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Reorientational Dynamics and Intermolecular Cooperativity in Reactive Polymers. 2. Multifunctional Epoxy−Amine Systems

Saša Andjelić, Benjamin Fitz, and Jovan Mijović*

Department of Chemical Engineering, Chemistry and Materials Science,
Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201

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ABSTRACT: An examination was carried out of the reorientational dynamics of dipoles during the network formation in multifunctional epoxy−amine systems. Experimental results were generated by simultaneous dielectric and Fourier transform infrared (FTIR) measurements. The observed changes in reorientational dynamics during the advancement of reactions were utilized to (1) describe the origin of the α relaxation during the network formation, (2) propose a methodology for the evaluation of the kinetics of network formation, and (3) advance an interpretation of network dynamics in terms of intermolecular cooperativity based on the interplay between molecular and dielectric architecture. Fragility or cooperativity plots proved most informative in relating intermolecular cooperativity to the molecular characteristics of the growing network.

Introduction

A detailed description of the general background to this topic was presented in the first part of this paper, which dealt with epoxy−amine model systems.[1] In this part of our study we examine a series of network-forming multifunctional epoxy−amine formulations.

Although dielectric cure monitoring has been a subject of interest to various groups,[2−6] fundamental investigations aimed at correlating the reorientational dynamics of dipoles with the molecular origin of relaxation processes and the intermolecular cooperativity in a reactive polymer network remain scarce. In reviewing the background of relevance to this specific theme, we shall cite only select examples of key references that examine dipole dynamics during cross-linking and are distinguished by the originality of their concepts.

The pioneering attempts at fundamental modeling of cure from dielectric measurements of dipole relaxations were reported in several papers by Seferis and coworkers.[7,8] They recognized and clearly expressed the need to relate the dielectric signal to the change of some fundamental property of polymer network during cure. The essential feature of their model is a correlation between complex permittivity (dielectric constant and loss) and network parameters (viscosity and degree of cure). The analysis of the dielectric response due to dipole relaxation is based on the well-known Havriliak−Negami equation, with a mean relaxation time that is allowed to vary as a function of degree of cure. The mean relaxation time is related to the viscosity by invoking analogy to the classic Debye expression for small spherical molecules in the liquid state. The viscosity, in turn, is correlated to the degree of cure by a multiparameter equation reported earlier by Seferis et al.[9] Good agreement was found between the measured and predicted results, despite the empirical nature of the model and an oversimplified physical picture. Mangion and Johari[10,11] studied dipolar relaxations during epoxy−amine cure and utilized the Kohlrausch−Williams−Watts (KWW) equation to describe their results. The KWW parameter β was replaced by the curing parameter γ, which was related to the progress of cure. Unfortunately, their results were obtained almost exclusively at a single frequency. Butta et al.[12] obtained high-frequency data during epoxy−amine cure and then arbitrarily selected a single frequency in the low-gigahertz range at which they followed the variations in dielectric constant. An excellent recent study by Fournier et al.[13] examines epoxy−amine cure in the frequency domain and seeks to correlate the evolution of dielectric properties to the reaction kinetics determined by differential scanning calorimetry. A particularly interesting aspect of their work was the definition of the conditions under which the dielectric loss peak in the frequency domain coincides with the diffusion-controlled kinetic regime.

The cooperative nature of a reactive system was first considered by Matsuoka et al.,[14] who proposed a model for the curing reactions of epoxy resins based on the similarity between chemical cross-linking and structural relaxation in glassy thermoplastics. During cross-linking, the configurational entropy will decrease while the temperature (T^*) below which the equilibrium state cannot be reached and the relaxation time will increase. The authors calculate T^* by assuming that it varies in proportion with the degree of cure and then substitute the calculated value in the Adam−Gibbs expression,[15] which is based on cooperative segmental motions, to obtain the relaxation time. The relaxation time, on the other hand, is contained within an "apparent" rate constant and is thus related to the reaction kinetics via a first-order expression. The Adam−Gibbs expression and a distribution spectrum obtained from dielectric relaxation of poly(vinyl acetate) were employed to model the curing process for both isothermal and nonisothermal histories. Diffusion-controlled epoxy−amine kinetics were also studied by Cole et al.[16] and Deng and Martin.[17,18]

Important contributions to the development of correlations between chemical structure and intermolecular cooperativity were made by various authors.[19] In general, segmental relaxation times in polymers with symmetrical and flexible backbones display a near-Arrhenius temperature dependence, while an increase in steric hindrance and rigidity lead to strong intermolecular cooperativity and a non-Arrhenius response. Roland[20] studied poly(vinylethylene) networks cross-linked to a different degree of dicumyl peroxide and

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* To whom correspondence should be addressed.

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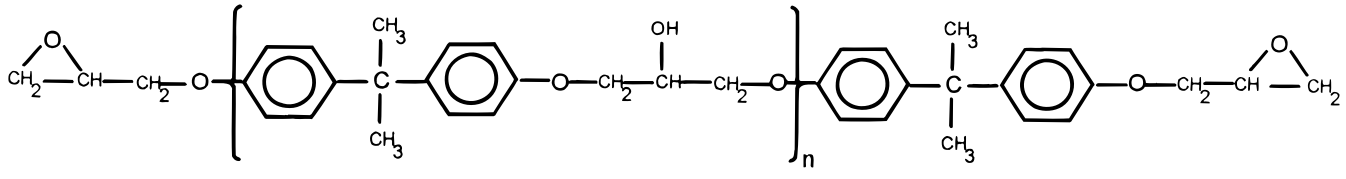
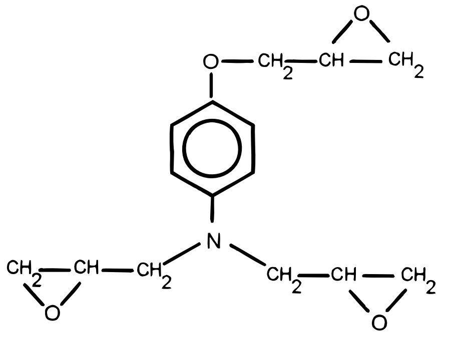
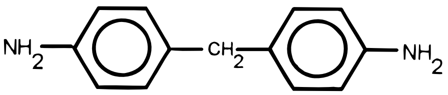
Table 1. Chemical Structures of Compounds Used in this Study



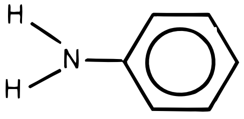
Diglycidyl Ether of Bisphenol A (DGEBA)



Triglycidyl ether of para-aminophenol (TGEPA)



Methylene dianiline (MDA)



aniline

examined the effect of constraints on the local segmental motions by dielectric spectroscopy. An increase in the cross-link density resulted in a higher glass transition temperature and a broader segmental relaxation function. Cooperativity plots of the segmental relaxation times indicate that cross-linking enhances intermolecular coupling and increases the noncooperative relaxation time, τ_0. We stress, however, that Roland[20] did not examine the effect of chemical reaction and the variations in the type and concentration of dipoles on intermolecular cooperativity.

The principal objective of this study is to establish how the changes in reorientational dynamics during the curing process can be utilized to elucidate the origin of relaxation processes in the network, the kinetics of network formation, and the intermolecular cooperativity in the growing network.

