

Dielectric Relaxation in Epoxy-Polyglycol Elastomers

A. S. GILBERT* and R. A. PETHRICK,[†] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland*

Synopsis

Dielectric relaxation data is reported on a series of elastomers formed between bisphenol A and either polyethylene glycol or polypropylene glycol. The observed dispersion may be ascribed to relaxation of the "soft" block and is found to vary with both change in the glycol block length and with the ratio of bisphenol A to polyglycol. Elastomers prepared with a poly-glycol component of mixed composition allowed the relaxation frequency at a particular temperature to be shifted over a frequency range of almost three decades. Activation parameters obtained from the temperature dependence of the mean relaxation frequency are used in evaluation of the factors influencing the molecular motion of the "soft" block.

INTRODUCTION

Resins and elastomers formed by the reaction of bisphenol A and various chain extending or crosslinking agents are well known^{1,2} and have wide commercial application. Mechanical measurements on epoxy resins³ and related elastomers^{4,5} indicate that these materials are capable of exhibiting a very wide range of physical properties. In this paper we attempt to study the effects of changes in chemical structure, glycol chain length, and epoxy-glycol composition on the position of the dielectric relaxation frequency in elastomers formed between bisphenol A and either polyethylene glycol or polypropylene glycol or their mixtures.

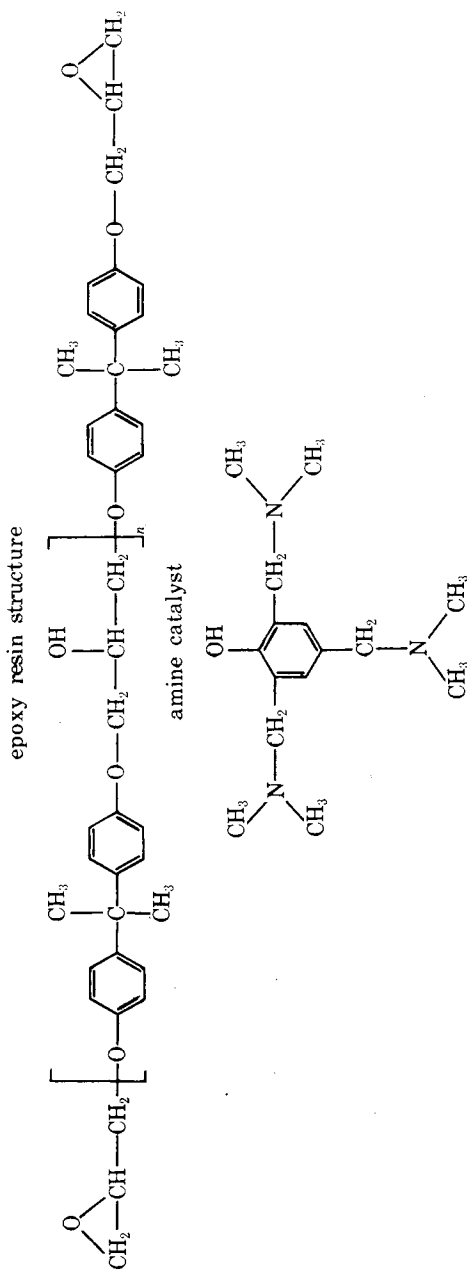
EXPERIMENTAL

Elastomer Preparation

The elastomers were prepared by reaction of epoxy resin with poly glycol in the presence of an amine catalyst. Two epoxy resins were used, both are commercial products of Ciba Geigy and conform to the general formula¹ The resin with $n = 0$ is a viscous liquid and is designated MY790; while that with $n = 1$ is a glassy yellow solid and is designated CT200. The polyglycols were also commercial polymers obtained from Dow Chemicals and are classified as *E* for polyethylene glycol and *P* for polypropylene glycol followed by a number corresponding to the average molecular weight. Two catalysts were used, Ciba Geigy HT973, a boron trifluoride ethylamine adduct, and DMP 30 which has the following structure:

* Present address: Wellcome Research Laboratories, Langley Court, Beckenham, Kent, BR3 3BS.

[†] To whom all communications should be addressed.



The latter, a liquid, was easier to use than the solid HT973 and has been used in the preparation of the majority of the elastomers described in this study.

