Dielectric relaxation spectroscopy of polymers revealing dynamics in isotropic and anisotropic stationary systems and changes in molecular mobility in non-stationary systems*

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Some recent studies of the dielectric properties of amorphous polymers, liquid crystalline polymers and polymerizing systems are discussed briefly and the theoretical interpretations of the observed relaxation phenomena are indicated.

(Keywords: dielectric properties; amorphous polymers; liquid crystalline polymers)

INTRODUCTION

Dielectric relaxation spectroscopy (d.r.s.) has been used for many years to study the molecular dynamics of polymer chains in the amorphous, crystalline and liquid crystalline states[1–5]. In the past most studies have been made manually by point-by-point frequency measurements but, owing to the advent of modern measuring equipment and modern data acquisition methods, computer control and modern data-processing methods, the d.r.s. method may now be used as a powerful method for studying molecular dynamics that is complementary to n.m.r. relaxation, quasi-elastic light scattering (q.e.l.s.) and time-resolved fluorescence depolarization. In the present paper we indicate briefly some areas of polymer science that are currently studied using d.r.s. These include stationary systems (i.e. a material of unchanging chemical composition and physical condition) and non-stationary systems in which the chemical or physical properties are changing with time.

SCOPE OF DIELECTRICS RESEARCH WITH POLYMERS

The d.r.s. method has a remarkable frequency/time range of 10^{-6}–10^{10} Hz/10^{5}–10^{-11} s. This may be covered in bands, with measurements being made normally in the frequency domain. Modern equipment includes transient response techniques[1,6], impedance (LCR) meters (10–10^9 Hz), time domain reflectometry techniques[7,8] (10^5–10^{10} Hz), network analysers (10^7–10^{10} Hz) and microwave transmission lines and cavity resonators (10^8–10^{11} Hz)[1,3,9,10]. For polymer systems the normal working range is 10^{-2}–10^7 Hz, especially for solid polymers[1,2,9].

Table 1 indicates some of the areas which are presently studied using d.r.s. and gives selected references in which further references to work published in those areas will be found. We summarize below the observations and essential conclusions of the dielectrics studies of some of these different systems below, and indicate briefly the nature of the dielectric theory and the different models that are used to fit the data.

FLEXIBLE POLYMER CHAINS

Conventional amorphous polymers such as acrylate and methacrylate polymers and polyesters, poly(vinyl halide)s

Table 1 Dielectric relaxation spectroscopy of polymers

Category	References
Flexible polymer chains	
Solution and	
Bulk amorphous state	1–4, 11–18
Bulk crystalline state	1–4, 19–22
Rod-like polymer chains	
Solution	23–31
Lyotropic nematic (liquid crystalline) state	23–31
Liquid crystalline polymers	
Nematic and smectic chiral nematic states	5, 32–55
Ferroelectric state	56
Time dependent systems	
1. Chemical change:	
Step (condensation) polymerization systems Addition (chain) polymerization systems	57–69
2. Physical change:	
Crystallizing systems Physical ageing	70, 71

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and poly(ethylene terephthalate) all exhibit multiple dielectric relaxations. The α and $\alpha\beta$ processes are due to micro-Brownian motions of chains and the β process is due to partial reorientation of chain segment dipoles[1-4]. The $\alpha\beta$ process is formed by the coalescence of α and β processes as the temperature is raised well beyond the glass transition temperature T_g. Such behaviour is not unique to glass-forming, amorphous polymers. As Johari, Goldstein and Smyth first showed, the pattern of α, β and $\alpha\beta$ relaxations is also observed for small-molecule, glass-forming liquids (for a review of this and earlier work see Williams[72]). The shapes of the α and β processes in plots of loss factor $\varepsilon''(\omega)$ against $\log f$ (where $f=\omega/2\pi$) are essentially the same for amorphous polymers and small-molecule, glass-forming liquids[72], and the loci of the average relaxation frequencies $f_{m\alpha}$ and $f_{m\beta}$ follow Vogel–Fulcher and Arrhenius laws, respectively, in both classes of system. Therefore chain connectivity is not the origin of α, β and $\alpha\beta$ dielectric relaxations in polymers. The behaviour is rationalized in terms of partial (β process) and total relaxation of the dipole moments $\boldsymbol{\mu}_j$ of chain segments[2,3]. The dipole moment time correlation function for the polymer chain is given by[3,73]

$$C_\mu(t)=\frac{\langle\mu_i^2\rangle\lambda_{ii}(t)+\sum_j\langle\boldsymbol{\mu}_i(0)\boldsymbol{\mu}_j(0)\rangle\lambda_{ij}(t)}{\langle\mu_i^2\rangle+\sum_j\langle\boldsymbol{\mu}_i(0)\boldsymbol{\mu}_j(0)\rangle} \tag{1}$$

where the autocorrelation function $\lambda_{ii}(t)$ refers to a reference dipole i in a chain and the cross-correlation functions $\lambda_{ij}(t)$ refer to dipoles i and j along the same chain

$$\begin{aligned}\lambda_{ii}(t)&=\frac{\langle\boldsymbol{\mu}_i(0)\boldsymbol{\mu}_i(t)\rangle}{\langle\mu_i^2\rangle}\\ \lambda_{ij}(t)&=\frac{\langle\boldsymbol{\mu}_i(0)\boldsymbol{\mu}_j(t)\rangle}{\langle\boldsymbol{\mu}_i(0)\boldsymbol{\mu}_j(0)\rangle}\end{aligned} \tag{2}$$

