

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

New chiral photochromic menthone-containing homopolymers and copolymers - synthesis, phase behaviour and photo-optical properties

A. Yu. Bobrovsky; N. I. Boiko; V. P. Shibaev

Online publication date: 06 August 2010

To cite this Article Bobrovsky, A. Yu. , Boiko, N. I. and Shibaev, V. P.(1999) 'New chiral photochromic menthone-containing homopolymers and copolymers - synthesis, phase behaviour and photo-optical properties', *Liquid Crystals*, 26: 12, 1749 – 1765

To link to this Article: DOI: 10.1080/026782999203373

URL: <http://dx.doi.org/10.1080/026782999203373>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

New chiral photochromic menthone-containing homopolymers and copolymers—synthesis, phase behaviour and photo-optical properties

A. YU. BOBROVSKY, N. I. BOIKO, V. P. SHIBAEV*

Chemistry Department, Moscow State University, Leninskie Gory,
119899 Moscow, Russia

(Received 9 February 1999; in final form 23 April 1999; accepted 24 June 1999)

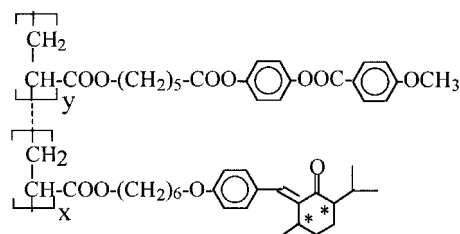
A new approach for the preparation of photosensitive materials for coloured data recording and storage is advanced. This approach involves the synthesis of copolymers containing nematogenic and combined (-)-arylidene-*p*-menthan-3-one chiral photochromic fragments in one monomer unit. The conditions for the formation of an LC phase in the chiral photochromic homopolymers as a function of the structure of the side groups have been identified; for a new series of copolymers, the effect of their composition on the phase behaviour and photo-optical properties is considered. Planarly oriented films of the copolymers show selective light reflection in the UV, visible, and near IR spectral regions. The photochemical behaviour of the homopolymers and copolymers in dilute solution and as films has been studied. In these systems, under UV radiation, the *E*-*Z* isomerization of the (-)-arylidene-*p*-menthan-3-one fragment is the dominating process. The kinetic features of the photoprocess are revealed, and the effective quantum yields calculated. The isomerization process leads to dramatic changes in the anisometry of the chiral side groups, and the helical twisting power decreases. Therefore, as a result of UV radiation of films of the copolymers, the selective light reflection peak is shifted to a longer wavelength spectral region. This means that such polymeric films can be considered as promising materials for colour data recording and as storage media.

1. Introduction

The development of light-sensitive media based on liquid crystalline compounds for data recording, storage, and reproduction is one of the most strongly developing areas of the modern physical chemistry of low molecular mass and polymer liquid crystals. Among various photochromic LC systems used for the above purposes, so-called comb-shaped polymers containing azobenzene fragments have been the most studied. As a result of the action of polarized light, films of such polymers experience the *trans*-*cis*-isomerization of the azo groups, which leads to the appearance of photoinduced birefringence. The possibility of light-induced local and reversible changes in the birefringence allows one to use such polymers for data recording and storage [1–9].

An alternative approach involving the application of photochromic polymers is directed at the development of so-called command surfaces [10–14]. The application of azobenzene-containing polymers as orienting film supports for the deposition of low molecular mass liquid crystals and the light-induced orientation of the liquid crystals on the surfaces of such films allows one to create quite unique systems.

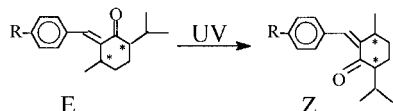
Despite numerous publications devoted to photochromic mesomorphic materials [1–14], until recently only a few have focused on preparing and studying photosensitive LC polymers which are able to produce chiral mesophases [15–17]. Only in our recent publications [18, 19] have we advanced new approaches for the development of novel photochromic cholesteric copolymers which are able to change their optical characteristics dramatically under light irradiation. In addition to phenyl benzoate nematogenic side units, such copolymers contain chiral photosensitive fragments, which are derivatives of 1-menthone†:



†A little later, a copolymer with a chemically similar structure was synthesized by the research group at Philips R&D, The Netherlands [20].

* Author for correspondence; e-mail: lcp@libro.genebee.msu.su

Under the action of UV light, the chiral photochromic side units of such copolymers experience *E*-*Z* isomerization:



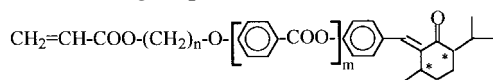
The twisting power of the *Z*-isomer is approximately 10 times lower than that of the *E*-isomer [21, 22]. Under the action of UV irradiation, in films of the cholesteric copolymer, untwisting of the cholesteric helix is observed, and this untwisting is accompanied by a shift of the selective light reflection to a higher wavelength spectral region.

Hence, by synthesizing cholesteric photochromic copolymers with different compositions and with a given helical structure and consequently strictly fixed optical properties, one may induce local changes in their supra-molecular structure and helical pitch by UV irradiation. This modification offers advantages for coloured data recording with a coloured background [18, 19].

We have continued our research activities in the direction of the synthesis and study of chiral photochromic LC polymers, with principal attention focused on finding the correlation between the molecular structure of chiral photochromic copolymers and their phase behaviour and photo-optical properties. To this end, we synthesized a set of chiral photochromic acrylic copolymers based on the same nematogenic phenyl benzoate monomer as in the copolymers mentioned above:



We also synthesized a set of chiral photochromic monomers with different lengths of spacer and different lengths of aromatic fragments containing one, two, or three benzene rings, which adjoin the chiral (-)-arylidene-*p*-menthan-3-one group:



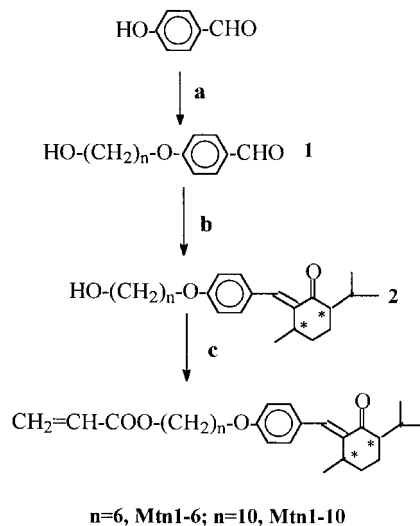
where $n = 6, 10$; $m = 0, 1$.

Hence, this work had two principal goals: (i) studying the phase behaviour of a set of the synthesized copolymers with different concentrations of chiral photochromic units with different chemical structures and (ii) studying the optical and photo-optical properties of the synthesized compounds from the viewpoint of their possible application as photosensitive materials for coloured data recording and storage.

2. Experimental

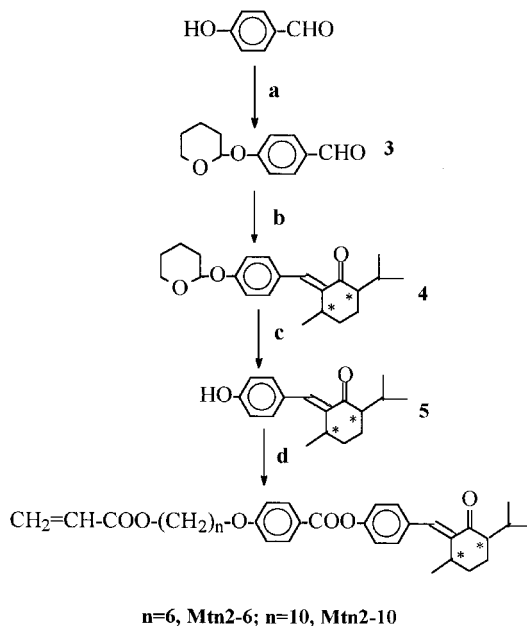
2.1. Synthesis of monomers

Nematogenic monomer A was prepared according to the procedure described in [23]. In figures 1–3 the schemes of synthesis of the photochromic monomers are presented. Synthesis techniques are described below.



$n=6$, Mtn1-6; $n=10$, Mtn1-10

Figure 1. Synthesis of chiral photochromic one ring monomers: (a) $\text{HO}-(\text{CH}_2)_n-\text{Br}$, acetone, K_2CO_3 ; (b) 1-menthone, DMSO, KOH; (c) $\text{CH}_2=\text{CH}-\text{COCl}$, NEt_3 , THF. The first number of the compound code shows the number of benzene rings in the mesogenic fragment; the second number corresponds to the spacer length.



$n=6$, Mtn2-6; $n=10$, Mtn2-10

Figure 2. Synthesis of chiral photochromic two ring monomers: (a) 3,4-dihydropyran, $\text{C}_2\text{H}_5\text{Cl}_2$, TosOH; (b) 1-menthone, DMSO, KOH; (c) MeOH, $\text{C}_2\text{H}_5\text{Cl}_2$, TosOH; (d) $\text{CH}_2=\text{CH}-\text{COO}-(\text{CH}_2)_n-\text{Ph}-\text{COOH}$, DCC, DMAP, THF.

2.1.1. Synthesis of Mtn1-6 and Mtn1-10 (figure 1)

2.1.1.1. Reaction (a): 4-(6-hydroxyhexyloxy)benzaldehyde and 4-(10-hydroxydecyloxy)benzaldehyde (1) [17]. A mixture of 4-hydroxybenzaldehyde (5.3 g, 43.7 mmol) and potassium carbonate (6.6 g, 48.1 mmol) in 100 ml

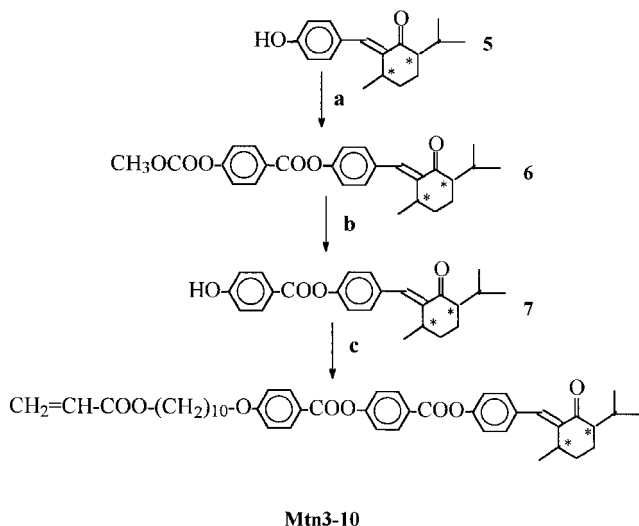


Figure 3. Synthesis of the chiral photochromic three ring monomer: (a) $\text{CH}_3\text{OCO}-\text{Ph}-\text{COOH}$, DCC, DMAP, THF; (b) NH_3 , H_2O , MeOH ; (c) $\text{CH}_2=\text{CH}-\text{COO}-(\text{CH}_2)_{10}-\text{Ph}-\text{COOH}$, DCC, DMAP, THF.

of dry acetone was heated under reflux with stirring for 0.5 h while 6-bromohexanol or 10-bromodecanol (48.1 mmol) was added dropwise; the reaction was then continued for 6 h, when the precipitate was filtered off and the filtrate evaporated. The oily residue was dissolved in 200 ml of diethyl ether and washed, first with a 10% aqueous Na_2CO_3 (triply) and then with water (triply). The solution was dried over MgSO_4 and evaporated. Finally, the residue was recrystallized from hexane and dried in vacuum.

