BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 9, pp. 1903–1910, 1995

0032-3861/95/$10.00+0.00

Synthesis and characterization of photo-crosslinkable main-chain liquid-crystalline polymers containing bis(benzylidene)cycloalkanone units

Gangadhara and Kaushal Kishore*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India
(Received 3 June 1994; revised 18 October 1994)

A series of new photo-crosslinkable main-chain liquid-crystalline polymers containing bis(benzylidene)cycloalkanone units have been studied. These units in the polymers function as mesogens as well as photoactive centres. Polyesters with three different bis(4-hydroxybenzylidene)cycloalkanones corresponding to three cycloalkanones, namely cyclopentanone, cyclohexanone and cycloheptanone, have been prepared. Three dicarboxylic acids with ether linkages, which were derived from oligoethylene oxides, namely triethylene glycol, tetraethylene glycol and pentaethylene glycol, have been used as spacers in these polymers. Polymerization was carried out by both solution and interfacial polycondensation; the latter method gave high-molecular-weight polymers. Structural characterizations were done by ultra-violet, infra-red and ^1H nuclear magnetic resonance spectroscopy. Liquid-crystalline properties were studied by differential scanning calorimetry and polarized-light optical microscopy. These polymers show a nematic mesophase. Liquid-crystalline transition temperatures were correlated with polymer structure. The decrease in transition temperature with increase in cycloalkanone ring size was explained in terms of the change in geometrical anisotropy of bis(benzylidene)cycloalkanone units. MNDO (modified neglect of differential overlap) calculations were performed on the model compounds, bis(4-acetyloxybenzylidene)cycloalkanones, to elucidate the geometrical variation of the mesogenic units with cycloalkanone ring size. Studies of photolysis reveal the two kinds of photoreactions that proceed in these polymer systems, namely photoisomerization and photo-crosslinking. The former reaction disrupts the parallel stacking of the chromophores and is reflected as an increase in the ultra-violet spectral intensity. The favourability of these two reactions depends on the mobility of the polymer chains. When the photolysis was done below T_g, photo-crosslinking dominates over photoisomerization. Above T_g, photoisomerization is followed by photo-crosslinking. The photosensitivity of the polymers decreases with increase in size of the cycloalkanone ring.

(Keywords: photo-crosslinking; liquid-crystalline polymers; bis(benzylidene)cycloalkanone)

INTRODUCTION

Owing to their macromolecular properties coupled with the properties of low-molar-mass liquid crystals, liquid-crystalline polymers (LCPs) have attracted considerable attention in recent years in a variety of applications[1–5]. Among these, photo-crosslinkable LCPs are potential candidates for applications in anisotropic network systems like LC elastomers and LC thermosets[6,7], non-linear optics[8], information storage devices[9] and in thin films with controlled orientation of functional groups, which are of interest in microelectronics and optoelectronics[10,11]. Besides, these polymers are also used for the selective permeation of gases and drugs[12,13]. The photochemistry of these polymers is of interest from topochemical points of view, since the reactions take place in an organized liquid-crystalline medium[14,15].

The studies so far reported in this class of LCPs have dealt with polymer systems containing cinnamate ester group[6–25] until a recent report from our laboratory on a new class of photo-crosslinkable LCPs containing bis(benzylidene)cycloalkanone units, where the main emphasis was to synthesize and understand the mechanism of photo-crosslinking[26]. In the present study we wish to understand the structure–property relationship in a large number of these polymer systems. MNDO (modified neglect of differential overlap) calculations have also been carried out on model mesogens to explain the observed trend.

EXPERIMENTAL

Materials

p-Hydroxybenzaldehyde, cycloheptanone, triethylene glycol, tetraethylene glycol, pentaethylene glycol, boron trifluoroetherate (Merck-Schuchart) and oxalyl chloride (Aldrich) were used without further purification. Cyclohexanone and the solvents were purified by distillation.

---

*To whom correspondence should be addressed

Synthesis

Bis(4-hydroxybenzylidene)cycloalkanone. Bis(benzylidene)cyclopentanone and bis(benzylidene)cyclohexanone are prepared from *p*-hydroxybenzaldehyde and corresponding cycloalkanones[27].

Bis(4-hydroxybenzylidene)cycloheptanone. To a mixture of 1.22 g (0.01 mol) of cycloheptanone and 2.44 g (0.02 mol) of *p*-hydroxybenzaldehyde, 3 ml of dry piperidine was added dropwise so that the temperature did not rise above 40°C. After the addition was complete, the mixture was stirred at 80°C for 6 h. Subsequently, it was diluted with 15 ml of pyridine and poured into 250 ml of cold water. The solution was then acidified with HCl and the separated yellow solid was filtered. Recrystallization from 3:1 mixture of methanol and water yielded fine light green crystals. Yield: 2.5 g (78%). M.p.: 252°C. I.r. (KBr): 3360 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{O-H}}$), 1654 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{C=O}}$), 1604 $\mathrm{cm^{-1}}$ ($\nu_{\mathrm{C=C}}$, exocyclic). ^{1}H n.m.r. (DMSO-d_6; TMS): δ (ppm) = 1.83 (m, 4h, $-\mathrm{CH_2}-$, α to the keto group of cycloheptanone), 2.6 (m, 4H, $-\mathrm{CH_2}-$, β to the keto group of cycloheptanone), 6.83 (d, 4H, aromatic), 7.14 (s, 2H, $-\mathrm{CH}=$, exocyclic olefinic), 7.36 (d, 4H, aromatic), 9.84 (s, 2H, $-$OH).