The equilibrium terms $\langle\boldsymbol{\mu}_i(0)\boldsymbol{\mu}_j(0)\rangle$ express the angular correlations between dipoles i and j. As $|i-j|$ is increased so the strengths of these terms decrease rapidly[2]. Although the cross-correlation terms contribute to the overall dielectric relaxation behaviour of amorphous polymers and glass-forming liquids, it has been reasoned[3,74] that the functions $\lambda_{ii}(t)$ and $\lambda_{ij}(t)$ are all similar for flexible chains, so the origin of multiple (α, β and $\alpha\beta$) dielectric processes may be understood simply by considering the autocorrelation function $\lambda_{ii}(t)$ for the motion of any reference dipole i in a chain. It is shown that partial relaxation of the dipole vector in a range of local environments (β process) followed by total relaxation (α process) leads to a correlation function of the form

$$\lambda_{ii}(t)=\varphi_\alpha(t)[A_\alpha+B_\beta\varphi_\beta(t)] \tag{3}$$

where $A_\alpha+B_\beta=1$ and

$$B_\beta\varphi_\beta(t)\equiv\sum_r {}^\circ p_r q_{\beta_r}\varphi_{\beta_r}(t) \tag{4}$$

where ${}^\circ p_r$ is the probability of obtaining a temporary local environment r, $\varphi_{\beta_r}(t)$ is the relaxation function for that local environment, $q_{\beta_r}=\langle\mu_i^2\rangle-\langle\boldsymbol{\mu}_i\rangle^2$ and is that part of $\langle\mu_i^2\rangle$ that is partially relaxed in environment r, and $\langle\boldsymbol{\mu}_i\rangle$ is the mean moment residing in environment r after partial relaxation (β process) has occurred. The remaining relaxation strength is relaxed at longer times by the α process, i.e. when the local environment is relaxed, with a relaxation function $\varphi_\alpha(t)$. Such a phenomenological model rationalizes the occurrence of α, β and $\alpha\beta$ relaxations, their behaviour with respect to changes in temperature and pressure and the experimental conservation rule $\Delta\varepsilon=\Delta\varepsilon_\alpha+\Delta\varepsilon_\beta$ for the total relaxation strength. All of this is well established and has been discussed and reviewed[2-4,72-75]. Clearly, the detailed mechanisms for α and β processes have not yet been specified in equations (3) and (4). The β process will be different for alkyl acrylate and methacrylate polymers (where side-group motions partially relax $\langle\mu_i^2\rangle$) and polyesters, oxide polymers and poly(vinyl chloride) (where main-chain motions partially relax $\langle\mu_i^2\rangle$). In practice, the β process is extremely broad[1-4] which is consistent with partial relaxations occurring in a wide range of local environments, as expressed in equations (3) and (4). The α process is very similar in its shape and has the same temperature dependence for a wide range of flexible polymers, with and without side chains, and for small-molecule, glass-forming liquids. It obeys the WLF equation[1] for the average relaxation frequency variation with temperature, and the relaxation function in the time domain $\varphi_\alpha(t)$ is well fitted over much of the relaxation range by a 'stretched exponential function' (KWW function) of the form[76,77]

$$\varphi_\alpha(t)=\exp[-(t/\langle\tau\rangle)^\beta] \tag{5}$$

for $0<\beta\leqslant 1$. This function gives loss curves in the frequency domain that are broad and asymmetrical in the Davidson–Cole sense[1,76-80] in agreement with experimental data. The function fails to fit experimental data in the high frequency tail[76,77]. This is expected since the KWW function is badly behaved at short times/high frequencies. From equation (5) we see that $|\mathrm{d}\varphi_\alpha(t)/\mathrm{d}t)|\rightarrow\infty$ as $t\rightarrow 0$, whereas a well behaved relaxation function (a time correlation function) should obey time reversal symmetry[81,82] that requires $\mathrm{d}\varphi_\alpha(t)/\mathrm{d}t\rightarrow 0$ as $t\rightarrow 0$.

Since the 1970s many attempts have been made to devise models that would lead to functions of the KWW form in order to fit the α process observed in dielectric, dynamic mechanical and n.m.r. relaxations, electron spin resonance (e.s.r.), q.e.l.s. and fluorescence experiments. Several of these models have been reviewed by Williams and coworkers[1,3,72,79,80,83] and include early defect diffusion models, the Shlesinger–Montroll conditioned diffusion model, dynamic Ising models and hybrid diffusion models (Litovitz). Ngai[84-86] and coworkers take the derivative $\mathrm{d}\varphi_\alpha(t)/\mathrm{d}t$ of equation (5) to be the master equation in time for application to diverse relaxation phenomena in polymeric systems, including dielectric relaxation. Quite recently Goetze[87,88] and coworkers and Mazenko[89] and coworkers have proposed 'mode–mode' coupling models to rationalize the α-relaxation behaviour in polymers, ionic materials and glass-forming molecular liquids. These models are essentially phenomenological and attempt to formulate $\varphi_\alpha(t)$ within a formal framework in which assumptions are made regarding the truncation of a continued fraction involving $\tilde{\varphi}_\alpha(\omega)$, the Laplace transform of $\varphi_\alpha(t)$, and assumed forms for particular memory functions. As will be discussed elsewhere[90], the results of such an approach appear to depend critically on the assumptions made in relating the unknown memory function to the unknown relaxation function. Also, the precise meaning of the relaxation function $\varphi_\alpha(t)$ is unclear in terms of molecular behaviour. It should be emphasized that the molecular properties that give rise to dielectric relaxation[1,10,81,82], Kerr effect relaxation[82,91], dynamic mechanical relaxation[1], n.m.r. and e.s.r.

