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Suspension polymerization of thermotropic monomer: Formation of droplets or beads

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Ordered beads were obtained by the suspension copolymerization of a mesogenic methacrylate-based monomer and methacrylic acid. The stability of these particles and the liquid crystal organization inside the particles depend mainly on the time of polymerization and on the crosslinking. Suspended droplets of monomers or polymers can be obtained as well as solid spheres. The solid particles exhibit ordered microstructures with a liquid crystal configuration that has a variable form depending on polymerization time and observation temperature. Bead characteristics such as morphology, size and polydispersity, and porosity are discussed and compared with those of non-mesomorphic beads. The mesomorphic beads are smaller and their porosity lower. The presence of a crosslinker during the polymerization process leads to more mechanically stable particles with retention of polymorphism.

1. Introduction

Over the past fifteen years, polymer dispersed liquid crystals (PDLCs) have been intensively investigated and applied to technological uses such as electro-optic displays or variable transmittance devices [1–3]. PDLCs are produced using a phase separation between a polymer and low molecular mass liquid crystal [3–8], leading to small droplets of liquid crystalline molecules. Difficulties lie in the choice of the polymer matrix and the control of the kinetics of demixing. In such systems, Terentjev showed [9] that the emulsion is stabilized by the orientational order within the droplet. A characteristic size of droplet is obtained (typically tens of micrometers), which is controlled by the balance of the elastic properties of the liquid crystal and the anchoring tension at the interface between the droplet and the isotropic liquid.

Robust liquid crystalline droplets were recently obtained by encapsulation using a polymerizable surfactant [10, 11]. These particles, whose diameter is a few micrometers, are stable for long periods above the clearing temperature. Furthermore, micron-sized capsules were prepared by swelling monodispersed polymethylmethacrylate particles with a mixture of liquid crystal, monomers and initiators [12].

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In this paper a new method is described for the formation of stable particles of liquid crystal from a mesogenic methacrylate monomer. The polymerization was performed from suspensions of these monomers in a non-miscible conventional solvent; a crosslinking agent could also be introduced. As the polymerization proceeds, the droplets of liquid crystal harden, the orientation of its molecules changes and its mobility decreases. So, by controlling the polymerization time, droplets or small beads of liquid crystals can be obtained. A better fundamental understanding of liquid crystals in confined geometries, will contribute to these materials finding application, for example, as paints or as temperature-switchable devices, opaque at low temperatures and transparent at high temperatures.

2. Experimental

2.1. Characterization techniques

The nature of the mesophases and the temperature at which they occur were determined by polarizing optical microscopy (POM) (Olympus microscope equipped with a Mettler FP82HT hot stage), differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 calorimeter, and X-ray scattering experiments. The transition temperatures recorded for the mesogenic monomer correspond to those determined from the maxima of the DSC peaks obtained on cooling at $5^{\circ}\text{C min}^{-1}$.

X-ray measurements were performed using CuK_α radiation of a 12 kW rotating anode X-ray generator. A flat pyrolytic germanium (1 1 1) monochromator delivered a $1 \times 0.9 \text{ mm}^2$ beam to the sample. The scattered radiation was collected on a two-dimensional detector from Mar Research (Hamburg). The detector system was an imaging plate (Fuji Photo Film Co. Ltd) read by scanning with a He-Ne laser. The diameter of the circular plate was 180 mm, and the pixel size $150 \times 150 \mu\text{m}^2$. The intensity map was stored as a $1200 \text{ pixel} \times 1200 \text{ pixel}$ numerical image on a Silicon Graphic work station. The sample-to-detector distance was 450 mm through helium in order to lower absorption and diffusion.

The average weight molecular mass and average number molecular mass (respectively \overline{M}_w and \overline{M}_n) of the polyacrylates were determined, by size exclusion chromatography (SEC) in toluene using three columns (Styragel® HR1-HR3-HR4-300 X 0.7 mm) and a refractometer detector (Waters, RI model 410). The flow rate was 1.2 ml min^{-1} and calibration was performed with polystyrene standards. Samples at a concentration of 2 mg ml^{-1} were injected after 24 h solubilization in toluene.

The size distributions of bead samples were analysed by laser light scattering from suspensions in distilled water (Malvern Instruments) and in the dry state by scanning electronic microscopy (SEM) and optical microscopy. The particles were characterized using a polarizing microscope (magnification $\times 200$) and a Sony camera. Pore volumes were determined by mercury intrusion porosimetry on a Carlo Erba model 2000 porosimeter (Milan, Italy). Before measurements, the samples were degassed under vacuum at 80°C for 24 h. Pore sizes (pore radii R_p) were calculated from the intruded pressure (P_{Hg}) using the Washburn equation, taking a mercury surface tension γ of 480 mN m^{-1} , a contact angle θ of 130° and assuming a cylindrical pore model according to the Washburn equation: $P_{\text{Hg}} = -2\gamma \cos \theta / R_p$

2.2. Synthesis

The synthetic route for the mesogenic monomer is shown in the scheme. Hydroquinone, methacrylic acid, 4-(dimethylamino)pyridine (DMAP), triphenylphosphine (TPP), pyridine and ethylene glycol dimethylacrylate (EGDMA) were purchased from Aldrich Fine Chemicals (Saint Quentin Fallavier, France). *N,N'*-Dicyclohexylcarbodiimide (DCC), 1,6-hexanediol, diethyl azodicarboxylate (DEAD), α,α' -azoisobutyronitrile (AIBN) and poly(vinyl alcohol) (PVA) ($\overline{M}_w = 100\,000 \text{ g mol}^{-1}$, 88% hydrolysed) were obtained from Fluka, Saint Quentin Fallavier, France. All the solvents used were HPLC grade.