Experimental Section

Materials. Three multifunctional epoxy–amine formulations, two network-forming and one linear polymer-forming, were prepared and investigated. The two network-forming formulations were (1) diglycidyl ether of Bisphenol A, or DGEBA (Epon 825, Shell Chemical Co.), and methylenedianiline, or MDA (XU HY 205, Ciba-Geigy); and (2) triglycidyl ether of *p*-aminophenol, or TGEPA (Araldite 0510, Ciba-Geigy), and MDA. The linear polymer-forming formulation consisted of DGEBA and aniline (Aldrich). The chemical structures of all compounds are shown in Table 1. All formulations contained the stoichiometric amounts of epoxy group and amine hydrogen. The components were mixed at an appropriate temperature, heated until a clear mixture was obtained, and immediately tested under a series of conditions of different frequencies, temperatures, and times.

Techniques. Dielectric Spectroscopy. A detailed description of our experimental facility for dielectric measurements is given in the first part of this communication.[1]

Infrared Spectroscopy. Infrared spectroscopy was performed using a Nicolet Magna-IR system 750 spectrometer with spectral range coverage from 15 800 to 50 cm^{-1} and the Vectra scanning interferometer with better than 0.1 cm^{-1} resolution. Near-infrared (NIR) data were obtained using a calcium fluoride beam splitter, a white light source, and an MCT detector cooled with liquid nitrogen. All spectra were measured at 4 cm^{-1} resolution using 35 scans. A silica type optical fiber was used for in-situ monitoring of reactions in the remote mode. The entire apparatus was designed and assembled in our laboratory and has been described in more detail elsewhere.[21]

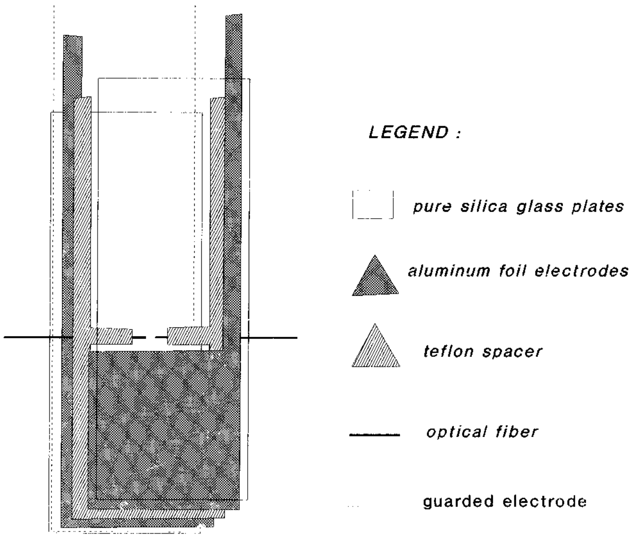


Figure 1. Schematic of the disposable measurement cell for simultaneous FT-IR and dielectric spectroscopy.

Simultaneous Dielectric/Remote Near-Infrared Spectroscopy. The experimental setup for simultaneous dielectric and infrared spectroscopy combines our dielectric and near-infrared (NIR) assemblies. The common element that ties the two assemblies together is a disposable sample cell, shown schematically in Figure 1. The cell consists of two glass slides separated by a Teflon spacer, with thin aluminum electrodes placed on the inside surface of each glass slide. A special high-temperature adhesive was used to bond Teflon to glass. A guarded electrode is introduced to minimize the fringe fields and eliminate the possibility of surface conduction. The

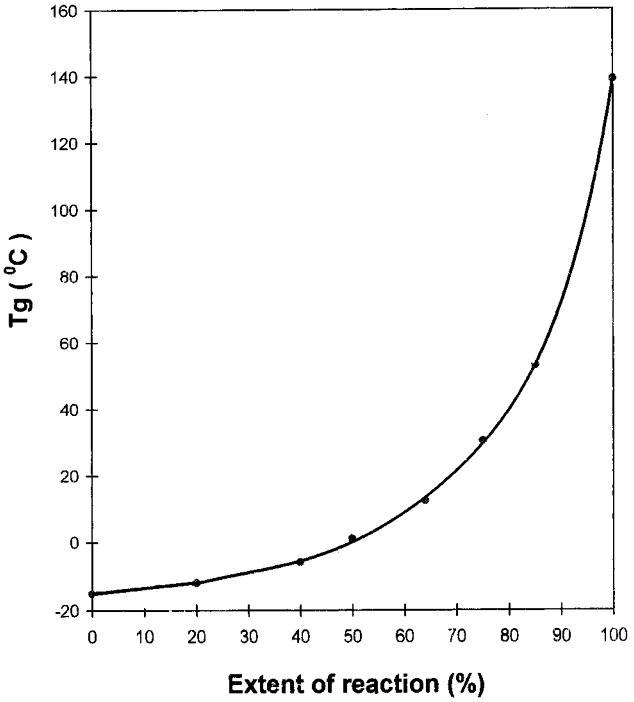


Figure 2. DSC T_g as a function of degree of cure for DGEBA−MDA formulation.

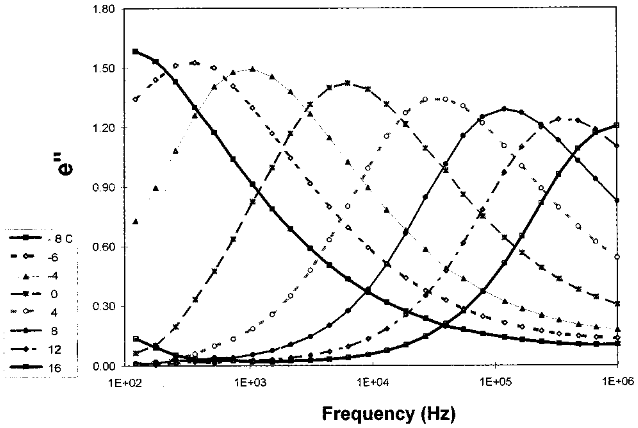


Figure 3. Dielectric loss in the frequency domain with temperature as a parameter for the DGEBA−MDA mixture prior to the onset of chemical reactions.

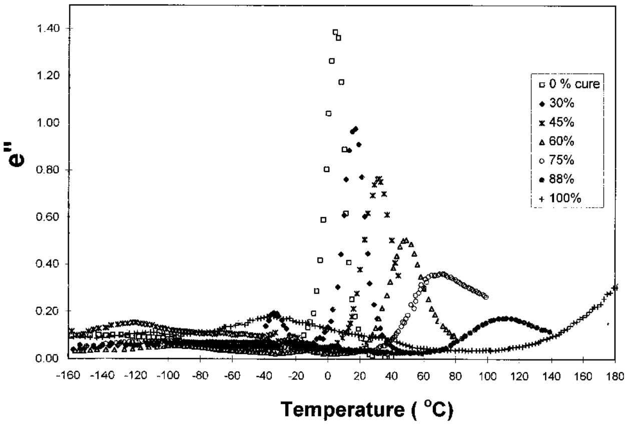


Figure 4. Dielectric loss as a function of temperature with extent of reaction as a parameter for DGEBA−MDA formulation.

receiving and transmitting legs of optical fiber were inserted through the Teflon spacer and centered inside the cell just above the electrodes. The measurements were conducted in a transmission mode.

