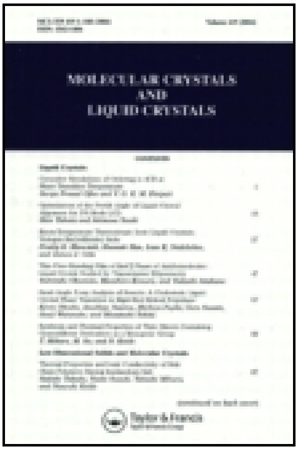

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Effect of Structure of Photoresponsive Molecules on Photochemical Phase Transition of Liquid Crystals IV. Photochemical Phase Transition Behaviors of Photochromic Azobenzene Guest/Polymer Liquid Crystal Host Mixtures

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Sixteen azobenzene derivatives were used as guests in a polymer liquid crystal (PLC) host with side-chain mesogenic phenyl benzoate groups, poly(4′-methoxyphenyl 4-(acryloyloxy)propoxybenzoate (PAPB3), and were examined on their ability to induce the photochemical isothermal phase transition of the guest/host mixtures. Although the rates of photoisomerization of the azobenzene guests were found to be similar to those of the mixtures composed of the same azo guests and a low molecular weight ester-type host, ECH206, the rates of the photochemical phase transition were retarded approximately by one order of magnitude compared to those of the same azo guest/ECH206 mixtures. This was interpreted as a consequence of low mobility of mesogenic moieties in PLC. The effect of mesogenic 4-cyanobiphenyl groups incorporated into the azobenzene guests on the photochemical phase transition behaviors of the guest/host mixtures was discussed with Reference to the effect of the methylene spacer length.

Keywords: photochemical phase transition, azobenzene, photoisomerization, order parameter, guest/host mixture, polymer liquid crystal

INTRODUCTION

In a course of the systematic studies on the effect of the structure of the photoresponsive molecules on the photochemical phase transition behaviors of the photochromic guest/host mixtures, we prepared 17 azobenzene derivatives in which mesogenic 4-cyanobiphenyl moieties were attached at one end or at both ends of

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‡Deceased on July 11, 1989.

the azobenzene cores through flexible methylene spacers or alkoxy substituents were solely incorporated.[1] We examined their ability to induce the photochemical isothermal phase transition of various host liquid crystals (LC) such as 5CB[2] and ECH206[3]. We found that the mesogenic 4-cyanobiphenyl moieties incorporated into the photochromic guests were effective in inducing the photochemical phase transition of the guest/host mixtures. However, the efficiency of the photochromic guests to induce the photochemical phase transition of the mixtures seems to depend on the affinity of the 4-cyanobiphenyl moiety to the host mesogens. The corrected rates of the photochemical phase transition were found to be higher by approximately two order of magnitude in the 5CB host than in the ECH206 host.[2,3]