2.2.1. 6-Hydroxyhexyl methacrylate **1**

DCC (250 mmol), 1,6-hexanediol (250 mmol), and DMAP (25 mmol) were dissolved in dichloromethane (500 ml). Methacrylic acid (250 mmol) was added dropwise and the resulting solution stirred overnight at room temperature. The solution was filtered and evaporated. These operations were repeated after the addition of cold heptane. The crude product was purified by chromatography on a silica gel column using dichloromethane as eluent. A yellow oil was obtained (90 mmol); yield 35%. Mass: m/z 186 $[\text{M}]^+$. Elemental analysis found (calculated): H = 9.9 (9.7), C = 64.4 (64.5)%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm/TMS): 1.3, 1.5, 1.6, 1.9, 3.6, 4.1, 5.5 and 6.0. $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3 , δ ppm/TMS): 18.5, 25.8, 28.7, 64.7, 125.4, 136.6 and 167.6.

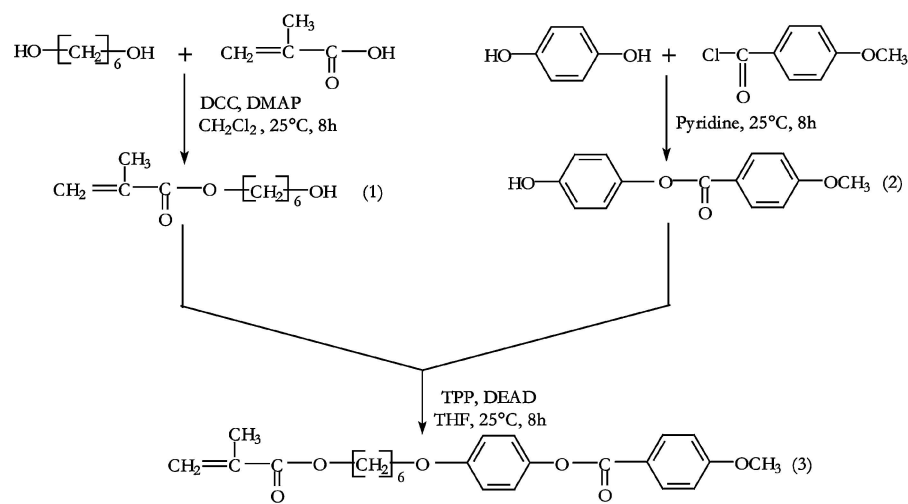
2.2.2. 4-Hydroxyphenyl 4-methoxybenzoate **2**

Hydroquinone (200 mmol) was dissolved in anhydrous pyridine (150 ml). 4-Methoxybenzoyl chloride (200 mmol), dissolved in anhydrous pyridine (50 ml), was added dropwise and the resulting solution stirred overnight at room temperature. The solution was diluted with water (50 ml). The diester obtained as a white precipitate was filtered. The solution was acidified with concentrated hydrochloric acid (10 mol %) then the crude product was filtered and purified by recrystallization in methanol. Compound **2** was obtained as white crystals, yield 50%. Mass: m/z 244 $[\text{M}]^+$. Elemental analysis found (calculated): H = 5.0 (5.0), C = 68.1 (68.8)%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm/TMS): 3.9, 6.8, 6.9, 7.0 and 8.1. $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3 , δ ppm/TMS): 55.6, 114.0, 116.2, 122.8, 132.4, 122.0, 144.6, 153.4, 164.0 and 164.7.

2.2.3. 4-(6-Methacryloyloxyhexyloxy)phenyl 4-methoxybenzoate **3**

Compound **1** (32 mmol), **2** (32 mmol) and TPP (32 mmol) were dissolved in tetrahydrofuran (THF). DEAD (32 mmol) was added dropwise, at 10°C , and the resulting solution stirred overnight at room temperature. The solution was evaporated and the residue diluted with cyclohexane/ethyl acetate (20/5 v/v) (25 ml). The white precipitate of phosphine was filtered off, and the solvent evaporated. The crude product was purified by chromatography on a silica gel column using dichloromethane as eluent. The product was finally recrystallized from ethanol. Compound **3** was obtained as white crystals; yield 60%.

