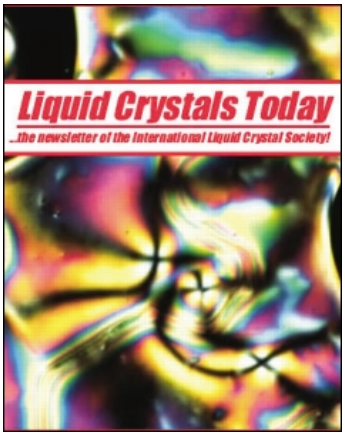

Liquid Crystals Today
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713681230

Thermal-lens effect of low-density lipoprotein lyotropic-like aggregates investigated by using the Z-scan technique

S. L. Gómez[a]; R. F. Turchiello[b]; M. C. Jurado[a]; P. Boschcov[c]; M. Gidlund[a]; A. M. Figueiredo Neto[d]
[a] Instituto de Ciencias Biomedicas, Universidade de Sao Paulo, Brazil [b] Instituto de Quimica, Universidade de Sao Paulo, Brazil [c] Escola Paulista de Medicina, Universidade Federal de Sao Paulo, Brazil [d] Instituto de Fisica, Universidade de São Paulo, Brazil

To cite this Article Gómez, S. L. , Turchiello, R. F. , Jurado, M. C. , Boschcov, P. , Gidlund, M. and Neto, A. M. Figueiredo(2006) 'Thermal-lens effect of low-density lipoprotein lyotropic-like aggregates investigated by using the Z-scan technique', Liquid Crystals Today, 15: 1, 1 — 3
To link to this Article: DOI: 10.1080/14645180600912093
URL: http://dx.doi.org/10.1080/14645180600912093

Liquid Crystals Today, Vol. 15, No. 1, March 2006, 1–3

Taylor & Francis
Taylor & Francis Group

Thermal-lens effect of low-density lipoprotein lyotropic-like aggregates investigated by using the Z-scan technique

S.L. GÓMEZ†, R.F. TURCHIELLO‡, M.C. JURADO†, P. BOSCHCOV§, M. GIDLUND† and A.M. FIGUEIREDO NETO*

†Instituto de Ciencias Biomedicas, Universidade de Sao Paulo, Brazil
‡Instituto de Quimica, Universidade de Sao Paulo, Brazil
§Escola Paulista de Medicina, Universidade Federal de Sao Paulo, Brazil
*Instituto de Fisica, Universidade de São Paulo, Brazil

(*Received 17 July 2006*)

The thermal nonlinear optical response of human normal and copper-oxidized low-density lipoproteins (LDLs) were investigated by using the Z-scan technique, as a function of temperature and concentration of LDL particles. The results show that the Z-scan signals from normal LDL are characteristic of a sample with negative thermo-optical coefficient. The amplitude of the Z-scan signal increases linearly with the LDL concentration, following the usual Beer–Lambert law. On the other hand, oxidized LDLs do not show thermal nonlinear optical response. This behaviour can be attributed to an absorbing element that is modified by the oxidative process. On the other hand, changes in the physical state of the cores and conformation of the ApoB100 protein, due to an increase in temperature, seems to enhance the native LDL thermal nonlinear optical response.

Low-density lipoproteins (LDLs) are the main carriers of cholesterol, playing a critical role in human cholesterol metabolism. LDLs are almost spherical lyotropic-type aggregates (typical diameter ~27 nm) composed of a hydrophobic core made mainly of cholesterol esters and triglycerides, an outer shell of phospholipids, and one copy of the protein apoB100 [1]. Their structure and composition resembles the micellar aggregates that form lyotropic liquid crystals [2].

Several pathological conditions are associated with oxidative modifications of the LDL particles [3]. The physical state of the LDL lipid core is highly dependent on the temperature, T, and influences the structural conformation of the apoB100 protein [4]. The physical state of the core also determines the shape-symmetry of the LDL particles. Cryo-electron microscopy experiments [5, 6] suggest that native LDL for $T<T_c$ (where T_c is the transition temperature of the core content from the liquid crystalline phase to the isotropic phase) has an oblate ellipsoidal shape.

An interesting problem that could be addressed is the response of the native and oxidized states of the LDL to electromagnetic fields, in particular the nonlinear optical response. The LDL particles have a number of components that may contribute differently to the nonlinear optical response. This response could depend also on the particular state of the LDL and its geometry. It is well known that self-assembly amphiphilic systems, like lyotropic liquid crystals, respond to optical fields in a way that depends on the structure and local ordering of the amphiphilic aggregates [7]. Therefore, this response could be used to identify different states (native or oxidized) of the LDL particles.

