

Study of pressure-induced transitions of polyisoprene by laser Raman spectroscopy

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This paper reports isothermal pressure-induced glass transitions and β transitions of polyisoprene in the pressure range 0–2 GPa studied by laser Raman spectroscopy at room temperature. The values obtained are supported by experimental results of piston-cylinder isothermal compression. Elementary discussions on the mechanism of pressure-induced transitions are also given.

(Keywords: glass transition; Raman spectroscopy; polyisoprene)

INTRODUCTION

It is significant in theory and practice to study the structure and properties of polymer under high pressure. A series of transitions and structure relaxations in polymer will happen under high pressure, which affect its properties strongly. Transition pressures, moreover, as transition temperatures, are important parameters in characterizing the bulk structure and molecular motion of polymer. Many methods of studying transitions of polymer under normal pressure can be used in principle to study the pressure-induced transitions if the high pressure technique can be realized. Recently, Sasuga and Takehisa¹ studied the glass transition of polyisoprene at pressures up to 0.8 GPa by means of a dilatometer. Dalal *et al.*² have reported the relationship between the glass transition of polyisoprene and pressure in the pressure range of 0–0.38 GPa by use of dielectric relaxation. Because of the difference between the effects of heat and pressure, some methods which cannot be used under normal pressure may be used successfully to study pressure-induced transitions of polymer. In this paper, we have investigated isothermal pressure-induced transitions of polyisoprene between 0 and 2 GPa by laser Raman spectroscopy. Changes of Raman spectra associated with glass transition and β -relaxation have been found; furthermore, the above results are supported by experimentation of isothermal compression by piston-cylinder high pressure apparatus.

EXPERIMENTAL

Sample

Polyisoprene was synthesized with anionic polymerization in our laboratory. Its $\bar{M}_w = 1.59 \times 10^4$, $\bar{M}_w/\bar{M}_n < 1.1$. The contents of cis-1.4, trans-1.4 and 3.4 structure was 60%, 33% and 7%, respectively.

Measurement of high pressure Raman spectra

Hydrostatic pressure in the range 0–2 GPa was applied to the bulk of the polyisoprene sample at room temperature by a Mao–Bell³ miniature type diamond anvil cell. The pressure was calibrated by ruby fluorescence⁴. The scattering spectra were scanned at each pressure by SPEX 1403 double-grating monochromator. The 4880 Å of an Argon ion laser was used as an excitation line, the output power 300 mW, the slit width 800 μm .

Isothermal compression with piston-cylinder

The isothermal compression of polyisoprene was carried out at room temperature up to 1.9 GPa by a piston-cylinder high pressure apparatus; for the arrangement of the measuring device, methods of experiment and dealing with the data refer to refs. 5 and 6.

RESULTS AND DISCUSSION

Analysis of Raman spectra

Raman spectra of polyisoprene (*Figure 1*) recorded at normal pressure by us were identical with those found by Cornell and Koenig⁷. The relevant bands were classified into two sorts for connecting them with the molecular motions of polyisoprene: those relevant to the motions of main-chain are =CC₂ rocking vibration band at 493 cm⁻¹, =CHCH₂ rocking vibration band at 996 cm⁻¹ (since the sample contains 93% 1.4-structure, the contribution of 3.4-structure side group to the above two bands can be neglected), C=C stretching vibration band at 1664 cm⁻¹ and –CH₂– in plane stretching vibration band at 2913 cm⁻¹. Those relevant to the motions of side-group are –CH₃ rocking vibration band at 1038 cm⁻¹. From *Figure 2* we see that 493 cm⁻¹, 1664 cm⁻¹ and 2913 cm⁻¹ are distinctly associated with main-chain motion shift clearly as the pressure is enhanced. The relationships between the frequency shifts

