Oriented polymer networks obtained by photopolymerization of liquid-crystalline monomers

Citation for published version (APA):

DOI:
10.1002/apmc.1990.051830103

Document status and date:
Published: 01/01/1990

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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ORIENTED POLYMER NETWORKS OBTAINED BY PHOTOPOLYMERIZATION OF LIQUID-CRYSTALLINE MONOMERS

D. J. Broer, R. G. Gossink and R.A.M. Hikmet

SUMMARY

In this paper a new class of oriented polymers is introduced: highly crosslinked polymer networks obtained by photopolymerization of oriented liquid crystalline (LC) monomers. Orientation of these monomers can be induced in the same manner as usual for conventional LCs applied in LCDs: with the aid of an electric or magnetic field, or using surface orientation. Photopolymerization offers the advantage that a temperature can be chosen right within the LC temperature region.

The resulting polymer networks show a high degree of ordering which is somewhat dependent on the polymerization temperature, as demonstrated by the amount of birefringence. This ordering is maintained over a wide temperature region, contrary to that in LC side-chain polymers. Apart from their optical properties, uniaxially ordered polymer networks show anisotropy also in other physical properties, such as the thermal expansion coefficient and modulus.

1 Paper presented at the meeting of the GDCh-Fachgruppe "Makromolekulare Chemie" on "Polymers and Light" in Bad Nauheim (W-Germany), May 7-9, 1990
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ZUSAMMENFASSUNG


Die Photopolymerisation bietet den Vorteil, dass eine Temperatur genau im LC-Bereich gewählt werden kann.


INTRODUCTION

In his classification of liquid-crystalline (LC) polymers containing mesogenic molecular units, Finkelmann (1) distinguishes between LC main-chain polymers, LC side-chain polymers and LC side-chain elastomers (Fig. 1).

In the present review of recent work at Philips Research Laboratories (2-10), we will describe a class of polymers that do not strictly belong to the LC polymers, since they do not form a mesophase, but constitute a logical extension of the Finkelmann classification: oriented polymer networks containing nematogenic bridging units. Such oriented networks can conveniently be formed by photopolymerization of preoriented LC diacrylates or similar monomers (Fig. 2).
This process of obtaining oriented polymer networks has the following main characteristics:

- Because of their LC behaviour, the monomers can easily be macroscopically oriented by external forces, such as an electric or a magnetic field, elongational flow or surface orientation (e.g. by a rubbed polyimide layer) as applied in LCDs.
This macroscopic orientation can be "frozen in" by polymerization. Using photopolymerization offers the great advantage over thermal polymerization that (i) a temperature can be chosen right inside the LC region of the monomer, and (ii) after the macroscopic orientation has been performed, the polymerization can be (photo)initiated and brought to completion. In other words: monomer orientation and initiation of polymerization are decoupled.

Summarizing, the process described combines the fields of low-molecular weight LC compounds, photopolymerization, and polymer orientation.

The polymer networks thus obtained behave anisotropically in a number of physical properties, such as thermal expansion coefficient, modulus of elasticity, and refractive index.

Contrary to the LC polymers in the Finkelmann classification, these networks have an orientation which is hardly dependent on temperature over a wide temperature range, and thus the anisotropy of the above-mentioned physical properties is also much stabler.

Another advantage over (preformed) linear LC polymers is that the orientation is brought about in a low-viscosity and moderate-temperature situation. This opens possibilities in the direction of foils and coatings, also on substrates with a complex form.

LC diacrylates are attractive monomers for the above described process, since they can be readily polymerized by a photo-initiated radical polymerization process (11). However, also other monomers such as di-epoxides and di-vinylethers can be chosen.

In this paper, the following aspects will be discussed:

- structure and synthesis of some suitable LC diacrylates.

- LC behaviour and orientation of these monomers and a related monoacrylate.

- photopolymerization behaviour of these monomers.
- thermal behaviour and physical properties of the anisotropic networks obtained.

- anisotropic networks containing non-polymerizable LC molecules ("anisotropic gels").

