Phase Transitions Induced by Electric Fields in Near-Critical Polymer Solutions

Denis Wirtz and Gerald G. Fuller

Chemical Engineering Department, Stanford University, Stanford, California 94305-5025

A time-dependent small-angle light scattering (SALS) study is presented which demonstrates the feasibility of electric-field-induced phase transitions in nonionic binary liquids near the critical point. Mixing of two-phase solutions induced by electric fields is shown to be a universal feature shared by a wide class of systems including upper and lower critical point polymer solutions and mixtures of low-molecular-weight molecules in a solvent. The shift of the critical temperature is computed from SALS measurements and is quadratic in the electric-field strength.

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Phase transitions in binary liquid systems can be induced under the influence of external forces. In particular, flow-induced phase behavioral transitions in complex polymeric systems have recently received attention [1–3]. Flows such as shear or extensional flows can induce polymer phase separation, phase dissolution, gelation, crystallization, and fiber formation in polymer solutions, as well as ordering transitions in block copolymers and liquid crystals [2]. Fundamental understanding of these various phenomena is still at an early stage. For example, several theoretical models have attempted to explain flow-induced turbidity measurements in polymer solutions. Such systems are not described by equilibrium means such as minimization of free energy, but by microscopic equations of motion of the appropriate internal degrees of freedom [3]. Electric fields offer an alternative method of inducing anisotropic mechanical and optical properties of polymeric materials [4]. Contrary to the flow case, nonionic polymeric systems subjected to a steady electric field are, once steady state is reached, in equilibrium. Therefore, a simple thermodynamic approach can be used to describe the collective structure and possible phase transitions of polymeric systems in an electric field. In 1965, Debye and Kleboth [5] observed a strong decrease of the absorption coefficient in near-critical binary mixtures subjected to an electric field. This effect was attributed to an electric-field-induced shift of the critical point [5]. In this Letter, we exploit these authors' original idea to show that electric fields can induce phase transitions in nonionic polymer-solvent systems near the critical point. The effect of shear on upper critical point (UCST) polymer solutions is to induce an apparent *demixing*, accompanied by a large increase in the turbidity at temperatures significantly higher than the coexistence curve [1–3]. In contrast, we demonstrate that an electric field can induce *mixing* of similar polymer solutions following a shallow quench in the two-phase region. The same stabilization effect of an electric field is observed for lower critical point (LCST) polymer solutions.

The equilibrium phase behavior of a mixture of high-molecular-weight polymer molecules dissolved in a low-molecular-weight solvent with a temperature between the Flory Θ point $(T = T_\Theta)$ and the coexistence curve can be approximately described by the sum of a local binary interaction and a local repulsive three-body interaction between neighboring molecules. In addition, the description of this equilibrium must include an entropy term due to the number of different macromolecular arrangements that can exist for a given polymer volume fraction φ. Starting from the classical expression of the Flory-Huggins free energy density of mixing [6], f, expressed in thermal energy unit $\beta = 1/k_B T$ for solutions of low polymer concentrations, one can add a free energy density term due to the presence of the electric field:

$$f = (\varphi/N)\ln\varphi + \tfrac{1}{2}(1 - 2\chi)\varphi^2 + \tfrac{1}{6}\varphi^3$$
$$+ (\beta E^2/2)[\varepsilon_0(\varphi) - (1 - \varphi)\varepsilon_s - \varphi\varepsilon_p], \qquad (1)$$

where N is the polymerization index of the macromolecules. The first three terms describe, in order, the entropic contribution and the binary and three-body interaction energy contributions to the free energy at small φ. The last term in Eq. (1) is the contribution to f due to the uniform electric field $\mathbf{E} = E\hat{\mathbf{x}}$ and is proportional to the "excess" electrostatic energy of the mixture. This excess free energy is equal to the difference between the electrostatic energy of the solution and the φ-weighted average of the pure polymer and the pure solvent [7]. Here ε_0 is the composition-dependent dielectric constant of the binary mixture, ε_s and ε_p are the dielectric constants of the pure solvent and the pure polymer, respectively. The location of the critical point, defined as the maximum (for an UCST system) or the minimum (for a LCST system) of the coexistence curve, is given by the two conditions $\partial\mu/\partial\varphi = 0$ and $\partial^2\mu/\partial\varphi^2 = 0$, where μ is the chemical potential of the polymer solution derived from the expression of f:

