Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Polymer 46 (2005) 4152–4159

polymer

www.elsevier.com/locate/polymer

Viscoelastic properties of 1,2-,1,4- and 1,2-1,4-diblock butadiene polymers

Adel F. Halasa*, William P. Francik

The Goodyear Tire and Rubber Company, 142 Goodyear Blvd, Akron, OH 44305, USA

Abstract

The use of polar modifiers to produce novel structures of butadiene polymers is well documented in the literature [Antkowiak TA, Oberster AE, Halasa AF, Tate DP. J Polym Sci 1972;10:1319; Langer AW. Polym Prep Am Sco Polym Div. 1966;7:132; Hay JN, McCabe JF, Robb JC. Polym Prep Am Chem Faraday Trans 1972;1:681; Halasa AF, Mochel VD, Frankel G. Polym Prep Am Chem Sco, Div Polym Chem 1980;21(1):13; Halasa AF, Schulz DN, Tate DP, Mochel VD. Adv Organomet Chem 1980;8:55 [1–5]]. Manipulating microstructures of 1,3-butadiene to produce diblock co-polymers has been reported by one of us [Halasa AF. Rubber Chem Technol 1981;54:627 [6]]. The discovery of polar modifier di-piperdinoethane to produce pure (100%) atactic 1,2-polubutadiene [Halasa AF, Lohr DF, Hall JE. J Polym Sci Polym Chem Ed 1981;19 [7]] provided scientists with a new tool to structurally engineer various block co-polymers of butadiene and styrene and study their structural and viscoelastic properties [Cohen RE, Torradas JM. MS Thesis, MIT, May 1980, PhD Thesis, MIT January, 1982 [8]].

Keywords: Diblock butadiene polymers; WLF; Viscoelasticity

1. Summary

The dynamic viscoelastic properties of 1,2 poly-butadiene (1,2 BR), 1,4 poly-butadiene (1,4 BR), and 1,2-1,4-block poly-butadiene (1,2-1,4 BR) have been examined using the Rheometrics System IV Mechanical Spectrometer. All results can be reduced to the mastercurve following the universal WLF relationship, confirming that chain mobility is important in controlling the viscoelastic properties of these materials. The obvious effects of increasing the 1,2 ratios in the molecular chains are (a) a displacement of the terminal zone toward lower frequencies, (b) a reduction in the breadth of the rubbery plateau and the value of the plateau modulus, and (c) a displacement of the transition zone toward the lower frequencies. These effects can be interpreted in molecular terms. A stronger chain interaction can occur between 1,2-BR chains due to the fact that the double bonds of vinyl side chains are easier to orient by rotation about a single carbon–carbon bond. This has been confirmed by the work of Nordsiek [9] where he has found that polymers containing high vinyl groups have higher resilience than those possessing a phenyl side group. Similarly, the dependence of hysteresis of vinyl groups on the frequencies and amplitude has been reported.

2. Discussion

The morphology of block co-polymers of various conjugated diene structures has been examined by many workers [10–12]. We are examining the viscoelastic properties of 1,2-BR (90% 1,2), 1,4-BR (10% vinyl, 35% cis, 55% trans), and 1,2-1,4-Block BR (58% 1,2 and 42% 1,4-microstructures). The molecular weight and molecular weight distribution of thes polymers are shown in Table 1.

The parallel plate geometry was used to carry out the dynamic shear measurements using the Rheometrics System IV Spectrometer. Figs. 1–3 show the results of the storage modulus (G′), loss modulus (G″), and tan δ vs. temperature for 1,2-BR, 1,4-BR, and 1,2-1,4-Block BR, respectively. The T_g of the polymers in this work, was taken as the temperature of maximum tan δ. The T_g values determined by dynamics measurements are somehow different from those determined by thermal analysis due to the fact that in

---

* Corresponding author.
E-mail address: adel.halasa@goodyear.com (A.F. Halasa).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.02.064

Table 1
MW and MWD of BR's

	Polymer		
	1,2-BR	1,2-1,4-Block BR	1,4-BR
Mw	116,000	224,000	144,900
Mn	100,000	155,000	129,000
MWD	1.16	1.44	1.12

the latter, the samples are taken in the unstrained state and at zero frequency.

The T_g values determined under the strain of 0.1% and the frequency of 0.1 Hz are: −8 °C for 1,2 BR, −95 °C for the 1,4-BR, and −35 °C for the 1,2-1,4-diblock BR. It is not surprising to see a single T_g for the two homo-polymers of the 1,2-BR and the 1,4-BR. An interesting feature of the 1,2-1,4-diblock BR is that instead of showing two tan δ peaks corresponding to two T_g's for 1,2 and 1,4 structures, a single broad tan δ peak is observed in the intermediate region. This result indicates that 1,2-1,4-diblock BR does not exhibit separated phases characterized by two well-defined T_g's. This might be due to the comparable very close χ parameters and not due to morphology.

