On the origin of multiple dispersions in acrylic polymers

S. Havriliak Jr*
Rohm and Haas Research, Bristol, PA 19007, USA

and S. J. Havriliak
Havriliak Software Development Co., Huntingdon Valley, PA 19006, USA

(Received 16 August 1990; revised 21 January 1991; accepted 25 January 1991)

Dielectric and infra-red experimental evidence on methacrylate polymers is reviewed. These results are discussed in terms of a model proposed for dielectric relaxation of polar polymer in a matrix of arbitrary compliance. As the side-chain length increases, the symmetry of the orienting segment *decreases*, causing the strain energy to offset any reduction in the free energy due to interactions of the dipoles, $\bar{\mu}$, with the applied electric field, $\bar{E}$.

(Keywords: acrylic polymers; dielectric relaxation; infra-red spectra; multiple dispersions)

INTRODUCTION

Many polymers exhibit multiple relaxation processes. For those polymers that are partially crystalline, such as polyesters, the interpretation is quite simple: relaxation in the crystalline and non-crystalline domains have different dynamic parameters so that their respective relaxation processes occur under different experimental conditions. Acrylic polymers are not thought to be partially crystalline, although there is some evidence to suggest that there may be a considerable amount of local structure. Not all acrylic polymers have two dispersions: those with short side chains exhibit two dispersions, while those with longer side chains have only one. It is the object of this work to review briefly the dielectric and infra-red evidence for acrylic polymers, and then interpret the relaxation process in terms of recent theoretical developments[1].

REVIEW OF DIELECTRIC RELAXATION

60 Hz loss peaks

A plot of the dielectric loss tangent with temperature for conventionally initiated polymethacrylates taken from the data of Steck, Dyvik and Bartoe[2,3] is given in *Figure 1*. This series clearly demonstrates several important features. First, poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) have two loss tangent maxima, while the other polymethacrylates have only one. The relative magnitudes of the higher-temperature loss peaks for these two polymers, i.e. α peaks, are much smaller than their corresponding β peaks. The magnitude of the loss tangent for these two β peaks is similar to the α peaks of the other methacrylate polymers. The β peaks for PMMA and PEMA do not correlate with the glass temperature, while the α peaks do correlate with that temperature. In other words, increasing the side-chain length to about three or four carbon atoms appears to 'freeze out' the β (glass phase) relaxation process.

Syndiotactic poly(methyl methacrylate)

The complex dielectric constant was measured over a frequency range of 30 Hz to 150 kHz and a temperature range of room temperature to 150°C. At a temperature of 105.1°C, i.e. 15°C below T_g, the dispersion is centred in the available frequency range. This process is referred to as the β relaxation process because it occurs in the glass phase. The parameters of the β relaxation process were represented in terms of the general Debye function:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = [1 + (i\omega\tau_0)^\alpha]^{-\beta}$$

and are given in ref. 4. In this expression ε_0 and ε_∞ represent, respectively, the low-(equilibrium) frequency and high-(infinite) frequency limiting dielectric constants for the particular process, i.e. the β process. In addition α and β represent the shape of the process when viewed in the complex plane. These parameters can also be interpreted in terms of a distribution of relaxation times or a time-dependent correlation function. Finally τ_0 is the relaxation time. It is always necessary to specify the process that these parameters represent, i.e. the α parameter for the β process or β parameter for the β process. This rather awkward specification is consistent with convention. Similarly we must also state the process to which the other parameters such as the equilibrium dielectric constant, i.e. ε_0, belongs, i.e. equilibrium dielectric constant of the β process or relaxation time of the β process.

At temperatures well above T_g, deviations from the β process were observed and were attributed to another or α process. The parameters of the general Debye equation

---

* To whom correspondence should be addressed

0032-3861/92/050938-06

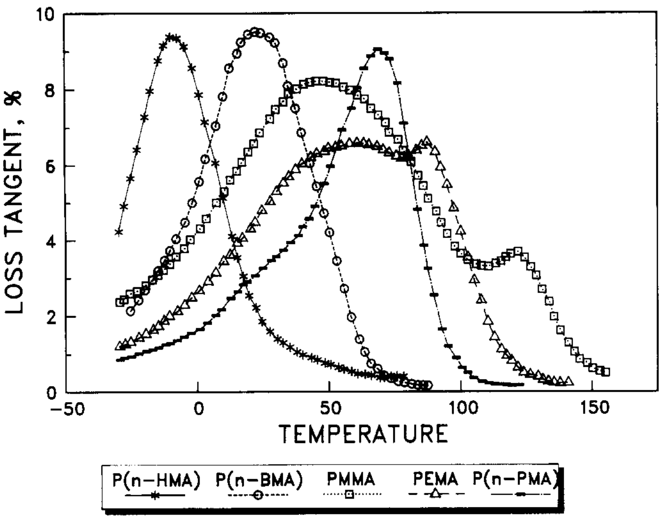

Figure 1 A plot of the loss tangent (×100) as a function of temperature (°C) for a number of methacrylate polymers. The polymers are identified in the legend and in the footnote to *Table 1*

