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Dielectric Spectroscopy of Liquid Crystalline Dispersions

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Received December 26, 2005

We describe dielectric spectroscopy measurements on dispersions of two thermotropic liquid crystals (5CB and 8CB) in a poly(dimethylsiloxane) matrix. 5CB exhibits nematic and isotropic phases, while 8CB exhibits smectic, nematic, and isotropic phases. The spectra of the dispersions exhibit a temperature-dependent dielectric relaxation in the interval from 100 to 1000 Hz, with relaxation times that depend strongly on whether the dispersed phase is isotropic, nematic, or smectic. The dielectric relaxation times also depend on the viscosity of the matrix fluid. These results suggest a coupling between the electric field and the mechanics of the interface that affects the spectrum of the dispersed phase and shifts the Maxwell–Wagner interfacial polarization peak.

1. Introduction

Dispersions of liquid crystalline droplets in an amorphous liquid matrix are of interest in a variety of applications, including display technology and as precursors for self-reinforced polymer composites, and the interface between a structured fluid and one without structure is itself of considerable inherent interest. Broadband dielectric relaxation spectroscopy is potentially a powerful technique for characterizing the dynamical processes in these multiphase systems, where the dynamics of the dispersed phase include molecular motions ranging from local processes to cooperative molecular rearrangements.

Dielectric spectroscopy has been applied to liquid crystals in a number of studies,^{1–9} and the theory of the dielectric response of monodomain and polydomain liquid crystals is addressed by Kozak et al.¹⁰ and Williams.¹¹ Most studies have addressed bulk liquid crystalline phases. Carius and co-workers⁴ measured the dielectric response of blends of polymer liquid crystals with polycarbonate. The studies most relevant to the work described here are those of Sinha and Aliev⁵ and Frunza and co-workers,⁶ who studied the dielectric response of molecular liquid crystals in highly confined environments, the former in porous glass matrixes and the latter in molecular sieves. Both found a strong effect of confinement on the dielectric response of the liquid crystals.

We report here on the dielectric response of dispersions in a poly(dimethylsiloxane) (PDMS) matrix of two biphenylcarbo-

nitrides (5CB and 8CB) that exhibit isotropic and liquid crystalline phases. The interfacial tensions between these carbonitriles and PDMS have the unusual property of increasing with temperature¹² because of coupling between the structure and the interface.

2. Experiment

2.1. Preparation. 4'-Pentyl-4-biphenylcarbonitrile (5CB) and 4'-octyl-4-biphenylcarbonitrile (8CB) were purchased from Sigma-Aldrich and used as received. 5CB undergoes a crystal-to-nematic transition at 21 °C and a first-order nematic-to-isotropic transition at 35 °C. 8CB undergoes a crystal-to-smectic-A transition at 22.5 °C, a relatively broad smectic-to-nematic transition between 32 and 34 °C, and a first-order nematic-to-isotropic transition at 41 °C. These transitions can be seen in the viscosity data of Rai et al.¹² The matrix fluid for most experiments was 60 cSt PDMS 200 fluid, which was purchased from Sigma-Aldrich and used without further purification; the molecular weight of PDMS 200 is about 2500. High-viscosity PDMS was used in some experiments to study the effect of suspending fluid viscosity; the number-average molecular weight of the 30 000 cSt PDMS used is 67 700, while that of the 60 000 cSt PDMS is 116 500.

The dispersions were prepared by adding measured amounts of 5CB or 8CB to the PDMS and stirring by hand with a spatula. Droplet size distributions were not obtained because of the opacity of bulk samples, but the average droplet sizes observed in the optical microscope near the sample surface were of order 20 μm. All experiments reported here were for dispersions containing 6.2% 5CB or 5.0% 8CB by weight; some 5CB data at other concentrations are reported by Rai.¹³ The batch-to-batch uncertainty in composition was estimated to be ±0.1%. The dispersion was allowed to rest for a few hours in a dry environment in order to expel entrapped air bubbles, after which the sample was loaded in the dielectric sample cell. The dispersed phases and PDMS 200 are density matched; hence, no settling or creaming of the dispersion occurred over periods much longer than the time from sample preparation to completion of an experiment. We assume throughout that the structural states of the biphenylcarbonitriles in the droplets are the same as in the bulk, but we do note that a small birefringent ring was observed in the 5CB droplets above the bulk isotropic transition temperature, indicating induced nematic order at the interface; this order appears to be analogous to Kocevvar and Musevic's¹⁴ observation of stable surface-induced order in 5CB at a silanated glass surface at 20 °C above the bulk nematic-to-isotropic transition. Molecular field theory

