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Novel atropoisomeric binaphthyl-containing liquid crystalline copolymers forming chiral nematic phases

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Novel liquid crystalline (LC) acrylate side group copolymers, which consist of nematogenic phenyl 4-methoxybenzoate acrylate monomer (**A**) and novel chiral binaphthyl (**BN**) methacrylate monomers (**MB**-n) have been synthesized. The copolymers prepared differ in the spacer lengths of **MB**-n ($n=3,5,11$) and in their compositions. The homopolymers of the three new chiral binaphthyl monomers **MB**-n were also prepared. Copolymers with a low concentration of binaphthyl monomer units (less than 16 mol %) display a cholesteric mesophase. The induced chirality in the polymers is due to atropoisomerism (C_2-symmetry) of the molecules. The helical twisting powers (β), caused by the atropoisomeric units in the synthesized copolymers, were determined, and their temperature dependencies studied. The unusually high negative temperature coefficient of β observed above the glass transition temperature is explained in terms of conformational changes of the **BN** molecules in the copolymers.

1. Introduction

Cholesteric side group (comb-shaped) polymers were synthesized for the first time about twenty years ago [1–6]. Since then they have attracted great attention due to their helical supramolecular structure. This unusual structure determines a number of unique optical properties, such as selective reflection of light in different wavelength ranges, high optical rotatory power, circular dichroism, etc. [7, 8]. All these remarkable optical properties of cholesteric polymers are displayed only with a definite orientation of the helix axis—when the mesogenic groups are arranged in the direction parallel to the film surface and the helix axis is normal to the latter (the so-called planar texture).

However, the synthesis of chiral polymers by means of homopolymerization of chiral monomers leads very often to liquid crystalline (LC) polymers which do not form only a cholesteric mesophase, but a smectic phase as well. In this case, in spite of the planar cholesteric texture formed at elevated temperatures (in the cholesteric mesophase), this texture is not preserved on cooling

and is transformed into the confocal smectic texture which strongly scatters light. As a result, all the unique and important optical properties caused by the planar cholesteric texture partially disappear in these polymeric films. They are therefore not of particular interest for practical applications. Here we do not consider the chiral tilted smectic C* phases which provide a basis for the creation of ferroelectrics.

Copolymerization of the chiral monomers referred to above with nematogenic monomers hinders the formation of a smectic phase and gives the opportunity to keep the planar texture inherent to cholesteric mesophases in the solid state. Thus polymeric films with desirable optical properties can be obtained. Chiral monomers, which form amorphous polymers are most likely to offer the best possibilities for the synthesis of chiral copolymers, which exhibit the cholesteric mesophase without any indications of layered packing (of the smectic type) of the mesogenic groups in the copolymers.

Only a limited number of chiral monomers such as cholesteryl acrylate, cholesteryl methacrylate and some menthyl derivatives which form amorphous homopolymers have so far been synthesized and studied in

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this context. In all these compounds chirality results from asymmetric carbon atoms located in the chiral fragments.

Another source of chirality originates from hindered rotation about single bonds leading to two conformationally stable optical antipodes (atropoisomers). Chirality based on atropoisomerism, which is due to hindered rotation about single bonds leading to two conformationally stable optical antipodes, has already been used in the area of low molecular mass liquid crystals [9, 10]. Whereas chiral monomers with asymmetric carbon atoms have been widely used and their chiral copolymers have been well studied [6–8], chiral monomers based on atropoisomerism have not yet been used in order to obtain chiral copolymers.

We therefore focus on the use of this type of chirality using binaphthyl derivatives **MB**-*n* (figure 1).

