Direct determination of stem length for chain-folded lamellar polymer crystals grown from solution: ozonolysis–g.p.c. measurements

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The application of selective ozonolysis together with high-resolution g.p.c. was performed to determine the crystalline stem lengths, in monomer units, of chain-folded lamellar crystals for *trans* and *cis* polyisoprene and polybutadiene. The *trans* polymer crystals were crystallized at −20°C in hexane directly from the dissolution temperature of 60°C, while the *cis* polymer crystals were crystallized by the same method at −70°C. The stem lengths of the *trans*- and *cis*-1,4-polyisoprene crystals were found to be 11 and 10 monomer units, respectively. Those for *trans*- and *cis*-1,4-polybutadiene crystals were found to be 12 and 13 monomer units, respectively.

(Keywords: selective ozonolysis; crystalline stem length; *trans* polyisoprene; *cis* polyisoprene; *trans* polybutadiene; *cis* polybutadiene)

Introduction

The surface fold lengths and the crystalline stem lengths of chain-folded lamellar *trans* polyisoprene crystals[1–3] and *trans* polybutadiene crystals[4,5] were calculated from the reacted and unreacted fractions obtained by a combination of selective epoxidation and ^{1}H or ^{13}C n.m.r. measurements of the resulting polymers.

We have successfully determined the sequence distribution of styrene units in styrene–butadiene copolymers by a combination of the selective ozonolysis of double bonds in butadiene units and high-resolution g.p.c. measurements of the resulting products[6].

The surface-folded structure of polyethylene single crystals was estimated from the molecular weight ratio between single traverses and double traverses obtained from oxidation using ozone[7–9].

In this paper, we propose the selective ozonolysis–g.p.c. method for analysing the stem length distribution of the chain-folded polymer crystals. The lamellar crystals used are the solution-grown *trans* and *cis* polyisoprene crystals as well as *trans* and *cis* polybutadiene crystals.

Experimental

The polymers used for this study were *cis*-1,4-polyisoprene (*cis*-1,4, 97%; $\bar{M}_n = 20 \times 10^4$; $\bar{M}_w = 10 \times 10^5$; IR-2200, Japan Synthetic Rubber Co.); *trans*-1,4-polyisoprene (*trans*-1,4, 99%; $\bar{M}_n = 7 \times 10^4$; $\bar{M}_w = 14 \times 10^4$; TP301, Kuraray Co., Japan); *cis*-1,4-polybutadiene (*cis*-1,4, 97%; $\bar{M}_n = 10 \times 10^4$; $\bar{M}_w = 57 \times 10^4$; BR-01, Japan Synthetic Rubber Co.); and *trans*-1,4-polybutadiene (*trans*-1,4, 95%; $\bar{M}_n = 11 \times 10^4$; $\bar{M}_w = 50 \times 10^4$; TRANS-4, Shell Co. Ltd). The polymers were purified in the usual way before use.

Trans polyisoprene and *trans* polybutadiene were rapidly crystallized at −20°C from dissolution temperatures (60°C) in 0.2% (w/v) hexane solutions. *Cis* polyisoprene and *cis* polybutadiene were crystallized by the same method at the lower crystallization temperature of −70°C. The suspension solutions of the polymer crystals in hexane were directly subjected to ozonolysis reaction at the low temperature of −20°C. About 1% of ozonized oxygen blew into the reaction vessel for various periods of time. The ozone uptake increased with increasing the reaction time. The resulting ozonides were decomposed to alcohols by using 1% (w/v) $LiAlH_4$ in diethyl ether. The oligomer fractions of single traverses were separated from the whole product by using methanol extraction. The monomers from the amorphous part or cilia were removed by washing the oligomer solution in chloroform with water three times.

G.p.c. and h.p.l.c. measurements were carried out using a Jasco 880-PU high-pressure pump and a Jasco 830-RI detector. Two preparative columns (21.2 mm i.d. × 600 mm) and two analytical columns (7.5 mm i.d. × 500 mm) packed with styrene–divinylbenzene gels[10] and with ODS–silica gels were used in series. The eluents used were chloroform for g.p.c. and ethanol for h.p.l.c.

