

## Mechanical and Dielectric Relaxations in Alternating Block Copolymers of Dimethylsiloxane and Bisphenol A Carbonate

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### Synopsis

Alternating block copolymers of bisphenol A carbonate and dimethylsiloxane at three different compositions were studied by mechanical and dielectric measurements. Both sets of data exhibit transitions characteristic of the primary glass transitions of the component polymers. This behavior is characteristic of heterophase polymers. Dielectric data for all three samples cast from methylene chloride solution are presented. In addition, one sample was also cast from the solution of methylene chloride-*n*-hexane. The resulting morphologic differences among the samples are reflected in the activation energies associated with the low-temperature transitions. The time-temperature superposition principle was invoked to construct master curves for both mechanical and dielectric data. It was found that there exist considerable discrepancies in the respective master curves and the shift factor data. These results indicate that this heterophase block copolymer is thermorheologically complex.

### INTRODUCTION

Although heterophase polymers such as block and graft copolymers and polyblends have been known for a long time, their full significance has only been actively explored relatively recently.<sup>1-6</sup> Many of the unique properties of these polymeric systems can be attributed to their microphase separation. Commonly, one of these phases is rigid (glassy or crystalline) and the other is soft (rubbery), thus giving the overall characteristic of being tough and highly impact resistant. In addition, since the rigid domains, especially in block copolymers, are believed to act as quasi-crosslinks, these materials form a new class of thermoplastic elastomers which is particularly convenient to process. Heterophase polymers are also interesting from a fundamental scientific point of view. Since the formation of domains alters the supramolecular structure of the polymers, their correlation with observed physical properties forms an important area of investigation.

One of the most versatile techniques employed in the study of physical properties of polymers is the construction of viscoelastic master curves (or

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relaxation spectra) through the time-temperature superposition principle.<sup>7,8</sup> The validity of this principle has been amply vindicated for homogeneous amorphous polymers. A number of investigators have applied this technique to heterophase block copolymers.<sup>9-17</sup> However, it has now become clear that heterophase polymers should in fact be considered thermorheologically complex, and that the simple time-temperature superposition is only valid in a limited way.<sup>17-19</sup> In this work, we shall further scrutinize this problem by comparing the viscoelastic master curve of an alternating block copolymer of dimethylsiloxane and bisphenol A carbonate with dynamic mechanical and dielectric data. Pertinent literature data<sup>20-24</sup> on this polymer will be compared with those reported here when appropriate.

## EXPERIMENTAL

Three alternating block copolymers of dimethylsiloxane and bisphenol A carbonate were kindly supplied by the General Electric Research and Development Center. All of them have constant average siloxane block lengths of 20 monomeric units. Sample 1 contains 75% bisphenol A carbonate with average block length 18; sample 2 contains 50% carbonate with length 6; while sample 3 contains 35% carbonate with length 3.5. The method of synthesis of these polymers has been previously described by Vaughn.<sup>20</sup> All samples were received in the form of powder. They were subsequently cast into films from solutions of the polymer in methylene chloride on mercury surface. Sample 3 was also cast from a mixed solvent of 50% methylene chloride and 50% hexane. The cast films were dried in a vacuum oven at 45°C to constant weight. Samples for viscoelastic testing were cut into strips of  $6.5 \times 0.5 \times 0.15$  cm<sup>3</sup>. Dielectric samples were cast into circular films 5 cm in diameter and 0.01 cm in thickness.

Stress-relaxation measurements were carried out on a Model TM-SM Instron Universal Testing Instrument, fitted with Missimers Model PITC temperature conditioner. Tensile mode was used for all measurements until the modulus reached  $10^9$  dynes/cm<sup>2</sup>, above which the flexural mode was utilized. In all cases strain was kept below 2-3% in order to avoid yielding.<sup>22</sup> Relaxations were recorded to 4000 sec.

