

## Amorphous State Transitions in Butadiene-Acrylonitrile Copolymers

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### Synopsis

Differential thermal analysis, creep measurements, and gas permeation rates are used to confirm the existence of a transition zone in three butadiene acrylonitrile copolymers in a temperature region that starts at roughly 15° to 25°C above the main glass transition temperatures of the copolymers and extends over a broad temperature range. The change appears to be slightly endothermic and softens the copolymers upon heating. It is speculated that the copolymers are in a mesomorphic state above their main glass temperature in which there is either a degree of ordering or a low-grade crystallinity of polybutadiene units along the copolymer chains. It is not until the copolymers are 50° to 75°C above their main glass temperature that they become truly amorphous.

### INTRODUCTION

The existence of transitions in polymers above the main glass transition temperature has been reported for a number of polymeric materials.<sup>1-7</sup> Fox and Flory<sup>3</sup> and Krimm and Tobolsky,<sup>4</sup> for example, found changes in the properties of polystyrene at 100°C and 160°C which appear to be glass-like transitions. In this case, the lower temperature appeared to be the conventional glass temperature. Boyer<sup>5</sup> has proposed that a glasslike transition above the main glass temperature involves a coordinated motion of an entire polymer molecule and that the temperature interval between these two transitions, and the relative magnitude of the two, will depend on the size of the group attached to the polymer chain and the value of the main glass temperature,  $T_g$ .

Amorphous transitions in polyacrylonitrile ( $T_g \sim 90^\circ\text{C}$ ) at 140°C, were reported by Kimmel and Andrews<sup>6</sup> and by Schmieder and Wolf.<sup>7</sup> Their presence is explained by Andrews to result from the dissociation of oriented nitrile groups. Nitrile groups have a high dipole moment and groups on adjacent chains tend to have their dipoles oppositely directed, a situation

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favoring association of dipoles. Saum<sup>8</sup> also suggests a possibility of association between adjacent nitrile groups in a hydrocarbon chain. The dissociation of these, upon the introduction of thermal energy, is offered as an explanation for the observed transition in polyacrylonitrile.

The existence of multiple main glass transition temperatures in butadiene-acrylonitrile copolymers has been reported by Chandler and Collins.<sup>9</sup> The authors suggest that the presence of the multiple transitions may arise from molecular structure differences along the polymer chains or from polymer mixtures of incompatible species that could form as a result of the slight difference in reactivity ratios of the two monomers.

In this paper we show several experiments which confirm the existence of a transition zone in three butadiene-acrylonitrile copolymers in a temperature region that starts at roughly 15° to 25°C above the main glass transition temperatures of the copolymers and extends over a broad temperature range. The change appears to be slightly endothermic and softens the copolymers upon heating. Differential thermal analysis of a series of polybutadienes shows a similar transition in about the same temperature range. This latter transition is in the melting range of poly-*cis*-1,4-butadiene. These facts lead us to speculate that the copolymers are in a mesomorphic state above their main glass transition temperature in which there is a degree of ordering, or perhaps a low-grade crystallinity, of polybutadiene units along the copolymer chains.

## EXPERIMENTAL

### Materials

The copolymers used in this study were butadiene-acrylonitrile copolymers obtained from The Firestone Synthetic Rubber and Latex Company, Akron, Ohio. Their designations are FRN-500, FRN-501, and FRN-502, corresponding to acrylonitrile contents of 24.3, 31.2, and 34.9% by weight, respectively. One of the polybutadiene polymers was also from Firestone and was designated as FRS 2004. The other two polybutadienes were reference standards supplied by the Phillips Petroleum Company, Special Products Division. The high *cis* material contains 95.3% *cis*, 1.4% *trans*, and 3.3% vinyl. The high *trans* material contains 8.9% *cis*, 88.5% *trans*, and 1.32% vinyl. The various experiments were conducted on as-received specimens, on films that were cast from dilute solution, and on compression-molded plugs. The manner of treatment did not appear to significantly alter the behavior of the materials.

