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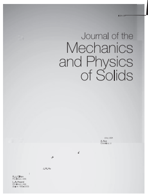

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Nomenclature

$\boldsymbol{A}$	rotation tensor
[illegible]	Avogadro's constant
[illegible]	length of a chain's segment
[illegible], [illegible]	solvent's concentration in the reference state and solvent concentration triggering the opening of all the switchable molecules in the unit volume, respectively
$\boldsymbol{E}$	Green–Lagrange deformation tensor
[illegible]	energy barrier between the two states of a single switchable molecule
$\boldsymbol{F}$, [illegible]	deformation gradient tensor
$\boldsymbol{F}$	deformation gradient tensor associated to the molecules opening mechanism
[illegible]	threshold force required to open a switchable molecule
[illegible]	force acting on a polymeric chain
[illegible]	average chain force value evaluated over all the chain lengths
[illegible] $(\boldsymbol{F},$ [illegible]$)$	ratio between the number of open and the number of switchable molecules joined to chains with a given length
[illegible] $(\boldsymbol{F},$ [illegible]$)$	number fraction of the open molecules with respect to the total number of switchable molecules in the polymer
	total relative volume change
[illegible], [illegible]	relative volume change due to the opening of the switchable molecules and to swelling, respectively
[illegible], [illegible]	activation and deactivation reaction rates of the switchable molecules
[illegible]	Boltzmann's constant
$\mathcal{L}$, $\mathcal{L}^{-1}$	Langevin function and its inverse
[illegible], [illegible]$_0$	end-to-end distance of a single polymer chain in the current and reference state, respectively
[illegible]	end-to-end distance of the polymer chain having the mean value [illegible] of Kuhn's segments
[illegible], [illegible]$_0$	length of a switchable molecule in the current and reference state, respectively
[illegible]	number of chains per unit volume
[illegible]	number of segments in a polymer chain
[illegible], δ[illegible]^2	mean value of the distribution of the number of Kuhn's segments, and its variance, respectively
[illegible]	current number of solvent molecules available for one switchable molecule
[illegible]	probability density function of the number of Kuhn's segments
$\boldsymbol{r}$	end-to-end distance
$\boldsymbol{P}$	first Piola stress tensor
[illegible]	stoichiometric ratio necessary for the activation of the opening reaction
[illegible]	absolute temperature
	molar volume of the switchable molecules
	molar volume of the solvent molecules
[illegible], [illegible]	volume of a switchable molecule in the close and in the open form, respectively
[illegible]	energy stored in the network
[illegible]	mixing energy
	energy associated to opening of the switchable molecules
	mechanical work necessary to open a single switchable molecule
α	relative size of the switchable molecule
χ	Flory–Huggins parameter governing the swelling phenomenon
δ[illegible]$_0$, δ[illegible]$_0$	energies required for the opening and the closing transformation, respectively
δ	size difference of the switchable molecule between the two states
φ	volume fraction of the switchable molecules
φ	volume fraction of the switchable molecules in the open state
φ	volume fraction of the switchable molecules in the close state
λ	stretch of a switchable molecule
λ	stretch of a single polymer chain
λ	stretch of the single polymer chain-switchable molecule system
λ_0	stretch value referred to the mean chain length [illegible]$_0$
$\tilde{\lambda}$	average (mesoscopic) stretch value evaluated over all the chain lengths
μ	shear modulus
ψ	deformation energy function

[illegible]

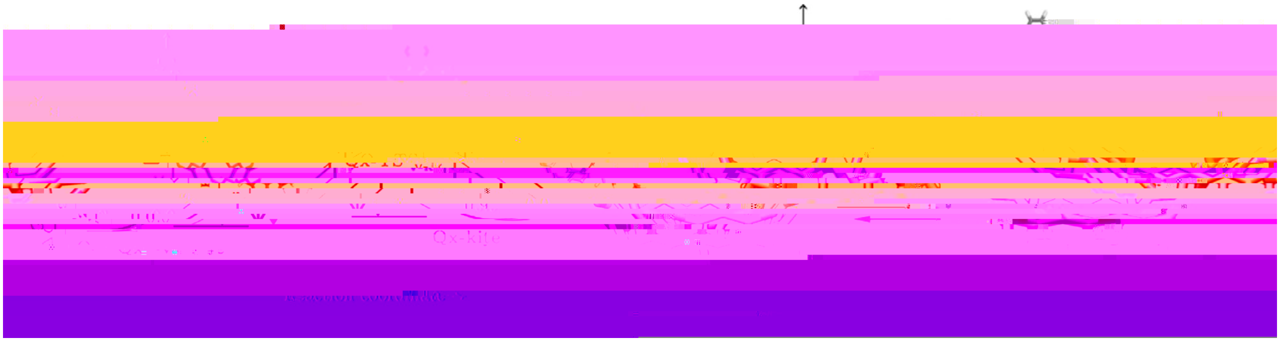


Fig. 1. (a) Shape of the two states, close and open, of the switchable quinoxaline cavitands. (b) Graph illustrating the energy of the cavitand during the transition between the two states; the vase (close) and the kite (open) conformations are the only stable ones and correspond to a minimum of the energy. The transition from one stable state to the other one requires passing through an energetic potential barrier.

model has been applied to the specific case of an elastomeric PDMS containing switchable cavitands and compared with the corresponding experimental results in the last part of Section 6.

