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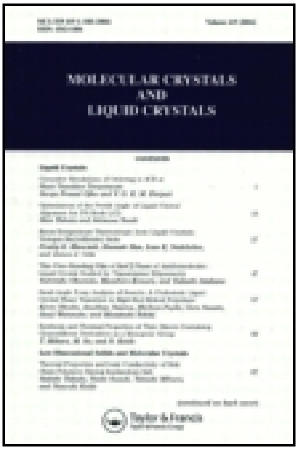

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Liquid-Crystalline Physical Gels Formed by the Aggregation of Trans-(1R,2R)-Bis(Dodecanoylamino)Cyclohexane in a Thermotropic Nematic Liquid Crystal. Phase Behavior and Electro-Optic Properties

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Liquid-Crystalline Physical Gels Formed by the Aggregation of *Trans*-(1*R*,2*R*)-Bis(Dodecanoylamino)Cyclohexane in a Thermotropic Nematic Liquid Crystal. Phase Behavior and Electro-Optic Properties

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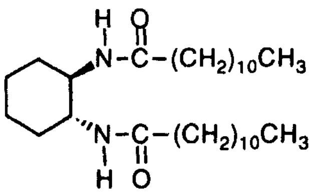
Liquid-crystalline physical gels have been obtained by the self-association of hydrogen-bonded molecules in a room-temperature nematic liquid crystal. Thermoreversible three states, isotopic liquid, *normal* (isotropic) gel, and anisotropic gel can be achieved for these mixtures. Electro-optic properties of the anisotropic gels have been examined with a twisted nematic cell.

Keywords: Liquid Crystal Gel; Physical Gel; Electro-optic Properties; Anisotropic Gel; Self-Assembly; Nematic; Hydrogen Bonds

INTRODUCTION

Anisotropic chemical gels fabricated by the dispersion of covalently crosslinked polymers in liquid crystals have attracted attention because of interesting electro-optic properties[1-3]. However, no liquid crystal physical gels had been prepared until we recently reported that anisotropic gels can be fabricated by the aggregation of *trans*-(1*R*, 2*R*)-bis(acylamino)cyclohexane (Cy11) in a room-temperature nematic liquid crystal, 4-cyano-4'-(pentyl)biphenyl[4]. This bis(amino)cyclohexane derivative and related compounds were developed as low molecular weight gelling agents for a variety of common organic solvents[5,6]. Reversible sol-gel transition behavior is observed for these anisotropic physical gels[4,7]. Anisotropic-isotropic and gel-sol transition temperatures could be designed by the combination of liquid crystals and gelling agents[4,7]. It is of interest to examine electro-optic properties of such new anisotropic materials. Preliminary results on such properties for these physical gels show that these gels are responsive to electric fields[4]. In the present study, thermal and electro-optical properties are examined for the liquid crystalline physical gels consisting of nematic liquid-crystal E7 based on cyanobiphenyl compounds and *trans*-(1*R*, 2*R*)-bis(dodecanoylamino)-cyclohexane (Cy11) as a gelling agent (Fig. 1).



Cy11

FIGURE 1 Chemical structure of *trans*-(1*R*,2*R*)-bis(dodecanoylamino)-cyclohexane (Cy11).

EXPERIMENTAL

A nematic mixture, E7 (Merck) was used as a room temperature liquid crystal material (T_{ni}=60 °C) without further purification. The gelation was tested for a mixture of E7 and diamide compound Cy11 in a sealed tube. The mixture was heated to an isotropic liquid state at 100 °C, then cooled to the desired temperature in a thermo-controllable oil bath. DSC measurements have been

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performed by a Mettler DSC30 in the heating and cooling rate of 5 °C/min. The electro-optic properties of anisotropic gels have been measured with ITO (indium tin oxide) glass sandwich cells (1 cm x 1 cm x 16 μm) coated with polyimide layers in which the rubbing direction of the two surfaces was perpendicular. AC fields (300 Hz) were applied to the cells.

RESULTS AND DISCUSSION

A room-temperature nematic liquid crystal, E7 can be efficiently gelled by compound Cy11. Figure 2 shows the phase transition behavior of the mixture of E7 and Cy11 as a function of the concentration of Cy11. The mol% of Cy11 is calculated based on the average molecular weight of E7. Three states, isotropic liquid, *normal* (isotropic) gel, and anisotropic gel states have been achieved for these mixtures. The minimum concentration of Cy11 for the gelation of E7 is 2.5×10^{-1} mol% in the mixture. It should be noted that the transitions are thermally reversible. When the mixture is heated above the sol-gel transition temperature, it fully becomes fluid isotropic liquid. Upon cooling, the *normal* gel based on the isotropic state of E7 is formed. It does not flow when the test tube is turned upside down for several months. The further cooling of the *normal* gel leads to the isotropic-anisotropic transition and the formation of the nematic liquid crystal gel. DSC curves clearly show such transitions. For the mixture containing 1 mol% of the gelling agent of Cy11, we observe two exothermic peaks at 76 and 58 °C corresponding to sol-gel and isotropic-anisotropic transitions, respectively. The enthalpy change at sol-gel transition due to the association energy of Cy11 is 1.2 J/g. The enthalpy change of transition between normal and nematic gels is observed to be 2.4 J/g. The glass transition is seen at -69 °C. With the increase of the concentration of the gelling agent, the sol-gel transition temperatures between the isotropic liquid and the *normal* gel increase. For the gel containing 9.1 mol% of Cy11, the sol-gel transition is observed at 112.2 °C. In contrast, the anisotropic-isotropic transition temperatures are kept to be constant.

