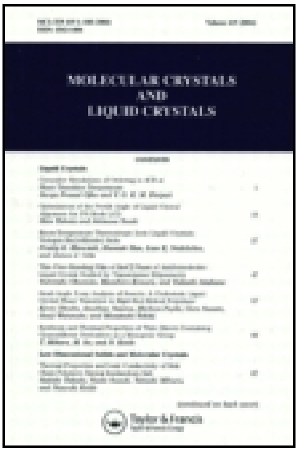

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Synthesis and Characterization of Liquid Crystalline Monomers and Side-Chain Polymers Containing Diphenyldiacetylene Mesogens

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Synthesis and Characterization of Liquid Crystalline Monomers and Side-Chain Polymers Containing Diphenyldiacetylene Mesogens

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Nine unsymmetrically diphenyldiacetylenic monomers were prepared. The phase behavior as well as thermal polymerization of the obtained monomers were characterized by optical polarizing microscopy and DSC measurement. UV absorption, refractive indices and dielectric constants of the monomers were also measured. The olefinic monomers were subjected to undergo hydrosilylation reaction with poly(methylhydrogensiloxane) to form the polysiloxanes. Thermal behavior of the prepared polysiloxanes were studied.

1. INTRODUCTION

The synthesis and characterization of diphenyldiacetylenic liquid crystals (LCs) have been extensively studied in recent years.[1-9] These LCs which have extended π-conjugation and perfect linear rod-like structure, exhibit extraordinary high birefringence and relatively low viscosity and have been demonstrated as a potential application in infrared spatial light modulators.[10] Furthermore, the unsymmetrically diphenyldiacetylenic LCs which contain an electron donating group at one end of the molecule and an electron withdrawing group at the other, have been found to possess pronounced second-order nonlinear optical properties.[4,5]

The goal of this study is to present the synthesis and characterization of some new unsymmetrical diphenyldiacetylenes. The particular examples refer to 4-al-

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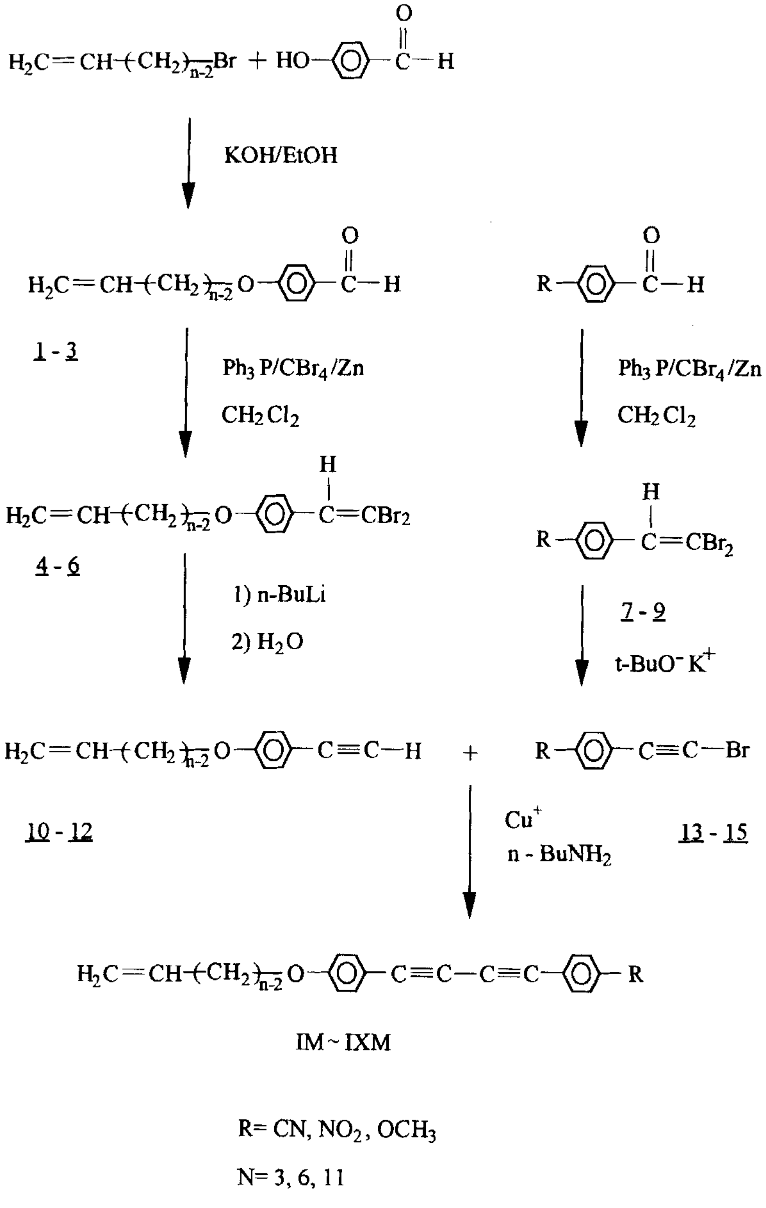


