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Synthesis and Properties of Comb-Like Liquid Crystalline Polymers with Electrooptically Active Mesogenic Side Groups

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Synthesis and Properties of Comb-Like Liquid Crystalline Polymers with Electrooptically Active Mesogenic Side Groups

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A system of non-centrosymmetric mesogens (4, nitrobenzylidene-2'-methylphenol(M2) and 4, cyanobenzylidene-2'-methylphenol(M5)) and their corresponding alkanol phenoxy ethers (M2C8 and M5C8) was investigated. The mesomorphic properties of mixtures of these low molecular mass compounds were established. The properties of homo and random copolymers of M2 and M5 attached as side-groups via a C8 spacer to a poly(methyl methacrylate) backbone were studied. A phase diagram was obtained. The thermo-mechanical relaxation properties of this system were also investigated by means of thermo-stimulated currents. While monotropic namatic mesophases dominate the low molecular mass M2C8–M5C8 system, the copolymers display an enantiotropic nematic behaviour. Two relaxation processes dominate the thermomechanical response of this copolymer system. One is interpreted as related to the segmental motion of the backbone (α-peak), the second, to the motion of the mesogenic groups (δ-peak). While the parameters related to the alpha peak relaxation such as the activation energy or relaxation times are not strongly affected by copolymer composition, the delta relaxation is affected by the composition of the copolymer.

Keywords: Electrooptical activity, L.C. Polymers, noncentrosymmetric mesogens

INTRODUCTION

The design of liquid crystalline polymers with moieties displaying large second and third order nonlinear polarizabilities is of considerable practical and theoretical interest (1). Of particular interest are comb like polymers in which structural moieties with a non-centrosymmetric acceptor-donor structure are attached as side groups to a polymer chain (2). Particular attention is devoted in this work to groups which in addition to their non-centrosymmetric structure and electron acceptor and donor substituents (features promoting nonlinear optical properties) display a high potential for liquid-crystallinity. Such moieties are for example cyano and nitro substituted

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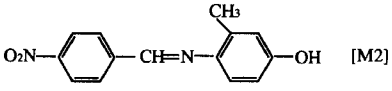
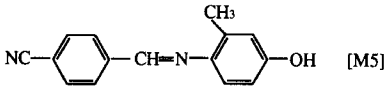
benzylidene phenols such as M2 and M5:



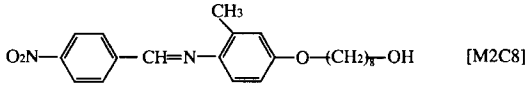
[M2]



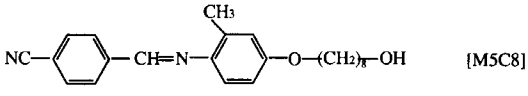
[M5]

The main features of M2 and M5 is the presence of acceptor-donor substituents on a rigid and anisotropic moiety, conjugation and non-centrosymmetry all promoting simultaneously liquid crystallinity and NLO properties.

A sequence of eight methylene groups is introduced into M2 and M5 by polyetherification leading to:



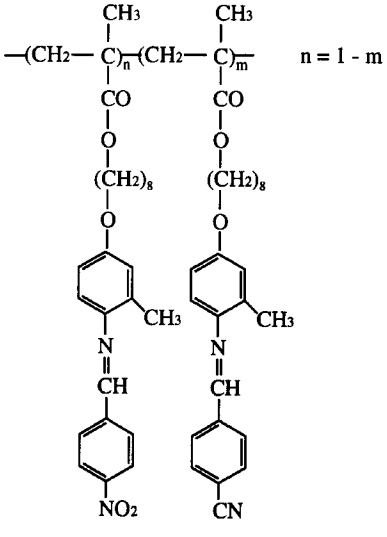
[M2C8]



[M5C8]

In what follows the properties of M2C8, M5C8 as well as the properties of the corresponding homo and copolymers are described.

The copolymer of M2C8MA and M5C8MA is a statistical copolymer with mesogenic side groups decoupled from a moderately rigid poly(methylmethacrylate) backbone via a flexible spacer containing a sequence of eight methylene groups:



Copolymer of M2C8MA and M5C8MA

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EXPERIMENTAL SECTION

Synthesis of monomers and polymers. Schemes 1 and 2 summarize the synthesis of intermediate low molecular mass compounds M2, M5, M2C8, M5C8 and monomers M2C8MA and M5C8MA and of their polymers and copolymers.

Synthesis of M2 and M5

0.2 moles of *p*-nitrobenzaldehyde (or *p*-cyanobenzaldehyde) and .2 moles of 4-amino *m*-cresol are added with 600 ml of benzene and 100 ml of absolute alcohol under stirring. After 30 min. of stirring the solution was slowly heated on a steam bath and the solvents slowly distilled off at ca. 60°C. The boiling temperature of the solution went gradually up. The reaction was stopped at 80°C and the excess of benzene was removed by evaporation. The crude product was dissolved in acetone and refluxed for 2 h in presence of activated charcoal. The solution was filtered and acetone evaporated. The final product was 4 times recrystallized from methanol. The final product was orange (M2) and yellow (M5). The yield in both cases was 70–80% and the results of the elemental analysis were satisfactory (see Table 1).