STRUCTURE AND SYNTHESIS OF LC DIACRYLATES

Most common low-molecular weight LCs consist of elongated molecules with a highly anisotropic polarizability and with a rigid (rod- or disc-like) molecular unit. Restricting ourselves to rod-like structures, a number of examples of basic LC structures is given in Fig. 3 (1). The mesogenic unit is built up of 2 or 3 aromatic or saturated six-rings, interconnected in such a way that their axes are in line. For our purpose these basic structures have to be functionalized at both ends with an acrylate or methacrylate moiety.

![Fig. 3. Examples of molecular structures of LC compounds with rod-like mesogenic moieties (1).](image)

We have synthesized the following class of monomers:
where: n = 4-10, but usually 6
R = H or CH₃

The synthesis route chosen for the compound with n=6 and R=H, i.e. 1,4-phenylene bis (4 - [6 - (acryloyl-oxy) hexyloxy] benzoate), is shown in Fig. 4 (4). The principle of this route is to first prepare the acrylate benzoate derivates, which are then joined together by reaction with hydroquinone. The mesogenic unit thus is only composed in the last reaction step. Overall yields were ≥ 20%.

Fig. 4. Synthesis route to LC diacrylate II.

LC BEHAVIOUR OF THE DIACRYLATES

The LC behaviour of the diacrylates synthesized as well as that of a related monoacrylate obtained from Finkelmann (2,3):

\[ \text{CH}_2=\text{CH} - \text{C} - \text{O} - (\text{CH}_2)_6 - \text{O} - \text{C} - \text{C}_{13},(1) \]
was studied by the following experimental procedures:

- phase transitions were detected with DSC (Perkin-Elmer DSC-2C; 5K/min)

- orthoscopic measurements were done with a polarization microscope (Leitz Laborlux 12 Pol) provided with a temperature controller (Perkin-Elmer).

A DSC scan for the diacrylate with n=6 and R=H (II) is shown in Fig 5. Upon heating, the monomer melts at 108°C and shows LC behaviour up to the clearing temperature of 155°C; orthoscopic measurements showed this to be a nematic region. Upon cooling, a transition to a smectic-C phase is observed at 88°C, and the compound crystallizes at 75°C. At temperatures of 65°C and lower a transition to more stable crystalline phases is seen.

![DSC scan of diacrylate II on heating and cooling](image)

Fig.5. DSC scan of diacrylate II on heating (a) and cooling (b).

An overview of transition temperatures measured on the monoacrylate I, and the diacrylates II and III (n=6 and R=CH₃) is given in Table I.
Table I: Transition temperatures of LC acrylates.

<table>
<thead>
<tr>
<th></th>
<th>Transition temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Monoacrylate I</td>
<td>92</td>
</tr>
<tr>
<td>+ 2 wt % A</td>
<td>89</td>
</tr>
<tr>
<td>+ 2 wt % B</td>
<td>88</td>
</tr>
<tr>
<td>Diacrylate II</td>
<td>108</td>
</tr>
<tr>
<td>+ 1 wt % B</td>
<td>107</td>
</tr>
<tr>
<td>+ 2 wt % B</td>
<td>107</td>
</tr>
<tr>
<td>Diacrylate III</td>
<td>86</td>
</tr>
</tbody>
</table>

c = crystalline  s = smectic  n = nematic  i = isotropic

For structures of LC acrylates I, II and III and photoinitiators A and B: see text.

Monoacrylate I shows a melting point of 92°C to a nematic phase, and a clearing temperature of 102°C. Upon cooling a transition to smectic-A is observed at 79°C.

