

Novel Atropisomeric Binaphthol Containing Comb-Shaped Copolymers Forming Chiral Nematic Phases

V. P. SHIBAEV,¹ H. J. DEUSSEN,² A. YU. BOBROVSKY,¹
P. V. SHIBAEV,³ N. I. BOIKO,¹ T. BJØRNHOLM,² K. SCHAUMBURG,²
and K. BECHGAARD⁴

*Chemistry¹ and Physics³ Departments
Moscow State University
119899 Moscow, Russia*

*²Centre for Interdisciplinary Studies of Molecular Interactions
Department of Chemistry, University of Copenhagen
DK-2100 Copenhagen Ø, Denmark*

*⁴Department of Solid State Physics
Risø National Laboratory
DK-4000 Roskilde, Denmark*

Novel comb-shaped liquid crystalline acrylic copolymers consisting of nematogenic methoxy-phenylbenzoate acrylic monomers (A) together with novel chiral binaphthol (BN) methacrylic monomers (MB-*m*) were synthesized in this study. The prepared copolymers differ in spacer lengths of MB-*m* (*m* = 3, 5, 11) and in their compositions. The homopolymers of the three new chiral BN monomers MB-*m* were also prepared. 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 atropisomerism (chirality due to hindered rotation around single bonds) of the BN molecules. The helical twisting power β (HTP) caused by the atropisomeric units in the synthesized copolymers was shown to decrease significantly on heating. The unusually high negative temperature coefficient of HTP observed above the glass transition temperature (T_g) could be explained in terms of conformational changes of the BN molecules in the copolymers.

INTRODUCTION

Cholesteric side chain (comb-shaped) polymers were synthesized for the first time about twenty years ago (1–6). Since then they have attracted 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 at 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 (so-called planar texture).

However, the synthesis of chiral polymers by means of homopolymerization of chiral monomers often leads to liquid crystalline polymers that not only form a cholesteric mesophase, but also a smectic one. In this case, regardless of the planar cholesteric texture formation at elevated temperature (in the cholesteric me-

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

Only a limited number of chiral monomers such as cholesteryl acrylate, cholesteryl methacrylate and some menthyl derivatives which create amorphous homopolymers have so far been synthesized and studied in this context (7). In all these compounds chirality results from asymmetric carbon atoms located in the chiral fragments. Whereas chiral monomers with asymmetric carbon atoms have been widely used and their chiral copolymers have been studied (6–8), chiral monomers based on atropisomerism (chirality originating from hindered rotation about single bonds which leads to two conformationally stable optical antipodes) have not yet been used in order to obtain chiral copolymers. However, atropisomerism has already been used in the area of low-molar-mass liquid crystals (LCs) (9, 10) in order to obtain cholesteric phases.

We therefore focused on the use of this type of chirality using binaphthol (BN) derivatives MB-*m* (Fig. 1). These molecules consist of two β -naphthol moieties connected in the 1,1'-positions with restricted rotation about the C₁-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 naphthol moieties (10, 11). An angle of $\theta > 90^\circ$ corresponds to transoid conformations and an angle of $\theta < 90^\circ$ 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). A number of different chiral BN derivatives were recently successfully used as effective chiral dopants for low-molar-mass LCs giving chiral nematic phases (9, 13, 14).

Because of the high twisting powers found in earlier studies (9, 13, 14), 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 monomers (A). Accordingly three new methacrylic monomers were synthe-

sized, in which the methacryl groups are connected via a flexible spacer of three different lengths ($m = 3, 5, 11$) to the BN moieties (Fig. 1). They were homopolymerized to give the homopolymers MB-*m* and copolymerized with the nematogenic monomer A to different copolymers MB-*m*-A.

The thermal and optical properties of the chiral copolymers MB-*m*-A of different compositions will be addressed as follows: the systematic study of phase behaviour and optical properties of synthesized copolymers MB-*m*-A depending on the concentration of the chiral BN units and different spacer lengths will be discussed; and the temperature dependence of the optical properties will be discussed by evaluation of the influence of possible BN conformations in the prepared copolymers.