Dicarboxylic acid dichlorides from oligoethylene glycols. Dicarboxylic acids were synthesized by the oxidation of the oligoethylene glycols using conc. $\mathrm{HNO_3}$ and then converted into corresponding dichlorides using oxalyl chloride[26].

Polymerization

Polymerizations of the photo-crosslinkable main-chain liquid-crystalline polymers (PMCLCPs) were performed in two ways: solution polycondensation and interfacial polycondensation.

Solution polycondensation. All the polymers are prepared by the same general procedure; a typical synthesis of PMCLCP-13* is described below.

First, 3.72 g (12.2×10^{-3} mol) of bis(4-hydroxybenzylidene)cyclohexanone was dissolved in 10 ml of dry pyridine and the solution was cooled to 0°C. To this solution 3.49 g (12.2×10^{-3} mol) of pentagolic acid* dichloride in chloroform was added dropwise. After the addition, the solution was stirred at room temperature for 24 h and the mixture was poured into 150 ml methanol. The precipitated polymer was filtered off, purified by reprecipitation and dried under vacuum. Yield: 6.12 g (85%).

Interfacial polycondensation. A procedure for the preparation of PMCLCP-13(PTC) is given below; a similar procedure was used for the other polymers as well.

First, 0.575 g (1.878×10^{-3} mol) of bis(4-hydroxybenzylidene)cyclohexanone was dissolved in 5 ml of water containing 0.165 g (4.13×10^{-3} mol) of NaOH. To this solution was added 0.063 g (1.878×10^{-4} mol) tetrabutylammonium bromide and the mixture stirred vigorously. During stirring 0.537 g (1.878×10^{-3} mol) of pentagolic acid dichloride in 5 ml of dry chloroform was added and stirring continued for 10 min. The reaction mixture was then diluted with 15 ml of chloroform. The chloroform layer was washed twice with 20 ml of 5% NaOH, once with 20 ml of 5% HCl and finally with 20 ml of distilled water. The chloroform layer was then concentrsted to 10 ml and poured into 50 ml of methanol. The precipitated polymer was collected by filtration, washed twice with methanol and dried under vacuum at room temperature. Yield: 1.03 g (93%).

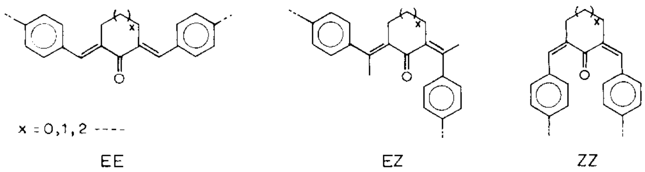


Figure 1 Isomeric structures of bis(benzylidene)cycloalkanones

Measurements

The intrinsic viscosity was measured in pyridine using a Schott–Gerratte Ubbelohde viscometer at 30°C. ^{1}H n.m.r. spectra were recorded on a 400 MHz Bruker AMX-400 *FT*n.m.r. spectrometer. The chemical shifts were calibrated from tetramethylsilane (TMS). Infra-red spectra were recorded on a Bio-Rad FTS 7 *FT*i.r. spectrophotometer using KBr pellets. The u.v.-vis. absorption spectra were recorded on a Hitachi U-3400 spectrophotometer. A DuPont TA9900 differential scanning calorimeter (d.s.c.) was used to determine the thermal transitions. The glass transition temperature (T_g) was taken as the midpoint of the heat-capacity change. All the heating and cooling rates were 10°C $\mathrm{min^{-1}}$ and the sample weight was 30 mg. A Leitz optical polarized microscope model BK-2, equipped with hot stage, was used to observe the thermal transitions and to analyse the anisotropic textures.

RESULTS AND DISCUSSION

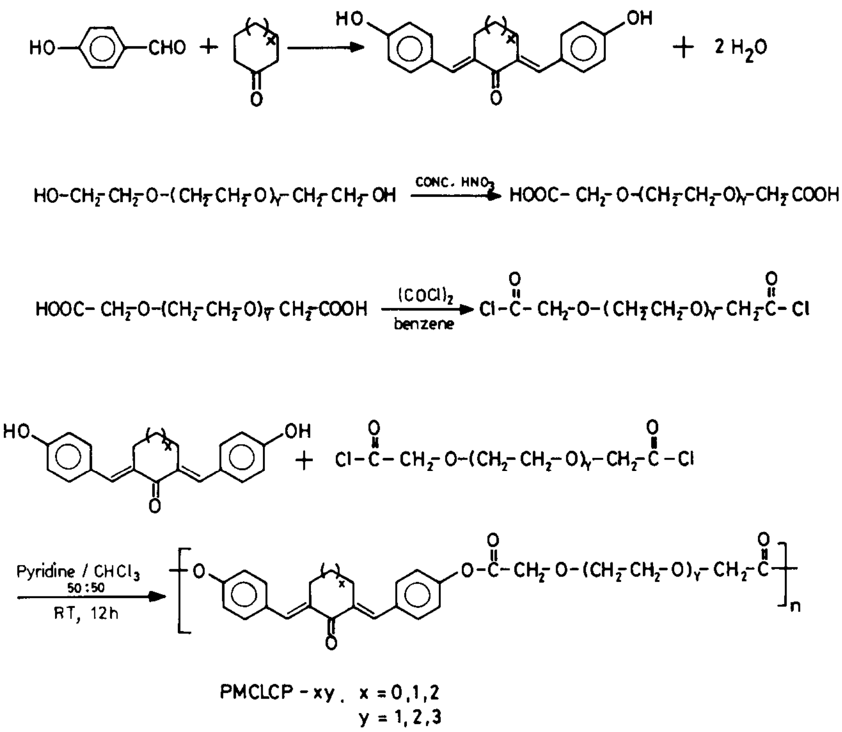
The bis(benzylidene)cycloalkanone units can have three isomeric structures, namely *EE*, *EZ* and *ZZ* (*Figure 1*). The *EE* isomer as a whole possesses a rod-like geometry and hence fulfils the requirements, such as geometrical anisotropy, necessary for mesogenic behaviour. The *EZ* and *ZZ* isomers do not have linear geometry. The α,β-unsaturated ketone functionality present in these structures has the capacity to undergo photoisomerization, photodimerization and photopolymerization reactions. The latter two reactions in polymers lead to the crosslinking of the chains. Hence the polymers with *EE*-bis(benzylidene)cycloalkanone units are expected to exhibit the dual property of liquid crystallinity and photo-crosslinking. In the present study, several polyesters with *EE*-bis(benzylidene)cycloalkanone units in the main chain containing oligoethylene oxide spacers have been synthesized. The ether linkages in the spacer units are expected to reduce the transition temperatures.

