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Chain Dynamics in Solid Polymers and Polymerizing Systems as Revealed by Broadband Dielectric Spectroscopy

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Summary: Broadband Dielectric Spectroscopy (BDS) provides a direct, powerful means of studying the chain dynamics of solid polymers. The present work discusses experimental data, phenomenological theories, molecular theories and recent molecular dynamics simulations of the relaxation functions and average relaxation times for the multiple dielectric relaxations observed for amorphous polymers. Examples of current applications of BDS are given, including studies of the dynamics of ultra-thin polymer films and real-time studies of (i) the crystallization behaviour of bulk polymers and (ii) thermo-polymerizing systems.

Keywords: amorphous polymers; chain dynamics; crystallization; dielectric relaxation; molecular dynamics; polymerization; thermosetting reactions; thin films

Introduction

Numerous techniques have been employed to study chain dynamics in solid polymers, including broadband dielectric spectroscopy (BDS),[1–4] dynamic mechanical relaxation (which includes dynamic mechanical thermal analysis, DMTA),[5] multi-nuclear NMR relaxation,[6] quasi-elastic dynamic light scattering (QELS),[7] quasi-elastic neutron scattering (QENS),[8] transient fluorescence depolarization (TFD)[9] and several optical relaxation techniques (see Ch.3 in ref.3). Such studies reveal multiple dielectric relaxation processes α_N, α, β, γ.... in decreasing order of temperature at a set frequency, which are characterized as a function of temperature and, increasingly in recent years, applied pressure.[3]

Data for average relaxation times $\langle\tau\rangle$ and time-dependent relaxation functions $\Phi(t)$ for each process are usually fitted using empirical equations. While this phenomenological approach is valuable in describing and quantifying the relaxation behaviour of amorphous, crystalline and liquid crystalline polymer systems, molecular theories of relaxation are required in order to connect the macroscopic observables (complex dielectric permittivity, dynamic moduli/compliances, scattering functions ....) to the molecular dynamics of the polymer chains.

Each of the above techniques involves its own, particular molecular probe of the dynamics of a polymer system. For dielectric relaxation the connections between complex permittivity $\varepsilon(\omega)$, complex conductivity $(\sigma(\omega) = i\omega\varepsilon(\omega)\varepsilon_v)$, where $\omega = 2\pi f/Hz$, and molecular behaviour are provided by Kubo-linear response theory. It is found that $\varepsilon(\omega)$ and $\sigma(\omega)$ are given by Fourier transforms of molecular time-correlation functions (TCFs) for the (i) reorientational motions of chain dipoles[10] and (ii) the translational motions of the ionic species.[11] Related studies using NMR.[6] QELS,[7] QENS[8] and TFD[9] yield information on the reorientational motions of specific chemical groups. Although DMTA is a leading technique for testing the practical applications of polymer materials, molecular interpretations of

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mechanical relaxation and creep behaviour remain elusive since in the theory, direct links between an applied macroscopic stress/strain (bulk/shear, moduli/compliances) and the *molecular response* of the polymer chains for bulk materials remain to be established.

While BDS is one of the older techniques used to study the dynamics of polymer systems, it has undergone a renaissance during the past 20 years[2–4] for several reasons: (i) It has an exceptionally wide frequency range, 10^{-6} to 10^{10} Hz, which is readily covered using modern, commercially-available equipment: (ii) Multi-frequency measurements may be achieved across the normal working range for polymers, 10^{-1} to 10^{7} Hz, within minutes, allowing systems undergoing *physical changes*, e.g. isothermal crystallization, volume and enthalpy relaxation, physical ageing, and *chemical changes* (e.g. thermo-polymerization and photo-polymerization) to be studied in real-time: (iii) Since the measured dielectric property (complex capacitance) increases with decreasing film-thickness, BDS is ideally suited for the study of thin and ultra-thin polymer films, and offers a distinct advantage over NMR and scattering techniques in those cases: (iv) Phenomenological and molecular theories underpinning dipole relaxation and ion-conduction in polymer systems are well-developed and are less complicated and sophisticated than those for multi-nuclear NMR relaxation, QELS, QENS and TFD. Taken together with its remarkable frequency coverage, BDS offers a directly-applicable and understandable means of studying molecular and ionic dynamics in polymer systems: (v) Large-scale computer simulations of dielectric relaxation functions for dipolar and ionically-conducting polymer systems have advanced considerably in recent years enabling close comparisons between experimental data and theory to be made.

In the present paper we describe how modern BDS studies yield vital information on the chain dynamics in both stationary and time-dependent polymer systems. Initially we consider elements of the basic theory of dielectric relaxation, then focus on the behaviour of amorphous polymers, their multiple relaxations, phenomenological descriptions of relaxation functions $\Phi(t)$ and relaxation times $\langle\tau(T,P,V)\rangle$ and a molecular theory of dielectric relaxation. We then consider physical models and recent molecular dynamics simulations of dielectric relaxation in amorphous polymers. This is followed by selected applications of BDS to study chain dynamics in thin polymer films and changes in dynamics (as revealed by real-time studies) during polymer-crystallization and thermosetting polymer reactions. BDS studies of global chain motions in amorphous polymers, ionic conduction in polymers, crystalline and liquid-crystalline polymers have large, important literatures[1–4] but will not be considered here in order to limit the length of the paper.

Broadband Dielectric Spectroscopy

The frequency-dependent complex dielectric permittivity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ is related to the macroscopic dielectric relaxation function $\Phi(t)$ as follows[1–4]

$$\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_o-\varepsilon_\infty} = R(i\omega) = \Im\left[-\frac{d\Phi(t)}{dt}\right] = 1 - i\omega\Im[\Phi(t)] \tag{1}$$

where $\Im$ indicates a one-sided Fourier transform and ε_0 and ε_∞ are limiting low and high frequency permittivities respectively. For a model system having a single relaxation time (SRT) process $\Phi(t) = \exp(-t/\tau)$, where τ is the relaxation time, we obtain the SRT equations

$$\varepsilon' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+\omega^2\tau^2}; \quad \varepsilon'' = \Delta\varepsilon\frac{\omega\tau}{1+\omega^2\tau^2} \tag{2a,b}$$

$\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ is the relaxation strength. Figure 1 shows the plots of $\varepsilon', \varepsilon''$ vs. $\log\omega\tau$ for chosen values of ε_0 and ε_∞; the loss-peak occurs at $\omega\tau = 1$.

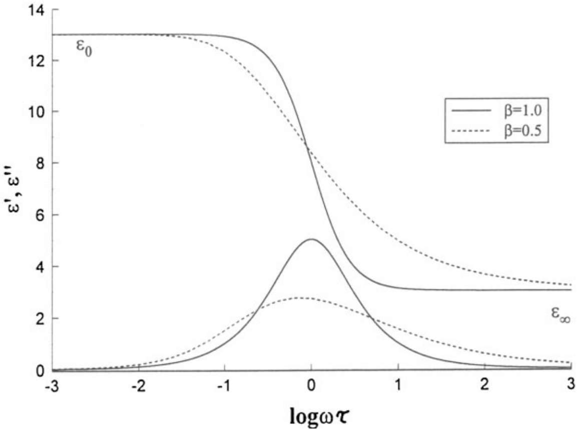

Figure 1.

Plots of ε' and loss ε''- vs. log$\omega\tau$ for a single relaxation time function (continuous lines) and a KWW stretched-exponential function with $\beta = 0.5$ (dotted lines).

If a material also has a low frequency (dc) conductivity σ_0 there is an additional loss at low frequencies $\varepsilon''_{ion} = \sigma/\omega\varepsilon_v$ where ε_v is the permittivity of free-space. However, for real polymer systems the behaviour is more complicated.[1–4] The ε' and ε''curves for dipole relaxation are far broader than that for a SRT process and for ac conduction the ω^{-1} relation is usually replaced by a power law, ω^{-m}, m < 1, together with $\varepsilon'(\omega)$ increasing with decreasing frequency, also as a power law.

