Introduction

The control of dielectric permittivity and loss of solid polymers, through an understanding of the origins of their dipole relaxation and ionic conduction processes, is essential for their use in electrical insulation, in electrical/electronic circuits, and devices operated over wide power ranges. This article discusses dielectric properties and behavior of polymers and briefly describes measurement techniques and applications.

Dielectric Properties

The dielectric properties of polymer materials are usually expressed in terms of the complex dielectric permittivity $\varepsilon(\omega)$ relative to vacuum, defined as $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, where $i = \sqrt{-1}$, $\omega = 2\pi f$, and f is the measurement frequency. The real permittivity ε' and loss factor ε'' for polymers depend on frequency due to (1) electric polarization arising from the tumbling motions of electric dipoles in the polymer chains and (2) conduction due to the translational motions of electric charges (intrinsic or extrinsic ions and electrons) (1–4). For essentially nonpolar polymers such as polyethylene, polypropylene, polystyrene, and polytetrafluoroethylene in their pure state, the absence of dipoles and ions results in (1) low values of ε' (in the range 2–3 since here $\varepsilon' \sim n^2$, where n is the optical refractive index), and (2) very small values of loss ($\varepsilon'' < 10^{-3}$) across the entire frequency range from 10^{-6} to 10^{12} Hz. These low permittivity, low loss materials are dielectric insulators and so find wide applications in electrical cables and capacitors and in electroic circuits. Polar polymers contain dipolar groups, such as

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ether, ester, halide, and amide groups, repeated regularly along the chains. Those polar polymers that are glasses (eg, poly(vinyl chloride), poly(methyl methacrylate), aliphatic and aromatic polyesters, and polycarbonates at room temperature) or are highly crystalline (eg, polyoxymethylene and polyoxyethylene at room temperature) also exhibit low values of ε' and ε'' since the dipoles and the extraneous ions present are immobilized. Polar polymers that are liquid or elastomeric (eg, polar polymers above their glass-transition temperature T_g) exhibit frequencydependent ε' values (typically in the range 3–20) together with complementary losses because above $T_{\rm g}$ the dipolar groups are mobile, allowing the dipole polarization to contribute to $\varepsilon(\omega)$. If such polymers also contain ions, as in polymer electrolytes, then ionic conduction and electrode polarization effects contribute to ε' and ε'' at low frequencies (<10⁵ Hz), leading to large values (>10²) of both ε' and ε'' . The dielectric properties of polymers, as observed in plots of ε' and ε'' against $\log f/Hz$, reflect contributions due to the reorientational motions of dipoles and the translational motions of ions and from the effects of interfacial and electrode polarizations (1-4).

When an electric field *E* is applied as a step at t = 0 to a slab of dielectric material the electric charge passing through the material has two components $q_{\rm P}(t)$ and $q_{\rm i}(t)$ due to electric polarization and ion conduction, respectively. For $q_{\rm P}(t)$ the initial response q_{∞} is rapid (<10⁻¹² s) and is due to both electronic polarization (arising from the displacement of electron charge clouds in the molecules) and atomic polarization (arising from the relative displacement of atomic positions in the molecules). There is a delayed response that takes $q_{\rm P}$ up to a steady value q_0 because the field perturbs the spatial distribution of dipole directions, giving a macroscopic dipole polarization P in line with the field. The timescale for this response is determined by the rate of the reorientational motions of the chain dipoles in the absence of the field, which will depend on the chemical structure of the polymer and its temperature. Below $T_{\rm g}$ the response time becomes very large and so there is little or no dipole polarization. The material appears to be nonpolar [except from a minor contribution to $q_{\rm P}(t)$ from small-amplitude motions of dipoles in the glassy state (see below)]. On removal of the field the process is reversed; the fast decay of $q_{\rm P}(t)$ is followed by the delayed response. The normalized rise and decay functions for dipole relaxation $\Phi(t) = [q_P(t) - q_\infty]/(q_0 - q_\infty)$ are equivalent; this is one condition for a linear dielectric material, the other being that $\varepsilon(\omega)$ is independent of the field strength. An average relaxation time $\langle \tau \rangle$ is defined as the time taken for the decay function to fall to 1/e of its original value at t = 0. For liquid water, $\langle \tau \rangle \sim 10^{-11}$ s. For polymers temperature has a large effect on the rate of molecular motions, eg, $\langle \tau \rangle$ for poly(vinyl acetate) increases from about 10^{-11} to 10^2 s as the temperature is reduced toward T_g .