These molecules consist of two β-naphthyl moieties connected at the 1,1′-positions with restricted rotation about the C_1–C_1 bond connecting the two aromatic systems. This leads to two optical antipodes, which can exist in different *cisoid* and *transoid* states defined by the dihedral (torsional) angle between the two naphthyl moieties [10, 11]. An angle $\theta > 90°$ corresponds to *transoid* conformations and an angle $\theta < 90°$ to *cisoid* conformations. It is well-known that 2,2′-disubstituted-1,1′-binaphthyl derivatives have been widely used in organic synthesis in order to induce chirality [12]. Also, a number of different chiral binaphthyl (**BN**) derivatives were recently successfully used as effective chiral dopants for low molecular mass liquid crystals giving chiral nematic phases [10, 13].

Because of high helical twisting powers (HTP) or β values found in refs. [10, 13], it was an obvious extension to use the special expression of chirality in the **BN** system for the synthesis of chiral monomers followed by copolymerization with nematogenic monomer (**A**). Accordingly three new methacrylate monomers **MB**-*n* were synthesized, in which the methacrylate groups are connected via flexible spacers of three different lengths (*n* = 3, 5, 11) to the **BN** moieties (see the scheme). They
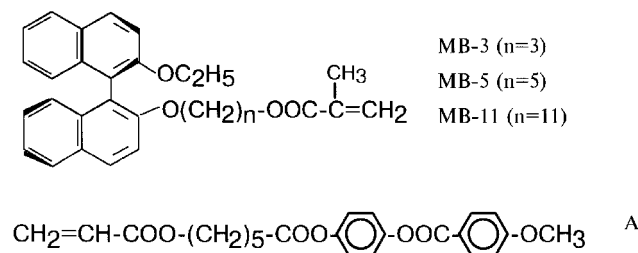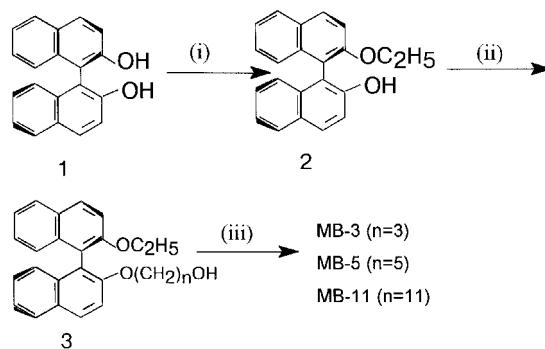

Figure 1. The formulae of the atropoisomeric chiral methacrylate binaphthyl monomers **MB**-*n* with different aliphatic chain lengths (*n* = 3, 5, 11) and the mesogenic acrylate monomer **A**.

Scheme. Synthetic pathway for the synthesis of the monomers **MB**-*n* (*n* = 3, 5, 11). (i) EtBr, K_2CO_3, acetone, reflux. (ii) $Br(CH_2)_nOH$, K_2CO_3, acetone, reflux. (iii) methacryloyl chloride, Et_3N, diethyl ether, reflux.

were homopolymerized and copolymerized with the nematogenic monomer **A**.

The thermal and optical properties of the chiral copolymers of different compositions and the results from the systematic study of phase behaviour and optical properties of the synthesized copolymers depending on the concentration of the chiral **BN** units and spacer lengths will be discussed first. Secondly, the determination of the helical twisting powers (β) of the **BN** fragments, followed by an evaluation of the influence of binaphthyl conformations on the optical properties of the copolymers will be presented.

2. Experimental
2.1. Synthesis of monomers MB-3, MB-5, MB-11 and their precursors

The general synthetic pathway to the three synthesized **BN** monomers **MB**-*n* is illustrated in the scheme. Optically pure (S)-2,2′dihydroxy-1, 1′-binaphthyl **1** (**BN**) was prepared according to a known procedure [14]. The optical purity of the starting material was verified by its specific rotation ($\alpha D^{22} = -34.0$; THF) prior to use in the subsequent steps.

