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Electro-Optic Effects and Phase Behavior of Liquid-Crystalline Physical Gels: Self-Assembly of Hydrogen-Bonded Molecules for the Formation of Dynamically Functional Composites

Takashi Kato*, Norihiro Mizoshita, Takaaki Kutsuna, Gohta Kondo

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Kenji Hanabusa

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan

SUMMARY: Anisotropic physical gels of liquid crystals are obtained by the formation of non-covalently-bonded networks through self-organization of low molecular weight compounds in nematic solvents. They exhibit thermoreversible transitions between isotropic liquid and isotropic gel, and between isotropic gel and liquid-crystalline gel, whose temperatures are dependent on the components. Electro-optic properties of liquid-crystalline gels are examined with twisted nematic cells. A nematic liquid crystal in a gel structure can respond to electric fields twice faster than a single liquid-crystalline component.

Introduction

Liquid crystals, which are dynamic anisotropic fluids, have been widely used as advanced functional materials for electro-optic applications(1). They possess organized structures and they are responsive to external fields, which may be important for the fabrication of novel dynamic materials. On the other hand, physical gels, which are macroscopically soft-solids of organic solvents, can be obtained by the self-aggregation of low molecular weight compounds in common solvents(2-5). They show thermoreversible sol-gel transitions. In many cases, hydrogen bonding is a key interaction for the association of low molecular weight gelling agents. These gels consisting of isotropic solvents are applicable to functional materials(6-8). We expected anisotropic functional soft-solids, which are a novel class of materials, would be obtained when liquid crystals were gelled by such low

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molecular weight compounds. We have recently succeeded in the physical gelation of liquid-crystalline materials by the hydrogen-bonded self-aggregation of a cyclohexane diamide and amino acid derivatives[9-12]. Anisotropic physical gels are obtained by self-organization of a small amount of gelling agents, while anisotropic chemical gels are fabricated by the covalently-bonded polymer networks[13,14]. Here we report phase behavior and electro-optic properties of anisotropic liquid-crystalline physical gels.