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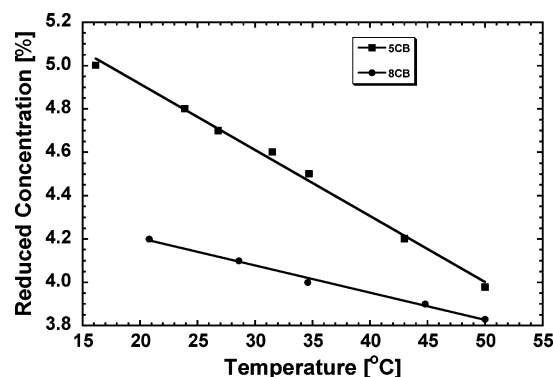


Figure 1. Reduced concentrations of a nominal 6.2% dispersion of 5CB and a 5% dispersion of 8CB in PDMS 200 as functions of temperature.

calculations and Monte Carlo simulations of the nematic-to-isotropic transition in surface-aligned nematic films by Lu et al.¹⁵ suggest an order parameter of 0.6 in a surface boundary layer at temperatures considerably above the bulk transition.

2.2. Solubility. 5CB and 8CB are slightly soluble in PDMS 200,^{16,17} but the solubility of PDMS in 5CB and 8CB is negligible.¹⁷ We refer to the concentration of 5CB or 8CB dispersed in pure PDMS 200 as the *nominal concentration*, while the concentration of 5CB or 8CB above the respective solubility limit in PDMS 200, which is a weak function of temperature, is referred to as the *reduced concentration*. Figure 1 shows the reduced concentrations of a nominal 6.2% dispersion of 5CB and a nominal 5% dispersion of 8CB in PDMS, using the data of Inn and Denn¹⁶ for a lower-viscosity PDMS; the 5CB solubility curve differs in detail from the data of Gogibus et al.,¹⁷ but the small differences have no effect on the conclusions. All concentrations reported here are nominal concentrations unless otherwise stated.

2.3. Dielectric Relaxation Spectroscopy. The dielectric relaxation spectroscopy (DRS) experiments were carried out on a commercial broadband dielectric spectrometer (BDS-80) from Novocontrol GmbH, using a cylindrical sample cell having a diameter of 19.21 mm and a gap of 0.27 mm between the plates. The reported temperature resolution is 0.01 °C, with a range from −196 to 400 °C. The accessible impedance range for the Alpha high-resolution dielectric and impedance analyzer is from 0.01 to 10¹⁴ Ω, with a reported tan(δ) accuracy of 3 × 10^{−5}. The root-mean-square voltage used in all experiments was 1.00 V.

The −C≡N end group on the aromatic backbone could be sensitive to water. Hence, one series of controlled experiments was carried out to determine the possible effect of trace amounts of water in the PDMS that might have migrated to the interface. A 5CB dispersion prepared in the usual manner was divided into three parts. The first was kept in a desiccator under vacuum for 144 h. The second was left open in the air for 144 h. The third was kept in a tightly capped vial. The dielectric spectrum at 33 °C was essentially the same in the three cases, and the results are not shown.

3. Experimental Results

3.1. Pure Components. The capacitive dielectric constant, ϵ' , and the dielectric loss factor, ϵ'' , of 5CB are shown as functions of frequency, with temperature as a parameter, in panels a and b of Figure 2, respectively. The corresponding data for 8CB are shown in Figure 3a and b. The lines are drawn to guide the eye. The high-frequency ($\sim 10^7$ Hz) peak in ϵ'' and the corresponding gradual decrease in ϵ' correspond to reorientation of the molecules around the short axis of the molecule in the applied alternating electric field. ϵ'' is more sensitive to temperature than is ϵ' .

