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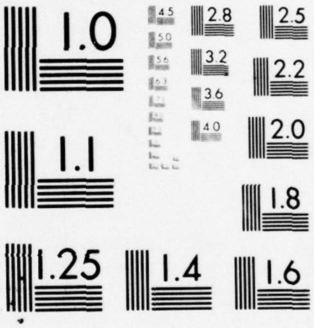

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⑥ Secondary Relaxation Behavior of Some Diene Polymers.

by ⑭ TR-16

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Secondary Relaxation Behavior of Some Diene Polymers

It is now well known that the chain microstructure of a polymer influences its secondary relaxation behavior. A case in point is the diene polymers. It has been found that below the glass transition temperature there are two distinct secondary loss peaks for the trans isomer of polybutadiene, but not for the cis isomer.[1] Two hypothetical molecular mechanisms were proposed by Morgan, Nielsen and Buchdahl[2] for this observation. The purpose of this work is to compare the dynamic mechanical loss curves of three polymers containing the diene groups in an effort to further scrutinize this interesting behavior.

Samples of polybutadiene (PB) were supplied by the Phillips Petroleum Company. The cis-PB contains 93% cis, 4% trans and 3% vinyl; while the trans-PB contains 73% trans, 17% cis and 10% vinyl structures. They were crosslinked by 0.16 and 0.32% of dicumyl peroxide respectively. A sample of polypentamer (PP), $[(CH_2)_3 - CH = CH -]_n$, was obtained from the Goodyear Rubber and Tire Company with 82% trans content, and cured with 0.5% dicumyl peroxide. A sample of polyoctenamer (PO), $[(CH_2)_6 - CH = CH -]_n$, also provided by Goodyear, had about 40% trans diene groups and was similarly cured. Dynamic mechanical experiments were carried out on a vibrating reed acoustic spectrometer previously described.[3] Samples were cut to appropriate reed dimensions. One end of the sample was then lightly clamped in the spectrometer, while a metal plate was bolted to the free end. This plate served to drive the reed in forced oscillation and was also used to measure deflection. Following a rapid quench into liquid nitrogen and reclamping, the entire assembly was enclosed in a chamber and submerged in liquid nitrogen. If desired, the chamber, which contained some liquid nitrogen, was pumped to reduce the reed temperature towards the triple point, 63°K. Modulus and loss measurements were taken during warmup at 0.5 - 1°K/minute.

Figure 1 shows the loss data for the two PB's. The large upturns at 170°K for cis-PB and 210°K for trans-PB are attributable to their respective primary glass (β) transition. Below these temperatures the trans isomer has a γ-relaxation at 150°K (104 Hz) and a very small and broad δ relaxation around 88°K (121 Hz). Previously Gupta[1] found loss peaks at 160°K and 110°K for trans-PB at a measurement frequency about 2000 Hz, and Morgan, et. al.[2] located a similar relaxations at 132°K and 85 - 103°K (7.5 Hz). The loss location of our data for trans-PB falls between that of these two authors as may be seen in Fig. 2. This Arhenius plot summarizes the glassy transitions of the polymers considered here and is particularly useful in that virtually all data refer to maxima in tan δ_G vs T. (The horizontal bars indicate uncertainty in the broad δ-peak position).

The activation energies of about 9 and 6 Kcal/m for the γ and δ peaks of trans-PB correspond to those for other polymers in this region of the Arhenius plots. Our data for cis-PB, as that of the other two authors, shows no resolved loss peak but a large shoulder on the side of the T_g peak, this shoulder appearing roughly in the region of the γ-peak of the trans polymer. It is conceivable that a small γ-peak does exist for the cis polymer but is hidden by the closely adjacent T_g peak. This would need to be resolved by working at very low frequencies.

The polyethylene γ-peak position is indicated by a line in Fig. 2. The line shown is the peak position found[7c] in branched polyethylene (i.e. PE of limited crystallinity such as high pressure PE and ethylene-propylene copolymer) which we believe to be representative of hydrogenated compounds discussed below.

