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ARTICLE TYPE

## New photoswitchable mesogenic polyurethanes with gelation ability

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5 We report a new series of thermotropic side-chain liquid crystalline polyurethanes comprising photosensitive three ring chiral mesogen and a flexible methylene spacer. All compounds, polymers as well as monomeric precursors, display the smectic type phases. Due to a presence of azo group in molecular structure, materials exhibit reversible photoisomerization process. It was also found that the polyurethanes show the gelation ability for several organic solvents, obtained gels are thermo- and photo-  
10 reversible.

### Introduction

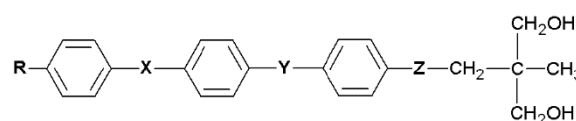
Introduction of the mesogenic molecules into the main chain or as side groups of a polymer may lead to liquid crystalline polymer (LCP), that combines the anisotropic properties of liquid crystals  
15 and the elastic properties of the polymeric materials.<sup>1-4</sup> Side-chain liquid crystalline polymers (SCLCP) have been known as an important class of polymers due to their distinctive features in the field of nonlinear optics and optical information storage devices<sup>5-7</sup>, thus designing of new SCLCP materials has become a  
20 fascinating area of current research. The structural properties of SCLCP are defined by the type of mesogenic group and polymer scaffold, but also by the grafting density of mesogenic groups, length and flexibility of spacer between mesogenic group and the polymer chain, etc.<sup>4,8-12</sup> For the SCLCP with sufficiently long  
25 spacers the order of mesogenic units decouples from the polymer backbone order, thus nematic, smectic and columnar phases can be easily formed.<sup>13-17</sup> Depending on the structure, the liquid crystalline polymeric systems might have different potential applications.<sup>18</sup>

30 Some polymeric materials have been also known for their gelation abilities. Gels formed by various classes of gelators have been studied over the decades for a broad range of their applications.<sup>19</sup> The chemical and physical organogels are formed by the self-assembling of organic molecules into an entangled  
35 network that entraps organic solvent molecules. In recent years there is increasing interest in mesogenic gelators due to their tuneable properties.<sup>20-26</sup>

Here, it is reported the synthesis and the mesogenic properties of a new series of side chain liquid crystalline polyurethanes,  
40 obtained by the reaction of hexamethylenediisocyanate with a mesogenic diols. The chiral mesogenic diols consisting of a three ring molecular core were chosen, as for such molecular structures ferroelectric behavior is anticipated.<sup>27</sup> Also, the gelation ability of the studied polyurethanes for various organic solvents is reported,  
45 with thermally and photo reversible sol-gel phase transition.<sup>28</sup>

### Results and discussions

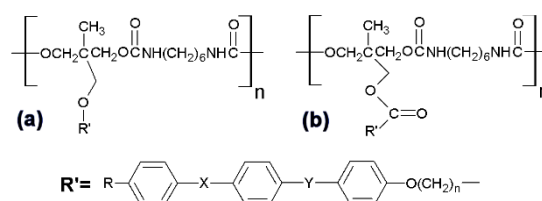
A general molecular structure of the diol monomers (M1-M4) and related polyurethanes (P1-P4) is presented in scheme 1 and 2  
50 respectively, along with the details provided in the Table 1. Mesogenes M1-M3 contain single chiral centre in terminal chains, derived from 2-methylbutanol, while M4 have two, additional one being derived from lactic acid.



