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Observation of blue phases in chiral networks

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We report the first observation of cholesteric blue phases in chiral anisotropic polymer networks. In two-component mixtures of a chiral and a non-chiral diacrylate, we observed typical textures of BPI, BPII and BPIII phases. By photopolymerization of these materials at constant temperature we obtained blue phase networks. After polymerization, the blue phases were stored, which enabled us to further study them without any temperature control.

1. Introduction

The blue phases (BP) occurring in chiral liquid crystals close to the clearing temperature have been extensively studied during the past decade [1–3] owing to some striking analogies to solid crystals, such as the occurrence of liquid single crystals, Bragg reflection (in the visible wavelength range), and electrostriction. Two modifications, BPI and BPII, are known to exhibit cubic structures while a third modification, BPIII, has yet to be identified. In addition to these structures, at least three modifications, namely a tetragonal, a two dimensional hexagonal and a three dimensional hexagonal blue phase can occur under the influence of electric fields.

Since this large variety of phases occurs typically in a narrow temperature range of about 1 K or less, attempts have been made either to find monomer materials with an unusually large blue phase temperature range [4, 5], or to store the blue phase structure in polymer materials by quenching below the glass transition temperature [6, 7]. So far, blue phases have been found in both side chain oligomers [6, 7] and side chain polymers [8] where mesogenic units are connected to a polysiloxane backbone. Recently, Gilli *et al.* [7] demonstrated that quenched blue phases are suitable for electron microscopy studies. Moreover, the same authors reported the occurrence of a new blue phase modification in oligomer liquid crystals which has yet to be identified.

In the present paper, we report the first observation of blue phases in cross-linked polymers, which are obtained by photopolymerization of chiral diacrylates. The properties of anisotropic gels formed by non-chiral polydiacrylates [9–13] and the occurrence of cholesteric phases in mixtures of non-chiral diacrylates with monomer chiral additives [14] have been described previously. In addition, we present recent microscopic studies which give evidence for the occurrence of blue phases in chiral diacrylates. These blue phases can be stored by *in situ* photo-polymerization.

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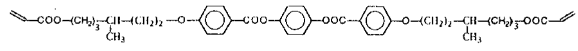
2. Experimental

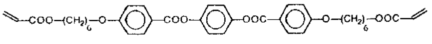
We have investigated binary mixtures of the chiral diacrylate

(1)



and the non-chiral diacrylates.

(2)



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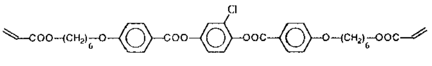

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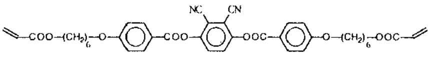


The compounds (**1**), (**3**) and (**4**) were prepared similarly to the synthesis of compound (**2**) which has been described previously [9–13]. In order to study the binary phase diagrams of the compounds (**1**) with a non-chiral compound (**2**), (**3**) or (**4**), we applied the method of contact preparation. For this purpose, a droplet of the chiral and the respective non-chiral compound was placed separately on a microscope slide and covered by a thin cover slide thereby flowing together when melted and producing a concentration gradient at the contact zone.

In order to identify the occurring phases in both the contact preparation and in mixtures with constant concentration, their textures were observed using a polarizing microscope in transmission with crossed polarizers. The temperature was controlled using a Mettler FP5 hot stage. Uniform orientations could be obtained by using glass cells with uniaxially rubbed polyimide layers and 7 μm spacers.

In order to obtain polymer networks, about 1 per cent of the photoinitiator α, α-dimethoxydeoxybenzoin (Irgacure 651, Ciba Geigy) was added to the diacrylates prior to microscopic investigation. Immediate photopolymerization was avoided by using only yellow light for the observation of the monomers. Complete polymerization was obtained by removing the hot stage from the microscope and illuminating the sample at constant temperature for a few seconds with UV light from a high pressure Hg lamp. The light intensity was $\approx 10\,\mathrm{mW/cm^2}$ at 366 nm.

3. Results

3.1. *Characterization of the pure compounds*

The transition temperatures of the pure diacrylates (**1**)–(**4**) are given in the table. In comparison to the non-chiral compound (**2**) which has been described previously [10], compound (**1**) shows a lower melting and clearing temperature due to the introduction of chiral centres in the alkyl chain. A lateral chloro substituent causes a decrease of the clearing temperature as well, as can be seen by comparison of the transition temperatures of compounds (**2**) and (**3**). Finally, compound (**4**) exhibiting two lateral cyano groups shows no nematic but a higher ordered smectic phase S_X which is not identified as yet.

