

## Viscoelastic Properties of Styrene-Acenaphthylene Copolymers in the Transition Region

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### Synopsis

A series of styrene-acenaphthylene copolymers was prepared by thermal polymerization. Homogeneous samples were obtained except for those compositions where the initial concentration of styrene monomer was 40-60 mole-%. Master curves and characteristic viscoelastic parameters were obtained for the homogeneous copolymers. The plot of  $T_g$  vs. copolymer composition yielded a linear relationship.

### INTRODUCTION

Although the preparation of homopolymers and copolymers of acenaphthylene has been reported by a number of authors,<sup>1-3</sup> relatively little work has been done on their characterization. Dunham et al.<sup>4</sup> made a study of the craze properties of acenaphthylene copolymerized with styrene-butadiene in which some of the mechanical properties of the styrene-acenaphthylene system were reported. Recently the solution properties of polyacenaphthylene have also been investigated.<sup>5</sup>

In this study the viscoelastic properties of styrene-acenaphthylene copolymers were observed in the transition region, and their characteristic parameters were obtained from modulus-temperature and relaxation master curves. These results were complemented by differential thermal analysis data.

### EXPERIMENTAL

#### Sample Preparation

Mixtures of styrene (Borden Chemical Company) and acenaphthylene (Aldrich Chemical Company) were degassed by repeated heating and freezing under high vacuum. Thermal polymerizations were carried out at 120°C. in sealed ampules for approximately 72 hr. The contents of the ampules were then dissolved in chloroform and the polymer was recovered from methanol. The styrene-acenaphthylene copolymers were then redissolved in chloroform and reprecipitated by adding the above solution dropwise to an excess of methanol. The yellow powder so obtained was dried in an air oven at 80°C. for 12 hr. and then in a vacuum oven at 110°C. for an additional 24 hr.

Differential thermal analysis measurements were made at a heating rate of  $10^{\circ}\text{C./min.}$  through the courtesy of Mr. R. W. Schwenker of the Textile Research Institute.  $T_g$  values of copolymers containing high acenaphthylene contents are not well defined in their thermograms, hence they are not included in our data below.

Polymer samples for torsional and penetrometric measurements were pressed (40,000 psi) at temperatures  $30^{\circ}\text{C.}$  above their glass transition temperatures for approximately 5 min. Although most of the samples pressed clear, those initially containing 40 and 60 mole-% styrene monomer concentrations were translucent, indicating inhomogeneity. Since the reactivity ratios for styrene-acenaphthylene copolymerization are quite different,<sup>6</sup> it is likely that large blocks of both monomer units are present, giving rise to the translucency observed. Since these polymers did not have well defined compositions, their physical properties were not investigated in this study.

### Ultraviolet Analysis

Figure 1 shows the ultraviolet spectra of polystyrene and polyacenaphthylene, measured in chloroform solution with a Perkin-Elmer 202 spectrophotometer. Polyacenaphthylene exhibits an absorbance peak at  $297\text{ m}\mu$  where polystyrene does not absorb appreciably. Copolymer compositions were measured at this wavelength with the use of a Beckman DU spectrophotometer. The extinction coefficient of polyacenaphthylene in chloroform solution at  $297\text{ m}\mu$  is 61.3 and that of polystyrene is 0.92.