Temperature-frequency sweeps were also carried out using the Rheometrics System IV in shear mode at 0.1% strain. Values of G′ at various temperatures and frequencies are given in Figs. 4–6 for 1,2-BR, 1,4-BR and 1,2-1,4-diblock BR, respectively. Fig. 7 shows the mastercurves of storage modulus (reference −5 °C). The experimental shift factor a_T used to transform the data to equivalent frequencies at −5 °C are shown in Fig. 8. Also, shown as solid lines in Fig. 8, are values of a_T calculated from the universal WLF relationship: [13].

$$\mathrm{Log}\, a_T = -17.44(T - T_g)/51.6 + T - T_g$$

As shown in Fig. 8, the experimental values and calculated values of a_T are in excellent agreement. Since the data can be horizontally shifted to form the mastercurve, this indicates that chain segmental mobility is important in controlling the viscoelastic properties of these materials.

As expected, the flow region of 1,2-BR is shifted to lower frequencies when compared with 1,4-BR. This observation might be explained by the fact that, in comparison with the double bond in the 1,4 BR chain, a double bond of a vinyl side chain is easier to orient by rotating about a single carbon–carbon bond [14]. Through this orientation, a stronger chain interaction is achieved. Because of the

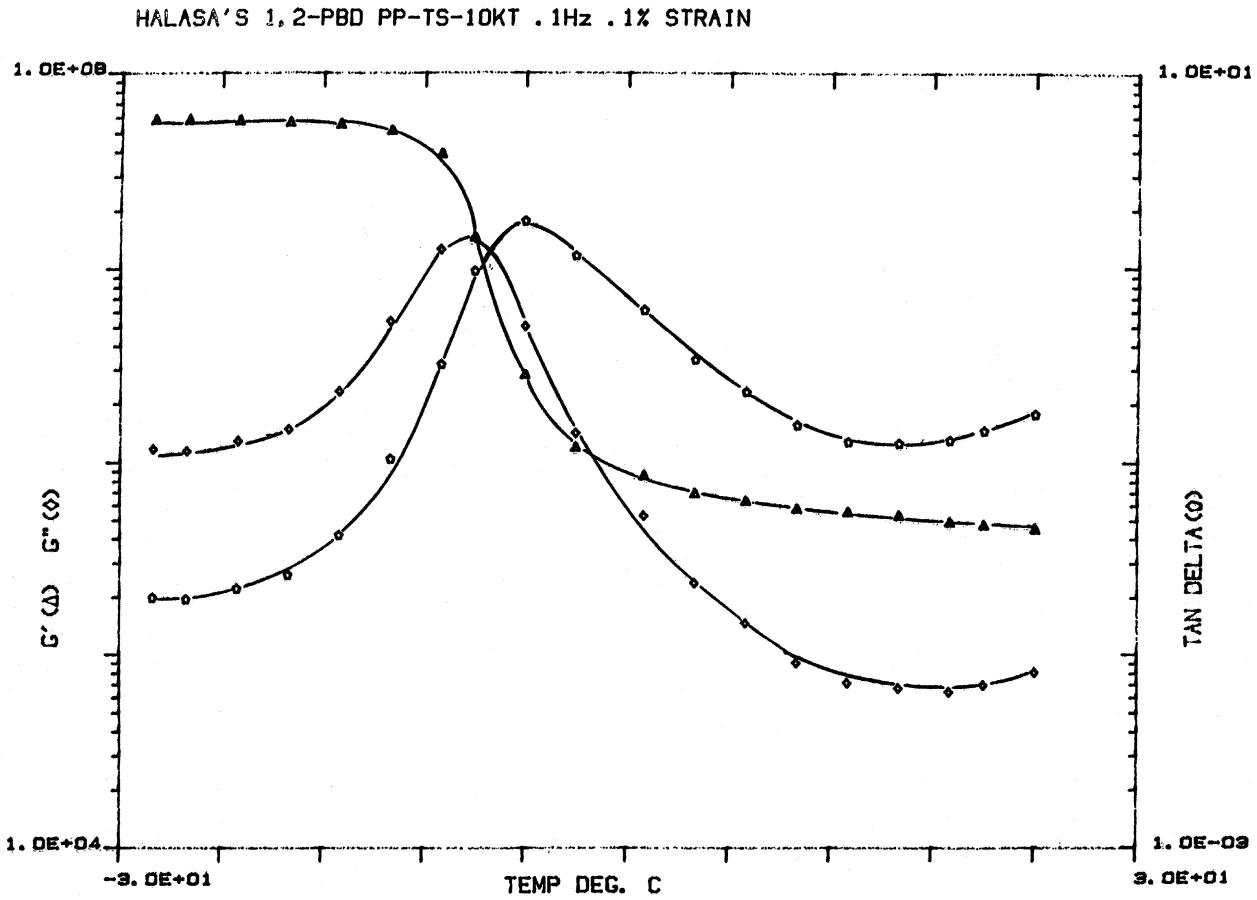

Fig. 1. The dynamic mechanical properties of 1,2-BR (I) as a function of temperature.