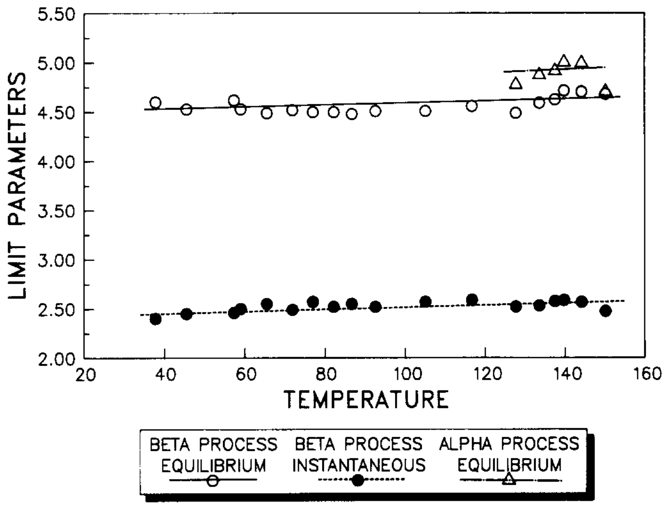

Figure 2 A plot of the instantaneous and equilibrium dielectric constants for the β process of s-PMMA as well as the equilibrium dielectric constant for the α process

for the α process were determined by assuming the experimental complex dielectric constants to be additive in terms of the two processes. The parameters of the general Debye function for the α process are also listed in ref. 4. This nomenclature is awkward and leads to statements such as the α parameter for the β process or β parameter for the α process. Although this nomenclature is awkward, it is consistent with previous definitiions. For the reasons stated above, the parameter and process should always be specified.

Another unusual condition arises that merits mention. The equilibrium dielectric constant for the β process turns out to be numerically the same as the instantaneous dielectric constant for the α process, at the same temperature. This comes about because the processes are assumed to be additive and the α process is considerably slower than the β process. The parameters and processes should always be specified.

A plot of the limiting dielectric constants with temperature is given in *Figure 2*. The full circles represent the instantaneous dielectric constant for the β process, the open circles represent the equilibrium dielectric constant for the β process as well as the instantaneous dielectric constant for the α process and finally the triangles represent the equilibrium dielectric constant for the α process. The three parameters do not appear to depend significantly on temperature, and there are no large changes in these constants in the vicinity of the glass transition temperature. A plot of these parameters in the original work did show a small discontinuity (12%) at the glass temperature. Inasmuch as ε_∞ is expected to be a function of density, the observed discontinuities were interpreted in terms of a cell constant change due to the releases of moulded-in stresses. Taking this into account gave the results shown in *Figure 2*. The α parameter for the β process also changes continuously through the glass transition temperature (see *Figure 3*). A plot of the relaxation time with temperature is given in *Figure 4* for the α and β processes, which intersect at a temperature of about 240°C. The relaxation time for the β process changes continuously through the glass transition region. The refracrtive index (η) is given in *Table 1* for s-PMMA as well as for other acrylic polymers at room temperature. The dielectric constants at infinite frequencies is believed to be equal to the square of the refractive index (η^2), also listed in *Table 1*, although some estimate of the atomic polarization must be added to η. About 7% of the refractive may be a reasonable estimate of the atomic polarization ($(1.07\eta)^2$), which is also listed in *Table 1.*

Poly(ethyl methacrylate)

Ishida and coworkers[4] studied the dielectric relaxation properties of poly(ethyl methacrylate) (PEMA) over extensive temperature and frequency ranges. PEMA, like PMMA, exhibits two relaxation processes. They were not able to resolve the α process parameters, while the results for an unbiased study of the β process are listed in *Table 1*. A rate plot of the relaxation times for the β process was found to vary continuously through the glass transition region. The α parameter for the β process was also found to change continuously through the glass transition temperature. The parameters listed in *Table 1* were obtained using unbiased methods[5].

