# Multiple Glass Transitions in
# Butadiene-Acrylonitrile Copolymers*

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## Synopsis

The second order transition temperatures (Tg) have been determined for a range of compositions of polybutadiene-acrylonitrile copolymers. It was found that copolymers having more than 36 percent acrylonitrile had a single Tg while copolymers with less than 36 percent acrylonitrile had two main Tg's. The analyses were carried out with differential thermal analysis (DTA). The two Tg's are interpreted as the result of incompatible phases which differ in BD and VCN ratio. The presence of two phases is discussed in terms of polymerization conditions and molecular structure.

## INTRODUCTION

Extensive studies on the effect of composition on the glass transition temperature have been made on few copolymers systems. Most of the studies deal with homogeneous systems that exhibit a single glass transition. Theoretical work has been directed to explaining these simple systems. An excellent review of the relation of transition temperatures to chemical structure has been made by Boyer.[1] Multiple transitions have been observed and discussed for a number of polymer systems and were the subject of a recent symposium.[2] Conforming to the nomenclature proposed by Boyer,[2] the multiple transitions referred to in this study deal with the main glass transition temperature, $T_g$.

Multiple main glass transitions of polymers have been reported previously by Angelo, Ikeda and Wallach,[3] who have described Tg relations in block copolymers and mixtures of incompatible homopolymers. Krause and Roman[4] have reported that mixtures of compatible homopolymers on the other hand, exhibit a single transition. The homogeneous polymer mixtures with a single transition form solid solutions. We have found, by differential thermal analysis, (DTA), that batch polymerized butadiene-acrylonitrile copolymers of various compositions exhibit multiple main glass transition temperatures. The purpose of this communication is to describe the compositional dependence of the multiple transitions in this system.

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To the best of our knowledge, multiple main glass transitions occurring within a single copolymer system have not been previously reported. This probably is related to the fact that generally low conversions are used in carrying out basic studies, and often the type of apparatus used to measure Tg precludes the detection of more than one transition.

## EXPERIMENTAL

The copolymers were prepared by emulsion polymerization at 5°C. Monomers were batch charged into the polymerization reactor. Antioxidant was added to the latexes prior to their coagulation with calcium chloride. As far as is known, no special polymerization technique is required for the formation of copolymers showing multiple glass transition temperatures. The samples were analyzed as uncured rubbers.

The percent acrylonitrile (VCN) of the charged monomers, the percent conversion, and the bound VCN content (calculated from Kjeldahl analyses for Nitrogen) are given in Table I. The Tg values for the copolymers are also tabulated in Table I. In some cases the transition temperatures re-

TABLE I
Polymerization, Percent Composition and Glass Transition
Temperature Data for Butadiene-Acrylonitrile Compolymers

| Sample | % VCN | % Conversion | % VCN | Number samples | First Heat | | Reheat | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Tg | Tg | Tg | Tg |
| 1 | 75.0 | 85* | 63 | 1 | — | −7 | — | −4 |
| 2 | 58.0 | 86 | 51 | 2 | — | −14 | — | −12 |
| 3 | 46.5 | 91 | 41.0 | 1 | — | −20 | — | −19 |
| 4 | 44.8 | 78 | 40.8 | 1 | — | −21 | — | −21 |
| 5 | 43.0 | 91 | 41.6 | 3 | — | −21 | — | −20 |
| 6 | 35.0 | 79 | 35.0 | 1 | −32 | −24 | −31 | −23 |
| 7 | 34.0 | 90 | 34.1 | 3 | −32 | −27 | −31 | −24 |
| 8 | 32.3 | 91 | 34.0 | 3 | −38 | −25 | −38 | −24 |
| 9 | 30.4 | 79 | 32.5 | 2 | −40 | −27 | −40 | −26 |
| 10 | 27.2 | 88 | 29.6 | 4 | −52 | −28 | −53 | −27 |
| 11 | 25.8 | 78 | 29.3 | 1 | −54 | −30 | −52 | −29 |
| 12 | 18.0 | 84 | 20.0 | 1 | −69 | −35 | −69 | −33 |
| 13 | 10.0 | 81 | 11.1 | 1 | −77 | — | −77 | — |
| 14 | 0.0 | — | — | 1 | −85 | — | −85 | — |

\* Estimated.

