Relaxations of Damped Debye Lattice; Partially Brominated Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: The damped Debye lattice (DDL) model has been useful in developing molecular interpretations of viscoelastic relaxation in the primary (glass-to-rubber) transition region. The steepness index (SI) of stress relaxation master curve is shown to vary in a predictable way when the structure of the polymer is changed by the addition of plasticizer or by chemical substitution. The DDL model has been applied to the viscoelastic behavior of the partially brominated poly(2,6-dimethyl-1,4-phenylene oxide) (PBrPO). PBrPO ordinarily conforms to a two-dimensional DDL model with the SI of 1.0. When PBrPO was plasticized with dioctyl phthalate (DOP) and dioctyl sebacate (DOS), as predicted by the model, an unusual sharpening of the transition region in stress relaxation master curve is shown by an increase in the SI from 1.0 to 1.5 and then a broadening of the transition region yielding a change in the SI from 1.5 to 0.5, on further plasticization. This behavior is associated with changes in the size of interchain force constants produced by various concentrations of plasticizer. This is the first experimental demonstration in which a system changes to a three-dimensional system and then to a one-dimensional system by an incorporation of diluents into a two-dimensional system. The interchain interaction suggested by the DDL model is demonstrated to be an important factor in determining the viscoelastic behavior in the primary transition region of an amorphous polymer.

Introduction

In the original development of theories presented by Rouse, Bueche, and Zimm (RBZ)[1] to treat the viscoelastic behavior of polymers, polymer chains are represented by a simple bead-spring model. Later, Ferry, Landel, and Williams (FLW)[2] suggested that the RBZ bead-spring model might be extended to interpret the behavior of bulk polymer. In this case, they argued that the friction generating fluid would be the entire ensemble of polymer chains, except for the one on the consideration, and concluded that two different friction factors were appropriate. A fundamental assumption of the RBZ theory, which was also adopted by FLW, is that there are no elastic interactions between the polymer chains. Tobolsky et al.[3] suggested a further development of the bead-spring model to account for interchain interactions. They defined the original RBZ linear bead-spring model to be a one-dimensional system and, further, allowed the inclusion of interchain elastic coupling to yield a two-dimensional or a three-dimensional damped Debye lattice (DDL). The latter model is also known as a three-dimensional damped torsional oscillator (DTO) model, and infers that inter- and intrachain interactions could be characterized by the same force constant. This idea becomes acceptable if one realizes that the beads themselves correspond to a substantial number of segment of the polymer chain.[3]

The DDL model considers that intermolecular interactions are important to determine the viscoelastic behavior observed in the primary (glass-to-rubber) transition region. This model was originally suggested to explain the observed differences in relaxation rate between polystyrene (PS) and polyisobutylene (PIB), in which PS actually decays 1000 times faster than PIB in the primary transition region (in Figure 1). In this figure, the steepness index (SI) of PS is 3 times larger than for PIB. Tobolsky rationalized this behavior by suggesting that the incorporation of interchain force constants fundamentally causes the distribution of relaxation times to become denser than is possible with only intramolecular interactions.[3] An increase in density of the distribution of relaxation times causes the observed stress relaxation behavior to decay very rapidly with time. Thus, PS is inferred to be a three-dimensional system in which the intermolecular interaction is balanced by the intramolecular interaction, while PIB is inferred to be a one-dimensional system in which intramolecular interaction is dominant.

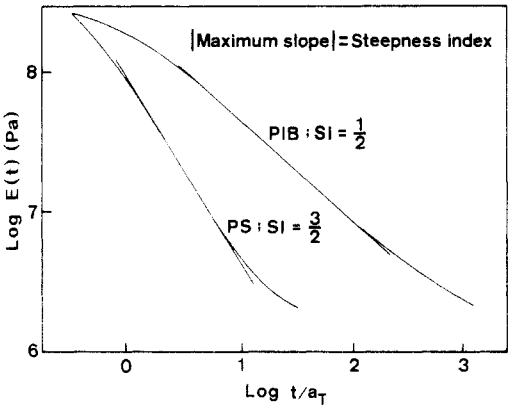

Figure 1. Stress relaxation master curves of polystyrene (PS) and polyisobutylene (PIB) in the primary transition region at different reference temperatures.

