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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Kuwahara, Y. and Shen, M.(1976) 'Thermoelasticity and Chain Conformation in Alternating Copolymers of Butadiene', *Journal of Macromolecular Science, Part A*, 10: 6, 1205 — 1214

To link to this Article: DOI: 10.1080/00222337608061245

URL: <http://dx.doi.org/10.1080/00222337608061245>

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Thermoelasticity and Chain Conformation in Alternating Copolymers of Butadiene

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ABSTRACT

The internal energy contribution (f_e/f) and the temperature coefficient of the unperturbed chain dimensions can be determined by thermoelastic measurements. A particularly convenient technique for such measurements is the determination of the variation of shear moduli as a function of temperature. In previous works, it was found that values of f_e/f for random copolymers bear no simple relation to those of respective parent homopolymers. In addition, the signs of the energy contributions are often the reverse of the homopolymers. In this work, thermoelastic measurements of several alternating copolymers were carried out. Specifically, these elastomers are alternating copolymers of butadiene with propylene, methylene, and tetramethylene units. Again no simple relation can be found between copolymers and their parent homopolymers. Implications of these observations will be discussed.

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INTRODUCTION

The study of the thermoelastic behavior of rubbers is important because of its relevance to the statistical theory of rubber elasticity. The energy contribution to the elastic force is

$$f_e/f = 1 - (\partial \ln f / \partial \ln T)_{V,L} \quad (1)$$

On the basis of the statistical theory, the energy contribution is related to the temperature coefficient of the unperturbed chain dimensions:

$$d \ln \langle r_0^2 \rangle / dT = f_e / fT \quad (2)$$

The latter is of particular interest because it is calculable from the rotational isomeric model of chain molecules [1]. Comparisons of the calculated and experimental values of $d \ln \langle r_0^2 \rangle / dT$ are satisfactory for most homopolymers, thereby reinforcing the essential validity of the model. In this work, thermoelastic data on several alternating copolymers will be reported.

EXPERIMENTAL

A sample of the alternating copolymer of propylene and butadiene was supplied by the Maruzen Petrochemical Company. Of the butadiene units, 96% are in the trans-1,4 configuration, and the remaining are 1,2-butadienes [2]. Two levels of cure were used, namely 0.4 and 0.8 phr of dicumyl peroxide (dicup). One sample each of poly-pentenamer [3, 4] or poly(methylene-co-butadiene) and polyoctenamer [3] or poly(tetramethylene-co-butadiene) was obtained from the Good-year Rubber and Tire Company. The former has 82% trans content, and the latter 40%. They were both cured with 0.5 phr of dicumyl peroxide.

Thermoelastic data were taken by measuring the thermal expansion coefficients of strips of rubber samples under a series of loads in nitrogen atmosphere. The temperature range of 20-80°C was selected for all measurements. As shown previously, the temperature coefficient of shear moduli can be determined [5] by Eq. (3):

$$\beta_L = \beta_L^\circ - \left(\frac{\lambda^3 - 1}{\lambda^3 + 2} \right) \left(\frac{d \ln G}{dT} + 2\beta_L^\circ \right) \quad (3)$$

where G is the shear modulus, λ is the elongation ratio, and β_L and β_L° are the linear thermal expansion coefficients of the stretched and unstretched samples, respectively. The energy contribution is readily calculated by [5]

$$\frac{f_e}{f} = 1 - \frac{d \ln G}{d \ln T} - \beta_L^\circ T \quad (4)$$

Agreement of data determined by this method with those by tension compression, torsion, and simple shear has been previously verified [6].

RESULTS AND DISCUSSION

Results of the thermoelastic measurements are shown in Figs. 1-3. They are plotted according to Eq. (3) for the determination of the temperature coefficients of shear moduli. Energy contributions calculated by Eq. (4) are summarized in Table 1. It is seen that all of the peroxide-cured alternating copolymers of butadiene have rather low values of f_e/f (~ 0.05).

