

Molecular Relaxations in the Glassy State of Polymers with Unsaturated Backbone Chains and Their Hydrogenated Derivatives

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SUMMARY

A study of the dynamic mechanical behaviour of poly-(propene-alt-1,4-butadiene), poly(styrene-b-isoprene) SIS triblock, and their hydrogenated derivatives has been carried out using torsional braid and rheovibron techniques. It was found that the existence of low temperature damping processes (120-160K/1Hz) depends on the molecular structure, particularly on the geometric isomerism of the double bond. Simple ring analogues have been used as models to elucidate the molecular mechanisms underlying these relaxation processes.

INTRODUCTION

While there is considerable interest in the sub-glass transitions which are detected in many polymers, the molecular mechanisms responsible are only firmly established in a few cases (COWIE 1979). Mechanisms have been proposed for relaxations involving either intramolecular motions in rings (HEIJBOER 1965) or sequences of methylene units both in the main chain (SCHATZKI 1962, BOYER 1963, BOYD AND BREITLING 1974) and in pendant side chains (SHIMIZU et alia 1975). Only limited attention has been afforded to structures containing sites of unsaturation in the main chain but some interesting data have emerged from work on polydienes and their hydrogenated derivatives.

MORGAN et alia (1971) noted significant differences in the dynamic mechanical spectra of cis and trans polydienes. In both trans 1,4 polybutadiene and trans 1,4 polyisoprene strong damping peaks centred on 130K and 150K respectively, were detected which were absent in the corresponding cis polymers. This difference due to geometric isomerism vanishes when an extra methylene unit is inserted between the double bonds, as evidenced by the appearance of damping maxima at 125K and 130K for both the cis and trans polypentenamers (BELL et alia 1974).

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In this work the dynamic thermomechanical response of two diene copolymers and their hydrogenated derivatives has been measured in order to assist identification of the sequences of atoms responsible for the low temperature damping processes and thereby determine the molecular mechanisms involved.

EXPERIMENTAL

SAMPLES: The copolymers used were (i) a triblock copolymer of styrene and isoprene (SIS) with the following characteristics: M_n (each styrene block) = 2.65×10^4 ; M_n (central isoprene block) = 1.43×10^5 with microstructure 70% cis 1,4, 25% trans 1,4, 5% 3,4 vinyl addition; and (ii) an alternating copolymer of propene and butadiene, $M_n = 1.36 \times 10^5$, with 97% trans 1,4 addition of the diene units.

HYDROGENATION: Samples were hydrogenated by refluxing a toluene solution of the polymer in the presence of p-toluene sulphonhydrazide (MANGO and LENZ 1973). The extent of hydrogenation was determined by n.m.r. analysis (COWIE and McEWEN 1977).

DYNAMIC MECHANICAL MEASUREMENTS: The mechanical damping index for each sample was measured as a function of temperature in the range 100K-470K by means of a torsional braid analyser (LEWIS and GILLHAM 1962) at a nominal frequency of 1Hz. Experimental procedures have been described elsewhere (COWIE et alia 1977). Frequency dependence measurements were made using a Rheovibron viscoelastometer DDVIIC, from which the activation energy ΔH^\ddagger for a given damping process could be determined.

RESULTS

The SIS series: The apparent thermomechanical damping index spectra for the unhydrogenated, the partially, and the fully hydrogenated samples are displayed in Fig.1. Significant differences can be seen, particularly the development of a strong damping process at 153K with increasing hydrogenation, which is absent in the spectrum of the starting material. A strong damping maximum at 215K is associated with the glass transition of the polyisoprene component and remains essentially unchanged with hydrogenation of the central isoprene block. The damping peak arising from the glass transition of the polystyrene block is relatively ill defined for all samples but can be located around 390K. There is evidence of a broad damping peak located between 270K and 320K in the partially and fully hydrogenated samples, and a similar feature was observed in the damping spectra of styrene-

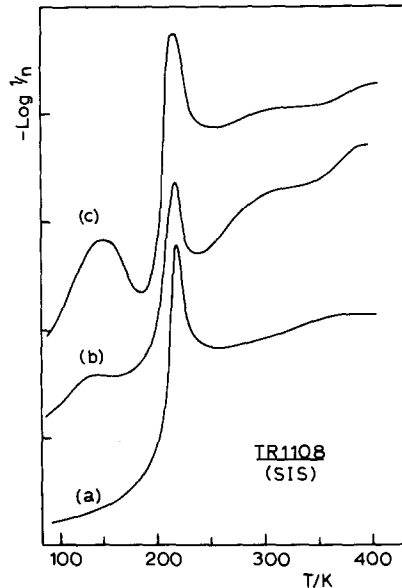


Figure 1. Damping spectra for (a) SIS copolymer (b) partially hydrogenated SIS and (c) fully hydrogenated SIS.

butadiene block copolymer films cast from carbon tetrachloride (BEECHER et alia 1969), which was attributed to phase blending in the system. The test samples investigated in this work were cast from toluene which has been shown to lead to dispersion of the polystyrene component in the matrix (SEGUELA and PRUD'HOMME 1978). This could encourage more extensive phase blending, but the results also suggest that hydrogenation of the polyisoprene results in a more compatible block copolymer system.