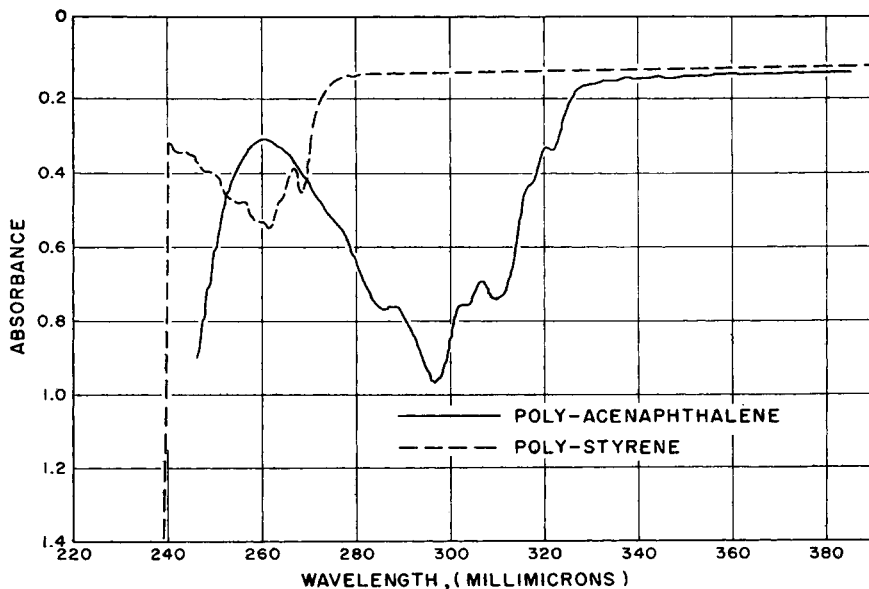


Fig. 1. Ultraviolet spectra of polystyrene and polyacenaphthylene.

### Intrinsic Viscosity Measurements

Samples were dissolved in benzene and solution viscosities were measured in a Cannon-Ubbelohde dilution viscometer at 25°C. The solvent efflux time was 207 seconds. The viscosity-average molecular weight ( $\bar{M}_v$ ) was calculated from the Mark-Houwink equation

$$[\eta] = K\bar{M}_v^a$$

where  $[\eta]$  is the intrinsic viscosity. The parameters  $K$  and  $a$  were taken from Moacanin et al.<sup>5</sup>

### Modulus-Temperature Curves

The 10-sec. modulus-temperature curves were constructed for the copolymer samples by using a modified Gehman torsion stiffness tester.<sup>7</sup> The heating rate was 1°C./min. In the lower temperature region (<150°C.) samples were measured in a Dow-Corning silicone oil bath, whereas at higher temperatures the measurements were made in an electric furnace under an atmosphere of dry nitrogen.

### Master Curves by the Ball Indentation Method

Since polymers containing high contents of acenaphthylene are quite brittle, the penetrometer<sup>8</sup> technique for obtaining relaxation master curves was employed in this study. Temperature control accurate to  $\pm 0.2^\circ\text{C}$ . was obtained with the use of an Aminco bimetallic thermo regulator with a supersensitive relay. At temperatures above 150°C. the penetrometer experiments were done in a specially constructed double walled chamber made from Maronite and insulated with glass wool. Below 150°C. a Tenney environmental testing chamber was used. High temperature measurements were again carried out in an atmosphere of dry nitrogen in order to minimize oxidation.

Time-dependent Young's moduli  $E(t)$  were calculated from the penetrometric measurements by use of the following relations:<sup>9,10</sup>

$$E(t) = 5.48 \times 10^4 L/d(t)^{3/2} D^{1/2} \quad (1)$$

where  $L$  is the applied load in pounds,  $D$  is the diameter of the penetrating sphere in inches, and  $d$  is the indentation in inches.  $E(t)$  was converted into units of dynes/cm.<sup>2</sup>. Master curves were then constructed from the modulus-time isotherms by shifting them along the time axis to yield a smooth curve.

## RESULTS AND DISCUSSION

The characteristic viscoelastic parameters of the styrene-acenaphthylene copolymers studied are listed in Table I. The inflection temperature ( $T_i$ ) as determined from 10-sec. modulus-temperature curves is defined as the temperature at which  $3G = 10^9$  dynes/cm.<sup>2</sup>, where  $G$  is

TABLE I  
Characteristic Viscoelastic Parameters of Styrene-Acenaphthylene Copolymers

AN in monomer, mole-%	AN in polymer, mole-%	$n$	$s$	$T_i$ , °C.	$T_g$ , °C.
0	0	0.72	0.22	104	100
5	9	0.63	0.22	120	117
10	12	0.75	0.22	122	119
20	16	0.65	0.14	134	127
80	89	0.66	0.08	252	
90	93	0.72	0.08	254	
100	100	0.77	0.09	264	

the torsional modulus and  $3G$  is approximately equal to Young's modulus;  $s$  is the slope of the tangent to the modulus-temperature curve at  $T_i$ .