Transition temperatures of the diacrylates.

(1)	Cryst	79°C	N*	87°C	Iso
(2)	Cryst	108°C	N	155°C	Iso
(3)	Cryst	68·3°C	N	114·3°C	Iso
(4)	Cryst	92·9°C	S_X	108·6°C	Iso

In order to characterize the helical twisting power of substance (**1**), we have investigated the selective reflection of the cholesteric phase in a mixture containing 50 per cent of compound (**1**) and 50 per cent of compound (**2**). The Bragg wavelength was found to be $\lambda \approx 600$ nm. Using an estimated value of $n = 1{\cdot}6$ for the mean refractive index, we conclude that the product of concentration and pitch is about $c \cdot p = c \cdot \lambda / n = 18{\cdot}8\ \mu\mathrm{m} \cdot \mathrm{wt}\%$. By linear extrapolation we find a value as small as $p = 188$ nm for the cholesteric pitch of the pure chiral compound. This small pitch can be explained by the presence two chiral carbon atoms in the molecule.

3.2. *Binary phase diagrams*

Investigations on binary mixtures of compounds (**1**) and (**2**) reveal the occurrence of up to three different blue phases in a narrow temperature range (a few tenths of 1 K) close to the clearing point. For example, a mixture containing 37·8 wt% of compound (**2**) shows the phase sequence N* 116·4°C BPI 116·6°C BPII 116·7°C BPIII 116·8°C BPIII/I 117·2°C I. The investigation of mixtures with different concentration indicates an almost linear dependence of the clearing temperature on concentration (see figure 1). From the relation between clearing temperature and concentration, the approximate concentrations for the appearance of BPI, BPII and BPIII phases can be determined from the observation of contact preparations. For the pure compound (**1**) and for compositions with high chirality (range *a* in figure 1) no blue phase could be detected. However the occurrence of blue phases cannot be excluded for these concentrations, since the BP selective reflection bands are expected to be in the UV region for high chirality. For compositions where the clearing temperature is between 110 and 115°C (range *b*), we observed the phase sequence Ch/BPI/BPIII/I. BPI exhibits a characteristic platelet texture, while BPIII shows no platelets but a diffuse selective reflection with very low intensity. In the range *c* three blue phases can be observed, as mentioned

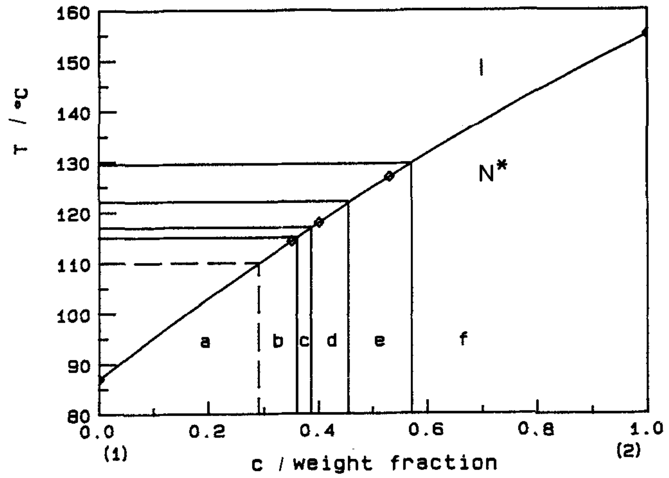


Figure 1. Clearing temperature versus composition in binary mixtures of compounds (**1**) and (**2**). According to studies on contact preparations, the concentration ranges (*a*)–(*f*) correspond to the compositions where (*a*) the selective reflection of the blue and cholesteric phase is in the UV region, and where the following phases can be observed close to the clearing temperature, respectively: (*b*) BPI and BPIII, (*c*) BPI, BPII and BPIII, (*d*) BPI and BPII, (*e*) BPI, and (*f*) no BP. The temperature range of the blue phases is very narrow and thus not presented in the diagram.

above. BPII exhibits larger platelets than BPI, and after cooling from BPII a cross-hatching texture can be observed in BPI which is very characteristic for the BPII–BPI transition. At lower chiralities (i.e. higher concentrations of compound (**2**)) only BPI and BPII (range *d*), only BPI (range *e*) and finally no blue phases (range *f*) occur close to the clearing point. With respect to the influence of the chirality on the stability of the BP modifications our results are in agreement with earlier observations.