EXPERIMENTAL

Synthesis of Monomers MB-3, MB-5, MB-11 and Their Precursors

The general synthetic pathway of the three synthesized BN-monomers MB-*m* is illustrated in Fig. 2. Optically pure (S)-1,1'-bi-2-naphthol (BN) **1** was prepared according to a known procedure (15). The optical purity of the starting material was verified by its specific rotation ($\alpha_D^{22} = -34.0^\circ$; $c = 1$, 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 catalytical amount of sodium iodide. The reaction procedure could be monitored by thin-layer chromatography (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 diethylether. The combined organic phases were washed with sodium hydroxide solution in order to remove most of the unreacted starting material. The remaining mixture of unreacted **1**,

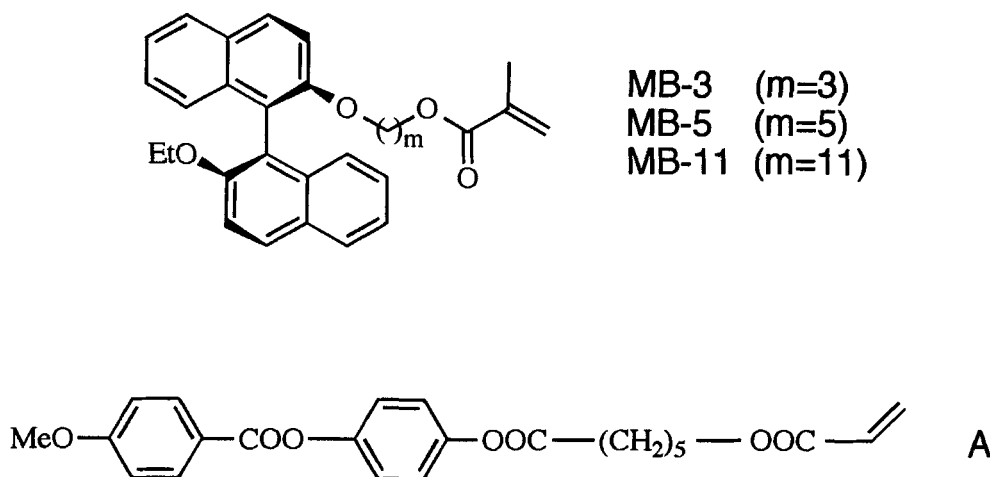


Fig. 1. The atropisomeric chiral methacrylic binaphthol (BN) monomers MB-*m* with different chain lengths ($m = 3, 5, 11$) and the mesogenic acrylic monomer A.