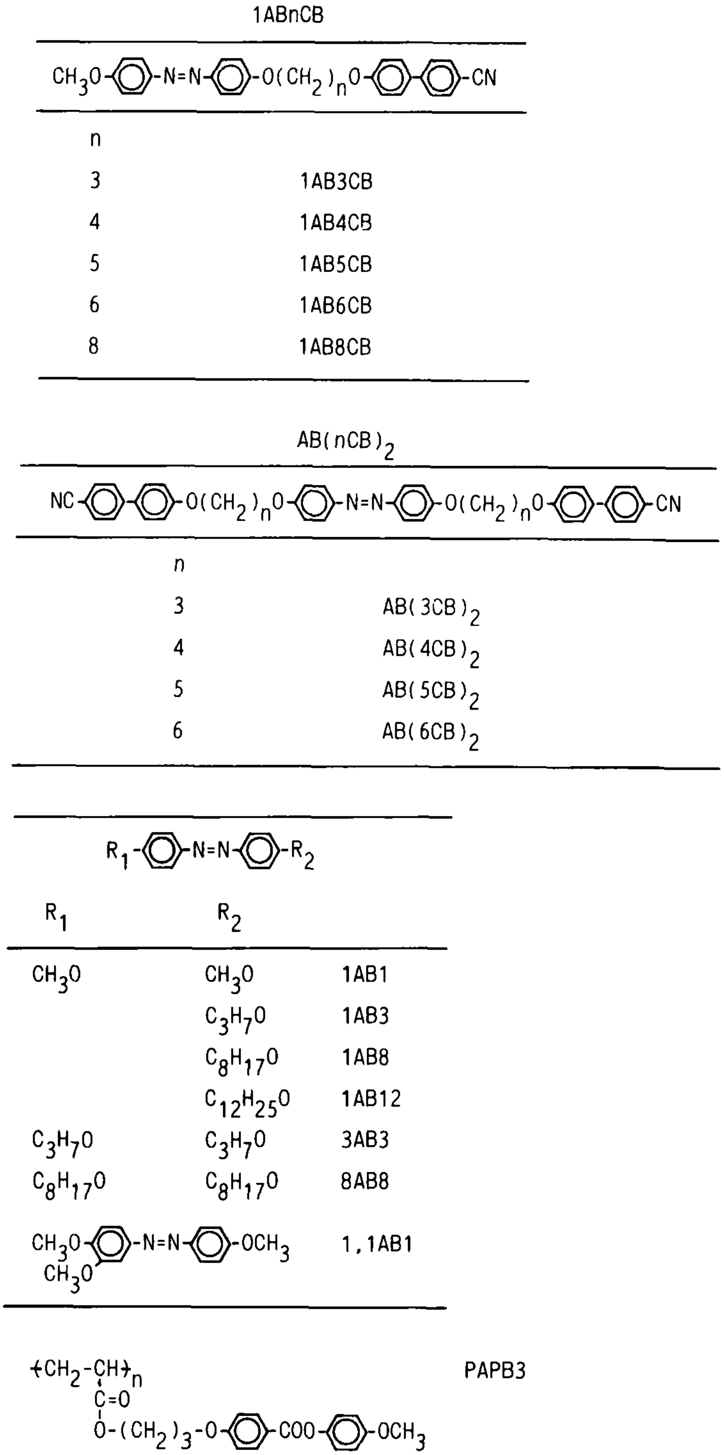
It appears to be a reasonable extension of our systematic studies on the effect of the photochromic guests on the photochemical phase transition of the guest/host mixtures to explore the photochemical phase transition behaviors of the azobenzene guest/polymer liquid crystal (PLC) host, since much attention has recently been paid to PLCs as optical-image storage materials. In fact, the use of PLCs as optical-image storage materials has become a current topic in view of a phenomenon of glass transition and the processability of the polymers. Below the glass transition temperature (T_g), the segmental motion of the polymer chains is frozen-in, thereby the stored information can be kept stable for a long period. Furthermore, cell-free polymer films with the ability of long-term storage are evidently favored from the viewpoint of processability.

Shibaev *et al.*[4] and Coles and Simon[5] reported on laser-addressed PLC storage devices in which heat-mode recording was exclusively employed. Photon-mode image storage in the PLCs was first demonstrated by Eich and Wendorff as "holographic" optical storage, in which photoirradiation caused isomerization of the photochromic groups incorporated into the PLCs, thus inducing "grating" in the PLCs.[6,7] We have demonstrated the *photochemical phase transition* in various PLCs[8-11] aiming at the optical-image storage materials. Our system is different from the previous works in that *photochemically induced isothermal phase transition of the matrix PLCs* is the principle involved in the image storage system, so that high sensitivity and a high signal-to-noise (S/N) ratio can be expected.

In the present study, 16 azobenzene derivatives were used as guests in a host PLC, poly(4′-methoxyphenyl 4-(acryloyloxy)propoxybenzoate (PAPB3), and were examined on their ability to induce the photochemical phase transition of the guest/host mixtures. As in the case of the azobenzene guest/low molecular weight LC mixtures, special attention was paid to the effect of the mesogenic 4-cyanobiphenyl groups covalently incorporated at one end or at both ends of the azobenzene derivatives on the photochemical phase transition behavior of the mixtures from the viewpoint of interaction between the mesogenic 4-cyanobiphenyl moieties and the host ester mesogens.