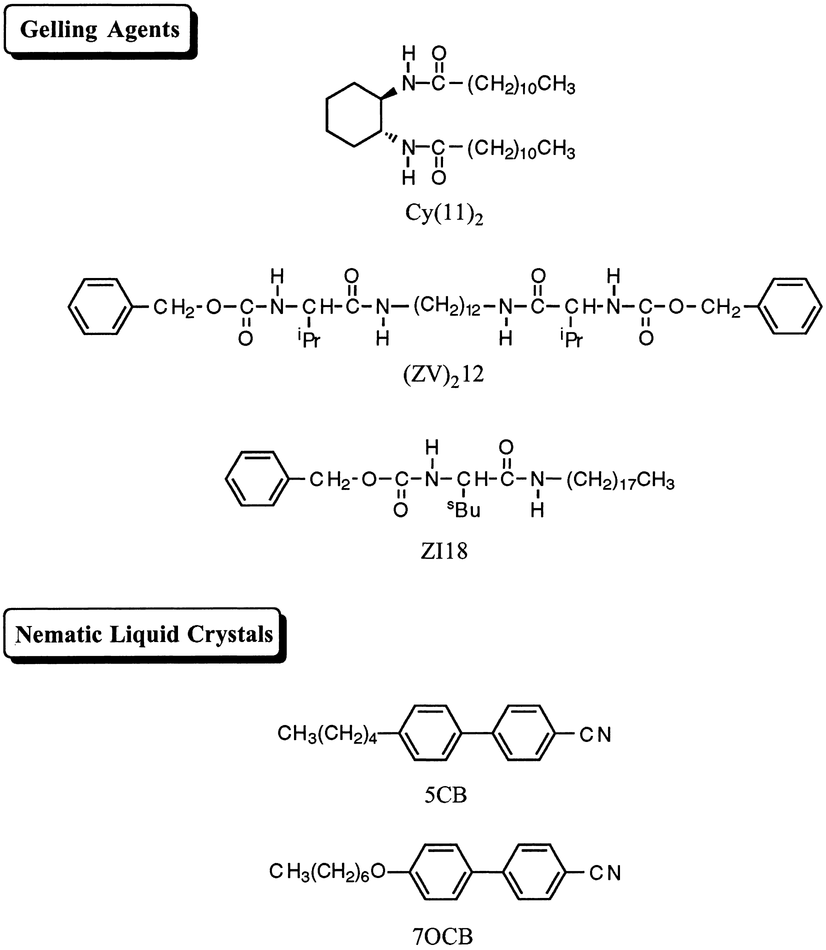

Fig. 1: Chemical structures of gelling agents and nematic liquid crystals.

Materials and Methods

Liquid crystals and gelling agents used for the formation of liquid-crystalline gels are shown in Fig. 1. *trans*-(1*R*,2*R*)-1,2-Bis(dodecanoylamino)cyclohexane ($Cy(11)_2$), dodecamethylenediamide of *N*-benzyloxycarbonyl-L-valine ($(ZV)_2 12$) and octadecylamide of *N*-benzyloxycarbonyl-L-isoleucine (ZI18) were reported to be effective gelling agents for various organic solvents[15-17]. 4-Cyano-4′-pentylbiphenyl (5CB, T_{NI} = 35 °C) and 4-cyano-4′-heptyloxybiphenyl (7OCB, T_{NI} = 74 °C) were used as nematic liquid-crystalline solvents. Anisotropic gels were obtained by mixing liquid crystals and gelling agents in test tubes. The mixtures were heated to isotropic states, then cooled to the required temperatures. Phase transitions of the mixtures were observed under a polarizing optical microscope and characterized by differential scanning calorimetry. The electro-optic effects of liquid-crystalline gels were measured with ITO glass sandwich cells (1 cm × 1 cm × 16 μm) coated with polyimide (JSR AL1254) layers whereby the rubbing direction of the two surfaces was perpendicular. AC electric fields (300 Hz) were applied to the cells. For the measurements of response time, the applied voltage for the cell was 10 V.

Results and Discussion

Self-aggregation of these low molecular weight gelling agents in liquid crystals has led to the formation of anisotropic physical gels. Fig. 2 shows the phase transition behavior of the liquid-crystalline gels containing $Cy(11)_2$ as a gelling agent. Thermoreversible three states, isotropic liquid, isotropic gel, and liquid-crystalline gel, have been achieved by this physical gelation of liquid crystals. The sol-gel transition temperatures increase as the concentration of the gelling agent increases. On the other hand, the transition temperatures from isotropic gel to liquid-crystalline gel are constant and independent of the concentration of the gelling agent, which shows that the microphase separation of liquid crystals and the fibrous aggregation of gelling agents occur in the gels.

All the gelling molecules have amide or urethane groups that can form one-dimensional hydrogen-bonded chains. Variable-temperature FT-IR measurements of liquid-crystalline gels have shown that the formation of intermolecular hydrogen bonds of gelling agents plays a key role for the gelation of liquid crystals. In the sol state of 5CB containing 4.8

mol-% of $Cy(11)_2$, N-H and C=O stretching bands of the amide group of $Cy(11)_2$ are observed at 3394 and 1675 cm^{-1}, respectively, which shows that the amide group is free of hydrogen bonding. Upon the transition from sol to gel, these absorption bands shift to 3278 and 1637 cm^{-1}, respectively, which indicates that intermolecular hydrogen-bonded chains are formed in the gelation process. Fig. 3 presents the phase transition behavior of the mixtures of 5CB and $(ZV)_2 12$ or ZI18. Figs. 2 and 3 show that each of sol-gel and isotropic-anisotropic transition temperatures can be tuned by the choice of components. In contrast to amino acid derivative ZI18, $(ZV)_2 12$ can be used for thermal stabilization of the gels (Fig. 3). For example, the sol-gel transition temperature of 5CB containing 1.0 mol-% of

