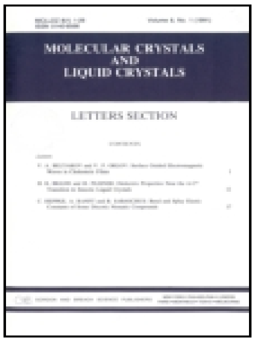

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Remoldable Crosslinked Liquid-Crystalline Polysiloxane with Side Chain Mesogens Based on Exchangeable Crosslinks

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Crosslinked liquid-crystalline polymers (CLCPs) show unique behavior of deforming macroscopically when stimulated with heat, electricity and light. However, they cannot be remolded and reshaped once prepared. Here, we designed crosslinked polysiloxane with side chain mesogens that contain exchangeable crosslinking points based on transesterification between phenyl benzoates and hydroxy groups. After the formation of a polymer network, a base catalyst was introduced into the CLCP. When heated at 80°C, a piece of the CLCP was reshaped into a film and separate pieces of the CLCP were fused together, indicating that the CLCP is remoldable.

Keywords Liquid-crystalline polymer; dynamic covalent bond; transesterification

Introduction

Crosslinked liquid-crystalline polymers (CLCPs) are novel soft materials that possess both the alignment order of liquid crystals and the elasticity of polymer networks [1–3]. Uniaxially aligned CLCPs exhibit a spontaneous contraction along the director axis when heated above nematic-isotropic phase transition temperature, due to the strong coupling between the alignment of mesogens and conformation of polymer main chains [4, 5]. When photochromic moieties such as azobenzene derivatives are incorporated into a CLCP system, an isothermal nematic-isotropic phase transition and deformation of a CLCP film can be induced by irradiation with UV light as a result of photoisomerization [6]. Furthermore, three-dimensional bending motions of CLCP films containing azobenzene moieties have been observed upon exposure to light [7–9].

The large deformation of CLCPs depends on the initial alignment of mesogens, and the alignment of mesogens should be fixed with high alignment order on preparation of the sample. One of the most widely used procedures for preparing large-size monodomain CLCPs is a two-step crosslinking method. In this method, a weakly crosslinked film is uniaxially stretched to align mesogens, and then the alignment is fixed by the post

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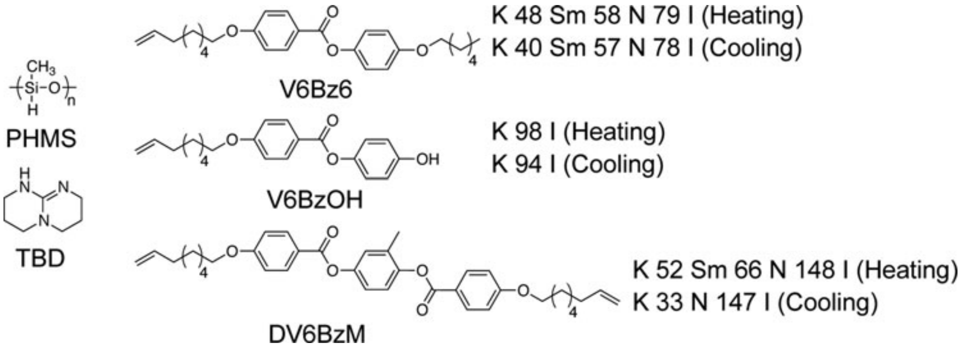

Figure 1. Chemical structures and phase transition temperatures of compounds used in this study. K, crystal; Sm, smectic; N, nematic; I, isotropic.

crosslinking [10]. Another method is copolymerization of aligned liquid crystalline (LC) monomers and crosslinkers in a glass cell with alignment layers [11]. However, there is an essential drawback in these methods: crosslinked polymers cannot be reshaped and reprocessed by heat or with solvent after the formation of the polymer network is completed. This fact restricts seriously the fabrication of CLCPs into various three-dimensional shapes.

Recently, introduction of dynamic covalent bonds into crosslinked polymers has been demonstrated as a powerful approach towards the design of self-healing and remoldable polymer materials [12]. In particular, vitrimers attract much attention due to changes of their topology through bond exchange reactions [13,14]. At high temperatures, activation of transesterification leads to a flow of vitrimers, even though the total number of crosslinks remains unchanged. Furthermore, the concept of exchangeable networks has been shown to be applicable to CLCPs based on epoxy resins, in which mesogens are uniaxially aligned and fixed by stretching the epoxy resins above an activation barrier temperature even after the formation of the network is completed [15].