SCHEME I Synthesis of monomers IM ~ IXM.

kenyloxy-4'-cyanodiphenyldiacetylenes, 4-alkenyloxy-4'-nitrodiphenyldiacetylenes and 4-alkenyloxy-4'-methoxydiphenyldiacetylenes. The obtained olefinic diphenyldiacetylene monomers are subjected to undergo hydrosilylation reaction with poly(methylhydrogensiloxane) to form the corresponding side-chain polysiloxanes. The thermal behavior of the prepared monomers and polymers, and the thermal polymerization and some physical properties of the monomers are described.

TABLE I

Characterization of monomers IM—IXM

Monomer	Yield(%)	400 MH$_z$ ^{1}H-NMR (CDCl$_3$, δ , PPM)
IM	38.7	4.56(d,2H,-C$\underline{H}_2$-O-), 5.37(m,2H,-CH=C$\underline{H}_2$) 6.02(m,1H,-C$\underline{H}$=CH$_2$), 6.88 and 7.47(d;d,4H, -O-$\underline{Ph}$-), 7.60(two doublet,4H,-$\underline{Ph}$-CN).
IIM	42.3	1.50-2.18(m,6H,$(C\underline{H}_2)_3$), 3.96(t,2H,-C$\underline{H}_2$-O-), 5.00(m,2H,-CH=C$\underline{H}_2$), 5.79(m,1H,-C$\underline{H}$=CH$_2$), 6.83 and 7.44(d;d,4H,-O-$\underline{Ph}$-), 7.57(two doublet,4H,-$\underline{Ph}$-CN).
IIIM	47.4	1.27-2.10(m,16H,$(C\underline{H}_2)_8$), 3.96(t,2H,-C$\underline{H}_2$-O-), 4.96(m,2H,-CH=C$\underline{H}_2$),5.79(m,1H,-C$\underline{H}$=CH$_2$), 6.85 and 7.46(d;d,4H,-O-$\underline{Ph}$-), 7.60(two doublet,4H,-$\underline{Ph}$-CN).
IVM	40.2	4.43(d,2H,-C$\underline{H}_2$-O-), 5.21(m,2H,-CH=C$\underline{H}_2$), 5.89(m,1H,-C$\underline{H}$=CH$_2$), 6.75 and 7.33(d;d,4H, -O-$\underline{Ph}$-), 7.51 and 8.06(d;d,4H,-$\underline{Ph}$-NO$_2$).
VM	48.4	1.50-2.18(m,6H,$(CH_2)_3$), 3.98(t,2H,-C$\underline{H}_2$-O-), 5.01(m,2H,-CH=C$\underline{H}_2$), 5.82(m,1H,-C$\underline{H}$=CH$_2$), 6.85 and 7.47(d;d,4H,-O-$\underline{Ph}$-), 7.64 and 8.19 (d;d,4H,-$\underline{Ph}$-NO$_2$).
VIM	46.3	1.27-2.10(m,16H,$(C\underline{H}_2)_8$), 3.97(t,2H,-C$\underline{H}_2$-O-), 4.97(m,2H,-CH=C$\underline{H}_2$), 5.79(m,1H,-C$\underline{H}$=CH$_2$), 6.86 and 7.48(d;d,4H,-O-$\underline{Ph}$-), 7.64 and 8.20(d;d,4H,-$\underline{Ph}$-NO$_2$).
VIIM	51.7	3.80(s,3H,-O-C$\underline{H}_3$),4.53(d,2H,-C$\underline{H}_2$-O-), 5.34 (m,2H,-CH=C$\underline{H}_2$), 6.01(m,1H,-C$\underline{H}$=CH$_2$), 6.83 and 7.44(2 overlapping doublet,8H,Aromatic protons).
VIIIM	53.5	1.50-2.18(m,6H,$(C\underline{H}_2)_3$), 3.80(s,3H,-O-C$\underline{H}_3$), 3.93(t,2H,-C$\underline{H}_2$-O-), 4.99(m,2H,-CH=C$\underline{H}_2$), 5.80(m,1H,-C$\underline{H}$=CH$_2$), 6.82 and 7.44(two overlapping doublet,8H,Aromatic protones).
IXM	37.8	1.27-2.10(m,16H,$(C\underline{H}_2)_8$), 3.80(s,3H,-O-C$\underline{H}_3$), 3.94(t,2H,-C$\underline{H}_2$-O-), 4.94(m,2H,-CH=C$\underline{H}_2$), 5.79(m,1H,-C$\underline{H}$=CH$_2$), 6.80 and 7.46(two overlapping doublet,8H,Aromatic protons).

