

An Enantiomorphic Crystal-Crystal Transition of *trans*-Polybutadiene

R. NAGAO

The behaviour of trans-polybutadiene in an enantiomorphic crystal-crystal transition was measured by X-ray diffractometry and volume dilatometry. The crystal-crystal transition ranges lay between 33.1° and 43.3°C for the formation of a modification II as a decreasing I modification in the heating process, and between 36.5° and 26.3°C for the formation of a I modification as a decreasing II modification in the cooling process, as determined directly by taking X-ray diffraction diagrams of trans-polybutadiene. The specific volume/temperature curve of trans-polybutadiene shows a characteristic shape at the crystal-crystal transition ranges.

NATTA *et al.*¹ indicated a crystal-crystal transition point of *trans*-polybutadiene at a characteristic point (76°C) of the specific volume/temperature curve in the heating process. According to my observation this point is an end point of the crystal-crystal transition at which the I modification transfers to the II modification completely.

EXPERIMENTAL

A *trans*-polybutadiene prepared at the Phillips Petroleum Co. was used in the study. The sample dissolves well in chloroform and carbon tetrachloride at room temperature. The *trans*-1,4 content of the sample is 91 mole per cent as estimated from infra-red analysis.

X-ray diffractometry was used in the temperature range between room temperature and 105°C in order to observe the enantiomorphic crystal-crystal transition. The apparatus used was a Geigerflex standard X-ray diffractometer constructed by the Rigaku-Denki Co. Ltd, of Japan. The powder X-ray diffraction spectra were taken by Cu K_α-rays.

Volume dilatometry was used to measure the temperature dependence of the specific volumes in relation to the crystal-crystal transition; the accuracy of specific volume was to four figures when 1 g of a specimen and 25 g of mercury as the confining liquid were used.

A rate of temperature variation of a sample in measurement was five minutes per degree.

RESULTS AND DISCUSSION

The X-ray spectra of temperature variation are shown in *Figure 1*. At 22.0°C the *trans*-polybutadiene shows a pure I modification pattern; at 55.0°C it shows a pure II modification pattern, and at 105.0°C it shows a melted state, while the other three spectra show the coexistence of the I and II modifications. The powder X-ray spectra of the annealed specimen measured from room temperature down to -196°C all showed the I modification pattern.

Figure 2 shows the ratio of the diffraction intensities of the main peaks of the I and II modifications (I_{II}/I_I and I_I/I_{II}) against the temperature in

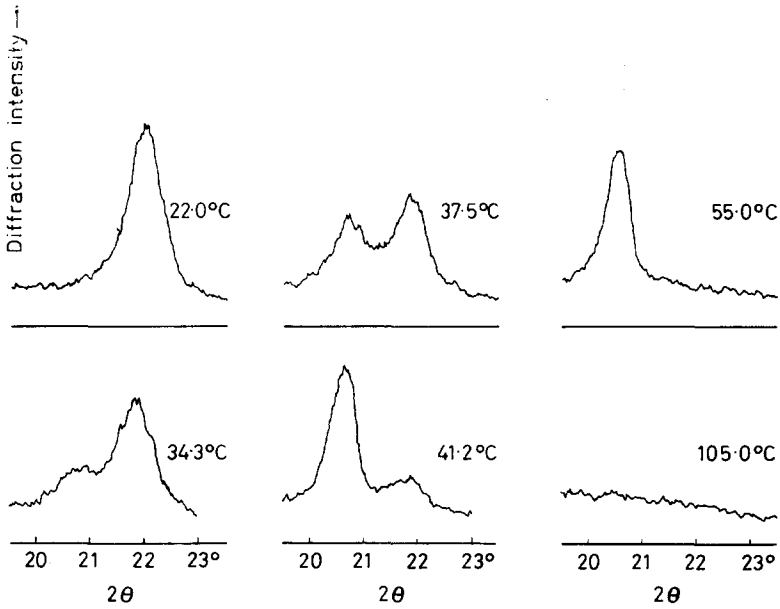


Figure 1—X-ray diffraction powder spectra of *trans*-polybutadiene (the annealed specimen) taken with 35 kV and 12 mA at the I-to-II crystal-crystal transition

