

Synthesis and Properties of Vinylic Copolymers with Fluorescent Moieties as Optical Brighteners for Liquid Crystals

I. GRABCHEV, I. MONEVA

Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Received 9 June 1998; accepted 9 January 1999

ABSTRACT: The synthesis and characterization of new side-group copolymers of styrene or methylmethacrylate with fluorescent 1,8-naphthalimide derivatives are described. Basic photophysical characteristics of produced low molar and polymeric fluorescent brighteners are reported. The utility of the brighteners in liquid crystalline displays of the guest-host type is discussed on the basis of their spectral properties and their effect on the behavior of nematic liquid crystal ZLI 1840 (Merck, Darmstadt, Germany) at phase transition. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 151–157, 1999

Key words: fluorescent side-group copolymers; 1,8-naphthalimide derivatives; optical brighteners; photophysical properties; guest-host liquid crystal displays

INTRODUCTION

The chemical modification of polymers using fluorescent units able to take part in polymerization processes is of great interest and promise. Products thus obtained can find use as colored polymers resistant to solvents that have high fluorescence-, photo- and thermostability.^{1,2}

Similar substances are recently reported to have a novel use as luminophores in liquid crystal (LC) systems for displays of the “guest-host” type.^{3,4} In general, guest-host displays are built up of units of nematic LC and dichroic dyes. Their action is based on the so called “guest-host” effect which consists in alignment of mesogenic units under applied voltage accompanied by close alignment of chromophorous units, with a resulting

selective absorption by chromophores depending on orientation.⁵ Guest-host displays need only one polarizer and have a wide viewing angle.⁶ The displays exhibit high image contrast when fluorescent dyes are involved. Introduction of polymeric components results in enhanced self-support of display systems.⁷

Dichroic dyes of different molecular structure have been used until now for the electro-optic applications mentioned.^{3,4,8,9} It is suggested that the class of fluorescent brighteners also can be of interest in this aspect. The fluorescent brighteners (FBs) absorb light in the near UV region of the spectrum and re-emit violet-blue fluorescence in the visible region. One can expect that introduction of the colorless but highly fluorescent luminophores into LC systems for displays will strongly enhance the black-white image contrast of displays.

An important group of fluorescent brighteners is based on naphthalimide derivatives which are effective compounds for attaining high degrees of whiteness.¹⁰ Introduction of polymerizing groups into the FBs allows combination of both processes, polymer formation and bleaching, when

Correspondence to: I. Moneva.

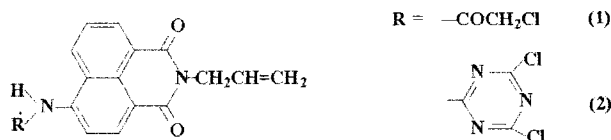
Contract grant sponsor: National Science Foundation of Bulgaria; contract grant number: X-556/95.

This article was presented at the 7th European Polymer Federation Symposium, Szczecin, Poland, September 1998, p. 87.

Journal of Applied Polymer Science, Vol. 74, 151–157 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/010151-07



Scheme 1

performing polymerization in the presence of FBs. In this article, we report on the ability of two unsaturated 4-acylamino-N-allyl-1,8-naphthalimide derivatives to copolymerize with styrene or methylmethacrylate (MMA) in bulk thus obtaining fluorescent side-group copolymers. Characteristic photo-physical properties of the novel low molar and polymeric FBs are determined in different media. Additionally, the effect of the low molar and polymeric FBs on phase-transition temperature and behavior of LC ZLI 1840 has been studied, and their utility for LC displays of the guest-host type is discussed.

EXPERIMENTAL

Materials

The monomeric FBs used in the copolymerization process were of the structure seen in Scheme 1. Their synthesis was described previously.¹¹

Commercial styrene (St) and MMA were used after purification. St was washed with an aqueous solution of NaOH, dried over CaH₂ and then distilled under reduced pressure in pure N₂ (of 99.99%) atmosphere. MMA was used after distillation under reduced pressure in N₂ atmosphere. As initiator of the radical copolymerization was used dibenzoylperoxide (DBP) (Fluka, Steinheim, Germany) which was recrystallized from CHCl₃.