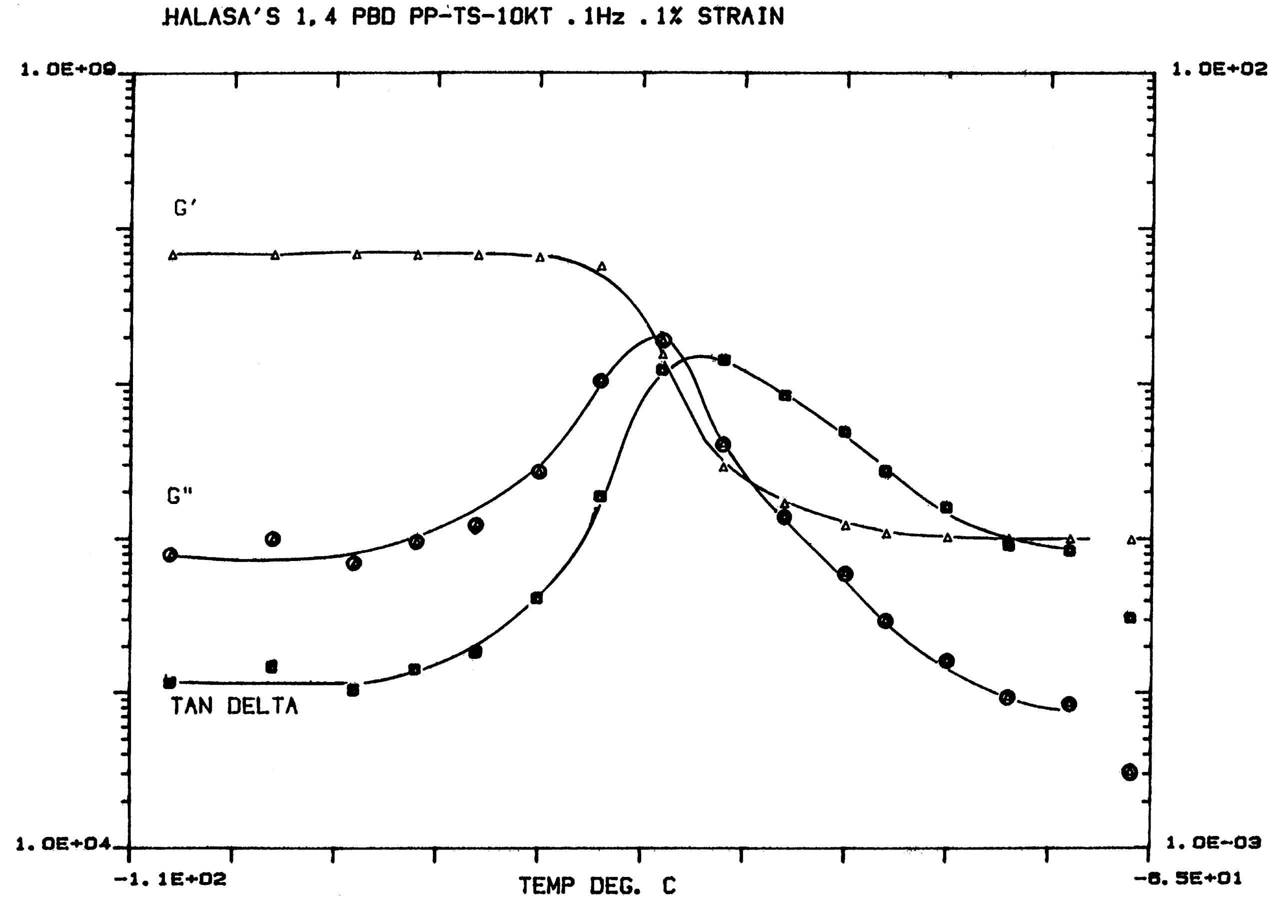

Fig. 2. The dynamic mechanical properties of 1,4-BR (II) as a function of temperature.

increased chain interaction, a longer time (lower frequency) is needed for the 1,2-BR chain to undergo long-range motion by disentangling and flowing past one another. Based on the same consideration, 1,2-1,4-diblock BR exhibits flow behavior at a frequency range between that of 1,2-BR and 1,4-BR. Likewise, the transition zones of the 1,2-1,4-diblock BR and the 1,2-BR are shifted to lower frequencies when compared with 1,4-BR. This is a consequence of the increased monomeric friction between chains with increasing 1,2-content.

Values of the entanglement moduli, G°ŋ, for these elastomers have been estimated from Fig. 7. The estimated G°ŋ values are tabulated in Table 2, along with the approximate frequency range of the 'rubbery plateau'. The G°ŋ values and the breadth of the entanglements region are reduced as the 1,2 content in the molecular chains is increased. Apparently, a stronger interaction between 1,2-BR chains makes chains stiffer, thereby hindering the chain bending which is needed to form entanglements. The decreased number of entanglement coupling caused G°ŋ to decrease. This occurs in spite of the enhanced chain interaction due to the vinyl side group.

The mastercurve of G″ and tan δ (constructed with same shift factor used for G′) are shown in Figs. 9 and 10, respectively. All three elastomers show both a maximum and a minimum tan δ. The maximum in tan δ is associated with the frequency at which the material undergoes its glass transition at −5 °C. Tan δ is high at sufficiently low frequencies for all these uncrosslinked polymers, since there is adequate time for the chains to slip and flow past one another in a viscous manner and entanglement couplings are inactive in this frequency region.