4-(6-Hydroxyhexyloxy)benzaldehyde: yield 3.5 g. (52%), white fine crystalline powder, $T_m = 25-26^\circ\text{C}$. IR (cm^{-1}): 3444 (OH), 2940, 2904, 2864 (CH_2), 1664 ($\text{C}=\text{O}$ in ArCHO), 1600 ($\text{C}-\text{C}$ in Ar), 1260 (COC).

4-(6-Hydroxydecyloxy)benzaldehyde: yield 4.75 g. (70%), white fine crystalline powder, $T_m = 52-53^\circ\text{C}$. IR (cm^{-1}): 3444 (OH), 2941, 2906, 2865 (CH_2), 1663 ($\text{C}=\text{O}$ in ArCHO), 1600 ($\text{C}-\text{C}$ in Ar), 1260 (COC).

2.1.1.2. Reaction (b): (-)-4-(6-hydroxyhexyloxy)benzylidenmenthan-3-one and (-)-4-(10-hydroxydecyloxy)benzylidenmenthan-3-one (**2**). A generalized method for the synthesis of similar compounds was described in [24]. To a solution of **1** (31.5 mmol) and l-menthone (31.5 mmol) in 10 ml of dry, freshly distilled dimethylsulphoxide, ground KOH (23.2 mmol) was added. The mixture was stirred for 12 h at room temperature, poured into 100 ml of cooled 3% aqueous acetic acid, kept with periodic shaking for 3 h, and then shaken with chloroform. The extract was triply washed with water, dried over calcined MgSO_4 , and evaporated. The resulting

oily product was doubly purified by chromatography eluting with a benzene–ethyl acetate mixture (first 10:1 and then 2:1, $R_f = 0.36$).

(-)-4-(6-Hydroxyhexyloxy)benzylidenmenthan-3-one: yield 15%, a light-yellowish oil. IR (cm^{-1}): 3444 (OH), 2956, 2888, 2872 (CH_2), 1676 ($\text{C}=\text{O}$), 1600 ($\text{C}-\text{C}$ in Ar), 1260 (COC). UV: (THF) $\lambda_{\text{max}} = 302 \text{ nm}$ ($\lg \epsilon = 4.16$). $[\alpha]_{\text{D}}^{22} = -146.9^\circ$, $[M]_{\text{D}}^{22} = -526^\circ$.

(-)-4-(10-Hydroxydecyloxy)benzylidenmenthan-3-one: yield 10%, a light-yellowish oil. IR (cm^{-1}): 3445 (OH), 2954, 2888, 2872 (CH_2), 1675 ($\text{C}=\text{O}$), 1600 ($\text{C}-\text{C}$ in Ar), 1260 (COC). UV: (THF) $\lambda_{\text{max}} = 302 \text{ nm}$ ($\lg \epsilon = 4.15$). $[\alpha]_{\text{D}}^{22} = -138.5^\circ$, $[M]_{\text{D}}^{22} = -529^\circ$.

2.1.1.3. Reaction (c): (-)-4-(6-acryloyloxyhexyloxy)benzylidenmenthan-3-one (**Mtn1-6**) and (-)-4-(10-acryloyloxydecyloxy)benzylidenmenthan-3-one (**Mtn1-10**). The syntheses were performed according to [25, 26]. A solution of substance **2** (4.7 mmol), triethylamine (7.1 mmol), and *N,N*-dimethylaminopyridine (0.71 mmol) in 20 ml of absolute tetrahydrofuran was cooled in ice-cold water. To this solution acryloyl chloride (7.1 mmol) was slowly added with vigorous stirring and the mixture then stirred for 12 h. The whole was then dissolved in 100 ml of ether, repeatedly washed with water, and dried over calcined MgSO_4 . The solvent was distilled off and the oily product dried in vacuum and purified by column chromatography (eluent benzene–ethyl acetate 2:1).

Mtn1-6: yield 30%, a light-yellowish powder, $T_m = 49-50^\circ\text{C}$. IR (cm^{-1}): 2956, 2888, 2872 (CH_2), 1720 ($\text{C}=\text{O}$ in $\text{CH}_2=\text{CH}-\text{COO}-\text{R}$), 1676 (ketone $\text{C}=\text{O}$), 1650 ($\text{C}=\text{C}$), 1600 ($\text{C}-\text{C}$ in Ar), 1260 (COC). UV: (THF) $\lambda_{\text{max}} = 303 \text{ nm}$ ($\lg \epsilon = 4.17$). $[\alpha]_{\text{D}}^{22} = -154.0^\circ$, $[M]_{\text{D}}^{22} = -634^\circ$.

Mtn1-10: yield 46%, a light-yellowish powder, $T_m = 44-47^\circ\text{C}$. IR (cm^{-1}): 2932, 2884, 2856 (CH_2), 1722 ($\text{C}=\text{O}$ in $\text{CH}_2=\text{CH}-\text{COO}-\text{R}$), 1678 (ketone $\text{C}=\text{O}$), 1635 ($\text{C}=\text{C}$), 1600 ($\text{C}-\text{C}$ in Ar), 1260 (COC). UV: (THF) $\lambda_{\text{max}} = 303 \text{ nm}$ ($\lg \epsilon = 4.16$). $[\alpha]_{\text{D}}^{22} = -140.0^\circ$, $[M]_{\text{D}}^{22} = -655^\circ$.

2.1.2. Synthesis of **Mtn2-6** and **Mtn2-10** (figure 2)

2.1.2.1. Reaction (a): 4-tetrahydropyranloxybenzaldehyde (**3**) [27]. To a stirred solution of 4-hydroxybenzaldehyde (10.4 g; 85.2 mmol) in 100 ml of dichloroethane cooled in an ice bath, 2,3-dihydropyran (9.3 ml; 102.8 mmol) was added dropwise over 10 min. Some crystals of *p*-toluenesulfonic acid were then added. The reaction was complete after about 15 min—thin layer chromatography (TLC) showed no starting material remaining. The reaction was quenched by addition of NaHCO_3 (1.0 g). The solvent was removed by rotary evaporation and the liquid product was purified by column chromatography using toluene as eluent. The

product **3** was a colourless oil: yield 4.93 g (30%). IR (cm^{-1}): 2948, 2872 (CH_2), 1692 (C=O), 1600 (C–C in Ar), 1120, 1260 (COC).

2.1.2.2. *Reaction (b)*. Compound **4** in figure 2 was synthesized according to the procedure described for the menthone derivatives **2**. Yield 25%, $T_m = 69\text{--}70^\circ\text{C}$. IR (cm^{-1}): 2956, 2892, 2872 (CH_2), 1664 (C=O), 1600 (C–C in Ar), 1244 (COC). $[\alpha]_D^{22} = -115.2^\circ$, $[M]_D^{22} = -394^\circ$.

2.1.2.3. *Reaction (c)*: (-)-4-hydroxybenzylidenmenthan-3-one (**5**). Substance **4** (2.74 g; 8.0 mmol) was dissolved in 20 ml of dichloroethane, and 35 ml of methanol and 0.1 g of *p*-toluenesulfonic acid were then added. The mixture was stirred at room temperature for 1 h. The reaction was controlled by TLC using a mixture of benzene–ethyl acetate 2:1 ($R_f = 0.76$). The solvent was evaporated and the pure phenol **5** obtained by column chromatography on silica gel using benzene–ethyl acetate (10:1) mixture as eluent. Yield 1.16 g (56%), yellow fine-crystalline powder, $T_m = 140\text{--}141^\circ\text{C}$. IR (cm^{-1}): 3320 (OH), 2992, 2960 (CH_2), 1664 (C=O), 1600 (C–C in Ar). $[\alpha]_D^{22} = -289.8^\circ$, $[M]_D^{22} = -751^\circ$.

2.1.2.4. *Reaction (d)*: (-)-4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-benzylidenmenthan-3-one (**Mtn2-6**) and (-)-4-[4-(10-acryloyloxydecyloxy)benzoyloxy]-2-benzylidenmenthan-3-one (**Mtn2-10**). 4-(6-Acryloyloxyalkyloxy)benzoic acid (4.7 mmol) synthesized according to [28], phenol **5** (4.0 mmol), and *N,N*-dimethylamino-pyridine (0.47 mmol) were dissolved in 3 ml of tetrahydrofuran. Dicyclohexylcarbodiimide (DCC) (4.7 mmol) was added and the resulting mixture stirred for 36 h. The reaction was monitored by TLC using a mixture of toluene–ethyl acetate 10:1 as eluent ($R_f = 0.3$). The precipitate was filtered off, washed with tetrahydrofuran and then diethyl ether (50 ml) was added to the filtrate. The solution was washed successively with water, a 5% solution of acetic acid, and finally with water to pH 7. The ether extract was dried over anhydrous Na_2SO_4 . After the solvent was distilled in vacuum, the product was purified by column chromatography using chloroform as eluent.

Mtn2-6: yield 25%, yellowish fine-crystalline powder, $T_m = 78\text{--}79^\circ\text{C}$. IR (cm^{-1}): 2944, 2884, 2868 (CH_2), 1723 (CO in $\text{CH}_2=\text{CH}-\text{COO}-\text{Alk}$), 1713 (CO in $\text{Ar}-\text{COO}-\text{Ar}'$), 1681 (ketone C=O), 1635 (C=C), 1600 (C–C in Ar), 1256 (COC). UV: (THF) $\lambda_{\text{max}} = 276\text{ nm}$ ($\lg \varepsilon = 4.49$). $[\alpha]_D^{22} = -85.1^\circ$, $[M]_D^{22} = -501^\circ$.

Mtn2-10: yield 35%, yellowish fine-crystalline powder, $T_m = 67\text{--}69^\circ\text{C}$. IR (cm^{-1}): 2945, 2885, 2868 (CH_2), 1722 (CO in $\text{CH}_2=\text{CH}-\text{COO}-\text{Alk}$), 1714 (CO in $\text{Ar}-\text{COO}-\text{Ar}'$), 1680 (ketone C=O), 1635 (C=C), 1600

(C–C in Ar), 1256 (COC). UV: (THF) $\lambda_{\text{max}} = 276\text{ nm}$ ($\lg \varepsilon = 4.50$). $[\alpha]_D^{22} = -108.3^\circ$, $[M]_D^{22} = -577^\circ$.

2.1.3. Synthesis of **Mtn3-10** (figure 3)

2.1.3.1. *Reaction (a)*: (-)-4-(4-methoxycarbonyloxybenzoyl)-2-benzylidenmenthan-3-one (**6**). This was synthesized according to the method described previously for **Mtn2-6**.