relaxation[22], quasi-elastic light scattering and fluorescence depolarization[22,82] are all understood and have been discussed extensively. In most cases specific time correlation functions are involved, e.g. for dielectric relaxation in amorphous polymers equation (1) shows that time correlation functions for the reorientational motions of dipole vectors are involved and that $C_\mu(t)$ is a weighted sum of autocorrelation and cross-correlation terms. As described[87–89], the mode–mode coupling theories do not include a specification of the molecular probes (dipole moment vector, polarizability tensor, bond vector, optical chromophore) that are responsible for the relaxation function considered in their formal equations and subsequently applied to data. Thus in one case[87] the relaxation functions of complex permittivity, $\varepsilon(\omega)=\varepsilon'(\omega)-\mathrm{i}\varepsilon''(\omega)$, and its reciprocal, $M=[\varepsilon(\omega)]^{-1}=M'(\omega)+\mathrm{i}M''(\omega)$, are each considered within the framework of the mode–mode coupling theory. For molecular dipole systems the relaxation function for $\varepsilon(\omega)$ is related, from linear response theory, to dipole moment time correlation functions, as we have seen, and no significance should be attached in this case to the relaxation function for electrical modulus. If, however, a system is ionic, so that dispersion/absorption of $M(\omega)$ may be the appropriate property to be discussed, then it remains to be established how $M(\omega)$ (or $\varepsilon(\omega)$) is related to the time correlation functions of the ionic motions, although some preliminary considerations have been outlined[92].

One further approach to the mechanism of the dielectric process in polymers is to consider that the relaxation function $\varphi_\alpha(t)$ obeys a memory function equation and that the memory kernel $K(t)$ takes a particular assumed form, e.g. that proposed by Douglas and Hubbard[93] (their equation (2.7b)) which reduces to the single relaxation time model, or a KWW function or Cole–Cole function, for different values of the two adjustable parameters. We shall show[90] that it is possible to derive the experimental memory function $\tilde{K}(\omega)$ in the frequency domain from dielectric data for amorphous polymers for comparison with the equation of Douglas and Hubbard.

A further topic of interest is the dielectric relaxation behaviour of flexible-chain polymers in solution or in the bulk state where the polymer chains have a cumulative dipole moment along their chain contour. Following on from the pioneering studies of Baur and Stockmayer[94], Adachi and Kotaka and coworkers[11–17] and Boese *et al.*[95], studies of single-arm and multiarm (star) polymers of polyisoprene have demonstrated convincingly that both segmental chain motions (through $\langle \boldsymbol{\mu}_i(0).\boldsymbol{\mu}_j(t)\rangle$ for all (i,j)) and end-to-end vector motions (through $\langle \mathbf{P}(0).\mathbf{P}(t)\rangle$ can be observed for bulk poly(propylene oxide)s and different polyisoprenes. The correlation function $\langle \mathbf{P}(0).\mathbf{P}(t)\rangle$ is due to fluctuations in the persistent dipole moment along the chain contour and we may write

$$\langle \mathbf{P}(0).\mathbf{P}(t)\rangle = \mu_{\mathrm{p}}^2\langle \mathbf{R}(0).\mathbf{R}(t)\rangle \qquad (6)$$

where $\boldsymbol{\mu}_{\mathrm{p}}$ is the dipole moment, per repeat unit, along the chain contour and $\mathbf{R}(t)$ is the end-to-end vector of the chain. The average correlation time for $\langle \mathbf{P}(0).\mathbf{P}(t)\rangle$ is strongly dependent on molecular weight, being proportional to M for low molecular weights and to $M^{3.7}$ for molecular weights above that for chain entanglement in the bulk polymer[11–17]. In the case of star-shaped polyisoprenes the long-range (Rouse mode) motions are observed[94,95], but the concept is extended to include the tethering of chains[95]. This modifies the τ values and their dependence on molecular weight, and experiment and theory are found to be consistent[95]. These studies, which are concerned with specially prepared and characterized polymers covering up to nine decades of frequency and measure accurately small dielectric loss factors, show the present experimental capability of modern d.r.s. and its value in giving information on both segmental and long-range motions of flexible polymer chains in solution and in the bulk amorphous state.