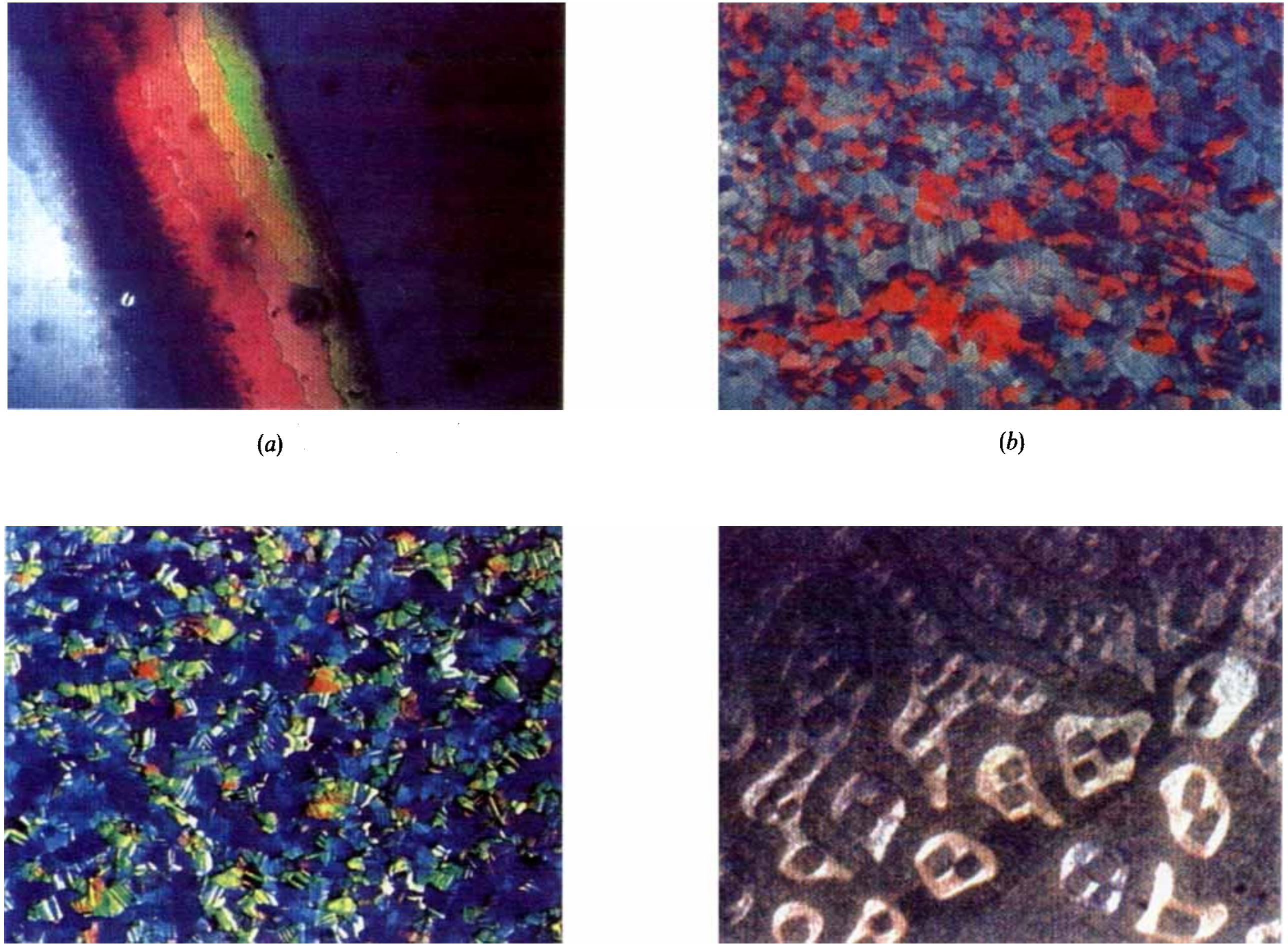
Blue phases occur also in binary mixtures consisting of the chiral component (**1**) and the chloro-substituted compound (**3**) or the cyano compound (**4**), respectively. Similar to the system described above, blue phases with visible selective reflection occur for weight fractions between about 0·3 and 0·6 of the nematic component. The latter mixtures show also BPI, BPII and BPIII phases. However, in the mixture (**1**)/(**3**) the modification BPIII appears only for very high chiralities where the cholesteric selective reflection is in the UV wavelength region.

