Our equipment enables measurements in the angular range 5–40°, which corre-

sponds to scattering vectors between $1.3 \cdot 10^{-3}$ and $1.02 \cdot 10^{-2}$ nm^{-1} when a He-Ne laser is used for illumination. The corresponding observable structure sizes are then *ca* 0.5–12 µm. The calibration curve, *i.e.*, a plot of the scattering vector magnitude, *q*, *vs* the detector distance from the lens, *l*, is shown in Fig. 2. The dependence is strongly non-linear especially for longer distances from the lens. To overcome the problem, thirty-eight non-equidistant measuring positions of the detector, *N*, were selected to get the quasi-linear calibration curve shown in Fig. 3. One step represents approximately 1° of scattering angle. The scanning of the intensity of scattered light with a photodiode is controlled by a computer which allows to vary the measurement speed in a wide range of times. The angular resolution is better than 0.5° in the whole measurement range of the apparatus. The time resolution of the apparatus is limited by maximal possible velocity of axial scans. If the integration time at each stop is 1 s, then we need about 1 min per scan. Since the angular resolution of the apparatus is strongly dependent on the detector position (increasing with increasing distance from
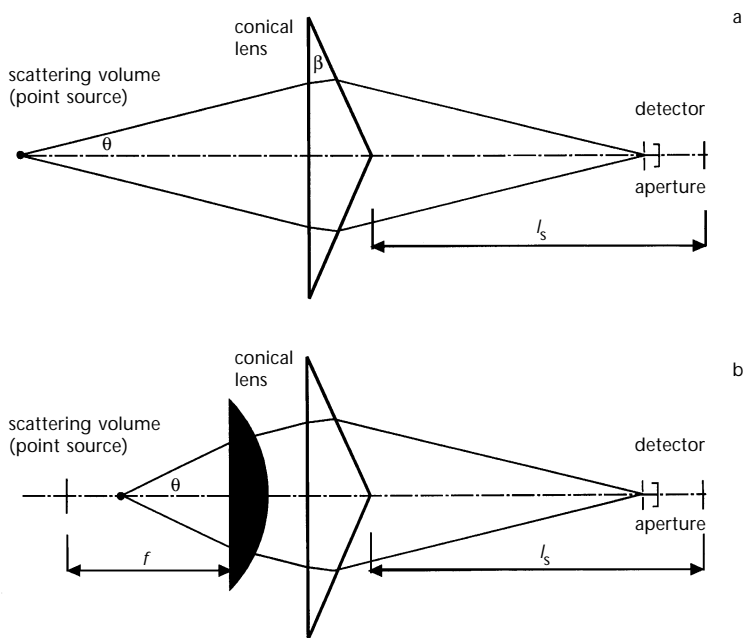

FIG. 1
Optical arrangement for conical lens; β is the cone angle, θ the scattering angle and l_s is the scanning length of the detector (a). Optical arrangement for conical lens using a spherical lens; *f* is the focal length of the spherical lens (b)

the lens), experimental data must be corrected to obtain the light intensity per unit solid angle. A suspension of small latex particles (r = 60 nm, c = 1.2 wt.%) with the known factor $S(q)$ was used for determination of the intensity correction. The concentration of latex particles was selected to minimise multiple scattering contribution. The correction function is shown in
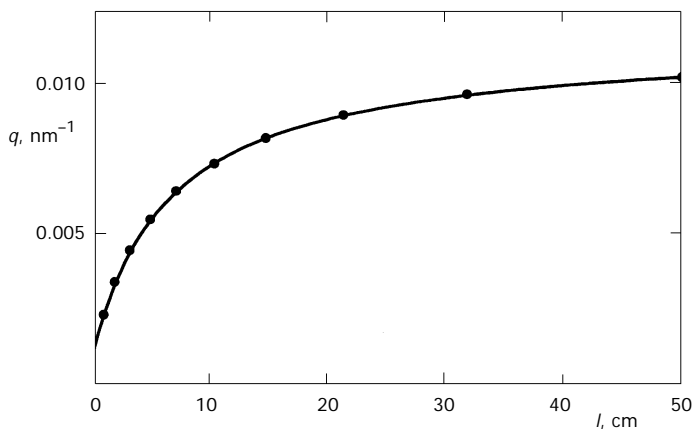

