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CHEMICAL INTERPRETATION OF THE RELAXED PERMITTIVITY
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The change in dielectric constant during cure of a diglycidyl ether of bisphenol-A resin (EPON 825) with diamino diphenyl sulfone was studied using microdielectrometry and differential scanning calorimetry. The dipole moments attributable to the epoxide and amine groups were obtained by dielectric measurements on the starting materials, and on related model compounds whose functionality precludes crosslinking. The decrease of the relaxed dielectric constant, ϵ_r , during cure can be attributed to the consumption of the polar		

reactive groups by the crosslinking reaction, and can be correlated with the extent of conversion measured by DSC. The DSC rate data was fit to a kinetic model, and the model used to calculate concentrations of reactive groups versus time. The Frohlich theory, which relates the static dielectric constant to the concentrations and moments of dipoles in the material, was used to interpret the ϵ_r curing behavior. Originator Supplied Keywords include:

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CHEMICAL INTERPRETATION OF THE RELAXED PERMITTIVITY

DURING EPOXY RESIN CURE

BY

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INTRODUCTION

The contribution of orientable dipoles to the measured dielectric permittivity of polar materials depends on the number of dipoles present and on their ability to orient with an applied electric field at the frequency of measurement. In the low frequency limit, all dipoles can orient, and a large permittivity, denoted by the term "relaxed" permittivity, ϵ_r , is observed. At high frequencies, where the dipole can no longer follow the applied field, a lower permittivity, called the "unrelaxed" permittivity, ϵ_u , is observed. This paper addresses the analysis of $\epsilon_r - \epsilon_u$, which measures the contribution of orientable dipoles, in terms of the chemical composition of the medium.

In epoxies cured with amines, both the epoxide and amine groups have appreciable dipole moments. The curing reaction will change the number and type of permanent dipoles present, which will be reflected in a changing relaxed permittivity. Soualmia et. al. have reported a correlation between $\epsilon_r - \epsilon_u$ and the concentration of epoxide groups as measured by chemical analysis [1]. Their analysis attributes the change in $\epsilon_r - \epsilon_u$ to both a decreasing number of epoxides and a decreasing epoxide dipole moment. This paper considers a more realistic model in which the contributions of other polar groups and their time variation are included.

The isothermal cure of a stoichiometric mixture of a DGEBA epoxy resin, EPON 825, with diamino diphenyl sulfone (DDS) was studied at temperatures between 410 K and 460 K using differential scanning calorimetry (DSC) and microdielectrometry [2]. This previously reported data is analyzed further in this work. All permittivities reported are relative to that of free space, denoted by ϵ_0 , and having the value 8.85×10^{-14} F/cm. Figure 1 is a plot of the permittivity versus time during the DGEBA/DDS cure at 410 K, measured at frequencies between 0.1 and 10,000 Hz [2]. For all but the highest frequency, a large permittivity is observed early in cure which is due to the effects of blocking electrodes [3]. As the cure proceeds, the contribution of the electrode blocking to the permittivity disappears, and the measured permittivity follows the relaxed permittivity curve ϵ_r for a brief interval, then drops abruptly to the unrelaxed value ϵ_u as the dipoles become immobilized due to vitrification [2]. Measurements over a wide frequency range are required to follow ϵ_r through the cure. The intent of this work is to analyze the decrease in ϵ_r with cure in terms of (1) the time varying concentrations of dipolar reactive groups and (2) theoretical models relating dielectric constant to the number and type of permanent dipoles. The DSC data will be fit to an existing kinetic model for the amine cure of epoxies. The model is then used to calculate the time-dependent concentration of polar reactive groups. The resulting concentrations are used with the

dielectric data in a model for the permittivity of materials containing permanent dipoles to extract estimates of the dipole moments of the functional groups.

DSC RESULTS AND DISCUSSION

There are a number of possible reactions taking place during the amine cure of an epoxy [4]. The principal reaction is the reaction of a primary amine with an epoxide to form a secondary amine which can subsequently react with another epoxide to form a tertiary amine. These reactions are catalyzed by hydrogen-bond donor molecules, including the hydroxyl groups formed by the epoxide reaction. A homopolymerization reaction in which the hydroxyl opens the epoxide ring to form an ether linkage is also possible, but the rate is considerably less than for amine addition.