The commercial LC mixture ZLI 1840 (Merck, Darmstadt, Germany) was used to prepare guest-host systems FB/LC. It has wide temperature range of nematic state (from -20°C to 90°C¹²). The monomeric and polymeric FBs had been screened initially for solubility in LC. For further studies, they were dissolved in LC at 0.5% w/w concentration, which usually guarantees an appropriate contrast ratio.¹³ The preparation of guest-host systems was performed as described previously.⁴

Synthesis and Characterization of Fluorescent Copolymers

The radical copolymerization of St or MMA with the unsaturated substances 1 and 2 was carried

out in ampoules, previously purged with pure dry N₂. The process of copolymerization was conducted under conditions used with other like monomers¹⁴: in the case of St at 80°C for 8 h and in the case of MMA at 70°C for 12 h, in the presence of 1.0% w/w FB and 1.0% w/w DBP under N₂. The side-group copolymers thus obtained were precipitated several times with ethanol from their solutions in benzene or chloroform for PS-based and PMMA-based copolymers, respectively. Precipitated copolymers were washed repeatedly with ethanol, recovered by filtration, and dried in vacuum to constant weight. Transparent fluorescent copolymers of intense blue emission were obtained.

The inherent viscosity [η] of the copolymers was determined in 0.5% w/w solutions of benzene or chloroform for copolymers with PS backbone and PMMA backbone, respectively.¹⁵ The data and related viscosity-average molecular masses M_v are reported in Table I. The equation [η] = $K \cdot M_v^a$ was used for the evaluation, using the following values of the constants: $K = 1.73 \times 10^{-3}$, $a = 0.69$ for PS-based polymers,^{16a} and $K = 0.71 \times 10^{-3}$ and $a = 0.73$ for PMMA-based polymers.^{16b}

Chemical binding of the monomeric FBs was proved by thin layer chromatography (TLC) and Fourier transform infrared (FTIR) analysis of the copolymers. TLC analysis was performed on silica gel plates (Fluka F60 254, 20 × 20 cm², 0.2 mm), using the system n-heptane:acetone (1 : 1) as eluent. FTIR spectra were taken on Perkin-Elmer (Norwalk, CT) 1600 spectrophotometer at 4-cm⁻¹ resolution, using KBr pellets for the low molar FBs, and on films for the copolymers. The quantity of bonded FB was determined by means of UV spectrophotometry, using the method of the stan-

Table I Molecular Characteristics of Fluorescent Copolymers of Vinylic Monomers with the Optical Brighteners FB1 and FB2

| Polymer | [η] cm · g ⁻¹ | M_v × 10 ⁻⁵ | Chem. Bound FB (%) |
|------------------|------------------------------------|-----------------------------|--------------------------|
| PS | 0.62 | 1.45 | — |
| poly(St-co-FB1) | 0.53 | 1.16 | 0.86 |
| poly(St-co-FB2) | 0.50 | 1.06 | 0.91 |
| PMMA | 1.04 | 5.09 | — |
| poly(MMA-co-FB1) | 0.92 | 4.30 | 0.85 |
| poly(MMA-co-FB2) | 0.86 | 3.92 | 0.93 |

dard line and the area of absorption bands of monomeric FBs for calibration.

UV-Vis absorption spectra were recorded on a Hewlett Packard (Palo Alto, CA) 8254A spectrophotometer, both in organic solvents and in LC for the low molar FBs, and in the respective solvent, benzene or chloroform, and on solid films for St-based or MMA-based copolymers. The films used in the study were sufficiently thin ($20\ \mu\text{m}$) and absorb in the range of validity of the Lambert-Beer law.

Fluorescence spectra of the monomeric and polymeric FBs were recorded on a Perkin-Elmer MPF 44 fluorimeter in solution and in LC. For excitation, monochromatic light of $\lambda = 360\ \text{nm}$ was used. The spectra in LC were taken on surface-stabilized display cells which consisted of two glasses covered from inside with oriented polymer layers in between having been sandwiched the doped LC systems.⁴

The quantum fluorescence yield Φ_F was determined on the basis of absorption and fluorescence spectra of the FBs in benzene and chloroform at a concentration of $1 \times 10^{-5}\ \text{M/l}$, using as standard quinone bisulphate ($\Phi_0 = 0.55^{17}$).