FIG. 2
Calibration curve: a plot of the scattering vector magnitude, q, *vs l*
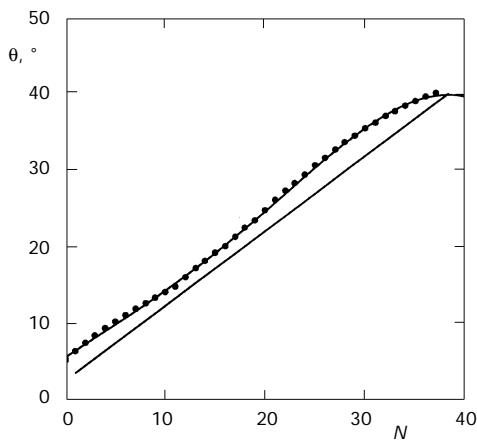

FIG. 3
Quasi-linear calibration curve for non-equidistant measuring positions, N

Fig. 4. The measured light scattering intensity should be multiplied by the function in Fig. 4 to obtain data normalised per unit space angle. Accuracy of intensity measurements is about 5% at $q^2 > 8 \cdot 10^{-5}$ nm^{-2} and smaller for $q^2 < 8 \cdot 10^{-5}$ nm^{-2}. Experimental data can be further analysed by software to evaluate, *e.g.*, sizes of phase-separated domains.

Since the light scattering intensity from phase-separated samples is high, only standard thin quartz cells (Hellma 124-QS, 0.1 and 0.2 mm) were used for the measurement. Such cells are not suitable for measurement of dilute polymer solutions but can be used for strongly scattering colloid suspensions.

Software Azimuthal Averaging of Scattering Patterns Detected with a CCD Camera

In these experiments, the light scattered from the sample at small angles is visualised on a screen and recorded with a CCD camera. The range of scattering angles is given by the distance between the scattering volume and the screen and can be fixed in the range 0.5–45°. Complete images with 600 × 400 pixels are transferred *via* a frame grabber into a PC with a maximum speed of 0.7 s per image. The CCD camera reading is controlled by a computer, which allows varying the measurement speed in a wide range of
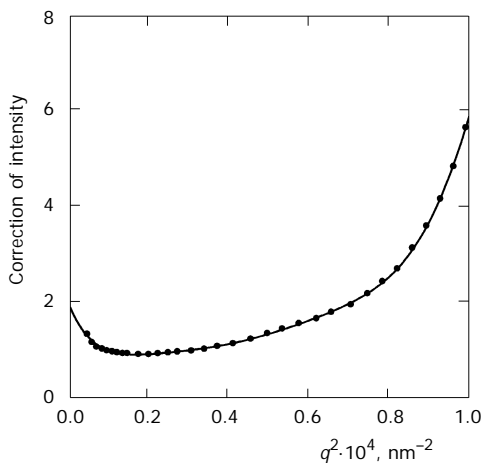

Fig. 4
Correction function for the scattered light intensity

times. Higher rates are also possible using a videorecorder at a fixed reading frequency of 24 images per second. Image identification is recorded on videotape in the space between frames and the images are analysed later on. Scattering patterns are analysed using a specially developed program which enables averaging of the intensity in a set of selected concentric spherical shells centred on the optical axis of the apparatus. In such a way, azimuthal averaging of the light scattering intensity is performed.

EXAMPLES OF APPLICATIONS

Latex Particles (Conical Lens)

In order to test the apparatus, a suspension of latex particles with the radius $r = 0.6$ μm ($c \approx 0.05$ wt.%) was used for measurements with conical lens. The angular range of θ was 4–13° (set up in Fig. 1a). The light scattering intensity, I_s, was collected for 240 positions of the detector. The reciprocal value of I_s is plotted as a function of q^2 in Fig. 5. The data were analysed using a model of solid spheres for $q^2 \leq 1/r^2$. As a result, we have obtained the value 0.61 ± 0.05 μm for the radius of particles, in a good agreement with the results given by the producer (Polysciences). An increase in I_s^{-1} at higher q^2 values is due to the Mie effect.
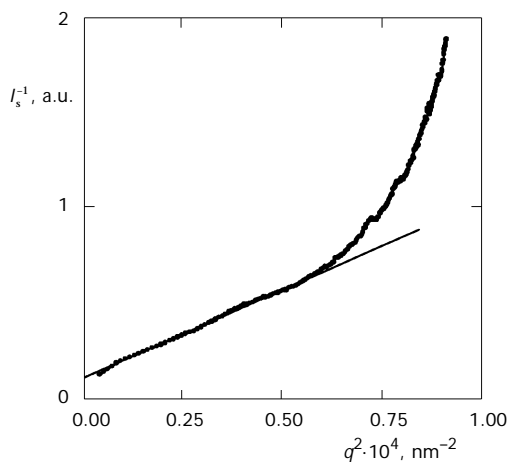

