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Reversible Deformation of Smectic Liquid-Crystalline Elastomers

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要旨：液晶エラストマーはポリマーネットワークの力学的性質と液晶相の異方性を併せ持つ新しいソフト固体として注目されており、応力場により配向制御ができるという特徴を持つ。その配向状態は架橋により記憶されるため、例えば、ネマチックエラストマーの場合、等方相⇌ネマチック相転移において可逆的・自発的な伸縮が観測される。いままで主に検討されてきたネマチックや SmA エラストマーの局所的な配向は円筒対称であり、一軸配向によりモノドメイン試料を得ることができた。しかし二軸性である SmC エラストマーの場合、単純な一軸配向ではモノドメインを得ることはできない。ここでは、せん断応力印加架橋によるダイレクターとスメクチック層の両方が配向したモノドメイン SmC エラストマーの合成について述べ、その相転移を伴う昇降温過程における可逆的な形状変化について報告するとともに、記憶形状のメカニズムについて議論する。

1 Introduction

Since Finkelmann and coworkers reported the reversible elongation and shrinkage of a uniformly aligned liquid-crystalline elastomer designated as a Liquid Single Crystal Elastomer (LSCE) along its director during the phase transformation between an isotropic to a nematic phases, an increasing attention has been paid to their reversible strain actuation and soft elasticity [1]. While there have been a few investigations on reversible shape change of nematic elastomers, much less work has been carried out on those of smectic. In particular there are few experimental reports about the deformation of chiral smectic C (SmC*) elastomers in spite of their potential properties due to the point group C_2 of the untwisted structure.

About a decade ago, Terentjev and Warner theoretically described the coupling between elastic deformation and the SmC order parameter for the limiting situation of small distortions [2]. These predictions have not been experimentally verified due to the lack of monodomain samples. Recently, we succeeded in obtaining these samples with macroscopic C_2 symmetry of the unwound SmC* state by two successive deformation processes and more perfectly by mechanical shear deformation [3,4]. The purpose of this paper is to show that the monodomain SmC* elastomer obtained by a mechanical shear field exhibits a biaxial-shape-memory effect, which means spontaneous and reversible deformation occurs in a heating and cooling process where successive phase transitions take place [5].

2 Experimental

An elastomer is synthesized by a hydro-silylation reaction of the liquid-crystalline side groups with a polysiloxane backbone. The chemical structures of the polymer backbone, the mesogens and the crosslinker are shown in Figure 1. The elastomer contains two different mesogenic moieties statistically linked to the monomer units of the network, and shows the following phase sequence; g -6 SmX* 32 SmC* 105 SmA 115 I (in °C). The transition temperatures listed above are confirmed by DSC measurements and temperature dependent X-ray investigations. After the reaction under centrifugation, the elastomer, which is removed from the vessel, is deformed uniaxially to obtain a uniform orientation of director. And then, it is fixed onto a simple shear apparatus and sheared.

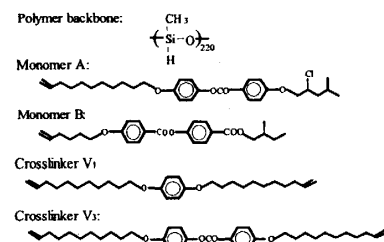


Fig. 1 System under investigation

3 Results and Discussion

To investigate deformational behavior of the monodomain SmC* elastomer during the successive phase transitions, the shape-change of the elastomer film is observed in a cooling and heating process. A photograph of the monodomain SmC* elastomer at room temperature is shown in Fig. 2(a), where the

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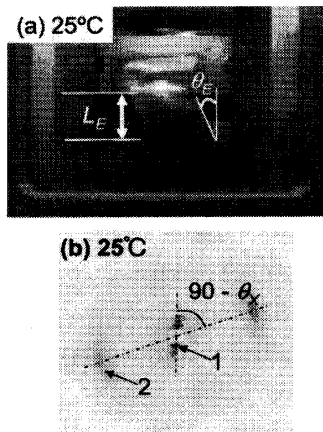


Fig. 2 (a) a photograph of monodomain SmC* elastomer and (b) its X-ray pattern.

room temperature, decreases with increasing temperature in the SmX* and SmC* phases. θ_E remains at about 10° in the temperature region of the SmA phase at 90°C and it also remains at several degrees even in the isotropic phase at 130°C . In the same manner as the sample length L_E , the reverse deformation is also recognized in the tilt angle θ_E of the elastomer. Namely, the monodomain SmC* elastomer possesses the ability to restore its shape spontaneously.

To analyze whether macroscopic shape changes directly correlate with molecular re-alignment processes, X-ray investigations are carried out. Fig. 2(b) shows the X-ray pattern of the monodomain SmC* elastomer observed at room temperature (25°C). While the layer reflection located near the meridian (arrow 1) indicates a uniform alignment of smectic layers in the tilted smectic phase at room temperature, reflection at wide angle (arrow 2) indicates that the mesogenic groups are aligned uniformly in the direction inclined as the molecular tilt angle θ_X with respect to the layer normal. The reverse change of θ_X is also confirmed during the heating and cooling process. In addition, the tilt angle of the elastomer film θ_E approximately agrees with the molecular tilt angle θ_X characterized in the X-ray patterns. The agreement between the sample observation and the X-ray analysis reveals that the macroscopic symmetry defined by the shape of the SmC* elastomer film is closely associated with the microscopic local symmetry due to the liquid-crystalline phase. Because crosslinking under mechanical shear field perpetuates the memory of the molecular alignment at the SmC* state, the monodomain SmC* elastomer exhibits a biaxial shape memory effect in the macroscopic feature of the film.

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topside of the elastomer is fixed to a sample holder, while the lower end can move freely. To measure the elastomer's shape, the sample length L_E (the distance between polyimide tapes) and the tilt angle of the elastomer film θ_E (the angle between the edge of the film and the direction of the first-uniaxial deformation) are defined as illustrated in Fig. 2(a). Both of them are plotted as a function of temperature in Figures 3(a) and (b), respectively. While L_E slightly increases with increasing temperature in the SmX* and SmC* phases, and it attains its maximum in the SmA phase, and then it rapidly decreases during the phase transformation from SmA to Iso (Fig. 3(a)). The reverse deformation is recognized on cooling; namely, the elastomer rapidly elongates at the phase transformation from Iso to SmA, and then L_E decreases slightly with decreasing temperature in the SmC* and SmX* phases. The temperature dependence of the tilt angle θ_E of the elastomer is shown in Fig. 3(b). θ_E is about 23° at

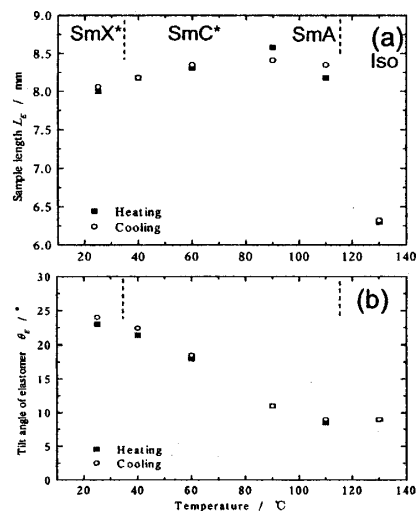


Fig. 3 Temperature dependences of (a) sample length L_E and (b) tilt angle θ_E of an elastomer film.