LIQUID CRYSTALLINE SIDE CHAIN POLYMERS

Figure 1 shows schematics of a flexible-chain backbone to which are attached mesogenic groups either longitudinally or transversely via a spacer group which is typically a $(\mathrm{CH_2})_m$ sequence with $3<m<10$. Also shown is a main-chain side-chain liquid crystalline (LC) polymer chain. Many other variations are possible (see e.g. Percec and Pugh in ref. 96) which include (i) carbon chains, phosphazene chains, siloxane chains and sulfone chains for the backbones and (ii) various mesogenic head-groups including cyanobiphenyls, aromatic esters and aromatic groups containing chiral attachments that render the LC polymer chiral nematic or chiral smectic. While liquid crystalline side chain (LCSC) polymers are interesting as hybrid materials with polymer and electroactive/magnetoactive LC properties, many studies are motivated by their promise of new organic materials for optical information storage, for optical elements such as optical waveguides and zone plates, and for non-linear optics, especially second harmonic generation. Such applications have been described in detail[96]. In all these applications it is required that the LCSC material be in the form of

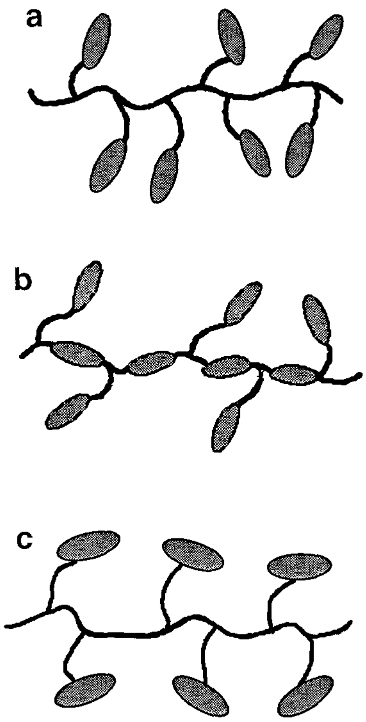


Figure 1 Schematic illustrations of different liquid crystalline polymers: (a) side chain with mesogenic group longitudinally attached; (b) main-chain side chain having mesogenic groups in both main chain and side chain; (c) side chain with mesogenic group transversely attached

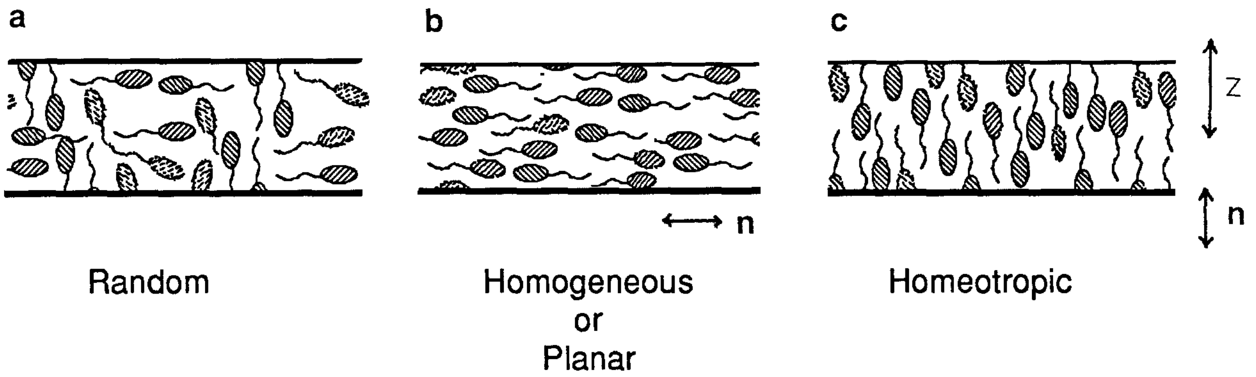


Figure 2 Schematic illustrations of (a) a random arrangement in the isotropic phase, (b) a homogeneous or planar alignment having **n** perpendicular to Z, and (c) a homeotropic alignment having **n** parallel to Z

a film 5–50 μm in thickness and aligned macroscopically in the homeotropic (H), homogeneous (H_s) or planar (P) condition. *Figure 2* indicates schematically the orientations of the mesogenic groups (heads plus tails) in these states compared with the isotropic (random) state. In the H state the average LC director **n** is perpendicular to the plane of the metal or glass electrodes, while for both H_s and P states **n** is parallel to this plane. Molecular motion in the LC state gives rise to dielectric properties that are anisotropic such that there are two principal permittivities $\varepsilon_{\parallel}(\omega)$ and $\varepsilon_{\perp}(\omega)$, where it can be shown that[39,41]

$$\begin{aligned}\varepsilon_{\parallel}(\omega)&=\varepsilon_{\infty\parallel}+\frac{G}{3kT}[A_{00}F_{00}(\omega)+A_{01}F_{01}(\omega)]\\ \varepsilon_{\perp}(\omega)&=\varepsilon_{\infty\perp}+\frac{G}{3kT}[A_{10}F_{10}(\omega)+A_{11}F_{11}(\omega)]\end{aligned}\tag{7}$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are measured parallel and perpendicular, respectively, to the macroscopic director **n**, $\varepsilon_{\infty\parallel}$ and $\varepsilon_{\infty\perp}$ are limiting high frequency permittivities ($\varepsilon_{\infty\parallel}\approx\varepsilon_{\infty\perp}$), G is a factor involving internal field terms and the A_{ij} and $F_{ij}(\omega)$ are strength factors and relaxation frequency functions, respectively. The A_{ij} are determined by the dipole moment components $\mu_{\parallel}$ and μ_t of the mesogenic group and the local order parameter S

$$\begin{aligned}A_{00}&=(1+2S)\mu_{\parallel}^2 & A_{01}&=(1-S)\mu_t^2\\ A_{10}&=(1-S)\mu_{\parallel}^2 & A_{11}&=(1+S/2)\mu_t^2\end{aligned}\tag{8}$$

