NANOSYSTEMS:
PHYSICS, CHEMISTRY, MATHEMATICS

Pleshakov I.V., et al. *Nanosystems: Phys. Chem. Math.*, 2022, **13** (5), 503–508.
http://nanojournal.ifmo.ru
DOI 10.17586/2220-8054-2022-13-5-503-508

Original article

Optical anisotropy in fullerene-containing polymer composites induced by magnetic field

Ivan V. Pleshakov[1,a], Olga V. Proskurina[1,2,b], Viktor I. Gerasimov[3,c], Yuriy I. Kuz'min[1,d]

[1]Ioffe Institute, St. Petersburg, Russia

[2]St. Petersburg State Institute of Technology (Technical University), St. Petersburg, Russia

[3]Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

[a]ivanple@yandex.ru, [b]proskurinaov@mail.ru, [c]viger53@rambler.ru, [d]iourk@yandex.ru

Corresponding author: Ivan V. Pleshakov, ivanple@yandex.ru

PACS 42.70.-a; 42.70.Jk; 78.40.Ri

ABSTRACT Using water-soluble hydrated fullerenes embedded in a polyvinyl alcohol matrix, samples were obtained that demonstrated the presence of optical anisotropy when they were formed in a magnetic field. Its existence was established in experiments on light scattering in films containing $C_{60}(OH)_n$ and $C_{70}(OH)_m$ molecules. The mechanism of the effect is presumably associated with the anisotropy of the shape of these molecules.

KEYWORDS carbon-containing composites, polymer matrices, fullerene, fullerenol, light scattering.

ACKNOWLEDGEMENTS The authors are grateful to A. V. Varlamov and D. M. Seliutin for their help in the experiments.

FOR CITATION Pleshakov I.V., Proskurina O.V., Gerasimov V.I., Kuz'min Yu.I. Optical anisotropy in fullerene-containing polymer composites induced by magnetic field. *Nanosystems: Phys. Chem. Math.*, 2022, **13** (5), 503–508.

1. Introduction

Composites, which are polymer matrices with embedded molecules or molecular complexes based on carbon, are currently being studied from various points of view. The interest in them is dictated by the desire to produce materials with special properties, for example, for improvement of mechanical characteristics, the need to obtain particular membranes and many other objectives [1–5]. One of the important trends in this field is fullerene-containing polymers and the possible creation of such optical media on their basis, the parameters of which could be controlled in one way or another, including control by the action of external fields.

In this paper, we consider the previously unexplored case of fullerene- and fullerenol-containing composites formed in the magnetic field H. As an experimental approach used to obtain information about this substance, the light scattering technique was applied.

2. Samples

The samples were made in the form of films of polyvinyl alcohol (PVA) with $C_{60}(OH)_n$ or $C_{70}(OH)_m$ molecules injected in it, solidified on glass substrates. Similar materials, but synthesized without the applying H, were studied by us earlier [6, 7]. In addition, films of epoxy resin with fullerene C_{60} were used as control samples.

Fullerene and its derivatives were obtained on the basis of principles outlined in [8]. Soot resulting from the erosion of graphite electrodes in an electric arc in a helium atmosphere was treated with xylene and separated in a chromatographic column. After multi-stage purification with a carbon sorbent, a product was formed, which was further hydrated using sodium hydroxide, and, as an interfacial catalyst, tetrabutylammonium hydroxide solution. At the final stage, drying was carried out in vacuum at 40 °C. According to the data of complex thermal and elemental analysis, the result was compounds that best correspond to the formulas $C_{60}(OH)_{42}\cdot 4H_2O$ or $C_{70}(OH)_{52}$ (hereinafter referred to as C_{60}HyFn and C_{70}HyFn, respectively).

