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A. Golemme^a, G. Arabia^a & G. Chidichimo^a

^a Dipartimento di Chimica, Università della Calabria, 87030, Rende, Italy

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Influence of the Phase Separation Mechanism on Polymer Dispersed Liquid Crystalline Materials

A. GOLEMME, G. ARABIA and G. CHIDICHIMO

Dipartimento di Chimica, Università della Calabria, 87030 Rende, Italy

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We have studied the phase separation mechanism accompanying the formation of polymer dispersed liquid crystals (PDLC). Different polymers and liquid crystals were used, including epoxy resins, fluorinated macromolecules, eutectic mixtures and single component mesophases. Various phase separation methods, such as solvent evaporation and polymerization of the components, have also been employed. Results show that PDLC's can be obtained by nucleation and growth and by spinodal decomposition of an initially homogeneous mixture. In samples formed via this last mechanism, the characteristic length of the fastest growing concentration modulation in the first stage of the decomposition is still evident, in the morphology of the cured samples, as an alignment of the droplets in rows. Other physical properties of the material are unaffected by the decomposition mechanism, except in the case of concentrations close to the spinodal line. Such last samples exhibit dramatically different electrical resistivity and also different x-ray patterns and IR spectra. Such differences are probably correlated with a particular packing of the polymer chains induced by the peculiar conditions of phase separation for samples near the spinodal line. Implications of these properties for PDLC technological applications are discussed.

I. POLYMER DISPERSED LIQUID CRYSTALS

Among the newly developed liquid crystalline materials Polymer Dispersed Liquid Crystals (PDLC) stand out as candidates for use in optoelectronic devices^{1,2} but also for the opportunities they offer of studying important physical properties of mesophases.^{3,4} PDLC's typically are solid materials in which the liquid crystal is dispersed in the form of microscopic droplets⁵ roughly spherical in shape, although highly non-spherical domains can be obtained and are in some cases desirable. The size of the mesophase domains is controllable and can range between less than 0.1 and several tens of micrometers, always with a certain degree of polydispersity. The materials used for PDLC preparation vary widely, depending on the desired final characteristics, but usually the solid matrix is an organic polymer while the mesophase is more often nematic, although both cholesteric^{6,7} and smectic⁸ phases have been successfully used.

The droplet morphology associated with PDLC's induces on such materials interesting and useful features. The most important one is probably the extremely high surface to volume ratio which is obtained. With droplets in the 1 μm range,

size which is typical of PDLC's that scatter visible light, surface effects are one of the main factors determining molecular orientation.⁹ When the material is not subjected to any kind of treatment to induce a particular preferred molecular orientation, liquid crystal molecules are oriented following regular director distributions within each droplet, but different droplets present different distributions and, on a macroscopic scale, we can say that the mesophase director is distributed along random directions under the influence of surface interactions. In such conditions, if the density of droplets is high enough and if they are in the appropriate size range, PDLC's scatter visible light and appear as white opaque materials, since the refractive indices in the droplet and in the external matrix are not equal. Upon the application of external fields the direction of the average molecular orientation can be affected and it can become homogeneous over the whole sample. In these conditions, if refractive indices of materials are properly chosen, PDLC's are transparent. This change in the transparency of the material is exploited in their application in optoelectronic devices.¹⁰

Although the basic principle of operation is rather simple, the use of PDLC's for any particular application requires a carefully controlled and tailored adjustment of the properties of the material. These include size, shape and density of droplets, indices of refraction, dielectric constants, elastic constants and electrical conductivity. Recently, a number of new materials have also been used, both with the purpose of optimizing such properties and to exploit new phenomena for PDLC's applications. For example, glasses have been used for the external matrix,¹¹ allowing a higher chemical stability in time. PDLC's made using cholesteric liquid crystals also seem to promise interesting applications.¹² In other cases the molecular orientation induced on the liquid crystal molecules via a shaping of the droplets has been useful for obtaining a PDLC modulator, exploiting the electroclinic effect of the smectic A* phase.⁸

All these different PDLC's, made using different materials and whose principles of operation are drastically different, have in common the droplet morphology. The only way such morphology can be obtained is through phase separation processes. Such processes constitute then a unifying element in PDLC technology, and a very important one, since the features of the resulting material are a direct consequence of the method used for its preparation. In the following we will first describe the different phase separation techniques used for PDLC preparation in the frame of what is already known from the general theories of phase separations. We will then present data to show that the control of the conditions of the phase separation process is important in determining some new and previously overlooked features of PDLC's. We will develop an analogy with ordinary phase transitions and, in particular, we will present data to show that the phase separation process used for PDLC preparation can be carried out under particular conditions and that the materials obtained in this case present peculiar features.

