MOLECULAR AGGREGATION IN OPTICAL GLASSES AS REVEALED BY LIGHT-SCATTERING

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1. *Introduction*

WHILE making a comparative study of the scattering of light in optical glasses with the incident light in different states of polarisation, Krishnan (1936) found that the depolarisation factors ρ_u and ρ_v corresponding to incident unpolarised light and light polarised with vibrations vertical respectively, were of the same order of magnitude as those usually observed in ordinary gases. On the other hand, when the incident light was polarised with vibrations horizontal, the depolarisation factor ρ_h instead of being equal to 1 as in the case of a gas or a liquid, was less than 1 as in the case of colloids containing particles not small compared with the wave-length of light. This anomalous depolarisation was explained by Krishnan as due to the existence of molecular aggregates in glasses. The actual magnitude of the effect is rather small and hence it is difficult to observe visually whereas it is easily seen with many ordinary colloids. The observation of the effect is also rendered more difficult by reason of the feeble intensity of scattering when the incident beam is polarised with the vibrations horizontal and by the weak fluorescence exhibited by the glasses. Krishnan (1938) therefore, devised an objective method based on photographic photometry for demonstrating the reversal of polarisation in optical glasses. In this method the transversely scattered light is photographed through a double-image prism using incident polarised light. Photographs of the two tracks were taken on the same negative for different orientations of the Nicol (polarising the incident beam) about the mean horizontal position. Microphotometric records of the negatives published in his paper show clearly the reversal of polarisation when the incident beam is polarised with vibrations horizontal.

It is well known that the light scattered by any medium whose elements of heterogeneity are not small compared with the wave-length of light, will be elliptically polarised when the incident beam is linearly polarised in a direction oblique to the plane of scattering. Elliptic polarisation has been observed by Hariharan (1942) in the light scattered by liquid mixtures very near the critical solution temperature, in which molecular clusters of appreciable size exist. The detection of elliptic polarisation in the light scattered by optical glasses under similar conditions would give us an entirely independent and conclusive evidence for the presence of molecular aggregates in such media. It is the object of this paper to present such evidence.

2. *Details of the Experiment*

The new technique for the study of light-scattering developed by Sir C. V. Raman (1941) has been used with success in the present investigation. This new method is based upon the use of a Nicol for polarising the incident beam in any desired azimuth and of a Babinet Compensator for observing the transversely scattered light. It enables one to demonstrate the reversal of polarisation or anomalous depolarisation and also to detect the existence of an elliptic polarisation in the scattered light.

The optical glasses used for the present study were the same specimens with which Krishnan (1936) carried out his investigations. These glasses were absolutely free from strains and did not show any measurable birefringence. Of the seventeen glasses only nine were selected for the present investigation. Their serial numbers were 1, 3, 4, 5, 6, 7, 8, 9 and 16.

Sunlight was reflected into a dark cabin by means of a heliostat and focussed by a Dallmeyer photographic lens of variable aperture. A rectangular glass cell containing a concentrated solution of alum was kept close to the lens in order to cut off the heat rays. A Nicol mounted on a graduated disc was placed in the path of the incident light before it entered the optical glass under investigation which was placed inside a wooden box. By rotating the Nicol the incident beam could be polarised with the direction of vibration inclined at any desired angle with the vertical. The specimen of optical glass to be examined was suitably blackened on the outside excepting for three windows, one for the entrance of light, one for its exit and the third for the observation of the transversely scattered light. To view the light transversely scattered by the specimen, a Babinet compensator was placed with its principal plane inclined at 45° to the plane of observation. The scattered light then passed through another Nicol oriented in such a manner as to transmit vibrations which had their electric vector horizontal. An eye-piece was used for making visual observations. The eye-piece was removed and substituted by a camera for taking photographs of the pattern of fringes in the field of vision.

3. *Sources of Error*

The main source of error in the present experiment is the presence of inclusions or specks inside the glass, which give rise to an intense polarised scattering. A preliminary survey was made of the seventeen optical glasses available in this Laboratory. A strong beam of sunlight was focussed into the glass prism and the track inside was examined visually along the direction of the incident beam. Any speck or inclusion of colloidal dimensions would give rise to an intense and localised forward scattering and would thus make itself visible. Only those glasses were selected for the present investigation inside which the scattered track was of uniform intensity and colour throughout the entire section of the specimen.