2. EXPERIMENTAL

2.1 Synthesis of Diphenyldiacetylenic Monomers

The synthetic routes used to prepare the monomers IM ~ IXM are outlined in Scheme I. All the unsymmetrical diacetylene were prepared by the Cadiot-Chodkiewicz coupling of the terminal acetylene with 1-bromoacetylene.[11] Both terminal acetylene and 1-bromoacetylene were synthesized according to the same procedures reported by Corey and Fuchs.[12] Table I summarized the yield and ^{1}H-NMR chem-

TABLE II

Elemental analysis and infrared absorption of C≡C band for monomers IM—IXM

Monomer	n	R	Elemental analysis; found (calculated)			Infrared absorption
			C/ %	H/ %	N/ %	$\bar{\nu}$ (C≡C) / cm^{-1}
IM	3	CN	82.75(80.57)	4.76(4.59)	4.85(4.95)	2212
IIM	6	CN	84.36(84.92)	6.08(5.85)	4.21(4.31)	2212
IIIM	11	CN	84.59(85.06)	7.45(7.34)	3.63(3.54)	2212
IVM	3	NO_2	74.88(75.25)	4.39(4.29)	4.62(4.62)	2208
VM	6	NO_2	76.23(76.52)	5.54(5.51)	4.01(4.06)	2209
VIM	11	NO_2	77.78(78.07)	7.13(6.99)	3.38(3.37)	2211
VIIM	3	OCH_3	82.98(83.33)	5.56(5.56)	————	2140
VIIIM	6	OCH_3	83.30(83.64)	6.78(6.67)	————	2136
IXM	11	OCH_3	82.95(84.00)	8.15(8.00)	————	2136

a) n and R according to Scheme 1 .

ical shifts. Table II summarized the elemental analysis results and the infrared absorptions of C≡C band for all synthesized diphenylic monomers.

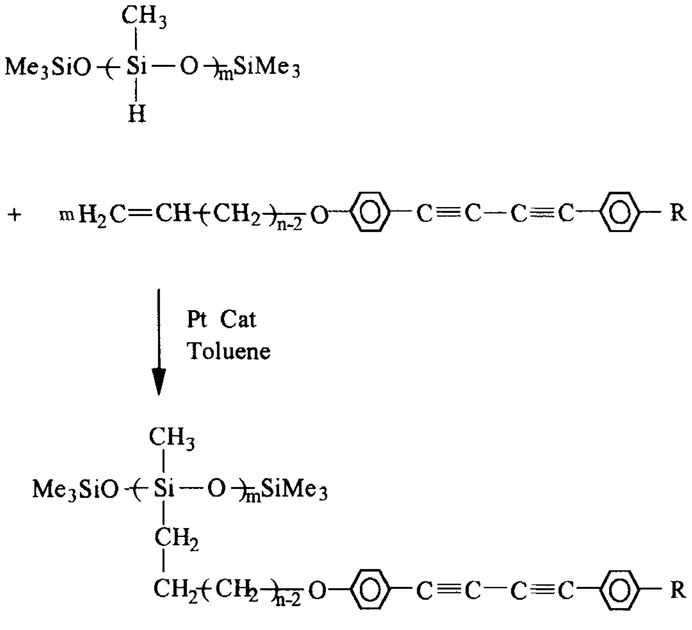
2.2 Synthesis of Polysiloxanes

The synthetic route used for the preparation of the polysiloxanes is outlined in Scheme II. Poly(methylhydrogensiloxane)($\overline{Mn}$ = 2270) was obtained from Patrarch System, Inc. and used as received. Hydrosilylation reaction was carried out in freshly distilled toluene with the proper amount of olefinic monomer and poly(methylhydrogensiloxane) by using dicycolpentadienylplatinum (II) chloride as the catalyst.[13,14]

3. RESULTS AND DISCUSSION

3.1 Mesomorphic Behavior of Monomers

The thermal properties as determined by differential scanning calorimetry (DSC) and optical polarizing microscopy for the diphenyldiacetylene monomers IM ~ IXM are summarized in Table III. All the obtained monomers except IM and IVM exhibit a liquid crystalline phase. Among the three monomers containing a cyano group, monomer IM shows no mesophase while both monomers IIM and IIIM exhibit respectively a monotropic nematic phase. The melting transitions of three monomers decrease with increasing the length of terminal alkenyloxy chains. For the three monomers containing a nitro group, monomer IVM presents no mesophase while monomers VM and VIM exhibit respectively a monotropic nematic and an enantiotropic smectic A phase. The result demonstrates that a longer al-