II. PHASE SEPARATION PROCESSES AND THEIR USE IN PDLC PREPARATION

The thermodynamics and kinetics of phase separation are subjects which in the last decades have been developed first in connection with the metallurgy of metal

alloys and glasses¹³ and more recently with the technology of polymer blends.¹⁴ Only in the last few years has the phase separation involving anisotropic media become the subject of theoretical^{15–19} and experimental^{20–25} investigations. While the theoretical works have tried to underline the peculiarities of this kind of phase separation, the few existing experimental results regard the kinetics of phase separation and do not show any real peculiarity due to the presence of mesophases. In the following we will review the methods of PDLC preparation within the frame of the phase separation theories.

All of the several techniques used for PDLC preparation involve a phase separation process. Among the first ones to be used is the so called polymerization induced phase separation, where a homogeneous mixture of a liquid crystal and a “monomer” is first prepared. Here by monomer we intend a substance, or a mixture of substances, that can undertake a polymerization reaction either spontaneously or under the effect of radiation. The reaction proceeds within a macroscopically homogeneous medium up to the point when the liquid crystal and the forming polymer are no longer miscible. At this stage a phase separation occurs between a polymer rich and a liquid crystal rich phase. In the appropriate conditions droplets of a liquid crystal rich phase (often quite pure) in a solid polymer are obtained after the reaction is complete.

A different method can be used with thermoplastic polymers. In this case the polymer can be melted before the liquid crystal is added. The homogeneous mixture is then cooled at an appropriate rate and eventually a temperature where the two substances are no longer miscible is reached. At this point a phase separation occurs and at the end a solid polymer matrix is obtained in which liquid crystal droplets are cast. In a third method the polymer and the liquid crystal are dissolved in a common solvent: in this case we have a three components homogeneous solution at the starting point. The solvent is then evaporated at a controlled rate and again a region of the phase diagram can be reached which corresponds to a miscibility gap, and a phase separation process develops. The solvent is then completely evaporated and a PDLC is obtained.

The three methods for PDLC preparation discussed above present of course a similarity, namely they are all phase separation processes. There is always a variation of a parameter that makes the components of an initially homogeneous solution no longer miscible. Such parameter can be the temperature, the composition of the mixture or even the chemical nature of the components. In any case the phase separation is a consequence of the variation induced on the free energy of the solution by the change in this parameter. For a homogeneous solution of a polymer and a liquid crystal the free energy can be expressed as²⁶:

$$\frac{F}{kT} = \chi \ln \chi + \frac{1 - \chi}{N_p} \ln(1 - \chi) + a\chi(1 - \chi) \quad (1)$$

where k is the Boltzmann constant, χ is the liquid crystal volume fraction, a an interaction parameter and N_p is the degree of polymerization of the macromolecular component. For the liquid crystal the degree of polymerization is 1. In the case of phase separation induced by polymerization N_p increases with time, and this cor-

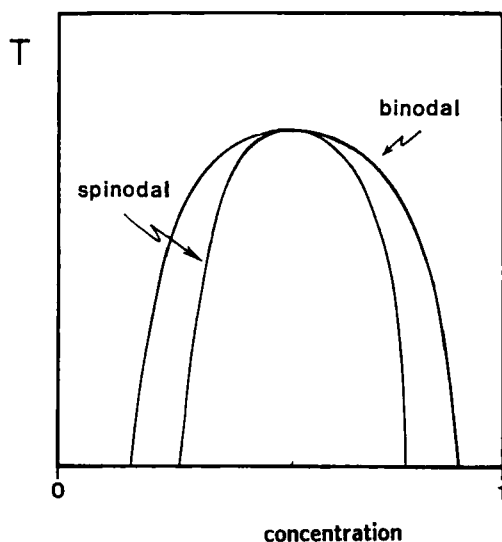


FIGURE 1 Typical phase diagram for a two components mixture. The solution is homogeneous and stable outside the binodal line. The region below the spinodal line corresponds to unstable conditions, where the system free energy second derivative is negative. For concentrations and temperatures between the binodal and the spinodal lines the system is metastable and phase separation is possible.

responds to a continuous time evolution of the free energy and of the associated phase diagram of Figure 1, which is a general example of a phase diagram in the case of a two components mixture which is unmiscible below a certain temperature. In particular, the bell shaped coexistence line shifts upwards as the reaction proceeds, and correspondingly the mixture can become unstable towards phase separation at a certain stage of the reaction.