The (S)-2-ethoxy-2′-hydroxy-1,1′-binaphthyl **2** was synthesized by alkylation of **1** with ethyl bromide in boiling acetone (3–4 days) using potassium carbonate as a base together with a catalytic amount of sodium iodide. The reaction procedure could be monitored by TLC (Merck Kieselgel 60 F_{254}, $d = 0.2$ mm) using methylene chloride as eluent. The reaction mixture was poured into water and extracted with diethyl ether. The combined organic phases were washed with sodium hydroxide solution in order to remove most of the unreacted starting material. After evaporation of the solvent, the remaining mixture of unreacted **1**, mono- and dialkylated product was purified by crystallization from ethanol, where by most of the dialkylated product could be removed. Subsequent column chromatography (Merck

Kieselgel 0·063–0·200 mm, 70–230 mesh ASTM) using a methylene chloride/hexane gradient for elution gave pure **2** ($\alpha D^{25} = +36$; CHCl$_3$).

The (S)-ω-(2-ethoxy-1,1′-binaphthyl-2′-yl)oxyalkanols **3** ($n = 3,5,11$) were prepared by alkylation of **2** with the corresponding ω-bromoalkanols using similar conditions to those described for the preparation of **2**. The compounds were purified by column chromatography on silica gel with methylene chloride/ethyl acetate (0–100%) gradient elution ($n = 3$, $\alpha D^{25} = -36$; CHCl$_3$), ($n = 5$, $\alpha D^{25} = -68$; CHCl$_3$), ($n = 11$, $\alpha D^{25} = -55$; CHCl$_3$).

The (S)-ω-(2-ethoxy-1,1′-binaphthyl-2′-yl)oxyalkyl 2-methylacrylates (**MB-**n) were obtained by esterification of the corresponding **BN** alkanoles **3** with methacryloyl chloride in the presence of triethylamine (usually three days in boiling diethyl ether). After usual work up, the monomers were purified by column chromatography on silica gel (methylene chloride). ($n = 3$, $\alpha D^{25} = -54$; CHCl$_3$), ($n = 5$, $\alpha D^{25} = -51$; CHCl$_3$), ($n = 11$, $\alpha D^{25} = -45$; CHCl$_3$).

Full details of the synthesis of the monomers **MB-**n and their precursors are described in ref. [15].

2.2. *Characterization of the monomers MB-n and their precursors*

All the newly synthesized chiral monomers and their precursors were characterized by ^{1}H NMR (Bruker AM-250 MHz) using solutions in CDCl$_3$ (tetramethylsilane as internal standard), and by mass spectrometry (EI/Jeol JMS-HX/HX110A Tandem Mass Spectrometer). It has been shown earlier that racemization does not occur on submitting such materials to similar reaction conditions, and the enantiomeric purity of all compounds is therefore assumed to be >99% [15]. This is consistent with the high values of the optical rotations measured on a Perkin-Elmer 141 polarimeter.

2.3. *Preparation of the polymers*

The homopolymers of the chiral binaphthyl-containing methacrylates **MB-**n, as well as the copolymers with nematogenic monomer **A**, were obtained by radical polymerization in toluene using 1 mol % of α,α'-azobisisobutyronitrile as initiator at 65°C. The polymers were precipitated several times from TGF solutions with methanol. The compositions of the copolymers are assumed to be equal to those of the monomer mixtures before polymerization, due to the comparable chemical structures of the monomers **A** and **MB-**n. The molecular masses of the copolymers were evaluated from viscometric data obtained using toluene solutions and an Ubbelohde viscometer at 25°C. The intrinsic viscosities of the copolymers varied in the range of 0·25–0·30, corresponding to the M_w range $(10–20) \times 10^4$.

2.4. *Optical microscopy*

A Polam P-221 polarizing microscope equipped with a Mettler FP-86 heating stage was used to study mesophase textures and to determine the phase transition temperatures of the compounds synthesized.

2.5. *Differential scanning calorimetry*

The phase transition temperatures and heats of phase transitions were measured with a Mettler FP-4000 Thermosystem differential scanning calorimeter. The scan rate was varied in the range of 5–10 K min^{-1}. The phase transition temperatures were taken at the endothermic maxima of the heating curves at a scan rate of 10 K min^{-1}. Glass transition temperatures were taken from the points of inflexion.