In the manufacture of samples, the fact that PVA and fullerenols are water-soluble substances was used. To obtain composite films, their solutions were mixed in different proportions at a temperature of about 90 °C, subjected to ultrasonic treatment for 30 min, applied to a glass substrate and dried in a magnetic field, forming films with a thickness of 30 to 60 μm. The concentrations of the starting compounds varied, but the best quality of the sample (acceptable transparency with a sufficiently high content of inclusions) was achieved by introducing 10 mg of fullerenol into a five percent solution of PVA (5 wt. % of dry material by weight of water), and the greatest effect associated with the magnetic field was observed at the maximum achievable value in the laboratory $H = 15$ kOe. The results below relate to these values.

The preparation of control samples was performed differently, since fullerene C_{60} does not dissolve in water. Initially, powdered fullerene was added to the epoxy resin hardener (commercially available transparent product *Artline Crystal Epoxy*), and this mixture was subjected to ultrasonic stirring for 30 minutes. Then the resulting mass was combined with the resin in a ratio of 2:1 and sonified for another 10 minutes. The weights of the ingredients were selected so that the concentration of C_{60} in the liquid was 1 wt. %. Next, the liquid was deposited on glass and placed in the field $H = 15$ kOe, in which it hardened to a solid state, while the thickness and visual optical characteristics of the film were approximately the same as in the case of PVA.

For comparison, samples were also made for all matrices and fillers at $H = 0$.

3. Measurements procedures and processing of data

The optical measurements performed in this work were experiments on static light scattering carried out according to the standard scheme. The setup included a semiconductor laser ($\lambda = 650$ nm), the radiation of which was directed at the sample, and a block rotating around the sample on the limb, consisting of a photodetector and a polarizer located in front of it, which allowed one to separate either horizontally or vertically polarized components of the scattered light.

A horizontally polarized laser beam was formed by a diaphragm with a sufficiently large aperture (more than 1 mm) and was applied to the sample from the side of the substrate perpendicular to it. The degree of laser radiation linear polarization P_0, which is known to be determined by the expression

$$P_0 = \frac{I_1 - I_2}{I_1 + I_2},$$

where I_1 is theintensity of the horizontally polarized light component, and I_2 is the intensity of the orthogonal (i.e. vertically polarized) light component, was about 95 %.

The experiment is reduced to determining the dependence of the intensity of scattered radiation I_s recorded by the photodetector on the angle θ, measured in the horizontal plane from the optical axis of the system to the direction of the scattered beam, that is, determining of the indicatrix $I_s(\theta)$. We also measured the degree of linear polarization of the scattered radiation given by the formula

$$P_s = \frac{I_{s1} - I_{s2}}{I_{s1} + I_{s2}},$$

where I_{s1} and I_{s2} are the intensities of horizontally and vertically polarized components of scattered light, respectively. Next, the relative value of P_s/P_0 was determined – an important parameter for our study that characterizes the degree of impact of the substance under investigation to light.

All measurements were performed for two positions of the sample: when the mutual orientations of the field H in which it was prepared and the polarizations p of incident beam were parallel or perpendicular.

The scattering indicatrices $I_s(\theta)$ were processed by fitting functions of the form $f(\theta) = a \cdot \cos^2(\beta\theta)$. This was necessary to estimate the value of $I_s(0)$ (of course, measurements are impossible in the region close to $\theta = 0$) and, thus, to determine the width of $I_s(\theta)$ at half intensity $\delta\theta_{0.5}$. It should be noted that this approach is rather rough, but it introduces a simple unified criterion for all indicatrices (accurate analytical processing is extremely complicated by the fact that the phenomenon under study is a complex case of scattering on a system of non-spherical and differing in size objects with internal anisotropy). The lines shown in the figures below are drawn using this fit.

4. Experimental results

Figure 1 shows the $I_s(\theta)$ indicatrices for two orientations of an epoxy resin-based sample obtained by recording scattered radiation with a polarization coinciding with the incident one (Fig. 1a) and perpendicular to it (Fig. 1b). It is noteworthy that these diagrams are rather narrow $\delta\theta_{0.5} \cong 6\,^\circ$) and practically the same for the geometries of the experiment corresponding to different orientations of the magnetic field. In order to note the not quite exact correspondence of the chosen approximation to experimental data, an additional curve is shown in Fig. 1a, which is a fit of $f(\theta)$ to points at $|\theta| > 5\,^\circ$. In Fig. 1b the calculated curve is a scaling transformation of the main diagram in Fig. 1a, that is, the ratio P_s/P_0 within the main peak remains constant at all angles θ and orientations of H.

