

## Temperature Dependence of Dynamic Mechanical Properties of Mixed Polymer Systems. II

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### INTRODUCTION

In an earlier communication<sup>1</sup> the temperature dependence at essentially constant frequency of the dynamic mechanical properties of a homologous series of butadiene-styrene copolymers was described. The discussion in this previous report was predicated on the assumption that corresponding to each possible mode of motion in the system there exists an equilibrium characteristic temperature, and that only in the vicinity of this characteristic temperature does the mode act as an energy-dissipating mechanism. On the basis of this assumption, and the further assumption that the transition is activated, it was shown that as a first approximation the magnitude of the viscous component,  $E_2(1/T)$ , of the dynamic modulus at a given temperature  $T = T_k$  was related to the number,  $H(1/T_k)$ , of mechanical modes of motion undergoing a transition at that temperature:

$$E_2(1/T)|_{T=T_k} = H(1/T_k)/\pi \quad (1)$$

It was found that the modal transition temperature,  $T'_k$ , i.e., the temperature of maximum  $E_2(1/T)$  for each copolymer, was related to that,  $T'_{k,s}$ , for styrene homopolymer by the expression:

$$1/T'_k - 1/T'_{k,s} = C \ln N_s \quad (2)$$

where  $N_s$  is the mole fraction styrene in the copolymer and  $C$  is a constant, at least at high mole fractions of styrene. A series of butadiene-acrylonitrile copolymers have been recently studied with similar results, as described in the present report.

The finding that the modal transition temperature of both styrene and acrylonitrile homopolymers is depressed by the "diluent" butadiene in a manner paralleling the depression of the melting temperature of a crystallizable polymer by a randomly copolymerized, noncrystallizing diluent<sup>2</sup> suggests that the influence of monomeric diluents on the modal transition temperature might parallel their influence on the melting temperature of crystallizing polymers. Some preliminary results were presented in the

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earlier communication as regards the effect of monomeric diluents on the temperature at which the peak in  $E_2(1/T)$  was observed. Additional experiments have recently been carried out and the results are given in the present communication. Also, as part of the earlier analysis, the influence of frequency on  $E_2(1/T)$  was predicted. The prediction has been subjected to experimental verification, as described in this report.

In the earlier work, and in the work presented here, the rubbery copolymers were incorporated into a thermoplastic matrix at a level of some 20 wt.-% in order to ensure that the frequency of the applied deformation did not vary significantly in the temperature range examined with respect to the rubbery copolymers. It was therefore necessary to assume that the dynamic mechanical properties of the rubbery copolymers and matrix were additive. Furthermore, it was assumed earlier that molecular weight was only a moderate factor as regards the magnitude of  $E_2(1/T)$  observed for the materials studied, all of which had a number-average DP in excess of 500. It was assumed also that the degree of dispersion of the rubbery polymers within the supporting matrix should have little effect on the observed magnitude of  $E_2(1/T)$  corresponding to the rubber component. The validity of the assumptions has been subjected to experimental scrutiny and the results are discussed in the present communication.

## EXPERIMENTAL

The vibrating-reed technique described fully in the earlier communication was used also in the present study. The experimental method and error were unchanged except for the study of the effect of frequency on  $T'_k$  (see below).

### Materials

The polymers utilized in the present study consisted of copolymers of butadiene and acrylonitrile covering a range of bound acrylonitrile, and copolymers of butadiene and styrene of essentially constant composition and covering a range of molecular weight. The butadiene-acrylonitrile copolymers were commercial materials from Naugatuck Chemical Corporation under the trade name of Hycar. The butadiene-styrene copolymers were experimental materials made with a "hot" recipe.<sup>3</sup> The molecular weight in the latter materials was controlled by variations in the quantity of mercaptan modifier charged in the recipe. The emulsion copolymers were salt-acid-coagulated and oven-dried prior to use.

The copolymers were incorporated into a thermoplastic matrix, polystyrene, by means of mill-blending for 10 min. at 165°C. on a standard two-roll rubber mill. The blended materials were flash-molded in a mold with cavities of the proper dimensions, ca.  $4.5 \times 0.30 \times 1.25$  cm. Since the thermoplastic matrix exhibited no transition in the temperature range in which the rubbery copolymers exhibited transitions, the specimens, containing some 80 wt.-% of the thermoplastic, did not undergo a significant

change of rigidity in this temperature range. Consequently, since the resonant frequency of the specimens is rigidity-controlled,<sup>4</sup> no significant change in frequency occurred in the temperature range of interest in regard to the rubbery copolymers.