A kinetic model relating the rate of consumption to the conversion of epoxides was proposed by Sourour and Kamal [4]. For a stoichiometric mixture of epoxy and amine their model is,

$$\frac{da}{dt} = (K_1 + K_2 a)(1-a)^2 \quad (1)$$

where a is the fractional conversion of epoxides, and K_1 and K_2 are rate constants. This model assumes that the primary and secondary amines have equal reactivity and that no etherification takes place.

The extent of conversion, a , calculated by the kinetic model, is the fraction of epoxides consumed. The fraction of primary amines consumed, a_1 , and the fraction of tertiary amines formed, a_2 , are related to the epoxide consumption by the following expressions [5],

$$a = a_1 + \frac{(1-a_1)}{2} \log(1-a_1) \quad (2)$$

$$a_2 = a_1 + (1-a_1)\log(1-a_1) \quad (3)$$

The fraction of amines as secondary amines will be given by $a_1 - a_2$. The rate constants K_1 and K_2 were determined from the experimental data by defining a reduced rate, a_r ,

$$a_r = \frac{da/dt}{(1-a)^2} = (K_1 + K_2 a) \quad (4)$$

and plotting versus a [4]. The measured DSC isothermal a versus time from reference 2 were analyzed in this manner. The plots of reduced rate were linear in a up to conversions of about 50%.

At higher conversions the reaction becomes diffusion controlled and the rate constants themselves become functions of the extent of reaction.

Figure 2 shows a comparison of the experimental α versus time data to that calculated using the kinetic model. Good agreement is obtained for conversions up to about 70%. As discussed above, deviations at higher conversions are expected. The rate constants K_1 and K_2 were determined over the temperature range 410 K to 460 K and activation energies were found from an Arrhenius plot. The activation energy for K_1 was 72.8 kJ/mol, and for K_2 , 60.0 kJ/mol. Barton [6], studying a similar epoxy, EPON 828, cured with DDS, found a value of 85.3 kJ/mol for his quantity that corresponds to the K_1 rate constant. On the other hand, excellent agreement was obtained between the times to reach 50% consumption of primary amine groups ($\alpha_1=0.5$) calculated using the kinetic model and those measured experimentally using infrared spectroscopy, again for EPON 828 cured with DDS [7]. Table I shows the calculated and experimentally determined values at cure temperatures from 383 K to 413 K.

The kinetic model will be used below to correlate the disappearance of polar functional groups with the decrease in relaxed permittivity during cure. To illustrate the cure dependence of the functional group concentrations, Fig. 3 shows the various extents of reactions, as determined from the kinetic model, for the curing reaction at 420 K. The epoxide and primary amine concentrations decrease monotonically with time, with the amine disappearing more rapidly. The secondary amine concentration rises to a peak and decreases, while the tertiary amine concentration continuously increases.

DIELECTRIC RESULTS AND DISCUSSION

The relaxed permittivity will increase as the number and/or moments of dipoles increases, and decreases with temperature due to thermal disorder. This behavior is illustrated in Fig. 4, which shows the permittivity versus temperature for a fully reacted mixture of phenyl glycidyl ether (PGE) with DDS. PGE is approximately half of the DGEBA molecule, and since it contains only a single epoxide, this material does not crosslink. At low temperatures and at all frequencies, the dipole relaxation time is large so no dipole orientation is possible and the permittivity is equal to ϵ_u . As the material is warmed, the dipoles gain sufficient mobility to orient, and the permittivity rises to ϵ_r . However, the conductivity increases also, which leads to electrode blocking effects and very high permittivities [3]. The temperature dependence of the relaxed permittivity is determined from a composite of measurements made over a wide frequency range.

