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STUDY OF REACTION KINETICS AND DEVELOPMENT OF ELASTIC
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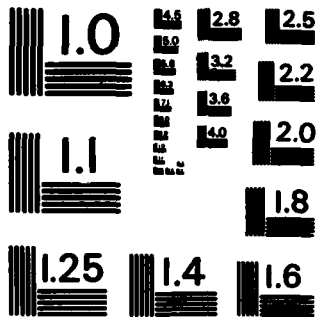
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STUDY OF REACTION KINETICS AND DEVELOPMENT OF ELASTIC
PROPERTIES IN NETWORK POLYMERIZATION SYSTEMS BY
THE IMPULSE TECHNIQUE

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**STUDY OF REACTION KINETICS AND DEVELOPMENT
OF ELASTIC PROPERTIES IN NETWORK POLYMERIZATION
SYSTEMS BY THE IMPULSE TECHNIQUE**

by

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ABSTRACT

The total impulse approach to linear viscoelasticity developed by Farris ⁽¹⁾ has been extended to the study of kinetics of network formation and development of mechanical properties in nonlinear polymerization reactions. A single experiment permits kinetic data and absolute measurements of viscosity and elastic parameters to be obtained during the evolution of a reacting system from a liquid to a glassy or rubber network.

The method was applied to the cure of an epoxy-amine system at different temperatures to obtain kinetic information (gel times), viscosities and elastic parameters.

Theoretical predictions of pre-gel and post-gel relations are in good agreement with the observed experimental values.

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INTRODUCTION

The study of gelation and network formation in nonlinear polymers presents several problems. The onset of gelation is a rather fast process and very difficult to follow with commonly available experimental techniques. Investigations of kinetic mechanisms and the relation between conversion and structure formation are restricted by the insolubility of the network polymer.

Elementary estimations of gel points by following the expected exponential increase in viscosity (pot life) depend on the geometry of the environment. Large errors are normally induced by heat transfer problems and acceleration.

Methods based on simultaneous viscosity measurements and titration are only applicable at very low conversions in the pre-gel state.

Other procedures to obtain information on the kinetics and the structure are based on running parallel experiments and separate measurements, i.e., dynamic mechanical analysis (DMA) and infrared spectroscopy (IR).

Tung et al. [2] established some semi-empirical criteria for the determination of gel times. Observations on dynamic mechanical analysis (DMA) for several thermosets indicate that the condition $\tan \delta = 1$ or $G' = G''$ correlates well with experimentally determined gel times. The condition $G' = G''$ was verified for gelations occurring above the glass transition temperature and interpreted as the passage from an essentially viscous response to an elastic response after network formation. Although experiments show good agreement, explanations based on DMA data are not straightforward. Gel times measured by this procedure are frequency-dependent.

An alternative method for the study of gelation and mechanical properties in reacting systems is presented here. It is based on an extension of the total

impulse technique developed by Farris [1], which separates elastic from viscous response in linear viscoelastic systems. For convenience, the most important aspects of the method are outlined below.

The constitutive equations for a linear isotropic and non-aging viscoelastic material can be written as:

$$(1a) \quad \sigma'_{ij}(t) = 2G_{\infty} \epsilon'_{ij}(t) + 2 \int_0^t G(t-\tau) \frac{\partial \epsilon'_{ij}}{\partial \tau} d\tau, \text{ and}$$

$$(1b) \quad \sigma_{kk}(t) = 3K_{\infty} \epsilon_{kk}(t) + 3 \int_0^t K(t-\tau) \frac{\partial \epsilon_{kk}}{\partial \tau} d\tau, \text{ where}$$

$$(2a) \quad \sigma_{ij} = \sigma'_{ij} + \delta_{ij} \sigma_{kk}/3, \text{ and}$$

$$(2b) \quad \epsilon_{ij} = \epsilon'_{ij} + \delta_{ij} \epsilon_{kk}/3.$$

In the above equations σ'_{ij} and ϵ'_{ij} are the deviatoric stress and strain and are related to the total stress and strain, σ_{ij} and ϵ_{ij} , in equation 2. The shear modulus G and the bulk modulus K have each been decomposed into two terms, a constant elastic term G_{∞} and K_{∞} and a time dependent viscoelastic term $G(t)$ and $K(t)$. Consistent with this definition we must require that $G(\infty)$ and $K(\infty)$ to be zero.

The simplest means by which to develop the total impulse approach is by applying some of the theorems of the Laplace transform to equation 1. The transform of equation 1 is simply

$$\bar{\sigma}'_{ij} = 2G_{\infty} \bar{\epsilon}'_{ij} + 2\bar{G}s \bar{\epsilon}'_{ij} \tag{5a}$$

$$\bar{\sigma}_{kk} = 3K_{\infty} \bar{\epsilon}_{kk} + 3\bar{K}s \bar{\epsilon}_{kk} \tag{5b}$$

where $\bar{f} = \bar{f}(s) = \int_0^{\infty} f(t)e^{-st} dt$

Several theorems in Laplace transform theory deal with the limits of \bar{f} as the Laplace parameter s approaches zero or infinity. Of particular use in the discussions below are two theorems which state

$$\lim_{s \rightarrow 0} \bar{f}(s) = \int_0^{\infty} f(t)dt, \text{ and} \quad (6)$$

$$\lim_{s \rightarrow 0} s\bar{f}(s) = \lim_{t \rightarrow \infty} f(t) = f(\infty) \quad (7)$$

