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ORIGINAL CONTRIBUTION

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^{2}H-NMR investigation after a polymerisation-induced phase separation process*

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*Dedicated to Professor V. Bertini for his 70th birthday

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Abstract Polymer-dispersed liquid crystals (PDLC) are composite materials consisting of micron-sized droplets of liquid crystal dispersed in a polymer matrix. The easiest method to obtain a PDLC film is the polymerisation-induced phase separation process (PIPS). The liquid crystal is mixed with a monomer of low molecular weight and polymerisation is induced by heat or UV light. The increasing molecular weight of the polymer causes the phase separation of liquid crystal from the polymer matrix as micron-sized droplets. In this work, we have studied the structural changes induced in the polymer matrix of a PDLC after the PIPS process by deuterium nuclear magnetic resonance. Two different selectively deuterated monomers have been synthesized and investigated: isobutyl methacrylate (IBMA-d_2) and methyl methacrylate (MMA-d_3). The main results were the disappearance of the characteristic two-site hop in poly-IBMA, due to liquid crystal molecules, and the lack of unreacted MMA molecules in the liquid crystal droplets. In this last case, we found that it is possible to confine temporarily the unreacted MMA molecules within liquid crystal droplets.

Keywords Polymer-dispersed liquid crystal · Phase separation · ^{2}H-NMR · Polymer-liquid crystal composite

Abbreviations

MMA	Methyl methacrylate
IBMA	Isobutyl methacrylate
PDLC	Polymer-dispersed liquid crystal
PIPS	Polymerisation-induced phase separation
^{2}*H-NMR*	Deuterium nuclear magnetic resonance

Introduction

Polymer-dispersed liquid crystals (PDLC) are composites consisting of micron-sized droplets of liquid crystal dispersed in a polymer matrix [1, 2]. They have aroused great interest for the production of smart windows, displays, and large area devices with an electrically variable transmittance. The most used method for the preparation of PDLCs is the polymerisation-induced phase separation process (PIPS) [2]. A homogeneous mixture of organic monomers and liquid crystal is polymerised by either thermal or UV initiators. As polymerisation proceeds, the mixture passes through a miscibility gap and a phase separation among components appears. Liquid crystal domains separate from the polymer matrix as small droplets, whose diameters generally range from a few tenths to some tens of micrometres. The rate of polymerisation determines the size and density of the liquid crystal droplets. PDLC thin films (thickness ≈ 10 μm) generally appear opaque due to the mismatch between the refractive indices of liquid crystal droplets and the polymer matrix. If the liquid crystal ordinary refractive index matches the index of the polymer matrix, the application of an electric field (E≈1–10 V μm^{-1}) will lead the film into an optically transparent state [3].

Even though such systems have been known for more than 15 years, there are some aspects of PDLCs which, if better understood, could be used to improve their electro-optical properties. In particular, very few experiments have been performed on the effects due to the presence of liquid crystal on the polymer structure and on the location of unreacted monomers. These data have an important role in the related application fields, as several technological parameters (operational fields, response times, mechanical properties, optical contrast ratios, ageing, etc.) depend on the physicochemical properties of the components used for preparation (liquid crystal, polymer, and monomer) and on the characteristics of their phase separation. Deuterium nuclear magnetic resonance (^{2}H-NMR) has been successfully used to determine some important properties of liquid crystals in PDLCs such as the director configurations, the anchoring parameters at the interfaces, and the molecular reorientation due to an electric field [4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Nevertheless, scant attention has been paid to the polymer matrix of PDLCs.

In this paper, we intend to show how detailed information on the polymerisation process can be obtained from ^{2}H-NMR spectra. We have investigated, by ^{2}H-NMR applied on selectively deuterated monomers (methyl methacrylate, MMA-d$_3$ and isobutyl methacrylate, IBMA-d$_2$), the distribution of unreacted monomers and the dynamic and structural changes in the polymer matrix due to a PIPS process. In particular, we have observed the disappearance of the characteristic two-site hop in poly-IBMA-d$_2$ [14] and the lack of unreacted MMA-d$_3$ molecules in the liquid crystal droplets. In addition, we found that it is possible to confine, temporarily, in droplets some unreacted MMA by means of a second thermally induced phase separation.

Experimental

The monomers used were: methyl methacrylate, selectively deuterated in its methyl chain (MMA-d$_3$) and isobutyl methacrylate, selectively deuterated in its methylene sites (IBMA-d$_2$). They were synthesized according to the strategy sketched in Fig. 1.

