Dielectric Properties during Free-Radical Bulk Polymerization: Visible Light-Induced Polymerization of Bisphenol-A Bis(2-hydroxyethyl ether) Dimethacrylate

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Received September 6, 1996; Revised Manuscript Received January 23, 1997[⊗]

ABSTRACT: The dielectric properties of the polymerized and unpolymerized bisphenol-A bis(2-hydroxyethyl ether) dimethacrylate have been studied, and the polymerization of this monomer using visible blue light (λ = 470 nm) and the system camphorquinone/(dimethylamino)ethyl methacrylate as a photochemical initiator has been followed in real time. Remarkable changes in the permittivity $\epsilon'(\omega,t,T)$ and the loss peak $\epsilon''(\omega,t,T)$ of the polymer have been observed and analyzed, as soon as the sample was illuminated, corresponding to a sudden fall of $\epsilon'(\omega,t,T)$ for all the frequencies of measurement, a shift to low frequencies, and a large decrease of the relaxation loss peak in the frequency domain. A thermal postcuring of the acrylic polymer has been performed, leading to small changes in the chemical properties but large changes in the dielectric absorption. The present work shows how dielectric relaxation spectroscopy may be used as a very sensitive technique to follow polymerization.

Introduction

The complex dielectric permittivity $\epsilon(\omega,T) = \epsilon'(\omega,T) - i\epsilon''(\omega,T)$, where $\omega = 2\pi f$/Hz and T is temperature, as measured over wide ranges of frequency and temperature, provides valuable information on the structures, interactions, and dynamics of polymers chains in the liquid and solid states. Dielectric relaxation spectroscopy (DRS) has become a leading method for studying the reorientational motions of molecules in polymer materials[1−4] or for following the course of thermosetting chemical reactions (see refs 5−14 and references therein). Dielectric spectroscopy of the bulk step polycondensation of epoxides with amines was studied several years ago by Lane and Seferis,[8] and related studies have been reviewed by Senturia and Sheppard.[9] Mangion and Johari have published a series of papers (see refs 10−13 and references therein) in which the dielectric properties of such systems were investigated in real time. However few publications[14] have been concerned with free-radical polymerization of bulk monomer as studied by DRS.

The polymerization of methacrylate monomer, for example, has been widely applied especially for medical applications, including optical lenses, implants, orthopedic cement, or dental composite resins. Indeed the photopolymerization of dimethacrylate resins has found ample applications in the dental field, using such initiator systems as the camphorquinone (CQ)/amine couple which produces free radicals on exposure to visible light at 470 nm. In spite of the technological applications of photopolymerization in visible light, only a few physical studies of this process have been published.[15]

The main purpose of the series of experiments in this paper is to monitor with real-time dielectric spectroscopy a photoinduced bulk polymerization process and to study the evolution of $\epsilon'(\omega,t,T)$ and $\epsilon''(\omega,t,T)$ as the sample changes from a viscous liquid to a glassy solid over a period of several minutes. Our interest is to obtain new information on the changes of the molecular mobility during the bulk polymerization of a representative dimethacrylate monomer, induced photochemically over a large range of reaction temperatures. Dielectric spectra can show different relaxation absorptions in glass-forming materials[1] giving the following main processes:

(i) The principal relaxation, labeled α, is referred to as a primary or glass−rubber relaxation, which appears at the lowest frequency (for a given temperature). From a molecular point of view, it has been widely accepted that it results from large scale conformational rearrangements of the polymer chain backbone.[1]

(ii) The secondary loss regions (β, γ, δ) result from local motions of the chains in the glasslike state. Since the molecules of amorphous polymers may contain side groups capable of undergoing hindered rotations independently of the chain backbone, the secondary relaxations are often ascribed to such motions. For example, the dielectric and mechanical β peaks in methacrylate polymers are generally thought to involve rotations of the −COOR side groups.[1]

The relative strength of the two dielectric dispersion regions is a function of the monomer structure. If the relaxations are well separated in the f-domain, then three items of information may be obtained for each process: (i) the dispersion magnitude $\Delta\epsilon$, (ii) the frequency f_m of maximum loss factor, and (iii) the form of the ϵ'' vs log f plot.

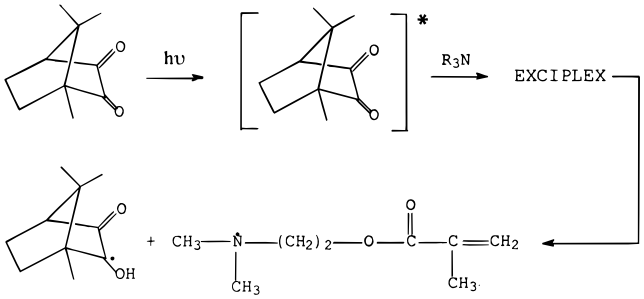
Theoretical Background

It is appropriate to summarize certain features of the photopolymerization process and the essential nature of the dielectric measurements in order to understand the variations we shall report of the dielectric properties as a result of photoinduced polymerization of bulk monomer.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1997.

S0024-9297(96)01319-8 CCC: $14.00

Photopolymerization Kinetic Theory. Three processes are involved in addition polymerization: *initiation*, *propagation*, and *termination*. The initiation of radical photopolymerization by aromatic ketones is relatively well known.[16,17] It is supposed to result from hydrogen atom abstraction from the monomer by the excited ketone or from an electron transfer reaction from a donor molecule to the excited ketone (in an exciplex) followed by a proton transfer. Thus it is assumed that camphorquinone (CQ) exposed to a blue light ($\lambda = 470$ nm) in the presence of an amine ((dimethylamino)ethyl methacrylate, DMAEM) produces an excited complex (exciplex) which in turn gives free radicals, as shown in the mechanism below:



Cook[18] explained that the absorption of one quantum of radiation promotes the carbonyl group to a singlet state. This excited singlet [CQ−C═O*(S)] may then: (i) return to the ground state by fluorescence or a radiationless transition, (ii) decompose to another species, or (iii) undergo intersystem crossing to the triplet state [CQ−C═O*(T)]. The excited triplet acts as an electron acceptor and forms an exciplex by charge transfer with the amine acting as an electron donor. This excited complex may be deactivated or may form a degradation product, but it is expected to produce two radicals, formed from the amine and the ketone. The amine radical is assumed to be responsible for initiating the polymerization. The lifetimes of excited singlet states are normally very short, and the concentrations of CQ−C═O*(S) and CQ−C═O*(T) are assumed to be low. Cook investigated this mechanism and proposed that the kinetics of consumption of CQ during irradiation or for a high concentration of amine (>0.3 wt %) were reasonably well fitted to a first-order expression, which we may write as:

$$\frac{-\mathrm{d}[\mathrm{CQ}]}{\mathrm{d}t} = k(I_o)[\mathrm{CQ}] \qquad (1)$$

where the rate coefficient k was found to be proportional to the radiation intensity I_o but independent of [CQ] and of the medium mobility.

