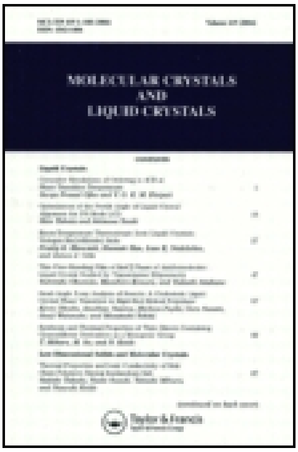

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Films Based on New Methacrylate Monomers: Synthesis, Characterisation and Electro-Optical Properties

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Films Based on New Methacrylate Monomers: Synthesis, Characterisation and Electro-Optical Properties

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A number of liquid crystal monomers based on methacrylate derivatives were synthesised by novel mild and solventless procedures under microwave irradiation. Their photo- and thermo assisted homo- and co-polymerizations with glycidyl methacrylate were investigated. The resulting polymers were characterised by NMR, GPC, DSC, and SEM to determine their structures and properties. The effects of the structures of the monomers on the electro-optical properties were correlated.

Keywords Electro-optical properties; green chemistry synthesis; liquid crystal polymer; PDLC

1. Introduction

The effects of the composition of the mixtures, the curing temperature, and the UV light intensity are known to influence on the microstructure of the polymer network in the PDLC films. Different liquid crystal domains imply different responses to an applied electrical field and thus the microstructure of the polymer network seriously affects their electro-optical properties.

The published synthesis works with a view for new PDLC devices focus mainly to the preparation of new mesogenic compounds to be incorporated in the polymer matrix, and new polymer synthesis have not the same attention.

As an approach, PDLC materials may be formed using a liquid crystalline bifunctional molecule, such as an acrylate, as the monomer (LC monomer) [1]. The LC monomers have an advantage over conventional acrylate monomers due

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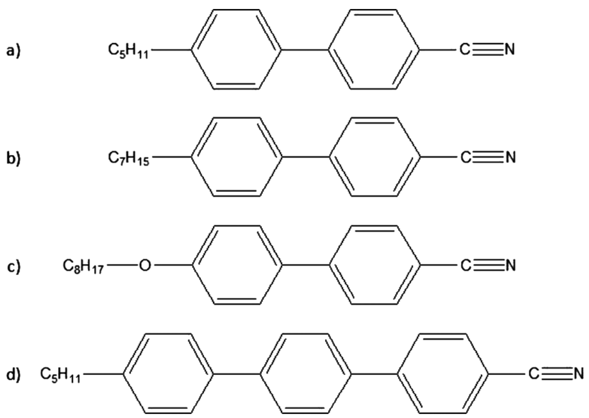


Figure 1. Components of E7 liquid crystal from Merck.

to their high compatibility with the low molecular weight nematic LC materials, thereby facilitating formation of high concentrations of low molecular weight LC and yielding a sample with high optical quality. The presence of higher concentrations of low molecular weight LCs in the PDLC material greatly lowers the switching voltages.

The stabilization of the liquid crystal domains is one important aspect in designing new polymeric materials for PDLC devices and this is related with the miscibility and compatibility between the LC molecules and the monomer(s) molecules. One possible approach for this stabilization can be achieved using a comonomer with the same mesogenic unit as the LC. Therefore, we synthesised a number of photo- and thermo-polymerisable monomers, mainly mono-methacrylates containing aromatic systems and nitrile group, mimicking some structural elements of a LC, a multicomponent nematic mixture E7 from Merck [2] (Fig. 1, Table 1) with a view for better miscibility and compatibility during preparation of PDLC films, possible control on the LC microdroplets size, and hence on the electro-optical properties of the resulting materials.

New mild and solvent-free procedures have been developed [3], with short reaction times, using microwave (MW) irradiation and which, in many cases, appears to be a more selective affording higher yields compared to classical thermal heating [4,5].

Table 1. Components and mass composition of E7 liquid crystal from Merck

Designation	Molecular formula	Molecular weight g/mol	IUPAC name	Composition w/w
a) 5CB	$C_{18}H_{19}N$	249.36	4-cyano-4′-n-pentyl-1,1′-byphenyl	51%
b) 7CB	$C_{20}H_{23}N$	277.41	4-cyano-4′-n-heptyl-1,1′-byphenyl	25%
c) 8OCB	$C_{21}H_{25}NO$	307.44	4-cyano-4′-n-octyloxy-1,1′-byphenyl	16%
d) 5CT	$C_{24}H_{23}N$	325.45	4-cyano-4″-n-pentyl-1,1′,1″-terphenyl	8%

The selected monomers were aromatic methacrylates because they are highly reactive due to the presence of aromatic ring and thus form an interesting class of polymerizable monomers. They were polymerised and copolymerised with glycidyl methacrylate by photo-, thermo-, and microwave assisted polymerization, and the resulting materials were fully characterised in here and elsewhere [3]. Five-carbon spacer arm was introduced into the structures between the aromatic ring and the methacrylate group to increase the flexibility of the molecule. The effects of the rigidity and flexibility of the polymerizable monomers on the microstructure of the polymer network were investigated.