In addition, ionic conduction causes a charge $q_i(t)$ to pass through the material, which rises from zero and then becomes linearly dependent on time to give a constant current $I(t) = dq_i/dt$. In contrast to $q_P(t)$, which becomes constant at long times (since the dipolar system reaches thermodynamic equilibrium in the presence of the steady field), $q_i(t)$ increases without limit in the absence of interfacial and electrode polarization effects, giving a continual dissipation of energy via the conduction process. The fact that the steady conduction current takes time to get established means that the ac real conductivity $\sigma'(\omega)$ is constant at low frequencies and becomes *f*-dependent at high frequencies. Although the nature of dipole polarization and ionic conduction are readily understood in the time domain, dielectric measurements for polymers are normally made in the frequency domain. The range $10^{-6}-10^{12}$ Hz can be covered using a combination of techniques, but the working range for most studies in the older literature was from about 1 to 10^7 Hz (1–5). Below 1 MHz the dielectric may be regarded as an electrical equivalent circuit comprising a capacitor C_p in parallel with a resistor R_p measured at a frequency $f = \omega/2\pi$ (1). Measurements made using an impedance analyzer allow the complex electrical admittance $Y(\omega)$ or its reciprocal—the impedance $Z(\omega)$ —to be determined where

$$Y(\omega) = G_{\rm P}(\omega) + i\omega C_{\rm P}(\omega) \tag{1}$$

Here $G_p(\omega) = [R_p(\omega)]^{-1}$ is the electrical conductance. The complex permittivity ε , complex conductivity $\sigma = \sigma' + i\sigma''$, and complex electrical modulus M = M' + M'' are determined from Y, using the relations

$$\varepsilon(\omega) = \frac{Y(\omega)}{i\omega C_0} = \frac{\sigma(\omega)}{i\omega \varepsilon_{\rm v}} = \frac{1}{M(\omega)}$$
(2)

Here ε_v is the permittivity of vacuum (= $8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$) and C_0 is the geometrical capacitance of the sample. The dielectric properties of polymers are variously reported in terms of $Z, Y, \varepsilon, M, \sigma$ and its reciprocal, the resistivity ρ . This is a source of confusion and makes it difficult to compare literature data for different polymer materials. The preferred representations of data when dipole polarization and ion conductivity are present will be indicated below.

At microwave frequencies $(f > 10^8 \text{ Hz})$ a polymer material is regarded as a distributed circuit having a complex propagation coefficient $\gamma = \alpha + i\beta$, where α and β are the electrical attenuation and phase factors of the material. These are measured using microwave techniques and ε' and ε'' follow as

$$\varepsilon'(\omega) = [n(\omega)]^2 \{1 - [\alpha(\omega)/\beta(\omega)]^2\}; \qquad \varepsilon''(\omega) = 2[n(\omega)]^2 \alpha(\omega)/\beta(\omega)$$
(3)

where $n(\omega) = c\beta(\omega)/\omega$ is the refractive index at ω and c is the velocity of light.

As an example of dielectric relaxation behavior, Figure 1 shows plots of ε' and ε'' against log f/Hz for glycerol, a polyhydroxyl liquid, studied over a wide temperature range. At each temperature, ε' at low frequencies is constant (at ε_0) and then falls with increasing frequency to values typical of a nonpolar material. Dispersion of ε' is accompanied by a loss peak whose frequency of maximum loss (f_{max}) determines the average relaxation time $\langle \tau \rangle = [2\pi f_{\text{max}}]^{-1}$. For glycerol $\langle \tau \rangle$ increases by 10 orders of magnitude as the temperature is reduced toward T_g . In addition, ionic conduction gives the increasing loss at low frequencies. The dielectric behavior of glycerol is representative of all amorphous polymers and glass-forming liquids that contain dipolar molecules (1–5).

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Fig. 1. Plots of (a) ε' and (b) ε'' against frequency (Hz) for glycerol at 10 K intervals from 193.15 K (+) to 333.15 K ()). Data provided by Dr G. Schaumburg, Novocontrol GmbH.