It appears that the diffusion of monomers and initiators does play an important role in the kinetics. Zang et al.[19−21] studied the diffusion of camphorquinone in a polymerizing host during the photopolymerization, particularly in poly(methyl methacrylate) as the glass transition. They showed that cross-linking of the polymer chains reduced the average free volume and, hence, reduced the diffusion rate of the penetrants (e.g., active centers). However they mentioned that the diffusion is facilitated by the cooperative motion of the polymer segments.

Regarding the influence of the amine as a coinitiator, the following have been established.[18] (i) Purified dimethacrylate monomers do not readily photopolymerize in the absence of amines. However it appears that the photopolymerization of commercial products can proceed to a limited extent (sufficient to cause gelation) without coinitiator, and this is due to the presence of reducing impurities in the material. (ii) The photopolymerization is extremely slow for primary amines and for amines with no α-hydrogens. (iii) The rate of photopolymerization is found to be greatest for tertiary amines followed by secondary amines and then primary amines. This may result from the mesomeric effects which stabilize the tertiary ionic intermediates.

Concerning the propagation stage, chain carriers are formed from the reactions of the free radicals and monomer units. Owing to the dimethacrylate structure of the monomer bisphenol-A bis(2-hydroxyethyl ether) dimethacrylate (bisHDMA) and the nature of the amine which also possesses a methacrylate group, the chain propagation proceeds rapidly by multiadditions to produce the network. Polymerization of divinyl monomers such as bisHDMA or bisphenol-A bis(glycidyl methacrylate)[18] (bisGMA) is characterized by a rapid loss of double bonds at low conversions and a rapid buildup in the propagating radical conversion.[15] The studies[15,18] of the propagation process in photopolymerization of a difunctional methacrylate monomer, e.g., bisGMA, initiated by visible light in the presence of a mixture (camphorquinone/tertiary amine) show a rapid increase of the extent of reaction as the light source is switched on until a certain value, usually up to ∼60%, and then the reaction progresses at a considerably slower rate.

The two most common mechanisms of termination involve bimolecular reactions of growing polymer chains. *Combination* involves the coupling of two growing chains to form a single polymer molecule. Alternatively, a hydrogen atom can be abstracted from one growing chain by another in a reaction known as *disproportionation*. In general, both types of termination reactions take place but to different extents depending upon the monomer and the polymerization conditions. Poly(methyl methacrylate)[22] was found to terminate mainly by disproportionation when the thermopolymerization took place above 60 °C but by both mechanisms below this temperature. In the case of the bulk polymerization of a polyfunctional monomer such as bisHDMA, the diffusion of the active center or the monomer is made difficult when the network reaches a certain degree of conversion. During the linear polymerization of monoacrylate monomer, the active units are found at the end of the chains and these 'double bonds' are free to diffuse to lengthen the chain. In the photopolymerization of bisHDMA in the presence of the CQ/amine couple, the reaction produces branched macromolecules, and these will develop into a large three-dimensional network containing both branches and cross-links. Thus the diffusion of the reactive centers is strongly restricted by densification and the topological constraints of the matrix so the cross-linking may 'stop' without radical termination,[23] but only because the active sites, which are tethered in the network, are unable to meet each other. However the polymerization of methyl methacrylate induced by visible light in the presence of the combination isatoic anhydride−Br_2 was found to terminate mainly through disproportionation reactions.[24]

Phenomenlogical Theory of Dielectric Relaxation. The fundamental relationship joining the time dependent and the frequency dependent dielectric complex permittivity $\epsilon(\omega) = \epsilon'(\omega) - \mathrm{i}\epsilon''(\omega)$ is expressed by the following Fourier transform relation:[1]

$$\frac{\epsilon(\omega) - \epsilon_0}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left[\frac{-\mathrm{d}\phi(t)}{\mathrm{d}t}\right] \exp(-\mathrm{i}\omega t)\, \mathrm{d}t$$

$$= 1 - \mathrm{i}\omega \int_0^\infty \phi(t) \exp(-\mathrm{i}\omega t)\, \mathrm{d}t \qquad (2)$$

where ϵ_0 and ϵ_∞ are the limiting low- and high-frequency permittivities and $\phi(t)$ is the normalized transient function [$\phi(0) = 1$, $\phi(\infty) = 0$] which expresses the time dependent decay of polarization following the step withdrawal of an electric field from a sample. $\phi(t)$ contains only contributions from relaxation processes, and it can be deduced by inversion of eq 2 if $\epsilon(\omega)$ is known over its entire relaxation range.[1]

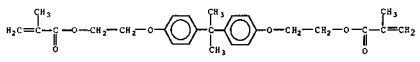
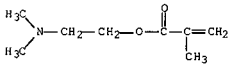
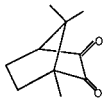
These important relations allow the conversion of dielectric measurements made in the time domain into permittivity and loss data in the frequency domain. The simplest form for $\phi(t)$ is the single-exponential decay $\phi(t) = \exp(-t/\tau)$, where τ is the macroscopic relaxation time. The single-relaxation time function, called the Debye equation, can be obtain by inserting this decay function into eq 2 giving:

$$\frac{\epsilon(\omega) - \epsilon_0}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau} \qquad (3)$$

One method to fit experimental data is to modify the single-relaxation time function, eq 3, in the frequency domain by insertion of empirical distribution parameters. The best known empirical expressions for normalized complex permittivity were Cole−Cole,[25] Davidson−Cole,[26] and Havriliak−Negami,[27] which are obtained by replacing the term $(1 + \mathrm{i}\omega\tau)$ in eq 3 by respectively $[1 + (\mathrm{i}\omega\tau)^n]$, $[1 + (\mathrm{i}\omega\tau)]^m$, and $[1 + (\mathrm{i}\omega\tau)^p]^q$. The parameters n, m, p, and q have different values in the interval [0;1]. Fuoss and Kirkwood[28] suggested that the single-relaxation time equation for loss factor could be written as $\epsilon''(\omega) = \epsilon_m''$ sech $\ln(\omega\tau)$, where ϵ''_m is the maximum loss factor, and they modified this expression as $\epsilon''(\omega) = \epsilon_m''$ sech $m' \ln(\omega\tau)$, where $0 < m' \leq 1$. A further empirical relation for dielectric relaxation was proposed by Williams and Watts,[29] who transformed the single-exponential decay function to a 'stretched exponential' $\phi(t) = \exp[-(t/\tau)^\beta]$, where $0 < \beta \leq 1$. The curves of $\epsilon''(\omega)$ vs $\log(\omega)$ derived from the empirical equations above exhibit different shapes in terms of broadness and symmetry or asymmetry. For a large number of polymers, the dielectric relaxation behavior can be fitted using the Williams−Watts approach with a single parameter β or equally well using the Havriliak−Negami function with two parameters. The α process observed in the time or frequency domain for amorphous polymers using different spectroscopic methods such dynamic−mechanical, NMR, ESR, light-scattering, or fluorescence depolarization methods is also well fitted using both of these functions.

