Korea Polymer Journal, Vol. 6, No. 4, pp 295-301 (1998)

A Study on Phase Transition Behavior of Low Molecular Weight Liquid Crystal and Its Blend with a Polymer Using Alternating Current Impedance Spectroscopy

Wonsool Ahn*, Seung-Hyun Lee, and Seung-Baik Rho

Department of Chemical Engineering, Keimyung University, Taegu 704-701, Korea

Lee-Soon Park

Department of Polymer Science, Kyungpook National University, Taegu 702-701, Korea

Chung Yup Kim

Polymer Materials Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

Received May 11, 1998

Abstract : Alternating Current Impedance Spectroscopy (ACIS) was used to characterize phase transition behavior of a low molecular weight liquid crystal, 4-cyano-4'-*n*-heptylbiphenyl (7CB) and its blend with an amorphous polymer, poly(methyl methacrylate) (PMMA). ACIS showed that pure 7CB has a single relaxation time due to a large permanent dipole moment associated with cyano (-CN) group in the 7CB molecule, which could be deduced from the Nyquist plot of the impedance spectra of 7CB. The Nyquist plot of 7CB showed a remarkable change in scale near T_{NI} and T_{CN}, but almost perfect semicircles in complex plane. Changes of the electrical properties of PMMA/7CB blend were also utilized to investigate the relationship between the electrical properties and the phase behavior. The maximum resonance frequency, f_{max}, at which -Z" of the blend becomes maximum, was considered to be a very sensitive probe to investigate the physico-chemical changes within the samples.

Introduction

In a practical application of liquid crystal display (LCD) as an information display, it is activated by an applied electric field. This opens the possibility for current flow and physico-chemical changes within the materials. It is, therefore, important to find a method to monitor the condition of the device under electric field through the life-cycles.

Alternating current impedance spectroscopy (ACIS)[1,2] is a powerful method to characterize many of the electrical properties of materials and their interfaces with electrically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charges in the bulk or in the interfacial regions of any kind of solid or liquid materials, i.e., ionic, semiconducting, mixed electronic-ionic, and even insulators (dielectrics). In the case of LCD device for the practical applications, ACIS may offer a natural route to probing the condition of the devices. Wang *et al.*[3] proposed the practical methods, using ACIS, to monitor the conditions of LCD devices throughout the life cycles, and also to apply for the quality control of the device fabrication. On the other hand, a polymer-dispersed liquid crystal (PDLC) is a kind of heterogeneous blend system in which liquid crystal (LC) is dispersed as droplets in a polymer matrix. It was found that ACIS could be directly applied to isolate the system permittivity and resistivity for a such a PDLC system. Kelly and Seekola[4] modelled PDLC system as a composite material consisting of two phases with different electrical characteristics, and compared with the experimental data for a PMMA/E7 (E7 is the trade name of EM Chemicals) blend using a dielectric analyzer (DEA). They suggested that the model, though having some limitations, was able to provide a useful framework for interpreting and predicting the general behavior of PDLC materials. DEA, therefore, can be an alternative method to measure the electrical properties and to probe the condition of PDLC materials, though it is particularly used for a non-conducting materials. Kajiyama and coworkers[5] investigated the relationship between the dielectric properties and light-switching characteristics of polymer/LC composite materials, and the ways to improve the response characteristics on the basis of the modulation of dielectric properties of matrix materials. They concluded that the polymer/LC materials can be approximated as a binary series-connected dielectric composite model composed of polymer matrix and LC phases. It is, however, noted that all the above studies for the polymer/LC blends did not take into considerations for the temperature effect on the relationship of electrical property with the phase behavior of blends. Though Kelly and Seekola[4] briefly described temperature effects on the PMMA/E7 system where the glass transition temperature (T_g) of the blend decreased by addition of LC and all the phase-separated samples show a pronounced changes in the dielectric constant in the vicinity of T_g, caused by the conductivity increase of LC with temperature, they did not mention any reason for the changes of states within PDLC materials.