### Diffusion and Permeation Coefficients

The diffusion and permeation coefficients of helium, neon, argon, and nitrogen were measured by the time lag technique.<sup>10</sup> A constant pressure technique for obtaining the time lag curve was employed, with constant pressures being maintained at both the upstream and downstream faces of a

TABLE I  
Films Used in Permeation Cell

Film	Polymer composition, wt-%	Approx. value of primary $T_g$ , °C	Thickness, cm	Area cm <sup>2</sup>
A	24.3% acrylonitrile	-53	0.194	43.7
B	31.2% acrylonitrile	-44	0.172	43.7
C	31.2% acrylonitrile	-44	0.077	43.7
D	34.9% acrylonitrile	-38	0.224	43.7
E	34.9% acrylonitrile	-38	0.060	43.7

polymer film during the permeation process. A detailed description of the constant-pressure permeation cell has been presented elsewhere.<sup>11</sup> The permeation coefficients obtained from the cell were found to be reproducible within 5% while the diffusion coefficients were reproducible to 15%.

A list of the films used in the permeation cell is given in Table I, indicating both the film thickness and the area exposed for permeation. The reported thickness is an average of at least ten measurements made with a micrometer. The films were cast from solution on a mercury surface and were not crosslinked. Chloroform was used as a solvent for the low acrylonitrile polymer while methyl ethyl ketone was found suitable for the other two materials. High purity gases containing less than 0.005% impurities were used for the permeation and diffusion measurements.

### Differential Thermal Analysis

The transitional behavior was also observed using the calorimeter attachment of a du Pont Differential Thermal Analyzer (DTA). The operating principle of the DTA has been described before.<sup>12</sup> The analyses were performed on the materials in the as-received state as well as after hot pressing and drying. Samples were cooled to -70°C with a liquid nitrogen bath and then heated at the rate of 15°C/min. Each sample was cycled from the highest temperature to -70°C several times to ascertain the reproducibility of the traces. In general, neither hot pressing nor cycling caused any major differences in the behavior of the materials. The only noticeable variation was in the absolute values of the transition temperatures; different handling conditions caused up to a 5° variation in the observed temperatures. This is expected from the nature of glass transitions.

### Mechanical Measurements

Mechanical creep tests were run in the environmental chamber of an Instron testing machine in which temperature could be controlled to  $\pm 1^\circ\text{C}$ . The materials were prepared by milling and hot pressing for 20 min at 175°C and 350 psi. Creep specimens were cut from the prepared material using a "dog bone" clicker die. These specimens were 4 in. long with an

initial cross-section of 0.2 by 0.2 in. and an initial gauge length  $l_0$  of 1.5 in. A specimen was gripped at the upper end and a constant load of 1.22 lb applied at its free end (corresponding to an initial stress of 30.6 psi). Deformation was monitored by a 10% incremental extensometer and was reported in terms of an effective compliance,  $j(t) = \epsilon(t)/\sigma$ , where  $\epsilon(t)$  is the reduced deformation,  $(l - l_0)/l_0$ , and  $\sigma$  is the stress based on the true cross-sectional area  $A$  (assuming no volume change on stretching  $Al = A_0l_0$ ).

## DISCUSSION OF RESULTS

### Diffusion and Permeation

The diffusion of gases in polymer films has long been recognized as an activated process and can be described by an Arrhenius-type equation.<sup>13,14</sup>

$$D = D_0 \exp(-\Delta E_d/RT) \quad (1)$$

where  $D$  is the diffusion coefficient,  $\Delta E_d$  is the activation energy for diffusion, and  $D_0$  is a "constant" given by Eyring.<sup>14</sup>

$$D_0 = e(\lambda_d)^2 \frac{kT}{h} \exp(\Delta S/R) \quad (2)$$

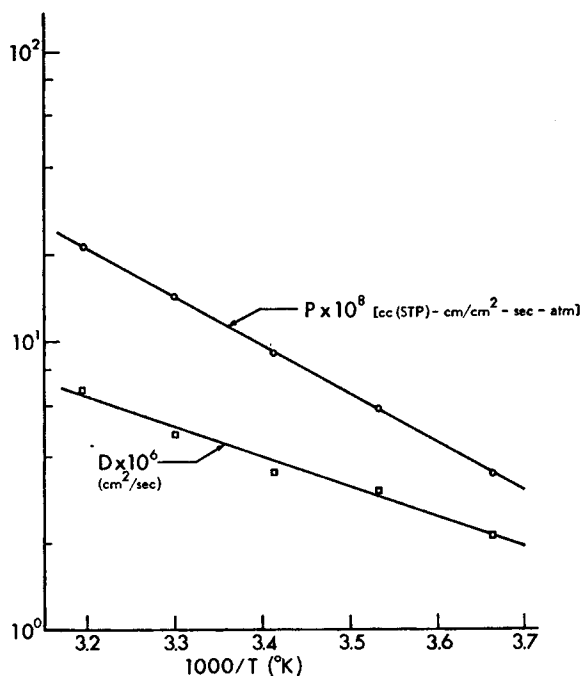


Fig. 1. Diffusion and permeation coefficients for helium in 31.2% acrylonitrile polymer as a function of reciprocal of absolute temperature.