The relaxation functions $F_{ij}(\omega)$ are given by the Fourier transform relation

$$F_{ij}(\omega)=1-i\omega f[F_{ij}(t)]\tag{9}$$

where the $F_{ij}(t)$ ($(i,j)=(0,1)$ combinations) are linear combinations of time correlation functions for the angular motions of $\mu_{\parallel}$ and μ_t in the local LC potential. Such motions have been described pictorially by several authors[51]

$$\begin{aligned}F_{00}(t)&=\Phi_{00}^1(t)\\ F_{01}(t)&=\Phi_{01}^1(t)+\Phi_{0-1}^1(t)\\ F_{10}(t)&=\Phi_{-10}^1(t)+\Phi_{10}^1(t)\\ F_{11}(t)&=\Phi_{-1-1}^1(t)+\Phi_{-11}^1(t)+\Phi_{1-1}(t)+\Phi_{11}^1(t)\end{aligned}\tag{10}$$

where

$$\Phi_{ij}^1(t)=\langle D_{ij}^{1}{}^*(\Omega_0)D_{ij}^1(\Omega)\rangle\tag{11}$$

and D indicates a Wigner rotation matrix element. The Ω_0 and Ω are initial and later (at time t) orientations of the moving group. The form of $\Phi_{ij}(t)$ has been specified[41] for all (i,j) and was further described subsequently[51,53]. The principal (or δ) process observed in most dielectric experiments with LCSC polymers[32–55] corresponds to the function

$$\Phi_{00}(t)=\langle\cos\beta(0)\cos\beta(t)\rangle\tag{12}$$

where β is the angle between $\mu_{\parallel}$ and **n**. Thus dielectric studies of LCSC polymers give information on four relaxation modes for the anisotropic motions of the mesogenic head-groups in the LC potential. Since materials need to be aligned by surface forces or by strongly directing electric (E) or magnetic (B) fields, it is of interest to see how the measured permittivity varies with the extent of macroscopic alignment, as expressed by the macroscopic director order parameter S_d, where[39]

$$S_d=\langle 3\cos^2\theta_{nZ}-1\rangle/2\tag{13}$$

and θ_{nZ} is the angle between a local director **n** and the laboratory Z direction (see *Figure 2*). S_d takes on the values 1 and -0.5 for $\theta_{nZ}=0$ (H alignment) and $\theta_{nZ}=\pi/2$ (P or H_s alignment), respectively.

For intermediate alignment the measured complex permittivity $\varepsilon(\omega)$ is given approximately by the weighted sum of the principal permittivities such that[39]

$$\varepsilon(\omega)=(1+2S_d)\varepsilon_{\parallel}(\omega)/3+2(1-S_d)\varepsilon_{\perp}(\omega)/3\tag{14}$$

Figure 3 shows how the real and imaginary parts of $\varepsilon_{\parallel}(\omega)$

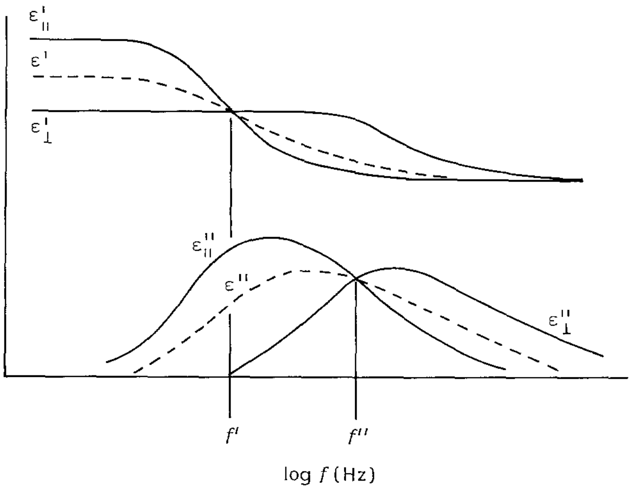


Figure 3 Plots of the real and imaginary parts of $\varepsilon_{\parallel}$, ε and $\varepsilon_{\perp}$ against $\log f$ for a dielectrically positive LC material showing the isosbestic frequencies f' and f''

