

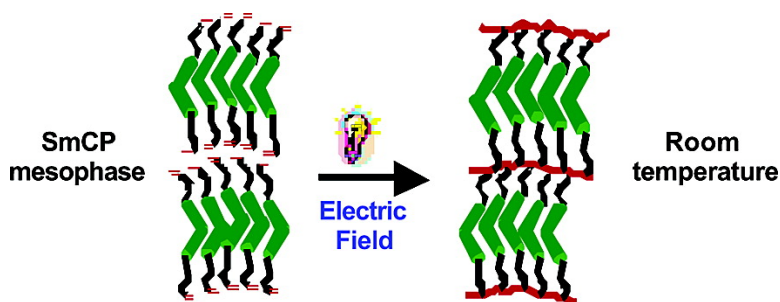
Communication

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SmCP-Networked Films Obtained by in Situ Photopolymerization of Neat Reactive Banana-Shaped Liquid Crystals

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The combination of liquid crystal order and in situ photopolymerization processes¹ is widely accepted to be a very versatile technique for producing materials that are suitable for a variety of applications. This strategy provides different types of materials that include gels, side-chain and cross-linked polymers, or anisotropic networks where a functional response along with thermal and mechanical stability are required in a well-aligned medium. The key goal is to incorporate the active structure in an aligned liquid crystalline medium that is able to transform into a macroscopically aligned high-molecular weight material.

Polymerizations in classic liquid crystal phases are reported quite regularly.^{1,2} However, among the different types of mesogenic materials, the new banana-shaped liquid crystals represent a topic of current interest from both academic and practical points of view.³ Interestingly, some compounds exhibit the unique feature of forming polar ordered mesophases (SmCP³) with achiral molecules, thus providing antiferroelectric, ferroelectric, or nonlinear optical properties. However, very few attempts at the polymerization of bent molecules in these mesophases have been reported. Ikeda et al.⁴ succeeded in preparing noncentrosymmetric polar networks by using blends of a nonmesogenic V-shaped bisacrylate with a nonreactive bent liquid crystal. And, with similar purposes, Gin et al.⁵ have used neat bent-core molecules bearing 1,3-dienes as reactive groups.

Here we report our studies on the in situ photopolymerization of neat V-shaped bisacrylates (Scheme 1) in which the SmCP order of their mesophase is also retained in the resulting polymer. These compounds incorporate an angular core that has a high tendency to promote the SmCP phase, namely, the 3,4'-disubstituted biphenyl unit.⁶

These compounds were prepared following synthetic routes similar to those reported in the literature.^{6,7} The thermal properties of the monomers were determined by polarizing optical microscopy, differential scanning calorimetry (DSC), and X-ray diffraction. The results of these studies are collected in Table 1.

Despite the fact that the compounds described here show a thermotropic SmCP mesophase that vitrifies at around room temperature on cooling, it is clear that the incorporation of the reactive end groups dramatically modifies the thermal stability of the liquid crystal order promoted by these angular structures.⁸

The SmCP mesophases of **A** and **M** were assigned on the basis of the *Schlieren* textures observed by microscopy as well as from the X-ray patterns taken both in the mesophase and the glassy state that appears on cooling (Table 2). The measured interlayer distance *d* is shorter than the molecular length estimated from Dreding stereomodels, and the differences between the measured layer thickness and the molecular length confirm that the molecules are tilted in the layers. The data shown in Table 2 indicate that there are no significant differences between either of the two compounds or between the high-temperature values and the values measured in the glassy state. Additionally the switching processes of these

Table 1. Liquid Crystal Properties of Reactive Banana Compounds

compound	phase transition (°C, [kJ mol ⁻¹]) ^{a,b}
A	K 83.6 [39.7], SmCP 104.1 [16.01] I
	I 102.3 [15.66], SmCP 30.0 SmCPg
	SmCPg ^c 37.0, SmCP 103.4 [16.23] I
M	K 85.9 [38.33], SmCP 108.6 [19.60] I
	I 106.7 [18.11], SmCP 30.0 SmCPg
	SmCPg ^c 35.0, SmCP 107.6 [18.00] I

^a Data determined by DSC from first scans at a scanning rate of 10 °C/min. ^b K, crystalline; SmCP, SmC polar mesophase; SmCPg, glassy SmC polar phase; I, liquid phase. ^c Data from a second scan.

compounds are clearly tristable, indicating an antiferroelectric switching (*P* around 600 nC cm⁻²) (Supporting Information).

Compounds **A** and **M** were subjected to both thermal and radical photopolymerization experiments to investigate the polymerization behavior of these reactive banana systems and to ascertain whether they can be cross-linked with retention of the liquid crystalline arrangement.⁹ However, our main interest was focused on the study of the in situ photopolymerization processes in the SmCP mesophase, which is without precedent in the literature. Neither **A** nor **M** absorb above 310 nm, and consequently, the polymerization can be induced by a photoinitiator absorbing at 365 nm.¹⁰ A study of the photopolymerization of the mixtures was carried out by DSC. The conversion vs irradiation time (Figure 1) and polymerization