Background

In the past, a single parameter called the steepness index (SI),[4] defined as the absolute value of the maximum negative slope in a stress relaxation master curve of log modulus vs log time in the primary transition region, has been used as a measure of sharpness of relaxation. According to the DDL model, a one-dimensional (1-D) system, like PIB, which is very similar to the familiar RBZ linear bead-spring model[10] with individual beads held together by springs in one dimension, is dominated by

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intramolecular interaction and has an SI of 0.5. A two-dimensional (2-D) system, in which intermolecular interaction plays the dominant role, produces an SI of 1.0. For example, experimentally observed results show that poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(methyl methacrylate) (PMMA), or poly(α-methylstyrene) (PαMS) belongs to 2-D system. As introduced, the DDL model also suggests the existence of a three-dimensional (3-D) system, in which inter- and intramolecular interactions are characterized by equal force constants. The 3-D model can be applied to PS and shows an SI of 1.5. Experimentally these numbers have usually been determined with an accuracy of ±0.1.

One approach to investigate the credibility of the DDL model is to measure changes in relaxation rate (i.e., SI) as the strength of interchain interactions is varied via plasticization or dilution of the bulk polymer with low molecular weight materials. In the case of PS, for example, with an SI near 1.5, a balance between inter- and intramolecular force constants can presumably be disrupted by dilution. Thus, the transition region is expected to broaden, and SI is decreased by dilution. Further experimental investigations on PS[4-8] have been carried out to assess the viability of the model.

In previous work, the earliest effort in this area concentrated on varying the dimensionality as shown by SI because a simple separation of polymer molecule should diminish the intermolecular interactions while leaving the intramolecular interactions more or less unaffected. This was done successfully by incorporation of diluents or plasticizers into a PS system.[5-8] They found that the incorporation of diluent leads to a broadening of the transition, i.e., a decrease in SI. In addition, they also found that the exception to this behavior occurs when the solubility parameters of the polymer and the diluent are matched.[6] In this result, no appreciable broadening of the transition region is observed and this is in accord with the prediction of the DDL model since dilution with a solvent of like solubility parameter should not affect the strength of intermolecular interactions and thus not lower the dimensionality of PS. This was extended to PMMA[9] which shows a two-dimensional system after using various plasticizers. The SI of the plasticized PMMA was experimentally indistinguishable from 1.0, despite the fact that substantial decreases in transition temperatures (such as T_g) were observed (a decrease in T_g was also observed in the PS system). Thus, this result leads to the conclusion that the PMMA system would be very sensitive to intermolecular interaction. In addition, Akionis[9] predicted that further plasticization would be accompanied by a very distinctive variation of SI with plasticizer concentration, if the 2-D system (SI = 1.0) consists of interchain force constants. The predicted variation in SI as a function of diluent concentration is schematically represented in Figure 2. In this figure, a 2-D system, in which intermolecular interactions are dominant over intramolecular ones, drifts to a 3-D system (SI = 1.5) upon adequate dilution with suitable solvents. At this point, inter- and intramolecular interactions are equally balanced and the system behaves like a three-dimensional one. Further incorporation of diluents, of molecular chain length shorter than polymer, continuously weakens intermolecular interaction and allows intramolecular interactions to dominate the system at higher concentration of diluent, and thereby a 1-D system is exhibited. In this case, a simple analysis of the model might suggest that the SI should be close to 0.5.

A continued investigation of the DDL model was carried out to some compatible polymer blends which offer a possibility to critically test the model.[9,10,13] The systems used in this study are PS–PPO, PS–PαMS, and PS–PBrPO (partially brominated PPO) and the results explored the generality of the observation. However, in the PS–PBrPO system,[13] the authors used three diluents which have various values of solubility parameters in the context of single-phase systems. Based on the behavior of homopolymers, the expected behavior was not observed in all cases because all three diluents appear to be approximately equally efficient in reducing intermolecular elastic force constants. For this, the authors reported that the oversimplification of the model may cause the above observations.

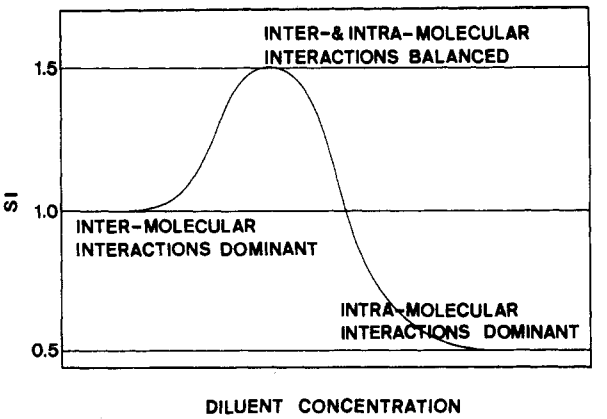

Figure 2. Predicted variation of SI with diluent concentration where intermolecular interaction dominated system in a two-dimensional DDL system.