Dielectric measurements were made over a frequency range of 50 Hz to  $10^6$  Hz. The equipment consists in a General Radio Model 1615A capacitance bridge, a Model 1232A null detector, and a Model 1310B signal generator. The sample was inserted between a two-terminal electrode. Measurements were carried out at constant temperatures in a Statham SD30 temperature test chamber.

## RESULTS AND DISCUSSION

### Mechanical Properties

Twenty-one modulus-time isotherms between -133.5°C and 111°C are shown in Figure 1 for the alternating block copolymer consisting of 50%

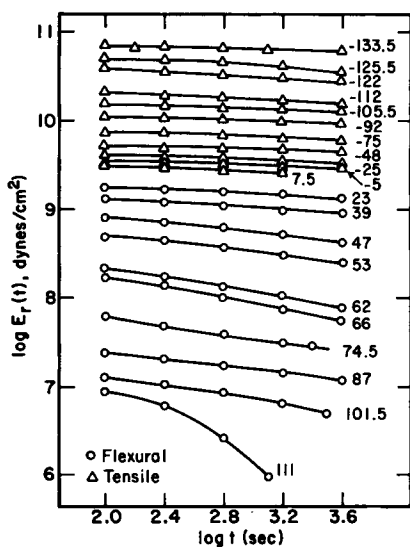


Fig. 1. Modulus-time isotherms for alternating block copolymer consisting of 50% dimethylsiloxane and 50% bisphenol A carbonate (sample 2). Triangles represent data obtained by the flexural mode, circles, those by the tensile mode. Numerals on the right-hand side of the figure indicate temperatures in  $^{\circ}\text{C}$ .

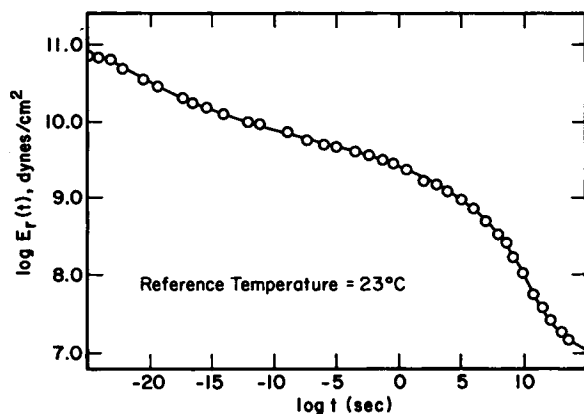


Fig. 2. Master curve for sample 2. Reference temperature,  $23^{\circ}\text{C}$ .

dimethylsiloxane and 50% bisphenol A carbonate (sample 2) cast from methylene chloride. Data taken by the flexural and tensile modes agree well with each other. These isotherms were readily superposed with each other by shifting horizontally along the log time axis to yield a smooth viscoelastic master curve (Fig. 2). Shift factors utilized in effecting superposition are given in Figure 3.

Isochronal (100 sec) modulus-temperature curve for the block copolymer may also be obtained from data in Figure 1. This curve is plotted in Figure 4. At very low temperatures, the polymer exhibits a very high

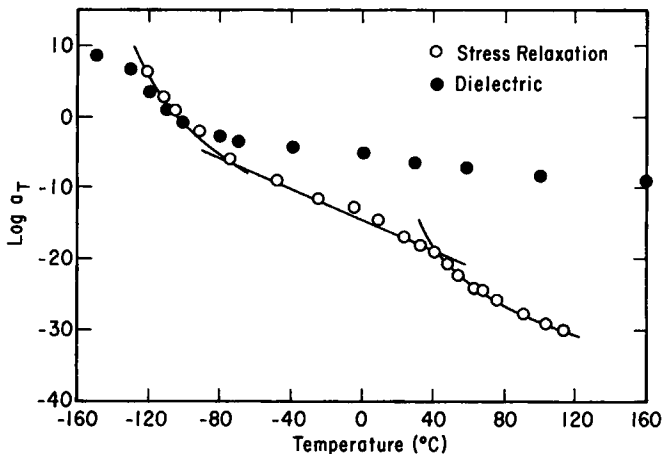


Fig. 3. Viscoelastic shift factors used in constructing the master curve of sample 2: (O) mechanical; (●) dielectric.