The product was purified by column chromatography using toluene as eluent. Yield 44%, $T_m = 85\text{--}87^\circ\text{C}$. IR (cm^{-1}): 2944, 2884, 2868 (CH_2), 1762 (C=O in MeOCOOAr), 1714 (CO in $\text{Ar}-\text{COO}-\text{Ar}'$), 1680 (ketone C=O), 1635 (C=C), 1600 (C–C in Ar), 1256 (COC). $[\alpha]_D^{22} = -129.6^\circ$, $[M]_D^{22} = -526^\circ$.

2.1.3.2. *Reaction (b)*: (-)-4-(4-hydroxybenzoyl)-2-benzylidenmenthan-3-one (**7**). Following [29], substance **6** (10 mmol) was dissolved in 140 ml of methanol, cooled in an ice bath, and a 25% aqueous solution of ammonia (70 ml) was added. The reaction was monitored by TLC ($R_f = 0.12$, CHCl_3). After 2 h reaction was complete. Then, the solution was acidified with acetic acid, diluted with water, and shaken several times with chloroform (the total volume of the extract was about 500 ml). The solution was dried over anhydrous Na_2SO_4 , and the solvent removed by rotary evaporation. Purification was performed by column chromatography using a mixture of toluene–ethyl acetate (10:1) as eluent. Yield 0.79 g (30%), $T_m = 136\text{--}138^\circ\text{C}$. IR (cm^{-1}): 3400 (OH), 2956, 2888, 2872 (CH_2), 1706 (CO in $\text{Ar}-\text{COO}-\text{Ar}'$), 1680 (ketone C=O), 1628 (C=C), 1600 (C–C in Ar). $[\alpha]_D^{22} = -137.9^\circ$, $[M]_D^{22} = -538^\circ$.

3.1.3.3. *Reaction (c)*: (-)-4-[4-(10-acryloyloxydecyloxy)benzoyloxy]benzoyloxy]-2-benzylidene-*p*-menthan-3-one (**Mtn3-10**). This was synthesized according to the technique for preparing **Mtn2-6** and **Mtn2-10** using DCC. Yield 67%, $T_m = 103\text{--}105^\circ\text{C}$. IR (cm^{-1}): 2932, 2880, 2856 (CH_2), 1728, 1715 (ester C=O), 1680 (ketone C=O), 1635 (C=C), 1600 (C–C in Ar). UV: (*n*-octane) $\lambda_{\text{max}} = 269\text{ nm}$ ($\lg \varepsilon = 4.68$), (THF) $\lambda_{\text{max}} = 277\text{ nm}$ ($\lg \varepsilon = 4.69$). $[\alpha]_D^{22} = -63.6^\circ$, $[M]_D^{22} = -458^\circ$.

2.2. Synthesis of polymers

The copolymers were synthesized by radical copolymerization of the monomers in benzene solution at 60°C ; AIBN was used as initiating agent. All the synthesized copolymers were purified by repeated precipitation with methanol and dried in vacuo.

2.3. Physicochemical methods of investigation

IR spectra were recorded with a Bruker WP-200 instrument in the range $4000\text{--}400\text{ cm}^{-1}$. The samples were prepared as KBr pellets. In the case of oil-like

substances, the compounds were applied as thin layers on a KBr plate. A BioRad FTS 6000 FTIR spectrometer was used to record the IR spectra of UV irradiated polymer samples.

The optical rotation of chiral compounds was measured with a Polarimeter-1 EPO using the D-line of sodium ($\lambda = 589 \text{ nm}$). Measurements were performed using 10% solutions of substances in dichloroethane.

The relative molecular mass of copolymers was determined by gel permeation chromatography (GPC). GPC analyses were carried out with a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made using a UV detector, THF as solvent (1 ml min^{-1} , 40°C), a set of PL columns of 100, 500 and 10^3 \AA ; a calibration plot was constructed with polystyrene standards. The copolymers obtained have the following molecular mass characteristics: $M_n = 12\,000\text{--}15\,000$, $M_w/M_n = 2.1\text{--}3.1$.

Phase transitions in copolymers were studied by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 thermal analyser (a scanning rate of 10 K min^{-1} ; prior to DSC measurement, samples were annealed for one month at 45°C). The optical polarizing microscope investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope.

Selective light reflection of chiral polymers was studied with a Hitachi U-3400 UV-Vis-IR spectrophotometer equipped with a Mettler FP-80 hot stage. The polymer samples with a thickness of $20 \mu\text{m}$ were sandwiched between two flat glass plates. Prior to tests, the polymer samples were annealed for 20–40 min at appropriate temperatures.

X-ray diffraction analysis was carried out using a URS-55 instrument (Ni-filtered CuK_α radiation, $\lambda = 1.54 \text{ \AA}$).

2.4. Photochemical investigations

Photochemical properties were studied using a special instrument [19] equipped with a DRSh-250 ultra-high pressure mercury lamp and UV (N_2) laser—ILGI-503 (337 nm). Using a filter, the 313 nm band of the linear radiation spectrum of the mercury lamp was selected. To prevent heating of the samples due to IR irradiation from the lamp, a water filter was used; to obtain a plane-parallel light beam, a quartz lens was used. During irradiation, a constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of UV irradiation was determined actinometrically [30] and was equal to $2.03 \times 10^{-9} \text{ Es s}^{-1} \text{ cm}^{-2}$ (0.77 mW cm^{-2}) for the Hg-lamp and $1.12 \times 10^{-7} \text{ Es s}^{-1} \text{ cm}^{-2}$ (42.9 mW cm^{-2}) for the UV laser.

In our studies of photochemical transformations in solution, *n*-octane and dichloroethane were used as solvents. Concentrations of solutions were $1\text{--}5 \times 10^{-5} \text{ M}^\ddagger$. For illumination, the solutions were placed in a 2 cm thick quartz cell. The process of isomerization was followed by recording the absorption spectra of the illuminated solutions.

The photochemical properties of copolymers in the condensed state were studied by illuminating $20 \mu\text{m}$ thick films at different temperatures. After a certain time of irradiation, the samples were annealed at a temperature 30°C higher than the glass transition temperature. During annealing, the selective light reflection spectra of samples were recorded and the clearing temperatures (T_{cl}) were determined periodically using the polarizing microscope. The samples were annealed until no changes in the selective light reflection wavelength or in T_{cl} were observed (usually about 40 min).

3. Results and discussion

3.1. Phase behaviour and photo-optical properties of the chiral photochromic homopolymers

3.1.1. Phase behaviour

Table 1 presents the data on the phase behaviour of the chiral photochromic homopolymers.

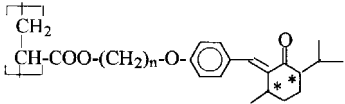
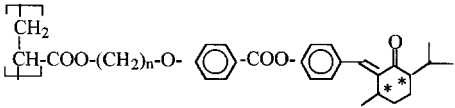
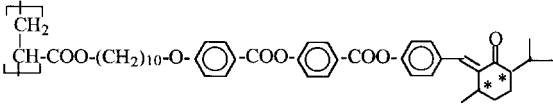
With the exception of **PMtn3-10**, all the chiral homopolymers are amorphous. The absence of the mesophase in the menthone-containing homopolymers is related to the presence of the bulky substituents [$-\text{CH}_3$ and $-\text{CH}(\text{CH}_3)_2$] in the chiral cyclohexanone fragment. As a result, the anisometry of the benzyldenementhan-3-one fragments is dramatically decreased, and development of a mesophase is impossible. Note that, among a great number of known low molecular mass derivatives of menthone [31, 32], none produces a mesophase.

Our three-ring homopolymer **PMtn3-10** provides an intriguing exception to this rule. According to the data obtained by polarizing optical microscopy, this homopolymer is characterized by a fan-like texture. The corresponding X-ray patterns obtained at temperatures below the isotropization temperature show a diffuse halo at wide scattering angles and an intense small angle X-ray reflection ($2\theta = 2.29^\circ$). The corresponding inter-layer distance ($d_{0,0,1} = 38.5 \text{ \AA}$) virtually coincides with the calculated length of the side group of the homopolymer (38–40 \AA). This shows the existence of a SmA phase with a single layer packing of the side mesogenic groups.

Comparing the glass transition temperatures (T_g) of the homopolymers presented in table 1, one may draw the following conclusions:

‡ In this paper 1 mol l^{-1}

Table 1. Properties of the chiral menthone-containing photochromic homopolymers

Structure of homopolymer and its abbreviated designation ^a	$T_g/^\circ\text{C}$	Phase behaviour and phase transitions/ $^\circ\text{C}$
	PMtn1-6 28 PMtn1-10 15	amorphous amorphous
	PMtn2-6 51 PMtn2-10 30	amorphous amorphous
	PMtn3-10 39	SmA 122 (0.8) ^b I

^a **Mtn-*m-n*** are abbreviated designations of the homopolymers **Mtn** corresponds to the presence of the menthanone group in the polyacrylate; *n* is the spacer length; *m* is the number of benzene rings in the side fragment.

^b Enthalpy of phase transition, J g⁻¹.

- (a) As the length of the spacer in the single-ring or two-ring homopolymer is increased, T_g decreases because of the plasticizing action of the methylene fragments [33].
- (b) As the length of the rigid aromatic fragment is increased, the reverse effect is observed; this effect is associated with enhanced interactions between the side groups.

Similar effects have been observed for a set of menthyl-containing chiral amorphous homopolymers [34, 35] with side groups of similar structure.

3.1.2. Photochemical properties

The photochemical behaviour of the chiral photochromic homopolymers with different lengths of the rigid fragments was studied for dilute solutions and the solid phase (film).

Figures 4(a–c) show the spectra for dilute solutions of the homopolymers in dichloroethane ($c = 2.6 \times 10^{-2}$ mg ml⁻¹) before and during UV laser irradiation. As follows from figure 4, as a result of light irradiation, the optical density of the solutions is decreased, and the absorption band is shifted to a shorter wavelength region (shown by the arrow in figure 4). According to results obtained in [21, 36], the above changes in the electronic spectra of this class of compound are associated with the occurrence of the *E-Z* isomerization.

Using the experimental data and equation (1) obtained in [19], we calculated the quantum yields of the isomerization process for homopolymers **PMtn1-6**

and **PMtn1-10**:

$$\varphi_E = - \left(\frac{dD_{337}}{dt} \right)_{t \rightarrow 0} \frac{V}{I_0(I - I_0^{-D_{337}}) \epsilon_E^{337} l} \quad (1)$$

where D_{337} is the optical density at the wavelength of the light source (337 nm); t is the time (min); I_0 is the intensity of the incident light (Es min⁻¹ cm⁻²); V is the volume of the solution (ml); l is the thickness of cuvette (cm); ϵ_E^{337} is the extinction coefficient at a wavelength of 337 nm (cm² mol⁻¹).