Thus dielectric relaxation studies of a polymer at a fixed temperature and applied pressure give four items of information:

(i) *Relaxation strength* $\Delta\varepsilon$ which, for dipolar systems, is related to the mean squared dipole moment $\langle \mu^2 \rangle$ of chain units and their concentration.
(ii) *Average relaxation time* $\langle \tau(T, P, V) \rangle$, which is related to the dynamics of chain dipoles and depends on sample temperature (T), pressure (P) and volume (V).
(iii) *Relaxation function* $\Phi(t)$ obtained, by Fourier inversion of Eq. 1, from the line-shape of plots of ε'' vs. log ω.
(iv) *Conduction behaviour* where $\sigma'(\omega) = \sigma_0$ at intermediate to low frequencies and follows a power law at high frequencies.[3,4,11]

Amorphous Polymers

General Features

By far the largest area of activity in BDS studies of polymers concerns the behaviour of amorphous materials. These exhibit distinct, multiple relaxation regions (α, β, $\alpha\beta$) associated with segmental motions of chains.[1–4,12] Certain polymers, e.g. polypropylene glycols and polyisoprenes, have a cumulative dipole moment along the chain contour which gives rise to the (global) α_N process whose relaxation time depends strongly upon molecular weight.[3,4,13–16] This behaviour will not be discussed further here but detailed accounts are given in the texts of Kremer and Schonhals,[3] Riande and Diaz Calleja[4] and by Adachi.[16] The α and $\alpha\beta$ processes arise from large-scale reorientational motions of chain dipoles (dynamic glass-transition process) while the β-process is due to limited motions of main-chains and/or side-chain dipoles.[1–4] For example, BDS studies in 1966[17] of polyethyl methacrylate (PEMA) as a function of (ω,T,P) showed that the α and β processes coalesced to form the $\alpha\beta$-process as temperature was raised above T_g. This phenomenon was observed subsequently for other methacrylate polymers and is a general occurrence for polymers containing rotatable dipolar side groups.[1–4,18] Johari and Goldstein in 1970 conducted studies in low molar mass (LMM) glass-forming liquids and found[19,20] that analogous dielectric α and β processes were observed, which demonstrated the ubiquity of such processes in organic glass-forming systems. For polymers having no rotatable dipolar side-groups, e.g. polyethylene terephthalate (PET) and aromatic polycarbonates, although α and β processes tend to merge with increasing temperature, coalescence is not fully attained.[1–4]

Phenomenological and Molecular Aspects of α, β and $\alpha\beta$ Processes

For amorphous polymers such as the aliphatic polyesters, polyacrylates, polyalkyl methacrylates, polypropylene oxides, polycarbonates, amorphous polyethylene terephthalate and polyvinyl halides, the dielectric α-process arises from the large-scale, cooperative motions of chain dipoles[1–4] and is strongly associated with the glass-transition behaviour observed in the usual (long-time) thermodynamic measurements. In addition, a broad, secondary dielectric β-process, due to limited motions of main-chain and side-chain dipoles, is observed both below and above T_g.[1–4,17] The large literature for the dielectric properties of such polymers is given in the texts by McCrum, Read and Williams,[1] Kremer and Schonhals[3] and Riande and Diaz-Calleja.[4] Most papers reporting multiple dielectric relaxations in these polymers fit data for each process using semi-empirical equations for the relaxation functions and relaxation times.

Relaxation Functions

The dielectric α-relaxation observed for amorphous polymers in the f-domain is broad and asymmetric to high frequencies and may be represented by "stretched-exponential functions", notably the Kohlrausch-Williams-Watts, KWW, function[21–23]

$$\Phi(t) = \exp -(t/\tau)^{\overline{\beta}} : \quad \overline{\beta} \leq 1. \tag{3}$$

and its Fourier transform, $\tilde{\Phi}(\omega)$ (for use in Eq. 1). Eq. 3 was first used in 1854 by Rudolf Kohlrausch[21] for charge-relaxation in the Leiden Jar, in 1863 by his son F. Kohlrausch for mechanical relaxation in galvanometer threads[22] then in 1970 by Williams and Watts[23] for the dielectric α-process in amorphous polymers. A history of this stretched-exponential function, and its applications, has been given recently by Cardona, Chamberlain and Marx.[24]

Williams and Watts[23] performed the transform in Eq. 1 for $\overline{\beta} = 0.5$ and derived the general transform for $0 < \overline{\beta} \leq 1$ in a subsequent paper with Dev and North[25] in which they gave plots of R' and R'' vs. $\log\omega\tau$ for a range of $\overline{\beta}$-values. Tables of these functions were given by Koizumi and Kita[26] using their method.[25] Figure 1 shows plots of $\varepsilon', \varepsilon''$ vs. $\log\omega\tau$ for $\overline{\beta} = 0.5$. The loss curve is broad and asymmetrical, as is observed for the α-process in amorphous polymers.[1–4]

The KWW function has found wide applications for relaxation and scattering processes in polymers and for time-dependent and history-dependent thermodynamic processes in the glass-transition region (the paper by Williams and Watts[23] has over 2000 citations at this time). Numerous examples of these applications are found in the five *International Discussion Meetings on Relaxations in Complex Systems* organised by Ngai and coworkers, published in *J. Non-Crystalline Solids*.[27a–e] Note that the Havriliak-Negami equation for $R(i\omega)$, with its two adjustable width-parameters, is widely-used to fit α-processes in amorphous polymers and has similar characteristics to the transformed KWW function $\tilde{\Phi}(\omega)$for broad relaxations.[1–4,28,29]

Average Relaxation Times

The following equations have been used extensively to fit dielectric relaxation data for both amorphous polymers and LMM glass-forming liquids[1–5,27a–e,30,31]

$$\langle\tau\rangle = A\exp[B/(T - T_0)] \tag{4a}$$

$$\langle\tau\rangle = A\exp[c\Delta\mu/TS_c] \tag{4b}$$

$$\langle\tau\rangle = A\exp[Q/kT]] \tag{4c}$$

These are the well-known Vogel-Fulcher, Adam-Gibbs and Arrhenius equations, respectively, where Q in Eq. 4c is TPV-dependent for α-relaxations and is a constant forβ-relaxations.

In Eq. 4a $\langle\tau\rangle$diverges as $T \rightarrow T_0$, which is often termed "super-Arrhenius behaviour". In Eq. 4b the model for cooperative motions involves a dynamic quantity $\Delta\mu$ (an energy) and an equilibrium quantity S_c (configurational entropy). Suitable choice of the form of $S_c(T)$ also leads to super-Arrhenius behaviour.[2–4,5c] In Eq. 4c the activation energy Q depends generally on the T,P,V condition of the material. Roland and coworkers[30,31] made extensive dielectric studies of α-relaxations as a function of temperature and pressure for glass-forming liquids and polymers. Combination of their results with their PVT data for these materials led them to propose that $Q = Q(V)$ and, importantly, scales as V^{-m} , where $m > 1$ and is a material constant (see ref. 31 for a discussion and a review of this and related work). For polymer β-relaxations, plots of ε'' vs. $\log\omega$ are very broad and symmetrical and are fitted[1–4] using Cole-Cole or Fuoss-Kirkwood empirical equations for the line-shape and the Arrhenius equation for $\left\langle\tau_\beta(T)\right\rangle$, with Q constant.

