Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Shindo, T. and Uryu, T.(1993) 'Induction of smectic mesomorphism by mixing a non-liquid-crystalline methacrylate with a nematic liquid-crystalline compound having a cyano-containing mesogen', Liquid Crystals, 15: 2, 239 — 246
To link to this Article: DOI: 10.1080/02678299308031954
URL: http://dx.doi.org/10.1080/02678299308031954

LIQUID CRYSTALS, 1993, VOL. 15, NO. 2, 239–246

PRELIMINARY COMMUNICATIONS

Induction of smectic mesomorphism by mixing a non-liquid-crystalline methacrylate with a nematic liquid-crystalline compound having a cyano-containing mesogen

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(*Received 28 August 1992; accepted 18 March 1993*)

The structure and phase diagram of a binary mixture of a non-liquid-crystalline, mono-functional (meth)acrylate monomer and a liquid-crystalline compound having a cyano group-containing mesogen were examined. The monomers had mesogenic units such as biphenylene and phenyl benzoate, but did not show liquid-crystallinity. The liquid-crystalline compounds possessed a cyanobiphenyl or a cyanophenyl benzoate mesogenic unit. The liquid-crystalline 4-cyanophenyl 4′-*n*-octyloxybenzoate did not show a smectic A phase, while the binary mixture of the 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl monomer with 4-cyanophenyl 4′-*n*-octyloxybenzoate showed the induction of a smectic A phase in a nearly equimolar composition range. However, the binary mixture of the monomer, containing a phenyl benzoate group, and the liquid-crystalline compound did not induce a smectic phase.

We have previously reported electron-beam irradiation polymerization of binary mixtures consisting of a liquid-crystalline or non-liquid-crystalline (meth)acrylate monomer and a non-polymerizable liquid-crystalline compound [1–3]. Various types of monomers and liquid-crystalline compounds were examined. When a mixture of the methacrylate monomer, 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl (BMHB), and the liquid-crystalline compound, 4-cyanophenyl 4′-octyloxybenzoate (8CPB), was polymerized by an electron beam, a remarkable acceleration of the polymerization occurred [2]. In addition, this effect depended on the molar ratio of 8CPB. Thus, it was suggested that the mixing of the two compounds caused orientation of the monomer suitable for polymerization.

Miscibility studies have been utilized for the identification of liquid-crystalline mesophases. There are several reports of enhanced mesophase temperature ranges for binary mixtures of two kinds of liquid-crystalline compounds [4]. It has also been reported specifically for smectogenic, low molecular weight, thermotropic liquid crystals in appropriate proportions [5–7]. In a few cases, it was found that even if none of the components used formed a smectic phase, the induced phase was smectic [8].

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0267–8292/93 $10·00

Moreover, a mixture of a liquid crystal, containing a cyano group mesogen and one having a phenyl benzoate unit, showed an induced smectic phase [8]. It was suggested that the mixture formed a dipole-induced lamellar structure.

In this study, we wish to report the induction of a new liquid-crystalline phase, i.e. smectic, by mixing a non-liquid-crystalline methacrylate with a nematic liquid-crystalline compound containing a cyano group mesogen. These binary mixtures were characterized by means of optical microscopic observation, differential scanning calorimetry, and X-ray diffraction measurement.

Three kinds of acrylate or methacrylate monomers, i.e. 4-alkyloxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl, and 4-alkyloxyphenyl 4′-(ω-acryloyloxyalkyloxy) benzoate, in which the alkylene spacer is ethylene or hexamethylene, were synthesized according to the literature [9, 10]. All the liquid crystals, except for 4-cyano-4′-*n*-octyloxybiphenyl, were prepared according to the literature [11, 12]. 4-Cyano-4′-*n*-octyloxybiphenyl (Merck Ltd.) was used without purification.

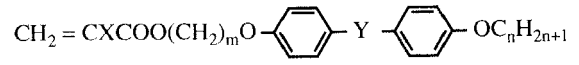
The structure and thermal properties of the acrylate or methacrylate monomers are shown in table 1. Although the monomers have such mesogenic units as biphenylene and phenyl benzoate, they did not show liquid-crystallinity. The structure and thermal properties of four cyano-group containing-mesogens are shown in table 2. 4-Cyanophenyl 4′-octyloxybenzoate, (8CPB), showed only a nematic mesophase in the first cooling, while the other three compounds exhibited smectic phases.