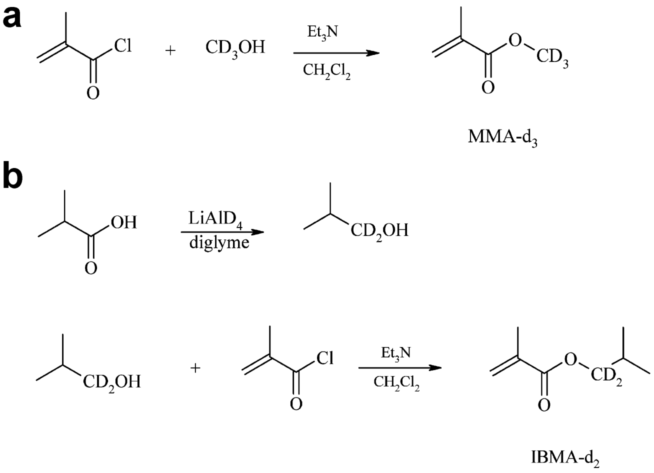

Fig. 1 Synthesis of selectively deuterated MMA and IBMA

Synthesis of 2-methyl-1-propanol-d$_2$

A suspension of LiAlD$_4$ (5.0 g, 130 mmol) in dry 2-methoxy ethyl ether (diglyme, 65 ml) was treated drop by drop (at 0 °C, under nitrogen) with 2-methylpropionic acid (11.4 g, 129 mmol) and stirred for 1 h at 100 °C. After dilution with 2-butoxyethanol (50 ml), the mixture was filtered and distilled at reduced pressure to provide a mixture of 2-butoxyethanol and 2-methyl-1-propanol-d$_2$ (20 ml in the first fraction). The distillation, at reduced pressure, of the latter mixture gave 2-methyl-1-propanol-d$_2$ (6 g, 78 mmol, yield 54%); b.p. 107–109 °C. MS *m/z*: 76 (M$^+$, 94%); 61 (M$^+$-15, 42%); 58 (M$^+$-18, 100%).

Synthesis of IBMA-d$_2$

A solution of 2-methyl-1-propanol-d$_2$ (6.0 g, 79 mmol) and dry triethylamine (12 g, 118 mmol) in dry dichloromethane (70 ml) was cooled to 0 °C and treated, under nitrogen, with freshly distilled methacryloyl chloride (7.7 ml, 79 mmol). The mixture was stirred for 15 h at room temperature, hydrolysed with water (300 ml), and extracted with dichloromethane (4×50 ml). All the organic phases were mixed and washed with 10% K$_2$CO$_3$ (2×100 ml), 1 N HCl (50 ml), and H$_2$O up to neutrality. After drying over anhydrous Na$_2$SO$_4$ and solvent evaporation at reduced pressure, the extracts were distilled to obtain IBMA-d$_2$ (7.6 g, 53 mmol, yield 92%); b.p. 70 °C/12 torr. IR (film) ν (cm^{-1}):1718 (C=O); 1182 (C–C(=O)–O); 940 (C=CH$_2$). MS *m/z*: 142(M$^+$, 1%); 87 (M$^+$-55, 24%); 68 (M$^+$-74, 100%). ^{1}H-NMR (CDCl$_3$) ppm: 0.84 (d, 6H, J=5.22 Hz); 1.84 (s, 3H); 1.85 (q, 1H, J=5.22 Hz); 5.46 (s, 1H); 6.02 (s, 1H). We found no signal at 4.1 ppm due to methylene groups. The deuterium substitution was larger than 99%.

Sample preparation

The liquid crystal used in this investigation was E7 (a eutectic mixture of cyanobiphenyls, Merck), characterised by a nematic-isotropic transition temperature of 59.0 °C. The components of E7 are shown in Fig. 2. The monomer-liquid crystal weight ratio was fixed at 1:1. Benzoyl peroxide (2 wt.%) was added as thermal initiator. Such homogeneous mixtures were polymerised for 15 h at 60 °C.

Experimental NMR parameters

^{2}H-NMR spectra were observed on a Bruker MSL 300 spectrometer, operating at 46.05 MHz in a 7-T magnetic field. The spectra, with a typical width of about 300 kHz, were recorded using a quadrupole technique (π/2-τ-π/2) with a pulse width of 9.1 μs, separated by a 40 μs delay. The free induction decay for each spectrum was averaged 300,000 times in order to achieve a good signal to noise ratio. The temperature was 18.0±0.1 °C.