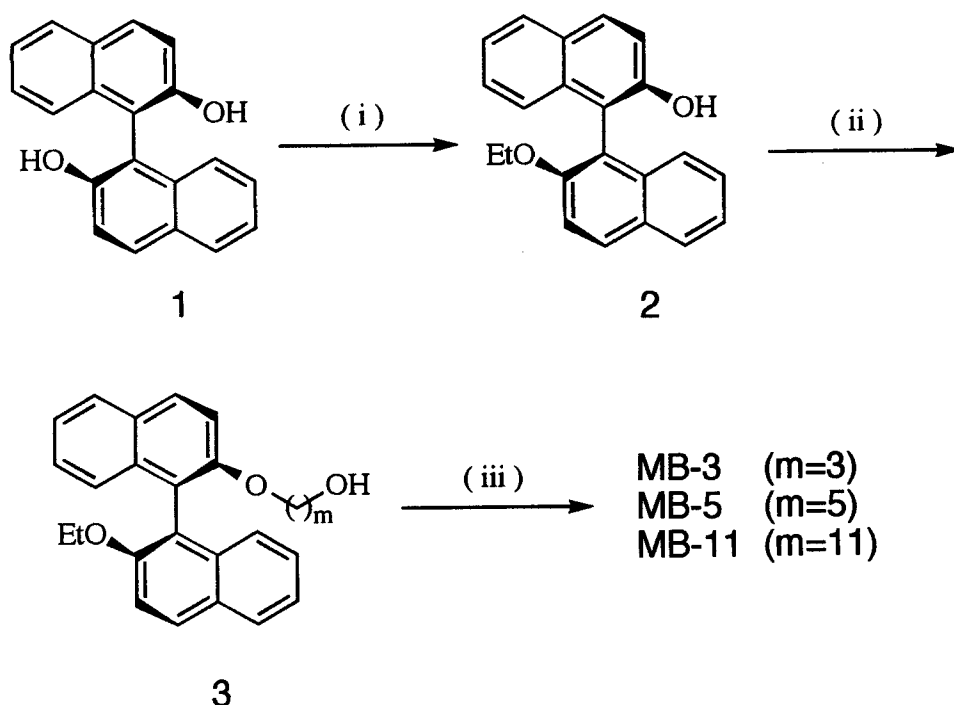


Fig. 2. Synthetic pathway for the synthesis of the binaphthol monomers (BN) MB-m ($m = 3, 5, 11$). (i) EtBr, K₂CO₃, acetone, reflux. (ii) Br(CH₂)_mOH, K₂CO₃, acetone, reflux. (iii) methacryloyl chloride, Et₃N, diethylether, reflux.

mono- and dialkylated product was purified by crystallization from ethanol after evaporation of the solvent, where most of the dialkylated product could be removed. Subsequent column chromatography (Merck Kieselgel 0.063–0.200 mm, 70–230 mesh ASTM) using a methylenechloride/n-hexane gradient gave pure **2** ($\alpha_D^{25} = +36^\circ$; $c = 0.1$, CHCl₃).

The (S)- ω -(2-ethoxy-1,1'-binaphthyl-2'-yl)oxyalkanols **3** ($m = 3, 5, 11$) were prepared by alkylation of **2** with the corresponding ω -bromoalkanols using similar conditions as described for the preparation of **2**. The compounds were purified by column chromatography on silica with a methylene chloride/ethyl acetate (0–100%) gradient ($m = 3$, $\alpha_D^{25} = -36^\circ$; $c = 0.2$, CHCl₃), ($m = 5$, $\alpha_D^{25} = -68^\circ$; $c = 0.2$, CHCl₃), ($m = 11$, $\alpha_D^{25} = -55^\circ$; $c = 0.2$, CHCl₃).

The (S)- ω -(2-ethoxy-1,1'-binaphthyl-2'-yl)oxyalkyl 2-methylacrylates (MB-m) were obtained by esterification of the corresponding BN-alkanols **3** with methacryloyl chloride in the presence of triethylamine (usually three days boiling in diethylether). After the usual workup, the monomers were purified by column chromatography on silica (methylene chloride). ($m = 3$, $\alpha_D^{25} = -54^\circ$; $c = 0.1$, CHCl₃), ($m = 5$, $\alpha_D^{25} = -51^\circ$; $c = 0.025$, CHCl₃), ($m = 11$, $\alpha_D^{25} = -45^\circ$; $c = 0.1$, CHCl₃).

Characterization of the Monomers MB-m and Their Precursors

All the new synthesized chiral monomers and their precursors were identified by ¹H-NMR (Bruker AM-250 MHz) in CDCl₃ (tetramethylsilane as internal standard), and mass-spectrometry (EI/Jeol JMS-HX/HX110A Tandem Mass Spectrometer). It has been shown that racemization does not occur under similar reaction conditions—the enantiomeric purity of all

compounds is therefore assumed to be >99% (16). This is consistent with the high values of optical rotation measured on a Perkin-Elmer 141 polarimeter.

Preparation of the Polymers

The homopolymers of the chiral BN-containing methacrylates MB-m and the copolymers with nematogenic monomer A were obtained by radical polymerization in toluene using 1 mol% of 2,2'-azobis(2-methylpropanenitrile) as initiator at 65°C. The polymers were precipitated into methanol and reprecipitated. The compositions of the random copolymers are assumed to be equal to the mol fractions of the monomer mixtures before polymerization due to the comparable chemical structures of the monomers A and MB-m. The obtained samples were uniform, i.e., no microphase separation was observed. The molar masses of the copolymers were estimated by measuring their intrinsic viscosity (0.2–0.3) to be approximately 100,000.