Poly(methyl acrylate)

Ishida and coworkers[5] also studied the dielectric relaxation properties of poly(methyl acrylate) (PMA)

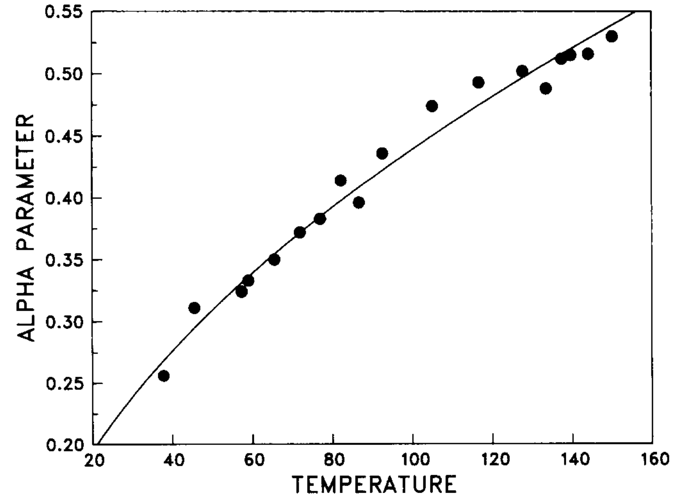

Figure 3 A plot of the α parameter with temperature (°C) for the β process of s-PMMA

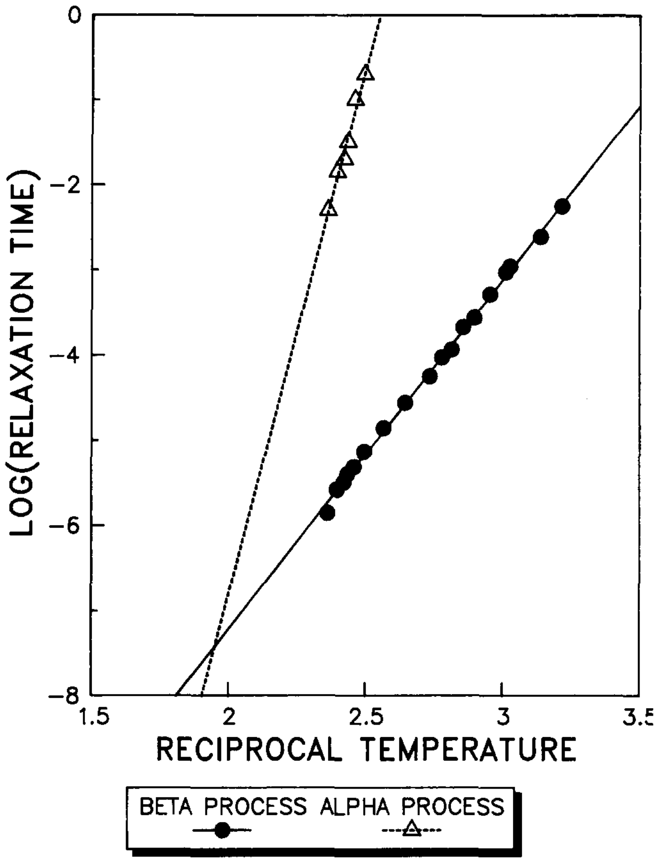

Figure 4 A rate plot for the α and β processes of s-PMMA

Table 1 Instantaneous and equilibrium dielectric constants for some acrylic polymers

				Beta process		Alpha process	
Polymer[a]	η	η^2	$(1.07\eta)^2$	ε_∞	ε_0	ε_∞	ε_0
s-PMMA	1.47	2.16	2.47	2.50	4.6	4.6	5.0
PMMA	1.49	2.22	2.54	–	–	–	–
PMA	1.48	2.19	2.51	–	–	4.11	7.42
PEMA	1.49	2.22	2.54	2.36	4.77	–	–
PnPMA	–	–	–	–	–	–	–
PnBMA	1.48	2.19	2.51	–	–	2.17	3.64
PiBMA	1.46	2.13	2.44	–	–	2.10	3.54
PAMA	–	–	–	–	–	–	–
PcHMA	1.51	2.28	2.61	–	–	2.21	3.86
PnHMA	1.48	2.19	2.51	–	–	2.60	4.25
PnOMA	–	–	–	–	–	2.53	4.22
PnNMA	–	–	–	–	–	2.37	3.42

[a] Abbreviations: s-PMMA, syndiotactic poly(methyl methacrylate); PMMA, poly(methyl methacrylate); PMA, poly(methyl acrylate); PEMA, poly(ethyl methacrylate); PnPMA, poly(n-propyl methacrylate); PnBMA, poly(n-butyl methacrylate); PiBMA, poly(isobutyl methacrylate); PAMA, poly(amyl methacrylate); PcHMA, poly(cyclohexyl methacrylate); PnHMA, poly(n-heptyl methacrylate); PnOMA, poly(n-octyl methacrylate); PnNMA, poly(n-nonyl methacrylate)

over extensive temperature and frequency ranges. PMA, like PMMA and PEMA, exhibits two relaxation processes. Their results for the α process in PMA are listed in *Table 1*, while the results for an unbiased study of the β process[6] are listed there along with the refractive index. A plot of the log of the relaxation time with reciprocal absolute temperature for the two processes of PMA is similar to that of PMMA (see *Figure 4*). In other words (see *Figure 4*), rate plots with low (β process) and high (α process) activation energies intersect at temperatures above the experimental range. The α parameter for the β process was found to change continuously through the glass transition temperature.