Theory

The normalized decay function $\Phi(t)$ of the dipole polarization is related to $\varepsilon(\omega)$ according to (1,5)

$$\frac{\varepsilon(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = 1 - i\omega\Im[\Phi(t)] \tag{4}$$

Where ε_0 and ε_∞ are the limiting low and high frequency real permittivities, and \Im indicates a one-sided Fourier transformation. A simple form for $\Phi(t)$ is the single exponential decay function

$$\Phi(t) = \exp(-t/\tau) \tag{5}$$

Insertion into equation 4 gives the paired relations

$$\frac{\varepsilon'(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1}{1 + \omega^2 \tau^2} \tag{6}$$

$$\frac{\varepsilon'(\omega)}{\varepsilon_0 - \varepsilon_\infty} = \frac{\omega\tau}{1 + \omega^2 \tau^2} \tag{7}$$

Here $\varepsilon_0 - \varepsilon_{\infty}$ (= $\Delta \varepsilon$, say) is the relaxation strength. Figure 2 shows plots of ε' and ε'' against log $\omega \tau$ for $\varepsilon_0 = 13$, $\varepsilon_{\infty} = 3$ for equations 6,7 [the single relaxation time (SRT) function]. $\omega_{\max} \tau = 1$ at the loss peak. Thus dielectric relaxation is characterized by $\Delta \varepsilon$ and τ for this function. The steady ionic conductivity σ_0 contributes an additional, rising loss at low frequencies given by $\varepsilon_i'' = \sigma_0/\omega\varepsilon_v$, but this process makes no contribution to $\varepsilon'(\omega)$ in this case.

In practice dielectric relaxation curves for polymers (1–5) and glass-forming liquids (eg, Fig. 1) are far broader than that for an SRT process. Numerous empirical relaxation functions have been proposed for this behavior (1,2,5). One function is the stretched exponential function of Kohlrausch, Williams, and Watts (KWW) (4–6), that is widely applied to dielectric and other relaxation data for amorphous polymers:

$$\Phi(t) = \exp[-(t/\tau)^{\beta}]$$
(8)

 $0 < \bar{\beta} \le 1$. Figure 2 includes curves for ε' and ε'' calculated using equation 4 and the KWW function for $\bar{\beta} = 0.50$. The loss curve is broad and nonsymmetrical, with a total half-width $\Delta_{1/2} \sim 2.2$ (cf 1.14 for the SRT process). The dielectric data for glycerol conform approximately to the KWW function ($\bar{\beta}$ increases from about 0.6 to 0.95 as temperature is increased). Thus dielectric relaxation in polymers and other materials is characterized by the *shapes* of the ε' and ε'' curves in addition to $\Delta\varepsilon$ and $\langle \tau \rangle$.

Molecular theories for the static permittivity ε_0 of dipolar liquids developed originally by Onsager, Kirkwood, and Fröhlich were adapted for linear bulk

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Fig. 2. Plots of ε' and ε'' against $\log_{10} \omega \tau$ for the SRT function (——) $\beta = 1.0$ and the KWW function (----) for $\bar{\beta} = 0.50$. The increasing loss ε_i'' at low frequencies (----) is due to the steady conductivity σ_0 .

polymers by Williams and co-workers (1,7) giving

$$\varepsilon_0 - \varepsilon_\infty = \frac{4\pi}{3kT} \left(\frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty} \right) \left(\frac{\varepsilon_\infty + 2}{3} \right)^2 c_r g \mu^2 \tag{9}$$

Where c_r is the concentration of the dipolar repeat units, each of dipole moment μ , and g is the Kirkwood–Fröhlich factor for orientational correlations of dipoles along and between chains.

$$g = 1 + \sum_{ij} \left\langle \cos \theta_{ij} \right\rangle \tag{10}$$

where $\langle \cos \theta_{ij} \rangle$ is the equilibrium average projection of dipole *j* on a reference dipole *i*, which can be calculated using statistical mechanics (4,5,8). Parallel or antiparallel alignment of dipoles leads to g > 1 and g < 1, respectively. The large values of ε_0 for glycerol (Fig. 1) arise since intermolecular H-bonding leads to g > 1. In liquid water, H-bonding gives $g \sim 2.5$, which raises ε_0 to ~ 80 at room temperature.