Optical Microscopy

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

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 Kmin⁻¹. The phase transition temperatures are given as endothermic maxima of the heating curves at the

rate of 10 Kmin⁻¹. Glass transition temperatures were taken as points of inflexion.

X-ray Diffraction

X-ray diffraction measurements were performed using CuK α -radiation with a URS-55 instrument equipped with a flat film cassette for recording X-ray diffraction pattern.

RESULTS AND DISCUSSION

Thermal Properties of the Homopolymers MB-m

All homopolymers obtained by polymerization of BN-containing monomers MB-m are glassy amorphous compounds. The glass transition temperature of homopolymers decreases with increasing spacer length corresponding to 90°C, 68°C 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 results in 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 of glass transition temperatures ($T_g = 25^\circ\text{C}$)—clearing temperature ($T_{cl} = 120^\circ\text{C}$) (17).

Thermal Properties of the Copolymers MB-m-A

The phase transition temperatures and the maximum wavelengths of selective reflection of light λ_{max} at 22°C for different copolymer compositions for all three BN-containing polymers of different spacer length are shown in Table 1.

All 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-m units the copolymers become amorphous. The flat plate of X-ray diffraction patterns for all copolymers shows only one broad diffuse halo at angles corresponding to 4.6–4.8 Å, which is charac-

teristic 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 con-focal texture which is easily transformed into a planar one while mechanically shifting the glass plates with respect to each other. This texture selectively reflects light in the IR-range (Table 1), a fact which supports the occurrence of a chiral or twisted nematic N* phase formation.

The phase determination data lead to the general phase diagram of the three copolymers (Fig. 3). As it can be seen from the phase diagram, the increase of BN-containing monomer units in the copolymers only leads to a minor rise of the glass transition temperature, whereas the clearing temperatures drastically decrease. This decrease is practically independent of spacer length of the BN-containing units.

Optical Properties of the Copolymers MB-m-A

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 Eq 1,

$$\lambda_{\text{max}} = nP \quad (1)$$

where n is the average refractive index of the chiral phase. Equation 1 is only valid at a 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 (HTP) β of the chiral monomeric unit (7, 9), which is defined as

$$\beta = 1/Px \quad (2)$$

where P is the induced cholesteric pitch (μm^{-1}), x is the concentration of the chiral monomeric units x (moles of chiral monomeric units/moles of liquid crystalline monomeric units). Inserting Eq 1 into Eq 2 and

Table 1. Phase Transition Temperature and Maximum Wavelength of Selective Reflection of Light λ_{max} at 22°C for Different Copolymer Compositions MB-m-A.

Copolymer MB-m-A	Chiral Monomer/Mol %	$T_{\text{glass}}/^\circ\text{C}$	$T_{\text{clearing}}/^\circ\text{C}$	λ_{max} at 22°C/nm
$m = 3$				
1	8	35	100	2300
2	12	37	84	—
3	16	39	—	—
$m = 5$				
4	6	33	104	1500
5	8	36	95	1320
6	10	35	91	1150
7	12	34	68	—
8	16	37	—	—
$m = 11$				
9	6	30	99	1870
10	8	29	90	1420
11	12	31	75	—
12	16	29	—	—