Another source of error is the weak fluorescence exhibited by the glasses. As was pointed out by Krishnan (1936), in order to eliminate the effect of fluorescence completely it is necessary to use an orange filter in the path of the incident beam. With the orange filter the intensity of scattering would be considerably reduced with the result that it might not be possible to photograph the fringe system within a reasonable time, especially when the incident light is polarised with vibrations horizontal. Therefore, in the present investigation a blue filter was used in the path of the scattered light. The width of the transmission band of the filter used was about 500 A.U. With this filter it was found that the vertical and horizontal component of the scattered light were almost of the same colour in all the glasses.

A third source of error is the parasitic illumination. This was avoided by eliminating all extraneous light other than that passing through the glass. A series of diaphragms and screens in the path of the incident beam cut off all parasitic light and there were similar diaphragms on the observation side.

To avoid errors arising from the finite angle of convergence of the incident beam, the aperture of the condensing lens was kept very small.

4. *Results*

The following general features were observed in all the glasses when the plane of polarisation of the incident beam was rotated. When the incident light was polarised with its vibrations vertical, the fringes in the Babinet compensator appeared very brightly in the field of vision. The compensator used was of the fixed type and was provided with a vertical cross-wire in the field of vision. The cross-wire appeared on the central dark band, indicating thereby that the scattered light which was partially polarised under such conditions, contained an excess of vertical component. As the Nicol polarising the incident beam was slowly rotated, the visibility of the fringes as well as the intensity of the pattern decreased progressively. At a particular inclination of the plane of polarisation of the incident beam, the fringes ceased to be visible and the field of vision was uniformly illuminated. For this setting of the Nicol in the path of the incident beam, the vertical and horizontal components of the scattered light were of equal intensity, *i.e.*, the depolarisation factor ρ_θ was equal to 1. θ is the inclination of the plane of polarisation of the incident beam to the vertical. The value of θ for which ρ_θ is equal to 1 can be calculated, using Krishnan's formula* (1939).

$$\rho_\theta = (1 + \tan^2\theta / \rho_h) / (\tan^2\theta + 1/\rho_v). \tag{1}$$

The observed value of θ for which the fringes disappeared, was in reasonable agreement with the calculated value.

Long before the fringe system disappeared, it was found that the pattern had shifted laterally and the cross-wire instead of appearing at the centre of the central dark band, appeared to have shifted towards the next bright band. The shift increased gradually as the polarising Nicol was rotated. Finally when the incident beam was polarised with vibrations horizontal, the cross-wire appeared at the centre of a bright band, showing thereby that the scattered light under such conditions was partially polarised with an excess of horizontal component, *i.e.*, ρ_h was less than 1. The existence of the anomalous depolarisation in glasses is thus indisputably established. For those settings of the polarising Nicol for which the cross-wire appeared neither at the centre of a bright nor at the centre of a dark band, but at some intermediate position, the transversely scattered light was a mixture of unpolarised and elliptically polarised light. On rotating the polarising Nicol further through 90°, the features described above appeared in the reverse order. Typical photographs showing the general features of the phenomenon are reproduced in the accompanying plate.

In order to measure the phase difference of the component vibrations in the elliptically polarised scattered light, the following procedure was adopted. The eye-piece used for visual observation was removed and the scattered light as seen through the compensator and the analysing Nicol was photographed. From the photograph the position of the cross-wire in relation to the nearest dark band was noted. Assuming the phase difference to be equal to π corresponding to a shift of the cross-wire from the dark fringe to the next bright fringe, the phase difference between the two components of the scattered light corresponding to this particular position of the cross-wire was evaluated. In this way the values of the phase difference for the various glasses for a series of orientations of the polarising Nicol were determined. The results obtained with glasses Nos. 1 and 5 are graphically represented in Fig. 1.

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* Perrin (1942) has since shown that Krishnan's formula must be true for any symmetrical medium.