EXPERIMENTAL

Figure 1 shows the structures of the photochromic azobenzene guests and the host PLC used in this study as well as their abbreviations. The azobenzene guest molecules are classified into three groups as described in the preceding paper:[3] AB(nCB)$_2$



1ABnCB

n	
3	1AB3CB
4	1AB4CB
5	1AB5CB
6	1AB6CB
8	1AB8CB

AB(nCB)$_2$

n	
3	AB(3CB)$_2$
4	AB(4CB)$_2$
5	AB(5CB)$_2$
6	AB(6CB)$_2$

R_1	R_2	
CH_3O	CH_3O	1AB1
	C_3H_7O	1AB3
	$C_8H_{17}O$	1AB8
	$C_{12}H_{25}O$	1AB12
C_3H_7O	C_3H_7O	3AB3
$C_8H_{17}O$	$C_8H_{17}O$	8AB8
		1,1AB1

PAPB3

FIGURE 1 Structure of photochromic azobenzene guests and a polymer liquid crystal host used in this study and their abbreviations.

in which 4-cyanobiphenyl moieties are attached to both sides of azobenzene at the para positions through various lengths of methylene spacers, 1ABnCB where the 4-cyanobiphenyl moiety is attached to one side of the azobenzene, and nABm or k,lABm which possess alkoxy substituents at both para positions of azobenzene or at various positions of the azobenzene phenyl rings. Synthesis and their thermotropic properties are described in full detail in the previous paper.[1]

The host PLC employed throughout this work, poly(4′-methoxyphenyl 4-(acryloyloxy)propoxybenzoate (PAPB3), was prepared and purified as reported previously[9] and its number-average molecular weight (M_n) was determined as 6100 by gel-permeation chromatography (GPC) using polystyrene as the standard. Thermotropic properties of PAPB3 was thoroughly investigated in the previous paper.[9] Briefly, PAPB3 shows only a nematic phase, and T_g and the nematic-to-isotropic phase transition temperature (T_{NI}) depend strongly on M_n. Both values increase with M_n up to $M_n = 10^4$, thereafter they become constant. T_g and T_{NI} of the present samples of PAPB3 were determined as 34°C (DSC) and 60°C (polarizing microscopy), respectively.

LC behavior and phase transition behavior were studied on an Olympus model BHSP polarizing microscope equipped with a Mettler hot stage model FP-80 and FP-82. The thermodynamic properties of the host/guest mixtures were determined with a differential scanning calorimeter (DSC; SEIKO I&E SSC-5000) at a heating rate of 10°C/min. At least four scans were performed for each sample to check reproducibility. Polarized absorption spectra were recorded with a Hitachi UV-200 spectrophotometer with the aid of a polarizer.

The photochemical phase transition behaviors of the guest/PLC host mixtures were investigated by means of the apparatus already reported.[2,10] By the use of this apparatus, the photochemical phase transition behavior of the guest/host mixtures as well as the photoisomerization behavior of the guest photochromic molecules could be followed simultaneously. Samples (polymer films containing 1 mol% of the azobenzene guests) were prepared by casting the polymer solution in chloroform onto glass plates. The films were then dried under reduced pressure, and their LC behavior was examined with a polarizing microscope. We were aware that annealing of the polymer films was crucial for PLC to show the LC phase, so that in the present study the PLC films were subjected to annealing in a thermostat at temperatures where the PLC films showed the LC phase. The PLC films containing 1 mol% of the guest were placed in a thermostated block and irradiated with a monochromatic light from a JASCO CRM-FA irradiator.

RESULTS AND DISCUSSION

Order parameters determination by UV dichroism

In order to measure the polarized absorption spectra for the determination of the order parameters of the azobenzene guest/PLC host mixtures, the isotropic melt of the mixture was injected into an LC cell with a 9 μm-cell gap and parallel homogeneous orientation, followed by cooling gradually to a temperature just below T_{NI} of the mixture. However, the preparation of the uniformly oriented samples of the guest/PLC mixtures seemed to be difficult even after prolonged annealing at this temperature. We next tried the orientation of the mixtures in a magnetic field. The mixture in the LC cell was placed in a magnetic field of 2.1 T and left at a temperature just below T_{NI} for 30 h. However, this method of the orientation was still unsuccessful, giving poorly oriented samples as judged by microscopic observation. Furthermore, the uniform orientation was tried for the PLC films containing the azobenzene guests in the magnetic field. In this case, again, uniformly oriented samples could not be obtained.