Stability towards phase decomposition is usually discussed in terms of the sign of the second derivative of the free energy respect to composition.^{13,14} It is important to stress that the failure of the usual parameter for phase stability, the convexity of the free energy, is not a necessary requirement for the onset of phase separation. Such criterion, in fact, refers only to local stability, i.e. to infinitesimal composition variations. When the second derivative of the free energy is positive the system could very well be only locally stable, i.e. in a metastable state, and a phase separation process in such conditions can occur as well. The mechanism of phase separation, at least in its first stages, is dramatically dependent upon whether the initial system conditions are the ones of instability or metastability, as we will see in the following.

If the concentration of components of a homogeneous solution are such that the mixture, which is no longer miscible, is in a metastable state, a phase separation can occur only if, as a consequence of concentration fluctuations, a nucleus of a new phase is formed. Moreover, for such nucleus to be stable, it must have a minimum size because of the new surface term in the energy, and only nuclei larger than this critical size can be formed by concentration fluctuations large enough to cross the energy barrier between the metastable (homogeneous solution), and the most stable state, corresponding in our case to the newly forming phase with a

larger liquid crystal concentration. The formed nucleus will then grow in size as a consequence of diffusion processes driven by differences in chemical potential. This kind of phase separation, which involves a nucleation of the new phase, followed by its growth, is known as binodal decomposition.¹³

A different process occurs when the system is unstable, i.e. the stability criterion of a convex free energy is not fulfilled. Under these conditions the phase separation process follows a completely different path. In this case any concentration fluctuation, no matter how small, corresponds to a lower free energy for the system. It is possible to show¹³ that under such conditions the concentration within the sample starts to change continuously in space. There will be areas of the sample richer in one component, when compared with the initial solution, and next to them areas poorer in the same component. It is possible to describe the concentration at this stage of the decomposition as a sinusoidal function of position. Although all concentration wavelength can be present, it is possible to show that some will be damped while the growth rate of the ones whose intensity increases is wavelength dependent. A narrow range of wavelengths will be growing much faster than the other ones, and which are these wavelengths is determined by how unstable the solution is, i.e. by the value of the energy second derivative. The concentrations will continue to change in the different areas of the sample driven by a negative diffusion coefficient, since molecular species will diffuse from regions of lower concentration to regions of higher one. When the final stable concentration will be reached, growth of the different domains will still be possible by coalescence. This second kind of phase separation is known as spinodal decomposition. In Figure 1 regions a typical phase diagram corresponding to spinodal and binodal decompositions are shown. They are separated by the spinodal line, where $\partial^2 F / \partial \chi^2 = 0$. In real systems phase diagrams are not as symmetrical as in Figure 1.^{20,23} This is particularly true for our systems, where polymer size is polydispersed and this feature can also shift the location of the critical point on the binodal line. In addition, the phase decomposition mechanism does not change abruptly at the spinodal line¹⁴ but it does so more smoothly, passing through intermediate, somehow mixed mechanisms.

As already said, such different kinetics have been studied experimentally especially in metal alloys and in polymer-polymer phase separations. Few studies have appeared in which mesophases were involved and only one in connection with PDLC preparation,²⁵ where only the later stages of phase separation were followed in their kinetics. One of the important consequences of the particular kinetics of phase separation lies, for us, in the morphology of the resulting phase separated material. It is well known that the particular evolution of the decomposition in the early stages of the spinodal mechanism is particularly important in determining such property.¹³ In fact the spinodal mechanism is characterized in its early stages by a typical dimension, i.e. the most rapidly growing wavelength of the concentration modulation. If the subsequent stages of growth and coalescence are then partially or totally inhibited, such dimension will be present and evident in the spatial distribution of the resulting phases. If instead the phase separation mechanism is the binodal one, the spatial distribution of the resulting phase, i.e. the droplets in the case of PDLC's, is completely random. We will see from the data

presented in section IV as such regularities are present or not in PDLC's, depending on whether they are obtained via a spinodal or a binodal decomposition mechanism.