Differential Scanning Calorimetry. Some supporting evidence was obtained from DSC using TA Instrument Co. DSC model 2920 at a heating rate of 10 °C/min.

Results and Discussion

1. Reorientational Dynamics and Network Formation.

We begin our discussion by examining the dielectric response before and during the cross-linking of a multifunctional epoxy−amine formulation composed of the stoichiometric amounts of diglycidyl ether of Bisphenol A (DGEBA) epoxy prepolymer (degree of polymerization, $x = 0.1$) and a liquid curing agent, methylenedianiline (MDA). The results are presented in the frequency and temperature domains. The molecular mechanism and the kinetics of this reaction have been elucidated by Fourier transform infrared (FTIR) spectroscopy[22] and other methods[23] and will not be revisited here. Prior to dielectric measurements, the kinetic data obtained from the FTIR investigation were combined with the results of differential scanning calorimetry (DSC) and used to establish a correlation (Figure 2) between the "calorimetric glass transition temperature" and the extent of reaction. No reactive epoxy groups remain in the network at 100% conversion.

The reorientational dynamics of a neat DGEBA prepolymer were described in detail in part 1 of this study and the moelcular origin of α relaxation was assigned to the segmental motions associated with the dielectrically active terminal epoxy groups.[1] The contribution of the phenoxy groups in DGEBA is quite small. We now examine the dielectric response of a stoichiometric mixture of DGEBA and MDA prior to the onset of chemical reactions.

Dielectric loss in the frequency domain with temperature as a parameter for a nonreacted (0% conversion) mixture is shown in Figure 3. The intensity of the loss peak decreases with increasing temperature, shifts to higher frequency, and displays a strongly non-Arrhenius response between 100 Hz and 1 MHz. A non-Arrhenius behavior was also observed in the unreacted model epoxy−amine mixture. In both instances, the observed response is a consequence of the specific dipolar interactions introduced upon mixing. These interactions impose conformational restrictions to the mobility of dielectrically active species, causing the observed non-Arrhenius response. With increasing temperature, however, these restrictions are relaxed and the reorientational ability of dipoles is enhanced. This mechanism is corroborated here by FTIR spectroscopy, which reveals an increase (with increasing temperature) in the absorption intensity of dipole-containing groups (epoxy, amine) that partake in specific interactions. On the other hand, the absorption intensity of the moieties (e.g., benzene rings, methylene groups) that do not engage in specific interactions display a characteristic decreasing trend with increasing temperature.

Changes in the dielectric response during cure were considered next. The salient features of the dielectric loss in the temperature domain for samples at various stages of cure are recapped in Figure 4. All spectra in this figure were generated at a constant frequency of 25 kHz. The breadth of α relaxation increases and its loss peak shifts to higher temperature as the cure progresses. The intensity of α relaxation decreases; this can be readily seen in the ϵ' versus T plots (not shown here) and can be quantified from ϵ'' versus $1/T$ plots, as described elsewhere.[24] In the fully cured (100%) sample, α relaxation is completely suppressed and the observed

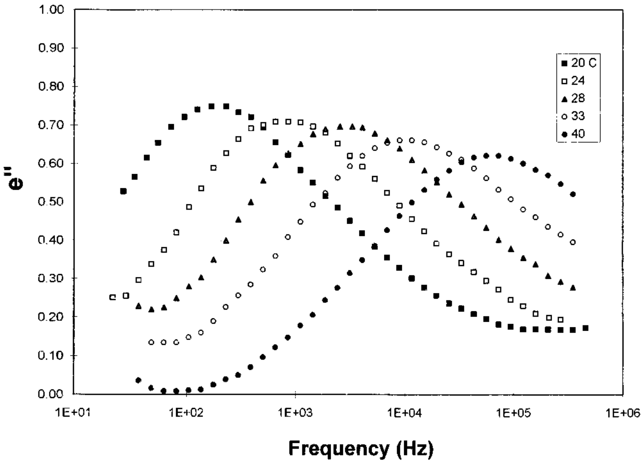


Figure 5. Dielectric loss in the frequency domain with temperature as a parameter for DGEBA–MDA formulation reacted to 50%.

increased in dielectric loss, which starts at about 120 °C, results from the conductivity due to migrating charges, which dominates the high-temperature response. For instance, the advancement of cure was accompanied by an increase in the breadth and intensity of the hydroxyl peak (β relaxation) located at about −30 °C, as well as a continuous decrease in intensity and a shift to higher temperature of the peak due to the sub-T_g motions of epoxy rings (γ relaxation).

Frequency sweeps were performed next on a series of samples of a precisely known degree of cure. An example of dielectric loss in the frequency domain, with temperature as a parameter, is shown in Figure 5 for a DGEBA–MDA sample cured to 50% conversion. A systematic decrease in the loss peak intensity and a shift to higher frequency with increasing temperature were common to all samples at all degrees of cure. The effect of the advancement of cure on the dielectric loss can be readily appreciated from the composite plot of Figure 6. Each curve in this figure was obtained at a different degree of cure and temperature and was shifted along the frequency axis so that the peak maxima approximately coincide. It is obvious that the intensity of dielectric loss diminishes with advancing cure. The observed decrease in α relaxation during cure is caused primarily by the disappearance of dipoles associated with epoxy (throughout cure) and primary amine (early stages of cure) groups, and we shall return to this argument later in the text.

Date obtained from the frequency sweep of each partially cured sample were used to construct the plots of frequency at maximum loss as a function of reciprocal temperature and to calculate the activation energy. An astonishing observation was made in that all except two partially cured formulations were characterized by an Arrhenius response at frequencies between 100 Hz and 1 MHz (at still higher frequencies and temperatures chemical reactions continue and α and β relaxations overlap). The two exceptions were the as-mixed (0% cure) and a 61% cured formulation, which displayed a strong non-Arrhenius response. The activation energy for each partially cured sample was calculated and plotted as a function of extent of reaction in Figure 7. The shape of the resulting curve is most curious, suggesting the existence of three different regimes (marked A, B, and C in Figure 7) of dipole dynamics during network formation. We remind the reader that the reaction between DGEBA and MDA proceeds according to a general two-step scheme shown in Figure 8 of the preceding paper,[1] except that a cross-linked polymer network is now formed. The mechanism and kinetics of cure have been reported earlier;[22,23] for the purpose of the discussion that follows it is sufficient to reiterate that an epoxy group reacts with a primary amine to form a secondary amine, which, in turn, reacts with another epoxy to give a tertiary amine. In regime A (Figure 7), which extends to approximately 35% cure, the dominant reaction in the mixture is between epoxy and primary amine groups and the principal product is a linear chain of continually increasing molecular weight. This mechanism has been corroborated by ample evidence from infrared spectroscopy[25] and high-performance liquid chromatography (HPLC).[26] The observed increase in activation energy with increasing chain length is also a well-established characteristic of