### Diluents

To study the effect of diluent concentration on the transition temperature of a rubbery copolymer, the following technique was used for the preparation of specimens. Increasing quantities of a diluent, alternatively *n*-butyl stearate and dioctyl phthalate, were added via mill-blending to aliquots of PR-3, an experimental rubbery copolymer of styrene and butadiene with a bound styrene level of 62%. After the milling step, the rubber was reduced to a fine powder (<0.5 mm. diameter) by means of a laboratory-scale grinder whose cutting head was maintained at low temperatures, to facilitate grinding, by passing liquid nitrogen through the grinder along with the rubber. The samples of powdered rubber containing lubricant were then stirred with aliquots (80 wt.-%) of the thermoplastic matrix, also in powder of the same size, and the mixtures were flash-molded into specimens of the desired size. A styrene-acrylonitrile copolymer was selected as matrix material because of its superior resistance to materials which are plasticizers for styrene homopolymer. Samples of the rubber prior to incorporation in the matrix were subjected to infrared analysis, to serve as a check on the quantity of lubricant present, calculated on the basis of the ingredients used. In view of the difficulty in quantitatively mill-blending liquids with rubber, the infrared data were taken as being correct.

### Frequency

To study the effect of frequency on the transition temperature it was necessary to use specimens of various dimensions, since the resonant frequency of the specimens is related<sup>4</sup> to dimensions as well as to the intrinsic rigidity of the material, viz.:

$$E_2 = 38.4 \rho (l^4/d^3) f_r \Delta f$$

where  $\rho$  is the density,  $l$  and  $d$  are the specimen length and thickness, respectively,  $f_r$  is the resonant frequency, and  $\Delta f$  is the half-power band width. Consequently, specimens of various lengths and thicknesses were flash-molded from mixtures of a rubbery copolymer and a matrix. Since the dynamic mechanical properties depend much more strongly on temperature (exponential dependence) than on frequency, it was felt that the specimens should be tested together during one experiment in order to prevent the small experimental variation in temperature,  $\pm 0.1^\circ\text{C}$ ., from obscuring, or superimposing a large experimental error on, the dependence of the dynamic properties on frequency. The equipment described earlier was altered so that the resonant frequency and band width of four specimens could be measured rapidly and consecutively at each temperature. The

alteration, involving an interesting combination of analogue computing devices, will be described in a subsequent communication.

## RESULTS AND DISCUSSION

As was the case in the earlier communication, the discussion below will be restricted to the temperature dependence of the viscous component of the dynamic modulus. The choice is based upon the fact that the distribution function  $H(1/T_k)$  is defined by  $E_2(1/T)$  without the need for geometric differentiation as is the case with  $E_1(1/T)$ , the elastic component of the dynamic modulus.

### $E_2(1/T)$ for the Matrix Materials

As noted above (under Experimental), the desire to maintain the frequency of the applied strain essentially constant through the temperature range encompassing the transitions of the rubbery copolymers led to the

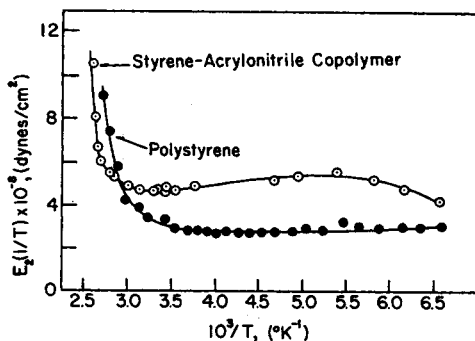


Fig. 1. Dependence of the viscous component of the dynamic modulus on reciprocal absolute temperature for the matrix materials polystyrene and a styrene-acrylonitrile copolymer.

technique of incorporating the rubbery copolymers at a relatively low level, generally 20 wt.-%, in a rigid (thermoplastic) matrix. On the assumption of linear additivity of the contributions of the several relaxation mechanisms in a particular material, the viscous component of the dynamic modulus corresponding to a given rubber can be determined from the experimental data by correcting for the contribution of the matrix material throughout the temperature range of interest. Consequently, the dynamic mechanical properties of the matrix materials were determined; plots of the viscous component of the dynamic modulus against reciprocal absolute temperature are given in Figure 1 for the two materials used as matrices in the present study, styrene homopolymer and a styrene-acrylonitrile copolymer.

The fact that  $E_2(1/T)$  of the styrene homopolymer is essentially independent of temperature at temperatures below the  $\alpha$  transition of the poly-

mer renders this polymer admirably suitable as supporting matrix for the majority of the rubbery copolymers studied. However, during a study of the influence of diluents on the transition temperature of a butadiene-styrene copolymer (see below) it was found necessary to replace the polystyrene as matrix material with a styrene-acrylonitrile copolymer because of the much lower solubility of the diluents in the latter polymer. Fortunately,  $E_2(1/T)$  of the styrene-acrylonitrile copolymer, while uniformly higher than that of polystyrene, is essentially independent of temperature at temperatures below the  $\alpha$  transition; only a small  $\beta$  transition is observed at very low temperatures (Fig. 1).