Dipole relaxation in polymers is conveniently considered in terms of the normalized dipole correlation function $\Phi_{\mu}(t)$ for the reorientational motions of dipolar groups.

$$\Phi_{\mu}(\mathbf{t}) = \frac{\langle \mu_i(0)\mu_i(\mathbf{t}) \rangle + \sum_j \langle \mu_i(0)\mu_j(\mathbf{t}) \rangle}{\langle \mu_i^2 \rangle + \sum_j \langle \mu_i(0)\mu_j(0) \rangle}$$
(11)

where $\langle \mu_i(0)\mu_i(t)\rangle$ and $\langle \mu_i(0)\mu_j(t)\rangle$ are the autocorrelation function (ACF) and cross-correlation function (CCF) for dipole motions of a reference dipole *i* and further dipoles *j* along and between chains. The ACF is readily understood. At time t = 0 the dipole *i* has a particular value $\mu_i(0)$. The normalized ACF $\langle \mu_i(0)\mu_i(t)\rangle/\langle \mu_i^2\rangle = \langle \cos \theta_{ii}(t)\rangle$ is the average projection of $\mu_i(t)$ at time *t* on $\mu_i(0)$ at t = 0. This decays to zero with time. The CCFs in equation 11 account for the dynamic cross-correlations between dipole *i* and the neighboring dipoles *j*. It is found (5) that $\Phi_{\mu}(t) \approx \Phi(t)$, the macroscopic relaxation function, and so $\varepsilon(\omega)$ can be determined using equation 4. $\Phi_{\mu}(t)$ may decay as a SRT function, a broadened function (eg, the KWW function), a weighted sum of SRT functions (known as a "distribution of relaxation processes"), or decay in several discrete stages—which leads to discrete multiple loss peaks in the *f*-domain (1,3,5). The overall loss curve gives information on the mechanism(s) of the dipole relaxation process(es) in the polymer material (1–5).

For ionic conduction the complex conductivity is given by (9,10)

$$\sigma(\omega) = \sum_{i} a_{i} \Im \langle v_{i}(0) v_{i}(t) \rangle = \omega^{2} \sum_{i} a_{i} \Im \left[\left\langle \Delta R_{i}^{2}(t) \right\rangle \right]$$
(12)

Here $a_i = [c_i q_i^2 / kT]$, c_i and q_i are, respectively, the concentration and charge of species *i* (anions and cations). $\langle v_i(0)v_i(t) \rangle$ and $\langle \Delta R_i^2(t) \rangle$ are, respectively, the velocity correlation function (VCF) and mean-squared displacement in time of species *i*. The steady current behavior at long times in the step-on experiment (see above) means that $\langle \Delta R_i^2(t) \rangle$ becomes linearly dependent on time, giving the Nernst–Einstein equation that connects the low-*f* conductivity $\sigma'(0) (=\sigma_0)$ to the diffusion coefficients D_i for the translational motions of the ions (9,10):

$$\sigma_0 = \sum_i a_i D_i \tag{13}$$

$$D_i = \frac{1}{3} \int_0^\infty \langle v_i(0) v_i(t) \rangle \mathrm{d}t \tag{14}$$

$$D_i = \frac{1}{6} \frac{\left\langle \Delta R_i^2(t) \right\rangle}{t} \tag{15}$$

Hopping motions of ions at short times are influenced by the surrounding molecules, leading to a "bounce-back mechanism" that causes $\langle \Delta R_i^2(t) \rangle$ to be lower at short times than it would be if the long time behavior was extrapolated to zero (9,10). As a result the real conductivity $\sigma'(\omega)$ for polymers and most amorphous disordered solids is a constant (σ_0) at low frequencies but obeys a power law (ω^m , $0 < m \leq 1.0$) at high frequencies (9,10).

In view of the above we note that plots of $\varepsilon''(\omega)$ against log f/Hz give information on the *reorientational motions* of chain dipoles through $\Phi_{\mu}(t)$ (eqs. 4, 6,7 and 11) while plots of $\sigma'(\omega)$ against log f/Hz give information on the *translational motions* of ions through $\langle v_i(0)v_i(t) \rangle$ and $\langle \Delta R_i^2(t) \rangle$ (eqs. 12 and 14,15).

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The other representations Z, Y, M, and ρ refer indirectly to these molecular dynamic properties (see eq. 2).

