polymer

Blending as a method of tuning reflection wavelength and helical twisting sense in films and composites of liquid crystalline cellulose derivatives

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Dedicated to Professor Imanishi on the occasion of his retirement

Abstract

Ethyl cellulose (EC) with a degree of substitution of 2.41 and a fully acetylated sample (AEC) of this material, form lyotropic liquid crystalline solutions in chloroform and acrylic acid. Above 35 wt% polymer, the solutions exhibit chiral nematic phases that reflect light selectively at a specific wavelength λ_0. For EC solutions the helical twist sense of the chiral nematic phase is left handed, whereas the AEC solutions are right handed.

The λ_0 and handedness of the system can be tuned to a given set of values by preparing solutions of EC and AEC in different blend ratios. These can be converted to films or composites, that retain the chiral nematic structure and the corresponding chiro-optical properties, by either casting from chloroform or photopolymerising the (EC + AEC)/acrylic acid solutions to form blend composites of EC/AEC in poly(acrylic acid).

The most effective way to control the chiro-optical properties of the dry films was to use the photopolymerisation technique to form composite films of the blends. Such films can be used either as coatings to reflect visible light of a particular colour, or act as a protective layer to reduce UV degradation. © 2002 Published by Elsevier Science Ltd.

Keywords: Lyotropic liquid crystalline; Cellulose derivatives composite formation; UV protection

1. Introduction

Many cellulose derivatives when dissolved in a variety of solvents, form lyotropic liquid crystalline solutions above a critical concentration, which usually lies in the range 30–50 wt% polymer [1]. When fully formed, these liquid crystalline phases are mainly chiral nematic (cholesteric) and possess the interesting chiro-optical properties associated with the helical supramolecular arrangement of the molecules found in these phases [2,3]. One of the more important of these properties is the ability of these systems to reflect circularly polarised light selectively over a narrow range of the spectrum. This is centred on a wavelength (λ_0) that is a function of the pitch length (P) of the helical structure. The relation is expressed in the equation, developed by de Vries [4]

$$\lambda_0 = \tilde{n}P \sin \Theta \tag{1}$$

where $\tilde{n}$ is the refractive index of the sample, and Θ is the angle of the incident light.

As the structure of the chiral nematic phase is represented schematically as comprising nematic layers of cellulose chains in which the director rotates clockwise or anti-clockwise on passing through the layers, thereby forming the supramolecular helical structure; $\sin \Theta = 1$ when the incident beam is parallel to the long axis of the helix and $\lambda_0 = \tilde{n}P$. The helical structure can have either a right handed twist or a left handed twist depending on the nature of the solvent/cellulose system, but not both in the same system. The chiral nematic phase also exhibits apparent circular dichroism, which means that one component of circularly polarised light will be reflected selectively while the other component is transmitted, together with the other wavelengths. As the plane of polarised light follows the direction of twist in the chiral nematic phase, the right handed circularly polarised component will be reflected from the phase with a right handed helical twisting sense and, vice versa.

The majority of lyotropic cellulose derivatives form right handed chiral nematic phases. Vogt and Zugenmaier [5] were the first to observe that lyotropic liquid crystalline

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solutions of ethyl cellulose (EC) in acetic acid form left handed chiral nematic phases and other examples have been found subsequently, usually when the substituent group on the cellulose was small. However, the size of the substituent group is not always an accurate guide to the handedness of the helical twist, as acetoxypropyl cellulose in acetic acid [6] and 6-*O*-trityl-2,3-*O*-hexyl cellulose in tetrahydrofuran [7] have bulky substituents but form a left handed chiral nematic structure. A more comprehensive coverage of the various systems and the effect of substituent, solvent, temperature, concentration and molar mass, on the chiro-optical properties has been compiled by Zugenmaier [8].