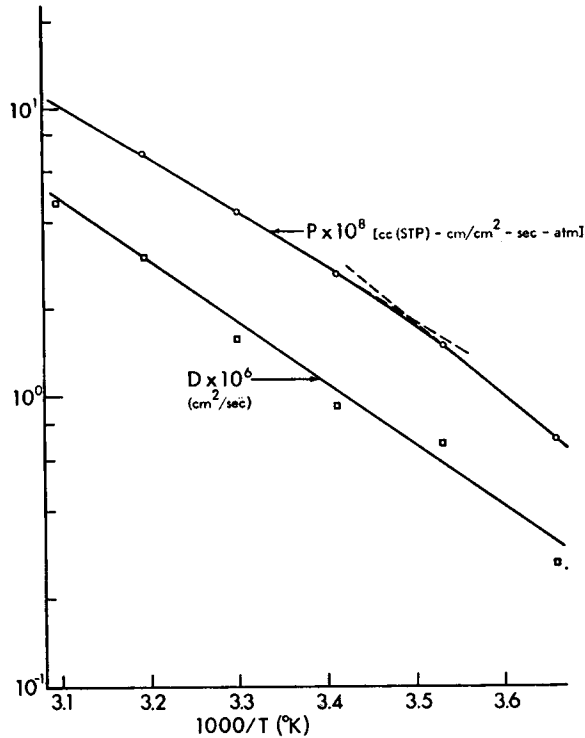


Fig. 2. Diffusion and permeation coefficients for neon in 31.2% acrylonitrile polymer as a function of reciprocal of absolute temperature.

Here,  $\lambda_d$  is the diffusional jump length,  $k$  and  $h$  are Boltzmann's and Planck's constants, respectively, and  $\Delta S$  is the entropy of activation for diffusion. The solubility coefficient of a gas in a polymer has also been found to follow an exponential relationship<sup>13</sup>

$$S = S_0 \exp(-\Delta H_s/RT) \quad (3)$$

where  $S$  is the solubility coefficient,  $\Delta H_s$  is the heat of solution of the gas in the polymer, and  $S_0$  is a constant. Since the permeation coefficient  $P$  is simply the product of  $D$  and  $S$ , it can also be given by an exponential relationship

$$P = P_0 \exp(-\Delta E_p/RT) \quad (4)$$

where  $\Delta E_p$ , the "activation energy" of permeation, is a sum of  $\Delta E_d$  and  $\Delta H_s$ , and  $P_0$  is the product of  $D_0$  and  $S_0$ .

Plots of the logarithm of the diffusion or permeation coefficient of an inert gas in a polymer against the reciprocal of temperature normally appear linear over temperature ranges of 20–30°C. Some nonlinearity has been reported over larger temperature ranges,<sup>15–18</sup> with the apparent activation energies for both diffusion and permeation decreasing with increasing temperature. Also, apparent activation energies will normally change

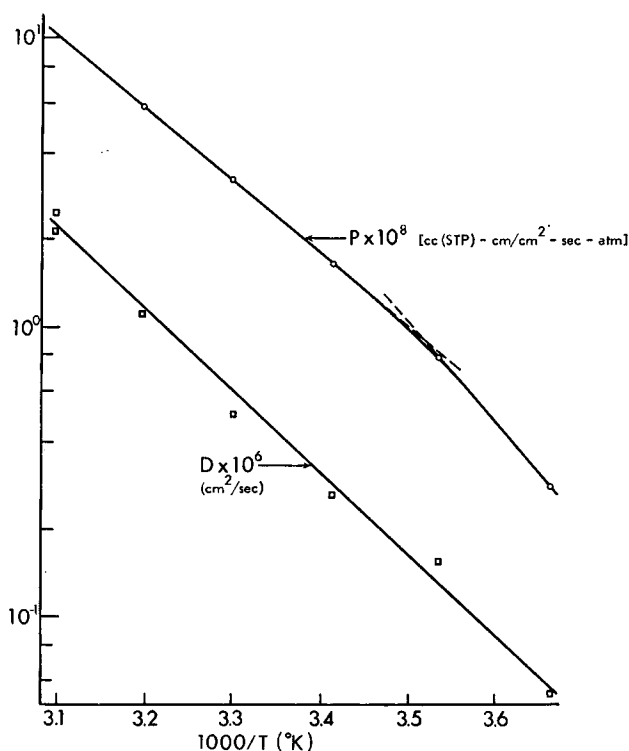


Fig. 3. Diffusion and permeation coefficients for argon in 31.2% acrylonitrile polymer as a function of reciprocal of absolute temperature.