The molecular structures of the oligomer products thus obtained were determined using a Jeol JNM FX-200 at 200 mHz for ^{1}H n.m.r. and at 50 MHz for ^{13}C n.m.r.. The measurements were carried out at room temperature in $CDCl_3$ solution with tetramethylsilane as an internal standard.

Results and discussion

The whole products obtained from the selective ozonolysis degradation are composed of a polymer part from the multilayer lamellae, oligomer fractions of single traverses from monolayers, oligomer fractions of double traverses from double layers and monomers from cilia. *Figure 1* shows a typical g.p.c. curve for the whole product obtained from ozonolysis of *trans* polybutadiene at 62.4 mol% ozone inlet. It can be seen that three peaks corresponding to polymer, oligomer fractions of double traverses and oligomer fractions of single traverses were clearly separated. The oligomer fractions obtained from

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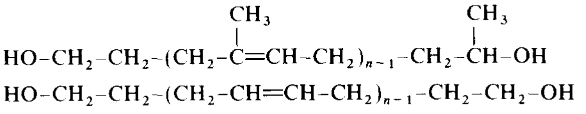
methanol extraction, which correspond to the single-traverse fractions, in the yield of 10.3% for *trans* polyisoprene were found to have a narrow molecular weight distribution up to polydispersity ($\bar{M}_w/\bar{M}_n$) of 1.01. *Figure 2* shows an example of ^1H n.m.r. and ^{13}C n.m.r. spectra for *cis* isoprene oligomer fractions obtained from methanol extraction which had a main fraction of 10 monomer units. The assignments of the signals are summarized in *Table 1*. The spectra obtained confirmed that the molecular structure of the resulting oligomers is a series of homologues of the isoprenoid or butadienoid compounds having hydroxy terminal groups as shown in structures (I) and (II), respectively:



$$HO\text{-}CH_2\text{-}CH_2\text{-}(CH_2\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH\text{-}CH_2)_{n-1}\text{-}CH_2\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}OH \qquad (I)$$

$$HO\text{-}CH_2\text{-}CH_2\text{-}(CH_2\text{-}CH{=}CH\text{-}CH_2)_{n-1}\text{-}CH_2\text{-}CH_2\text{-}OH \qquad (II)$$

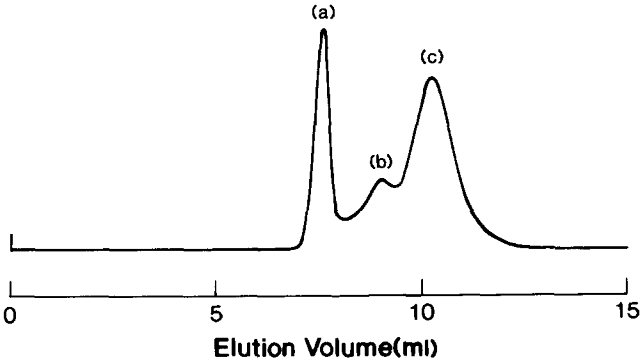


Figure 1 Typical g.p.c. curve for the whole product obtained from ozonolysis of solution-grown *trans*-1,4-polybutadiene crystals. (a) Polymer fractions from stacked lamellae; (b) oligomer fractions from double traverses; (c) oligomer fractions from single traverses

The selective ozonolysis was expected to be performed on the folded parts of the lamellar surfaces. By increasing the amount of the ozonized oxygen into the suspension of polymer crystals, it was observed that the degree of polymerization of the resulting oligomers decreased. The optimum stage of etching, in which all the surface folds were completely reacted, would give information of the stem length distribution, and the main fraction of resulting oligomer fractions from methanol extraction was estimated to have an average chain length equal to the crystalline stem length.