Previous investigations[3-13] were not able to reduce SI to 0.5 at high dilutions, as the model predicted, since experiments on highly plasticized systems could not be performed at low enough temperatures to test this feature. The lowest values of SI observed were 1.0 for a 25 wt % DOP diluted PS–PPO system[11] and 1.1 for the inclusion of 25 wt % DOP in a PS–PBrPO system.[13]

We have now extended our studies to investigate the stress relaxation behavior of a partially (1/4 equivalent) brominated poly(2,6-dimethyl-1,4-phenylene oxide) diluted with plasticizers in the primary transition region. Intermolecular force constants are substantially changed by the chemical substitution of molecular bromine into PPO.[11] We have chosen this system since we predicted that the experimental temperature should be adequate to generate a 1-D system. Therefore, in this work, we evaluate the DDL model as a predictor of intermolecular interaction in order to rationalize viscoelastic relaxations in amorphous polymers.

Experimental Section

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, $\bar{M}_n$ = 35 000) was obtained from the General Electric Co., Schenectady, NY. The bromination of PPO was carried out by substitution of molecular bromine into the polymer.[14] The amount of molecular bromine necessary to produce a desired extent of reaction was directly added to the PPO as a 10 wt % polymer solution in toluene. After the mixture was stirred for several hours in the dark, the brown bromine color disappeared and a halogenated orange color polymer was isolated by dropping the reaction mixture slowly into 10-fold excess methanol with vigorous stirring. Brominated polymers with 0.25, 0.50, 0.75, and 1.0 equiv of bromine per repeating phenyl ring in the PPO were prepared in this way.

Glass transition temperatures (T_g) were measured using a Perkin-Elmer differential scanning calorimeter (DSC-7). Samples were heated to 70 °C above their anticipated T_g's at a heating rate of 20 °C/min, then they were quench cooled to room

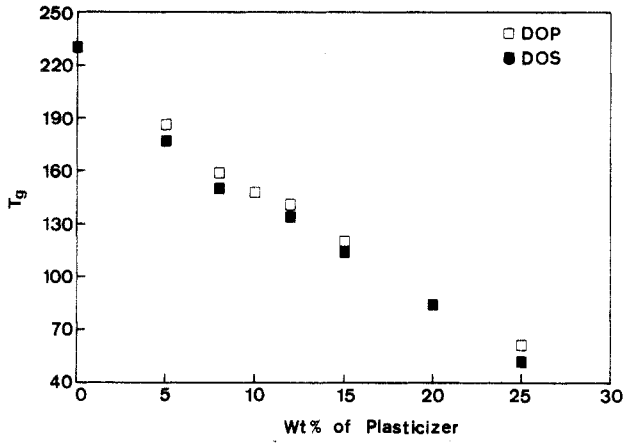

Figure 3. Experimental glass transition temperatures of PBrPO (1/4 equivalent) plasticized with DOP (□) and DOS (■).

temperature. The T_g was determined during a second heating, again at a rate of 20 °C/min.

Quantitative bromine content in brominated PPO was measured with a Varian EM-360, 60-MHz proton NMR. A 30–50-mg portion of a 4 wt % solution (in $CDCl_3$ solvent) of each sample was used with TMS as reference material.

Samples were molded into 0.1 by 1.0 by 5.0 cm strips for stress relaxation experiments. Molding was effected at temperatures approximately 50 °C above T_g of each sample. In order to add diluent, a dry precipitated polymer was pressed into a film at a temperature approximately 50 °C above T_g and the required amount of diluent dropped onto the sample and slightly pressed. The pressed film was broken into small pieces and repressed many times so that homogeneously plasticized samples coule be prepared with considerable mechanical mixing of the polymer. Plasticized samples were shaped into strips as described above.

The diluents used in this study were dioctyl phthalate (DOP) and dioctyl sebacate (DOS) purchased from the Aldrich Chemical Co., Milwaukee, WI.