Synthesis

The bisphenol monomers, bis(4-hydroxybenzylidene)cycloalkanones, were prepared by reacting 2 mol of *p*-hydroxybenzaldehyde with 1 mol of cycloalkanones. Three different bisphenols were prepared in this series corresponding to three cycloalkanones, namely cyclopentanone, cyclohexanone and cycloheptanone. The other set of monomers is dicarboxylic acid containing

---

* For further details on nomenclature/notation, see 'Results and discussion' section under 'Synthesis' subheading



Scheme 1

Table 1 Yield and physical characteristics of the polymers

Polymers, PNCLCP-xy	Colour	Yield (%)	Solubility[a] Py	DMF	CHCl$_3$	THF	MeCN	Viscosity[b] [η]
Solution polycondensation								
PMCLCP-01	green	75	−	−	−	−	−	−
PMCLCP-02	green	82	+	−	−	−	−	0.08
PMCLCP-03	yellowish green	86	+	+	−	−	−	0.13
PMCLCP-11	yellow	89	+	+	+	−	−	0.16
PMCLCP-12	yellow	85	+	+	+	−	−	0.15
PMCLCP-13	yellow	80	+	+	+	−	−	0.18
PMCLCP-21	pale yellow	86	+	+	+	−	−	0.21
PMCLCP-22	pale yellow	83	+	+	+	−	−	0.11
PMCLCP-23	brown	60	+	+	+	+	+	0.10
Interfacial polycondensation								
PMCLCP-11	yellow	90	+	+	+	−	−	0.24
PMCLCP-12	yellow	93	+	+	+	−	−	0.26
PMCLCP-13	yellow	92	+	+	+	−	−	0.21

[a] Solvents are, respectively, pyridine, dimethylformamide, chloroform, tetrahydrofuran and acetonitrile

[b] Measured in pyridine: + = soluble, − = insoluble

ether linkages, which were prepared by the oxidation of oligoethylene glycols. Three different glycols, namely triethylene glycol, tetraethylene glycol and pentaethylene glycol, were used, and the resulting dicarboxylic acids are correspondingly called trigolic acid, tetragolic acid and pentagolic acid. These dicarboxylic acids were then converted into the respecctive dicarboxyloyl chlorides by treatment with oxalyl chloride.

Polymers were synthesized according to *Scheme 1*; both solution and interfacial polymerization methods were followed. These polymers are abbreviated as PMCLCP-xy, where $x=0$, 1, 2 denotes the number of $-CH_2-$ units on the cycloalkanone ring of the bisphenol monomer and $y=1$, 2, 3 denotes the $-CH_2-CH_2-O-$ units on the dicarboxylic acid monomer. The yield and the physical characteristics of the polymers are shown in *Table 1*. All the polymers, except PMCLCP-23, were obtained in good yield (>80%). However, highest yields were obtained for the polymers prepared by interfacial polycondensation. Most of the polymers were soluble only in highly polar solvents, and the solubility increases with increasing values of x and y. The polymers prepared

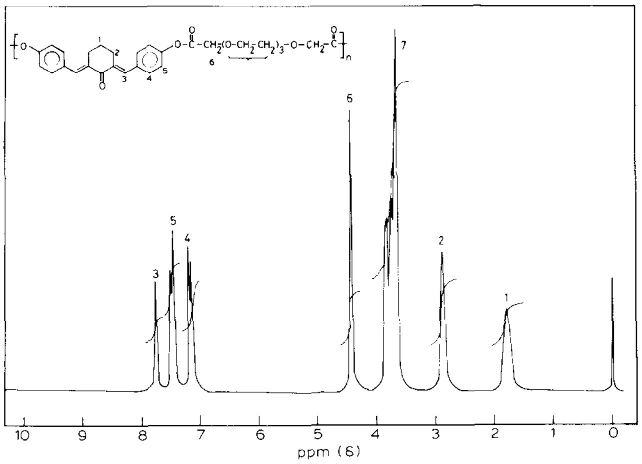


Figure 2 Representative 400 MHz ^{1}H n.m.r. spectrum of PMCLCP-13 in $CDCl_3$

Table 2 Thermal transition temperatures of PMCLCP-*xy* obtained by d.s.c.