As observed by POM and DSC, this compound exhibits a monotropic nematic phase: Cr-I 40.6°C , I-N 33.6°C ($\Delta H_{\text{I-N}} = 1.9 \text{ J g}^{-1}$). Mass: m/z 412 $[\text{M}]^+$. Elemental analysis found (calculated): H = 6.6 (6.8), C = 70.0 (69.9)%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm/TMS):



1.4, 1.7, 1.8, 1.9, 3.9, 4.1, 5.5, 6.1, 6.8, 6.9, 7.0, and 8.1. ^{13}C NMR (62.9 MHz, CDCl_3 , δ ppm/TMS): 18.5, 25.9, 26.0, 28.7, 29.3, 55.6, 64.8, 68.3, 114.0, 115.2, 122.1, 122.7, 125.4, 136.6, 144.5, 156.8, 164.0, 165.4 and 167.7.

2.3. Suspension polymerization

Suspension polymerization was carried out by suspending a solution of monomers and crosslinker in toluene (to allow the solubilization of all the solid compounds) as droplets in water. Toluene accounted for 70 wt % of the organic phase. Toluene was also used as a porogenic agent. The droplets were prevented from coalescing by stirring at 400 rpm in the presence of a suspension stabilizer such as poly(vinyl alcohol) solubilized in distilled water at a concentration of 20 g l^{-1} . The free-radical initiator used was azobisbutyronitrile (AIBN) soluble in the monomer droplets at the concentration of 2% per mole of monomers. A 15% molar ratio of methacrylic acid was always introduced in the different samples for its hydrophilic nature, so promoting copolymerization at the toluene/water interface. Figure 1 and table 1 report the chemical compositions of the samples prepared. Sample 1, without mesogenic groups, was prepared as a reference. Sample 2 was not crosslinked.

Table 1. Chemical composition of the samples. Each sample contains a 15% molar ratio of methacrylic acid ($X + Y + 15 = 100\%$).

Sample	% Mesogenic monomer X	% Crosslinker (EGDMA) Y
1	0	85
2	85	0
3	70	15

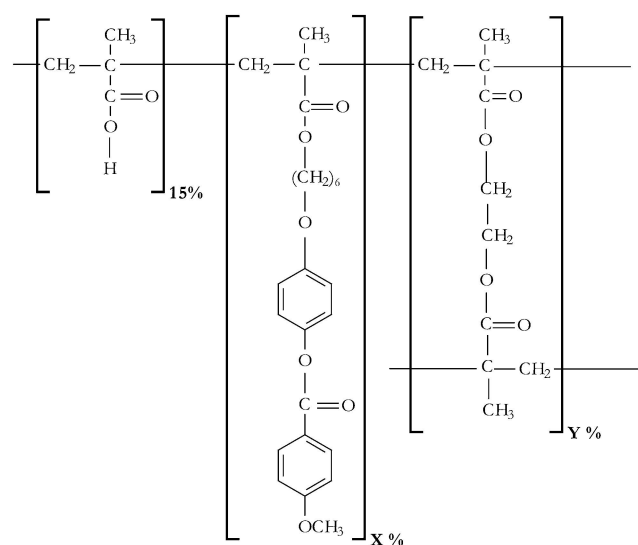


Figure 1. Chemical structures of the samples described ($X + Y + 15 = 100\%$).

A 500 ml batch reactor was used for the suspension polymerization process. The polymerization occurred at 80°C under a nitrogen flow. The water/organic volume ratio was typically 10/1. The organic phase contained the AIBN initiator, the monomers (methacrylic acid, mesogenic monomer) and, when present, the EGDMA crosslinker; the total volume was 200 ml. Mixing was complete after 3 min sonication.

The batch reactor was equipped with a bottom ball valve, through which samples were removed at different polymerization times. Periodically a small amount of the sample was examined under POM; generally, polymerization continued for 24 h. After polymerization, the beads obtained (about 1 g) were washed twice in hot water (200 ml) to remove PVA from their surface.

3. Results and discussion

3.1. Particle morphology

3.1.1. Non-crosslinked sample

Figure 2 shows the photomicrographs of sample 2 after different polymerization times. Particles were observed for all polymerization times. For short reaction times (*a*), the particles were typically primary beads or droplets in which the monomers were incompletely polymerized; the photomicrograph exhibits deformable droplets. The droplets were progressively transformed into solid spherical particles or beads while the sizes of the particles were unchanged (*b*, *c* and *d*) even after 24 h polymerization. Furthermore, these pictures show the perfectly spherical nature of the beads and suggest a polydispersity of bead sizes.

The evolution of the polymer chain length during polymerization was studied. Comparative chromatograms are given in figure 3. The chromatograms reveal two main peaks elute at about 18 (peak 1) and 29 ml (peak 2) after 4 h polymerization. Peak 2 reveals the presence of short polymer chains in the sample or residual monomer. This peak decreases and totally disappears after 24 h polymerization to leave peak 1 (18 ml). This may be attributed to the presence of long polymer chains in the sample (109 000 g per mol eq polystyrene).

3.1.2. Crosslinked samples

The SEM photographs in figure 4 confirm both the spherical nature and the broad polydispersity of the beads whatever sample is considered. It is well known that suspension polymerization leads to a broad bead size distribution depending on the reactor shape, stirring speed or nature and concentration of the surfactant. If we compare samples 1 and 3 after 24 h polymerization, there is a large difference in the average bead diameter (100 and 40 μm , respectively). The size distribution of the beads was 60–130 μm for sample 1, figure 4(*a*), against 20–60 μm for sample 3, figure 4(*b*). The particle sizes depend mainly on the chemical composition of the mixtures before reaction, if all other experimental conditions are unchanged. The reduction of bead size appears to be due to the presence of mesogens as described previously [8, 9].

