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Phase separation kinetics in mixtures of polymers and liquid crystals

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Light scattering has been used to study phase separation kinetics in mixtures containing liquid crystals and epoxy resins. In the samples studied, phase separation was induced by the polymerization of the resins with an appropriate curing agent. Experiments were carried out at different compositions and at different temperatures. The results show that the kinetic mechanism of phase separation is composition dependent. For high liquid crystal content the data are in qualitative agreement with existing theories describing spinodal decomposition; at lower concentrations the mechanism is different. The physical properties of the resulting materials are independent of the decomposition mechanism. The data have also been analysed considering the scaling behaviour expected for late stages of phase separation in polymeric mixtures. Samples obtained in a narrow concentration range, where the two kinetic mechanisms overlap, exhibit peculiar physical properties.

1. Introduction

Dispersions of polymers and liquid crystals have been studied for more than 10 years and they are used for practical purposes in several devices, ranging from displays to switchable windows [1]. They are generally prepared via phase separation methods from initially homogeneous solutions. The morphology of the dispersion can be quite variable, depending on the composition of the initial mixture and the conditions under which phase separation is carried out. Among the morphologies observed, we can mention the dispersion of almost spherical liquid crystalline droplets in a polymeric matrix, or the dispersion of a continuous polymeric network within the mesophase. Not only the morphology, but also the physical properties of the final material can be varied by controlling the separation process. This is a consequence of the fact that, as in our case, phase separation may often be far from an equilibrium process and the features of the phase separation material can be controlled by kinetic factors.

The phase separation process used to prepare polymer/liquid crystal dispersions can be induced by a thermal quench or by a polymerization reaction. The phase separation of a binary mixture after a thermal quench is a relatively well understood process [2–4], but fewer studies exist in the case of phase separations

induced by the polymerization of one component of a mixture [5–10]. In addition, in the large majority of cases, the homogeneous starting solutions contain several components and are substantially different from 'ideal' binary mixtures. For such reasons, experimental studies of phase separation driven by polymerization are at this stage necessary to understand better the kinetic process and to supply reliable data for further theoretical developments.

Studies of phase separation from mixtures of liquid crystals and polymers are relatively recent. They have focused both on the thermodynamic [11, 12] and on the kinetic [13] aspects of the separation process. In this work we deal with the dynamics of the phase separation driven by polymerization in mixtures of liquid crystals and reacting monomers. Light scattering has been used to follow the kinetics of the separation as a function of liquid crystalline content and data will be shown which support the hypothesis of a separation dynamic which depends on mesophase content.

2. Experimental

Samples were prepared by mixing an epoxy resin, a curing agent and a liquid crystal. The resin was the diglycidyl ether of neopentyl glycol, also known by the commercial name WC68, from Wilmington Chemicals (USA). The curing agent was a fatty polyamine, component B of an off-the-shelf epoxy glue (Bostik brand). As a liquid crystal we chose 4-pentyl-4'-cyanobiphenyl, from Merck Ltd, UK, also known by the commercial

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name K15. The required amounts of the three components were placed in a test tube, thoroughly mixed and lightly centrifuged to eliminate air bubbles. The homogeneous solution was then placed between two glass slides to obtain a 100- μm -thick liquid film. The thickness was controlled using glass spacers at the corners of the cell, which was then placed in a controlled temperature chamber with an accuracy of $\pm 1^\circ\text{C}$. Experiments were performed at 21 and 40°C . In all samples the resin/curing agent weight ratio was 1:2. The content of K15 was varied between 40 and 69 wt %.

Light scattering measurements were performed using a set-up equipped with a 5 mW He-Ne laser. The beam was chopped, expanded and collimated before impinging upon the sample. The scattered intensity was recorded using a photodiode mounted on a rotating arm controlled by a computer through a stepping motor. The photodiode signal was pre-amplified and then passed through a lock-in amplifier interfaced to the computer.

Resistivity measurements were carried out on cured samples prepared in the same way, but placed between two indium tin oxide coated glasses. The thickness of the resulting films was 10 μm , controlled using glass spacers. The temperature of the curing samples was controlled with an accuracy of $\pm 1^\circ\text{C}$. Resistivity measurements were performed at room temperature using a Hewlett Packard 4284A LCR meter.