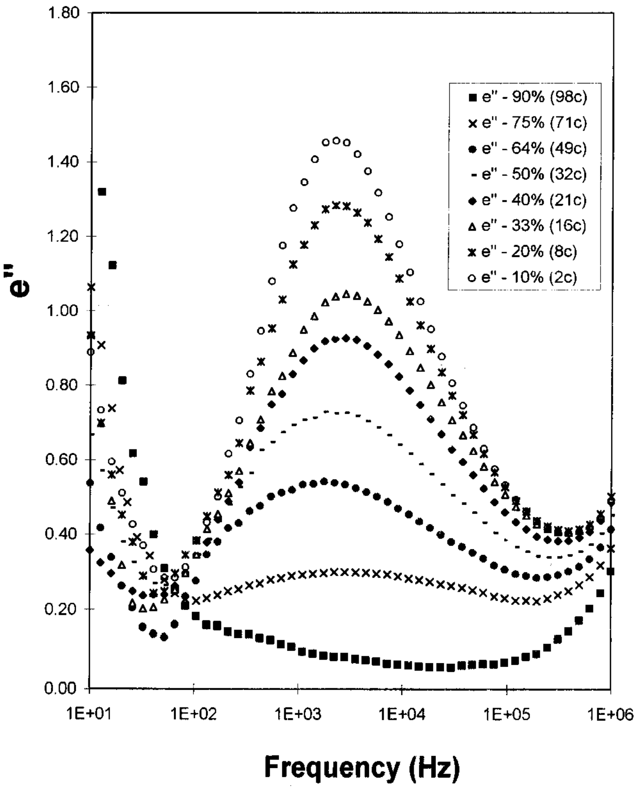


Figure 6. Dielectric loss in the frequency domain with extent of reaction as a parameter for DGEBA–MDA formulation. The temperature for all curves is chosen such that T_g/T is a constant.

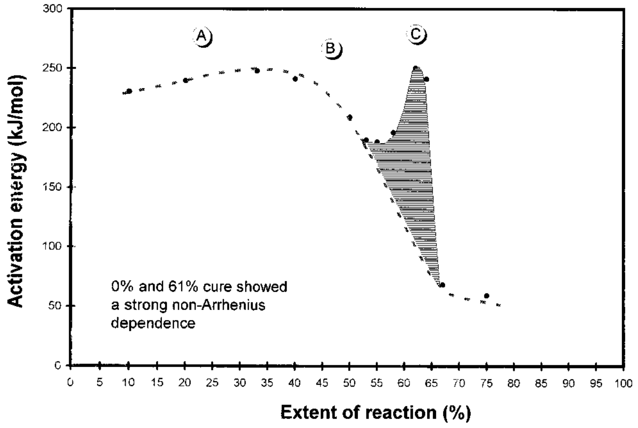


Figure 7. Activation energy versus extent of reaction for DGEBA–MDA formulation. Zones A, B, and C indicated on plot are discussed in text.

a number of homologous series of organic molecules (e.g., alcohols).

Above approximately 35% cure we enter regime B, where secondary amine−epoxy reactions become important and a cross-linked network begins to form. Dipoles that contribute strongly to α relaxation (mostly epoxy and some primary amine) continue to be replaced by less dielectrically active secondary and tertiary amines and hydroxyl groups. At this stage of cure it is important to establish how the dynamics of dipole relaxation are influenced by cross-linking. The rotational movement of each terminal epoxy group on a molecule whose other end is attached to a cross-link site (i.e., tertiary amine) will be further restricted by the other two chains connected to the same cross-link site. Therefore, a direct consequence of the proliferation of cross-link sites throughout the growing network would be a decrease in the interactions between the epoxy dipole and other dipoles, and a lower activation energy (and cooperativity, as will be shown later) of the α relaxation process. For clarity, we term this phenomenon "dipole dilution effect" and submit that it is an inherent characteristic of epoxy cure that links dipole dynamics with network formation. Intuitively, one would expect this trend to persist with continuing cross-linking, giving rise to a further decrease in activation energy along the "expected" dashed line in Figure 7. But that does not happen; instead, a most peculiar change in the activation energy is noted between about 55 and 67% cure. We first observed a steep increase in activation energy between 55 and 62% conversion and then an abrupt drop to 67% conversion, as shown in Figure 7. We stress that the reliability and reproducibility of the measured data have been firmly established by repeated runs and that analogous observations were made in other multifunctional formulations, as will be shown later in the text. Here is what we believe happens in this conversion range. The activation energy reverses its decreasing trend at around 55% cure, begins to increase, and reaches a maximum at approximately 62% conversion. We note that the gel point in this system, as determined from IR spectroscopy, occurs at about 60% conversion.[27] Two important phenomena, one physical and the other chemical in nature, occur on the molecular level as the network approaches the gel point. The physical change is manifested as a decrease in the distance (densification) between the polar groups in the mixture, whereas the chemical change is associated with the formation of a new type of hydrogen-bonding complex. The emergence of this three-dimensional hydrogen-bonded complex is contingent upon reaching a critical combined concentration of epoxy, amine, and hydroxyl groups, and its existence has been confirmed by spectroscopic evidence.[28] The molecular composition of a hydrogen-bonded complex is likely to vary throughout the mixture because of a multitude of possible complex structures involving hydroxyl, epoxy, and/or amine groups. The most likely scenario, we believe, includes cyclic structures composed of epoxy and/or amine groups and bridged by hydroxyl groups, as shown in a two-dimensional schematic of Figure 8. Once formed, these complexes increase the steric hindrance and intermolecular rigidity of the network, while at the same time impeding the reorientational motions of terminal epoxy groups that are at the origin of the α relaxation process at this stage of cure. This, in turn, leads to the creation of a higher activation energy state. The lifetime of complex(es), however, is confined to a narrow conversion range. With a continuation of reactions and the concomitant decrease in the concentration of epoxy and amine groups, the critical conditions for the coexistence of epoxy, amine, and hydroxyl groups in a three-dimensional hydrogen-bonded structure are not met anymore, and the three-dimensional complex breaks up. The extreme sensitivity of the complex to the chemical state of the matter is exemplified by the precipitous drop in activation energy above 64% conversion. The shaded area in Figure 7 highlights the difference between "intuitively expected" and measured activation energy in the conversion range between about 55 and 67%.

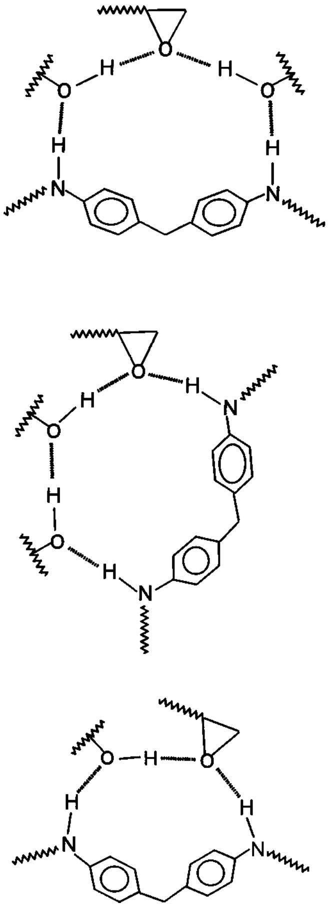


Figure 8. Two-dimensional schematic view of cyclic hydrogen-bonded complexes that co-involve hydroxyl, epoxy, and/or amine groups.