Table 2
Values of the entanglement moduli and the approximate frequency range of the entanglement plateau for 1,2-PBD 1,4-PBD, and 1,2-1,4-Block PBD

Sample	Log G°n (N/m^2)	Approximate frequency range of entanglement plateau (rad/s)
1,4-BR	6.0	40–10^6
1,2-1,4-Block BR	5.85	6(10^{-2})–6
1,2-BR	5.70	2(10^{-5})–6(10^{-4})

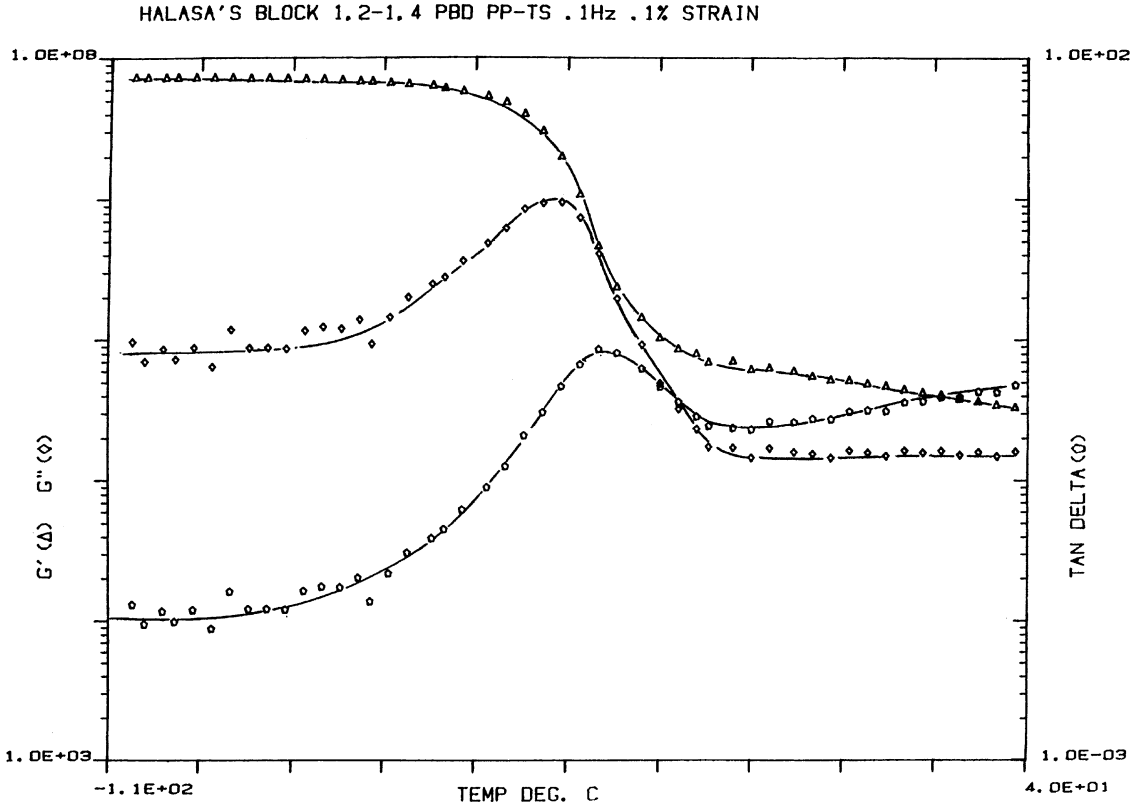

Fig. 3. The dynamic mechanical properties of 1,2-1,4-block BR (III) as a function of temperature.