A theoretical expression relating the relaxed, ϵ_r , and unrelaxed, ϵ_u , permittivities to the dipole moments present in a material was developed by Onsager and modified by Fröhlich and is shown as equation 5 [8].

$$\frac{(\epsilon_r - \epsilon_u)(2\epsilon_r + \epsilon_u)}{\epsilon_r(\epsilon_u + 2)^2} = \frac{\sum N_i \mu_i^2}{9\epsilon_0 kT} \quad (5)$$

This model predicts that a plot of the function of the unrelaxed and relaxed permittivities on the left hand side versus $1/T$ should have a slope proportional to the sum of the products $N\mu^2$, and should pass through the origin. As the reaction proceeds and dipoles are consumed, we would expect the slope to vary. Since it is impossible to stop the reaction at a given extent of reaction and then measure the permittivity versus temperature, the kinetic model was used to determine the times to reach a given conversion at each of the isothermal cure temperatures. It was then possible to go back to the dielectric data and determine the temperature dependence of the permittivity at fixed chemical conversion. Figure 5 shows such a plot for conversions of 0% and 50%, as well as the 100% conversion represented by the PGE/DDS data. The plot shows that there is a systematic change in slope during curing, as expected. A result not accounted for by the theory is that the extrapolated line does not intercept the origin but the inverse temperature axis, and furthermore, that the "intercept temperature", T_{int} , varies with extent of reaction.

The Onsager theory assumes that the potential energy of a dipole depends only on its orientation with respect to the applied field and does not take into account other possible interactions. A temperature dependence similar to that of Fig. 5 has been reported for poly(acetaldehyde) by Williams [9]. He has shown that the energetically favored all-trans conformation has the C-O-C dipoles aligned in parallel. As temperature is increased, other higher-energy but less polar conformations become more likely and the relaxed permittivity decreases more rapidly with temperature than predicted by the Onsager relation. The corresponding origin of the intercept in Fig. 5 is not understood. Nevertheless, there is a systematic shift of this intercept temperature with increased curing, as shown in Fig. 6, which can be described by a linear decrease of the intercept temperature with extent of cure.

COMBINED KINETIC/DIELECTRIC MODEL

We have shown above that the dielectric data could not be fit to the standard theory, so we have chosen to modify the Onsager equation empirically, as follows:

$$\frac{(\epsilon_r - \epsilon_u)(2\epsilon_r + \epsilon_u)}{\epsilon_r(\epsilon_u + 2)^2} = \frac{\sum N_i(\alpha)\mu_i^2}{9\epsilon_0 k} \left[\frac{1}{T} - \frac{1}{T(\alpha)_{int}} \right] \quad (6)$$

where T_{int} depends on α as in Fig. 6. We expect that this equation will allow us to represent the experimental values of ϵ_r taken from isothermal curing experiments. For a given reaction temperature and reaction time, the kinetic model provides us with α , which in turn gives values for N_i and T_{int} . The only unknowns in the above equation are then the dipole moments μ_i . Previous work has demonstrated that both the amine and epoxy have large dipole moments [10]. To simplify modeling, we will consider that the product of an amine/epoxy reaction, be it secondary or tertiary amine, has a single dipole moment. This means that there are three contributions to the right hand side of Eq. 6 above. A least-squares fit was done using 10 data points at each of six temperatures to determine the best values of the three dipole moments. The dipole moments were 7.6E-30 C-m for the epoxide, 14.8E-30 C-m for the primary amine, and 12.6E-30 C-m for the reacted amine. A similar analysis applied to unreacted mixtures having varying ratios of DGEBA and DDS gave an epoxy dipole moment of 8.5E-30 C-m and an amine dipole moment of 19.8E-30 C-m [10]. The experimental data and the curves calculated from the best fit moments are shown in Fig. 7.

CONCLUSION

This work has demonstrated a relationship between the decrease in the relaxed permittivity and the consumption of polar reactive groups during the cure of DGEBA with DDS. Isothermal extent-of-conversion versus time results from differential scanning calorimetry were fit to a kinetic model, which was then used to predict reactive group concentrations. The cure time and temperature dependence of the calculated reactive group concentrations and the experimental relaxed permittivity were used to determine dipole moments for the reactive groups by fitting the data to an empirically modified Onsager relation for the permittivity. The dipole moments had reasonable values and were consistent with previous work. Further investigation is needed to understand the origin of the deviation from the Onsager behavior.

ACKNOWLEDGEMENTS

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TABLE I. Experimental and calculated times to reach 50% primary amine conversion versus cure temperature.