2. Experimental Methods

2.1. *Materials and Methods*

Reagents and solvents were purified before use.The nematic liquid crystals (LC) used were E7 obtained by Merck.

Average molecular weights of the prepared polymers were determined by gel permeation chromatograph (GPC), Knauer Equipment with Pump Smartline 1000, UV detector Smartline2500, IR detector Smartline 2300, ELS detector PL-ELS 1000 and Autosampler Smartline 3800. The results were obtained using light scattering and refractive index detectors in a temperature controlled oven (set at 85°C) coupled to a integrated solvent and sample delivery module (degasser, pump and auto sampler), at a flow rate 1 mL/min, using DMF as eluent, and with an injection volume of 150 μl. The detectors alignment and instrument sensitivity parameters were previously calibrated using a low molecular weight distribution PMMA standard. Glycidyl methacrylate have been chosen as a co-monomer (50% w/w) because of its well-known action as a reactive solvent in polymerization systems in order to solubilise the mixtures [6].

2.2. *General Procedure for Photo-Polymerization*

Photo-polymerisations of the monomers and their co-polymerisations with GMA were carried out by mixing the monomers with DMPA (1% by weight with respect to the monomer mixture). The mixtures were flushed with Ar, sandwiched between two KBr-plates and irradiated by UV-light (Oriel Hg lamp, 366 nm filter). The polymer films were obtained by dissolving the KBr-plates in distilled water, washed several times with distilled water, and dried under vacuum.

For SEM studies of PDLC films, mixtures of monomer/E7 (30/70 w/w) were photo-polymerised with DMPA between two KBr-plates. After dissolving the KBr-plates in distilled water, the films were dipped in acetonitrile for three times to dissolve the E7 and then dried under vacuum for 24 h. SEM studies were performed in a Hitachi, model S-2400.

For electro-optical studies of PDLC films, mixtures of monomer/E7 (30/70 w/w) were introduced by capillarity into a ITO 20 μm cell spacing optical cell and photo-polymerised with DMPA.

2.3. *General Procedure for Thermo-Polymerization*

Thermo-polymerisations of the monomers and their co-polymerisations with GMA were carried out by mixing the monomers with AIBN (1% by weight with respect to the monomer mixture). The mixtures were flushed with Ar, sandwiched between two KBr-plates and heated at 74°C in an oven for several hours. The polymerization of the material was followed by FTIR measuring the amount of the methacrylate carbon double bonds present. By the end of the polymerization, the set were cooled to room temperature. For SEM and electro-optical studies, the procedure was similar to the one reported above.

2.4. *General Procedure for DSC Analysis*

DSC measurements were performed in a Setaram, model DSC131, with heating and cooling scanning rates of 10 K/min.

2.5. *General Procedure for Electro-Optical Analysis*

The electro-optical studies were performed using a laser (He-Ne 632.8 JDS Uniphase) equipped optical bench, with an AC voltage programmable pulse generator Agilent 33220A for sample excitation and a photo diode detection system for light transmission analysis.

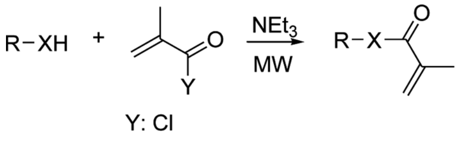
3. Results and Discussion

3.1. *Monomer Syntheses*

A number of photo- and thermo-polymerisable monomers have been designed for mimicking some structural elements of E7. The synthesis details of monomethacrylated monomers are reported in Table 2.

Spectroscopic characterization data (NMR and FTIR) of the synthesised monomers is presented elsewhere [3].

