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Small angle light backscattering of polymer blends: 1. Multiple scattering

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A novel apparatus and the principle are presented. The small angle light backscattering is used to measure the morphology of polymer blends. In spite of the absorption by the sample of incident light, the scattering from a rough surface and a thick sample are discussed. The backscattering of the sample with a rough surface mainly comes from diffusion (random reflection), which obeys the diffusion speckle theory, and that of the sample with a smooth surface comes from density fluctuation in the internal medium, which corresponds to the Rayleigh scattering theory. The random scattering from the surface can be ignored when the roughness of surface is no more than $0.237\,\mu\mathrm{m}$. For the thick sample which has a smooth surface, the experimental result shows that the backscattering is almost independent of the thickness of the sample. © 1997 Elsevier Science Ltd.

INTRODUCTION

Light scattering techniques which give information on optical properties have been proven to be useful for obtaining deep insights into the molecular and structural parameters of polymers. These techniques are especially useful for polymeric systems with supermolecular structures in solutions, liquids and solids. The main advantage is that the measurement does not damage or interrupt the system.

Since light scattering was first applied to polymers[1], small angle light scattering (SALS) was successfully applied to solid polymers and their blends in 1949[2]. Light scattering techniques have developed extensively. A serial research by light scattering reveals the relationship between multistructure and heterogeneity of the polymer and its blend[3–7]. Elastic light scattering is a convenient and valid method. The elastic scattered intensity generally depends on density, concentration, and orientation fluctuations and their spatial correlation[8]. For polymer solutions, liquid crystals and mixtures, the latter two fluctuations dominate the former[8–12]. For traditional SALS, the central speckle usually covers the scattering information with thin samples and the multiple scattering complicates the process of scattering information with thick samples.

This paper presents a new technique, which has experimental differences from SALS. Small angle light backscattering (SALBS) is the scattering part in reverse. It is independent of the central speckle. Although SALBS has never been reported or investigated previously, it is believed to give direct information on the formation, dissolution and deformation of molecular aggregates.

Therefore, this technique is believed to be important and must be thoroughly explored in the future. In this paper we describe an apparatus used for investigating SALBS and give preliminary experimental results to demonstrate its possible use in studying the condition of the sample and in the fundamental theory of amorphous polymers. Further discussion of SALBS on crystal, solution, liquid crystal and rheological properties are beyond the scope of this paper, and will be presented in the future.

THEORY

Backscattering is the part of elastic scattering resulting from the medium. The scattering angle $\theta < 90°$ is forward scattering and $\theta > 90°$ is backscattering. It is assumed that there is no energy loss accompanying the scattering and that the scattering medium is sphere symmetric. Debye and Bueche[2] applied statistical theory to heterogeneous solid scattering and proposed that, in the range of small scattering angles, the scattering light is described by

$$I_{(\mathbf{h})} = K' \int_0^\infty \gamma_{(\mathrm{r})} \frac{\sin(\mathbf{hr})}{hr} r^2 \mathrm{d}r \qquad (1)$$

when $\gamma_{(\mathrm{r})}$ is a correlation function corresponding to fluctuation of the medium. Generally, for polymers:

$$\gamma_{(\mathrm{r})} = \exp(-r/a_{\mathrm{c}}) \qquad (2)$$

a_{c} is the correlation distance and $h = (4\pi/\lambda)\sin(\theta/2)$ is a scattering vector. Substituting equation (2) into equation (1) and integrating, we can obtain correlation distance a_{c} as follows:

$$\frac{1}{[I_{(h)}]^{1/2}} = \frac{1}{(k''a_{\mathrm{c}}^{1/2})^3}(1 + h^2 a_{\mathrm{c}}^2) \qquad (3)$$

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When $r = 0$, $\gamma_{(r)} = 1$, we obtain integral area Q:

$$\overline{\eta^2} = K' \int_0^\infty I_{(h)} h^2 \mathrm{d}h \tag{4}$$

$$Q = \int_0^\infty I_{(h)} h^2 \mathrm{d}h \tag{5}$$

The parameter a_c describes the distance the heterogeneity expands in the scattering medium, and Q is the intensity of heterogeneity of the scattering object.