Our loss data for polypentanamer is given in Figure 3. Below the primary glass transition of 170°K, there is but a single loss peak at 142°K (33 Hz, tan δ = 0.044). Another sample resulted in a substantially higher peak (145°K, 64 Hz, tan δ = 0.067) but of the same shape. The reason for this difference is unclear. Polypentenamer has also been measured by Sanui, MacKnight and Lenz[5] and by Gillham and Benci.[6] An activation energy of 7.6 Kcal is computed (Fig. 2), but this may be a bit low because the peak temperature of the broad low frequency peak[6] is hard to establish. Again, our data fall between those of these two observers. One notes that the PP peak falls between the trans-PB and the PE peaks; rather closer to the trans-PB. This is as might be expected on the basis of the microstructure. When trans-PP is hydrogenated[5] an additional peak appears at approximately the position of the irregular branch of PE. [Note that even fully hydrogenated material was only 85% crystalline]. The fact that we see two peaks in hydro-PP rather than a single shifted one suggests that the hydrogenation is relatively blocky. Furthermore, Gilliam and Benci[6] have shown that unhydrogenated cis-PP and trans-PP both show a loss at low frequency as a broad peak of the same intensity. The situation thus differs from that in PB where only trans-PB shows a large peak.

Polyoctenamer is an interesting analogue of partly hydrogenated PP. Its loss curve is also shown in Fig. 3. Here two samples gave similar results. Note that only a single peak appears below T_g, which is shown in Fig. 2 to fall just in the area of branched PE. No vestige of a trans-PB peak seems to remain. No activation energy can be determined since the frequency range is quite small. The loss peaks might be affected by the crosslinking, but we do not believe this is to be the case. It has been shown previously[8] that crosslinking PE at levels 15-25 times higher in dicumyl peroxide has only a relatively small effect on peak shape and position.

In their work, Morgan, Nielsen and Buchdahl[2] proposed two possible mechanisms for the β-relaxations involving trans-PB and trans-polyisoprene. One mechanism (Model A) involves the motion of C_3- C_4 in $C_1-C_2=C_3-C_4-C_5-C_6$, specifically a crankshaft like rotation about the virtually colinear (vinyl) C_1-C_2 and C_5-C_6 bonds. The other mechanism proposed (Model B) involves a libration of the $C_2=C_3$ unit in an all trans configuration of $C_0-C_1-C_2=C_3-C_4-C_5$ with hydrogen wagging but minimal motion of the C_1 and C_4 carbons themselves. Atoms C_0 and C_5 remain fixed. Models A and B are only possible for trans configuration around the double bond, whether PB, PP or PO.

It is useful to interpret the additional data on PP and PO in the light of these models. Replacement of PB by PP changes the C_5-C_6 bond in Model A from vinyl to allyl. In PO that bond becomes alkyl. In either case the chemical nature of the C_1-C_2 bond in Model A remains unchanged. In Model B the C_0-C_1 and C_4-C_5 bonds are biallyl (i.e. allyl to 2 double bonds) in PB, allyl/alkyl in PP and PO. We expect the vinyl bond to be weak (relatively free rotation), while the allyl bond should be rather similar to the alkyl bond. We have seen that the δ-transition occurs in trans-PB[0,1,2] (ref 0 refers to this work) but is absent for for cis-PB[2], trans-PP[0] and 40% trans-PO[0]. The γ-transition is found to be strong for trans-PB[0,1,2], probably weak for cis-PB[0,1,2], and present for trans-PP[0,5,6], cis-PP[6] and 40% trans-PO[0]. When we compare the proposed models to the data we see that Model A can account for the δ-transition if we assume that two vinyl bonds are required for the rotor. Model B fails here, the change of an allyl to alkyl bond seems too slight to account for the loss of the transition when we go to PP. Neither model can account for the γ-transition, at least in cis-PP.