The elastomers were fabricated as disks, 5 cm in diameter and approximately 5 mm thick. Reaction was achieved by stirring in catalyst (usually DMP 30) to the preheated and thoroughly mixed reactants.¹ The mixture was then poured into the mould and cured at between 80°–100°C for about 12 hr. Generally very small amounts of catalyst were used but one or two samples were cured with up to 20% by weight of DMP 30. This large increase in the proportion of catalyst did not appear to have any significant effect on the relaxation properties of the elastomer; nor did the alternative use of HT973 as catalyst.

The cured materials were often transparent and colored yellow to brown depending on the amount of catalyst used. It was not possible using DMP 30, to prepare materials containing polypropylene glycol of higher molecular weight (MW) than 400 except as small amounts mixed with the polyethylene glycols. Use of HT973 did allow elastomers of polypropylene glycols of MWs 1000 and 2000 to be prepared, however the "cloudy" nature of the sample raised doubts about the homogeneity of the product and these materials were not studied.

Dielectric Measurements

The dielectric data were obtained using a Wayne Kerr transformer ratio arm bridge to cover the frequency range 334 Hz–50 kHz and a Scriber bridge from the range 5–310 Hz. Contact was made between the samples and the dielectric cell with either aluminium or graphite electrodes. The latter were preferred in this study as they lead to more consistent results. The techniques and methods of computation of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant have been described elsewhere.⁶ Variable temperature studies were performed using a water bath.

RESULTS AND DISCUSSION

Typical dispersions are shown in Figure 1. Certain selected elastomers were studied as a function of temperature and the variation in the mean relaxation frequency used to derive an "activation" energy for the process.⁷ The use of such plots is highly suspect as the implicit condition of a unimolecular reaction mechanism is rarely applicable.⁸ The activation-energy approach, however, is useful in comparing data obtained from similar systems, provided the process being studied is not substantially modified between samples. The magnitude of the incremental change in E' observed in these studies is consistent with the loss process arising from motion of the main backbone of either the polyethylene glycol or polypropylene glycol blocks. Inspection of a typical rate plot, Figure 2 indicates that the expected linear variation of relaxation time with reciprocal temperature is only observed over a limited temperature range. Curvature in the activation energy plots has been observed in the viscoelastic and dielectric relaxation of both polypropyleneoxide and polyethyleneoxide polymers.^{10–17} The form of the relaxation spectrum of the pure glycols was found to be dependent upon molecular weight.^{12,16} The lower molecular weight glycols, approximately $M_n = 400$, exhibit a single relaxation process which has a temperature dependence similar to that for other simple glass-forming liquids.^{18–22} In contrast, the high molecular weight glycols (approximately $M_n = 4000$), exhibit

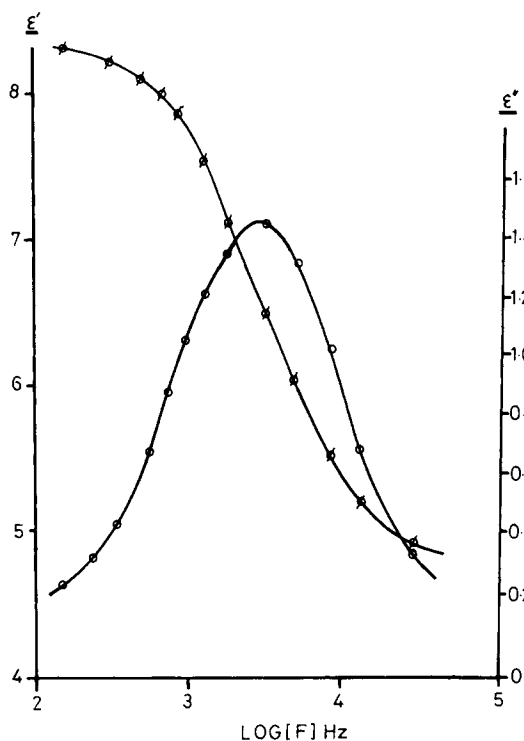


Fig. 1. Dielectric dispersion in a polyethylene glycol epoxy resin. Data obtained at 293 K from a sample of 0.637 mole ratio of glycol to epoxide using aluminium foil electrodes.

relaxation properties more typical of polymeric materials consisting of a dominant high-frequency relaxation process which was found to be independent of molecular weight and a secondary relaxation of smaller amplitude which varies with molecular weight. This latter feature exhibits a temperature dependence describable by a Rouse model^{23,24} and appears to be associated with collective motions of the whole chain.¹⁶ The main relaxation feature dielectrically in the pure glycol is associated with local reorientational motion of main backbone.

