Structure of solution-grown *trans*-1,4-polyisoprene crystals: 1. Determination of stem length and fold surface structure by ozonolysis–g.p.c. measurement

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Crystallization of synthetic *trans*-1,4-polyisoprene (TPI) at $-20°C$ in hexane and amylacetate solutions gave chain-folded α-type crystals with 53% and 57% crystallinity, respectively. Selective ozonolysis degradation of the isoprene units in the surface folds associated with high-resolution g.p.c. measurement was used to determine the crystalline stem length, stem length distribution and fold surface structure of the α-TPI crystals. As ozone uptake increased, the isoprene units of the main fraction of oligomer products were found to decrease from 13, reaching a constant value at 11 for hexane and 12 for amylacetate. The polydispersity of the oligomer fractions was found to be in the range of 1.01–1.02. These findings suggested that the chain fold structure might be tight folding with slightly irregular folds, with a stem length of 11 monomers and a dispersion of 2.3 for lamellae grown from hexane, and 12 monomers with dispersion of 2.3 for those grown from amylacetate.

INTRODUCTION

Recently, the stem length and the fold length of solution-grown *trans*-1,4-polyisoprene (TPI) crystals have been determined by selective epoxidation[1–3] and hydrochlorination[4] in combination with electron microscopy or [13]C n.m.r. The stem length and the fold length were estimated from the average unreacted and reacted chain lengths, respectively. The average unreacted and reacted chain lengths were found to be in the range of 15–17 isoprene units and 9–13 isoprene units, respectively, by employing epoxidation in suspension of β-TPI lamellae. For hydrochlorination, the average number of isoprene units in crystalline traverse and per fold were found to be 10–16 and 4.5–5.2, respectively.

The fold surface of polyethylene single crystals was studied by oxidation using nitric acid[5–7], fuming nitric acid[8–10] and ozone[7,11,12]. The two peaks obtained from g.p.c. measurement were thought to relate to molecular lengths corresponding to single and double traverses of the lamella. These experimental values of the molecular length were in the ratio of 1:2 within 5% as would be expected for tight folding, although the condition used for oxidation was not clarified.

So far, we have successfully applied selective ozonolysis in combination with high-resolution g.p.c. to determine the stem lengths of solution-grown crystals for *trans*- and *cis*-1,4-polyisoprenes as well as for *trans*- and *cis*-1,4-polybutadienes[13].

This paper describes the application of this method under well controlled conditions for the determination of the crystalline stem length in isoprene units and the fold surface structure of α-TPI crystals which were crystallized at $-20°C$ in hexane solution and in amylacetate solution.

EXPERIMENTAL

Synthetic TPI (TP301, Kuraray Co., Japan) was purified by precipitation from toluene solution into methanol in the usual way. Its microstructure was found to be composed of 99% *trans*-1,4 by [1]H n.m.r. G.p.c. measurements showed $\bar{M}_w = 1.4 \times 10^5$, $\bar{M}_n = 7.0 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 2.0$.

Crystallization of TPI was carried out in 0.2% (w/v) solutions by dissolution of 200 mg polymer at 60°C in hexane solution and at 80°C in amylacetate solution, followed by cooling rapidly to a crystallization temperature of $-20°C$ and holding at that temperature for 5 h in hexane solution and 24 h in amylacetate solution. The suspended TPI crystals in hexane were subjected to ozonolysis. The TPI crystals were washed and then dried in a vacuum oven at room temperature before being characterized by d.s.c., density and X-ray diffraction measurements.

D.s.c. measurements were made with a Rigaku TAS-200 thermal analyser. The samples (about 2 mg)

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were heated from $-20°C$ to $100°C$ at a scanning rate of $10°C\,min^{-1}$. The melting temperature was obtained from the maximum of the endothermic peak.

Densities of the dried polymer crystals were determined by the flotation method using the density of a mixture of acetic acid and ethanol. Density measurements were carried out at 20°C by using pycnometers with a nominal volume of 25 cm^3. Weight-fraction crystallinity, W_c, was calculated using the well known equation:

$$W_c = (\rho_c/\rho)[(\rho - \rho_a)/(\rho_c - \rho_a)]$$

where ρ, ρ_a and ρ_c are the densities of the sample, the totally amorphous and totally crystalline polymer, respectively. For TPI crystals, ρ_a and ρ_c were reported to be 0.905 g cm^{-3} and 1.05 g cm^{-3} for α-type crystals[14], respectively.

