Fluorescence Correlation Spectroscopy on Liquid-Crystalline Elastomers

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Fluorescence Correlation Spectroscopy (FCS)[1] and Confocal Fluorescence Microscopy (CFM)[2] imaging are powerful methods mainly used in the investigation of biological or colloidal systems.[3] Our aim was to leverage the methodology to the study of dynamics in polymer networks.[4] Fluorescent labelled networks in swollen state show continuous fluctuations while the emitted signal can be related to the different time scales.[5]

This work used spatially-resolved FCS to study swollen polymer chains of different main-chain liquid-crystalline elastomers with different crosslinking densities, all labelled with dye molecules (azobenzene compounds) for their structural and morphologic characterization (Figure 1).

The results indicate that the autocorrelation function ($G(\tau)$) has a bimodal distribution of the residence time (τ_D) of the dye, due to the different localization of the emitting molecules in the polymer chains. There are three statistically possible locations: close to the crosslinking points (slow mobility), in the middle of the polymer chains or in a free-hanging chain ends (fast mobility). The technique showed that the homogeneity and degree of crosslinking of the network can be thus evaluated, while the obtained results fit the known chemical composition (Figure 2).

The importance of these findings lays in opening a new characterization method to the study of polymer dynamics while also enabling a better understanding of the structure of polymer systems.

(1) M.N. Berberan-Santos, *"Fluorescence of Supermolecules Polymers, and Nanosystems"*, Springer-Verlag, **2008**
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(3) Ch. Zander, J. Enderlein, R.A. Keller, *"Single Molecule Detection in Solution: Methods and Applications"*, Wiley-VCH Verlag, **2002**
(4) Y. Hirokawa, H. Jimai, Y. Nishikawa, T. Okamoto, T. Hashimoto *Macromolecules* **1999**, *32*, 7093
(5) J.U. Sommer, S. Lay *Macromolecules* **2002**, *35*, 9832

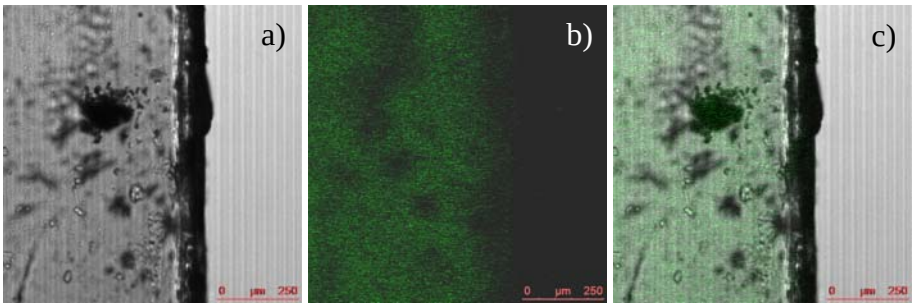

Figure 1. Microscopy of an elastomer with azobenzene co-monomer irradiated at 633 nm: a) transmission, b) fluorescence, and c) overlapping of both images

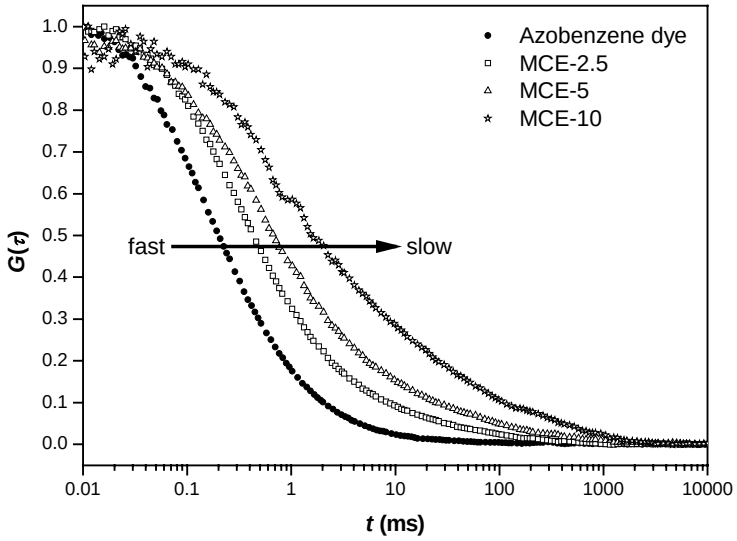

Figure 2. Normalized autocorrelation function ($G(\tau)$) on the free azobenzene dye (monomodal) and three main-chain liquid-crystalline elastomers (bimodal) at different crosslinking densities (2.5, 5 and 10 mol-%). The arrow is in the direction of slower mobility