Table 2. Synthesis of monomethacrylated monomers



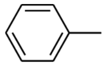
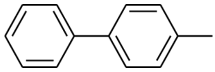
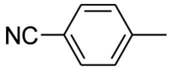
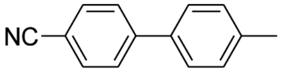
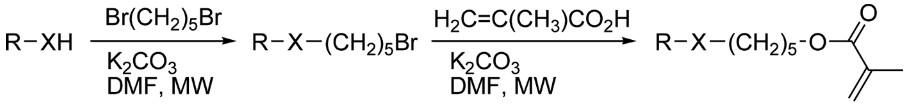
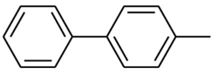
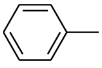
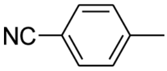
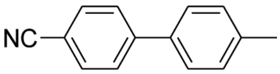
	R	X	Reaction conditions at MW	Yield [%]
PhM		O	200 W, 1 min	95
biPhM		O	200 W, 1 min	71
NCPhM		O	200 W, 2 min	64
NCbiPhM		O	200 W, 1 min	88

Table 3. Synthesis of monomethacrylated monomers with a 5-C spacer arm between the aromatic system and the methacrylate group



	R	X	Step 1	Yield [%]	Step 2	Yield [%]
biPhOSpM		O	200 W, 3 min	52	200 W, 1 min	70
PhOSpM		O	250 W, 5 min	76	250 W, 5 min	47
NCPhM		O	200 W, 5 min	38	200 W, 5 min	57
NCbiPhOSpM		O	200 W, 2 min	65	200 W, 1 min	57

The synthesis of monomethacrylated monomers with a 5-C spacer arm between the aromatic system and the methacrylate group are reported in Table 3.

Spectroscopic characterization data (NMR and FTIR) of the synthesised monomers is presented elsewhere [3]. The structures of the synthesised monomers are presented in Table 4. We included the commercial monomer phenyl methacrylate (PhM), acquired from Sigma-Aldrich andit was used as received.

3.2. *Polymer Structures and Molecular Weights Evaluation*

The average polymer molecular weights were determined by GPC using a 50/50 w/w monomer mixture with glycidyl methacrylate in order to solubilise the solid monomers. The results for thermal- and photo-polymerization are shown in Tables 5 and 6, respectively.

Typical GPC results for a mixture monomer/glycidyl methacrylate (50/50 w/w) for thermal- and photo-polymerisation are shown in Figure 2.

Generally, the polymers with lower molecular weight possess a lower polydispersion, but no correlation is observed with the molecular structure. For the thermal-polymerization, the polymers have a number average molecular weight, M_n, around e^8 or e^{13}, and for photo-polymerization polydispersions are higher and M_n is around e^{12}. All chromatograms and SEM images are available in the Supporting Information file, accessed via Internet.

3.3. *Polymer Calorimetric Characterisation*

The PhM and PhOSpM monomers, liquids at room temperature and both with only one aromatic ring, show the same calorimetric behaviour. For the PhOSpM monomer, a −3.6°C melting temperature (T_f) with an enthalpy of fusion of $\Delta_f H = 115.5$ J g^{-1}, a $T_g = -86°C$ and a cold crystallization at $T_{cc} = -40°C$ with an enthalpy of

Table 4. Monomers chemical structures

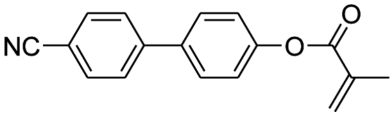
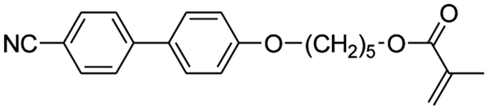
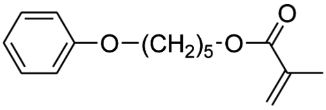
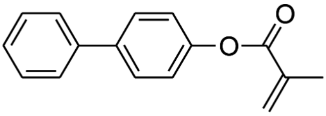
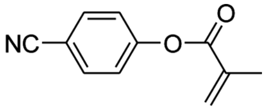
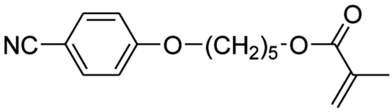
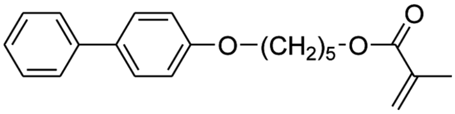
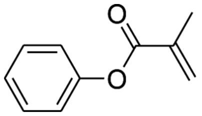
IUPAC name	Monomers chemical structure	Reference
4′-isocyanobiphenyl-4-yl methacrylate		NCbiPhM
5-(4′-cyanobiphenyl-4-yloxy)pentyl methacrylate		NCbiPhOSpM
5-phenoxypentyl methacrylate		PhOSpM
Biphenyl-4-yl methacrylate		biPhM
4-isocyanophenyl methacrylate		NCPhM
5-(4-cyanophenoxy) pentyl methacrylate		NCPhOSpM
5-(biphenyl-4-yloxy)pentyl methacrylate		biPhOSpM
Phenyl methacrylate		PhM