3. Results and discussion

We have quantitatively analysed the dynamics of the phase separation by following the time evolution of the scattering pattern from samples curing at a controlled temperature. In particular, we carried out experiments on samples at different concentrations of the liquid crystal K15 and observed two different regimes in the phase separation kinetics, one for higher and one for lower K15 concentrations. In the following account, to distinguish between these two regimes, we will talk about high and low concentration ranges. Figure 1 shows the typical time evolution of the scattering profile obtained from a sample in the high K15 concentration range. These data show several distinct features. The first one is better visible from figure 2, where the time evolution of the scattered intensity at different scattering angles is shown. It is evident that during the initial stage of the separation, i.e. the first 1–2 min, the intensity grows exponentially with time; this is more evident at smaller scattering angles. The exponential growth of the intensity is typical of the early stages of the so-called spinodal decomposition. In fact, at the beginning of the separation in unstable systems, small concentration fluctuations are present. It can be shown that this 'linear' regime leads to an exponential growth in the concentration difference among different regions in the sample and consequently

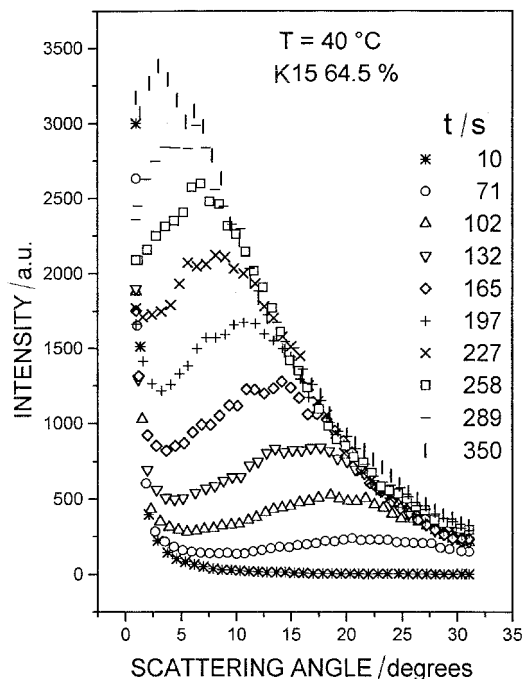


Figure 1. Typical time evolution of the scattering pattern for a sample in the high K15 concentration range.

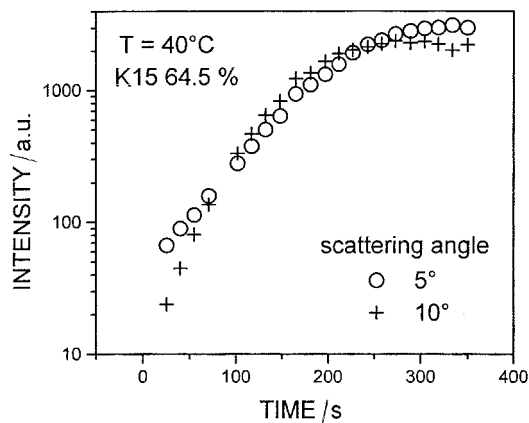


Figure 2. Time dependence of the scattered intensity at different scattering angles for a sample in the high K15 concentration range. Exponential growth of the intensity is evident for the initial stage of the separation.

to an exponential growth of the scattered intensity [14]. To our knowledge this is the first observation confirming the existence of a spinodal mechanism during the first stages of decomposition in mixtures of liquid crystals and polymerizing materials. Another important feature, directly visible from figure 1, is the shift of the scattering maximum towards lower wavenumbers as the separation evolves. This is also typical of spinodal decomposition, at a later stage, when different domains coarsen in time to minimize surface energy. We have observed exponential growth of scattering intensity and a shift of

the scattering maximum for all samples in the high K15 concentration range, for both curing temperatures of 21 and 40°C.

The evidence described above indicates that at high liquid crystal content the solution is unstable during phase separation. As we decrease the K15 concentration closer to the thermodynamic solubility limit, we expect to move towards a region of metastability, where small concentration fluctuations decay while those with large enough amplitude grow with time. This can be seen more clearly through figure 3, where we show what can be expected for the time evolution of the solubility limit (solid line) and of the spinodal (dotted line) with increasing molecular mass of the resin, i.e. as the polymerization evolves. All the states under the spinodal line are unstable towards phase separation, while the region between the spinodal and the solubility curves represents metastable states. The two crosses in figure 3 represent two systems at different concentration curing at the same temperature. As the polymerization (time) progresses, the system with the higher K15 concentration will rapidly fall into the unstable region. The system at lower concentration will instead experience conditions of metastability for a much longer time.

