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Raman study of a liquid crystalline gel consisting of photochromic 4-methyl-*N*-(4-*n*-heptyloxysalicylidene)aniline and a gelling agent (*R*,*R′*)-1,2-bis(dodecanoylamino)cyclohexane

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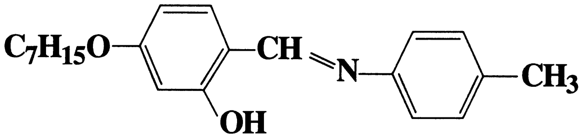
A liquid crystalline physical gel has been prepared from the mixture of a nematic liquid crystal and a low molecular mass gelling agent containing a hydrogen-bonding moiety. The newly synthesized liquid crystalline compound exhibited photochromism in the crystalline solid phase. Although photochromism was not observed in the nematic gel state of the mixture, the lifetime of photochromism in the solid phase became longer, compared with that of a single liquid crystalline compound. Some Raman bands of the mixture showed a marked change in both intensity and frequency through the phase transitions. These bands have been assigned to the vibrational modes related to the core part of molecule.

1. Introduction

Thermotropic liquid crystals are well known as dynamic anisotropic fluids and have an established position in advanced materials for electro-optical applications [1]. Moreover, much attention has been recently drawn to the fact that small amount of low molecular mass gelling agents can effectively gel a large liquid crystal volume, resulting in liquid crystalline physical gels [2–8]. The gelation occurs through the formation of a three-dimensional network self-assembled by fibrous aggregates of the gelling agents, with the aggregation process driven by a specific intermolecular interaction such as hydrogen bonding. These gels can be expected to have great potential as functional soft materials. It has also been reported that the aggregation of *trans*-(1*R*, 2*R*)-bis(dodecanoylamino)cyclohexane (DAC) through intermolecular hydrogen bonds results in the efficient gellation of liquid crystalline compounds [3, 9, 10]. DAC has been employed for the gelation of 4-*n*-pentyl-4′-cyanobiphenyl to examine the effect of gelling agents on the dynamic behaviour of liquid crystals. For example, it have been reported that faster electro-optic responses of nematic materials are induced by the physical gelation to be achieved in a nematic cell [3].

Recently, studies on photochromic or thermochromic materials have increased because of their possible application in the optical processing of information, in addition to the scientific interest [11, 12]. Generally, photochromic or thermochromic behaviour is observed only in a crystalline solid phase, i.e. not in a liquid crystalline phase [13]. It is now of interest to determine whether photochromic or thermochromic behaviour is observed in the liquid crystalline phases in an anisotropic physical gel formed by low molecular mass gelling agents.

In this study, we have synthesized a new liquid crystalline compound, 4-methyl-*N*-(4-*n*-heptyloxysalicylidene)aniline (MHSA). This compound has a core



frame of *N*-salicylideneaniline (SA), which exhibits photochromism or thermochromism in the solid state [11, 12]. MHSA also exhibited photochromism only in the solid phase. The molecular self-aggregation of the gelling agent DAC in the liquid crystalline compound MHSA results in the formation of an anisotropic physical gel. To investigate the properties of the mixture of MHSA and DAC, we employed Raman spectroscopy; this is known as a powerful technique in the study of the phase transitions in liquid crystals, enabling the analysis of either internal or external molecular vibrations [14]. The internal vibrations are

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those of the isolated molecule perturbed by the molecular field of neighbouring molecules. The analyses of internal vibrations are expected to provide a good picture of the molecular conformational changes [14–18]. The Raman bands ascribed to the external modes disappear when the three-dimensional crystal lattice order is lost through the solid–liquid crystal phase transition [19, 20]. Some Raman bands of the mixture drastically change in intensity and frequency at the solid–nematic gel phase transition, but they do not significantly change in sequential higher temperature phases. The temperature dependence of these bands is explained by the change in molecular conformation through the phase transitions.