Many polymers exhibit a principal α relaxation and β relaxation and further secondary relaxations, but not all relaxation processes are observed in dielectric experiments. The processes appear in DRS only if they involve reorientations of dipole moment vectors. The α relaxation corresponds to microbrowian motions of polymer chains, related to the "dynamic glass transition" of the polymer, while the β process is related to limited motions of side groups in the chains. Thus the β relaxation appears generally as a broad loss curve in the higher frequency domain, for temperatures below T_g, the apparent glass transition temperature, while the α process occurs for $T > T_g$ and lower frequencies. As the temperature increases above T_g, both α and β processes tend to coalesce to a single $\alpha\beta$ process, implying that all three processes are inter-related.[34] As we shall see, the monomer in the present work behaves as a simple glass-forming liquid, and the derived polymer has the features typical of a glassy amorphous material. We note that the monomer used here contains phenoxy and ester dipolar groups, and these same groups are present in both the monomer and the final polymer network.

Table 1. Reagents Used for the Photopolymerization

Reagant	Formula	Supplier
BisHDMA		*Pilkington Glass*
DMAEM		*Aldrich*
CQ		*Aldrich*

Experimental Section

The dimethacrylate monomer studied was the bisphenol-A bis(2-hydroxyethyl ether) dimethacrylate (bisHDMA) supplied by Pilkington Glass under the name Diacryl 101 (see Table 1). We used the camphorquinone (CQ)/2-(dimethylamino)ethyl methacrylate (DMAEM) couple to initiate the photopolymerization under visible light. Both chemicals were supplied by Aldrich. They were 98% pure and used without further purification. The sample was prepared by mixing 12 g of bisHDMA with 0.05 g of CQ (0.5 wt %) and 0.05 g of DMAEM (0.12 wt %) with a magnetic stirrer. Heating of this sample to about 50 °C for a few minutes was needed to facilitate the solubility of the camphorquinone in the medium. As only small quantities of the mixture were used for each experiment, the sample was stored in a dark chamber at 5 °C. It was found to be stable for at least 8 weeks.

Photopolymerization was initiated with an Elipar-2 dental photocuring source (ESPE, Germany). This source consists of a 100 W tungsten halogen lamp, a series of optical filters and lenses, and a fused fiber-optic light guide with a 10 mm exit window. The spectral characteristics of the source are similar to those described by Cook.[30] The emission spectrum of the unit has been coordinated with the absorption of camphorquinone, occurring between 400 and 500 nm. The light source fluctuations due to the variations of the main's voltage or aging effects of the lamp are recorded by a microprocessor and immediately equalized in order to obtain a constant level of light. When the light delivery is activated by means of the switch activator, the fan in the transmitter runs and the light is emitted for 25 s. For all the experiments, the bulk polymerization was induced by three exposures of 25 s occurring in the first 6 min of the experiment. The distance between the extremity of the light guide and the sample was fixed at 3 mm.

Indium tin oxide (ITO) conducting glass cells, which are transparent to visible light, were used to contain the sample during the photoinduced bulk polymerization. The bottom and top plates were stuck together with epoxy adhesive and separated by two PTFE spacers, whose thickness was 70 μm, to form the conducting glass dielectric cell. The liquid monomer sample was drawn in between the plates by capillary attraction. In order to apply a measuring electric field to the cell, conducting wires were connected to the edges of the ITO plates, using gold-plated clips. This kind of cell presents great advantages: (i) it allows a photoinduced polymerization of the

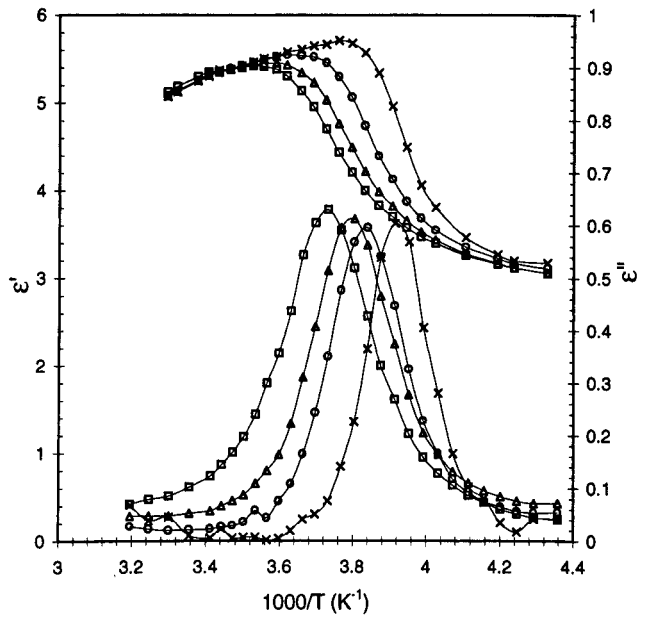


Figure 1. Plots of the permittivity ϵ' and the loss factor ϵ'' against reciprocal temperature for the bisHDMA monomer at the frequency of measurement $f = 10^3$ Hz (×), 10^4 Hz (●), $10^{4.6}$ Hz (▲), and 10^5 Hz (■).

monomer in situ with visible light ($\lambda = 470$ nm), which is not absorbed by the glass; (ii) the small thickness of the cell gives good dielectric measurements; and (iii) such a cell is readily fabricated. The ITO gives additional dielectric losses of high frequencies in Figures 2 and 9.

Dielectric measurements were made for many frequencies in the range $10^{1.2}-10^5$ Hz and temperatures in the range −80−80 °C using the GenRad Digibridge 1693. The capacitance $C(\omega)$ and the dissipation factor $D(\omega)$ were chosen to be measured in a parallel equivalent circuit mode. They allowed the determination of the real permittivity $\epsilon'(\omega) = C(\omega)/C_o$ and the loss factor $\epsilon''(\omega) = D(\omega)C(\omega)/\omega C_o$, where C_o is the empty cell capacitance.

The photopolymerization kinetics were monitored with a FTIR instrument (Perkin Elmer 1725X spectrometer). The sample was contained between two NaCl plates separated by two PTFE spacers whose thickness was 70 μm. Complete spectra of the sample, from 4000 to 400 cm^{-1}, were obtained every 5 min during the initial 15 min of illumination and then every 15 min during 1 h 45 min. The polymerization was induced by three illuminations (of 25 s) as 470 nm during the first 6 min of the experiment. We also plotted the spectrum of the unreacted monomer and those of the polymer samples obtained (i) after 2 h at room temperature, (ii) after 2 days at room temperature, and (iii) after 8 days at $T = 80$ °C.