A sample cured to 61% conversion was of particular interest to us because of its anomalous response. We recall that this was one of the two samples in which a strong non-Arrhenius behavior was noted, as seen in Figure 9. But was that non-Arrhenius response specific to this particular conversion (61%) and, if not, over what conversion range it did persist? This query was addressed by subjecting the 61% cured sample to additional incremental cure. By increasing the temperature to 45.5 °C, we increased the extent of reaction by (only) 1%, in an effort to establish if such a small advancement in cure would have an effect on the activation energy of the α relaxation process (our remote near-IR setup enables us to monitor the degree of cure with such high precision). Had the additional excursion to 45.5 °C not increased the degree of cure, the activation energy at that temperature would have fallen on the extrapolated curve in Figure 9. Instead, a dramatically different result was obtained; the activation energy of the sample, now at 62% conversion, increased notice-

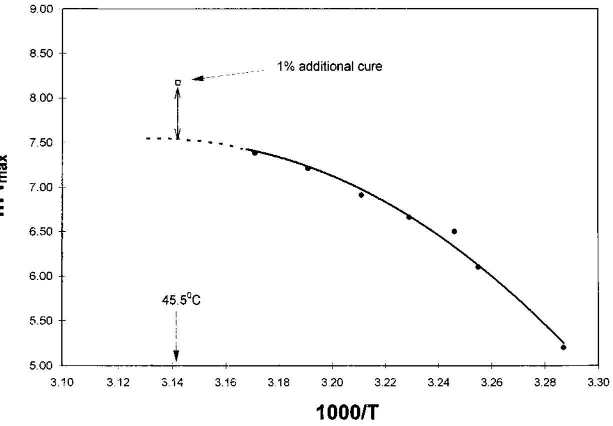


Figure 9. ln frequency at dielectric loss maximum ($f_{\max}$) versus 1/T for DGEBA−MDA formulation reacted to 61% conversion. Dahsed line indicates expected values of $f_{\max}$ at elevated temperatures, were further reactions not to occur. An additional datum point indicated on the chart is for DGEBA−MDA formulation reacted to 62%.

ably and reverted to the Arrhenius form! But what makes the conversion of 61% so distinctly different from those just below and/or above it? The answer is that at 61% conversion the combined concentration of epoxy, amine, and hydroxyl groups, and their proximity caused by the densification of the network, create the conditions that are just right for the formation of the above-described hydrogen-bonded complexes, which, in turn, strongly affect the relaxation dynamics. An important question is whether it is feasible that a cross-linked network should exhibit unique dipole dynamics at a specific conversion near (or at) the gel point? We believe so. In this regard, it is also worth noting that a highly specific response observed at the gel point and not in its immediate vicinity has a precedent in the work by Winter and Scanlan.[29] These authors employed dynamic mechanical measurements to study the cross-linking of various divinyl-terminated poly(dimethylsiloxane) prepolymers with a tetrafunctional cross-linker, tetrakis(dimethylsiloxane)silane and *cis*-dichlorobis(diethyl sulfide)platinum as a catalyst. The interpolated value of the phase angle was found to be independent of frequency at the critical gel time. A short time before the gel point, however, the sample was in a liquid state and the phase angle showed a downward trend in the (decreasing) frequency domain. Similarly, a sample cured just beyond the gel time showed an upward trend in the (decreasing) frequency domain. The pertinent point in support of our claim is that a chemically cross-linked network can respond uniquely to a dynamic mechanical field at gel point only, but not just above or below it.[29]

Although the findings shown in Figure 7 have been repeatedly verified experimentally, we were not sure if the observed behavior was entirely specific to the DGEBA−MDA system or had a broader validity. To answer that question, we decided to examine another multifunctional epoxy−amine formulation. We chose a stoichiometric formulation composed of a trifunctional epoxy resin (triglycidyl ether of *p*-aminophenol or TGEPA) and methylenedianiline (MDA). The mechanism and kinetics of cure of this formulation have also been recently investigated in our laboratory, and the results have been reported.[28,30] Hydrogen-bonded complexes were present in this system as well,[28] and the gel point was detected (by FTIR) at 40% cure (Flory's theoretical value is 41%). We performed simultaneous dielectric and NIR measurements and conducted frequency sweeps on a large number of partially cured TGEPA−MDA samples. The observed trends were analogous to those in DGEBA−MDA formulation and are not shown here. All partially cured TGEPA−MDA formulations were characterized by an Arrhenius response in the frequency−temperature window at the conditions of this study. The only exception was the as-mixed (0% cure) formulation, which displayed a characteristic non-Arrhenius response for the same reasons as its DGEBA−MDA counterpart. The activation energy was calculated for each partially cured TGEPA−MDA sample from the data in Figure 10 and then replotted as a function of extent of reaction in Figure 11. The plot in Figure 11 is again characterized by the presence of three different regimes (see discussion of Figure 7) of dipole dynamics during crosslinking. The shaded area in Figure 11 highlights the difference between "intuitively expected" and measured activation energy. The analogy in the observed response in bi- and trifunctional formulations is striking. The characteristic abrupt increase in the calculated activation energy was observed at the conversion that corresponds to the gel point, as determined by IR spectroscopy. Although the width and the magnitude of the activation energy jump (enclosed by the shaded area in Figure 11) for TGEPA−MDA formulation were not as pronounced as in the DGEBA−MDA case (Figure 7), it is clear that the same underlying phenomenon is responsible for the

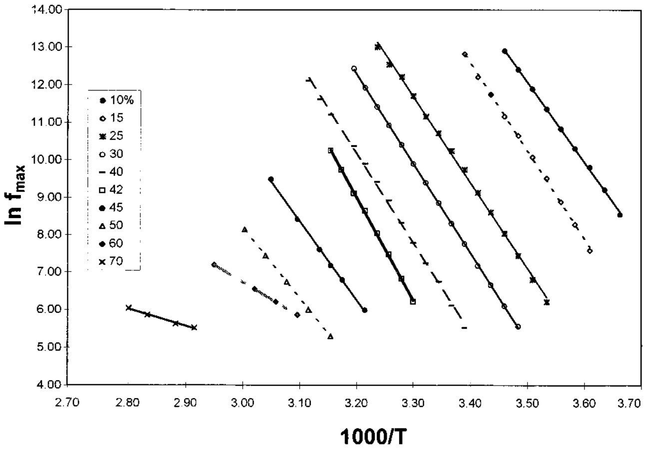


Figure 10. ln frequency at dielectric loss maximum ($f_{\max}$) versus 1/T for TGEPA−MDA formulation with degree of cure as a parameter.