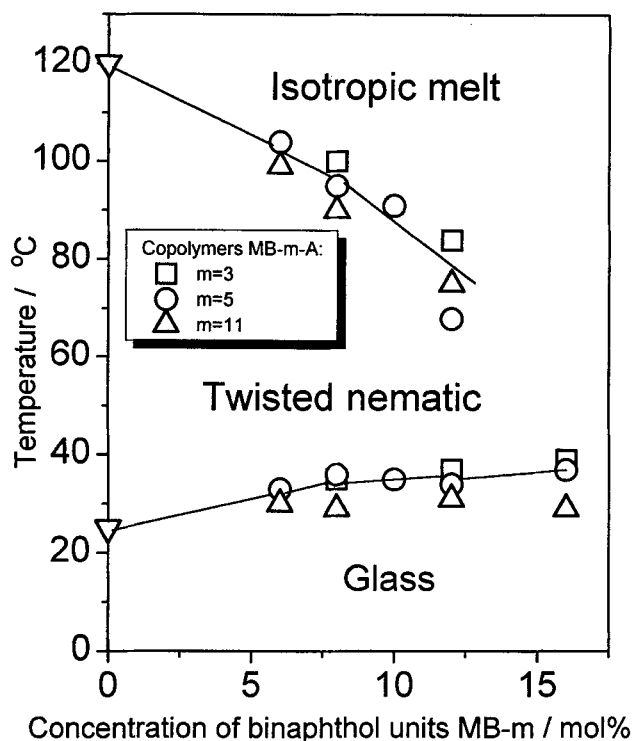


Fig. 3. Phase diagram of the three copolymers MB-m-A ($m = 3, 5, 11$) for different compositions.

assuming n to be constant leads to Eq 3:

$$\beta = n d \lambda_{\max}^{-1} / dx \quad (3)$$

Thus the HTP β is determined by the slope of the dependence of $\lambda_{\max}^{-1}$ on x . Figure 4 shows this depen-

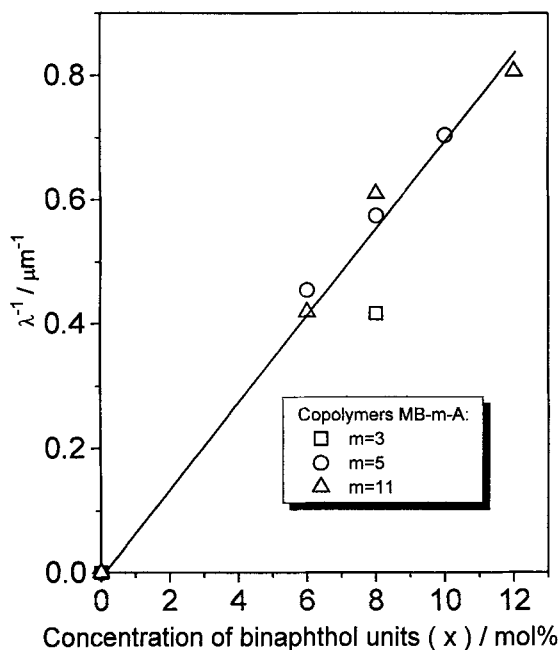


Fig. 4. Dependence of $\lambda_{\max}^{-1}$ on the molar fraction of BN-containing monomeric units MB-m for the three copolymers (MB-m-A, $m = 3, 5, 11$).

dence of $\lambda_{\max}^{-1}$ on the molar fraction of BN-containing monomeric units for all three copolymers.

It can be seen that the two copolymers MB-5-A and MB-11-A practically show the same dependence of $\lambda_{\max}^{-1}$ on the concentration of the chiral monomeric units x . The point obtained for copolymer MB-3-A does not obey this tendency. The different behavior 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 liquid crystalline packing of the mesogenic groups. The calculated HTP β of all BN-units in the copolymers is about $10\text{--}12 \mu\text{m}^{-1}$. This value is slightly higher in comparison with the values of cholesteryl-containing copolymers described in (7). However, in the case of BN-containing copolymers the disturbance of the mesophase begins with lower concentration ($\sim 15 \text{ mol}\%$) whereas the cholesteryl-containing copolymers preserve the chiral mesophase up to a cholesteryl concentration of $25 \text{ mol}\%$.