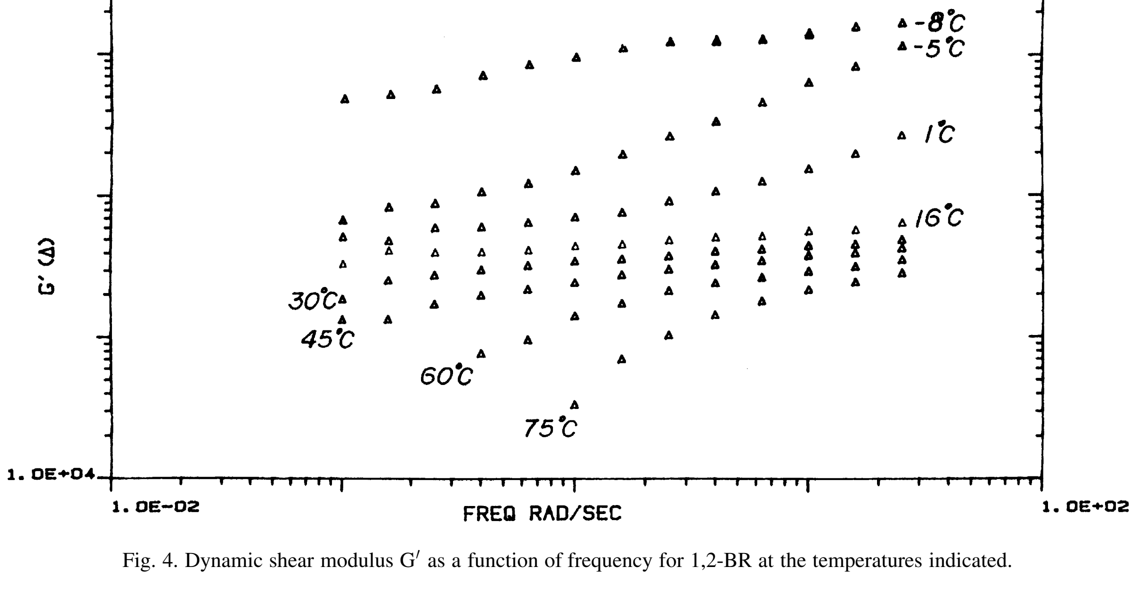

Fig. 4. Dynamic shear modulus G′ as a function of frequency for 1,2-BR at the temperatures indicated.

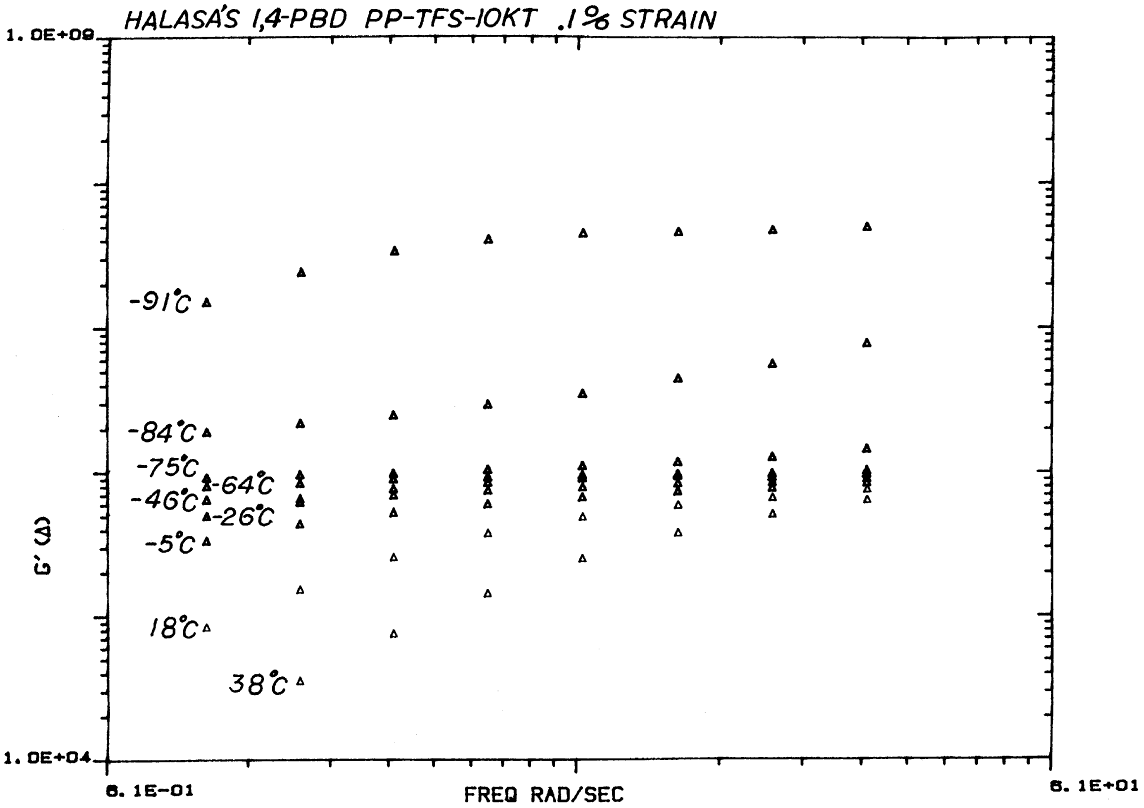

Fig. 5. Dynamic shear modulus G′ as a function of frequency for 1,4-BR at the temperatures indicated.