For homopolymers **PMtn1-6** and **PMtn1-10**, the calculated values of the quantum yield are $\varphi_E \approx 0.36$, and this value agrees with the values of the quantum yields obtained for the direct process of *E-Z* isomerization in low molecular mass compounds containing a benzylidene-*p*-menthan-3-one fragment, $\varphi_E \approx 0.31$ –0.43 [36]. However, in the case of the two-ring and three-ring homopolymers, the spectral changes are negligible, figures 4(b) and 4(c). Therefore, calculation of the quantum yield using the above equation is not possible. In passing from the single-ring to the two-ring or three-ring homopolymers, the changes in the absorption spectra are likely to be provided by a marked contribution from phenyl benzoate chromophore, whose absorption dominates in the case of the multi-ring homopolymers.

Figures 5 and 6 show the absorption of films of the single-ring and two-ring homopolymers versus the time of UV irradiation at two fixed wavelengths. The temperature of the irradiated samples was maintained at a constant level of 20°C.

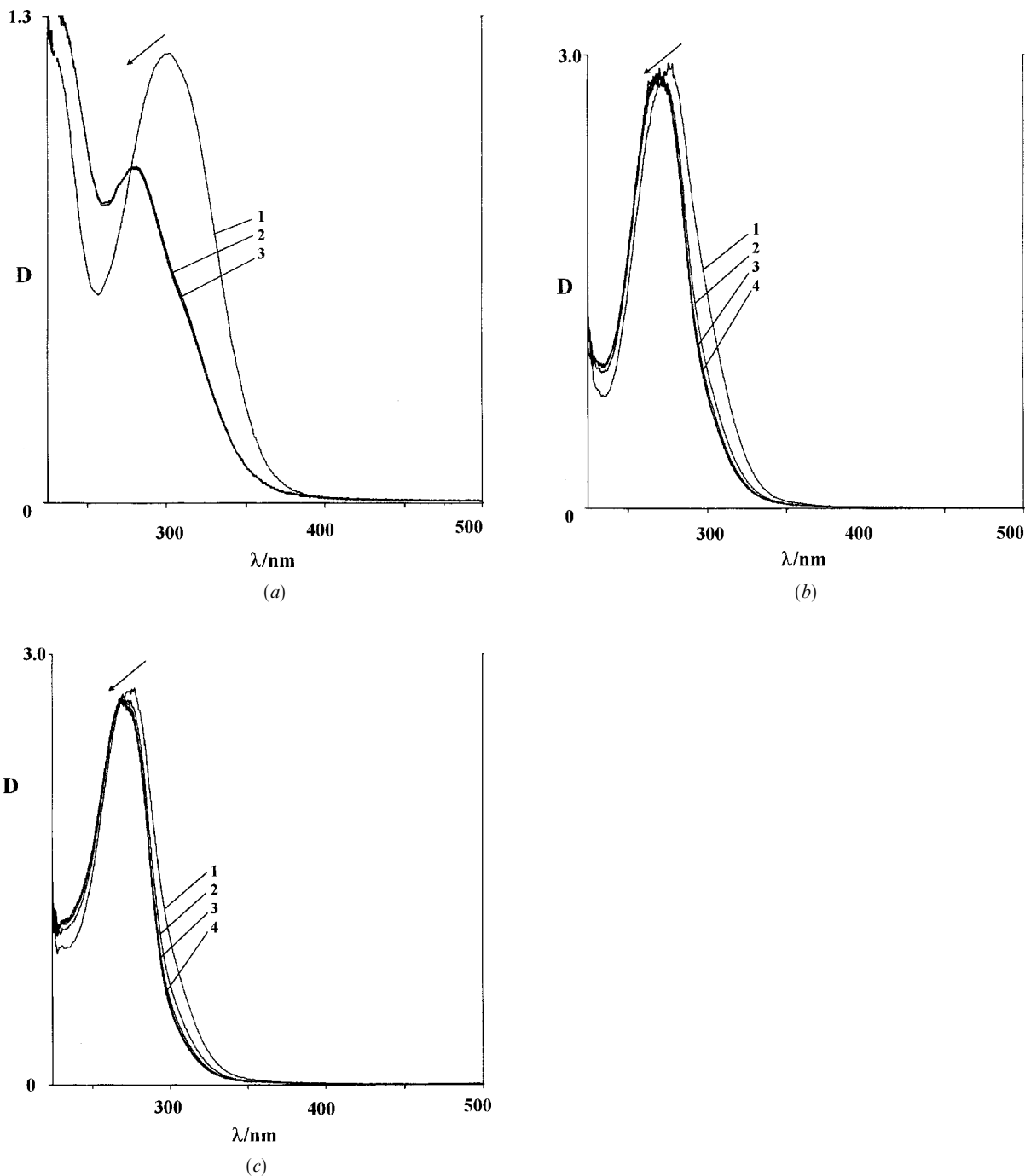


Figure 4. Changes in the absorption spectra of the chiral homopolymers **PMtn1-10** (a), **PMtn2-10** (b) and **PMtn3-10** (c) during UV irradiation (laser, 337 nm). 1: spectrum of initial solution before irradiation; 2, 3 and 4: spectra recorded at 5 min intervals during irradiation.

In the case of the single-ring chiral homopolymer (figure 5), even at long irradiation times (above 3 h), the optical density of the films gradually decreases. Upon irradiation, the two-ring and three-ring homopolymers show a quite different behaviour (figures 6(a) and 6(b)).

During the first 10–20 min of irradiation, the optical density rapidly decreases. Then, the absorption gradually increases. The initially colourless polymer film turns yellow and becomes insoluble in organic solvents. This behaviour is likely to be associated with cross-linking.

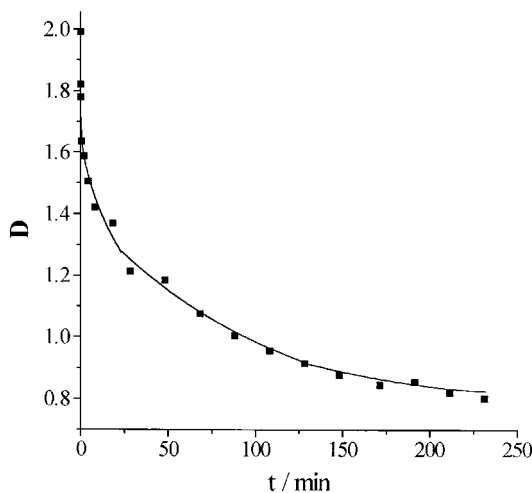
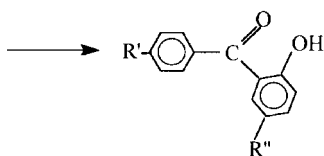
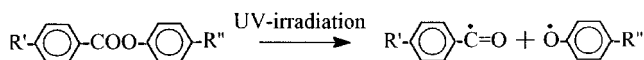


Figure 5. Change in the optical density D_{360} for a film of homopolymer **PMtn1-10** on irradiation (laser, 337 nm). Film thickness $d = 10 \mu\text{m}$, $T = 20^\circ\text{C}$.

According to data related to the photochemical transformations of menthone derivatives [21, 36], no photocycloaddition reaction $\{2 + 2\}$ leading to the formation of intermolecular chemical bonds is observed (probably, because of steric hindrance).

Analyzing the above experimental evidence, one may conclude that, in the early stages of irradiation, both homopolymers experience only one process of photoisomerization. However, in the case of the two-ring and three-ring homopolymers containing phenyl benzoate fragments, with long irradiation times, the secondary process related to a photo-Fries rearrangement is observed [37–39]:



To prove the above assumption, we used FTIR spectroscopy to examine the photochemical behaviour of thin films of the homopolymers. Dilute solutions of the polymers in chloroform were cast onto KBr plates and the solvent was slowly evaporated. Then, the as-cast films were exposed to UV irradiation, and the corresponding FTIR spectra were recorded within the specified periods of time.

It follows from figures 7(a) and 7(b) that UV irradiation shifts the absorption band of the carboxylate CO group in the benzylidene-*p*-menthan-3-one fragment to a higher frequency region (lower wavenumber).

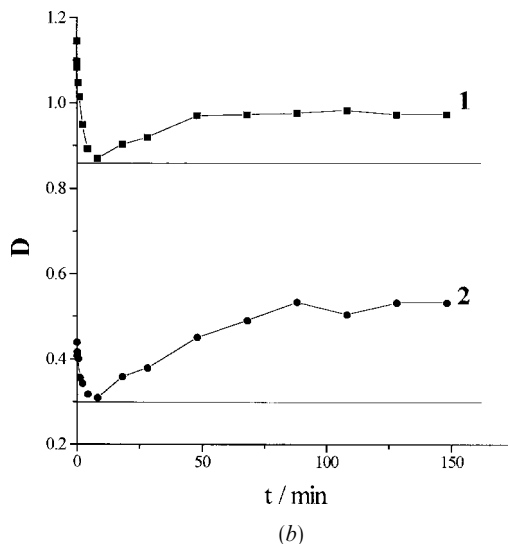
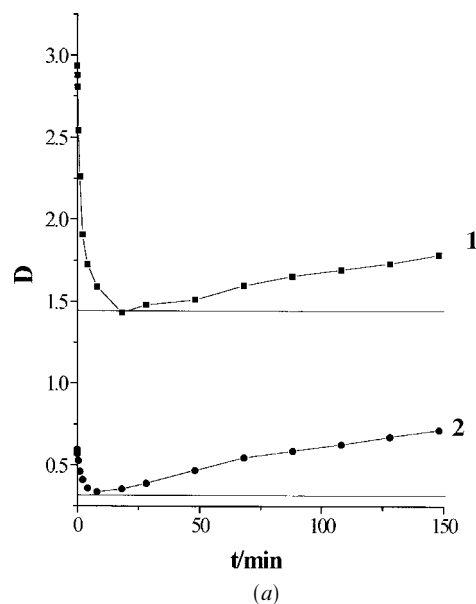


Figure 6. Changes in the optical densities D_{337} (1) and D_{360} (2) on irradiation for films of homopolymer **PMtn2-10** (a) and **PMtn3-10** (b); UV-laser, 337 nm. Films thickness $d = 10 \mu\text{m}$, $T = 20^\circ\text{C}$.

These changes are associated with the occurrence of *E-Z* isomerization [36]. However, in the case of the two-ring homopolymer, an additional band at 1625 cm^{-1} appears, and this is likely to be a result of the Fries rearrangement [40, 41]. The position of this band in a comparatively low frequency spectral region is probably related to the presence of hydrogen bonds, $\text{C}=\text{O} \cdots \text{H}-\text{O}-$, in the photoreaction products. The corresponding FTIR spectra of the three-ring homopolymers show quite similar photoinduced changes.