X-ray diffraction patterns from the powder specimens were recorded with a cylindrical camera, 50.0 mm in radius, using nickel filtered CuKα radiation (Rigaku Denki Co., Ltd).

The morphology of some TPI crystals was investigated using a H-700H Hitachi transmission electron microscope (TEM). A crystal suspension was dropped onto a carbon-coated grid, dried and then shadowed with Pt-C before viewing with the TEM.

The ozonolysis technique involved blowing about 1.0% ozonated oxygen into the suspension solution of TPI crystals in hexane at about $-20°C$. The resulting ozonides were decomposed to alcohols by reduction with 1% (w/v) LiAlH$_4$ in diethyl ether. The oligomer fractions of the single traverses and the double traverses were separated by extraction of the whole product with methanol and acetone, respectively. The dry oligomer product was dissolved in 20 ml CHCl$_3$ from which 1,4-pentanediol, resulting from the amorphous part, was removed by washing three times with 10 ml water. The ozone uptake increased corresponding to the increase of reaction time and was calculated from the difference between the total amount of ozone (moles) blown into the vessel and the excess ozone (moles) from the reaction vessel, which was trapped by potassium iodide aqueous solution.

G.p.c. measurements were made using a Jasco 880-PU as a high pressure pump and a Jasco 830-RI detector. Chloroform was used as an eluent. The chromatographic columns used were two analytical columns in series (7.5 mm i.d. × 500 mm, theoretical plate number 19 800 and 21 000) and two preparative columns in series (21.2 mm i.d. × 600 mm, theoretical plate number 20 000 and 28 000). The columns were packed with styrene–divinylbenzene gel[15] having an exclusion limit of 3000 for high-resolution measurements.

Further fractionation of each fraction of oligomer products was carried out by high performance liquid chromatography (h.p.l.c.). Two ODS-silica columns (21.2 mm i.d. × 600 mm) were used in series. The molecular weights of some fractions obtained were determined by field-desorption mass spectroscopy measurements.

The ^1H and ^{13}C n.m.r. spectra of oligomer fractions were obtained using a Jeol JNM FX-200. The measurements were carried out at room temperature in CDCl$_3$ solution with tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

Properties of the solution-grown TPI crystal

The TPI crystals were found by X-ray diffraction to be α-type[16,17]. *Table 1* summarizes the properties of solution-grown TPI crystals from hexane and amylacetate, including melting endotherm, density and weight-fraction crystallinity. The crystal grown from amylacetate has a higher melting temperature and also weight-fraction crystallinity than that grown from hexane.

Figure 1 compares the d.s.c. thermogram of the TPI crystal grown from hexane to that grown from amylacetate. The appearance of a single peak in d.s.c. together with the X-ray evidence indicates that crystallization of TPI at $-20°C$ for 5 h in hexane solution and at $-20°C$ for 24 h in amylacetate solution, after rapid transfer from dissolution temperature, gave only α-type crystals. The heats of fusion of the TPI crystal grown from hexane and that grown from amylacetate were found to be 9.1 kJ mol^{-1} and 8.4 kJ mol^{-1}, respectively, after correction for the crystallinity, and the latter crystal exhibits a higher melting temperature by 1.5°C. From electron microscopy evidence, the chain-folded TPI crystals were found to be a mixture of monolayers, bilayers and piled-up lamellae (*Figure 2a*). The existence of the TPI single crystals was confirmed by the electron diffraction pattern shown in *Figure 2b*. Information on the crystal form and thermodynamic properties, including crystallization conditions of the solution-grown TPI crystals, are reported in detail in subsequent papers[17,18].

Stem length and fold surface structure

The oligomer fraction, obtained by ozonolysis of solution-grown TPI crystals in hexane followed by reduction with LiAlH$_4$, was found by ^1H and ^{13}C n.m.r.