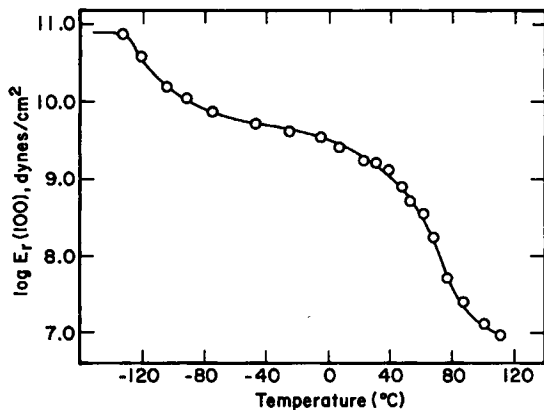


Fig. 4. Isochronal modulus-temperature curves for sample 2. Time scale, 100 sec.

glassy modulus ( $\approx 7 \times 10^{10}$  dynes/cm<sup>2</sup>). We note that the 10-sec glassy shear modulus for this sample reported by Narkis and Tobolsky<sup>24</sup> is  $2.1 \times 10^{10}$  dynes/cm<sup>2</sup>. Since the tensile modulus is approximately three times higher than the shear modulus, our data are thus consistent with those of Tobolsky ( $7.0 \times 10^{10}$  versus  $6.3 \times 10^{10}$  dynes/cm<sup>2</sup>).

A transition is seen to occur in Figure 4 near  $-120^\circ\text{C}$ , which may be attributable to the primary glass transition of the silicone blocks. The literature value for the glass transition temperature of poly(dimethylsiloxane)<sup>7</sup> is  $-123^\circ\text{C}$ . Following the transition there is an extended plateau region of fairly high modulus ( $10^9$ - $10^{10}$  dynes/cm<sup>2</sup>), which is quite characteristic of block copolymers. Such plateau regions have also been observed by Narkis and Tobolsky<sup>24</sup> and Kambour<sup>21,22</sup> for this sample. Above  $60^\circ\text{C}$ , another transition is apparent. This high-temperature transition is related to the glass transition of the polycarbonate blocks, the

temperature for which was reported by Kambour to be 70°C. This temperature is considerably lower than that of the pure homopolymer of bisphenol A carbonate (160°C).<sup>25</sup> The depression of  $T_g$  was shown by Kambour to be due to the lower molecular weight of the polycarbonate, assuming that the silicone blocks attached to the ends of the former are so mobile that they exert little restraint.

Narkis and Tobolsky also found that a rubbery plateau region follows the second transition, extending to above 200°C before the onset of rubbery flow occurs. In Figure 4, the beginning of such a plateau is clearly visible.

### Dielectric Properties

Dielectric data for the three block copolymer samples cast from methylene chloride are presented in Figures 5–7. In Figure 5 (sample 1), we note that there is a small loss peak located near -120°C and the onset of a large peak above 100°C. The sample contains 25% dimethylsiloxane and 75% bisphenol carbonate. Sample 2, containing 50% siloxane in Figure 6, has a similar loss curve, except that here the low-temperature peak is shifted toward higher temperatures and is of greater intensity. This trend is continued in Figure 7 for the sample containing 65% siloxane. In all instances, higher frequency produces a loss peak at a higher temperature, as expected. It is of interest to note that the loss tangent keeps increasing at the higher temperature end. In contrast, the dynamic mechanical loss<sup>21,22</sup> exhibits a peak at 80°C for sample 2 and begins to decrease above this temperature.<sup>21</sup>