Cross-linking of polymers is likely to occur by an intermolecular rearrangement. In this case, one can

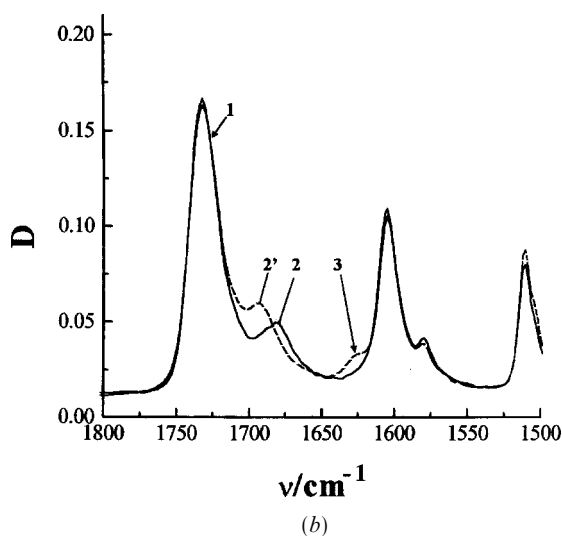
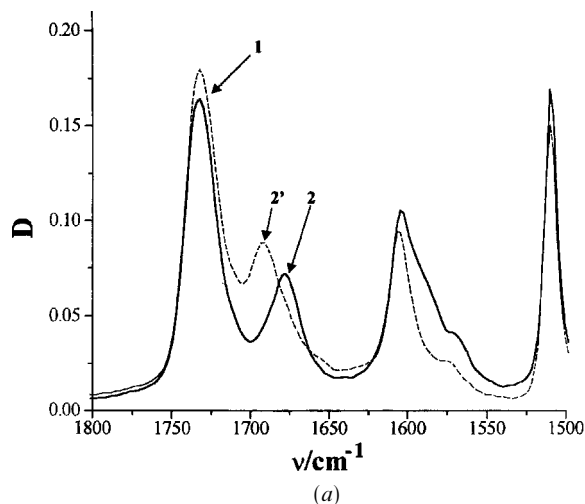


Figure 7. IR spectra of films of homopolymer **PMtn1-10** (a) and **PMtn2-10** (b) before (solid line) and after (dashed line) UV irradiation (unfiltered light from 100 W Hg lamp). Polymer films were obtained from chloroform solution. 1: vibration of ester CO groups; 2 and 2': CO in arylidene-menthan-3-one fragment (before and after irradiation, respectively); 3: CO in photo-Fries rearrangement product. Irradiation time 15 min.

hardly exclude the possible death of the radicals formed at the C=C bond of the arylidene-*p*-menthan-3-one fragment. However, we note that the occurrence of this photoreaction is very pronounced only for long irradiation times or under irradiation with a short wavelength UV light (< 313 nm) [42]. In the case studied, the occurrence of this process may however provide an additional contribution to a reduction in anisotropy of the chiral side units and lead to an additional decrease in helical twisting power.

Hence, to study quantitatively the contribution from the photochemical processes of *E*-*Z* isomerization and Fries rearrangement, we estimated the value of $\phi\epsilon_{360}$, which characterizes the quantum efficiency of the photo-processes (ϕ is the apparent quantum yield, ϵ_{360} is an unknown extinction coefficient of the homopolymer in the film). The calculations were performed using the following equation [39]:

$$\phi\epsilon_{360} = - \frac{dD_{360}}{dt} \frac{I}{I_0(I - 10^{-D_{337}})} \quad (2)$$

where D_{337} is the optical density of the sample at 337 nm; t is the radiation time (min); I_0 is the intensity of UV irradiation (Es min^{-1}). In this case, dD_{360}/dt stands for the change in optical density per unit time at a wavelength of 360 nm§.

Table 2 shows the calculated values of dD_{360}/dt and $\phi\epsilon_{360}$ for the three chiral photochromic homopolymers. Comparing the values of $\phi\epsilon_{360}$ for the two competing processes, one may suggest an insignificant role of the photoinduced Fries rearrangement (the values of $\phi\epsilon_{360}$ are more than two orders of magnitude lower than those obtained for the *E*-*Z* isomerization). As the length of the rigid aromatic fragment is increased, the value of $\phi\epsilon_{360}$ decreases, and this behaviour is likely to be related to the decrease in the extinction coefficient ϵ_{360} in the

§The choice of this wavelength is arbitrary and related to the fact that, in a shorter wavelength spectral region, the absorption of the films is so high that any kinetic measurements are impossible.

Table 2. Values of dD_{360}/dt and $\phi\epsilon_{360}$ for chiral photochromic homopolymers (at 20°C). The films were obtained from chloroform solutions of the polymers.

Homopolymer	<i>E</i> - <i>Z</i> isomerisation		Photo-Fries rearrangement	
	$dD_{360}/dt/\text{min}^{-1}$	$\phi\epsilon_{360}/\text{M}^{-1} \text{cm}^{-1}$	$dD_{360}/dt/\text{min}^{-1}$	$\phi\epsilon_{360}/\text{M}^{-1} \text{cm}^{-1}$
PMtn1-6	- 0.62	1876	—	—
PMtn2-6	- 0.58	1758	0.0027	8.2
PMtn3-10	- 0.08	236	0.00065	2.0

following order of the homopolymers: from **PMtn1-6** to **PMtn2-6** and **PMtn3-10**, see figures 4(a–c).

Studying the irradiation of the three-ring chiral photochromic homopolymer **PMtn3-10** at different temperatures, we evaluated the effect of temperature on the efficiency of both processes (figure 8). It follows from figure 8 that temperature has a strong effect on the apparent quantum yield of isomerization, whilst the efficiency of the photoinduced rearrangement depends slightly on temperature and is negligibly small compared with that observed during photoisomerization.

Concluding this consideration of the photochemical behaviour of the homopolymers, let us note that all the above photochemical reactions are thermally irreversible (at least, at temperatures below 150°C). This fact does not allow one to observe reversible changes in the optical properties of the systems studied. The irreversible character of the *E*–*Z* isomerization is likely to be related to a high energy barrier between the two isomeric forms of benzylidenementhan-3-ones [21, 36].

3.2. Phase behaviour, optical and photo-optical properties of the chiral photochromic copolymers

3.2.1. Phase behaviour

For the copolymerization with nematogenic phenyl benzoate monomer (**A**), we selected single-ring and two-ring chiral photochromic monomers because their corresponding homopolymers do not produce an LC phase. This approach may allow the development in the

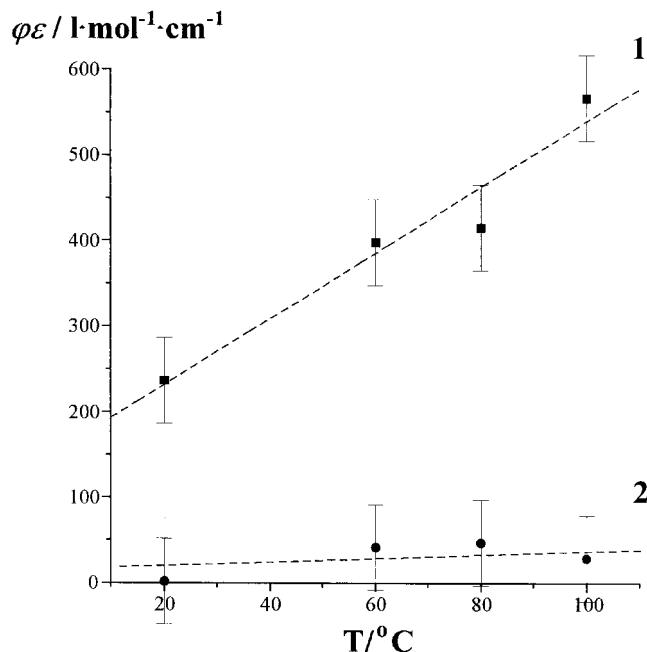


Figure 8. Temperature dependence of the quantum efficiency of *E*–*Z* isomerization (1) and photo-Fries rearrangement (2) for homopolymer **PMtn3-10**.

copolymers of a chiral nematic phase which is not complicated by the elements of a layered structure, as was usually observed for copolymers with mesogenic cholesterol-containing chiral units [43, 44]. As a result, one may dramatically simplify the system and find out the influence of the structure of chiral side groups on the thermal and photo-optical properties of the chiral nematic phase.

Using the data from polarizing optical microscopy, DSC measurements, and X-ray analysis, phase diagrams were constructed for the copolymers of the three types, figures 9(a–c). From figure 9, it can be seen that all copolymers with a relatively low content (less than 30–40 mol %) of chiral units are able to produce the chiral nematic phase. Concentration and temperature regions for the existence of this mesophase are controlled by the structure of the chiral photochromic units in the copolymers. In the case of the copolymers with single-ring chiral fragments and with a spacer containing six methylene units—copolymers **PMtn1-6-A**, figure 9(a)—loss of the mesophase is observed at a content of chiral component less than 30 mol %. As the length of spacer is increased, the concentration region of the existence of the LC phase widens, to about 40 mol %, figure 9(b). This trend is associated with an increased freedom of the chiral fragments with increasing length of spacer. The chiral non-mesomorphic fragments have the possibility of orientational ordering under the influence of the nematogenic matrix; as a result, the thermal stability of the mesophase increases.

An increase in the length of the rigid aromatic fragments of the chiral photochromic units—copolymers **PMtn2-6-A**, figure 9(c)—also leads to a widening of the interval of the existence of the mesophase. In this case, one may assume that the chiral units containing the phenyl benzoate (potentially mesogenic) fragment are characterized by a high orientational order parameter in the nematic matrix. In this case, the bulky menthanone group destroys the LC order to a much lesser extent.

Let us note specially that for the three types of copolymer with a low content of chiral units (less than 15–20 mol %), one observes the development of a unique chiral mesophase characterized by a local order which is typical for a *K* mesophase. This phase is likely to develop due to the ordering of phenyl benzoate mesogenic groups, as was observed in the case of homopolymer **A**, and is characterized by a two dimensional local order of the monoclinic type; this phase is referred to as the TDK phase (two dimensional *K* phase)¶. A detailed description of the structure of this mesophase was given in [45].

¶Earlier, this mesophase was referred to as a nematic B phase, N_B [46].