55 Scheme 1. General structure of LC diol monomers.

**Table 1** Structures of molecular parts of all the diol monomers.

Monomer	R	X	Y	Z
M1	CH <sub>3</sub> CH <sub>2</sub> C*H(CH <sub>3</sub> )CH <sub>2</sub> O	CH <sub>2</sub> O	N=N	O(CH <sub>2</sub> ) <sub>8</sub> O
M2	CH <sub>3</sub> CH <sub>2</sub> C*H(CH <sub>3</sub> )CH <sub>2</sub> O	CH <sub>2</sub> O	N=N	O(CH <sub>2</sub> ) <sub>10</sub> O
M3	CH <sub>3</sub> CH <sub>2</sub> C*H(CH <sub>3</sub> )CH <sub>2</sub> O	N=N	OCH <sub>2</sub>	O(CH <sub>2</sub> ) <sub>10</sub> O
M4	CH <sub>3</sub> CH <sub>2</sub> C*H(CH <sub>3</sub> )CH <sub>2</sub> OCOC*H(CH <sub>3</sub> )OCO	CH <sub>2</sub> O	N=N	O(CH <sub>2</sub> ) <sub>10</sub> COO



Scheme 2. Polymer skeleton of LC (a) P1, P2 and P3 (b) P4.

60 All the studied materials form liquid crystalline phases, observed phase sequences and phase transition temperatures, detected by DSC, are collected in Table 2. Similar clearing temperatures were observed for all the monomers with the single chiral centre. For the lactate derivative M4 the isotropisation temperature decreased  
65 due to the presence of two chiral centres in the terminal chain.

Table 2. Phase transition temperatures (in °C) and related thermal effects (in parentheses, kJ mol<sup>-1</sup>) for studied compounds determined by DSC.

	m.p. / g.t. <sup>a</sup>	HexI <sup>b</sup>	SmC*	SmA	Iso			
M1	112.6 (6.52)	•	121.0 (1.09)	•	135.1 (10.89)	•	143.0 (22.41)	•
P1	105.8 (0.39)	105.8 (0.39)	•	•	121.6 (3.65)	•		•
M2	131.6 (21.74)	•	137.7 (2.10)	•	144.2 (24.77)	•		•
P2			•	•	110.6 (1.08)	•	124.0 (14.20)	•
M3	97.5 (41.71)	•	131.4 (2.15)	•	138.8 (9.08)	•		•
P3	58.5 (7.81)	58.5 (7.81)	•	•	126.5 (0.49)	•	135.3 (0.65)	•
M4	96.9 (2.18)		•	•	116 (10.64)	•		•
P4	53.7 (14.03)	53.7 (14.03)	•	•	88.3 (9.18)	•		•

<sup>a</sup> melting of crystal was observed for monomers while glass transition for polymers

<sup>b</sup> in case of P3 the type of hexatic phase (HexF or HexI) was not identified

Polymers exhibit isotropization at lower temperatures relative to the corresponding monomers, apparently partial decoupling of smectic layers by polymer chains takes place. The monomers undergo the transition to crystalline phase on cooling, whereas the polymers exhibit glassy state of LC phase instead; the crystallization process of polymers is disfavoured due to the long polymer chain structure and high viscosity of materials. All the studied compounds, monomers and polymers, form tilted liquid-like smectic C phase (SmC\*). The tilted smectic phase was identified from a characteristic schlieren texture with four brush defects (Fig. 1), lack of two brush defects suggests synclinal smectic phase.<sup>29</sup>

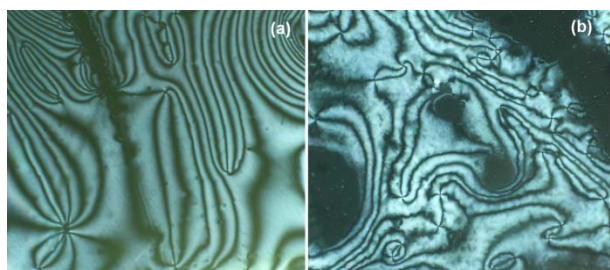


Fig. 1 Schlieren texture showing four brush defects, characteristic of SmC<sub>s</sub> (tilted, synclinal) phase (a) M3 and (b) P2 under POM.