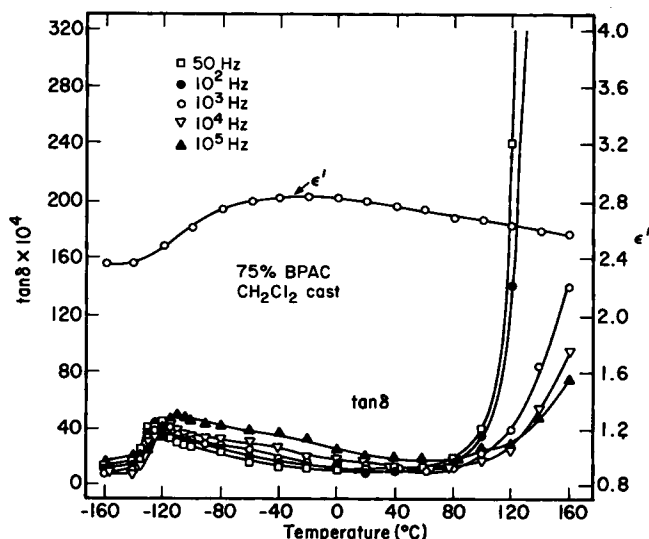


Fig. 5. Dielectric constant and loss tangent for alternating block copolymer of 25% dimethylsiloxane and 75% bisphenol A carbonate (sample 1) cast from methylene chloride solution, as a function of temperature.

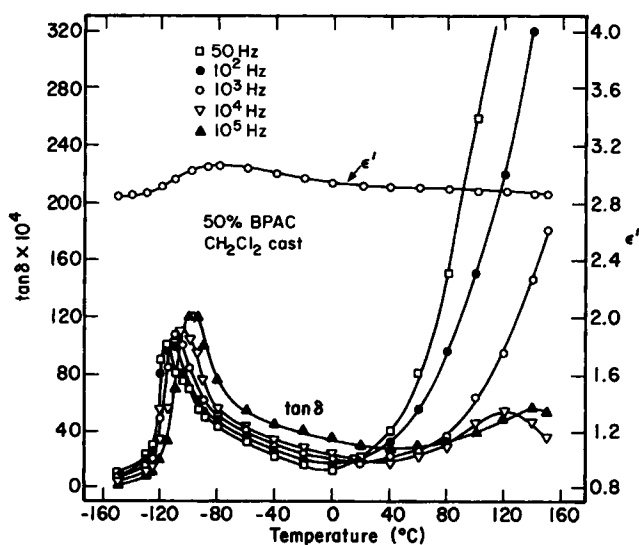


Fig. 6. Dielectric constant and loss tangent for alternating block copolymer of 50% dimethylsiloxane and 50% bisphenol A carbonate (sample 2) cast from methylene chloride solution, as a function of temperature.

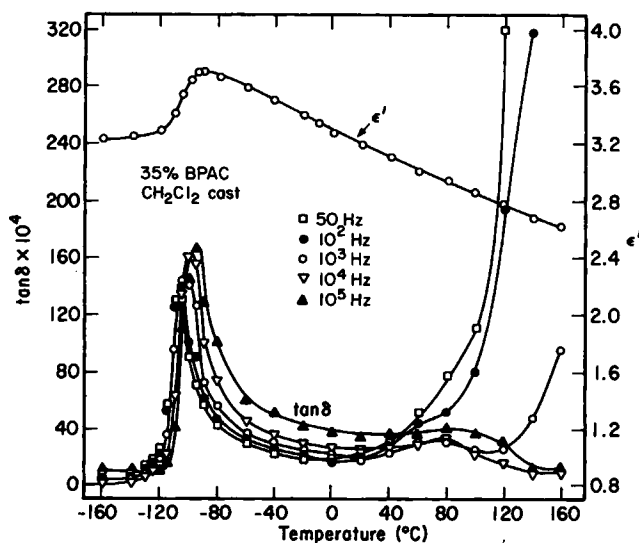


Fig. 7. Dielectric constant and loss tangent for alternating block copolymer of 65% dimethylsiloxane and 35% bisphenol A carbonate (sample 3) cast from methylene chloride solution, as a function of temperature.