ported are averaged values for polymers from several polymerization experiments. The average values fell within 3°C range except the lower transition temperatures of sample 8 which varied 4°C. The transition temperatures were taken as the inflection point of the DTA thermograms. This point is easily measured and reproducible. Typical thermograms are shown in Figure 1.
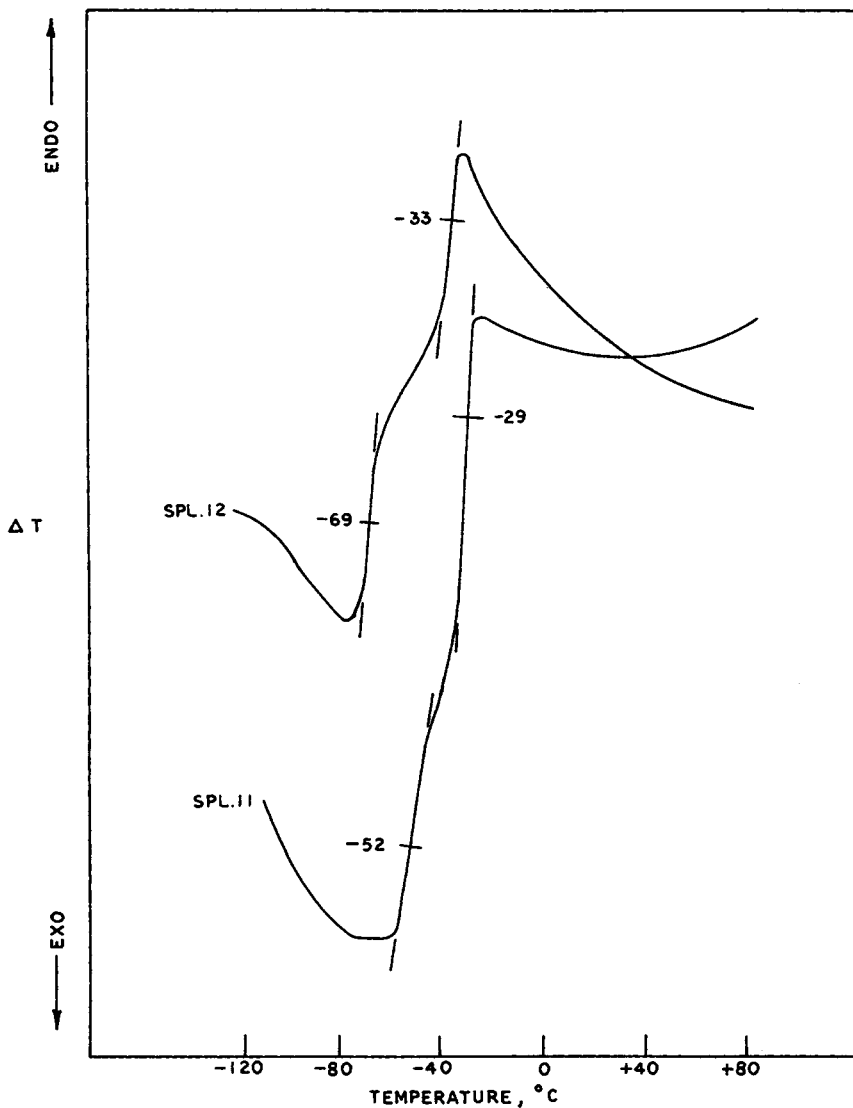
Fig. 1. DTA thermograms for samples 11 and 12.

Details of the DTA apparatus used in this study have been described elsewhere.[5]  The samples were analyzed by cooling from room temperature with liquid nitrogen to $-150°C$ at rates of 10 to $20°C/min$ and programed heating at $1°C/min$ to $+130°$.  The samples were then recooled and reheated at the same respective rates.  The transition temperatures tabulated first in Table I were obtained during the first heating and the second set on the second heating.  It was found that the data on reheating were more reproducible for the same charges ($\pm1°C$).  The differences in

transition temperatures between the first and second heatings are, for the most part, due to changes in the higher transition temperature. These changes are probably associated with losses of small amounts of volatile material (monomer, water) which produce on the thermograms very low and diffuse endotherms between about $+35°C$ and $+100°C$. The Tg of the reheated samples is considered the more accurate result. Generally, we have found that the practice of reheating improves the reproducibility and accuracy of thermal transition measurement with DTA. In addition to the removal of trace volatiles, as mentioned above, the procedure imparts a known and controlled heat history fundamental to the study of thermal events. Also, since the sample remains undisturbed from the first to the second analysis, the effects of sample movement due to softening, strain relief etc. are minimized. Although this paper deals with glass transitions, these comments on reheating apply to an even greater degree in the study of crystallization and melting phenomena.