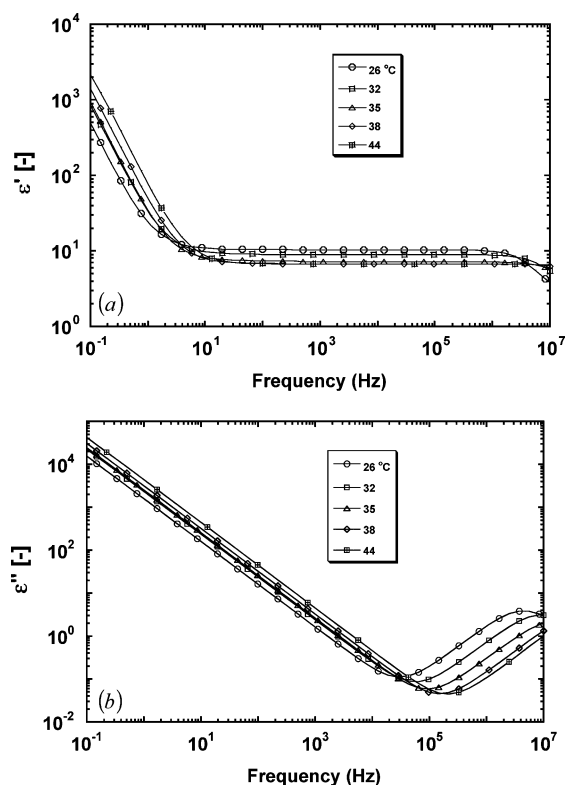


Figure 2. Frequency-dependent (a) capacitive spectrum, ϵ' , and (b) loss spectrum, ϵ'' , of 5CB at different temperatures.

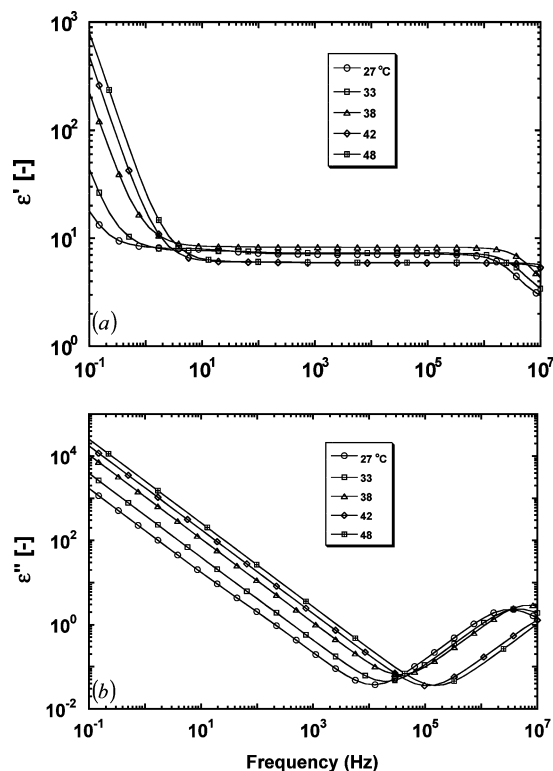


Figure 3. Frequency-dependent (a) capacitive spectrum, ϵ' , and (b) loss spectrum, ϵ'' , of 8CB at different temperatures.

The capacitive dielectric constants, ϵ' , and the dielectric loss factors, ϵ'' , of PDMS 200 saturated with 5CB at different temperatures are shown in panels a and b of Figure 4, respectively. The fluctuation in ϵ'' near 3×10^6 Hz appears to be a systematic error in this frequency range at small values ($\sim 10^{-3}$) of ϵ'' . These spectra are indistinguishable within experimental uncertainty from those of pure PDMS 200.