The stress relaxation experiments were carried out at various temperatures on a table model Instron (TM 1833) equipped with an environmental test chamber, designed to limit temperature variation to ±0.1 °C. The constant strain employed was 1–2% in the high modulus region and was increased to a maximum of 15% as the rubbery plateau region was approached. All experiments were repeated and data were consistent to better than ±5%. All measurements are in the domain of linear viscoelasticity. Modulus values were calculated by a method described elsewhere.[9]

Results and Discussion

The extent of bromination of PPO was measured using proton NMR. Analysis of NMR data indicated that bromine quantitatively reacted with PPO, and at the highest bromine concentration, less than 10% of the phenyl rings were dibrominated. Among these, quantitative proton NMR results of 0.25 equivalent brominated PPO agree well with the calculated ones.

T_g's of the brominated samples are similar to previous results.[13] T_g's of 1/4 equivalent bromine substituted PPO (we designate this sample as PBrPO in this study) as well as PBrPO plasticized with DOP or DOS are plotted in Figure 3. T_g's of plasticized PBrPO were decreased with plasticizer content up to 25 wt %. Reasonable agreement between data points for DOP and for DOS indicates that DOP and DOS are acting as ordinary plasticizers in this system. This observation, along with the fact that only a single T_g was observed for all samples and that all samples were optically clear, is an indication of a homogeneous single phase polymer system.

Measurements at each temperature were carried out at least 5 times to assess reproducibility. In most cases (experimental scatter was less than 5 wt %), logarithmic

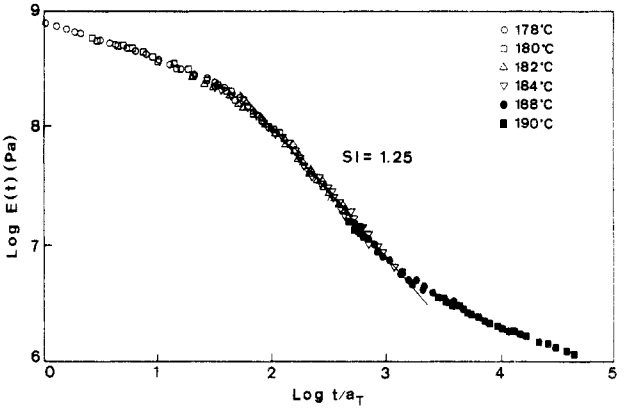

Figure 4. Stress relaxation master curve of PBrPO plasticized with 5 wt % DOP at reference temperature 182 °C.

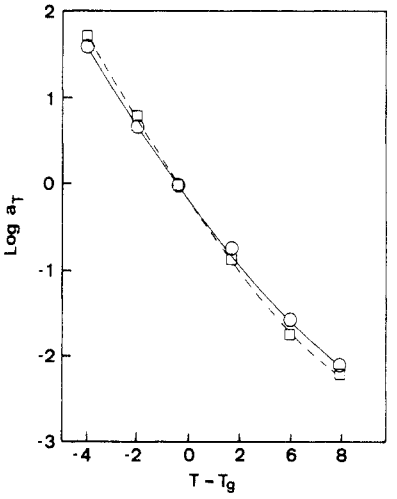

Figure 5. Shift factors of PBrPO with 5 wt % DOP (open circles with solid line; experimental results at reference temperature 182 °C and squares with dotted line; calculated values by WLF equation with T_g = 182 °C, C_1 = 17.4, and C_2 = 51.6).

$E(t)$ (modulus as a function of time) at various temperatures were successfully superposed by simple horizontal shifts along the log time axis[15] without employing longitudinal shifts. A typical stress relaxation master curve shown in Figure 4 for a 5 wt % DOP–PBrPO system in the primary transition region was constructed by shifting individual stress relaxation modulus curves. The shift factors employed to prepare this master curve at reference temperature 182 °C are plotted in Figure 5 while the calculated ones using a WLF equation[15] with C_1 = 17.4 °C, C_2 = 51.6 °C, and T_g = 182 °C. Experimental values are slightly different from the ones calculated. The SI measured graphically from Figure 4 is 1.25 ± 0.02.