To facilitate a more detailed discussion of these data, they are recalculated as $d \ln \langle r_0^2 \rangle / dT$ through Eq. (2). These values are given in Table 2, along with the available theoretical and experimental data for the homopolymers. Before discussing these results, it would be of interest first to review the known data on random copolymers. One would expect the temperature coefficients of the unperturbed dimensions of copolymer chains to depend on the chemical composition, the sequence distribution of the comonomers, the configuration of the chain microstructure (tacticity and cis-trans isomerism) and its sequence distribution. In a previous publication [7], we have found that values of $d \ln \langle r_0^2 \rangle / dT$ for a series of random, atactic acrylic copolymers were intermediate between those of the homopolymers as a function of chemical composition. However, this simple correlation

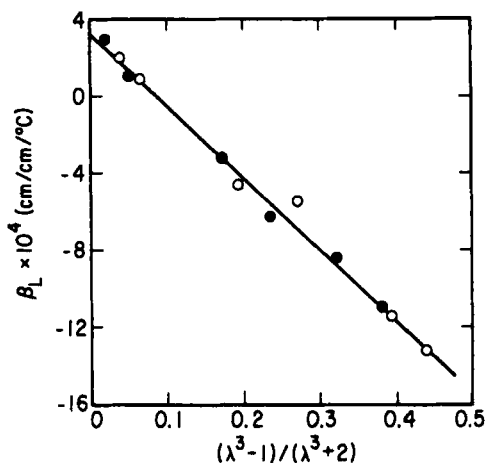


FIG. 1. Linear thermal expansion coefficients of stretched elastomers plotted as a function of $(\lambda^3 - 1)/(\lambda^3 + 2)$ for the alternating copolymer of propylene and butadiene containing 96% trans structures: (○) cured with 0.4 phr dicumyl peroxide; (●) cured with 0.8 phr dicumyl peroxide.

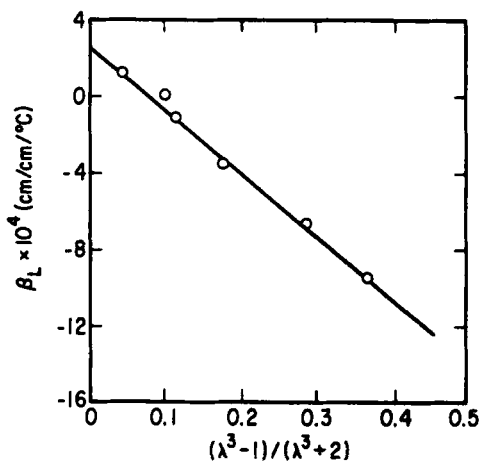


FIG. 2. Linear thermal expansion coefficients of stretched elastomers plotted as a function of $(\lambda^3 - 1)/(\lambda^3 + 2)$ for the alternating copolymer of methylene and butadiene containing 82% trans structure and cured with 0.5 phr dicumyl peroxide.

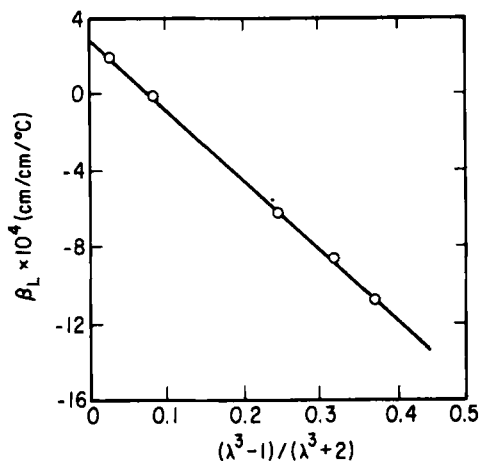


FIG. 3. Linear thermal expansion coefficients of stretched elastomers plotted as a function of $(\lambda^3 - 1)/(\lambda^3 + 2)$ for the alternating copolymer of tetramethylene and butadiene containing 40% trans structures and cured with 0.5 phr dicumyl peroxide.