Polymer, PMCLCP-*xy*	Transition temperature (°C)				
	T_g	T_1	T_2	T_3	T_i
Solution polycondensation					
PMCLCP-01	–	–	205	248	–
PMCLCP-02	–	135	157	175	198
PMCLCP-03	18	–	–	139	152
PMCLCP-11	50	–	149	182	196
PMCLCP-12	36	106	123	137	148
PMCLCP-13	15	–	–	53	125
PMCLCP-21	43	–	–	111	154
PMCLCP-22	31	–	107	117	132
Interfacial polycondensation					
PMCLCP-11	66	–	184	204	221
PMCLCP-12	26	–	108	125	158
PMCLCP-13	19	–	53	61	126

by the interfacial polymerization method show high intrinsic viscosity, indicating the high molecular weight obtained by this method. The structural characterization of these polymers was done by u.v.-vis., i.r., ^{1}H and ^{13}C n.m.r. spectroscopic techniques. A typical ^{1}H n.m.r. spectrum of PMCLCP-13 is shown in *Figure 2*.

Thermal properties

The liquid-crystalline properties of these polymers were studied by d.s.c. and polarized-light optical microscopy (p.o.m.). The transition temperatures are summarized in *Table 2*. The temperatures T_1, T_2, T_3 and T_i refer to the peak temperatures of successive endotherms observed in the heating scan for the annealed samples. Generally, for the highest transition temperature, there is a single endotherm corresponding to the liquid crystalline to isotropic transition. The transition from crystal to liquid crystal gives rise to one or more endotherms, and the one occurring at the highest temperature was attributed to the crystal to mesophase transition. The p.o.m. studies show no evidence for fluidity below this temperature. The remaining lower-temperature endotherms represent unidentified crystal to crystal transitions.

Figure 3 shows the d.s.c. thermograms for PMCLCP-03. In the first heating scan (curve a) the endotherm appearing at 146°C was assigned to the mesomorphic transition from the crystalline state. The endotherm at 155°C was assigned to the transition to the isotropic state. In the cooling scan (curve b), exotherms at 156 and 130°C were assigned respectively to the transitions from isotropic to mesophase and from mesophase to crystalline states. The second heating scan (curve c) also shows transition endotherms quite similar to the first heating scan, but with smaller enthalpy of transition. Annealing makes the transition peaks appear more distinctly (curve d).

The d.s.c. characteristics of PMCLCP-13 are shown in *Figure 4*. In the first heating scan (curve a) T_g is observed at 14°C, followed by an endotherm at 54°C for melting to anisotropic fluid. The endotherm at 133°C was assigned to the transition from anisotropic to isotropic phase. The broad endotherm centred at 93°C could not be assigned to any known transition since p.o.m. did not show any noticeable change in this temperature range. The cooling scan (curve b) showed only T_g at 14°C, and no clear exotherms were seen either for the isotropic to anisotropic or for the anisotropic to crystalline transitions. However, the p.o.m. observation confirms that the isotropic melt slowly changes over to the nematic phase at 109°C and, on further cooling, the nematic melt freezes into the glassy state with the retention of LC order. The second heating scan (curve c), besides T_g at 17°C, shows a small endotherm at 123°C for the mesophase to isotropic transition. Annealing the sample above T_g reproduces the melting endotherm at 52°C and the broad endotherm centred at 123°C for the isotropization (curve d).

The transition temperatures of the polymers are given in *Table 2*. All of them except PMCLCP-01 and PMCLCP-23

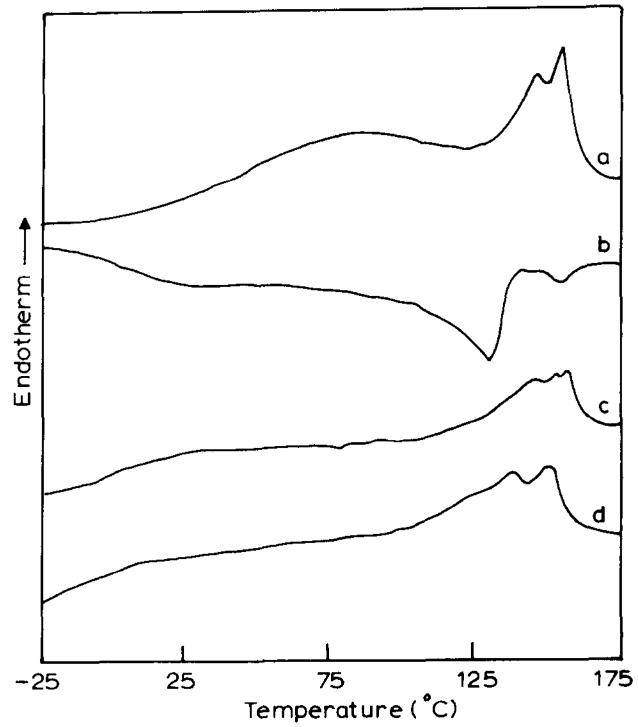


Figure 3 D.s.c. thermograms for PMCLCP-03: (a) first heating scan, (b) first cooling scan, (c) second heating scan and (d) heating scan for the annealed sample (90°C, 12 h)