### Influence of Matrix and Degree of Dispersion on $E_2(1/T)$

The data given in Figure 2 for the butadiene-styrene copolymer PR-3, which was separately incorporated by milling at the level of 20 wt.-% in the two matrices, indicate that the size and shape of the peak corresponding to the rubber are essentially independent of matrix composition. This finding supports the hypothesis that the dynamic properties of the rubber and

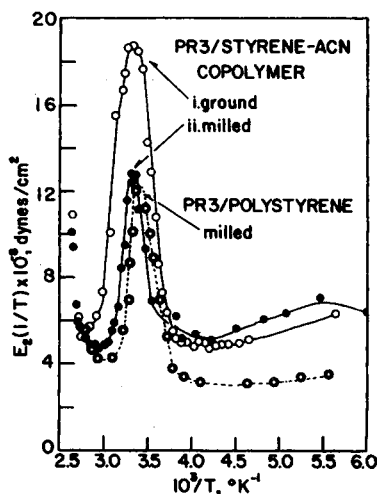


Fig. 2. Dependence of the viscous component of the dynamic modulus on reciprocal absolute temperature for the experimental copolymer PR-3 incorporated at the level of 20 wt.-% in the matrix materials: (O) PR-3 and matrix ground and mixed prior to molding of specimen; (●, ⊙) PR-3 and matrices milled prior to molding.

matrix are linearly additive within the limits of experimental error. Although the modal transition temperatures of the two peaks differ slightly, the difference is attributed to the difference between the base lines of the matrix materials (see Fig. 1) and to experimental error. Similarly, in the cases of the butadiene-acrylonitrile copolymer H-1014, separately incorporated in styrene homopolymer and in the styrene-acrylonitrile copolymer (see below), the area under the peak was larger in the latter system as a

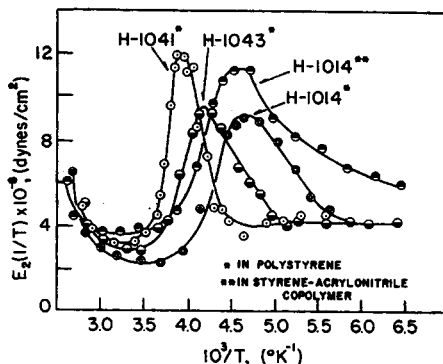


Fig. 3. Dependence of the viscous component of the dynamic modulus on reciprocal absolute temperature for the butadiene-acrylonitrile copolymers studied. Mole fractions of bound acrylonitrile in copolymers: H-1014, 0.21; H-1043, 0.28; H-1041, 0.41.

result of the  $\beta$  transition of the styrene-acrylonitrile copolymer (Fig. 1). The modal transition temperatures were, however, found to be the same in each case within experimental error.

The peak, also shown in Figure 2, for a sample of PR-3 mixed in powder form with the copolymer matrix also in powder form (see under Experimental) differs grossly in size from the peaks corresponding to the samples of PR-3 mixed with the matrices by means of milling. Microscopic examination of the samples revealed that the degree of dispersion of the PR-3 in the milled samples was considerably finer than that in the ground sample. We must conclude, therefore, that major changes in the degree of dispersion will exert an influence on the dynamic mechanical properties observed for mixed polymer systems. It is felt, however, that small differences in degree of dispersion, for example, the differences possibly encountered among the mill-blended materials, has little effect on the relative magnitude of the properties measured. A significant difference in the degree of dispersion obtainable through milling for a fixed length of time could arise, however, in cases in which the two polymers are strongly incompatible, i.e., when the interfacial free energy between the dispersed phase and matrix phase is high. In the case of incompatible polymers, the degree of dispersion would be expected to be coarser than that obtained for compatible polymers with the same expenditure of mechanical energy during milling. It is probable that the overly large peak observed for emulsion polybutadiene (G-2104, Figure 3 of the earlier communication) is a result of the incompatibility of polystyrene and polybutadiene and a concomitantly coarser dispersion than that obtained for the other rubbers, all of which contain copolymerized styrene and therefore exhibit increased compatibility with polystyrene. However, as yet no attempt has been made to determine via microscopic examination the degree of dispersion obtained throughout the homologous series of copolymers studied.

$E_2(1/T)$  for Butadiene-Acrylonitrile Polymers

In Figure 3,  $E_2(1/T)$  is plotted against reciprocal absolute temperature for the butadiene-acrylonitrile copolymers studied. The peak in each case corresponds to the rubbery polymer present in the blended mixture, while the incipient peak at high temperatures corresponds to the onset of the  $\alpha$  transition within the styrene homopolymer matrix. Temperatures in the vicinity of, and above, this transition are, of course, experimentally inaccessible with the present apparatus because of the thermal distortion of the reed specimens.

As was the case with the butadiene-styrene copolymers described earlier,<sup>1</sup> a nonzero magnitude of  $E_2(1/T)$  obtains for the butadiene-acrylonitrile copolymers at temperatures well below the maximum; i.e., the  $E_2(1/T)$  curves for the copolymers do not meet that of the matrix at low temperatures. The magnitude of  $E_2(1/T)$  for each of the copolymers is, however, zero at temperatures well above the maximum, in agreement with theory.