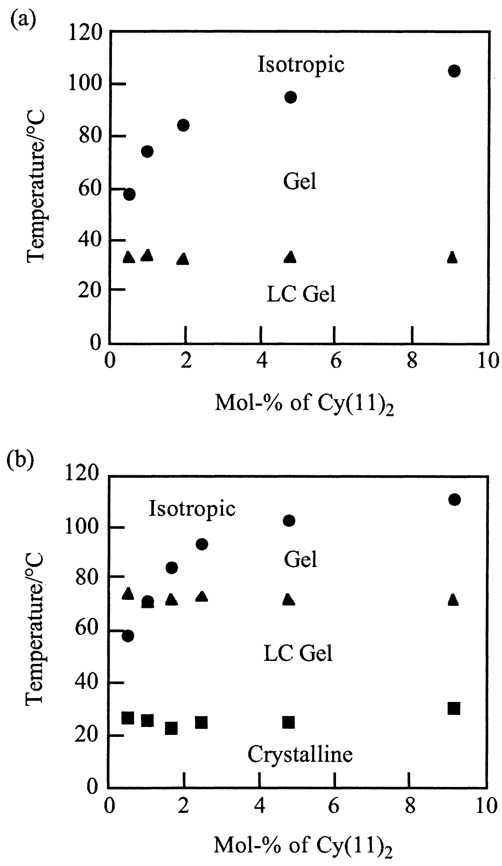

Fig. 2: Phase behavior of liquid-crystalline gels based on $Cy(11)_2$: (a) $Cy(11)_2$ and 5CB; (b) $Cy(11)_2$ and 7OCB. LC: liquid-crystalline.

$(ZV)_212$ is 82 °C, whereas 1.0 mol-% of ZI18 gels 5CB at 44 °C. This significant stabilization is due to the increase of the number of hydrogen bonding moieties. 7OCB with higher T_{NI} than 5CB is suitable for the induction of thermally stable liquid-crystalline gel state (Fig. 2).

Liquid-crystalline physical gels form microphase-separated structures as schematically illustrated in Fig. 4. A liquid-crystalline gel state consists of two independent materials: one is an anisotropic liquid crystal solvent, and the other is an aggregate formed by intermolecular hydrogen bonds (Fig. 5). Anisotropic physical gels exhibit thermoreversible

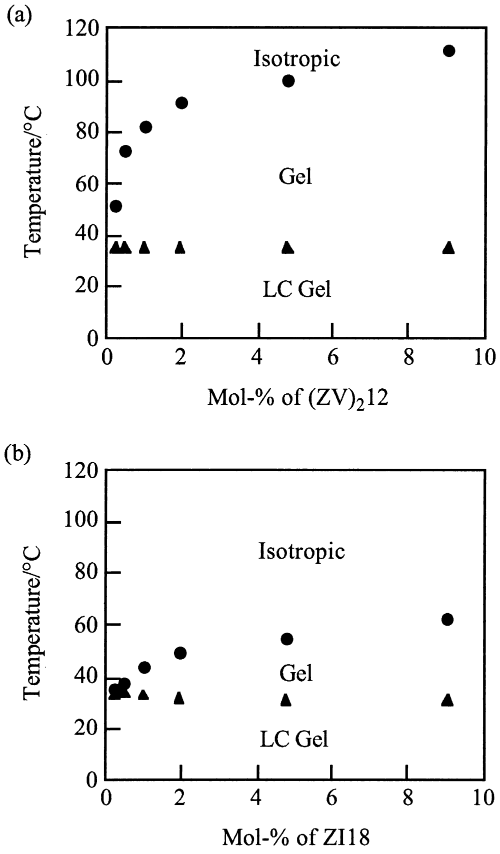

Fig. 3: Phase behavior of liquid-crystalline gels based on amino acid derivatives: (a) $(ZV)_212$ and 5CB; (b) ZI18 and 5CB.

transitions, each of which can be tuned independently by on-off switching of molecular orientation or hydrogen bonding.