RESULTS AND DISCUSSION

Copolymers and Composition

The following components were studied by means of TLC: unprecipitated copolymers (they comprise also some amount of unreacted FB), precipitated copolymers, monomeric FBs and mixtures of homopolymer and FB. Development of the chromatographic system reveals that the FBs in the mixtures (a mechanical blend of homopolymer and FB) were characterized by the same parameters as monomeric FBs whereas FBs in the copolymers, being chemically bonded to the main chain, remained at the start with the polymer. This is an indication of different absorbencies of bonded and nonbonded FBs and qualitatively confirms their binding to polymer chain in copolymers.

The presence of a covalent bond in copolymers between the monomeric units of St and MMA and the low molar FBs is also proved when comparing IR absorption spectra of copolymers with those of homopolymers and low molar FBs. Thick films, $50\text{--}70\ \mu\text{m}$, were used to achieve a good resolution in the relevant frequency ranges of copolymer spectra necessary for their proof. Figure 1(a) plots

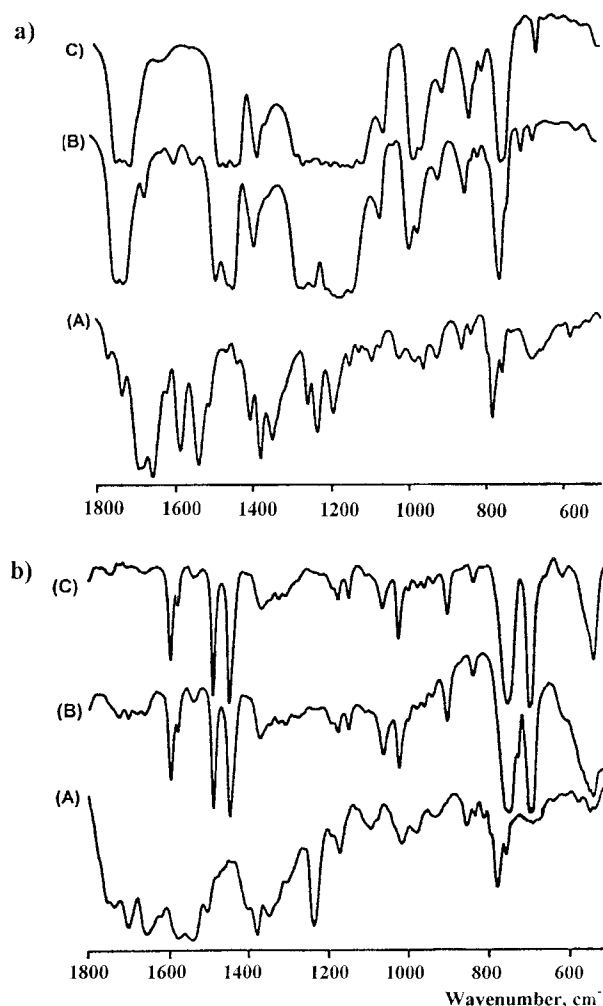


Figure 1 FTIR spectra: (a) FB1 (A), poly(FB1-co-MMA) (B) and pure PMMA (C) and (b) FB2 (A), poly(FB2-co-St) (B) and pure PS (C).

FTIR spectra of PMMA-based polymers and of low molar FB1. The spectrum of poly(MMA-co-FB1) differs considerably from that of homo-PMMA in the range $600\text{--}750\ \text{cm}^{-1}$ and $1500\text{--}1600\ \text{cm}^{-1}$ where it exhibits the characteristic bands of FB1 from vibrations $\nu(\text{C—C})$ and deformations $\delta(\text{C—H})$, vibrations of the aromatic system groups, and such of the carbonyl group from its naphthalimide structure. Figure 1(b) presents FTIR spectra of homo-PS and poly(St-co-FB2) compared with that of FB2. Notable are the differences in the range $500\text{--}700\ \text{cm}^{-1}$ where peaks appear which are characteristic of the chlorine atoms from the triazine ring of FB2 $\nu(\text{C—Cl})$ and at $1726\ \text{cm}^{-1}$ where carbonyl groups absorb.