Several techniques have been developed to measure photo-induced effects in a medium. The single-beam Z-scan (ZS) technique [8], initially developed to study nonlinear optical effects from an electronic origin, and the thermal-lens technique [9, 10], were employed successfully in the field of photothermal spectroscopy for studying lyotropic liquid crystals [11, 12]. This technique, with laser pulses in the millisecond time-scale regime, is particularly sensitive to the electronic polarizability of the LDL particles, their modifications with temperature, and geometrical factors. The ZS technique does not need to use an extrinsic probe, which can be considered as an advantage of this technique in the face of other techniques usually employed in the study of LDL.

In this study we report on the thermal nonlinear optical response of LDL from normolipidemic blood donor volunteers. Details of the protocols to promote

*Corresponding author. Email: afigueiredo@if.usp.br

Liquid Crystals Today
ISSN 1358-314X print/ISSN 1464-5181 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/14645180600912093

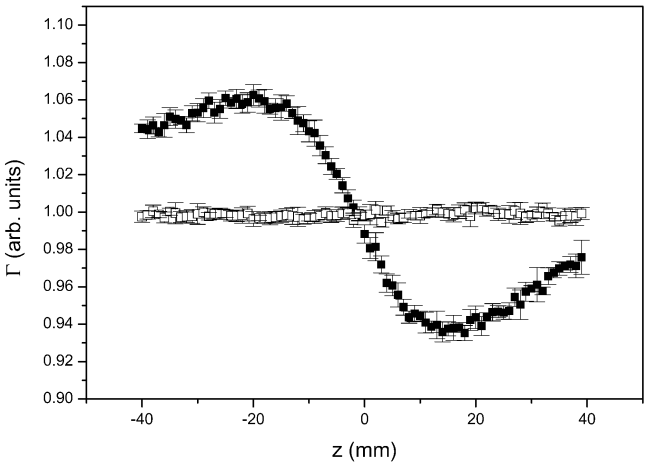

Figure 1. Typical Z-scan curves of LDL samples: (■) normal LDL; (□) oxLDL. The peak-valley Z-scan transmittance curve for a normal LDL sample corresponds to a sample with $dn/dT<0$.

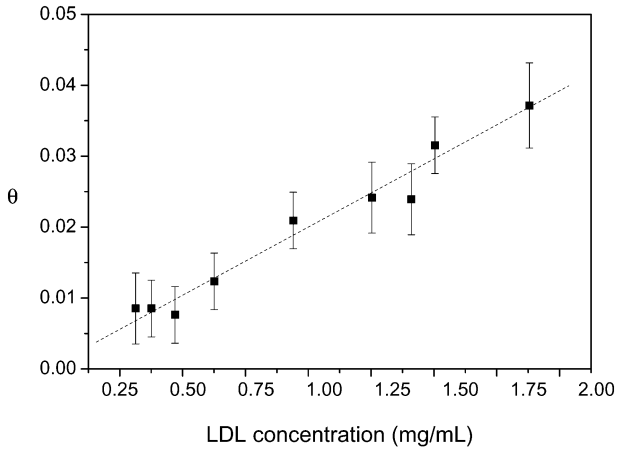

Figure 2. Z-scan signal peak-to-valley amplitude-related coefficient as a function of the concentration of LDL. Measurements made at the same conditions of temperature, power of incident laser beam and sample thickness. The dotted line is a linear fit.

the oxidative modifications of the LDL particles by Cu^{+2} as well as on the Z-scan technique can be found elsewhere [13, 11]. The laser-beam pulses used in the ZS experiments were of 20 ms. In this time-scale, the optical response of the sample is of a thermal origin. The samples were prepared in a slab geometry, with the LDL dispersed in water forming a film 200 μm thick.

Figure 1 shows typical ZS (peak–valley) curves of normal LDL and oxidized LDL (oxLDL) samples. Samples of normal LDL, at temperatures between 23 and 43°C, exhibit a ZS signal characteristic of an absorbing medium, with negative thermo-optical coefficient ($dn/dT<0$). On the other hand, copper-oxidized LDL particles do not exhibit any ZS signal under the same experimental conditions. This means that normal LDL responds to the optical field stimulus by forming a thermal lens, differently from the oxLDL that, in the same conditions, does not form a thermal lens.

Figure 2 shows a plot of the peak-to-valley amplitude-related coefficient in a ZS measurement θ [14] as a function of concentration of LDL particles c. Figure 2 also displays a linear fit showing that the nonlinear optical response is proportional to c, following the Beer–Lambert law. So, the Z-scan technique is highly sensitive for quantitative determination of the normal LDL concentration.