Poly(propene-alt-butadiene). The damping spectra for both the hydrogenated and unhydrogenated alternating copolymer are shown in Fig.2. In both samples, prominent damping peaks are seen at 150K followed by the large glass transition peaks representing T_g 's of 204K for the unhydrogenated sample and 209K for the hydrogenated polymer. In the parent copolymer a very broad damping peak is found at temperatures above T_g which is similar to that observed in low molecular weight polybutadienes (COWIE and McEWEN 1979). This feature becomes much sharper in the hydrogenated sample and may be related to the so-called $T_{\beta\beta}$ transition which has been observed in a large number of polymer systems (BOYER 1963).

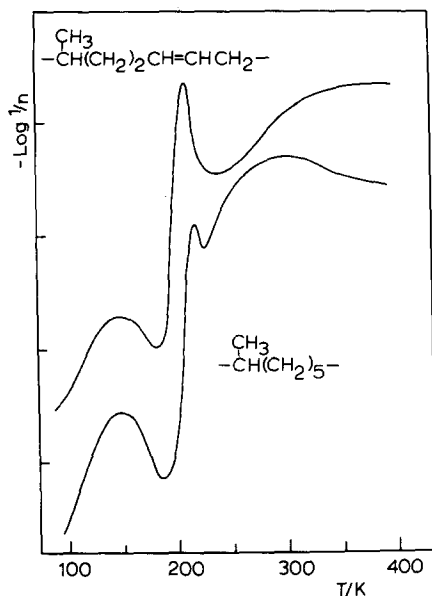


Figure 2. Thermomechanical damping spectra for hydrogenated and unhydrogenated poly(propene-alt-butadiene).

The activation energy for the damping process at 150K was measured in the frequency range 1-110 Hz and found to be $40 \pm 6 \text{ kJ mol}^{-1}$.

DISCUSSION

Glass and sub glass transition temperatures for structures containing unsaturated units in the main chain, and their hydrogenated counterparts, are summarised in Table 1. No significant relaxations are detected in the cis forms of poly(1,4-butadiene) or poly(1,4-isoprene) but the corresponding trans structures display mechanical damping peaks at 132K and 156K. It has been proposed (MORGAN et alia 1971) that the complex twisting motion, shown schematically in Fig.3, is a possible relaxation in the trans polymers. This is not a suitable mechanism for relaxation in the cis polymers and it is found that limited motion is much more difficult when the cis form is present in the backbone chain. Our earlier work (COWIE and McEWEN 1977) on hydrogenated cis 1,4-polybutadiene substantiates this observation, as it was demonstrated that a low temperature damping peak (150K/1Hz) was absent in the parent cis polydiene but developed progressively as the chain was hydrogenated.

TABLE 1

Glass and subglass transitions in polymers containing unsaturated units in the main chain and their hydrogenated analogues

| Polymer Structure | T _g /K | T _β /K | Ref. |
|---|-------------------|-------------------|--------------------------|
| a) $\{CH_2-CH=CH-CH_2\}$ | | | |
| cis | 177 | - | COWIE & McEWEN (1977) |
| trans | 215 | 132 | MORGAN et alia (1971) |
| b) $-CH=CH-(CH_2)_3-$ | | | |
| cis/trans ratio 18/82 | 160 | 125 | BELL et alia |
| 95/5 | 164 | 130 | (1974) |
| c) $\{CH_2-\underset{\substack{ \\ CH_3}}{C}=CH-CH_2\}$ | | | |
| cis | 215 | - | THIS WORK |
| trans | 215 | 156 | MORGAN et alia (1971) |
| d) $\{CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_2-CH_2\}$ | 218 | 150 | THIS WORK |
| e) $\{CH_2-\underset{\substack{ \\ CH_3}}{C}-CH_2-CH=CH-CH_2\}$ (trans) | 204 | 150 | THIS WORK |
| f) $\{CH_2-\underset{\substack{ \\ CH_3}}{C}-CH_2-CH_2-CH_2-CH_2\}$ | 209 | 150 | THIS WORK |

The peak first appeared when units of four to six consecutive methylene units were formed in the chain, imparting greater flexibility.