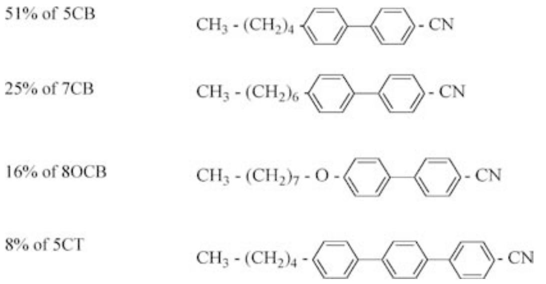

Fig. 2 Composition of the nematic eutectic mixture E7

Basic NMR theory

The ^{2}H-NMR line shape of quadrupolar nuclei is determined by the interaction between the nuclear quadrupole moment and the electric field gradient tensor generated by the surrounding environment [15]. The magnitude of such interaction depends on three factors: nature of chemical bonds, and orientation and motion of nuclei with respect to the external magnetic field, B_0. Since chemical bonds between deuterium atoms and carbon atoms are stable, the ^{2}H-NMR spectrum essentially depends on the orientation and motion of nuclei. In the absence of motion, the spectrum line shape depends only on the angle that the C–^{2}H bonds form with respect to B_0. The resonance frequencies for deuterons can be written as [15]:

$$\nu^{\pm} = \pm\frac{3}{8}\nu_Q\left(3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\phi\right) \qquad (1)$$

where θ and φ are the polar angles specifying the orientation of B_0 in the principal axis system of the electric field gradient tensor. $\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$ is the asymmetry parameter, V_{ii} are the three main elements of the electric field gradient tensor. η will be zero in the case of an electric field gradient tensor axially symmetric around the C–^{2}H bond, as in most aliphatic and aromatic compounds. The quadrupolar constant, ν_Q, is about 175 kHz in static C–^{2}H bonds and the resulting line shape for a sample with uniaxial symmetry and random orientation will be a characteristic powder pattern with a spectral width $\Delta\nu = {}^3/_2\ \nu_Q$ (about 262 kHz) and a peak separation between 90 ° singularities of $^3/_4\ \nu_Q$ (about 131 kHz). If nuclei are oriented parallel to the external magnetic field ($\theta = 0$ °), there will be two lines at $\pm\,{}^3/_4\ \nu_Q$. If the nuclear orientation is perpendicular to B_0 ($\theta = 90$ °), the spectrum will be characterised by two lines separated by $\Delta\nu = {}^3/_4\ \nu_Q$. Fast molecular motions average the ν_Q and η values, as they change the orientation of C–^{2}H bonds with respect to B_0. Consequently, ν_Q and η must be replaced in Eq. 1 by their average values $<\nu_Q>$ and $<\eta>$. Generally, molecular motions change the width and shape of NMR spectra in a significant and sometimes predictable way. For example, the fast rotations of methyl groups will shrink the static quadrupolar splitting of C–^{2}H bonds to about 1/3 (peak separation between 90 ° singularities of about 43 kHz), while the two-site hop of methylene C–^{2}H bonds will reduce the static quadrupolar splitting to about 1/2 (spectral width of about 131 kHz) and increase η to 1 [14, 15].

Results and discussion

^{2}H-NMR experiments on MMA-d_3

Figures 3a and b show the NMR spectra of samples obtained after the polymerisation of pure MMA-d_3 and a mixture of MMA-d_3 and E7 (1:1).The spectrum in Fig. 3a is formed by the superposition of a small, shrunk peak and a powder pattern, whose splitting between the central peaks (90 ° singularities) is around 38 kHz ($^3/_4$ $<\nu_Q>$). Such a powder pattern can be attributed to the free rotation of C–$^2H_3$ moieties of poly-MMA-d_3, in agreement with theoretical expectations, which predict a reduction in the static splitting by a factor of 3 (from 131 kHz to about 43 kHz). The difference between