In this work, therefore, the electrical properties of a low molecular weight liquid crystal, 4-cyano-4'-*n*-heptylbiphenyl (7CB) and its blends with poly(methyl methacrylate) (PMMA), were measured as a function of temperature using an ACIS spectrometer equipped with a temperature controller. Their relationships with phase transition behaviors were also discussed. The results will show that marked electrical property changes occur near the phase transition of 7CB and PMMA/7CB blends. Furthermore, it will be considered that this method of an electrical property measurement for these materials is particularly useful for the investigation of phase transition behavior of a heterogeneous blend system having a small refractive index difference between the components, which is hard to detect by such a method like dynamic light scattering.

Experimental

Liquid crystal 7CB was purchased from Merck Co. and used without further purification. Pure 7CB has two transition temperatures, nematic-to-isotropic (T_{NI}) at 43℃ and crystal-to-nematic (T_{CN}) at 30℃, according to its own phase transition. 7CB was sandwiched between two ITO-coated glass plates and placed on a hot plate, controlled at about 130℃. The area and thickness of samples were controlled by spacer films with various thicknesses. Cables from the both sides of electrodes were connected to the working- and counter-electrode of differential electrometer (a high impedance-adaptor) of the measuring unit.

For the AC impedance measurement of the PMMA/7CB blend samples, a flat steel electrode of circular type with about 10 cm of diameter was employed. Thermocouple of Pt-100 Ω was inserted from the side wall of electrode into the center position to read sample temperature more accurately. Polyimide film of 50 μm-thickness was used to separate the electrodes. Samples were set on a hot plate, controlled at about 130℃. Temperature of the sample with steel electrodes was controlled in MTP-8 hot press of Tetrahedron (USA) over a temperature range of *ca.* 20~120℃. Real temperature of the sample was independently measured using the thermocouple inserted into the electrode. The computer-controlled AC impedance measuring system was Solatron 1255 digital frequency response analyzer (FRA) with Potentiostat/galvanostat (Model 273, EG&G). Impedance range of the system was 10^2-10^9 Ω and Stray capacitance was less than 0.5 pF. Frequency was controlled by a computer over the range of 1.0×10^{-3}-1.0×10^5 Hz. A monochromatic sinusoidal voltage generated by FRA, with specified frequency range (10^{-3}-10^4) and amplitude (20 mV), was applied to the test sample across the two electrodes. From the response-to-stimulus ratio, impedance of the sample was calculated by the computer for all specified frequencies ranging

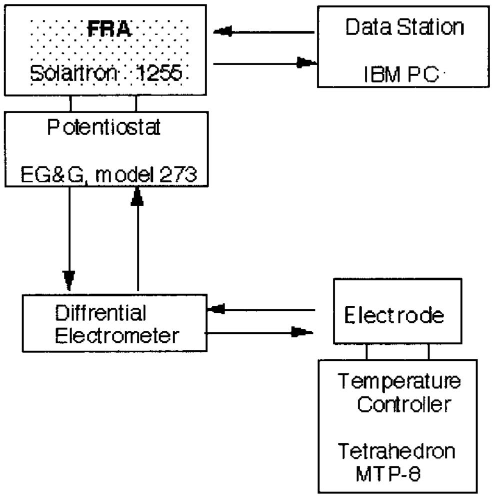

Figure 1. Schematic representation of the impedance measuring system.

over 10^{-3} to 10^{4} Hz. Schematic diagram of the impedance measuring system is represented in Figure 1.

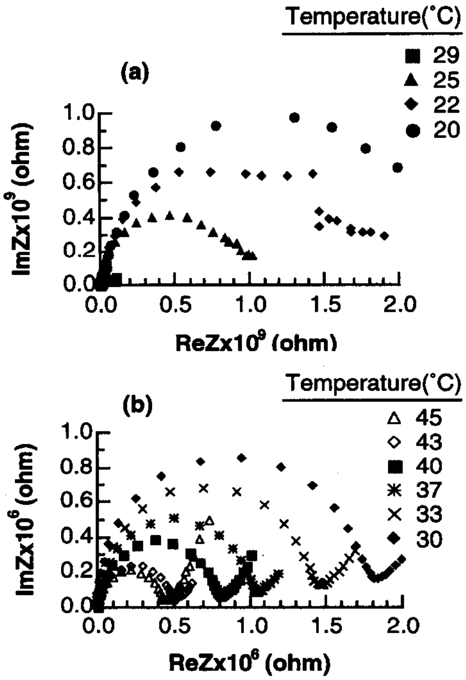

Figure 2. Impedance spectra of pure 7CB at different temperatures: (a) below 30 °C and (b) above 30 °C.