Figure 2 demonstrates the $I_{s1}(\theta)$ indicatrix (Fig. 2a) and the relative degree of linear polarization P_s/P_0 (Fig. 2b), obtained for C_{60}HyFn film at different magnetic field orientations. The width $\delta\theta_{0.5} \cong 5.8\,^\circ$ measured from $I_{s1}(\theta)$ turned out to be approximately the same for every H direction (the dots that not described by the main peak function $f(\theta)$ were not recorded here). However, in this case, the approximations of $I_{s1}(\theta)$ and $I_{s2}(\theta)$ differed not only by the scale factor, i.e., there was a pronounced angular dependence of the parameter P_s/P_0, which, moreover, was different for different orientations of the field. As an example, Fig. 2b shows the curves calculated from the above expressions using fitting functions I_s.

Another picture was observed for the C_{70}HyFn sample (Fig. 3). At different orientations of the field, the $I_{s1}(\theta)$ indicatrices were noticeably different in width (Fig. 3a), and the difference in $P_s(\theta)/P_0$ became very significant, reaching a value of about 10–15 %.

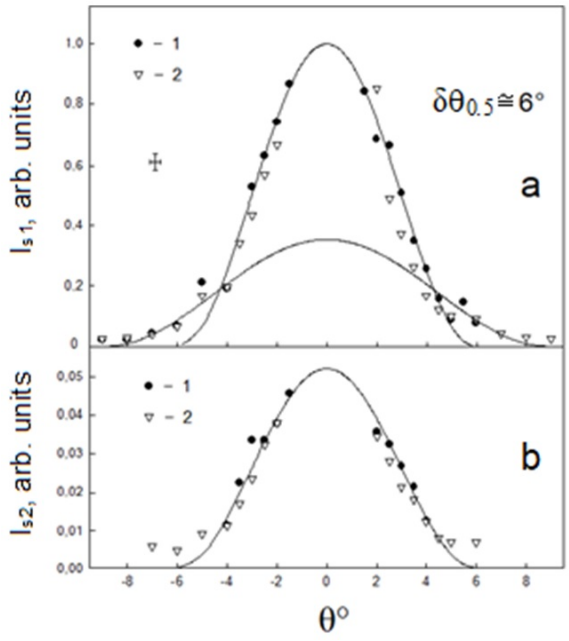

FIG. 1. Indicatrices of epoxy-based sample for registration of scattered light with polarization parallel (a) and orthogonal (b) to polarization p of incident beam. 1 – Perpendicular orientation of H to p, 2 – parallel orientation of H to p

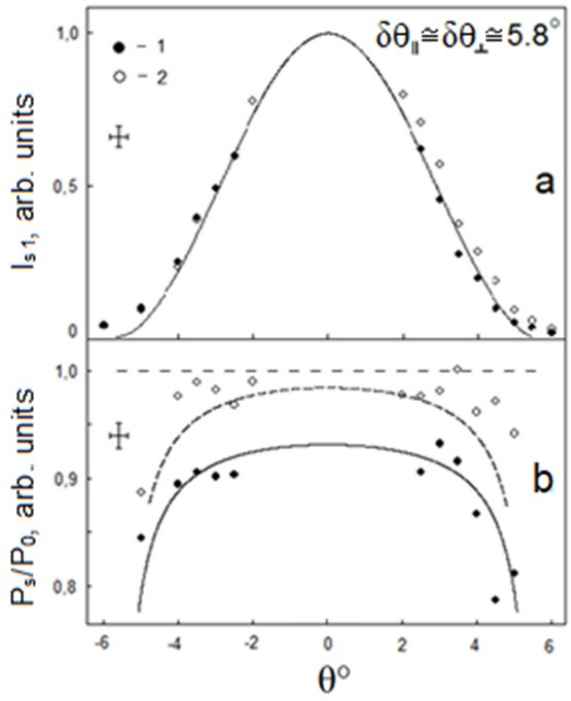

FIG. 2. Results of the experiment with the sample C_{60}HyFn: indicatrix $I_{s1}(\theta)$ (a) and relative degree of linear polarization P_s/P_0 (b). 1 – Perpendicular orientation of H to p, 2 – parallel orientation of H to p