Properly applying these theorems to the transforms of equation 1, one finds

$$\int_0^{\infty} \sigma'_{ij}(t)dt = 2G_{\infty} \int_0^{\infty} \epsilon'_{ij}(t)dt + 2\epsilon'_{ij}(\infty) \int_0^{\infty} G(t)dt \text{ and} \quad (8a)$$

$$\int_0^{\infty} \sigma_{kk}(t)dt = 3K_{\infty} \int_0^{\infty} \epsilon_{kk}(t)dt + 3\epsilon_{kk}(\infty) \int_0^{\infty} K(t)dt \quad (8b)$$

The terms on the left hand side of equation 8 are the total stress impulses. The first term on the right hand side of these equations involves what might be termed the total strain impulses. The usefulness of the technique is apparent from equation 8 when one considers applying strain disturbances where $\epsilon'_{ij}(\infty) = \epsilon_{kk}(\infty) = 0$. For this situation the equations simply become

$$\int_0^{\infty} \sigma'_{ij}(t)dt = 2G_{\infty} \int_0^{\infty} \epsilon'_{ij}(t)dt \text{ if } \epsilon'_{ij}(\infty) = 0, \text{ and} \quad (9a)$$

$$\int_0^{\infty} \sigma_{kk}(t)dt = 3K_{\infty} \int_0^{\infty} \epsilon_{kk}(t)dt \text{ if } \epsilon_{kk}(\infty) = 0 \quad (9b)$$

Obviously when these conditions are met the total impulse approach can be simply used to separate elastic from viscoelastic contributions since $G(t)$ and $K(t)$ never appear in equations 9. The equilibrium moduli G_{∞} and K_{∞} can be determined simply by taking the ratio of the stress and strain total impulses. If the material is a fluid then G_{∞} must be zero, hence the deviatoric stress impulse to any strain disturbance must be zero. Any deformation history that starts and ends at zero strain can be used, providing the strain impulse is not zero as it would be for a single full sine wave. Alternatively, if the beginning and ending strain is zero and a wave form is used wherein the total strain impulse is zero, the stress impulse must be zero for all linear viscoelastic materials including Newtonian fluids and elastic solids. From these types of experiments one can check linearity assumptions, determine if the material is a true solid and obtain the equilibrium moduli.

If the material in question is a viscoelastic liquid, $G_{\infty} = 0$ from the previous experiments, then the total impulse of stress in equation 8a simply becomes

$$\int_0^{\infty} \sigma'_{ij}(t) dt = 2\varepsilon'_{ij}(\infty) \int_0^{\infty} G(t) dt \quad (10)$$

Hence, any strain disturbance starting at zero and ending at $\varepsilon'_{ij}(\infty)$ gives a total stress impulse proportional to the integral of the time dependent part of the relaxation modulus. Molecular or mechanical models of viscoelastic behavior demonstrate that this integral is equal to the steady state shear viscosity of the system

$$\eta = \int_0^{\infty} G(t) dt \quad (11)$$

Therefore the total stress impulse can be represented as

$$\int_0^{\infty} \sigma'_{ij}(t) dt = 2G_{\infty} \int_0^{\infty} \epsilon'_{ij}(t) dt + 2\eta \epsilon'_{ij}(\infty) \quad (12)$$

If the material is a fluid, the steady state viscosity can be obtained by

$$\eta = \int_0^{\infty} \sigma'_{ij}(t) dt / 2\epsilon'_{ij}(\infty) \quad (13)$$

It again should be emphasized that these relations are valid for all strain histories providing the simple conditions mentioned above are satisfied.

Summarizing previous results, the elastic parameters G_{∞} and K_{∞} can be calculated from equation 9 by application of a strain pulse satisfying $\epsilon'_{ij}(\infty) = \epsilon_{kk}(\infty) = 0$. Viscosity can be obtained through equation 13 by application of a strain pulse satisfying $\epsilon'_{ij}(\infty) \neq 0$.

Clearly, two different pulse inputs are required. However, a reformulation permits all previous information to be obtained from a single experiment.

Starting with the transformed equation 5a,

$$\bar{\sigma}'_{ij} = 2G_{\infty} \bar{\epsilon}'_{ij} + 2\bar{G}s \bar{\epsilon}'_{ij} \quad (14)$$

a division by s gives

$$\frac{\bar{\sigma}'_{ij}}{s} = 2G_{\infty} \frac{\bar{\epsilon}'_{ij}}{s} + 2\bar{G} \bar{\epsilon}'_{ij} \quad (15)$$

Applying the theorem on limits given by equation 6,

$$\int_0^{\infty} \int_0^{\infty} \sigma'_{ij}(\epsilon) d\epsilon dt = 2 \int_0^{\infty} \int_0^{\infty} G_{\infty} \epsilon'_{ij}(\epsilon) d\epsilon + 2 \int_0^{\infty} G(t) dt \int_0^{\infty} \epsilon'_{ij}(t) dt \quad (16)$$

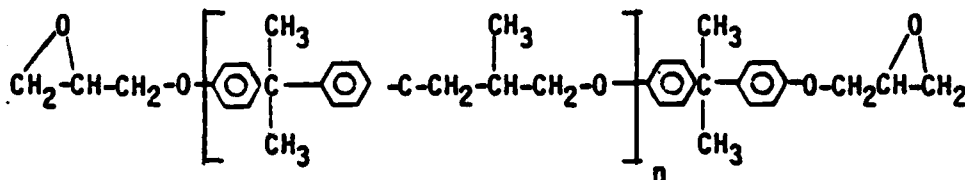
from which results that

$$\eta = \frac{\int_0^t \int_0^\infty [\sigma'_{ij}(\epsilon) - 2G_\infty \epsilon'_{ij}(\epsilon)] d\epsilon dt}{2 \int_0^t \epsilon'_{ij}(t) dt} \quad (17)$$

The usefulness of this procedure becomes obvious, since equations 9 and 17 can now be related to a single experiment wherein $\epsilon'_{ij}(\infty) = 0$.