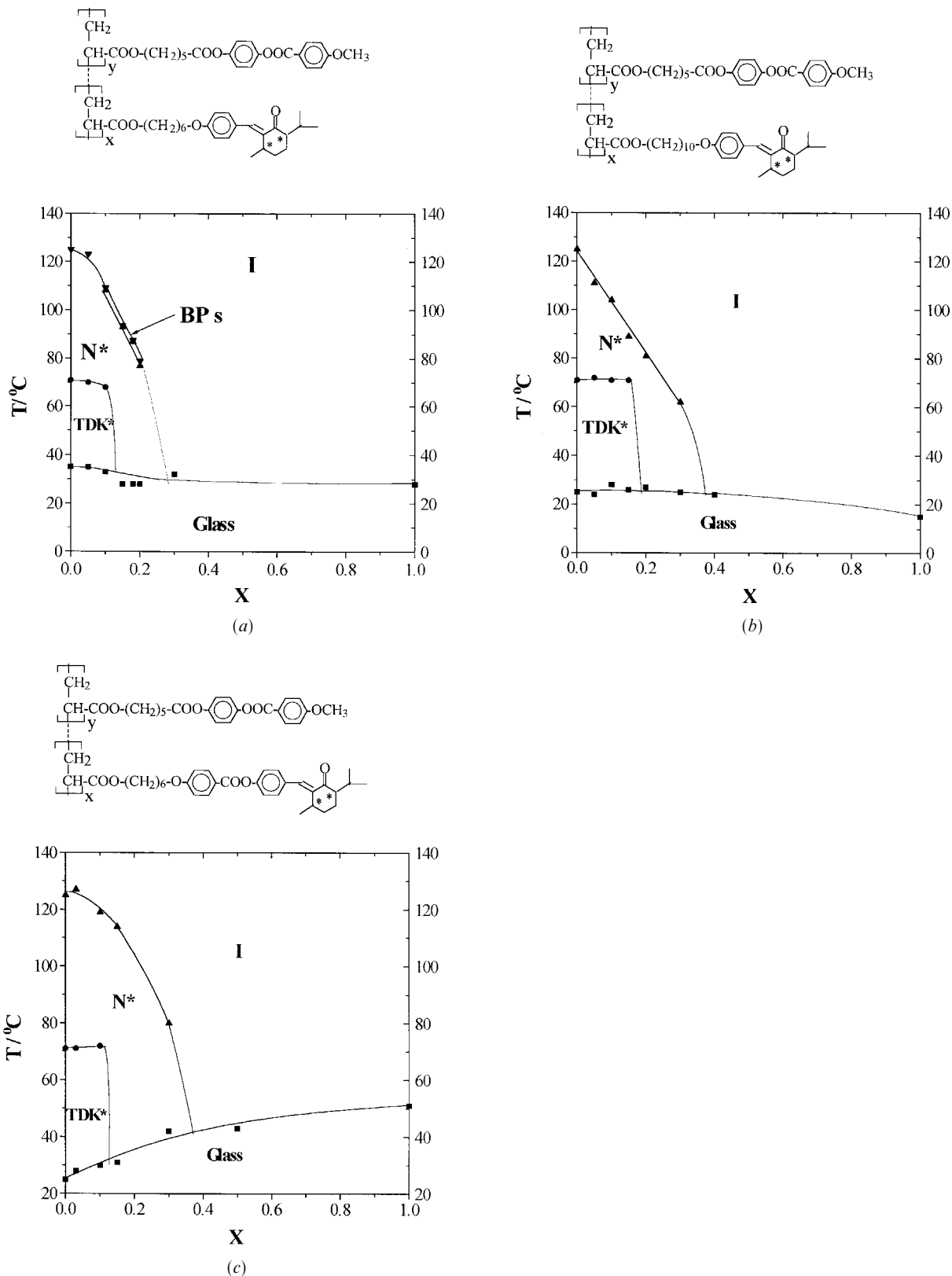


Figure 9. Structural formula and phase diagrams for the copolymers **Mtn1-6-A** (a), **Mtn1-10-A** (b) and **Mtn2-6-A** (c); X is the molar fraction of chiral units.

In the case studied here, we deal with a helically twisted TDK phase, whose model was presented in [35]. Let us emphasize that the planar texture of this phase is characterized by a selective light reflection; however, the development of this phase requires an additional annealing process (from several days to one month depending on the annealing temperature [47]).

In addition to the chiral TDK* phase, the copolymers **PMtn1-6** also show blue phases over a narrow temperature region near the clearing temperature, figure 9(a). These phases are characterized by a platelet texture and give selective light reflection in the visible spectral region (when the content of chiral units is equal to 10–20 mol%). The development of these phases is possible only in systems with a high chirality [48–52], that is with a short pitch of the helix (200–400 nm).

It is interesting to note that the two other types of copolymer **PMtn1-10-A** and **PMtn2-6-A** do not produce blue phases even though they are also characterized by a short pitch of the helix (see §3.2.2.). The reasons for this behaviour are open to speculation.

3.2.2. Optical properties

For all three types of copolymer containing less than 30 mol % of chiral component, their planar textures are characterized by selective light reflection in the IR, visible, and UV spectral regions. The difficulties related to the preparation of a uniform planar texture do not allow one to observe selective light reflection for the copolymers with a higher content of chiral units. Furthermore, for such copolymers, the selective light reflection maximum should be located in the region of high absorption, and this situation substantially complicates the study of their optical properties.

Figures 10(a) and 10(b) show the temperature dependences of the maximum wavelength of selective light reflection for the copolymers with single-ring chiral units containing spacers with different lengths. The dependences agree with model speculations advanced in [53–55] for the temperature dependences of the helical pitch in the absence of anharmonism of the rotational vibrations. Near the clearing temperature, one may observe a slight increase in the pitch of the helix due to a decrease in the orientational order parameter. The temperature coefficient of the selective light reflection $\gamma = (1/\lambda) \times (d\lambda/dT)$ is equal to 0.004 and is independent of the content of chiral units.

Another situation is observed for the copolymers, in which chiral side groups contain a two-ring rigid fragment (figure 11). In this case, the temperature coefficient of the above dependences is negative and depends linearly on the concentration of chiral component (see inset in figure 11). Usually, negative values of the temperature

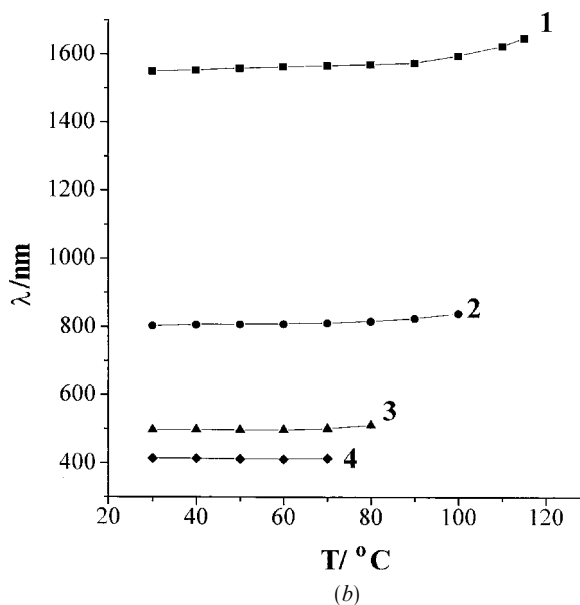
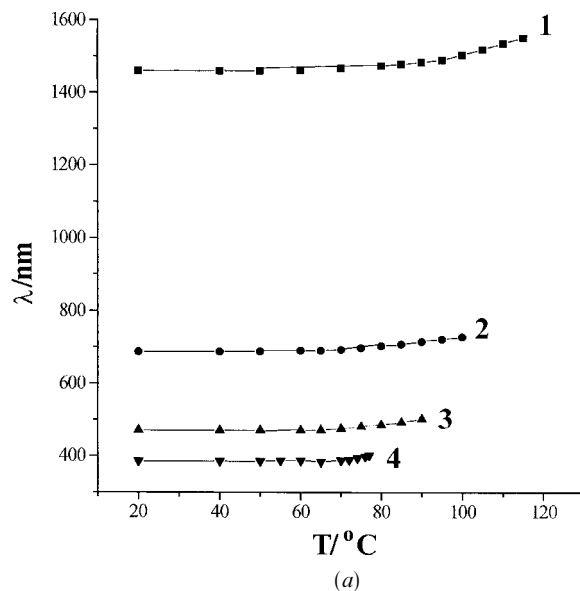


Figure 10. Temperature dependences of the maximum of selective light reflection for copolymers **PMtn1-6-A** (a) and **PMtn1-10-A** (b) Chiral unit content: 5 (1), 10 (2), 15(3) and 20 (4) mol %.

coefficient have been observed earlier for cholesteryl-containing copolymers [25, 43, 44, 56], and this behaviour is related to smectic fluctuations in the N* mesophase (according to X-ray data). In the case studied here, the situation is quite unusual. First, our structural studies revealed the absence of any small angle reflections in the corresponding X-ray patterns; second, the absolute value of the temperature coefficient γ decreases with increasing concentration of chiral units (inset in figure 11). This experimental evidence suggests that the chiral side units are not smectogenic.

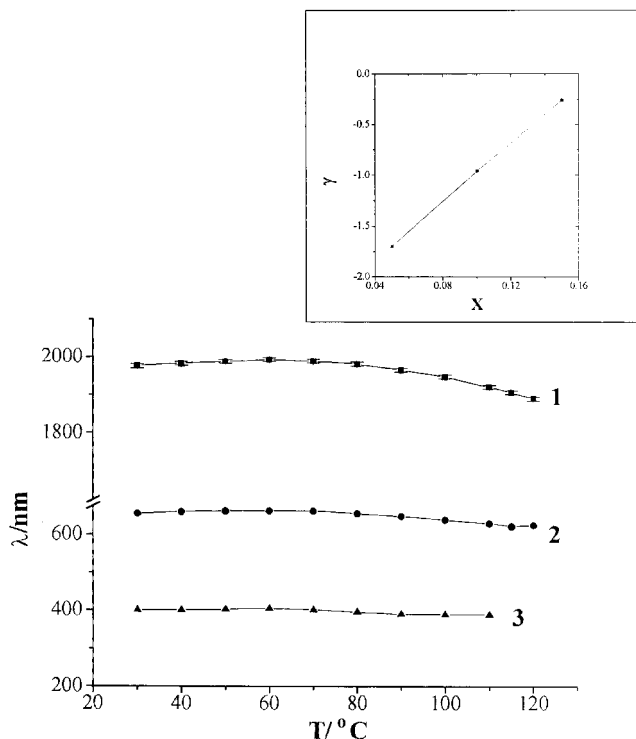


Figure 11. Temperature dependence of the maximum of selective light reflection for copolymers **PMtn2-6-A** Chiral units content: 3 (1), 10 (2) and 15 (3) mol%. Inset: dependence of temperature coefficient $\gamma = (1/\lambda)(d\lambda/dT)$ on the content of chiral units.

This is the first time that such abnormal behaviour of the temperature dependences of the helical pitch have been observed. The only exception is provided by [57] where a similar behaviour of the temperature dependences of λ_{max} was described for phenylethylamine-based copolymers with chiral units. According to the authors of [57], the negative coefficients γ and the decrease in the absolute value of this coefficient with increasing content of chiral component may be explained by the presence of hydrogen bonding between amide and carboxylic groups. However, in the case of the menthone-containing copolymers, this explanation seems to be invalid, because one can hardly expect the presence of strong hydrogen bonding between the different chain units in the copolymers. Furthermore, copolymers with menthyl chiral units of similar structure do not show this abnormal behaviour [34, 35]. The origin of this behaviour is still open to speculations.