Cure Temperature (K)	IR data [7]	kinetic model
383	200	212
393	121	125
403	76	75
413	48	46

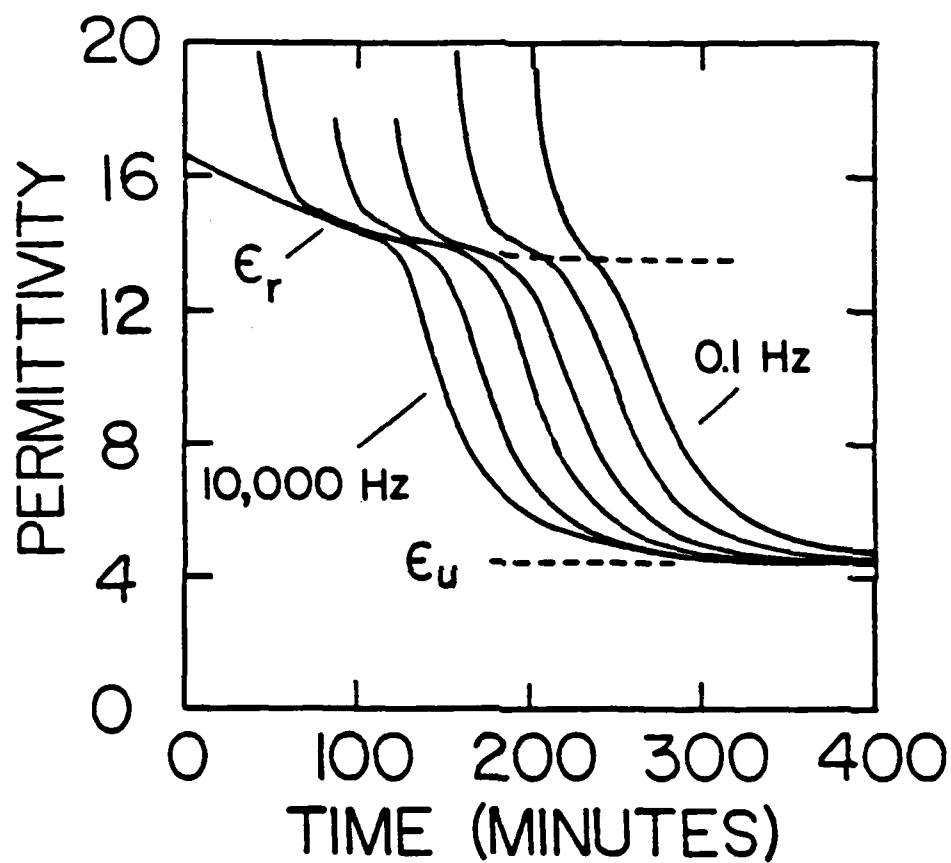


Figure 1 - Relative permittivity versus cure time for EPON 825 cured with DDS at 410K, showing relaxed, ϵ_r , and unrelaxed, ϵ_u , permittivities [2].