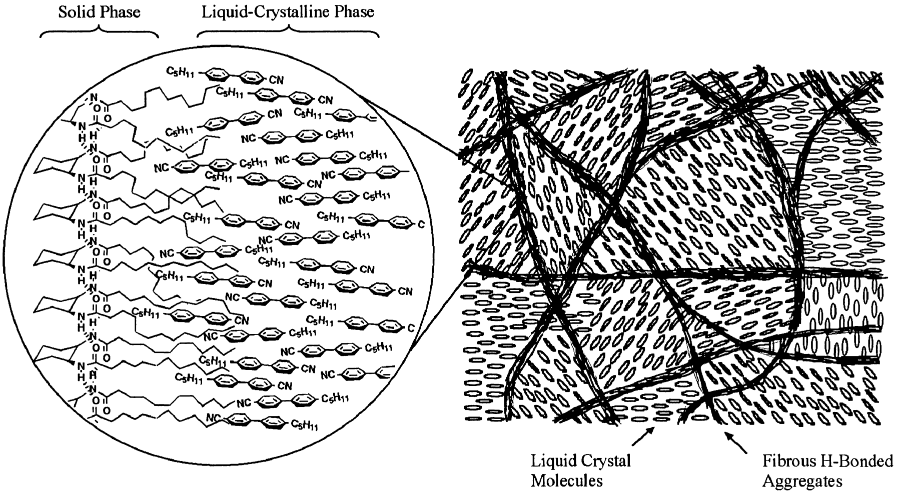

Fig. 4: Schematic representation of the microphase-separated structure of the liquid-crystalline gel consisting of $Cy(11)_2$ and 5CB.

	LC Gel	Iso. Gel	Iso. Liquid
Orientation (LC Molecule)	***ON***	***OFF***	***OFF***
H-Bond (Gelling Agent)	***ON***	***ON***	***OFF***

Fig. 5: Molecular self-organization in the formation process of a LC gel state.

The responses of these liquid-crystalline gels to electric fields have been measured with twisted nematic (TN) cells. The liquid-crystalline gels by $Cy(11)_2$ and ZI18 exhibit TN molecular alignment and electro-optic responses when the concentration of the gelling agent is less than 0.5 mol-%. Electro-optic responses of anisotropic gels consisting of ZI18 and 5CB are shown in Fig. 6. As the concentration of ZI18 decreases, the responses of the gels become similar to that of 5CB alone. For the anisotropic gels obtained by $(ZV)_2 12$, however, neither TN molecular alignment nor response has been observed. The electro-optic properties of these gels are summarized in Table 1. Significant effect of gelling agent ZI18 on response time is observed even though the fraction of the gelling compound is less than 0.25 mol-%.

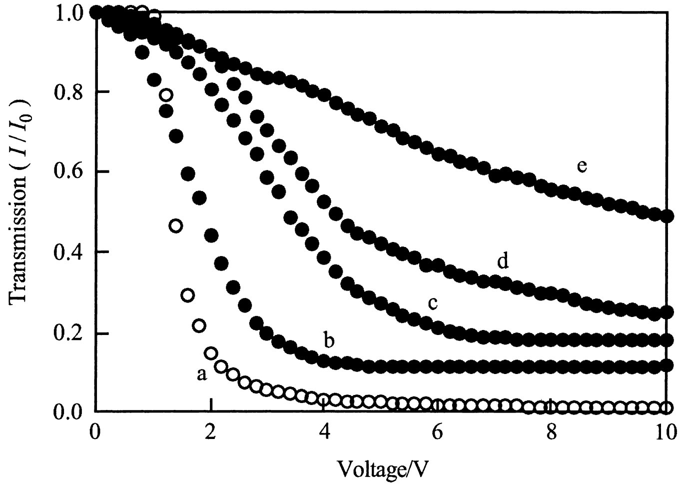

Fig. 6: Relationship between transmittance and applied voltage for liquid-crystalline gels consisting of ZI18 and 5CB in a TN cell: Concentration of ZI18 in the mixture: (a) 0 mol-%; (b) 0.25 mol-%; (c) 0.33 mol-%; (d) 0.50 mol-%; (e) 1.00 mol-%.