FIG. 5
The reciprocal value of the scattered light intensity I_s plotted as a function of q^2 for latex particles with the radius of 0.6 μm

Time Evolution of Phase Separation in a Statistical Styrene and Methyl Methacrylate Copolymer (Conical Lens)

The phase separation kinetics was studied on statistical copolymers of styrene (S) and methyl methacrylate (MMA) having composition 20 vol.% of styrene and 80 vol.% of methyl methacrylate prepared by radical copolymerization[7]. The molecular parameters of the copolymer obtained by GPC are $M_w = 2.9 \cdot 10^5$, $M_w/M_n = 1.8$. Composition of samples was selected to provide the maximum chemical heterogeneity[8] $\sigma^2 \approx 2 \cdot 10^{-3}$. The samples were softened with 30 vol.% of dibutyl phthalate to decrease the glass transition temperature from 110 to 40 °C. The phase separation was observed on cooling at about 95 °C. The results of SALS measurements on the statistical S/MMA copolymer are shown in Fig. 6 where time evolution of I_s is plotted as a function of q. Experimental data were taken at a variety of delays, t_d, after a fast temperature jump from 105 °C (above the phase separation temperature) to 60 °C in the multiphase region (the duration of phase separation). Light scattering experiments have revealed the occurrence of a conspicuous, unexpected maximum at q_{max} in the scattering profiles. The position of this maximum is virtually independent of time but the light scattering intensity I_s^m at q_{max} increases linearly with t_d. The occurrence of the maximum arises probably from a liquid-like order between the phase-
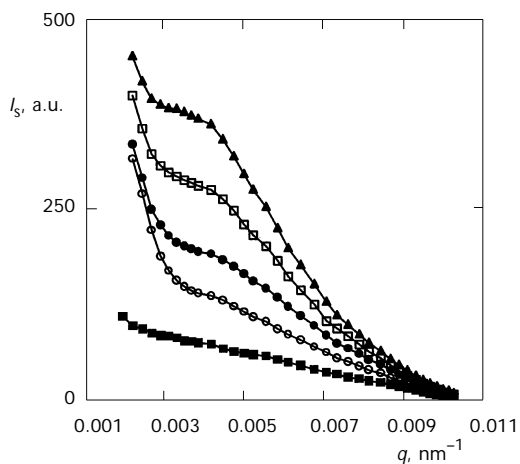

FIG. 6
Time evolution of light scattering intensity profiles for a statistical copolymer of styrene and methyl methacrylate after a fast temperature jump from 105 °C (above the phase-separation temperature) to 60 °C in the multiphase region. The duration of the phase separation, t_d (in min): ■ 2, ○ 6, ● 20, ❑ 60, ▲ 120

separated domains. The size of these domains, ζ, estimated from a monotonic background light scattering, is independent of t_d ($\zeta \approx 220$ nm). Thus, the domain formation should be a very fast process. The near-invariance in position of I_s^m implies that the distance between ordered domains is roughly independent of t_d. The hard-sphere interaction radius of domains estimated from q_{max} ranges from 1.1 (after 6 min) to 1.3 μm (after 120 min). On the other hand, an increase in I_s^m with time implies that the volume fraction of the ordered liquid-like structure increases with time. Thus, the domain ordering is a slow process which can be investigated using the SALS apparatus used The phase separation is probably driven by the incompatibility of copolymer chains due to the chemical composition inhomogeneity[9]. Full analysis of data is in progress.