To photopolymerize the acrylate monomers, a radical photoinitiator has to be added. Two suitable photoinitiators are the following:

\[
\begin{align*}
\text{Q} & \quad R^1 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{C} & \quad \text{OCH}_3 \\
\text{C} & \quad \text{OH} \\
\text{R}^1 & \quad \text{R}^2 \\
\text{R}^1 & \quad \text{C}_6\text{H}_5
\end{align*}
\]

Addition of 2 weight % of these photoinitiators to monomer I leads to some decrease of the transition temperatures (see Table I); in particular the clearing temperature is sensitive to photoinitiator addition.
Coming back to monomer II, it is interesting to compare its transition temperatures with those of a similar compound without the acryloyl end groups. A compound with the same mesogenic moiety but with hexyl end groups was reported by Dewar and Schroeder (12) to have a comparable melting temperature, but stabler (higher transition temperature) smectic and nematic phases.

In the case of monomer II, the addition of photoinitiator again leads to lower transition temperatures. The clearing temperature is even decreased by 10°C upon addition of 2 weight % of photoinitiator B.

Finally, introduction of a methyl substituent to the central aromatic ring (monomer III), thus somewhat disturbing the rod-like structure, leads to some distinct changes of the mesoscopic behaviour in comparison to monomer II:

- the melting temperature is reduced by 21°C;
- the clearing temperature is reduced by 29°C;
- no smectic phase is observed, although the temperature region of supercooling is extended.

Mixing of different LC compounds is a common practice to bring down the melting temperature and increase the LC region in LCs for LCDs. In a mixture of monomer II and III, $T_c$ proves to be a linear function of the monomer ratio; $T_m$ shows an eutectic of 80°C at 80 weight % of monomer III.

The birefringence of uniaxially oriented monomers in the nematic state was measured in two ways. In spaced glass cells (6 μm), provided with rubbed polymer layers on their inside surfaces, the birefringence was determined with the polarization microscope. In addition, the ordinary and extraordinary refractive indices ($n_0$ and $n_e$) were measured at 589 nm by means of an Abbe refractometer using a rubbed prism.

Fig. 6 shows the refractive index data of monomers II and III and their eutectic mixture. Above $T_c$, the monomers have one isotropic refractive index $n_i$ (about 1.52). Below this transition, the refractive index is split up in the ordinary ($n_0$) and extraordinary ($n_e$) refractive index. In particular $n_e$ is strongly temperature
dependent, which can be understood from the fact that loss of orientation and decreasing density upon temperature rise for $n_e$ work in the same direction.

![Graph showing refractive index vs. temperature](image)

**Fig. 6.** Ordinary, extraordinary and isotropic refractive index (at 589 nm) vs. temperature of diacrylate I (○), diacrylate III (□), and their eutectic mixture (△).

Using the Halder method (14) the order parameter $S$ of the oriented nematic state was calculated from the $n_e$ and $n_o$ measurements. The value of $S$ is 0.7 in the highest ordered (lowest temperature) state, decreasing to 0.4 at $T_c$ (6).

**PHOTOPOLYMERIZATION OF THE MONOMERS AND ORIENTATION OF THE POLYMERS OBTAINED**

The isothermal photoinitiated polymerization of the LC (di)acrylates I, II and III was studied at different temperatures, using a DSC apparatus modified for UV irradiation (13). The grooves present in the Al sample pans were found capable to orient the LC monomer; this was checked by polarisation microscopy of the polymerized films after dissolving the pans in a NaOH solution.

Fig. 7 shows some typical DSC photopolymerization curves at various temperatures using 1 weight % of photoinitiator B. Directly from the onset of photopolymerization, the rate increases rapidly. Under the irradiation conditions
used (Philips TL08 lamp; maximum intensity at 350 nm; total intensity 0.2 mW/cm²), the maximum rate is reached after about 5 s.

![Graph showing isothermal DSC trace of photoinitiated polymerization of diacrylate II at various temperatures.](image)

**Fig. 7.** Isothermal DSC trace of the photo-initiated polymerization of diacrylate II (containing 1 wt.% of photoinitiator B) at various temperatures.

![Graph showing photopolymerization rate of diacrylate II as a function of conversion at 120°C.](image)

**Fig. 8.** Photopolymerization rate of diacrylate II (1 wt.% of B) at 120°C as a function of the conversion of double bonds.