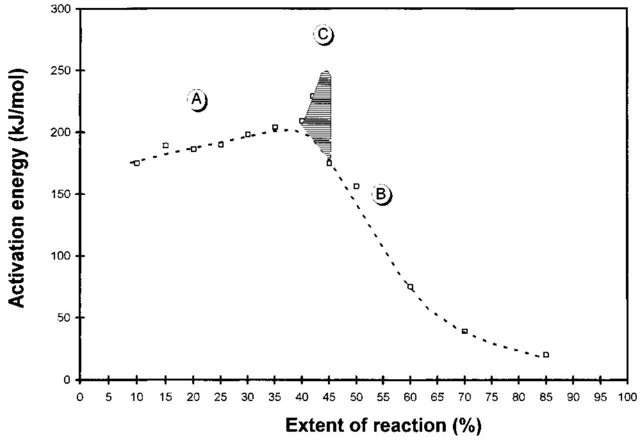


Figure 11. Activation energy versus extent of reaction for TGEPA−MDA formulation. Zones A, B, and C indicated on plot are discussed in text.

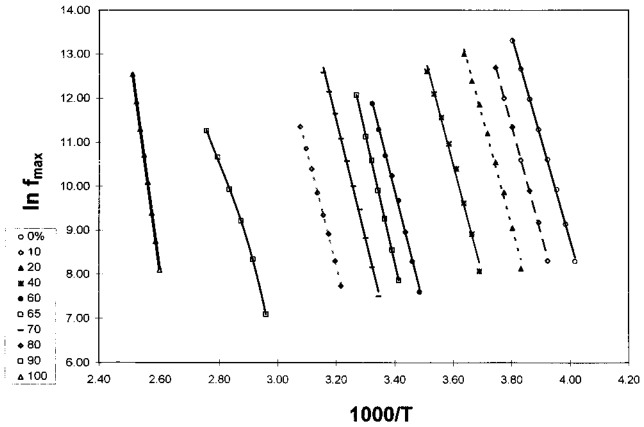


Figure 12. ln frequency at dielectric loss maximum (f_{max}) versus $1/T$ for DGEBA−aniline formulation with degree of cure as a parameter.

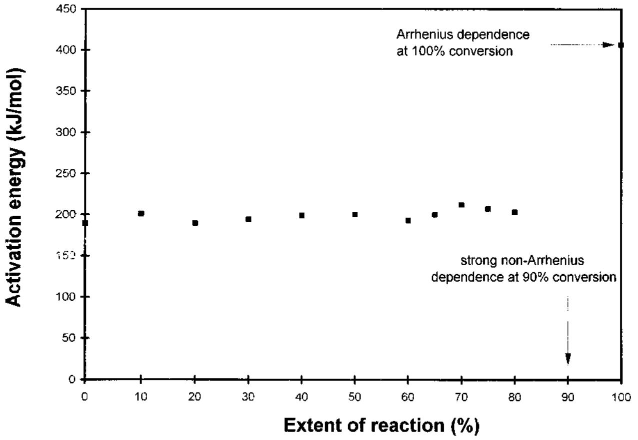


Figure 13. Activation energy versus extent of reaction for DGEBA−aniline formulation. Extent of reaction where non-Arrhenius behavior is observed is indicated by an arrow on the plot.

observed trends in both systems. We now believe that the experimentally observed sudden increase and a subsequent drop in the activation energy in the vicinity of gel point represent an inherent characteristic of the network-forming epoxy−amine formulations.

But how about an epoxy−amine formulation that reacts to form a linear polymer instead of a cross-linked network and, hence, does not gel? To test that, we examined a formulation composed of the same DGEBA prepolymer ($x = 0.1$) and aniline, the model aromatic amine utilized in part 1 of this study. The reaction between these two bifunctional components (DGEBA and aniline) results in the formation of a linear chain. We again employed simultaneous dielectric and NIR measurements and conducted frequency sweeps of a large number of partially reacted samples. This time all partially reacted formulations up to 90% conversion were characterized by an Arrhenius response at frequencies between about 1 kHz and 1 MHz, as shown in Figure 12. The activation energy was calculated for each partially reacted sample and plotted as a function of extent of reaction in Figure 13. No significant change in the activation energy was noted up to 80% conversion. The 90% reacted sample displayed a strong non-Arrhenius response, while the fully reacted sample had a considerably higher activation energy than the partially reacted samples. The relatively constant activation energy during the first 80% of the reaction can be rationalized in terms of the interplay between molecular and dielectric architecture in the reactive mixture. An increase in the molecular weight during polymerization augments rigidity and steric hindrance and alters the molecular architecture in the direction of higher cooperativity and activation energy. Dielectric architecture, on the other hand, contributes to lower cooperativity and activation energy during reaction, as the dipoles associated with epoxy and primary amine groups are gradually depleted and less dielectrically active components are generated during reaction. The term “dielectric architecture” was defined in the preceding paper[1] and is meant to include the type and concentration of dielectrically active species (mostly dipoles) as well as the various specific interactions that can affect the reorientational dynamics of dipoles. The effects of molecular and dielectric architecture on the cooperativity of the reactive mixture up to 80% conversion are approximately of equal strength but opposite sign, and hence their interplay gives rise to a relatively unchanged activation energy. But at 90% conversion, where epoxy groups are almost completely consumed, the cooperativity requirements for α relaxation become dominated by the type and concentration of relaxing dipoles. We stress that at this point the molecular origin of α relaxation has changed greatly from its initial form. The contribution to α relaxation at 90% conversion comes from the small remaining fraction of unreacted epoxy groups and a much larger number of less dielectrically active glycidyl ether moieties. Dielectrically, this stage of cure can be viewed as a transition region characterized by the coexistence of two different relaxation mechanisms with similar time scales. Upon further reaction, the activation energy increases abruptly and almost doubles in value in going from 80 to 100% conversion. But in contrast to the cross-linked systems, where α relaxation all but disappears at 100% conversion, the intensity of the α relaxation peak in a fully reacted DGEBA−aniline sample decreases only to about one-third of its initial value. Reorientational dynamics of dielectrically active species are restricted to a lesser degree in non-cross-linked systems, as already shown in the case of the model epoxy−amine system described in part 1 of this communication.[1]

2. Reorientational Dynamics and Reaction Kinetics. We now turn our attention back to the multifunctional network-forming formulations. Data obtained from the frequency sweeps of a partially cured DGEBA−MDA and/or TGEPA−MDA sample were replotted in the form of normalized dielectric loss versus frequency. All samples, with the exception of DGEBA−MDA reacted to 61% conversion, were “dielectrically simple”, i.e., giving loss curves whose shapes were independent of temperature. Examples of such plots for DGEBA−MDA samples cured to 5%, 33%, and 64% conversion are shown in Figure 14A−C, respectively. Jonscher’s power law parameters[31] m and n were calculated for a number of partially cured DGEBA−MDA and TGEPA−MDA samples and were found to vary in a systematic manner, as seen in Table 2. A very interesting and hitherto not reported observation was made when we attempted to correlate the measured dielectric response with the reaction kinetics determined by near-IR spectroscopy. A careful reexamination of all normalized curves (see Figures 14A−V) revealed that a relative change in the width at half-height of the normalized loss peak was in excellent agreement with the degree of cure determined by near-IR. A comparison of the dielectric and near-infrared degree of cure as a

Table 2. Jonscher's Parameters for Reactive DGEBA–MDA and TGEPA–MDA Systems[a]

extent of reaction (%) based on NIR data		m		$1 - n$	
DGEBA–MDA	TGEPA–MDA	DGEBA–MDA	TGEPA–MDA	DGEBA–MDA	TGEPA–MDA
0	0	0.87	0.60	0.50	0.42
5		0.77		0.49	
10	10	0.75	0.47	0.48	0.39
20	20	0.67	0.41	0.45	0.36
33	30	0.60	0.32	0.43	0.31
40	40	0.55	0.26	0.42	0.26
50	50	0.54	0.225	0.37	0.22
64		0.48		0.33	

[a] MDA parameters: $m = 0.74$; $1 - n = 0.53$.