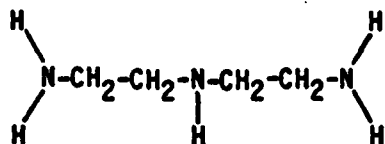
EXPERIMENTAL

A commercial epoxy-resin EPON 828 having approximate equivalent weight of 189



diglycidyl ether of bisphenol-A (DGEBA) ($n = 0.1$)

was cured with a pentafunctional amine



diethylenetriamine (DETA)

with a stoichiometric imbalance $r = fA_f/B_2 = 1.08$. A_f notes the concentration of amine with functionality f , and B_2 is the concentration of epoxy molecules.

The material was placed between parallel plates connected to a load cell in an Instron testing equipment. Cures were performed at several temperatures between 25 C and 55 C. Thin gaps between plates (in the order of 1 mm) permit

good heat transfer and uniform temperature throughout the reacting mass.

The cure process was followed by applying small deformation pulses as indicated in Figure 1. It is important to ascertain that no appreciable changes in the structure by chemical reaction occur while the pulse response is being measured. For the particular conditions of the experiment, pulses in the order of 6 seconds were effective in tracking the rapid change in properties at the onset of gelation. Figure 1 contains a succession of typical curves obtained during a cure process. The symmetric character of the pulses at the beginning of the reaction is associated with a predominantly viscous response. On the inception of gelation, a well defined positive area is observed, which can be attributed to the development of elastic properties due to network formation. At that point, analysis of the pulses reveal drastic changes in viscosity and elastic moduli.

THEORETICAL PREDICTIONS

The mathematical modeling of the curing reactions and gel formation are essential for an interpretation and evaluation of the previous experimental results.

Theoretical treatment permits the estimation of kinetic data as well as parameters related to the structure like molecular weights, fraction of solubles, concentration of crosslinks, etc.

Several simplifying assumptions are normally introduced in the models, like

- 1) all functional groups of the same type have equal reactivity
- 2) all groups react independently of one another
- 3) no intramolecular reactions (cyclizations) occur in the pre-gel

state.

As proposed by Flory [3,4,5] in his original work, the above conditions are normally used to define an "ideal" system.

The diepoxide-polyamine system under study fails to meet the first two requirements simultaneously. The first condition is not satisfied because of substitution effects, that is, all reaction events at the molecule sites are not statistically independent.

In the presence of substitution effects, the probability of reaction between two unreacted sites on two monomers depends on the configuration of the two molecules to which those monomers belong, respectively. The most extreme case is when the reaction probability depends on the configuration of the entire molecule [6].

The least extreme case of a substitution effect is when the instantaneous probability of reaction at a site depends on the status (reacted or unreacted) of the remaining sites at a molecule and is independent of the configuration of the rest of the molecule. This case is known as "first shell substitution effect", and typically occurs in epoxy-polyamine systems, where the primary hydrogen is nearly twice as reactive as the secondary hydrogen.

Original work on modeling and analysis of substitution effects was developed by Gordon [7] and Gordon et al. [8,9] by use of the theory of branching processes. A good perspective on the applicability of the theory of branching processes in the description of network formation can be found in the work by Důšek [10]. Důšek et al. [11] extended some of these techniques to the calculation of post-gel relations. The curing of epoxy-resins with diamines was statistically treated as an irreversible alternating polyaddition under the assumption

of negligible polymerization of epoxi-groups and cyclization. Lunák et al. [12] compared those findings with experimental results.

Miller et al. [6] extended Gordon's original work on substitution effects to the calculation of post-gel relations. Instead of following the formalism of the theory of branching processes, these authors applied their own techniques [13,14,15] developed earlier for the solution of other simpler problems in non-linear polymerization.

The present system (DGEBA + DETA) combines the problems of unequal reactivity and first shell substitution effects. The modeling is based on the works by Důšek et al. [11] and Miller et al. [6].

The main assumptions are:

- 1) no reaction between epoxi-groups or cyclization,
- 2) reactivity of epoxi-groups in diepoxide and amino groups in polyamines are independent of each other, i.e., only first shell substitution effects are considered,
- 3) the difference in reactivity of primary and secondary amines is only due to steric effects (no inductive effects are considered). Accordingly, the ratio of rate coefficients of secondary amines to primary amines k_2/k_1 remains constant and independent of temperature.

The first two assumptions are easily justified in the case of monomers with a considerable separation between reacting groups like DGEBA and DETA. The third one is also valid for these chemical species, and supported by the experimental findings of Kakurai et al. [19], where the independence of k_2/k_1 from temperature and conversion was tested for several epoxi-amine systems.

The formation of all possible reacting species is indicated in Figure 2.
The balances are given by the following set of equations:

$$\frac{dA_0}{dt} = -4K_1A_0B - K_2A_0B$$

$$\frac{dA_{11}}{dt} = -2K_1A_{11}B - 2K_2A_{11}B + 4K_1A_0B$$

$$\frac{dA_{12}}{dt} = -4K_1A_{12}B + K_2A_0B$$

$$\frac{dA_{21}}{dt} = -3K_2A_{21}B + 2K_1A_{11}B$$

$$\frac{dA_{22}}{dt} = -2K_1A_{22}B - K_2A_{22}B + 2K_2A_{11}B + 4K_1A_{12}B$$

$$\frac{dA_{31}}{dt} = -2K_2A_{31}B + 3K_2A_{21}B + 2K_1A_{22}B$$

$$\frac{dA_{32}}{dt} = -2K_1A_{32}B + K_2A_{22}B$$

$$\frac{dA_4}{dt} = -K_2A_4B + 2K_2A_{31}B + 2K_1A_{32}B$$

$$\frac{dA_5}{dt} = K_2A_4B$$

$$\frac{dB_0}{dt} = -2B_0(K_1A_p + K_2A_s)$$

$$\frac{dB_1}{dt} = -B_1(K_1A_p + K_2A_s) + 2B_0(K_1A_p + K_2A_s)$$

$$B = 2B_0 + B_1$$

$$A_p = (4A_0 + 2A_{11} + 4A_{12} + 2A_{22} + 2A_{32}) / (f A_{00})$$

$$A_s = (A_0 + 2A_{11} + 3A_{21} + A_{22} + 2A_{31} + A_4) / (f A_{00})$$

A_p and A_s) note the fractions of primary and secondary amino-groups in the system.