Results and Discussion

The values of ϵ' and ϵ'' for the unreacted monomer were measured from $T = -40$ to 30 °C for 30 temperatures at the different frequencies and are displayed as a function of $1/T$ in Figure 1. The high-T (relaxed) permittivity of the unreacted material does not change significantly with the frequency of measurement but varies considerably with the temperature of measurement. As the temperature is lowered, the values of $\epsilon'(\omega,T)$ drop substantially for all the measurement frequencies. Thus we observe the dynamic T_g process for the unreacted monomer. For $f = 10^5$ Hz, ϵ' falls from 5.5, at 10 °C, to 3.5, at −20 °C. The corresponding values of $\epsilon''(\omega,T)$ exhibit dielectric relaxation peaks over the same range of temperature. As predicted by dielectric theory,[1] the loss peak moves to low temperatures on lowering the measuring frequency. No loss peak can be observed at room temperature in our f-range. At T = 25 °C the dielectric absorption of the monomer is situated at a frequency approximately equal to 10^{10} Hz. The experimental data for $\epsilon''(\omega,T)$ can be plotted as a function of log(f/Hz) for a fixed temperature of measurement, as shown in Figure 2. In this representation, the loss peaks for the monomer are broad and somewhat similar to those obtained during the thermopolymerization of the epoxy resin.[8−14,31,32] The shift of the peak from high to low frequencies, when the temperature is lowered, is clearly shown in Figure 2, $\epsilon''(\omega,T)$ is found to vary from 0.01 to about 0.6. Depending on the sample temperature, the *monomer* can be considered as a liquid, a viscous liquid, a viscoelastic liquid, or a glass. Thus the evolution of $\epsilon'(\omega,T,t)$ and $\epsilon''(\omega,T,t)$ during the polymerization of the material should be very different if the initial material is a glass ($T < -30$ °C), a viscoelastic liquid (−30 °C < T < 0 °C), or a viscous liquid ($T > 0$ °C). As seen in Figure 1, the loss peak becomes slightly broader and the temperature of maximum loss increases, when the frequency is increased. For a single relaxation time, the loss factor versus $1/T$ is symmetrical about $1/T_{max}$, while the curves in Figure 1 are slightly unsymmetrical, being broader on the high-T side. The relationship between the time or frequency dependence of relaxation parameters and temperature dependence is easily understood for a single-relaxation time model and can be expressed as follows:

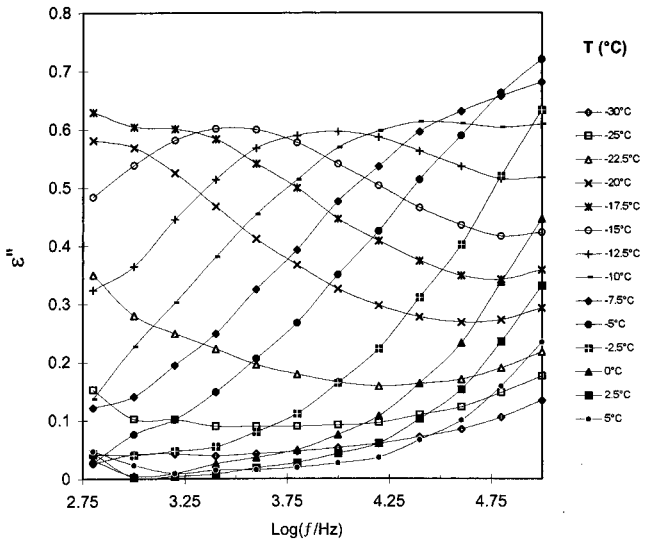


Figure 2. Plots of the loss factor against the frequency on a logarithmic scale for the bisHDMA monomer at 14 different temperatures.

$$\tau = \tau_0 \exp\left[\frac{H}{kT}\right] \tag{4}$$

As $\tau = 1/(2\pi f_m)$ for ϵ''_{max}, we may write:

$$f_m = f_m(0) \exp\left[\frac{-H}{kT}\right] \tag{5}$$

In Figure 3 the values of log(f_m/Hz) corresponding to the maximum loss peak were plotted versus $1/T$ and found to be linearly dependent on $1/T$.

The dashed lines in Figure 3 indicate the position of the dielectric loss maxima for conventional polymethyl methacrylate[1] (PMMA), corresponding to an α or β process. It is noticed that at fixed frequency, the α relaxation process of the monomer bisHDMA occurs at much lower temperatures than those for PMMA. The energy of activation H, from eq 5, was calculated for our

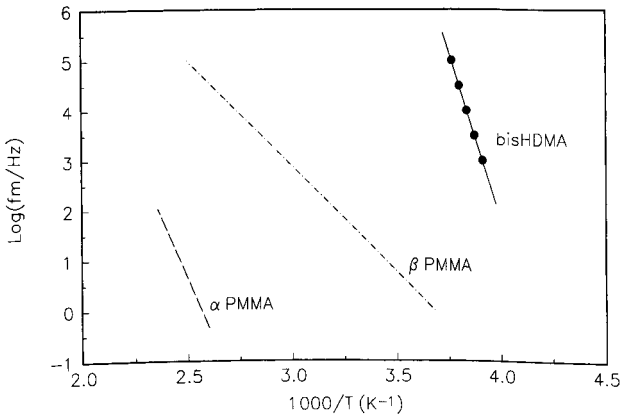


Figure 3. Plots of log(f_m/Hz) against reciprocal temperature for the bisHDMA monomer and the poly(methyl methacrylate).[1]

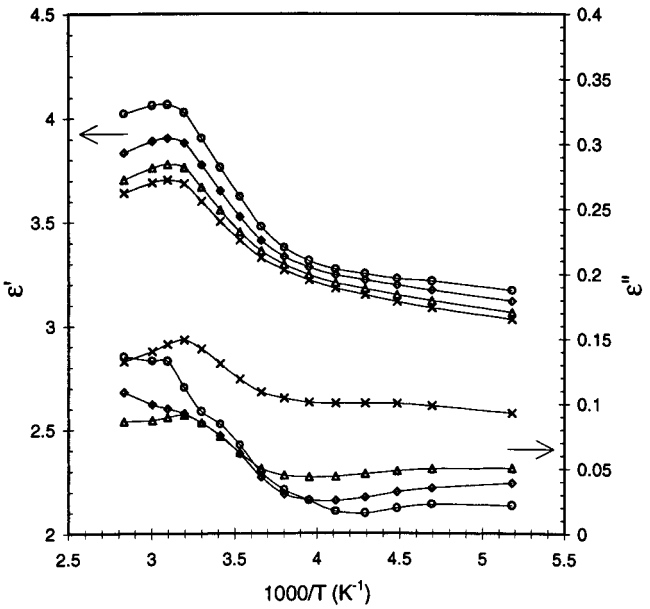


Figure 4. Plots of the permittivity and the loss factor against reciprocal temperature for the fully reacted polymer at the frequency of measurement $f = 10^2$ Hz (●), 10^3 Hz (◆), 10^4 Hz (▲), and 10^5 Hz (×).

sample, and we found $H = 250$ kJ/mol. Such a high value is usually attributed to an α process, but the frequency−temperature location of the relaxation in bisHDMA corresponds rather to a β process. Hence we may assume that the dielectric relaxation observed for our monomer sample in the temperature range between −25 and 0 °C for $10^2 < F < 10^5$Hz corresponds to an α process or a coalesced $\alpha\beta$ process due to the large scale motions of the molecules just above T_g.

