Stress-Strain Isotrimers for Stereoregular and Stereoblock Cis-Trans Polybutadienes

M. A. SHARAF and J. E. MARK
Department of Chemistry and the Polymer Research Center
University of Cincinnati
Cincinnati, Ohio 45221

B. GUNESIN
Central Research Laboratories
Firestone Tire and Rubber Company,
Akron, Ohio 44317

and

M. JULEMONT and P. TEYSSÉE
Laboratoire de Chimie Macro moléculaire et de Catalogue Organique
Université de Liège
Liège 4000, Belgium

Introduction

Polybutadiene (PBD) can be prepared so as to have 1,4 repeat units [CH=CH-CH=CH-] that are either cis or trans, or 1,2 vinyl units [CH2=CH-CH2=CH-] of meso or racemic stereochemistry (1). Samples of PBD prepared using most catalysts or initiators have a random mix- 90-10 of cis and trans vinyl monomer units. They are highly elastomeric, but the irregularity of their structures is expected to greatly diminish their capacity for strain-induced crystallization (3-4), which is known to occur in high-cis (4-8) and high-trans PBD (8).

The elastomers of interest in the present investigation were prepared from samples of PBD which have neither high-cis nor high-trans contents. One

* Research Laboratories, Mobil Chemical Company, Elizabeth, N. J., U.S.A.

** National Bureau of Standards, Washington, D.C.

*** U.S. Patent 3,017,926.

**** B. Gunesin, J. E. Mark, and M. Julemont, unpublished data.

Polymer Engineering and Science, January, 1966, Vol. 6, No. 2

Stress-Strain Isotrimers for Stereoregular and Stereoblock Cis-Trans Polybutadienes

The elongation isotrimers were obtained on unswollen strips (~1.5 by 5.0 by 40) mm cut from the extracted network sheets, with most of the data being obtained at 5°C. In the case of the stereoblock networks, the measurements were generally carried out at several temperatures, including the minimum temperature which would make the networks elastomeric. Some of the specific temperatures employed are given in column nine of Table 1.
The measurements were carried out in the usual manner (14-17), using an atmosphere of nitrogen to suppress oxidative degradation and rubber-lined clamps to minimize premature rupture. Most of the data were taken in the direction of increasing values of the elongation or relative length \( \xi = L/L_0 \), but some were taken out of sequence to test for reversibility. Experiments were continued to the point of rupture (which generally occurred away from the clamps).

RESULTS AND DISCUSSION

The elongation results were interpreted in terms of the reduced stress or modulus (2, 4, 17, 18)

\[
[f' = f/\xi^{\alpha} (\alpha = \alpha^*)
\]

(1)

where \( f' \) is the equilibrium elastic force, and \( \alpha^* \) is the undeformed cross-sectional area of the sample. Values of \( f'/\xi^2 \) were plotted against reciprocal elongation \( \alpha^* \) as suggested by the equation (10, 17-19).

Table 1. Character of Crosslinking Methods, and Elongation and Swelling Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Character of Crosslinking</th>
<th>Elongation Results</th>
<th>Swelling Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Designation</td>
<td>Crosslinking</td>
<td>T, (^\circ)C</td>
<td>( \xi_{\text{m}} )</td>
</tr>
<tr>
<td>Cis-</td>
<td>Trans</td>
<td></td>
<td></td>
</tr>
<tr>
<td>131-A</td>
<td>25.0</td>
<td>67.0</td>
<td>8.0</td>
</tr>
<tr>
<td>1515-73-3</td>
<td>3.16</td>
<td>66.7</td>
<td>1.6</td>
</tr>
<tr>
<td>3.04</td>
<td>55.0</td>
<td>11.0</td>
<td>0.888</td>
</tr>
<tr>
<td>35.0</td>
<td>63.1</td>
<td>1.9</td>
<td>0.900</td>
</tr>
<tr>
<td>3.04</td>
<td>47.0</td>
<td>10.0</td>
<td>0.943</td>
</tr>
<tr>
<td>43.0</td>
<td>68.4</td>
<td>20.0</td>
<td>0.855</td>
</tr>
<tr>
<td>5.00</td>
<td>49.0</td>
<td>20.0</td>
<td>0.855</td>
</tr>
<tr>
<td>6.00</td>
<td>49.0</td>
<td>20.0</td>
<td>0.855</td>
</tr>
<tr>
<td>7.00</td>
<td>49.0</td>
<td>20.0</td>
<td>0.855</td>
</tr>
<tr>
<td>8.00</td>
<td>49.0</td>
<td>20.0</td>
<td>0.855</td>
</tr>
<tr>
<td>9.00</td>
<td>49.0</td>
<td>20.0</td>
<td>0.855</td>
</tr>
<tr>
<td>10.00</td>
<td>49.0</td>
<td>20.0</td>
<td>0.855</td>
</tr>
</tbody>
</table>

* Number of units per stereonetwork.