Chiral additives or chiral side units are characterized by a very important parameter called the helical twisting power (A) [58]:

$$A = \left(\frac{d\lambda_{\text{max}}^{-1}}{dX} \right)_{X=0} \quad (3)$$

To calculate A values, the reciprocal value of the wavelength maximum of the selective light reflection (at $T = 0.95T_{\text{cl}}$) was plotted against the molar fraction of chiral units X (figure 12). An approximation of the plotted curves was obtained using the following formula [34, 35]:

$$\lambda_{\text{max}}^{-1} = AX/(1 + BX) \quad (4)$$

where B is the parameter characterizing the deviation of this plot from linearity. The calculated values of the helical twisting power A and of parameter B are summarized in table 3.

Analysis of the calculated values allows one to recognize the effect of the structure of the chiral units on their twisting power. In the order of the copolymers from **PMtn1-6-A** to **PMtn1-10-A**, as the length of spacer is increased, the values of A decrease. This behaviour has been observed earlier [34, 35, 59, 60], and is likely to be related to a decrease in the rotational order parameter of chiral side units [61]:

$$S_R = \cos 2\psi \quad (5)$$

where ψ is the rotation angle about the long axis of the chiral group.

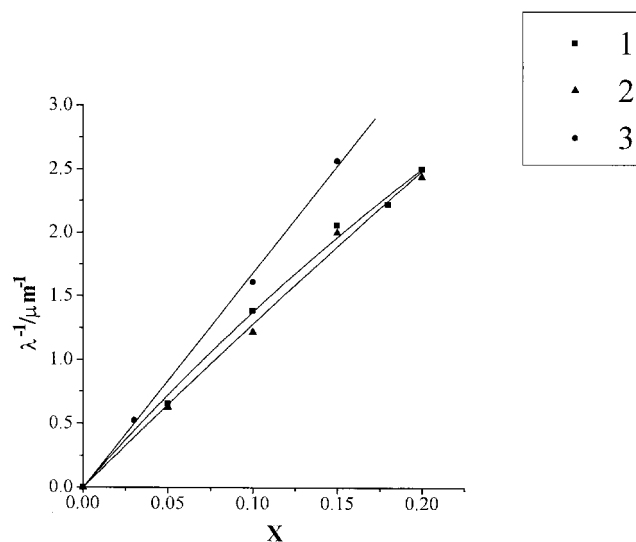


Figure 12. Dependence of λ^{-1} on the molar fraction of chiral units (at $T = 0.95T_{\text{cl}}$) for copolymers **PMtn1-6-A** (1), **PMtn1-10-A** (2), and **PMtn2-6-A** (3).

Table 3. Values of the helical twisting power (A) and parameter B for chiral photochromic copolymers of different series.

Copolymers	$A/\mu\text{m}^{-1}$	B
PMtn1-6-A	15.3 ± 1.3	1.1 ± 0.6
PMtn1-10-A	13.2 ± 1.3	0.3 ± 0.6
PMtn2-6-A	16.9 ± 1.1	0.0 ± 0.5

On the other hand, as the length of the rigid aromatic fragment is increased (copolymers **PMtn2-6-A**), quite the reverse effect is observed: the helical twisting power increases. This behaviour may be explained by an increase in the orientational order parameter of the chiral units in the nematic phase. However, for the chiral photochromic copolymers, the values of A only slightly increase (from $15.3 \mu\text{m}$ for **PMtn1-6-A** to $16.9 \mu\text{m}^{-1}$ for **PMtn2-6-A**). On the other hand, in menthyl-containing copolymers, when the length of the mesogenic moiety is increased by one benzene ring [34, 35], an almost two fold increase in A is observed.

For the copolymers studied here, somewhat different changes in parameter B are observed. As the length of the spacer is increased, B decreases. With increasing length of the mesogenic fragment, the decrease in parameter B is even more pronounced (table 3). In the latter case, the dependence is almost linear. These features are likely to be related to an increase in the orientational order parameter of the chiral units in the following order: **PMtn1-6-A**—**PMtn1-10**—**PMtn2-6-A**. As the lengths of the spacer and the aromatic fragment are increased, ‘compatibility’ of the chiral units with the nematogenic matrix is improved, and the distortions in the LC order induced by the chiral component are minimized. Hence, the presence of chiral photochromic units in the copolymers first allows one to prepare polymer films with selective light reflection in the visible, IR, and UV spectral regions, and secondly provides a unique opportunity to control the maximum wavelength of selective light reflection via UV irradiation.

3.2.3. Photochemical and photo-optical properties of the chiral photochromic copolymers

The photo-optical properties of the chiral photochromic copolymers were studied for planar oriented films with a thickness of $20 \mu\text{m}$ under UV irradiation. After each 5 min of irradiation, the samples were annealed at $T = T_g + 30^\circ\text{C}$ until no changes in the maximum wavelength of selective light reflection were observed (about 40 min).

Figure 13 shows the maximum wavelength of selective light reflection as a function of the time of irradiation. As is seen, irradiation leads to a marked increase in the maximum wavelength of selective light reflection. However, on prolonged exposure to UV radiation, degeneration of the selective light reflection peak is observed. This degeneration may be explained by an increased inhomogeneity of composition of the sample in the irradiated zone. As a result of the high extinction coefficients of the copolymers, the photoreaction zone is likely to be small (less than $1 \mu\text{m}$) as compared with the film thickness ($20 \mu\text{m}$). Hence, the rate of this process is

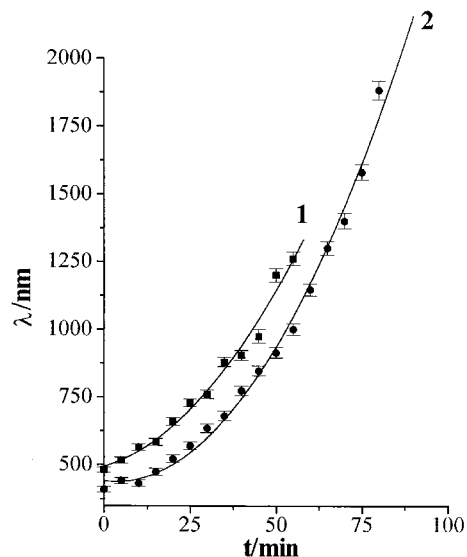


Figure 13. Selective reflection wavelength as a function of UV irradiation time for the copolymers **PMtn1-6-A** (1) and **PMtn2-6-A** (2) with 15 mol % of chiral units. Temperature of irradiated samples $T_{\text{ir}} = T_{\text{cl}} + 20^\circ\text{C}$.

strongly limited by the thermal diffusion of macromolecules with a high content of the *Z*-isomeric chiral units formed in the film thickness [62]. It seems likely that mixing of the samples is so hindered that one may observe a gradual ‘accumulation’ of the photoreaction products in the surface layer near the light source. Furthermore, a disturbed anisometry of the chiral units in the *Z*-form disturbs the LC order. As a result, the isotropization temperature is decreased (figure 14), and the selective light reflection peak is widened (more defects in the planar texture).

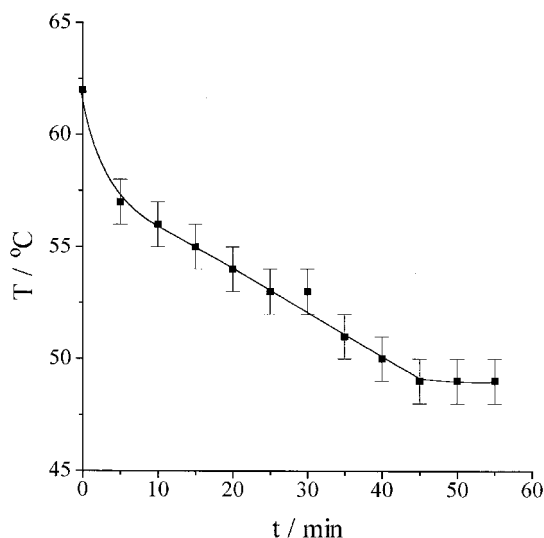


Figure 14. Clearing temperature depression of the chiral photochromic copolymer **PMtn1-10** with 30 mol % of chiral units during UV irradiation.

Table 4. Values of $(d\lambda_{\text{max}}^{-1}/dt)_{t=0}$ and apparent quantum yield ϕ'_E for copolymers measured at different temperatures.

Chiral units concn./mol%	Temperature of irradiation of films/ $^{\circ}\text{C}$	$(d\lambda_{\text{max}}^{-1}/dt)_{t=0}/\mu\text{m}^{-1} \text{min}^{-1}$	ϕ'_E
<i>Copolymers of series PMtn1-6-A</i>			
10	$T_{\text{cl}} + 10 = 130$	- 0.016	0.037
	60	- 0.061	0.014
	25	- 0.0012	0.003
15	$T_{\text{cl}} + 20 = 124$	- 0.030	0.070
	100	- 0.017	0.041
	80	- 0.012	0.029
	60	- 0.0075	0.018
	25	- 0.0045	0.011
<i>Copolymers of series PMtn1-10-A</i>			
15	$T_{\text{cl}} + 20 = 108$	- 0.032	0.074
<i>Copolymers of series PMtn2-6-A</i>			
10	100	- 0.0177	0.041
15	$T_{\text{cl}} + 20 = 143$	- 0.0343	0.080

Analysis of the photo-optical behaviour of the copolymers with chiral photochromic units with various structures showed that as the length of the spacer was increased, no changes in the kinetics of this process were observed. A tendency to widening and degeneration of the peak is also preserved.

The copolymers with chiral units containing aromatic fragments with different lengths show a somewhat different behaviour (figure 13). In the case of copolymers with two-ring menthone-containing units, 'degeneration' of the selective light reflection occurs somewhat later (curve 2, figure 13). With increasing length of the aromatic fragment, the anisotropy of the chiral side groups increases, and the planar texture contains more defects at longer irradiation times. Hence, increasing the length of the aromatic fragment allows an almost two fold increase in the shift of the selective light reflection band ($\Delta\lambda \approx 800$ and 1400 nm for the single-ring and two-ring copolymers, respectively, figure 13).

Analysis of the kinetic curves of helix untwisting induced by UV radiation allows one to estimate the apparent quantum yield of the photoisomerization (ϕ'_E) [19]:

$$\phi'_E = (\phi_E)_{t=0} = - \frac{\rho l}{MAI_0} \left(\frac{d\lambda_{\text{max}}^{-1}}{dt} \right)_{t=0} \quad (6)$$

Here, m is the mass of the sample (g); ρ is the density of the sample (g cm^{-3}); l is the thickness of the sample (cm); M is the average molecular mass of the copolymer units (g mol^{-1}); A is the helical twisting power of the chiral moiety (μm^{-1}); I_0 is the intensity of the incident light beam ($\text{Es min}^{-1} \text{cm}^{-2}$); λ_{max} is the maximum wavelength (μm) of selective light reflection.

Apparent quantum yields were calculated for all three types of copolymer, and the calculated values are presented in table 4.

We emphasize that these values primarily characterize the efficiency of the diffusive mobility of the macromolecules in the copolymer. As a result, a pronounced temperature dependence of ϕ'_E is observed. Calculations of the true quantum yield present a more complicated task [63, 64]. As follows from the data presented in table 4, the values of ϕ'_E are almost independent of the structure of the chiral photochromic side units.

