Reactive & Functional Polymers 73 (2013) 885–890

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Review

Switching shapes of nematic elastomers with various director configurations

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A R T I C L E I N F O

Article history:
Available online 27 October 2012

Keywords:
Liquid crystal elastomers
Nematic elastomers
Soft actuators

A B S T R A C T

We review our recent studies for various types of thermally driven deformations of nematic elastomers (NEs) such as elongation, contraction, bending, spiral and helical deformations. The shape of NEs is very sensitive to a change in local nematic order as a result of pronounced coupling of rubber elasticity and molecular orientational order. A variety of the types of director configurations such as planar, vertical, hybrid and twist alignments lead to various types of thermal deformation. The inhomogeneous thermal deformations such as bending, spiral and helical deformations are quantitatively predictable from the data of the thermal uniaxial deformation of the corresponding NE with planar alignment on the basis of the continuum elastic theories.

Contents

1. Introduction

Nematic elastomers (NEs) are a novel class of materials. NEs have both the hyperelasticity of rubbers and the orientational properties of liquid crystals (LCs) [1,2]. A marked feature of NEs is that the macroscopic shape and molecular orientational order are strongly coupled with each other. The shape of NEs is very sensitive to external stimuli that change the orientational order of mesogens. In the case of thermotropic LCs, the temperature change across the nematic–isotropic transition temperature (T_{NI}) greatly varies the orientational order of the mesogens. In fact, the thermotropic NEs with globally planar alignment exhibit large degrees of uniaxial elongation or contraction in response to cooling or heating each of which causes an increase or decrease in nematic order, respectively [3–5]. Importantly, this thermally induced deformation is reversible, and no appreciable effect of thermal history on deformation is observed. This indicates that NEs are a kind of shape-memory materials. The origin of the shape memory in NEs is the director configuration memorized in the stage of cross-linking reaction for the formation of permanent polymer networks with infinite molecular weight. For instance, the NEs with planar alignment are prepared by cross-linking reaction in the globally aligned state of the mesogens. The initial planar director configuration memorized by cross-linking is not erased by repeating the thermal transition between the aligned nematic state and the randomly oriented isotropic state. Thermally induced large deformation of NEs with planar alignment received much attention in the early stage of the researches of NEs. In general, the main chain type NEs where the mesogens are incorporated into the network backbone exhibit considerably larger degrees of thermal strain than the corresponding side chain type NEs where the mesogens belong to the chains dangling from the network backbone [5]. The larger degrees of thermal deformation of the main chain type NEs is due to the direct coupling between the alignments of the mesogen and network backbone. In the case of side chain type NEs, the alignment of network backbone is in indirect manner caused by that of dangling mesogen. In fact, several types of main chain type NE

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http://dx.doi.org/10.1016/j.reactfunctpolym.2012.10.008

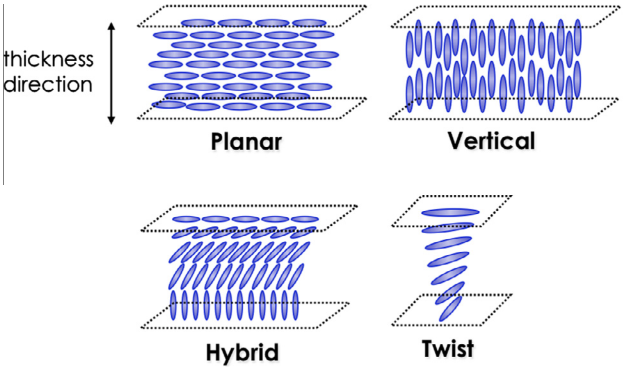

Fig. 1. Various types of director configuration.

exhibit a remarkable strain of ca. 300% in response to a temperature change across T_{NI} [5,6]. NEs showing the large thermal deformation have potential as thermally driven soft actuators and sensors. The performance of NEs as thermally driven actuators and sensors was examined by several researches [3,7,8].

Various complicated types of thermal deformation other than simple elongation/contraction can be achieved if the corresponding inhomogeneous director configurations are introduced into NEs. In the field of LC displays, various types of director configuration have been employed in electro-optical cells [9]. They include inhomogeneous configurations such as "hybrid" and "twist" alignments. In hybrid alignment, the director smoothly changes from planar orientation to vertical one between two substrates (Fig. 1). In twist alignment, the director continuously rotates by 90° between the substrates (Fig. 1). Broer et al. [10] demonstrated that the glassy LC networks with hybrid or twist alignment exhibit a curled or saddle-like shape, respectively, in response to temperature change. In the glassy state, there is no pronounced coupling of macroscopic shape and orientational order, and the local nematic order is insensitive to temperature. The main origin of the thermal deformation in the glassy LC networks is a finite gradient of thermal expansion coefficient in the thickness direction due to anisotropic orientation. Recently, we have fabricated the NEs with these inhomogeneous configurations, and demonstrated that the temperature change gives rise to markedly large degrees of bending and twist deformations [11,12]. A pronounced coupling between the shape and nematic order in the elastomeric LC networks boosts up the thermally induced deformations. These results not only extend the possibility of NEs as soft actuators and sensors, but provide important basis to understand fully the coupling between nematic order and rubber elasticity. A primary goal of this article is to review our recent studies for the fabrications and thermal deformation of NEs with various types of director configurations.