From Fig. 8 it is seen that this maximum rate occurs at a conversion of 20% of the double bonds. The polymerization rate drops to a low value after 60% conversion, but with FT-IR spectroscopy it could be shown that prolonged irradiation (15 min) drives up the conversion to more than 95% (4).
Fig. 9 shows the maximum photopolymerization rate of II and the conversion reached at the point that the rate becomes virtually zero, both as a function of temperature. After an initial increase, both the maximum rate and the conversion drop down with rising temperature. It is tempting to ascribe this to loss of monomer orientation upon passing the clearing temperature of 151°C. However, in non-mesogenic diacrylates of comparable molecular structure, the same phenomenon was observed, be it that the decrease in maximum rate and the conversion sets in at considerably lower temperature (90°C). A possible explanation is that in an ordered system suppression of the Trommsdorff effect due to chain transfer is less predominant than in an isotropic diacylate.

The degree of ordering in the monomer and the polymer state can be compared on the basis of birefringence measurements on uniaxially ordered samples. Fig. 10 shows the birefringence as a function of temperature for the monoacrylate I before and after photopolymerization at 85°C, i.e. from the nematic phase. The monomer shows a behaviour very similar to that of conventional mesophases: Upon cooling to the clearing temperature, a rapid increase of \( \Delta n \) is observed, with a transition from nematic to smectic at 77°C. Also the birefringence values are comparable with those of conventional mesophases.
Photopolymerization leads to a considerable increase of birefringence. Birefringence values exceeding 0.2 are high compared with those of conventional ordered polymers. This result demonstrates that the preorientation of the monomer can indeed be maintained (and improved!) by in-situ photopolymerization. The polymer obtained shows liquid crystallinity over a wide temperature region, with a smectic region between 87 and 169°C and a narrower nematic region from 169°C to 186°C. When the polymer is heated above its clearing temperature and cooled down again, the uniaxial ordering is partly lost.
Turning to the LC diacrylates II and III, we have seen the birefringence of the monomers as a function of temperature in Fig. 6. Upon photopolymerization of II, a negative or positive birefringence effect depending on polymerization temperature is observed (see Fig. 11): below 118°C the birefringence is decreased by polymerization and above this temperature the birefringence is increased. Neglecting some small changes in molecular polarizability during polymerization, it is concluded that part of the ordering is lost when the monomer is polymerized in a state of high ordering, whereas at lower monomer ordering, polymerization leads to an increase of ordering.

![Fig. 12. Birefringence An of oriented polydiacrylate II as a function of temperature, with the photopolymerization temperature as the parameter (a = 80°C, b = 90°C, c = 100°C, d = 110°C, e = 130°C, f = 140°C).](image)

This does not mean that the birefringence of the polymer is the same irrespective of photopolymerization temperature. Fig. 12 shows the birefringence of the uniaxially oriented polymer II as a function of temperature, with the photopolymerization temperature as the parameter. Two observations can be made:

- Over a wide temperature region (room temperature to 300°C) the birefringence shows only a moderate decrease with temperature, when compared with the polymerized monoacrylate (Fig. 10). Moreover, the birefringence behaviour of these ordered 3D networks proves to be completely reversible upon heating to 240°C. Above this temperature, some thermal degradation takes place.
Within a certain region (Δn = 0.12 to 0.15 at room temperature) the birefringence can be tuned by choosing the appropriate photopolymerization temperature.

FURTHER PHYSICAL PROPERTIES OF THE ORIENTED POLYMER NETWORKS

A study was made of the mechanical properties and the thermal expansion coefficient of the oriented polymer networks obtained (7). Uniaxially oriented polymer films with a thickness of 60 μm were made by sandwiching the monomer between two spacered glass substrates provided with uniaxially rubbed polymeric films; these monomer films were then photopolymerized with a high pressure Hg lamp in a nitrogen atmosphere, with the rubbing directions of the substrates parallel. Samples with a twisted orientation were made in a similar way, with the rubbing directions perpendicular.