2. Experimental

2.1. *Materials*

The gelling agent, (*R*,*R*′)-1,2-bis(dodecanoylamino)-cyclohexane (DAC), was obtained commercially and employed without further purification. The preparation of 4-methyl-*N*-(4-*n*-heptyloxysalicylidene)aniline (MHSA) used commercially obtained 4-*n*-heptyloxy-2-hydroxybezaldehyde, as starting material. The benzaldehyde was coupled with methylaniline by refluxing in an ethanol solution, and the crude product was purified by successive recrystallization from a mixture of ethanol and benzene. The liquid crystalline texture and phase transition temperatures were determined by means of a Nikon polarizing microscope equipped with a Mettler FP-52 microfurnace. Transition temperatures were determined using a Shimazu differential scanning calorimeter (DSC). Each sample was heated and cooled under a flow of nitrogen gas to prevent decomposition. The phase transition temperatures based on texture change were in good accord with those measured from DSC. The following phase transitions were found: crystalline solid (Cr)–63°C–nematic (N)–82°C–isotropic liquid (I).

2.2. *Preparation of liquid crystal gel*

The liquid crystal and DAC must be heated into the isotropic state to ensure homogeneous mixing. However, because DAC has a melting temperature of 192°C, heating to that temperature is liable to cause thermal decomposition. DAC and MHSA were therefore dissolved in tetrahydrofuran (THF) to obtain a homogeneous solution; the gel was then obtained on removing the solvent by first heating the mixture at 80°C and then at 40°C in a vacuum oven [2]. For all experiments, the mixture was heated to the isotropic phase for a least 5 min before cooling to the solid state.

2.3. *Raman spectroscopy*

The Raman spectra were obtained using a SPEX 1403 double monochromator equipped with a photon-counting system in a back-scattering geometry. Radiation of 632.8 nm from a helium-neon laser (NEC GLG 7500) was used to excite the Raman spectra to avoid fluorescence in the specimen. The sample was contained in a glass capillary; its temperature was controlled to within 0.5°C during the recording of the spectra.

2.4. *UV measurements*

UV irradiation was performed using a Moritex high pressure mercury lamp filtered through a band pass-glass filter with a transmission maximum around 365 nm; the irradiation time was 10 min. Absorption spectra were obtained with a Jasco V-550 spectrometer at room temperature. For UV irradiation and absorption measurement, the polycrystalline film prepared from the melt was held between a pair of quartz plates separated by about 20 µm. The sample film was kept overnight in a dry box before measurements.

3. Results and discussion

3.1. *Phase diagram*

The mixture of MHSA and DAC showed two kinds of gel state, an isotropic gel (ordinary gel, IG) and a nematic liquid crystalline gel (NG), at a DAC concentration greater than 1.4 mol%. Figure 1 shows the

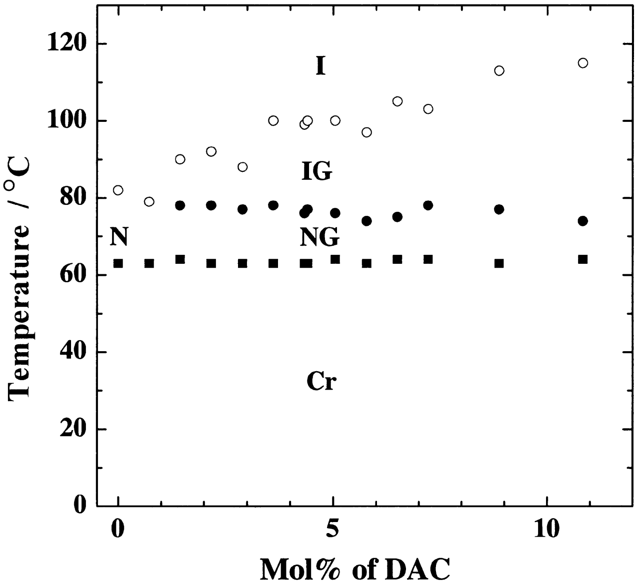

Figure 1. Phase behaviour of the mixture of MHSA and DAC; Cr=crystalline solid, N=nematic phase, NG=nematic gel, IG=isotropic gel, I=isotropic liquid phase.