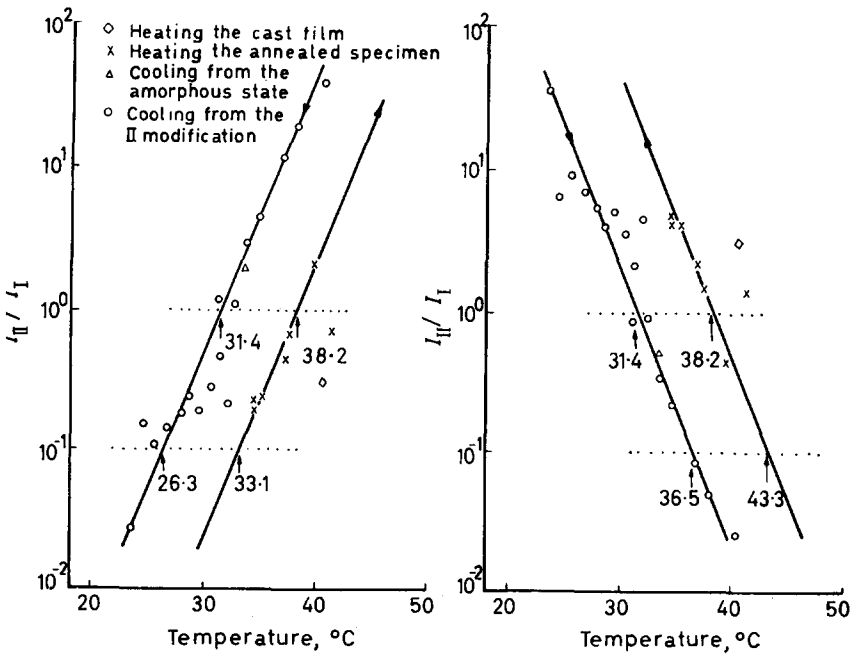


Figure 2—Diffraction intensity ratio/temperature curves

the crystal-crystal transition range; the intensities are free from the incoherent and amorphous-part diffraction. Measurements were carried out for four processes; heating the cast film from room temperature to the amorphous state, cooling the amorphous state to room temperature, heating the annealed specimen from room temperature to the amorphous state, and cooling the II modification to room temperature. From *Figure 2* the crystal-crystal transition points for the heating (the I-to-II transition) and cooling (the II-to-I transition) processes were determined as temperatures corresponding to the 1.0 value of the longitudinal axis; these temperatures are 38.2° and 31.4°C respectively. The crystal-crystal transition ranges for the heating and cooling processes were determined at temperatures corresponding to the 0.1 value of the longitudinal axis being regarded as nearly 0.0 because values less than 0.1 were within the error of measurement; thus ranges were obtained between 33.1° and 43.3°C and between 36.5° and 26.3°C respectively.

Figure 3 shows the temperature dependence of the crystal-plane distances (d_{hkl}) in the crystal-crystal transition ranges.