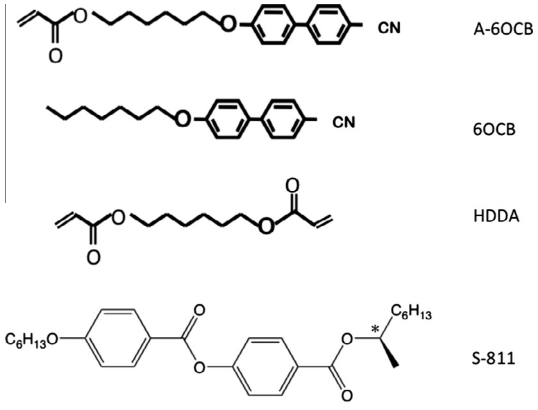

Fig. 2. Chemical structures of employed materials.

2. Fabrication of NEs with various director configurations

Various types of director configurations (planar, vertical, hybrid and twist alignments) for monomeric and polymeric LCs can be achieved in glass cells with small gap using surface effects. The surfaces of glass substrates are coated by uniaxially rubbed polymer layers. Polyimide (PI) is a familiar polymer employed for the alignments of LCs. The surface coated by rubbed PI layer often promotes the orientation of the mesogens parallel to the rubbing direction. For planar configuration, the LCs are sandwiched between the two substrates with this type of PI (P-PI). For vertical configuration, a special type of polyimide (V-PI) to induce the mesogen orientation normal to the surface is coated on the two substrates. Hybrid configuration is achieved by the combination of the substrate with P-PI and that with V-PI. For twist configuration, the two substrates with P-PI are placed so that the rubbing directions are crossed each other. The handedness and the degree of twisting are controlled by the kind and amount of a substance with molecular chirality ("chiral dopant") that is mixed with LCs.

In order to obtain the NEs with these types of director configuration, it is required to conduct the cross-linking reaction in the low-temperature nematic state of the LC molecules with the corresponding alignments. We employed the photopolymerization of monoacrylate mesogen (A-6OCB) and diacrylate cross-linker (HDDA), whose chemical structures are shown in Fig. 2, with a photoinitiator bis(cyclopentadienyl)bis [2,6-difluoro-3(1-pyrryl)phenyl]titanium (Irgacure® 784). The resulting network is a side chain type NE with acrylate backbone. The amount of HDDA (cross-linker) is sufficiently low (typically less than 10 mol%) to make the networks elastomeric. A-6OCB is highly crystallizable, and the temperature range of the nematic state is very narrow (less than a few degree). In order to broaden the nematic state, the miscible unreactive nematic solvent 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) is mixed with A-6OCB at a mixing molar ratio of 1/1.

The reactant mixtures are loaded in the glass cells with the PI-coated surfaces. The cell gap is usually less than 100 μm below which the surface effect works sufficiently. The photopolymerization is conducted by irradiating the light with a wavelength of

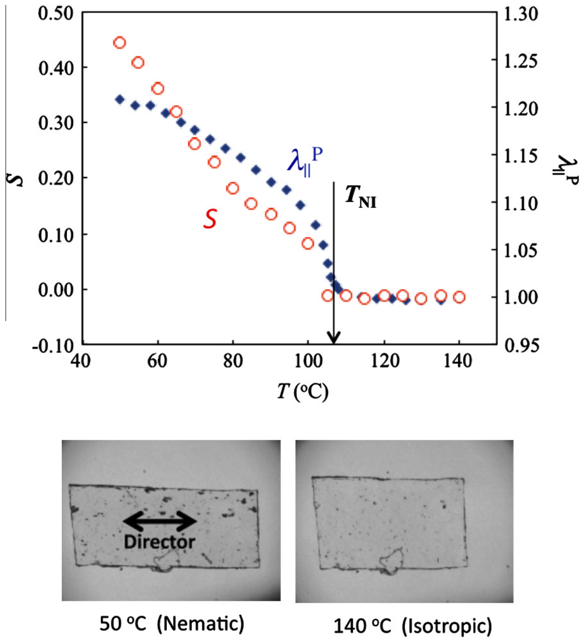

Fig. 3. Reduced dimension along the director and orientational order parameter for P-NE as a function of temperature.