IP ~ IXP

R= CN, NO_2, OCH_3

N= 3, 6, 11   m = 40

SCHEME II Synthesis of polysiloxanes IP ~ IXP.

kenyloxy group can not only decrease the melting temperature but also lead to the formation of a more stable mesophase. All three monomers containing a methoxy group present respectively an enantiotropic nematic phase. Figure 1 presents the DSC heating and cooling scans of monomer VIIM. Monomer VIIM shows a melting transition of 174°C on the heating scan. Upon the cooling scan, it presents an isotropic to nematic phase transition at 173°C and a crystallization transition at 65°C. Figure 2 shows the representative nematic texture displayed by monomer VIIM. Comparing the monomers IIM, VM and VIIIM which contain the same electron donating hexenyloxy group at one end of the molecule, monomer VIIIM containing another electron donating methoxy group, displays a fairly wide range of nematic mesophase whereas monomers IIM and VM containing respectively the other electron withdrawing cyano group and nitro group display two very narrow nematic phases. The results demonstrate that the nature of both terminal groups in a diphenyldiacetylene molecule has a pronounced effect on the thermal stability of the mesophase.

Thermal polymerization of the synthesized diphenyldiacetylenic monomers were investigated by DSC and an optical polarizing microscope equipped with a heating stage. Figure 3 show the DSC thermograms of monomers IM ~ IXM which were heated to about 400°C. A big exothermic transition corresponding to the thermal

TABLE III

Phase transitions and phase transition enthalpies for monomers IM—IXM

Monomer	n	R	Phase transitions, °C (Corresponding enthalpy changes, KJ/mol) Heating Cooling
IM	3	CN	K 210(20.06) I I 203(20.69) K
IIM	6	CN	K 164(39.84) I I 154(0.21) N 150(37.08) K
IIIM	11	CN	K 148(52.54) I I 142(0.88) N 133(47.23) K
IVM	3	NO_2	K 205(31.73) I I 191(18.94) K
VM	6	NO_2	K 148(30.10) I I 146(0.21) N 143(29.22) K
VIM	11	NO_2	K 128(25.75) S_A 142(3.72) I I 140(4.47) S_A 124(23.74) K
VIIM	3	OCH_3	K 120(29.76) N 174(1.42) I I 173(1.67) N 65(24.12) I
VIIIM	6	OCH_3	K 83(18.35) N 150(1.46) I I 148(1.46) N 66(18.35) K
IXM	11	OCH_3	K 74(30.72) N 123(1.38) I I 121(1.46) N 68(30.10) K

a) n and R according to Scheme 1.
b) K=crystalline, N=nematic, S=smectic, I=isotropic.

polymerization of the diacetylene monomer was observed in each DSC curve. The exothermic changes begin near 210°C for monomers with cyano or nitro groups and near 240°C for monomers with methoxy groups. The subsequent DSC scans show no exothermic peak for all monomers. This means that thermal polymerization could be complete at 400°C. The enthalpy changes vary in the range from 160 KJ mol^{-1} to 386 KJ mol^{-1}. The polymerization of diacetylenic compounds occurs in the solid state by a 1,4-addition reaction, following a photochemical mechanism described previously.[15,16] The polymerization of diacetylenic liquid crystals has been proven to easily occur in a smectic or even a nematic mesophase.[4–9] Among three kinds of monomers, the one containing a nitro group has a larger thermal polymerization ethalpy. This could be due to the more ordered molecular packing of this kind of monomer. Monomer VIM which presents a smectic A mesophase, has the largest value of thermal polymerization ethalpy. Evidence for the formation of polymers was obtained by optical polarizing microscopy. On initial heating at 220°C, the monomer underwent reversible phase transitions at the temperatures which have only a few degrees difference with those which have been shown in DSC