Solution of the previous system permits calculation of the vector $\bar{p} = (p_1, p_2, \dots, p_f)$, where p_i represents the extent of reaction of site i in an f -functional monomer A_f . These magnitudes are essential for the calculation of the reaction probabilities at each site. All pre-gel and post-gel information has been calculated by following the procedures already indicated.

RESULTS AND DISCUSSION

The DGBFA - DETA system was cured at several temperatures between 25 C and 55 C. The typical response to a shear pulse is described in Figure 1. Each individual curve contains all the information for the calculation of the viscosity and the shear modulus. These magnitudes can be readily obtained by performing the integrations specified in formulas 9 and 17, either numerically, or by use of a recorder with integrator.

Results from these calculations are presented in Figure 3 for viscosity, and Figure 4 for shear modulus.

Under the particular experimental conditions of these tests, the evolution of the system at gelation was followed by monitoring changes of about three orders of magnitude in viscosity and shear modulus. However, measurements can be readily extended until the end of the cure process if the test equipment has the required capacity and stiffness.

The relation between reaction temperature, chemical structure, and the glass transition temperature of the reacting system is of special importance. If the glass transition temperature is at some point lower than the reaction temperature, the reaction will be virtually stopped by formation of a solid, glassy network normally containing a high proportion of unreacted material. According to the experimental findings of Tanaka et al. [16], cures of DGEBA with DETA in stoichiometric ratio at room temperature are known to retain 50% of unreacted epoxy groups after several weeks.

In order to evaluate the present experimental results, all relevant parameters of the cure and gelation were calculated according to the methods previously discussed. Simulations were performed with $K_1 = 9.22 \cdot 10^4 \exp(-13000/RT)$ [l/mole-sec] and $K_2/K_1 = 0.6$, as obtained from a regression analysis of the experimental data.

The resulting gel times are:

<u>TEMPERATURE [C]</u>	<u>GEL TIME [SEC]</u>
35	4620
40	4020
45	2280
55	1620

Figure 5 contains all the pre-gel and post-gel information. The conditions for the gel point are coincident with those for an infinite weight-average molecular weight.

The probability of a finite chain (P_{fc}) (or extinction probability) that a bond in a monomer unit is not connected to an infinite sequence, remains constant and equal to unity throughout the pre-gel state.

The concentration of effective crosslinks is required for a theoretical evaluation of the elastic moduli. An f -functional A_f unit will be an effective crosslink if at least three of its A groups lead to an infinite network [6]. For a pentafunctional unit (DETA), it is necessary to account for units containing three, four and five linkages to an infinite network. The corresponding probabilities (P_3, P_4, P_5) are also presented in Figure 5. According to the theory of rubber elasticity, the shear modulus of an ideal rubber is given by

$$G = \nu_e RT$$

where R is the gas constant, T is the absolute temperature, and ν_e is the concentration of effective network chains. A network chain will be considered effective if it is long and its ends are effective crosslinks which are separated so as to permit random coil behavior.

If the factors affecting chain effectiveness can be estimated, it is possible to obtain a relation between the concentration of effective crosslinks and the concentration of effective network chains. In the analysis of chemical crosslinks, the most important problem is the presence of chain defects like dangling ends or finite chains. The influence of these defects on the effectiveness of chains having different number of links to the infinite network has

been estimated according to the criteria of Duisier et al. [17], and Graessley [18].

Once these concepts are used to obtain the concentration of effective chains, it is possible to predict elastic moduli according to the theory of rubber elasticity. Calculations for shear moduli are presented in Figure 6.

The experimental moduli, also indicated in Figure 6, are in very good agreement with the predicted values. A departure from the predictions of the kinetic theory is indeed expected at higher conversions and viscosities, given the loss of the Gaussian character of the chains.

CONCLUSIONS

The study of gelation and formation of network structures in nonlinear polymerization faces important limitations in both theoretical and experimental aspects. Investigation of the kinetics (conversion) and its relation to structure formation is restricted by the insolubility of the network polymer.

The present preliminary application of the impulse technique to the study of gelation presents several advantages in comparison with viscosity-titration methods, running of parallel experiments, or gel point determinations by DMA. A single experiment yields kinetic data and absolute measurements of viscosity and elastic parameters while the reacting system evolves from a liquid to a glassy or rubbery network.

Several general applications of the impulse technique were already described by Farris [1]. The extension of the method to reacting systems offers a new perspective in the study of the development of mechanical properties, effect of

chemical structure, stoichiometry, physical transitions combined with gelation, etc.