Table 1 Properties of solution-grown TPI crystals from hexane and amylacetate

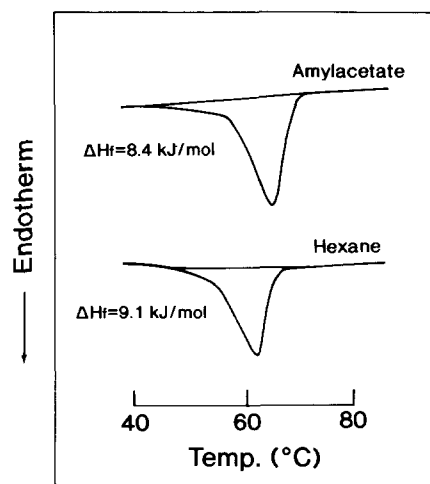| Solution	Crystal form	T_m (°C)	ρ (g cm^{-3})	W_c
Hexane	α	61.5	0.9765	0.53
Amylacetate	α	63.0	0.9822	0.57

Figure 1 D.s.c. thermograms of α-TPI crystals crystallized isothermally from hexane and amylacetate at $-20°C$. Scanning rate 10°C min^{-1}
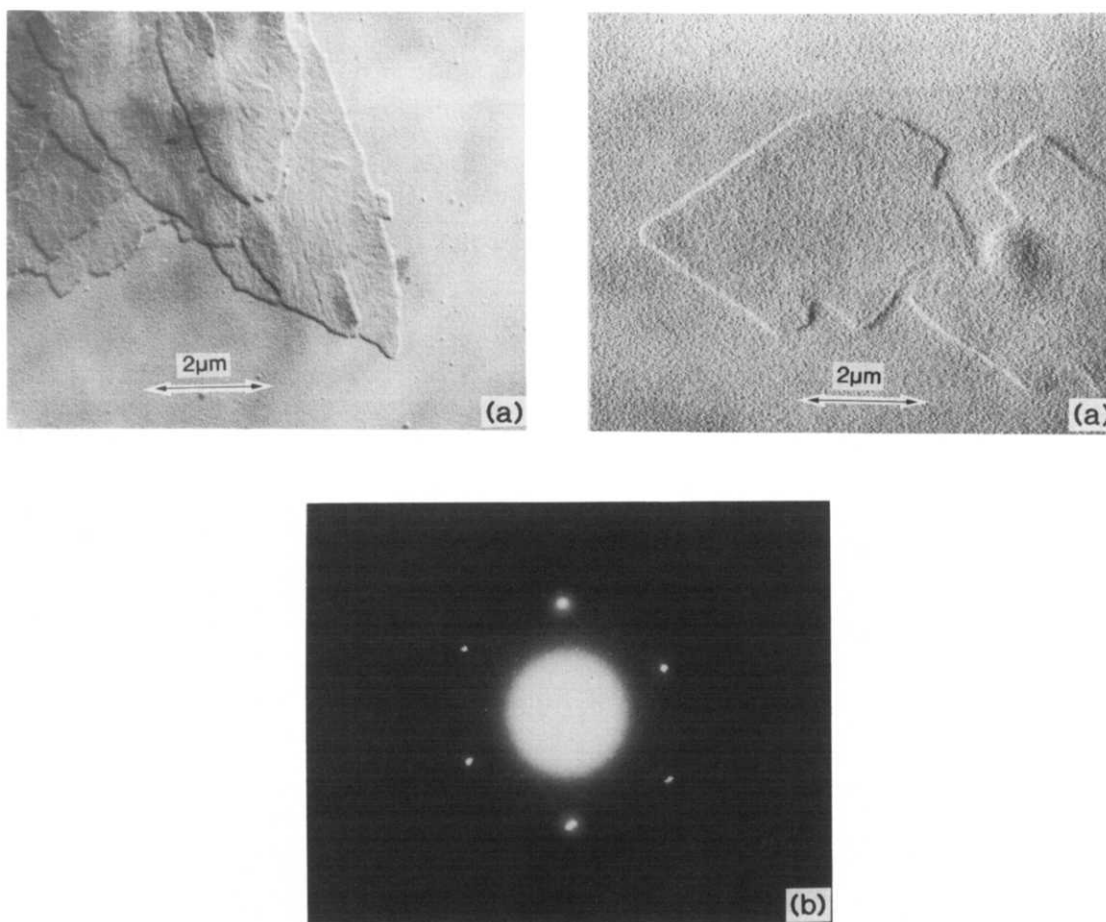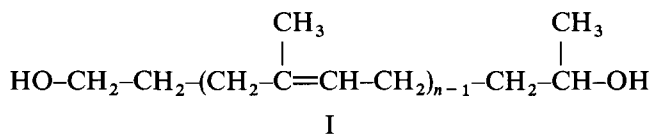
Figure 2 (a) Lamellar morphology of the chain-folded TPI crystals grown from hexane solution at −20°C (shadowed with Pt-C). (b) Electron diffraction pattern from a TPI crystal