The phase diagram of a mixture of the 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl, (BMHB), monomer and 8CPB, measured by means of polarizing microscopic observation, is depicted in figure 1. Although 8CPB showed a nematic mesophase, the binary mixture containing BMHB, in the proportion between 50 mol% and 66 mol%, showed a smectic A phase. Thus, the mixing of a non-liquid-crystalline methacrylate, BMHB, with the nematogen, 8CPB, induced the formation of the smectic A phase. In addition, a mixed phase of smectic texture and crystal was observed in the mixture containing BMHB between 66 mol% and 80 mol%.

As shown in figure 2, a binary mixture of 33 mol% of BMHB and 67 mol% of 8CPB exhibited a nematic texture at 72°C. On the other hand, figure 3 is a photomicrograph of a binary mixture of BMHB and 8CPB, in an equimolar composition at 71°C, showing a smectic A phase with a focal-conic fan texture.

Sigaud *et al.* [7], studied a phase diagram of a binary mixture of a polar rod-like mesogen, as an acceptor, and a non-liquid-crystalline amino-substituted plate-like molecule, as a donor, revealing that the mixtures with the molar fraction of the plate-like compound between 0·1 and 0·2 showed induction of smectic A phases.

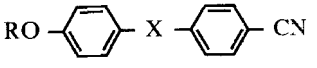
Table 1. Structure and thermal properties of monomers.



Monomer†	*X*	*Y*	*m*	*n*	Melting point/ °C
BMHB	CH_3	None	6	4	98–99
MPAEB	H	COO	2	1	87–89
EPAHB	H	COO	6	2	101–103

†BMHB: 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl. MPAEB: 4-methoxyphenyl 4′-(ω-acryloyloxyethoxy)benzoate. EPAHB: 4-ethoxyphenyl 4′-(ω-acryloyloxyhexyloxy)benzoate.

Table 2. Structure and thermal properties of liquid crystals.



Compound†	*R*	*X*	Thermal properties‡§/°C													
			First cooling							Second cooling						
8CPB	n-C_8H_{17}	COO	C	44	N	82	I			C	73	N	82	I		
10CPB	n-$C_{10}H_{21}$	COO	C	51	S	79	N	90	I	C	83	N	92	I		
CBOB	$CH_3(CH_2)_5CH(CH_3)CH_2$	$COOC_6H_4$	C	86	S	196	I			C	102	S	199	I		
8OCB	n-C_8H_{17}	None	C	30	S	66	N	79	I	C	55	S	67	N	80	I

†8CPB: 4-cyanophenyl 4′-*n*-octyloxybenzoate. 10CPB: 4-cyanophenyl 4′-*n*-decyloxybenzoate. CBOB: 4-cyanobiphenyl 4′-(2-methyloctyloxy) benzoate. 8OCB: 4-cyano-4′-octyloxybiphenyl.

‡Abbreviations: C, crystal; S, Smectic; N, nematic; I, isotropic melt.

§Measured by DSC at a scanning rate of 10°C min^{-1} and with a cross-polarizing microscope equipped with hot stage.

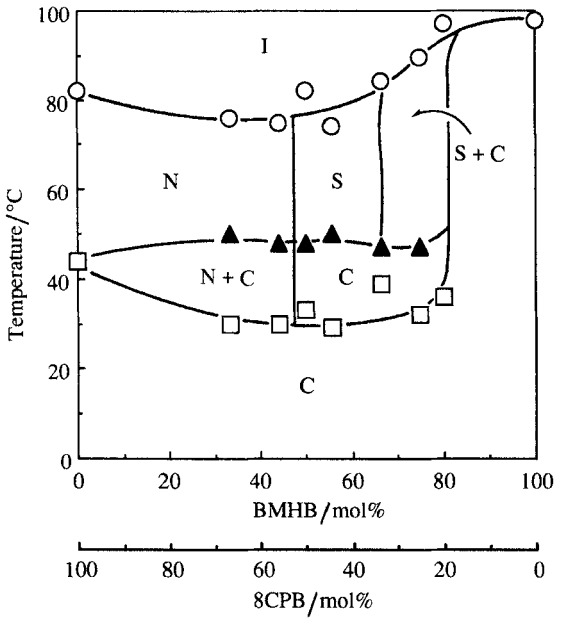


Figure 1. Phase diagram of binary mixture of 4-butoxy-4′-(ω-methacryloyloxyloxy)biphenyl and 4-cyanophenyl 4′-*n*-octyloxybenzoate. Phase identities: I, isotropic melt; N, nematic; S, smectic; C, crystal.