** Density of \( \xi = 20^\circ\)C, respectively.

*** Elasticity constant in the equation \( f' = f/\xi^2 \) for the reduced stress.

**** Molecular weight between crosslinks.

***** Swelling factor of polybutadiene equilibration swelling in benzene at room temperature.
\[ |
\] where \( 2C_1 \) and \( 2C_2 \) are constants independent of \( a \).

The isotherms for the stereochemically random PBD networks are shown in Figs. 1 to 4. The reversibility is generally satisfactory and the results are well represented by the least-square lines shown. There are no upturns in the reduced stress, which is consistent with the non-crystallizability of these polymers. In the case of the high-trans polymers studied previously (8, 14), large amounts of crystallinity were observed for trans contents as low as 72 mol percent, but these polymers were relatively blocky.

The four stereoblock polymers found to be crystalline, with melting points as cited in Table I. Stress-strain isotherms were determined at several temperatures, and some of the results are shown in Fig. 5. The tabulated results pertain to temperatures just high enough to make the networks elastomeric. At none of the temperatures employed was it possible to induce significant amounts of additional crystallinity, as would have been evidenced by upturns in the reduced stress. The amount of crystallinity must therefore have been relatively insensitive to deformation over the temperature and elongation ranges investigated.

Values of the elongation constants \( 2C_1 \), \( 2C_2 \), and \( 2C_2/2C_1 \) obtained from least-squares analysis of the isotherms are given in columns ten through twelve in Table I. The constant \( 2C_1 \) is a direct measure of the crosslink density or inverse measure of the molecular weight \( M \) between crosslinks (19). It was found to increase with increase in radiation dose, as expected. The other constants, \( 2C_2 \) and \( 2C_2/2C_1 \), are due to increase in nonuniformity of the deformation with increase in elongation (20). The values are generally large, which suggests a heterogeneous distribution of crosslinks of relatively high functionality (21). In any case, decrease in \( M \) should decrease the amount of chain junction entanglement which, in turn, should decrease the extent to which the network deformation can become more nonuniform with increasing elongation (11, 20). The relevant results for the five types of random networks are shown in Fig. 6. Two curves are seen to represent all of the results and both show the expected (20) decrease of \( 2C_2/2C_1 \) toward zero as \( M \) decreases.

Values of \( M \) were calculated from the relationship

\[ M = \frac{A_3\rho RT}{2C_1} \]

where \( \rho \) is the network density, \( R \) is the gas constant, and \( T \) is the absolute temperature. The structure factor \( A_3 \) is given by (11, 20)

\[ A_3 = 1 - 2/\phi \]

where \( \phi \) is the junction functionality; it should therefore be \( \phi \) for the usual functionality of four. Values of \( M \), thus calculated are given in column thirteen of Table I. They are, of course, only approximate because of difficulties in the extrapolations for the \( 2C_1 \) estimate of the high deformation modulus (32) and uncertainty in the most appropriate value to use for \( A_3 \).

Fig. 1. Stress-strain isotherms at 5°C for the (stereochemically random) 131-A PBD networks cured by γ-radiation. Each of these isotherms is labelled with the radiation dose the sample received, and the rupture points are shown by dashed vertical lines. Results were generally obtained using a series of increasing values of the elongation \( a \). Results obtained out of sequence to check for reversibility are shown by the filled symbols.

Fig. 2. Stress-strain isotherms at 5°C for the 1515-73-3 and 1515-79-2 networks.

Fig. 3. Stress-strain isotherms at 5°C for the Durene-25 networks.

Fig. 4. Stress-strain isotherms at 5°C for the Phillips Sylprene 255 networks.

Fig. 5. Typical stress-strain isotherms for the stereoblock networks. Each isotherm is labelled with the network designation, and the temperature at which it was determined. The isotherm for \( n = 3 \) has been shifted upward by 0.15 N m\(^{-2}\) in order to prevent overlapping of some of the points.

Fig. 6. The elastic constant \( 2C_2 \), normalized to constant crosslink density (as specified by \( 2C_1 \)) shown as a function of the average molecular weight between crosslinks. The results pertain to networks 131-A (9), 1515-73-3 (2), Durene-25 (3), 1515-79-2 (4), and Phillips Sylprene 255 (5).