phase diagram as a function of DAC concentration. The transition temperatures between Cr and NG phases, and between NG and IG phases, remain almost unchanged with DAC concentration. These transition temperatures are almost the same as those of Cr–N and N–I transitions for pure MHSA. This suggests that the intrinsic properties of MHSA molecules in a liquid crystalline phase are unaffected by gelation. In contrast, the IG–I transition temperature rises with increasing DAC concentration. Similar behaviour has been reported for the gel of 4-*n*-pentyl-4′-cyanobiphenyl and 4-methoxybenzylidene-4′-butylaniline [10].

3.2. *Photochromism*

The compound MHSA was yellow or pale yellow when freshly prepared. At room temperature, the color deepened to orange under UV irradiation; MHSA exhibited photochromism only in the solid phase. We expected that if the more ordered liquid crystalline state were realized by gelation, photochromism would also be observable in the liquid crystalline phase. Figure 2 shows the difference in absorption between non-irradiated and irradiated samples as a function of temperature. The absorption difference gradually decreases with increasing temperature, and ultimately becomes unobservable in the nematic gel phase, contrary to expectation. This may be due to a change in both regularity and rigidity through the Cr–NG transition. Similar behaviour has been observed in SAs because of a fast thermal back reaction [21, 22].

The colour of the DAC-MHSA mixture after UV irradiation faded with time at room temperature. In figure 3 the rate constant of fading is plotted against the concentration of DAC. The thermal fading process of photochromic SA has been described as a double-exponential decay with two transient stages [21]. In the present case, interestingly, the decay process changes from double- to single-exponential decay with increasing the concentration of DAC, although its change is negligibly small, i.e. the averaged value of two rate constants is smaller than that of pure MHSA. This may be ascribed to an increase in both regularity and rigidity of the mixture in the solid phase through the formation of a phase–segregated structure. Each LC domain is separated from the others by gel sheets. Therefore, photochromic behaviour appears to be dominated by the effect of the sheet interfaces. However, the rate constants do not depend significantly on the concentration of DAC, as shown in figure 3. It is thus supposed that the environment around photochromic molecules hardly changes in the range of DAC concentration studied.

3.3. *Raman spectra*

We measured the Raman spectra for pure MHSA in the range 15–1800 cm^{-1} at various temperatures. Figure 4 shows typical Raman spectra in the crystalline solid (Cr,

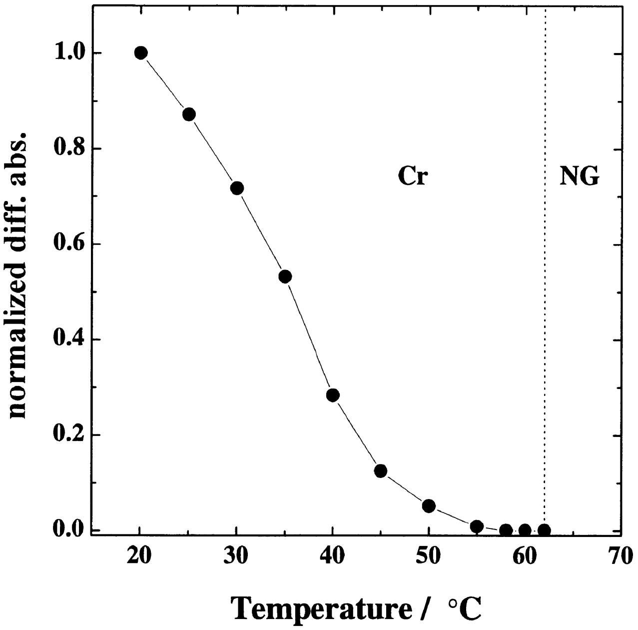

Figure 2. Absorption difference at a wavelength of 440 nm between UV-irradiated and non-UV-irradiated samples of 4.33 mol% DAC content, as a function of temperature.