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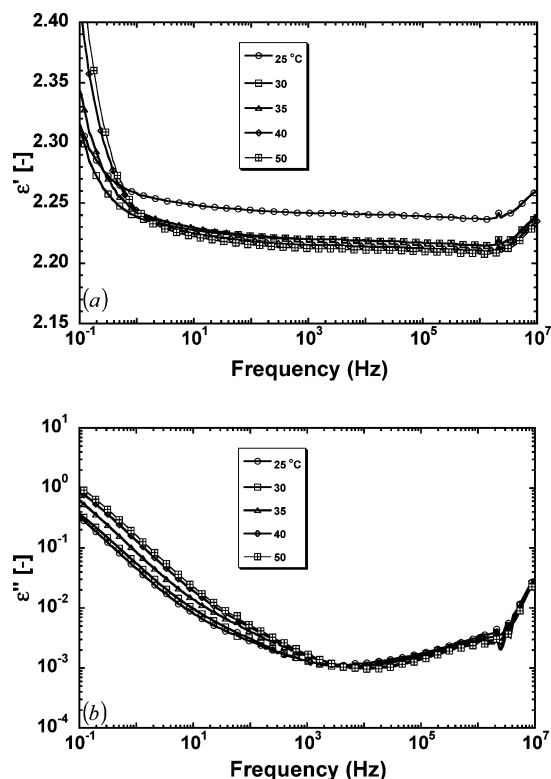


Figure 4. Frequency-dependent (a) capacitive spectrum, ϵ' , and (b) loss spectrum, ϵ'' , of PDMS 200 saturated with 5CB at different temperatures.

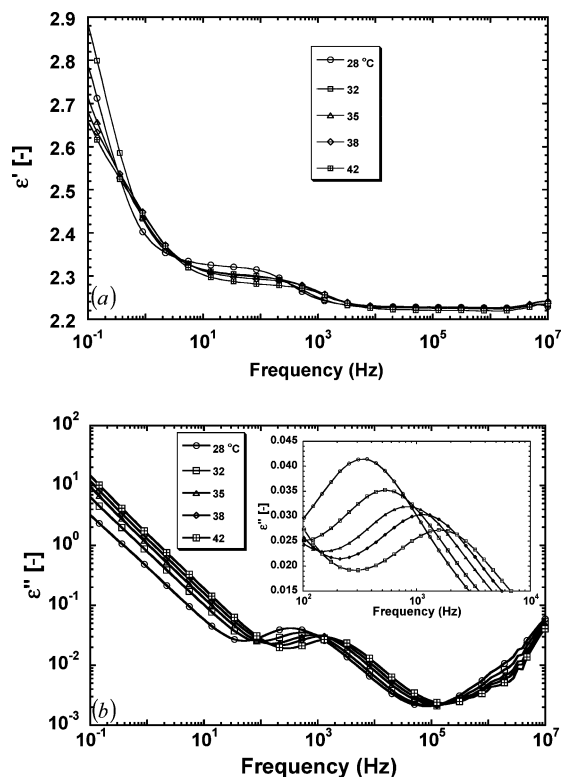


Figure 5. Frequency-dependent (a) capacitive spectrum, ϵ' , and (b) loss spectrum, ϵ'' , of a nominal 6.2% dispersion of 5CB in PDMS 200 at different temperatures.

3.2. Spectra of Dispersions. Figure 5 shows the dielectric spectrum of a dispersion containing nominal 6.2% 5CB in PDMS 200 at temperatures in both the isotropic and nematic phases. These five spectra are representative of data at more than 20