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and pressure are shown in Figure 3. There are considerable changes of frequency shift within 0.60–0.80 GPa. We have also found that the intensity of the side group $-\text{CH}_3$ rocking vibration band enhances and that of the main chain group $=\text{CHCH}_2$ rocking vibration band weakens as the pressure is raised. Plotting the relative intensity ratio of those two bands $\{I(-\text{CH}_3)/I(=\text{CHCH}_2)\}$ versus pressure in Figure 4, we see that the curve has two considerable turning regions at 0.60–0.80 GPa and 1.70 GPa, respectively. These results indicate that the sample must undergo structure transitions at about 0.7 and 1.7 GPa. The sample having 60% cis-1,4, 33% trans-1,4 and 7% 3,4 structures is difficult to crystallize⁸. No crystallization has been found and no chemical change occurred during the experimental pressure. Thus, the transition at approximately 0.70 GPa, as stated above, is believed to be the glass transition characterizing the forced freezing of main-chain motion. It is suggested that the relative intensity ratio of two bands suddenly changes to a new value at about 1.70 GPa and should be correlated to the β transition characterizing the forced freezing of side-group motion.

RESULTS OF ISOTHERMAL COMPRESSION

Boyer⁹ has indicated that the jump point of B_T corresponds to the secondary transition pressure when the isothermal compressibilities are treated with linear Tait equation:

$$\exp(-\Delta V/V_0 C_T) = A_T + P/B_T \quad (1)$$

where $C_T=0.0894$ is a universal constant for polymer. Yang⁶ also suggested that when using the linear

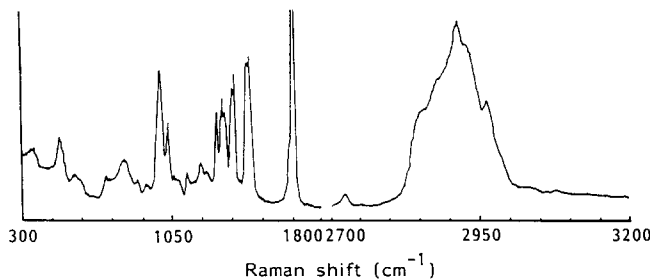


Figure 1 Raman spectra of polyisoprene at normal pressure

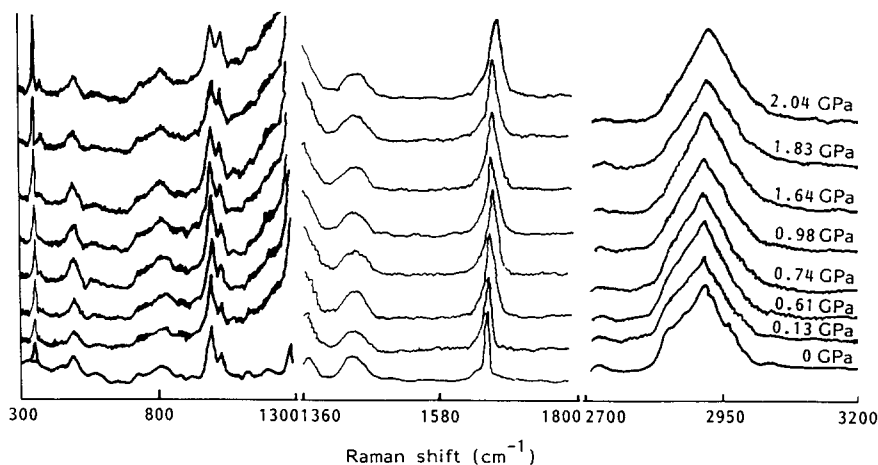


Figure 2 Raman spectra of polyisoprene at several pressures

Murnaghan equation

$$(V_0/V)^{1/C_M} = A_M + P/B_M \quad (2)$$

where $C_M=0.1016$ is also a universal constant for polymer, the value of B_M also jumps at the point of pressure-induced transition and the transition pressure can be evaluated by

$$P_i = B_i B_{i+1} \Delta A_i / \Delta B_i \quad (3)$$

Figure 5 shows the results of fitting the isothermal compressibilities by use of the linear Tait and linear Murnaghan equations. It is found that four transitions happened at 0.46 GPa, 0.63 GPa, 0.80 GPa and