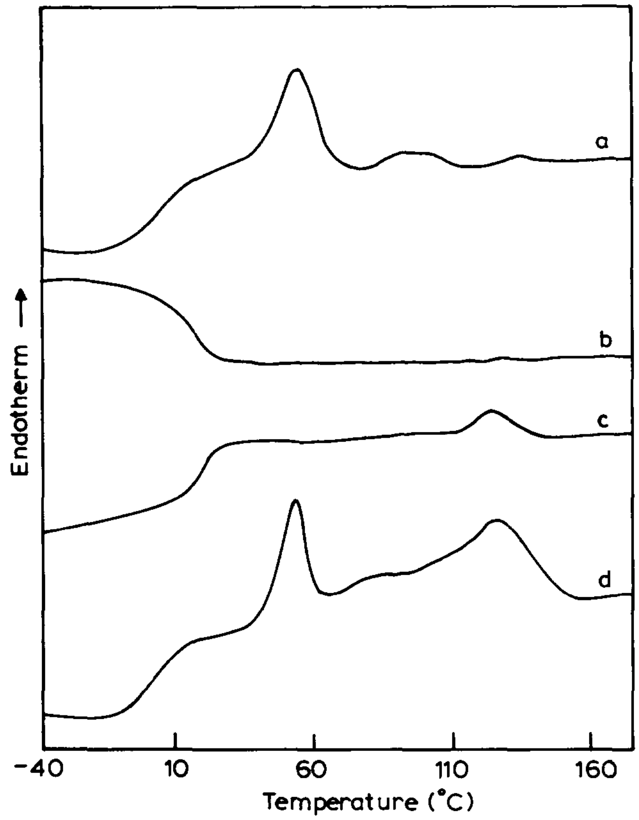


Figure 4 D.s.c. thermograms for PMCLCP-13: (a) first heating scan, (b) first cooling scan, (c) second heating scan and (d) heating scan of the annealed sample (25°C, 24 h)

exhibit liquid-crystalline properties and p.o.m. studies confirm that they show nematic mesophase. PMCLCP-01 undergoes thermal degradation immediately after the melting at 248°C, and hence the identification of LC phase, if any, was rendered difficult. PMCLCP-23 is amorphous and slowly changes over to isotropic liquid, above T_g at -25°C. Most of the polymers exhibit multiple endotherms for melting. Transition temperatures are dependent on the structures of the mesogens (hard segments) and the spacer units (soft segments). Comparing the transition temperatures among the polymers with different mesogenic units and having similar spacer length, the one with bis(benzylidene)cyclopentanone mesogens shows highest transition temperatures followed by the polymer having bis(benzylidene)cyclohexanone units. The polymer possessing bis(benzylidene)cycloheptanone groups shows the lowest transition temperatures. It can then be generalized that the transition temperatures are inversely proportional with the size of the cycloalkanone ring of the bis(benzylidene)cycloalkanone units. A plausible explanation could be that, the smaller the ring size, the more linear and rigid is the hard segment, which leads to closer packing of the chains and hence higher transition temperatures. As the ring size increases, the hard segments start losing their linear rigid structure and become slightly kinked semirod-like in structure, which can reduce the transition temperatures.

The above explanation for the dependence of transition temperature on the anisotropy geometry of the mesogens was supported by the MNDO (modified neglect of differential overlap) calculations on the model mesogens, namely bis(4-acetyloxybenzylidene)cycloalkanones. An attempt was made to achieve a local minimum near all *trans–trans* conformations using the MOPAC package. The Pluto diagrams of fully optimized structures for the three model mesogens are shown in *Figure 5*. The deviation from the linear geometry of the mesogen with cycloalkanone ring size is conspicuously seen. In bis(4-acetyloxybenzylidene)cyclopentanone, the two phenyl and the cyclopentanone rings lie in the same plane and the molecule acquires an overall rod-like geometry. In mesogens having a cyclohexanone ring, the two phenyl rings stretch out of plane with respect to the cyclohexanone rings and show a deviation from the linear geometry. This deviation is greater for the cycloheptanone mesogen.

For polymers with the same mesogenic unit but having different spacer lengths, the transition temperatures decrease with increase in the spacer length. The greater the spacer length, the higher will be the number of ether linkages, which will induce flexibility to the polymer chains, thus bringing down the transition temperatures.

Taking the effect of mesogen and the spacer together, a polymer having rigid mesogen and shorter spacer

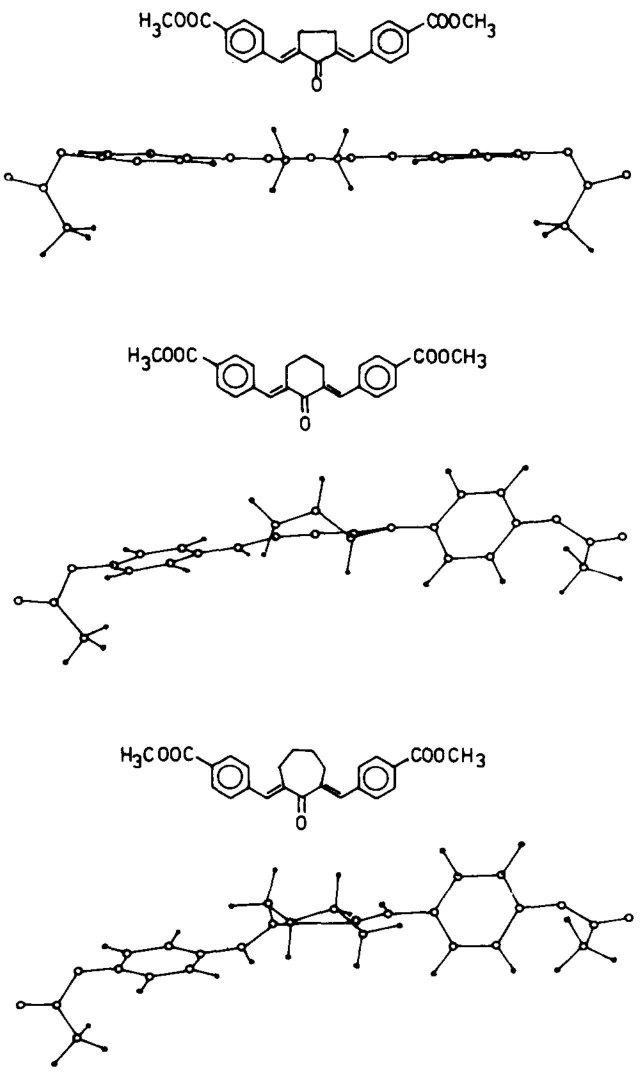


Figure 5 Pluto diagrams of model mesogens bis(4-acetyloxybenzylidene)cycloalkanone