Synthesis of M2C8 and M5C8

Mixture of .05 mole of M2 (or M5) and .055 mole of 8-bromo-octanol, .075 mole of K2CO3 and 350 ml of distilled acetone was mixed and stirred in a dry nitrogen atmosphere followed by refluxing for 7–9 days until the color of the solution became orange in the case of M2C8 (or yellow in the case of M5C8). After evaporation of the solvent the crude product was added with 200 ml of methylene dichloride and 100 ml of water and shaken in a separatory funnel. The organic layer was separated and washed with 100 ml of water (twice) followed by a 70 ml of aqueous 2N NaOH solution (3 times). It was than dried over $MgSO_4$, filtered and the solvent evaporated. The crude product was dissolved in acetone and refluxed in presence of activated charcoal for 2 h, this was followed by filtration and evaporation of the solvent. The product was recrystallized from methanol (twice) and from acetone (twice). Orange colored crystals (M2C8) and yellow colored crystals (M5C8) were obtained. The yield was in both cases 60–70%. The results of elemental analysis were satisfactory. (Table I)

Synthesis of monomers M2C8MA and M5C8MA

0.01 mole of M2C8OH (or M5C8OH) were added with 1.5 ml of triethylamine and dissolved in 30 ml of pure tetrahydrofurane (THF). To the above solution was added dropwise a solution of .011 M of freshly distilled methacryloylchloride in 10 ml of THF. The mixture was than stirred for 10 h and refluxed for 2 h. After cooling the solution was acidified with 2N HCl (until a pH of 4–6) and 50 ml of methylenedichloride and 30 ml of saturated NaCl solution were added. The organic layer was decanted and washed repeatedly with 30 ml of 2N NaOH (5 times), followed by 30 ml of concentrated NaCl solution (3 times), and finally with 30 ml of distilled water (2 times). After

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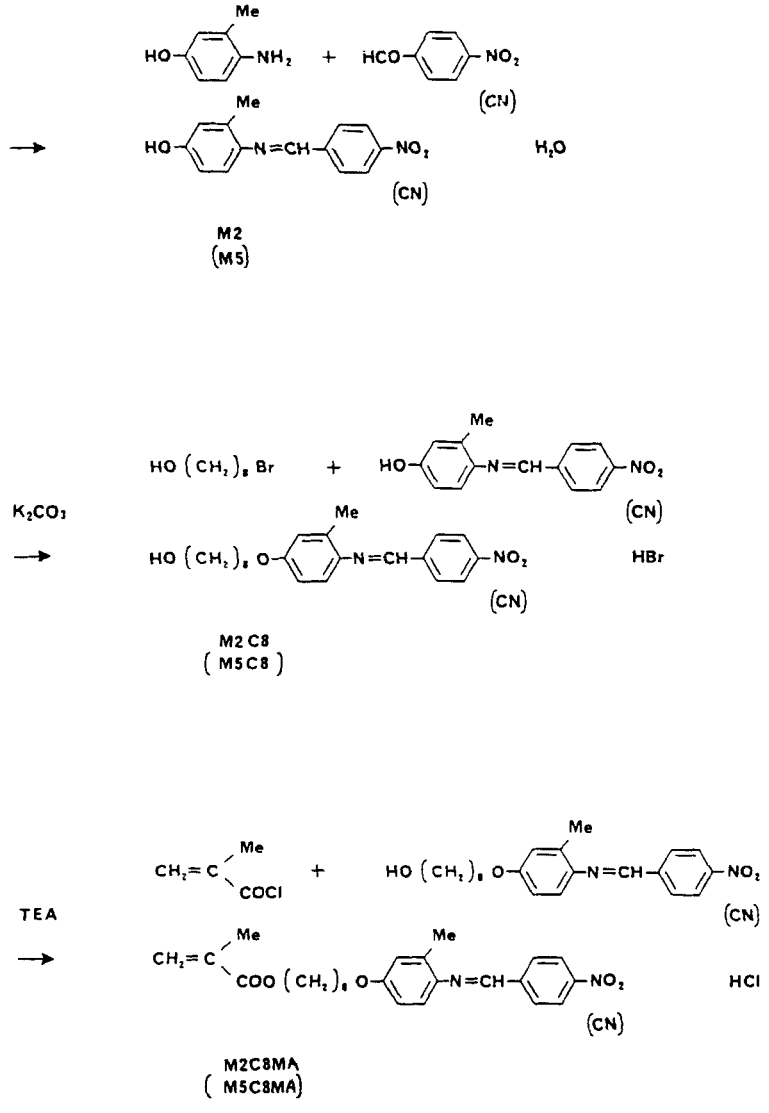

SCHEME 1 Synthesis of intermediate M2, M5, M2C8, M5C8 and of monomers M2C8MA and M5C8MA.

evaporation of the solvent the product was repeatedly recrystallized from acetone. Yield 60–80%. The results of elemental analysis were satisfactory.