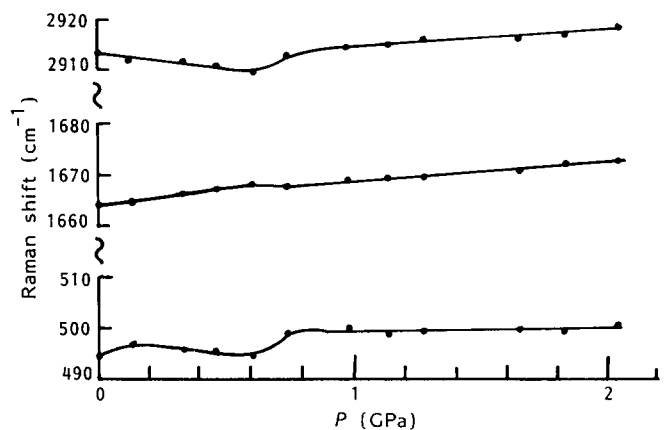


Figure 3 Relationship between frequency shifts and pressure

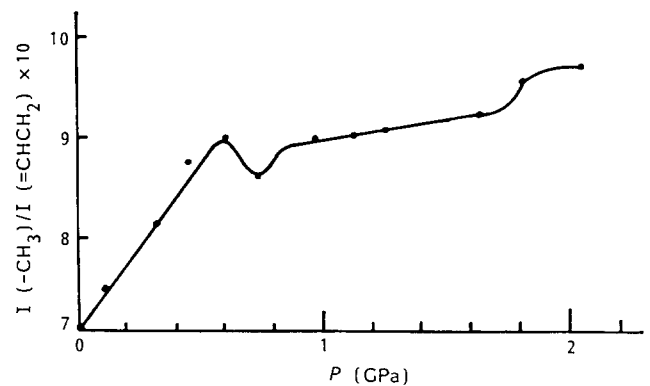


Figure 4 Relative intensity ratio of $I(-\text{CH}_3)/I(=\text{CHCH}_2)$ versus pressure

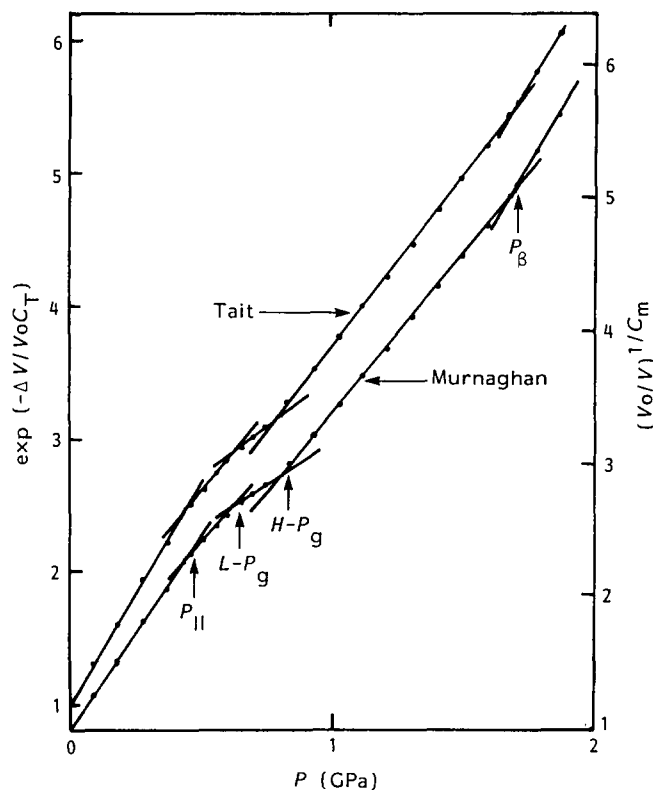


Figure 5 Isothermal compressibilities fitted by linear Tait and Murnaghan equations

1.70 GPa, respectively. According to the theory of polymer multiple transitions¹⁰, the liquid₂-liquid₁ transition (P_{II}), low-pressure glass transition (L-P_g), high pressure glass transition (H-P_g) and β transition (P_{β}) are concluded from lower to higher pressure as stated above, respectively. Therefore, it is shown that the transition within 0.6–0.8 GPa reflected by Raman spectra is the glass transition, and the transition at 1.7 GPa is β transition. The P_g given by us is consistent with that measured by Sasuga and Takehisa¹ using a dilatometer. The liquid₂-liquid₁ transition at 0.46 GPa, however, has not been reflected by Raman spectra.