Thus we have the important result that stretched-exponential relaxation functions for $\Phi(t)$, e.g. Eq. 3, *together with* super-Arrhenius functions for $\langle\tau(T,P,V)\rangle$, e.g. Eqs. 4a–c, may be used to fit data for dielectric α-relaxations in amorphous polymers. These functions are also used to fit NMR, QELS, QELS and FDP data for α-relaxations in amorphous polymers.[6–9] In addition, it has been established that the time-dependent, thermal-history-dependent thermodynamic behaviour (volume, enthalpy, C_p) observed in the glass-transition region for amorphous polymers and glass-forming liquids, and physical-ageing phenomena of polymer glasses near their T_g, may be fitted using combinations of (i) stretched exponential relaxation functions, especially the KWW function, with (ii) super-Arrhenius functions, especially Eqs. 4a and 4b, as demonstrated by the many works of Kovacs, Aklonis and Hutchinson, Struik, Angell, Hodge, Moynihan, Ngai, Matsuoka, Simon and McKenna, and their coworkers (see e.g. refs. 32–37 and refs therein, especially the seminal paper by Kovacs and coworkers[32] and the comprehensive reviews by Hodge[36] and Hutchinson.[37]

In 1995 Nobel Laureate P.W. Anderson commented[38]:-

"*The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade. The solution of the problem of spin glass in the late 1970's had broad implications in unexpected fields like neural networks, computer algorithms, evolution and computational complexity. The solution of the more important and puzzling glass problem may also have a substantial intellectual spin-off. Whether it will help to make better glass is questionable.*"

In view of the successes noted above in applying equations for stretched-exponential relaxation *together with* those for super-Arrhennius behaviour of relaxation times in fitting (i) relaxation and scattering data for the α-relaxation and (ii) thermodynamic data in the glass-transition region for glass-forming materials, we suggest that a *practical solution* to the problem posed by Anderson has now been achieved using what are, essentially, phenomenological or semi-empirical theories for relaxation behaviour. This is a significant achievement since the methodology provides a framework, or "working model", that has predictive qualities and which may be applied to a wide range of glass-forming materials of very different chemical composition. The next step is to find molecular theories of relaxation that lead to behaviour similar to those given by Eq. 3 and 4a–c.

Molecular Theories of Dielectric Relaxation

In order to "see what the molecules are doing" during α, β and $\alpha\beta$ relaxation processes, the following question needs to be addressed – *how do the dielectric observables relate to the dynamics of the chain molecules?* A solution is found in the use of time-correlation functions (TCFs)[10,39] for the reorientational and translational motions of molecules, an approach that has been well-established for over forty years for NMR relaxation[6] and dielectric relaxation.[2–4,10,12,39] It is surprising, and disappointing, that most papers reporting experimental dielectric relaxation data for polymers make no reference to the TCF approach in the interpretations of results. The most direct route from a molecular model for a relaxation process to a prediction of the experimental behaviour (e.g. in NMR and dielectric relaxation) uses Kubo linear-response theory[2–4,10,39] rather than deducing the dielectric susceptibility of a system in an applied field for each proposed model of relaxation.[1,4] Recent molecular dynamics simulations of the dynamics (including dielectric properties) of polymers use the TCF approach (see below). In an attempt to remedy the limited use of the TCF approach for the dielectric relaxation of polymers we outline here its essential points for application to multiple dielectric relaxation regions.

In 1970 Cook, Watts and Williams[40] used Kubo linear response theory, developed by Glarum and Cole[41,42] for dielectric relaxation, to show for an ensemble of flexible dipolar chain molecules that

$$\frac{\varepsilon(\omega)-\varepsilon_{\infty}}{\varepsilon_{0}-\varepsilon_{\infty}}p(i\omega) = 1 - i\omega\Im[C_{\mu}(t)] \tag{5a}$$

$$C_{\mu}(t) = \frac{\left\langle \vec{M}(0).\vec{M}(t)\right\rangle}{\left\langle \vec{M}^{2}\right\rangle} = \frac{\sum\limits_{ij}\left\langle \vec{\mu}_{i}(0).\vec{\mu}_{j}(t)\right\rangle}{\sum\limits_{ij}\left\langle \vec{\mu}_{i}(0).\vec{\mu}_{j}(0)\right\rangle} \tag{5b}$$

where $C_{\mu}(t)$ is the time correlation function for the angular motions of chain dipoles $\vec{\mu}_i$, in the ensemble and p(iω) is an internal field factor. $C_{\mu}(t)$ is a weighted sum of auto- and cross-correlation functions, but for flexible chains these have approximately the same t-dependence so $C_{\mu}(t) \approx \langle\vec{\mu}_i(0).\vec{\mu}_i(t)\rangle / \langle\vec{\mu}_i^{2}\rangle$, which is the auto-correlation function for the motions of a reference chain-dipole. Also in 1970 Williams and Watts[43] introduced the concept of *partial* and *total* relaxations of dipolar groups to rationalise the dielectric α, β and $\alpha\beta$ processes in amorphous polymers. The following equation was obtained (see Appendix 1 for definitions and further details)

$$C_{\mu}(t) = A_{\alpha}\varphi_{\alpha}(t) + B_{\beta}\varphi_{\alpha}(t)\xi_{\beta}(t) \tag{6}$$

where $\xi_{\beta}(t)$ is a weighted sum of relaxation functions for the partial-reorientations of chain dipoles, which relax a portion B_{β} of the total relaxation strength. The α-process, due to large-scale microbrownian motions of chains, has a relaxation function $\varphi_{\alpha}(t)$ and relaxes the remaining strength A_{α}, where $A_{\alpha} + B_{\beta} = 1$. Eq. 6, which is sometimes called "The Williams Ansatz", couples α and β processes together when they are due to *motions of the same reference group, but on different time-scales.* It predicts *inter alia* :-

(i) That α and β processes merge at high temperatures to form the $\alpha\beta$-process, which is a continuation of the α-process to higher temperatures but now incorporates the relaxation-strength of the β-process.
(ii) A "conservation rule", $\Delta\varepsilon = \Delta\varepsilon_{\alpha} + \Delta\varepsilon_{\beta}$, so if $\Delta\varepsilon_{\beta}$ decreases with increasing pressure, $\Delta\varepsilon_{\alpha}$ will increase in a complementary manner in order to conserve the total relaxation strength $\Delta\varepsilon$.

(i) and (ii) are observed for dielectric relaxation in polymers such as the polyalkyl acrylates and methacrylates, polyvinyl halides, polycarbonates and in aliphatic and aromatic polyesters.[1–4,12,17,18]

Eq. 6 is general in the sense that the functional-forms of the individual relaxations are not specified. These will be determined by the chemical structure and actual mechanisms for the dynamics of chains for each polymer. Partial reorientations of different chemical groupings in main-chains and side groups (e.g. ester, benzoate) and small pendant groups (e.g. methoxy) will all have different mechanisms, leading to a variety of of

β-relaxation processes, as is observed experimentally.[1–4] Starting with a molecular model for relaxation or using a computer simulation of the dynamics of an ensemble of polymer molecules, the dipole moment TCF, $C_\mu(t)$, may be determined using Eqs. 5 for comparison with experimental dielectric data for theα, β and $\alpha\beta$ processes in amorphous polymers.[1–4,12]

Model Theories for α-Relaxations

Numerous theories for the α-relaxation process in amorphous polymers and LMM glass-forming liquids have been proposed that seek to obtain stretched-exponential behaviour for $\Phi(t)$, or $C_\mu(t)$, together with super-Arrhenius behaviour for $\langle\tau(T,P,V\rangle$. Some models are essentially *phenomenological* and introduce empirical relaxation functions, while others propose specific *molecular mechanisms* for motion that predict the TCFs for chain-dipole relaxations and motions of particular molecular-groups, as in multi-nuclear NMR relaxation and fluorescence depolarization experiments. A full account of these models is beyond the aims of this paper so in Table 1 we indicate only a selection of the theories and include key references. Further details of these and related models may be found in the standard texts[2–4] and key references.[44–51] See especially the many experimental and theory papers in ref.[27] that make use of these theories.