Liquid crystal droplets in emulsions have been discussed in terms of the shape of the droplets and orientation of the director within a droplet. The size distribution of sample 1 after 24 h polymerization reveals the good correlation between microscopy and laser light scattering measurements, see figure 5. The polydispersity of the beads of sample 3 seemed to be greater than that of the reference when the analysis was based on laser light scattering in water as the suspension medium. Thus, an aggregation phenomenon between beads is truly observed (see also figure 4). This is possibly due firstly to a self-

association between mesogenic groups at the bead surfaces and secondly to a problem of bead wettability in water. In fact, water does not favour the dispersion of the particles.

The porosity of the particles also appears to be governed by the presence of the mesogens. Figure 6 represents the variation of the cumulative intruded mercury volume with the pore radius for samples 1 and 3. This analysis was performed only with crosslinked samples to ensure maximum mechanical resistance. At low pressures, the variation of mercury volume corresponded to the void volume between particles. The lack of macroporosity was clearly revealed in sample 3: the void volume was lower in accord to the behaviour of mesomorphous beads, which tended to associate with each other, in suspension in water as well as in the dry state. The reference sample showed meso- and micro-porosity (pore radii <100 nm), while sample 3 exhibited only low microporosity (pore radii <30 nm). The variation of the porous volume and pore size distribution in the two samples was very different and could be attributed to:

- (i) The interactions between mesogenic groups contracting the network. The resulting porosity was therefore considerably reduced.
- (ii) Toluene as porogenic agent having different affinities for the two materials and generating different pore size ranges. Other porogens should now be investigated.

Figure 7, obtained by SEM, also shows the difference in surface porosity between the samples. With the mesomorphic material, no porosity is observed in the photograph.

3.2. Mesomorphic properties

In this section, we discuss the mesomorphic properties of the samples and the liquid crystalline organization within the droplets or beads. Table 2 gives the transition temperatures versus the polymerization time for sample 2 (non-crosslinked) and sample 3 (crosslinked). These results show a good correlation with the average

Table 2. Isotropic–nematic transition temperature (T_{IN}) of the mesomorphic samples (2 and 3) versus polymerization time; ND = not determined. T_{IN} of pure monomer is 34°C.

Polymerization time	$T_{\text{IN}}/^\circ\text{C}$	
	Sample 2	Sample 3
90 min	32	ND
4 h	71	98
8 h	94	ND
24 h	108	120