EXPERIMENTAL

The backscattering apparatus was constructed by Tianjin University, Tianjin, P.R. China. *Figure 1* shows a schematic diagram of the apparatus. The system can measure polymers and their blends in crystal and amorphous solid, liquid crystal, melt and solution states. The SALBS measurement consists of eight parts. A He–Ne laser (L) is used as an incident light source ($\lambda_0 = 6328$ Å). The parallel beam is filtered by a filter (F) to change the intensity of the incident light. The polarization direction of the laser beam can be varied by rotating a polarizer (P_1). The incident beam is reflected by a half-reflecting and half-transmitting mirror (M) and irradiates the sample (S). The backscattered light from the sample is passed through the mirror (M), optical system (O) and the polarization analyser and is detected by a CCD connected to a computer. The optical system is specially designed not to broaden the laser beam. Thus, the back reflected element depends only on the diameter of the laser beam, which covers a small angle ($< 0.5°$). The scattering-angular range covered by the present apparatus is typically from 1 to 15°.

The polymer samples are commercial—both polystyrene (PS) and ethylpropylene rubber (EPDM) are from Yanshan Chemical Industry Company. As a simple amorphous system, PS with EPDM has general incompatibility[13]. The two phases of their blend are easy to separate and there is no third phase. As a preliminary result to demonstrate the prospects of SALBS, we present here optical investigations of PS/EPDM with a weight ratio of 4/1.

The blend was mixed in a mixer for 6 min at 180°C. The mixed polymer blend was model pressed into a 1 mm film. The surface of the samples were processed as set out in *Table 1* for investigating the effect of the surface on the scattering. The roughness of the samples was measured by interference microscope (MNN-4, Shanghai) and
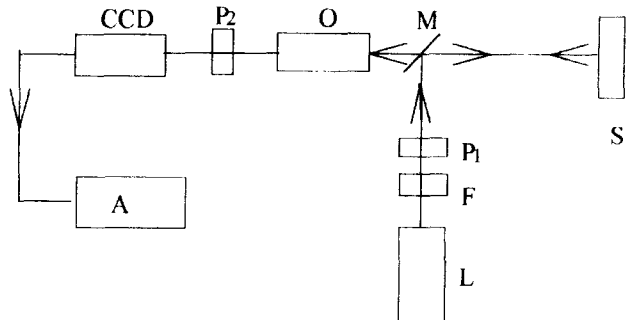

Figure 1 Schematic representation of the backscattering apparatus: (L) He–Ne laser; (F) density filter; (P_1, P_2) polaroid to change the polarization direction; (M) half-transparent reflective mirror; (S) sample; (O) optical system; (A) analysis system

Table 1 Surface processing of the sample [PS : EPDM, 4/1]

Sample number	Surface process	Roughness (μm)
S11	Covered with glass	Smooth
S12	Smoothed 20 min by smoother	0.237
S13	Smoothed 10 min by smoother	0.645
S14	Smoothed by rough cloth	4.582
S15	Smoothed by sand paper	8.613

Table 2 Different thickness samples for [PS : EPDM, 4/1]

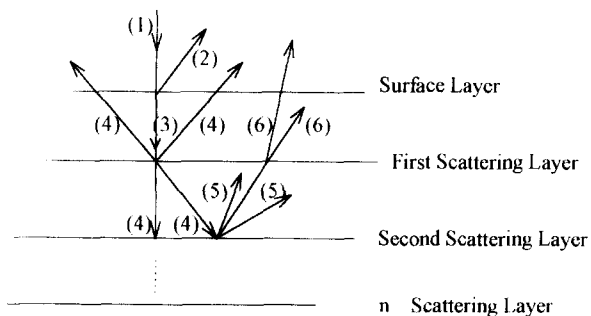| Sample number	S21	S22	S23	S24	S25	S26	S27
Thickness (mm)	0.023	0.076	0.132	0.287	0.325	0.567	1.084

Figure 2 Diagram of multiple scattering

light cross-section microscope (Ziess, Germany). The other samples were pressed into different thicknesses (*Table 2*) and covered with glass at 180°C in order to obtain smooth surfaces. These samples were used to study the multiple backscattering from samples of different thickness.

