polymer communications

Solid cholesteric films for optical applications

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Cholesteric liquid crystals selectively reflect visible light and exhibit brilliant chloesteric colours when their cholesteric helical pitches are comparable with the wavelength of visible light[1]. The temperature-sensitive effects associated with the selective reflection have been utilized for various kinds of applications, such as thermal indicators and radiation sensors[2]. Also, some applications of the unique optical properties of cholesteric liquid crystals to passive optical devices have been proposed[3-5].

In the latter case, it is desirable that the wavelength of selective reflection is insensitive to temperature. In this communication, we wish to report the preparation of polymer films in which cholesteric liquid crystalline organization is frozen-in. These films are applicable to passive optical devices, such as circular polarizers, bandpass filters, notch filters, and reflective displays.

We have reported that cholesteric organization in polypeptide–vinyl monomer liquid crystalline systems can be easily immobilized by causing the vinyl monomers acting as solvents to polymerize[6-9]. In previous publications[7-9], we dealt with poly(γ-butyl-L-glutamate) (PBuLG)–butyl acrylate systems; the cholesteric pitches of the polymer composites obtained by the polymerization of butyl acrylate ranged between 5 to 10 μm, which were far longer than the wavelength of visible light. Recently, we found that PBuLG dissolved in triethylene glycol dimethacrylate (TGDM) exhibited irridescent cholesteric colours, when the PBuLG/TGDM (wt/wt) ratio was between 40/60 and 60/40. Furthermore, we succeeded in immobilizing the coloured cholesteric liquid crystalline structures by polymerization of the TGDM component.

PBuLG and TGDM were weighed into small screw vials and were kept at 40°C for 2 days with intermittent mechanical stirring. Homogeneous liquid crystalline solutions with the PBuLG/TGDM compositions 40/60, 45/55, 50/50, and 55/45, were prepared. After the addition of 2.0% benzophenone as a photosensitizer, small portions of the solutions were sandwiched between pairs of microscope slides, allowing a 0.2 mm gap by use of spacers. The sample cells were immersed in a thermostatically-controlled bath, allowed to stand for 1 h, and irradiated with a high-pressure mercury lamp for 2 h to cause the TGDM component to polymerize. Stiff polymer films ~0.2 mm thick, which appeared red to violet depending on both the PBuLG/TDGM compositions and polymerization temperatures, were disengaged from the cells by hand.

Figure 1 shows the transmission spectra of coloured films prepared by the polymerization at 30°C. The sharp 'apparent absorbance' peaks reveal that the selective reflection due to cholesteric structures occurs in the visible wavelength region, and that the position of the peaks depends strongly on the compositions of the starting solutions. In addition, they indicate that the helical axes of cholesteric structures were aligned perpendicularly to the film surfaces (planar textures)[1,2]. Each peak wavelength, λ_{max}, was practically insensitive to observation temperatures between 0° and 100°C. The peak positions were highly sensitive, however, to the temperatures at which the polymerization was carried out. In *Figure* 2, the relations between λ_{max} and the PBuLG content in the films polymerized at 20° and 30°C are shown. Guided by these curves, we were able to produce polymer films that selectively reflected visible light at any desired wavelength simply by controlling the PBuLG/TGDM ratio and the polymerization temperature.

Cholesteric liquid crystals are known to give rise to a circular dichroism for a light beam propagating parallel to the helical axis[1,2]. As *Figure* 3 shows, the polymer films obtained in this study fully retained the circular dichroism exhibited by the original PBuLG/TGDM cholesteric liquid crystals. Their detailed optical properties will be published later.