Dielectric Behavior of Polymers

Dielectric spectroscopy (DS) provides a means of studying chain dynamics of amorphous, crystalline, and liquid crystalline (LC) polymers (1,3–5,11). As one example Figure 3 shows plots of ε'' against log f/Hz for the amorphous polymer poly(vinyl acetate) at different temperatures. The α loss peak (Fig. 3a) is due to the large-scale motions of chain dipoles and moves to ultralow frequencies as T_g is approached. $\langle \tau_{\alpha}(T) \rangle$ obeys the Vogel–Fulcher–Tammann equation

$$\langle \tau_{\alpha}(T) \rangle = A \exp[B/(T - T_{\infty})]$$
(16)

where A, B, and T_{∞} are material constants. T_g is often defined operationally as the temperature at which $\langle \tau_{\alpha} \rangle = 10^2$ s. The loss curves for poly(vinyl acetate) may be fitted approximately using the KWW function ($\bar{\beta}$ increases from 0.6 to 0.8 in this T-range). Below T_g a small secondary loss process (β process) is observed (Fig. 3b) because of limited motions of chain backbones and side chains. $\langle \tau_{\beta}(T) \rangle$ obeys the Arrhenius equation with activation energy $Q_{\beta} \sim 40$ kJ·mol⁻¹. All dipolar amorphous polymers (and small-molecule glass-forming liquids) give dielectric behavior similar to poly(vinyl acetate) (1–5) [ie, they exhibit an α process (lower-f process with large $\Delta \varepsilon_{\alpha}$) and a β process (higher-f process with small $\Delta \varepsilon_{\beta}$)]. Syndiotactic poly(methyl methacrylate) is an exception, having $\Delta \varepsilon_{\beta} > \Delta \varepsilon_{\alpha}$ (1,3). Static permittivities $\varepsilon_0(T)$ have been reported for numerous amorphous polymers and (using eq. 9) have enabled $g\mu^2$ to be determined in several cases (1,5,8).

Dielectric relaxation data for individual polymers are frequently compared with complementary data obtained from NMR, dynamic mechanical, quasi-elastic light/neutron scattering, and time-resolved fluorescence depolarization experiments (12). Many studies show (1–5,12) that the β process is due to spatially limited motions of chain segments or side chains occurring in a range of local environments, leading to a dielectric relaxation strength $\Delta \varepsilon_{\beta} \propto \langle \mu^2 \rangle - \langle \mu \rangle^2$], where $\langle \mu \rangle$ is the mean dipole moment that remains after the local motions (β process) have taken place. The α -process is due to the large-scale motions (micro-Brownian motions) of chains and has a relaxation strength $\Delta \varepsilon_{\alpha} \propto \langle \mu \rangle^2$. If pressure is applied in order to reduce $\Delta \varepsilon_{\beta}$, there is a complementary increase in $\Delta \varepsilon_{\alpha}$ [as demonstrated for poly(alkyl methacrylates) (3–5)]. For polymers with rotatable side groups [eg, poly(alkyl methacrylates)] the dielectric α and β processes merge in the MHz region to form the $\alpha\beta$ process (1–5,13). For polymers without rotatable side groups, eg, poly(ethylene terephthalate), polyesters and polycarbonates, the α and β processes merge only at very high frequencies $(>10^9 \text{ Hz})$ (1-5,13). The origins of α,β and $\alpha\beta$ relaxations, their relaxation functions, and their *T*-dependencies for amorphous polymers and glass-forming liquids have received much attention (1– 5,11–13). Models for chain dynamics based on mode-coupling theories, transient energy landscapes, and local "dynamic heterogeneities", together with large-scale molecular dynamics/Monte Carlo simulations of assemblies of polymer chains, have been developed and applied to relaxation, spectroscopic, and scattering data



Fig. 3. Plots of ε'' against frequency (Hz) for poly(vinyl acetate): (a) the α -relaxation region from 293.15 K (+) to 333.15 K (Δ) in intervals of 10 K and (b) the β -relaxation region from 183 K(z) to 253 K (+) in intervals of 10 K. Data provided by Dr G. Schaumburg, Novocontrol GmbH.

(see, eg, Ref. 12). At a more practical level, DS is used to study the structure and dynamics of complex amorphous polymer systems. For example local inhomogeneity in polymer blends and random copolymers that exhibit a single T_g was revealed for blends of poly(o-chlorostyrene)/polystyrene and their random copolymers using broadband DS (see Ref. 14 and references therein). The width $\Delta_{1/2}$ of the α -peak was far broader than those for the pure homopolymers and broadened further as temperature was reduced, showing the presence of microphase separation and allowing the distribution of local concentrations to be determined (14). In certain polymers (eg, polypropylene oxide and polyisoprene) there is a small cumulative dipole moment along the chain contour and so for these materials DS can monitor the long-range motions (Rouse modes) of linear chains and multi-armed stars (11,15,16). The dependence of dielectric relaxation time $\langle \tau \rangle$ on molecular weight M is of interest; eg, for linear *cis*-polyisoprenes, $\langle \tau \rangle \sim M^2$ for $M < M_c$ and $\langle \tau \rangle \sim M^{3.7}$ for $M > M_c$, where M_c is the critical value for chain entanglements (15). The dielectric and dynamic mechanical relaxation data for the normal-mode relaxations in such polymers may be compared.