It is instructive to consider the phase separation processes within the frame of the generalized phase transitions. In the language of phase transition a phase separation with the binodal mechanism is a first order transition, since there is an energy barrier working against the formation of the new phase, and since the original unstable phase and the newly forming one lie in regions of the thermodynamic parameters space which are not contiguous. In each nucleus, from the time of its formation, the concentration already corresponds to the final one. The spinodal decomposition is instead a continuous transformation of a phase into two new ones, without a real phase transition. In each point of the system the concentration changes continuously, approaching the final equilibrium concentrations of the two resulting phases. As already said, whether one or the other mechanism is followed, depends on the free energy of the mixture. For a given system the free energy is in general a function of composition and temperature. When we change one of these parameters we can induce a variation of the second derivative of the free energy from negative, corresponding to an area of the phase diagram associated with spinodal decomposition, to positive, in a region where the system is metastable. It is reasonable to expect that somewhere in between there should be a point where the second derivative vanishes. At this point the phase separation process occurs under "critical" conditions, where by critical we mean that, in terms of generalized phase transitions, we have a second order phase transition. We will see in the following how PDLC's can be obtained in a variety of conditions, including such "critical" ones, and how their properties can be drastically influenced depending on such conditions.

III. SAMPLE PREPARATION AND ANALYSIS

In our effort to test the character of the different phase separation mechanisms in PDLC preparation and their influence on the properties of the final materials we purposely chose different materials and phase separation techniques. We have then prepared PDLC's using phase separation induced by two different means: direct polymerization of components and solvent evaporation. This of course implies the use of polymers whose chemical nature is quite different. We also chose for the mesophase both single component substances and mixtures containing several chemical components. All such efforts to diversify materials and techniques have been made in order to be able to isolate and evaluate the distinctive nature of the different mechanisms of phase separation regardless of the details of the method used for PDLC preparation.

Polymer/liquid crystal composite films based upon epoxy resins were prepared carefully mixing monomer, curing agent and liquid crystal, at different concentrations, in a small test tube. The solution is homogenized by mixing and centrifugation and then cured at a controlled temperature. Both bulk samples and thin films of different thickness have been prepared using this technique. Films for resistivity measurements were prepared between In/Sn oxide coated conductive glasses and

TABLE I
Composition of Samples

Polymer	Liquid crystal	Curing temperature
Epon 828/Capcure 3-800 1:1	K21 up to 50%	70°C
Epon 828/Bostik B 1:1	E7 up to 44%	70°C
Epon 828/Capcure 3-800 1:1	E7 up to 37%	70°C
PVDF	E7 up to 37%	100°C

their thickness was controlled with 35 μm spacers. The resins and curing agents used were all commercially available, Epon 815, Epon 828 and Capcure 3-800 from Shell-USA and a polyamine, part B of Bostik from Bostik-Italy. Measurements were made several weeks after sample preparation, when the PDLC properties became stable. As liquid crystals we used the eutectic mixture E7 and the single component mesophase K21, both from BDH-England. In all these cases a polymerization takes place in the initially homogeneous mixture and it induces a phase separation. Table I lists the composition of all the series of samples analyzed.

We also prepared PDLC's by solvent evaporation. In this case we used polyvinylidene fluoride (PVDF), from Aldrich and E7 in different concentrations. Both components were dissolved in the minimum possible quantity of *N-N*-dimethylformamide. Solubilization was achieved by stirring at 70°C and subsequently the solution was left unstirred for one hour at room temperature to eliminate air bubbles. Films of the resulting homogeneous mixture were drawn on a flat substrate and the solvent was then removed by evaporation at 100°C for one day. In some cases the resulting 60 μm solid film was coupled to a second substrate, like conducting glass, for resistivity tests. In this case the coupling was performed under the action of both pressure and temperature. Some of these films were also used for IR measurements on a Perkin Elmer 1330 spectrophotometer. A Philips 1730/10 instrument was used to record x-rays diffractograms from 4 mm thick samples of PDLC obtained both from PVDF and epoxy resins. PDLC morphology was studied using electron microscopy. Both thin films and bulk samples were cut along random directions and, after evaporation under vacuum of the liquid crystal, the exposed surface was coated with a thin gold layer and then analyzed using a Jeol T330A scanning electron microscope. Resistivity measurements were performed using a Hewlett Packard 4284 A impedance analyzer.