The samples were cut to 2 mm wide strips. Dynamical mechanical measurements were carried out with a Polymer Laboratories DMTA apparatus at a frequency of 1 Hz. Thermal expansion coefficients were measured with a Perkin Elmer TMA-7 unit.

Fig. 13. Mechanical loss tangent as a function of temperature for polymerized LC diacrylates with spacer length (CH₂)n between n = 2 and 10.
Fig. 13 shows the mechanical loss tangent as a function of temperature for a series of oriented and photopolymerized LC diacrylates with R=H and spacer lengths varying between n=4 and 10:

\[
\text{CH}_2= \text{CH-} \text{COO--(CH}_2\text{)}_n\text{O--COO--OOC--O-...}
\]

\[-(\text{CH}_2\text{)}_n\text{OOC--CH=CH}_2\]

Three relaxation peaks are observed (following convention indicated by \(\alpha, \beta\) and \(\gamma\) in order of decreasing temperature). The position of the \(\beta\) and \(\gamma\) peaks are almost independent of spacer length, whereas that of the \(\alpha\) peak decreases with temperature. This phenomenon is not particular to our oriented networks, but is typical for a larger class of highly crosslinked networks (15). Our interpretation of the three loss peaks is:

- **\(\alpha\) peak:** network relaxation.
- **\(\beta\) peak:** sum of overlapping relaxation modes of the mesogenic unit. Introduction of a methyl group at the middle aromatic ring considerably changes the position of this peak.
- **\(\gamma\) peak:** crankshaft motion of \(\text{--CH}_2\text{--}\) groups. This peak is absent for a diacrylate with \(n=2\), and a similar structure (central ester groups reversed).

Fig. 14. Dynamic tensile modulus as a function of temperature for polydiacrylate II. 

\(//\) = parallel to direction of orientation \(\perp\) = perpendicular

\(\text{twist}\) = twisted orientation \(\text{iso}\) = isotropic polymer.
The dynamic tensile modulus for the polymer with n=6 measured as a function of temperature is shown in Fig. 14. The modulus of the uniaxially oriented polymer shows a clearly anisotropic behaviour. The modulus in the direction of molecular orientation is much higher than that in the perpendicular direction (2.5 versus 1 GPa). On the other hand the modulus in the orientation direction for this network is much lower than can be reached with linear main chain LC polymers (16). This must be explained by the fact that the oriented mesogenic units in the network are separated by more flexible acrylate regions.

The modulus for the twisted polymer and that polymerized from the isotropic state lie closely together.

![Graph showing linear thermal expansion for polydiacrylate II in the direction of orientation (z), and in the two perpendicular directions (x, y).](image.png)

Fig. 15. Linear thermal expansion for polydiacrylate II in the direction of orientation (z), and in the two perpendicular directions (x, y).

The linear thermal expansion behaviour of the n=6 polymer II measured in three directions is shown in Fig. 15 (17). Again a distinct anisotropy is observed. In the direction of molecular orientation the linear thermal expansion coefficient behaves negatively, as is common for oriented polymers and can be ascribed to entropic forces. In the perpendicular direction, a positive expansion is found.
TWO SPECIAL NETWORK STRUCTURES: HELICOIDAL NETWORKS AND ANISOTROPIC GELS

The combination of monomer orientation by methods common for low-molecular LCs with photopolymerization offers possibilities to come to unique polymer network structures. One possibility is to vary the monomer orientation over the layer, e.g. by applying an electric field over certain areas whereas leaving the uniaxial orientation unaltered in the other areas, in the way of an LCD; this situation can then be fixed by photopolymerization (8). Another possibility is to use masking techniques to achieve a patternwise orientation of the mesogens (2).

In the final section of this paper, however, we would like to elaborate on two other network structures based on the network formation process that we have described: helicoidal networks and anisotropic gels.