While most theories in Table 1, with their adjustable parameters, may be applied successfully to experimental data for dielectric α-relaxations in polymers, further information on the dynamics is needed, from complementary experiments and from applications of constraints on the interpretations of data, in order to discriminate between different models – thus rejecting some and favouring others. An immediate difficulty is that dielectric, NMR and fluorescence studies give information, through their TCFs, on the motions of chain vectors and tensors (dipole moments, bond directions, polarizability tensors) while most of the theories in Table 1 (defect diffusion, tilings, mosaics, energy landscapes, mode coupling theory, Ngai coupling model and the Adam-Gibbs model) are *scalar theories* that make no specific reference to these molecular quantities. Also these theories are not able to relate α and β relaxations to each other or derive their relative intensities. Exceptions are dynamic Ising models, but these use linear or circular chains that are unrealistic for 3D-polymers, and the models of Sillescu, Diezemann and coworkers[49,50] where the motions of a relaxor between

Table 1.
Model Theories for α-Relaxations

Theory	Nature of theory	Authors
Defect diffusion	Targeted diffusion of defects, controlled random walks on lattices	Glarum 1960[41] , Shlesinger, and Montroll 1984[91]
Dynamic Ising chains	Conditioned flips in long linear chains	JE Anderson 1970[92a], Skinner and Wolynes 1980[92b]
Rotation-isomeric models	Conformational dynamics of flexible polymer chains	Jernigan 1972[93a] Beevers and Williams 1975[93b]
Hierarchical models	Motions in multi-level spin systems	Palmer, PW Anderson et al, 1984[94]
Tiling models, mosaics, frustrated domains	Dynamics of conditioned rearrangements of tiled area	Weber, Stillinger and Frederiksen 1986[95]
Energy landscapes	Motions in a multi-barrier spin system	Sillescu, Diezemann, Hinze, Bohmer[49,50]
Coupling model	Two-piece relaxation function; single exponential + KWW	K. Ngai[46]
Mode-coupling theory	Continued fraction for C(t) relating second order memory function M(t) to C(t)	Goetze 1988[96], Cummins[97]
Configurational entropy	Dynamics of a cooperative region	Adam and Gibbs 1985[98]
Dynamic heterogeneity	Motions of temporary local regions in an ergodic system	Spiess and Schmidt-Rohr 1991[6,51,48]

different energy states are accompanied by specified changes in its direction, thus allowing orientational TCFs of different order to be determined (see below).

The concept of ‘‘dynamic heterogeneity’’ proposed by Schmidt-Rohr and Spiess[51] has been well-received. It has strong experimental support from multinuclear NMR studies by Spiess and coworkers[6,51] of the motions of selected sub-ensembles of molecular groups in amorphous polymers - see especially the excellent reviews by Bohmer and coworkers[48,52] who describe how dynamic heterogeneity in amorphous systems can be probed by NMR techniques[6,48] and by pulsed and non-resonant hole-burning dielectric techniques.[52] Further evidence for dynamic heterogeneity in amorphous polymers was obtained by Israeloff and coworkers[53] through novel dielectric-probe studies of surface regions, ~50 nm in depth, in poly(vinyl acetate) just above its T_g. They showed[53] that the dielectric relaxation behaviour for the α-process of the regions fluctuate with time, indicating the presence of a dynamic heterogeneity. Superposition of the individual responses gave KWW behaviour for the process.

In the model of ‘‘dynamic heterogeneity’’ it is proposed[6,51] that a bulk polymer above T_g at an arbitrary time $t = 0$ has a spatial distribution of local states, of mesoscopic to nanoscopic dimensions, which have their own local dynamics, leading to relaxations of chains and an apparent non-ergodic behaviour of the system within the time-scale of those dynamics. A cartoon of the system is shown in Figure 2.

As time develops the system fluctuates, allowing local states to change their energies, and hence their dynamics, so at long times the entire system becomes ergodic and, therefore, thermodynamically-stationary, for which the ensemble-averaged TCFs and the time-averaged TCFs for chains are equal.[39] As a result of such a ‘‘dynamic heterogeneity’’, relaxations of chains can occur, leading to α, β and $\alpha\beta$ processes, as observed in dielectric, NMR and related experiments.[1–4,6–9,47–53] The forms of the multiple relaxations, α, β and $\alpha\beta$, are not specified in this general model of dynamic heterogeneity and are to be determined by experiment[6,48,51,52,53] or through computer simulations of the dynamics of polymer chains in the bulk state (see below).

Computer Simulations of Chain Relaxations

Most theories in Table 1 provide practical ‘‘working models’’ for application to relaxation, fluorescence and scattering data for α-processes in polymers and LMM liquids. However, in order to gain a deeper understanding of the *molecular processes* involved, large-scale ‘‘Molecular Dynamics’’ (MD) and ‘‘Monte Carlo’’(MC) computer-simulations of the dynamics of chains in the bulk state have been made in recent years. A detailed account of these major advances is well-beyond the aims of this paper so we consider only briefly some of the MD studies and their essential conclusions. Note that MD studies are normally limited to times ranging from picoseconds to about 10 nanoseconds, which are smaller than those for most dielectric and NMR studies

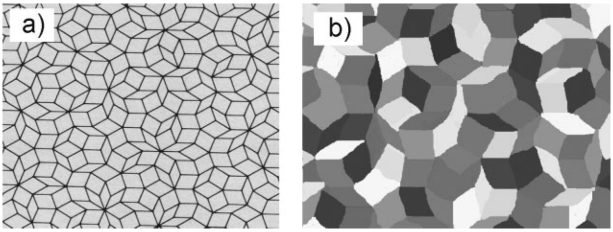

Figure 2.
A cartoon of Dynamic Heterogeneity. (a) Penrose tiling of a mesoscopic region. There is no symmetry so the region is disordered. (b) Paint in the energies at $t = 0$. Local regions span the range of dynamical behaviour, giving from slow to fast relaxations. Continual exchange of energy ensures ergodicity of the system.

of polymers, and are many orders of magnitude less than those for thermodynamic studies of glass-transition behaviour. Thus MD simulations give information on relaxation and scattering behaviour above $\sim 10^8$ Hz, which is in the range where α and β processes coexist or merge to form the $\alpha\beta$ process.[1–4,17,18] In the early 1990's Roe[55,56] and Monnerie[57] and coworkers pioneered MD studies of the dynamics of polymer chains in the bulk state. For a model of polyethylene Roe[56] determined $C_\mu(t) = \langle P_1(\cos\theta(t))\rangle$ for segmental chain-motions, where P_1 is the first-order Legendre polynomial. It was shown that at short times $C_\mu(t)$ decreased slightly over a wide t-range (β-process) then decayed to zero at longer times through the α-process, which was fitted by the KWW function, Eq. 3, with $\overline{\beta} = 0.59$. Also the higher order TCFs, $\langle P_n(\cos\theta(t))\rangle$, were determined and their relaxation times scaled as $[n(n+1)]^{-1}$, so $\langle P_2(\cos\theta(t))\rangle$, the TCF for NMR, QELS and fluorescence depolarization studies, relaxed approximately three times faster than $\langle P_1(\cos\theta(t))\rangle$. These simulations demonstrated, and quantified, the local (β) and large-scale-cooperative (α) relaxations of chain segments. The recent major developments in large-scale simulations of the dynamics of flexible-chain polymers are summarized in the texts by Binder[58] and Boyd and Smith,[59] the reviews by Binder and Paul,[60] Smith and Bedrov[61] (for poly(butadiene)), Paul and and Smith[62] and by Logotheti and Theodorou[63] (for poly(propylene)).