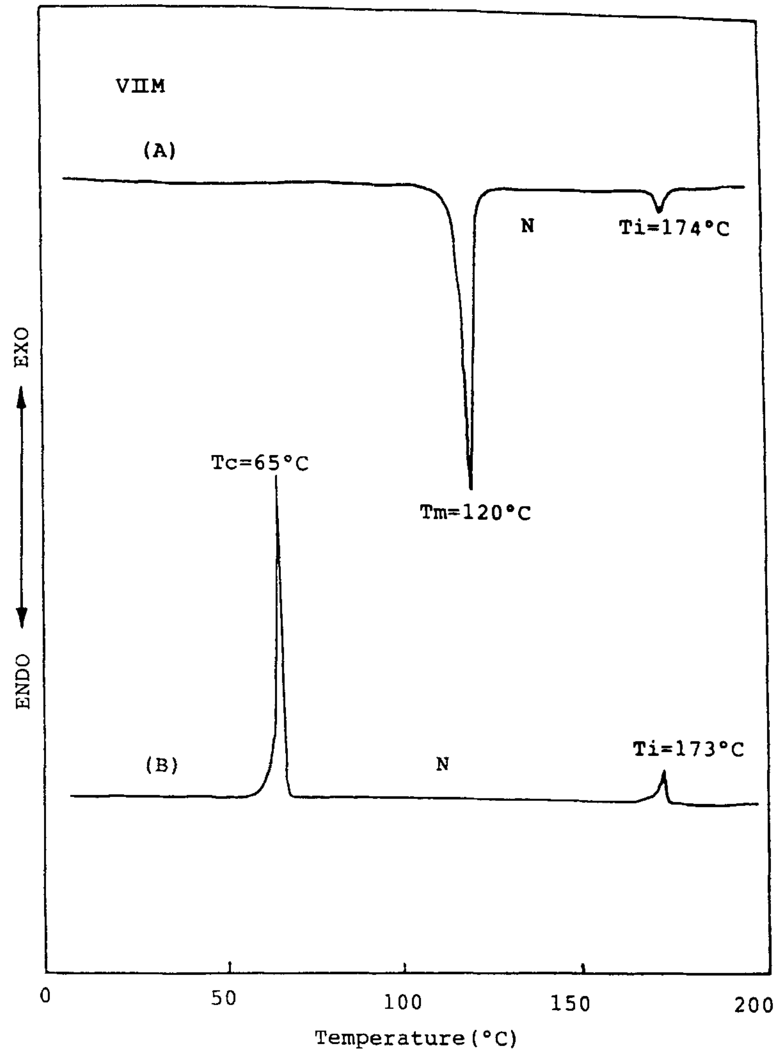


FIGURE 1 DSC thermograms (10°C/min) of monomer VIIM: (A) Second heating scan; (B) Cooling scan.

scans. Further heating to higher temperature formed the dark red or brown polymers of low solubility in common solvents.

3.2 Physical Properties of Monomers

3.2.1 UV. Absorption. Polarized UV absorption of a LC determines the refractive index dispersion of the LC.[17] The absorption spectrum of three asymmetric diphenyldiacetylenic LCs with different terminal groups: CN(IIM), NO_2(VM) and OCH_3(VIIIM) were studied. The UV absorption coefficient of a conjugated LC is very large[18] owing to the resonant $\pi \rightarrow \pi^*$ electron transitions. Thus, the guest-

FIGURE 2 Typical nematic texture exhibited at 171°C by monomer VIIM. See Color Plate I.

host system[16] turns out to be a convenient method for characterizing the polarization effect of a LC substance. In the guest-host method, 1% of the LC substance was dissolved in a host LC: ZLI-2359 (Merck, Germany), which is highly transparent in the UV region. In addition, this host mixture has a wide nematic range (−20 to 68°C) so that adding 1% of LC guest does not affect the clearing temperature of the host. A Glan-Taylor polarizer made of calcite crystal was used to polarize the incoming light. However, its cutoff wavelength is about 220 nm; below this wavelength, a deep UV polarizer[18] has to be used. This is not done in the present study. Two parallel-aligned LC cells with identical thickness (6μm) were used in the measurements: one with a LC guest and one without. Thus, the obtained data represent the normalized optical density for the 0.06-μm-thick LC guest. The absorption coefficient can then be calculated accordingly.

Figures 4–6 show the measured optical density of IIM, VM and VIIIM, respectively, at $T = 23°C$ which is equivalent to a reduced temperature $T_r = 0.865$. The top, middle and bottom traces in each figure represent the absorption of the extraordinary ray, unpolarized light and ordinary ray, respectively. Among CN, NO_2 and OCH_3 terminal groups, NO_2 exhibits the longest absorption wavelength, followed by CN and finally OCH_3. The LC consisting of the NO_2 group actually shows a yellowish color. Therefore, the birefringence of VM is expected to be the highest among the three when they are compared at the same wavelength and same reduced temperature.

Due to the long absorption wavelength of these diphenyldiacetylenic LCs, their photostability in the UV and blue spectral regions is expected to be poor. However, for IR application, photostability of these LCs is not a problem. Some localized molecular vibrational absorption band exist,[19] but there is still a broad region where LCs are transparent, and useful electro-optic modulation can be realized.