when going through a transition. Illustrative plots of the logarithms of the diffusion and permeation coefficients (obtained in this work) versus the reciprocal of the absolute temperature are shown in Figures 1 to 4. All other systems behave in a similar fashion. The plots of the permeation data look quite linear for some of the gas-polymer systems, while for other systems the experimental points are better represented by either a smooth curve or by two intersecting straight lines, with a lower activation energy for permeation occurring at the higher temperatures. The higher degree of scatter in the diffusion data made it impossible to differentiate between linear and nonlinear behavior. A least mean square fit of a straight line to the data gave an "average" activation energy for the temperature range.

The Arrhenius parameters for both diffusion and permeation are listed in Table II. Where curvature exists, the activation energies above and below the "transition" zone are reported along with the temperature region of maximum curvature. The activation energy for permeation is probably accurate to  $\pm 300$  cal/mole, while the average activation energy for diffusion is probably accurate to  $\pm 1,000$  cal/mole.

The experimental results for neon, argon, and nitrogen clearly indicate a decrease in activation energy of roughly 1,000 to 3,000 cal/mole in the

TABLE II  
Arrhenius Parameters For Diffusion and Permeation

Polymer composition, wt-%	Gas	$\Delta E_d$ , cal/mole	$D_0$	Above transition zone		Below transition zone		Transition °C
				$\Delta E_p$ , cal/mole	$P_0$	$\Delta E_p$ , cal/mole	$P_0$	
24.3% acrylonitrile	He	6,600	0.44	—	—	7,200	0.03	—
	Ne	7,800	0.87	8,200	0.059	10,400	3.19	0-5
	A	10,000	6.7	10,200	1.61	—	—	—
	N <sub>2</sub>	9,600	2.6	10,500	0.80	—	—	10-15
31.2% acrylonitrile	He	4,700	0.013	—	—	7,600	0.045	—
	Ne	9,700	16.2	8,600	0.07	11,500	100	10-15
	A	12,800	450	11,600	7.4	13,500	190	10-15
	N <sub>2</sub>	13,900	2,460	12,600	11.8	—	—	0-10
34.9% acrylonitrile	He	6,800	0.53	—	—	7,700	0.04	—
	Ne	8,200	1.30	8,200	0.031	9,700	0.34	25-30
	A	12,800	460	12,300	17.3	14,200	540	10-15
	N <sub>2</sub>	13,200	700	13,400	41	14,200	150	15-20

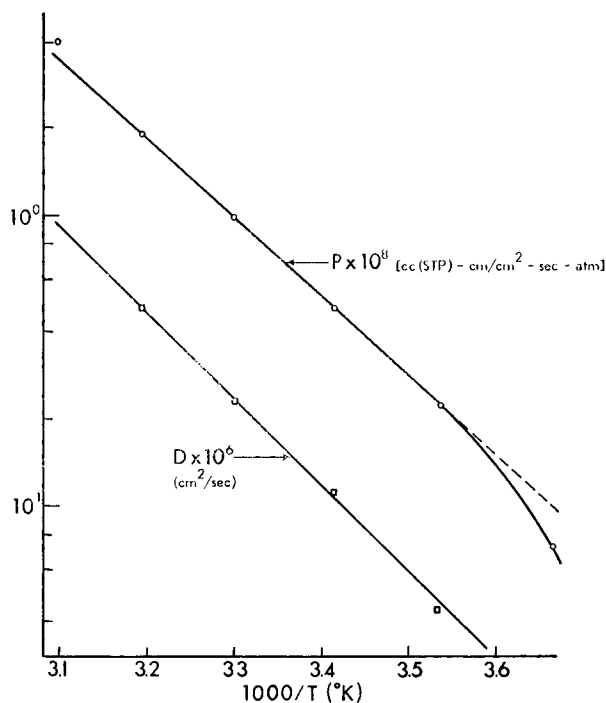


Fig. 4. Diffusion and permeation coefficients for nitrogen in 31.2% acrylonitrile polymer as a function of reciprocal of absolute temperature.

temperature range of 0° to 20°C for each of the polymers. This is roughly 50° to 60°C above the main glass transition temperatures of these copolymers. Similar permeation and diffusion behavior for inert gases in natural rubber, butadiene-acrylonitrile copolymers, butadiene-styrene copolymers, and neoprene have been reported by Barrer and Skirrow<sup>16</sup> and by van Amerongen.<sup>17</sup> In all cases, this behavior is found in a temperature range where the polymers are generally considered amorphous and where no significant transition in the bulk properties of the polymers have previously been reported. In polybutadiene, there is no change in the activation energy for permeation of the inert gases over the same temperature range.