To display the effect of the magnetic field on the studied composites more clearly, the data obtained for C_{60}HyFn and C_{70}HyFn are presented together on a separate graph (Fig. 4), where the angular dependences of the relative degree of linear polarization are shown in the region $-5\,^\circ < \theta < 0\,^\circ$.

In control samples fabricated at $H = 0$, the effects described above were not observed.

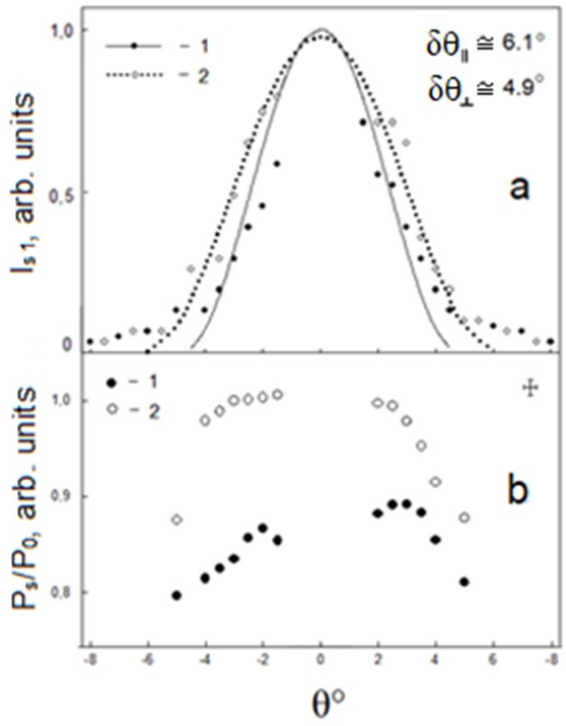

FIG. 3. Results of the experiment with the sample C_{70}HyFn: indicatrix $I_{s1}(\theta)$ (a) and relative degree of linear polarization P_s/P_0 (b). 1 – Perpendicular orientation of H to p, 2 – parallel orientation of H to p

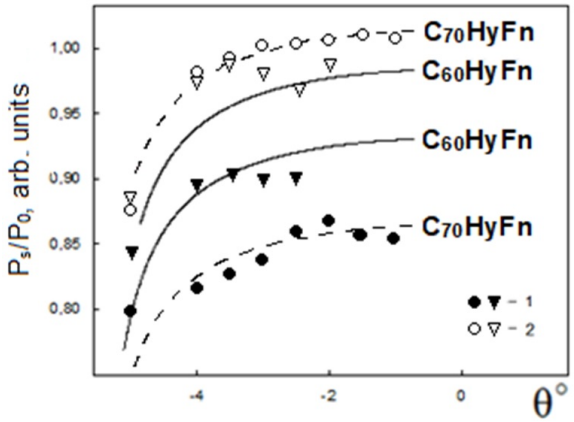

FIG. 4. Comparison of the dependences of relative linear polarization degree on the scattering angle in PVA films. 1 – Perpendicular orientation of H to p, 2 – parallel orientation of H to p

