Small angle X-ray study of phase transitions in chiral liquid-cristalline polymers confined in porous media

Experiment CRG 02-01-106

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In this experiment the SAXS profiles were obtained in the q range $0.10 \leq q \leq 0.9$ Å $^{-1}$ and the reflection peaks were studied as a function of temperature for all the samples. The measurements were made at 16 keV in order to overcome the strong absorption due to chlorine atoms in the samples.

In the first part of the experiment, the mesophase behaviour of two new chiral side chain liquid-crystal polyacrylates P_{13} and P_{14} were studied by SAXS. The polyacrylate with eleven methylene units in the spacer, P_{13}, exhibits a chiral smectic A phase whereas the polyacrylate with a spacer containing four methylene units, P_{14}, presents a chiral nematic phase. SAXS profiles are presented in figures 1 and 2, together with some data from the SAXS analysis. Thermal analysis and SAXS reveals that mesomorphic behaviour was dependent on both molecular weight and spacer length. These results are beeing prepared for publication.[1]

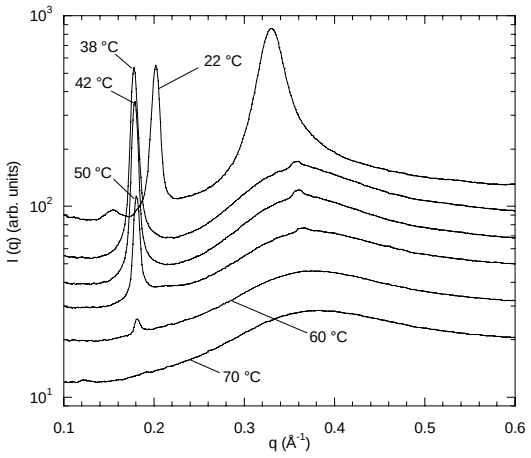

Figure 1: SAXS profiles of the P_{13}

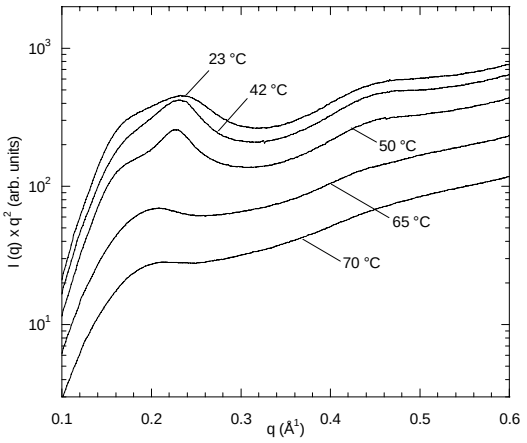

Figure 2: SAXS profiles of the P_{14}

T (°C)	P_{13} [a]			P_{14} [b]	
	d (Å)	$I(q)/I(q)^{max}$	$\sqrt{\Delta x^2}/L$ [c]	d (Å)	θ_t (°) [d]
22	31.12	0.10	-	27.04	39.73
38	35.30	1.0	0.0	-	-
42	35.08	0.92	0.07	27.32	39.10
50	35.84	0.34	0.14	27.61	38.28
60	34.56	0.08	0.19	-	-

[a] Mw: 21.200 gmol^{-1}; $T_{G\rightarrow S}$: 37.3 °C; $T_{G\rightarrow I}$: 68.2 °C [b] Mw: 113.300 gmol^{-1}; $T_{G\rightarrow N}$: 20.5 °C; $T_{N\rightarrow I}$: 63.1 °C
[c] Mean mesogenic fluctuation amplitude; L (35.18 Å) is the extended conformation from the monomer repeat unit.
[d] Tilt angle: $cos^{-1}\ (d/L)$.

For the second part of the work, the chiral liquid crystalline acrylate used for prepare P_{13}, was transformed into a linked network via photopolymerization (N_2 atmosphere, 40°C - 65 °C) with UV light (1.50 mW/cm^2 at 365 nm), in the presence of Irgacure 651® as photoinitiator, at different polimerization times. The polyacrylate crosslinked in bulk (CPB) and crosslinked in aerogel (CPA) was obtained. The silica aerogel consisted of a network of fractal agregates (D_m=1.7±0.1) with a mean pore size of 80±5.0 Å and density of 0.18 g/cm^3.[2] The uncrosslinked polyacrylate P_{13} (UP) was taken as reference.

The CPB was obtained after polymerization for 30 s and shows similar layered structure as the UP. Photo-crosslinking inside silica aerogels gives similar polyacrylates (CPA) as the CPB. Unreacted monomer was detected in the smaller pores, independently of the polymerization time. The CPB and CPA samples show also a smectic A mesophase. SAXS profiles of CPB and CPA can be seen in figures 3 and 4.

Some of these results were recently presented in the Workshop *Fibers and Polymers*, organized by the ESRF.[3]

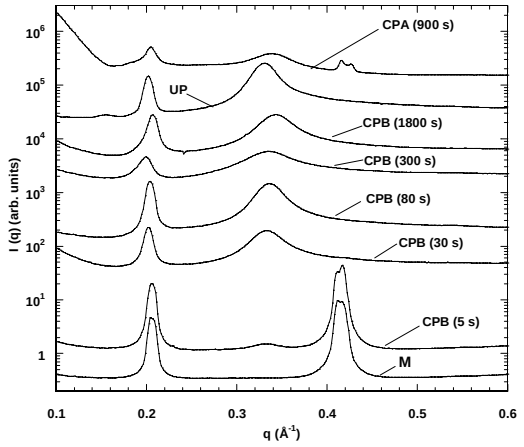

Figure 3: SAXS profiles of the UP.

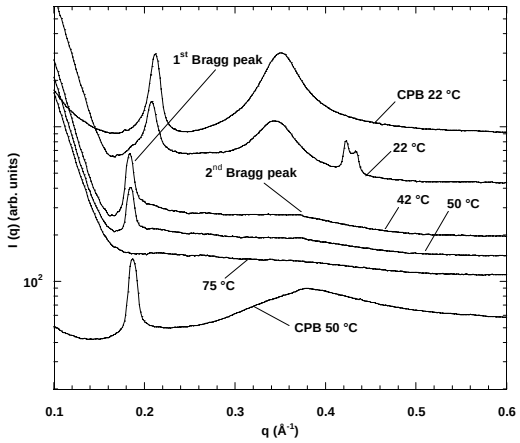

Figure 4: SAXS profiles of CPB. M: mesogenic moiety.

References

1) Ritter, O. M. S., Merlo, A. A., Pereira, F. V., Pesce da Silveira, N., Geissler, E., Zukerman-Schpector, J. *Synthesis and characterization of new chiral liquid-crystalline polyacrylates form L-isoleucine.* To be submitted.

2) Rigacci, A., Ehrburger-Dolle, F., Geissler, E., Chevalier, B., Sallée, H., Achard, P., Barbieri, O., Berthon, S., Bley, F., Livet, F., Pajonk, G. M., Pinto, N., Rochas, C, *J. Non-Crystalline Solids* **285**, 187 (2000).

3) Pesce da Silveira, N., Rigacci, A., Ehrburger-Dolle, F. Geissler, E. *Liquid Crystalline Polymers Confined in a Silica Aerogel: A SAXS Study.* In: Fibers and Polymers Workshop, ESRF, February 11-12, 2002.