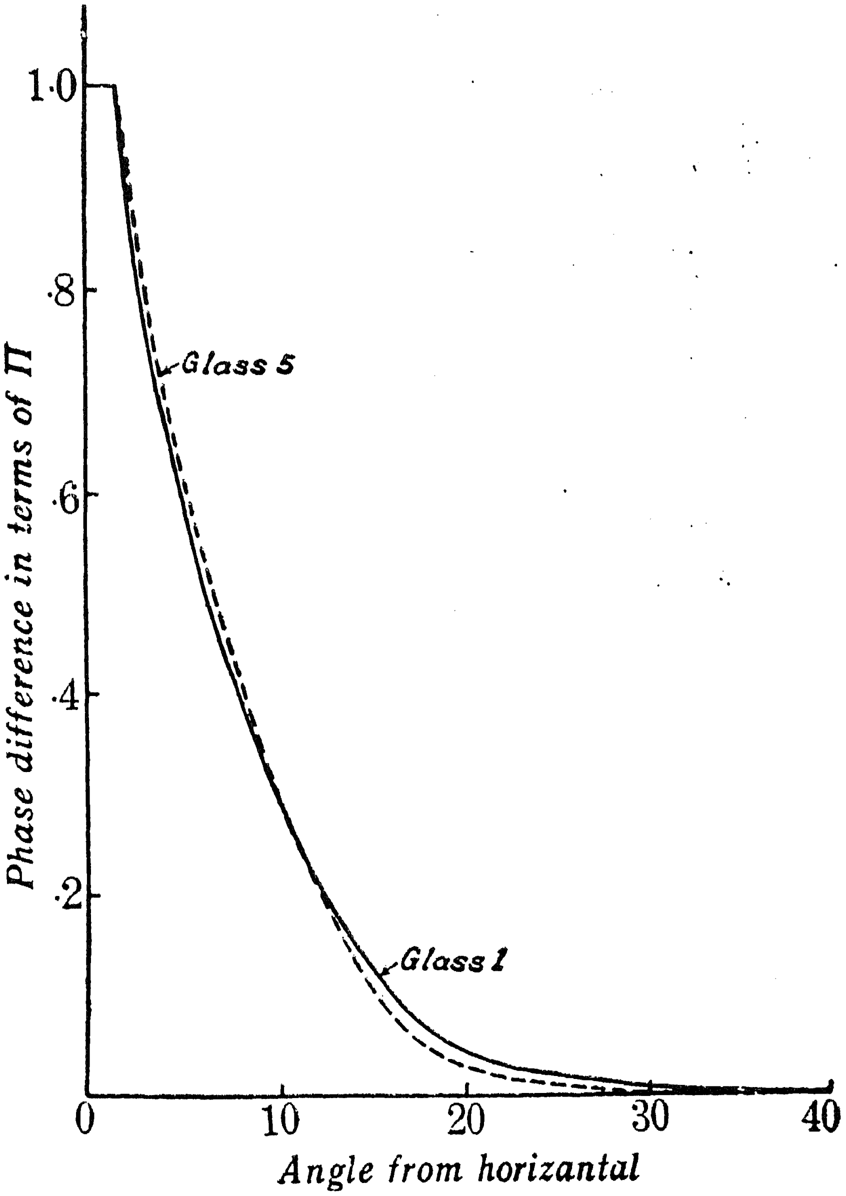

FIG. 1

Table I gives the values of ρ_u, ρ_v and ρ_h for the glasses examined.

TABLE I

Glass No.	Observed			Calculated		Range of θ in which ellipticity is found
	ρ_v %	ρ_u %	ρ_h %	ρ_h %	$\Delta\rho_u$ %	
1	12·7	26·1	78	77	3·36	39°
3	3·5	8·1	72	72	1·31	33°
4	0·46	1·2	68	62	0·28	8°
5	3·6	8·1	80	75	1·16	30°
6	3·5	7·5	85	82	0·74	27°
7	2·4	5·2	78	82	0·51	12°
8	3·0	6·1	91	91	0·28	8°
9	2·1	4·8	81	75	0·68	24°
16	2·5	5·3	87	85	0·43	15°