measurements to comprise a series of homologues of the *trans*-1,4-isoprenoid compounds of structure I[13].

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\text{HO-CH}_2\text{-CH}_2\text{-(CH}_2\text{-}\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}\text{=CH-CH}_2)_{n-1}\text{-CH}_2\text{-}\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{CH}\text{-OH}
$$

I

The whole product obtained was composed of high-molecular-weight fractions, which are assumed to come from the piled-up lamellae, and also oligomer parts of single traverses and double traverses, which are assumed to come from monolayers and bilayers, respectively, as shown by the g.p.c. trace of *Figure 3*. The purified oligomer fractions of single traverses were subjected to high-resolution g.p.c. in order to determine the molecular weight of each fraction via the standard calibration curve (see *Figure 5*).

Figure 4 shows an example of the g.p.c. curve for the single traverse oligomer fraction comprising isoprene 7–14mers obtained from ozonolysis at 50.7% ozone uptake. The molecular weights of three selected peaks were confirmed by f.d.-m.s. measurements to be 716, 784 and 852, respectively. The molecular weights of the other fractions could be determined by calculation using the number of isoprene units in a molecule. *Figure 5* shows the standard calibration curve plotted between log molecular weight and elution volume of the eight peaks by using the least-squares method. Each peak in the g.p.c. curves could be assigned by interpolation based on this calibration curve.
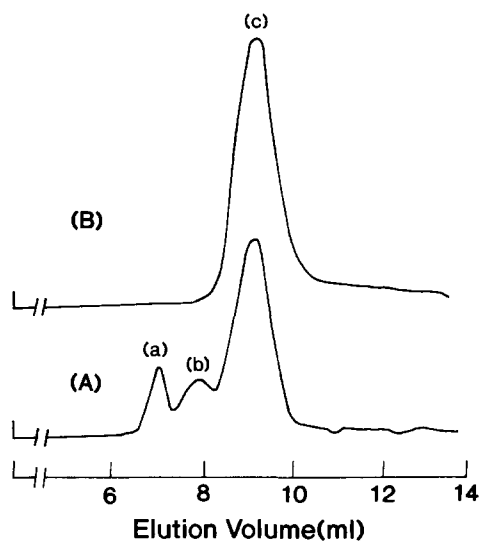

Figure 3 Typical g.p.c. curves of the whole products (A) and product from methanol extraction (B) obtained from ozonolysis of TPI crystals. (a) Polymer part; (b) the oligomer fractions of the double traverses; (c) the oligomer fractions of the single traverses