A better idea of the molecular mechanism can be obtained if a model system can be examined and in this respect it is instructive to consider a simple ring analogue of the appropriate unit present in the polymer chain. If limited motion can occur in a segment of the ring without causing undue disturbance in the rest of the system, then this relaxation is likely to occur in

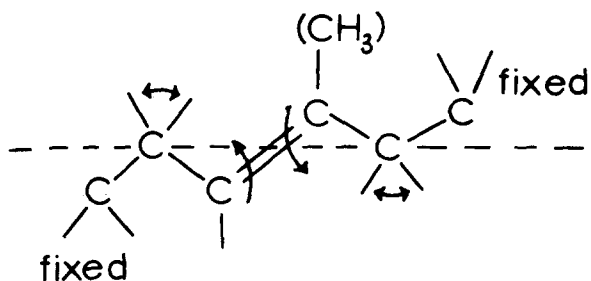


Figure 3. Suggested motion for trans polydienes

in comparable small units in a linear polymer chain, where the rigid polymer matrix will act in a restrictive manner similar to a ring system.

A useful analogue to consider is then cis,cis,cis, cyclododeca-1,5,9-triene which is in effect a cyclic trimer of cis 1,4-butadiene. Nmr studies have shown (BRICKWOOD et alia 1973) that conformational changes in this ring are difficult to accomplish and have to overcome energy barriers of over 70 kJ mol⁻¹. Thus comparable restricted motion in a cis 1,4-polydiene chain would have to surmount energy barriers of similar magnitude. The activation energy for the glass transition process in cis 1,4-polybutadiene was measured and found to be on average 90-100 kJ mol⁻¹. Thus the energetics of limited chain motion are virtually the same as that required for cooperative chain motion resulting in the merging of the processes so that they become essentially indistinguishable. This would explain why no sub-glass relaxations are found in the cis 1,4-polydienes.

A suitable model for the trans diene polymers is trans,trans,trans, cyclododeca-1,5,9-triene studied by DALE (1976) who has suggested that rotation of the trans double bond can be accomplished in this system with a much lower activation energy of about 36 kJ mol⁻¹ for the process. This would correspond to a 1Hz mechanical damping maximum around 140-160K in agreement with the experimental data for the trans polydienes. As the glass transitions take place at much higher temperatures and have activation energies of the order 100-120 kJ mol⁻¹, a sub-glass relaxation will be resolved in the trans diene systems.

The restrictive aspect of geometric isomerism is removed when one extends the sequence of methylene units in the

chain such as in the polypentenamers. Here both cis and trans structures display relaxations in the glass. In the ring cis,cis, cyclodeca-1,6-diene, the chair-chair conformational change, shown in Fig.4, has been identified and an activation energy of about 40 kJ mol^{-1} is estimated for the process (ROBERTS et alia 1974). The relaxation involves site exchange of geminal hydrogens with double bond rotation and would be an

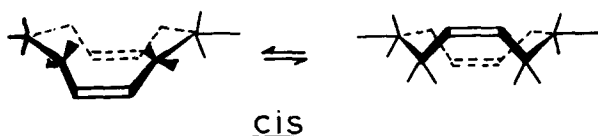


Figure 4. Chair-chair conformational change in cis,cis cyclodeca-1,6-diene.

appropriate mechanism for molecular motion in the cis polypentenamer or the partially hydrogenated cis polydienes. The extra methylene unit makes it easier for movement to take place in the cis chain and one could even postulate a reasonable crankshaft motion such as shown in Fig.5. The disadvantage of this model is that it requires co-linearity of the stem bonds and may therefore be a low probability structure.

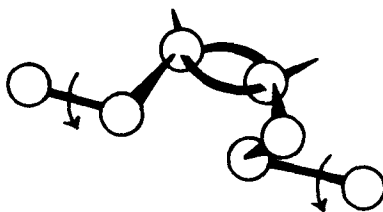


Figure 5. Crankshaft motion incorporating a double bond.

In the trans polypentenamer or the partially reduced trans polydiene, the molecular mechanism illustrated in Fig.6 can be postulated from an examination of models. Rotation around bond 1 activates bond 6 and moves the intervening three carbon unit through 120° with an estimated activation energy of about 35 kJ mol^{-1} .