### Differential Thermal Analysis

Figure 5 is a sketch of the DTA tracings for the three FRN copolymers studied. The first breaks in the curves at about -38°C for FRN-502 and at about -44°C for FRN-501 are due to the main glass transition temperatures of these copolymers. (The FRN-500 exhibits a main glass transition at about -53°C.) The curves break again at about -17°C for FRN-502, -22°C for FRN-501, and -26°C for FRN-500. As heating continues, the traces exhibit reasonably well-defined minima and then slowly increase with temperature. The minima occur at roughly 35° to 40°C above the main



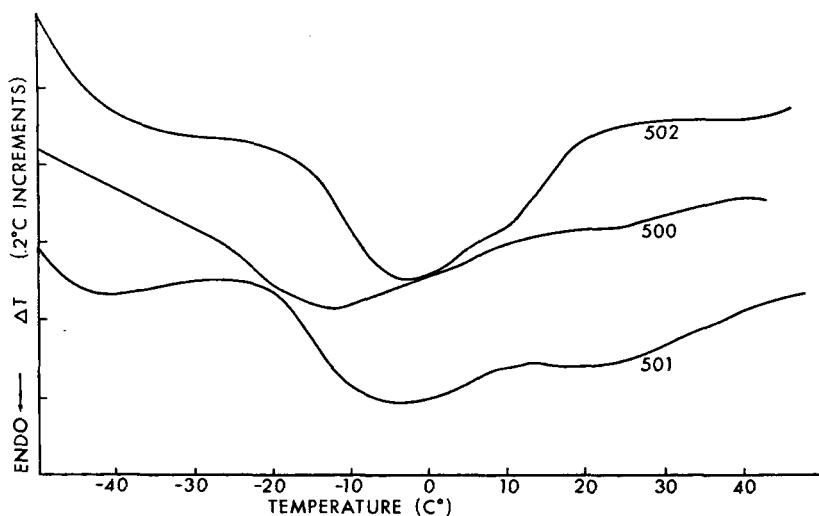


Fig. 5. Sketch of DTA tracing for FRN butadiene-acrylonitrile copolymers.

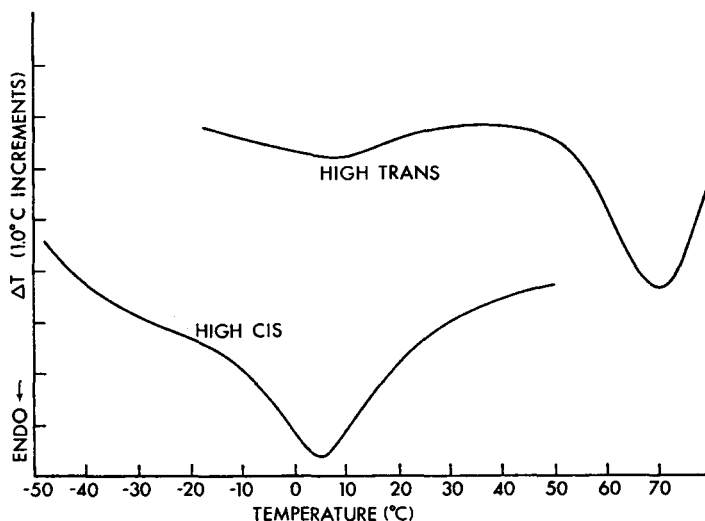


Fig. 6. Sketch of DTA tracings for Phillips polybutadienes.

glass temperature and the region of change is between  $-20^{\circ}$  and  $+20^{\circ}\text{C}$  for the three copolymers.

These traces indicate that there are slight endothermic changes in the copolymers occurring over the temperature range  $-20^{\circ}$  to  $+20^{\circ}\text{C}$ . These changes could be associated with a gradual disordering of the polymer structure.