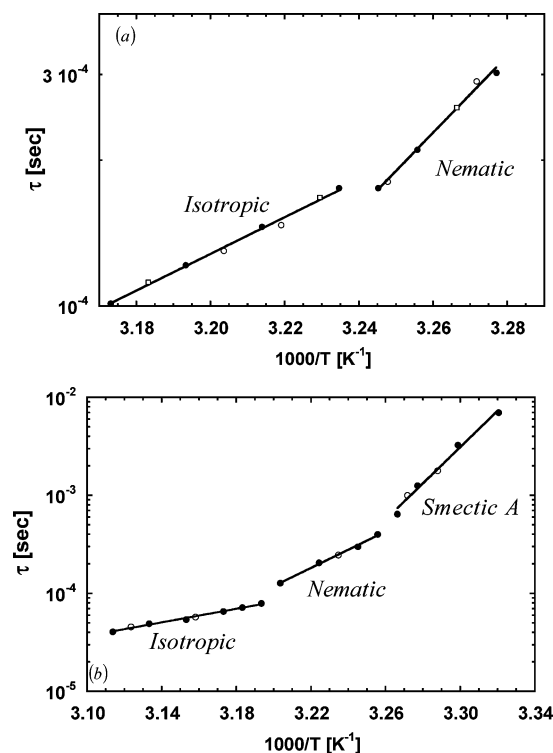


Figure 6. Characteristic relaxation times of (a) a nominal 6.2% dispersion of 5CB in PDMS 200 and (b) a nominal 5% dispersion of 8CB in PDMS 200 plotted versus reciprocal temperature. The different symbols represent different samples that were prepared and run on different days.

temperatures, all from the same sample. The positive slope in ϵ'' at high frequencies corresponds to the peak at around 10^7 Hz in the pure component that is associated with reorientation around the short axis. There is a new temperature-dependent peak in ϵ'' , as well as a corresponding shoulder in ϵ' , at around 1000 Hz; the region around the peak is shown on a larger scale in the insert. This peak decreases in magnitude and moves to higher frequencies with increasing temperature. The same behavior is observed for a dispersion containing nominal 5% 8CB in PDMS 200 in the smectic, nematic, and isotropic regimes of the dispersed phase.

The peak in the dielectric loss factor characterizes a new dynamic process that is associated with the presence of the biphenylcarbonitrile droplets in the PDMS matrix. The relaxation time, τ , is defined as $1/(2\pi f_{\max})$, where f_{\max} is the frequency in Hz at which the maximum occurs. The relaxation time is plotted versus reciprocal absolute temperature in panels a and b of Figure 6 for the 5CB and 8CB blends, respectively. The different symbols represent different samples that were prepared and run on different days. The data can be fit in each structural regime of the dispersed phase with a temperature dependence of the form $\exp(E_a/RT)$, with a substantial change in slope at the phase transitions. The values of E_a in the isotropic phase are 32 kJ/mol for the 5CB dispersion and 30 kJ/mol for the 8CB dispersion; in the nematic phase, they are 62 kJ/mol for 5CB and 77 kJ/mol for 8CB. E_a is 175 kJ/mol for the 8CB blend in the smectic phase. Hence, the relaxation process is highly dependent on the structure of the dispersed phase: smectic, nematic, or isotropic.

3.3. Effect of Matrix Viscosity. The strong sensitivity of the activation energy associated with the intermediate peak to the structure of the dispersed phase (i.e., smectic, nematic, or isotropic), particularly the extremely high activation energy in the constrained smectic state, suggests that resistance to deformation may play a role in the dielectric response, in which

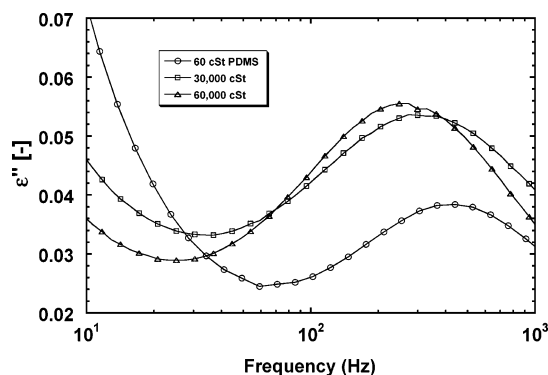


Figure 7. Frequency-dependent loss spectrum of nominal 6.2% dispersions of 5CB in three PDMSs of different viscosities at 30 °C.

case the viscosity ratio between dispersed and matrix phases would be important. High-molecular-weight PDMS has a sufficiently different density from the biphenylcarbonitriles that sedimentation is a problem, and data could be obtained only for a single temperature per run and in a limited temperature range. Loss spectra for dispersions of nominal 6.2% 5CB in the two high-viscosity PDMS matrixes at 30 °C are shown in Figure 7. The peaks in ϵ'' move to lower frequencies and larger magnitudes relative to the PDMS 200 suspension.