Polymerization and co-polymerization of M2C8MA and M5C8MA

The polymerization technique was similar to the procedure of Shibaev *et al.* (3) with some modifications: polymerization ampoules were filled with a 10% by wt. solution of

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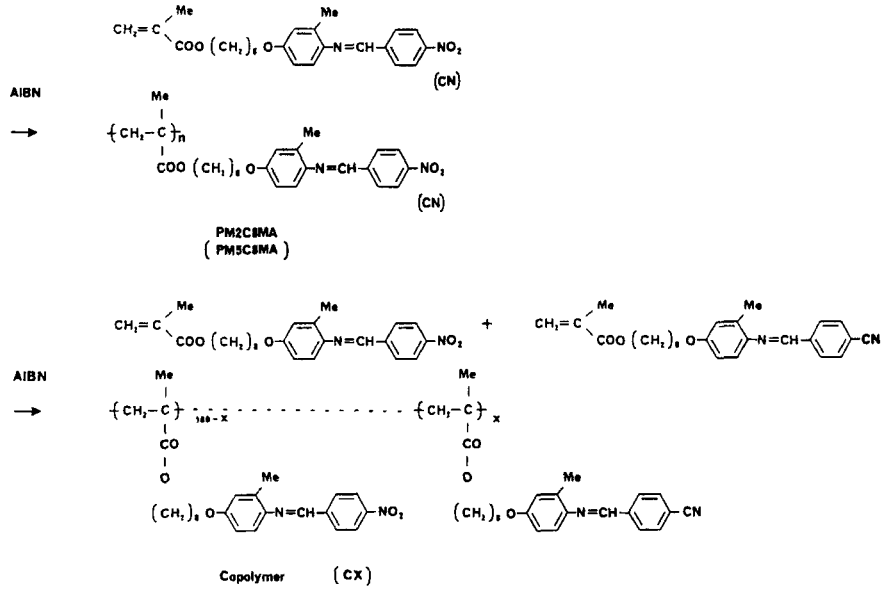

SCHEME 2 Polymerization and co-polymerization of M2C8MA and M5C8MA.

the monomer in benzene to which was added 0.05% by wt. of AIBN (Azoisobutyronitrile). The ampoules were cooled (dry ice) and evacuated to 10–3 mm and thawed. This process was repeated several times before the ampoule was sealed and placed for 50–70 h at 60°C. (Polymerization at higher temperatures may lead to some insolubility of the polymer) The empoule's content was than stirred drop-wise into hexane. The precipitated polymer was filtered, redissolved in methylenedichloride and precipitated first into methanol and than into methanol–acetone (1:1). After filtration the polymers were dried in vacuo at 40°C. The yield was 10–40%.

Characterization of Synthesized Compounds

Standard characterization included IR and UV spectroscopy, DSC measurements, polarizing microscopy, GPC and capillary viscometry. Molecular masses of polymers and co-polymers were determined by GPC. Standard samples of polystyrene were used for calibration. Table 2 illustrates the molecular masses of homo- and co-polymers of M2C8MA and M5C8MA system.

DSC thermograms were used to locate the phase transitions in monomers and polymers (Perkin Elmer 2C Model). Both DSC and I.R. spectroscopy (Perkin–Elmer 1600 series Fourier Spectrometer) were used to characterize the polymers and co-polymers. In order to determine the actual composition of copolymers in addition to elemental analysis, quantitative IR measurements were performed: $\nu C{=}N$ at $2228\,cm^{-1}$ and $\nu C{-}NO_2$ ($1522\,cm^{-1}$ and $1342\,cm^{-1}$) were taken as vibrations characteristic of M2C8MA and M5C8MA units respectively and $\nu C{=}O$ as the

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TABLE 1

Elemental Analysis of Monomers and Polymers

Compounds	C (F)	C (C)	H (F)	H (C)	N (F)	N (C)
M2	64.17;	65.63;	5.18;	4.69;	10.38;	10.94;
M5	76.21;	76.27;	5.13;	5.08;	11.82;	11.86;
M2C8	68.68;	68.75;	7.35;	7.29;	7.28;	7.29;
M5C8	75.75;	75.79;	7.74;	7..74;	7.78;	7.69;
M2C8MA	68.96;	69.01;	7.20;	7.13;	6.17;	6.19;
M5C8MA	75.14;	74.97;	7.67;	7.46;	7.12;	6.48;
PM2C8MA	68.96;	69.01;	7.20;	7.13;	6.17;	6.19;
PM5C8MA	74.98;	74.97;	7.36;	7.46;	6.43;	6.48;
Copolymer Mole%PM5C8MA						
20	69.84;	70.20;	7.19;	7.20;	6.39;	6.25;
30	71.04;	70.80;	7.26;	7.23;	6.32;	6.28;
50	72.25;	71.99;	7.34;	7.30;	6.52;	6.34;
60	72.28;	72.59;	7.40;	7.33;	6.49;	6.36;
70	73.38;	73.18;	7.37;	7.36;	6.50;	6.39;
80	73.52;	73.78;	7.39;	7.39;	6.35;	6.42;
90	74.32;	74.37;	7.39;	7.43;	6.47;	6.45;

TABLE 2

Thermal Properties of the PM5C8MA-PM2C8MA Copolymers

Copolymer Mole % PM5C8MA	M_n	T_g °C	T_{NI} °C	ΔH_{NI} cal/g
00	72,800	38.3	–	–
20	49,400	42.7	59.7	0.04
30	49,400	42.2	60.9	0.04
50	51,900	42.0	65.6	0.16
60	57,000	41.9	69.4	0.28
70	49.400	41.0	69.3	0.32
80	60,000	42.3	68.2	0.23
90	54,500	41.4	73.6	0.53
100	45,000	42.9	75.1	0.58

internal reference. Films were cast on KBr crystal plates. Figure 1a and b gives the FTIR spectra of the copolymers and the IC=N/IC=O at $\lambda = 1342\,\text{cm}^{-1}$, versus the composition of the copolymer in Mole % of M5 in the feed. The dependence is linear suggesting a random distribution of comonomeric units.