Our previous study on the thermotropic properties of PLCs revealed that in homologs of PAPB3, poly(4′-methoxyphenyl 4-(acryloyloxy)alkoxybenzoate (PAPBn) where *n* is the number of methylene units in the spacer alkyl chain, PAPB3 exhibited specifically low orientational ordering in comparison with the other set of the homologs with $n = 2$, 5 and 6, which was evaluated by thermodynamic parameters and IR dichroism.[9] Coupled with this result, it may be said that the orientational ordering of the mesogenic moieties in PAPB3 is very low. Furthermore, another difficulty was associated with the determination of the order parameter of the guest/PAPB3 mixtures by UV dichroism. Namely, significant scattering and interference of the PLC films prevented reliable measurements of the polarized absorption spectra of the samples. This problem was still present when the mixtures were placed in LC cells. We, therefore, will not discuss the order parameters of the guest/PLC host mixtures in the present study.

Photochemical phase transition behaviors of the guest/host mixtures

A typical example of the photochemical isothermal phase transition behavior of the azobenzene guest/PAPB3 mixtures is shown in Figure 2 where a 1AB12/PAPB3 mixture containing 1 mol% of the guest was irradiated at 360 nm at the reduced temperature ($T_{red} = T/T_{NI}$) of 0.99. In the upper part of the figure, the change in absorbance of the azobenzene guest at the irradiation wavelength (360 nm) is indicated as a function of the irradiation time and in the lower part of the figure the change in transmittance of the linearly polarized light (633 nm), I_t, is shown as a function of time. The transmittance was measured through the crossed polarizers between which the sample was placed. It is clearly seen that photoirradiation caused trans → cis isomerization of 1AB12 doped in PAPB3 as evidenced by a decrease in absorbance at 360 nm, and the trans → cis photoisomerization of the dopant induced concomitantly nematic (*N*) → isotropic (*I*) phase transition of the host PLC as demonstrated by a complete loss of birefringence ($I_t = 0$). As described in the preceding paper,[3] we defined the response time, τ, as the time required to reduce the transmittance, I_t, to 10% of the maximum value in order to discuss the photochemical phase transition behavior quantitatively. In addition, the rate of the trans → cis photoisomerization of the azobenzene guests was different depending on the structure of the guest molecules, and we determined the isomerization rate from the initial slope of the change in the absorbance and termed it as R_{t-c}.

We explored the effect of temperature on the photochemical phase transition of the guest/PLC host mixtures and found that the rate of the phase transition, eval-

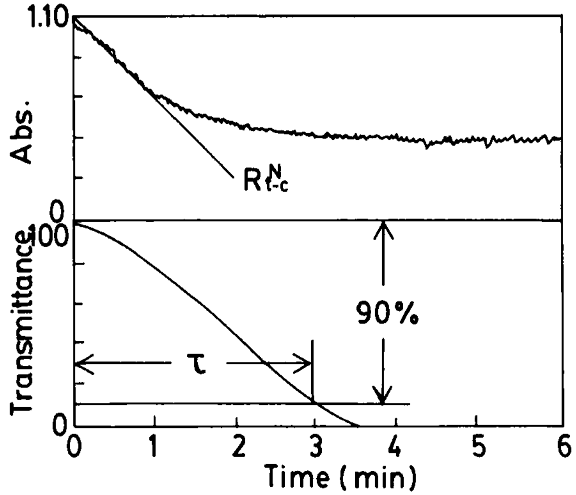


FIGURE 2 Photochemically induced isothermal phase transition behavior of PAPB3 doped with 1 mol% of 1AB12 (lower part) and the photoisomerization behavior of the photochromic dopant (upper part). Change in absorbance of 1AB12 in PAPB3 at 360 nm is plotted as a function of irradiation time in the upper part and the transmittance between a pair of the crossed polarizers is plotted in the lower part of the figure as a function of the irradiation time (λ_{ex} = 360 nm). Irradiation was performed at T_{red} = 0.99.

uated by the reciprocal of the response time (τ^{-1}), decreased with decreasing temperature. This is a general tendency that has been observed for the photochemical phase transition of the azobenzene guest/host LC mixtures.[1-3,8-11] The rationale for this tendency lies in the fact that the photochemical phase transition is closely related to the lowering of T_{NI} of the mixture brought about by accumulation of the cis-form of the azobenzene guests. T_{NI} of the guest/host mixtures decreases as the concentration of the cis-form increases and when T_{NI} of the system is lowered below the irradiation temperature, the isothermal phase transition is induced. In the present study, all the photochemical phase transition behaviors were evaluated at T_{red} = 0.99.