The amount of FBs 1 and 2 incorporated into macromolecules was determined spectrophoto-

Table II Photophysical Characteristics of the Optical Brighteners FB1 and FB2 Measured in Organic Solvents and in LC

| FB | Benzene | | Chloroform | | Acetone | | Liquid Crystal | |
|------------------------------------|---------|-------|------------|-------|---------|------|----------------|-------|
| | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| λ_A nm | 360 | 362 | 368 | 372 | 362 | 360 | 358 | 363 |
| $\log \varepsilon$ | 3.99 | 4.00 | 4.03 | 4.05 | 4.18 | 4.22 | 4.66 | 4.90 |
| λ_F nm | 450 | 457 | 456 | 459 | 447 | 450 | 416 | 422 |
| $(\nu_A - \nu_F)$ cm^{-1} | 5555 | 5742 | 5244 | 5095 | 5253 | 5555 | 3894 | 3851 |
| f | 0.214 | 0.229 | 0.271 | 0.283 | 0.28 | 0.40 | — | — |
| E_{S1} kJ mol^{-1} | 291.9 | 290.5 | 285.7 | 284.1 | — | — | 288.5 | 292.3 |
| Φ_F | 0.53 | 0.58 | 0.51 | 0.53 | — | — | — | — |

metrically to be within 0.85–0.93% at 1% w/w initially introduced FB for PS- and PMMA-based copolymers (Table I). Considering that the values are obtained for repeatedly precipitated polymers in which low molar fractions have been removed during precipitation, results are rather satisfactory and imply that both FBs are suitable for obtaining fluorescent copolymers.

Spectral Characteristics of Low Molar and Polymeric Fluorescent Brighteners in Isotropic and Anisotropic (LC) Media

Table II shows basic electronic characteristics of the monomeric FBs in organic solvents and LC: the values of the ground-state position of absorption maximum (λ_A), the extinction ($\log \varepsilon$), the fluorescence maximum (λ_F), the Stoke's shift ($\nu_A - \nu_F$), the oscillator strength (f) for the long-wave absorption band, the energy of the singlet state (E_{S1}), and the quantum yield of fluorescence (Φ_F).

The monomeric FBs absorb in the near UV region at $\lambda_A = 360$ – 372 nm and have intense blue fluorescence ($\lambda_F = 447$ – 459 nm). The substitutes at fourth position have a small effect on λ_A , λ_F , and Φ_F , whose values are slightly higher for FB2. In terms of electron donor-acceptor interactions, which govern the polarization of this type of luminophores, this implies that the electron-donating ability in the case of FB2 is somewhat higher than that of FB1, at equal conjugation length.

Table II reveals clearly the effect of organic solvents on λ_A and λ_F of the FBs. As expected, λ_A and λ_F exhibit bathochromic shift (8–10 nm) in the more polar chloroform with regard to benzene. However, in the case of acetone, the most polar solvent used, the effect of solvent polarity is obviously disturbed since λ_A and λ_F values are close to those in benzene. This can be due to

intermolecular hydrogen bonding between the carbonyl group of the solvent and the acylamino group at fourth position of FB which leads to decrease of its electron-donating ability.

The absorption and emission spectra of both low molar FBs in LC are displayed in Figure 2. In LC, λ_A values of FBs are very close to those in benzene whereas λ_F values are strongly hypsochromically shifted (34–35 nm). Consequently, Stoke's shift is lower, whereas extinction ε is high (Table II). The E_{S1} values for FB1 and FB2 in LC are the lowest among all solvents.

The Stoke's shift was found by the expression

$$(\nu_A - \nu_F) = (1/\lambda_A - 1/\lambda_F) \times 10^7 \quad (1)$$

Another important parameter for luminophores is the oscillator strength which shows the effective