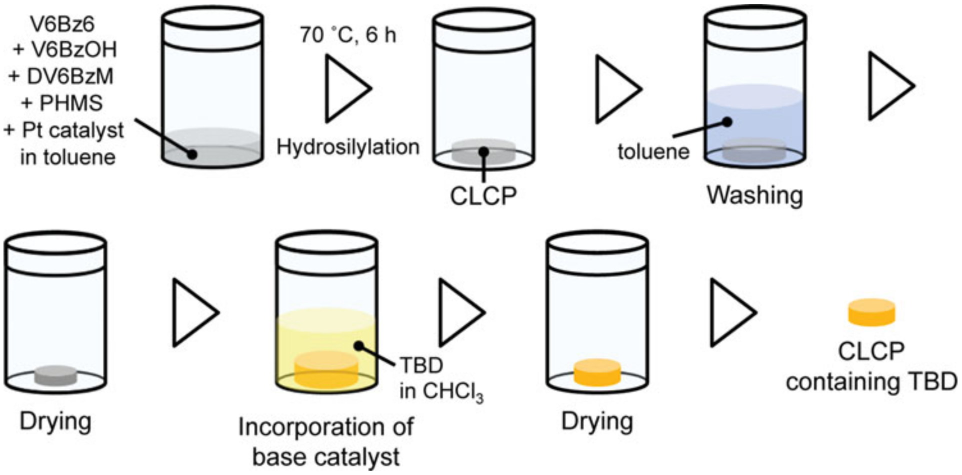

Figure 2. Schematic illustration of the procedure for preparing CLCP.

Crosslinked polysiloxanes are representative elastomers with excellent mechanical properties. CLCPs based on the polysiloxane backbone show large deformation up to 400% upon heating [5]. The processability of polysiloxane elastomers would be improved by introduction of exchangeable crosslinks. In this work, we prepared CLCPs with a polysiloxane backbone and side chain mesogens, which are subject to transesterification, and explored their ability to be reshaped and remolded.

Experimental

Chemical structures of compounds used in this study are shown in Figure 1. We designed the CLCP that undergoes transesterification between phenyl benzoates and hydroxy groups. A crosslinker (DV6BzM) was prepared according to a previously reported method [16]. A phenyl benzoate mesogen with a vinyl group (V6Bz6) was synthesized from 4-(oct-7-enyloxy)benzoic acid [17] and 4-hexyloxyphenol with *N,N′*-dicyclohexyl carbodiimide (DCC) and *N,N′*-dimethyl-4-aminopyridine (DMAP) in dry CH_2Cl_2 at room temperature. A phenyl benzoate derivative containing a hydroxy group and a vinyl group (V6BzOH) was obtained via an esterification reaction between 4-(oct-7-enyloxy)benzoic acid and hydroquinone using DCC and DMAP in dry THF at room temperature.

CLCPs were prepared through hydrosilylation reaction (Figure 2). V6Bz6 (60 mol%), V6BzOH (30 mol%), DV6BzM (10 mol%) and polymethylhydrosiloxane (PMHS, $M_n =$ 2,100) were dissolved in dry toluene, and then a toluene solution of Karstedt's catalyst was added. The reaction mixture was heated at 70°C for 6 h. The resultant gel was washed with toluene, and dipped in chloroform containing triazabicyclodecene (TBD), which was incorporated as a base catalyst of transesterification reactions. Furthermore, the gel containing TBD was dried under reduced pressure.

The mesomorphic properties of the CLCP were examined by polarizing optical microscopy (POM).

Results and Discussion

Figure 3 shows POM images of a CLCP sample. The sample showed a LC phase between room temperature and 155°C on heating. Although the CLCP contains V6BzOH units, which show no LC phase (Figure 1), the polymer exhibited a LC phase in a wide temperature range.