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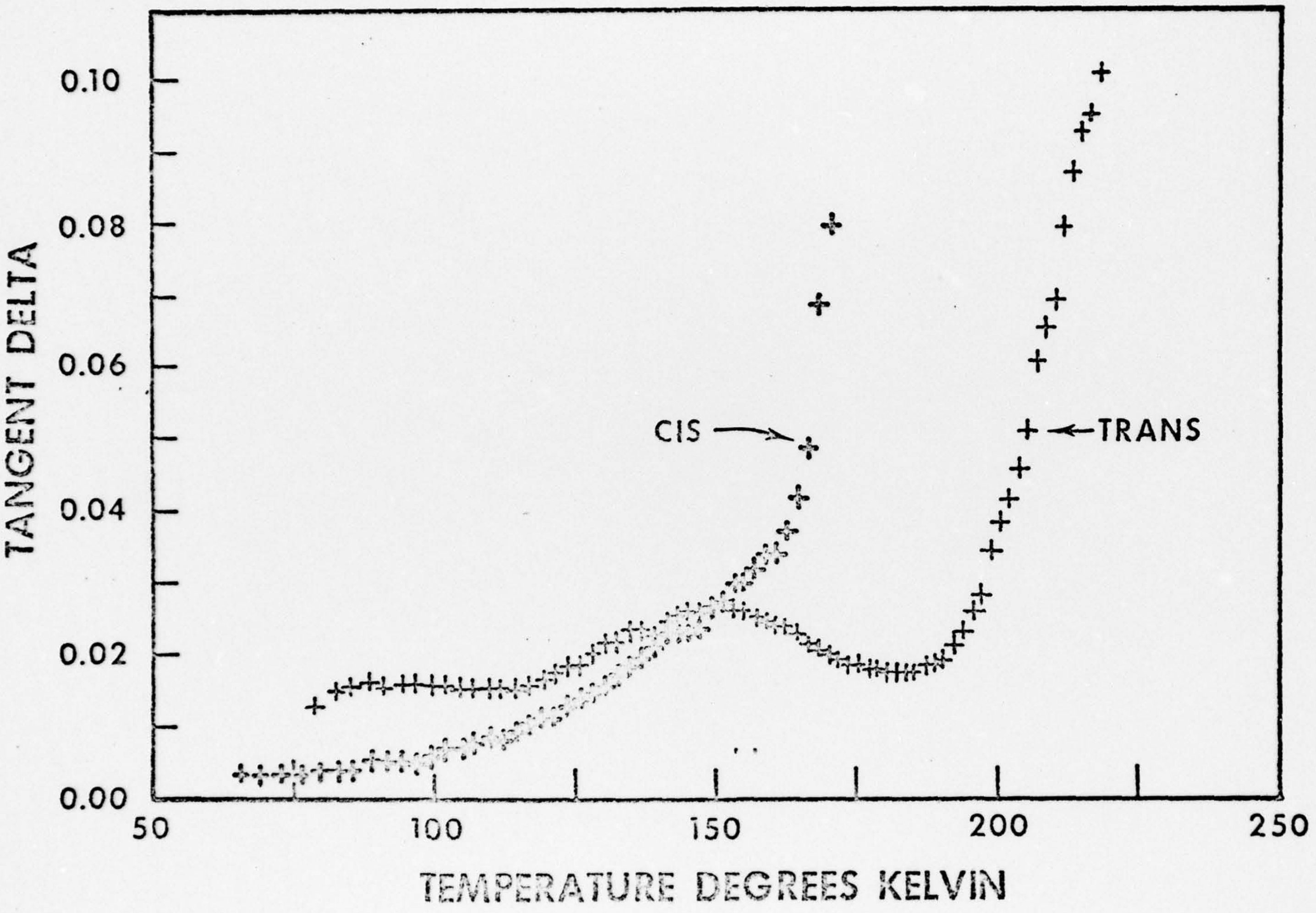
Captions for Figures

Figure 1: Loss tangent as a function of temperature for trans-polybutadiene and cis-polybutadiene.

Figure 2: Arhenius plot of trans-dienes and related polymers, maxima in tan δ_G vs T.