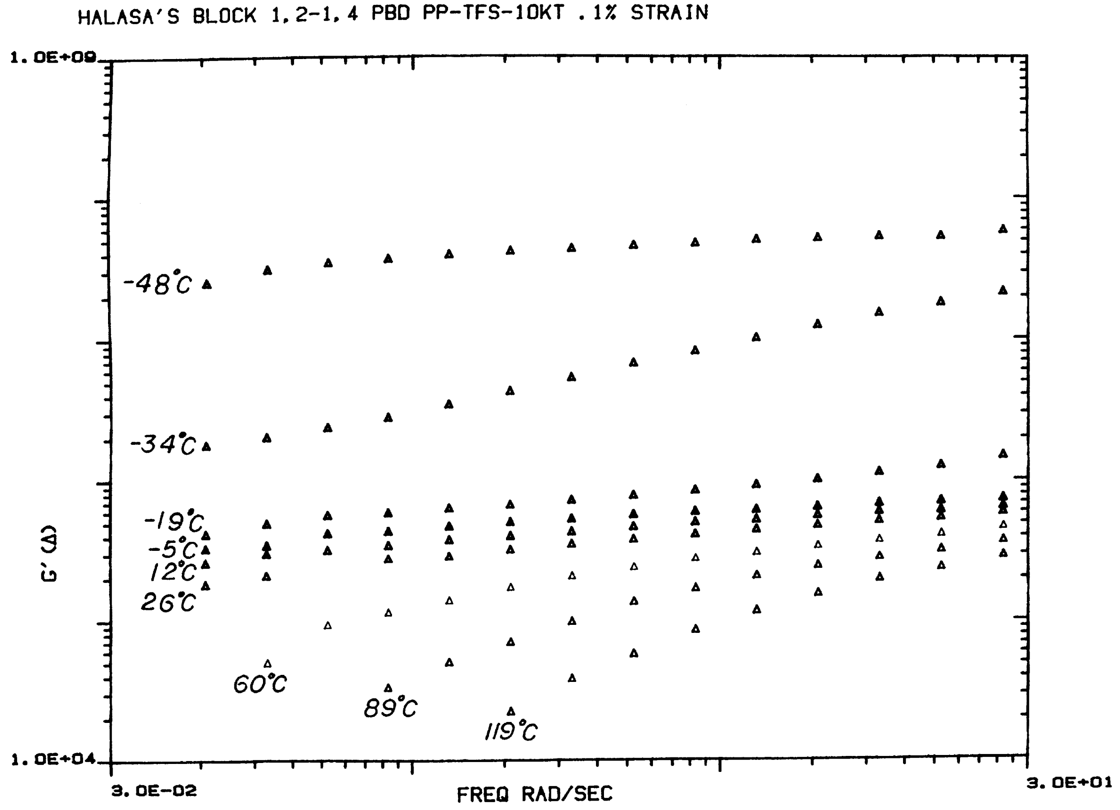

Fig. 6. Dynamic shear modulus G′ as a function of frequency for 1,2-1,4-diblock BR at the temperatures indicated.

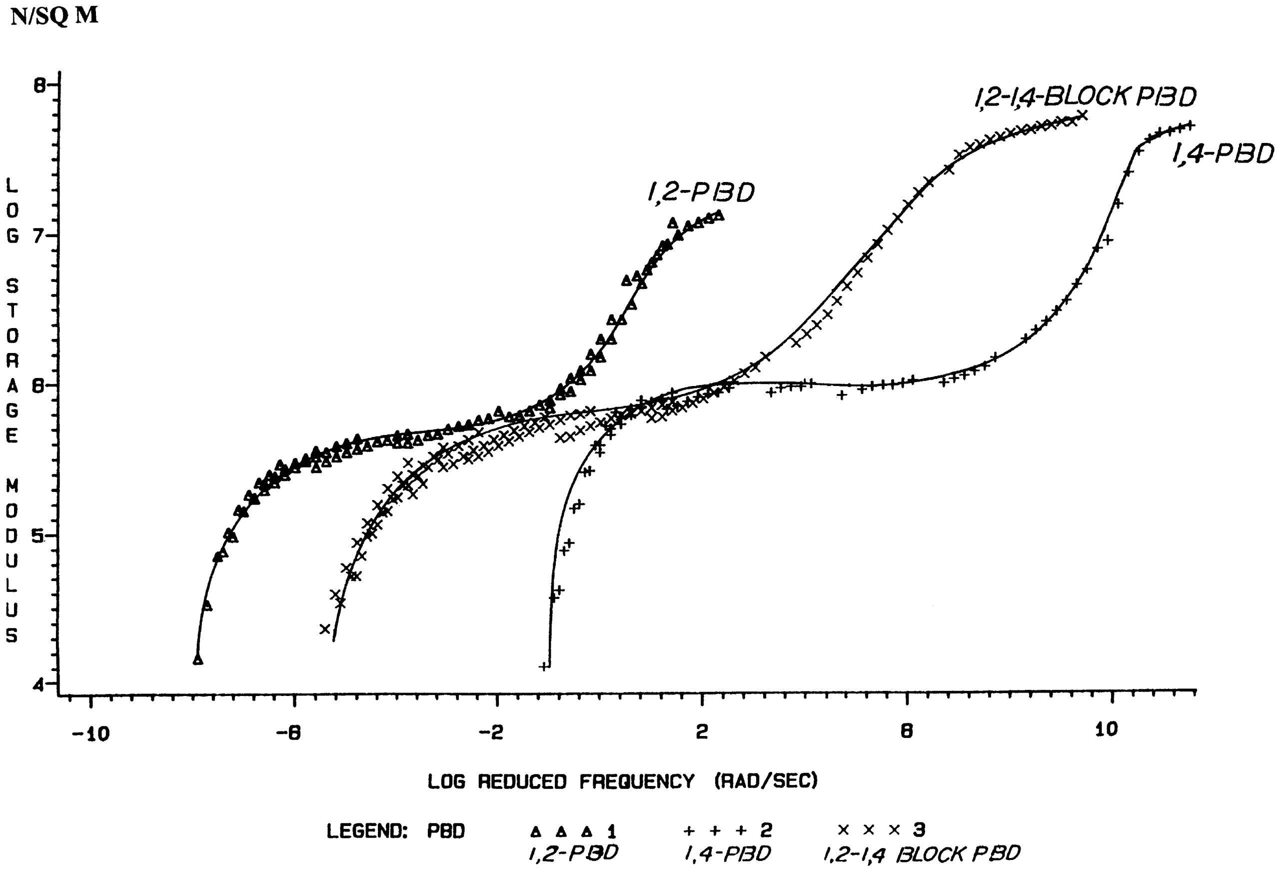

Fig. 7. Master curve for the dynamic shear modulus G′ as a function of reduced frequency. (Referenced to −5 °C).