It is evident that two different timescales are relevant to our discussion, one connected with the kinetics of the polymerization reaction and one with the phase separation kinetics. We always observed the beginning of phase separation between 1 and 2 h after the beginning of the polymerization reaction, i.e. the reaction timescale is of the order of hours. The phase separation in contrast lasts between 5 and 10 min, as observed by the evolution of the light scattering profile. We can then conclude that the composition of the reacting mixture, i.e. the polymer

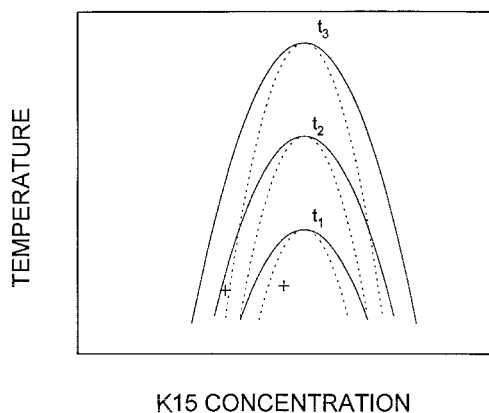


Figure 3. Schematic representation of the time evolution of the spinodal (dotted line) and of the solubility curve (solid line) with time as the polymerization reaction progresses. The two crosses represent two systems with different K15 content, but curing at the same temperature and $t_3 > t_2 > t_1$.

molecular weight, changes only to a small extent during phase separation. For samples with low enough K15 concentration, we then expect that the whole phase separation will evolve in the metastability region. In fact, in the lower K15 concentration range an exponential growth of the scattered intensity is not observed in the initial stages of the decomposition (as shown in figure 4) but rather a linear growth. Moreover, although we still observed a scattering maximum, at these lower concentrations, its shift in time is greatly reduced or totally absent (as shown in figure 5). In the lower K15

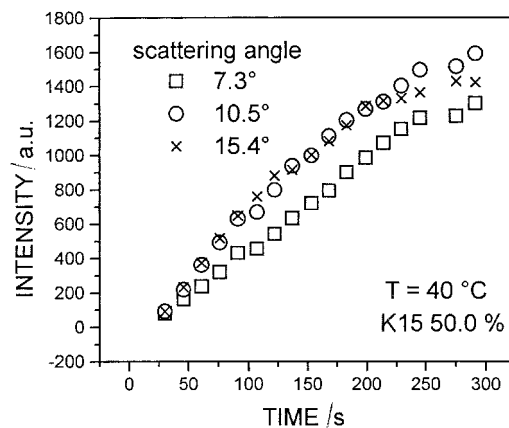


Figure 4. Time dependence of the scattered intensity at different scattering angles for a sample in the low K15 concentration range. A linear growth of the intensity is evident for the initial stage of the separation.

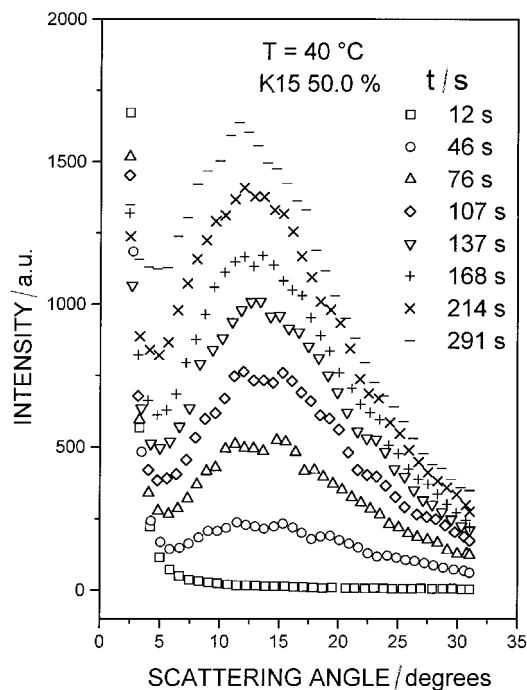


Figure 5. Typical time evolution of the scattering pattern for a sample in the low K15 concentration range.

concentration range the observed mechanism is then different. We believe that the two mechanisms are associated with the fact that the homogeneous mixture is unstable for high K15 concentrations and metastable for lower ones.