In Table I, the modal transition temperatures for the butadiene-acrylonitrile copolymers are given along with the mole fraction of bound acrylonitrile. It will be noted that in Figure 3  $T'_k$  increases with increasing acrylonitrile content, and that the peaks become more symmetrical and increase in height with increasing acrylonitrile content. The increasing symmetry is attributed to a decreasing probability of long sequences of butadiene as the acrylonitrile content is increased to ca. 0.5 mole fraction. The increasing height reflects the increasing population density of molecular structures with the modal composition. It would be expected that as the mole fraction of butadiene were decreased below 0.5 the peaks would again decrease in height and become skewed in the direction of high temperatures. Unfortunately, the presently available model compounds and matrix materials do not permit definition of the peaks of copolymers containing less than 0.5 mole fraction of butadiene. It will be noted that in Figure 3 the area under the peaks per unit weight of rubber decreases with decreasing butadiene content; similar behavior was observed earlier for butadiene-styrene copolymers.<sup>1</sup>

As shown in Figure 4, where  $10^3/T'_k$  is plotted against mole fraction

TABLE I  
Modal Transition Temperature and Mole Fraction Acrylonitrile for the Butadiene-Acrylonitrile Copolymers Studied

Sample <sup>a</sup>	Modal transition temp., $T'_k$ (°K.)	Bound acrylonitrile, <sup>b</sup> mole fraction
H-1041 (20 wt.-%)	256	0.41
H-1043 (20 wt.-%)	238	0.28
H-1014 (20 wt.-%)	211	0.21

<sup>a</sup> Numbers in parentheses indicate loading of rubber in polystyrene.

<sup>b</sup> Determined via Dumas analysis for total nitrogen.

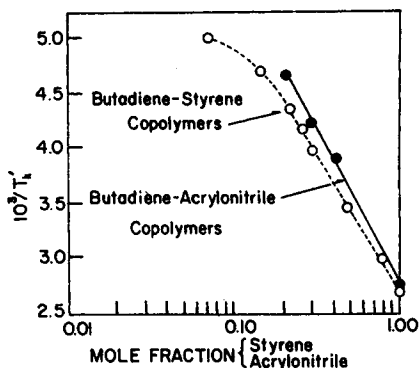


Fig. 4. Plot of reciprocal modal temperature against mole fraction of styrene or acrylonitrile for, respectively, butadiene-styrene copolymers and butadiene-acrylonitrile copolymers.

acrylonitrile for the present samples, a behavior is observed for butadiene-acrylonitrile copolymers similar to that observed in the case of butadiene-styrene copolymers, for which some data are here repeated to facilitate comparison. It appears, therefore, that for any homologous series of random copolymers, whose corresponding homopolymers are a plastic and a rubber, the transition temperatures are related to that of the plastic homopolymer by an equation of the form of eq. (2); i.e., the rubbery comonomer acts as a "diluent" in depressing the transition temperature of the plastic homopolymer.

Pressing the analogy between first- and second-order transitions, the enthalpy change  $\Delta H$  associated with the transitions for polystyrene and polyacrylonitrile can be calculated from the slopes of the lines in Figure 4; i.e., the constant  $C$  of eq. (2) is identified with  $-R/\Delta H$ . A value for  $\Delta H$  of about 800 to 900 cal./mole of repeating unit is thus obtained for both polystyrene and polyacrylonitrile. This magnitude of  $\Delta H$  is, as would be expected, somewhat lower than the magnitude of the enthalpies of fusion normally observed for semicrystalline polymers in which the degree of order is greater than that in glassy polystyrene or polyacrylonitrile.

#### Influence of Monomeric Diluents on $E_2(1/T)$

Representative data obtained for the copolymer PR-3 to which the diluents *n*-butyl stearate and dioctyl phthalate were separately added at various levels are given, respectively, in Figures 5 and 6. The modal temperatures,  $T'_k$ , are given in Table II, and their reciprocals,  $10^3/T'_k$ , are plotted in Figure 7 against diluent loading. The data of Flory and Fox<sup>6</sup> for the system polystyrene-diethyl benzene, and the data of Kelly and Bueche<sup>6</sup> for the system polymethylmethacrylate-diethyl phthalate, are given in Figure 8, where the reciprocal of the glass transition temperatures determined dilatometrically are plotted against volume fraction diluent. It can be seen that the data in Figures 7 and 8 suggest that the influence of diluents



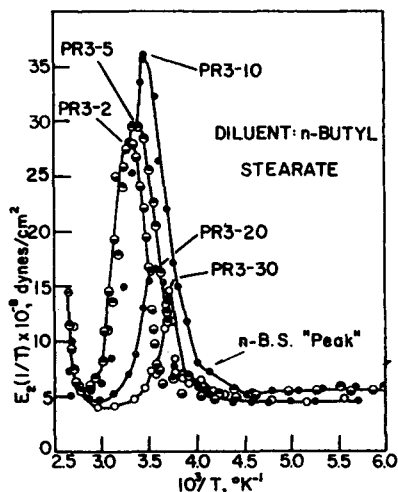


Fig. 5. Dependence of the viscous component of the dynamic modulus on reciprocal absolute temperature for samples of PR-3 containing *n*-butyl stearate and supported in a styrene-acrylonitrile matrix. Volume fraction diluent: PR3-2, 0.0185; PR3-5, 0.0529; PR3-10, 0.0835; PR3-20, 0.166; PR3-30, 0.228.