Results and Discussion

Low Molecular Weight Liquid Crystal, 7CB. Impedance response of 7CB can be represented by a RC parallel circuit model.[1] Resistance is obtained from the low frequency impedance region, i.e., the diameter of semicircle of a complex plane. Capacitance is determined from the top of semicircle with the relation, $\omega=1/RC$. These values are then converted into resistivity (ρ) and relative permittivity (ε) with known electrode area and sample thickness. Figure 2 shows Nyquist plot (imaginary vs. real part of impedance, -Z" vs. Z') of pure 7CB obtained at fixed temperatures during heating from 20 °C. Several features are clearly observed from the figure. First, almost perfect semicircles irrespective of temperatures are shown, indicating that 7CB has a single relaxation time due to the large permanent dipole moment associated with cyano (-CN) group in the molecule. For a simple semicircle, Debye function, $D(\omega\tau)$ is defined as:[1]

$$D(\omega\tau) = 1/(1 + j\omega\tau) \quad (1)$$

where $\tau=RC$ (single relaxation time constant). And, then, the above equation can be described in terms of $Z=Z'-jZ''=RD(\omega\tau)$, which represents the semicircle in the complex plane for the parallel connection. Second, the radius of semicircle decreases as temperature increases. Moreover, this change is remarkable near T_{NI} at 43 °C and T_{CN} at 30 °C, which are nematic-to-isotropic and crystal-to-nematic phase transition temperatures of 7CB, respectively. It should be noticed that the scale in Figure 2(b), for example, is smaller by the order of three than that in Figure 2(a), which clearly shows the drastic step-wise changes of electrical properties near T_{CN}. These phenomena are clearly due to the phase transition of 7CB. Considering at molecular level, it seems to be difficult for dipoles of 7CB at a solid crystalline state below T_{CN} to response with the external AC field. The bond associated with this moment, however, becomes activated as temperature increases near transition temperatures, showing a marked decrease of the impedance (i.e., the decrease of diameter of semicircle). A similar change occurs to the transition from nematic state to isotropic state, though the impedance change is comparatively smaller than that of the

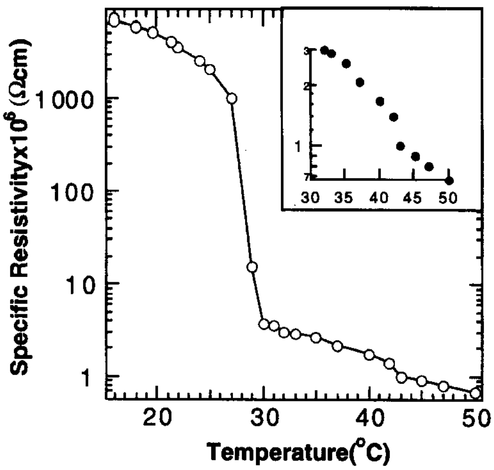

Figure 3. Specific resistivity of pure 7CB as a function of temperature. Inset represents magnified temperature range near T_g.

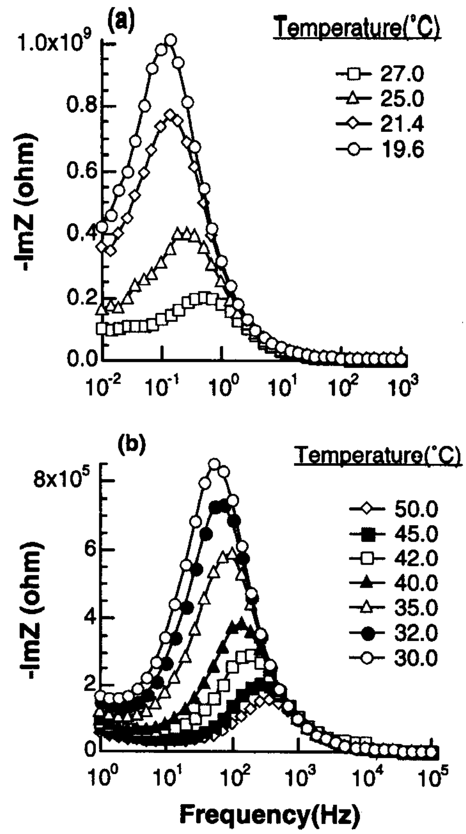

Figure 4. Plot of -Z" vs. log f of pure 7CB: (a) below 30 °C and (b) above 30 °C.