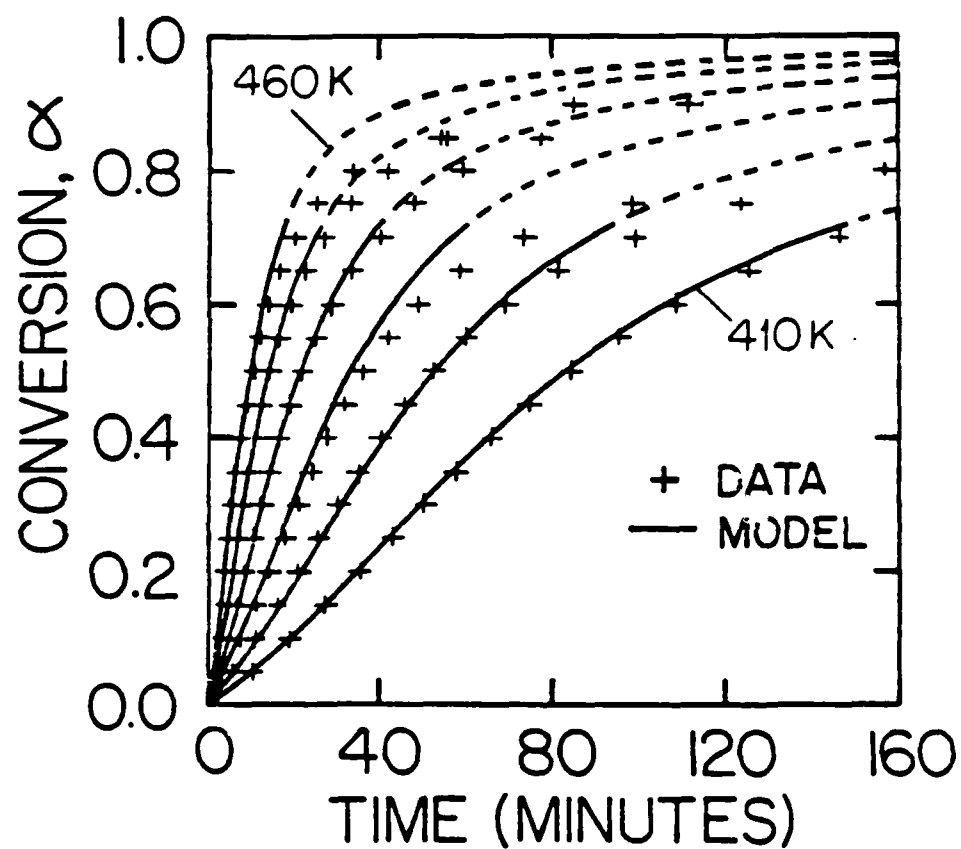


Figure 2 - Extent of conversion versus time from differential scanning calorimetry. Crosses - experimental data from [2]. Solid curve - kinetic model, equation 1.

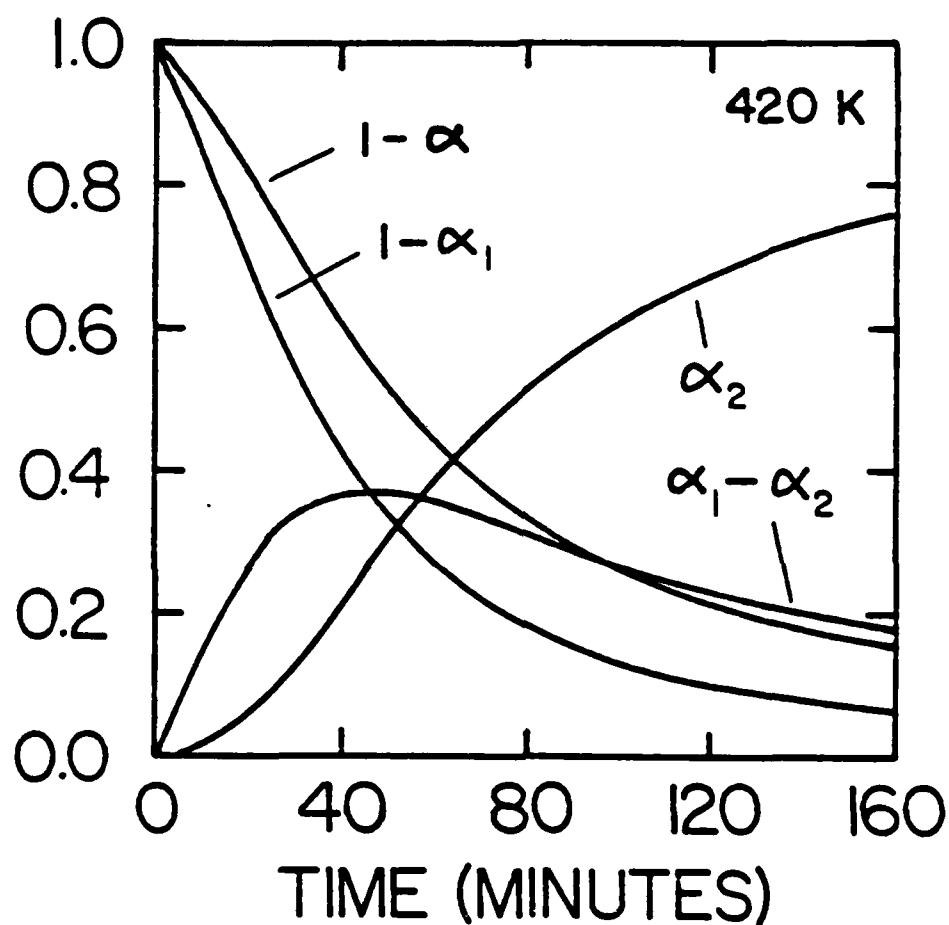


Figure 3 - Time dependence of functional group concentrations for an isothermal cure at 420K, as calculated from kinetic model. $1-\alpha$ - fraction epoxides remaining. $1-\alpha_1$ - fraction primary amines remaining. α_2 - fraction tertiary amines formed. $\alpha_1-\alpha_2$ - fraction secondary amines present.