Polarizing microscopy was performed using a Leitz Ortholux polarizing microscope equipped with a hot stage and a Mettler FP-52 temperature programmer. Viscosity measurements were done in tetrachloroethane at 30°C using an Ubbelohde dilution viscometer.

X-ray diffractograms were obtained with a Warhus flat plate camera mounted on a Hitachi generator, using Ni-filtered CuK alpha radiation of 1.54 A with a sample to film distance 5 cm (WAXS) and 17 cm (SAXS).

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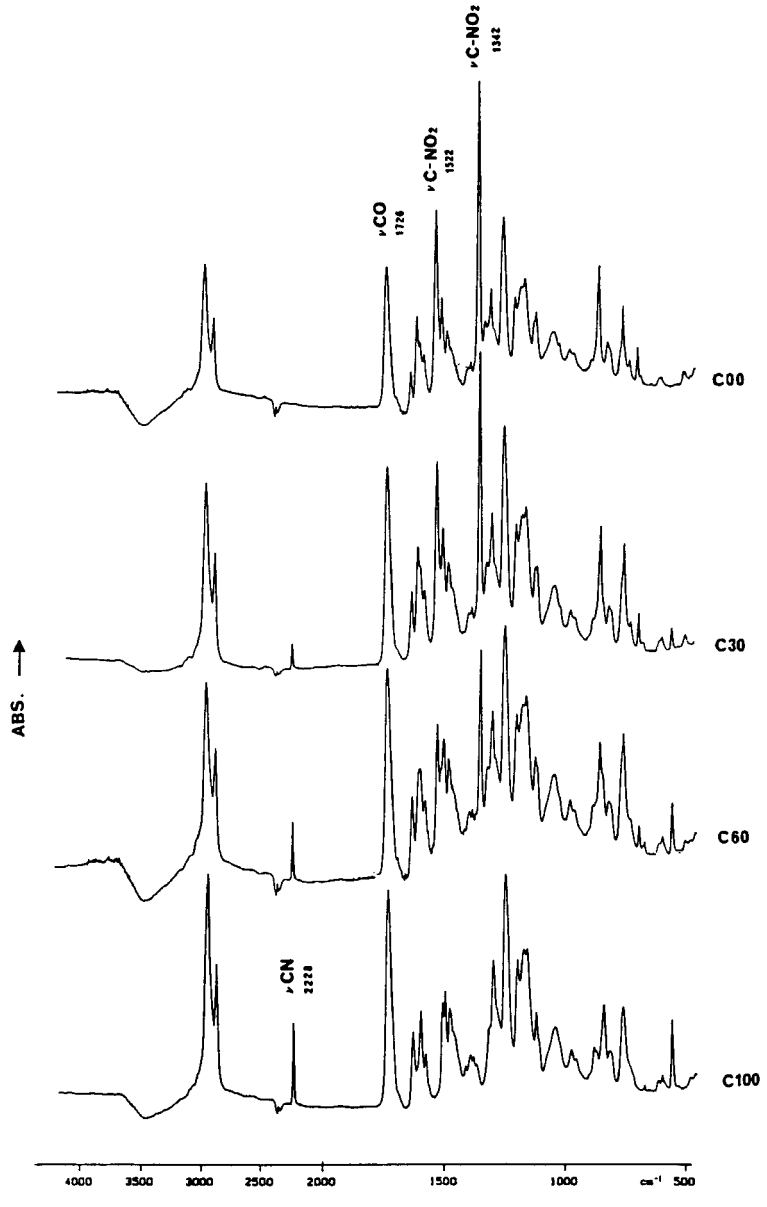
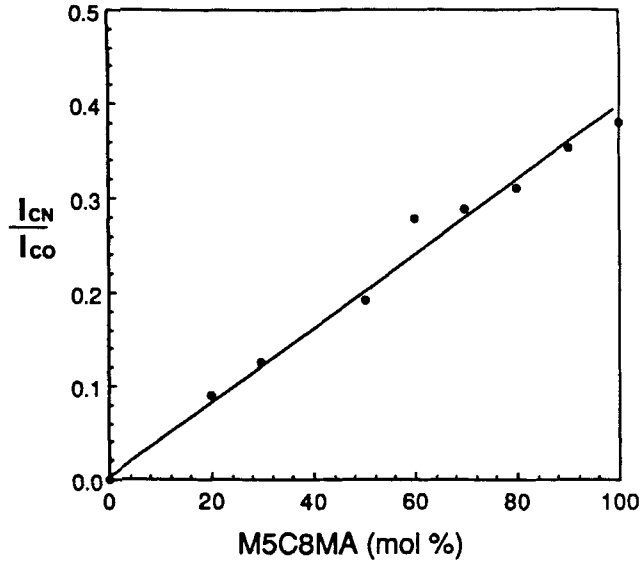


FIGURE 1a FTIR spectrum of the M2C8MA-M5C8MA copolymer system.