Higher methacrylates

A number of poly(alkyl methacrylates) were studied by Ishida *et al.*[4] as well as Strella and coworkers[6,7]. These polymers do not show any evidence for a *dielectric* glass phase (β) relaxation process. The high-frequency limiting values of the dielectric constant, i.e. ε_∞, should approach η^2. The parameters listed in *Table 1* were obtained from published data using unbiased statistical techniques.

REVIEW OF INFRA-RED SPECTRA IN THE ESTER OXYGEN REGION

Syndiotactic poly(methyl methacrylate)

The dipole moments of the acrylic polymers just described lie in the planes of the ester groups, and nearly pointing in the direction of the carbonyl group. For this reason an understanding of the infra-red characteristics of the ester group is basic to an understanding of the dielectric relaxation properties of acrylic polymers. The spectra of s-PMMA in the ester oxygen region (1000 to 1300 cm^{-1}) is considerably more complex than the infar-red spectra of simple esters such as methyl acetate[8]. Specifically, in the case of methyl acetate only one strong band is observed in this region while in s-PMMA at least four strong bands and three weak or hidden bands are observed. Some of these strong bands are associated with the C–C–O coupled with C–O stretching vibrations. The large number of bands in s-PMMA was interpreted in terms of splittings due to intramolecular interactions rather than intermolecular interactions because the splittings persisted in dilute solutions such as 1% chloroform. In addition these bands disappeared in copolymers of methyl methacrylate and styrene in a 1/3 ratio. In other words separating the polar ester groups with non-polar phenyl groups reduced the number of bands in the infra-red spectra, albeit a very broad one, to that observed in methyl acetate. The results suggest that the number of bands is due to polar intramolecular interactions caused by different and specific arrangements of the dipole moment associated with the ester side chain. The possibility of changing the distribution between these arrangements was obtained from thermal cycling studies. The absorbance ratio of neighbouring groups ($\nu_1/\nu_2 = A(1268\ \text{cm}^{-1})/A(1238\ \text{cm}^{-1})$ shows *important* effects of thermal hysteresis (see *Figure 5*) on films that were cast from solution. The open squares in *Figure 5* represent measurements made at constant temperature by allowing the temperature to equilibrate for 1 h after the temperature was changed 5–10°C. After 200°C was reached, the test specimen was quenched to dry-ice temperatures and the measurements were repeated as before. These results are represented by the full circles in *Figure 5*. The ratio is significantly lower and independent of temperature until about 120°C is reached. Above this temperature, the initial behaviour was observed. Once 200°C was reached, the test specimen was cooled slowly (overnight) and the heating measurements repeated. This third heating run (full squares in *Figure 5*) repeated the results of the first warming run. These results can be used to construct the following model for local structure of s-PMMA in the non-crystalline phase. The main-chain carbon atoms form a *planar* zig-zag arrangement. The ester groups are in planes perpendicular to the