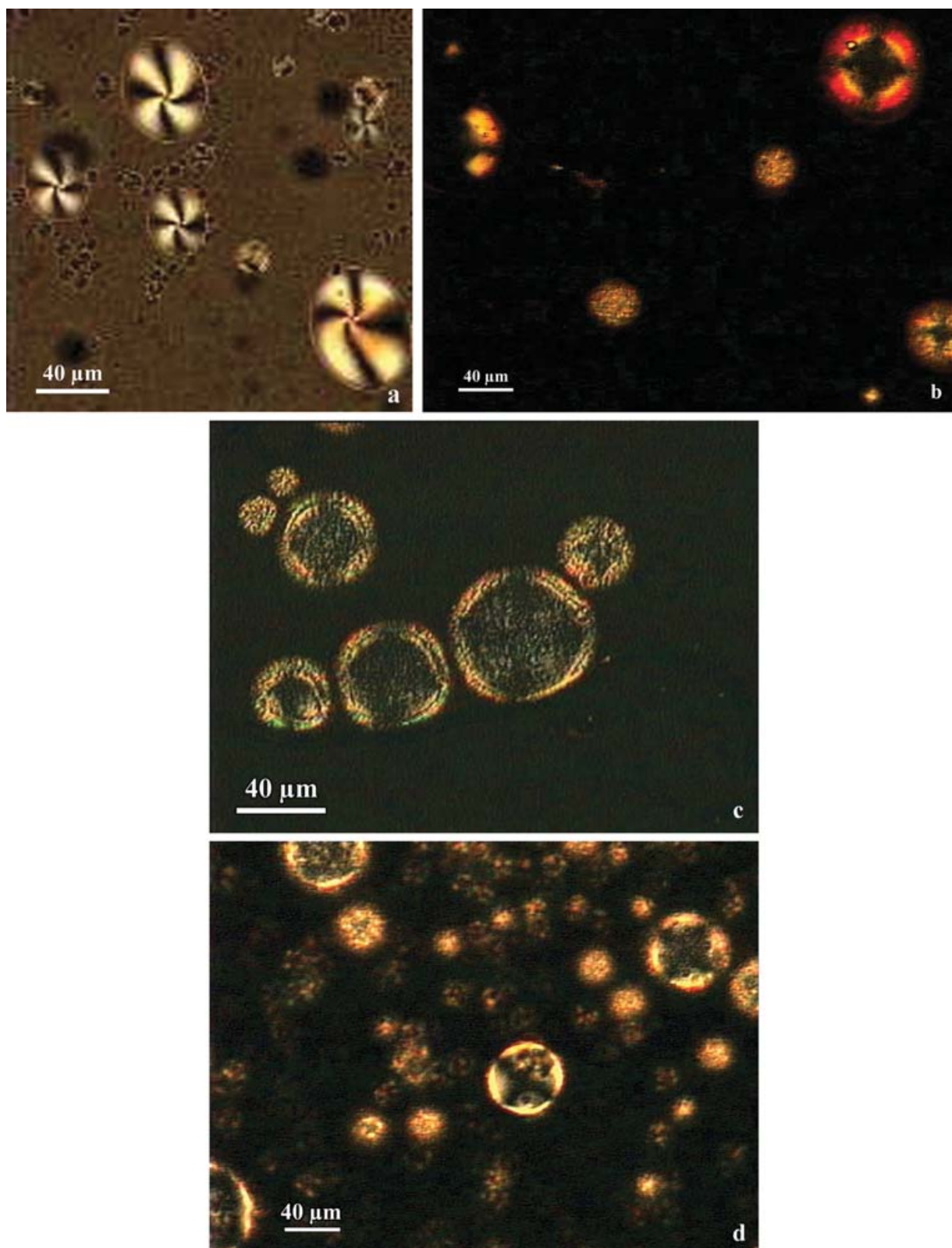


Figure 2. POM photographs for sample 2 with varying polymerization time and observation temperature. (a) 90 min, 25°C; (b) 4 h, 25°C; (c) 8 h, 90°C; (d) 24 h, 90°C.

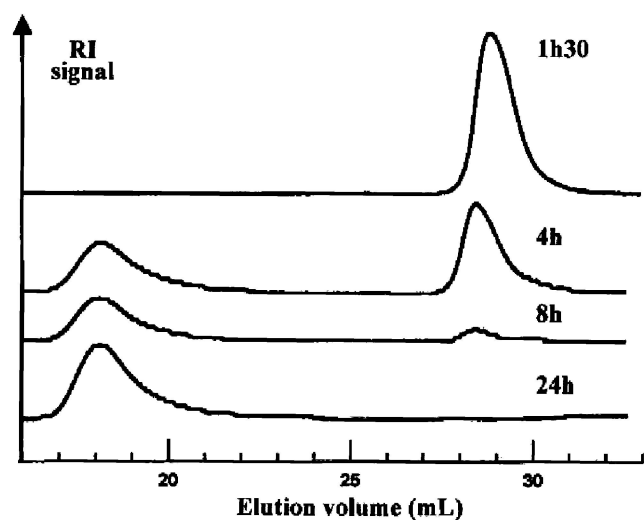


Figure 3. SEC chromatograms of sample 2 versus polymerization time. The elution profiles were obtained in toluene at 1.2 ml min^{-1} .

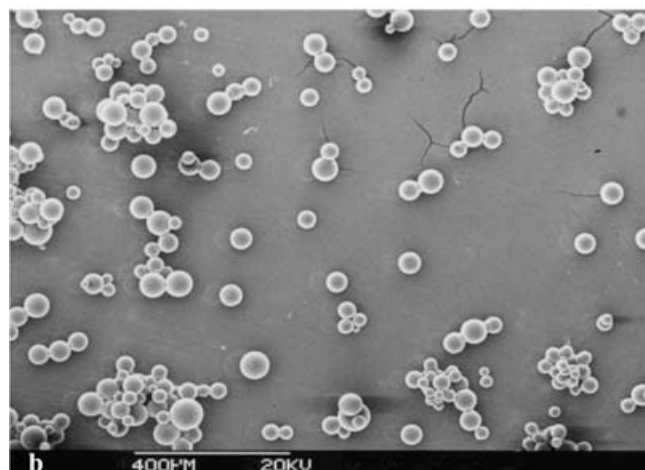
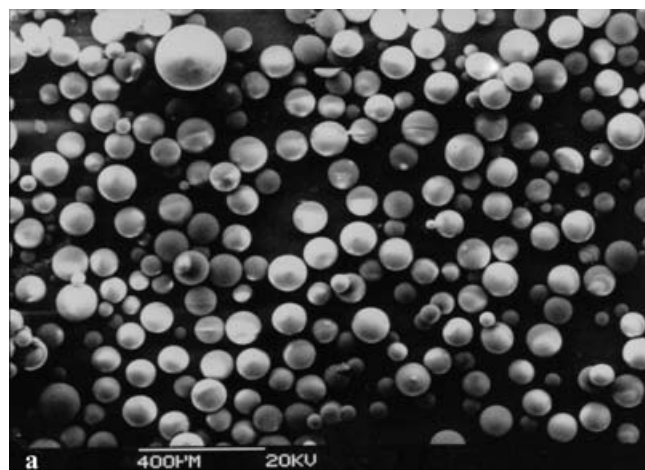


Figure 4. SEM photographs of (a) sample 1 and (b) sample 3 after 24 h polymerization.