Figure 2 shows a plot of  $T_i$  and  $T_g$  versus mole fraction of acenaphthylene in the copolymers. A linear relationship is in each case in agreement with the previously reported work of Dunham et al.<sup>4</sup> The  $T_g$  values obtained by these authors were considerably lower than those found in this study, e.g. 214°C., compared to 264°C. for polyacenaphthylene. We

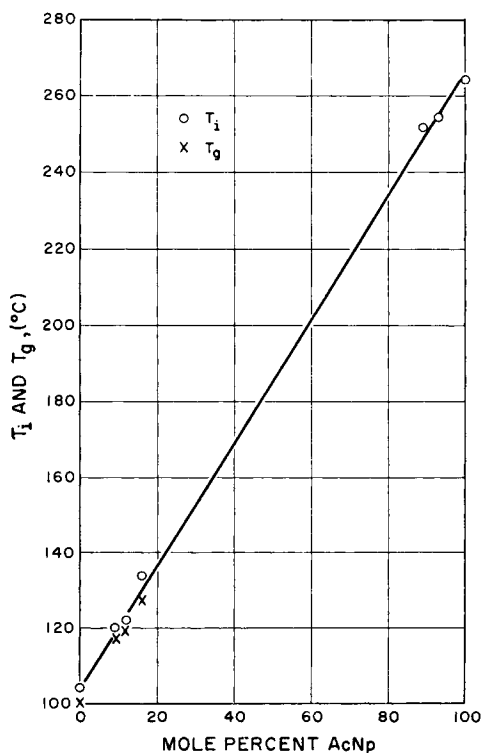


Fig. 2.  $T_i$  and  $T_g$  vs. composition for styrene-acenaphthylene copolymers.

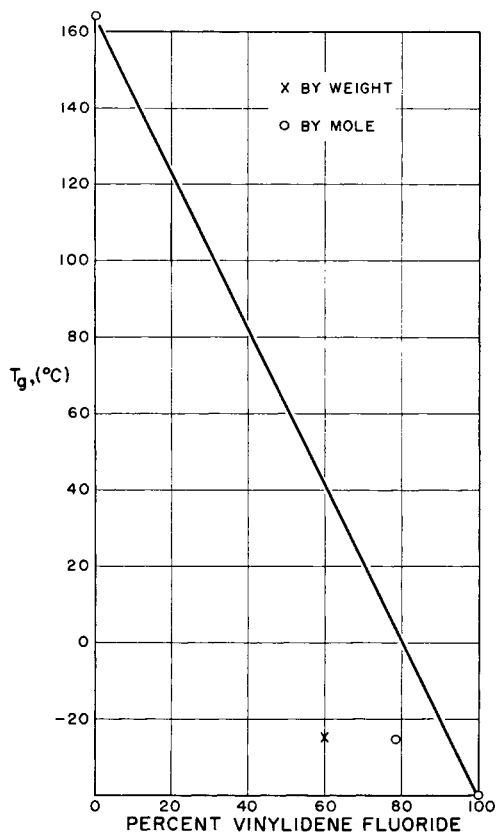


Fig. 3.  $T_g$  vs. composition of vinylidene fluoride in copolymers of perfluoropropylene and vinylidene fluoride.

have taken precautions in our sample preparation to obtain "dry" polymers. It is possible that the discrepancy is due to the fact that the samples studied in the previous work may have contained small amounts of residual monomer or solvent which acted as a plasticizer and lowered  $T_g$ .<sup>11</sup>

The linearity in the  $T_g$ -copolymer composition curves that we obtain for the styrene-acenaphthylene system (on a mole fraction basis) is not always observed in similar plots for other comonomer pairs. For instance, the experimental value of the glass transition temperature of polyperfluoropropylene is reported as 165°C.;<sup>12</sup> that of polyvinylidene fluoride is -39°C.<sup>13</sup> However, the  $T_g$  of Viton A (duPont) which is a copolymer of perfluoropropylene (40 wt.-%) and vinylidene fluoride (60 wt.-%) is -25°C.<sup>12</sup> Obviously, the deviation from linearity in this case is very considerable, as shown in Figure 3. A possible explanation is that the introduction of a few "flexible hinges" in a polymer chain which shows great resistance to internal rotation might produce a disproportionately large lowering of the  $T_g$  of the stiff copolymer chain. A similar explana-

tion may also obtain for the alternating copolymers of tetrafluoroethylene-trifluoronitrosomethane ( $T_g = -51^\circ\text{C}.$ ), and tetrafluoroethylene-1-nitro-2-nitrosotetrafluoroethane ( $T_g = -42^\circ\text{C}.$ ),<sup>14</sup> although the  $T_g$  of polytetrafluoroethylene homopolymer is reported to be  $100^\circ\text{C}.$ <sup>15</sup> Obviously the "flexible hinge" interpretation does not apply in our styrene-acenaphthylene system. Here the styrene units are perhaps not flexible enough to yield a nonlinear relationship in its  $T_g$ -copolymer composition curve.