Oh [8], reported that a binary mixture of a 4-cyano-4′-*n*-alkoxybiphenyl and 4′-*n*-hexyloxyphenyl 4-*n*-butylbenzoate, in an approximately equimolar composition, exhibited an induced smectic A phase. They postulated a lamellar structure in which the two compounds are oriented by aggregating through the alternating cyano-containing dipole.

The phase diagram of the binary mixture of BMHB and 10CPB as depicted in figure 4 was examined in detail. When the proportion of BMHB was in the range of 10 to 40 mol%, the binary mixture caused an increase in the temperature range of the nematic phase. When the proportion of BMHB was increased to the range of 50 to 65 mol%, the smectic phase temperature range was enhanced with complete disappearance of the nematic phase.

Effects of the structure of the liquid-crystalline compounds on the orientation of molecules were then examined. Phase diagrams of the binary mixture of BMHB with 4-cyanobiphenyl-4′-(2-methyloctyloxy)benzoate, (CBOB), containing the cyanobiphenyl benzoate mesogenic unit, or 4-cyano-4′-octyloxybiphenyl, (8OCB), possessing a biphenyl mesogenic unit, both of which exhibit smectic mesophases, are shown in figures 5 and 6, respectively. In these binary mixtures, the mesophase, thermal stabilities of the pure mesogens were not enhanced by mixing with the BMHB monomer. Although 8OCB has the same mesogenic group as that of BMHB, its miscibility with BMHB was lower than that of 8CPB with BMHB.

By fixing 8CPB as the liquid-crystalline compound, the effects of two monomer structures were examined. The monomers contained the mesogenic, phenyl benzoate unit such as MPAEB and EPAHB. Neither mixture exhibited an induced smectic phase, or an enhancement in mesophase stability.

The thermal properties, examined by means of differential scanning calorimetry (DSC), are summarized in table 3. Liquid-crystalline 8CPB and non-liquid-crystalline

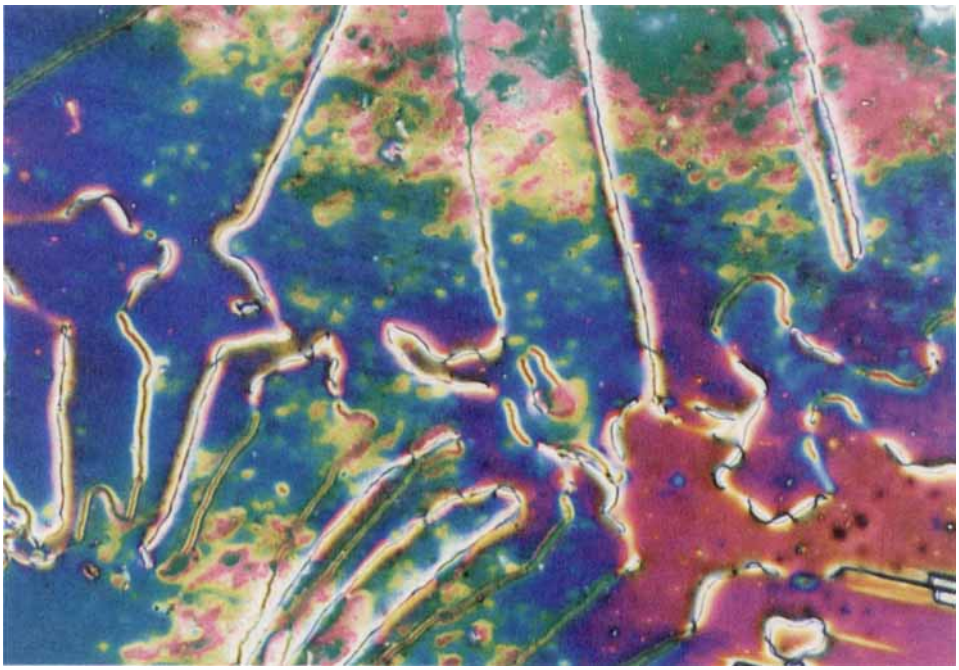


Figure 2. Photomicrograph of the binary mixture of 33 mol% of 4-cyano-4′-(ω-methacryloyloxyhexyloxy)biphenyl and 67 mol% of 4-cyanophenyl 4-*n*-octyloxybenzoate at 72°C.