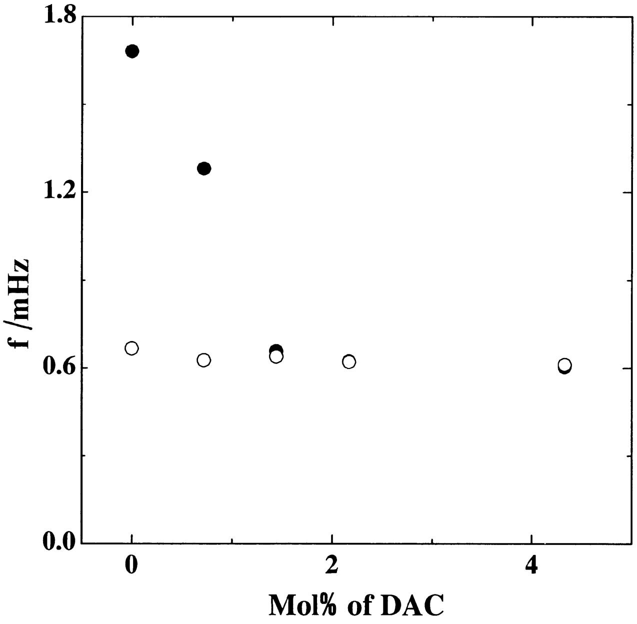

Figure 3. Rate constant of thermal fading at a wavelength of 440 nm and temperature of 20°C, as a function of DAC concentration.

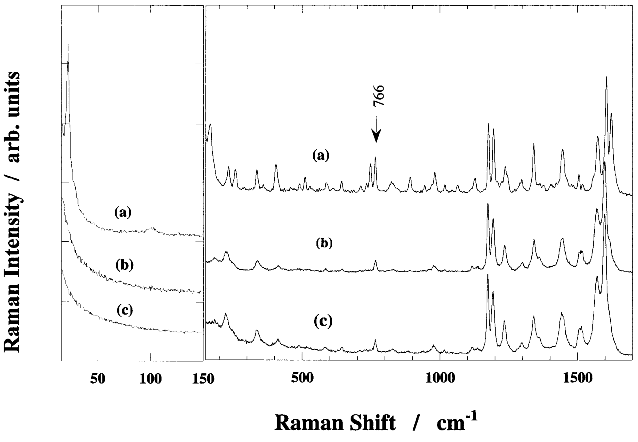

Figure 4. Raman spectra of MHSA in (*a*) solid (25°C), (*b*) nematic (71°C), and (*c*) isotropic (90°C) phases.

25°C), nematic (N, 69°C) and isotropic liquid (I, 90°C) phases. The spectra were measured at temperatures up to 120°C, because of thermal decomposition of MHSA beginning at about 130°C. The Raman spectroscopic technique has been widely utilized to investigate the lattice mode region (below 150 cm^{-1}) and the conformationally sensitive end chain (alkoxy/alkyl) mode region (200–700 cm^{-1}) [14]. Raman bands assigned to lattice modes disappear when the three-dimensional crystal lattice order is lost through the transition to higher temperature phases [19, 20]. The end chains melt in the liquid crystal phases, in the same manner as in the isotropic phase. The intensity of the end chain modes then decreases due to the increase of randomness in orientational order in liquid crystal phases. Raman bands due to lattice modes (below 150 cm^{-1}) disappear in the N and I phases, and the 257 cm^{-1} band due to alkoxy chain deformation vibration disappears in the N phase. We will not be concerned with Raman bands in these two regions, because these bands showed similar behaviour to those reported previously.