The dielectric behavior of crystalline polymers is more complex (1,2,4,17). For most materials (eg, the nylons, polyesters) motions of dipoles in the crystalline regions are totally suppressed. Polyethylene is an exception since chain rotation accompanied by translation of whole chains occurs within the lamellar crystals (17). Chain motions are possible in disordered regions on the surfaces of the lamellae (as occur in linear polyethylenes) or in the abnormal amorphous regions between the lamellar (as in the nylons). For polyethylene, which is nonpolar, motions occurring within the lamellae (α_c and γ_c processes) and the amorphous regions (β_a and γ_a processes) are activated for dielectric studies by incorporating carbonyl or C-Cl dipoles into the chains (1,3,17). Melt-crystallized polyamides (nylons) and polyesters are 100% spherulitic (by optical microscopy) but may be only \sim 50% crystalline. The motions of the amorphous phase within spherulites are severely influenced by the crystals, giving an α' process that is far broader and slower than the normal α process for the amorphous form of the polymer. Real-time dielectric studies of such polymers [eg, poly(ethylene terephthalate)] made during crystallization monitor the disappearance of the α process and the appearance of the α' process (18), thus providing a novel means of studying both the kinetics of crystallization and the dynamics of chains in the abnormal amorphous regions within spherulites.

Dielectric studies have been made for thermotropic LC polymers having mesogenic (LC-forming) dipolar groups in the side chains. These are a rare example of *dielectrically variable materials*, ie materials whose dielectric properties can be changed *in situ* using applied electric or magnetic fields. Motions of the mesogenic groups give four active dielectric relaxation modes (00, 01, 10, and 11) while motions of the chain backbone contribute to an α process (3,4,19,20). Aligned LC polymer films are made using strong ac electric fields of high and low frequencies ("two-frequency addressing principle"), yielding samples having homeotropic (H), planar (P), or intermediate (I) alignment of the LC director (*n*) with respect to the measuring field direction (the *z*-axis normal to the the plane of the film) (19,20). H samples ($n \parallel E$) and P samples ($n \perp E$) exhibit [00, 01] and [10,11] modes, respectively, and so have very different dielectric properties. The δ process (00 mode) is dominant for the H material but is absent for the P material. In general

$$\varepsilon(\omega) = (1 + 2S_{\rm d})\varepsilon_{\parallel}(\omega)/3 + 2(1 - S_{\rm d})\varepsilon_{\perp}(\omega)/3 \tag{17}$$

 $S_{\rm d}$ is the "director order parameter" and is 1, 0, -1/2 for H-unaligned and P-aligned materials, respectively. $\varepsilon_{\parallel}(\omega)$ and $\varepsilon_{\perp}(\omega)$ are the principal permittivities of the LC phase and are related to dipole moment components μ_{\parallel} and μ_{\perp} of the side groups and the local order parameter S_l of the phase. Ferroelectric polymers, made by introducing chiral polar groups as mesogenic groups in side-chain LC polymers (21), exhibit two low frequency dielectric processes, (1) the Goldstone mode and (2) the soft mode, both having large relaxation strengths. The soft mode occurs only in the chiral S^*_c phase and is suppressed by application of a biasing electric field (21).