crystal-to-nematic transition due to the larger molecular mobility in the nematic state than in the crystal state. It is well known that other properties of liquid crystal besides the electrical properties, such as magnetic susceptibility, and refractive index, also show non-linear change near the phase transition.[6]

Conductivity or Resistivity of 7CB can be calculated from Z' value along x-axis of impedance spectra and the sample dimension. Figure 3, thus, may be drawn from Figure 2, showing the change of specific resistivity with temperature. Sharp changes near the transition temperatures are more clearly shown as expected. The inset of Figure 3 shows the drastic change of specific resistivity near T_{NI} of 7CB as found in most liquid crystals.[6,7] In nematic temperature range, since Z' value along x-axis in Figure 2(b) varies from ca. 0.4×10^6 to 1.8×10^6 Ω, specific resistivity of 7CB is calculated to be 3.6×10^9 $\Omega\cdot$cm at 30 °C and 1.5×10^9 $\Omega\cdot$cm at 40 °C, respectively, showing a good agreement with the literature value.[2]

To investigate the effect of temperature on phase transitions of 7CB more clearly, it is possible to obtain the resonance frequency at a given temperature by plotting -Z" vs. log(frequency), where -Z" becomes the maximum as shown in Figure 4. And, thus, the relationship between log (frequency maximum), log f_{max}, and temperature

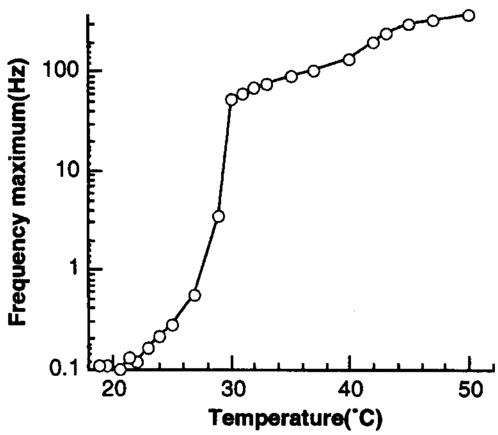

Figure 5. Change of the maximum resonance frequency of 7CB, f_{max}, at which -Z" becomes maximum at a given temperature.

can be easily obtained. Figure 5 could be drawn based on Figure 4, by plotting log f_{max} vs. temperature. It is clearly observed from the figure that log f_{max} changes remarkably near the transition temperatures of 7CB, i.e., 43℃ (T_{NI}) and 30℃ (T_{CN}). The drastic decrease of the resonance frequency near T_{CN} compared to that near T_{NI} exhibits the difficulty of dielectric response of 7CB to the applied field at solid crystalline state because, even though the molecule has a large dipole moment, it cannot contribute to the dielectric response if not free to reorient to the applied field.[4]

PMMA/7CB Blends. Since there are little works for the investigations of electrical property in relation with phase transition behavior of a polymer/LC blend, it is interesting to study the electrical property-phase behavior relationship of a polymer/LC blend such as PMMA/7CB blend. Electrical properties of such a heterogeneous blend system are approximately predicted by combining the electrical properties of each constituent with known relations.[1] The electrical properties of a binary polymer/LC blend, therefore, can be approximately described in terms of the intensive properties of each component such as the complex conductivity (σ), the complex resistivity (ρ), and the complex dielectric constant (ε).[3-5]

It is well known that the dielectric constant of an amorphous polymer matrix shows a peak near T_g.[5] Above the glass transition temperature, the dipole moments in the polymer molecule attain sufficient freedom and the thermal agitation causes a decrease in their ability to align along the field. Addition of small amounts of LC to the polymer shifts T_g of the matrix to a lower temperature as described earlier.[8] It is, however, expected that more amounts of LC in the polymer above a threshold LC concentration will cause the phase separation, resulting the marked changes of electrical properties with temperature.