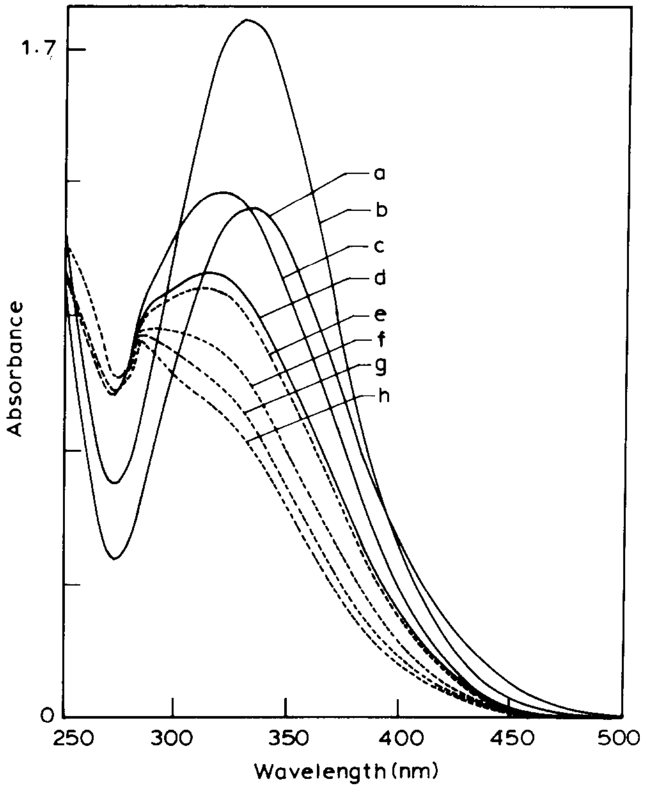


Figure 6 Changes in the u.v. spectral characteristics during the photolysis of PMCLCP-13 films at 40°C for different time intervals: (a) 0 min, (b) 1 min, (c) 3 min, (d) 6 min, (e) 9 min, (f) 15 min, (g) 25 min and (h) 35 min

should show the highest transition temperatures. This is corroborated by the fact that the polymers with cyclopentanone unit and trigolic acid spacer degrades before melting to the mesophase because the transition temperature is much higher. On the other hand, the polymer with bis(benzylidene)cycloheptanone mesogen and the longest spacer, i.e. pentagolic acid, shows low T_g (−25°C) and does not exhibit LC properties. A few of the polymers failed to crystallize during the d.s.c. cooling scan, indicating that these transitions are kinetically controlled and polymers freeze into liquid-crystalline glassy state. Annealing the sample at a temperature between T_g and T_m induces crystallization and was clearly seen as a melting endotherm in the subsequent d.s.c. heating scan. The polymers prepared by the interfacial method showed higher transition temperatures compared to those of polymers prepared by solution polycondensation owing to the high molecular weight of the polymer prepared by the former method.

Photolysis of the polymers

The effect of irradiation on the polymers was studied both as a thin film and in solution and was followed by u.v.-vis. spectroscopic techniques. *Figure 6* shows the change in the u.v. spectral pattern of PMCLCP-13 film for different intervals of photolysis at 40°C. At the initial stage (curve a), the polymer shows an absorption band at 332 nm, which corresponds to $\pi \rightarrow \pi^*$ transition. After 1 min of irradiation there is an increase in the intensity together with a small blue shift of the 332 nm peak (curve b). This increase in intensity reverses on further irradiation and decreases regularly thereafter. After 35 min of irradiation, the peak at 332 nm disappears completely and a new peak emerges at 283 nm (curve h). The polymer film becomes insoluble at this stage of photolysis, indicating crosslinking of the polymer chains. The increase in intensity at the initial stages of photolysis is due to the disruption of the near-parallel orientation of the chromophores[19,26]. This kind of disorder could be introduced by the *trans* to *cis* photoisomerization of the bis(benzylidene)cyclohexanone chromophores present in the polymer backbone[28–30]. The resulting *cis* isomer being non-linear in shape, it loses its mesogenic character and also disturbs the ordered arrangement of the surrounding mesogens. The decrease in the intensity at the latter stages of photolysis was attributed to the crosslinking of the polymer chains[26], which involves the $2\pi + 2\pi$ cycloaddition of the exocyclic double bond of the bis(benzylidene)cyclohexanone mesogens[31–34]. Hence there occur two kinds of photoreactions, namely isomerization of the bis(benzylidene)cycloalkanones and crosslinking of the polymer chains. The former, being of higher quantum yield, predominates over the crosslinking reaction.