3.2.2 Refractive indices. For a LC with high melting temperature and narrow

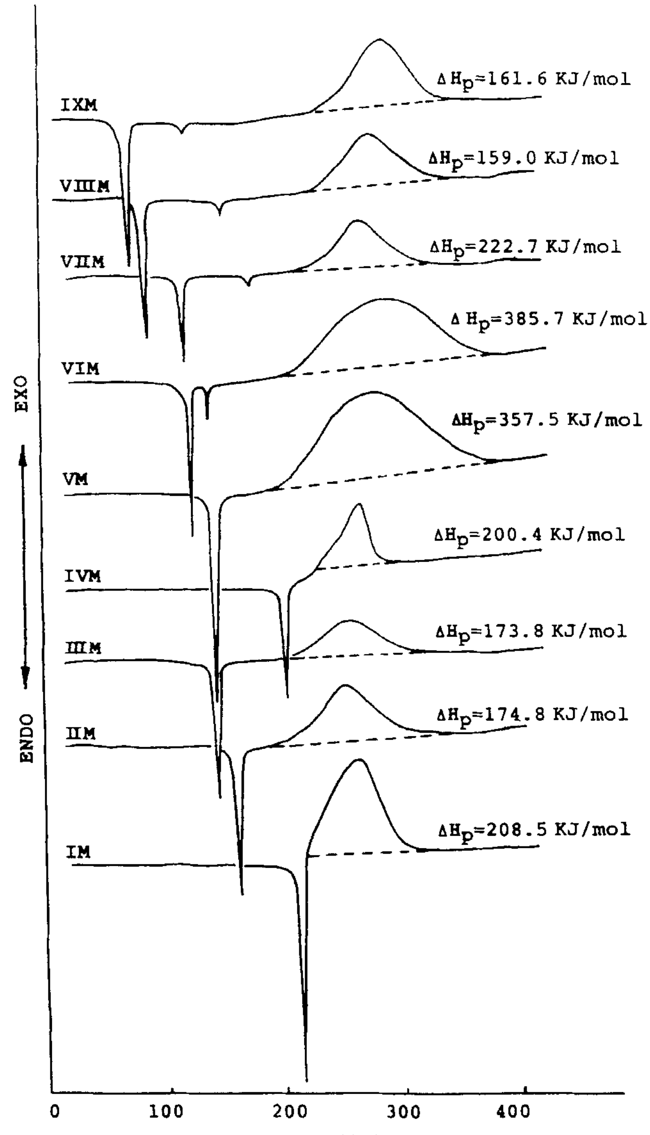


FIGURE 3 DSC thermograms (10°C/min) of monomers IM ~ IXM.

nematic range, its physical properties are difficult to evaluate in its nematic range. Furthermore, the measured properties correspond to T_r nearly equals unity, which is often far from practical application. Thus, the guest-host system was again employed. The concentration of the guest depends on its solubility. For the three diphenyldiacetylenic LCs studied, we found that 10% of VIIIM was still soluble to ZLI-1132 (Merck, Germany). However, for IIM and VM, their solubility is poor; even 5% of these LCs is enough to solidify the host. Thus, the refractive indices of these two LCs were not evaluated.

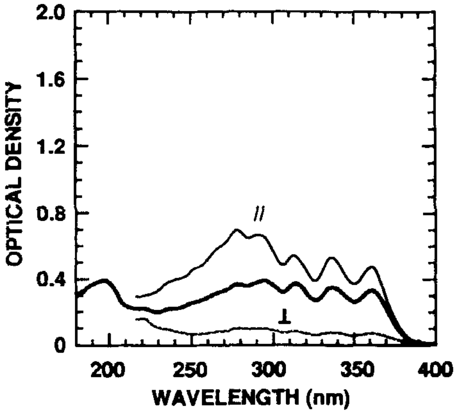


FIGURE 4 Optical density of 1% IIM dissolved in ZLI-2359. LC cell thickness is 6 μm. Measurement temperature T_r = 0.865. // and ⊥ are for extraordinary and ordinary rays and middle curve is for unpolarized light.