$$\mu = \frac{\partial f}{\partial \varphi} = \frac{1}{N} + \frac{1}{N}\ln\varphi + (1 - 2\chi)\varphi$$
$$+ \frac{\varphi^2}{2} + \frac{\beta E^2}{2}\left[\frac{\partial\varepsilon_0}{\partial\varphi} + \varepsilon_s - \varepsilon_p\right]. \qquad (2)$$

These two conditions give rise to two equations for the new critical concentration $\varphi_c(E)$ and the new critical two-body interaction Flory parameter $\chi_c(E)$. $\varphi_c(E)$ is given by

$$\varphi_c(E) = \varphi_c \left[1 + \frac{\beta_c E^2}{2} \left(\frac{\partial^3 \varepsilon_0}{\partial \varphi^3} \right)_c \right]^{-1/2} \cong \varphi_c , \qquad (3)$$

where the refractive index increment $\partial n_0/\partial\varphi$ can be assumed to be a constant for a semidilute polymer solution. Using this last equality, $\chi_c(E)$ is given by

$$\chi_c(E) - \chi_c \cong \frac{\beta_c E^2}{4} \left(\frac{\partial^2 \varepsilon_0}{\partial \varphi^2} \right)_c \cong \frac{\beta_c E^2}{2} \left(\frac{\partial n_0}{\partial \varphi} \right)^2 > 0 . \qquad (4)$$

Here $\varphi_c = N^{-1/2}$ and $\chi_c = 0.5 + N^{-1/2}$ are the mean field, quiescent values of the critical polymer volume fraction and the critical Flory parameter, respectively [6]. From (4), it can be inferred that the effect of an electric field is to *increase* the critical Flory parameter: Demixing occurs when $\chi < \chi_c(E)$ instead of $\chi < \chi_c$. More generally, χ_c is shifted if the dielectric constant as a function of the polymer concentration varies in a nonlinear fashion. This critical shift is quadratic in the electric-field strength, quadratic in the refractive index increment, and independent of the molecular weight of the polymer. As a consequence, the shift of the critical point (and subsequent stabilization of the system) is a universal feature also shared by near-critical low-molecular-weight systems. Since polymer solutions belong to the same critical universality class as simple binary mixtures [8], a similar behavior for both types of systems is expected in the presence of an electric field. In most UCST and LCST polymer solutions, the two-body interaction parameter is an inverse function of the temperature and can be written as $\chi(T) = b + a/T$ [9], where a and b are enthalpy and entropy coefficients which can be experimentally determined and depend on the concentration, the molecular weight and the molecular architecture. If a is positive (negative) and b is negative (positive), an UCST (LCST) coexistence curve may result. The corresponding shift of the critical temperature is given by $T_c/T_c(E) \cong 1 \pm E^2 \times (\partial n_0/\partial\varphi)^2/2|a|k_B$. Here, the negative sign reflects an increase of the critical temperature for a LCST solution, and the positive sign represents a decrease of the critical temperature for an UCST solution. Therefore, our mean field theory predicts that phase-separated UCST and LCST systems with a temperature close to the critical point mix in the presence of an electric field. Figure 1 shows that similar conclusions hold for polymer systems with an overall concentration different from the critical concentration. This phase diagram [6] displays the Flory parameter as a function of the polymer volume fraction, in the presence and in the absence of an electric field. These curves are predicted with Eq. (2) based on the equality of both the chemical potential and the osmotic pressure, $\pi = \varphi \partial f/\partial\varphi - f$, in the two phases [6]. The corresponding quiescent coexistence curves (T as a function
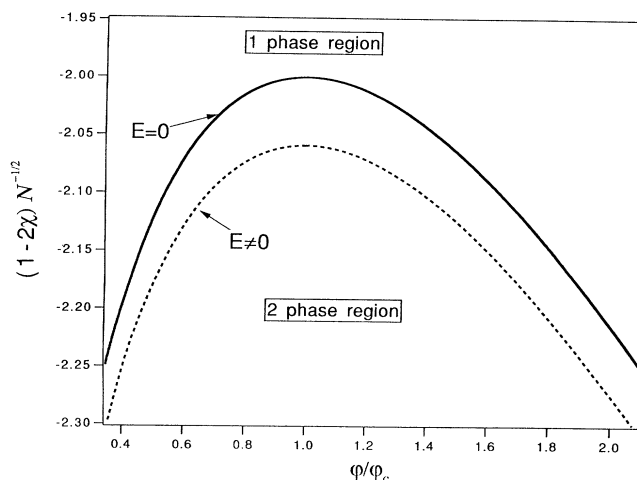