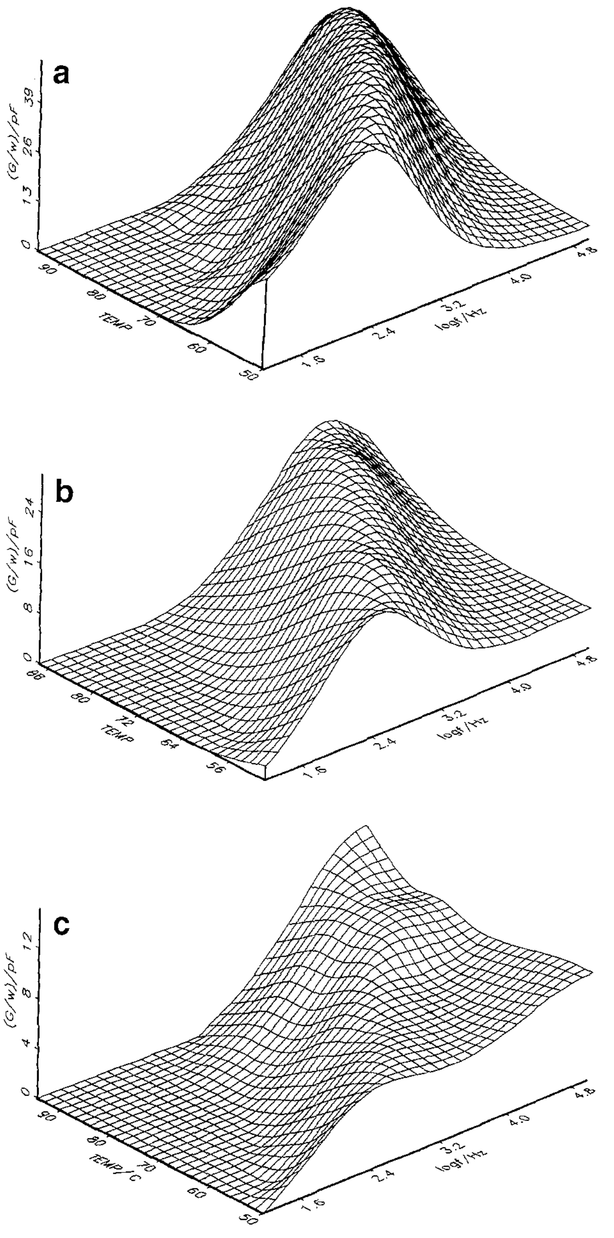
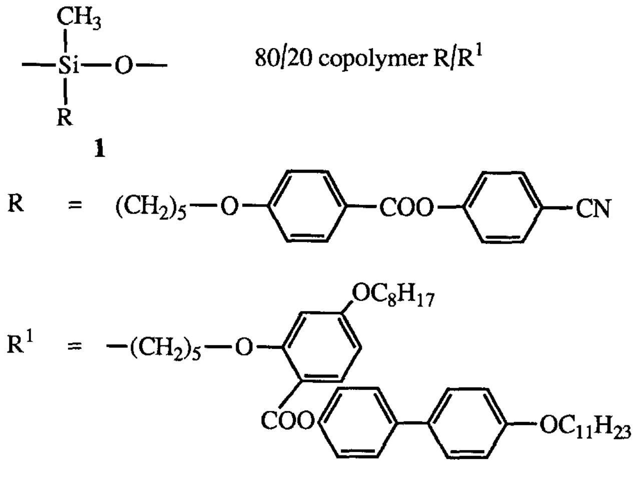


Figure 4 Dielectric loss behaviour of siloxane copolymer **1** as a function of frequency and temperature. Here $(G/\omega)=\varepsilon''C_o$, where C_o is the interelectrode geometric capacitance of the sample. Plots (a) to (c) correspond to H-aligned, unaligned and P-aligned conditions of the same sample, respectively

and $\varepsilon_\perp(\omega)$ vary with $\log\omega$ for a dielectrically positive material[48]. Also shown in the figure are the curves for $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for a sample of intermediate alignment. All $\varepsilon'(\omega)$ curves pass through f', which is the 'crossover frequency', and all $\varepsilon''(\omega)$ curves pass through f''. This follows from equation (14), i.e. when $\varepsilon'_\parallel(\omega)=\varepsilon'_\perp(\omega)$, $\varepsilon'(\omega)$ is independent of S_d. This occurs at f'. Similarly, when $\varepsilon''_\parallel(\omega)=\varepsilon''_\perp(\omega)$, $\varepsilon''_\perp(\omega)$ is independent of S_d. This occurs at f''. These crossover frequencies are also called 'isobestic points' by analogy with the ultra-violet/visible spectra of organic dyes.

It follows[48] that if a strongly directing a.c. electric field of frequency f is applied, then for $f<f'$, $\Delta\varepsilon'>0$ and H alignment is favoured, while for $f>f'$, $\Delta\varepsilon'<0$ and P alignment is favoured. Using this 'two frequency addressing principle', H-aligned, P-aligned and intermediately aligned samples may be prepared either by cooling from the melt with the appropriate field of chosen frequency applied or in the LC state with the chosen field applied, as we have described[35,38,39,48]. Note that f' and f'' are not simply related. The curves shown in *Figure 3* move to the right when the sample temperature is increased, leading to a marked increase in f' and f'' for LCSC polymers[48]. The kinetics of electric field induced alignment is affected by surface forces and is, in principle, determined by $\Delta\varepsilon(\omega)$, bulk viscosities and elastic constants, as we have described[42,48]. We have carried out studies of the alignment of a chiral nematic LCSC polymer[42,55], and have fitted the data using the theory of Esnault *et al.*[97]. A significant finding is that the alignment reaches a plateau whose level is determined by the strength of the applied field, a result similar to that observed in magnetic field induced alignment of main-chain LC polymers[98].