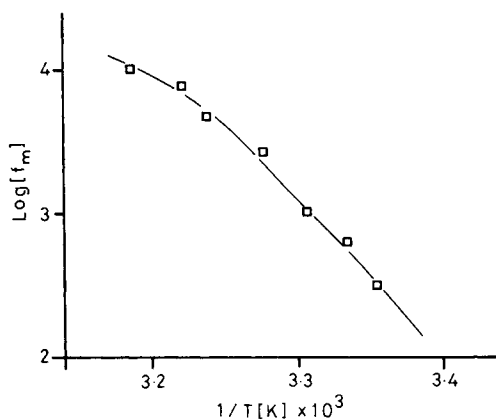


Fig. 2. Rate plot for a polyethylene glycol (1000)-epoxy resin of 0.623 mole ratio glycol to epoxide. Mean activation energy from the "linear" portion of the curve, 176 kJ/mole.

The temperature dependence of the relaxation frequency in the polyethyleneoxides was found to be describable in terms of the well-known WLF equation²⁵

$$\log b_T = -c_1(T - T_s)/(c_2 + T - T_s) \quad (1)$$

with $T_s = 243$ K, $c_1 = 7.80$, and $c_2 = 81$ K for a 2000 M_W polymer. Application of eq. (1) to the data obtained for the epoxy-glycol copolymers yielded values of the constants of similar magnitude to those reported for the pure glycols¹² and other polymers.²⁶ The values of the WLF constants cannot easily be compared since the morphologies of the copolymers may be expected to vary both with glycol type and composition.

Deviations from a linear variation of relaxation time with reciprocal temperature were found over a limited temperature range and suggest that deviations from the ideal behavior may be ascribed to an increasing degree of cooperation of neighboring segments and the surrounding environments in the motion of a particular segment. This hypothesis is further supported by the observation that the breadth of the relaxation increases as the temperature is lowered.^{19,22} The activation energies obtained from these plots must therefore be ascribed as mean energies for the segmental relaxation process and no attempt will be made to correlate these data with the detailed form of the potential energy variations expected for reorientational motions of the polymer.

Effect of Varying and Proportion of Epoxy to Glycol in the Elastomer

Figure 3 illustrates the effects of varying the epoxy to glycol content for E600, E750, and E1000 each separately with MY790 and E600 with CT200. The data

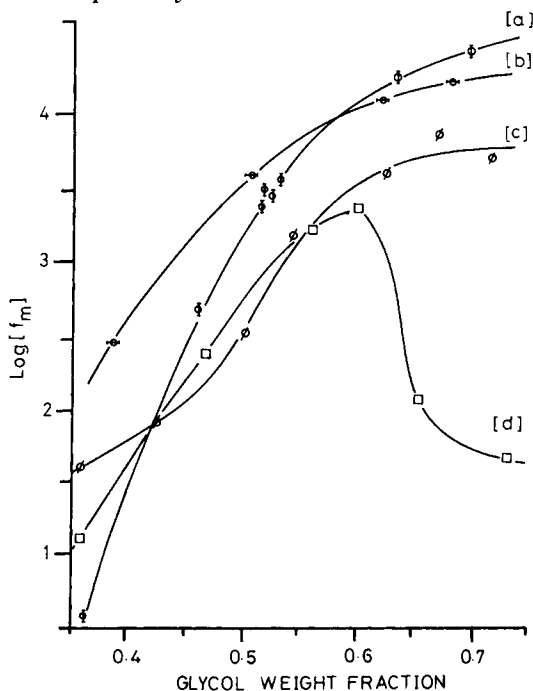


Fig. 3. Effect on the relaxation frequency at 293 K of variation of the proportion of polyglycol to epoxide in elastomer. (a)— \circ —E600, MY790; (b)— \diamond —E750, MY790; (c)— \square —E1000, MY790; (d)— \square —E600, CT200.

are displayed as logarithm relaxation frequency (f_m) vs the glycol fraction of the total weight (GFW) at room temperature.

If only the MY790 materials are considered, two trends are readily apparent. At low values of GFW up to about 0.5 the relaxation frequency can be seen to increase with increase in glycol content and to be not particularly dependent on the specific glycol used. At higher concentrations of glycol, however, it is evident that chain-length effects become predominant. Two effects can be identified: firstly, the shorter the glycol chain length, the higher the measured relaxation frequency; and secondly, the higher the GFW the smaller the rate of increase in f_m ; indeed for the case of E1000 the frequency actually drops.