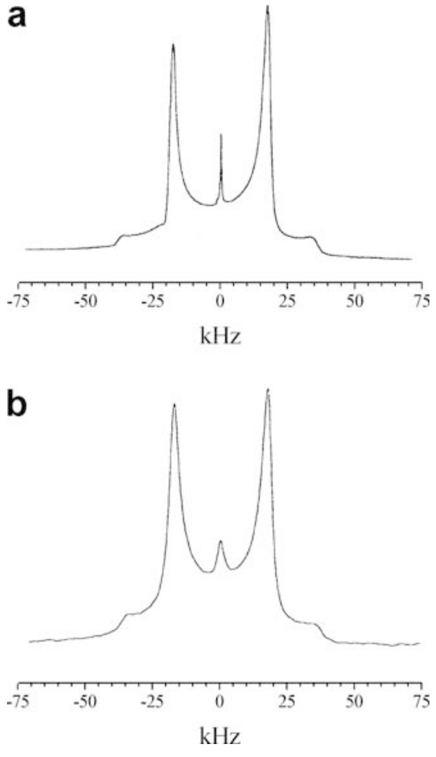

Fig. 3 ^{2}H-NMR spectra from: **a** poly-MMA-d_3 and **b** a PDLC obtained from a mixture of MMA-d_3 and E7 (1:1). Spectra were observed on a Bruker MSL 300 spectrometer, operating at 46.05 MHz in a 7-T magnetic field. The free induction decay was averaged 300,000 times in order to achieve a good signal to noise ratio. The temperature was 18.0 ± 0.1 °C

experiments (38 kHz) and theory (43 kHz) is that the average of Eq. 1 takes into account just the rotation of methyl groups and no other conformation motion. The small central peak can be due to the MMA-d_3 molecules dispersed in the thermoplastic matrix. Such unreacted molecules cannot be considered immobile and isotropically dispersed in the polymer matrix, as they would give a full powder pattern. A sharp peak is given by a rapid isotropic motion of reorientation, as in the case of a liquid phase. As a consequence, we can suppose either the presence of fast reorientation of unreacted monomers dispersed in the polymer matrix or the existence of small, nano-sized pockets of mobile MMA-d_3. Nevertheless, no void is detected on a scale of 50 nm by a scanning electron microscope investigation into thin films. The amount of unreacted MMA-d_3 is around 5–7%, as calculated by the spectrum integral.

Figure 3b does not show significant changes with respect to Fig. 3a. Even the presence of liquid crystal at a high percentage (50 wt.%) does not alter the line shape. It is possible to observe only an increase in the central peak intensity and a larger half height width (~3.7 kHz, area ~12%).

The methyl groups of poly-MMA-d_3 in PDLCs show a degree of order as large as that measured for the same groups in a pure polymer matrix (Fig. 3a). The powder pattern in Fig. 3b shows just a larger half height width due to the increased mobility of chains because of the presence of liquid crystal molecules. No unreacted MMA-d_3 is dispersed in liquid crystal droplets, at least within our experimental accuracy (1–2%). In fact for the above-mentioned case, we expect the presence of a doublet due to the fact that monomer molecules should be in an environment (liquid crystal droplets) which is aligned parallel to the external magnetic field (see later). As a consequence, monomer molecules are mainly dispersed in the matrix. Only a low percentage (less than 1–2%) of unreacted monomer can contaminate the liquid crystal droplets.

Nevertheless, after performing an NMR experiment on samples that were melted to a homogeneous mixture and later fast cooled (through a thermally induced phase separation), we obtained the spectrum shown in Fig. 4. In addition to the usual powder pattern, Fig. 4 shows at the base of the central peak a doublet, whose splitting is about 10.5 kHz. This doublet is due, in our opinion, to unreacted MMA-d_3 dispersed in liquid crystal droplets. The alignment of liquid crystal molecules in the presence of an NMR magnetic field produces a preferential alignment of unreacted MMA-d_3 molecules along the field direction and, consequently, it causes the appearance of a doublet in the spectrum. It is interesting to observe that the doublet of Fig. 4 disappears within a few days, giving rise to a spectrum similar to that reported in Fig. 3. This means that, after the thermally induced phase separation, the unreacted monomer can be trapped in liquid crystal droplets but monomer molecules can diffuse in the polymer matrix little by little. Consequently, it is quite important to take into consideration such a diffusion process in experiments dealing with the imprinting of droplet walls with monomers different from the polymer matrix [16].