To investigate the effect of the temperature ($23 \leqslant T \leqslant 43$°C) on the amplitude of the Z-scan signal, we performed experiments with the LDL as a function of temperature [13]. Our results show that the absolute value of θ increases almost linearly with T. The hydrophobic core of LDL undergoes a reversible thermal transition close to physiological temperature [15]. The transition temperature T_c varies in between individuals and has a strong dependence on the composition of the lipid core. Usual values of T_c are in the range of 24–30°C [16]. The temperature, and the physical state of the lipid core of LDL, have multiple consequences for many processes associated to oxidation of the LDL. The susceptibility of LDL to oxidation was shown to be dependent on the molecular packing of the core lipid, i.e., its physical state [17], being enhanced above T_c. The physical state of the lipid core also influences the conformation of the secondary structure of the protein moiety [4], revealing that its conformation is more stable above T_c, depending strongly on temperature, but less on the composition of the core. As a last observation we stress that, in the present state of our investigation, the nonlinear optical response of the ApoB itself and its effect in the integrity of the outer shell structure of the LDL is not determined.

Summarizing, we have shown that the ZS technique is sensitive for quantitative determination of concentrations of LDL in a broad range. Normal LDL has a thermal nonlinear optical response depending on T but oxLDL does not show any ZS signal at this time-scale. These results indicate the possible application of a nonlinear optical technique as a spectroscopic tool to investigate the structure of LDL. In addition to the structural properties implicated, the methodology allows the detection of changes associated to inflammatory-stress and thus indirectly can measure the LDL stability and vulnerability to thermal or oxidative stress. As this is associated to the presence of the risk of heart

disease we can also envisage a practical application as a diagnostic technique.

Acknowledgements

This work is a constituent of the research interests of the Millennium Institute of Complex Fluids, and has financial support from the State of São Paulo Research Foundation (FAPESP) and the National Council for Scientific and Technological Development (CNPq).

References

[1] T. Hevenoja, M.O. Pentikäinen, M.T. Hyvönen, P.T. Kovanen, M. Ala-Korpela. *Biochim. Biophys. Acta*, **1488**, 189 (2000).
[2] A.M. Figueiredo Neto, S.R. Azevedo Salinas. *The Physics of Lyotropic Liquid Crystals, Phase Transitions and Structural Properties*. Oxford University Press, New York (2005).
[3] M.D. Carvalho, L.M. Harada, M. Gidlund, D.F.J. Ketelhuth, P. Boschcov, E.C.R. Quintão. *J. Cell Biochem.*, **84**, 309 (2002).
[4] A. Coronado-Gray, R. Van Antwerpen. *FEBS Lett.*, **533**, 21 (2003).
[5] R. Van Antwerpen, M. La Belle, E. Navratilova, R.M. Krauss. *J. Lipid Res.*, **40**, 1827 (1999).
[6] E.V. Orlova, M.B. Sherman, W. Chiu, H. Mowri, L.C. Smith, A.M. Gotto Jr. *Proc. Natl. Acad. Sci. USA.*, **96**, 8420 (1999).
[7] F.L.S. Cuppo, A.M.F. Neto. *Langmuir*, **18**, 9647 (2002).
[8] M. Sheik Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Vanstryland. *IEEE J. Quantum Electron.*, **26**, 760 (1990).
[9] J.P. Gordon, R.C.C. Leite, R.S. Moore, S.P.S. Porto, R.J. Whinnery. *J. Appl. Phys.*, **36**, 3 (1965).
[10] C. Hu, J.R. Whinnery. *Appl. Opt.*, **12**, 72 (1972).
[11] S.L. Gómez, F.L.S. Cuppo, A.M. Figueiredo Neto, T. Kosa, M. Muramatsu, R.J. Horowicz. *Phys. Rev. E*, **59**, 3059 (1999).
[12] S.L. Gómez, A.M.F. Neto. *Phys. Rev. E*, **62**, 675 (2000).
[13] S.L. Gómez, R.F. Turchiello, M.C. Jurado, P. Boschcov, M. Gidlund, A.M. Figueiredo Neto. *Chem. Phys. Lip.*, **132**, 185 (2004).
[14] F.L.S. Cuppo, A.M. Figueiredo Neto, S.L. Gómez. *J. Opt. Soc. Am. B*, **19**, 1342 (2002).
[15] R.J. Deckelbaum, G.G. Shipley, D.M. Small, R.S. Lees, P.K. George. *Science*, **190**, 392 (1975).
[16] M. Pregetter, R. Prassl, B. Schuster, M. Kriechbaum, F. Nigon, M.J. Chapman, P. Laggner. *J. Biol. Chem.*, **274**, 1334 (1999).
[17] B. Schuster, R. Prassl, F. Nigon, M.J. Chapman, P. Laggner. *Proc. Natl. Acad. Sci. USA.*, **92**, 2509 (1995).