If the rotational potential defining the relaxation of the soft block is assumed to be composed of three contributions, namely an intramolecular glycol term (P_G), an intermolecular glycol-glycol term (P_{GG}), and an intermolecular glycol-epoxy term (P_{GE}), then it is evident from the data presented in Figure 3 that the increased contribution from P_{GE} that must occur with increase in epoxy content can be correlated with the decrease in relaxation frequency. The relative contribution from the P_{GE} term seem also to be responsible for the changes observed on variation of the epoxy block size. Comparison of E600/MY790 and E600/CT200 materials shows that at high glycol concentrations the relaxation times are comparable but at low GFW's the material with the larger epoxy block yields a higher relaxation frequency. This is evidently due to the fact that in the polymer formed with CT200 ($n = 1$), the epoxy content is more highly concentrated thus leading to fewer glycol-epoxy interactions and therefore a decreased contribution from P_{GE} for similar values of the GFW.

At high GFWs it is expected that P_G and P_{GG} will predominate with the greatly increased number of intermolecular glycol-glycol interactions and it is expected that the polymers will begin to show relaxation behavior akin to the pure glycols. Thus materials incorporating E600 and E750 which in the pure state at room temperature are both mobile solids (on a warm day, E600 is liquid) should behave as flexible rubbers. On the other hand materials containing E1000, which at room temperature is a crystalline solid, should undergo an incipient crystallisation which is evidently reflected in the decrease in relaxation frequency observed at GFW's higher than 0.6. At higher temperatures, above the "melting point" of the glycol chains, the E1000 samples will behave in similar fashion to the lower MW materials are illustrated in Figure 4 where it can be seen that at 45°C no decrease of relaxation frequency is observed at high values of GFW.

It is interesting to note that all the above changes in relaxation frequency are paralleled by corresponding changes in the subjectively perceived mechanical properties.²⁷ For example, in the E600 series at room temperature the highest epoxy content samples are hard rubbers; the flexibility of the other samples increases as GFW. For the series flexibility again increases with GFW up to about 0.6 but then decreases as the frequency falls to higher glycol concentrations. For instance the sample with GFW = 0.647 is a hard rubber, whereas that with GFW = 0.6 is fairly flexible.

The effects of change in glycol are paralleled in the variation in magnitude of the activation energy Table I. Within the E600 series increasing the glycol content raises the relaxation frequency and lowers the activation energy. Similarly increasing the glycol chain-length leads to an apparent drop in the activation energy and a corresponding increase in the relaxation frequency. The relative shifts with molecular weight in the relaxation frequency are paralleled closely by the activation energy.

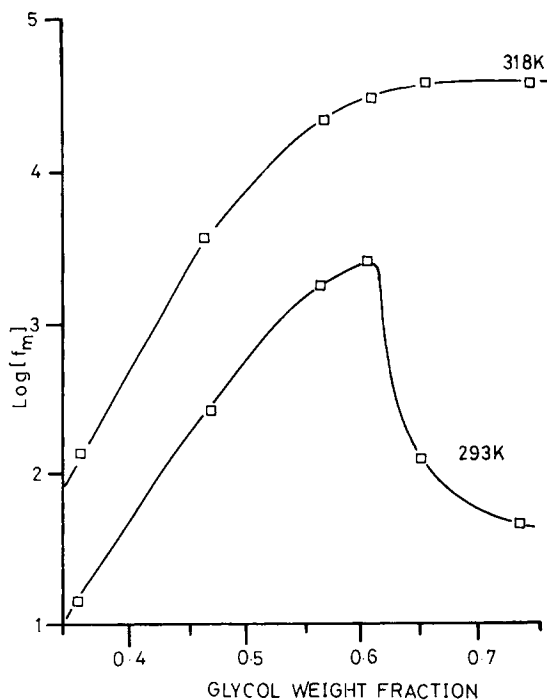


Fig. 4. Effect of temperature on the variation of relaxation frequency with polyglycol-epoxy composition. The dramatic drop in relaxation frequency at 0.625 polyglycol epoxide weight fraction observed at 293 K disappears on raising the temperature to 318 K.