The fact that a scattering maximum is still observed for samples in the low K15 concentration range deserves a comment. A scattering maximum is not expected for a conventional heterogeneous nucleation and growth mechanism in a metastable system. There can be at least two reasons to explain why we observe it. One may be evinced from the observation that the morphology of the final cured material, as observed by electron microscopy, shows droplets with a diameter of 0.3–1.0 μm , depending on concentration, separated from each other by 1–3 μm . Coherent effects among spheres, affecting the scattering structure factor, are then possible. One other explanation could be given by considering that, according to Hayward *et al.* [15], some spinodal features can be expected even for smaller supersaturations than those corresponding to the spinodal line. In other words, we can expect the real stability diagrams to be more complex than the simple one shown in figure 3.

At intermediate compositions, over a 3–4 wt % K15 concentration range, the two mechanisms overlap and it is not possible to distinguish clearly between them, at least using our experimental set-up. These intermediate concentration ranges are centred around 56 wt % of K15 at 40°C and around 50 wt % at 21°C. This is as expected for an upper critical point, where both the spinodal and the solubility curves move towards higher concentrations at higher temperatures near the solubility limit. In fact, in samples with 35 wt % K15 we do not observe any phase separation at 40°C. The variation of the growth rate law with K15 concentration during the first stages of the decomposition can clearly be seen from figure 6, where the scattering intensity for different samples has been shifted along the vertical axis for clarity. It is evident how in the spinodal region, i.e. for high K15 content, the growth is exponential at the beginning of the separation, but tends to be linear as the concentration is decreased.

Besides the usual increase in droplet size and number with increasing K15 content, scanning electron microscopic observations of the samples obtained for high, low and intermediate K15 concentrations did not reveal any different droplet structure in the final cured material. We believe that this is due to the fact that, during the final stages of the phase separation, coarsening and coalescence of droplets can substantially change the structures that develop at the beginning. In fact, we concentrated observations of the kinetic mechanism in the first few minutes of the separation. A detailed study of the final stages would be necessary to understand the

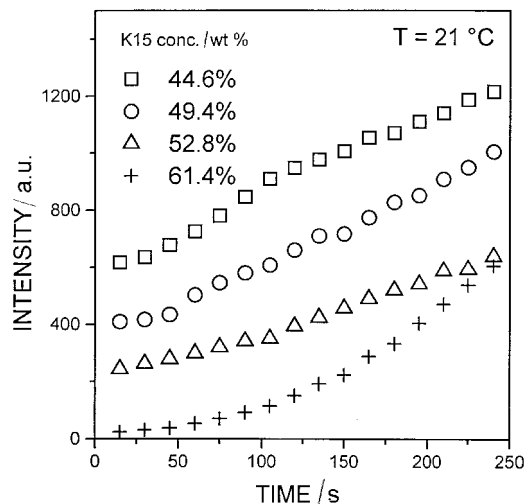


Figure 6. Time dependence of the scattered intensity at a scattering angle of 15° for samples with different K15 concentrations. Successive curves are shifted vertically by 200 units for clarity.

reason why the final droplet structure is independent of the initial separation mechanism and which conditions should be modified to induce such a dependence.

We also analysed the growth rate of the separating domains during the late stage of the decomposition by fitting our data to the power laws $I_{\max} \propto t^\beta$ and $q_{\max} \propto t^{-\alpha}$, where I_{\max} is the intensity of the scattering maximum and q_{\max} is the wavenumber at the scattering maximum, defined as:

$$q_{\max} = \frac{4\pi}{\lambda} \sin \frac{\theta_m}{2}, \quad (1)$$

where λ is the wavelength of the light in the medium and θ_m is the angle of the maximum scattering intensity. Several theoretical treatments have been developed to predict the value of the exponent α in thermally quenched binary mixtures. A cluster dynamic model [16] predicted $\alpha = 1/3$, while Langer *et al.* [17] obtained $\alpha = 0.21$. Siggia [18] considered critical compositions and his results are $\alpha = 1/3$ for an initial diffusion controlled growth and $\alpha = 1$ at later times, when coalescence due to surface tension becomes dominant. Our samples are not binary mixtures, due to the non-homogeneous molecular mass of the polymer, and the analogy with a thermal quench is only partial because the polymerization process can be considered as a slow cooling. Nonetheless it is instructive to look at our results for α and β .