FIG. 1. Phase diagram for both LCST and UCST polymer solutions: $(1 - 2\chi)/\sqrt{N}$ as a function of φ/φ_c in the presence (dashed line) and in the absence (solid line) of an electric field. Here χ is the Flory-Huggins parameter, φ_c is the critical concentration, and $\beta_c E^2(\partial n_0/\partial\varphi)^2 = 0.12$ (see text for notations).

of φ) are respectively lowered and raised for UCST and LCST solutions in the presence of an electric field.

In order to study the dynamics of electric-field-induced phase transitions in nonionic binary liquids, we have built a time resolved small-angle light scattering apparatus [10]. The light of a He-Ne laser illuminates a small scattering volume in the gap between the electrodes of a well-thermostated ($\pm 0.005\,^\circ$C) Kerr cell containing the solution. The electrode's separation and height are 1.65 and 4 mm, respectively. Measurements of the temperature increase of the system due to the combined effects of the applied field and the laser light indicated a negligible heating during the experiments. Scattering patterns are formed on a screen normal to the incident light and recorded on a framegrabber using a charge coupling device camera at a rate of 8 frames per second. Scattering patterns correspond to isointensity lines of the scattered light intensity which is proportional to the structure factor [11]. Since the structure factor is the Fourier transform of the equal time correlation function for the concentration fluctuations, information on the collective structure of binary systems can be inferred from scattering intensity measurements [11]. Three different systems were utilized to test the above theoretical predictions: an UCST polymer solution for which $T_\Theta - T_c > 0$, a LCST polymer solution for which $T_\Theta - T_c < 0$, and an UCST binary mixture of small molecules in a solvent. Critical and off-critical, semidilute solutions of polystyrene of different molecular weights in cyclohexane (PS in CH) were prepared using the procedure described in Ref. [10]. A PS/CH solution forms an UCST solution. In contrast, poly(p-chlorostyrene) in ethylcarbitol (PC in EC) forms a LCST solution. The cloud-point temperature of a 17 wt.% PC/EC solution was measured to be $T_c = 35.2\,^\circ$C
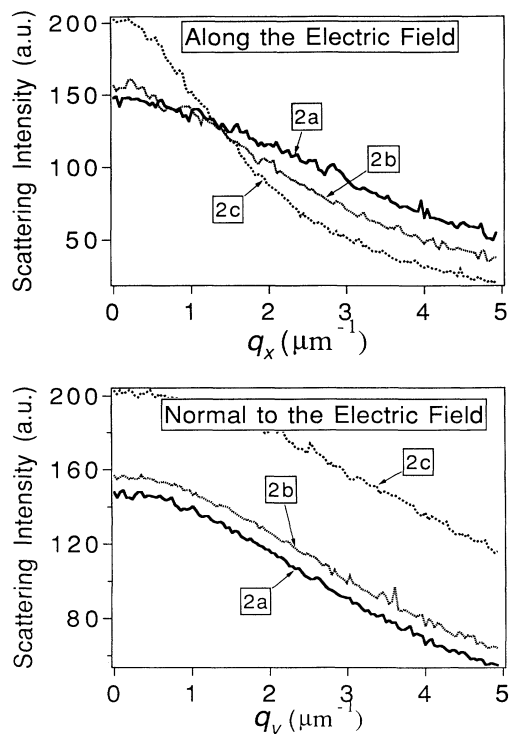
FIG. 2. Evolution of the scattering intensity profiles as a function of q_x and q_y for an electric-field-induced mixing of a two-phase UCST polymer solution. The electric field is turned on at $t = 1.5$ s; (a) $t = 1.5$ s (quiescent state); (b) $t = 1.8$ s; (c) $t = 2.5$ s (steady state). $T - T_c = -0.04$°C, $E = 5000$ V/cm. PS/CH solution ($M_w = 400\,000$, $\varphi = 5.89$ vol%, $T_c = 26.35$ °C).