Study of the Dielectric Behavior of the PM2C8MA-PM5C8MA Copolymer System by Thermally Stimulated Currents

The thermostimulated currents method (TSC) (4) is closely related to dielectric relaxation. The material is poled in a dc electric field at a temperature $T > T_g$. The



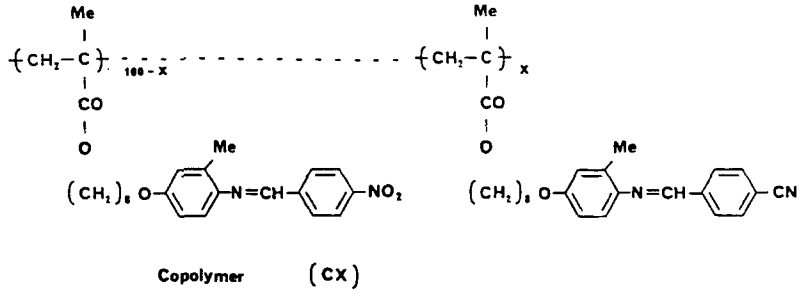


FIGURE 1b I_{CN}/I_{CO} versus copolymer composition.

dipole orientation is than quenched by rapid cooling and than reheated at a controlled rate while monitoring closely the current due to dipole disorientation (depolarization current). The stronger the alignment of dipoles the more intense the current $J(T)$. A peak of $J(T)$ at Tm reflects therefore a relaxation temperature of a specific set of dipoles. The method has been successfully used in the study of side-chain polymer liquid-crystals (see e.g., (5) The relaxation time τ is given by $\tau(T) = P(T)/J(T)$, with $P(T)$-polarization and $J(t)$ the depolarization current and $\tau = \tau_0 . \exp(E_a/kT)$, with E_a the activation energy of the relaxation determined from the slope of $\ln P[(T)/J(T)]$ as a function of $1/T$. On the other hand the knowledge of $Po = J(t)dt$ allows the determination of the relative dielectric dispersion $\Delta\varepsilon = \varepsilon_s - \varepsilon$, since $Po = (\varepsilon_s - \varepsilon)E$ with E the applied field, ε_s and ε the static and the high frequency dielectric permittivity.

The experimental set up is described originally by Laj (6) and is given in Figure 2. The sample is placed between the plates of a condenser. The voltage used is of a few

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THERMOSTIMULATED CURRENTS

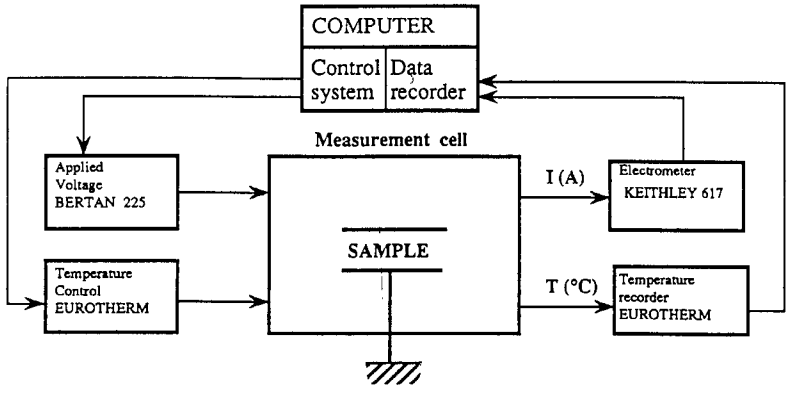

FIGURE 2 Thermostimulated currents (TMC): the set-up (5)

thousand volts and the film thickness of the sample is .5–.7 mm. The whole apparatus is placed in a cryostat-thermostat in which the temperature can vary from − 180 up to 300°C under controlled atmosphere and which provides an electrostatic caging of the condenser. The plates are insulated by means of teflon. The depolarization current is measured with an electrometer (Keithley 617) coupled with a two channel recorder, recording the temperature of the sample (thermocouple).

RESULTS AND DISCUSSION

Texture of M2C8 and of M5C8 in their nematic phase close to their isotropic-nematic transitions at 55.5 and 73.4°C respectively are given in Figure 3a and b. One observes in both cases a tendency for homeotropic anchoring. Such a tendency is not surprising since the paraffinic chain of 8-CH_2-units increases the amphiphilic character of these molecules.

The transition temperature versus composition for mixtures of low molecular mass intermediates M2C8–M5C8 are given in Figure 4. Both compounds are monotropic giving a nematic mesophase on cooling Mixtures of M2C8–M5C8 give an eutectic at 20 mole%. The attachment of methacrylic radical to these nematic moieties appears to destroy their liquid-crystalline character as M2C8MA monomer displayed a crystalline melting between 63.2 and 63.7°C, while crystals M5C8MA melt between 57–58°C.