These simulations provide detailed information on both the equilibrium and dynamic properties of large ensembles of chains. The following is demonstrated for the dielectric relaxation behaviour:-

Partial and total relaxations of chain dipoles occur leading to α andβ-processes occur, as envisaged in Eq. 6. In the dielectric β-process, chain segments move via a series of local conformational changes that do not change substantially their local environments.[59,61,62] These motions, do not relax all of $\langle\mu^2\rangle$ for individual group-dipoles so the remaining relaxation strength is relaxed by the α-process (see Eq. 6 above). As shown by Smith and Bedrov[61] for polybutadiene, different packing arrangements of chains with neighbouring chains in the bulk state impose a wide range of local barriers between conformational states for each of the chain units, so local conformational rearrangements occur at very different rates, leading to a very broad β-relaxation. Thus the long-term, unanswered problem of the large breadth of β-processes in amorphous polymers is addressed and explained in terms of the details of the local conformational dynamics of chain segments.

In the simulations by Boyd and coworkers of the dynamics of melt polyethylene,[59] the dielectric α-process arises from large-scale motions of chains. It is found that (i) the relaxation function exhibits KWW behaviour, (ii) $\overline{\beta}$ decreases with decreasing temperature, (iii) $\langle\tau(T)\rangle$ exhibits Arrhenius behaviour at high temperatures and super-Arrhenius behaviour at low temperatures. A detailed study of the dynamics of a chosen chain provides a physical interpretation for this behaviour.[59] Starting at $t = 0$ from an initial chain-conformation and chain-environment for individual, numbered groups along a chain, they monitored the trajectories of these groups in time and showed that they relaxed (a) at the same rates at high temperatures and (b) very different rates at low temperatures - giving the appearance of *dynamic homogeneity* at high temperatures, and *dynamic heterogeneity* at low temperatures, for the local system. The non-equivalence of the dynamics of these chemically-equivalent groups in the time-scale of the α-process at low temperatures gives KWW-behaviour for the α-relaxation process. When the trajectories are continued to much longer times, slow-relaxors become fast-relaxors, and vice-versa, so the dynamics of these groups become equivalent, ergodic behaviour is established and the system becomes thermodynamically-stationary. At low temperatures *dynamic heterogeneity* in the chain dynamics gives rise to super-Arrhenius behaviour for

$\langle\tau(T)\rangle$ while at higher temperatures *dynamic homogeneity* is approached, so Arrhenius behaviour is obtained.[59]

These MD simulations[55–63] give far more detailed information on the average (equilibrium) structures and molecular dynamics of model polymer chains in the bulk state than we have described here. Further simulations, especially those to longer time-scales, would yield *premonitory behaviour* for thermodynamic properties in the glass-transition region and would clarify further the molecular dynamics in polymers, copolymers and polymer blends of different chemical composition and encourage comparisons to be made between dielectric, NMR, fluorescence depolarization and scattering data for multiple relaxations.

Another approach would be to build on the physical insights obtained from these MD simulations to construct simple working models that lead to multiple relaxation behaviour. For example, in the simulations of polyethylene by Boyd and coworkers[59] (see figs.8.25 in ref.59), chain units move at different rates but we notice that the relaxation functions of individual groups appear to be similar, except their time-origins are displaced relatively. It should be possible to construct a simple model for the α-process where the relaxation of a set of chemically-equivalent relaxors is given by a weighted sum of the relaxations of individual relaxors, each having the same relaxation function $\lambda(t - t_0)$, $t > t_0$, but with their time-origins, t_0, distributed away from the arbitrary time $t = 0$.

Applications of BDS to Polymer Systems

The literature on the dielectric properties of polymers is now extremely large (see e.g. refs. 1–4, and the papers in refs. 27a–e) and it is evident that much progress has been made both in documenting the dielectric properties of amorphous polymers and in understanding the *fundamentals* of their relaxation behaviour. As a result, BDS, with its wide frequency range and facility of measurement, is being increasingly-applied to complex polymer systems that have a practical interest. As examples of such applications of BDS, we describe briefly the following – the apparent glass-transition of thin polymer films and real-time studies of (i) polymer crystallization and (ii) bulk-polymerization.

Thin Polymer Films

The emergence of thin-film technologies has brought considerable attention to the question - *do the physical properties of ultra-thin polymer films differ significantly from those in the bulk state?* Starting in the mid-1990's, studies by Keddie, Forrest, Jones and coworkers.[64–66] indicated that large decreases in T_g occurred for polymers, such as polystyrene, for films having a thickness <50 nm. These works initiated a host of publications since they imply, *inter alia*, that ultra-thin films of polymers have different thermodynamic and dynamic properties from those in the bulk state. If that were the case, technological applications of ultra-thin films of glassy polymers would need to be re-assessed since their dimensional stability could be reduced by such a large lowering of Tg. The subject has become increasingly controversial, with many studies reporting apparently conflicting results. These developments cannot be given here in any detail, so the reader is referred to recent reviews and key papers.[67–70]

There are several difficulties associated with studies of the dynamics and apparent T_g of ultra-thin polymer films, which include:

(i) Films are normally made by spin-coating of a solution onto a support-surface or by solvent-evaporation of a solution at a liquid or solid surface. In the absence of further heat treatment, the films may not be in their thermodynamic equilibrium state so the their physical properties may depend not only on film-thickness but also on the procedures used during their fabrication.

(ii) Films are studied in different configurations; as free-standing, one-side-supported and two-side-supported films (as in normal BDS measurements). Interactions at the polymer/template interface may affect the physical properties of the material, giving different results for the dynamics and apparent T_g behaviour of films prepared and studied in the three configurations.

(iii) Experimental techniques used to study the dynamics and apparent Tg of films include those of optical ellipsometry, neutron and X-ray reflectivity, positron-annhilation, thermal-probe measurements, capacitative scanning dilatometry and Brillouin light scattering (see ref. 67). These give only *indirect information* on an apparent glass-transition process. Clearly a glass-transition temperature observed by conventional thermodynamic methods is the consequence of a dynamical process, a ''motion to non-motion'' transformation, which is strongly associated with the α-relaxation and its temperature dependence, as discussed above. ''T_g'' takes different values depending on the thermal/time path chosen for its study and the method adopted for its determination. In some studies, e.g. differential scanning calorimetry (DSC), large, variable heating rates are employed ($>10\,K\,min^{-1}$) and the analysis of such data to yield meaningful information on the underlying transformation is difficult, even for bulk materials. It is clear that the ''glass-transition'' of an amorphous polymer, which extends over a range of temperature exceeding tens of K[1,5] and involves a change of several orders of magnitude in the mechanical moduli/compliances,[1,5] should be determined through measurements of changes in relaxation properties over the temperature range of the transformation, using e.g. dynamic-mechanical, dielectric, $C_P(\omega)$ and photon-correlation spectroscopy techniques at fixed temperatures. This is now being addressed in recent researches, especially those by Kremer and coworkers (see below).