FIG. 3. Critical temperature shift $T_c - T_c(E)$ as a function of the square of the electric-field strength PS/CH solution ($M_w = 900\,000$, $T_c = 29.17$°C, $\varphi = 4.03$ vol%) above the critical point ($T - T_c = 0.05$°C). The line is only a guide to the eye.

for a molecular weight of $M_W = 528\,000$ and a polydispersity of $M_W/M_N = 1.09$. The third system consisted of nitrobenzene dissolved in spectrophotometric n-hexane to form a mixture with $\varphi = \varphi_c = 37.7$ vol%, and $T_c = 19.06$°C [12].

Figure 2 shows a typical set of small-angle light scattering intensity profiles describing electric-field mixing of a phase-separated UCST PS/CH solution ($T - T_c = -0.04$°C) as a function of q_x and q_y in the plane normal to the incident light. Here q_x and q_y are the components of the scattering vector parallel and normal to the electric field, respectively. The electric field is applied along q_x ($E = 5000$ V/cm), and the times at which intensity curves were taken are shown in the figure. For the first intensity profiles, 2(a), taken prior to the application of the field, the maximum scattering intensity is very low since the turbidity of the phase-separated PS/CH solution is high. Intensity profiles 2(b) and 2(c) show the response following application of the field at $t = 1.5$ s. A dramatic increase of the scattering intensity is observed, and simultaneous formation of elliptical patterns is induced. In the present case, the steady state structure is approximately reached after 1 s [intensity profiles 2(c)].
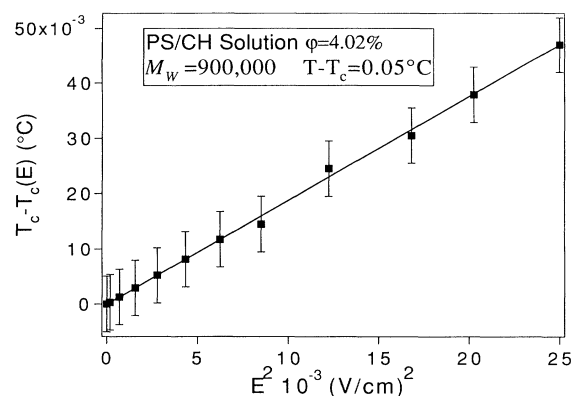
As was shown in an earlier paper [10], elliptical scattering patterns elongated in the direction normal to the electric field are a signature of a system above its critical point in an electric field. Light is scattered by concentration fluctuations which are deformed due to interfacial dipolar coupling with the electrostatic field. The deformation of the fluctuations in the direction of the electric field can be described by a free energy function which includes terms quadratic in the gradients of the order parameter fluctuation ($\propto [\nabla \varphi(\mathbf{r})]^2$) [13]. When the field is turned off, the elliptical patterns relax towards circular patterns while the scattering intensity decreases due to demixing of the solution. To compute the shift of the critical temperature $T_c(E) - T_c$, the mean field critical exponent $\nu = 0.5$, and the nonuniversal amplitude ξ_0 of the quiescent correlation length were determined from SALS measurements in the absence of the electric field for each system above the critical point. Plots of the inverse of the scattering intensity versus q_y^2 can determine the change in the correlation length $\xi_E = \xi_0\{[T - T_c(E)]/T_c\}^{-\nu}$ of fluctuations with a wave vector normal to the field, and, therefore, $T_c(E)$. Figure 3 demonstrates that, at least for low field strength, the shift $T_c - T_c(E)$ is quadratic in the electric-field strength.