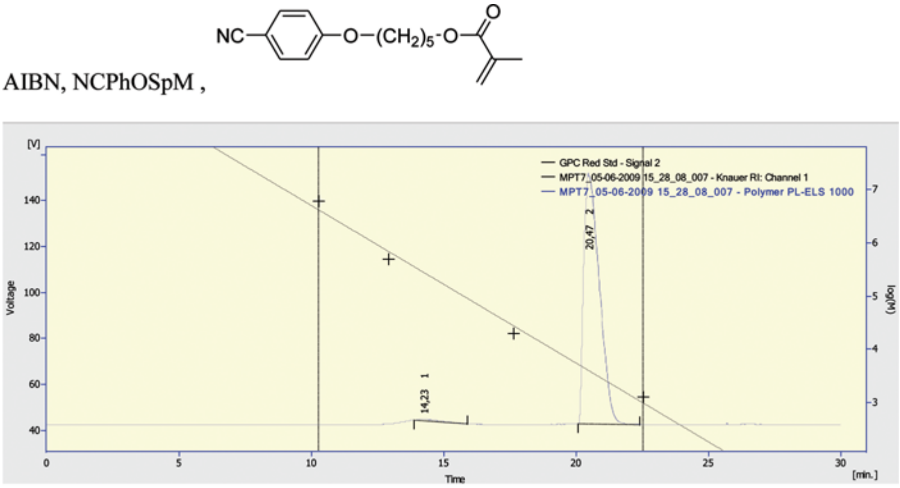
Table 5. Average polymer molecular weights by GPC for thermal-polymerization with (50/50 w/w) glycidyl methacrylate

Monomer reference	PD	Peak/min	Ln M_W	Ln Mn
biPhM	1.04	20.51	8.13	8.09
NCPhM	1.04	20.81	8.02	7.99
NCPhOSpM	1.04	20.47	8.16	8.12
biPhOSpM	1.05	20.14	8.22	8.17
NCbiPhM	1.91	13.86	12.80	12.15
NCbiPhOSpM	1.4	14.97	12.51	12.16
PhOSpM	1.44	13.57	13.05	12.69

Table 6. Average polymer molecular weights by GPC for photo-polymerization with (50/50 w/w) glycidyl methacrylate

Monomer reference	PD	Peak/min	Ln M_W	Ln Mn
biPhM	1.24	15.78	11.67	11.45
NCPhM	1.08	14.37	12.30	12.23
NCPhOSpM	1.38	15.63	11.72	11.39
biPhOSpM	1.36	22.36	6.99	6.68
NCbiPhM	1.51	14.28	12.80	12.39
NCbiPhOSpM	1.47	14.68	12.36	11.98
PhOSpM	1.35	15.06	12.04	11.74

AIBN, NCPhOSpM ,



DMPA, NCPhOSpM ,

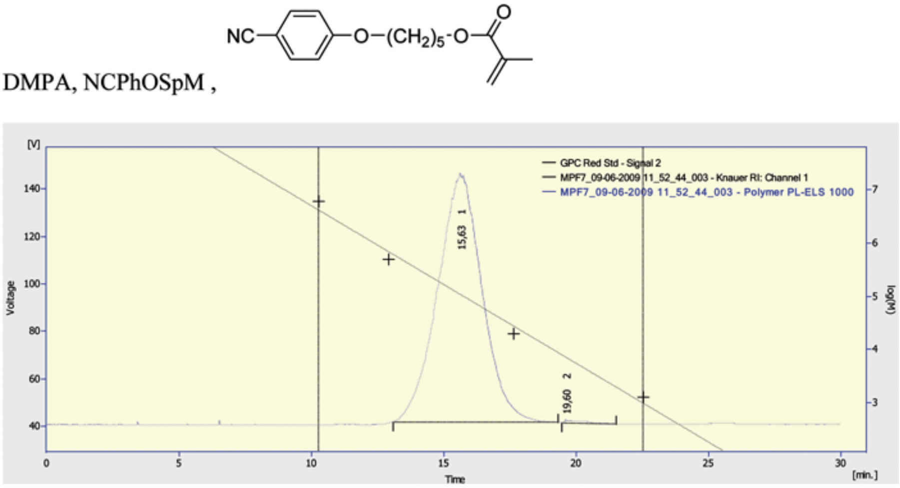


Figure 2. A typical GPC result for a mixture monomer/glycidyl methacrylate (50/50 w/w) for thermal- and photo-polymerisation. (Figure appears in color online.)