The gelation of E7 is induced by the association of Cy11 through the formation of hydrogen bonds between the amide groups[4]. In this case, the assembled Cy11 forms fibrous solids, which are phase-separated from the nematic phase of E7. The hydrogen bonds between amide linkages have also lead to the induction and stabilization of the single mesomorphic phases[8-11]. The reversibility of the formation and the break for hydrogen bonds results in the reversible sol-gel transitions of these anisotropic mixtures. The reversible feature of hydrogen bonds was also used for the reversible phase transition of supramolecular liquid-crystalline networks[12].

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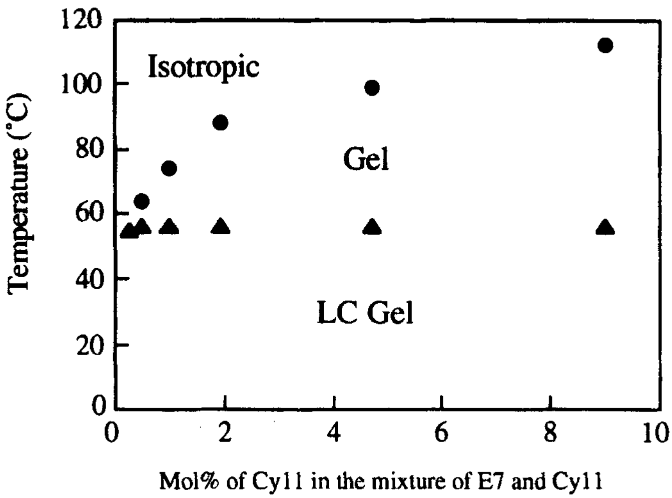

FIGURE 2 Phase behavior of the mixture of E7 and Cy11 on cooling. LC: liquid crystalline.

Electro-optic properties of these anisotropic gels have been examined with a twisted nematic (TN) cell. The gels containing no more than 0.5 mol%

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of Cy11 show TN molecular alignment. Figure 3 presents relationships between transmittance and applied voltage for the anisotropic gels and the single component of E7. These anisotropic gels are responsive to electric fields. The value of the threshold voltage (V_{th}) for the gel with 0.25 mol% of Cy11 is 1.9 V, while E7 shows the V_{th} value of 1.3 V. The response time of the gel with 0.25 mol% of Cy11 at 10 V is 23 ms, which is the same as that observed for only E7.

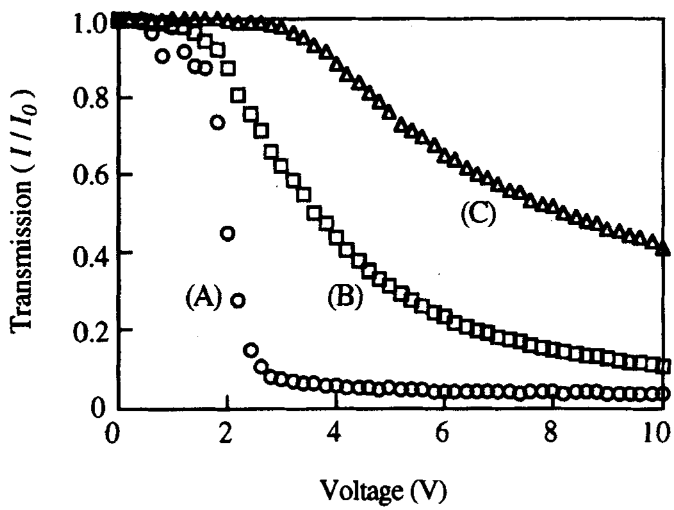

FIGURE 3 Relationship between transmittance and applied voltage for liquid-crystalline gels consisting of E7 and Cy11 in a TN (twisted nematic) cell: (A) E7; (B) E7 containing 0.25 mol% of Cy11; (C) E7 containing 0.5 mol% of Cy11.

The liquid-crystal gels reported here is a novel gel material, which possess the properties of liquid crystal materials and self-organized physical gels. These gels may be used for electro-optic materials and functional systems responsive to external stimuli.

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