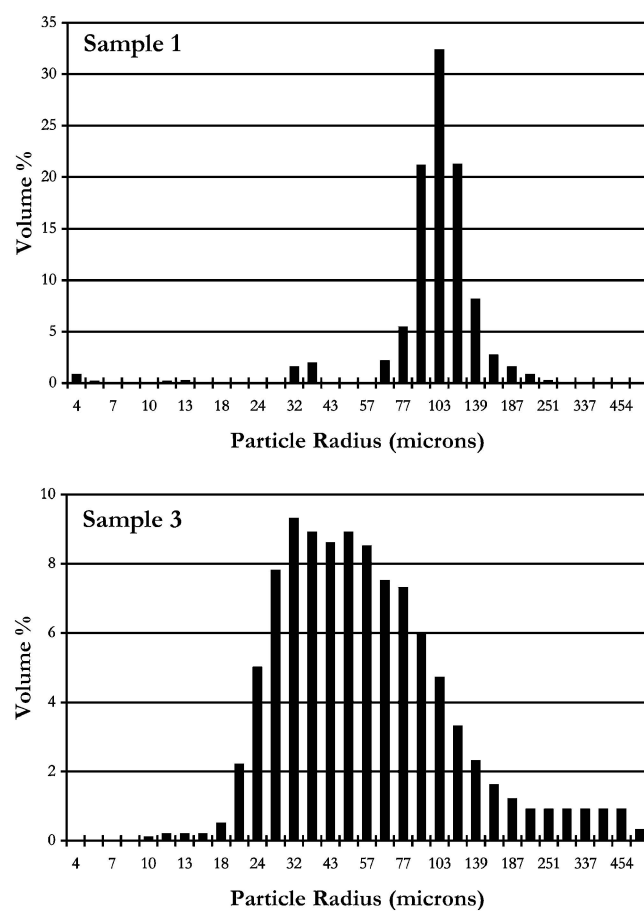


Figure 5. Bead size distribution of samples 1 and 3 after 24 h polymerization; by laser light scattering in water.

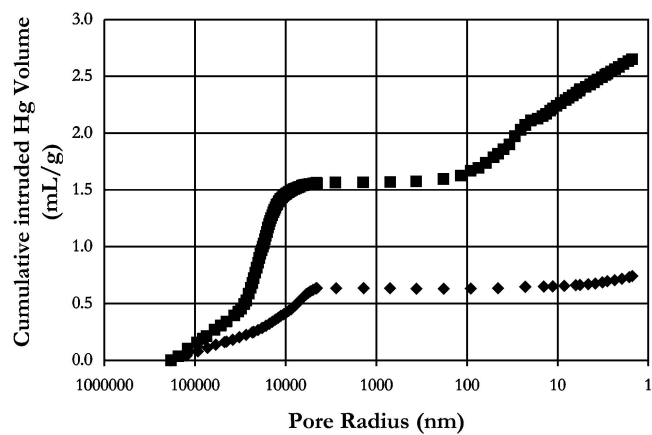


Figure 6. Comparative Hg porosimetry curves of samples 1 (■) and 3 (◆).

molecular weights determined from the chromatograms depicted in figure 3. Thus, T_{IN} (isotropic–nematic transition temperature) increases with increasing molecular weight during the polymerization process. In all cases, the transition temperatures of the samples (2 and 3) were higher than those obtained for pure

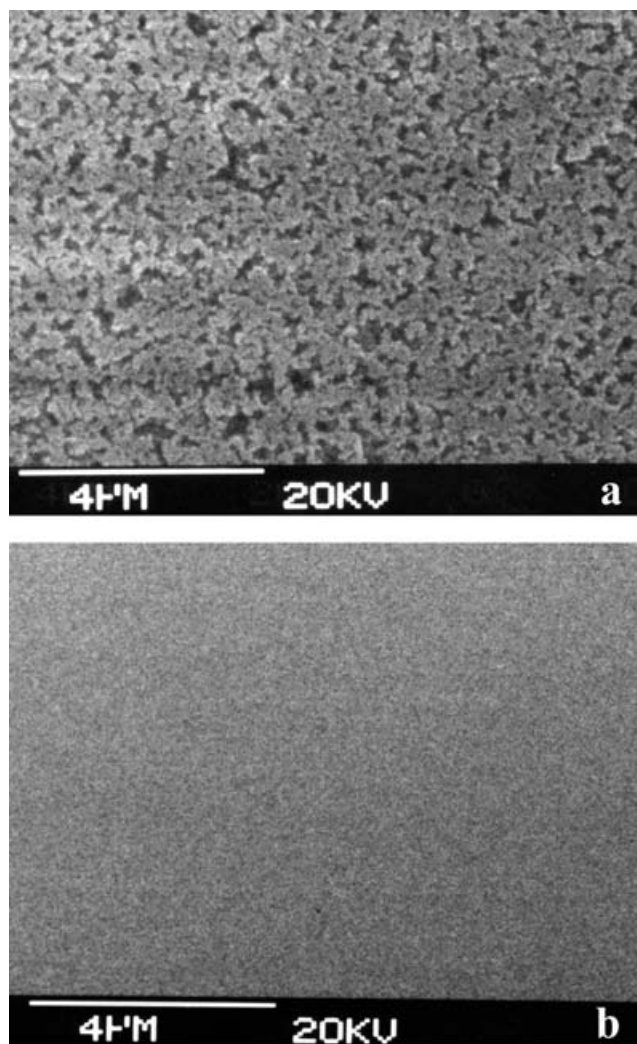


Figure 7. Surface porosity as seen by SEM photographs of crosslinked samples (a) 1 and (b) 3 after 24 h polymerization.