Most techniques, e.g. NMR and QELS, are not suited for measurements of ultra-thin films, but BDS is particularly appropriate, as we indicated in the Introduction. BDS studies by Fukao and coworkers[67] of high molecular weight polystyrene films revealed a well-defined α-process, of unchanging contour from the bulk material down to 14 nm-thick films. A decrease in T_g of $\sim$15 K was observed in this range ,which is a much smaller than those reported earlier for this polymer. Later, Kremer, Serghei and coworkers, using BDS, made a series of major investigations of the dynamics of ultra-thin polymer films[67–69] (see especially the recent review by Serghei[68] and refs. therein). The films were:- (a) prepared/fabricated in different ways (residual stresses can lead to metastable states); (b) subjected to different environments (polymer degradation, due to oxidation, and plasticization effects, due to moisture, are magnified for ultra-thin samples, due to the high ratio for sample area/thickness); (c) measured in different configurations (see (ii) above). Kremer and coworkers investigated the effects of (a)-(c) for films ranging from the bulk to nm-thicknesses for a several amorphous polymers. Large systematic variations in the dynamics of the α-process were observed under different conditions.[67–69] As one example, we describe their recent BDS results[71] for films of isotactic poly(methyl methacrylate), poly(vinyl acetate) and poly(2-vinyl pyridine). Samples were prepared by spin-coating solutions onto highly-conducting Si-wafers, had a free upper surface and, importantly, were annealed in N_2 for several hours before study. In this geometry, $\varepsilon(\omega)$ was calculated from the measured impedance as a dielectric-film in series with an air-gap capacitance. Figure 3 shows their data for the dielectric α-relaxation as plots of normalised loss vs. T/K at set frequencies for samples ranging from several hundred nm to 8 nm in thickness.

The loss peaks superpose for each polymer, showing the polymer dynamics, and hence the apparent T_g, *is independent of film-thickness* for each of these well-annealed polymers. In parallel studies, Huth and

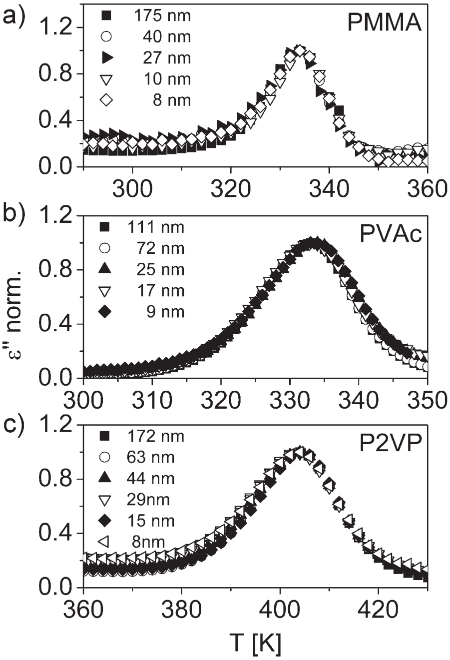

Figure 3.

Plots of normalised loss factor vs. temperature (K) at fixed frequencies showing the dynamic glass transition in thin films of (a) i-PMMA (0.12 Hz); (b) PVAc (120 Hz) and (c) P2VP (1.3 k Hz). Data of A. Serghei, H. Huth, C. Schick, F. Kremer, *Macromolecules*, **2008**, 41, 3636, reprinted with permission from The American Chemical Society, Washington DC.

coworkers[72] developed a chip-calorimeter to measure ultra-thin, spin-coated polymer films of poly(styrene) and poly(methyl methacrylate). They determined the real and imaginary parts of the complex heat capacity $C(i\omega)$ as a function of frequency and temperature for films down to 4 and 10 nm thickness, respectively, and found that the apparent T_g for PSt(at 40 Hz) and PMMA (at 80 Hz) *is independent of film-thickness*.

These new studies, in which the dynamics of the α-process (and hence T_g) for thin polymer films in particular configurations are determined directly by dielectric and calorimetric techniques, brings into focus earlier studies where the T_g of films appeared to decrease greatly on entering the nm range. A re-consideration of those results appears to be necessary in order to clarify if the samples (i) were in a non-equilibrium state, (ii) were affected chemically or physically by their preparation/environment and (iii) whether some of the physical methods used were able to determine, unambiguously, the T_g of the films.

Real-Time Studies of Polymer Crystallization

Despite the extensive studies made in the past 50 years or so, a full understanding of the processes occurring during crystallization and the physical state and the chain-dynamics of the resultant partially-crystalline materials is far from complete. Most studies of these materials use spectroscopic, X-ray and neutron scattering techniques together with electron microscopy[73] and are concerned primarily with the details of molecular ordering, lamellar and related structures, the different textures (e.g. spherulites) and gross morphologies. However, since bulk polymers are only partially crystalline they contain disordered regions which can possess molecular mobility ($T > T_g$) or be in a glassy state.

While high degrees of crystallinity (χ) are achieved for polymers such as linear poly(ethylene) and isotactic poly(propylene), this is not the case for many polymers of practical importance such as aromatic polyesters (e.g. polyethylene terephthalate) and aliphatic polyamides (e.g. the nylons). In those cases χ does not exceed 50%, but the materials appear to be composed entirely of spherulites when viewed in an optical microscope. The essential mechanical properties of strength, toughness and ductility for polymers of medium degree of crystallinity are enhanced as a result of the connections, and interplay, between the disordered regions and crystalline regions, where the disordered regions exist both between and within the ordered regions (e.g. spherulites). While there is a vast literature concerned with the structures and textures of the crystalline regions in partially crystalline polymers,[73] a full understanding of these materials requires that the nature and dynamics of their disordered regions, which may amount to over 50% of the material, be clearly established.

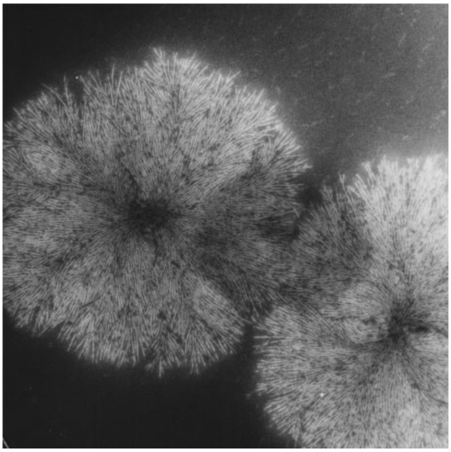

Figure 4.
Electron micrograph of two spherulites growing in a film of *cis*-poly(isoprene). The growth was terminated prior to completion by reaction with the staining agent, osmium tetroxide. Data of Paul J.Phillips, *Rep. Progr. Phys.*, **1990**, 53, 549, reprinted with permission from IOP Publishing Ltd, Bristol.

To illustrate the nature of spherulite growth in a bulk polymer, Figure 4 shows an electron micrograph observed by Paul J. Phillips[74] for two impinging spherulites growing in a film of cis-poly(isoprene).

Crystallization was terminated prior to completion of reaction by treatment with a staining agent, osmium tetroxide vapour, which allowed the lamellar crystals to be seen in contrast with (i) the normal-amorphous (NA) regions of the melt and (ii) the constrained-amorphous (CA) regions both between and within the growing spherulites. The micrograph suggests that the CA regions interact strongly with the lamella crystals and will have dynamical properties that are different from the NA regions of the isotropic melt.

In contrast to many relaxation, scattering and spectroscopic techniques, BDS provides a direct means of studying the developments of both NA and CA regions during the crystallization process, through *real-time* measurements made over a wide frequency range. Crystallization may be conducted from the melt or from the quenched amorphous glassy state (termed "cold-crystallization"). Numerous real-time BDS studies have been made over the years that started with the preliminary work in 1979 of Tidy and Williams, reported by Williams,[75] who showed plots of loss vs. log f/Hz as a polyethylene terephthalate (PET) sample was cold-crystallized at a temperature just above Tg. As the loss peak for the NA phase disappeared due to crystallization, a new broader peak appeared at lower frequencies which was due to motions of chains within and between the spherulites, i.e. motions in the CA regions.[75] At very long times the CA peak decreased slightly due to secondary crystallization.[75] These preliminary studies were followed by comprehensive, definitive real-time BDS studies by Ezquerra, Balta-Calleja and coworkers for the crystallization behaviour of a number of polymers including PET,[76,77] polyaryl ether ether ketone (PEEK)[78] and polybutylene isophthalate.[79] These studies showed how chain motions in the NA regions and CA regions evolved during crystallization and, through their SAXS and WAXS X-ray scattering studies, how changes in dynamics during the crystallization process are correlated with accompanying changes in the physical structures within the materials.