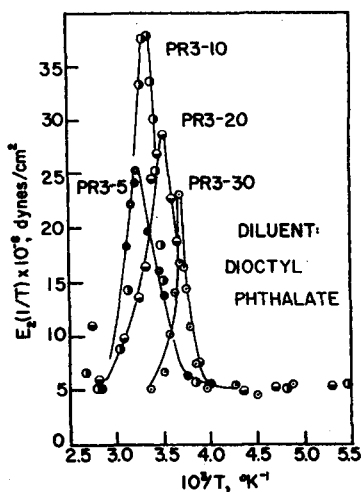


Fig. 6. Dependence of viscous component of the dynamic modulus on reciprocal absolute temperature for samples of PR-3 containing dioctyl phthalate and supported in a styrene-acrylonitrile matrix. Volume fraction of diluent: PR3-5, 0.0430; PR3-10, 0.0967; PR3-20, 0.178; PR3-30, 0.234.

on the transition temperature parallels the effect of diluents on the melting temperature of a crystallizing polymer.<sup>2</sup> The fact that linear relations are obtained indicates that the polymer-solvent interaction parameter,  $\chi_1$ , is small.<sup>7</sup> This finding is consistent with the fact that diluents of the type considered here, i.e., plasticizers, tend to "bloom" from the polymers at concentrations above about 5 wt.-%.

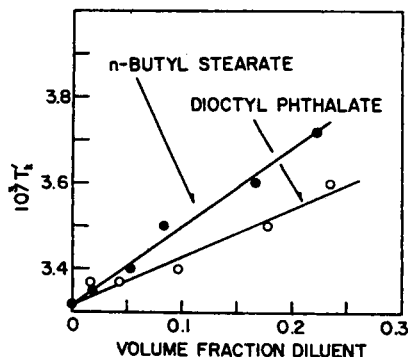


Fig. 7. Plot of reciprocal modal temperature against volume fraction of diluent for samples of PR-3 containing *n*-butyl stearate and dioctyl phthalate.

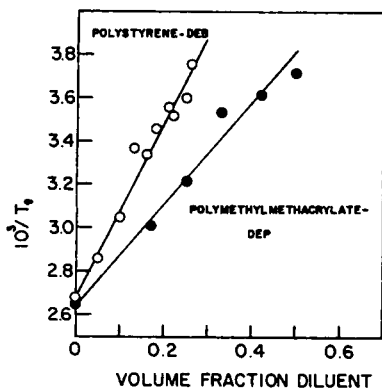


Fig. 8. Plot of reciprocal glass temperature determined dilatometrically against volume fraction of diluent for polystyrene-diethyl benzene (DEB)<sup>6</sup> and for polymethyl methacrylate-diethyl phthalate (DEP).<sup>6</sup>

Again pressing the analogy between first- and second-order transitions, the enthalpy changes associated with the transitions for these polymers can be calculated<sup>2</sup> from the slopes of the lines given in Figures 7 and 8. A value for  $\Delta H_{\mu}$  of 175 cal./mole of repeating unit is obtained for PR-3 with the diluent *n*-butyl stearate, and 240 cal./mole of repeating unit with the diluent dioctyl phthalate. The repeating unit for PR-3 was taken as 0.46 styrene units and 0.54 butadiene units. The difference between these values for  $\Delta H_{\mu}$  is probably attributable to diffusion of dioctyl phthalate from the rubber to the matrix (see below). For polystyrene, considering the repeating unit to consist of one styrene unit, a value for  $\Delta H_{\mu}$  of about 300 cal./mole of repeating unit is obtained from the slope of the line in Figure 8. While this value does not agree very well with that (800 to 900) calculated from the data in Figure 4, it is of the same order of magnitude. Closer agreement would be obtained if the repeating unit were considered to consist of two rather than one styrene unit.

TABLE II  
 Modal Transition Temperatures and Diluent Loading for Samples of PR-3 Containing *n*-Butyl Stearate and Dioctyl Phthalate and Supported in a Styrene-Acrylonitrile Matrix

Sample <sup>a</sup>	Modal transition temp., $T'_\alpha$ (°K.)	Diluent loading, <sup>b</sup> vol. fract. based on rubber
PR-3-0	305	0
<i>n</i> -Butyl stearate		
PR-3-2	298	0.0185
PR-3-5	294	0.0529
PR-3-10	286	0.0835
PR-3-20	278	0.166
PR-3-30	268	0.288
Dioctyl phthalate		
PR-3-2	297	0.0162
PR-3-5	297	0.0430
PR-3-10	294	0.0967
PR-3-20	286	0.178
PR-3-30	278	0.234

<sup>a</sup> Sample preparation described under Experimental.