As one example, *Figure 4* shows the loss data[99] for a siloxane copolymer **1** in the H-aligned, P-aligned and nominally unaligned states at 70°C. The prominent loss peak in the H-aligned sample is the δ process (00 mode), as described in the earlier works of Araki and Attard[100] and by Williams and coworkers[32–55]. On forming the P-aligned sample the δ process is effectively removed, leaving a small loss curve rising to higher frequencies.



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The apparent activation energy for the δ process is extremely large[98] ($Q\approx180\,\mathrm{kJ\,mol^{-1}}$), which emphasizes the cooperative nature of the process and that it is coupled to the chain backbone motions. It was shown from combined mechanical and dielectric measurements[50] that on heating an LCSC polymer from below T_g into the T_g range the chain backbone motions occur prior to mesogenic group motions as the sample is heated. In addition, memory effects have been observed[101] and have been modelled[102], demonstrating that aligned samples form on cooling from the melt in the presence of a directing electric field by a process of 'template-induced crystallization' on preformed, prealigned LC nuclei. Such studies demonstrate, *inter alia*, the following.

1. LCSC polymers may be aligned to different states in a controlled and reproducible manner in directing electric fields[32–35,98,100–102].
2. Alignment changes may be monitored using broad band dielectric relaxation spectroscopy and continuum theory may be applied[42,55].
3. The anisotropic motions of dipolar mesogenic groups may be studied by d.r.s.[32–41,98,100–103]. Also, the molecular theory of dielectric relaxation[41,53,103] which

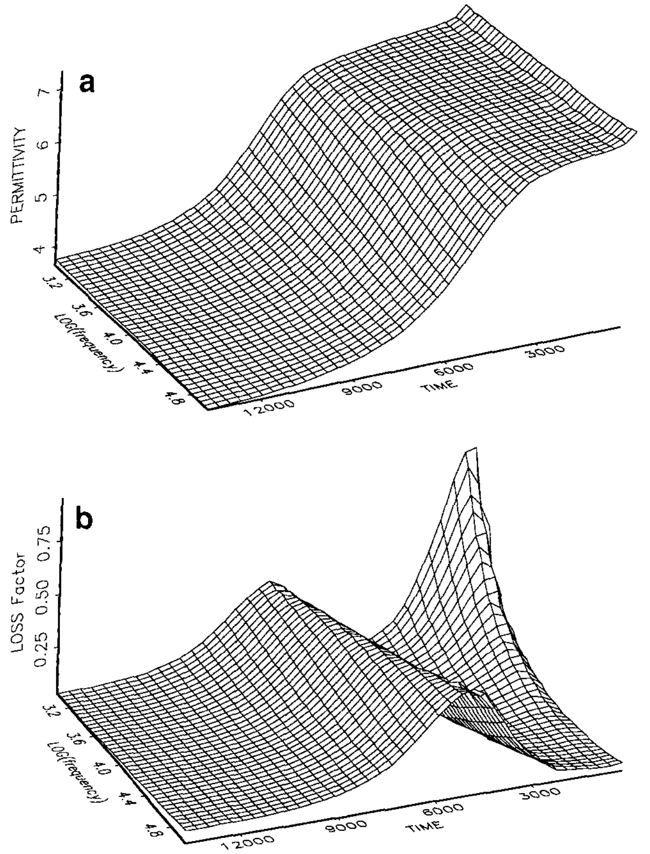

Figure 5 (a) Permittivity ε' and (b) loss factor ε'' as functions of frequency and reaction time (in seconds) during the reaction of a 2:1 (mol/mol) mixture of a diepoxide and an alicyclic diamine at 40°C

we have described, showing that four active relaxation modes will be involved, may be applied to the data, allowing determination of the dipole moment ratio $\mu_{\parallel}/\mu_t$, the local order parameter S and the relaxation functions $\Phi_{ij}(t)\,((i,j)=(0,1)$ combinations).

Such studies, which have direct relevance to the optical and electro-optical properties of LCSC polymers, represent an extension of the dielectric studies of isotropic polymers, which form the bulk of the dielectrics literature, to anisotropic polymer systems.

TIME DEPENDENT SYSTEMS

Dielectric relaxation spectroscopy has been used for many years to monitor the course of thermosetting polymer systems[57,58], and has been of increasing interest recently largely through the series of papers by Mangion and Johari[59–66]. In addition, Pethrick and co-workers[67,68] have shown how dipole relaxations and space charge relaxations evolve during the course of thermosetting reactions, and Maistros *et al.*[69] have also observed similar phenomena. As a liquid mixture polymerizes the material transforms slowly into the glassy state, leading to a drop (a dispersion) in $\varepsilon'(\omega)$ and a corresponding peak in $\varepsilon''(\omega)$ as the reaction proceeds. As one example of the dielectric cure-monitoring experiment, *Figure 5* shows the permittivity data $\varepsilon'(\omega,t,T_R)$ and loss data $\varepsilon''(\omega,t,T_R)$ for a diepoxide/diamine mixture (2:1 mol/mol) at a reaction temperature of 40°C which we obtained recently[104]. At such reaction times (t) and low frequencies ($f=\omega/2\pi$) a conductivity-related loss process is seen, and at higher frequencies for all reaction times a well defined relaxation process that is due to the micro-Brownian motions of molecular chain segments is observed which moves to lower frequencies as the reaction time t increases. Such measurements show how the rate of chain motions (dynamic T_g process) decreases as t increases. Clearly the rate of chemical reaction will be affected by these motions, but the connection is not immediately apparent, as we shall describe below.