Figure 7 shows the plot of relative change in the intensity of the absorption (A_t/A_0) at 332 nm with photolysis time at different temperature for PMCLCP-13 film. Here A_t represents the intensity at 323 nm peak for the photolysis time t and $A_0 = A_t$ when $t = 0$. Films were formed by solution casting and annealed at LC phase at 60°C for 5 min before irradiation at appropriate temperature. Curve a is for the photolysis at 10°C; below T_g, a slow decrease in intensity was observed with time. Between T_g and T_i, first an increase and then a decrease in the intensity was observed (curves c to g). However,

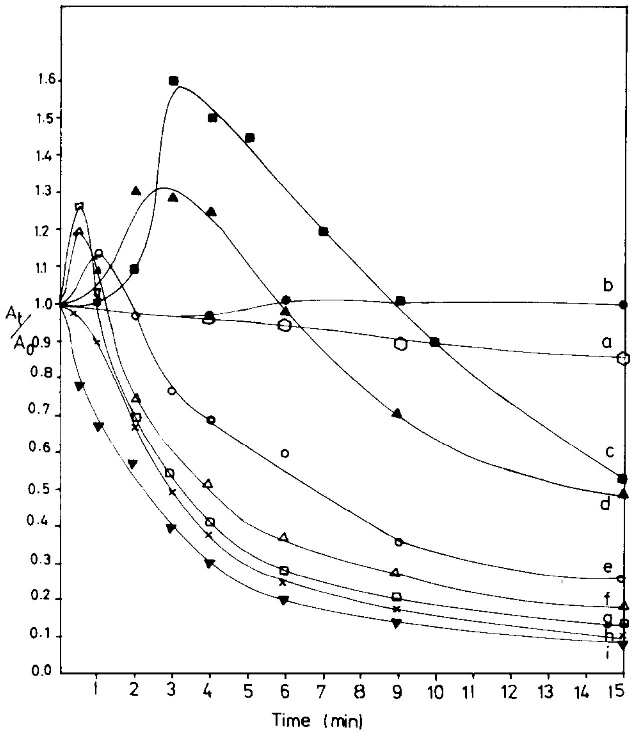


Figure 7 Variation in 332 nm peak intensity with photolysis time at different temperatures: (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 60°C, (f) 80°C, (g) 100°C, (h) 120°C and (i) 140°C

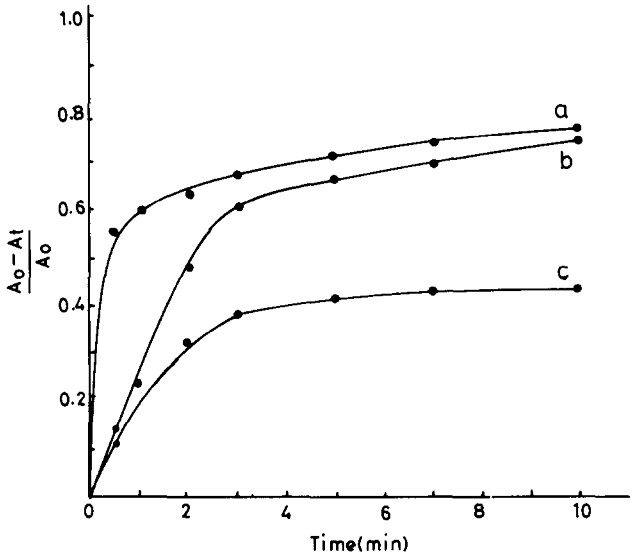


Figure 8 Relative change in the u.v. spectral intensity with photolysis time for (a) PMCLCP-02, (b) PMCLP-12 and (c) PMCLCP-22

when the photolysis was done above T_i, only a decrease in the intensity with photolysis was observed, but the rate of decrease was higher compared to the photolysis carried out below T_g. The intensity changes could be explained in terms of chain mobility and disorder introduced by the photoisomerization on the chromophores. Below T_g, the chains have negligible mobility and hence the polymer matrix will be rigid. Owing to the restriction on the motion of the polymer chains, photoisomerization is rendered difficult and hence photo-crosslinking dominates over photoisomerization. Above T_g, polymer chains gain sufficient mobility, which facilitates the photoisomerization reactions at the initial stages of photolysis. This, in turn, induces the disruption of the parallel stacking of the chromophores, which is reflected as an increase in the intensity. This phenomenon was observed when the irradiation was done between T_g and T_i where the polymer chains possess both order and mobility. When polymer films were irradiated in the isotropic state, although the chains have higher mobility, the chromophores do not have an ordered arrangement. Consequently the photoisomerization reaction will not be reflected as an increase in the intensity of the u.v. spectra.

It would be of interest to compare the photoreactivity of polymers of various mesogenic structures. This was done by comparing the rate of decrease of intensity at the absorption maxima in the u.v. spectra of the polymers. *Figure 8* shows the plot of $(A_0 - A_t)/A_0$ against irradiation time for the polymers PMCLCP-02, PMCLCP-12 and PMCLCP-22, which have different mesogenic structures. It is clear from *Figure 8* that photoreactivity decreases with increase in the ring size of cycloalkanone. The reason for this trend in the photoreactivity may be drawn from the geometry of the model chromophores obtained by MNDO calculations (*Figure 5*). The chromophores with linear structure are likely to favour bimolecular reactions leading to the crosslinking of the polymer chains. On the other hand, chromophores without such a linear geometry may find themselves in an unfavourable alignment for the photo-crosslinking reaction.