Figure 7 shows the time dependence of q_{\max} for two samples, one in the high and one in the low K15 concentration range. The exponent α starts at small values at all concentrations and then tends to grow. In the later stages of the decomposition, in the high K15

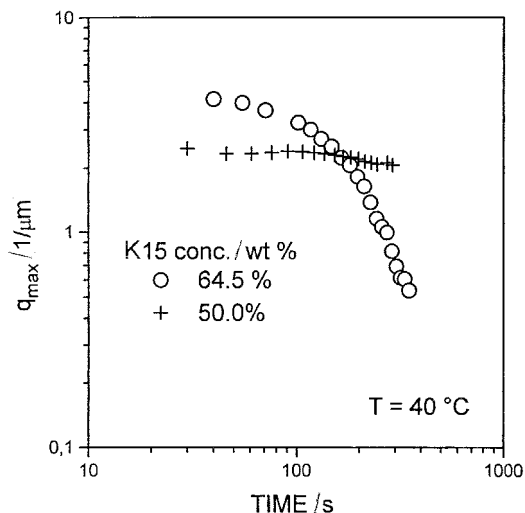


Figure 7. Time dependence of the wave vector of the scattering maximum for two samples in the high (circles) and low (crosses) K15 concentration ranges.

concentration range α tends to a value around 1.5–2.5, but it tends to a smaller value for the lower concentration range. In particular, for low K15 concentrations $0.4 \geq \alpha \geq 0.2$, not too far from Siggia's prediction [18]. One feature of the data of figure 7 for the 50 wt % concentration should be underlined. During the first 100 s of the separation we notice a slight but significant increase of q_{\max} . This unusual behaviour could be explained in the framework of the nucleation initiated spinodal decomposition theory, recently proposed by Kyu and Lee [10] to interpret similar experimental data. In the low K15 concentration range, the q_{\max} curves are always quite flat at the beginning of the separation, but we observed an increase of q_{\max} with time only for this concentration. Figure 8 shows the variation of α with K15 concentration at a curing temperature of 40°C. This figure confirms that there

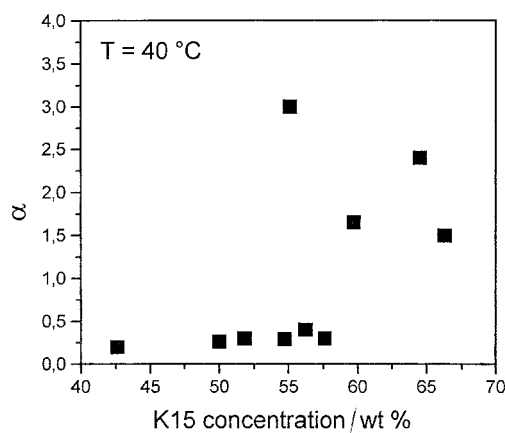


Figure 8. The exponent α measured in the later stage of the decomposition for samples at different K15 concentrations.

is a variation of the phase separation kinetics for a concentration of K15 around 56 wt %.

Figure 9 shows the typical time dependence of the scattered intensity at the scattering maximum for two different samples. In the low concentration range, at the beginning of the decomposition, during the initial stage, the exponent $\beta \approx 2$, but it decreases continuously, going through $\beta \approx 1$, during the late stage of the decomposition. During the late stage then, the relationship $\beta \approx 3\alpha$, predicted by Binder and Stauffer [16], holds approximately for K15 concentrations below 56 wt %, i.e. for concentrations where the initial linear regime is not observed. At other stages of the decomposition and/or in the high K15 concentration range, $\beta \neq 3\alpha$. In particular, in the high concentration range, β starts at values around 1.3–1.5 during the initial linear regime and grows to values around 2.1–2.3 during the later stage.

We also noticed a peculiar behaviour of the samples obtained in the narrow concentration range where the two mechanisms overlap. On measuring their resistivity, we notice in some cases a dramatic decrease compared with the values obtained for neighbouring concentrations (as shown in figures 10 and 11). At the low frequencies where the resistivity was measured, conduction is due to ionic transport and, since the number of charges must be quite similar in all samples, we can suppose that their mobility increases dramatically in the samples obtained when the separation mechanism is neither of the two observed, but of an intermediate nature. We could speculate that phase separation in the intermediate range induces a different molecular packing of the polymeric chains and thus a different ionic conductivity.