Figures 5 and 6 show the temperature dependence of $\lambda_{\max}$ for copolymers MB-m-A 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 $\lambda_{\max}$ are practically not changed in the temperature range from 20°C to $60\text{--}65^\circ\text{C}$ but a further increase of the temperature leads to a pronounced increase of $\lambda_{\max}$ that results in untwisting of the chiral nematic phase. This behavior is different from the majority of cholesteryl-containing polymers, where $\lambda_{\max}$ does not significantly rise with increasing temperature (7). Untwisting of the cholesteric helix is often observed at temperatures near to the region of cholesteric-smectic transition, i.e., at the appearance of the nuclei layered structure preceding the smectic phase formation.

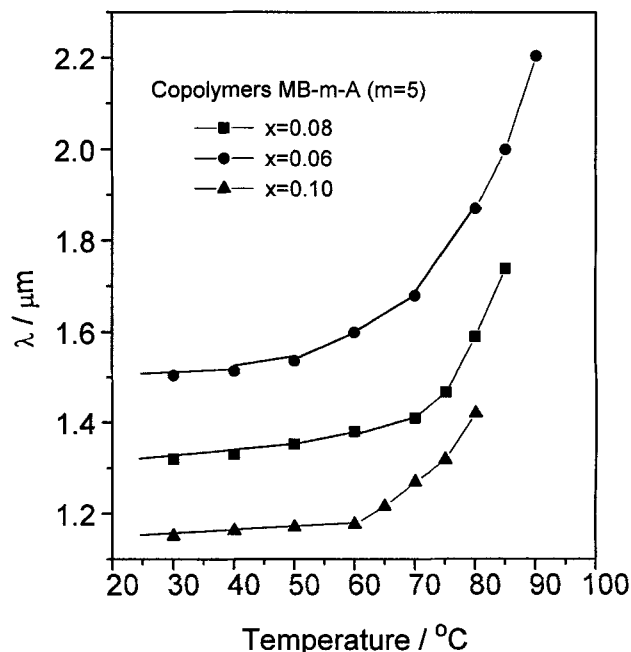


Fig. 5. Temperature dependence of $\lambda_{\max}$ for copolymer MB-m-A ($m = 5$) of different compositions.

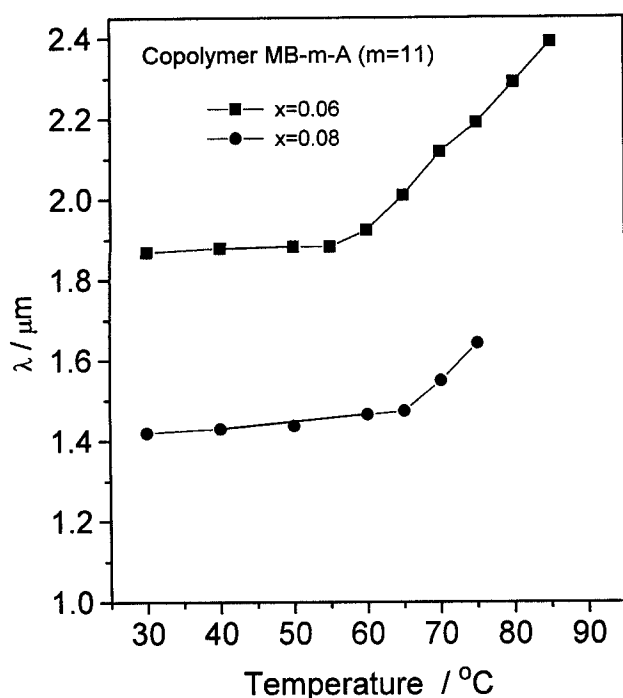


Fig. 6. Temperature dependence of $\lambda_{\max}$ for copolymer MB-m-A ($m = 11$) of different compositions.

Here, all BN-containing copolymers show opposite behavior and untwisting of the helix is observed when the temperature increases.

