Abstract

Several series of reversible physical networks based on polydimethylsiloxane (PDMS) chains and liquid crystalline (LC) structural units were synthesized and studied, which belong to three different architecture types:

(1) LC-grafted PDMS (with LC quartets at the grafting sites),

(2) LC-end-capped linear PDMS,

(3) and linear ‘infinite’ LC-PDMS copolymers (with alternating LC and PDMS segments).

PDMS spacers of different lengths of were tested, as well as 6 different polyaromatic mesogens of azo type and azo-free type.

Hydrosilylation coupling of vinyl-functional mesogens, obtained as part of an international cooperation, with commercial Si-H-functional PDMS was employed to synthesize all the studied materials.

The copolymers were physically crosslinked by the nano-aggregation of the LC units contained in their macromolecules. The thermotropic properties of the LC-nano-aggregates lent interesting physical properties to the whole material, making some of the copolymers attractive as potential smart materials.

The PDMS spacer segments were selected for the sake of their extreme flexibility, which should provide elastic properties to the physically crosslinked copolymers, and also because of their (desired) incompatibility with the mesogens. This latter effect was highly helpful for achieving the desired physical crosslinking.

The LC-grafted architecture achieved the strongest physical crosslinking, if copolymers with identical (or nearly) identical mesogens, and with PDMS spacers of the same length were compared. The linear infinite copolymers were less strongly crosslinked, and the crosslinking was the weakest in the LC-end-capped ones. The latter materials were rubbery only at low temperatures, but behaved like temperature-sensitive smart oils (containing

physical crosslinks) at ambient *T*. The efficiency of the crosslinking in the grafted copolymers is apparently greatly enhanced by the occurrence of LC units as quartets at the graft sites.

In the series of the linear ‘infinite’ LC-PDMS copolymers, it was possible to vary the strength of the physical crosslinking by changing the size of the incorporated mesogen. The melting point of the elastomers could be increased up to temperatures exceeding 160°C in the extreme case.

The presented work includes a comprehensive characterization of the copolymers by mechanical, thermo-mechanical and rheological methods. The complex phase behaviour of the nano-segregated LC-copolymers was elucidated by correlating DSC, X-ray and PLM analyses with thermo-mechanical and rheological ones.

Very attractive, application-related material properties of the copolymers include their re-processability (useful e.g. for 3D printing, recycling, or simple processing), multiple temperature-induced viscoelastic transitions in the rubbery or molten state (interesting for smart applications), melt thixotropy with very rapid recovery of the initial properties, as well as self-healing in the rubbery state (connected with the physical nature of the crosslinking).