The values of the depolarisation factors given in the table are those reported by one of the authors in an earlier paper (Krishnan, 1936). The column 6 in the table gives the values of $\Delta\rho_u$ which is the difference between the observed values of ρ_u and the anisotropic part of ρ_u which can be considered to be equal to $2\rho_v/(1+\rho_v)$ to a first approximation. $\Delta\rho_u$ therefore represents the depolarisation due to the finite size of the scattering centres. $\Delta\rho_u$ can be expressed in terms of either ρ_u and ρ_v or ρ_v and ρ_h, and the corresponding expressions are given below. Equation (2) or (3) can be used for the

$$\Delta\rho_u = \rho_u - 2\rho_v/(1 + \rho_v) \tag{2}$$

$$\Delta\rho_u = \left(\frac{1}{\rho_h} - 1\right)\Big/\left(\frac{1}{\rho_v} + 1\right) \tag{3}$$

evaluation of $\Delta\rho_u$ depending upon the accuracy in the determination of ρ_u or ρ_h respectively. The last column in Table I gives the range of θ over which the scattered light is elliptically polarised.

5. *Discussion*

From an analysis of the results obtained, it is clear that in all the glasses examined, the light scattered in the transverse horizontal direction when the incident light is polarised with vibrations horizontal, is partially polarised with the horizontal component stronger than the vertical component. These results confirm Krishnan's conclusion that the optical heterogeneity in glass cannot be identified as due to the individual molecules but is due to molecular aggregates, thus presenting an analogy with the case of liquid mixtures in the neighbourhood of the critical solution temperature and in protein solutions.

According to the theory of Mie, in directions other than parallel and perpendicular to the incident electric vector, the light scattered by large spherical particles would be elliptically polarised. The existence of such elliptic polarisation in the scattered light has been detected experimentally in the case of emulsions by Darbara Singh (1942), in the case of liquid mixtures very near the critical solution temperature and in silver sols by Hariharan (1942) and in some typical colloids by Rao and Krishnan (1944). The present investigation reveals that in glasses also the scattered light is elliptically polarised when the incident light is plane polarised. The curves of ellipticity show a striking similarity with those obtained with colloids in which the particles are known to be not small compared with the wave-length of light. These observations also support the view that molecular aggregates do exist in amorphous substances like glass.

Another important fact which emerges out of the present investigation is that those glasses which give larger values of $\Delta\rho_u$ exhibit ellipticity to a correspondingly larger extent. Compare columns 6 and 7 in Table I. This is not surprising because a larger value of $\Delta\rho_u$ corresponds to an increase in the size of the scattering units which in turn should give rise to a more pronounced elliptic polarisation. Comparing the values of ρ_h and $\Delta\rho_u$ given in Table I for the various glasses, one finds that the range of θ over which elliptic polarisation is detected, is directly correlated with $\Delta\rho_u$ and not with ρ_h. It follows therefore that no reliable estimate of the size of the particles in two different scattering media could be had from a knowledge of the values of ρ_h in the two cases, as they would be influenced to a large extent by the anisotropy of the particles. On the other hand, a comparison of the values of $\Delta\rho_u$ or the extent of ellipticity in the two cases would give us a better estimate of the relative sizes of the particles. Of the nine glasses investigated, No. 1 contains molecular aggregates of largest size and Nos. 4 and 8 contain those of smallest size.

In a paper on the polarisation of light scattered by glasses Parthasarathy and others (1941) claim to have obtained negative results (*i.e.*, ρ_h was not less than 1) in a few specimens of glass some of which were highly strained. Their experimental method of determining the values of the depolarisation factors was not free from defects. It is well known that all glasses exhibit fluorescence. Fluorescence will enhance the value of ρ_h as determined by photographic photometry. Their method for detecting the reversal of polarisation is far less sensitive than either the method of Krishnan (1938) or the new method of Sir C. V. Raman (1941) employed in the present investigation. Parthasarathy and others have worked with glasses having strains of macroscopic dimensions and tried to compare their results with Mueller's theory [Hans Mueller (1938)] which on the other hand is based on the existence of frozen-in strains of microscopic dimensions.