IV. RESULTS AND DISCUSSION

For all the polymer/liquid crystal combinations described in the previous section we have prepared a series of samples at different liquid crystal content. In all the series of samples we analyzed we always found, using SEM, that above a certain concentration of liquid crystal the morphology of the resulting PDLC is peculiar, since there is a tendency for the droplets to be aligned in parallel rows. This feature is not present in all samples with the same degree and in some cases the SEM analysis of several sections of the same sample was necessary to find a region of

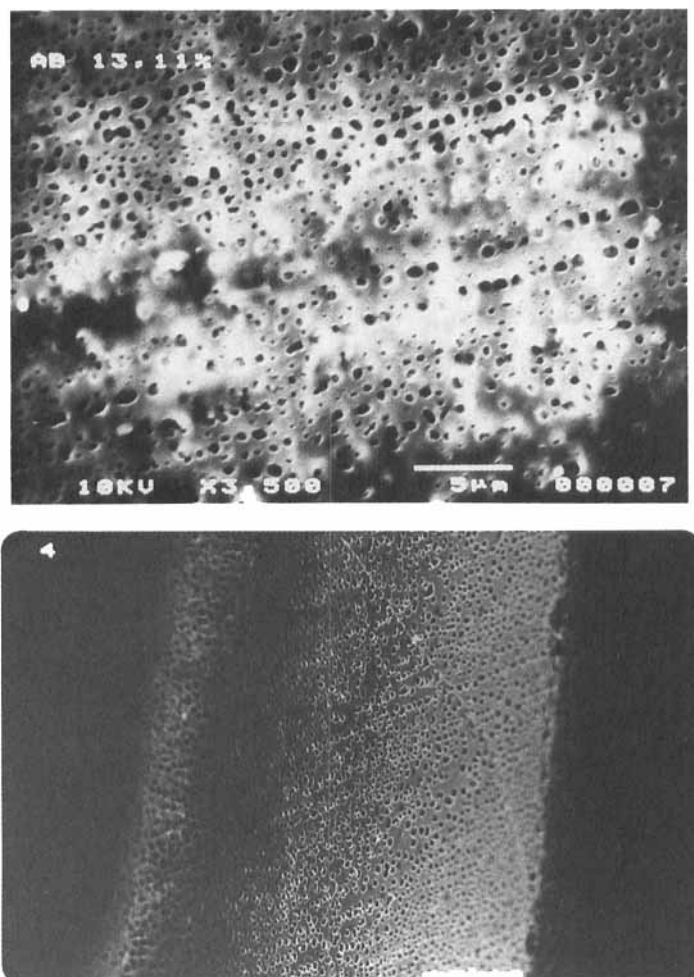


FIGURE 2 SEM pictures of sections of two PDLC's showing droplet alignment. Sample (a) contains 23.1% of E7 in an Epon 828/Bostik B resin and sample (b) 27.5% of E7 in PVDF. Picture (b) is obtained from one of the films used for resistivity measurements.

clear alignment. Droplets alignment in PDLC has been reported by several authors but never became a subject of deeper investigation, except in one case,²⁷ where the samples were obtained by solvent evaporation and the alignment was correlated with convective motions in the curing system during the early stages of the decomposition. The droplet alignment has been observed in all the different series of samples we have studied only above a certain liquid crystal concentration, which depends on the materials chosen. Below such concentration the position of droplets seems to be uncorrelated, at least for distances larger than the typical droplet size. SEM pictures of sections of two typical PDLC samples where the droplet alignment is visible are shown in Figure 2.

Such phenomenon can be understood in terms of the influence of the phase separation process on the morphology of the resulting phases. A different com-

position of the sample is associated with a different free energy and the phase separation mechanism can change from nucleation and growth to spinodal for different liquid crystal concentrations. In view of what is already stated in the previous section, the samples with ordered droplets should derive from spinodal phase decomposition while the binodal mechanism was acting for the formation of samples with randomly distributed ones. In our case then, the spatial regularity due to the fastest growing concentration modulation resulted in a regular alignment of droplets. Not always such regular distribution has been preserved totally in the final cured sample. This is due to the later stages of droplet diffusion and coalescence, typical of all decompositions, which tend to destroy the initial spatial regularity. In our case the later stages of decompositions must have been slowed down, by the increased viscosity of the forming, polymer rich new phase, enough to preserve, at least partially, the morphology induced by the early stage of concentration modulation typical of spinodal decomposition.