monomers, except after 90 min polymerization. This may be due to the presence of the other compounds used, which affected the transition temperatures; they are considered as impurities. Figure 8 shows an example of the beads obtained after 4 h polymerization and observed at two different temperatures. The textures observed reveal a nematic mesophase in each case (see also figure 2). The nature of the mesophase is confirmed by the X-ray measurements in which no lamellar structure was observed. The increase of the observation temperature from 74°C, figure 8 (a), to 98°C, figure 8 (b), gives higher birefringence.

At the beginning of polymerization (figure 2), the high mobility of the liquid crystal was apparent and the liquid crystal molecules showed homeotropic anchoring. The microscopic texture of all the droplets is a typical star pattern (Maltese cross) and invariant with respect to rotation of the microscope stage, thus proving that the

director field is radial. This kind of nematic droplet had already been studied [1, 5, 10, 13, 14]. When polymerization and crosslinking take place, the birefringent textures inside the beads change, resulting in inhomogeneities in the orientational ordering. This is indicative of the disordering effect due to growing polymer chains and/or the monomer consumption. This was also previously observed [13]. Furthermore, the final particles still exhibit, in their core, a liquid crystalline organization and a high mobility of the mesogen. This observation suggests that polymerization/crosslinking essentially occurs at the surface of the particles. The beads would have a core-shell structure in which the low molecular mass liquid crystal (monomer or oligomer) is still mobile. The shell, composed of the network, could induce a modification of the orientation of the free mesomorphic molecules.

Volovik and Lavrentovich [14] studied the topological dynamics of similar defects by varying the surface interaction energies of the liquid crystal molecules at the droplet wall. In our case, the same phenomenon occurs while polymerization takes place. It may be possible that the co-monomer MAA plays a role at the suspension medium/liquid crystal interface because of its hydrophilic nature. In fact, the polymerization of MAA may be faster than that of the mesomorphic monomer, leading to the formation of no random copolymers. It would be important to know the reactivity coefficients of the monomers.

After heating above the clearing temperature, the organization remains in the mesomorphic state in the case of crosslinked particles. Crosslinking provides robust and stable beads (in the dry state and in suspension media) in which the mesomorphic orientation is preserved even after heating to the isotropic state or one year after preparation, as shown in figure 9 which compares sample 2 (non-crosslinked), figures 9(a) and 9(b), and sample 3 (crosslinked), figure 9(c). Close to the clearing temperature, particles of the non-crosslinked sample coalesce, whereas they are stable in the crosslinked material.

4. Conclusion

We have shown that it is possible to prepare solid mesomorphic particles from a liquid crystal methacrylate monomer. The orientational order was observed in each case but its configuration inside the beads mainly depends on the polymerisation time and the temperature. Liquid crystals were 'encapsulated' in polymer beads by the suspension copolymerisation process using a hydrophilic co-monomer. Beads were stabilised by crosslinking. The average diameter of these new beads is smaller than that obtained without liquid crystal monomer and the porosity is much lower. Investigation