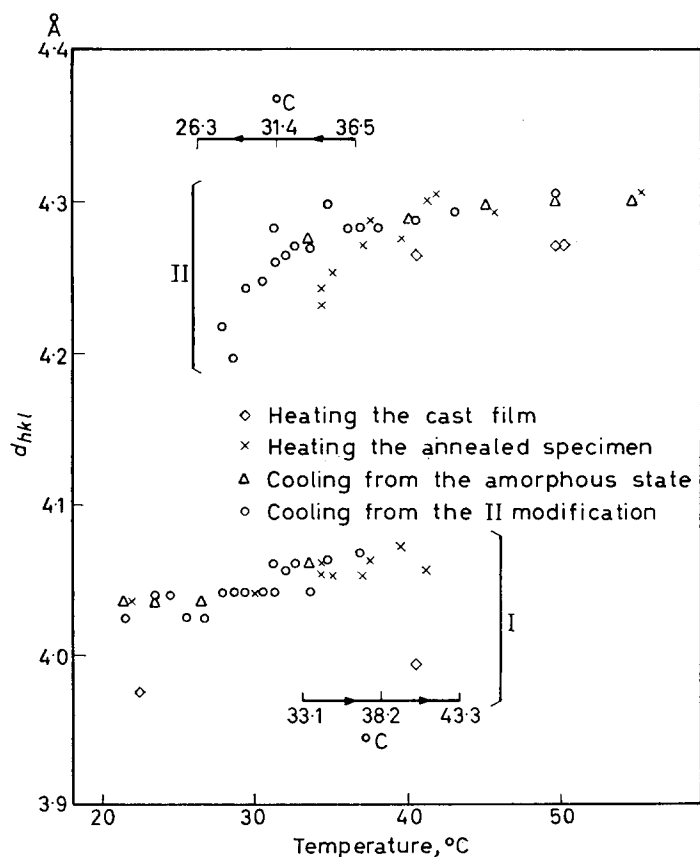


Figure 3—Crystal-plane distance/temperature relationship

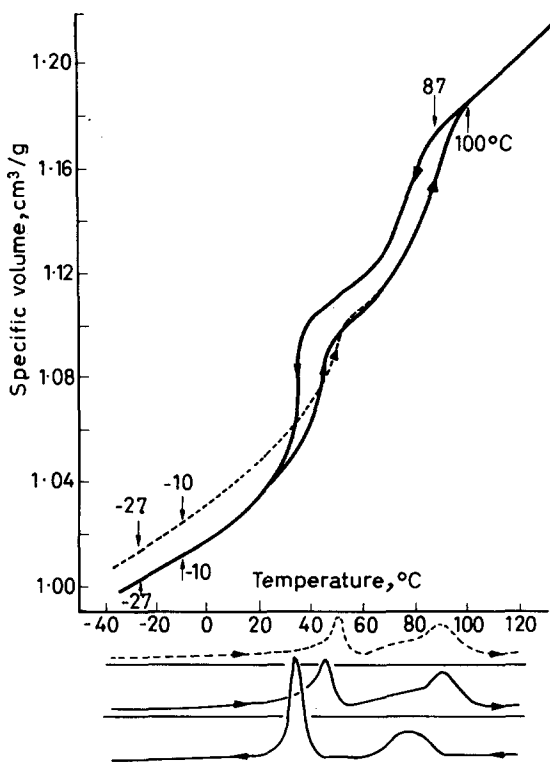


Figure 4—Specific volume/temperature curves and the derived curves

Figure 4 shows the specific volume/temperature curve. The dotted line, the solid line with the lower values, and the solid line with the higher values show the behaviour, respectively, of the cast film in the heating process, of the annealed specimen in the heating process, and of the specimen during the cooling process from the amorphous state. The specific volumes of the cast film are larger than those of the annealed specimen between -38° and 45°C and between 52° and 70°C , as with cast *trans*-polyisoprene, in which the same phenomenon occurs below 55°C though on a larger scale than this. The derived curves of the specific volume/temperature curves of the above three cases are gathered in Figure 4. As the fourth case, the behaviour of the specimen during the cooling process from the II modification at various temperatures is shown in Figure 5 in terms of the volume/temperature relationships, which possess, regarding the temperature axis, the same characteristics as the specimen during the cooling process from the amorphous state (the upper dotted line). Therefore, in the crystal-crystal transition we can only remark the three cases, the case of the cast film (the I-to-II transition), the case of the annealed specimen (the I-to-II transition), and the case of the specimen during the cooling process from the amorphous state or II modification at various temperatures (the II-to-I transition).