Time Evolution of Dissolution in PS/PMMA/PS-b-PMMA Blends (CCD Camera)[10]

We present here an example of dissolution study in PS/PMMA (30/70 by wt.%) blends with 2 wt.% of PS-b-PMMA copolymer for an annealing temperature of 160 °C. The polymers used are PS with $M_w = 8.9 \cdot 10^4$ (Polysciences), PMMA with $M_w = 7.4 \cdot 10^4$ (Pressure Chem.) and symmetri-
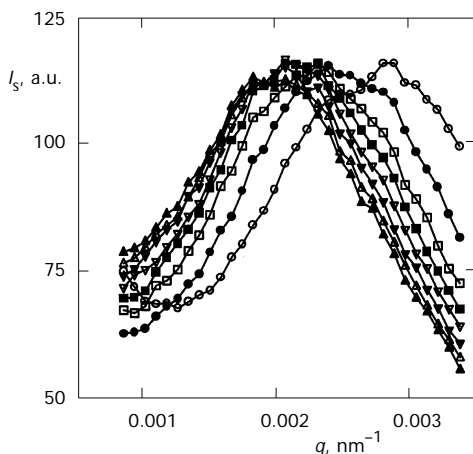

FIG. 7

Experimental time evolution of intensity profiles for PS/PMMA/PS-b-PMMA blends. Eight intensity profiles with 8-min time delay between measurements were selected for demonstration of the results measured with CCD camera at 160 °C. The first measurements (open circles) were taken 1.5 min after attaining the annealing temperature. The last measurement is marked with stand-up solid triangles

cal PS-*b*-PMMA copolymer with $M_w = 8.0 \cdot 10^4$ (Polysciences). The selected eight intensity profiles taken with 8-min delays between measurements are shown in Fig. 7 where the q-dependence of I_s is plotted. The initial morphology of samples used for dissolution investigation is a co-continuous structure in the two-phase region of blends as stated from a SEM image. Contrary to statistical copolymers, q_{max} decreases with increasing dissolution time[11]. Since the size scale of the morphology is related to $2\pi/q_{max}$, we can conclude that the characteristic size of the structure increases during annealing. Thus, the coarsening of the co-continuous structure of the blend is observed in agreement with theoretical predictions[11]. The intensity I_s^m is almost independent of the annealing time. This means that the structure of the blend does not substantially melt under the experimental conditions used.

CONCLUSIONS

A time-resolved light scattering apparatus has been constructed for investigation of phase separation problems in polymer systems. Since the speckle effect decreases the signal-to-noise ratio of the scattered light intensity as measured by point-like detectors, two procedures performing the azimuthal averaging of the scattered light intensity were used: (i) optical integration by means of a conical lens and (ii) software analysis of scattering patterns detected with a CCD camera using a specially developed program. A substantial increase in the signal-to-noise ratio is thus achieved. An important advantage of both the systems used is their much lower price in comparison with commercially available instruments. The use of the apparatus for investigation of a time evolution of phase separation and dissolution of phase-separated domains in concentrated solutions of statistical copolymers and polymer blends is demonstrated.

REFERENCES

1. Flory P.: *Principles of Polymer Chemistry*. Cornell University Press, Ithaca 1953.
2. Mallamace F., Micali N. in: *Light Scattering Principles and Development* (W. Brown, Ed.), Chap. 12, p. 381. Clarendon Press, Oxford 1996.
3. Holoubek J., Krug H.: *Makromol. Chem., Macromol. Symp.* **1988**, *18*, 123.
4. Ferri F.: *Rev. Sci. Instrum.* **1997**, *68*, 2265.

5. Lehnern D., Kellner G., Schnablegger H., Glatter O.: *J. Colloid Interface Sci.* **1998**, *201, 34*.
6. Pine D. J.: *Rev. Sci. Instrum.* **1984**, *55*, 856.
7. Dvořánek L., Koňák Č., Neuhousl T., Macková L., Šorm M.: *Angew. Makromol. Chem.* **1992**, *194*, 149.
8. Stejskal J., Kratochvíl P.: *J. Appl. Polym. Sci.* **1978**, *22*, 2925.
9. Koňák Č., Bansil R.: *Polymer* **1998**, *39, 6179*.
10. Holoubek J.: *Macromol. Symp.* **2000**, *162*, 307.
11. Akcasu A. Z., Klein R.: *Macromolecules* **1993**, *26*, 1429.