In order to confirm such a hypothesis, we prepared a sample in which a low percentage of MMA-d_3 (~5 wt.%) was dissolved in pure E7 liquid crystal. We obtained the spectrum reported in Fig. 5. The spectrum is formed by the superposition of a central peak and of a doublet consisting of MMA-d_3, aligned by liquid crystal, whose splitting is around 8 kHz. The difference between the splitting of the doublets in Fig. 4 and Fig. 5 arises from the increase in the order parameter of liquid crystal and, consequently, of MMA-d_3 when they are confined in drops. The central peak indicates that a phase separation occurs in the sample, i.e. a biphasic system is formed by a nematic liquid crystal-rich phase and an MMA-d_3-rich phase. The temperature variation of the

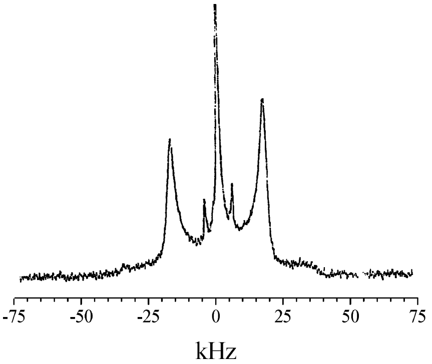

Fig. 4 ^{2}H-NMR spectrum after the melting and fast cooling of a PDLC obtained from a mixture of MMA-d_3 and E7 (1:1). Spectrum was observed on a Bruker MSL 300 spectrometer, operating at 46.05 MHz in a 7-T magnetic field. The free induction decay was averaged 300,000 times in order to achieve a good signal to noise ratio. The temperature was 18.0 ± 0.1 °C

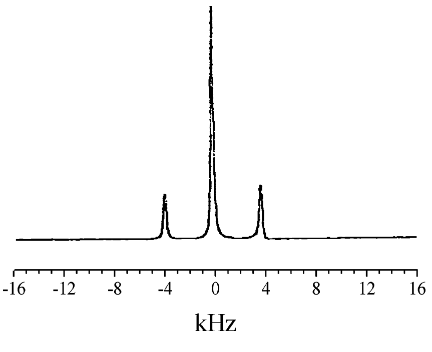

Fig. 5 ^{2}H-NMR spectrum from MMA-d_3 dispersed in E7 (5 wt.%:95 wt.%). Spectrum was observed on a Bruker MSL 300 spectrometer, operating at 46.05 MHz in a 7-T magnetic field. The temperature was 18.0 ± 0.1 °C

spectrum in Fig. 5 confirms the existence of two phases, as the central peak height and area increase, while the splitting width and area of the doublet decrease, till their disappearance at E7 clearing temperature. At 18 °C the solubility of MMA-d_3, as regards the liquid crystal, is around 2 wt.%.

As a further confirmation, we polymerised the sample which gave the spectrum reported in Fig. 5. Subsequently we obtained the spectrum shown in Fig. 6, which clearly shows the presence of a powder pattern with a separation between the central peaks (90° singularities) of around 38 kHz (arising from poly-MMA-d_3) and a doublet due to the aligned unreacted MMA-d_3. The doublet splitting in such a spectrum is around 15 kHz, due to the additional order induced by the polymerisation.

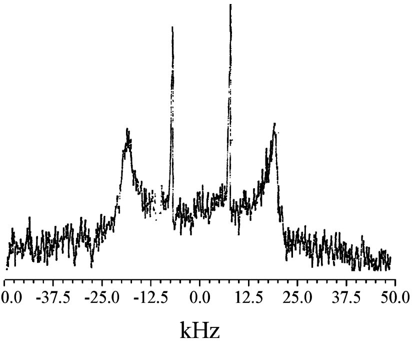

Fig. 6 ^{2}H-NMR spectrum from poly-MMA-d_3 dispersed in E7 (5 wt.%:95 wt.%). Spectrum was observed on a Bruker MSL 300 spectrometer, operating at 46.05 MHz in a 7-T magnetic field. The temperature was 18.0 ± 0.1 °C

^{2}H-NMR experiments on IBMA-d_2

Figures 7a and b show the NMR spectra of samples obtained after the polymerisation of pure IBMA-d_2 and a mixture of IBMA-d_2 and E7 (1:1). The spectrum in Fig. 7a is a powder pattern with a biaxial symmetry and a spectral width between the lateral edges (0° singularities) of about 114 kHz ($^3/_2$ $<\nu_Q>$). Such a powder pattern can be attributed to the particular conformational dynamics of the C–$^2H_2$ moiety of poly-IBMA-d_2. In agreement with theoretical expectations, the two-site hop of methylene bonds gives a reduction in the static spectral width by a factor of 2 (from 262 kHz to about 131 kHz). The difference between experiments (114 kHz) and theory (131 kHz) is that the average of Eq. 1 takes into account just the two-site hop of methylene bonds and no other conformation motion. In addition, a zero value is found for one of the diagonal components of the electric gradient tensor (i.e. V_{xx}), the other two being characterised by similar but opposite intensities ($V_{yy} \sim V_{zz}$) [14].