A simple observation of the morphology consequent to a phase separation is usually not sufficient to characterize a phase decomposition mechanism, which is mainly a kinetic effect, although it is a good indicator and it is often used for such purposes in the case of polymer mixtures.²⁸ In our case though there are other observations that contribute to such an interpretation. The first one is the fact that spatial regularity is observed only in sample above a certain liquid crystal concentration, and no regularity has been observed for samples with concentrations below this limit. This is in agreement with typical phase diagrams of polymer-polymer or metal-metal phase separations, where, as the concentration of one component is increased, a solution goes from homogeneous to metastable to unstable. It is also important to underline that such behaviour has been observed in PDLC prepared using different materials, as illustrated in the experimental section, and it cannot be attributed to the peculiarities of a particular composition. Moreover, the phenomenon has been observed in PDLC prepared via different techniques, such as phase separation induced by polymerization or by solvent evaporation, and it is not then typical of any of them. Such considerations, and the data presented in the following, support the thesis that the regularity in the droplet distribution is a consequence of the nature of the phase separation itself.

It comes natural to ask whether the PDLC's obtained via different decomposition mechanisms exhibit any diversity in their physical properties. One of the most interesting differences we found was in their electrical resistivity. In Figure 3 we can see the resistivity measured, at different frequencies, on samples obtained using different materials and phase separation techniques. It is evident how the resistivity is completely uncorrelated to the droplet spatial order, i.e. to the kinetics of the phase separation, but it changes by several orders of magnitude for the composition range corresponding to the switching from ordered to randomly distributed droplets. In some cases this range is extremely narrow, and this is another reason why such property has never been previously observed. In this concentration range the resistivity can increase or decrease by several orders of magnitude and it can become much higher or lower than the resistivity of each pure component. It also becomes much less frequency dependent, at least in the frequency range we analyzed. The resistivity is then affected only if the phase separation is carried out in samples

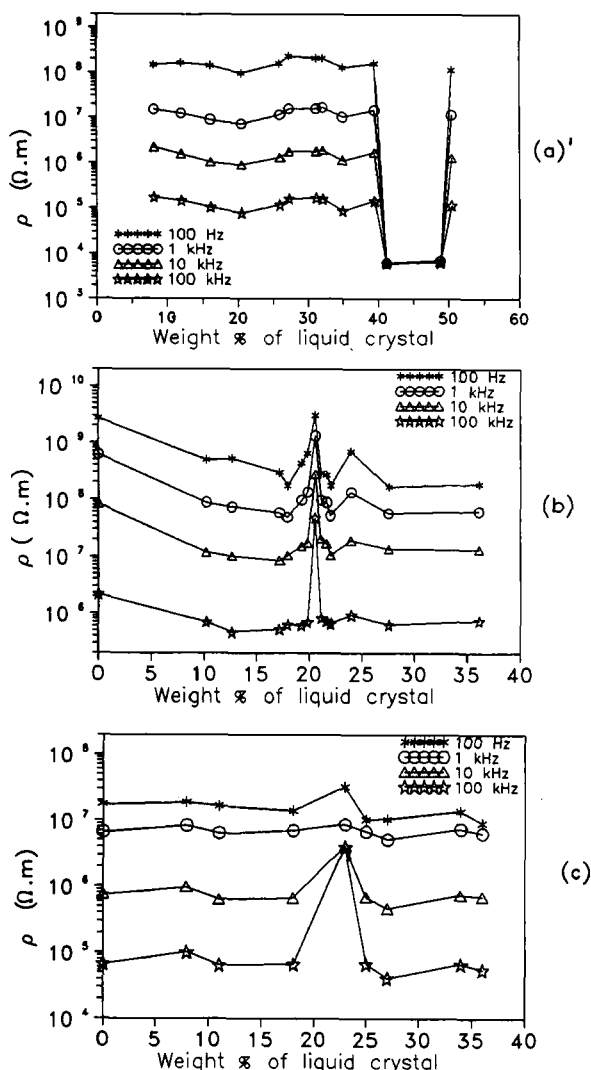


FIGURE 3 Semilog plots of the resistivity of PDLC's at different liquid crystal content for samples of Epon 828/Capcure 3-800/K21 (a), PVDF/E7 (b) and Epon 815/Capcure 3-800/E7 (c).

with those particular concentrations of liquid crystal corresponding to the boundary between the binodal and the spinodal regions, i.e. around the spinodal line.