4. Maxwell–Wagner Polarization

The Maxwell–Wagner model of interfacial polarization for a random distribution of noninteracting isotropic homogeneous spheres with complex permittivity $\epsilon_D^* = \epsilon_D' - j\epsilon_D''$ in an isotropic matrix with complex permittivity $\epsilon_M^* = \epsilon_M' - j\epsilon_M''$ leads to an effective medium theory (EMT), or a mixing rule, for the complex permittivity $\epsilon_B^* = \epsilon_B' - j\epsilon_B''$ of the blend:

$$\epsilon_B^* = \epsilon_M^* \frac{\epsilon_D^* + 2\epsilon_M^* - \phi(\epsilon_D^* - \epsilon_M^*)}{\epsilon_D^* + 2\epsilon_M^* + 2\phi(\epsilon_D^* - \epsilon_M^*)} \quad (1)$$

The dielectric data for PDMS 200 saturated with 5CB or 8CB are used for the continuous matrix for all of the following calculations, in which case ϕ in eq 1 is the reduced concentration. The dispersed 5CB and 8CB phases are assumed to be pure, which is consistent with thermodynamic calculations for the 5CB/PDMS system.¹⁷

Figure 8 compares the experimental data for the nominal 6.2% (reduced 4.55%) 5CB dispersion at 32 °C to the EMT calculation. The EMT does show an intermediate peak in ϵ'' and an intermediate shoulder in ϵ' , but the peak location is displaced to lower frequencies than the experimental peak and the magnitude is larger. A similar result is obtained for the 8CB dispersion. The relative locations of the experimental and EMT peaks for the 5CB and 8CB blends are shown as functions of temperature in Figure 9. The difference between the EMT and experiment is well outside the range of experimental uncertainty. The closest agreement is for the smectic phase of 8CB. The data for the 5CB dispersions in high-molecular-weight PDMS at 30 °C are also shown; here, the agreement between EMT and experiment is improved relative to the more mobile suspending fluid.

The dispersion also shows a higher steady-state conductivity than would be predicted from the pure component data, possibly because of the migration of trace amounts of impurities. The EMT calculation in the region of the peak is unaffected by the value of the steady-state conductivity, which can be adjusted so that the EMT and experimental blend data agree at frequencies below 10 Hz. Similarly, the presence of adsorbed water or other

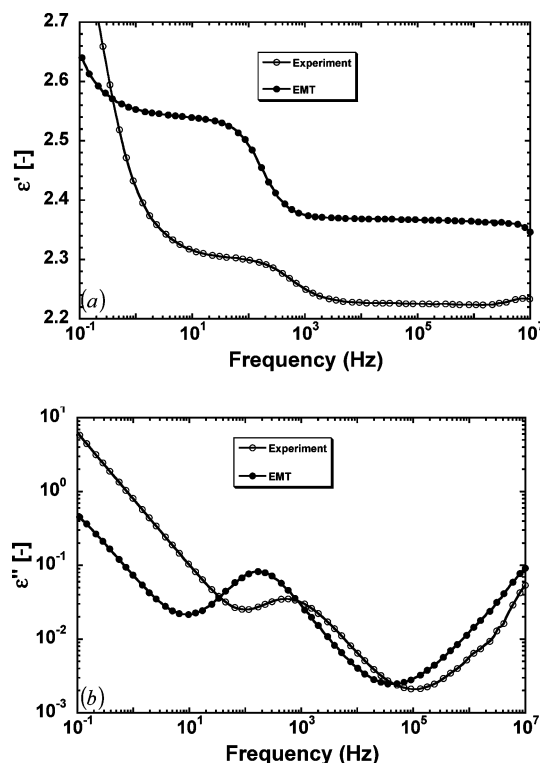


Figure 8. Comparison of effective medium theory prediction of (a) capacitive spectrum, ϵ' , and (b) loss spectrum, ϵ'' , with dielectric experiments for a nominal 6.2% dispersion of 5CB in PDMS 200 at 32 °C.