One possible use of the chiro-optical properties of these systems is to prepare thin film coatings that will reflect a particular colour in the visible region or reflect in the UV region thereby providing some protection against UV degradation. Such protective coatings prepared from a cellulose derivative of only one helical twist sense would of course reflect a maximum of only 50% of the UV radiation. This might be improved if a double layer of film combining both left and right handed structures was prepared where the expectation would be that the transmission of the UV radiation is reduced to a minimum.

Control of both wavelength of reflection and handedness are then necessary criteria in the preparation of such films on a scale which would be commercially viable, but the conversion of a lyotropic solution to a dry film that retains the required chiral nematic state can be problematic.

Simple casting processes from concentrated solutions can be unreliable because shearing can distort the mesophase structure. More importantly, the chiro-optical properties usually change with concentration, so that as the concentration increases (i.e. solvent evaporates) the wavelength of reflection moves to shorter wavelengths. Thus the resulting films may not reflect in the desired region of the spectrum [9,10]. Shimamoto and Gray [11] have developed a three stage casting technique which gives greater control over the structure of the cast film but this would be difficult to use on a large scale.

Alternative techniques can be used. The chiral nematic state can be retained by crosslinking the cellulose derivative prior to film preparation [12,13], but a more promising approach is to prepare lyotropic solutions using a polymerisable monomer as solvent, then photopolymerising, thereby locking in the required structure [14–17].

The control of handedness and wavelength of reflection can depend on the type of cellulose derivative, the solvent used, the concentration and temperature. Guo and Gray [18,19] have reported that EC, with a degree of substitution (DS) of 2.5, forms lyotropic liquid crystalline solutions with a left handed helical twist in chloroform and several other solvents. If the remaining hydroxyl groups are then acetylated progressively, λ_0 increases up to a critical DS (acetylation) of 0.18–0.2, then the system switches from a left handed to a right handed helical structure and λ_0 decreases

until a fully acetylated sample (AEC) is obtained (DS acetylation = 0.5). Thus both wavelength (λ_0) and helical twist sense can be tuned by the acetylation process.

As control over the precise degree of acetylation is not easily achieved, we report here on the use of blends of EC and AEC to control the wavelength and handedness of solid films and composite materials suitable for coatings.

2. Experimental section

2.1. Materials

EC was used as purchased from Aldrich which had a viscosity of 100 cps (80/20 solution toluene/ethanol). It had a degree of substitution $DS_{ethyl} = 2.41$ as determined by analysis of the ethoxy content. All other reagents were obtained from Aldrich and either used as received or purified using standard procedures.

2.2. Acetylation of EC

EC (3 g) was dissolved in pyridine (50 ml) to give a homogeneous solution, in a three necked flask. Acetic anhydride (6–12 ml) was added and the solution was stirred at 40 °C, under nitrogen, for periods of 0.5 h up to 2 days, in order to achieve different levels of acetylation. After the appropriate reaction time, the acetylated product was isolated by precipitation in excess of water. The material was filtered, washed then dried and redissolved in tetrahydrofuran. The solution was precipitated in water again and this procedure was repeated three times, after which the acetylated EC was separated and dried under vacuum. The DS with respect to the ester groups was determined as described by Gray [18], using FTIR spectroscopy and comparing the ratios of the relative absorbance values (I) of the OH stretch and carbonyl stretch for a sample of unknown DS with the fully acetylated EC as reference. The DS value for the acetyl content can be calculated from

$$(DS)_x = 0.5(I^{C=O}/I^{OH})_x (I^{C=O}/I^{OH})_{fullysub} \tag{2}$$

where x represents the particular sample under study.

2.3. Instrumentation

All infra red spectra were recorded using a Perkin–Elmer 1720 × FTIR spectrophotometer. The CD spectra were measured at the BBSRC Scottish Circular Dichroism Facility in the University of Stirling (now located in the University of Glasgow) and we thank Professor N. Price and Dr I.S. Kelly for their help and co-operation. Samples were measured on a Jasco 600 spectropolarimeter at a scanning speed of 50 nm/min and at a temperature of 20 °C. The upper wavelength range was 450–1000 nm, and the lower range used was 200–700 nm. The optical behaviour of the samples was followed using an Olympus polarising microscope fitted with a Linkam PR600 hot stage.