Figures 6 and 7 are sketches of DTA tracings for the three polybutadiene samples. The Firestone FRS 2004 polybutadiene exhibits a minimum at about  $0^{\circ}\text{C}$  which is quite similar to those observed on the copolymers. In

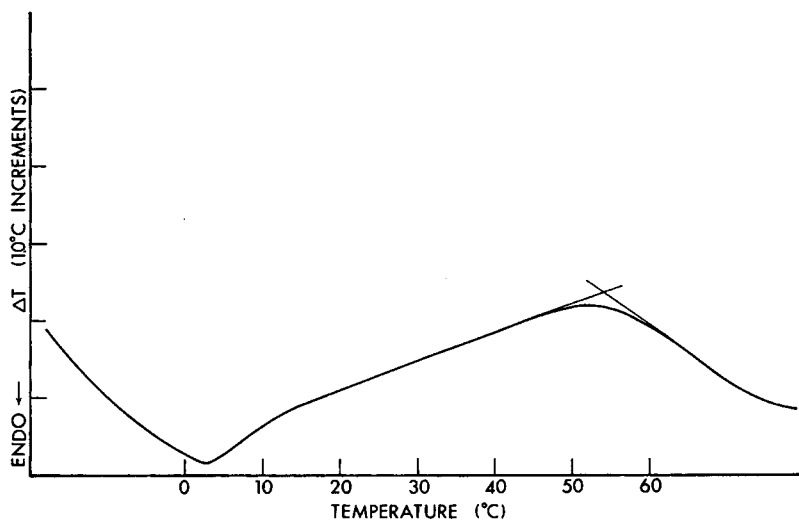


Fig. 7. Sketch of DTA tracing for Firestone 2004 FRS poly-*cis*-1,4-butadiene.

addition, a glasslike transition is observed at about 50°C, which is at least 130°C above the main glass transition temperature. The Phillips high poly-*cis*-1,4-butadiene shows an endotherm in the temperature range 0° to 5°C, which is the melting point for this isomer. The Phillips high poly-*trans*-1,4-butadiene shows a slight minimum in the DTA trace at about 0°C and then exhibits a sharp endotherm at about 70°C. The former is probably associated with the melting of the 8.9% *cis*-isomer in the material, while the latter endotherm is the polymorphic transformation of the poly-*trans*-1,4-butadiene.

These results lead one to the speculation that the changes in the copolymers in the temperature region -20 to +20°C are associated with conformational changes in the butadiene portions of the copolymer chains.

### Mechanical Tests

The deformation of the three copolymers was measured as a function of time at constant temperature. A typical set of deformation-time curves is shown in Figure 8. The behavior of the FRN-501 and 502 copolymers is identical to that of FRN-500, which is shown in the figure. There is a very rapid initial deformation followed by a region of relatively slow flow. The data may be replotted in terms of the "effective compliance"  $J(t) = \epsilon(t)/\sigma$ . Since  $Al = A_0 l_0$  and  $\epsilon(t) = (l/l_0 - 1)$ , the "effective compliance" may be written in terms of the initial stress as  $J(t) = [(l - l_0)/30.6l]$  psi<sup>-1</sup>. This expression is plotted in Figure 9 for the FRN-500. After the rapid initial deformation period, the "effective compliance" increases about linearly with time and can be extrapolated back to zero time to give an apparent initial compliance  $J(0)$ . These values are plotted in Figure 10 for the three copolymers. (Since the three materials behave in a quite similar fashion, a