We now focus on Raman bands in the 700–1700 cm^{-1} region, which is mainly involved with the core part of the molecule. It is of interest to relate the changes of the Raman bands in this region to those in intra/intermolecular interactions, since some of the bands show an abrupt change in intensity through the Cr–N phase transition, as shown in figure 4. The 766 cm^{-1} band significantly decreases in intensity in the N phase, with little change on entering in the I phase. The 748 cm^{-1} band adjacent to this band in the Cr state disappears in a higher temperature phase. These bands have been assigned to the rocking mode of the CH_2 group (heptyloxy chain) [23, 24]. The characteristic of these bands is that they are always double in the solid phase and become single in the liquid phase. This allows these bands to be distinguishable from others in the same spectral region [23]. Figure 5 shows the intensity change and frequency shift of the 766 cm^{-1} band as a function of temperature. The band due to the rocking vibration of the alkoxy chain decreases in intensity through the Cr–N transition, since the end chain melts in the N phase, as described above. Furthermore, this band exhibits a small discontinuous decrease in intensity through the N–I transition. The change in intensity may be due to the fact that molecules move more freely in higher temperature phases. In contrast, the frequency shift is negligibly small through the phase transitions. This may be because the alkoxy/alkyl chains are far apart, so that the intermolecular interaction is too small to be observed [25].

Figure 6 shows Raman spectra of the DAC-MHSA mixture at a DAC concentration of 6.5 mol% in the crystalline solid (Cr), nematic gel (NG), isotropic gel (IG) and isotropic liquid (I) phases. The spectra are similar to those of the single component MHSA shown in figure 4. As the addition of DAC is small, the Raman bands ascribed to DAC are relatively weak compared with those from MHSA, and consequently cannot be observed in the spectrum. It should be noted that the S/N ratio of the spectrum in the NG phase is heightened compared with that in the Cr phase. Gelled materials have been reported to show limited light scattering [26]. As a result, the S/N ratio of the spectrum in the NG phase is considered to become relatively higher than that in the Cr phase.

Some bands showed abrupt changes in intensity at the Cr–NG transition. Figure 7 shows the intensity change and the frequency shift of the 766 cm^{-1} band as a function of temperature in the DAC-MHSA mixture.

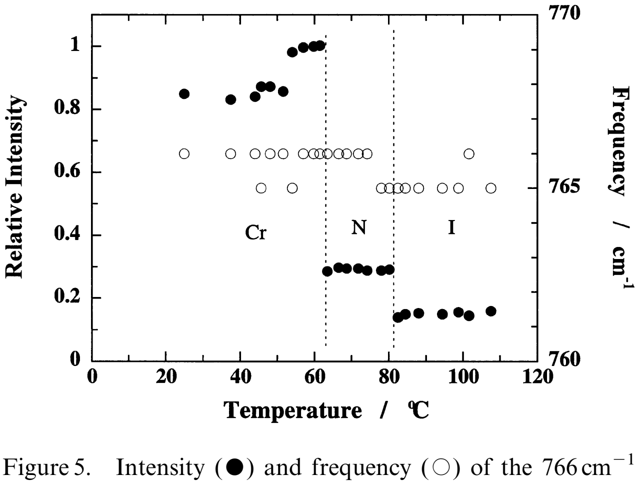

Figure 5. Intensity (●) and frequency (○) of the 766 cm^{-1} band of MHSA as a function of temperature, where the intensity is measured relative to that of the 1604 cm^{-1} band; Cr, N and I denote solid, nematic, and isotropic phases, respectively.

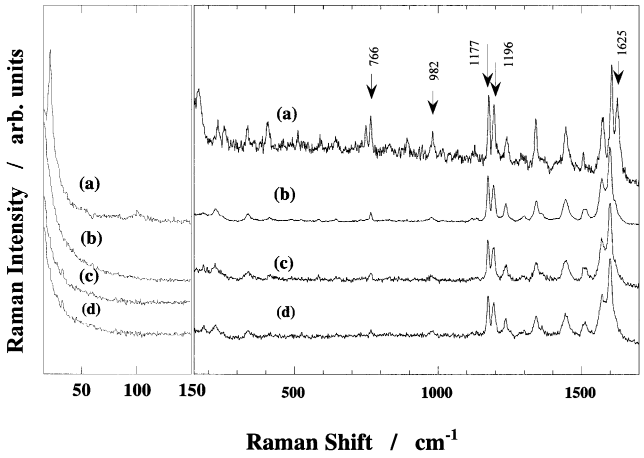

Figure 6. Raman spectra of the MHSA-DAC mixture containing 6.5 mol% DAC: (*a*) solid (25°C), (*b*) nematic gel (65°C), (*c*) isotropic gel (86°C), (*d*) isotropic (106°C) phases.