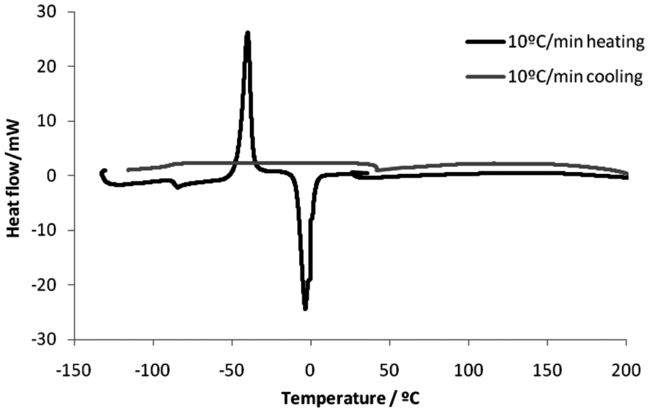


Figure 3. DSC heating and cooling scans at 10 k/min for PhOSpM monomer.

$-97.4\,\mathrm{J\,g^{-1}}$, indicate a partial amorphous material when a cooling rate of 10 K/min is used, Figure 3.

For the PhM, a $T_f = 18.9°C$ with $\Delta_f H = 109.0\,\mathrm{J\,g^{-1}}$, a $T_g = -89°C$ and a cold crystallization at $T_{cc} = -55.1°C$ with an enthalpy of $-107.7\,\mathrm{J\,g^{-1}}$ can be observed.

For the other monomers, the inclusion of nitrile groups or one more aromatic ring moved the heating and the cooling curves to higher temperatures, and the insertion of one 5-C spacer group moved the curves to lower temperatures, as can be seen in Table 7. After one heating cycle, a 10 K/min cooling rate was fast enough to avoid crystallization and no phase transition on cooling was observed. It was detected on cooling as well that different textures from the initial one appear. This polymorphism was detected with 8OCB molecule and its homologues, with similar structure to these monomers [7,8].

For NCbiPhM and NCbiPhOSpM monomers, more rigid than the others, both methacrylates with one nitrile group and two aromatic rings, the crystalline form melts and partially crystallises on cooling. The NCbiPhOSpM melts at $T_f = 78.7°C$ with $\Delta_f H = 102.9\,\mathrm{J\,g^{-1}}$ and crystallises on cooling at 96.9°C with an enthalpy of $-5.9\,\mathrm{J\,g^{-1}}$. The partial amorphous solid formed melts at 100.7°C with an enthalpy of $5.5\,\mathrm{J\,g^{-1}}$ and partially crystallises again on cooling at 98.5°C with an enthalpy of $-5.5\,\mathrm{J\,g^{-1}}$.

Table 7. Calorimetric data from DSC for the synthesised monomers

Monomer reference	$T_f/°C$	$\Delta_f H/\mathrm{Jg^{-1}}$
biPhM	107.7	91.8
NCPhM	85.0	129.4
NCPhOSpM	50.0	129.7
biPhOSpM	35.9	48.2
NCbiPhM	123.2	53.5
NCbiPhOSpM	78.7	102.9
PhOSpM	−3.6	115.5
PhM	18.9	109.0

All the DSC results are available in the Supporting Information file, accessed via Internet.

3.4. *Electro-Optical Properties*

All these polymer/E7 (30/70 w/w) show a very poor electro-optical response. This is due to the low mobility of the mesogenic parts of the polymeric matrix compared with the high mobility of the E7 molecules. Thus, with application of an external electric field there is only the reorientation of E7 molecules along the direction of electric field. Because of the high birefringence of liquid crystal molecules, it will strongly scatter incident light when mesogenic parts of the polymeric matrix are not oriented with the electric field but E7 molecules are.

4. Conclusions

In conclusion, we presented a set of new functionalized monomers that were used with E7 to obtain PDLC films. The selected monomers were aromatic methacrylates and they were thermal- and photo-polymerised. The resulting materials were characterised by several structural, calorimetric and optical methods. Although the chemical similarity between the E7 used as liquid crystal and the matrix network, no electro-optical response was detected for these PDLC films. This was due to the lack of mobility of the mesogenic part of the polymeric matrix and it's no reorientation along the direction of applied electric field.

Acknowledgment

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