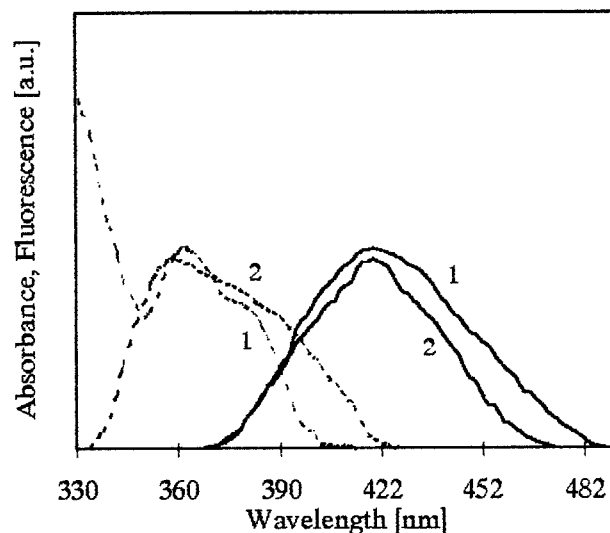


Figure 2 UV-Vis absorption and fluorescence spectra of low molar fluorescent brighteners FBs 1 and 2 in LC ZLI 1840.

Table III Spectral Characteristics of the Fluorescent Copolymers Recorded in Solution and on Thin Films

| Polymer | Solution | | | Solid Film | | |
|------------------|---------------------|---------------------|---|---------------------|---------------------|---|
| | λ_A (nm) | λ_F (nm) | $(\nu_A - \nu_F)$ (cm^{-1}) | λ_A (nm) | λ_F (nm) | $(\nu_A - \nu_F)$ (cm^{-1}) |
| PS | — | — | — | 286 | — | — |
| poly(St-co-FB1) | 360 | 451 | 5604 | 364 | 442 | 4848 |
| poly(St-co-FB2) | 360 | 455 | 5799 | 362 | 442 | 4999 |
| PMMA | — | — | — | 264, 286 | — | — |
| poly(MMA-co-FB1) | 365 | 455 | 5344 | 365 | 450 | 5175 |
| poly(MMA-co-FB2) | 368 | 458 | 5339 | 366 | 451 | 5149 |

number of electrons whose transition from ground to excited state gives the absorption area in electron spectrum. It was calculated by eq. (2)¹⁸:

$$f = 4.32 \times 10^{-9} \Delta \nu_{1/2} \epsilon_{\max} \quad (2)$$

where $\Delta \nu_{1/2}$ is the width of the absorption band (in cm^{-1}) at $1/2 \epsilon_{\max}$. The values found for FB1 and FB2 increase with solvent polarity being higher for FB2 and correlate well with the hypochromic effect observed (cc. log ϵ).

Whereas oscillator strength and extinction are smaller in nonpolar benzene, Stoke's shift is bigger. Accordingly, the energy of activation of first excited state E_{S1} , calculated from the point of intersection of absorption and fluorescence spectra at corresponding wavelength λ_{S1} , has higher values in benzene than in chloroform. It is noteworthy that the novel FBs exhibit high fluorescence ($\Phi_F = 0.51$ – 0.58) both in benzene and chloroform, without significant difference.

Table III presents data evaluated from the absorption and fluorescence spectra of poly(FB-co-St) and poly(FB-co-MMA) in isotropic state. The absorption and fluorescence maxima of copolymers in solution are identical with those of monomeric FBs in the respective solvent, benzene or chloroform. This indicates obviously that during the copolymerization process there is no change in the chemical structure of the chromophorous system. The absorption maxima of copolymer films are close to those of monomeric FBs in nonpolar solvent whereas the fluorescence maxima are hypsochromically shifted with respect to them, in the case of PS-based copolymers with 9–13 nm and for PMMA-based copolymers with 5–7 nm, probably due to conformational effects.

The long-wave fluorescence maxima λ_F of all low molar and polymeric FBs in isotropic media and in LC are interrelated in Figure 3 for better illustration. The histogram clearly shows that the fluorescence maxima of polymeric brighteners in LC are strongly hypsochromically shifted with respect to their values in solution and in solid state as in the case of low molar FBs. This fact and a strong increase in extinction ϵ (about $\times 4$ – 7) can be connected to hydrogen bonding in LC, between carbonyl and cyano groups present in LC and acylamino groups at fourth position of the FBs.