After the polymerization of the sample at 25 °C, the resultant transparent glass film was left for 2 days at room temperature. The dielectric properties of the glassy polymer were then measured over a large range of temperature, from −80 to 80 °C, and are shown in Figure 4. The permittivity of the fully polymerized material is found to decrease when the temperature of measurement is lowered. The dielectric absorption peaks observed for the monomer have disappeared. It must be pointed out that the high values of ϵ'' obtained at low and high frequencies in our range result from the ionic conductivity and the contribution of the ITO electrodes, respectively. For $2.4 < \log f < 4.2$, ϵ'' varies from 0 to 0.1, increasing gradually with the temperature in the range −20 to −50 °C. It then reaches a near

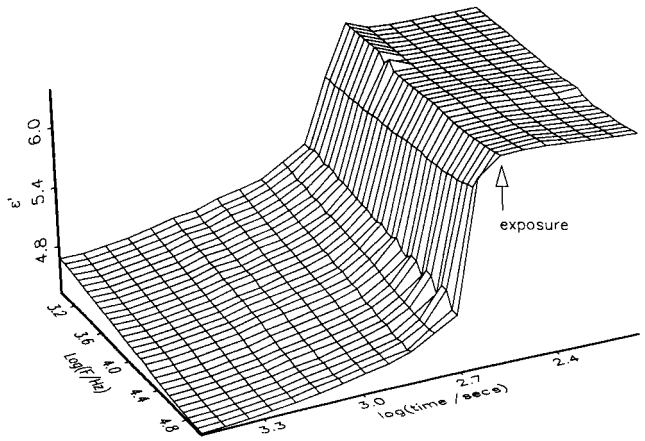


Figure 5. Evolution of the dielectric permittivity $\epsilon'(\omega,T,t)$ against the time and the frequency on a logarithmic scale during the photopolymerization of bisHDMA at 20 °C.

constant value around 0.1 for the temperatures above 50 °C. This may be considered as a broad relaxation process, whose small magnitude characterizes a polymerized material.

The studies of the temperature dependent relaxation process in the monomer and the polymer materials give us different information on dipole motions. We can visualize the frequency domain where the dielectric peaks occur by changing the temperature of measurement. From −30 to 0 °C, the dielectric loss factor ϵ'' appears as a peak of the *monomer* in the measurement frequency range allowed by the equipment, $10^{1.2}$−10^5 Hz. The measurement of the *polymer* properties under the same conditions shows that the loss peaks have disappeared. Thus, large variations in molecular dynamics of the material are to be expected during the polymerization, if the sample temperature is chosen to be in the range from −30 to 20 °C. For an α relaxation process, arising due to the microbrownian motions of molecules, a shift from high to low frequencies is to be expected as the polymerization progresses at a given temperature, because the motions of the growing polymer chain become restricted by the network. This result has been clearly established[8−14] during the thermopolymerization of an epoxy resin. As regards the β process, resulting from partial reorientations of dipoles in a distribution of local environments, the dielectric loss region may not move significantly in the frequency domain as the cure proceeds. Thus by following the reaction with DRS at chosen temperatures between 20 and −30 °C, the different aspects of the dielectric absorption can be observed. Eight different polymerization experiments were performed, at 20, 10, 0, −8, −10, −15, −20, and −27 °C. Only representative data are shown in the following figures for brevity, but the analyses take into account all our results.

Figure 5 presents a typical 3D-plot of $\epsilon'(\omega,T)$ during the photopolymerization of bisHDMA. For this experiment, the temperature was 20 °C, but similar plots were obtained at other experimental temperatures. As soon as the sample is exposed to the light, the curves $\epsilon'(t)$ vs time at a fixed frequency, fall markedly to lower values, in several minutes. They then continue to decrease slightly as the time progresses. The ϵ'' data corresponding to Figure 5 are shown in Figure 6 where it is seen that the loss values increase with increasing frequency before and after exposure to light. The loss levels for the polymerized material are higher than those for the unpolymerized material. We shall see that the behavior

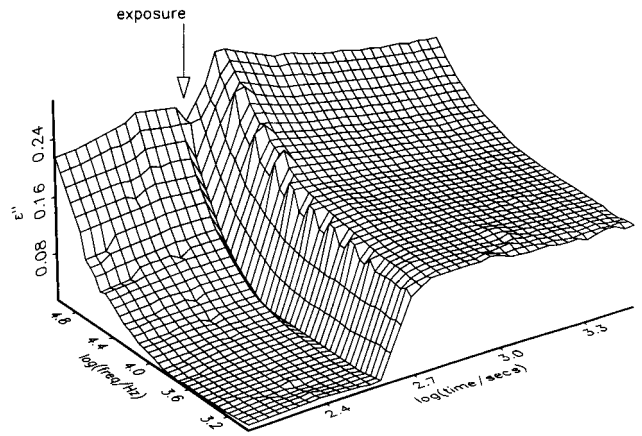


Figure 6. Evolution of the dielectric loss factor $\epsilon''(\omega,T,t)$ against the time and the frequency on a logarithmic scale during the photopolymerization of bisHDMA at 20 °C.

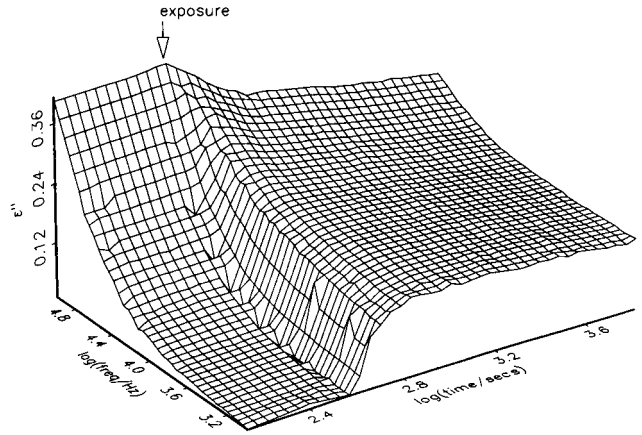


Figure 7. Evolution of the dielectric loss factor $\epsilon''(\omega,T,t)$ against the time and the frequency on a logarithmic scale during the photopolymerization of bisHDMA at 0 °C.

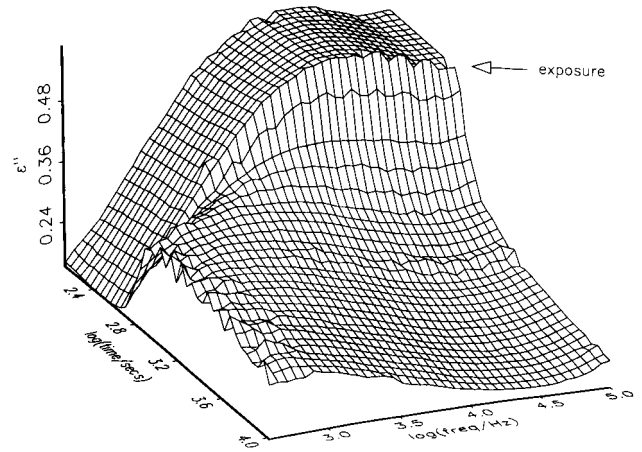


Figure 8. Evolution of the dielectric loss factor $\epsilon''(\omega,T,t)$ against the time and the frequency on a logarithmic scale during the photopolymerization of bisHDMA at −20 °C.

shown in Figures 5 and 6 is consistent with Figure 10 to be discussed below. We also show the 3D-plots of the evolution of ϵ'' as a function of the measurement frequency and the time at $T = 0$, −20, and −27 °C in Figures 7−9, respectively. A study of these figures suggests that the relaxation peak moves slightly to a lower frequency and its magnitude decreases considerably as the material changes from a liquid to a glassy solid in the first minutes of the experiment. This result appears obvious in Figure 8 for the experiment performed at −20 °C. We see that the $\alpha\beta$ relaxation peak