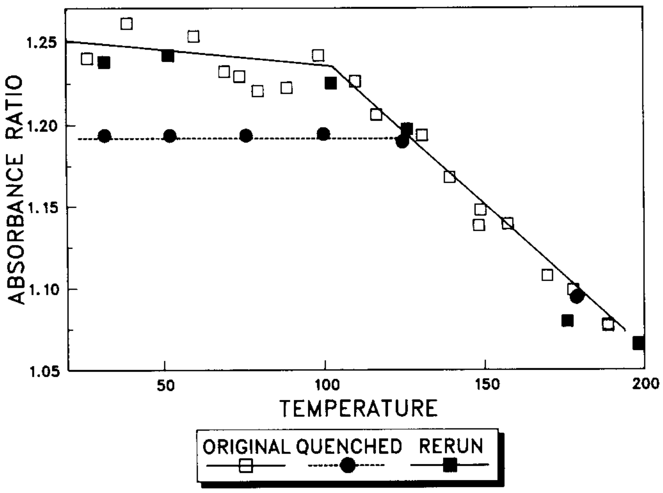

Figure 5 Infra-red absorbance ratio for s-PMMA demonstrating thermal hysteresis

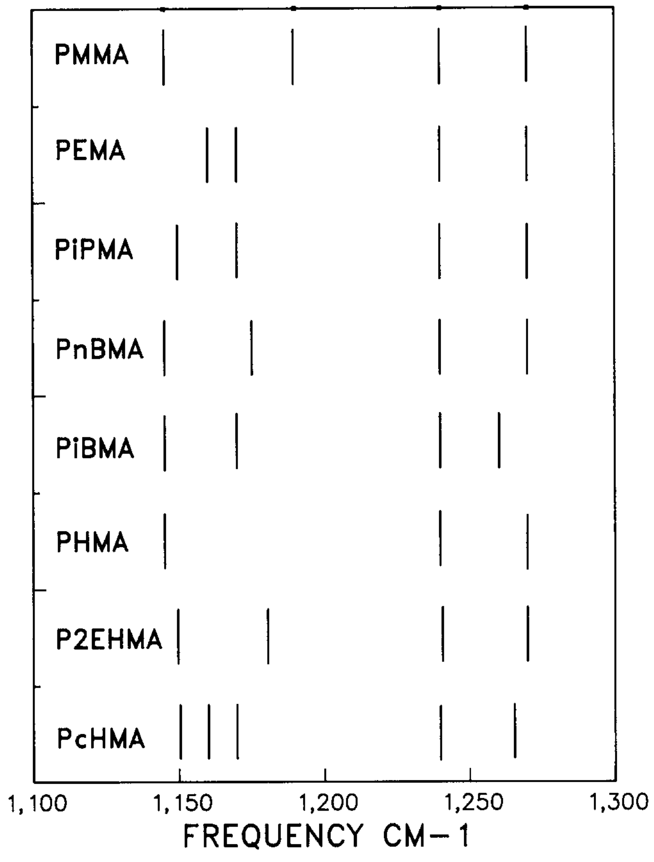

Figure 6 Location of the absorption peaks in free-radically initiated polymethacrylates: PiPMA, poly(isopropyl methacrylate); PHMA, poly(hexyl methacrylate); P2EHMA, poly(2-hydroxyethyl methacrylate); others can be found in footnote to *Table 1*

main-chain plane and alternate from side to side in s-PMMA.

Higher acrylic polymers

Structural information about higher poly(alkyl methacrylates) is less definitive. There is, however, some information made on a study of films and in dilute solution. Examination of polymethacrylates in catalogues of spectra[9,10] shows that the whole family of free-radically initiated methacrylates exhibit a multiplicity of ester oxygen peaks, often with a weak absorption band around 1070 cm^{-1}. These results are summarized in *Figure 6* for a series of methacrylates. Polyacrylates show a similar band structure but the bands are not as distinctly split, suggesting that the intramolecular interactions are not as specific as they are in the polymethacrylates.

Local structure for acrylic polymers

The results of computer modelling of a hypothetical syndiotactic methacrylate backbone with different side *chains* is given in *Figure 7*. Starting from the top of the figure, the first monomer unit is methyl methacrylate; the second, connected to the first in a syndiotactic placement, is ethyl methacrylate; the third, also connected in a syndiotactic placement, is propyl methacrylate; and so on down the chain. The calculations to produce that figure were performed using MacroModel developed at Columbia University by Professor C. Still and modified by Rohm and Haas for polymer modelling. The arrangements shown in *Figure 7* are in their local minimum and not a global minimum because the figure is used to illustrate the following points. The labels in *Figure 7* identify the side chains and are placed near the carbonyl group. The carbonyl groups were positioned to be pointing in the same direction (towards the viewer) to demonstrate their proximity to the main chain. An arrangement with dipoles pointing in the same direction is inconsistent with dipole moment calculations based on trial structures[4], which suggest that they alternate towards and away from the position of the viewer. The side chains are in their extended conformation to emphasize their length. It is clear from *Figure 7* that increasing side-chain length serves to separate main chains, consistent with experimental evidence[4]. Since the ester group is always in the same relative position to the main chain, one would expect the infra-red absorption characteristics to be independent of side-chain length.

Figure 8 is an end view of the same structure shown in *Figure 7*. In this view the dipole moments would be pointing up. It is the dipole moments of several ester groups that interact with the applied electric field. Restricting that orientation at equilibrium is the equilibrium tensile compliance surrounding the unit. *Figure 9* is a schematic representation of the polymer chain taken in the same direction as in *Figure 8*.

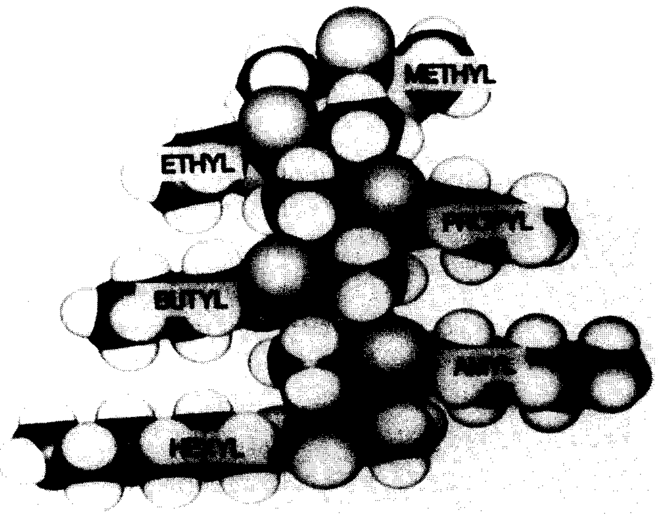

Figure 7 Computer-simulated model illustrating the effect of side-chain length on the width of the polymer chain. The side chains are labelled, while the main chain is in the y axis of the figure