5. Discussion

An obvious conclusion from the above data is that in systems containing C_{60}HyFn and C_{70}HyFn molecules, an external magnetic field induces optically detectable anisotropy. Comparison of the characteristics of the latter with the characteristics of the control sample shows that the shape of the molecules should play an essential role in this phenomenon. Assuming C_{60} to be a spherically symmetric object, it can be expected that no preferred direction under the action of H in a substance with "pure" fullerene can appear, which is confirmed by the measurement results of an epoxy-based composite (Fig. 1). At the same time, the width of the indicatrix (or, more precisely, the part of it that corresponds to the

most intense scattering) of the C_{60}-containing sample differs little from the value of the same parameter for C_{60}HyFn and C_{70}HyFn. This indicates that in all cases the scatterers are particles larger than individual molecules. The obtained values of the $\delta\theta_{0.5}$ allow us, based on [9] and the references therein, to estimate qualitatively their average size d as units of microns ($d \geq \lambda$), that is, to assume that we deal with a scattering close to the scattering of Mie (which is not quite strict, since the shape and structure of the scatterers, as mentioned above, differs from homogeneous sphere). An additional wide low-intensity line in Fig. 1a, corresponds, most likely, to the existence of a fine fraction of carbon inclusions in C_{60}-containing sample. The absence of angular dependence of P_s/P_0 in the epoxy-based composite, while conserving the value of this parameter close to the same in incident beam, is a sign of the high symmetry of scatterers associated with C_{60} molecules.

In the C_{60}HyFn -containing sample, such a dependence exists (Fig. 1b), and, what is most important, it is different for different sample orientations, while the change in the width of the indicatrix is not observed also (Fig. 1a). It can be assumed that in this case, the optical anisotropy induced by the magnetic field mainly is owing to the internal anisotropy of the clusters formed by fullerenol C_{60}HyFn molecules, which, in turn, is determined by a certain deviation of their shape from spherical. Of course, there is a question about how noticeable this effect is, since the carbon skeleton of this molecule continues to remain the same as that of fullerene C_{60} However, according to the results of the simulation carried out in [10], the attachment of a certain amount of OH groups to the core of the C_{60}HyFn molecule can form structures with a fairly well-defined asymmetry.

Figure 3, referring to C_{70}HyFn, shows the most striking manifestation of field-induced anisotropy. Here, in addition to the very different for the two orientations of H angular dependences of the relative degree of linear polarization (Fig. 3b), a noticeable broadening of the scattering indicatrix appears (Fig. 3a), which probably reflects both the existence of internal anisotropy and the non-sphericity of the clusters formed by the molecules of this fullerenol. The difference in the values of $\delta\theta_{0.5}$ when light is scattered on extended objects of a different physical nature, but with the same experimental geometries as in present work was observed, for example, in [11]. Nucleation of structures elongated in the field, the constituents of which are the C_{70}HyFn molecules, is more obvious than in the case of C_{60}HyFn, since their carbon skeleton is already has an anisotropy of the shape, which persisting or increasing when the hydrate shell is formed. The significantly stronger influence of the magnetic field on such samples is illustrated by comparing the plots of $P_s(\theta)/P_0$ of composites with C_{60}HyFn and C_{70}HyFn in a large scale (Fig. 4).

In the cases discussed above, and even if clustering does not occur at all, induced anisotropy required that non-magnetic molecules should line along the field. Of course, any molecules can be considered non-magnetic only in a certain approximation; it is more correct to take into account their diamagnetic properties, as is done, for example, when analyzing the behavior of liquid crystals. Therefore, as a simple explanation for the effects we observed, a mechanism similar to what occurs in these substances is proposed: non-spherical molecules, due to their anisotropy of dielectric susceptibility, rotate in the field, minimizing the corresponding energy and forming further larger objects (clusters). Being hypothetical, this model, of course, can be refined or modified, for instance, taking into account the complicated nature of the interaction of the hydrate shell of fullerenol molecules with the matrix.

Note that the structure of clusters does not necessarily imply the presence of a large number of closely packed molecules in them. It is possible, for example, that variations in the density of the additive distribution in the matrix creates a scattering medium with a spatially varying refractive index, in which fullerenol molecules are separated by PVA. A certain role in the formation of scattering objects can also be played by PVA crystallites [12], which are usually present in this polymer.

6. Conclusion

In the work, the light scattering method revealed the effect that a magnetic field can create optical anisotropy in a composite medium containing inclusions in the form of polyhydroxylated fullerenes molecules.

References

[1] Liming Dai, Albert W.H. Mau, Xiaoqing Zhang. Synthesis of fullerene- and fullerol-containing polymers. *J. Mater. Chem.*, 1998, **8**(2), P. 325–330.