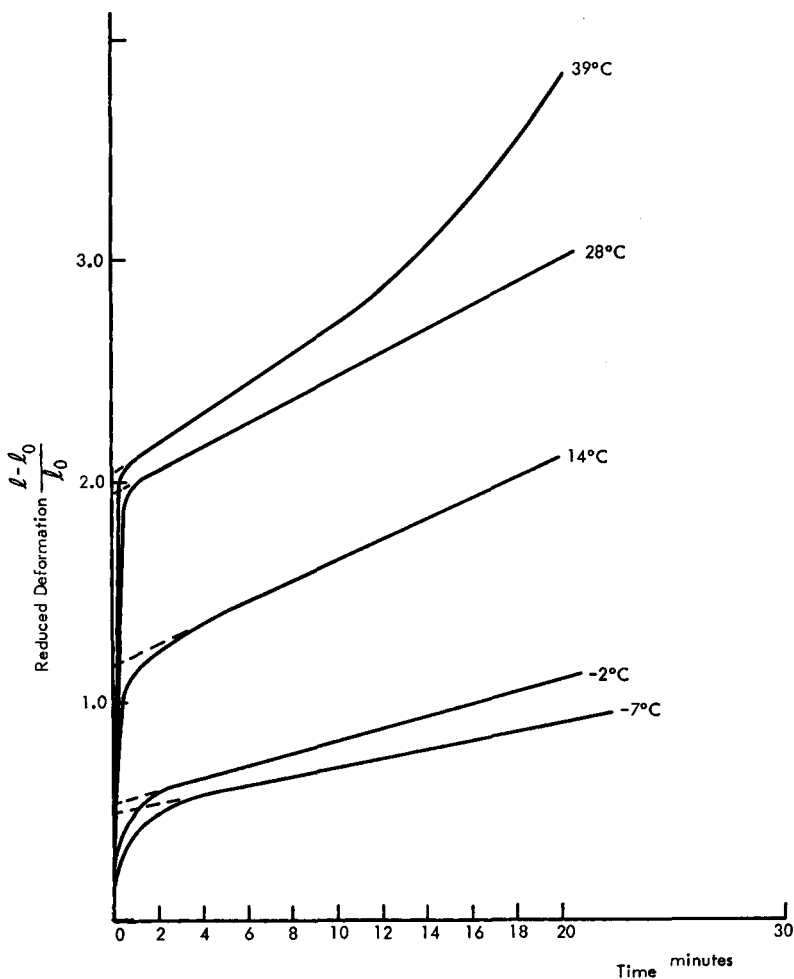


Fig. 8. Creep curves for FRN-500 copolymer.

single smooth curve was drawn through the points for the FRN-500 copolymer.) It is quite apparent that a mechanical transition starts at approximately 20–25°C and appears to end at about 0–5°C. The copolymers at low temperatures are stiffer than one would expect from the high-temperature behavior. The response is similar to that of a partially crystalline polymer when it is cooled through its crystalline melting point.

The rate of change of the apparent compliance with time,  $dJ/dt$ , is a measure of the fluidity of the copolymers. If one defines a strain rate as  $d\gamma/dt = (1/\ell) (d\ell/dt)$ , then  $dJ/dt = (1/\sigma) (d\gamma/dt) = 1/\eta$ , where  $1/\eta$  is the apparent fluidity. The linear portion of the curves of Figure 9 thus represents a steady flow region. For FRN-500 copolymer, the  $(1/\eta)$  are  $1.9 \times 10^{-4}$ ,  $2.5 \times 10^{-4}$ ,  $2.2 \times 10^{-4}$ ,  $1.4 \times 10^{-4}$ , and  $1.8 \times 10^{-4}$  psi<sup>-1</sup>/min for -7°C, -2°C, 14°C, 28°C, and 39°C, respectively. These correspond to

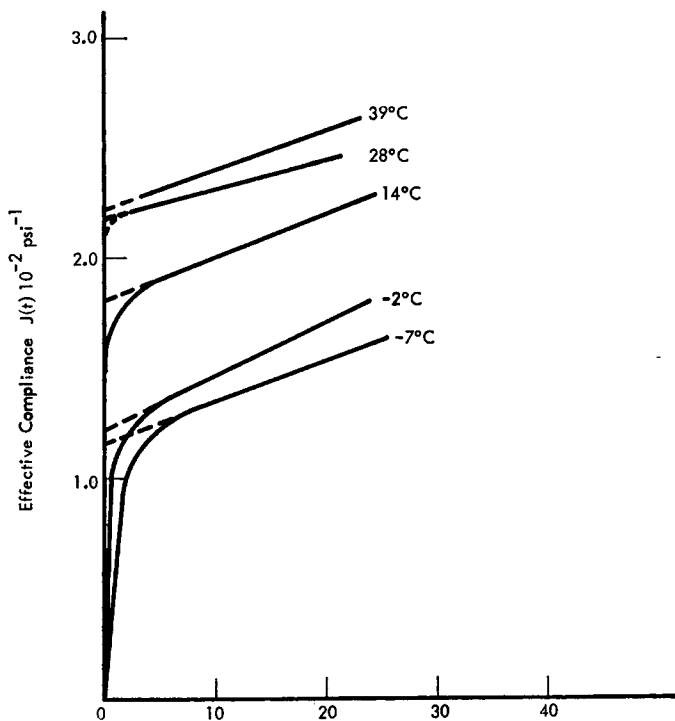


Fig. 9. Compliance curves for FRN-500 copolymer.