## RESULTS AND DISCUSSION

The transition temperatures determined on the second heating are plotted in Figure 2 versus the bound acrylonitrile content. The plot shows that the higher of the two transition values below 36 percent VCN and the transition values above 36 percent form a continuous, almost linear, relation which best approximates the relations derived from theory.[6-9] The lower of the two transition temperatures below 36 percent VCN shows a nonlinear relation with percent VCN down to $-85°C$, the transition of the polybutadiene homopolymer.

Several workers have reported low temperature transitions for butadiene-acrylonitrile copolymers; however, none has reported multiple glass transition temperatures. Borders and Juve[10] reported brittle points (which are closely related to glass transition temperatures) which were plotted as a straight line relation by Salomon.[11] However, the data originally tabulated by Borders and Juve when replotted (Fig. 3) indicate a discontinuity in the vicinity of 30 percent VCN. Wiley and Brauer[12] also tabulated brittle points which when plotted (Fig. 4) indicate a discontinuity around 36 percent VCN, although the original plot was shown as a straight line. However, their transition data from index of refraction measurements did

TABLE II
Brittle Points, Gehman Freeze Points and DTA for Cured Samples

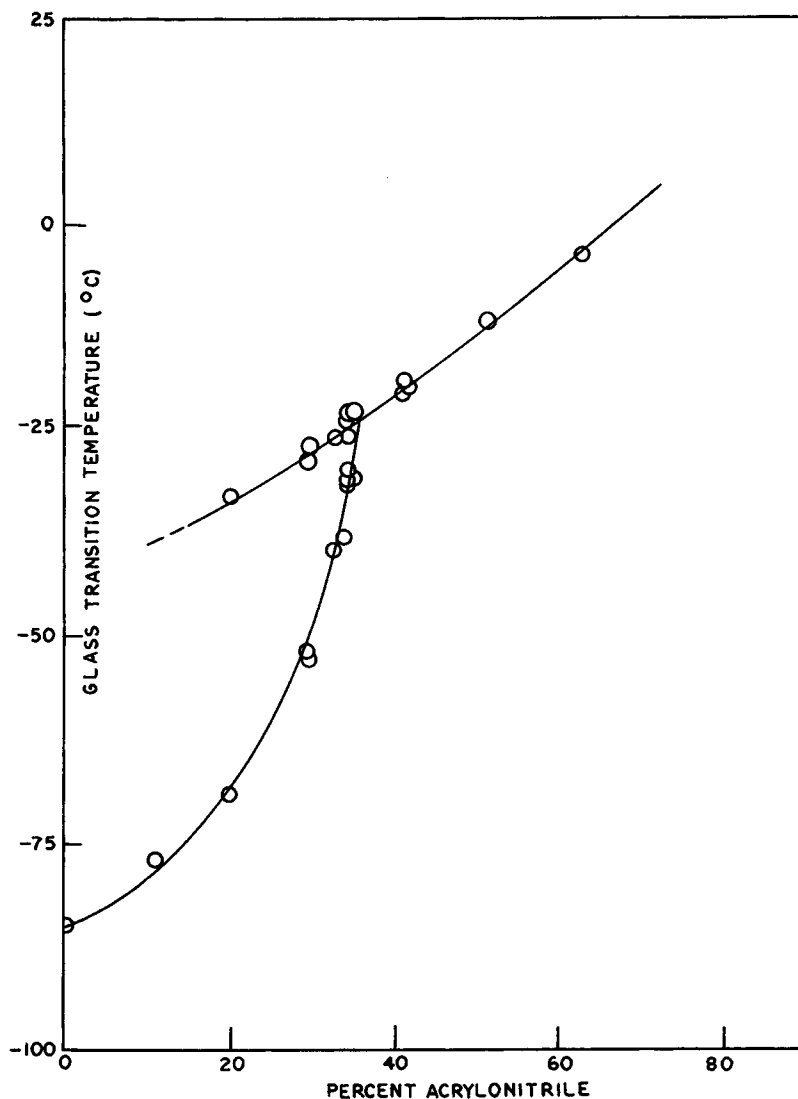| Sample number | % VCN | Brittle point °C | Gehman freeze °C | DTA °C | |
|---|---|---|---|---|---|
| 2 | 51 | −13 | −11 | — | −7 |
| 5 | 41.6 | −23 | −16 | — | −15 |
| 8 | 34.0 | −38 | −26 | −30 | −22 |
| 10 | 29.6 | −44 | −27 | −42 | −23 |
| 12 | 20.0 | −64 | −44 | −63 | −32 |

Fig. 2. Glass transition temperature versus acrylonitrile content for uncured rubbers as determined by DTA.

not indicate a discontinuity. Robbins, et al.,[13] report several values for the glass transition as determined dilatometrically which agree partially with the brittle point data of Wiley and Brauer; however, there are too few points to evaluate these data independently.