Formation of the schlieren texture, characteristic for the optically biaxial phase, indicates that the helix, expected for chiral tilted smectic phase, is not formed or the pitch is much longer than the thickness (several microns) of the sample under observation. The phase identification was verified by x-ray diffraction studies, the pattern recorded in SmC\* phase consisted of commensurate Bragg reflections at small angle range, associated with the layered structure, and a diffused signal at high angle range (corresponding to 4.5Å periodicity) confirming the liquid-like order in the smectic layers (Fig. 2a). For compounds M1 and P2 the orthogonal smectic A phase (SmA) has been also observed above the SmC\* phase. For all the monomers with one chiral centre (M1-M3), on cooling the transition from SmC\* phase to a hexatic smectic phase was found, manifested by a change of

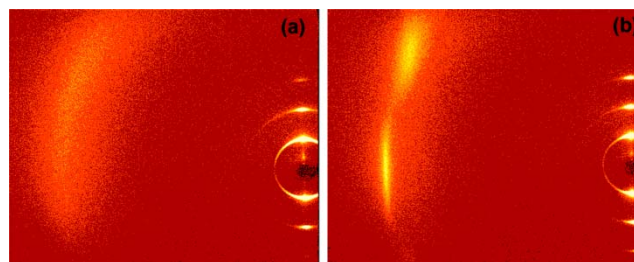


Fig. 2 Two dimensional X-ray patterns for M3 monomer in: (a) SmC\* phase and (b) HexI phase.

optical texture. On a basis of XRD studies of oriented samples the phase was identified as HexI phase; its XRD pattern (Fig.2b) shows azimuthally split signals at high angle region, which are significantly narrower than in SmC\* phase, reflecting the increased correlation length of positional order inside the layers in the hexatic phase. From the position of the high-angle peaks with respect to the equatorial plane, the direction of the long molecular axis tilt can be determined, in this case being towards the apex of the pseudo-hexagonal unit cell.<sup>30</sup> Also for a polymeric material P3 the SmC\* - hexatic smectic phase transition was observed, however the type of the hexatic phase was not identified, as no well aligned sample could be obtained.

The smectic layer thickness, *d*, has been measured for studied compounds as a function of temperature in the whole range of the liquid crystalline phases. The observed *d*(*T*) dependences (Fig. 3) confirmed phase sequences determined previously: at the SmA-SmC phase transition layer spacing decreases reflecting the tilt of the molecules, while upon approaching SmC\* - HexI phase transition the layer spacing increases gradually due to the increase in the orientational order of molecules and the stretching of the alkyl tails.

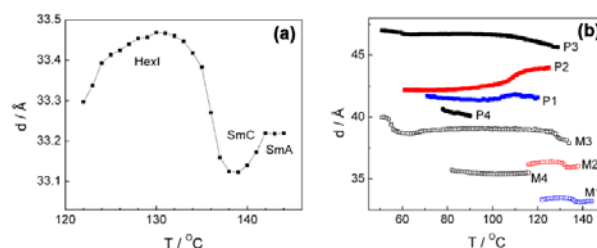


Fig. 3 Layer thickness as a function of temperature (a) *d*(*T*) dependence is presented for M1 (b) Temperature dependences shown for all compounds for comparison.

Comparing phase sequences of materials 1 and 2, it could be observed that changing the length of methylene spacer (unit Z in Table 1) has an opposite influence on monomers and polymers. In case of monomers, for which the spacer plays a role of terminal chain, increasing its length leads to destabilization of orthogonal SmA phase. For polymers, in which the spacer Z links the mesogenic cores to the polymeric backbone, the SmA phase was observed for longer homologue. Despite different influence on phase sequence, increasing the number of methylene groups in the spacer always leads to the slight increase of phase transition temperatures. Changing the positions of azo and ether linkage units in mesogenic core has only a minor effect on phase properties of monomeric compounds M2 and M3; in polymeric counterparts it induces/destabilizes hexatic smectic phase – the

hexatic phase is observed for P3 while absent for P2 material.