The high-temperature peaks in the dielectric data for all three samples can be attributed to the  $\alpha$ -relaxation (primary glass transition) of the polycarbonate.<sup>26,27</sup> The low-temperature peaks are probably composites of two relaxation processes. One is the  $\alpha$ -relaxation of the polysiloxane,<sup>28,29</sup> and the other, the  $\beta$ -relaxation of the polycarbonate. At 1 kHz, the former

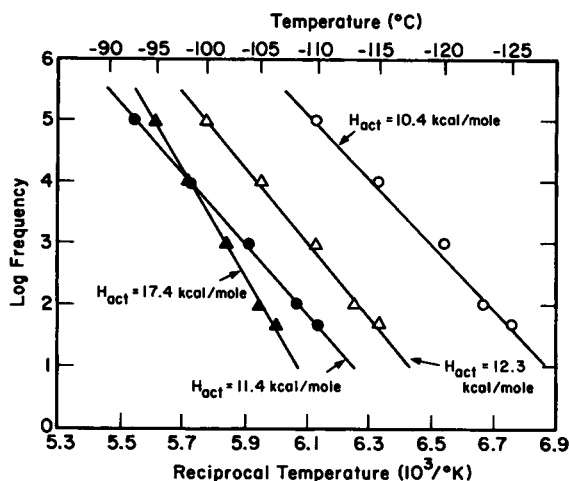


Fig. 8. Log frequency plotted against reciprocals of temperatures of loss maxima for methylene chloride-cast block copolymer with 25% silicone (open circles), 50% silicone (open triangles), 65% silicone (closed triangles). Closed circles represent the 65% silicone sample cast from a mixed solvent of methylene chloride-*n*-hexane.

is located around  $-120^{\circ}\text{C}$ , and the latter, near  $-70^{\circ}\text{C}$ . This is probably the reason why the low-temperature peak is very asymmetric. It is also known that the polycarbonate  $\beta$ -peak is very much broader than the polysiloxane  $\alpha$ -peak, which explains the extended plateau region at intermediate temperatures.

The frequency dependence of the temperature locations at which the value of the loss tangent reaches a maximum can be expressed by the activation energy ( $H_{\text{act}}$ ) as follows.

$$\omega = \omega_0 \exp(-H_{\text{act}}/RT) \quad (1)$$

where  $R$  is the ideal gas constant,  $T$  is absolute temperature, and  $\omega_0$  is a normalization constant. Activation energies can therefore be determined by taking the slopes off a log frequency versus the reciprocal of temperature plot. Figure 8 shows such a plot for the low-temperature peaks of the three samples. Here we find that the activation energies for samples containing 25%, 50%, and 65% siloxane are, respectively, 10.4, 12.3, and 17.4 kcal/mole.

For the sake of comparison, we note that values of  $H_{\text{act}}$  for the  $\alpha$ -process of poly(dimethylsiloxane) have variably been reported to be 37 kcal/mole<sup>30</sup> and 24 kcal/mole,<sup>31</sup> those for the  $\beta$ -process of bisphenol A polycarbonate, about 10–12 kcal/mole.<sup>26,27</sup> That the activation energies of the block copolymer low-temperature relaxation are intermediate between these values reinforces the composite nature of this process.

One possible interpretation consistent with the above observation is that the silicone domains contain some polycarbonate segments. The low temperature loss peaks are attributed to the primary glass transitions of

these "impure" silicone domains. The polycarbonate segments mixed in the silicones act as "antiplasticizers" to elevate the  $T_g$ 's of the latter. The higher silicone content may be expected to provide more extensive mixing, thus resulting in higher observed  $T_g$ 's. The increased activation energies with increasing silicone contents are consistent with this interpretation.