ACKNOWLEDGEMNT

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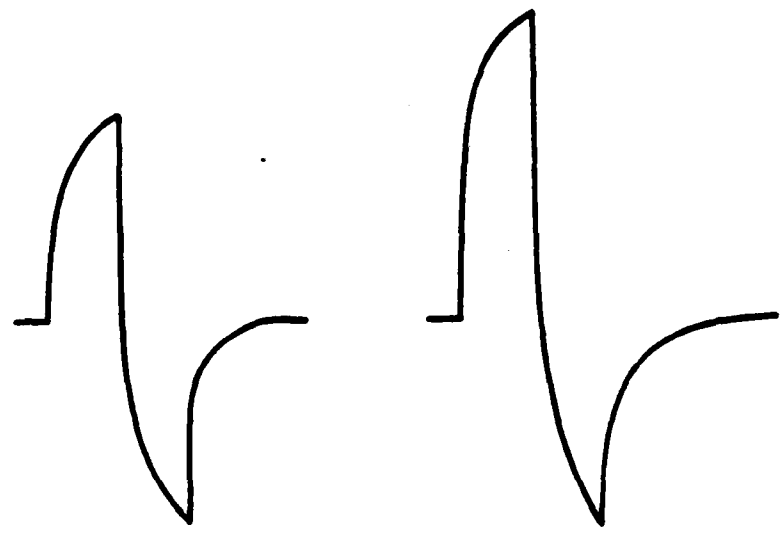
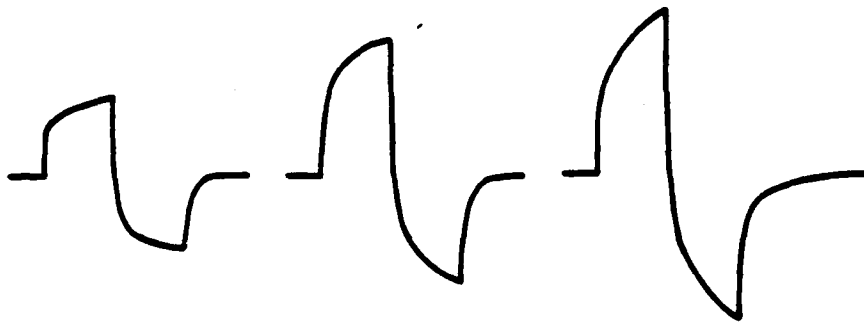
FIGURE CAPTIONS

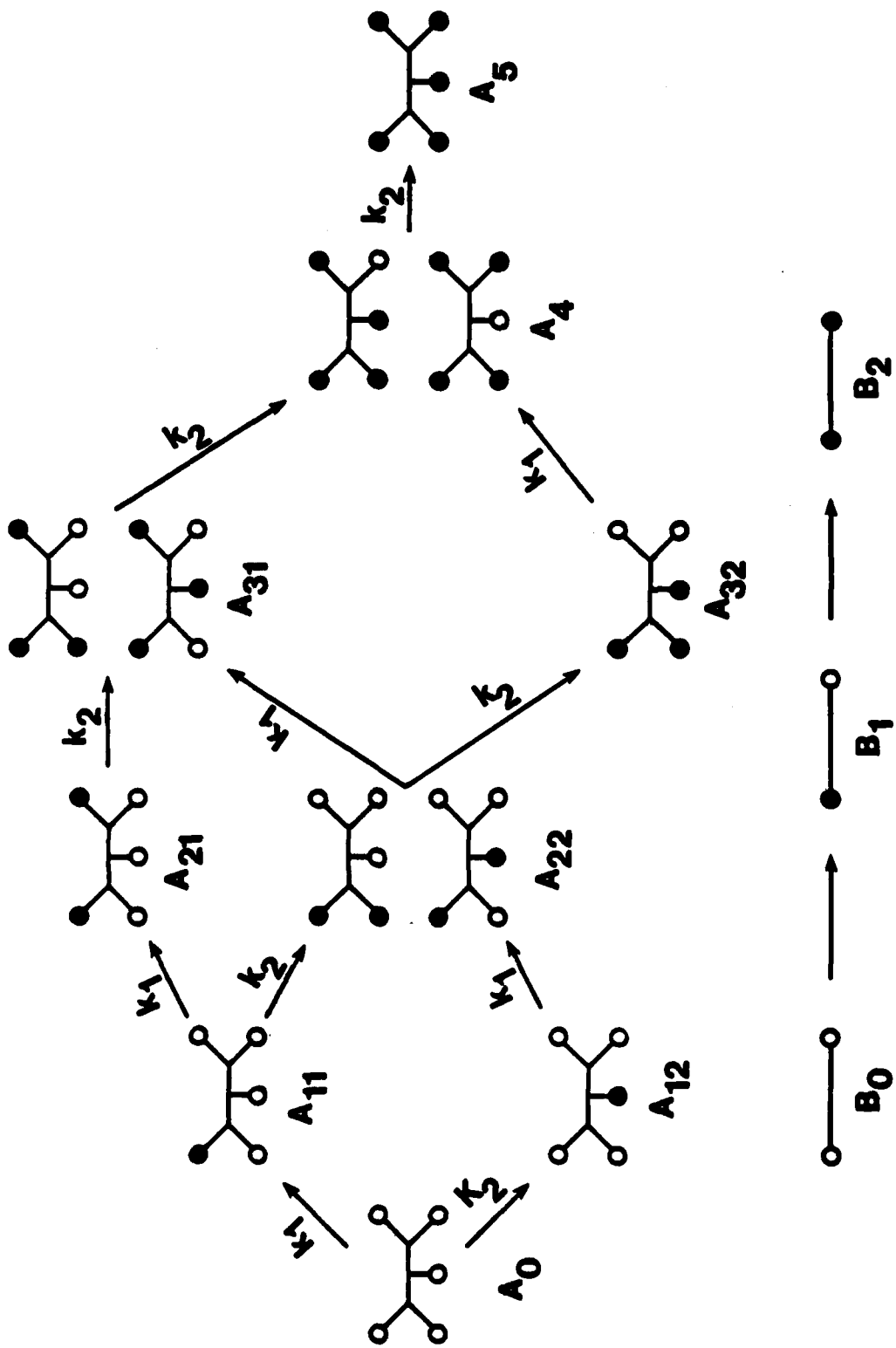
- Figure 1 Cure of DGEBA + DETA at 55 C ($r = 1.08$). Succession of typical response curves to a shear pulse before and after gelation.
- Figure 2 Kinetic scheme for the reaction of DGEBA (B) with DETA (A) indicating all possible species with different number of reacted functionalities.
- Figure 3 DGEBA-DETA system. Viscosity vs. time.
- Figure 4 DGEBA-DETA system. Shear modulus vs. time.
- Figure 5 Cure of DGEBA with DETA at 55 C ($r = 1.08$). Structural parameters vs. conversion (P_{fc} : probability of a finite chain; W_s : fraction of solubles; \bar{M}_n : number average molecular weight; \bar{M}_w : weight average molecular weight; P_i : probability of a crosslink with i reacted groups; P : total probability of a crosslink).
- Figure 6 Cure of DGEBA with DETA at several temperatures ($r = 1.08$). Experimental ($^\circ$) and theoretical shear modulus vs. time. Predictions based on the theory of rubber elasticity contain corrections for dangling ends or finite chains [17,18].