Table 1. Electro-optic properties of liquid-crystalline gels consisting of hydrogen bonding gelling agents and 5CB in a TN cell.

Gelling Agent	Concentration	Threshold Voltage	Response Time
	mol-%	V	ms
none		1.0	12
Cy(11)$_2$	0.50	1.5	19
(ZV)$_2$12	0.25	–[a]	–[a]
ZI18	0.50	1.7	7
ZI18	0.25	0.8	6

[a] Neither TN alignment nor response was observed.

For the gels formed by Cy(11)$_2$, they can respond to electric fields. However, the response time is longer than that of the single liquid-crystalline component, which is expected for such composite systems. Interestingly, a significantly faster response is achieved by the physical gelation of 5CB with ZI18. The response time of the gel of 5CB containing 0.25 mol-% of ZI18 is 6 ms, while only for 5CB it is 12 ms (Fig. 7). Threshold voltage for the gel containing 0.25 mol-% of ZI18 is slightly lower than that of 5CB. These differences on electro-optic responses of liquid-crystalline gels would result from a number of factors. One of the most effective factors is considered to be difference of morphologies of the mixtures in the cells. Microscopic observation of the gels formed by ZI18 shows that the fibrous aggregates of ZI18 are dispersed more finely in liquid crystal solvents than those of Cy(11)$_2$ and (ZV)$_2$12. The fact that the sol-gel transition temperatures of the gels based on ZI18 are lower than those based on other gelling agents suggests that ZI18 is less strongly aggregated in the liquid crystals. The formation of liquid-crystal domains by the network of finely dispersed aggregates and the decrease of the interaction from the polyimide surface due to the existence of the gelling molecules are consistent with the observed faster response.

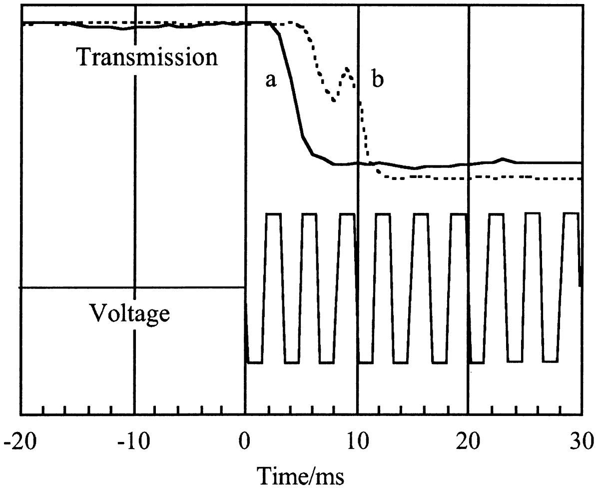

Fig. 7: Comparison of the response to an electric field: (a) liquid-crystalline gel consisting of ZI18 and 5CB (ZI18: 0.25 mol-%); (b) 5CB (broken line).

Conclusions

The liquid-crystalline physical gels have been prepared by the gelation of nematic liquid crystals with hydrogen-bonded networks. The formation of self-organized structures and their phase transitions are thermoreversible. The transition temperatures are dependent on components of the gel. The nematic liquid-crystalline gels can respond to electric fields in TN cells and their electro-optic properties can be tuned by the choice of gelling molecules. The acceleration of the electro-optic response has been observed for the physical gels of liquid crystals with an amino acid derivative, which suggests they have potential for electro-optic devices. Such *heterogeneous* anisotropic materials reported here are a new family of liquid-crystalline materials, while hydrogen-bonded *homogeneous* (non-phase-separated) mesogenic materials have been developed recently[18-20)]. The design and control of the hierarchically-ordered structures of these gels would lead to the fabrication of new dynamically functional materials. We are currently examining the gelation of various mesomorphic materials such as smectic liquid crystals[21)].

Acknowledgment

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