The polymer films with cholesteric order described here have several advantages as materials for optical devices. First, they need no supporting matter, and therefore, are easy to handle. Second, films with large areas, 500 × 500

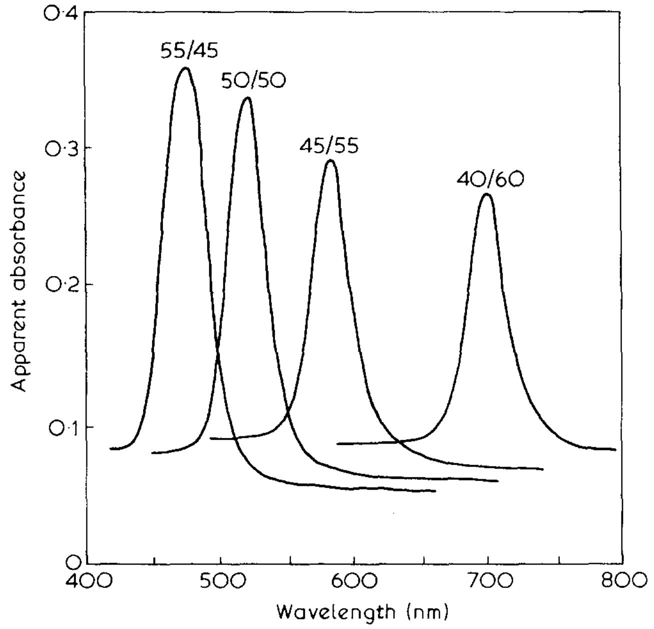

Figure 1 Transmission spectra of the PBuLG/TGDM composite films polymerized at 30°C. Numerals in the Figure indicate the PBuLG/TGDM (wt/wt) ratios. The spectra were taken at room temperature

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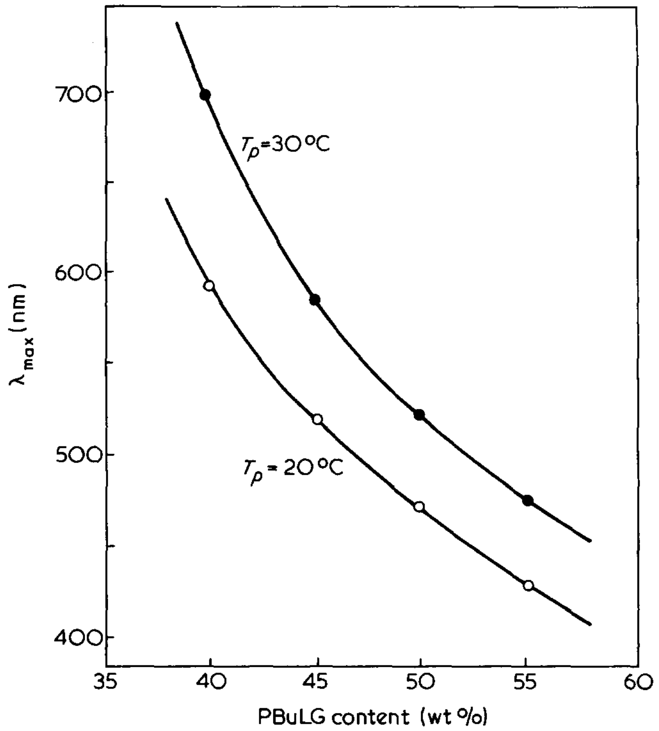

Figure 2 Peak wavelength of selective reflection plotted against the PBuLG content. T_p designates the temperature of polymerization