[2] Changchun Wang, Zhi-Xin Guo, Shoukuan Fu, Wei Wu, Daoben Zhu. Polymers containing fullerene or carbon nanotube structures. *Prog. Polym. Sci.*, 2004, **29**(11), P. 1079–1141.

[3] Eletskii A.V., Knizhnik A.A., Potapkin B.V., Kenny J.M. Electrical characteristics of carbon nanotube doped composites. *Phys. Usp.*, 2015, **185**(3), P. 225–270.

[4] Penkova A.V., Acquah S.F.A., Sokolova M.P., Dmitrenko M.E., Toikka A.M. Polyvinyl alcohol membranes modified by low-hydroxylated fullerenol $C_{60}(OH)_{12}$. *J. Memb. Sci.*, 2015, **491**, P. 22–27.

[5] Dmitrenko M., Liamin V., Kuzminova A., Mazur A., Lahderanta E., Ermakov S., Penkova A. Novel mixed matrix sodium alginate–fullerenol membranes: development, characterization, and study in pervaporation dehydration of isopropanol. *Polymers*, **12**(4), P. 2020864.

[6] Karpunin A.E., Gerasimov V.I., Mazur A.S., Pleshakov I.V., Fofanov Ya.A., Proskurina O.V. NMR investigation of composite material, formed by fullerenol in polymer matrix of polyvinyl alcohol. *Proceeding of "International Conference on Electrical Engineering and Photonics (EExPolytech)"*. Saint Petersburg (Russia), 22–23 Oct. 2018, IEEE, 2018, P. 168.

[7] Karpunin A.E., Pleshakov I.V., Proskurina O.V., Gerasimov V.I., Nechitailov A.A., Glebova N.V., Varlamov A.V., Parfenov M.V. Optical study of composite material with nanosized fullerenol inclusions. *Journal of Physics: Conference Series*, 2019, **1236**, P. 012012.

[8] Li J., Takeuchi A., Ozawa M., Li X., Saigo K., Kitazawa K. C_{60} fullerol formation catalysed by quaternary ammonium hydroxides. *J. Chem. Soc. Chem. Commun.*, 1993, **23**, P. 1784–1785.
[9] Bohren C.F., Huffman D.R. *Absorption and scattering of light by small particles*. John Wiley & Sons, Inc., NY, 1998, 544 p.
[10] Keshri S., Tembe B.L. Thermodynamics of hydration of fullerols $[C_{60}(OH)_n]$ and hydrogen bond dynamics in their hydration shells. *J. Chem. Phys.*, 2017, **146**(7), P. 074501.
[11] Pleshakov I.V., Prokof'ev A.V., Bibik E.E., Kuz'min Yu.I. Investigation of structures formed by magnetic fluid nanoparticles in polymer matrices by static light scattering. *Nanosystems: Phys. Chem. Math.*, 2022, **13**(3), P. 285–289.
[12] Thomas D., Cebe P. Self-nucleation and crystallization of polyvinyl alcohol. *J. Therm. Anal. Calorim.*, 2017, **127**, P. 885–894.

Submitted 8 September 2022; revised 17 September 2022; accepted 18 September 2022

Information about the authors:

Ivan V. Pleshakov – Ioffe Institute, 26 Politechnicheskaya str., St. Petersburg, 194021, Russia; ivanple@yandex.ru

Olga V. Proskurina – Ioffe Institute, 26 Politechnicheskaya str., St. Petersburg, 194021, Russia; St. Petersburg State Institute of Technology (Technical University), 26 Moskovsky ave., St. Petersburg,190013, Russia; proskurinaov@mail.ru

Viktor I. Gerasimov – Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya str., St. Petersburg, 195251, Russia; viger53@rambler.ru

Yuriy I. Kuz'min – Ioffe Institute, 26 Politechnicheskaya str., St. Petersburg, 194021, Russia; iourk@yandex.ru

Conflict of interest: the authors declare no conflict of interest.