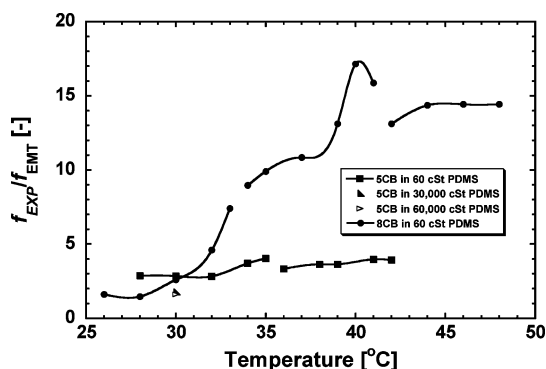


Figure 9. Location of experimental peak relative to the effective medium calculation. The lines are broken at the phase transitions of the dispersed phases.

surface effects at the droplet interface could cause tangential surface conductivity, which would increase the effective dielectric loss of the dispersed phase. Increasing the dielectric loss of the droplet phase by 30%, however, does not change the predicted EMT loss peak by any significant amount. Finally, we considered the possible existence of an outer droplet layer with dielectric properties different from the inner core, using the formalism of Jones¹⁸ for different shell thicknesses. Unacceptable values of the dielectric properties of the shell region (negative ϵ'' , for example) were always required in order to bring the EMT and experimental peaks together.

5. Interface Deformation

The strong sensitivity of the activation energy associated with the intermediate peak to the structure of the dispersed phase (i.e.,

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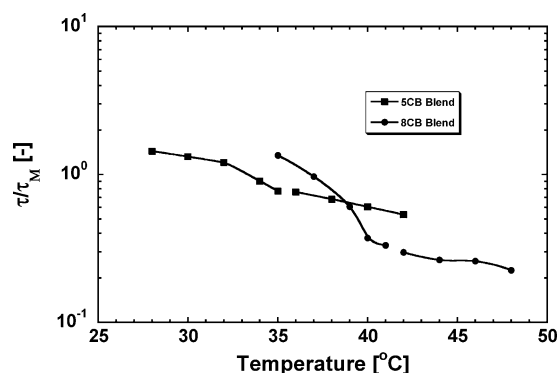


Figure 10. Ratio of experimental dielectric relaxation time to predicted mechanical relaxation time for a nominal 6.2% dispersion of 5CB in PDMS 200 (■) and a nominal 5% dispersion of 8CB in PDMS 200 (●) as functions of temperature. τ_M for smectic 8CB is not available. The lines are broken at the nematic–isotropic transitions of the dispersed phases.

smectic, nematic, or isotropic), particularly the extremely high activation energy in the constrained smectic state, and the sensitivity of the peak to the viscosity ratio suggest that droplet deformation may play a role in the dielectric response. There is a characteristic frequency regime in which a droplet interface is sensitive to an imposed mechanical deformation, with a corresponding relaxation time, τ_M , given by¹⁹

$$\tau_M = \frac{R\eta_M F\left(\frac{\eta_D}{\eta_M}\right)}{\gamma} \quad (2)$$

R is the droplet radius, η_M the viscosity of the matrix phase, η_D the viscosity of the dispersed phase, and γ the interfacial tension. $F(\eta_D/\eta_M)$ is a known function of the viscosity ratio for isotropic Newtonian fluid droplets in a Newtonian fluid matrix, and we use the Newtonian fluid relation here. The shear viscosities of the biphenylcarbonitriles and the interfacial tensions between the biphenylcarbonitriles and PDMS are reported by Rai et al.¹² The frequency range corresponding to the time scale given by eq 2 is not attainable in mechanical rheometry for the density-matched system studied here. The mechanical theory does describe the linear viscoelastic response of nematic and isotropic 8CB dispersions in a more viscous PDMS over the full frequency range, including that defined by eq 2, but it does not describe the mechanical response of dispersions of smectic 8CB droplets.¹⁶ Agreement over the full frequency range is not as good for 5CB dispersions, but the mechanical signature of droplet relaxation does occur in the frequency range defined by eq 2.