RESULT AND DISCUSSION

The diagram of multiple scattering is shown in *Figure 2*. According to the effect of the sample on the incident light, the sample can be divided into a surface layer, a first scattering layer, a second scattering layer, etc. Because the incident light first impinges on the surface of the sample the first scattering comes from the surface (random reflection) of the medium. The second one comes from the first scattering layer (because of the internal heterogeneity) and the third in turn. It shows that the surface is the main barrier to detecting the internal scattering. When the surface is smooth enough, such as when covered with glass, the surface random reflection can be ignored and we can obtain directly the internal scattering.

Figure 3 shows the spectra of backscattering light intensity *versus* scattering angle of samples with different surface processes. The sample number in *Figure 3* corresponds to the number in *Table 1*. The scattering light intensity changes with different rough surfaces. The curve S15 (*Figure 3*) is typical of diffusion caused by a rough surface. The scattering light intensity curve (*versus* scattering angle) obeys diffusing speckle theory[14,15]. According to the simple model of Cheng, one can calculate the random reflecting light distributing under different surface roughness conditions as in *Figure 4*. Comparing the scattering curves and the random reflecting curves (dashed lines) in *Figure 5*, one can find that the scattering curve S15 corresponds to the
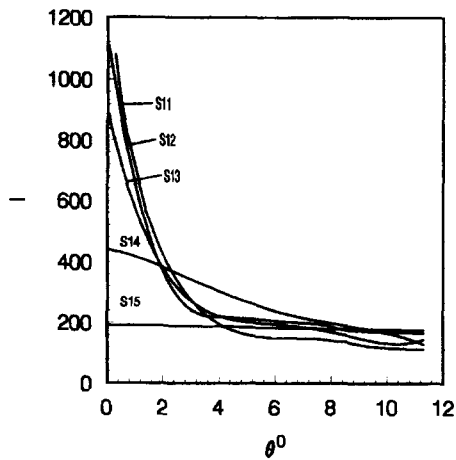
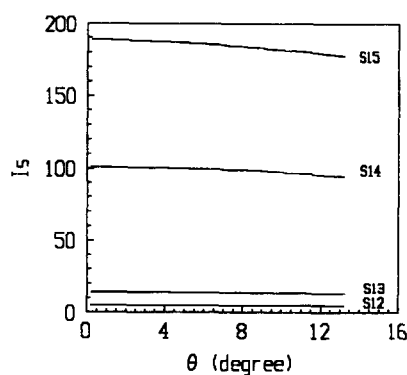**Figure 3**   Scattering spectra of different rough surfaces

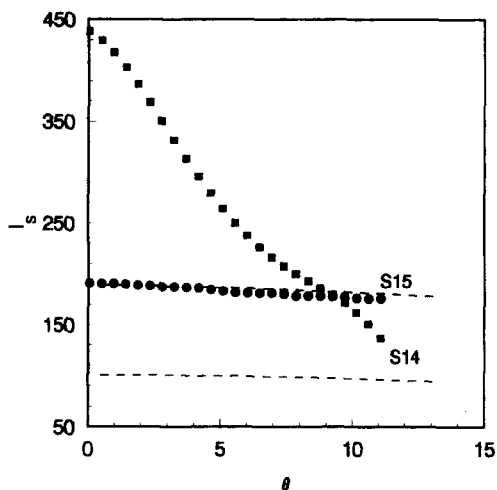**Figure 4**   Random reflecting light from Cheng's theory with different surface roughnesses