As discussed above, a two-dimensional DDL is predicted to sharpen and then broaden in relaxational behavior upon plasticization with an appropriate soluble diluent because of a continuous decrease in intermolecular interactions in the system. Representative stress relaxation master curves for PBrPO diluted with 5, 8, 10, 12, 15, and 25 wt % DOP are shown in Figure 6. These have been shifted onto each other by arbitrary factors to minimize overlap. Curve A, which is diluted with 5 wt % DOP, shows an SI of 1.25, whereas, curve C, which is diluted with 10 wt % DOP, has an SI of 1.52 showing a considerably sharpened relaxation. For the system diluted with 12, 15, and 25 wt % DOP, the SIs decrease to 1.33, 1.19, and 0.59, respectively. Here, a dramatic increase in SI at low concentration of plasticizer is observed, followed by a decrease in SI up to 0.6 at higher content of plasticizer. The variation in SI as a function of plasticizer DOP concentration is plotted in Figure 7.

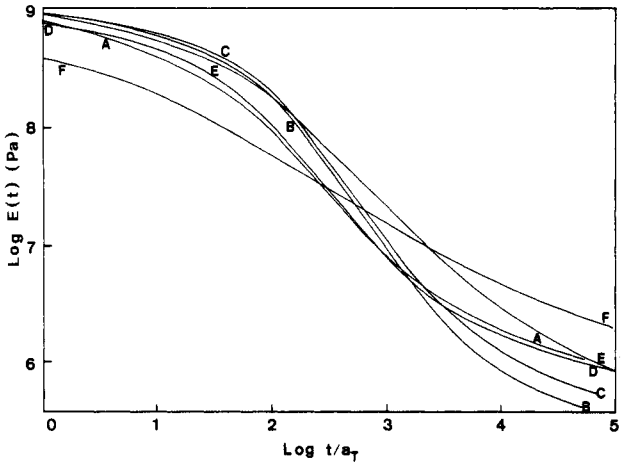

Figure 6. Stress relaxation master curves for PBrPO plasticized with six different concentrations of DOP: A, 5 wt % (182 °C); B, 8 wt % (148); C, 10 wt % (143); D, 12 wt % (136); E, 15 wt % (114); F, 25 wt % (49). Curves have been shifted along the log modulus and log time axis to emphasize slope changes in this region. Numbers in parentheses represent reference temperatures.

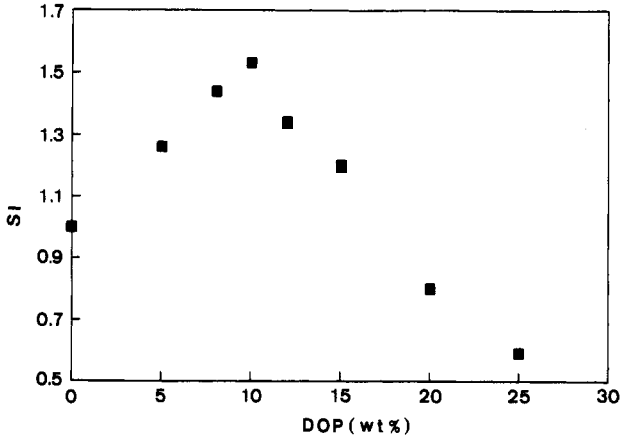

Figure 7. SI variation as a function of DOP concentration in PBrPO system.

To our knowledge, this is the first report of a sharpening followed by a broadening of the relaxation master curve, with SI approaching to 0.5 in the primary transition region by the introduction of plasticizers. Figure 7 is reminiscent of the predicted SI behavior using a DDL interpretation as shown in Figure 2.

In most cases, the previous work in this area concentrated on one particular diluent, DOP. As far as the DDL model is concerned, the diluent merely functions to separate the polymer molecules and thus diminishes the intermolecular elastic force constant. Some plasticizers having different solubility parameters have been reported to sharpen the relaxation master curves in the transition region while substantially affecting the glass transition temperatures.[4,5] In addition, it has been observed[4,7,8] that dilution of PS with a particular diluent having a solubility parameter[16,17] equal to that of PS caused no substantial decrease in SI in spite of the fact that the usual decrease in T_g is observed. Such behavior has been interpreted by Aklonis et al.[6] by suggesting that separation of polymer molecules with a diluent of identical solubility parameter is not sufficient to alter the local environment of the polymer chains in terms of the energetics of intermolecular interaction to change the dimensionality of the system. The solubility parameters of the diluents used in this system are DOP 7.9 and DOS 8.6 and the solubility parameter of the PBrPO is 9.8 as calculated by a method proposed by Fedors.[18]