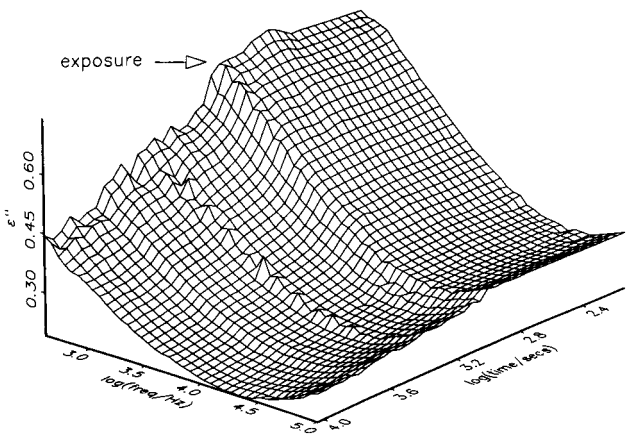


Figure 9. Evolution of the dielectric loss factor $\epsilon''(\omega,T,t)$ against the time and the frequency on a logarithmic scale during the photopolymerization of bisHDMA at −27 °C.

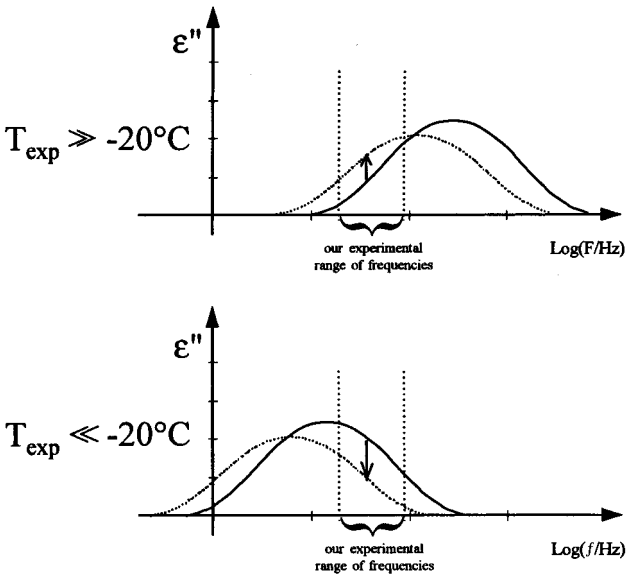


Figure 10. Schematic evolution of the dielectric relaxation at the onset of the photopolymerization for two different ranges of temperature.

for the monomer is changed as a result of polymerization to yield a smaller, broader peak that occurs at frequencies lower than that for the monomer. In this figure, $f_m = 10^4$ Hz for the unpolymerized sample, and it moves below 10^3 Hz when the polymer is formed. The chief observations from these plots are (i) the loss peak shifts rapidly to a lower frequency at the beginning of the experiment, and (ii) the value of maximum loss decreases and the peak becomes broader, as polymerization occurs.

The behavior shown in Figure 8 is also observed for the other seven temperatures studied, and a similar interpretation applies. As regards the experiment at $T > -10$ °C, shown in Figures 6 and 7, the dielectric absorption of the monomer is situated in a higher frequency range compared with our measurement range, so only the low-frequency behavior of the peak can be seen. When the polymerization proceeds, the loss peak moves to lower frequencies, and the values of ϵ'' measured in our frequency domain increase. This change in the dielectric loss factor is explained schematically in Figure 10. When a similar experiment is performed at −27 °C (see Figure 9) the loss peak, characterizing the molecular dynamics of the monomer, is located at lower frequencies than those available to

our equipment. Then the decrease of the value of ϵ'' when the reaction starts is consistent with the shift of the loss peak to the lower frequencies as demonstrated in Figure 10. Thus, by changing the temperature of the experiment, it is possible to visualize different parts of the dielectric loss peak and to monitor in real time its evolution when the sample changes from a viscous liquid (monomer) to a solid state (polymer). We should notice that this reaction proceeds in a short period of time, during which important changes of ϵ' and ϵ'' are observed. Afterward, the dielectric properties of the material change only slowly with time, for all the experimental temperatures. We note that the effective final values of ϵ'', obtained after 3 h, increase as the temperature is lowered. The values of the loss factor ϵ'', obtained at the end of the photopolymerization of the sample at the temperature T ($T < 10$ °C), are much greater that the values of ϵ'' for the fully reacted material polymerized at 25 °C and measured at the temperature T. This means that the dielectric parameters measured for the polymer change if the polymerization is performed at 20, 0, or −20 °C, for example. Thus, from a molecular dynamics point of view, the structures and the compositions of the resultant polymers obtained at 20, 0, and −20 °C are not the same. However, the dielectric experiments give information on molecular mobility and do not readily give direct information about the chemical changes in the material during the photopolymerization.

Thus FTIR spectrometry was used to investigate the chemical changes in the sample during the photopolymerization at room temperature. As the extent of reaction $\alpha(t)$ increases from zero to the final degree of conversion, irreversible changes in the material are observed in both dielectric and FTIR experiments. For our kinetics study, the conversion was measured by determining the loss of monomer and the increase in polymer using the evolution of the absorption band at 1637 cm^{-1} corresponding to the C═C stretching band in our material. Figure 11 shows the variation of the peak at $\nu_{C=C} = 1637$ cm^{-1} during the photopolymerization of bisHDMA at room temperature. We see that the concentration of double bonds in the sample decreases dramatically after the first illumination of the monomer. The peak then decreases slightly as the sample is further illuminated. The variation of the concentration in double bonds is extremely fast during the first exposure of 25 s; afterward it becomes very slow. Indeed it took 2 days to pass from peak 2 to peak 5 in Figure 11, which corresponds to a diminution in monomer concentration of 15% while in several minutes at the onset of the reaction the monomer decreased by 45%. The peak at 1608 cm^{-1}, attributed to the aromatic ring of bisHDMA, was also taken as a reference peak, and the conversion of double bonds of monomers was calculated using eq 6:

$$\text{conversion (\%)} = 1 - R(t)/R(0) \qquad (6)$$

where $R(t)$ = absorption at 1637 cm^{-1} at time t/absorption at 1608 cm^{-1} at time t.