CONCLUSION

A set of new photosensitive polymers with liquid-crystalline properties have been synthesized. These polymers contain bis(benzylidene)cycloalkanone moieties in their structures and exhibit a nematic mesophase. Two kinds of photochemical reactions operate in these polymer systems. When the polymer chains are mobile, photoisomerization is followed by a photo-crosslinking reaction. However, the photoisomerization is rendered difficult when the polymer chains are rigid but photo-crosslinking still proceeds. Photoisomerization induces disorder into the chromophoric order in the mesophase, and this phenomenon can suitably be exploited for developing information storage devices[25]. These polymers may be potentially useful in the poling of non-linear optical (n.l.o.) materials. The mesophase-mediated poling promotes the easy orientation of n.l.o. molecules in an electric field[8], and their ability to undergo crosslinking can be utilized to permanently freeze in the oriented n.l.o. molecules after poling[35].

ACKNOWLEDGEMENTS

The authors are grateful to Professor N.V. Madhusudana, Raman Research Institute, Bangalore, for his help in p.o.m. studies. This research was supported by the Department of Science and Technology, New Delhi.

REFERENCES

1 Chaopy, L. L. (Ed.) 'Recent Advances in Liquid Crystalline Polymers', Elsevier Applied Science, London, 1985
2 McArdle, C. B. (Ed.) 'Side Chain Liquid Crystal Polymers', Chapman and Hall, New York, 1989
3 Noel, C. and Navard, P. *Prog. Polym. Sci.* 1991, **16**, 55
4 Ober, C. K., Jin, J.-I. and Lenz, R. W. *Adv. Polym. Sci.* 1984, **59**, 103
5 Hani, R. and Lenz, R. W. 'Silicon Based Polymer Science, A Comprehensive Resource', American Chemical Society, Washington, DC, *Adv. Chem. Ser.* 1990, **224**, 741
6 Ikeda, T., Itakura, H., Lee, C., Winnik, F. M. and Tazuke, S. *Macromolecules* 1988, **21**, 3537
7 Keller, P. *Chem. Mater.* 1990, **2**, 3
8 Ulrich, D. R. *Mol. Cryst. Liq. Cryst.* 1990, **189**, 3
9 Griffin, A. C., Hoyle, C. E., Gross, J. R. D., Venkataram, K., Creed, D. and McArdle, C. B. *Makromol. Chem.* 1988, **9**, 463
10 Tillman, N., Ulman, A., Shildkraut, J. S. and Penner, T. L. *J. Am. Chem. Soc.* 1988, **110**, 6136
11 Walda, D., Keller, P., Parmar, D. S. and Wand, M. D. *J. Am. Chem. Soc.* 1989, **111**, 8273
12 Koch, T., Ritter, H. and Buchholz, N. *Makromol. Chem.* 1989, **190**, 1369
13 Loth, H. and Euschem, A. *Makromol. Chem., Rapid Commun.* 1988, **9**, 35
14 Creed, D., Griffin, A. C., Hoyle, C. H. and Venkataram, K. *J. Am. Chem. Soc.* 1990, **112**, 4049
15 Noonan, J. M. and Caccamo, A. F. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1984, **30**, 501
16 Krigbaum, W. R., Ishikawa, T., Watanabe, J., Toriumi, H. and Kubota, K. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 1851
17 Peter, K. and Ratzsch, M. *Makromol. Chem.* 1990, **191**, 1021
18 Whitcombe, M. J., Gilbert. A. and Mitchell, G. R. *J. Polym. Sci., Polym. Chem. Edn.* 1992, **30**, 1681
19 Creed, D., Griffin, A. C., Gross, J. R. D., Hoyle, C. E. and Venkataram, K. *Mol. Cryst. Liq. Cryst.* 1988, **155**, 57
20 Ikeda, T., Itakura, H., Lee, C., Winnik, F. M. and Tazuke, S. *Macromolecules* 1988, **21**, 3537

21 Keller, P. *Chem. Mater.* 1990, **2**, 3

22 Whitcombe, M. J., Gilbert, A., Hirai, A. and Mitchell, G. R. *J. Polym. Sci., Polym. Chem. Edn.* 1991, **29**, 251

23 Whitcombe, M. J., Gilbert, A. and Mitchell, G. R. *Br. Polym. J.* 1990, **23**, 77

24 Griffin, A. C., Hoyle, C. E., Gross, J. R. D., Venkataram, K., Creed, D. and McArdle, C. B. *Makromol. Chem.* 1988, **9**, 463

25 Legge, C. H., Whitcombe, M. J., Gilbert, A. and Mitchell, G. R. *J. Mater. Chem.* 1991, **1**, 303

26 Gangadhara and Kishore, K. *Macromolecules* 1993, **26**, 2995

27 Borden, D. G. *J. Appl. Polym. Sci.* 1978, **22**, 239

28 George, H. and Roth, H. T. *Tetrahedron Lett.* 1971, **43**, 4057

29 Wargnier, F. B., Feigenbaum, A. and Muzart, J. *J. Chem. Educ.* 1978, **55**, 339

30 Aizeshtat, Z., Hausmann, M., Pickholtz, Y., Tal, D. and Blum, J. *J. Org. Chem.* 1977, **42**, 2386

31 Forward, G. C. and Whiting, D. A. *J. Chem. Soc.* (*C*) 1969, 1868

32 Frey, H., Behmann, G. and Kaupp, G. *Chem. Ber.* 1987, **120**, 387

33 Kaupp, G. and Zimmermann, I. *Angew. Chem., Int. Edn. Engl.* 1981, **20**, 1018

34 Theocharis, C. R., Jones, W., Thomas, M. J., Molevalli, M. and Hursthouse, B. M. *J. Chem. Soc., Perkin. Trans. II* 1984, 71

35 Chen, M., Yu, L. and Dalton, L. R. *Macromolecules* 1991, **24**, 5421