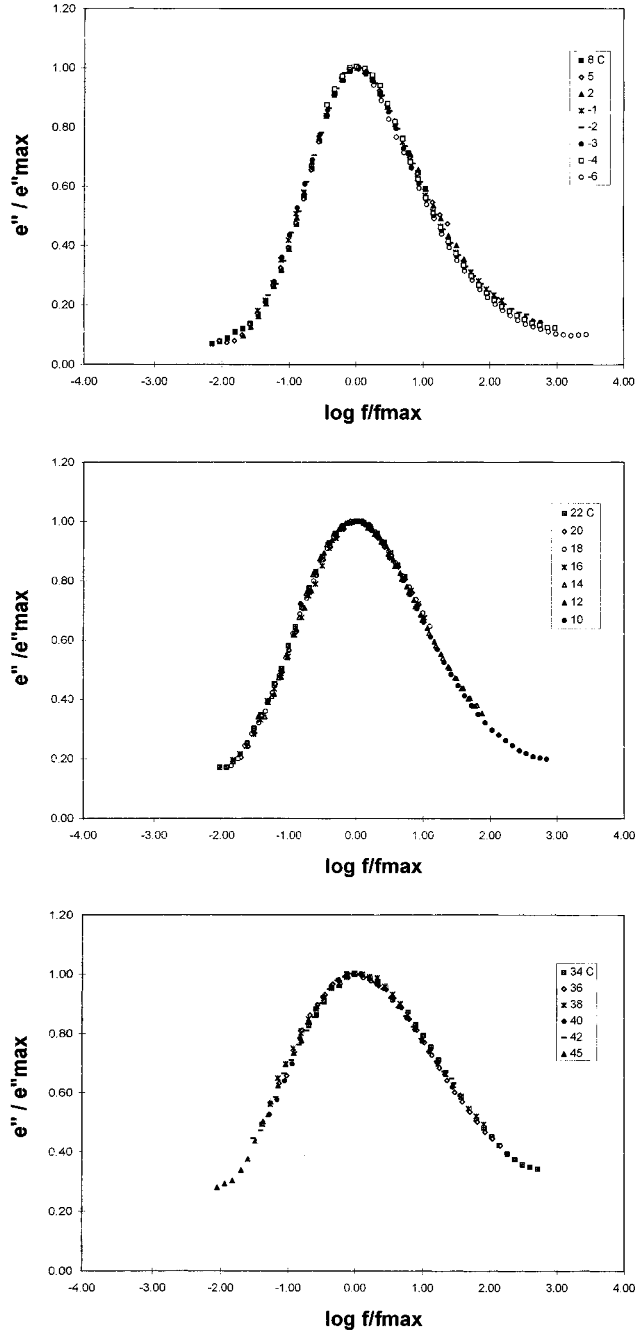


Figure 14. Normalized dielectric loss versus normalized frequency with temperature as a parameter for DGEBA–MDA formulation reacted to (A) 5%, (B) 33%, and (C) 64%.

function of reaction time for DGEBA–MDA and TGEPA–MDA formulations, is presented in Table 3.

Table 3. Comparison between Degree of Cure (%) Calculated from the NIR and Dielectric Data for DGEBA–MDA and TGEPA–MDA Curing Systems

NIR		half-bandwidth increase of the normalized relaxation peak	
DGEBA–MDA	TGEPA–MDA	DGEBA–MDA	TGEPA–MDA
10.0	10.0	10.7	9.3
20.0	20.0	19.4	19.8
33.0	30.0	29.5	31.4
40.0	40.0	38.0	39.8
50.0	50.0	50.0	49.4
64.0		66.5	

This methodology constitutes a novel way of quantifying the rate of formation of a thermoset network from dielectric measurements of dipole dynamics. Moreover, since the molecular origin of α relaxation can be assigned to (a) specific molecular entity(ies), such as epoxy and/or amine groups, our findings suggest a possibility that dielectric measurements of dipole dynamics in multifunctional epoxy–amine formulations during cure could be useful in the mechanistic kinetic studies.

An alternative method of data analysis consists of fitting the data to a stretched exponential (or KWW) expression[32]

$$\Phi(t) = \exp[-(t/\tau)^{\beta}] \tag{1}$$

and examining how the empirical parameter β varies with the degree of cure. In eq 1, $\Phi(t)$ is the normalized relaxation function, τ is the characteristic relaxation time, and β is the stretched exponential parameter ($0 < \beta \le 1$). For clarity, we describe briefly here the fitting process. It is first necessary to establish if the normalized dielectric loss data are "dielectrically simple"; if not, no fitting can be performed. We then convert the data to the complex general form expressed as[33]

$$\epsilon^*(\omega) - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)[1 - i\omega\int_0^\infty \Phi(t)\exp(-i\omega t)\,dt] \tag{2}$$

where ω is angular frequency, ϵ_0 and ϵ_∞ and low- and high-frequency permittivity, and $\Phi(t)$ is the normalized relaxation function. The KWW expression (eq 1) then replaces the normalized relaxation function in the above integral and a computer routine[34] solves for the best fit β parameter. A plot of the KWW β parameter as a function of degree of cure for DGEBA–MDA formulation results in a straight line, as seen in Figure 15. It thus appears that either the width at half-height (or the β parameter, since they are directly related[21]) can be used to correlate dipole dynamics to the kinetics of network formation.

3. Reorientational Dynamics and Intermolecular Cooperativity. Another way of interpreting our findings and quantifying the dispersion and temperature dependence of segmental motions is by constructing the fragility or cooperativity plots, first utilized by Angell[35] and later redefined by Ngai,[36] as discussed in detail in the first part of this paper.[1] The use of cooperativity plots to relate the progress of chemical reactions to the evolving network structure has not been reported in the literature hitherto and has yielded most interesting information in this study, as can be surmized from Figure 16 for DGEBA–MDA formulation. Briefly, cooperativity plots contain the most probable relaxation time as a function of normalized reciprocal temperature,

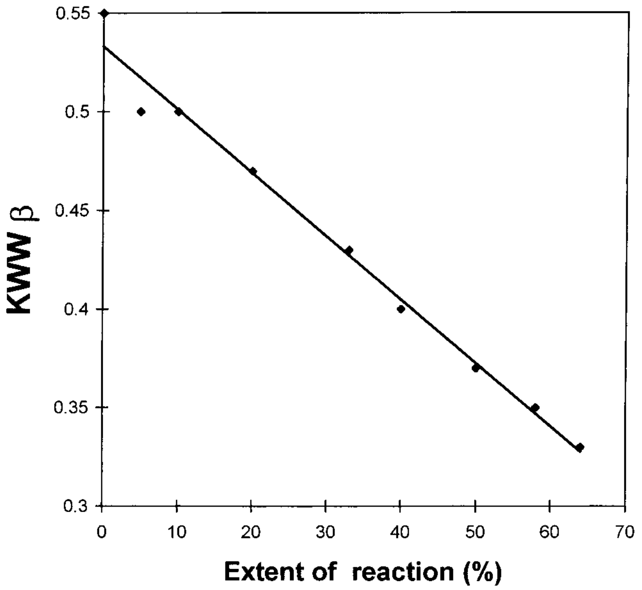


Figure 15. Stretched exponential (KWW) β parameter versus extent of reaction for DGEBA−MDA formulation.