The intensity decreases drastically but the frequency shift is negligibly small, as the Cr–NG transition is approached. Furthermore, both decrease slightly through the NG–IG and IG–I transitions. The band is assigned to the rocking mode of the CH_2 group, as described above. The decrease in intensity can be explained from analogy with the case of the single component MHSA. The intensity appears to decrease in steps at successive phase transitions between the Cr and I phases, although the changes at the NG–IG and IG–I transitions are small. This is considered to reflect a stepwise change of molecular conformation and interaction through the phase transitions. Self-assembly of DAC in the liquid crystal mediated by hydrogen bonding results in the fabrication of a liquid crystalline physical gel, leading to micrometer-scaled segregation [4]. In such a segregated structure, the free movement of liquid crystalline molecules will be restricted due to a reduction in the size of an effective free volume. In the IG phase, MHSA molecules are already in the isotropic phase, but the segregated structure is still maintained. It is therefore presumed that some difference in surroundings around MHSA molecules exists between the IG and I phases. The band definitely changes through the IG–I transition, although only slightly.

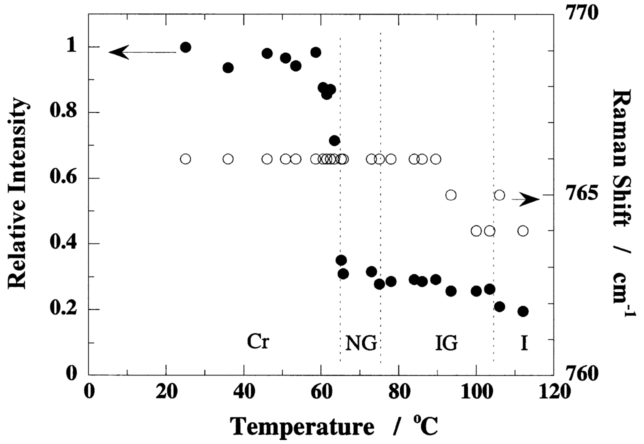

Figure 7. Temperature dependence of intensity (●) and frequency (○) of the 766 cm^{-1} band in the mixture containing 6.5 mol% DAC, where the intensity is measured relative to that of the 1604 cm^{-1} band; Cr, NG, IG and I denote crystalline solid, nematic gel, isotropic gel, and isotropic liquid phases, respectively.

Figure 8 shows the intensity change and the frequency shift of the 982 cm^{-1} band as a function of temperature. Both intensity and frequency decrease significantly at the Cr–NG transition, but remain almost unchanged in the IG and I phases. Their temperature dependences are similar to those of single MHSA and also that of liquid crystalline compounds, *N*-[4-(4-*n*-alkoxybenzoyloxy)-2-hydroxybenzylidene]-methylanilines (AHMAs), with the same core frame as MHSA [27]. This band can be assigned to the CH in-plane deformation mode of the aniline rings [27–29]. It is possible that the twist angle of the aniline ring out of the C=N–C plane changes through the phase transition [13]. Such a change in the molecular conformation causes a change in the steric interaction between the hydrogen of the Schiff's base and the hydrogen atoms of the aniline ring. Consequently, the CH in-plane deformation vibrational modes will be affected by the change in the force constant of the steric interaction. In the molecular conformation with a large twist angle, the band assigned to the CH in-plane vibration would be strong in intensity and high in frequency because of a weak steric interaction coming from the large