<sup>b</sup> Data obtained via infrared analysis.

For the above calculations, molar volumes  $V_1$  of 400, 350, and 150 ml. were used for *n*-butyl stearate, dioctyl phthalate, and diethyl benzene, respectively, and molar volumes  $V_u$  of 83 and 100 were used for the repeating units of PR-3 and polystyrene, respectively.

Evidence of the "freezing" or immobilization of the *n*-butyl stearate itself can be seen in the small peak occurring at  $10^3/T \approx 4.0$  in Figure 5 for the samples of PR-3 containing large quantities of the diluent. Although dioctyl phthalate does not "freeze" at temperatures of interest in the present study, it, unlike *n*-butyl stearate, resulted in a slight depression of the transition of the matrix material. This finding, indicated by the onset of the  $\alpha$  transition of the matrix at  $10^3/T \approx 2.7$  vs. 2.6 in the case of *n*-butyl stearate, suggests that the dioctyl phthalate diffused from the rubber phase into the matrix, but at present no reliable estimate of the extent of diffusion can be made. The decreased slope of the curve in Figure 7 for the dioctyl phthalate diluent possibly results from this diffusion of the diluent from the rubber to the matrix. In this regard, it should be mentioned that in a series of samples wherein polystyrene was utilized for the matrix component, the characteristic temperature of the matrix was depressed considerably by the presence of the diluent *n*-butyl stearate, reflecting a substantial degree of diffusion of the diluent from the rubber phase to the matrix.

As noted above, samples for the study of the effect of diluents were prepared by grinding of the copolymer containing the diluent, followed by mixing of the copolymer with the matrix also in powder form. It was found that the peak in  $E_2(1/T)$  was considerably larger for the ground sample of

PR-3 than for the milled samples (see Fig. 2). The peaks in  $E_2(1/T)$  shown in Figures 5 and 6 are also considerably greater than those shown in Figure 2 for the milled materials. In fact, the peaks for the lower lubricant levels, 2, 5, and 10 wt.-%, are higher than that for the ground sample containing no lubricant. The increase in size of the peaks at the lower diluent loadings is not understood at this time. The decrease in the size of the peaks at the higher diluent loading reflects, of course, the decrease in the loading of rubber in the matrix; in the present study the weight of lubricant plus rubber was maintained constant at the level of 20%.

### Influence of Molecular Weight on $E_2(1/T)$

The dynamic mechanical properties were measured for a series of copolymers of essentially constant composition but of varying molecular weight. The temperature dependence of  $E_2(1/T)$  for these materials, each incorporated at the level of 20 wt.-% in a styrene homopolymer matrix, is shown in Figure 9. It can be seen that the shape of the peaks and their modal transition temperatures are not significantly dependent on molecular weight as measured over a sixfold range of intrinsic viscosity. The pertinent data for the four samples PR-3A through PR-3D are collected in Table III.

While there is a slight decrease in  $T'_k$  with decreased molecular weight, it is of the same order as the experimental error, even when  $T'_k$  for PR-3B and PR-3C is corrected for their slightly increased styrene content (see Fig. 4). We conclude that molecular weight, as hypothesized earlier, does not play a significant role in the results obtained in the present work. The finding

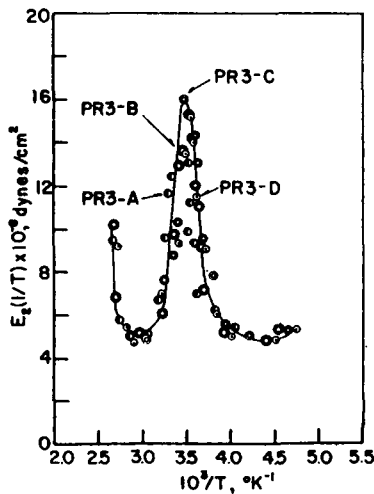


Fig. 9. Dependence of the viscous component of the dynamic modulus on reciprocal absolute temperature for samples of PR-3 of various molecular weights, each supported at the level of 20 wt.-% in a polystyrene matrix: PR-3A,  $[\eta] = 1.00$  dl./g.; PR-3B,  $[\eta] = 0.56$  dl./g.; PR-3C, Dilute solution viscosity = 0.35 dl./g.; PR-3D, DSV = 0.17 dl./g.

TABLE III  
 Modal Transition Temperatures, Intrinsic Viscosity, and Mole Fraction Styrene for  
 Samples of PR-3 of Various Molecular Weights

Sample <sup>a</sup>	Modal transition Temp., $T'_k$ (°K.)	$[\eta]$ , dl./g. at 30°C. in toluene	Bound styrene, <sup>c</sup> mole fraction
PR-3A	292	1.00	0.46
PR-3B	286	0.56	0.50
PR-3C	286	0.35 <sup>b</sup>	0.50
PR-3D	282	0.17 <sup>b</sup>	—

<sup>a</sup> Preparation of the PR-3 samples is described under Experimental. Samples were supported at the level of 20 wt.-% in a polystyrene matrix.