The resistivity results seem to indicate the possibility of a variation in the structure of the polymeric part of the PDLC. The liquid crystalline component maintains a composition very similar to the bulk one, indicating a good purity, and it does not have other possibilities to influence the total PDLC resistivity. To investigate such point we performed x-ray scattering experiments on our samples. Figures 4 and 5 show x-ray scattering patterns from PDLC samples at concentrations corresponding to phase separations in the binodal, spinodal and intermediate region. An evident difference in the patterns is visible for samples in the intermediate region. In the

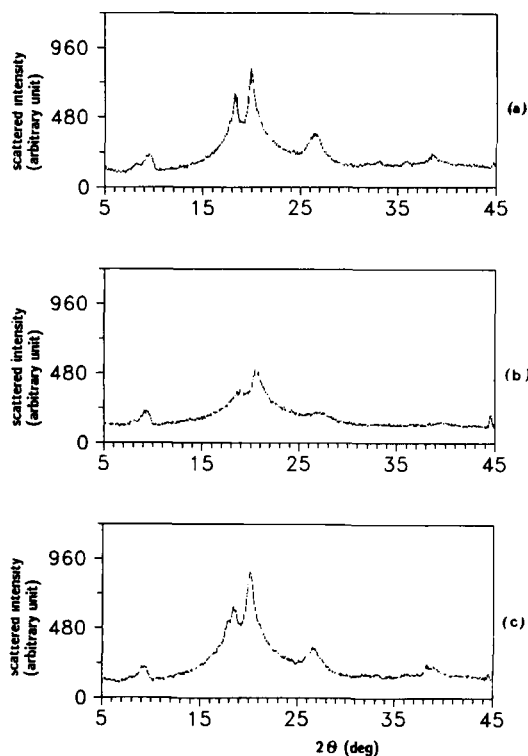


FIGURE 4 X-ray scattering patterns from PVDF/E7 samples at different liquid crystal concentration: 19.6% (a), 20.1% (b) and 22.1% (c). The concentration of sample (b) is the one for which an increased resistivity is measured.

case of polyvinylidene fluoride the pattern is associated with a decrease of the degree of crystallinity in such region while for the Epon 828/Capcure samples we see the appearance of peaks at low angles indicating an increase of crystallinity. Specimens of crystallizable plastics usually contain both amorphous and crystalline regions. In our case we see from the x-ray analysis that the degree of crystallinity can increase or decrease in the intermediate region of liquid crystal concentration. In both cases the variation of the degree of crystallization is not dramatic but it is anyway clearly evident. In the case of polyvinylidene fluoride the decreased crystallinity is also reflected in the more intense IR bands for the C-F bendings around 700 cm^{-1} , as shown in the spectra of Figure 6, which indicate a different packing in the polymer rich phase. Such different polymer chain arrangements must also be quite stable, since we found the resistivities stable and reproducible, after the first few days when polymer curing is still going on, after 2 years from sample preparation. There is one exception to such behaviour, for the Epon 828/Capcure/K21 system, where the anomalous low resistivity of samples with concentrations around the spinodal line (see Figure 3a) is stable for about one year and then it suddenly levels off to values of the same order of magnitude typical of other concentrations. We believe that in this case an unstable polymer packing is obtained during phase separation.

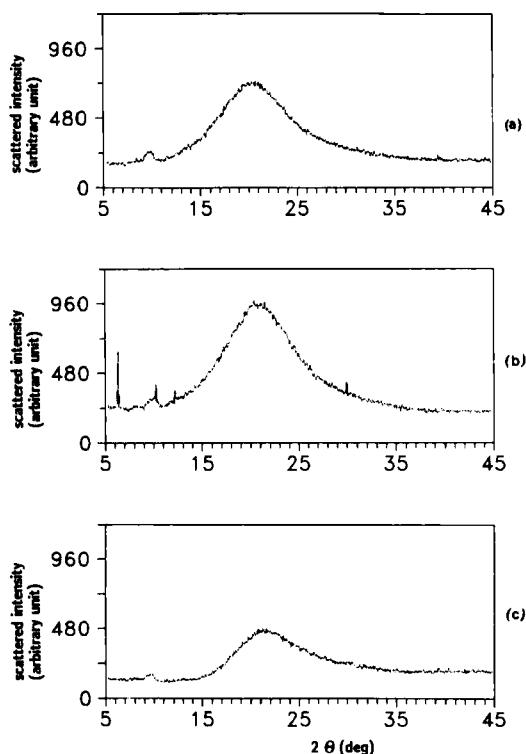


FIGURE 5 X-ray scattering patterns from Epon 828/Capcure 3-800/K21 samples at different liquid crystal concentration: 39.0% (a), 42.9% (b) and 50.0% (c). The concentration of sample (b) is the one for which a lower resistivity is measured.