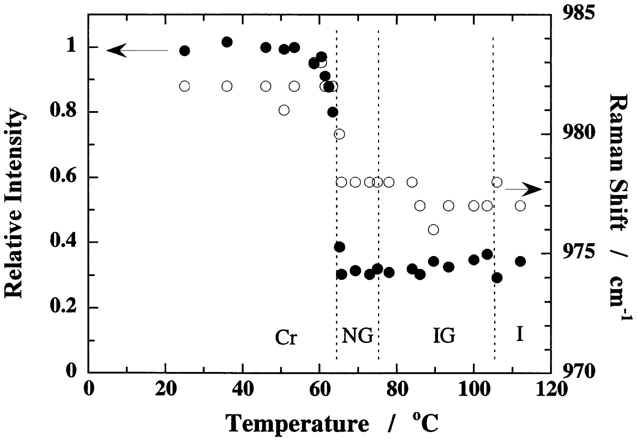

Figure 8. Temperature dependence of intensity (●) and frequency (○) of the 982 cm^{-1} band in the mixture containing 6.5 mol% DAC.

separation between the hydrogen of the Schiff's base and that of the aniline ring.

The SA core frame of MHSA shows photochromism or thermochromism in the crystalline solid phase. In the photochromic crystal, the salicylaldimino part of the molecule is planar, but the aniline ring lies 40°–50° out-of-plane, and the resulting structure is relatively open with no close face-to-face contacts between molecules [11, 12]. In the thermochromic crystal, in contrast, the molecules are planar and pack face-to-face with short intermolecular contacts normal to the molecular planes. Accordingly, photochromism and thermochromism are generally mutually exclusive properties in the series of crystalline SAs [11, 12]. In the case of photochromic AHMA compounds, the SA part has been considered to adopt a non-planar conformation [11, 12]. As the compound MHSA is photochromic and has the same SA core frame as AHMAs, we suppose that MHSA adopts the conformation with the large twist angle, from analogy with the Raman spectra of AHMAs. In MHSA with such a conformation in the solid, the twist angle between the aniline ring and the Schiff's base presumably decreases through the Cr–NG transition. Hence both the intensity and the frequency of the band decrease in the NG phase. Thus, it seems that the disappearance of photochromism in the NG phase is due to the change in molecular conformation, as well as to fluidity in the liquid crystalline phase.

The band at 1196 cm^{-1} slightly decreases in intensity and frequency at the Cr–NG transition, as shown in figure 9. This band is assigned to the C(ring)–N(Schiff's base) stretching vibrational mode [28]. The temperature dependence is similar to that of single component MHSA and can be explained by the change in the twist angle, from analogy with the CH in-plane deformation vibration. Such a rotation around the C–N bond would result in an increase in the degree of disorder in the molecular structure. As the band slightly decreases in intensity, the C–N stretching mode is considered to be less sensitive than the CH in-plane deformation mode to the change in molecular conformation.

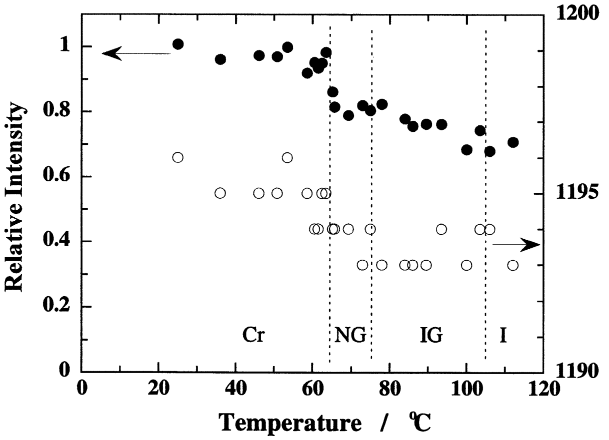

Figure 9. Temperature dependence of intensity (●) and frequency (○) of the 1196 cm^{-1} band in the mixture containing 6.5 mol% DAC.