<sup>b</sup> Dilute solution viscosity measured at only one concentration within the range 0.1 to 0.3 g./100 ml.

<sup>c</sup> Determined via infrared analysis.

that  $E_2(1/T)$  is independent of the degree of polymerization over the range  $1000 \leq DP \leq 100$  indicates that, at the frequencies involved in the present study (200 to 300 cycles/sec.), the transition and the absorption of energy must involve the coordinated motion of repeating-unit sequences considerably less than 100 units in length. If this were not the case, the "concentration" of chain ends would be appreciable, particularly at low DP's and a reduction in  $T'_k$  of the transition peak would be expected to occur.<sup>2</sup> Furthermore, as noted above in connection with monomeric diluents, considering the repeating units to consist of only a very few monomeric units leads to enthalpies of the magnitude to be expected for the transition.

### Influence of Frequency on $E_2(1/T)$

The influence of frequency on the temperature dependence of  $E_2(1/T)$  is shown in Figure 10 for specimens prepared from the copolymers PR-3 and PR-2 in separate admixtures with a matrix of styrene homopolymer. The dimensions of the specimens, the modal temperatures  $T'_k$ , and the frequency at the temperature  $T'_k$  are given in Table IV. It can be seen that, although the experimental error is increased at high frequencies, the prediction illustrated in Figure 1 of the earlier communication is generally fulfilled; i.e., a fourfold increase in frequency of the applied strain results in an increase of about 0.1 unit in the reciprocal modal transition temperature of sample PR-3.

On the other hand, it can be seen from the data for sample PR-2 that a 50% increase in frequency leads only to a marginal increase in  $T'_k$ . In fact, had the experiments not been carried out concurrently, the fluctuations in temperature normally encountered within the thermostat would probably have obscured the marginal increase in  $T'_k$  (see under Experimental).

It should be pointed out that the difference between the sizes of the peaks for the samples of PR-3 and PR-2 arises from the fact that the samples of PR-3 were prepared with grinding while the samples of PR-2 were prepared with milling with the polystyrene matrix.

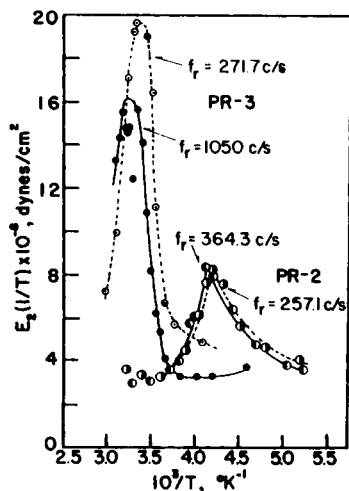


Fig. 10. Influence of frequency on the temperature dependence of the viscous component of the dynamic modulus of PR-3 and PR-2 each supported at the level of 20 wt-% in a polystyrene matrix. The resonance frequencies given in each case are for the modal transition temperatures. The PR-3 samples were prepared via grinding and the PR-2 samples via milling with the matrix.

TABLE IV  
Modal Transition Temperatures, Central Frequency, and Dimensions of PR-3 Used for Frequency Study

Sample <sup>a</sup>	Specimen size, cm. <sup>b</sup>		Modal transition temp., $T'_k$ (°K.)	Central frequency at $T'_k$ , cycles/sec.
	Length	Thickness		
PR-3X	5.02	0.313	296	271.7
PR-3Y	2.51	0.312	308	1050
PR-2X	5.42	0.248	237	257.1
PR-2Y	5.41	0.352	241	364.3

<sup>a</sup> Samples consist of 20 wt.-% PR-3 and 20 wt.-% PR-2 separately incorporated in a polystyrene matrix. The PR-3 samples were prepared with grinding and the PR-2 samples with milling.

<sup>b</sup> Specimen dimensions measured after 4 weeks' annealing at 65°C.

## CONCLUSIONS

Through a study of appropriate model compounds it has been established that the transition temperature of a given plastic homopolymer, as measured from dynamic mechanical properties at essentially constant frequency in the range 200–300 cycles/sec., is depressed by the presence of a copolymerized rubbery diluent in a fashion parallel to the depression of the melting point of crystalline polymers by the presence of noncrystallizing comonomers. It has also been shown that the transition temperature of polymers

is depressed by the presence of nonpolymeric diluents, again in a fashion parallel to the depression of the melting point of crystalline polymers by the presence of nonpolymeric diluents. These findings suggest that the glass transition, or second-order transition, is a transition for which usual thermodynamic expressions can be used. This conclusion, along with a dependence on frequency in accord with predictions, supports the proposed treatment of dynamic mechanical properties measured in the vicinity of the glass transition temperature.