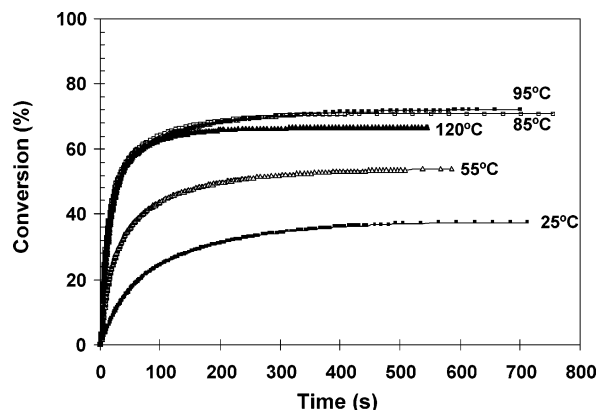
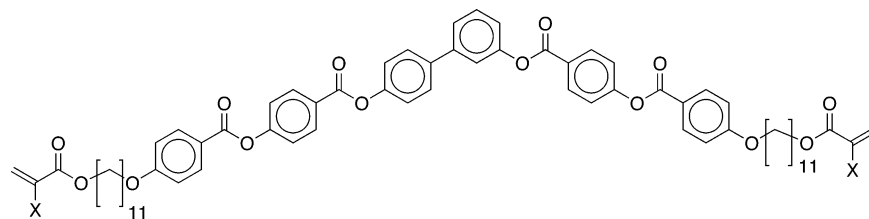


Figure 1. Conversion vs time at different temperatures (cooling) for the photopolymerizable sample prepared with monomer **M**.

rate vs conversion relationships were evaluated from the photopolymerization exotherms of the DSC curves (see Supporting Information).

The final conversion for both monomers, determined by DSC was around 75% in the polar mesophase, in the range 95–85 °C. A faster polymerization rate was observed for the bisacrylate **A**, and the Rp/% conversion curves are very similar to those reported

Scheme 1. Compounds Studied: A (X = H) and M (X = CH₃)**Table 2.** X-ray Data of the Studied Materials

compound	<i>T</i> (°C)	phase	measured spacings (Å)	Miller index	parameters (Å)
A	94	SmCP	41.3	001	<i>d</i> = 41.2
	room temp	SmCPg	13.7	003	<i>d</i> = 40.3
			40.2	001	
M	98	SmCP	42.0	001	<i>d</i> = 42.0
	room temp	SmCPg	14.0	003	<i>d</i> = 41.1
			41.2	001	
free film- A	room temp	SmCP	13.7	003	<i>d</i> = 45.5
			45.1	001	
			22.8 (weak)	002	
free film- M	room temp	SmCP	15.3	003	<i>d</i> = 43.9
			43.7	001	
			22.0 (weak)	002	
			14.7	003	

for bisacrylate and bismethacrylate monomers in calamitic mesophases.^{1d}

To demonstrate that the banana monomers had cross-linked to form polar networks, samples of compounds **A** and **M** were placed between two uncoated glass plates and the photopolymerizations were performed in the SmCP mesophase. Free thin films, mechanically stable at room temperature, were removed from between the glasses, and different techniques provide evidence that the films are networks, with a lamellar order at room temperature similar to the SmCP mesophase exhibited by monomers prior to polymerization. Their X-ray patterns are consistent with a SmCP order. Additionally, the second-order maximum (002 reflection), was visible (albeit with a weak intensity) for the polymers (Table 2).¹¹

To investigate the possibility of obtaining noncentrosymmetric networks from these neat SmCP photopolymerizable materials, a sample of monomer **M** was polymerized under an electric field.¹² The optical texture of the film after polymerization showed that it was still a polydomain, but the polar arrangement could be kept stable for long time over a wide temperature range from room temperature to 150 °C and higher. More interestingly, the polymerized material showed SHG activity at room temperature and in the absence of an electric field. The maximum intensity of the SHG signal from the sample was comparable of that of quartz.¹³ However, it must be noted that proper characterization of the *d_{ij}* coefficients of these materials requires well-aligned samples,¹⁴ and more precise measurements will be performed as part of a future project.

In conclusion, we have shown that the versatility of in situ photopolymerization can be extended to the new SmCP mesophases and that, through suitable molecular design, reactive bent molecules exhibiting these mesophases can be explored. These results open very interesting ways to design many different materials based on the singular banana-shaped molecules. Furthermore, attractive properties such as noncentrosymmetric polar order and helical arrangements, which have been claimed for some of the mesophases

exhibited by these compounds, can be targeted through these high-molecular weight materials. The resulting systems have potential applications as new linear- and nonlinear optical, ferro-, antiferro-, pyro-, or piezoelectric materials.

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Supporting Information Available: Synthesis, experimental details, and characterization of monomers and polymerized films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Nonreactive homologue with terminal chains C₁₄H₂₉O— shows K 85 °C SmCP 162 °C I₆ A broad SmCP range in a nonreactive V-shaped molecule seems to ensure the SmCP order for the bisacrylate homologues.⁴
- (9) Indeed, care should be taken when manipulating samples above 130 °C, even in the presence of a thermal inhibitor.
- (10) Photopolymerization of the monomers was carried out using a photo-DSC experimental setup equipped with a 365 nm lamp and samples containing 1% (w/w) Irgacure 369 and 200 ppm of the thermal inhibitor 2,6-di-*tert*-butyl-4-methylphenol. The liquid crystalline properties of the monomers were not noticeably modified for the blends.
- (11) The 10% increase of *d* in the SmCP order upon cross-linking has been attributed to a less tilted packing of the bent cores in the network. Using stereomodels, we deduced tilt angles of ca. 50° for both monomers in the mesophase and 45–47° in the networks assuming a bent angle of 120° and all-trans conformations of the chains.
- (12) Monomer was placed in a 5 μm ITO cell (from Linkam) and photochemically polymerized in the SmCP mesophase (at 100 °C) using a DC voltage (40 V/μm) to ensure a noncentrosymmetric polar order (also called SmCP_F)^{3c}.
- (13) Activity of this sample (thickness of 5 μm) was compared at room temperature with that of a *x*-cut quartz crystal (1 mm).
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