Polymeric FBs, both PMMA- and PS-based, exhibit as a rule bathochromic shift and higher emission intensity in LC with respect to their monomeric counterparts. These observations can be connected to hindered hydrogen bonding when

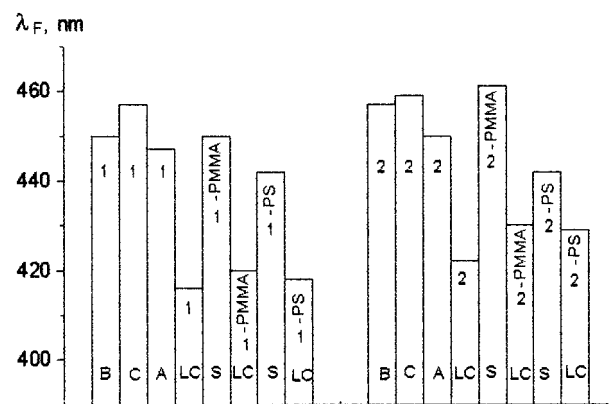


Figure 3 Fluorescence maxima of low molar optical brighteners FBs 1 and 2 and their PMMA-based and PS-based copolymers in different media: benzene (B), chloroform (C) and acetone (A), on solid films (S) and in liquid crystal (LC).

Table IV Effect of Low Molar and Polymeric Fluorescent Brighteners on the Temperatures T_N and T_I of the Nematic-Isotropic Phase Transition of Liquid Crystal ZLI 1840 (in K)

| System | T_N | T_I | $T_I - T_N$ | ΔT_N | ΔT_I | T_{NI} | ΔT_{NI} |
|-----------------------|-------|-------|-------------|--------------|--------------|----------|-----------------|
| LC | 362.5 | 368.5 | 6.0 | — | — | 365.5 | — |
| LC + FB1 | 360.8 | 361.8 | 7.3 | -1.5 | -0.3 | 364.5 | -1.0 |
| LC + FB2 | 360.3 | 367.6 | 7.3 | -2.0 | -0.8 | 364.0 | -1.5 |
| LC + PS | 358.1 | 366.3 | 8.2 | -4.4 | -2.2 | 362.2 | -3.3 |
| LC + Poly(FB1-co-St) | 356.4 | 365.6 | 9.2 | -6.1 | -1.9 | 361.0 | -4.5 |
| LC + Poly(FB2-co-St) | 356.1 | 365.8 | 9.7 | -6.4 | -2.7 | 361.0 | -4.5 |
| LC + PMMA | 357.1 | 366.0 | 8.9 | -5.4 | -2.5 | 361.6 | -3.9 |
| LC + Poly(FB1-co-MMA) | 356.2 | 365.1 | 8.9 | -6.3 | -3.4 | 360.7 | -4.8 |
| LC + Poly(FB2-co-MMA) | 356.1 | 365.4 | 9.3 | -6.4 | -3.4 | 360.8 | -4.7 |

chromophores are chemically bonded. Thus λ_F maxima of copolymer solid films where H-bonding surely cannot take place are close to those in solvents without solvation. λ_F for bonded FB1 and FB2 tend to higher values in the case of PMMA-backbone which is related to conformational effects.

Phase-Transitional Behavior of FB/LC Systems

It is well known that the addition of nonmesogenic solute to a nematic LC changes its normal nematic-isotropic phase transition temperature, in most cases causing its decrease. Another specific feature of the phase transition is the appearance of two-phase regions predicted by theory and observed experimentally.¹⁹

The effect that low molar and polymeric FBs have on the phase transitional behavior of LC ZLI 1840 was studied by means of a polarizing microscope with a heating stage. The results of temperature investigations on pure LC, binary FB(0.5%)/LC, and ternary FB(0.5%)/homopolymer(40%)/LC mixtures are given in Table IV. The following characteristic temperatures of the nematic-isotropic phase transition are determined: T_N , at which the first drop of the isotropic liquid appears, and T_I , at which the last drop of the nematics disappears. Their difference ($T_I - T_N$) is the range of the two-phase region, and ΔT_N and ΔT_I are the shifts of T_N and T_I with respect to the relevant temperatures of pure LC. $T_{NI} = 1/2(T_N + T_I)$ is the average temperature of the nematic-isotropic transition of guest/LC mixtures and ΔT_{NI} is its shift with respect to pure LC.