4. Conclusion

Finally, one may conclude that the copolymers synthesized are quite unique materials which have no analogues. These materials do offer substantial advantages for coloured data recording on a coloured background.

This research was supported by the Russian Foundation of Fundamental Research (Grant 96-03-33495), INTAS Project 96-922, the International Soros Science Educational Program (Grant a98-2199) and the Russian Research Program 'Universities of Russia' (grants 5177). The authors thank Prof. F. Kremer and Dr S. Shilov (University of Leipzig) for assisting with the FTIR.

References

- [1] *Applied Photochromic Polymer Systems*, 1992, edited by C. B. McArdle (Blackie & Son Ltd).
- [2] *Polymers as Electro-optical and Photo-optically Active Media*, 1996, edited by V. P. Shibaev (Berlin Heidelberg Springer-Verlag), p. 37.
- [3] SHIBAEV, V. P., KOSTROMIN, S. G., and IVANOV, S. A., 1997, *Polym. Sci. A*, **39**, 118.

- [4] IVANOV, S. A., YAKOVLEV, I. A., KOSTOMIN, S. G., SHIBAEV, V. P., LASKER, L., STUMPE, J., and KREYSIG, D., 1991, *Makromol. Chem. rapid Commun.*, **12**, 709.
- [5] STUMPE, J., LASKER, L., FISCHER, TH., KOSTROMIN, S., IVANOV, S., SHIBAEV, V., and RUMANN, D., 1994, *Mol. Cryst. liq. Cryst.*, **253**, 1.
- [6] BROWN, D., NATANSOHN, A., and ROCHON, P., 1995, *Macromolecules*, **28**, 6116.
- [7] ROMANUJAM, P., HOLME, N., and HVILSTED, S., 1996, *Appl. Phys. Lett.*, **68**, 1329.
- [8] NATANSOHN, A., ROCHON, P., MENG, X., BARRET, C., BUFFETEAU, T., BONENFANT, S., and PEZOLET, M., 1998, *Macromolecules*, **31**, 1155.
- [9] WU, Y., DEMACHI, Y., TSUTSUMI, O., KANAZAVA, A., SHONO, T., and IKEDA, T., 1998, *Macromolecules*, **31**, 1104.
- [10] CREAUGH, L. T., and KMETZ, A. R., 1973, *Mol. Cryst. liq. Cryst.*, **24**, 59.
- [11] ICHIMURA, K., SUZUKI, Y., SEKI, T., HOSOKI, A., and AOKI, K., 1988, *Langmuir*, **4**, 1214.
- [12] ICHIMURA, K., SUZUKI, Y., TAKAHIRO, S., KAWANISHI, Y., and AOKI, K., 1989, *Makromol. Chem. rapid Commun.*, **10**, 5.
- [13] RINGSDORF, H., URBAN, C., KNOLL, W., and SAWODNY, M., 1992, *Makromol. Chem.*, **193**, 1235.
- [14] REN, Y., TIAN, Y., SUN, R., XI, S., ZHAO, Y., and HUANG, X., 1997, *Langmuir*, **13**, 5120.
- [15] KREUZER, F. H., 1996, *Polymers as Electro-optical and Photo-optically Active Media*, edited by V. P. Shibaev (Berlin, Heidelberg Springer-Verlag).
- [16] PETRY, A., BRAUCHLE, CH., LEIGEBER, H., MILLER, A., WEITZEL, H.-P., and KREUZER, F.-H., 1993, *Liq. Cryst.*, **15**, 113.
- [17] GANGADHARA, K. H., 1995, *Macromolecules*, **28**, 806.
- [18] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Polym. Sci. A*, **40**, 232.
- [19] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Liq. Cryst.*, **25**, 393.
- [20] VAN DE WITTE, P., GALAN, J. C., and LUB, J., 1998, *Liq. Cryst.*, **24**, 819.
- [21] YARMOLENKO, S. N., KUTULYA, L. A., VASHCHENKO, V. V., and CHEPELEVA, L. V., 1994, *Liq. Cryst.*, **16**, 877.
- [22] VINOGRADOV, V., KHIZHNYAK, A., KUTULYA, L., REZNIKOV, YU., and RESHETNYAK, V., 1990, *Mol. Cryst. liq. Cryst.*, **192**, 273.
- [23] BOIKO, N. I., 1987, PhD thesis, Moscow State University (in Russian).
- [24] KUTULYA, L. A., NEMCHENOK, I. B., and TISCHENKO, V. G., 1987, *Referativnii Zhurnal Khimii*, 7N135P (in Russian).
- [25] BOOTH, C. J., DUNMUR, D. A., GOODBY, J. W., and TOYNE, K. J., 1996, *Liq. Cryst.*, **20**, 815.
- [26] NIESES, B., and STEGLICH, W., 1978, *Angew. Chem. int. Ed. Engl.*, **17**, 522.
- [27] BOUCHTA, A., NGUYEN, H. T., ACHARD, M. F., HARDOUIN, F., and DESTRADE, C., 1992, *Liq. Cryst.*, **12**, 575.
- [28] PORTUGALL, M., RINGSDORF, H., and ZENTEL, R., 1982, *Makromol. Chem.*, **183**, 2311.
- [29] CHIN, E., and GOODBY, J. W., 1986, *Mol. Cryst. liq. Cryst.*, **141**, 311.
- [30] KURIEN, K. C., 1971, *J. chem. Soc. B*, 2081.
- [31] KUTULYA, L. A., NEMCHENOK, I. B., and HANDRIMAILOVA, T. V., 1990, *Kristallografiya*, **35**, 1234 (in Russian).
- [32] KUTULYA, L. A., NEMCHENOK, I. B., and HANDRIMAILOVA, T. V., 1990, *Kristallografiya*, **35**, 1242 (in Russian).
- [33] NGAI, K. L., ETIENNE, S., ZHONG, Z. Z., and SCHUELE, D. E., 1995, *Macromolecules*, **28**, 6423.
- [34] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1997, *Polym. Sci. A*, **39**, 798.
- [35] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Liq. Cryst.*, **24**, 489.
- [36] YARMOLENKO, S. N., CHEPELEVA, L. V., KUTULYA, L. A., VASHCHENKO, V. V., DRUSHLYAK, T. G., and PONOMAREV, O. A., 1995, *J. Obsch. Chimii*, **65**, 145 (in Russian).
- [37] WHITCOMBE, W. J., GILBERT, A., and MITCHELL, G. R., 1991, *J. Polym. Sci. A: polym. Chem.*, **30**, 1681.
- [38] *Einführung in die Photochemie*, 1976, edited by H. O. Bekker (Berlin: VEV Deutscher Verlag der Wissenschaften).
- [39] STUMPE, J., ZIEGLER, A., BERGAHN, M., and KRICHELDORF, H. R., 1995, *Macromolecules*, **28**, 5306.
- [40] SMITH, A. L., 1979, *Applied Infrared Spectroscopy. Fundamentals, Techniques, and Analytical Problem-Solving* (New York: John Wiley and Sons).
- [41] LI, S.-K., and GUILLET, J. E., 1977, *Macromolecules*, **10**, 840.
- [42] CREED, D., GRIFFIN, A. C., HOYLE, C. E., and VENKATARAM, K., 1990, *J. Am. chem. Soc.*, **112**, 4049.
- [43] SHIBAEV, V. P., and FREIDZON, YA. S., 1989, *Side Chain Liquid Crystalline Polymers*, edited by McArdle, C. B. (New York: Blackie).
- [44] FREIDZON, YA. S., and SHIBAEV, V. P., 1993, *Liquid Crystal Polymers*, edited by N. A. Platé (New York: Plenum Press), p. 251.
- [45] OSTROVSKII, B. I., SULIANOV, S. N., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Liq. Cryst.*, **25**, 153.
- [46] FREIDZON, YA. S., TALROZE, R. V., BOIKO, N. I., KOSTROMIN, S. G., SHIBAEV, V. P., and PLATÉ, N. A., 1988, *Liq. Crystals*, **3**, 127.
- [47] BOIKO, N. I., OSTROVSKII, B. I., WOLFF, D., SPRINGER, J., and SHIBAEV, V. P., 1998, Abstracts of Workshop *Chemistry and Characterization of Mesophase Materials*, Bayreuth, 4–6 October 1998, P22.
- [48] STEGEMEYER, H., BLUMEL, TH., HILTROP, K., ONUSSEIT, H., and PORSCH, F., 1986, *Liq. Cryst.*, **1**, 3.
- [49] DEMIKHOV, E., and STEGEMEYER, H., 1993, *Liq. Cryst.*, **14**, 1801.
- [50] CROOKER, P. P., 1989, *Liq. Cryst.*, **5**, 751.
- [51] STEGEMEYER, H., and ONUSSEIT, H., 1989, *Makromol. Chem., rapid Commun.*, **10**, 571.
- [52] GILLI, J. M., and SIXOU, K. M., 1989, *J. Phys. Fr.*, **50**, 2911.
- [53] LISEZKY, L., TIMAN, B., TISCHENKO, V., and POLOTI, T., 1977, *Solid State Physics*, **19**, 3461 (in Russian).
- [54] CHILAYA, G. S., and LISETSKY, L. N., 1981, *Usp. Phis. Nauk*, **134**, 279 (in Russian).
- [55] FINKELMANN, H., and STEGEMEYER, H., 1978, *Ber. Bun., phys. Chem.*, **82**, 1302.
- [56] SHIBAEV, V. P., FINKELMANN, H., KHARITONOV, A., PORTUGALL, M., PLATÉ, N. A., and RINGSDORF, H., 1981, *Vysokomol. Soedin.*, **A 23**, 919.
- [57] ZHU, X., BOIKO, N. I., and SHIBAEV, V. P., 1997, *International Symposium New Approaches in Polymer Synthesis and Macromolecular Formation*, June 16–20, 1997, Saint-Petersburg P-085.

- [58] ADAMS, J. E., and HAASE, W. E. L., 1971, *Mol. Cryst. liq. Cryst.*, **15**, 27.
- [59] FINKELMANN, H., and REHAGE, G., 1980, *Macromol. Chem., rapid Commun.*, **1**, 859.
- [60] FINKELMANN, H., and REHAGE, G., 1982, *Macromol. Chem., rapid Commun.*, **3**, 859.
- [61] FINKELMANN, H., and STEGEMEYER, H., 1978, *Ber. Bunsenges, Phys. Chem.*, **82**, 1302.
- [62] VOROBIEV, A. KH., 1995, PhD thesis, Moscow State University (in Russian).
- [63] SHEATS, J. R., DIAMOND, J. J., and SMITH, J. M., 1988, *J. phys. Chem.*, **92**, 4922.
- [64] MINAYLOV, V. V., VOROBIEV, A. KH., and GURMAN, V. S., 1995, *J. Photochem. Photobiol. A: Photochem.*, **87**, 67.