The tilted smectic phases observed for monomers and polymers are expected to be polar, due to the broken inversion symmetry of tilted lamellar phase made of chiral molecules.<sup>27</sup> In case of polymer P4, having two chiral centres attached to mesogenic core through ester group bridge, clear electrooptical switching was observed, i.e. rotation of extinction brushes in fan-like texture upon application of electric field, indicating tilt angle  $\sim 30$  deg. However, optical switching was not accompanied by detectable polarization reversal current peak, indicating small electric polarization for this material ( $< 5$  nC/cm<sup>2</sup>). Moreover, the material had a rather high ionic conductivity. Similar results were seen for monomer M4 – clear optical switching with no detectable polarization reversal current. For none of compounds having a single chiral centre attached to mesogenic core by methylene group any optical or electric response was measured, indicating that polarization is even smaller than for P4 and M4 materials. Small electric polarization, below the measuring limit, suggests that the average transverse dipole moment of the mesogenic units is very small.

#### Effect of UV irradiation on the structure of polymer

Polyurethanes were also investigated by XRD under application of the UV light to determine the influence of the change in the molecular conformation on the formed structures. When the polymeric compound being in the SmC\* phase was illuminated with UV radiation, the x-ray signal related to the lamellar structure disappeared (Fig. 4a). Apparently, the Z isomeric form, induced by absorption of UV light lacks the mesogenic properties. If the UV light is turned off, the signal reappears that verifies the reversible change between Z and E isomers. For polymers in the glassy state of SmC\* phase it takes much longer time ( $>30$  min) to attain isotropization by UV irradiation, probably lack of translation freedom of the molecular fragments in the glassy state strongly weakens conformational changes of azo units.

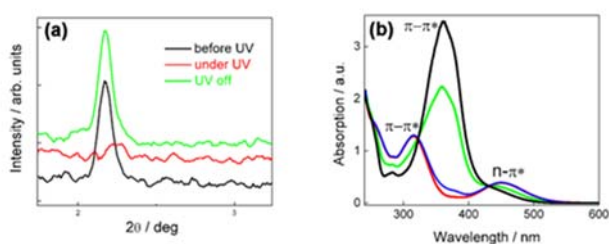


Fig. 4 (a) X-ray signal related to the layer spacing in SmC\* phase of polymer P3: (black) before irradiation, (red) under irradiation with UV light, 365 nm, (green) 20 min after irradiation. (b) UV-VIS absorption spectra for polymer P3 dissolved in chloroform: (black) before irradiation, (red) just after irradiation with UV light, 365 nm, (blue) 20 min after irradiation and (green) after irradiation with visible light.

The E-Z conformation change was confirmed by UV-Vis spectroscopic measurements.<sup>31</sup> The polyurethanes containing azo groups exhibited a strong  $\pi$ - $\pi^*$  absorption band with maximum centered at 360 nm and 310 nm, for E and Z isomer, respectively. When the solution of polyurethane in chloroform was irradiated with UV light, the E to Z isomerization was observed, monitored by the blue shift of  $\pi$ - $\pi^*$  absorption and the appearance of weak n- $\pi^*$  band at 450 nm (Fig. 4b). In solution, the Z isomer was

stable after the UV irradiation had been stopped, the E form was restored by irradiation with visible light,  $\lambda > 400$  nm. Similar results were also observed for all the diol monomers in solution.

#### Polymer gels

All the studied polymers exhibited gelation ability for various organic fluids, such as toluene, nitrobenzene, 3-methylcyclohexanone, (-)-menthone, (+)-menthone, at concentrations ca. 10 wt%. No gelation was observed for polar or mediate organic solvents (DMF, ethanol, methanol, dichloromethane, chloroform). The gels were formed after the mixture of polymer and solvent was heated and subsequently cooled to room temperature; it should be stressed that gelation occurred in the whole volume of the sample, no precipitation of crystallites from solution was observed. The gel and sol states are thermoreversible with the phase transition temperature dependent on the organic solvent (see ESI). The sol-gel phase transition temperatures monitored optically coincide with those detected by the DSC method (Fig 5a). The morphology of gels was examined by the scanning electron microscopy (SEM). The SEM picture of the dried xerogel (Fig. 5b) revealed the formation of a three-dimensional network made of long, entangled, weakly twisted helical fibrous aggregates. The x-ray patterns of gel and the xerogel are similar, with a very weak diffused signal at small angle region and a stronger diffused signal at a high angle range, corresponding to  $\sim 5$  Å, which indicates amorphous character of fibrous aggregates forming a gel.