We examined if the CLCP can be reshaped and reprocessed. At room temperature, a piece of the CLCP deformed under stress and returned to the initial shape when the stress was removed. When a piece of the crosslinked polymer was cramped between two glass

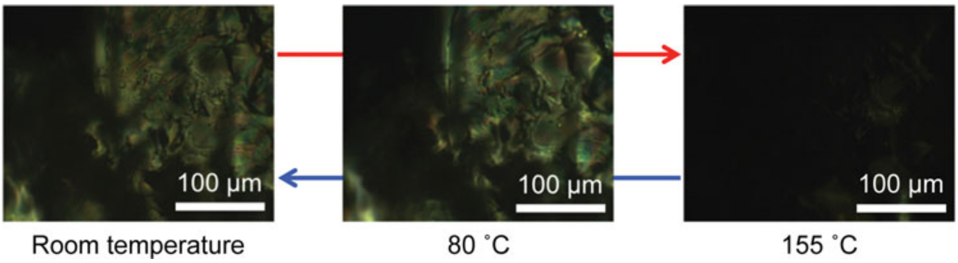

Figure 3. POM images of a CLCP.

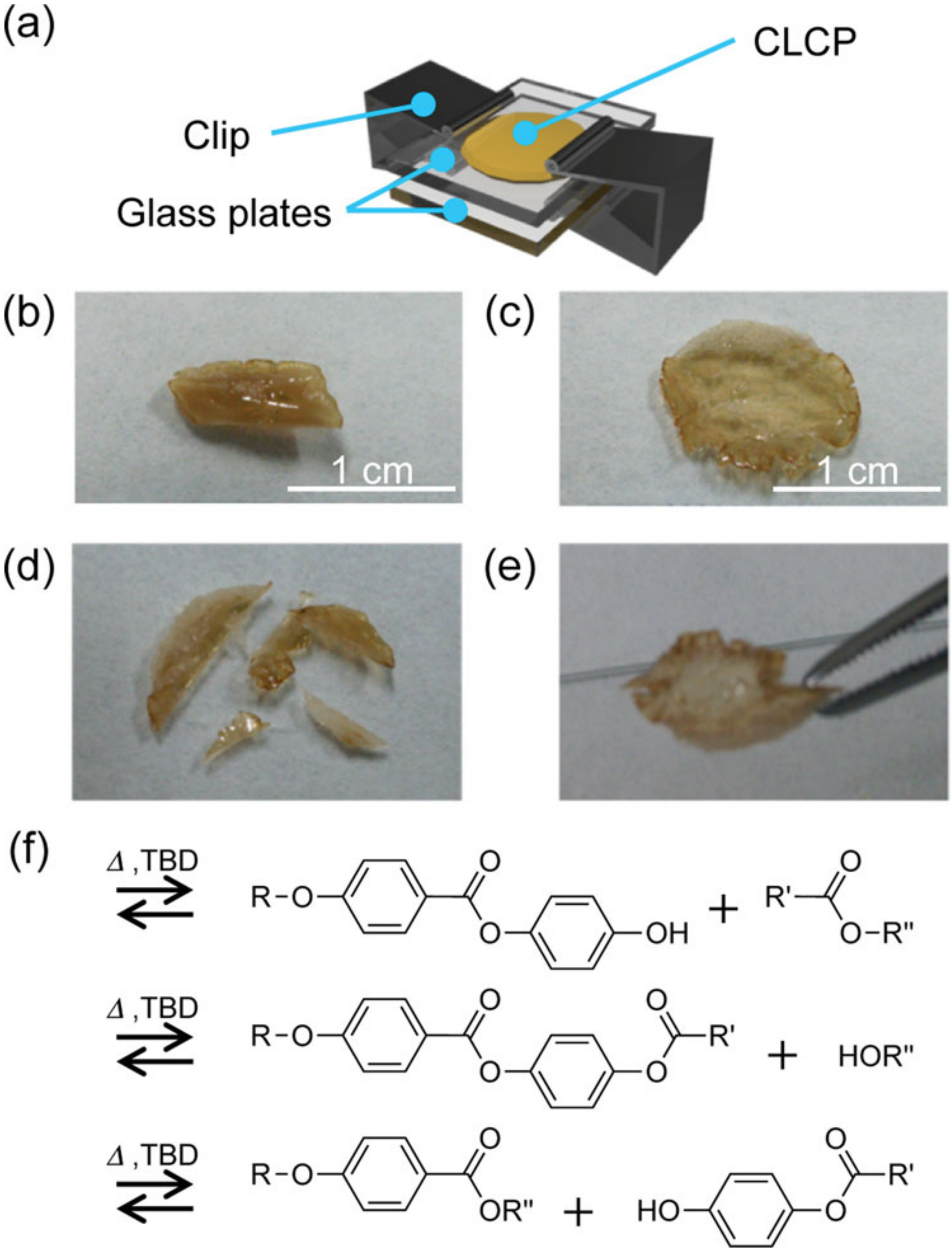

Figure 4. Reshaping and reprocessing of the CLCP at 80°C for 1 h. (a) Schematic illustration of the experimental setup; Photographs of a piece of the CLCP (b) before and (c) after reshaping; Photographs of (d) several pieces of the CLCP and (e) after fusion of them; (f) Scheme of reversible transesterification.

plates (Figure 4a) and left at 80°C for 1 h, it was reshaped into a film (Figure 4b and c). The shape of the resultant film was stable both at room temperature and 80°C. This result indicates that transesterification proceeds between phenyl benzoates and hydroxy groups in the crosslinked polymer at 80°C (Figure 4f), and it can be reshaped through the exchange of crosslinking points. The reshaping temperature was lower than that of the epoxy resin-based exchangeable networks [13,15], presumably reflecting the flexibility of the polysiloxane main chains. Furthermore, small pieces of CLCP were fused together into a film under the same condition (Figure 4d and e), and the resultant film could be picked up with tweezers without separating into initial small pieces. This fact implies that the crosslinks are exchangeable even between the different pieces of the CLCP, which enables the molding of the polymer through such processes as extrusion and injection molding usually applied for thermoplastics.

Conclusion