Alternative values of \( M \) were obtained from the swelling results through the relationship (2, 5, 10, 22)

\[ M = \frac{-m_V(i_{sm} - m_{sw})}{\ln(1 - i_{sm}) + i_{sm} + X_1 i_{sm}} \]

where \( V \) is the molar volume of the benzene and \( X_1 \) is the free energy of interaction parameter (2) for polybutadiene in benzene. Reliable values of \( X_1 \) as a function of composition are not available, unfortunately, and the constant value 0.335 (5) reported for a polybutadiene sample of unspecified stereoregular composition (23) had to be used. The experimental values of \( m_{sw} \) and the values of \( M \) they yield are given in the final two columns of Table I. These estimates of \( M \), are seen to be in very good agreement with those obtained from the elongation results. The agreement is much better than was obtained in the case of the crystallizable PBD elastomers (8, 14). In that case, there were probably difficulties in the extrapolations for \( 2C_1 \) arising from the strain-induced crystallization, and there may have been more of a difference between the stereoregular-composition of these samples and the PBD sample used to obtain the cited value of \( X_1 \) (23).

The present results clearly demonstrate the effects of stereoregular structure on several elastomeric properties. A detailed analysis (14) of its effect specifically on ultimate properties will be reported elsewhere (24).

ACKNOWLEDGMENTS

JEM wishes to acknowledge with gratitude the financial support provided by the National Science Foundation through Grant DMR-7918003 (Polymer Program, Division of Materials Research), and the hospitality of the IBM Research Laboratory, San Jose, during a sabbatical visit when the manu...
script was written. We also wish to thank Mr. T. Ryle for carrying out the differential scanning calorimetry measurements, and the Phoenix Laboratory at the University of Michigan for assistance in the γ irradiations.

REFERENCES


INTRODUCTION

Silica filler may be precipitated into an already cross-linked elastomer by the hydrolysis

\[
\text{Si(OCH}_3\text{)}_2 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_6\text{OH}
\]

to form tetraethylorthosilicate (TEOS) as a diluent in the network structure. The concept of such an "in-situ" precipitation is novel, and of practical importance since hard mineral fillers, although introduced, can give considerable reinforcement to an elastomer. A variety of substances have been found to act as catalyst for this hydrolysis, but very little has been done to characterize the rate of the reaction.

The most important concerns the use of aqueous solutions of ethylamine and ammonia as catalysts for this in-situ precipitation reaction. They were chosen because of their volatility, which makes them easy to remove from the filled polymer network. Of primary interest is the effect of the hydrolysis conditions on the amount of silica precipitated and the elastomeric properties of the resulting filled elastomers.

EXPERIMENTAL DETAILS

The networks investigated were prepared from two samples of hydroxyl-terminated poly(dimethylsiloxane) (PDMS) [Si(CH}_3\text{)}_2\text{O} - ] having number-average molecular weights of 5.0 and 21.3 \times 10^4 g mol^-1, respectively. The samples were generously provided by the Dow Corning Corporation of Midland, MI. They were crosslinked and then cured with stannous-2-ethylhexanoate as catalyst, in the usual manner (12, 13). The resulting networks were extracted with tetrahydrofuran and then toluene for several days to remove soluble material (found to be present to the extent of a few percent).

Two series of samples were cut from the extracted and dried network sheets. The first consisted of a large number of relatively small pieces to be used to obtain the amount of filler precipitated as a function of hydrolysis time. The second consisted of a smaller number of larger pieces, in the form of strips suitable for stress-strain measurements in elongation. The dependence of the wt percent filler on time and catalyst concentration can be expected to differ somewhat for the two series since the TEOS hydrolysis and its loss to the surrounding solution would depend on the ratio of sample surface area to volume, and thus on sample size and shape.

One strip cut from each network sheet was set aside as a reference material (0 wt percent filler). The other network strips were swelled with TEOS to the maximum extent attainable, corresponding to a volume fraction of polymer of approximately 0.3 and 0.2, respectively. The swollen strips were then placed into aqueous solutions of either ethylamine or ammonia, at a series of concentrations. The hydrolysis of the TEOS was permitted to occur at room temperature for various periods of time, and values of the wt percent filler incorporated, were obtained from the weights of the dried strips.

The strips cut from the networks were used in elongation experiments to obtain the stress-strain isotherms at 25°C (12-15). The elastomeric properties of pre-strain interest were the nominal stress

\[
f' = f/A'
\]

where \(f\) is the equilibrium elastic force and \(A'\) the undeformed cross-sectional area, and the reduced stress or modulus (15-18)

\[
f'' = f/(\alpha L)
\]

where \(\alpha = L/L_0\) is the elongation or relative elongation.