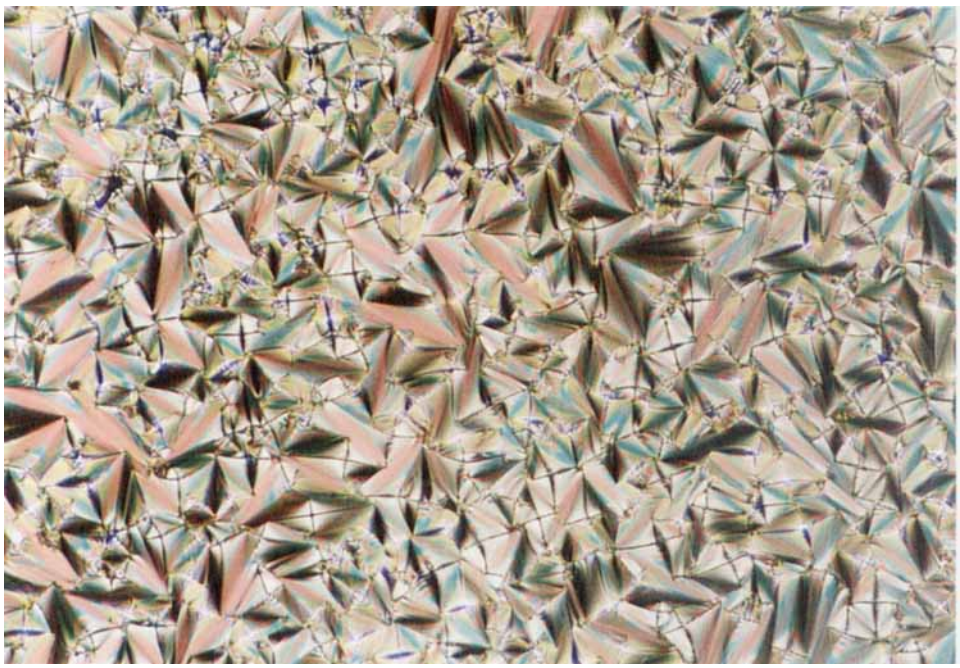


Figure 3. Photomicrograph of the binary mixture of 4-cyano-4′-(ω-methacryloyloxyhexyloxy)benzoate and 4-cyanophenyl 4-*n*-octyloxybenzoate in an equimolar composition at 71°C.

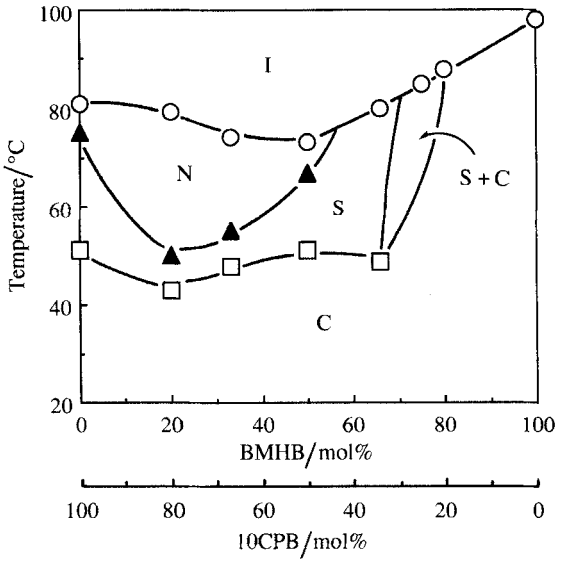


Figure 4. Phase diagram of the binary mixture of 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl and 4-cyanophenyl 4′-*n*-decyloxybenzoate. Phase identities: I, isotropic melt; N, nematic; S, smectic; C, crystal.

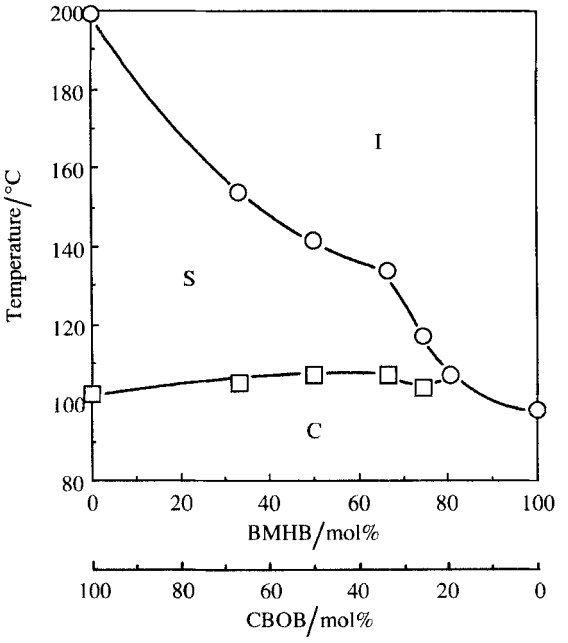


Figure 5. Phase diagram of the binary mixture of 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl and 4-cyanobiphenyl-4′-(2-methyloctyloxy)benzoate. Phase identities: I, isotropic melt; S, smectic; C, crystal.