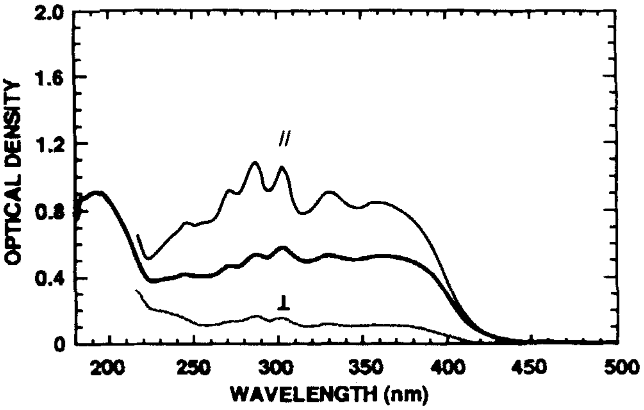


FIGURE 5 Optical density of 1% VM dissolved in ZLI-2359. LC cell thickness is 6 μm. Measurement temperature T_r = 0.865. // and ⊥ are for extraordinary and ordinary rays and middle curve is for unpolarized light.

For the 10% VIIIM in ZLI-1132, the clearing point of the guest-host system increases to 75°C, as compared to 71°C for the host LC. The n_e and n_0 of both guest-host and host-only were measured using the Jelley-Leitz refractometer at T = 23°C (or T_r = 0.856) and λ = 589 nm. From these two sets of data, the refractive indices of the guest LC (VIIIM) are extrapolated to be n_e = 1.852 and n_0 = 1.525. The high Δn (0.327) of VIIIM results from its long absorption bands as shown in Figure 2. Although the accuracy of this extrapolation method remains debatable, it does provide a crude way for estimating the refractive indices of a LC with high melting temperature and narrow nematic range, which is difficult to measure in the pure substance.

3.2.3 Dielectric constant. The dielectric constant of VIIIM was evaluated in a similar way to that of refractive index. A 10% guest-host mixture was used for

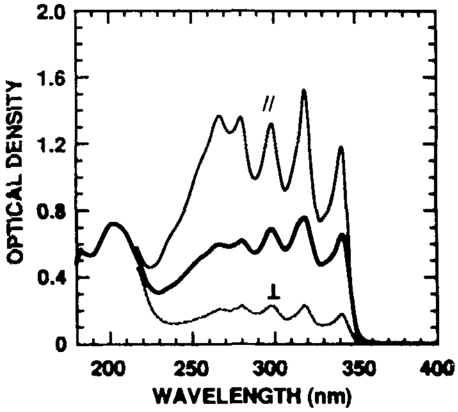


FIGURE 6 Optical density of 1% VIIIM dissolved in ZLI-2359. LC cell thickness is 6 μm. Measurement temperature T_r = 0.865. // and ⊥ are for extraordinary and ordinary rays and middle curve is for unpolarized light.

TABLE IV

Phase transitions and phase transition entropies for polymers IP—IXP

Polymer	n	R	Phase transitions, °C (Corresponding entropy changes, J/mru °K)
IP	3	CN	G 28 I
IIP	6	CN	G 26 I
IIIP	11	CN	G 20 S 125(8.62) I
IVP	3	NO_2	G 25 I
VP	6	NO_2	G 21 I
VIP	11	NO_2	G 20 I
VIIP	3	OCH_3	G 27 I
VIIIP	6	OCH_3	G 25 I
IXP	11	OCH_3	G 23 I

a) n and R according to Scheme 2.
b) mru= mole repeating units.
c) G= glassy, S = smectic, I= isotropic.

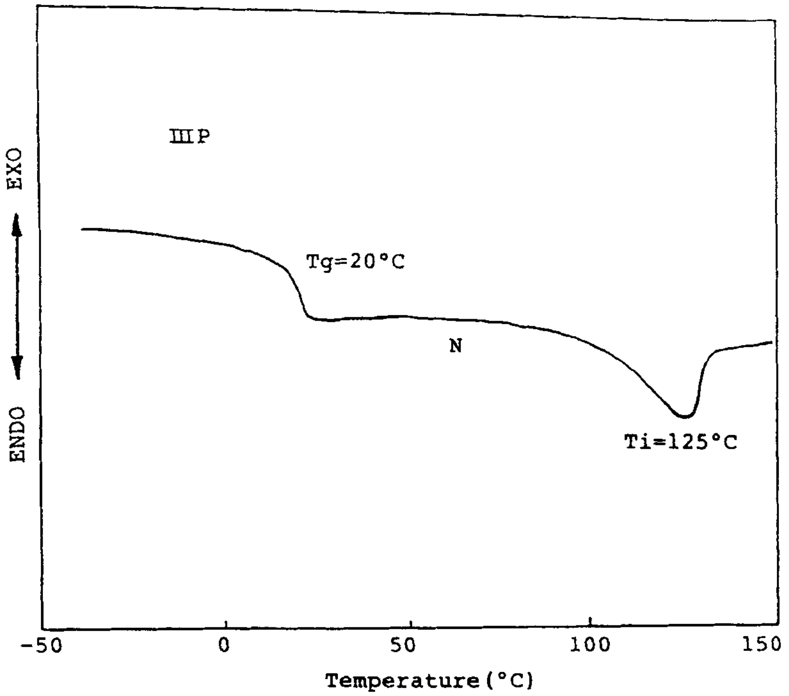


FIGURE 7 DSC thermograms (10°C/min) of polymer IIIP.