High-resolution g.p.c. was applied to the oligomer fractions of the single traverses. The separation of each

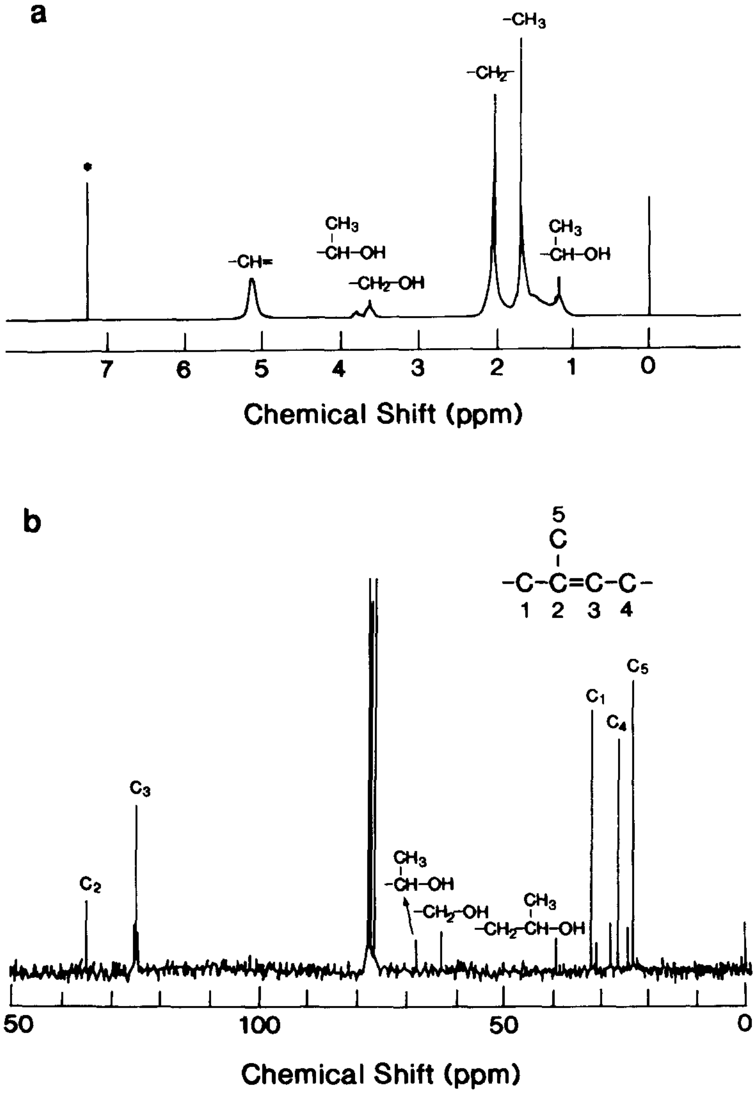
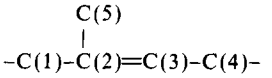


Figure 2 (a) ^1H n.m.r. and (b) ^{13}C n.m.r. spectra for *cis* isoprene oligomers having a main fraction of 10 monomer units

Table 1 Assignments of ^1H and ^{13}C n.m.r. signals in isoprene oligomer from *cis*-1,4-polyisoprene. The carbon atoms in isoprene units including both the terminal units are designated as follows:



$$-C(1)-\overset{\displaystyle C(5)\atop |}{C(2)}=C(3)-C(4)-$$

^1H n.m.r.		^{13}C n.m.r.	
Chemical shift (ppm)	Assignment	Chemical shift (ppm)	Assignment
1.19	$-C(C\underline{H_3})-OH$	23.5	C(5)
1.68	$-C(C\underline{H_3})=CH-$	24.3	$-CH(\underline{C}H_3)-OH$
2.03	$-C\underline{H_2}-C(CH_3)=CH-C\underline{H_2}-$	26.4	C(4)
3.64	$-C\underline{H_2}-OH$	31.0	$-\underline{C}H_2-\underline{C}H_2-OH$
3.80	$-C\underline{H}(CH_3)-OH$	32.2	C(1)
5.14	$-C(CH_3)=C\underline{H}-$	39.5	$-\underline{C}H_2-CH(CH_3)-OH$
		63.0	$-\underline{C}H_2-OH$
		67.9	$-\underline{C}H(CH_3)-OH$
		125.0	C(3)
		135.2	C(2)