The morphology of heterophase polymers can often be altered by the nature of casting solvent. For instance, methylene chloride is a good solvent for both poly(dimethylsiloxane) and bisphenol A polycarbonate. *n*-Hexane, on the other hand, is a good solvent for poly(dimethylsiloxane) only, and is actually a nonsolvent for polycarbonate. Casting our alter-

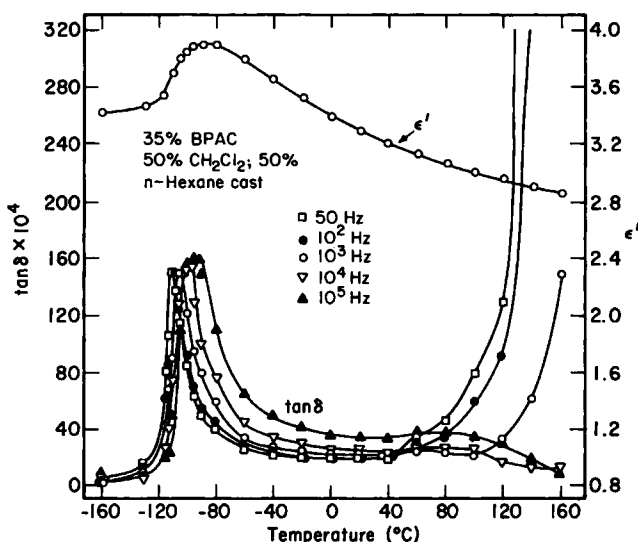


Fig. 9. Dielectric constant and loss tangent for alternating block copolymer of 65% dimethylsiloxane and 35% bisphenol A carbonate (sample 3) cast from a mixed solvent of methylene chloride-*n*-hexane, plotted as a function of temperature.

nating block copolymer from the solution of a 50–50 mixture of methylene chloride and *n*-hexane will cause the polycarbonate to coacervate.<sup>22</sup> In this case, we would expect a "purer" silicone domain as a consequence of this demixing. Figure 9 shows the dielectric data of our sample 3 (65% siloxane) cast from such a mixed solvent. Here we see that the low-temperature loss peaks are shifted to lower temperatures in comparison with the same sample cast from pure methylene chloride. This is what one would expect if the silicone domains contain less polycarbonate segments acting as antiplasticizers. Consistent with this conclusion is that the activation energy for the mixed solvent-cast sample is now lowered (Fig. 8), being 11.4 kcal/mole compared with 17.4 kcal/mole for the methylene chloride-cast sample.



### Time-Temperature Superposition

Figure 3 shows that the shift factors used in the time-temperature superposition do not follow the classical WLF equation.<sup>13-19</sup> In a recent publication, three distinct regions of temperature dependence for shift factors were noted for A-B-A triblock copolymers.<sup>13</sup> Near the glass transition temperatures of the A and B blocks, the shift factors still obey the WLF equation with "universal constants":<sup>7,8</sup>

$$\log a_T = \frac{-16.14(T - T_d)}{56 + T - T_d} \quad (2)$$

where  $T_d$  is the characteristic temperature. Intermediate between these two  $T_d$  values there is a region of constant slope, i.e., the  $\log a_T - T$  plot here is a straight line. This region is presumably an interfacial mixed region, the composition of which is a gradient depending on the distance from the pure A or B blocks. In Figure 3, we apply this model to our alternating block copolymers, using a low-temperature  $T_d = -110^\circ\text{C}$ , a high-temperature  $T_d = 45^\circ\text{C}$ , and a constant slope of  $d \log a_T/dT = -0.1/^\circ\text{C}$  for the intermediate region. The agreement with data is very good.