Table 2 lists the degree of polymerization ($\overline{DP}_{n-1}$) of the main fraction, the isoprene units of the main fraction, polydispersity ($\overline{M}_w/\overline{M}_n$) and oligomer conversion in connection with the mole percentage of ozone uptake. The per cent ozone uptake was derived from the mole ratio of ozone reacted with some C=C double bonds to the total amount of C=C double bonds in the isoprene
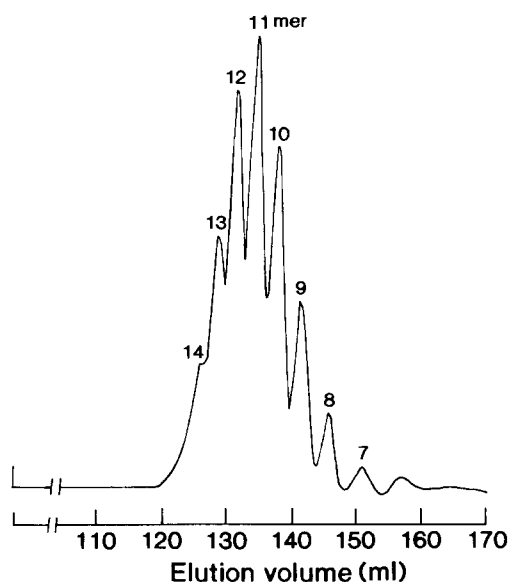
Figure 4 Typical g.p.c. curve of low-molecular-weight oligomer fractions obtained from ozonolysis at 50.7% ozone uptake
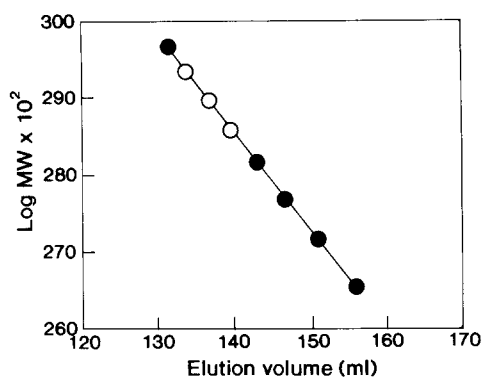

Figure 5 G.p.c. calibration plot of log molecular weight *versus* elution volume: ○, determined by f.d.-m.s. measurements

Table 2 Degree of polymerization, stem length distribution, isoprene units of the main fraction and oligomer conversion obtained at various ozone uptakes

Solution	Ozone uptake (%)	$\overline{DP}_{n-1}$	$\overline{M}_w/\overline{M}_n$	Main fraction (mer)	Oligomer conversion (%)
Hexane	10.3	12.0	1.02	13	0.5
	20.9	10.5	1.01	12	12.8
	39.9	9.7	1.02	11	6.6
	41.7	10.5	1.01	11	4.5
	50.7	10.1	1.02	11	22.5
	64.3	8.3	1.03	9	1.2
	80.7	8.1	1.04	9	5.6
Amylacetate	16.4	11.1	1.02	12	1.9
	32.0	11.3	1.01	12	26.0
	43.5	9.4	1.03	11	1.5
	48.2	8.5	1.01	10	1.4

units. The oligomer conversion was obtained from the weight ratio of oligomer fractions of the single traverses to the total initial weight of the polymer. The oligomer conversion might depend not only on concentration of the crystallization solution but also on ozone uptake. For the present study, however, the concentration of the crystallization solution was kept constant. Therefore, the

oligomer conversions obtained could be assmed to vary preferentially due to the variation of ozone uptake. At low percentages of ozone uptake, random cutting is presumed to occur on the surface folds, giving not only single traverses but also double or triple traverses. This resulted in a low percentage of oligomer conversion of the single traverses. A drastic increase in oligomer conversion (22% for hexane and 26% for amylacetate) was observed when ozone uptake increased to around the value of the amorphous content of each crystal. It was noted that polydispersity of the single-traverse oligomer part is in the range of 1.01–1.02 for 10.3–50.7% ozone uptake in hexane and 16.4–32.0% ozone uptake in amylacetate. The narrow distribution of the stem lengths obtained from ozonolysis on the surface folds of the lamellae suggested that the surfaces of solution-grown α-TPI crystals, crystallized at −20°C in hexane solution and in amylacetate solution, might have slightly irregular chain folding. More precise information about the fold length and fold length distribution, which clarifies the surface structure of lamellae, will be reported in a subsequent paper.