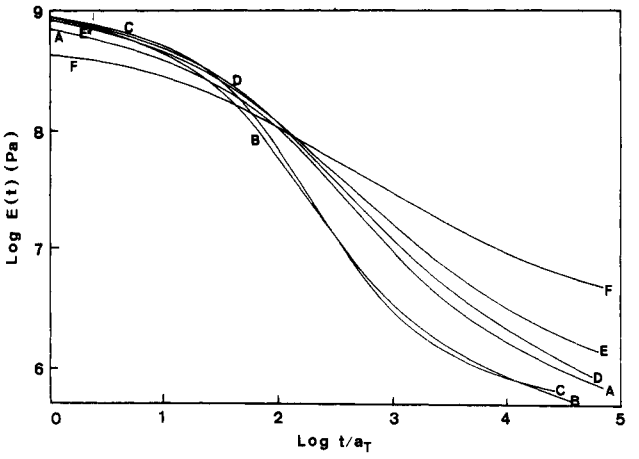

Figure 8. Stress relaxation master curves for PBrPO at six different concentrations of DOS: A, 5 wt % (169 °C); B, 8 wt % (149); C, 12 wt % (128); D, 15 wt % (107); E, 20 wt % (80); F, 25 wt % (44). Curves have been shifted along the log modulus and log time axis to emphasize slope changes in this region. Numbers in ( ) represent reference temperatures.

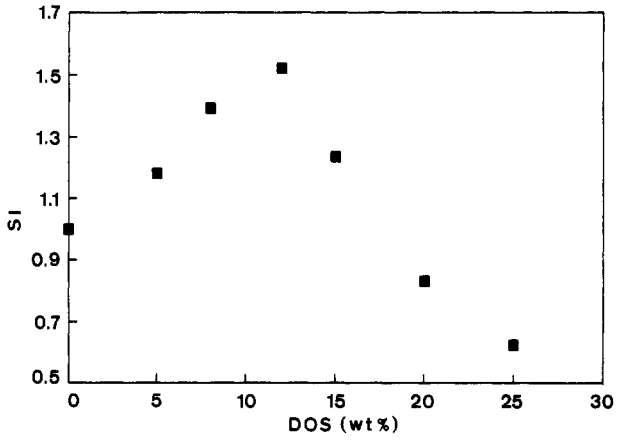

Figure 9. SI variation with different concentration of DOS in PBrPO system.

Further test of the model was also feasible by using DOS as a plasticizer whose solubility parameter is rather close to that of PBrPO. Differences in solubility parameter had been suggested to affect the degree of separation of polymers and, thus, the model predicts that the incorporation of diluent having a solubility parameter close to the polymer should be less effective in modifying the SI. Experiments were carried out with samples containing six different concentrations of DOS in the PBrPO system. The results of stress relaxation master curves are also collected in Figure 8 and a summary of SI as a function of DOS concentration is plotted in Figure 9. This figure shows a result very similar to that of the DOP–PBrPO system given in Figure 7 and again is reminiscent of Figure 2. It is clear that, under these conditions, the two diluents appear to be equally effective in changing the polymer dimensionality, and therefore the solubility parameters of the plasticizers used are less effective in controlling the SI in the PBrPO system. This result is consistent with the behavior shown in the PS–PBrPO blend system,[13] specially with modest concentration of PBrPO, diluted with three different plasticizers, DOP, DBP, and DOS. Based on the behavior of homopolymers in terms of the DDL model, SI measurements in the transition region afford a critical test of the viability of the DDL model.

Conclusion

Tobolsky's DDL model has been used to rationalize the viscoelastic behavior of amorphous polymers in the

primary transition region and a steepness index (SI) has been used as a reference measure of viscoelastic relaxations.

We have observed that the behavior of partially brominated poly(2,6-dimethyl-1,4-phenylene oxide) is in complete accordance with all the predictions of the DDL model upon plasticization with DOP and DOS. DOP and DOS having widely varying solubility parameters to that of PBrPO have not shown a great effectiveness in reducing the degree of intermolecular elastic force constants. Thus the two diluents used appear to be approximately equally efficient in controlling SI.

At this point, our experimental observations indicate that the DDL model is useful to interpret viscoelastic relaxation in the transition region and that the intermolecular interactions of which the model suggests are important factors to rationalize in terms of molecular base.

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