2.6. *X-ray diffraction*

X-ray diffraction measurements were performed using CuK$_\alpha$-radiation with a 'URS-55' instrument equipped with a flat film cassette for recording X-ray diffraction patterns.

3. Results and discussion

All homopolymers obtained by polymerization of the binaphthyl-containing monomers **MB-**n are glassy amorphous compounds. The glass transition temperatures of the homopolymers decrease with increasing spacer length corresponding to 90, 68 and 38°C, respectively. These results are in accordance with the well-known relationship between the glass transition temperature and length of the spacer: an increase in the length of the aliphatic spacer enhances its plasticizing effect on the polymer, leading to a decrease in the glass transition temperature [5,8]. The homopolymer of **A**, on the other hand, is characterized by a wide temperature interval of LC phase formation in the range from the glass transition temperature ($T_g = 25$°C) to the clearing temperature ($T_{cl} = 120$°C) [16].

First of all, let us consider the thermal properties and the phase behaviour of the copolymers **MB-**n-**A** obtained by copolymerization of the corresponding **BN**-containing monomers **MB-**n with the nematogenic monomer **A**. The phase transition temperatures and the maximum wavelengths of selective reflection of light, λ_{max}, for different copolymer compositions for all three **BN**-containing polymers of different spacer length are shown in the table.

All the copolymers synthesized form a chiral LC-phase, provided that the concentration of **BN**-containing monomeric units does not exceed 12 mol %. Above this concentration of **MB-**n units, the copolymers become amorphous. The X-ray diffraction patterns for all copolymers show only one broad diffuse halo at angles corresponding to 4·6–4·8 Å, which is characteristic

Table. Phase transition temperatures and maximum wavelengths of selective reflection of light λ_{max} (at 22°C) for the copolymers **MB-*n*-A** of different composition.

Copolymer **MB-*n*-A**	Chiral monomer content/mol %	T_g/°C	T_{cl}/°C	λ_{max} at 22°C/nm
		n = 3		
1	8	35	100	2300
2	12	37	84	—
3	16	39	—	—
		n = 5		
4	6	33	104	1500
5	8	36	95	1320
6	10	35	91	1150
7	12	34	68	—
8	16	37	—	—
		n = 11		
9	6	30	99	1870
10	8	29	90	1420
11	12	31	75	—
12	16	29	—	—

for a nematic structure. Polarization-microscopic studies of the three series of copolymers of different composition, containing less than 12 mol % of **BN** monomer units, show that they all display a confocal texture which is easily transformed into a planar texture on mechanically shifting the glass plates with respect to each other. This texture selectively reflects light in the IR range (see the table), a fact which supports the occurrence of a chiral nematic N* phase formation.

Knowing the phases formed and the transition temperatures, the phase diagrams of the three copolymers (figure 2) may be drawn.

As can be seen from the phase diagram, increase in the **BN**-containing monomer units in the copolymers leads only to a minor rise in the glass transition
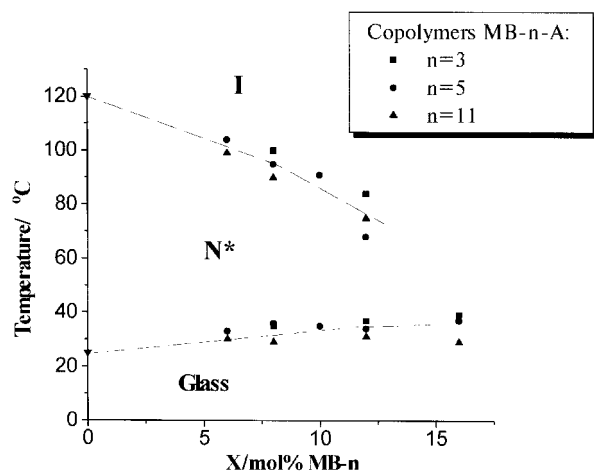
temperatures, whereas the clearing temperatures drastically decrease. This decrease is practically independent of spacer length of the **BN**-containing units.