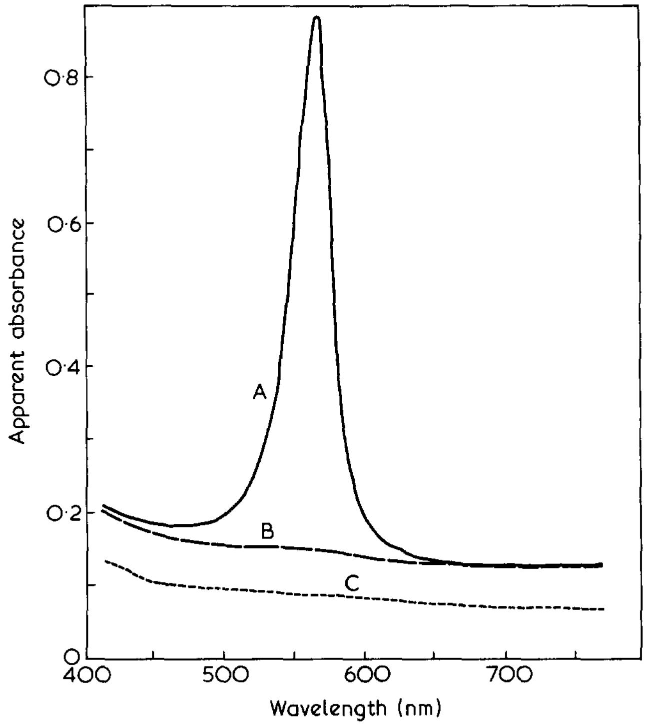

Figure 3 Transmission spectra of the PBuLG/TGDM 50/50 composite films polymerized at 40°C: A, incident light was right circularly polarized; B, incident light was left circularly polarized; C, shifted zero line due to a circular polarizer

mm for example, can easily be prepared. Polymer composites of any shape (and not just thin films) can be moulded, if the cells for the polymerization of the PBuLG/TGDM solutions are properly designed. Third, the wavelengths of their selective reflection can be varied continuously through the entire visible spectral region and tuned precisely to requirements. Finally, the method of preparation is extremly simple: it only requires homogeneous mixing of the two components followed by photo-irradiation.

References

1 Fergason, J. L. *Mol. Cryst.* 1966, **1**, 293
2 Elser, W. and Ennulat, R. D. 'Advances in Liquid Crystals', (Ed. G. H. Brown) Academic Press, New York, 1976, vol 2, page 73
3 Kahn, F. J. *Appl. Phys. Lett.* 1971, **18**, 231
4 Adams, J., Haas, W. and Daily, J. *J. Appl. Phys.* 1971, **42**, 4096
5 Scheffer, T. J. *J. Phys.* (*D*) 1975, **8**, 1441
6 Tsutsui, T. and Tanaka, T. *J. Polym. Sci.* (*Polym. Lett.*) 1977, **15**, 475
7 Tsutsui, T., Tanaka, R. and Tanaka, T. *J. Polym. Sci.* (*Polym. Lett.*) 1979, **17**, 511
8 Tsutsui, T. and Tanaka, R. *J. Polym. Sci.* (*Polym. Lett.*) 1980, **18**, 17
9 Tsutsui, T. and Tanaka, R. *Polymer* 1980, **21**,

Chain transfer induced by molecular hydrogen in the 'living' polymerization of propene with soluble $V(acac)_3/Al(C_2H_5)_2Cl$

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Introduction

Polymers with a narrow Poisson distribution of chain lengths can be obtained by living polymerization, because propagation of all chains is initiated simultaneously and chain transfer and termination are absent[1,2]. Recently, we found that the low-temperature polymerization of propene initiated by the soluble system, $V(acac)_3$ (acac = acetyl acetonate) with $Al(C_2H_5)_2Cl$ gives a syndiotactic polypropylene having a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.05\text{–}1.20$)[3,4]. This was the first Ziegler-type catalyst exhibiting 'living' character comparable with that of sodium naphthalene or lithium alkyl in anionic polymerization[2]. Here we report the change in the molecular weight distribution of polypropylenes during living polymerization involving molecular hydrogen as a transfer agent. Hydrogen is known to be an effective transfer agent in the polymerization of α-olefins with Ziegler-type catalysts[5–9]. However, there are few reports[10] on the effect of hydrogen on the molecular weight distribution of polymers.

Experimental

A three-necked glass flask (~300 ml) with a magnetic stirrer was used as a reactor. Propene (0.83 mol) was condensed into toluene in the reactor, and kept at −78°C by a methanol/dry ice bath. The amount of toluene was

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