Figure 3: Loss tangent as a function of temperature for polyoctenamer and polypentenamer.



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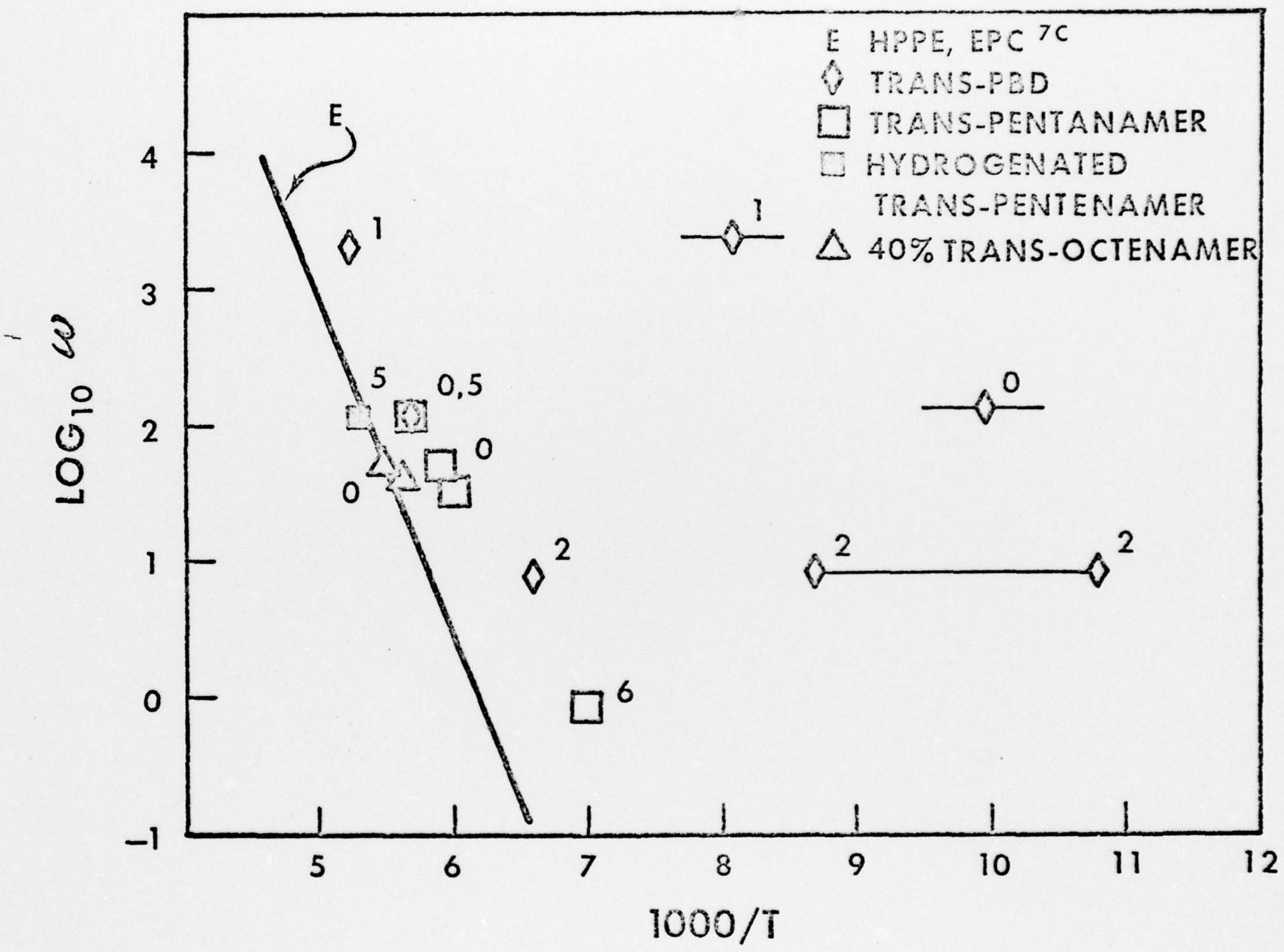