FREQUENCY SHIFT

Under the effect of pressure, intermolecular distance, intramolecular space and molecular conformation of polymer will all change. The contribution of change of molecular conformation is more important with regard to the pressure-induced transitions. As apparent from Figure 3, the frequencies of the bands of =CC₂ and -CH₂ in the main-chain shift first to lower frequencies before L-P_g and then to higher frequencies, and after H-P_g, tended to be stable. Meanwhile, it can be found that below L-P_g the band of C=C vibration shifts to a higher frequency, after L-P_g is almost unchanged, and after H-P_g shifts very slowly to a higher frequency again. Generally, the frequency slow-down is due to the extension of corresponding chemical bonds or groups, which implies the local stretching of the molecular chain. On the other hand, the increased frequency is due to the shrinking of chemical bonds or groups, which implies local contraction of the molecular chain. Thus, the above situation indicates that the C-C single bonds of main-chain extend first with increasing pressure, and

simultaneously the C=C double bond of main-chain shrinks; as a result, they cause the molecular dimension to shrink slowly, and the segmental motion to weaken. Up to L-P_g the C-C single bonds begin to shrink rapidly. The unanimous contractions of molecular chain lead the molecular dimension to shrink rapidly, and segmental motion to stop. After H-P_g, the C-C and C=C bonds all shrink slowly, so that the frequencies after 0.80 GPa are bigger than the base frequencies. This indicates that no matter what the process is the total change tendency of the dimension of the molecular chain becomes smaller with increasing pressure. Combining with the above two processes we can obtain a scheme such that at viscous-flow state, the molecular chains of polymer are random coil; there is great space or free volume between and within the molecules. With increasing pressure, the distance between molecules shortens, and the contraction of space between molecules intensifies. To compensate for these changes, the conformation of the molecular-chain rearranges and this makes the axial ratio of the chain coil become bigger, the dimension gradually smaller. After L-P_g this rearrangement becomes slower. Until H-P_g the conformation of the molecular chain has been stabilized and a glassy state is reached; the globate form of the molecular coil is replaced by the oval form or the rod form. If the pressure field is considered as a closed tube, of which the diameter is continuously condensing, the above-mentioned changes of polymer coil may be easily understood.

RELATIVE INTENSITY

The weakening in intensity of the =CHCH₂ rocking vibration band associated with the motion of main-chain with increasing pressure, as shown in Figure 2, is due to the hardening of the molecular chain and contraction of the chemical bond. In contrast, the increase of the intensity of the side group -CH₃ rocking vibration band results from the relative stretch of the group. Brown¹¹ has indicated that the intensity of the band for a particular group is related to its space configuration. The intensity of the vibration band of the methyl group with plane configuration is much weaker than that of the methyl group with tetrahedral configuration. It may be considered that at viscous-flow state the motion of the polyisoprene main-chain was so strong that the configuration of the methyl group was arrested and behaved to a large extent as a plane configuration. With increasing pressure the motion of the main chain is controlled, and the motion of the side-group is gradually isolated, so the methyl group is gradually restored to a tetrahedral configuration. At P_g the long-range motions of the main-chain stop, the coordinative long-range motions of the side group and main-chain do not exist, so that the relative intensity is changed. At P_β the contribution of the methyl configuration becomes more important and leads to another change of relative intensity. Thus, Raman information of β transition can also be detected.

CONCLUSION

The pressure-induced glass transitions and β transitions in a pressure range of 0–2 GPa have been measured by laser Raman spectroscopy and confirmed by experimental results of piston-cylinder isothermal

compression. The values of P_g given by Raman spectra are consistent with those reported by the literature. The information on the molecular motion and structure relaxation mechanism of polymer under pressure can also be drawn from Raman spectra.

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