According to Eq. (4), electric-field-induced mixing is also possible for polymer solutions of small molecular weights and in the limit of mixtures of small molecules in a solvent (data not shown here). In the latter case, mixing still occurs until about 0.02 °C below the cloud point of an UCST nitrobenzene/n-hexane critical mixture for a field strength of $E = 10\,000$ V/cm. Here, time scales are an order of magnitude shorter than for the polystyrene solutions. However, a detailed study of the kinetics of mixing still remains to be done both experimentally and theoretically. Note that the experiments conducted at temperatures smaller than the shifted critical tempera-
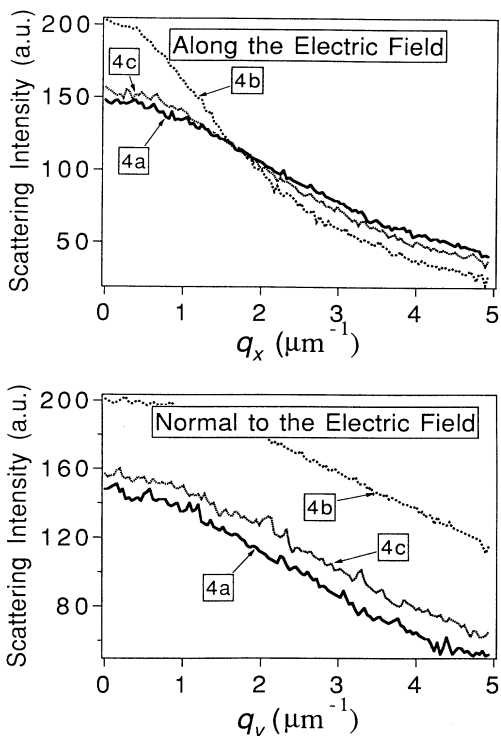
FIG. 4. Intensity profiles for a two-phase LCST polymer solution subject to an electric field. The electric field is turned at $t = 1.5$ s and turned off at $t = 2.5$ s; (a) $t = 1.5$ s (quiescent state); (b) $t = 2$ s (steady state); (c) $t = 10.5$ s (relaxation). $T - T_c = 0.03\,°C$, $E = 5000$ V/cm. PC/EC solution ($M_w = 528\,000$, $\varphi = 17$ wt%).

ture of UCST solutions showed that mixing is infeasible. Instead, scattering patterns were first distorted in the direction of the applied field and then suddenly reoriented in the direction normal to the electric field. This structural transition induced by electric fields in polymer/solvent systems well below the coexistence curve will be the subject of a future publication [13].

Electric-field-induced mixing of a two-phase LCST system (PC/EC) is demonstrated in Fig. 4 ($T - T_c = 0.03\,°C$ and $E = 5000$ V/cm). As in the UCST case, when a uniform electric field is applied [intensity profiles 4(a) and 4(b)] the scattering intensity is rapidly enhanced at small scattering angles, and rendered anisotropic by dipolar coupling of the fluctuations with the electric field. When the field is turned off ($t = 2.5$ s), the system is driven back into the two-phase region, producing scattering intensity [intensity profiles 4(c)]. This last intensity curve describes the relaxation of the concentration patterns and the early stage of phase separation of the PC/EC system.

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