evaluation. The single cell method[20] was employed for these measurements. The extrapolated results are: $\varepsilon_{\parallel} = 5.87$ and $\varepsilon_{\perp} = 3.12$ at 1KHz sinusoidal frequency and $T_r = 0.856$. As T_r increases, $\varepsilon_{\parallel}$ decreases and $\varepsilon_{\perp}$ increases gradually. The dielectric anisotropy ($\Delta\varepsilon = 2.75$) of VIIIM is larger than the corresponding symmetric diphenyldiacetylene ($\Delta\varepsilon \approx 0.8$).[10,21] This difference originates from the asymmetric alkoxy terminal in VIIM.

The dielectric anisotropy of IIM is expected to be quite large due to the cyano terminal group. Unfortunately, the solubility of IIM and VM is so poor that even an extrapolated result is not obtainable.

3.3 Thermal Properties of Polysiloxanes

Table IV summarizes the thermal properties of the obtained polysiloxanes. All polymers except IIIP exhibit only a glass transition at a temperature range from 20°C to 28°C. The glass transition temperature decreases with increasing the length of the flexible spacer. The fact that most of the polymers show no mesomorphic transition could be due to the possible reaction between the diacetylene group and the Si—H group under the hydrosilylation reaction condition. Both NMR and IR spectra reveal that most diacetylene groups disappeared for all polymers except polymer IIIP. Polymer IIIP, containing 4-undecanyloxy-4′-cyanodiphenyldiacetylene mesogenic side groups, is the only polymer that displays mesomorphic behavior. Figure 7 shows the representative DSC thermogram of IIIP. A glass transition is presented at 20°C, followed by a smectic phase which undergoes isotropization at

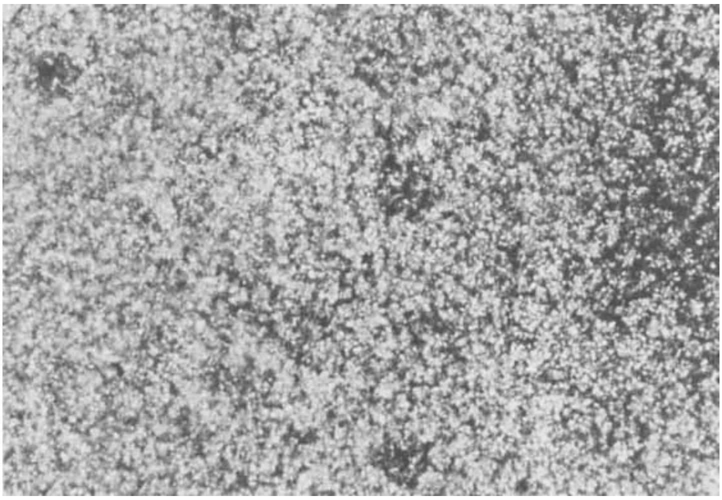


FIGURE 8 Typical smectic texture exhibited at 120°C by polymer IIIP. See Color Plate II.

125°C on the DSC heating scan. Figure 8 presents the typical smectic texture exhibited by polymer IIIP. X-ray diffraction measurement of IIIP, shows a sharp low angle diffraction maximum with d-spacing of 24.95 A° together with a broad outer maximum corresponding to an intermolecular distance of 4.54 A°. The X-ray result indicates the formation of a S_A or S_C phase.

4. CONCLUSION

A number of diphenyldiacetylenic LCs with three different terminal groups, i.e. CN, NO_2 and OCH_3, were synthesized. Most of the LCs present a nematic mesophase. The terminal groups have a pronounced effect on the thermal behavior of the LCs. The diphenyldiacetylenic LCs exhibit pretty long absorption wavelengths in UV spectra. Their photostability in the UV and blue spectral regions is expected to be poor. However, for IR application, photostability of these LCs is not a problem. The birefringence of the LCs is proved to be very large. The olefinic monomers were subjected to undergo hydrosilylation reaction with poly(methylhydrogensiloxane) to form the polysiloxanes. All of the obtained polysiloxanes except one show no mesophase transition. This result could be due to the possible reaction of the diacetylene group with the Si—H group under the hydrosilylation reaction condition.

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