2.4. Photopolymerisation [20]

Cellulose derivatives EC, AEC and blends of both were dissolved in acrylic acid. Lyotropic liquid crystalline solutions formed when the concentration exceeded 30 wt% polymer. The photoinitiator Daracur 1173 (Ciba) was added to a concentration of 0.05 wt%. Photopolymerisation was then achieved by radiating these solutions, contained in a special cell which produced a thin film, at room temperature, using a Blak-Ray UV lamp, (Model B, 100AP) for 30 min per sample. This resulted in the formation of solid composites that retained the chiral nematic structure. This was particularly obvious when the solutions reflected in the visible region as the colour remained largely unchanged after photopolymerisation.

2.5. Liquid crystalline behaviour

Solutions of EC and AEC in chloroform and acrylic acid were examined using polarising light microscopy. In all cases lyotropic liquid crystalline behaviour was observed then the solution concentrations exceeded 40 wt%. Strong birefringence was observed for the unaligned samples and on shearing typical striated patterns were obtained characteristic of chiral nematic (N^*) systems. Examination of solutions of blends of the two materials showed that the liquid crystalline characteristics were retained essentially unchanged. Solutions retained the N^* characteristics up to the clearing temperatures which were in the range 60–70 °C.

3. Results and discussion

In order to test the effectiveness of blending as a means of tuning the λ_0 and handedness of chiral nematic films, the simple system reported by Guo and Gray [18,19] of EC and AEC was used.

3.1. Acetylated EC in chloroform

Samples with various degrees of acetylation were prepared and their chiro-optical properties in 40 wt% solutions in chloroform were examined using CD. The results are recorded in Table 1 and show that there is an inversion from a left handed helical twist to a right handed one with increase in the degree of acetylation as reported previously [18]. This occurs in the DS (acet) range 0.04–0.13. There is an initial progressive increase in λ_0 indicating an unwinding of the helicoidal structure that will eventually reach a compensated nematic state in this range of DS (acet) after which it contracts with the opposite handedness as the acetylation progresses. The EC has a $\lambda_0 \sim 550$ nm and a left hand helical twisting sense while the AEC has $\lambda_0 \sim 440$ nm and a right handed twisting sense. The CD spectra in the DS (acet) range (0.04–0.13) are very broad and indistinct.

Table 1

Variation of reflected wavelength (λ_0) and handedness of solutions of partially and fully acetylated (AEC), ethyl cellulose with degree of acetylation DS (acet)

Degree of acetylation DS (acet)	Wavelength of selective reflection, λ_0 (nm)	Helical twisting sense
0.00	550	Left
0.014	610	Left
0.02	685	Left
0.04	Broad reflection band	Left
0.13	590	Right
0.21	550	Right
0.37	470	Right
0.59	440	Right

3.2. Blends of EC and AEC in chloroform

The earlier behaviour can now be compared with blends of EC and the fully acetylated AEC in chloroform solutions with a total polymer concentration of 40 wt%. The ratio of (EC/AEC) can be varied to give an equivalent DS (acet) and a selection of blends were prepared in this way. The optical behaviour of the blends in chloroform was similar to the single polymer solutions, showing typical chiral nematic textures, in particular the banded textures on shearing. The results for the CD measurements are shown in Table 2. The blends exhibit the same general trend in chloroform solution as the partially acetylated EC samples only now the change in helical twisting sense occurs around a (50/50) blend or an equivalent DS (acet) of approximately 0.3. This is higher than that shown by the partially acetylated EC samples. There is also the corresponding change in λ_0 with change in blend composition. The average pitch of the apparent helical structure in the blend seems to unwind more slowly in the left handed solutions and then rewinds more slowly in the right handed systems after the change in optical rotation.