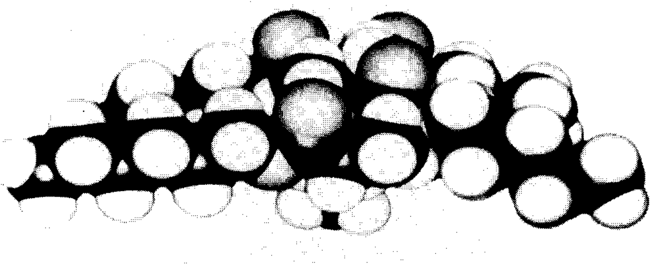

Figure 8 Same structure as shown in *Figure 7* except that the structure has been rotated so that the polymer chain is perpendicular to the plane of the figure

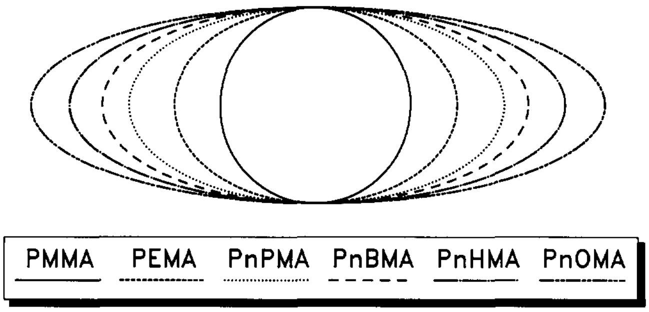

Figure 9 Elliptical cross section of acrylic polymers with increasing side-chain length

A MODEL FOR MULTIPLE DISPERSIONS

In a previous study the inhibiting nature of tensile compliance on the equilibrium polarization process was derived for a number of cases. We shall ignore the Onsager–Kirkwood case because their reaction field by itself is probably an inadequate representation of long-range correlations, particularly for the case of long stiff polar polymer chains. Instead, we shall pursue the discussion along the lines of inconsequential electrostatic interactions[1]:

$$\left(\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\right)\frac{3V}{4\pi} = \frac{N}{3kT}\left(1 + \frac{\zeta^2 V g_r \mu^2}{6D_0 NkT}\right)^{-1} g_r\mu^2 \qquad (1)$$

In this expression, $g_r\mu^2$ is the effective *squared* dipole moment, ζ is in general a *tensor* that relates a molecular shape factor (γ) to the dipole moment, i.e. $\gamma = \zeta\mu$, and D_0 is the equilibrium tensile compliance. It is these molecular shape factors that sum to a macroscopic strain, which in turn leads to a strain energy. The quantity γ^2/D_0 is the strain energy increase, which offsets the lowering of the polarization energy decrease when the electric field is turned on. This expression was derived for the case when the long-range interactions cannot be represented by an electrostatic reaction field.

Let us assume that the relaxation time τ_0 of the dielectric process is very fast, i.e. $t_0 \ll 10^{-6}$, that our experimental frequency range is 1 to 10^6 Hz, i.e. the timescale is 1 to 10^{-6} s, and that D_0 depends on the frequence (time) of measurement. For this case equation (1) becomes:

$$\left(\frac{\varepsilon_0(t) - 1}{\varepsilon_0(t) + 2}\right)\frac{3V}{4\pi} = \frac{N}{3kT}\left(1 + \frac{\zeta^2 V g_r \mu^2}{6D_0(t) NkT}\right)^{-1} g_r\mu^2 \qquad (2)$$

Let us further assume the following form for the time dependence of $D(t)$:

$$D(t)/\gamma^2 = 1 \times 10^{-l} + (1 \times 10^{-k} - 1 \times 10^{-l}) \times [1 - \exp(t/\tau_0)] \qquad (3)$$

This expression is a simple exoponential rise with limits of 10^{-l} at time 0 and 10^{-k} at infinite time. The lower limit of tensile compliance for most polymers is about 10^{-12} cm^2 dyn^{-1} for polymeric glasses at very low temperatures and 10^{-5} cm^2 dyn^{-1} for the rubbery transition region well above the glass transition temperature. For purposes of calculation let us set $l = 12$ and let k range from 5 to 8.5 in increments of 0.5. Since the quantity γ is a shape factor and is not known with certainty, we shall assume that it is lumped in with $D(t)$. Presumably the range would be nearly zero for symmetrical units and perhaps 10 to 100 for highly unsymmetrical units. The results of this calculation are given in *Figure 10*. The relaxation time was adjusted to centre the relation process in the experimental frequency range. At first, k shifts the relaxation process to longer times (lower frequencies), and finally decreases the magnitude of the relaxation process. The effects of l are observed by setting $k = 5$ and varying l from 11 to 14. The results of this calculation are given in *Figure 11*.