The dashed line in Figure 11 represents the base line used for the evaluation of the absorbance at 1637 cm^{-1}, corresponding to 100% conversion. The large change in composition of the material during the first minutes of experiment is observed. The values of the conversion are summarized in Table 2 during the polymerization and after thermal postcuring. The conversion is seen

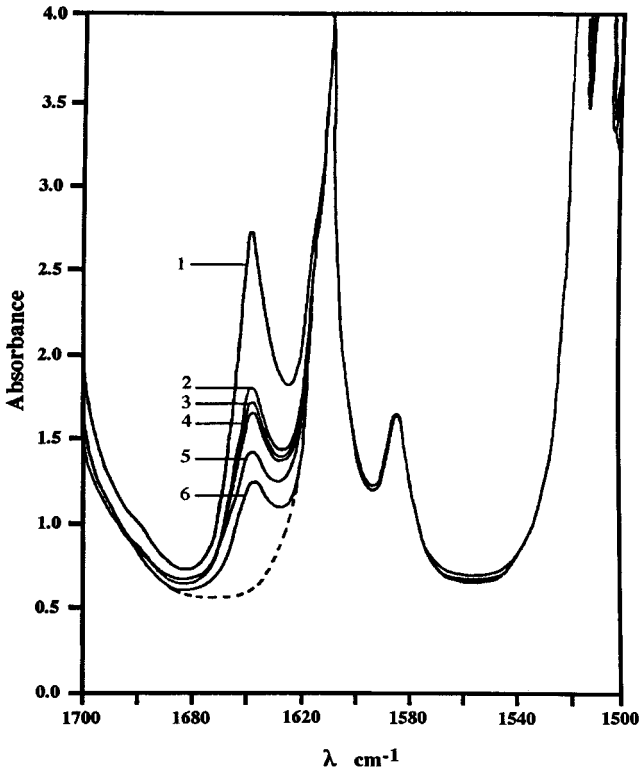


Figure 11. Evolution of peaks (1) for the monomer, (2) after 25 s of exposure, (3) after 50 s of exposure, (4) after 75 s of exposure, (5) after 2 days at 25 °C, and (6) after 8 days at 80 °C.

Table 2. Conversion of bisHDMA Monomers during the Photopolymerization and after a Thermal Postcuring

no. of curves in Figure 11	time of exposure (s)	postcuring	conversion (%)
1	0		0
2	25		44
3	50		52
4	75		54
	100	2 h at 25 °C	57
5	100	2 days at 25 °C	60
6	100	8 days at 80 °C	69

to increase dramatically from 0% to 54% in only 75 s. Then it increases slowly at room temperature, attaining 60% conversion after 2 days. That would probably represent the final degree of conversion of the polymer obtained at 25 °C, but a postcuring of the sample, consisting of heating the polymer at 80 °C for 8 days, proves that the degree of conversion can increase with a thermal treatment. Thus this FTIR study of the photopolymerization gives us the following indications on the bulk polymerization reaction. (i) The initiation of the reaction is fast and is followed by an immediate propagation process which occurs in a few minutes, increasing the degree of conversion to about 55%. (ii) The postheating of the sample allows the extent of reaction to increase gradually. We may assume that termination processes are ineffective at the end of the reaction, when the polymer may be considered 'alive', as it still contains some active centers. That means that at 25 °C, for instance, the reaction effectively stops at 60% conversion because the dense structure of the network at this temperature restricts the mobility of the polymer chains and prevents the active centers in the network from meeting each other. By heating the sample, we increase the mobility of the chains in the network which allows further reactions including crosslinking to occur. As seen in the different 3D-plots, the

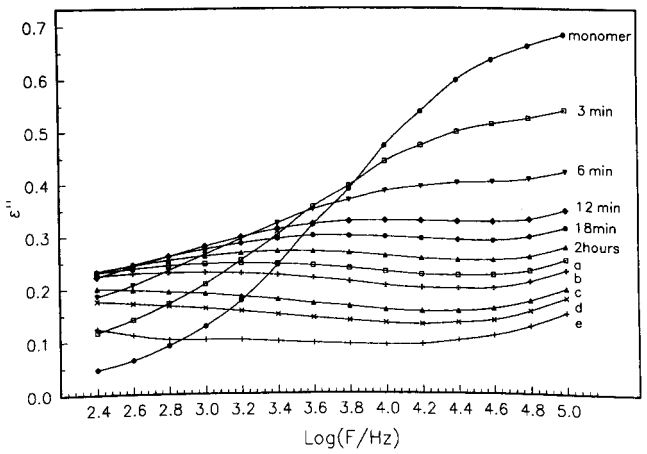


Figure 12. Evolution of the loss factor against the frequency on a logarithmic scale for the bisHDMA photopolymerization at $T = -8$ °C. The number adjacent to each curve indicates the average measurement time of ϵ'' during the 'normal' reaction, and the labels a−e correspond to the data measured at −8 °C but after a postcuring of 6 min at 0, 5, 10, 20, and 30 °C, respectively.

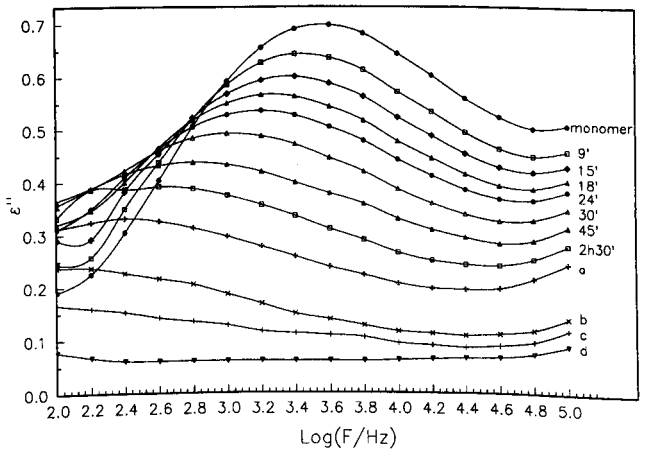


Figure 13. Evolution of the loss factor against the frequency on a logarithmic scale for the bisHDMA photopolymerization at $T = -15$ °C. The number adjacent to each curve indicates the average measurement time of ϵ'' during the 'normal' reaction, and the labels a−d correspond to the data measured at −15 °C but after a postcuring of 10 min at −10, 5, 10, and 25 °C, respectively.

dielectric curves of ϵ' and ϵ'' versus time at any frequency and temperature of measurement are composed of two distinct stages during the photocuring: (i) the onset of the reaction characterized by large variations of ϵ' and ϵ'' in a short time period, during which the chemical changes in the material are important, and (ii) the second part of the curves, appearing approximately 20 min after the beginning of the reaction. In this region, the evolution of the dielectric and kinetic parameters is extremely slow.

We know that the degree of conversion of the polymer can be increased by heating the sample after the photopolymerization. Thus the molecular dynamic changes occurring in the polymer were monitored through changes in ϵ' and ϵ'' during such a postcuring. Two similar experiments were carried out at $T = -8$ and −15 °C, and the resultant curves ϵ'' vs log(f/Hz) obtained for these experiments at fixed reaction times are plotted in Figures 12 and 13, respectively. Once the photopolymerization process appears to be effectively completed, following illumination at a fixed temperature T_{exp}, being −8 or −15 °C, and a postcuring of the polymer during approximately 2 h at T_{exp}, the sample was successively heated to higher temperature and cooled back to T_{exp} for the measurement. The dielectric absorption of the monomer, occurring between 10^2 and 10^5 Hz, is seen to decrease rapidly as the sample is illuminated. We notice that the values of $\epsilon''(\omega,t)$ do not change significantly between $t = 15$ min and 2 h, during the cure at −8 °C, and between $t = 45$ min and 2 h 30 min at $T = -15$ °C. The sample was heated to $T > T_{exp}$ during a few minutes and then cooled to T_{exp} and the dielectric measurement recorded. In both Figures 12 and 13, lower values of ϵ'' were observed at each frequency with increasing time. This heating−cooling process was repeated at higher temperature, allowing further postcuring, and the progressive decrease in ϵ'' curves was observed.