Second, the optical properties of the copolymers **MB-*n*-A** will be discussed. The optical properties of chiral polymers are described by the wavelength of selective reflection of light, λ_{max}, which is related to the pitch of the cholesteric helix P by equation (1),

$$\lambda_{max} = nP \qquad (1)$$

where n is the average refractive index of the chiral phase. Equation (1) is only valid for normal incidence of light for a planar cholesteric texture. Another feature of chiral compounds as guests in a liquid crystalline host is the helical twisting power β of the chiral monomeric unit [10, 11]. The relation between β, the induced cholesteric pitch P, and the concentration of the chiral monomeric units x (mol fraction of chiral monomeric units **MB-*n***) is given in equation (2).

$$\beta = 1/Px, \qquad (2)$$

Inserting equation (1) into (2) leads to (3) assuming n to be constant:

$$\beta = nd\lambda_{max}^{-1}/dx, \qquad (3)$$

Thus the helical twisting power β is determined by the slope of the dependence of λ_{max}^{-1} on x.

Figure 3 shows this dependence of λ_{max}^{-1} on the molar fraction of **BN**-containing monomeric units for all three copolymers at the same reduced temperature. It can be seen that the two copolymers **MB-5-A** and **MB-11-A** show practically the same dependence of λ_{max}^{-1} on the concentration of the chiral monomeric units. The single
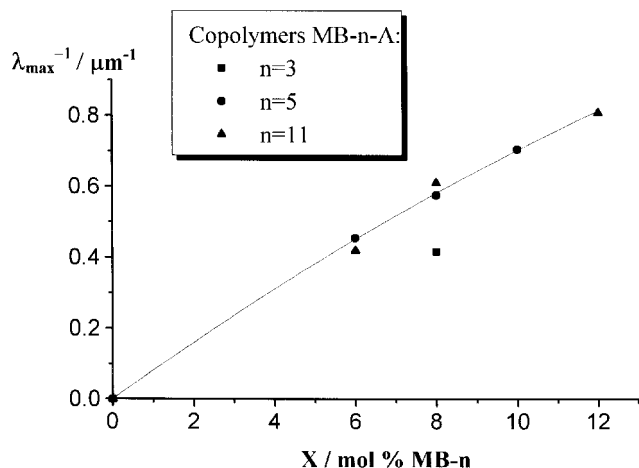

Figure 2. Phase diagrams for the three copolymers **MB-*n*-A** (*n* = 3,5,11) as a function of composition.

Figure 3. Dependence of λ_{max}^{-1} on the molar fraction of **BN**-containing monomeric units for the three copolymers (**MB**-*n*-**A**, *n* = 3, 5, 11) at the same reduced temperature.

Figure 4. Temperature dependence of λ_{max} for copolymers **MB**-*n*-**A** (*n* = 5) of different compositions.

Figure 5. Temperature dependence of λ_{max} for copolymers **MB**-*n*-**A** (*n* = 11) of different compositions.

point obtained for copolymer **MB**-3-**A** does not fit and obey this tendency. The different behaviour of **MB**-3-**A** could be attributed to the short spacer length. This results in a greater steric hindrance imposed by the **BN** units on the LC packing of the mesogenic groups. The calculated helical twisting power of all the **BN** units in the copolymers is about $\beta = 10$–$12\,\mu m^{-1}$. This value is slightly higher in comparison with the values for cholesteryl-containing copolymers described in [7]. However, in the case of **BN**-containing copolymers, the disturbance of mesophase order begins at a lower concentration (16 mol %), whereas the cholesteryl containing copolymers preserve the chiral mesophase up to a concentration of 25 mol % of cholesteryl moieties.