Table 2 and Figure 5 summarize the thermal data on polymers and copolymers of M2C8MA and PM5C8MA. The polymers and copolymers display a strong tendency for supercooling and no crystallization of PM5C8MA and of copolymers of M2C8MA and M5C8MA was observed. PM2C8MA displayed on the first heating a small endothermic peak at 51–52°C which disappeared on cooling and was not observed on reheating. From thereon PM2C8MA displayed a T_g only. No birefringence was

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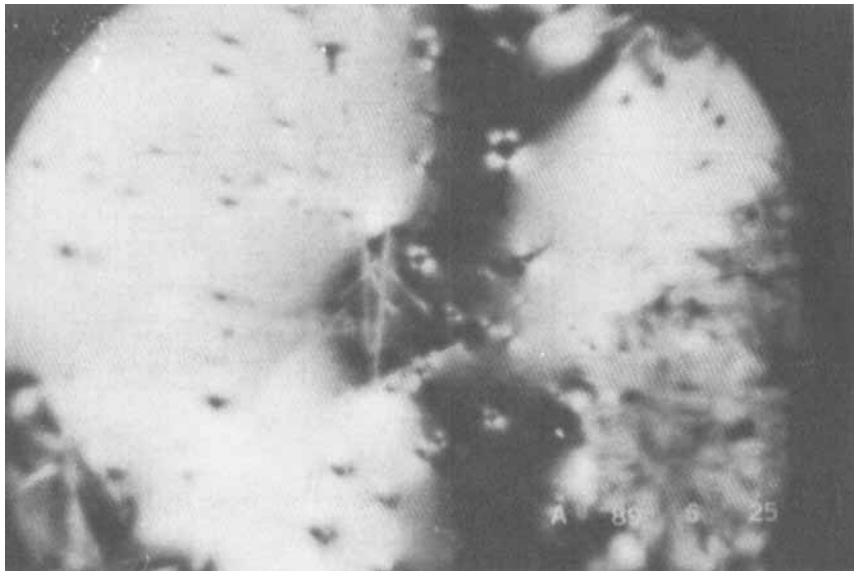

FIGURE 3a Polarizing micrograph of the nematic phase of M2C8 at 55.6°C (X 200). Homeotropic nematic anchoring destroyed by pressure (needle). See Color Plate V.

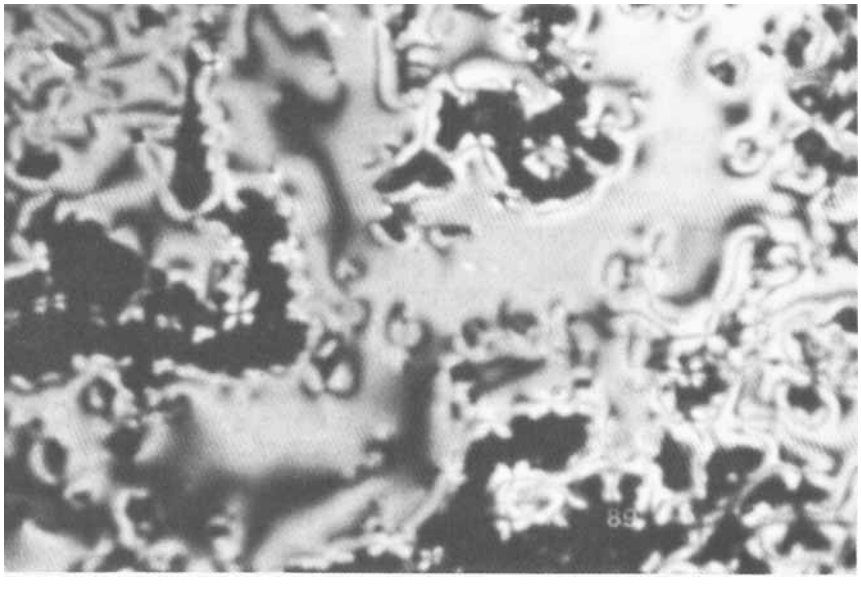

FIGURE 3b Polarizing micrograph of the nematic phase of M5C8 at 74.3°C. Tendency to homeotropic anchoring. See Color Plate V.

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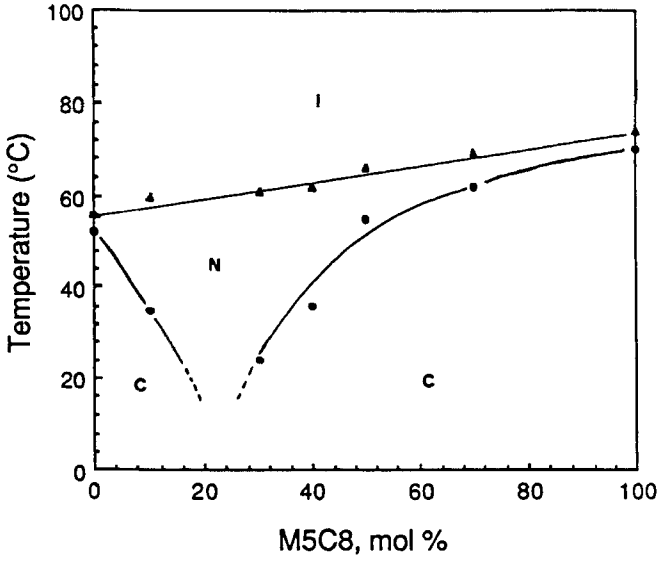