6. *Conclusion*

The finite size in comparison with the wave-length of light, of the elements of heterogeneity of any scattering medium is indicated by the existence of some anomalous depolarisation (*i.e.*, $\rho_h < 1$) and/or ellipticity in the scattering of polarised light in such medium. Of the two effects, the anomalous depolarisation or the reversal of polarisation is more easily observed and is very sensitive to the size of the scattering elements. Colloids such as gold sols, ferric hydroxide sol, vanadium pentoxide sol, etc., contain particles which are large enough to exhibit anomalous depolarisation but too small to show any measurable ellipticity in the scattered light. The detection of anomalous depolarisation in any scattering medium is therefore a more *delicate* test for the existence of molecular aggregates than the detection of ellipticity. The one drawback for this test lies in the fact that the observed anomalous depolarisation may also be caused by the finite angle of convergence of the incident beam and/or secondary scattering. The effect of secondary scattering will be pronounced in the case of emulsion, protein solutions and liquid mixtures very near the critical solution temperature. It is therefore necessary to eliminate the effects due to these disturbing factors in the determination of ρ_h. On the other hand, convergence of the incident beam and secondary scattering cannot give rise to any ellipticity in the scattering, as long as the medium is isotropic and contains particles which are small compared with the wave-length of light. Perrin (1942) has therefore rightly remarked that " the existence of some ellipticity in the scattering for an incident beam linearly obliquely polarised would be a much more *sure* test of the multipolar character of the scattering, and consequently of the non-negligible magnitude, in comparison with wave-length, of the elements of heterogeneity of the scattering medium ".

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Summary

Sir C. V. Raman's new technique for the study of light-scattering based on the use of a Babinet compensator, has been successfully applied for the detection of the anomalous depolarisation in optical glasses. Thus the existence of the reversal of polarisation when the incident beam is polarised with vibrations horizontal, has been definitely established by the new method which is of an objective character. The present investigation further reveals that in glasses the scattered light is elliptically polarised when the incident beam is linearly polarised in a direction oblique to the scattering plane. These observations support the view that molecular aggregates do exist in glasses. One important point which emerges out of the present investigation is that those glasses which give larger values of $\Delta\rho_u$ exhibit elliptic polarisation to a correspondingly larger extent. $\Delta\rho_u$ is the difference between the observed value of ρ_u and the anisotropic part of ρ_u which can be considered to be equal to $\frac{2\rho_v}{(1+\rho_v)}$. It has been pointed out that for making comparative estimates of the sizes of particles in any two scattering media a knowledge of the values of $\Delta\rho_u$ in the two cases is by far more important than the corresponding values of ρ_h.

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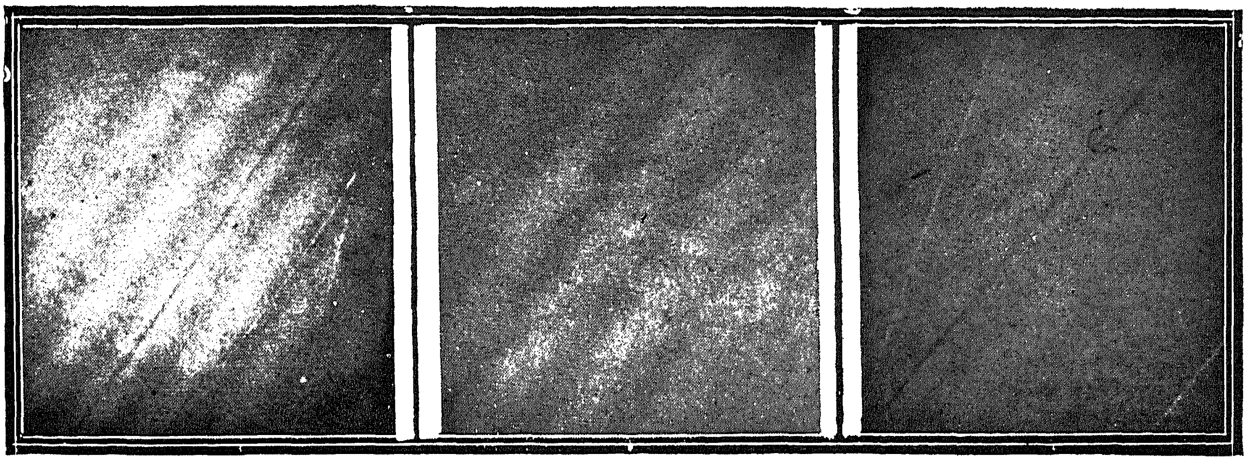