Solid polymer electrolytes are of interest for battery applications, and are either homogeneous polymers having electrically charged chains with labile counterions or blends of neutral polymers with inorganic salts. A practical aim is to prepare stable films having dc conductivities $\sigma_0 > 10^{-5}$ S·cm⁻¹ at room temperature. Many materials have been investigated (22). In all cases σ_0 decreases by up to 8 orders of magnitude as temperature is reduced toward $T_{\rm g}$ (polymer) as a result of two effects: (1) reduced ion mobility, due to the slowing down of molecular motions, and (2) increasing ion-association, which removes ions and creates dipolar aggregates that exhibit dielectric relaxation. Plots of $\sigma'(\omega)$ against log f/Hz feature (1) a plateau over a wide intermediate f-range that provides $\sigma_0(T)$ values, (2) a decrease in σ' at low frequencies as a result of electrode polarization, and (3) a power-law increase of σ' at high frequencies (see, eg, Refs. 22 and 23) as a result of the short-time "backlash effect" mentioned above. Such data for a polymer electrolyte at different temperatures or applied pressures (23) are used to construct a master curve of log $\sigma'(\gamma \omega)/\sigma_0$ against log $\gamma \omega$, where log γ is a horizontal shift factor (9,10). Near-universal behavior for these master plots is obtained for polymer electrolytes and many other disordered amorphous materials (9,10). Models proposed to account for this behavior include those for the hopping of charge carriers over local barriers between temporary sites in the solid (9,10). In general, polymer electrolytes contain dipolar species in addition to the ions, and so give dipole relaxation processes in addition to ionic conduction. Insufficient attention has been given in the literature to the separation of dipole relaxation and conduction processes in the plots of $\sigma'(\omega)$ and $\varepsilon''(\omega)$ against log *f*/Hz for polymer electrolytes.

Real-time dielectric studies of polymerizing systems give information on the changes in molecular dynamics that occur during reaction. Condensation (step) and radical-chain (addition) reactions yielding glassy or elastomeric products, initiated thermally or photochemically, have been studied in this way (see Refs. 24–26 and references therein). Figure 4 shows 3D plots of ε' and ε'' against {log f/Hz, time/s} for the reaction of an equimolar mixture of a diepoxide DGEBA (diglycidyl ether of bisphenol A) with an alicyclic diamine at 60°C (27). ε' values (Fig. 4a) decrease from those of a liquid at t = 0 to a glass at long times. The ε'' curves (Fig. 4b) exhibit (1) losses at low frequencies/short times due to ionic conduction, that decrease rapidly as the viscosity of the reaction mixture increases, and (2) the α -relaxation process, which moves to ultralow frequencies with time as the glass is formed. These data, taken together with those for the extent of reaction with time, show that decreasing molecular mobility (as monitored by the location of the α -process) causes the reaction to become diffusion-controlled, leading to a

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Fig. 4. Plots of (a) ε' and (b) ε'' against {log₁₀ f/Hz, time/s} for an epoxide/amine thermosetting reaction at 60°C. Data provided by Dr I.K. Smith (27).

chemically unstable glass at long times. In other cases reaction is completed before diffusion-control sets in, and so a chemically stable elastomer is formed (25,26). The "floor temperature" $T_{\rm f}$, below which the product is a glass and above which the product is an elastomer, can be determined using DS for thermopolymerization reactions (25,26).

Measurement Techniques and Applications

Measurements of $\varepsilon(\omega)$ and $\sigma(\omega)$ are made using commercial frequency-reponse analyzers (10⁻⁵ - 10⁶ Hz), impedance analyzers (10² - 10⁶ Hz), time-domain

reflectometers $(10^6 - 10^9 \text{ Hz})$, and network analyzers $(10^7 - 10^{12} \text{ Hz})$ (28). At very high frequencies (GHz to THz) special quasi-optical and far-infrared spectrometers have been developed (28,29). At ultralow frequencies $(10^{-5} - 1 \text{ Hz})$ transient charge/current methods provide an alternative (and faster) method to ac methods (1,28). Thermally stimulated current methods (30) provide a very useful way of observing multiple relaxation peaks for polymers at low effective frequencies (< 10^{-2} Hz).

The control of dielectric permittivity and loss of solid polymers, through an understanding of the origins of their dipole relaxation and ionic conduction processes, is essential for their use in electrical insulation, in electrical/electronic circuits, and devices operated over wide power ranges. DS provides information on chain dynamics and charge transport in amorphous, crystalline, LC polymers, and polymer electrolytes. It is ideally suited to the study of polymers in confined environments (eg, in sol–gel–glass) and thin films [since capacitance $\propto 1/(film thickness)$]. Real-time DS can be applied inter alia to polymer systems undergoing crystallization and polymerization; the switching behavior of LC polymers and polymer-dispersed liquid crystals; phase separation in polymer mixtures/blends induced by chemical reaction or heating [that gives an additional loss process in the product due to interfacial (Maxwell–Wagner) polarization (1,25,31)].

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