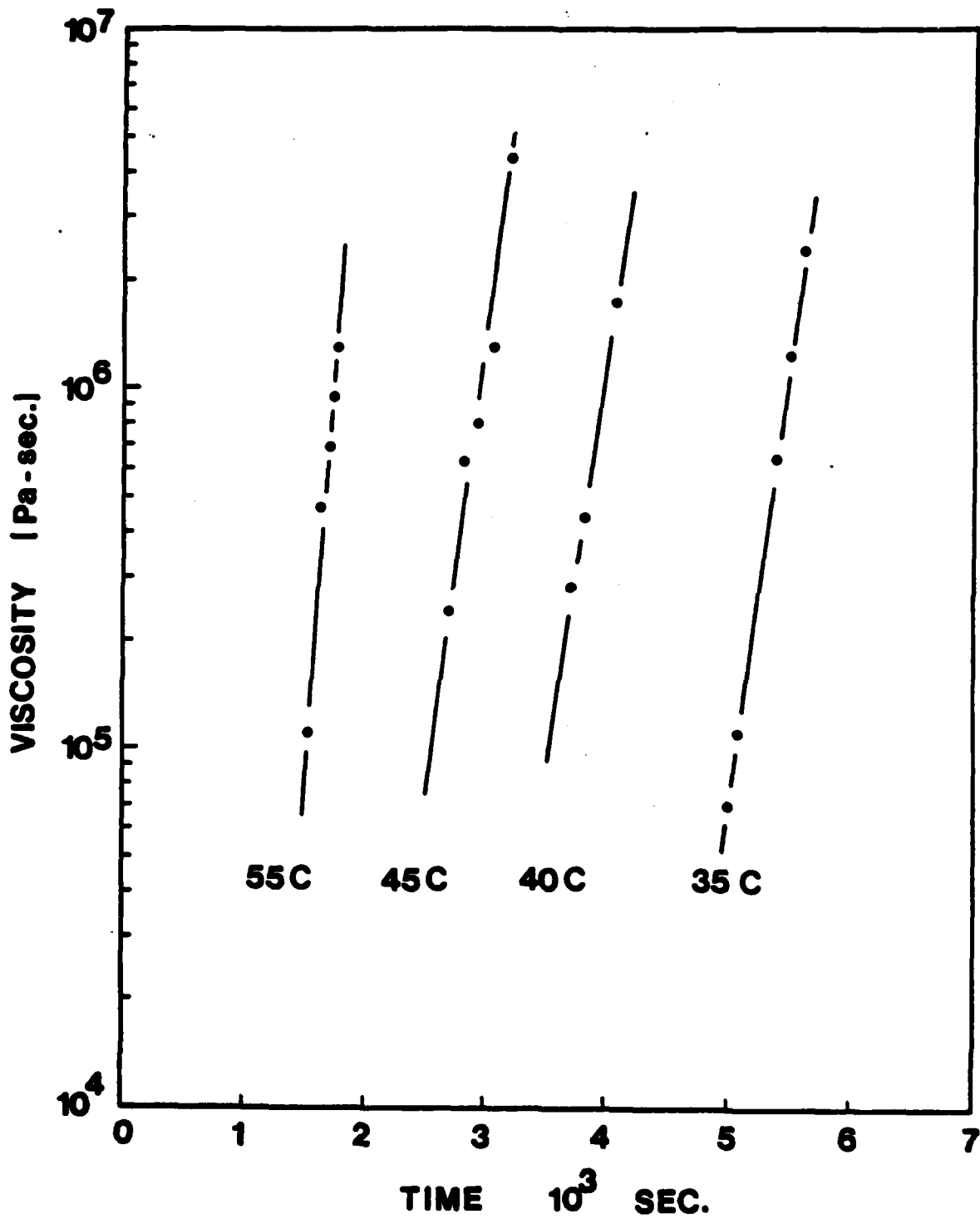
INPUT $\epsilon(t)$

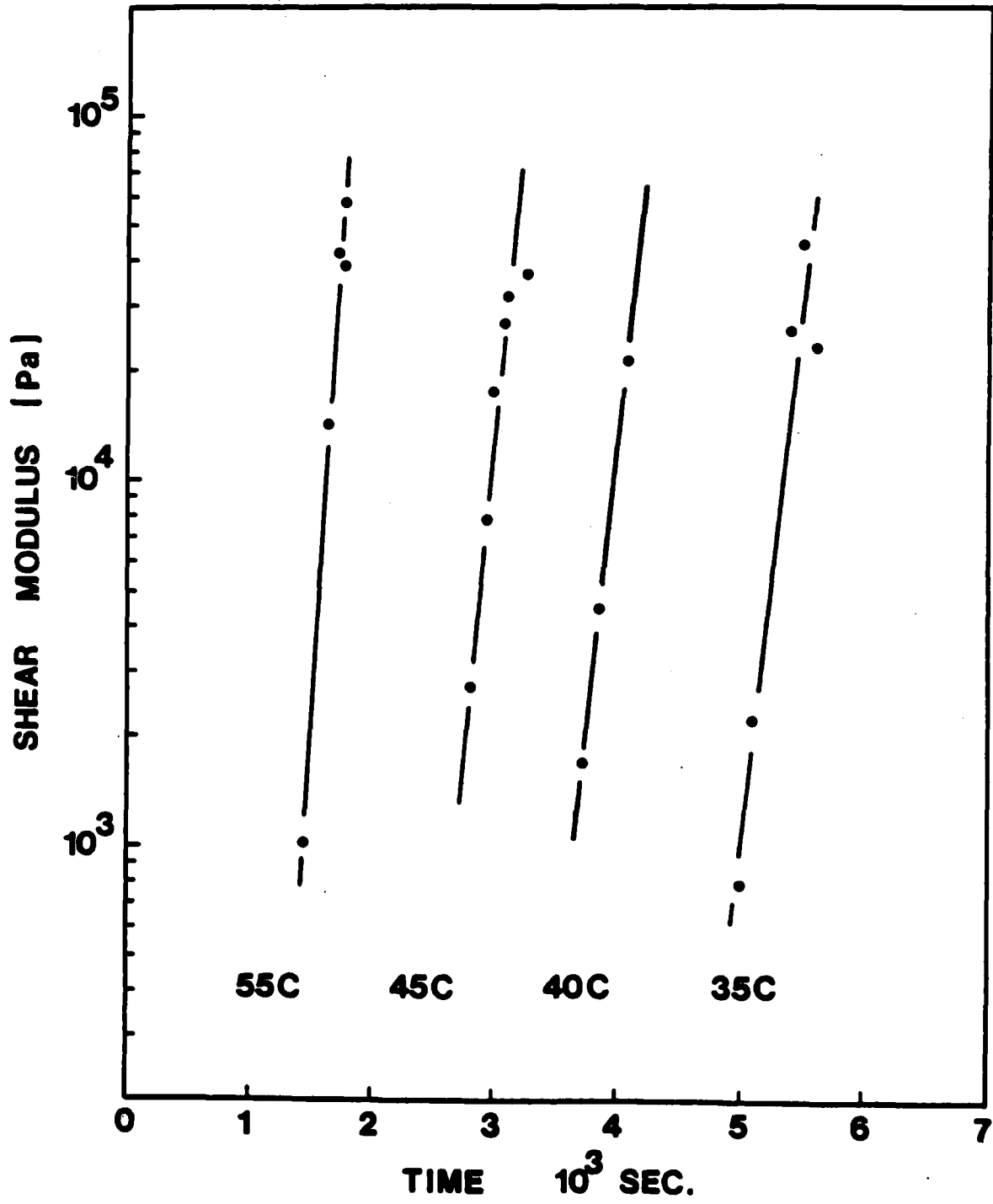