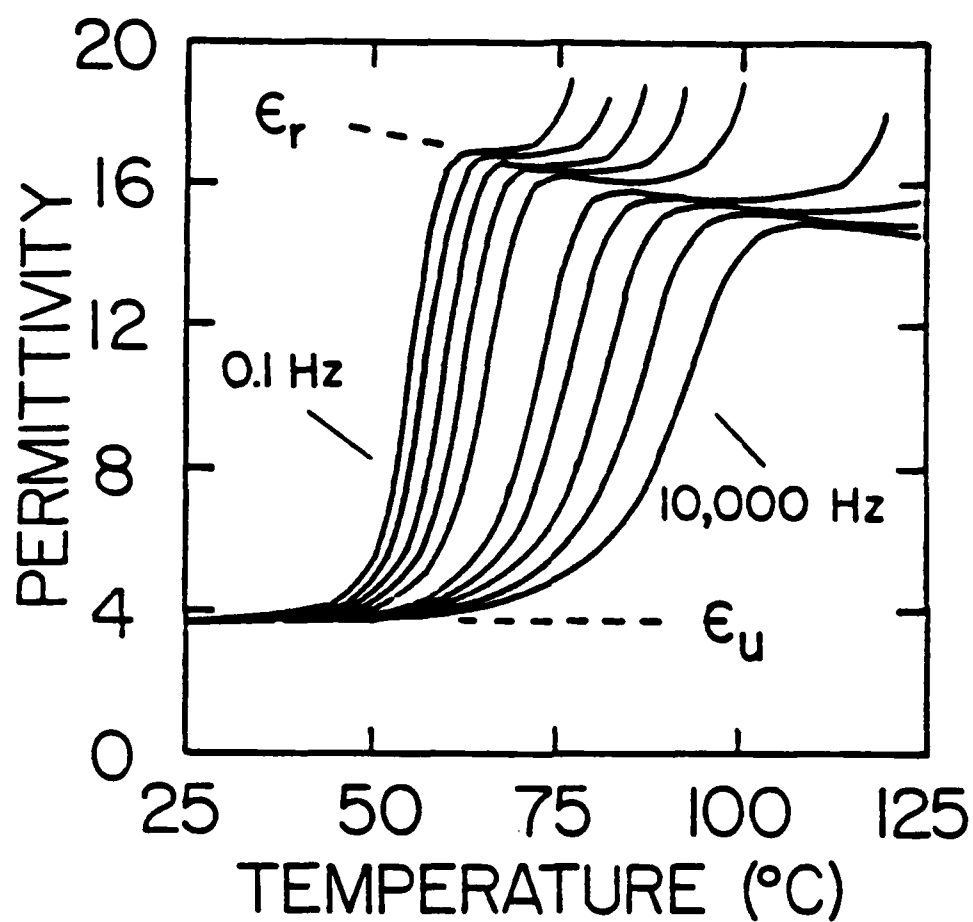


Figure 4 - Relative permittivity versus temperature for fully reacted sample of a stoichiometric mixture of phenyl glycidyl ether (PGE) with DDS.