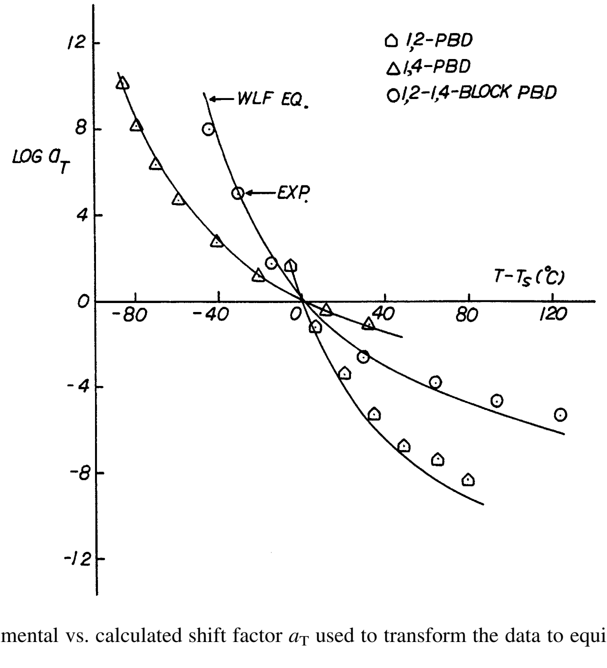

Fig. 8. Comparison of experimental vs. calculated shift factor a_T used to transform the data to equivalent frequencies at −5 °C.

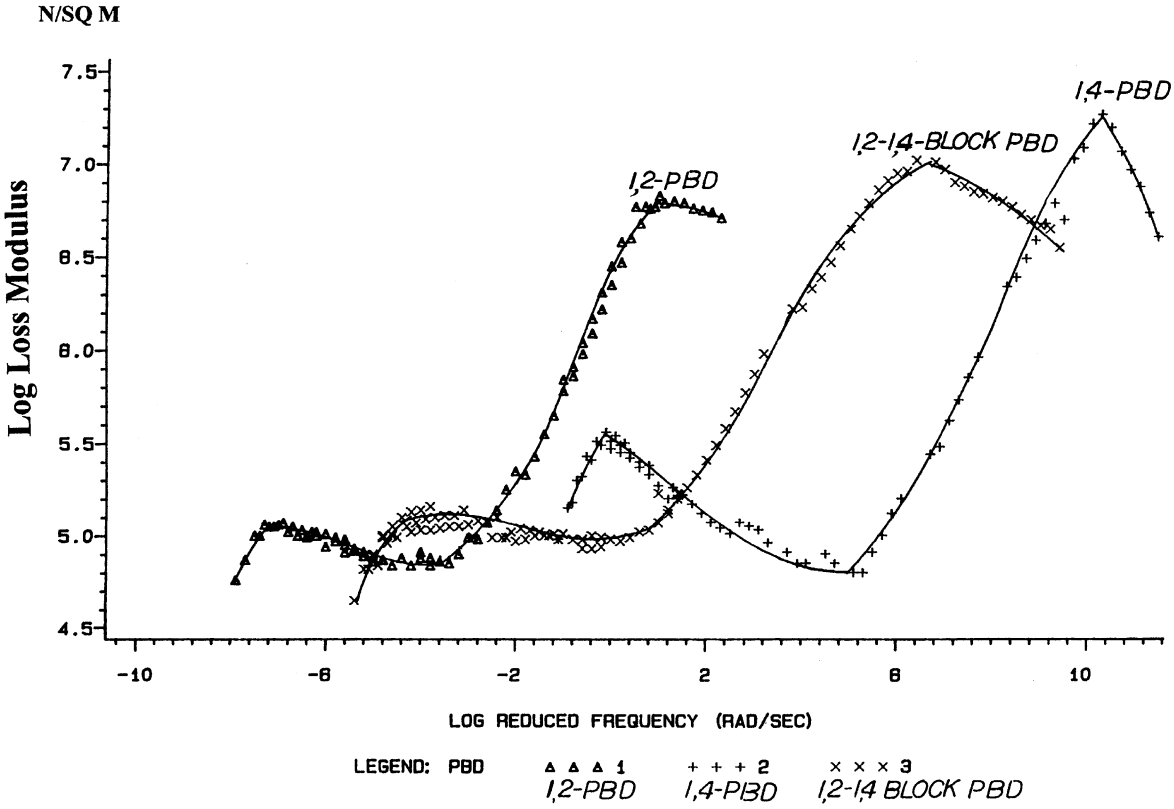

Fig. 9. Master curve for the dynamic loss modulus G″ as a function of reduced frequency. (Referenced to −5 °C).