Even though the time-temperature superposition technique can be employed for our heterophase polymer without difficulty in obtaining a viscoelastic master curve and the resulting shift factors can be interpreted with a reasonable model, there is still some question if the procedure is indeed valid. The time-temperature superposition principle states that the modulus of a material at a given time and temperature may have the same value at a different time if the temperature is appropriately changed.

$$E(t, T) = E(t/a_T, T') \quad (3)$$

In other words the effect of changing temperature from  $T$  to  $T'$  is to apply a multiplicative factor  $a_T$  to the time scale (or an additive factor to the log time scale). Materials obeying this principle are said to be thermorheologically simple. The shift factor for thermorheologically simple materials is defined by the ratio of the relaxation (or retardation) times at the two different temperatures.

$$(\tau_i)_{T'}/(\tau_i)_T = a_T \quad (4)$$

The implication here is that all the relaxation times must have the same temperature dependence. In the case of a heterophase system, even though the component phases are by themselves thermorheologically simple, which is true for bisphenol A polycarbonate<sup>25</sup> and poly(dimethylsiloxane),<sup>28</sup> there is no *a priori* reason that the composite is also thermorheologically simple. In fact, time-temperature superposition can be accomplished only if relaxation is dominated by one mechanism in a given temperature region, or if the two relaxation mechanisms happen to have the same temperature dependence.

An important criterion for testing thermorheological simplicity is that the viscoelastic shift factors used for one set of viscoelastic data must also be valid for a different set.<sup>8</sup> It is thus of interest to compare the mechanical master curve, which were obtained from isotherms in the time range of  $10^2$  to  $10^4$  sec, with a dielectric master curve (time range of isotherms: approximately  $10^{-2}$  to  $10^{-5}$  sec). To accomplish this comparison, we first crossplot the dielectric data in Figure 6 for the alternating block copolymer of 50% DMS and 50% BPAC into isotherms of  $\tan \delta$  versus log frequency. By using  $23^\circ\text{C}$  as the reference temperature, these curves are shifted into a smoothed master curve. Shift factors used for the time-temperature superposition are shown as filled circles in Figure 3. The mechanical master curve in Figure 2 in terms of  $\log E_r(t)$  versus  $\log t$  can be readily converted to  $\tan \delta$ -versus- $\log \omega$  master curve by linear programming.<sup>29</sup> Both of these master curves are shown in Figure 10.

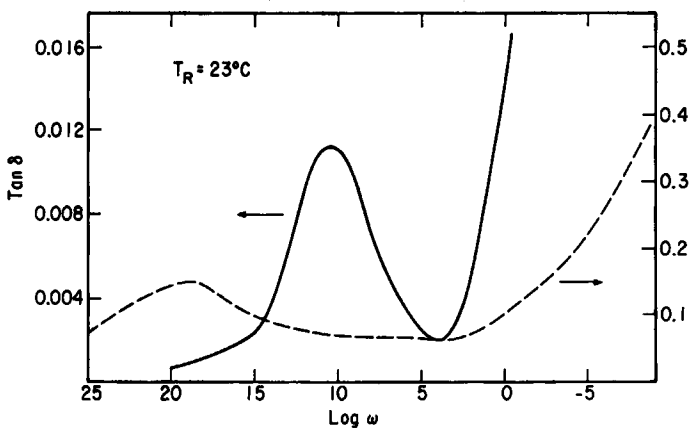


Fig. 10. Comparison of dielectric (solid line) and mechanical (broken line) master curves.

It is evident that both the shift factors and the master curves from mechanical and dielectric data for the same polymer show considerable discrepancy from each other. Even though in the mechanical and dielectric measurements different excitations are provided for the macromolecules, the molecular motions should nevertheless be affected by the same viscoelastic responses.<sup>8,32-34</sup> We see in Figure 10 that these master curves are similar in shape, but differ in time (or frequency) axis, which is a consequence of the rather different shift factors for the mechanical and dielectric data shown in Figure 3. The implication here is that the master curve for our block copolymer is not unique, but depends on the time range of isotherms. Those materials whose shift factors are not only temperature dependent but also time dependent must be considered thermorheologically complex. This observation is in agreement with the deductions of Fesko and Tschögl<sup>17</sup> through model calculations for styrene-butadiene-styrene block copolymers.

We conclude that time-temperature superposition can only be used for heterophase polymers in the range where one relaxation mechanism is dominant, or if both relaxation mechanisms by chance have the same temperature dependence. Only under these circumstances, the heterophase polymer is apparently thermorheologically simple.

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