The ratios of the experimental dielectric relaxation times for the dispersions in PDMS 200 relative to the computed mechanical relaxation times are shown in Figure 10. (There are no data for the interfacial tension of the 8CB–PDMS system in the smectic regime; hence, there are no computed mechanical peaks.) The times are of comparable magnitude, indicating that the response to droplet deformation will occur in the same frequency range as the dielectric response to the applied field.

Whether or not the imposed electric field can cause a deformation of the droplet depends on the relative values of the electric pressure and the Laplace pressure, γ/R . 5CB and 8CB have permanent dipole moments,²⁰ in which case the electric pressure is of order NpE_0 , where N is the number of permanent

dipoles per unit volume, p is the dipole moment, and E_0 is the root-mean-square magnitude of the imposed field. The permanent dipole moment of 5CB is 7.1 D,²¹ which gives a ratio NpE_0R/γ of order unity. Alternatively, O’Konski and Harris’s²² formalism for the mean deformation of a nearly spherical isotropic droplet suspended in a dielectric medium in a constant field, which does not include the presence of permanent dipoles, predicts an eccentricity of 0.2% under our experimental conditions; a deformation of this magnitude could be significant. A similar deformation is obtained from the dynamic analysis of Torza et al.,²³ although the latter work predicts a dynamic shape response at twice the input frequency. None of these calculations takes the anisotropy or the entropic (Frank) elasticity of the liquid crystalline state into account.

6. Discussion

The dielectric response of the biphenylcarbonitrile dispersions in PDMS exhibits an unusual dielectric relaxation at frequencies in the range 100–1000 Hz that depends strongly on the structural state of the dispersed fluid, whether isotropic, nematic, or smectic. It is tempting to identify this relaxation with Maxwell–Wagner polarization, since an intermediate Maxwell–Wagner peak is predicted by the effective medium theory, eq 1. This simple explanation is problematic, however; the predicted Maxwell–Wagner relaxation is shifted considerably from the experimentally observed peak.

An alternative explanation is that this intermediate relaxation is associated with the restricted motion of oriented molecules at the interface. This explanation is consistent with Sinha and Aliev’s⁵ observation of a relaxation process at frequencies below 10^4 Hz in 5CB and 8CB in porous glass matrixes with pores sizes of 10 and 100 nm and Frunza and co-workers’⁶ observation of a slow relaxation in 5CB and 8CB confined to mesopores with diameters less than 2.5 nm in a molecular sieve, both of which were attributed to confined molecular motion. There are problems with this explanation as well, however. First, it is unlikely that such a relaxation would depend on the viscosity of the matrix fluid. Second, the separation between this peak and the expected Maxwell–Wagner peak is sufficiently large that one would then expect to see the latter peak as well, especially since the predicted Maxwell–Wagner peak has a magnitude that is more than twice that of the experimentally observed peak.

The most likely explanation consistent with the experimental observations is that the effective dielectric response of the dispersed phase is altered because of an interaction with the imposed field that causes a small deformation of the droplets. The observed peak is then the expected Maxwell–Wagner relaxation, but shifted because of the coupling between the dipolar motion and the interfacial mechanics. Interfacial motion would be greatly reduced in the high-viscosity suspending fluids, and droplet deformation would be expected to be least in the smectic phase and less in the nematic than in the isotropic.

7. Conclusions

The fact that the dielectric response of the 5CB and 8CB dispersions depends strongly on the structural state of the droplets and the viscosity of the suspending PDMS is suggestive of a coupling with the mechanics of the interface that affects the spectrum of the dispersed phase and shifts the Maxwell–Wagner

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peak. This result is unexpected, but it is the most consistent explanation of the observation of a single relaxation in the 100–1000 Hz range that is displaced from the expected Maxwell–Wagner relaxation. The mechanics of the interaction between an oscillating electric field and a droplet of a material that can undergo a liquid crystalline transition and contains a permanent dipole

is an unsolved problem, so our explanation must remain speculative.

Acknowledgment. This work was supported in part by the National Science Foundation under Grant No. CTS-0112358.

LA053489O