TABLE 1. Thermoelastic Data of Alternating Copolymers of Butadiene

| Polymer | β_L° ($10^{-4}/^\circ\text{C}$) | $d \ln G/dT$ ($10^{-3}/^\circ\text{C}$) | f_e/f |
|--|---|--|---------|
| Poly(propylene-co-butadiene), PPB | | | |
| 96% trans, 0.4 phr dicup-cured β | 3.2 | 3.1 | 0.05 |
| 96% trans, 0.8 phr dicup-cured | 3.2 | 3.1 | 0.05 |
| Poly(methylene-co-butadiene), PMB | | | |
| 82% trans, 0.5 phr dicup-cured | 2.7 | 2.8 | 0.06 |
| Poly(tetramethylene-co-butadiene), PTB | | | |
| 40% trans, 0.5 phr dicup-cured | 3.0 | 3.1 | 0.05 |

TABLE 2. Temperature Coefficients of Unperturbed Chain Dimensions of Alternating and Copolymers Homopolymers

| Polymer | $d \ln \langle r_0^2 \rangle / dT, (10^{-3} / ^\circ\text{C})$ | | | |
|--|--|-----------|----------------|------------------|
| | Experimental | Ref. | Calculated | Ref. |
| Alternating Copolymers | | | | |
| Poly(propylene-co-butadiene), PPB | | | | |
| 0.4 phr dicup-cured, 96% trans | 0.17 | This work | | |
| 0.8 phr dicup-cured, 96% trans | 0.17 | " | | |
| Poly(methylene-co-butadiene), PMB | | | | |
| 82% trans, 0.5 phr dicup-cured | 0.21 | " | | |
| Poly(tetramethylene-co-butadiene), PTB | | | | |
| 40% trans, 0.5 phr dicup-cured | 0.18 | " | | |
| Homopolymers | | | | |
| Polymethylene, PM | -1.00 | [24] | -1.10 -1.00 | [23] [22] |
| Polypropylene, PP | | | | |
| Highly isotactic | | | -0.99 | [26] |
| Atactic | | | -0.56 | [26] |
| Highly syndiotactic | | | -1.21 | [26] |
| Polybutadiene, PB | | | | |
| Cis | 0.26-0.65 | [12-16] | 0.56 0.16 | [17] [18] |
| Trans | -0.65 | [16] | -0.65 -0.11 | [17] [18] |

is not expected to be generally true for all copolymers because of the other factors. To wit, $d \ln \langle r_0^2 \rangle / dT = -0.39 \times 10^{-3} / ^\circ\text{C}$ for SBR, a random copolymer of styrene and butadiene [8]. Commercial SBR normally contains about 18% cis, 65% trans, and 17% vinyl structures [9]. The temperature coefficient for atactic polystyrene [10, 11] determined by thermoelastic measurements is between 0.37×10^{-3} and $0.51 \times 10^{-3} / ^\circ\text{C}$. No data exist for isotactic and syndiotactic PS. Experimental values for poly-cis-butadiene [12-16] range from 0.26×10^{-3} to $0.65 \times 10^{-3} / ^\circ\text{C}$, while only one preliminary experimental determination has been attempted for poly-trans-butadiene [16] ($-0.65 \times 10^{-3} / ^\circ\text{C}$). Theoretical calculations by Mark [17] yielded values of 0.56×10^{-3} and $-0.65 \times 10^{-3} / ^\circ\text{C}$, respectively, for cis-PB and trans-PB; while those by Abe and Flory [18] are 0.16×10^{-3} and $-0.11 \times 10^{-3} / ^\circ\text{C}$. The latter authors also showed that $d \ln \langle r_0^2 \rangle / dT$ for PB increases monotonically with increasing cis fraction in the chain. However, no experimental or theoretical data are known for poly-1,2-butadiene.