We designed a CLCP with a polysiloxane backbone and side chain mesogens, which is able to undergo transesterification between phenyl benzoates and hydroxy groups. The CLCP showed a LC phase in a wide temperature range between room temperature and 155°C. The reshaping and reprocessing of the crosslinked polymers were accomplished at 80°C. This novel class of crosslinked polymers is possibly used for the development of soft actuators with various shapes through simple fabrication processes.

References

[1] de Gennes, P. G. (1975). *C. R. Acad. Sci. B*, *281*, 101.
[2] de Gennes, P. G., Hebert, M., & Kant, R. (1997). *Macromol. Symp.*, *113*, 39.
[3] Warner, M., & Terentjev, E. M. (2003). *Liquid Crystal Elastomers*, Oxford University Press: Oxford, UK.
[4] Finkelmann, H., Kock, H., & Rehage, G. (1981). *Makromol. Chem. Rapid Commun.*, *2*, 317.
[5] Wermter, H., & Finkelmann, H. (2001). *e-polymers*, *1*, 111.
[6] Finkelmann, H., Nishikawa, E., Perieira, G. G., & Warner, M. (2001). *Phys. Rev. Lett.*, *87*, 015501.
[7] Yu, Y., Nakano, M., & Ikeda, T. (2003). *Nature*, *425*, 145.
[8] Ikeda, T., Nakano, M., Yu, Y., Tsutsumi, O., & Kanazawa, A. (2003). *Adv. Mater.*, *15*, 201.
[9] Ube, T., & Ikeda, T. (2014). *Angew. Chem. Int. Ed.*, *53*, 10290.
[10] Küpfer, J., & Finkelmann, H. (1991). *Makromol. Chem. Rapid Commun.*, *12*, 717.
[11] Broer, D. J., Finkelmann, H., & Kondo, K. (1988). *Makromol. Chem.*, *189*, 185.
[12] Kloxin, C., & Bowman, C. (2013). *Chem. Soc. Rev*, *42*, 7161.
[13] Montarnal, D., Capelot, M., Tournilhac, F., & Leibler, L. (2011). *Science*, *334*, 965.
[14] Capelot, M., Montarnal, D., Tournilhac, F., & Leibler L. (2012). *J. Amer. Chem. Soc.*, *134*, 7664.
[15] Pei, Z., Yang, Y., Chen, Q., Terentjev, E. M., Wei, Y., & Ji, Y. (2014). *Nat. Mater.*, *13*, 36.
[16] Donnio, B., Wermter, H., & Finkelmann, H. (2000). *Macromolecules*, *33*, 7724.
[17] Wang, W., Sun, X., Wu, W., Peng, H., & Yu, Y. (2012). *Angew. Chem. Int. Ed.*, *51*, 4644.