TABLE I
Effects of Variation of Glycol Block Size and Epoxy Content on Relaxation Frequency and Activation Energy

Glycol type	Glycol weight fraction	Relaxation frequency ^a	Activation energy kJ/mole
E200	0.257	13 Hz	72.8
E600	0.694	30 kHz	—
	0.632	20 kHz	—
	0.579	4.5 kHz	—
	0.522	2.7 kHz	56.5
	0.459	511 Hz	111.0
E750	0.362	2.5 Hz	100.5
	0.358	42 Hz	63.6
E1000	0.647	113 Hz	184.0
	0.561	1.8 kHz	90.5
	0.358	13.5 kHz	16.9
E1450	0.703	105 Hz	74.5
P400	0.429	10 Hz	85.0

^a Values of relaxation frequency at 293 K.

It is interesting to compare the relaxation behavior of the polymer backbone observed in the copolymers with that of the pure glycols. The variation of the relaxation frequency in the copolymers is the reverse of that observed in the glycols, reflecting the role in the copolymers of the epoxy block in restricting the motion of the glycol block. It should also be noted that the position of the relaxation in the copolymers containing the short chain glycols is typically 7–9

decades lower than in the pure glycols and only 4–6 decades in the higher molecular weight glycols.

Relaxation of Epoxy Mixed Glycol Composites

Polyethylene Oxide 600 Polyethylene Oxide 4000 Mixtures

The variations of the relaxation frequency with composition of the glycol mixture are presented in Figure 5. The relaxation frequency of the longer chain analog occurs below 1 Hz at room temperature. The data demonstrate a significant drop in the relaxation frequency on the addition of a small amount of the higher molecular weight material. This trend is, however, apparently not monotonic and little change in the position of the relaxation frequency is observed for an increase in the fraction from 0.1 to 0.25. Above this fraction the relaxation frequency starts to fall again towards the E400 limit of below 1 Hz.

The observations were performed at approximately fixed epoxy glycol ratios and it may be suggested that the contribution arising from epoxy interaction is essentially constant throughout. A possible explanation for the observed effects can be obtained by assuming that the probability of significant neighboring interaction increases with chain length. Hence the addition of a small amount of E4000 increases the occurrence of P_{GG} interactions and lowers the relaxation frequency. The apparent insensitivity of the relaxation frequency to changes in composition in the range 0.1–0.25 may be a consequence of a compensation between the disorder introduced by the short-long chain mixture and the increased P_{GG} interactions. Above 0.25 the P_{GG} is dominant and the relaxation frequency tends towards the limit of the pure polymer.

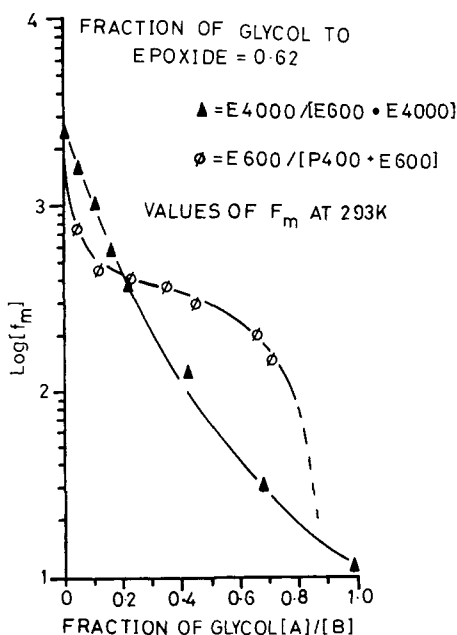


Fig. 5. Variation of relaxation frequency with composition for mixtures of polyglycols and epoxy.

Polyethylene Oxide 600 Polypropylene Oxide 400 Mixtures

The variations of the relaxation frequency with composition of the glycol mixtures are presented in Figure 5. The addition of P400 to E600 leads to a lowering of the frequency in a monotonic fashion. These observations may be explained partially on the basis that the introduction of the methyl group will tend to increase the steric contribution to the intermolecular potential. The methyl group will also introduce a steric contribution to the intramolecular potential (P_G) and the net effect of this will be a lowering of the relaxation frequency. In this study the ratio of the epoxy resin to the glycol was kept constant and it may be assumed that the effects of the epoxy contribution to the rotational profile will to a first approximation be constant through out the series. It appears that the decrease of the relaxation frequency with increasing P400 is a consequence of increased steric interactions influencing both the P_{GG} and the P_G terms in the rotational energy profile.

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