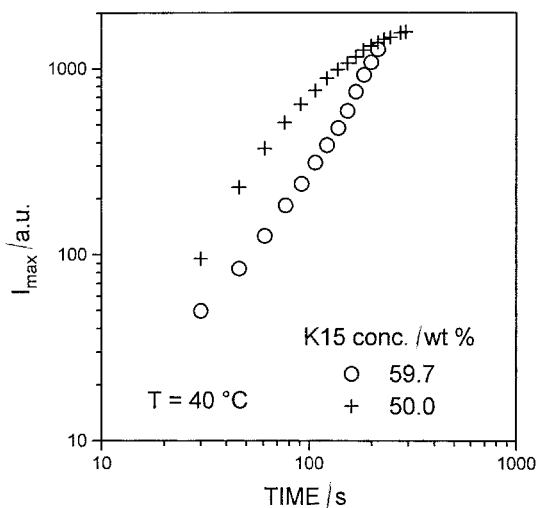


Figure 9. Time dependence of the intensity of the scattering maximum for two samples in the high (circles) and low (crosses) K15 concentration ranges.

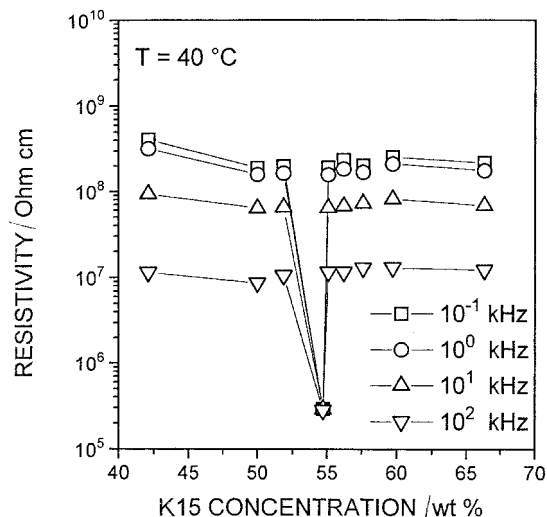


Figure 10. Dependence of the resistivity on K15 concentration for samples cured at 40°C.

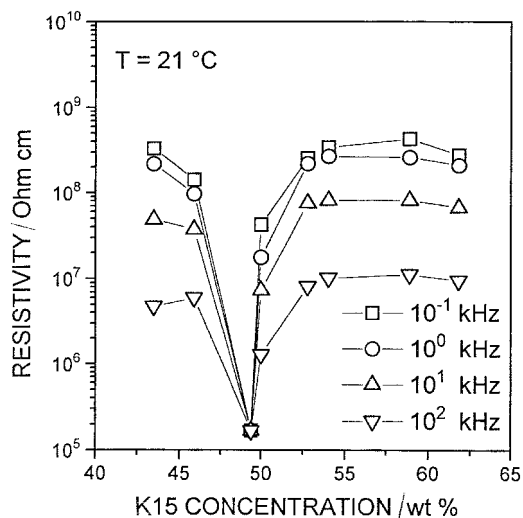


Figure 11. Dependence of the resistivity on K15 concentration for samples cured at 21°C.

4. Conclusions

We have performed time resolved light scattering measurements on mixtures of a mesogen and a polymerizing material during the phase separation process. The phase separation kinetics showed two different regimes, depending on mesogen content. For the high concentration regime we observed: (a) exponential growth of the scattering intensity in the early stage of the decomposition, (b) considerable shift of the scattering peak wave vector to smaller values with time during the later stage, and (c) values of the exponent α , describing the shift of the scattering peak ($q_{\max} \propto t^{-\alpha}$), between 1.5 and 3. In the low concentration regime we observed: (a) linear growth of the scattering intensity, (b) much smaller shift of the scattering peak, and (c) α exponents

between 0.2 and 0.4, roughly decreasing with decreasing K15 concentration. In all the samples, at the end of the curing process droplets of liquid crystals dispersed in a polymer rich matrix were obtained, and this morphology was independent of the curing mechanism.

In an intermediate composition range of K15 (3–4 wt % wide) the two kinetic mechanisms are not clearly distinguishable using our experimental method. Some samples with these concentrations show higher conductivity, probably connected with increased ionic mobility. We believe that this is a consequence of a different packing of polymeric chains in the matrix obtained in the intermediate concentration range when the kinetic mechanism is neither of the two described above, but intermediate, i.e. when the system undergoing phase separation is on the spinodal or very close to it.

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