Our FTIR and ϵ'' data in Figures 11−13 show the increase in conversion when the sample is postcured by heating. These data show that small changes in conversion lead to large changes in molecular mobility in the system. Figures 12 and 13 represent, to our knowledge, one of the first systematic studies of the changes that occur in dipole mobility as a monomeric diolefinic compound is converted to a polymer network by bulk polymerization. It is appropriate to consider further the information given in the DRS data presented here, especially as seen in Figures 12 and 13.

As we have stated above it is well known that dipole relaxation in amorphous polymers comprises the α, β, and αβ relaxations and that α and β relaxations coalesce to form the αβ relaxation at high temperatures.[33,34] In conventional poly(*n*-alkyl methacrylate)s the strength of the β process may exceed that of the α process[1,33,34] showing that motions of the ester side groups are extensive without the motions of the backbone. In the present system the unreacted monomer shows a dynamic glass transition process which relaxes essentially all of the mean square dipole moments of the molecules (see Figure 1, $\epsilon_\infty \sim 3$), so we expect a small higher frequency process due to limited motions of backbone and side groups. The high-temperature permittivities seen in Figure 4 for a cured material are also ∼4, so it seems likely that the high-f process in the monomer would also occur in the cured polymer. Therefore the observations in Figures 12 and 13, in our low-frequency range, relate to changes in the relaxations of the ester dipoles and phenoxy dipoles that are present in both the unreacted monomer and the polymer.

Consider now the data of Figure 13 when the αβ process of the monomer is centered at log(f/Hz) ∼ 3.5. The formation of linear polymers and the subsequent network formation at the early stages of polymerization lead to a marked increase in macroscopic viscosity of the medium which would move the αβ process of the monomeric species present to lower frequencies. The other species present (long-chain molecules forming a dilute cross-linked network in the initial stages of polymerization) will be unable to undergo the free-tumbling motion (αβ process) of the unreacted monomeric species, but the chain backbones, free side chains, and cross-links will all contribute an α and β or αβ process of their own to the overall loss curve. In Figure 13 we see a shift of the broad loss peak to lower frequencies, accompanied by a marked decreased in its intensity, corresponding to removal of monomer and increased medium viscosity, as we have described. After 2 h 30 min in Figure 13 one broad loss peak is observed in our range. Further heating, as indicated in the figure

caption, reduces the magnitude of the peak and moves it to still lower frequencies. Inspection of the data of Figure 12 (studies at −8 °C) shows that the loss peak after 2 h is diminished in intensity and moves to still lower frequencies as the material is postcured by heating. In both experiments, the materials postcured show only a very broad loss feature in our range. This shows that molecular mobility of the ester groups becomes effectively inhibited in the cured material, which is a dense network of chains. Thus the motions of ester groups and the phenoxy groups are suppressed in the network polymer product.

It is not possible to decompose the overall loss curves of Figures 12 and 13 into contributions arising from free monomer, free side groups of the form $-C(CH_3)COOCH_2-CH_2OPh-C(CH_3)_2-PhOCH_2CH_2OOCCH{=}CH_2$ (S, say), and ester and phenoxy groups in chains that are linked at each end to the polymer network. Qualitatively, the data of Figure 12 suggest that after 2 h the process being observed is the β process due to motions of ester groups and phenoxy groups in free side chains of the type S above and that subsequent curves a−e see the removal of free side chains as the network densifies, giving little motion in the cured product. Similarly in Figure 13 curve a appears to be a β process that is lost on further curing. The broad nature of curve a in Figure 12 and curve a in Figure 13 suggests a β process, but it is possible that unreacted monomer moving in a highly viscous medium for these conditions of material may also make a contribution to the overall loss curves. In any event, Figures 12 and 13 clearly show that a mobile liquid system is transformed to a glassy polymer system as reaction proceeds.

We note that photopolymerization at the low temperatures used here is effective and glassy products are obtained but postcuring is required to complete the reaction. In future studies it would be desirable to incorporate the high-frequency range 10^5-10^{10} Hz so the loss peak for monomer at room temperature and above would occur in this range and as the photopolymerization occurred curves analogous to our Figures 12 and 13 would be obtained.

Conclusion

The study of the photopolymerization of the system bisHDMA, DMAEM, and CQ in DRS gives results that are qualitatively different from those of typical thermosetting systems during cure that are extensively described in the literature.[6−13,31,32] In the time domain, the shape of the dielectric curves $\epsilon'(\omega,t)$ vs time and $\epsilon''(\omega,t)$ vs time cannot be fitted by a single-time relaxation function or a convenient semiempirical equation involving a distribution of relaxation times. The permittivity falls suddenly for all the frequencies of measurement, as soon as the sample is illuminated (Figures 5−7). Large changes appear in $\epsilon'(\omega,t)$ during the polymerization process; depending on the experimental temperature, $\epsilon''(\omega,t)$ is seen to decrease or increase in our range. This behavior has been rationalized as follows. In the frequency domain, the $\alpha\beta$ relaxation peak is seen to shift slightly to lower frequency and to decrease significantly in magnitude. The dielectric loss peak moves from high to lower frequencies during the first minutes of the photopolymerization reaction; however, its magnitude has decreased strongly. FTIR studies show that the initiation and the propagation are extremely rapid. The bulk polymerization occurs in a few minutes, when the extent of the reaction increases dramatically, and then it progresses only slowly with time. The final degree of conversion obtained at the experimental temperature can be increased by postheating the sample, whereas some further illuminations with light do not change significantly the chemical or dielectric properties of the newly formed polymer. Therefore by heating the sample, the rigidity of the network decreases slightly and the extent of the reaction is increased by a few percent through diffusion of reactive species to radical sites and vice versa. This postcuring leads also to large changes in the dielectric properties of the polymer. The influence of the thermal treatment of the polymer on the loss peak has been studied. A significant decrease and shift of the loss curve to lower frequencies has been observed as a result of the postcuring of the polymer.

These experiments demonstrate the usefulness of the dielectric relaxation spectroscopy technique in studies of photocuring systems. The present work shows clearly that photopolymerization of a dimethacrylate monomer can be investigated by following the remarkable changes in the permittivity and the loss peak of the sample as the reaction proceeds (see, e.g., Figures 12 and 13). Small changes in the chemical structure, as those observed using FTIR during the postcuring of the acrylic polymer, correspond in the present case to large changes in the dielectric properties, which are readily observed and rationalized in terms of molecular mobility.

Acknowledgment. We are pleased to acknowledge an Erasmus Grant to J. Fournier and EPSRC for support. We also wish to thank Dr. D. Brown of London University (Guys Hospital) for providing us with commercial dental resins for preliminary studies to those reported here and Dr. I. Lancaster (Pilkington Group Research) for his helpful discussions. We thank Mr. N. Edney for the loan of an Elipar lamp for our initial studies and Mr. G. A. Aldridge for technical support.

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MA9613190