PMMA is a very poor conductor in glassy state with the conductivity of 10^{-13} mho/cm. PMMA has also a permanent electrical dipole moment on side chain, which is originated from the ester linkage (-COO-). It is expected, therefore, that the effect of multiple relaxation time constants for the PMMA/7CB blend should appear in the impedance spectra, showing a Cole-Cole

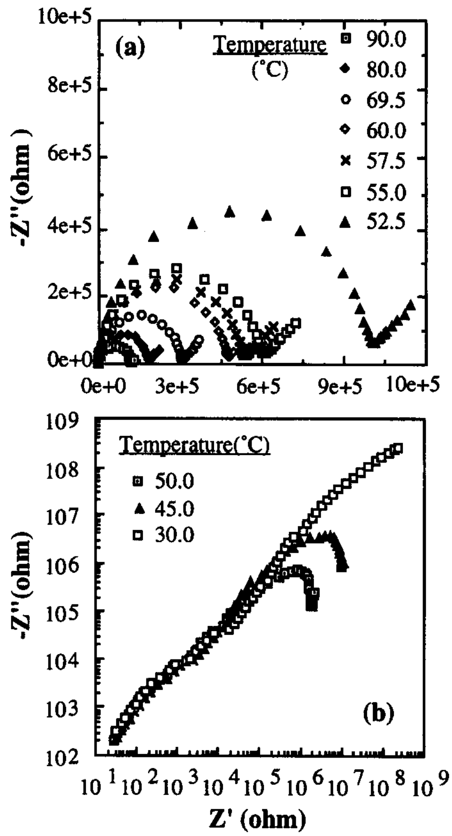

Figure 6. Impedance spectra of the 4/6 PMMA/7CB (w/w) blend with temperature: (a) above 50℃ and (b) below 50℃.

broadening.[1,6] Figure 6 shows Nyquist plots of -Z" vs. Z' of the 4/6 PMMA/7CB blend as a function of temperature, showing almost perfect semicircles in the experimental temperature range. Note that Figure 6(b) is plotted using log-log scale due to the much larger scale of Z than that of the scale in Figure 6(a). This result explains that the major response in impedance measurement is originated from 7CB in the blend because it is considered that the response of PMMA is weak and difficult to detect compared with that of 7CB due to the high molecular weight. The 4/6 PMMA/7CB blend must show several different phase states with temperature change according to Ref. 8. It shows the phase separation near 55℃ during cooling from the homogeneous state above the cloud point, heterogeneous-to-homogeneous transformation temperature (T_{cloud}), and an isotropic two-phase state until tem-

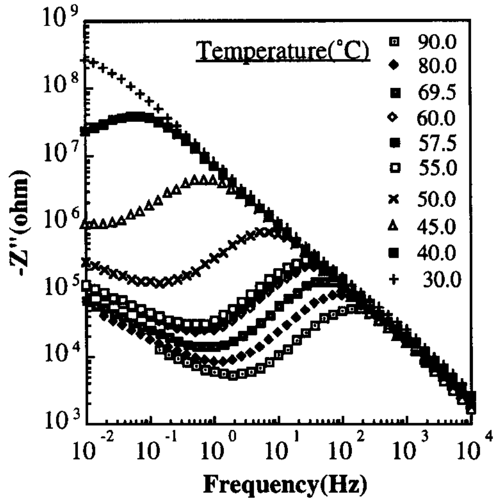

Figure 7. Plot of -Z" vs. log f of the 4/6 PMMA/7CB (w/w) at several given temperatures.

perature goes down below T_{NI} of LC-rich phase. These characteristics are also shown in Figure 6, exhibiting the stepwise change of impedance near each transition temperature.

When -Z" is plotted against log (frequency) as shown in Figure 7, one can easily find the maximum resonance frequency, f_{max} at which -Z" becomes maximum at a given temperature. The transition points can be deduced from the plot of log f_{max} vs. temperature as seen in Figure 8. Comparing this result with the phase diagram of the PMMA/7CB blend,[8] one may conclude that the change near 55 ℃ is originated from the phase separation of PMMA/isotropic-7CB, while the change near 43 ℃ exhibits the isotropic-to-nematic transition temperature of 7CB.