The temperature investigations on the binary systems show that low molar FBs slightly de-

crease both phase transition temperatures T_N (1.5–2.0K) and T_I (0.3–0.8K) of pure LC. The depression is much more enhanced when homopolymer is introduced into the system being within 4.4–5.4K for T_N and 2.2–2.5K for T_I . The polymeric FBs cause even larger depression of LC phase transition temperatures (6.1–6.4K) and a wider two-phase region (1.9–3.4K). Thus, the destructive influence on mesophase of the three types of guests increases in the row: low molar FBs, their mixtures with homopolymers, copolymers.

This behavior is in accordance with theoretical predictions (based on Helfand's lattice model) describing the effect that flexible polymer guests have on the nematic-isotropic phase transition of low molar LCs.²⁰

CONCLUSIONS

In this article, the idea is suggested and first studies are performed on the utility of fluorescent brighteners, both low molar and polymeric, as luminophores in guest-host LC displays.

Two monomeric optical brighteners of high fluorescence yield were obtained which were able to copolymerize with styrene and methylmethacrylate giving fluorescent side-group copolymers. Both the low molar brighteners and their copolymers are well soluble in LC ZLI 1840 (at 0.5% w/w concentration) and emit intense violet fluorescence. The low molar brighteners do not affect the phase transitional behavior of LC and can be suitable components in systems for guest-host displays working both in passive and active regimes.

The polymeric fluorescent brighteners have a more intense emission in LC compared with their monomeric counterparts. They exhibit, however, larger destructive influence on the mesophase which is comparable to that of polymeric dyes (comprising 1,8-naphthalimide) for use in LC.⁴ It seems that the main problem is the compatibility of polymer backbone to nematic LC as in the case of polymeric dyes.

The authors acknowledge financial support by the National Science Foundation of Bulgaria under Contract X-556/95, and are grateful to Merck (Germany) for LC sample ZLI 1840.

REFERENCES

1. Gothrie, J. *Rev Prog Coloration* 1990, 20, 40.
2. Miley, J. *Pure Appl Chem* 1996, 68, 1423.
3. Scherowsky, G. *Makromol. Chem, Makromol Symp* 1993, 69, 87.
4. Grabchev, I.; Moneva, I.; Wolarz, E.; Bauman, D. *Z Naturforsch* 1996, 51a, 1186.
5. Heilmeier, G.; Zanoni, L. *Appl Phys Lett* 1968, 19, 91.
6. Wolarz, E.; Moryson, H.; Bauman, D. *Displays* 1992, 13, 171.
7. Kim, B.; Ok, I.; Choi, C. *J Polym Sci, Part B: Polym Phys* 1995, 33, 707.
8. Ringsdorf, H.; Schmidt, H. *Makromol Chem* 1984, 185, 1327.
9. Grabchev, I.; Moneva, I. *Dyes Pigm* 1998, 37, 155.
10. Anliker, R.; Muller, G. *Fluorescent Whitening Agents in Environmental Quality and Safety*; Thieme, Darmstadt, Germany, 1975; Vol. IV.
11. Grabchev, I.; Konstantinova, T. *Dyes Pigm* 1997, 33, 197.
12. Merck Prospect: *Liquid Crystal Mixtures for Electro-Optic Displays*, Merck AGaA, Stuttgart, Germany, October 1994.
13. Gray, G. *Chimia* 1980, 34, 47.
14. Philipova, Tz.; Grabchev, I.; Petkov, I. *J Polym Sci, Part A: Polym Chem* 1997, 35, 1069.
15. Solomon, O.; Cinta, I. *J Appl Polym Sci* 1962, 6, 683.
16. *Encyclopedia of Polymer Science and Tehnology*; Wiley: New York, 1964; (a) Vol. 1 and (b) Vol. 13.
17. Olsbach, J. *J Chem Phys* 1979, 20, 25.
18. Gordon, P.; Gregory, P. *Organic Chemistry in Color*; Chimia, Moskva, 1987.
19. Martire, D. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G.; Gray, G., Eds. Academic: New York, 1979.
20. Chen, Y.; Li, J.; Yang, Y. *Mol Cryst Liq Cryst* 1995, 25, 37.