As ozone uptake increased, $\overline{DP}_{n-1}$ gradually decreased from 12.0 to 8.1 for hexane and from 11.1 to 8.5 for amylacetate, as shown in *Figure 6*. This suggested that ozonolysis started randomly from the surface folds until all double bonds of the surface folds were completely reacted, then penetrated into the crystalline core. The expected fold-cutting process on ozonolysis is shown schematically in *Figure 7*. Here, (a) represents the original chain-folded lamellae, (b) represents the initial stage of degradation with some surface folds randomly cut and (c) shows that all double bonds of isoprene units in surface folds or the amorphous part are fairly cut. This stage of reaction is thought to give the oligomer fraction that has isoprene units with the same length as the crystalline stem of the lamellae. Finally, (d) represents the stage at which degradation penetrated into the crystalline core, when ozone uptake increases to above the amorphous
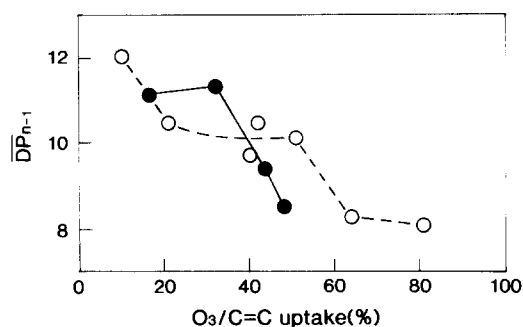

Figure 6 Plots of degree of polymerization *versus* ozone uptake for hexane (○) and amylacetate (●)
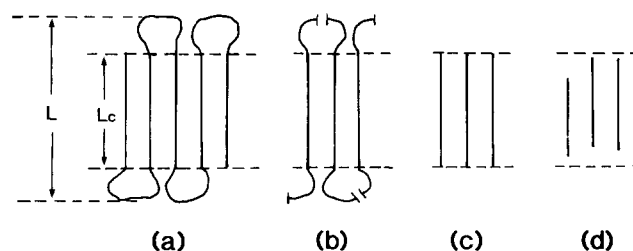

Figure 7 Schematic representation of fold cutting. *L*, lamellar thickness; *L_c*, crystalline stem length. (a)–(d) are explained in the text
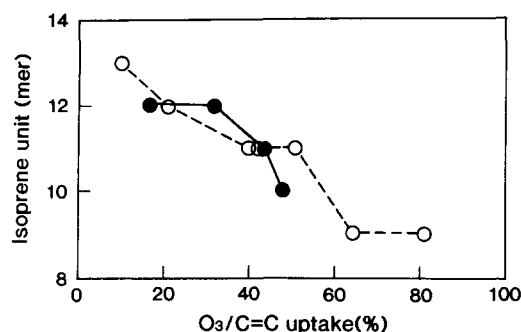
Figure 8 Relation between number of isoprene units of the main fraction and ozone uptake. Oligomer fraction obtained from ozonolysis of α-TPI grown from hexane (○) and from amylacetate (●)

content. At this stage, the oligomer fraction apparently has a shorter stem length than the lamellae.

Figure 8 shows the relation between the number of isoprene units of the main fraction and ozone uptake. It was revealed that the isoprene units reached a constant value at 11 for TPI crystals grown from hexane and at 12 for those grown from amylacetate. According to the etching mechanism proposed above, in which the double bonds of isoprene units in the amorphous part reacted with ozone first, it could be concluded that these values of 11 and 12 were the stem lengths of chain-folded α-TPI lamellae grown at −20°C from hexane and from amylacetate, respectively. This idea was confirmed by the remarkably high yield of oligomer fractions obtained due to complete cutting of the double bonds of the isoprene units in the amorphous part. This etching also demonstrated that the surface folds of the TPI lamellae grown from hexane are longer, on average, than those grown from amylacetate. These findings are in good agreement with the results from X-ray measurements[18] in which the lamellar thicknesses of crystals grown from hexane and from amylacetate are 90.3 Å and 87.6 Å, respectively.

CONCLUSIONS

It was demonstrated that selective ozonolysis under well controlled conditions associated with high-resolution g.p.c. may be used to determine the stem length and the stem length distribution of chain-folded lamellae, hence giving new information on the fold surface structure. The stem lengths of chain-folded α-TPI crystals grown from hexane and amylacetate at −20°C were found to be 11 and 12 isoprene units, respectively, with dispersion of 2.3. The surface folds of these lamellae are likely to be rather tight and involve slight irregularity. From etching evidence it was also found that the surface folds of lamellae grown from hexane are longer than those grown from amylacetate.

ACKNOWLEDGEMENTS

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