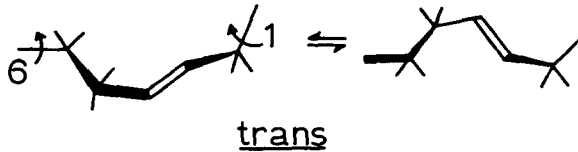


Figure 6. Possible mechanism for relaxation of unit containing a trans double bond in partially hydrogenated polydienes or polypentenamers.

No low temperature sub-glass transition damping peak was found in the spectrum of the SIS block copolymer studied. As the microstructure was predominantly cis 1,4-addition the result is in agreement with the analysis above. The development of a damping peak at 150K reflects a reduction in the restrictions to motion in the chain with the creation of extended methylene sequences. Most evidence points to the requirement that for a relaxation to occur in this temperature range, the chain must contain minimum sequence lengths of four to six σ -bonded atoms (KAJIYAMA and MACKNIGHT 1969). BOYD and BREITLING (1974) have examined some of the mechanisms used to explain sub-glass transition relaxations in a simple chain such as polyethylene. They concluded that the well known SCHATZKI (1962) crankshaft motion required too much volume but that a modified BOYER (1963) unit could undergo what they termed a "flip-flop" motion which was energetically feasible for a relaxation at 150K.

The change is depicted as a $tg^+tg^-t \rightarrow tg^-tg^+t$ movement and has an activation energy of 42 kJ mol^{-1} . An alternative, and equally feasible, mechanism has been proposed (COWIE 1979) which involves a $ttg^- \rightarrow g^-tt$ sequence change. Strain energy calculations (DALE, 1976) for this elementary process suggest an activation energy of about 34 kJ mol^{-1} , corresponding to a 1Hz mechanical damping maximum at a temperature in the range 150-160K. The mechanism is shown in Fig.7 with the minor modification that a pendant methyl group is now included in the chain. This should not alter the activation energy significantly and would explain the damping observed for structure (d) in Table 1. This structural unit also appears in the alternating copolymer, omitting the double bond, and so one would expect to find a low temperature relaxation in structure (e). This is indeed the case. However, as the double bond is in the trans configura-

tion a contribution from the relaxation of this unit is also likely.

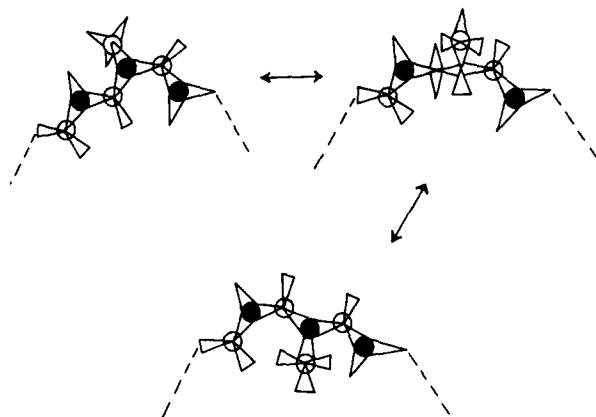


Figure 7. Elementary movement of a gauche bond two positions, i.e. $ttg^- \rightarrow g^-tt$.

The hydrogenated analogue, structure (f), has a variety of options open to it; a Boyd-Breitling "flip-flop", elementary migration of a gauche bond two places (Fig.7) and rotation of the methyl group are all mechanisms with the required activation energy. A recent ^{13}C study of the alternating copolymer in the melt led GRONSKI and MURAYAMA (1979) to suggest that three, five and seven bond rearrangements may take place. The first two of these are shown in Fig.8, but whether either occur in the glassy state remains open to speculation.

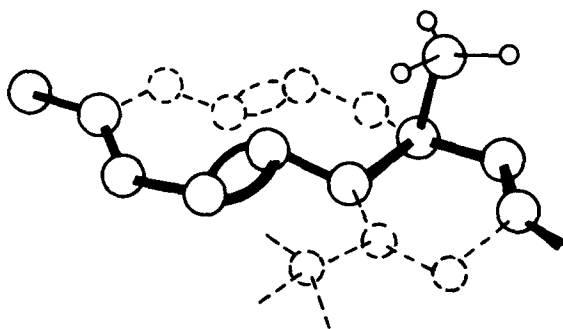


Figure 8. Three and five bond rearrangements in poly(propene alt-1,4-butadiene) melts, after GRONSKI and MURAYAMA (1979).

CONCLUSION

The study of intramolecular motions in ring systems which are model analogues for polymer chain segments can aid the understanding of molecular mechanisms responsible for relaxation processes in the glassy state. These have been used to explain (i) why the damping process seen at 120-160K in transpolydienes is absent when the cis form is examined, and (ii) why low temperature damping is detected in both cis and trans forms of polypentenamers or partially hydrogenated polydienes.

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