Thus the incorporation of chiral atropoisomeric **BN**-containing substituents in a nematic polymer matrix leads to formation of a chiral twisted nematic (cholesteric) phase in the same way as has been shown before for cholesteryl containing copolymers (where the chirality is due to asymmetric carbon atoms in the side groups) [7, 16]. Furthermore, the magnitudes of β of **BN**-containing units are slightly higher, but comparable with the helical twisting power of cholesteryl derivatives. These results suggest that the geometrical shape of the binaphthyl group in the side chain is the decisive factor responsible for the helical twisting power.

However, there is a crucial difference between the behaviour of cholesteryl based chiral units and atropoisomeric **BN**-based chiral units in polymers: this is the temperature dependence of λ_{max} and β.

Figures 4 and 5 show the temperature dependencies of these important parameters for copolymers with different spacer lengths of the **BN**-containing monomeric units.

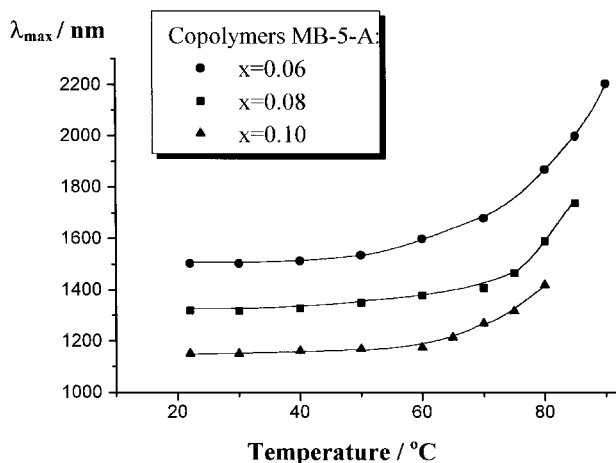Both copolymers (**MB**-5-**A** and **MB**-11-**A**) are characterized by similar curves $\lambda_{max} = f(T)$: the values of λ_{max} are practically unchanged in the temperature range from 20°C to 60–65°C, but a further increase in the temperature leads to a pronounced increase of λ_{max} that results in untwisting of the cholesteric helix. This behaviour is different from the majority of cholesteryl containing polymers, where λ_{max} does not significantly rise with increasing temperature [7]. Untwisting of the cholesteric helix is often observed at temperatures near to the region of a cholesteric–smectic transition, i.e. on the appearance of the nuclei of the layered structure preceding smectic phase formation. Here, all **BN**-containing copolymers show the opposite behaviour, and untwisting of the helix is observed when the temperature increases.
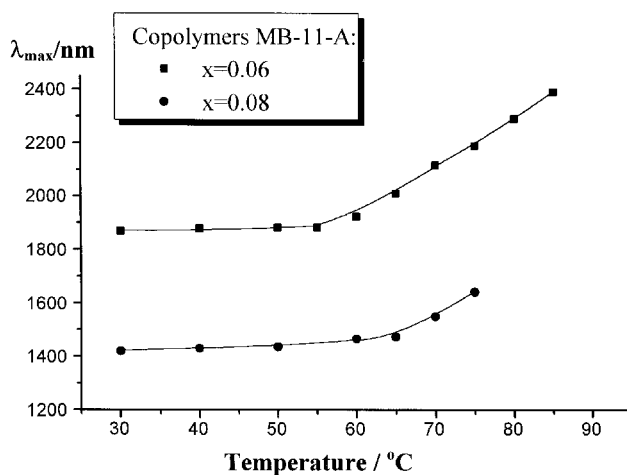
Furthermore, the values $(1/\lambda_{max})\,(d\lambda_{max}/dT)$ of the investigated copolymers lie in the region of 0·012–0·016

(depending on copolymer composition); this exceeds by three–four times the same value theoretically predicted for mixtures of low molecular mass nematics and chiral non-mesomorphic dopants [17]. Temperature dependencies of λ_{max} (i.e. positive sign of $d\lambda_{max}/dT$) have been observed before for two cholesteryl containing copolymers [18]. However, in this case the values of $(1/\lambda_{max})$ $(d\lambda_{max}/dT)$ did not exceed 0·001–0·002.