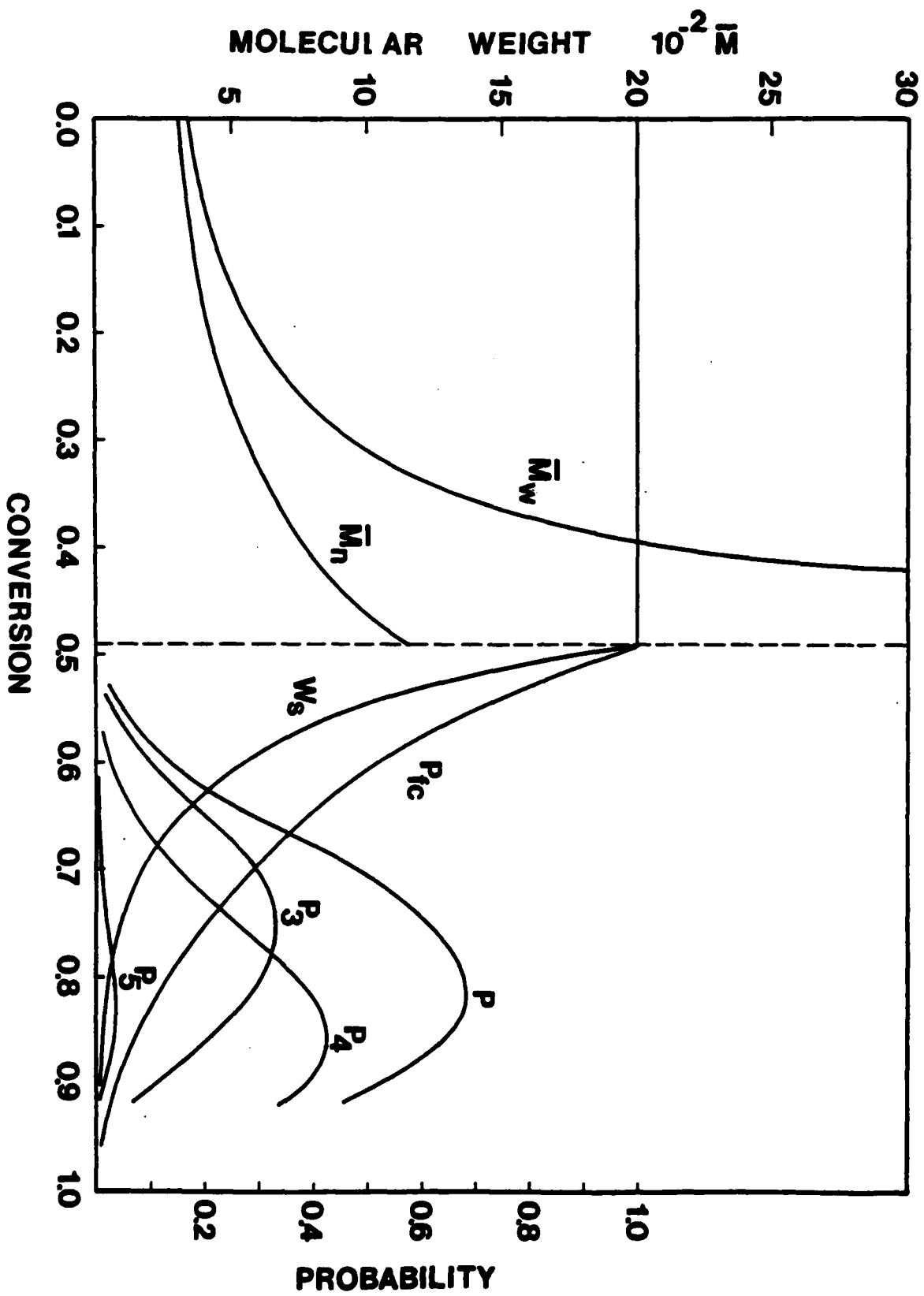
OUTPUT $\sigma(t)$