Previously it was argued that the  $T_g$  of perfluorinated polymers were high because of the high barrier to internal rotation, and despite low cohesive energy density. A  $T_g$  value of  $11^\circ\text{C}.$  was obtained<sup>15</sup> for polyperfluoropropylene on the basis of the data in Figure 3 and the  $T_g$ -copolymer equation of Fox.<sup>16</sup> It is our present belief that the  $T_g$  value of perfluoropropylene reported by duPont<sup>12</sup> is correct, and the argument presented in the previous paper<sup>15</sup> concerning high  $T_g$  values for perfluorinated polymers is now further confirmed and made more exact. It would appear however that no simple universal formula for  $T_g$  versus copolymer composition is available at the present time.

To observe the extent of degradation that occurred during molding and measuring, the molecular weight of polyacenaphthylene was determined immediately after purification and again after all measurements were completed. Data in Table II show that some degradation did indeed take place, as evidenced by the decrease in molecular weight. Fox and Flory<sup>17</sup> have shown that glass transition temperatures of high molecular weight polymers are not sensitive to slight changes in molecular weight. It is also recognized that the transition region of viscoelastic behavior is independent of molecular weight.<sup>18</sup> This was rechecked in this study by repeating the modulus-temperature curve measurements on the same sample. The agreement was within experimental error. The DTA thermograms also show that extensive decomposition did not occur until the temperature is much higher than  $300^\circ\text{C}.$  Hence the viscoelastic parameters presented in Table I can be accepted with reasonable confidence.

In order to check the dependability of the ball indentation method in constructing master curves, a few parallel experiments were made with the use of a stress-relaxation balance which has been previously described.<sup>18</sup>

TABLE II  
Physical Properties of Polyacenaphthylene

$[\eta]$ (before pressing) in benzene	0.203
$[\eta]$ (after run) in benzene	0.117
$a$ in benzene at $25^\circ\text{C}.$	0.68
$K \times 10^4$ in benzene at $25^\circ\text{C}.$ <sup>a</sup>	0.53
$\bar{M}_v$ (before pressing)	$1.86 \times 10^5$
$\bar{M}_v$ (after run)	$1.15 \times 10^5$
Extinction coefficient in chloroform at $297 \text{ m}\mu$	61.3

<sup>a</sup> Data of Moacanin et al.<sup>5</sup>

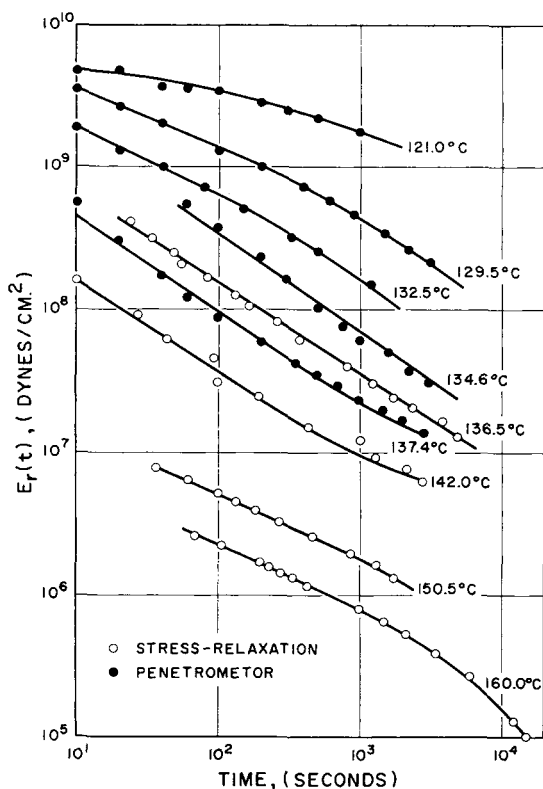


Fig. 4. Comparison of stress-relaxation and penetrometer data for the copolymer containing 16 mole-% polyacenaphthylene.

The comparison of stress-relaxation and penetrometer data for the copolymer containing 16 mole-% polyacenaphthylene (Fig. 4) indicates that excellent agreement was obtained.

Inspection of the data in Table I reveals that  $s$  (the slope of the modulus-temperature curve at  $T_i$ ) decreases with increasing acenaphthylene content. However,  $n$  (the slope of the master curve in the transition region) is relatively constant.