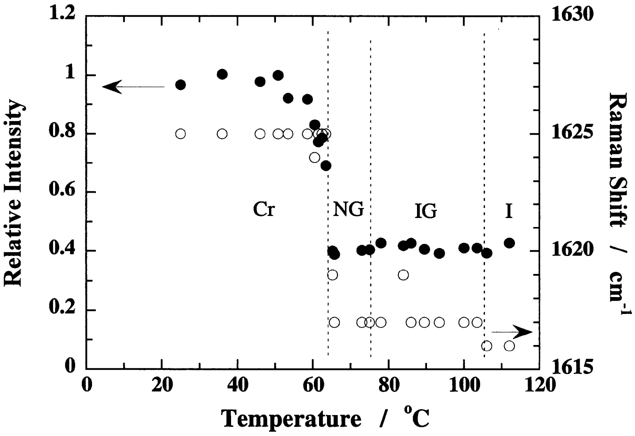

Figure 10. Temperature dependence of intensity (●) and frequency (○) of the 1625 cm^{-1} band in the mixture containing 6.5 mol% DAC.

The change of molecular conformation described above may be expected to affect the other vibrational modes associated with the core. The band at 1625 cm^{-1} decreases in intensity and frequency at the Cr–NG transition, while it remains unchanged in higher temperature phases, as shown in figure 10. This band becomes a shoulder at the higher frequency side of the strong band, due to the ring vibration above the Cr–NG transition temperature. Therefore, the temperature dependence of the band may have some uncertainty. This band is assigned to the coupling mode of the C=N stretching vibration and the ring vibration [27, 29]. The ring vibrational mode is considered to be unchanged through the successive phase transitions. Hence, the observed changes in intensity and frequency are possibly due to the change of the C=N stretching vibration influenced by the change in molecular conformation mentioned above.

The other significant band assigned to the vibrational mode of the core, i.e. the prominent band at 1176 cm^{-1}, exhibited no significant change in intensity, as shown in figure 11. This band is assigned to the C(ring)–O(alkoxyl) stretching vibration [30]. Thus, the C–O stretching mode of the MHSA molecule is scarcely influenced by change of molecular conformation through the phase transitions.

4. Summary

We have investigated, using Raman spectroscopy, successive phase transitions in the nematic liquid

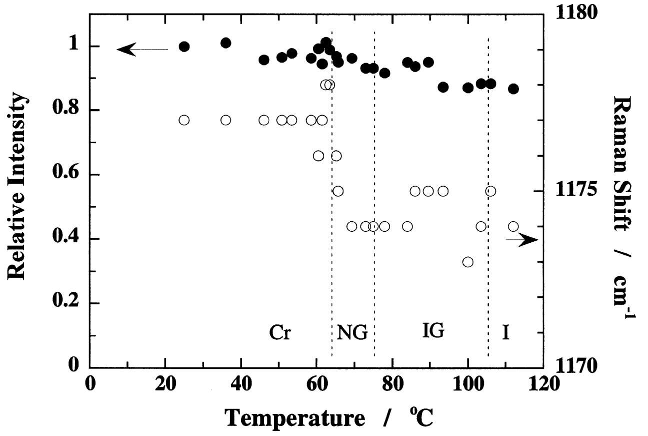

Figure 11. Temperature dependence of intensity (●) and frequency (○) of the 1177 cm^{-1} band in the mixture containing 6.5 mol% DAC.

crystalline physical gel prepared from a mixture of a liquid crystalline compound exhibiting photochromism and a low molecular mass gelling agent. Some Raman bands related to the core part of the molecule show a marked change in intensity and frequency through the phase transitions. Unfortunately, photochromism was not observed in the nematic gel state, but its thermal fading process in the solid phase became slow compared with the single liquid crystalline compound. It is certain that gelation exerts some positive effects on the retention of photochromism. Hence, the appropriate selection of gelling agent might permit the observation of photochromism in a liquid crystalline phase.

Acknowledgements

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