Figure 5   Scattering curve and corresponding random reflecting curve

Table 3   Integral constant changes with different surface roughnesses

Sample number	Surface roughness (μm)	Total integral area (Q)	Integral area (Q) from Cheng Lu theory	a_c (μm)
S11	Smooth	344	—	1.95
S12	0.237	403	1.90	2.00
S13	0.645	461	5.14	1.67
S14	4.582	482	297.4	—
S15	8.613	445	458.6	—

angle and the reverse for a large scattering angle. This is dependent on both the Rayleigh scattering theory and diffusion theory, which tends to make an extensive distribution in the range $0°-90°$. The diffusing speckle theory is ideal, but it is not possible to process and obtain the information on the internal structure from curves S15 and S14 because the total light intensity is not a simple addition of surface random reflection and internal scattering.

The curves S12 and S13 correspond to 0.237 and 0.645 μm surface roughnesses, respectively. The scattering mainly comes from the heterogeneity internal sample and the effect from surface is very low (*Figure 4*). *Table 3* shows the integral area Q changing with the varying surface roughness and the integral area from only random reflection. The change is mainly caused by the surface. One cannot obtain the pure internal scattering information by means of subtracting random reflecting light from total scattering light. The effect of the surface can be ignored when the surface is smooth enough, as when the roughness is no more than 0.24 μm.

The special condition is curve S11 (*Figure 3*) with a surface covered by glass. The main difference between curves S11 and S12 is that the scattering intensity of S11 is much stronger in the range $0°-0.2°$ scattering angle and less in the large scattering angle than that of S12. It is because the mirror backreflection of glass increases the small angle intensity and decreases the intensity of incident light impinging on the sample. Furthermore, because of the refractive index difference between glass and the sample, the effect of the interface between glass and sample is unavoidable. The light scattering of the sample covered by glass does not provide the best internal structure information. It is reasonable to consider S12 as the best scattering profile.

Assuming that the backscattering curves correspond to the Debye theory [equation (1)] and the correlation function is of the same type as equation (2), according to equation (3), we obtain the correlation distance as shown in *Figure 6*. In the small angle range the linear relationship corresponds rigidly and the structural parameter is shown in *Table 3*. That is to say the Debye theory is appropriate for small angle light backscattering.

Figures 7 and *8* show the backscattering light intensity under varying thicknesses. The change is small and random. For a smooth surface, the diffusion from the surface can be ignored and one can obtain the scattering light almost from the internal medium. Excluding the surface layer, for the multiple scattering shown in *Figure 2*, the first scattering is represented by line (4), the second one by line (5) and the third one by line (6). The scattering received comes from the addition of the first one (line 4), the third one (line 6), the fifth, etc. The scattering light is independent of the sample thickness,
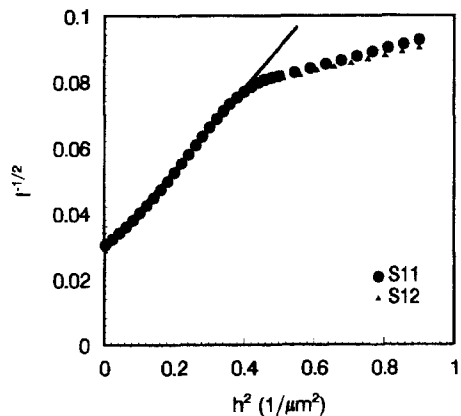
theoretical value (S15 dashed line) very well, which shows that the scattering from the surface of 8.613 μm roughness is almost from the random reflection of the surface. The deviation is because of the small internal scattering. The curve S14 is very different from the curve S15. The scattering intensity comes from both the random reflecting of the rough surface and the heterogeneous internal structure, but the surface reflecting (S14 dashed line) is much smaller than that of 8.613 μm roughness surface (S15 dashed line). It is typical of multiple scattering. The less the surface roughness is, the more intensive the scattering is for a small scattering