Figure 6 shows the temperature dependence of the helical twisting power β for two chiral copolymers both based on one and the same nematogenic acrylate monomer **A**. The first copolymer contains the atropoisomeric units of binaphthyl and the second one contains chiral menthyl groups located in the side groups:
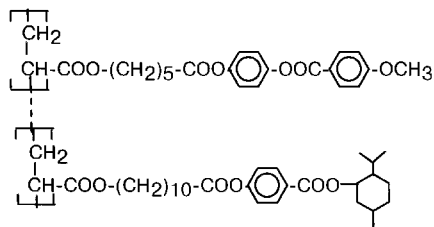
As can be seen from figure 6 the menthyl containing copolymer shows only a slight decrease of β on heating up to $T/T_{cl}=0\cdot925$; β then becomes larger on approaching the clearing temperature. It can be seen for the **BN**-containing copolymer, in comparison, that β decreases more significantly with increasing temperature even at low ratios of T/T_{cl}. This is in full accordance with recently obtained results [13], where similar changes of β were observed for a variety of mixtures of low molecular mass **BN** derivatives as chiral dopants. The temperature dependences of β there were explained by conformational changes of the **BN** molecules on heating. The closer the dihedral angle between the
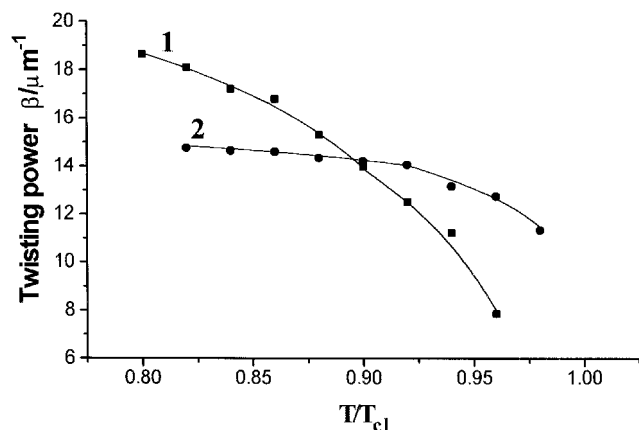
naphthyl moieties is to 90°, the smaller is the helical twisting power [13]. Therefore in the chiral polymers now synthesized, the two naphthyl moieties should have a tendency to orient more perpendicularly with respect to each other within a **BN** molecule on heating. This leads, in accordance with the earlier results [13], to a very significant decrease in the helical twisting power β on heating the copolymers.

4. Conclusion

Three different, novel liquid crystalline acrylate copolymers **MB**-*n*-**A** ($n=3,5,11$) of different compositions were prepared. They all consist of the known nematogenic phenyl 4-methoxybenzoate acrylate monomer (**A**) together with novel chiral binaphthyl (**BN**) methacrylate monomers (**MB**-*n*) with three different spacer lengths. The homopolymers of the corresponding **BN** monomers show decreasing glass transition temperatures with increasing spacer length. The copolymers with a low concentration of **BN** monomeric units (less than 16 mol %) display a cholesteric mesophase. The induced chirality in the polymers is due to atropoisomerism (C_2-symmetry) of the **BN** molecules. This is, to the best of our knowledge, the first example of the use of atropoisomerism in order to induce chirality in copolymers. The helical twisting power β, caused by the atropoisomeric units in the synthesized copolymers, was shown to decrease significantly on heating. As a result, the maximum wavelength of selective reflection of light decreases on heating. These unusual properties of chiral copolymers above the glass transition temperature were explained in terms of conformational changes of the **BN** molecules in the copolymers in accordance with earlier results for mixtures of low molecular mass liquid crystals with low molecular mass **BN** derivatives used as chiral dopants.

Figure 6. Temperature dependence of the helical twisting power β for the copolymer **MB**-5-**A** (1) and the menthyl containing copolymer (2) as a function of reduced temperature.

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