3.3. CD behaviour of mixtures of EC/AEC in acrylic acid

While the behaviour of blends in chloroform is satisfactory it is useful to examine the same blends of EC and AEC

Table 2

Chiro-optical properties of mixtures of EC and AEC in chloroform for 40 wt% polymer concentration solutions

DS (acet)	Composition ratio (EC/AEC)	λ (nm)	Helical twisting sense
0.00	100/0	550	Left
0.06	90/10	590	Left
0.18	70/30	850	Left
0.30	50/50	Flat	Compensated
0.41	30/70	900	Right
0.53	10/90	760	Right
0.59	0/100	440	Right

Table 3
Chiro-optical properties of solutions of (EC + AEC) in acrylic acid at a total polymer concentration of 55 wt%

Wt% ratio (EC/AEC)	λ_0 (nm)	Helical twisting sense
100/0	370	Left
90/10	380	Left
80/20	440	Left
60/40	Broad reflection	–
40/60	Broad reflection	–
20/80	900	Right
10/90	650	Right
0/100	430	Right

in a polymerisable monomer. Both EC and AEC exhibit lyotropic liquid crystalline phases when dissolved in acrylic acid at concentrations in excess of 35 wt%.

Solutions of EC and AEC were prepared at 55 wt% total polymer concentration and the CD spectra were measured. The results are listed in Table 3 and show the same general trends as the data in Table 2 for the chloroform solutions. Compensated nematic solutions again appear to form around the (60/40)–(40/60) wt% ratio of (EC/AEC) mixtures. The system does show some promise, as reflection wavelengths tend to shorten on conversion of solutions into films.

3.4. Films prepared by casting

During a casting process the evaporating of solvent effectively increases the solution concentration and the pitch of the chiral nematic helical structure tends to shorten. To some extent this could be countered by raising the temperature at which the casting is done. This is because an increase in temperature for these lyotropic solutions at a fixed concentration, leads to a clearing temperature at which the solution passes into the isotropic state. This is accompanied by a shift in λ_0 towards longer wavelengths as the helix unwinds. Films of partially and fully acetylate EC were cast from chloroform at 20, 30 and 40 °C, but results were disappointing and highlight the difficulties in controlling evaporation rate and the chiral nematic structure (see Table 4).

Table 4
Effect of casting temperature on the chiro-optical properties of acetylated EC, cast from chloroform solutions

DS (acet)	λ_0 (nm)			Helical twisting sense		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
0.02	< 300	< 300	< 300	Left	Left	Left
0.03	< 300	< 300	< 300	Left	Left	Left
0.04$_5$	410	< 300	< 300	Left	Left	Left
0.13	> 700	> 700	600	Right	Right	Right
0.21	530	> 700	500	Right	Right	Right
0.26	–	–	400	–	–	Right
0.37	370	350	430	Right	Right	Right
0.59	< 300	< 300	< 300	Right	Right	Right

Table 5
Chiro-optical properties of thin films of (EC/AEC) blends cast from chloroform solutions at room temperature

Wt% blend composition (EC/AEC)	λ_0 (nm)	Helical twisting sense
100/0	350	Left
90/10	360	Left
80/20	430	Left
70/30	500	Left
50/50	Broad reflection	–
30/70	Broad reflection	–
20/80	600	Right
10/90	380	Right
0/100	260	Right

Better results were obtained when films were cast from chloroform solutions of EC/AEC mixtures at room temperature. The CD results are listed in Table 5 which were obtained from 40 wt% solutions cast, in very thin films, with rapid evaporation of the solvent. The general behaviour was the same as for solutions of EC/AEC blends (Table 2), only now the casting process tends to move λ_0 to shorter wavelengths in films with both left and right handed helical twisting sense. Thus the (90/10) blend ratio had $\lambda_0 = 550$ nm in solution and $\lambda_0 = 360$ nm in the cast film (left hand twist) and in the (10/90) blend λ_0 (solution) = 760 nm and λ_0 (solid) = 380 nm (right hand twist).

3.5. Photopolymerisation

The casting method can be used to lock the chiral nematic phase into the films formed, but in situ photopolymerisation of lyotropic solutions of EC, AEC and EC/AEC blends in acrylic acid can present fewer problems in control of λ_0 and helical twisting sense.