Furthermore, the values $(1/\lambda)(d\lambda/dT)$ of the copolymers investigated are in the region of 0.012–0.016 (depending on copolymer composition), this exceeds three-four times the same value theoretically predicted for mixtures of low-molar-mass nematics and chiral non-mesomorphic dopants (17). Temperature dependencies $\lambda_{\max} = f(T)$ (i.e. positive sign $d\lambda/dT$) have been observed earlier for two cholesteryl-containing copolymers (18). However, in this case the values of $(1/\lambda)(d\lambda/dT)$ did not exceed 0.001–0.002.

Figure 7 shows the temperature dependency of the HTP β for two chiral copolymers consisting of the same nematogenic acrylic monomer A, but different chiral units in the side chains. The first copolymer contains the atropisomeric units of BN and the second one chiral menthyl groups in the side chains. As it can be seen from Fig. 7, the menthyl-containing copolymer shows only a slight decrease of β on heating up to T/T_{cl} of 0.925 which then becomes larger approaching clearing temperature. It can be seen for BN-containing copolymers in comparison that β decreases more significantly with increasing temperature already at low ratios of T/T_{cl} .

CONCLUSIONS

The incorporation of chiral atropisomeric BN-containing substituents in a nematic polymer matrix leads to a chiral twisted nematic (cholesteric) phase formation in the same way as it has been shown before for cholesteryl containing copolymers (where the

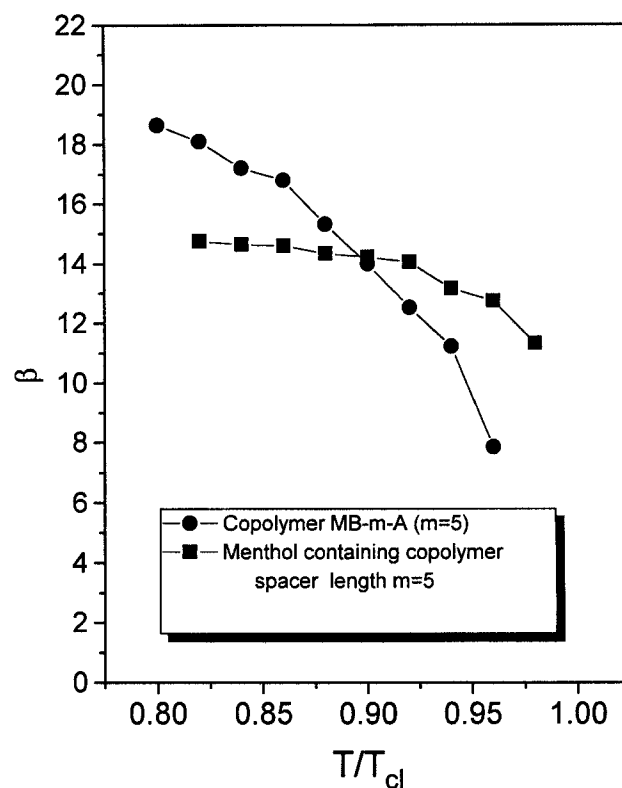


Fig. 7. Temperature dependencies of the helical twisting power β for the copolymers MB-m-A and a typical menthyl containing copolymers at reduced temperature (T/T_{cl}).

chirality is due to asymmetric carbon atoms in the side chains) (7, 19). The magnitudes of HTP β of BN-containing units are comparable with the HTP β of cholesteryl derivatives. These results suggest that the geometrical shape of the BN group in the side chain is the decisive factor responsible for their HTP. This is to the best of our knowledge the first example of the use of atropisomerism in order to induce chirality in copolymers.

The crucial difference between the behavior of cholesteryl based chiral units and atropisomeric BN-based chiral units in polymers, the temperature dependence of $\lambda_{\max}$ and HTP β can be explained by the special expression of chirality (atropisomerism) in the BN-units: The observed temperature dependence of HTP β of the copolymers MB-m-A is in full accordance with recently obtained results (13, 14), where similar changes of HTP β were observed for a variety of mixtures of low-molar-mass LCs with BN-derivatives as chiral dopants. The temperature dependencies of HTP β in (13, 14) 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 HTP β (13, 14). Therefore, in the chiral polymers synthesized, the two naphthol moieties should have the tendency to orient more perpendicular with respect to each other within a BN-molecule on heating. This leads, in accordance with the earlier obtained results (13, 14), to the significant decreases of the HTP β on heating in the copolymers.