Figure 3 shows the rates of the trans → cis photoisomerization of the azobenzene guests (1ABn) in two different phases of the host PLC as a function of the number of methylene chains in the flexible spacers: N (T_{red} = 0.99, ○); and I (T_{red} = 1.02, △) phases. The same plots for a series of the 1ABnCB/PAPB3 mixtures and the AB(nCB)$_2$/PAPB3 mixtures are shown in Figures 4 and 5, respectively. In all mixtures, the concentration of the dopant was 1 mol% in PAPB3.

It is interesting to note that the rate of photoisomerization of the azobenzene guests in the PLC matrix was not so depressed in comparison with those in the low molecular weight LC (ECH206),[3] although it apparently is a generally accepted concept that the mobility of the mesogenic groups in PLCs is much lower than that in low molecular weight LCs.[12] However, the photoisomerization of the azobenzene dopants in polymer matrices is affected mainly by free volume available for the dopants and not by the mobility of the matrices alone.[13,14] As discussed previously,

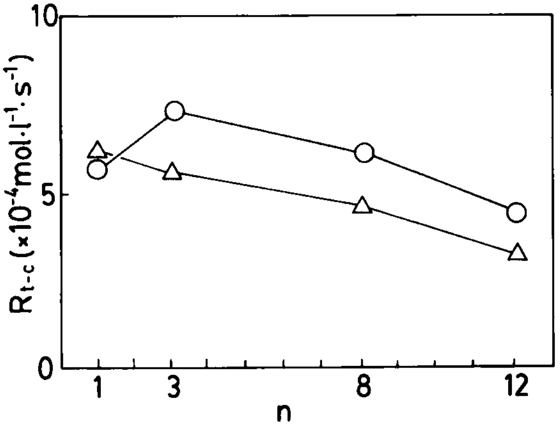


FIGURE 3 Rates of photoisomerization of 1ABn doped in PAPB3 in the nematic (○, T_{red} = 0.99) and isotropic phases (△, T_{red} = 1.02) as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm.

it seems likely that there is much free volume in PAPB3 available for the dopants owing to much less orientational ordering of the mesogenic moieties in this PLC.[9] Another point that should be mentioned is that in the 1ABn/PAPB3 and 1ABnCB/PAPB3 mixtures the rates of the photoisomerization were higher in the *N* state than in the *I* state. This is in sharp contrast to the photoisomerization behaviors of the azobenzene guest/low molecular weight LC mixtures so far examined.[2,3] This is interpreted most probably in terms of thermal reverse isomerization of the azobenzene dopants. Since T_{NI} of PAPB3 used in the present study was high (60°C), the irradiation temperature corresponding to T_{red} = 0.99 was high enough for the

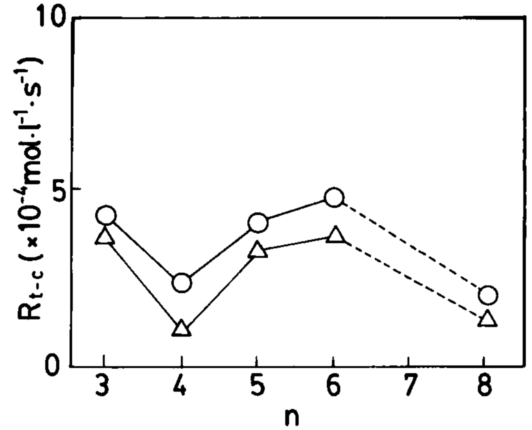


FIGURE 4 Rates of photoisomerization of 1ABnCB doped in PAPB3 in the nematic (○, T_{red} = 0.99) and isotropic phases (△, T_{red} = 1.02) as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm.