The nature of the brittle point[14] test precludes the determination of more than one transition since the specimen is destroyed at the brittle point. We have obtained brittle point data for a few samples and have found that the brittle point is, in fact, related to the lower transition temperature
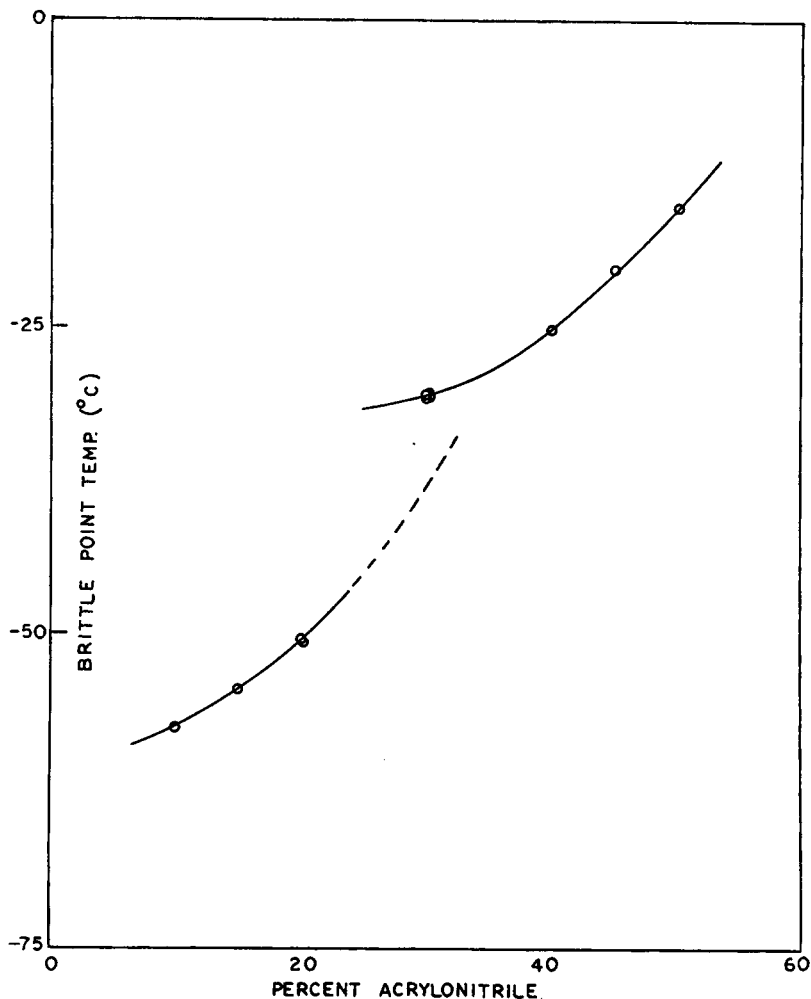
Fig. 3. Brittle point temperature versus acrylonitrile content after Borders and Juve.
Data on filled cured rubbers.