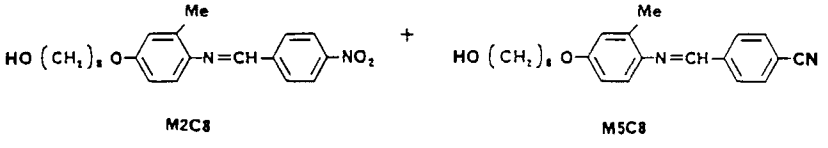

FIGURE 4 The phase diagram of mixture of M2C8 and M5C8.

detected on heating or cooling of PM2C8MA thereby confirming the isotropic nature of this polymer. In contrast, PM5C8MA displayed a rather large temperature interval of nematic flow on both, heating and cooling. On cooling below T_g a nematic glass was obtained as judged from a typical nematic "schlieren" texture under the polarizing microscope. It is interesting that an enantiotropic nematic polymer is obtained from a monomer (M5C8MA) which itself is not mesomorphic.

The nematic nature of M5C8MA and M2C8MA copolymers was also confirmed by absence of a small angle X-ray scattering pattern (SAXS pattern) and the presence of a single halo in the wide angle X-ray diffraction region (WAXS diffraction pattern). The copolymer appears to have a random composition of repeating units as is suggested by the linear variation of relevant I.R. absorption bands with composition (Figure 1) and by the uniform variation of the isotropization enthalpy ΔH_{NI} with composition (see Table 2). One can see from the phase diagram (Figure 5) that copolymerization of M5C8MA with M2C8MA did not affect strongly the nematic interval up to compositions of 80–90 mole% of M2C8MA. This is most interesting as the nitro substituted mesogen is contributing in a predominant way to NLO and copolymers composition-

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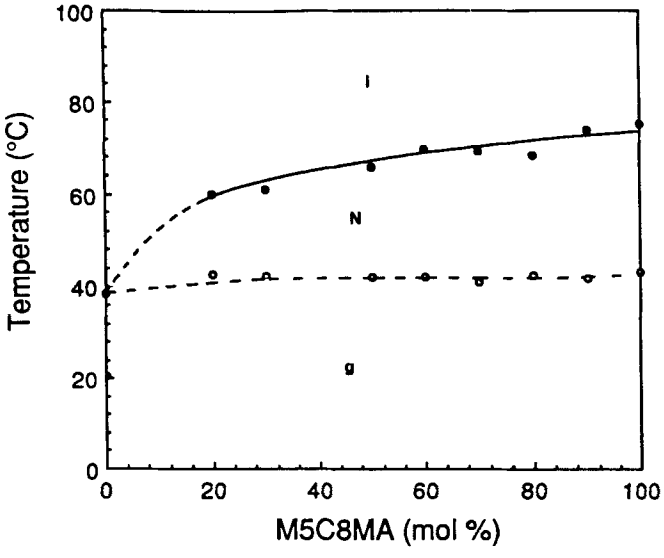

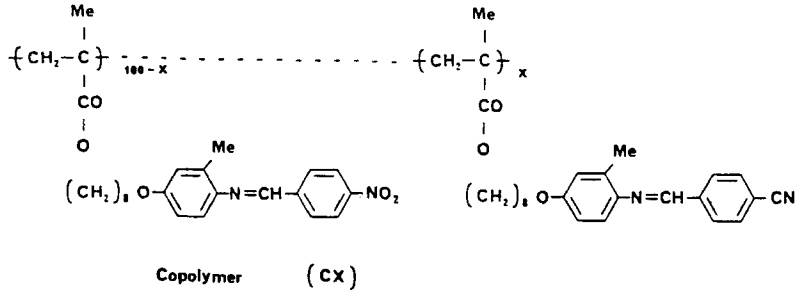

FIGURE 5 The phase diagram for the M2C8MA–M5C8MA copolymer system.

ally rich in the nitro-group can still preserve large nematic intervals and therefore display a high potential for orientation.

The dielectric relaxation of this copolymer system was studied by the thermo-stimulated currents technique. A typical experimental run is shown in Figure 6. Cooling from above T_g one can observe two relaxation peaks: one located at low temperature $T_{M\alpha}$ (high frequency) at temperature between 48–50°C or the α-relaxation peak, the second located at higher temperature $T_{M\delta}$ (low frequency) at temperatures between 70 and 80°C or the δ-relaxation peak. For copolymers in the mid compositional range (about 40–60 mole%) a splitting of the δ-peak into two peaks was observed. For PM5C8MA only a single peak was observed at an intermediate T_M of 59°C possibly indicating a coalescence of the alpha and delta relaxation peaks.