We assume that the relaxation time, τ_0, is given by a typical Arrhenius rate plot:

$$\ln \tau_0 = (\Delta E/RT) + \ln(\Delta S) \qquad (4)$$

In this expression the activation energy ΔE is taken to be 100 kcal mol^{-1}, a number similar to the activation energy of s-PMMA, and $\ln(\Delta S)$ is set to -125, which places the rate plot in the experimental temperature and frequency range. The results of the calculation are given in *Figure 12*.

DISCUSSION

The α and β dispersions of s-PMMA can be discussed in terms of *Figure 12*. In the glass phase, γ^2/D_0 is such that the polymer segment orients with respect to the electric field and results in a value of $\varepsilon_0 = 4.6$ (*Table 1*). At temperatures above the glass transition region the ratio γ^2/D_0 changes by several orders of magnitude not because γ^2 changes but because D_0 changes by five decades. The relaxation observed in *Figure 12* labelled 'alpha process' is entirely due to the assumed relaxation of D_0. In other words the polarization process is not complete until the strain-energy term approaches zero. The activation energy of this dielectric α process is the

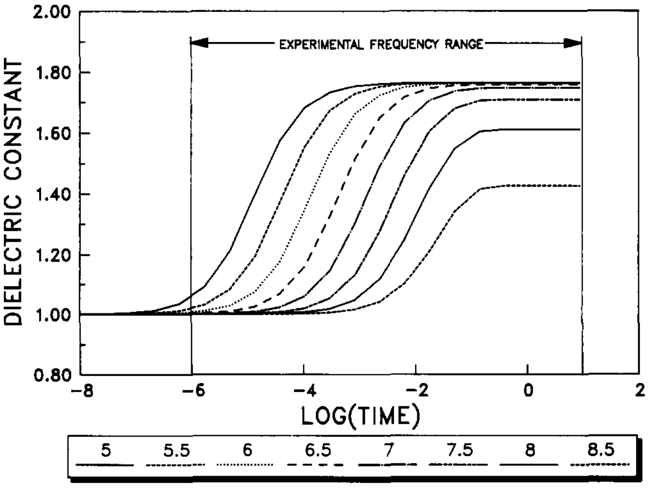

Figure 10 Dependence of the dielectric constant on various values of the equilibrium tensile compliance (k in equation (3)) listed below the figure

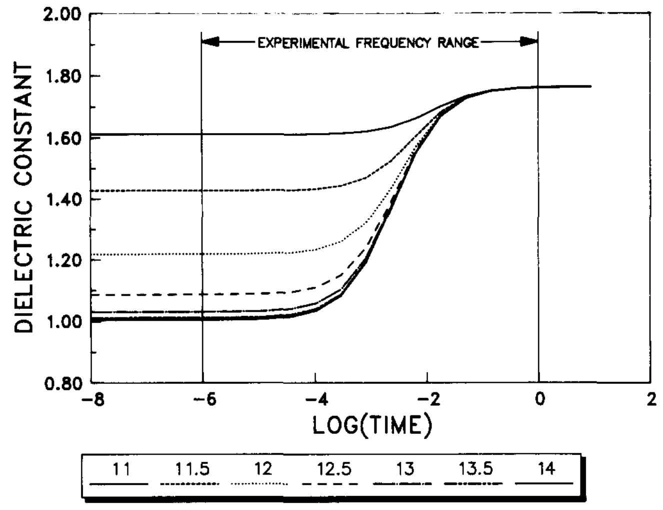

Figure 11 Dependence of the dielectric constant on various values of the instantaneous tensile compliance (l in equation (3)) listed below the figure

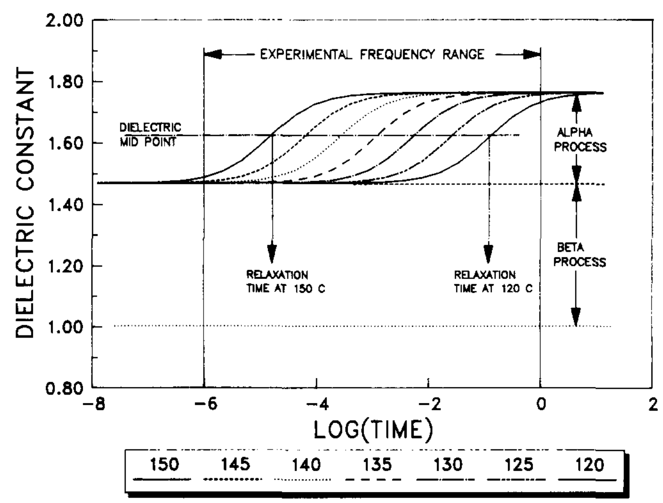

Figure 12 Dependence of the dielectric constant for fixed values of the instantaneous and equilibrium tensile compliance but for various values of the relaxation times given by equation (4) and the temperatures listed below the figure