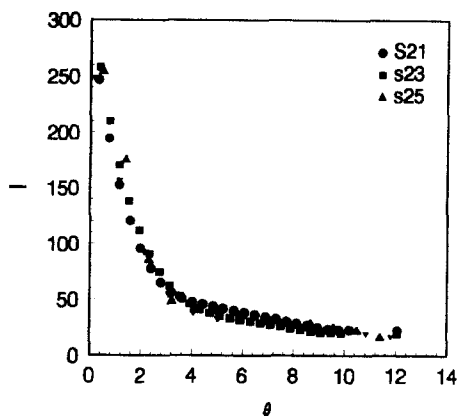**Figure 6** Ln(I) *versus* h^2 diagram for correlation distance

Figure 7 Backscattering intensity distribution *versus* scattering angle for different thicknesses (θ scattering)
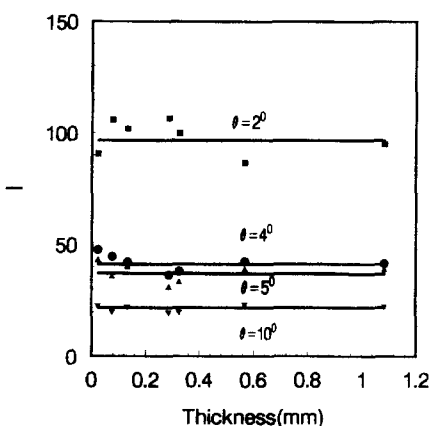

Figure 8 Backscattering intensity with different thicknesses (θ scattering)

which indicates the third and after scattering is much smaller than the first scattering.

For forward scattering, the multiple scattering from the thickness of medium usually becomes diffusive. In order to avoid the effect of multiple scattering, it is important to prepare a very thin sample. If the material has a high viscosity and cannot be made thin enough, a revision must be made[16]. It is the advantage of back-scattering that the thickness of the sample has almost no effect on the information received.

The corresponding structural parameters are calculated according to equations (3) and (5) as shown in *Figure 9*. For a sample made of the material PS : EPDM
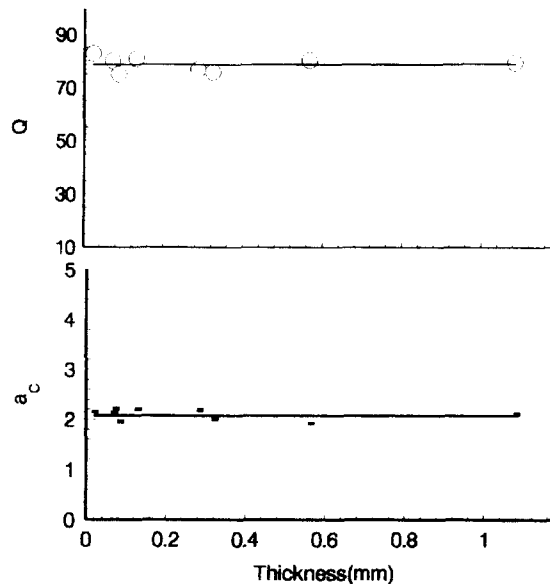

Figure 9 Structural parameters kept constant with various thicknesses

(4/1, w/w), the structural parameters undergo a small fluctuation because of the hetero-distribution of the two-phase structure. The thickness of the sample has hardly any effect on the scattering information.

CONCLUSIONS

The SALBS method is a better elastic light scattering technique than traditional SALS in investigating the two-phase morphology of polymer blends. When the surface roughness is no more than 0.237 μm, the surface diffusion does not interrupt detection of the scattering coming from the internal medium. A glass cover on the surface of the sample has a great effect on the scattering light distribution because of the difference in the refractive index between glass and the scattering medium. For a smooth surface (roughness < 0.237 μm), the thickness of the sample hardly affects the scattering information.

ACKNOWLEDGEMENT

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