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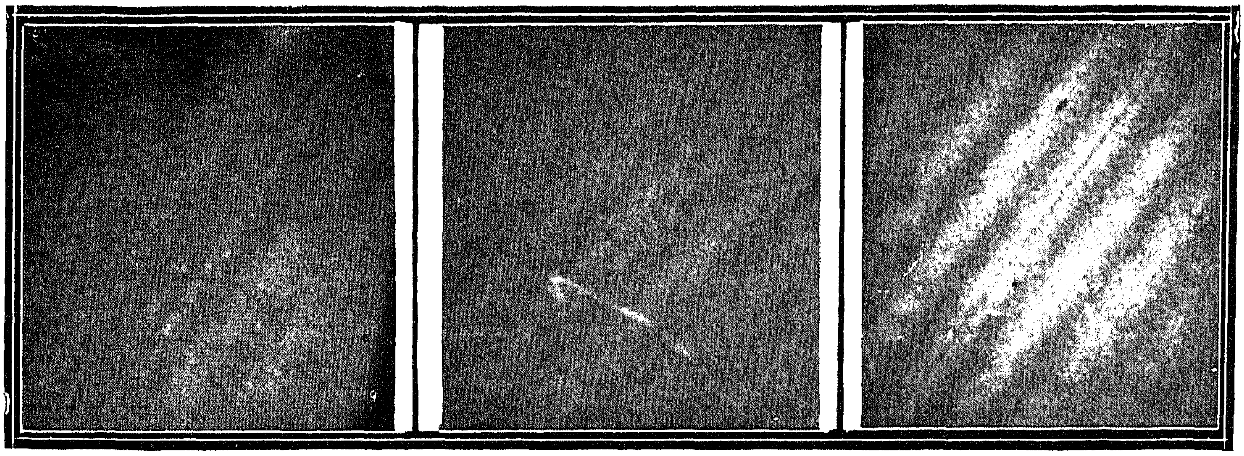

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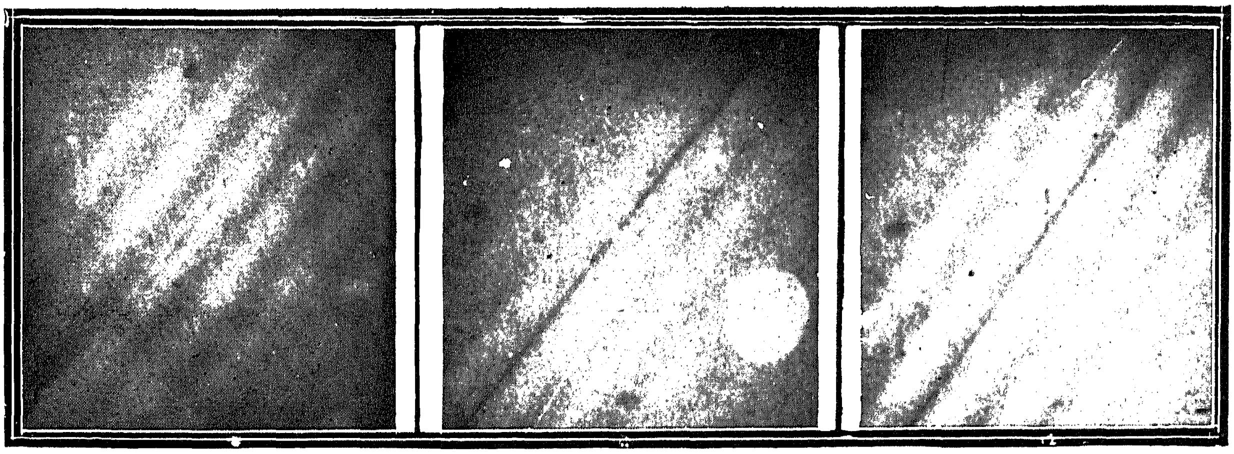

7 8 9

FIGS. 1 — 6. Photographs showing anomalous depolarisation in glasses Nos. 6, 7, 4, 9, 5 and 8 respectively when the incident beam is polarised with vibrations horizontal, *i.e.*, $\theta = 90°$.

FIGS. 7 — 9. Photographs showing elliptic polarisation in the scattered light in glass No. 8 for $\theta = 87°$, 84° and 81° respectively.