Comparing the x-ray and resistivity measurements we see that, in our PDLC's at concentrations around the spinodal line, a lower crystallinity is associated with a higher resistivity. A higher resistivity in the area of intermediate concentration is the case we always observed, with one exception, the Epon 828/Capcure samples, where a lower resistivity is associated with a higher degree of crystallinity. What we can deduce from such measurements is that the phase separation in the critical concentration range between the binodal and the spinodal mechanisms, can induce a modification in the local packing of the polymer chains of the resulting PDLC. Since in the frequency range we investigated the electrical conductivity is mainly associated with ion transport, we can reasonably correlate the different packing with a variation of the ion mobility and of the resistivity.

Besides the qualitative picture obtained from the x-ray analysis we have no other experimental evidence on the nature of such packing modification or on the reason why a lower chain crystallinity should correspond to a higher resistivity. Some speculations can nevertheless be considered. It is known that crystalline areas of polymers are practically unpenetrable to most charge carrying ions and this makes crystalline polymers less conductive than amorphous ones.²⁹ This is in contrast with our observations. It is possible though that, since the total number of charge carriers is the same, independent of the phase decomposition mechanism, the presence of

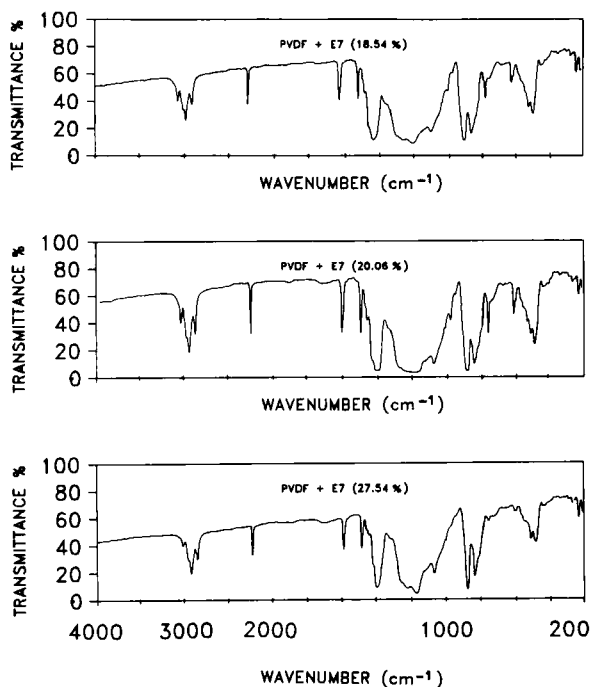


FIGURE 6 IR spectra of PDLC's at different liquid crystal content for samples of PVDF/E7.

larger crystalline domains forces a general redistribution of ions, may be increasing the conductivity of the mesophase domains, with a resulting higher carrier mobility.

Phase separations involving polymers have been studied both theoretically and experimentally.¹⁴ The final polymer chains configurations are determined by the diffusion occurring during phase separation by processes such as reptation or more local adjustments involving configuration variations. For longer concentration fluctuations, which are expected to occur around the spinodal line, reptation processes are expected to dominate. It is also known that in the vicinity of the spinodal concentration of a fluid mixture the viscosity increases, with a simultaneous drop of the diffusion coefficient.³⁰ A higher viscosity was actually typical of the initial homogeneous fluid mixtures of our PDLC samples in the critical region. We believe that the particular conditions of long wavelength concentration fluctuations and slowed down diffusion are at the origin of a different polymer chain packing in PDLC obtained from samples with the spinodal concentration.

V. CONCLUDING REMARKS

We have seen how PDLC's can be obtained by different phase separation mechanisms. Both the nucleation and growth and the spinodal mechanisms can lead to the desired final droplet morphology. We have seen how the properties of the final material are basically unaffected by the decomposition mechanism. The only noticeable peculiarity lies in the residual droplet alignment in rows found in the

PDLC's obtained via a spinodal mechanism. Only for concentrations near the spinodal one, where the free energy second derivative of the mixture is small or vanishes, the decomposition mechanism has a strong influence on the properties of the final material. We presented evidence that these samples differ from the usual ones in their crystallinity and, in general, in the polymer chain packing. Such feature has a dramatic influence on the electrical resistivity, which can change by more than 4 orders of magnitude. This is extremely important for PDLC technological applications, since the resistivity of the material is one of its most important parameters. The understanding of the details of the phase separation is then also important to obtain PDLC's with the desired conductivity. To better understand the dynamics of the decomposition process, especially in the region of the spinodal line, further experimental light scattering work is in progress.

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