ACKNOWLEDGMENTS

H.-J. Deussen wishes to thank the Gottlieb Daimler-und Karl Benz-Stiftung for a PhD grant. V. P. Shibaev and P. V. Shibaev thank the International Science Foundation (ISF) for grants of MME-000 and MME-300. Thanks also to the Russian Foundation for Fundamental Research (RFFI) for financial support. Support by the Danish Material Research Program (MUP) is gratefully acknowledged.

REFERENCES

1. Ya. S. Freidzon, V. P. Shibaev, and N. A. Plate, *Proceedings of the 3rd All-Union Conference on Liquid Crystals*, Ivanovo, 214 (1974) (in Russian).
2. V. P. Shibaev, Ya. S. Freidzon, and N. A. Plate, Abstracts of the papers of *XI-Mendeleev Congress on General and Applied Chemistry*, **v. 2**, Nauka, Alma-Ata, 164 (1975) (in Russian).
3. V. P. Shibaev, Ya. S. Freidzon, and N. A. Plate, USSR Inventor's Certificate No. 525 709 (1975), *Bull. Isobret.* No. 31 (1976) (in Russian).
4. V. P. Shibaev, Ya. S. Freidzon, and N. A. Plate, *Docl. Acad. Nauk of USSR*, **227**, 1412 (1976) (in Russian).
5. V. P. Shibaev and N. A. Plate, *Vysokomolek. Soedin.*, **A19**, 923, (1977).
6. H. Finkelmann, H. Ringsdorf, and W. Stöl Wendorff, *J. Makromolek. Chem.*, **179**, 829 (1978).
7. V. P. Shibaev and Ya. S. Freidzon, in *Side Chain Liq. Crystal Polymers*, McArdle, ed., Blackie, Glasgow-London, 260 (1988).
8. N. A. Plate and V. P. Shibaev, *Comb-Shaped Polymers and Liquid Crystals*, Plenum Press, New York (1988).
9. G. Gottarelli, M. Hibert, B. Samori, G. Solladié, G. Spada, and R. Zimmermann, *J. Am. Chem. Soc.*, **105**, 7318 (1983).
10. J. C. Bhatt, S. S. Keast, M. E. Neubert, and R. G. Petschek, *Liq. Crystals*, **18** (3), 367, (1995).
11. M. Kranz, T. Clark, and P. von Ragué Schleyer, *J. Org. Chem.*, **58**, 3317, (1993).
12. M., Smreina, J. Polakova, S. Vyskocil, and P. Kocovsky, *J. Org. Chem.*, **58**, 4534 (1993).
13. P. V. Shibaev, H. J. Deussen, R. A. Vinokur, K. Schaumburg, K. Bechgaard, T. Bjørnholm, V. P. Shibaev, and A. F. Alexandrov, *Izv. Acad. Nauk* (1996), (in Russian).
14. P. V. Shibaev, H. J. Deussen, R. A. Vinokur, K. Schaumburg, K. Bechgaard, T. Bjørnholm, and V. P. Shibaev, *Liq. Crystals* (1996).
15. R. Kazlauskas, *Org. Synth.*, **70**, 60 (1992).
16. H.-J. Deussen, E. Hendrickx, C. Boutton, D. Krog, K. Clays, K. Bechgaard, A. Persoons, and T. Bjørnholm, *J. Am. Chem. Soc.* (1996).
17. L. Lisezky, B. Timan, V. Tischenko, and T. Poloti, *Solid Fysics (in Russia)* **19**, 34 (1977).
18. V. P. Shibaev, H. Finkelmann, A. Kharitonov, M. Portugal, N. A. Plate, and H. Ringsdorf, *Vysokomol. Soedin.*, **A23**, 919 (1981).
19. N. I. Boiko, Ph.D. Thesis, Moscow State University, Moscow (1988).