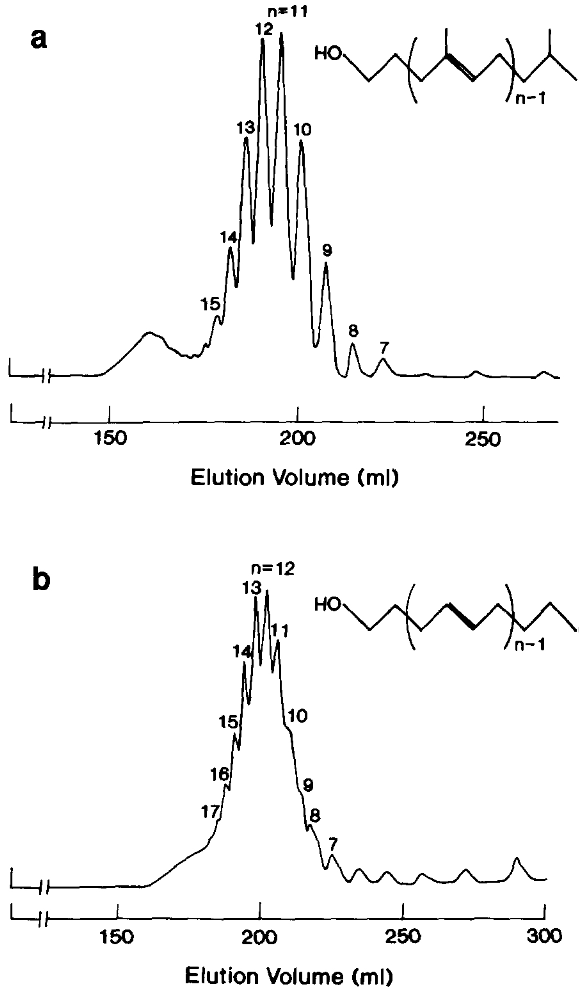


Figure 3 Typical g.p.c. curves for (a) *trans* isoprene oligomer fractions and (b) *trans* butadiene oligomer fractions

Table 2 Summary of crystalline stem lengths in monomer units and lamellar thicknesses of the chain-folded lamellar crystals grown in hexane

Polymer crystals	T_c (°C)	Stem length[a] (monomer units)	Lamellar thickness[b] (Å)
Trans-1,4-polyisoprene	−20	11	90.3
Cis-1,4-polyisoprene	−70	10	-
Trans-1,4-polybutadiene	−20	12	107.4
Cis-1,4-polybutadiene	−70	13	-

[a] Determined by selective ozonolysis–g.p.c. method
[b] Determined by small-angle X-ray method

fraction was clearly observed. *Figure 3* shows examples of g.p.c. curves for *trans*-1,4-isoprene oligomer fractions (*Figure 3a*) and *trans*-1,4-butadiene oligomer fractions (*Figure 3b*) obtained from ozonolysis degradation at the optimum stage of etching. The three collected fractions of each sample were subjected to field-desorption mass spectroscopy measurements; their molecular weights were found to be 716, 784 and 852 corresponding to $n = 10$, 11 and 12 monomer units, respectively, for *trans* isoprene oligomers and 684, 738 and 792 corresponding to $n = 12$, 13 and 14 monomer units, respectively, for *trans* butadiene oligomers.

Table 2 summarizes the crystalline stem lengths in monomer units as estimated from the selective ozonolysis degradation in connection with the crystallization temperatures and lamellar thicknesses determined by X-rays. The crystalline stem lengths for *trans* polyisoprene and *trans* polybutadiene crystals grown at −20°C were found to be 11 and 12 monomer units, respectively, whereas, those for *cis* polyisoprene and *cis* polybutadiene crystals grown at −70°C were found to be 10 and 13 monomer units, respectively. The relationship between the stem length and the lamellar thickness will be discussed in a subsequent paper.

Conclusion

Selective ozonolysis associated with high-resolution g.p.c. proved to be a direct method for determination of the crystalline stem length of chain-folded lamellae. Details of the surface-folded structure and stem length distribution of chain-folded polymer crystals will be included in a subsequent paper.

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