A number of thermoelastic studies of ethylene-propylene random copolymers have been carried out. Values for $d \ln \langle r_0^2 \rangle / dT$ range between 0.1×10^{-3} and $-1.6 \times 10^{-3} / ^\circ\text{C}$ for those containing approximately 50% of each comonomer [8, 19-21]. The theoretical values for polymethylene are $-1.00 \times 10^{-3} / ^\circ\text{C}$ by Hovee [22] and $-1.10 \times 10^{-3} / ^\circ\text{C}$ by Abe, Jernigan and Flory [23], in excellent agreement with experimental values determined by both thermoelastic [24] and by viscosity-temperature [25] measurements. For polypropylene, calculations by Boyd and Breitling [26] showed that $d \ln \langle r_0^2 \rangle / dT$ gave values of -0.99×10^{-3} , -0.56×10^{-3} , and $-1.21 \times 10^{-3} / ^\circ\text{C}$ for isotactic, atactic, and syndiotactic isomers, respectively. The only reliable experimental values were from viscosity-temperature measurements. These are $-4.0 \times 10^{-3} / ^\circ\text{C}$ [27], and $-3.0 \times 10^{-3} / ^\circ\text{C}$ [28], for the isotactic polymer and $-3.3 \times 10^{-3} / ^\circ\text{C}$ [29] and $-1.8 \times 10^{-3} / ^\circ\text{C}$ [28] for the atactic polymer. No data are available for the syndiotactic PP. The calculated temperature coefficients for 1:1 ethylene-propylene random copolymers are -1.5×10^{-3} , -1.1×10^{-3} , and $-1.1 \times 10^{-3} / ^\circ\text{C}$ for those containing highly isotactic, atactic, and highly syndiotactic propylene units [30]. For 1:1 copolymers containing long sequences of the respective comonomers, the values are $-1.8 \times 10^{-3} / ^\circ\text{C}$ for the highly isotactic; $-1.2 \times 10^{-3} / ^\circ\text{C}$ for the atactic and the highly syndiotactic configurations. In the case of the alternating copolymer, $d \ln \langle r_0^2 \rangle / dT = -1 \times 10^{-3} / ^\circ\text{C}$. No experimental data are known for the alternating copolymer.

It is obvious from the above that it is in general not possible to draw any inference about the temperature coefficient of unperturbed

copolymer chain dimensions from those of the respective homopolymers. Certainly there is no simple relation on the basis of chemical composition alone because of the importance of the detailed microstructure and sequential distributions. However, alternating copolymers provide an interesting case for study, since for these polymers comonomer composition and distribution is fixed.

Inspection of Table 2 shows that, even for alternating copolymers, the temperature coefficient is not simply related to that of the homopolymers. In all instances, values of $d \ln \langle r_0^2 \rangle / dT$ of the alternating copolymer of butadiene studied here are positive while those of polymethylene, polypropylene and poly-trans-butadiene are negative. Only the value calculated by Abe and Flory for poly-cis-butadiene is similar in magnitude, perhaps fortuitously. The value for poly(tetramethylene-co-butadiene) is close to that of the other peroxide-cured alternating copolymers, even though butadiene units in PTB are predominantly cis in configuration. The PPB samples crosslinked at two levels gave identical temperature coefficients, in agreement with our previous data on cis-PB and natural rubber [15]. However, in general there does not appear to be any simple relation between values of $d \ln \langle r_0^2 \rangle / dT$ of alternating copolymers and those of homopolymers, just as in the case of random copolymers. These findings emphasize the importance of chain microstructure configurations and their sequence distributions, since chemical compositions of the alternating copolymers are fixed. The sulfur-cured poly(methylene-co-butadiene) has a very highly positive temperature coefficient in comparison with the peroxide cured samples. It is not likely that this is due to its slightly higher trans content than the other PMB. It is also not likely to be attributable to the possible differences in degrees of crosslinking, since for poly(propylene-co-butadiene) in Table 2 and for a number of other elastomers [15] the degree of crosslinking is not found to be a factor in affecting the values of the temperature coefficient. The only other possible source of discrepancy appears to be the nature of the crosslink. In the case of natural rubber, sulfur-cured samples usually have lower values of $d \ln \langle r_0^2 \rangle / dT$ than the peroxide-cured ones [31]. The exact cause for this observation is, however, difficult to ascertain.

In conclusion, we can state that the thermoelastic behavior of copolymers is in general not related to that of the component homopolymers in a simple manner. Further theoretical work is indicated for the elucidation of the observed phenomena.

ACKNOWLEDGMENT

We wish to thank Drs. J. P. Bell, R. H. Boyd, and K. W. Scott for helpful discussions, and Drs. A. Kawasaki, N. Calderon, K. W.

Scott, R. A. Livigni, and S. Aggarwal for supplying the samples. This research was made possible by a Camille and Henry Dreyfus Teacher-Scholar Grant awarded to one of us (M.S.).

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Accepted by editor August 1, 1975

Received for publication October 27, 1975