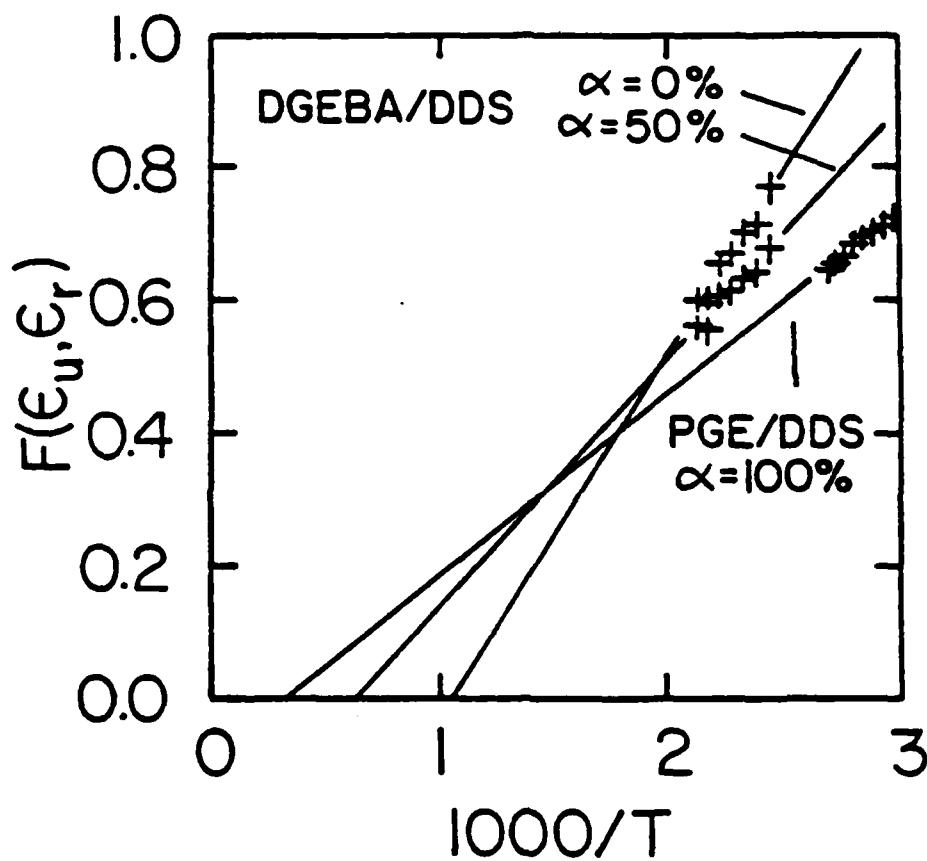


Figure 5 - Plot of the left hand side of the Onsager relation, equation 5, versus inverse temperature for varying extents of conversion. For DGEBA/DDS curves, individual points are taken from isothermal cure experiments. For PGE/DDS sample, points are taken from fig. 4.