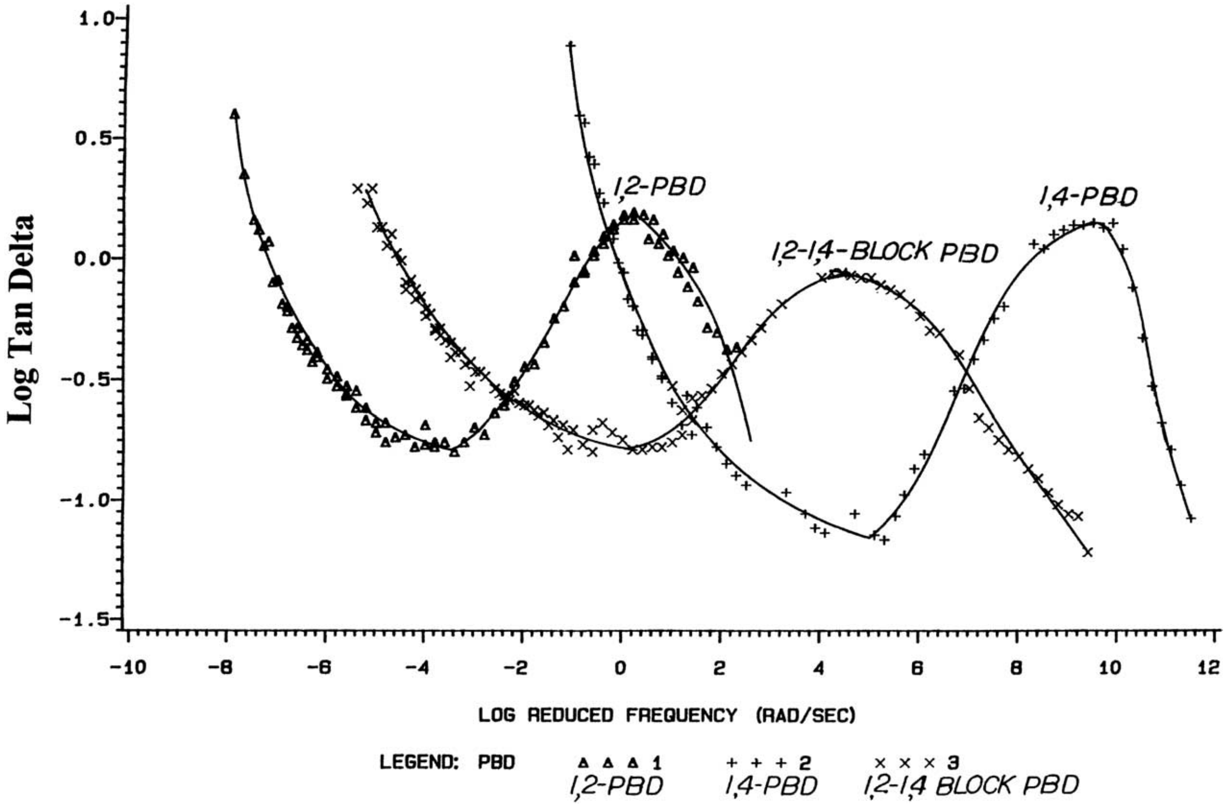

Fig. 10. Master curve for tangent delta as a function of reduced frequency. (Referenced to −5 °C).

References

[1] Antkowiak TA, Oberster AE, Halasa AF, Tate DP. J Polym Sci 1972;10:1319.
[2] Langer AW. Polym Prepr Am Soc Polym Div 1966;7:132.
[3] Hay JN, McCabe JF, Robb JC. Polym Prepr Am Chem Faraday Trans 1972;1:681.
[4] Halasa AF, Mochel VD, Frankel G. Polym Prepr Am Chem Soc Div Polym Chem 1980;21(1):13.
[5] Halasa AF, Schulz DN, Tate DP, Mochel VD. Adv Organomet Chem 1980;8:55.
[6] Halasa AF. Rubber Chem Technol 1981;54:627.
[7] Halasa AF, Lohr DF, Hall JE. J Polym Sci Polym Chem Ed 1981;19.
[8] Cohen RE, Torradas JM. MS Thesis, MIT, May 1980, PhD Thesis, MIT January 1982.
[9] Nordsiek, K. H. International Rubber Division Gotenborg, Sweden; 1986.
[10] Cohen RE, Torradas JM, Wilfong DE, Halasa AF. Polym Prep Am Chem Div Polym Chem 1980;21(2):216.
[11] Cohen RE, Ramos. Macromolecules 1979;12:131.
[12] Hashimoto M, Fujimura, Hashimoto T, Kawal H. Macromulecules 1981;14:844.
[13] Williams ML, Landel RF, Ferry JD. J Chem Soc 1955;77:3701.
[14] Bothe L, Rehage G. Rubber Chem Technol 1982;55:1308.