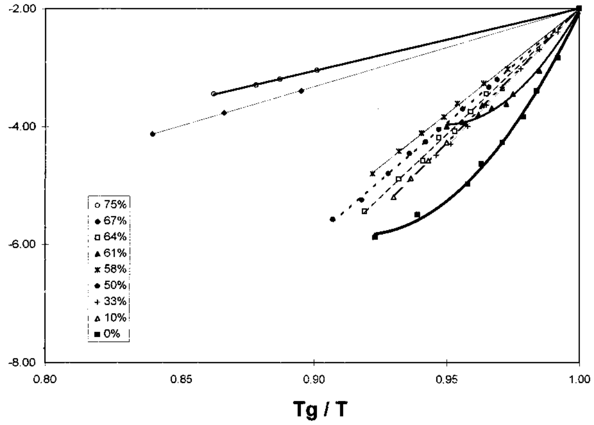


Figure 16. Cooperativity plot of log relaxation time as a function of reduced temperature for DGEBA−MDA formulation at various extents of reaction.

expressed as T/T_g or $(T - T_g)/T_g$, where T_g is commonly taken to represent the temperature at which the relaxation time attains an arbitrary value between, e.g., 0.01 and 100 s. The advancement of reactions in cross-linking systems affects molecular architecture by increasing the intermolecular dynamic constraints as a result of the reduced mobility and dielectric architecture as a consequence of the change in the concentration and type of dielectrically active species during reaction. The initial mixture is characterized by high intermolecular cooperativity and a distinctly non-Arrhenius response. Soon after the onset of reactions in a DGEBA−MDA formulation, the response becomes linear and the steepness of the cooperativity plot decreases as a result of the combined effect on cooperativity induced by the changes in molecular and dielectric architecture that accompany network formation. A careful examination of Figure 16 reveals that this situation prevails through 58% of cure. At 61% cure, however, a dramatic change is observed; the curve shifts back toward an increase in cooperativity and reverts to a non-Arrhenius response. This increase in cooperativity is caused by the formation of a hydrogen-bonded complex in the vicinity of gel point, as described earlier in the text, and it is evident that this phenomenon has a strong effect on the cooperativity plot. Above 61% conversion, however, the previously described dipole dilution effect becomes dominant again and the plot reverts to the Arrhenius form with a rapidly decreasing slope with further cure.

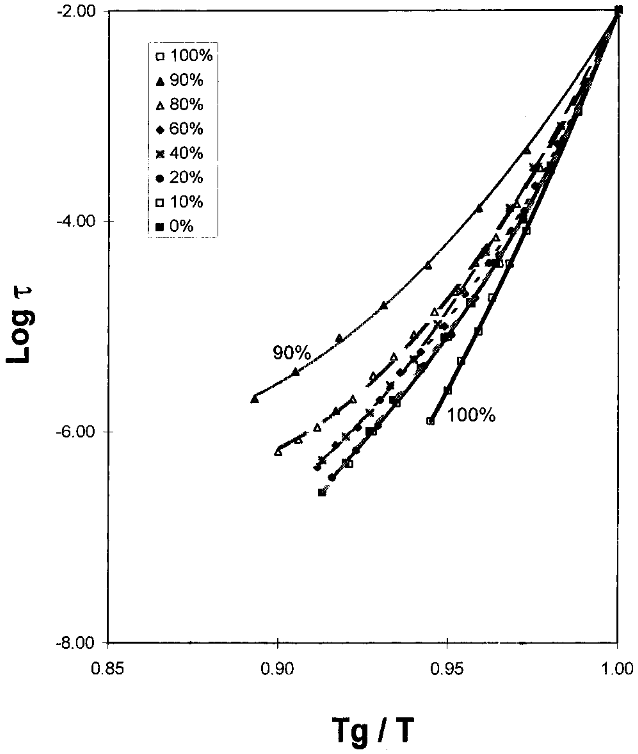


Figure 17. Cooperativity plot of log relaxation time as a function of reduced temperature for DGEBA−aniline formulation at various extents of reaction.

Finally, we would like to show that the cooperativity plot is equally informative in describing the formation of linear polymers. An example is shown in Figure 17, where a cooperativity plot is constructed for DGEBA−aniline formulation at various stages of polymerization. The steepness of the fragility curves (or the coupling parameter n^*) varies slightly for the samples between 0 and 80% conversion, while a dramatic change is noted at 90% conversion and in the fully cured (100% conversion) system. We remind the reader that the activation energy of this system at different extents of reaction (Figure 13) was calculated from the data in the frequency range between 1 kHz and 1 MHz (Figure 12), while the results in Figure 17 include a broader frequency range and hence there is no inconsistency. The pronounced change in cooperativity is caused by the change in the molecular origin of α relaxation at this stage of reaction, as discussed earlier.

Conclusions

We have employed simultaneous dielectric and FTIR measurements to study the reorientational dynamics of dipoles in reactive multifunctional epoxy−amine formulations. The variation in activation energy (determined from the temperature dependence of the dielectric loss peak) as a function of degree of cure, revealed interesting information. Three zones of dipole dynamics were identified: an initial zone where activation energy increases with degree of cure, an intermediate zone between about 55 and 67% conversion where activation energy displays a peculiar trend, and a third zone where activation energy decreases as cure approaches completion. The unusual behavior in the intermediate zone was caused by the chemical and physical changes in the growing network in the vicinity of the gel point. More specifically, dipole dynamics are strongly affected by the densification of the network and the formation and breakup of a three-dimensional hydrogen-bonded complex that co-involves hydroxyl, epoxy, and amine groups.

The changes in dipole dynamics during cure were also utilized to describe the kinetics of network formation. The normalized loss peak half-width was shown to decrease in a systematic manner during cross-linking, allowing us to calculate the degree of cure based on dipole dynamics. An excellent agreement was noted between the calculated dielectric and spectroscopic (near-infrared) degree of cure. This finding suggests a possibility that dielectric measurements of dipole dynamics during cross-linking of multifunctional epoxy−amine formulations could be used in the mechanistic kinetic studies, provided that the molecular origin of α relaxation can be established.

Finally, the fragility or cooperativity plots were used to relate dipole dynamics at any stage of cure to the intermolecular cooperativity of the growing network. Systematic trends were observed and it was concluded that cooperativity plots offer an informative picture of the advancement of cure. An explanation of the observed trends in intermolecular cooperativity during cure must be sought in terms of the interplay between molecular and dielectric architecture of the growing network.

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