$4.6 \times 10^{-11}$ ,  $6.1 \times 10^{-11}$ ,  $5.3 \times 10^{-11}$ ,  $3.4 \times 10^{-11}$ , and  $4.4 \times 10^{-11}$  in units of  $\text{poise}^{-1}$ . The values are probably accurate to  $\pm 10\%$ , so that the fluidity appears to pass through an anomalous zone in the same temperature region.

### CONCLUSIONS

Three independent experiments suggest that there exists a complex transition zone in the amorphous state of butadiene-acrylonitrile copolymers. The transition zone appears to start roughly  $15^\circ$  to  $40^\circ\text{C}$  (depending on the measuring technique) above the main glass transition temperature of the copolymers. The temperature range is roughly  $-20^\circ$  to  $+20^\circ\text{C}$ , being only slightly different for the three copolymers.

In speculating on the nature of the transition, the authors have considered the following factors: Firstly, many polymers apparently have transitions above the main glass transition temperature. In general, the temperature interval between these transitions and the relative magnitude of the two will depend on the size of the atomic units attached to the carbon chain and the absolute  $T_g$ . Secondly, the observed transition in the copolymers appears to be slightly endothermic, leads to a softening or "loosening" of the polymeric structure, and appears to occur over a broad range of temperature.

Thirdly, the observed behavior of the copolymers is similar to the behavior of amorphous polyacrylonitrile at 50°C above its main glass temperature. Fourthly, it is known that poly-*cis*-1,4-butadiene melts at about 5°C and that when the 1,4 *cis*-structure is diluted (as it is in high poly-*trans*-1,4-butadiene) a response similar to that observed in the copolymers may also be observed.

These factors lead us to speculate that when the copolymers are heated above the main glass transition temperature, a mesomorphic state is formed which has a certain amount of molecular order. This structural order

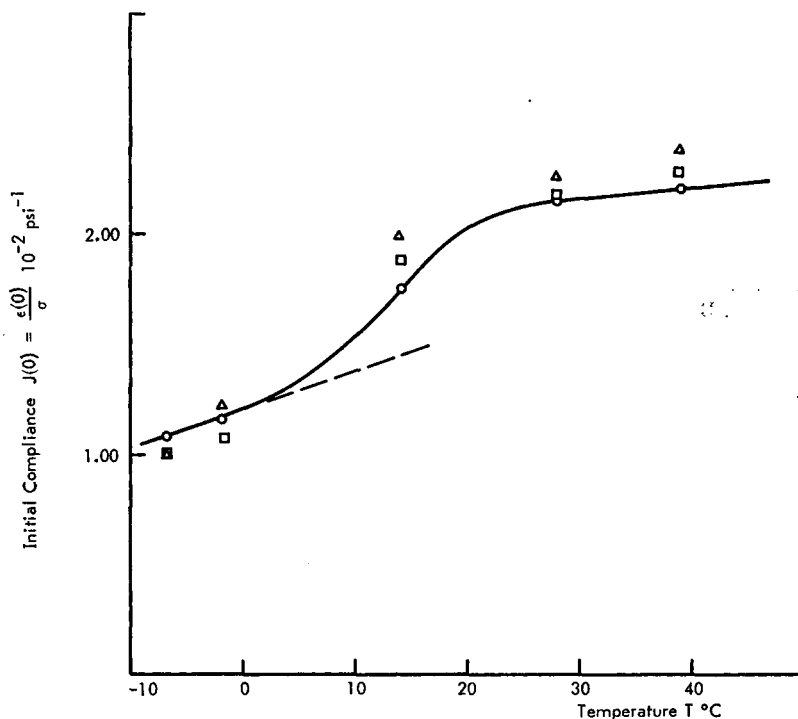


Fig. 10. Initial compliance as a function of temperature for the butadiene-acrylonitrile copolymers: (Δ) FRN-502; (□) FRN-501; (○) FRN-500.

might be induced by a partial association between adjacent nitrile groups along the carbon chains. A clustering, or short-range ordering, of the polybutadiene portions of the main chain might result in a nonuniform distribution of interchain distances in this state and a tendency for a low grade of crystallinity. Continued heating to 50° to 75°C above the main glass transition temperature could then cause a "melting" of these "crystalline" regions, leaving the polymer in a truly amorphous state. Although the interpretation is speculative, it can account for all the observations and is also consistent with prior interpretations of amorphous state transitions.

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