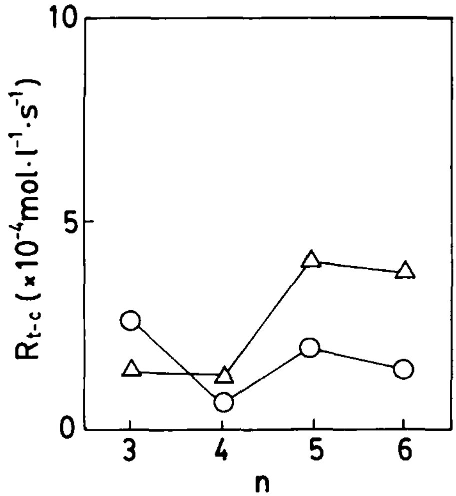


FIGURE 5 Rates of photoisomerization of $AB(nCB)_2$ doped in PAPB3 in the nematic (○, T_{red} = 0.99) and isotropic phases (△, T_{red} = 1.02) as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm.

cis-forms of the azobenzene chromophores to conduct the cis → trans reverse isomerization effectively.[14] Particularly, in this temperature range the rate of the thermal cis → trans isomerization is quite sensitively dependent on the temperature; a small rise in temperature possibly results in a large increase in the thermal reverse isomerization.[14] Thus, it is possible that in the *I* phase of the present mixture the rate of thermal reverse isomerization is much higher than in the *N* phase, leading to an apparently opposite trend in the rate of the photoisomerization. On the other hand, in the azobenzene guest/low molecular weight LC host mixtures (5CB and ECH206), T_{NI} was low and the thermal reverse isomerization did not take place appreciably, thereby the rates of the photoisomerization were higher in a less viscous phase (*I*) than in a viscous phase (*N*).

Although in the 1ABn/PAPB3 mixtures the rate of the photoisomerization was not affected significantly by the spacer length *n* (Figure 3), it was influenced by the methylene spacer in the 1ABnCB/PAPB3 (Figure 4) and $AB(nCB)_2$/PAPB3 (Figure 5) mixtures and those guest molecules with $n = 4$ showed the lowest rates of the photoisomerization in both mixtures. This may be a consequence of strong interaction of those guests with the matrix PAPB3 as in the case of 1AB4CB/5CB, $AB(4CB)_2$/5CB and $AB(4CB)_2$/ECH206 mixtures.[2,3]

The results shown in Figures 3, 4 and 5 have demonstrated that the rate of the photoisomerization of the photoresponsive azo compounds depends on the structure of the azo compounds, thereby for the quantitative evaluation of the photochemical phase transition behaviors of the guest/host mixtures, the apparent rate (τ^{-1}) was corrected for the rate of the photoisomerization of the guest molecule (R_{t-c}) measured in the *N* phase at T_{red} = 0.99 (R_{t-c}^{N}) as discussed in the preceding

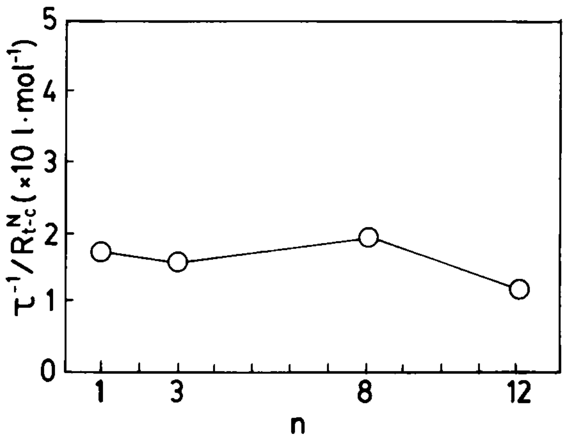


FIGURE 6 Corrected rates of the photochemical phase transition (τ^{-1}/R^{N}_{t-c}) of the 1ABn/PAPB3 mixtures as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm at T_{red} = 0.99.

paper.[3] In Figures 6–8 are shown the corrected rates of the photochemical phase transition (τ^{-1}/R^{N}_{t-c}) thus calculated.