To illustrate further the application of modern BDS techniques to polymer crystallization, we consider the recent study by Lund, Alegria, Colmonero and coworkers[80] of the cold-crystallization of poly(dimethyl siloxane) (PDMS). Figure 5 shows plots of

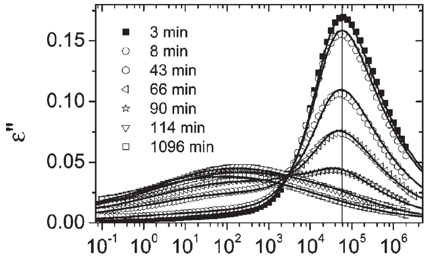

Figure 5.
The time-evolution of plots of loss factor vs. logf/Hz for polydimethyl siloxane ($M_N = 74\,000$) during cold crystallization at 162 K. Data of R. Lund, A. Alegria, L. Goitandia, J. Colmonero, M.A. Gonzalez, P. Lindner, *Macromolecules*, **2008**, 41, 1364 reprinted with permission from The American Chemical Society, Washington DC.

the loss spectra as a sample was crystallized at 162 K, some 16 K above the T_g (dsc).

Under these conditions, a maximum degree of crystallinity $\chi \sim 0.33$ was attained after ~180 min, as determined by a WANS scattering method. These real-time studies cover a wide frequency range (10^{-1} to $10^{+6.5}$ Hz), which allows the loss peak due to the NA and CA regions to be determined simultaneously during crystallization. It is evident from Figure 5, without any detailed analyses or adoption of assumed models for the crystallization process, that as time progresses the NA loss peak decreases, due to the disappearance of the NA regions, and the CA loss peak appears at lower frequencies as the CA regions form within and between the crystals. At long times the height of the CA loss peak decreases and it moves to lower frequencies, being indicative of secondary crystallization during which the chain motions in the CA regions become increasingly hindered. These results give information on (i) the relative amounts of CA and NA regions in the crystallizing sample and (ii) the dynamics in the NA and CA regions as a function of crystallization time t_X. Lund and coworkers[80] also studied the changes in physical structures during crystallization of the material, using WANS and SANS scattering techniques. Combination of the information gained from these BDS and scattering experiments allowed a quantitative analysis and interpretation of the crystallization process,[80] which showed (i) before any significant crystallinity is detected by WANS, the NA phase is changed at short times through the formation of nuclei that act as attachment centres for crystal growth, (ii) the dynamics of the CA regions is ~3 orders of magnitude less than that for the NA regions due to grafting of amorphous chains to the crystalline parts, (iii) in the secondary-crystallization regime, changes in the dynamics of the CA regions can be assigned to free chain-ends becoming attached to emerging crystals to form trans-lamellar cross-links.

Thus real-time BDS studies reveal the evolution, and quantify the dynamics, of the NA and CA regions for crystallizing systems. Since the nucleation density of crystals (e.g. spherulites) in polyesters, polyamides, polysiloxanes and other crystallizable polymers that achieve only medium χ-values can be varied by adding nucleating agents or using different cooling/heating protocols, it should be possible to combine real-time optical-microscopy with real-time BDS measurements to monitor the physical state (crystalline content, spherulite density, gross morphology) and the dynamics (of NA and CA components) during crystallization in order to optimize the essential mechanical properties of a material.

Real-Time BDS Studies of Bulk-Polymerization

Thermosetting resins, formed by the bulk polymerization of reactive monomers such as epoxides and amines, form an important class of materials that are used primarily as adhesives and electrical insulators. Starting with a liquid mixture of monomers, polymerization is initiated with heat and proceeds to form a cross-linked polymer that is, at room temperature, a rigid glass. The step-polymerization process involves the rates of diffusion of reactant species, which decrease markedly since molecular mobility decreases during reaction. Changes in molecular mobility are conveniently studied using real-time BDS, so a large literature has accumulated.

The first BDS studies were reviewed in 1986 by Senturia and Sheppard[81] and since that time many real-time, multi-frequency BDS studies have been made for thermosetting materials including those by the groups of Kranbuehl, Johari, Rolla, Mijovic, Williams and Pethrick, which have established BDS as a prime technique for monitoring, and quantifying, the cure-behaviour of thermosets. Key references are listed by Williams, Smith, Holmes and Varma[82] while Mijovic[83] has reviewed the method. In most cases, plots of ε' and ε'' vs. cure-time, t_c, are made at set frequencies which reveal an α-relaxation, due to motions of all dipole groups, which moves to low frequencies with time as the dynamics become increasingly retarded due to the formation of chain-polymers and networks. A polymer glass is formed when the α-process has moved to ultra-low frequencies.

In a series of major papers for epoxide-amine systems, Johari and coworkers[84] (see also ref.82 for a listing of key references to his works) showed that plots of ε'' vs. ε', obtained at set frequencies during cure, were similar to those for the KWW function. They applied a modification of the KWW-function to their curing data and determined how $\langle\tau(t_c)\rangle$ varied with cure-time t_c at different cure-temperatures T_{cure}. These and related studies show[81–86] that a reaction becomes diffusion-controlled at long times, through the reduced mobility of chains, and leads to the formation of a polymer glass. Fournier and coworkers[85] proposed a kinetic theory for diffusion-controlled step-polymerization reactions to quantify their extensive real-time BDS data for an epoxide-amine thermosetting system.

For the majority of systems studied in this way, the product at long times is a rigid glass, which is chemically-unstable since

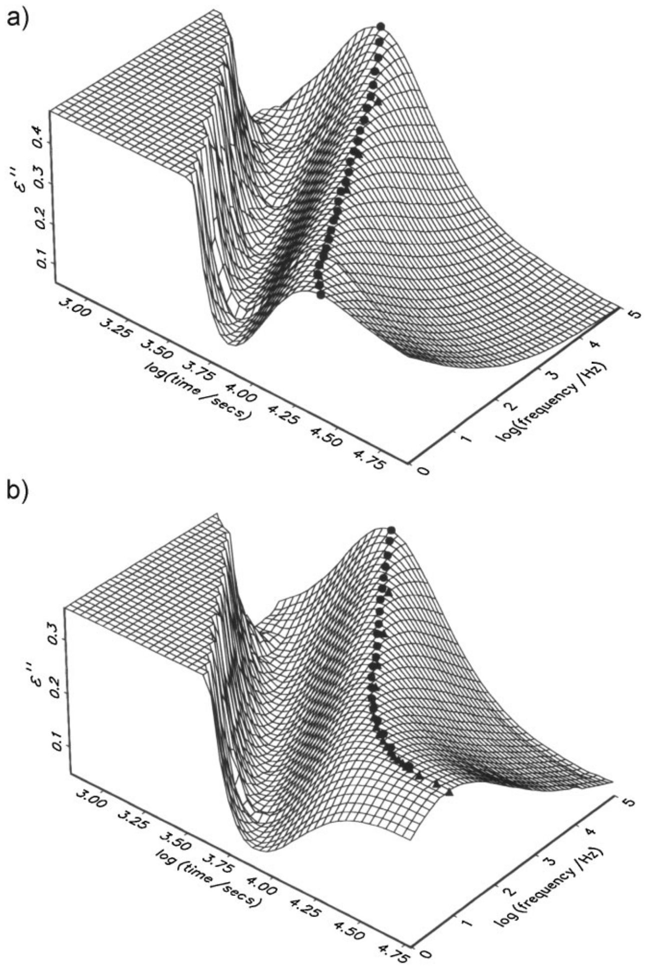

Figure 6.