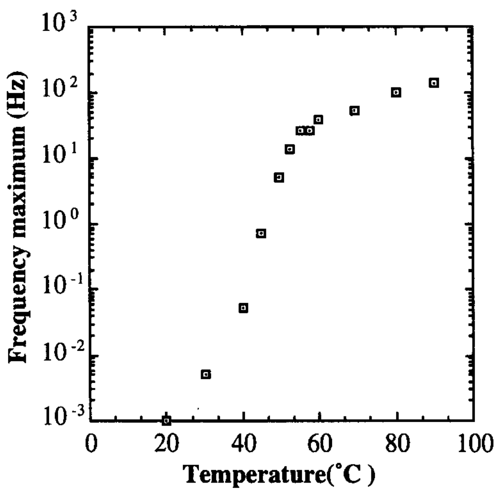

Figure 8. Change of the maximum resonance frequency of 4/6 the PMMA/7CB (w/w), f_{max}, at which -Z" becomes maximum at a given temperature.

It is notable at this point that ACIS measures sample impedance at a fixed temperature with frequency scanning over a wide range. It may not be used for such a sample of which state at a fixed temperature is time-dependent during test. In case of PMMA/7CB blends, however, it is considered that time for the usual frequency scanning (10^{-2}-10^{4} Hz) may not alter the sample condition at a given temperature during the experiment. Another difficulty to use ACIS for the impedance measurement of PMMA/7CB blend is that data scattering becomes serious at a low frequency as LC concentration decreases in the blend. With the present instrument, in fact, the impedance spectra of blend below T_g could be hardly obtained because of high impedance near or beyond the limit of the instrument. It was considered that the present instrument should be modified to measure the impedance of a material having such a low conductivity.[9]

Conclusions

ACIS to measure the electrical properties of pure 7CB and PMMA/7CB blends were utilized to investigate the relationship of electrical property-phase transition behavior of the samples. ACIS showed that pure 7CB had single relaxation time due to the large permanent dipole moment associated with cyano (-CN) group in the molecule, showing a remarkable change near T_{NI} at 43 ℃ and T_{CN} at 30 ℃ in Nyquist plot of the impedance spectra, which represented a semicircle in complex plane.

Calculated specific resistivities of 7CB at different temperatures showed good agreements with literature, which were 3.6×10^{9} Ω·cm at 30 ℃ and 1.5×10^{9} Ω·cm at 40 ℃, respectively.

For the polymer/LC systems, ACIS could be applied to isolate resistivity and permittivity. It could also be applied to the investigation of phase transition behavior of the blends. The maximum resonance frequency at which -Z" becomes maximum was found to be a very sensitive probe to investigate the physico-chemical changes within the blends, showing the marked changes of electrical properties including resistance and capacitance near T_{NI} and T_{cloud}.

Acknowledgement. This work was supported by the Korea Science and Engineering Foundation (Grant No. 95-0300-20-01-3) and partially by the Center for Automotive Parts Technology of Keimyung University.

References

(1) *Impedance Spectroscopy*, ed. by J. R. Mcdonald, John Wiley & Sons Inc., 1987.

(2) P. G. Bruce, in *Polymer Electrolyte Review*, eds. by J. R. MacCallum and C. A. Vincent, Ch. 8, Elsevier, N.Y., 1987.

(3) Y. Wang, D. D. Snyder, and G. J. Nelson, *Mol. Cryst. Liq. Cryst.*, **149**, 163 (1987).

(4) J. Kelly and D. Seekola, *Proc. SPIE*, **1257**, 17 (1990).

(5) A. Myamoto, H. Kikuchi, S. Kobayashi, Y. Morimura, and T. Kajiyama, *Macromolecules*, **24**, 3915 (1991).

(6) A. Chelkowski, *Dielectric Physics*, Ch. IV, Elsevier, N.Y., 1980.

(7) P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1974.

(8) W. Ahn, H. Kim, S. C. Kim, and C. Y. Kim, *Macromolecules*, **25**, 5002 (1992).

(9) Y. Wang, S. W. Liu, and R. Huo, *SAE Paper*, No. 860352 (1986).