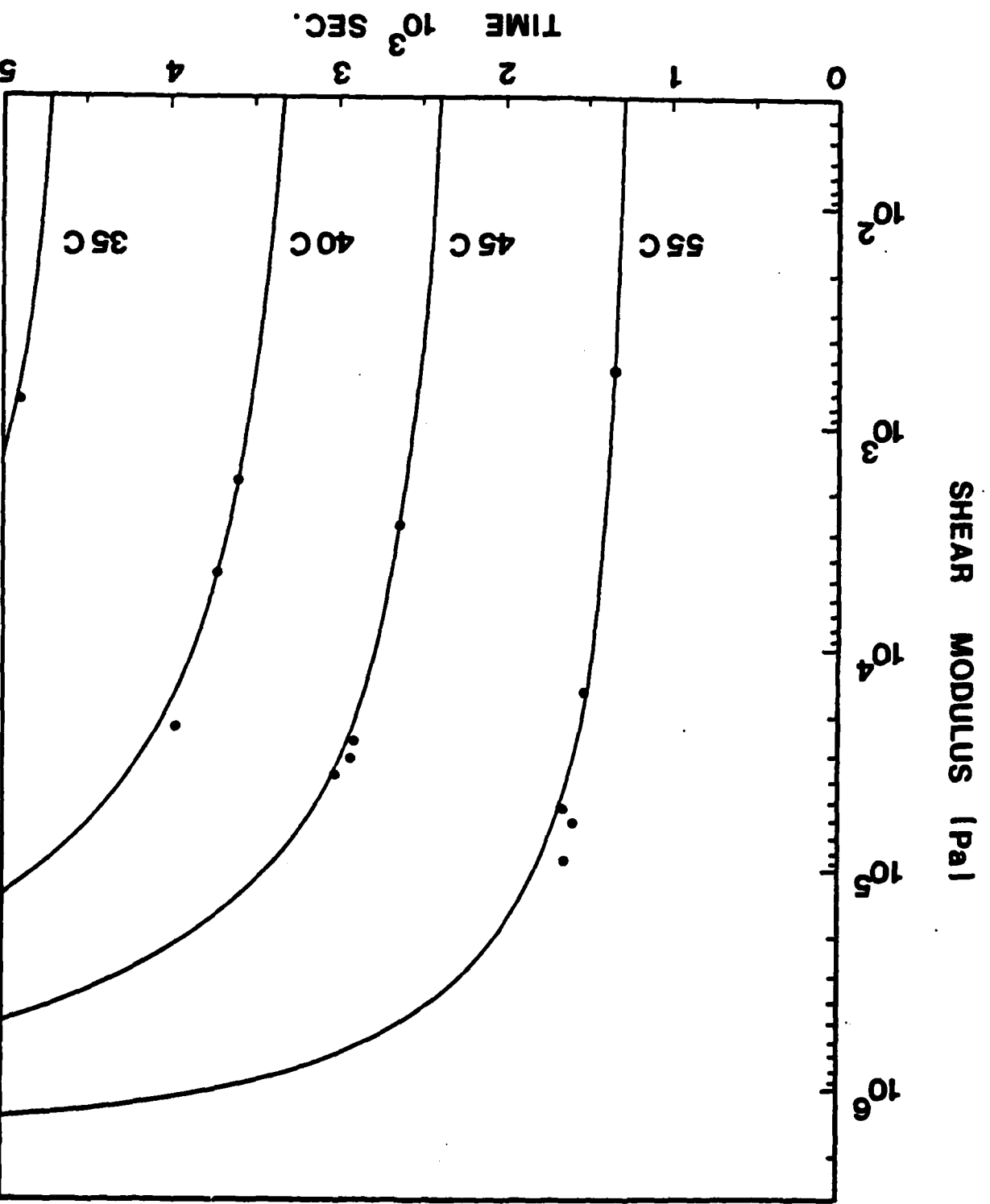












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