The small central peak can be attributed to the IBMA-d_2 molecules dispersed in the thermoplastic matrix, as in the case of the MMA-d_3 sample. The amount of unreacted IBMA-d_2 is around 4–5%, as calculated by the area integral.

Figure 7b shows significant changes compared to Fig. 7a. The presence of liquid crystal largely alters the line shape. It is possible to observe the superposition of a larger central peak and a powder pattern, whose separation between the central peaks (90° singularities) is around 57 kHz ($^3/_4$ $<\nu_Q>$). The presence of liquid crystal dispersed in the polymer matrix stops the two-site hop of the methylene groups (and the consequent average) and produces a uniaxial powder pattern with a doubled spectral width. The central peak area of Fig. 7b is now around 18–20% of the signal and the half height width is about 2.5 kHz. This means that IBMA monomers in a polymer matrix are characterised by an increased mobility and that a large amount of IBMA remains unreacted in the sample. No appreciable quantity of IBMA-d_2 molecules is found inside droplets. In fact we found no doublet due to IBMA-d_2 confined in liquid crystal droplets. As a consequence, IBMA molecules are mainly dispersed in the matrix. As previously done with MMA, we performed ^{2}H-NMR experiments

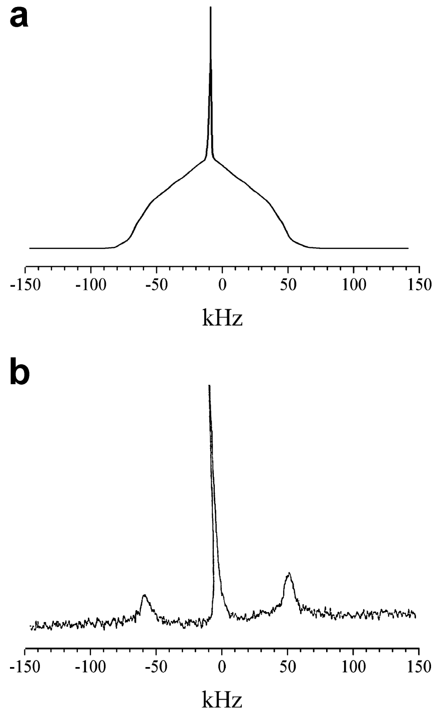

Fig. 7 ^{2}H-NMR spectra from: **a** poly-IBMA-d_2 and **b** a PDLC obtained from a mixture of IBMA-d_2 and E7 (1:1). Spectra were observed on a Bruker MSL 300 spectrometer, operating at 46.05 MHz in a 7-T magnetic field. The free induction decay was averaged 300,000 times in order to achieve a good signal to noise ratio. The temperature was 18.0 ± 0.1 °C

on polymerised samples (prepared with IBMA-d_2), which were melted into a homogeneous phase and then fast cooled (thermally induced phase separation). Unlike experiments on MMA-d_3, we obtained spectra similar to that reported in Fig. 7b, i.e. they are constituted only by the superposition of a powder pattern and a central peak with no lateral doublet. The lack of doublets in this case can be attributed to several differences between samples, including polymerisation rate, monomer diffusion coefficient, and polymer molecular weight. Just for sake of completeness, we prepared a sample in which a low percentage (~5 wt.%) of IBMA-d_2 was dissolved in E7 liquid crystal. We obtained a biphasic spectrum similar to that reported in Fig. 5. It was formed by the superposition of a central peak (due to IBMA-d_2 present in the monomer-rich phase) and a doublet (due to IBMA-d_2, aligned by liquid crystal, in the E7-rich phase) whose splitting was around 21 kHz. No evident doublet with similar or larger width was detected around the central peak of Fig. 7b.

Conclusions

In this paper we have found through a ^{2}H-NMR investigation that in the preparation of PDLCs, the presence of liquid crystal in homogeneous mixtures increases the percentage of unreacted monomer molecules after a polymerisation-induced phase separation. Such unreacted monomer molecules are dispersed in the polymer matrix rather than in liquid crystal droplets. In some PDLCs it is possible to trap temporarily monomers in liquid crystal droplets, but then they can diffuse into the polymer matrix in a short time.

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