CRYSTAL-CRYSTAL TRANSITION OF *TRANS*-POLYBUTADIENE

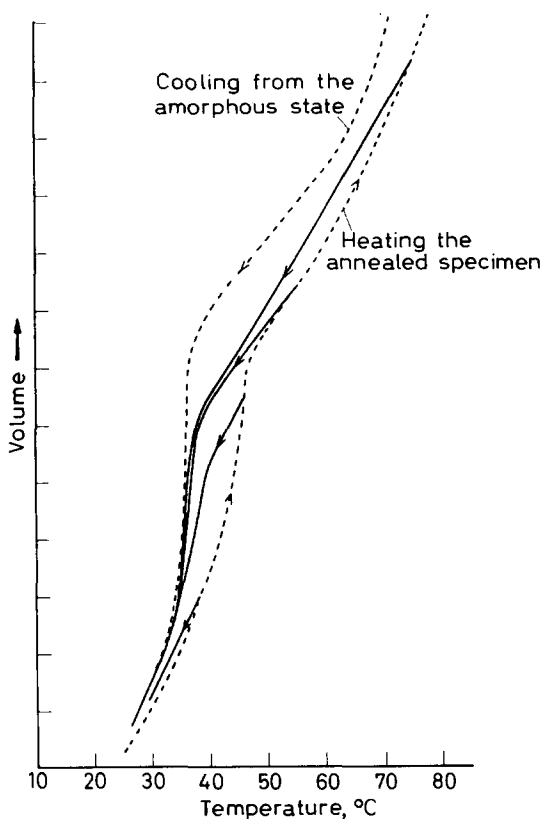


Figure 5—Volume/temperature curves during cooling from the II modification

The temperatures in the crystal-crystal transition range corresponding to the characteristic shape of the specific volume/temperature curve are compared in *Table 1* with the transition ranges and points determined by X-ray diffractometry. The crystal-crystal transition points defined in the present paper by the X-ray method exist around the abrupt increase or decrease in specific volume shown in *Figure 4* but not at the peaks of the derivative curves of the specific volume/temperature curves. Therefore, the range and point of the enantiomorphic crystal-crystal transition of *trans*-polybutadiene can be assumed roughly from dilatometric data.

The degree of crystallinity was estimated from the specific volume using the 100 per cent crystalline specific volume of the I and II modifications (0.9795 and 1.076 cm^3/g respectively)^{4,5}. They are set out in *Table 2*.

CONCLUSIONS

At an enantiomorphic crystal-crystal transition of an annealed *trans*-polybutadiene with a 91 mole per cent *trans*-1,4 unit the transition ranges were 33.1° to 43.3°C (the I-to-II modification) and 36.5° to 26.3°C (the

Table 1. Transition temperatures, °C

Crystal-crystal transition				
<i>Cast</i> (I-to-II)	<i>Annealed</i> (I-to-II)	<i>During cooling</i> (II-to-I)		<i>Method</i>
—	33.1–43.3 (38.2)	26.3–36.5 (31.4)	Range Point	X-ray: intensity
31–54 (42.5)	33–50 (41.5)	25–40 (32.5)	S-shaped range Middle point	Dilatometry: volume
40–57 (50.5)	35–52 (45.5)	27–43 (34.0)	Peak range Peak point	Dilatometry: temperature coefficient of volume
In the literature				
	35–56		Range	Sound velocity ²
	54		Point	Damping factor ²
	44		Point	Specific heat ³
	76		Point	Specific volume ¹
II Modification				
<i>Melting</i>	<i>Crystallization</i>		<i>Method</i>	
97	84	Point	X-ray: intensity	
100	87	Point	Dilatometry: volume	
80–100 (90)	65–90 (77)	Peak range Peak point	Dilatometry: temperature coefficient of volume	

Table 2. Degree of crystallinity as a weight per cent

<i>Sample</i>	<i>I modification</i> at 20°C	<i>II modification</i> at 50°C
Cast	47.6	77.7
Annealed	57.8	62.9

II-to-I) and the transition points were 38.2° and 31.4°C for the I-to-II and II-to-I transitions respectively as determined by X-ray diffractometry.

The transition range and point can be estimated roughly from the characteristic shape of the specific volume/temperature curve.

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Department of Chemistry,
Tokyo Science University,
Shinjuku, Tokyo, Japan

REFERENCES

- ¹ NATTA, G. and MORAGLIO, G. *Rubber Plastics Age*, 1963, **44**, 42
- ² BACCAREDDA, M. and BUTTA, E. *J. Polym. Sci.* 1961, **51**, S39
- ³ DAINTON, F. S., EVANS, D. M., HOARE, F. E. and MELIA, T. P. *Polymer, Lond.* 1962, **3**, 297
- ⁴ NATTA, G. and CORRADINI, P. *Nuovo Cimento*, 1960, **15**, Suppl. 1, 9
- ⁵ NATTA, G., CORRADINI, P. and PORRI, L. *Atti Accad. Nazl. Lincei*, 1956, **20**, 728