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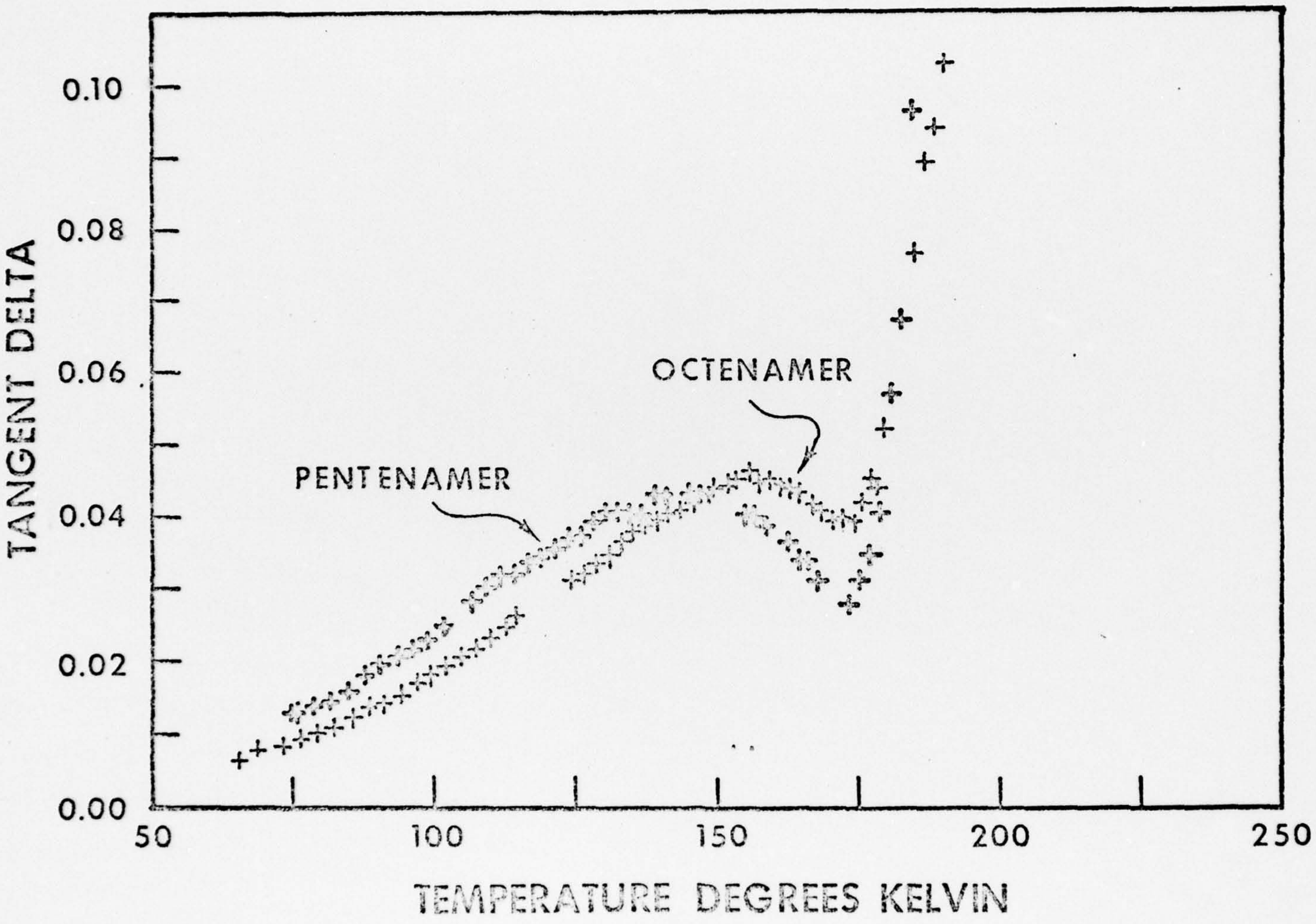
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