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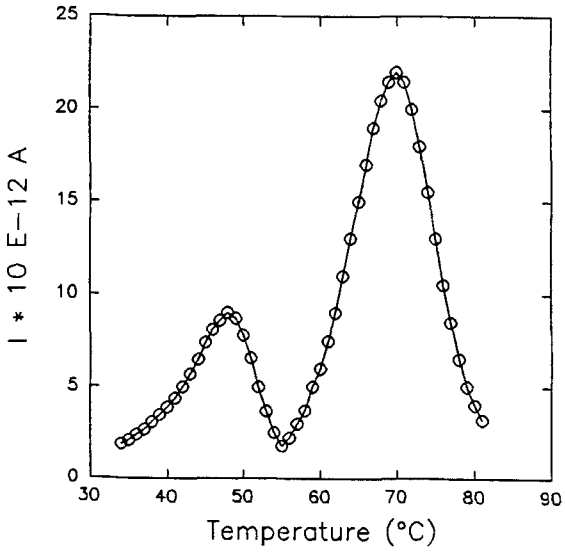

FIGURE 6 TMC spectrum for the homopoly (M2C8MA).

The Table 3 shows the evolution of $T_{M\alpha}$, $E_{a\alpha}$ and τ_α with composition for the copolymer system. One can see that as expected the α-relaxation peak follows closely the T_g of the copolymer. For very high or low compositions in M5C8MA one records a small decrease of τ_α (scaled to 50°C). For all other compositions $\tau\alpha$ is approximately constant and close in value to the relaxation times for both homopolymers. The energy of activation for the alpha relaxation $E_{a\alpha}$ follows approximately T_g. The relaxation times at 20 and 80 mole% of M5C8MA show a small increase with respect to other compositions.

The delta relaxation behaviour is shown in Table 4. The homopolymer PM5C8MA gave only one peak at 59°C a possible coalescence of the α and δ peaks or an artifact due to enhancement of conductivity in the sample interfering with the recording of the δ peak. Two compositional regions can be clearly distinguished, one in which both

TABLE 3

Evolution of the α-Peak Parameters with Copolymer Composition

PM5C8MA (Mole %)	T_g (°C)	$T_{n/i}$ (°C)	ΔH (cal/g)	TM_α (°C)	$E\alpha$ eV	τ_α (50 °C)	$\Delta\varepsilon\alpha$
0	38.3	–	–	48	1.75	26	1.43
20	42.7	59.7	0.04	50	1.85	35	1.72
30	42.2	60.9	0.04	49	1.79	30	1.30
50	42.0	65.6	0.16	49	1.77	30	2.14
60	41.9	69.4	0.28	49	1.71	30	1.17
70	41.0	69.3	0.32	49	1.70	32	1.19
80	42.3	68.2	0.23	–	–	–	–
90	41.4	73.6	0.53	50	1.81	37	0.35
100	43.1	81.5	0.58	59	1.84	24	0.73

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TABLE 4

Evolution of the δ-Peak Parameters with Copolymer Composition

PM5C8MA (Mole %)	TM δ (°C)	$E\delta$ (eV)	$\tau\delta$ (60°C) in s	$\tau\delta$ (80°C) in s	$\Delta\varepsilon_\delta$	$\Delta\varepsilon_\alpha + \Delta\varepsilon\delta$
0	71	1.93	340	8	3.4	4.83
20	74	1.61	422	18	0.6	2.32
30	77	1.48	620	34	2.0	3.30
50	69	1.75	220	7	0.3	2.43
60	74	1.90	590	18	0.7	1.87
70	80	1.52	1095	55	7.7	8.89
80	–	–	–	–	–	–
90	66	1.62	130	5	0.3	0.65
100	–	–	–	–	–	0.73

comonomers are in similar amounts and in which a split in the δ-relaxation peak is observed, the other in which the amount of one co-monomer predominates and is characterized by a single δ-relaxation peak. In this last region one can note an increase of $T_{M\delta}$ and of the relaxation time τ_δ. If we attribute the δ-relaxation to molecular motions of mesogenic side-groups our results suggest that a cooperative motion of both mesogenes predominate at extreme compositions (one single δ-peak) while at equivalent compositions each mesogene is trying to move separately.

The values of $\Delta\varepsilon_\delta$ (between 0.2–3) are small for mesogens endowed with strong dipoles such as M5 or M2 and this suggest a rather extensive interdigitation of mesogens canceling out some of the dipolar components.

In conclusion two low molecular mass mesogenic compounds a *p*-nitrosubstituted Schiff base and a *p*-cyano substituted Schiff base with strong acceptor-donor properties as well as the corresponding side chain homo- and copolymers were synthesized and studied. Monotropic nematic mesophases were found in the corresponding low molecular mass compounds. Homopolymer and copolymers containing the cyano substituted mesogen displayed enantiotropic nematic mesophases. The homopolymer containing the nitro-substituted mesogen was not liquid crystalline. While the nitro substituted polymer is not mesomorphic, small amounts of the cyano component induce an enantiotropic nematic mesophase in the copolymer. Hence a copolymer with a strong nitro-component of up to 90 mole% (with higher NLO potential) displays an enantiotropic nematic mesophase in a broad interval of temperatures. Two processes dominate the relaxation behaviour of this copolymer system: the first centered around 50°C is coupled with the glass transition (α-relaxation) and is related to segmental motion of the polymer chain, the second, centered around 70°C and related to the motion of the mesogenic molecular groups (δ-relaxation). A cooperative motion of mesogenic groups appears to predominate at extreme compositions while at equivalent comonomer compositions the motions of cyano and nitro mesogenic groups appear to be segregated.

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