(Table II) for samples below 36 percent VCN.   The Gehman freeze point,[15] on the other hand, appears related to the higher transition temperature (Table II) for the same polymers.   These tests were run on cured polymers. The presence of two glass transition temperatures at acrylonitrile contents lower than 36 percent provides an explanation to the discrepancy long observed between Gehman freeze point and brittle point in these types of materials.   Dilatometric data are often taken at temperature increments and may not detect a second transition depending on the temperature interval.   Robbins, et al., however, used a continuously recording apparatus which might be expected to detect both transition temperatures.   Only two materials having less than 36 percent VCN, were run by them and for
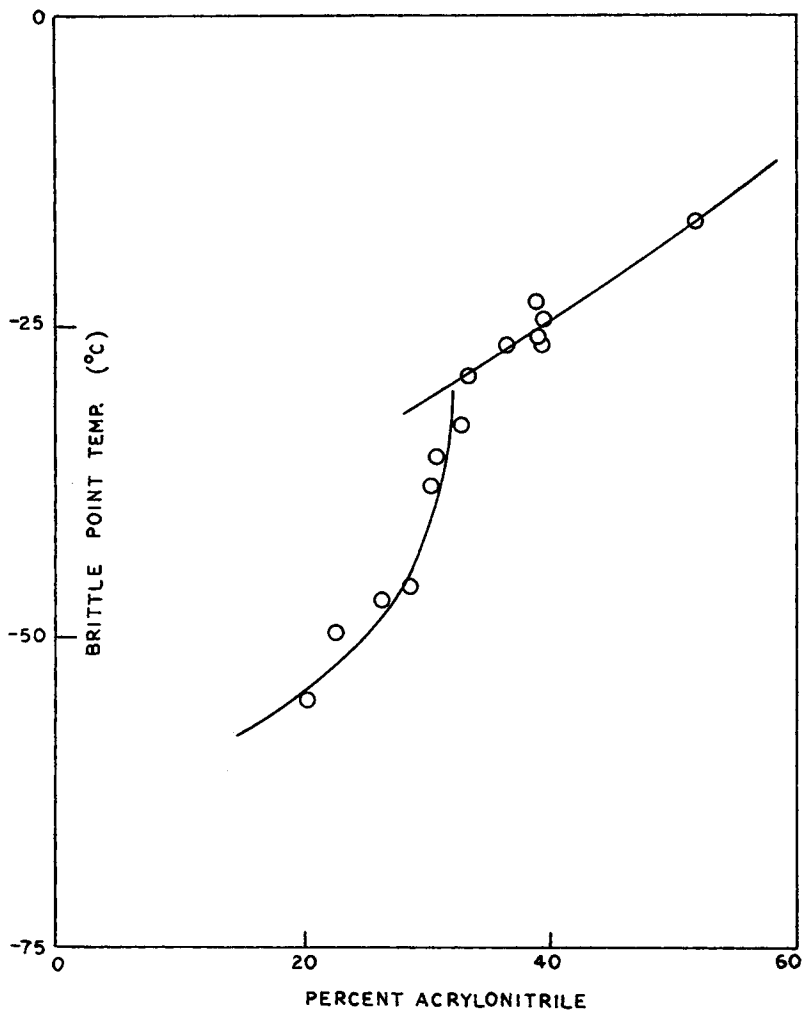
Fig. 4. Brittle point temperature versus acrylonitrile content after Wiley and Brauer. Data on unfilled cured rubbers.

one of these, 30 percent VCN, it would have been particularly difficult to detect two glass transitions since the transitions overlap. We were not able to detect two glass transitions for the 18 percent VCN polymers. It is possible a second transition was overlooked or that the polymer was prepared by a method which results in a single transition. Examination of the plots of the data of Borders and Juve and of Wiley and Brauer suggest quite strongly that the materials used by these researchers were copolymers which would, by DTA, exhibit more than one transition for compositions below 36 percent VCN. Their results are in good agreement with the results reported in this paper, as is shown in Figure 2.

The presence of two main glass transitions can be explained by (a) block or graft copolymer formation, (b) polymer mixtures of incompatible species, and (c) physical separation of different species formed in the latex and subsequently not subjected to conditions which favor solubilization. The last of these possibilities is readily tested by dissolving the polymer and casting a film from solution. Sample 12 formed a clear solution in methyl ethyl ketone with no visible gel. A film cast from this solution when examined with the DTA showed transition temperatures at $-51°$, $-28°$, and $-54°$, $-26°$ for first and second heatings, respectively. These results discount the possibility of a simple physical separation in the latex as the cause for the presence of the two transitions.

In considering the reactivity ratios of the two monomers ($r_1$ ($M_1$ = BD) = 0.28, $r_2(M_2 = VCN) = 0.02$), it is expected that in a batch type polymerization[16] that latex particles formed first would be acrylonitrile-rich and those formed in the later stages would be acrylonitrile-poor. What is surprising, however, is that the two species are incompatible. Recent work on block copolymers,[17] however, has shown that a homogeneous polymer can behave as a two-phase system. In the case of the butadiene-acrylonitrile copolymers there may be more than simple composition differences to be taken into account. The transition temperatures which fall along the nearly linear curve extending both above and below 36 percent acrylonitrile are the expected or normal transition of the copolymers. It can be seen on examining Figure 2 that some samples have low glass transition temperatures that are at the same temperature as the high glass transition temperatures in other samples. For example, the higher of the two glass transition temperatures of sample 12 is at $-33°C$ while the lower of the two glass transition temperatures for sample 7 is at $-31°C$. This reflects the fact that average values of acrylonitrile are plotted in Figure 2 and do not represent the composition of the components having different glass transitions. This suggests the incompatibility of the polymer phases is not simply compositional, but originates from molecular structure differences. More work will be necessary for a complete understanding of this system, especially work directed towards defining structural differences.

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