An earlier hypothesis, that molecular weight should play only a minor role at the frequencies involved in the present work, has been substantiated. However, it has been found, contrary to an earlier prediction, that the degree of subdivision of the rubbery polymer in the matrix plays a significant part as regards the area under the peak per unit weight of the rubber; the modal transition temperature, however, is not affected by the degree of dispersion.

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### Synopsis

The temperature dependence at constant frequency of the viscous component  $E_2(1/T)$  of the dynamic modulus has been determined for a homologous series of butadiene-acrylonitrile copolymers supported in a matrix of styrene homopolymer. The results, which agree with those reported earlier for a homologous series of butadiene-styrene copolymers, indicate that the transition temperature of a given plastic homopolymer, as measured from dynamic mechanical properties at essentially constant frequency in the range 200-300 cycles/sec., is depressed by the presence of a copolymerized rubbery diluent as the melting point of crystalline polymers is depressed by the presence of noncrystallizing comonomers. In addition, it has been found that the transition temperature is depressed by the presence of monomeric diluents much as the melting point of crystalline polymers is depressed by the presence of monomeric diluents. Two earlier assumptions, that the dynamic properties in the frequency range of interest should be independent of both the molecular weight of the rubbery copolymer and the degree of dispersion of the copolymer in the thermoplastic matrix, have been subjected to experimental scrutiny. The assumption regarding the dependence on molecular weight has been substantiated, at least for DP's in excess of 100. The assumption regarding the dependence on the degree of dispersion has been negated; the area under the  $E_2(1/T)$  peak was found to be considerably greater for a coarse dispersion than for a fine one.

### Résumé

On a déterminé pour une série homologue de copolymères butadiène-acrylonitrile supporté dans une matrice d'homopolystyrène, l'influence de la température vis-à-vis du module dynamique,  $E_2(1/T)$ , à une fréquence constante du composant visqueux. Les résultats sont en accord avec ceux décrits antérieurement pour une série homologue de copolymères butadiène-styrène, et montrent que la température de transition d'un homopolymère donné, celle que mesurée via les propriétés mécaniques dynamiques à une fréquence essentiellement constante de l'ordre de 200 à 300 c/s, est abaissée par la présence d'un comonomère, et de la même manière l'introduction de comonomères non cristallisables diminue le point de fusion de polymères cristallins. De plus on a trouvé que la température de transition est abaissée par la présence de diluants monomériques et de la même façon ceux-ci abaissent le point de fusion de polymères cristallins. Deux hypothèses antérieures prévoyaient que les propriétés dynamiques, à des fréquences qui sont intéressantes étaient indépendantes à la fois du poids moléculaire du copolymère et du degré de dispersion du copolymère dans la matrice thermoplastique; ces deux hypothèses ont été soumises à un examen expérimental. L'hypothèse concernant l'influence du poids moléculaire a pu être confirmée, tout au moins pour des D.P. Supérieurs à 100. L'hypothèse concernant l'influence due degré de dispersion s'est avérée erronée; on a trouvé que la région en dessous du pic  $E_2(1/T)$  était considérablement plus grande pour une dispersion grossière que pour une fine dispersion.

### Zusammenfassung

Die Temperaturabhängigkeit der Viskositätskomponente,  $E_2(1/T)$ , des dynamischen Modulus wurde bei konstanter Frequenz für eine homologe Reihe von Butadien-Acrylnitrilcopolymeren in einer Polystyrolmatrix als Träger bestimmt. Die Ergebnisse, welche mit den früher für eine homologe Reihe von Butadien-Styrolcopolymeren mitgeteilten übereinstimmen, lassen erkennen, dass die durch die dynamisch-mechanischen Eigenschaften bei im wesentlichen konstanter Frequenz im Bereich von 200 bis 300 Hz gemessene Umwandlungstemperatur eines gegebenen plastischen Homopolymere durch die Gegenwart eines copolymerisierten kautschukartigen Stoffes in ähnlicher Weise herabgesetzt wird, wie der Schmelzpunkt von kristallinen Polymeren durch die Gegenwart nicht kristallisierbarer Comonomerer. Außerdem wurde festgestellt, dass die Umwandlungstemperatur durch die Gegenwart von Monomeren in ähnlicher Weise erniedrigt wird, wie der Schmelzpunkt von kristallinen Polymeren durch die Gegenwart von Monomeren. Zwei frühere Annahmen, dass nämlich die dynamischen Eigenschaften in dem interessierenden Frequenzbereich sowohl vom Molekulargewicht des kautschukartigen Copolymeren als auch vom Dispersitätsgrad des Copolymeren in der thermoplastischen Matrix unabhängig sein sollten, wurden einer experimentellen Überprüfung unterzogen. Die Annahme bezüglich der Abhängigkeit vom Molekulargewicht wurde, wenigstens für D.P. oberhalb 100, als richtig erwiesen. Die Annahme bezüglich der Abhängigkeit vom Dispersitätsgrad wurde widerlegt; die Fläche unter dem  $E_2(1/T)$ -Maximum war bei einer groben Dispersion beträchtlich grösser als bei einer feinen.

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