3D ordered polymer networks with a helicoidal structure can be made by addition of small amounts of chiral material to a nematic LC diacrylate to induce a cholesteric arrangement; this arrangement is then fixed by photopolymerization (9). The same arrangement occurs when a chiral substituent is attached to an LC side-chain polymer (18). The advantage of a crosslinked oriented network, however, is that (i) the ordering in the monomer can be exactly controlled, and (ii) can be "frozen-in" by polymerization to be stable over a wide temperature range, as we have seen before.

![Fig. 16. Natural pitch p of the helicoidal structure in diacrylate II (2a) and the eutectic mixture of II and III (3) vs. the concentration of chiral dopant.](image-url)
To obtain cholesteric ordering, the left-handed chiral material 1-4 (4-hexyloxy benzoyloxy)-benzoic acid-2 octyl ester (S 811, Merck) was added to the LC diacrylate II and to the eutectic blend of II and III in both cases provided with 1 wt% of photoinitiator B.

The natural pitch $p$ of monomer II and the eutectic blend as a function of concentration of chiral dopant is shown in Fig. 16. This pitch is defined as the distance of a $2\pi$ screw rotation of the molecular packing. It is measured by the Cano wedge method (19). This consists in inserting the LC material between a flat and a planoconvex substrate, both provided with an uniaxially rubbed polymer film; from the distance between the Grandjean-Cano disclinations, which reflect a discontinuous step of $\pi$ radians in the rotation angle of the LC material, the natural pitch can be calculated. Such Grandjean-Cano disclinations for a sample after photopolymerization are shown in Fig. 17.

![Segment of the circular Grandjean-Cano disclination lines observed through a polarization microscope between crossed polarizers.](image)

During photopolymerization the distance of the disclination lines towards the centre of the wedge cell did not change. The resulting pitch was only found to differ from that in the monomer by the polymerization shrinkage (about 10% at 120°C) and by the thermal shrinkage upon cooling to room temperature (an additional 3%).
By the procedure described, foils of twisted polymer can be made with controllable rotation angle, thickness and birefringence.

Another special class of oriented polymer networks can be produced by UV-irradiating an oriented mixture of LC diacrylates and non-polymerizable LC molecules (10). In this way anisotropic gels can be made containing LC molecules which can be switched by an external electric or magnetic field, but align themselves with the mesogenic groups in the network when this external field is switched off. In this way light scattering can be induced upon application of an electric field.

A 6μm cell was filled with a mixture of 5 wt% of monomer and 95% of the commercial LC mixture E7 (BDH), after which the monomer was photopolymerized to a gel. The response of this cell in a polarization microscope between crossed polarizers when various voltages are applied, is shown in Fig. 18.

![Fig. 18](image)

**Fig. 18.** Response of 5 wt.% polydiacrylate II / 95 wt.% E7 mixture to various voltages applied across a 6μm cell.

CONCLUSIONS

Highly crosslinked oriented polymers can be made by photopolymerization of preoriented LC monomers.
Suitable monomers for this process are diacrylates with a mesogenic group based on di(benzoyloxy)benzene. This monomer shows stable LC behaviour with a melting temperature of 108°C and a clearing temperature of 155°C. A methyl substituent on the middle aromatic ring reduces these temperatures to 86 and 116°C, respectively.

Addition of 2 wt% of a photoinitiator leads to a decrease of these transition temperatures by a maximum of 10°C.

Photopolymerization kinetics of these diacrylates are not much different from those of similar diacrylates without LC behaviour.

Upon photopolymerization of the LC diacrylates the ordering shows some increase or some decrease depending on the polymerization temperature, as indicated by birefringence measurements. The resulting birefringence is very stable with temperature, and is completely reversible upon heating to ≤ 240°C.

Apart from the refractive index also the thermal expansion coefficient and the tensile modulus of the oriented networks show a clear anisotropy. In the case of the modulus, this is not as outspoken as reached in linear main chain LC polymers.

Two special cases of oriented network structures are helicoidal networks and anisotropic gels, the latter consisting of a mixture of photopolymerized LC diacrylates and non-polymerizable LCs.

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