3.3. *Photopolymerization*

By exposing blue phase samples to UV light for a few seconds, the mixtures were found to polymerize, thereby preserving their characteristic texture. After polymerization, the samples could be removed from the hot stage and the phases were found to be entirely stable at room temperature. Figure 2 (*a*) shows a micrograph of such a polymer network which was obtained from a mixture containing 63·9 per cent of compound (**1**) and 36·1 per cent of compound (**2**) by polymerization at about 110°C. (The addition of the photo-intiator caused a small decrease of the clearing temperature compared to the pure monomer mixtures described above.) Due to slight gradients of temperature and concentration, the cholesteric phase, BPI, BPIII and the isotropic phase appear in the same preparation. As usual, BPI shows a decreasing wavelength of selective reflection along the temperature gradient. Since polyimide coated glasses were used, the selective reflection wavelength does not change continuously but Cano steps occur in the BPI texture.

In the figures 2 (*b*) and (*c*), very typical BPI textures are shown which were obtained from a mixture with slightly lower concentration of the chiral compound. In the respective monomer mixture, BPII occurred in the temperature range between BPI and BPIII, and consequently the well-known cross-hatching pattern [2] appeared in parts of the sample when cooling from BPII to BPI. This behaviour has been discussed previously [2] and the striations are a characteristic feature for BPI textures.

Finally we wish to report another observation which is similar to the paramorphic effect observed by Stegemeyer *et al.* [15] at the BPII–BPI transition: In a sample consisting of about 60 per cent of compound (**1**) and 40 per cent of compound (**2**) we have observed characteristic square shaped platelets of BPII. These platelets have been described previously. They are known to occur when a fourfold axis, for example the [001] axis, is aligned along the direction of observation, and their shape is determined by the (110), ($\bar{1}$10), (1$\bar{1}$0) and ($\bar{1}\bar{1}$0) planes [16]. When we exposed the sample to UV light, the temperature was accidentally changed and the cholesteric phase appeared instead of the blue phase. However, since the polymerization was started prior to the BP–Ch transition, the square shape of the platelets could still be seen even in the resulting cholesteric network (see figure 2 (*d*)). This behaviour is very similar to the well-known effect that the shape of BPII single crystals grown in the isotropic phase can still be seen in the BPI texture appearing at lower temperature. However, in our case the partially polymerized sample even became cholesteric thereby storing the shape of the former BPII single crystal.



(*a*) (*b*)

(*c*) (*d*)

Figure 2. Micrographs of the textures observed after polymerization. The pictures were taken at room temperature in transmission, the sample was placed between crossed polarizers. (*a*) Coexistence of the N* phase, BPI, BPIII and the isotropic phase (from the left to the right) due to small gradients of temperature and concentration (nominal composition of the sample: 64 per cent (**1**), 36 per cent (**2**)). (*b*), (*c*) Textures of BPI in a sample with slightly lower chirality. (*d*) Shape of BPII single crystals stored in the cholesteric phase.

4. Conclusions

We succeeded in producing polymer networks exhibiting a blue phase structure by *in situ* photopolymerization of mixtures containing a chiral and a non-chiral diacrylate. The blue phase textures and the topology of the binary phase diagram for the respective monomer material reveal the appearance of the well-known modifications BPI, BPII and BPIII. By short exposure to UV light these textures can be permanently stored which indicates that the order parameter describing the orientation of the mesogenic units in the resulting polymer network is the same as for the monomer material.

To conclude, the new compounds may be used to perform experimental investigations on the blue phase structure without having the problem of temperature control. In this respect, the diacrylates and their respective polymers are as useful as the known side chain polymers which have been used by Gilli *et al.* [6, 7] for electron microscopy studies. However, in contrast to the material used previously, the preparation of our samples requires no rapid cooling from the clearing point to a temperature below the glass transition (which is typically 100°C lower). Instead, polymerization is performed at constant temperature.

Finally, we wish to point out that—in principle—the new method of preparing durable blue phases is also suitable to store the structures of field-induced blue phases such as the tetragonal, three dimensional hexagonal and two dimensional hexagonal blue phases [3]. With respect to this aim, we expect compounds (**3**) and (**4**) to be suitable due to their negative dielectric anisotropy. The extensive study of chiral nematic mixtures of these compounds in electric fields is the subject of future investigations.

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