It is worth mentioning here that the corrected rates of the photochemical phase transition obtained for the azobenzene guest/PAPB3 mixtures were lower by approximately one order of magnitude than those observed for the azobenzene guest/ECH206 mixtures,[3] although the rates of the photoisomerization were nearly identical in both mixtures. This result may be explicable in terms of low mobility of the mesogenic groups of PLC. The photoisomerization of the dopants proceeds approximately at the same rate in ECH206 and PAPB3 because of the effective

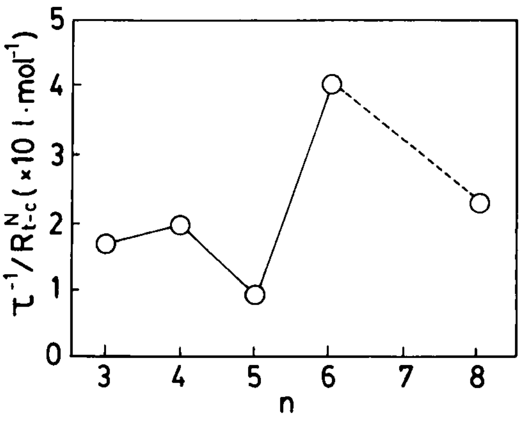


FIGURE 7 Corrected rates of the photochemical phase transition (τ^{-1}/R^{N}_{t-c}) of the 1ABnCB/PAPB3 mixtures as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm at T_{red} = 0.99.

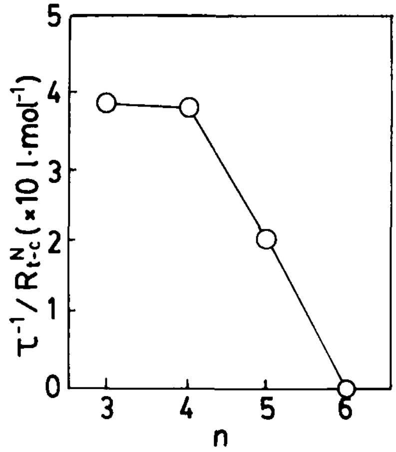


FIGURE 8 Corrected rates of the photochemical phase transition (τ^{-1}/R_{t-c}^{N}) of the AB(nCB)$_2$/PAPB3 mixtures as a function of the number of methylene units in the spacer chains. The concentration of the dopant was 1 mol % in the mixtures and photoirradiation was performed at 360 nm at T_{red} = 0.99.

free volume available for the dopants in the latter medium, so that the depression of T_{NI} of the mixtures is expected to occur to a similar extent in both media on photoirradiation. However, owing to the low mobility of the mesogenic groups in PLC, the isothermal phase transition is considered to take place much more slowly in the PLC matrix.

In the 1ABn/PAPB3 mixtures, the corrected rate of the photochemical phase transition was not affected by the methylene spacer *n* (Figure 6). This behavior seems reasonable in view of the fact that the rate of the photoisomerization was not significantly influenced by the spacer length (Figure 3). In contrast, in the 1ABnCB/PAPB3 mixtures an apparent odd-even effect of the methylene spacer length on the rates of the photochemical phase transition was observed (Figure 7). Namely, in the mixtures with guests of an even number of methylene chains the rate was high and in those of an odd number of *n* the rate was rather low. The AB(nCB)$_2$/PAPB3 mixtures showed a peculiar behavior for the photochemical phase transition (Figure 8). In the mixtures with *n* = 3 and 4, the rate of the photochemical phase transition was relatively high, but then it decreased rather monotonically with increasing *n*. In the mixture with *n* = 6, the phase transition could not be induced photochemically even though the photoisomerization of the dopant was found to proceed at a higher rate than that of the AB(4CB)$_2$/PAPB3 mixture (Figure 5). At the present stage of study, full interpretation can not be given to this result.

CONCLUSION

In the present study, various azobenzene derivatives were used as photochromic guests in PAPB3 and their ability to induce the photochemical phase transition of the guest/host mixtures was investigated. The photoisomerization of the azobenzene dopants was found to proceed at a similar rate to those mixtures composed of the same azobenzene dopants and a low molecular weight ester-type LC, ECH206, however, the rate of the photochemical phase transition was retarded approximately by one order of magnitude in comparison with those mixtures of the azo guest and ECH206. This is well interpreted in terms of the low mobility of the mesogenic moieties of PLC. PLCs are favored as hosts in the optical-image storage systems in view of the high stability of stored information, however, response is to be improved from the applicational point of view.

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