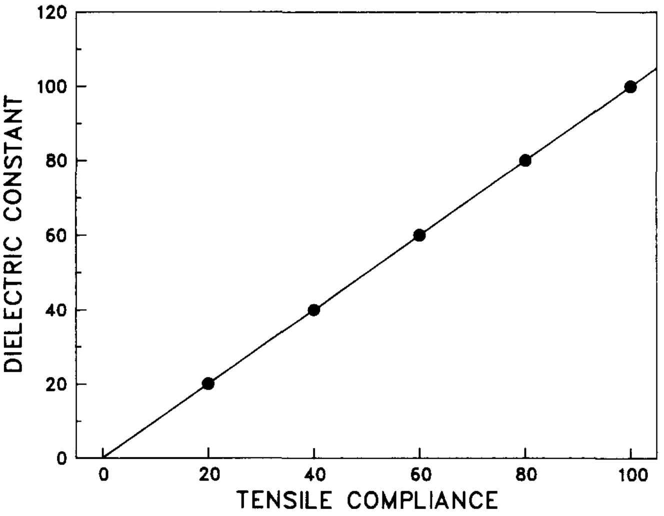

Figure 13 Dependence of the dielectric relaxation time defined in *Figure 12* with the tensile compliance relaxation time defined in equation (4)

same as the activation energy of D_0 because it is the rate-limiting step. In other words the rate of polarization (α process) due to softening of the matrix is determined by the matrix rate parameters even though the β process has a much faster rate.

The dielectric relaxation time can be defined as the time that the dielectric constant (for the α process) reaches half its final value (see *Figure 12*). An activation energy can be calculated from a plot of these relaxation times with reciprocal absolute temperature. In *Figure 13* we have plotted the dielectric activation energies for a range of assumed activation energies (20 to 100 in increments of 20) for the relaxation time in equation (4). $D(t)$ values were calculated using equation (3) and finally the relaxation time was calculated for $\varepsilon_0(t)$. The dielectric relaxation time was used to calculate the activation energy. As expected, the dielectric activation energy is determined by the activation energy for D_0.

Increasing the side-chain length from methyl to ethyl, i.e. from PMMA to PEMA, alters some of the details for the α and β processes but the results, and hence the interpretations, are similar. PMA is also similar to these two polymers, and hence the interpretation is similar. No other acrylic polymer listed in *Table 1* exhibits a β or glass phase process. This point is verified by the refractive indices (η) listed in *Table 1*. The result of squaring η with or without some allowance for atomic polarization is similar if not the same as the ε_∞ for the other methacrylates. This agreement suggests that there are no higher-frequency relaxation processes.

Inasmuch as D_0 values for acrylic polymers in the glass phase appear to be the same, it is the γ^2 values that are different, and consequently inhibit the orientation processs. *Figure 9* gives the reason for the dependence of γ^2 on side-chain length. As the side chain increases in length, the cross section of the polymer becomes less cylindrical and more elliptical. At a side-chain length of 4, i.e. butyl, the ratio γ^2/D_0 in the glass phase inhibits the polarization process.

ACKNOWLEDGEMENT

The authors would like to express their appreciation to Dr T. Pierce of the Rohm and Haas Co. who prepared *Figures 7* and *8*.

REFERENCES

1 Havriliak, S., Jr *Macromolecules* 1990, **23**, 2384
2 Steck, N. S. *SPE Trans.* 1964, January, p. 34
3 Dyvik, G. K., Bartoe, W. F. and Steck, N. S. *SPE Trans.* 1964, April, p. 98
4 Ishida, Y. and Yamafuji, K. *Kolloid Z.* 1961, **177** (7), 7
5 Havriliak, S., Jr *Colloid Polym. Sci.* 1990, **268**, 426
6 Strella, S. and Chinai, S. *J. Polym. Sci.* 1958, **31**, 45
7 Strella, S. and Chinai, S. *J. Colloid Sci.* 1958, **13**, 459
8 Havriliak, S., Jr and Roman, N. *Polymer* 1966, **7**, 387
9 Hummel, D. O. and Scholl, F. (Eds.) 'Atlas of Polymer and Plastics Analysis', Carl Hanser Verlag, Munich, 1981
10 Pauchert, C. T. 'The Aldrich Library of FT-IR Spectra', 1st Edn, Aldrich Chemical Co., 1985