Dielectric cure-monitoring. Plots of ε'' vs. log(f/Hz) and log(t_{cure}/sec) for a PY306/TMB/BA epoxide-boroxine mixture at a T_{cure} of (a) 65 °C and (b) 75 °C. Data of G. Williams, I.K. Smith, G.A. Aldridge, P.A. Holmes, S. Varma, *Polymer*, **2001**, 42, 3533, reprinted with permission from Elsevier Ltd.

reaction is incomplete under these conditions. However, the product for reactions conducted at high temperatures will be an elastomer, which becomes a glass on cooling to room temperature. This is the preferred route to obtain practical materials in the form of adhesives and electrical insulators. Williams and coworkers[86] made real-time multi-frequency BDS studies of an epoxide/boroxine mixture of a fixed composition, at cure-temperatures in the range 60–120 °C. Figures 6a and 6b show the 3D-plots of ε'' vs. {log f/Hz, temperature / °C} for T_{cure} equal to 65 °C and 75 °C, respectively.

In Figures 6 the α-loss peak due to motions of chain dipoles is seen together with a large low-frequency process, due to ionic conduction in the materials. At $T_{cure} = 65\,^{\circ}C$, the loss peak moves steadily to ultra-low frequencies showing that a glass is formed at long times at this temperature, which is the well-known result.[81–85] At $T_{cure} = 75\,^{\circ}C$ the loss peak moves initially to lower frequencies, but then stabilises beyond 40 ksec to become invariant with time, showing that a product having the molecular mobility of an *elastomer* is formed. Reactions conducted below 65 °C gave behaviour similar to Figure 6a , i.e. a glass is formed, while reactions above 75 °C give behaviour similar to Figure 6b, i.e. an elastomer is formed. Williams and coworkers[86] demonstrated that there was a *Floor Temperature* T_{Floor} at 72 °C for this reaction mixture. For $T_{cure} > T_{Floor}$ sustained molecular mobility during reaction allows it to go to chemical-completion, so an elastomer is formed. For $T_{cure} < T_{Floor}$ progressive reductions in molecular mobility with time leads to glass-formation before the reaction can achieve chemical-completion. This is a general principle for all thermo-polymerizing systems.

On the basis of their results, Williams and coworkers[86] proposed an extension to the well-known TTT contour-diagram of Gillham[87,88] for the temperature-time behaviour of bulk thermosetting reactions to include T_{Floor}. This is shown schematically in Figure 7.

In Figure 7 the time-scale is arbitrary; the ordinate T'$_g$ is the difference between T$_g$(reacting mixture) and T$_g$(unreacted mixture) at each cure-temperature, T_R, and increases with cure-time. ''Normalised temperature'' is the difference between T_R and Tg(unreacted mixture). We set $T_{Floor} = 70\,^{\circ}C$ in the figure. For $T_R > T_{Floor}$, reactions go to completion, elastomers are formed, all having the same T$_g$. For $0 < T_R < T_{Floor}$,

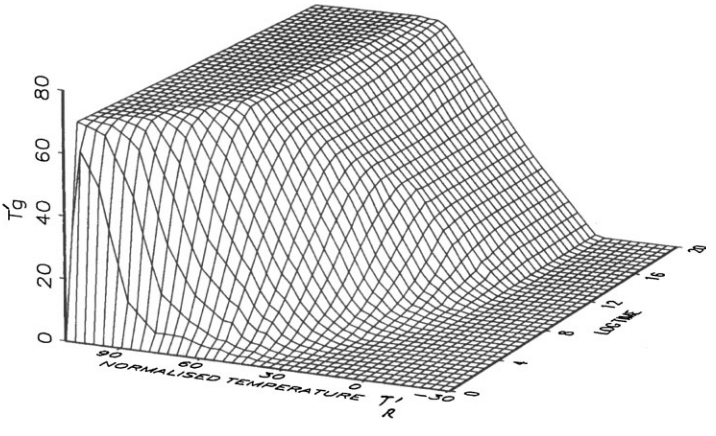

Figure 7.
Schematic plot of the variation of the normalized glass-temperature T'g with log(time) during isothermal curing at different temperatures T_R , indicating: (a) the rise in Tg during reaction and (b) the occurrence of a ''Floor Temperature'' at 70 °C. Data of G. Williams, I.K. Smith, G.A. Aldridge, P.A. Holmes, S. Varma, *Polymer*, **2001**, 42, 3533, reprinted with permission from Elsevier Ltd.

T_g(mixture) increases during reaction until a glass is formed. This behaviour continues until $T_R = T_{Floor} = 70$. For $T_R < 0$ (glassy-reaction-mixture) some reaction will occur very slowly, increasing T_g slightly.

Thus BDS provides a powerful method for studying the cure of thermosetting systems where the products may be a glass or an elastomer. We have considered here only the changes in dipole relaxation behaviour during cure, but many studies, especially those of Kranbuehl and coworkers, use complex conductivity rather than complex permittivity to monitor cure-behaviour.

Conclusion

This account has described some of the basic aspects of Broadband Dielectric Spectroscopy and how the technique is used to study chain-motions in solid polymers, especially amorphous materials, and in crystallizing and thermo-polymerizing systems.

Considerable progress has been made in the experimental techniques and in theories of dielectric relaxation for polymers, especially those involving dipole TCFs that lead, *inter alia*, to molecular dynamics simulations of multiple relaxations that are observed experimentally. In addition to further BDS studies along current themes, many new developments of BDS can be envisaged including, e.g., studies of chain-dynamics in bulk samples of "gradient" copolymers,[89] to reveal the molecular origins of their exceptionally broad glass-transition regions, and real-time studies of reactions of photoactive species (e.g. photo-isomerizable, photo-chromic) in polymer matrices where molecular mobility of the host will affect reaction rates.

While we have not considered conduction behaviour of polymer materials in this paper, recent studies by Alig and coworkers[90a–d] should be noted since they demonstrate an important new application of BDS to nano-composite systems and changes in their behaviour under processing conditions. BDS and rheological studies of [polymer]-[carbon multi-walled nanotube (MWNT)] composites were made, for MWNT contents $< 5\%$; the host polymers were polycarbonate[90a–d] and poly(propylene).[90b] These composites show extremely large conductivities ($\sigma > 10^{-3}$ S cm^{-1}) arising from charge-percolation through a network of nanotube structures embedded in the polymer matrix. While the materials were extruded it was shown that σ decreased by up to *six orders of magnitude*, providing clear evidence that the percolation network responsible for conduction was disrupted by flow. When the flow was stopped the large conductivities recovered with time, showing the networks re-formed in a one-stage[90d] or two-stage process.[90c] These studies provide quantitative information on the connectivity of the conducting networks, their disruption during flow and their recovery on removal of the flow field. Such information is not readily obtained by other means for these complex systems.

Appendix 1

Let p_r^0 be the probability that a reference dipole $\vec{\mu}_i$ finds itself in a local environment 'r' at t = 0. The dipole partially relaxes by motions in the local environment with relaxation strength $q_{\beta r} = 1 - [\langle\vec{\mu}_i\rangle_r^2]/\mu_i^2$ and relaxation function $\varphi_{\beta r}(t)$, where $\langle\vec{\mu}_i\rangle_r$ is the residual dipole moment after local relaxation has occurred. The residual relaxation strength, $1 - q_{\beta r}$, is relaxed by the α-process, with relaxation function $\varphi_\alpha(t)$. Summing up over all initial environments gives Eq. 4 of the text. $A_\alpha = \sum_r p_r^0 q_{\alpha r}$and $B_\beta \xi_\beta(t) = \sum_r p_r^0 q_{\beta r}\varphi_{\beta r}(t)$.

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