The method was first tested for the individual components EC and AEC. The cellulose derivative was dissolved in acrylic acid at various wt% concentrations between 45 and 55 wt%. The photoinitiator Darocur 1173 was added (0.05 wt%) to the solution and photopolymerised at room temperature to produce solid composite films of cellulose derivative in poly(acrylic acid) (PAA).

Table 6
Chiro-optical properties of composite films comprising EC and AEC in poly(acrylic acid) PAA

Wt% composition EC or AEC in composite	λ_0 (nm)		Helical twisting sense	
	EC	AEC	EC	AEC
45.0	840	950	Left	Right
47.5	610	710	Left	Right
50.0	500	630	Left	Right
55.0	375	470	Left	Right

Table 7
Chiro-optical properties of composite blends of (EC & AEC) total 55 wt% in PAA

Wt% ratio (EC/AEC)	λ_0 (nm)	Helical twisting sense
100/0	375	Left
90/10	410	Left
70/30	480	Left
50/50	510	Left
40/60	Broad reflection	–
20/80	650	Right
10/90	500	Right
0/100	470	Right

The CD results for composites of EC/PAA and AEC/PAA are shown in Table 6 as a function of composition.

These show that the handedness of the lyotropic solution is retained in the composite irrespective of concentration. There is a strong dependence of λ_0 on concentration, however, and illustrates the decrease in the helical pitch of the chiral nematic phase as the solution concentration increases. Based on these results, a suitable solution concentration for the preparation of the blends was selected as 55 wt%, as this should give the broadest range of λ_0 in the blend composites.

The CD measurements for a total (EC and AEC) concentration of 55 wt% of EC/AEC blends, photopolymerised at room temperature, are collected in Table 7. The data show that the λ_0 can be altered with a change in the (EC/AEC) ratio and that a change in helical twisting sense can also be achieved. There is a small change in the reflection wavelength when compared with the solutions but not as large as when a casting technique was used.

3.6. Combined films

The preparation of the cellulose derivative composite is the most reliable way of producing films reflecting in a particular wavelength region either visible or in the UV, and of retaining a given helical twisting sense. The UV region could be of particular interest where such coatings could provide protection against UV degradation. The chiro-optical properties mean that for a film of one handedness at least 50% of the radiation will be transmitted and only up to 50% reflected. While this might be enough to make a significant improvement in the lifetime of a material being protected, a layered combination of two films reflecting in the same wavelength region, but of opposite handedness, could be even more effective. Thin films of EC/PAA (50 wt%) and AEC/PAA (55 wt%) composites were prepared. Both films reflect wavelengths around 500 nm, but are of opposite handedness. The films were combined (one on top of the other) and the CD spectra were measured. As expected, the spectrum recorded was similar to that of the single film, depending on which side of the bilayer film

was placed next to the spectrophotometer beam. One could not determine whether these reflections were enhanced, so transmission spectra were measured using a UV/VIS spectrophotometer. These showed that the transmission of the combined film was less than 1% around $\lambda_0 = 500$ nm, irrespective of the film orientation. Thus the use of combined films would appear to be a promising way to prepare protective coatings using systems that reflect in the UV region.

4. Conclusions

Both the wavelength of selective reflection and the helical twist sense of the chiral nematic phase can be altered by a simple blending procedure using EC and AEC. While casting can be used to prepare films that retain the chiro-optical properties of the solutions the method can be unreliable because of the difficulties encountered in trying to control the solvent evaporation rate.

A more reliable approach is to prepare lyotropic solutions, using a polymerisable monomer as solvent. Subsequent photopolymerisation of the mixture locks in the chiral nematic structure to form composite films exhibiting the chiro-optical properties of the solutions. The latter can be changed by using different blend ratios of (AC/AEC) in the composite which in this case also includes PAA as the third component. This approach is general as other derivatives can be used in other polymerisable monomers as we have demonstrated previously [17,20].

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