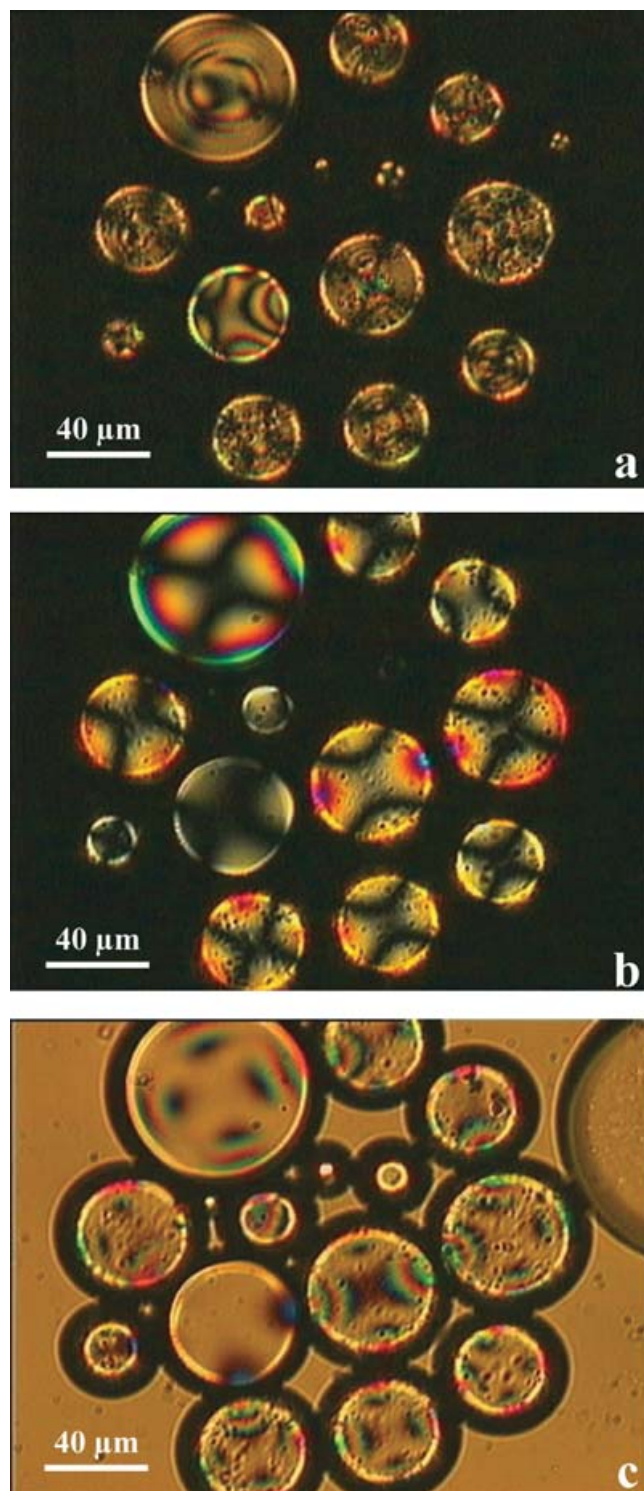


Figure 8. POM textures of sample 3 after 4 h polymerization (magnification $\times 200$): (a) at 78°C; (b) at 94°C (crossed polarizers); (c) at 94°C (uncrossed polarizers).

into the role of the co-monomer should now be pursued. The kinetics of polymerisation and its effects on the heterogeneities could be studied. Furthermore, a methacrylate

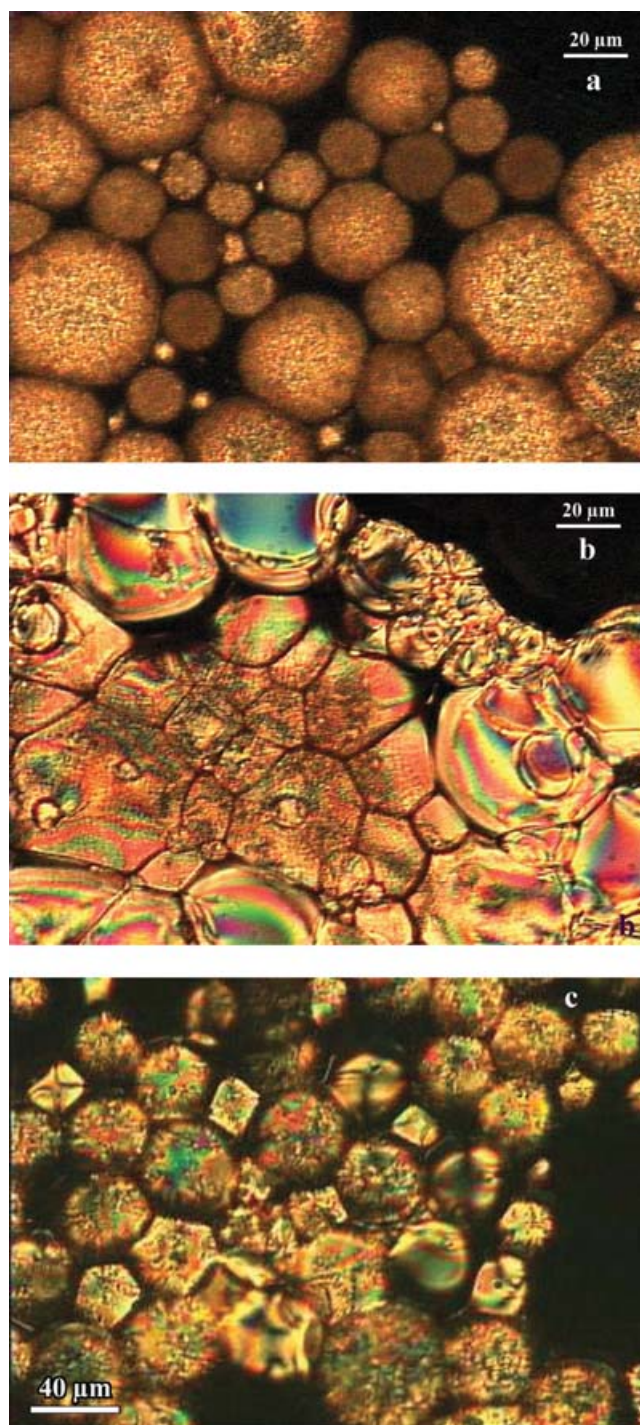


Figure 9. Effect of crosslinking on the thermal stability of bead samples 1 and 3 after varying polymerization conditions; observed by POM. (a) Sample 2, 25°C, 8 h; (b) sample 2, 80°C after heating above clearing temperature, 8 h; (c) sample 3, 50°C after heating above clearing temperature, 4 h.

monomer bearing a cyano-group could also be considered for its possible alignment under electric or magnetic field or by mechanical stress.

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