2. Motivation of the study

The development of a suitable

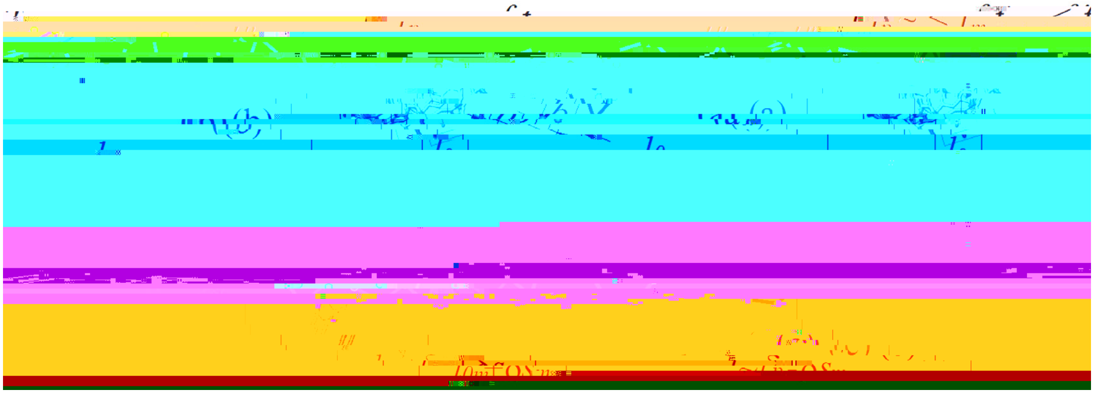
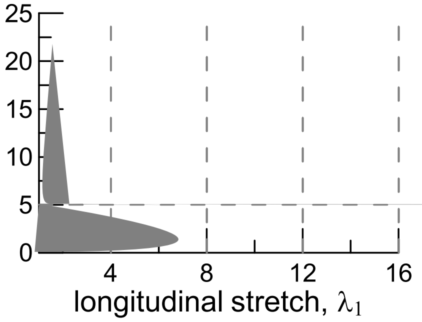


Fig. 2. Scheme of the switchable molecule joined in series with a polymeric chain. Stress-free state (a), loaded state before switching

Due to the small size of the

The value of the chain force [illegible] influences the value of the force [illegible] at which the transition takes


25
20
15
10
5
0
4
8
12
16
longitudinal stretch, λ_1

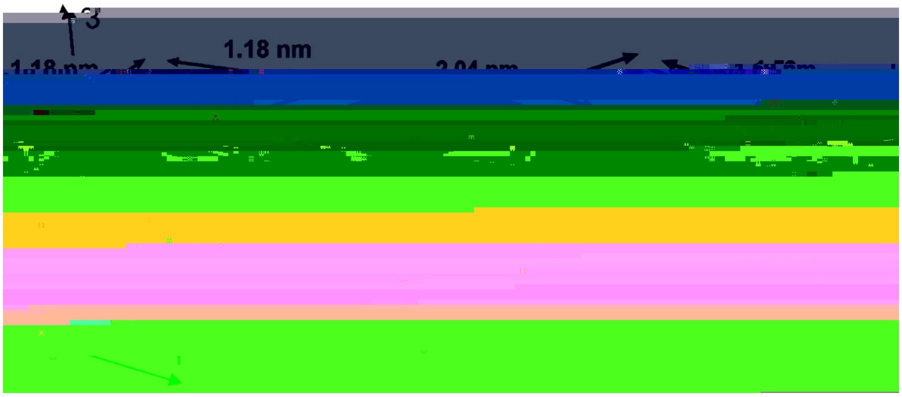


Fig. 9. Dimensions of the switchable molecule (quinoxaline

reported; at the steady state the volumetric expansion due only to the opening is equal to about 1.2%, which represents a remarkable volume change by considering that the volume fraction of the switchable molecules is equal to only 0.41%.

Experimental tests involving the stress-driving of the switchable molecules have not been performed yet and will be the object of a future research work.

7. Conclusions

In the present paper, the mechanical behavior of responsive materials has been considered. Responsive

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