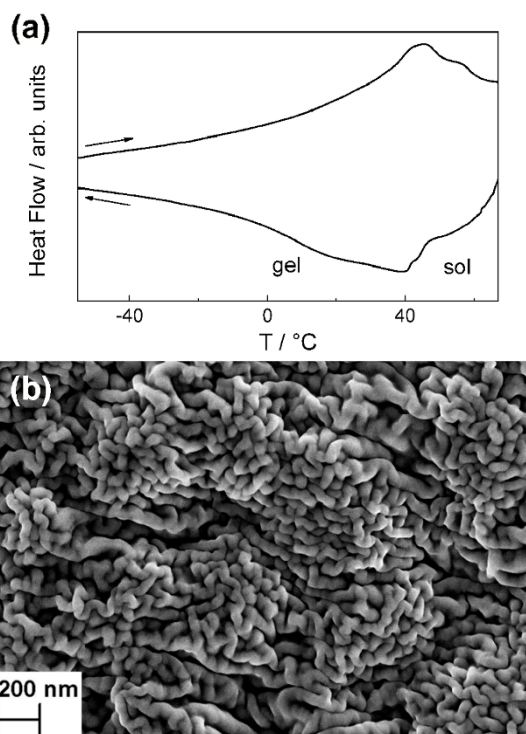


Fig. 5 (a) DSC scan showing reversible sol-gel phase transition for a P3 polymer in (+)-menthone and (b) SEM picture of xerogel.

As the investigated compounds have photoactive azo groups in their molecular structures,<sup>32</sup> the gel-sol transition could also be induced by illumination of the sample with the UV light; the resulting sol state is stable for hours after switching off the UV

light. At room temperature the mixture returns to a gel state only after irradiation with visible light ( $\lambda = 400$  nm) that restores the E conformation of azo units.

## Conclusions

New mesogenic diols were prepared and studied, and their liquid crystalline properties were compared with the respective polyurethanes. All the obtained compounds displayed SmC\* phase, however, with low electric polarization. Those with two chiral centres attached to the mesogenic core by stiffer ester linkage show electrooptic response, however not accompanied with measurable switching current. Lack of detectable polar properties for other materials, with the single chiral centre, can be attributed to its distant position in terminal chain and flexible connection between asymmetric carbon atom and mesogenic core. The presence of azo unit in the mesogenic units enables E/Z photoisomerization, the irradiation of the sample by UV light induced smectic-isotropic phase transition. Polymers were found to exhibit the gel forming ability for different solvents with thermo- and photo-reversible sol-gel phase transition.

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## Notes and references

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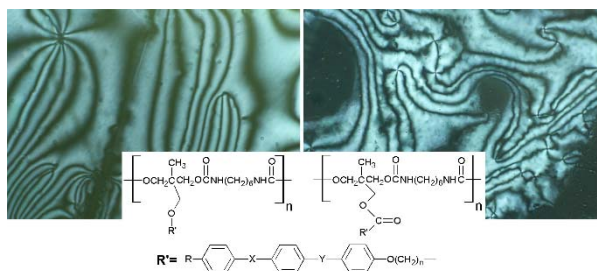
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† Electronic Supplementary Information (ESI) available: Experimental section, details of synthetic procedures and characterization of studied materials. See DOI: 10.1039/b000000x/

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TOC



5 New liquid crystalline polyurethanes are presented, that show the gelation ability for several organic solvents.