Master curves were constructed by using the time-temperature superposition principle according to which the effect of temperature on the viscoelastic properties of a polymer is to multiply the time scale of the experiment by a constant factor. This factor is expressed in terms of a characteristic relaxation time,  $K(T)$ , which is defined<sup>18</sup> as the time required for the polymer to relax to a value of  $\log E = 10^9$  dynes/cm.<sup>2</sup> at any temperature  $T$ .  $K(T)$  is evaluated by measuring the magnitudes of the shift along the time axis of the modulus-time plots in constructing a smooth curve by superposition.

An expression relating the characteristic relaxation time at temperature  $T$  to that at a reference temperature  $T_a$  has been derived by Williams,

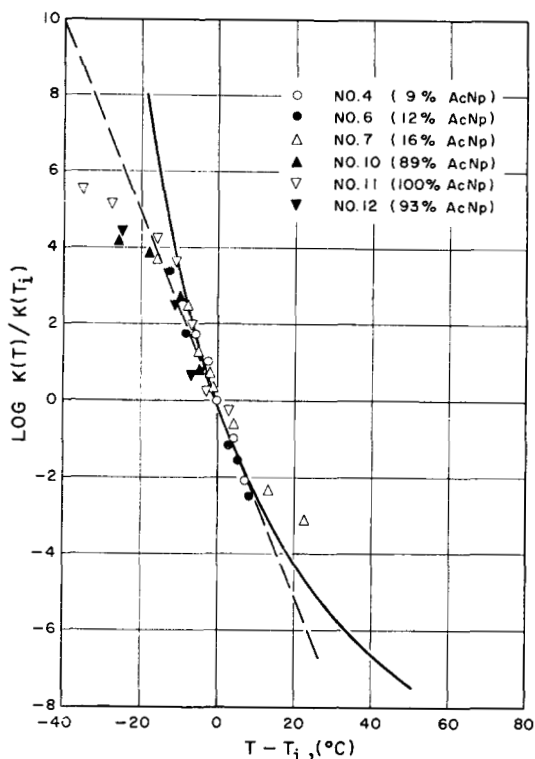


Fig. 5. Plot of  $\log K(T)/K(T_i)$  vs.  $T - T_i$  for the homogeneous copolymers investigated.

Landel, and Ferry.<sup>19</sup> As modified by Tobolsky and Catsiff<sup>20</sup> it assumes the following form:

$$\log \frac{K(T)}{K(T_d)} = \frac{-16.1 (T - T_d)}{56 + T - T_d} \quad (2)$$

where  $T_d$  is the characteristic temperature which we have chosen to be  $T_i$  in this study. Figure 5 shows a plot of  $\log K(T)/K(T_i)$  versus  $T - T_i$ . The experimental points for all the copolymers studied agree within experimental error in the transition region. At temperatures 20°C. below  $T_i$ , the points deviate appreciably from the calculated line. The reason for this deviation has already been discussed in a previous publication.<sup>8</sup>

At temperatures close to  $T_i$  eq. (2) may be rewritten:

$$\log [K(T)/K(T_i)] = -p(T - T_i) \quad (3)$$

In previous publications from this laboratory,<sup>8,21</sup> it was shown that  $p = 0.240$  for a variety of polymers. The best straight line through the points in Figure 5 has a slope of 0.240 in agreement with the former results.

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### Résumé

On a préparé une série de copolymères de styrène-acénaphthylène par polymérisation thermique. On a obtenu des échantillons homogènes sauf dans les copolymères où la concentration initiale en styrène était de 40 à 60 moles pour cent. On a obtenu des courbes principales et des paramètres viscoélastiques caractéristiques pour les copolymères homogènes. Le graphique  $T_g$ /composition du copolymère obéit à une relation linéaire.

### Zusammenfassung

Eine Reihe von Styrol-Acenaphthylencopolymeren wurde durch thermische Polymerisation dargestellt. Mit Ausnahme des Bereiches mit Ausgangskonzentrationen an Monostyrol zwischen 40-60 Molprozent wurden homogene Proben erhalten. Für die homogenen Copolymeren wurden Masterkurven aufgestellt und die charakteristischen viskoelastischen Parameter erhalten. Im Diagramm  $T_g$  gegen Copolymerzusammensetzung ergab sich eine lineare Abhängigkeit.

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