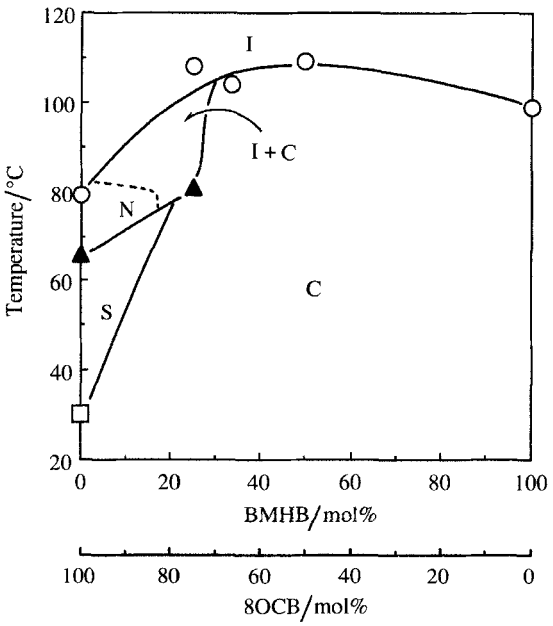


Figure 6. Phase diagram of the binary mixture of 4-butoxy-4′-(ω-methacryloyloxyhexyloxy) biphenyl and 4-cyano-4′-*n*-octyloxybiphenyl. Phase identities: I, isotropic melt; N, nematic; S, smectic; C, crystal.

Table 3. Thermal properties of binary mixtures.

BMHB/8CPB or 10CPB† Molar ratio	Thermal properties ‡§/°C						
8CPB							
33:67	C	31	N+C	50	N	76	I
50:50	C	33	C_2	48	S	82	I
66:34	C	32	C_2	47	S+C	83	I
10CPB							
20:80	C	48	S	54	N	79	I
33:67	C	48	S	55	N	74	I
50:50	C	48	S	67	N	73	I

†BMHB: 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl. 8CPB: 4-cyanophenyl 4′-*n*-octyloxybenzoate. 10CPB: 4-cyanophenyl 4′-decyloxybenzoate.

‡Abbreviations: C, C_1, C_2, crystal; S, smectic; N, nematic; I, isotropic melt.

§Measured by DSC at a scanning rate of 10°C min^{-1} and with a cross-polarizing microscope equipped with hot stage.

BMHB exhibited two peaks and one peak, respectively, while the DSC curve of the binary mixture of the two compounds showed several peaks due to different phase transitions. By addition of 33 mol% of BMHB to 8CPB, the mixture showed a nematic phase from 50 to 76°C. The binary mixture in an equimolar composition exhibited three peaks, indicating the transition from crystal to crystal at 33°C, from crystal to smectic at 48°C, and from smectic to isotropic melt at 82°C.

Wide-angle X-ray diffraction patterns of 8CPB, BMHB, and binary mixtures of BMHB and 8CPB were measured. 8CPB had sharp reflection patterns, while BMHB did not show regular reflection patterns, indicating that BMHB has a lower crystallinity than 8CPB. In comparing the two mixtures, one consisting of 33 mol% BMHB and the other of 50 mol% BMHB, it was recognized that by mixing 8CPB with BMHB of low-crystallinity many additional sharp diffractions appeared.

The examination of the phase diagrams of binary mixtures of non-liquid-crystalline acrylate or methacrylate monomers and a liquid-crystalline compound containing a cyano group mesogen, revealed a higher molecular orientation of the two compounds. The binary mixture of 4-butoxy-4′-(ω-methacryloyloxyhexyloxy)biphenyl and 4-cyanophenyl 4′-*n*-octyloxybenzoate showed the induction of the smectic A phase in a nearly equimolar composition range, though pure compounds alone exhibited no smectic phases.

The binary mixtures were prepared in glass tubes by cooling from the heated isotropic melt. The mesophase behaviour was examined using a polarizing microscope equipped with a Linkam TH-600RMS, or a Mettler FP 82HT, hot stage with a FP 80HT central processor, at a cooling rate of $10°C\,min^{-1}$ in the first cooling. Thermal analysis was carried out with a Perkin–Elmer DSC-7 calorimeter. X-Ray diffraction was measured with a Rigaku RINT-1500 X-ray diffractometer.

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