Analysis of data such as those in *Figure 5* gives the following information: (i) the variation in $\langle\tau\rangle=(1/2\pi f_m)$ with reaction time t (here $\langle\tau\rangle$ is an average correlation (relaxation) time and f_m is the frequency of the maximum loss factor obtained by extracting plots of ε'' *versus* $\log f$ at fixed t from the data of *Figure 5*); and (ii) the changes in extent of motion associated with the dielectric α process (there is also partial relaxation associated with a high frequency (β) process at frequencies higher than the range 10–10^5 Hz) as the reaction proceeds.

However, such data relate only to the changes in molecular dynamics of chains as the reaction mixture becomes more viscous, and eventually a glass. Users of dielectric cure monitoring wish to draw firm conclusions regarding the cure directly from the $\varepsilon(\omega,t,T_R)$ data, but the connection between the chemical process in the diffusion-controlled regime that leads to vitrification and the molecular dynamics in that regime can only be obtained by direct comparison of both sets of data (chemical kinetics, $\varepsilon(\omega,t,T_R)$ data) obtained experimentally for a given system at different reaction temperatures. We have recently completed such studies[104], and they indicate that diffusion control sets in around the reaction time at which the dielectric loss peak is observed for a measuring frequency of 1 Hz, and vitrification is effectively achieved around the reaction time at which the loss peak is observed for a measuring frequency of 10^{-5} Hz (as determined by linear extrapolation of the high frequency dielectric data). Precise definitions of the phrases 'onset of diffusion control' and 'vitrification is effectively achieved' have been made[104]. It is evident from these and related studies of thermosetting systems that d.r.s. provides an important means for studying changes in molecular dynamics as the reaction proceeds to give vitrification of a specimen, and that this is an entirely practical method of monitoring such reactions given the availability of modern dielectrics instrumentation. In addition to its use for thermosetting reactions, d.r.s. may also be applied to vinyl polymerizations initiated by thermal or photochemical means. Some results have been reported[105–108] for the bulk polymerization of butyl acrylate, where changes in $\varepsilon(\omega,t,T_R)$ with reaction time t were monitored at microwave frequencies using time domain reflectometry. It is anticipated that d.r.s. will be applied to acrylate and dimethacrylate polymerizations where a liquid monomer is transformed to a bulk glass. The kinetic processes in the vitrification region are entirely different from those for thermosetting polymers and qualitative differences between the real-time dielectric properties of these two classes of bulk polymerization are anticipated. We have recently obtained such evidence for a dimethacrylate polymerization initiated photochemically[109].

Other time dependent phenomena that can be studied using d.r.s. include the crystallization of polymers, phase separation in polymer blends and alignment phenomena in liquid crystals and liquid crystalline polymers. Some preliminary studies of the time dependent dielectric properties of poly(ethylene terephthalate) as it is crystallized from the amorphous state just above the T_g were reported many years ago by Tidy and Williams (see ref. 70, Figure 3), giving useful information on the distinction between the motions of chains in the normal amorphous state and those in the abnormal amorphous state within the polymer spherulites. We have described above the use of d.r.s. for the study of the time dependent alignment behaviour of LC polymers, but in this case the dielectric properties are normally measured for a 'stationary sample' in the absence of a directing electric field. The dynamics of phase separation in polymer blends and mixtures may be studied using d.r.s., but we are unaware of such studies. Indeed, such studies would provide useful information on the changes in phase composition with time as the separation proceeds.

CONCLUSIONS

It should be apparent from the above account that d.r.s. has provided valuable information on the molecular dynamics of polymer chains in amorphous, crystalline and liquid crystalline materials. An area of considerable promise, made practical owing to modern instrumentation, is that involving time dependent ('non-stationary') polymer systems, exemplified by polymerizing systems, crystallizing systems and, for the future, phase-separating blends.

For future researches using d.r.s. several new subjects should be investigated, including the following.

1. The development of routine broad band, high frequency techniques for the range 10^6–10^{10} Hz, which would extend the d.r.s. method very considerably, especially for time dependent phenomena. Such facilities are in routine operation in the laboratory of F. Kremer at the Max Planck Institüt für Polymerforschung at Mainz, but are not generally available.
2. The development of non-linear dielectric spectroscopy for the range 10^{-2}–10^7 Hz, which would enable higher-order moments of the time dependent orientational distribution function for molecular reorientations to be determined for amorphous, crystalline and LC polymers. The technique has been developed by Furukawa[110] and shows considerable promise.
3. The study of hybrid liquid crystal/polymer films known as 'polymer-dispersed liquid crystals' (PDLC), in which the electro-optical switching, and hence the optical properties, is determined by the dielectric properties.
4. The development of theoretical molecular models for linear and non-linear dielectric relaxation in ferroelectric LC polymers, for non-stationary polymer systems, multiphase systems (e.g. PDLC materials) and for non-linear dielectric relaxation in amorphous, crystalline and LC polymers.

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