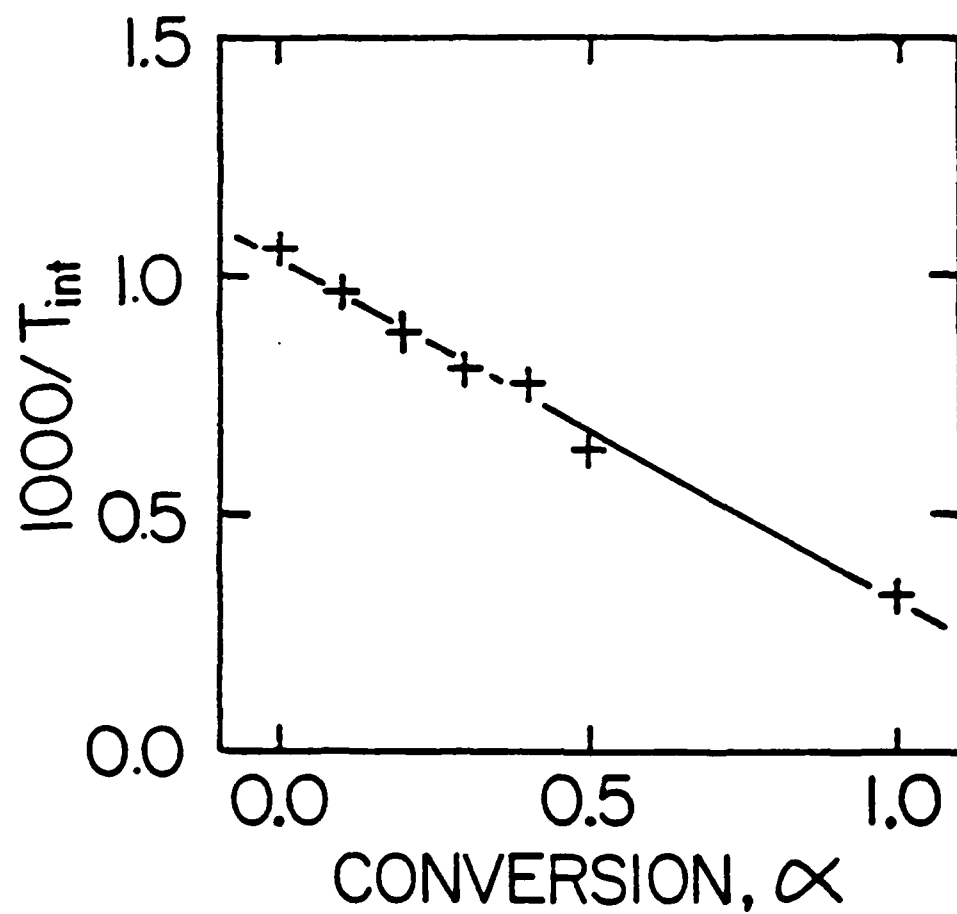


Figure 6 - Dependence of the extrapolated "intercept temperature" versus extent of conversion.

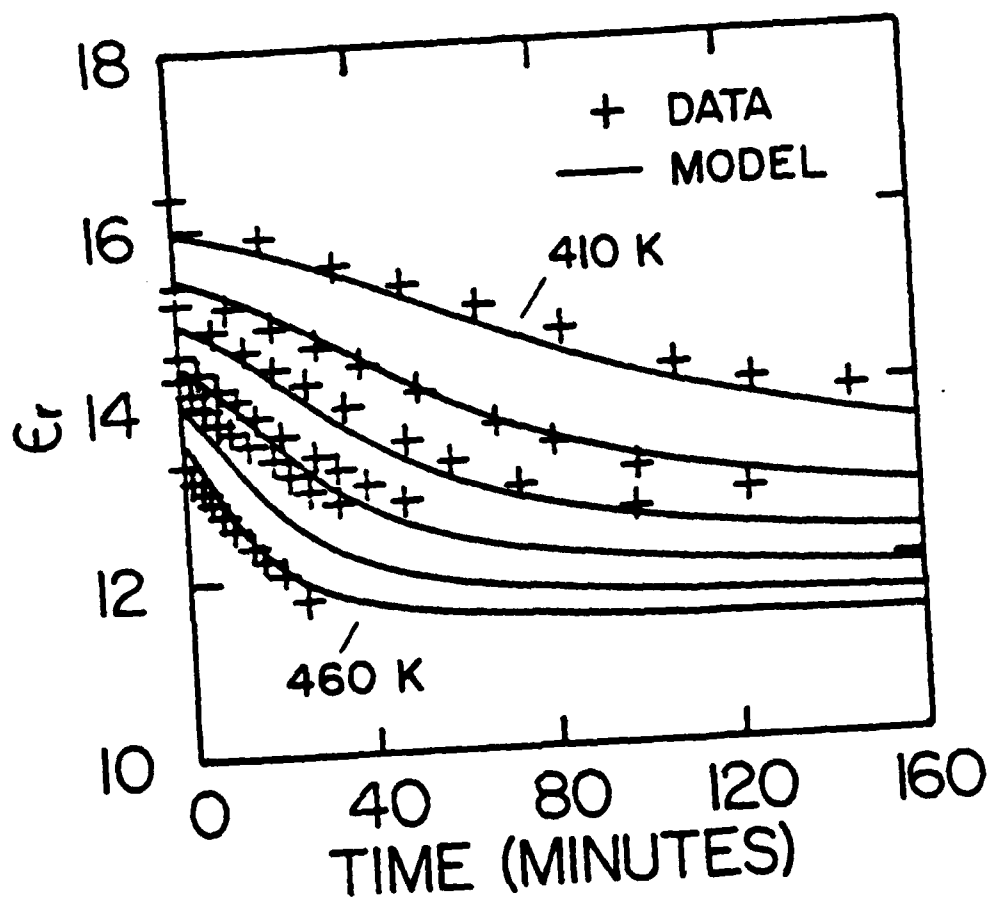


Figure 7 - Dependence of the relaxed permittivity versus cure time at temperatures between 410K and 460K. Crosses represent experimental points. Solid curves represent model of equation 6 evaluated using fixed dipole moments determined from least-squares fit to the experimental data.

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