

# Telechelic *cis*-1,4-Oligoisoprenes through the Selective Oxidolysis of Epoxidized Monomer Units and Polyisoprenic Monomer Units in *cis*-1,4-Polyisoprenes

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**ABSTRACT:** Telechelic *cis*-1,4-oligoisoprenes were prepared by the selective cleavage of weak epoxidized units (E) in epoxidized *cis*-1,4-polyisoprenes (EPIs) and by the random cleavage of isoprenic units (I) in *cis*-1,4-polyisoprene (PI). In both cases, cleavage by periodic acid (H<sub>5</sub>IO<sub>6</sub>) in tetrahydrofuran led to aldehydic and ketonic chain ends. Through variations in the E/(I + E) molar percentage (E%) in the cleavage of EPI and through variations in the H<sub>5</sub>IO<sub>6</sub>/I molar percentage (PA%) in the cleavage of PI, a polydispersity

index near 2 and a number-average molecular weight of  $2 - 20 \times 10^3$  were obtained. The correlation of the degree of scission with E% and PA%, combined with kinetic, led to the proposal of a two-step mechanism for the H<sub>5</sub>IO<sub>6</sub> cleavage of double bonds. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 42–46, 2002

**Key words:** degradation; telechelics; oligomers

## INTRODUCTION

Because of their important role in the preparation of advanced polymeric materials, for low molar mass polymers bearing specific functional groups at their chain ends, a large variety of techniques have been developed for synthesis and characterization.<sup>1,2</sup> In addition to polymerization methods, such telechelics can be prepared by the selective cleavage of a polymer with synchronous functionalization.<sup>3</sup> In this field, the controlled degradation of polymers and copolymers of dienes are usually studied, and the oxidative cleavage of double bonds, including ozonolysis<sup>4,5</sup> and RuO<sub>4</sub> oxidation,<sup>6</sup> has been found to be efficient (Scheme 1).

Because of the value of the *cis*-1,4 structure in high molar mass synthetic polyisoprene and natural rubber, this technique makes it possible to produce liquid telechelics high in *cis*-1,4 contents. The methods for synthesizing telechelic natural rubber derivatives have been reviewed;<sup>7</sup> redox and photochemical methods, as well as ozonolysis, have been widely exploited to produce natural rubber telechelic derivatives. Those processes involve the random scission of equireactive

monomer units in homopolymers, but the means to obtain telechelic products with reproducible chain lengths, chain length distributions, and end groups have not been systematically checked.

However, periodic acid (H<sub>5</sub>IO<sub>6</sub>) is an effective scission agent in partially epoxidized natural rubber<sup>8</sup> and natural rubber.<sup>8,9</sup> The work reported here extends the scope of these earlier studies and also forms an accurate comparative structural investigation of the resulting telechelic polymers with respect to the number-average molecular weight ( $M_n$ ), the polydispersity index ( $I_p$ ), and the structure of functional groups at the chain end.

For the removal of epoxides expected in some natural rubbers before the reaction, this study was performed with a synthetic *cis*-1,4-polyisoprene (PI; *cis*-1,4 content > 99%,  $M_n = 800 \times 10^3$ ) and its partially epoxidized derivatives [epoxidized *cis*-1,4-polyisoprene (EPI); Scheme 2].

The results were interpreted with reference to the scission of randomly distributed weak epoxidized monomer units in EPI and to the random scission of the unsaturated units in PI.

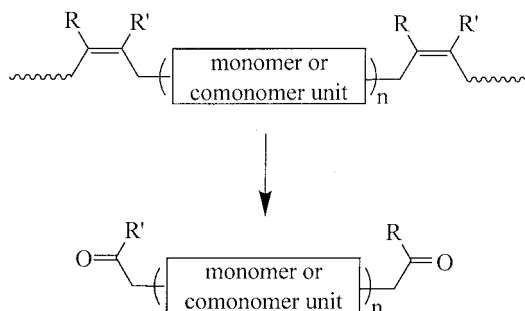
## EXPERIMENTAL

### Reagents

*m*-Chloroperbenzoic acid (MCPBA; 70–75%, Janssen, Geel, Belgium), H<sub>5</sub>IO<sub>6</sub> (99%, Acros Organics, Noisy-le-Grand, France), toluene, ethanol, and tetrahydrofuran (THF; ACS reagent, Acros Organics) were used as

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**Scheme 1** Selective cleavage of the polymer with synchronous functionalization.

received. Chloroform and methylene chloride (technical-grade) were dried on calcium chloride and distilled over  $P_2O_5$ .

The MCPBA content in the commercial product was determined by the titration of iodine liberated from a standard potassium iodide solution. Quantofix peroxide test sticks (Macherey-Magel, Hoerdt, France) were used for the semiquantitative monitoring of peracid conversion.

PI (PI<sub>800</sub>, cis-1,4 content > 99, average molecular weight =  $800 \times 10^3$ , Acros Organics) was reprecipitated from a methylene chloride solution (30–40 g L<sup>-1</sup>) into methanol until size exclusion chromatography (SEC) traces showed no traces of 2,6-di-*tert*-butyl-4-methyl phenol. The product was then dried in vacuo.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.67 (3H), 2.02 (4H), 5.11 (1H).

### Characterization

SEC data were obtained at room temperature on a Waters chromatograph equipped with a model 410 differential refractometer. The chromatograph was fitted with a set of two 60-cm columns packed with Jordi gel beads with 500-Å and 5-mm pore sizes. THF was

**TABLE I**  
Compositions of the Reaction Solutions During Epoxidation and Compositions of the Resulting EPI

| EPI Sample        | Feed composition |              |                        | Polymer composition |    |
|-------------------|------------------|--------------|------------------------|---------------------|----|
|                   | PI (mmol)        | MCPBA (mmol) | CHCl <sub>3</sub> (mL) | E%                  | I% |
| E <sub>1</sub> PI | 46               | 0.45         | 176                    | 1                   | 99 |
| E <sub>2</sub> PI | 46               | 0.9          | 176                    | 2                   | 98 |
| E <sub>4</sub> PI | 141              | 6            | 588                    | 4                   | 96 |

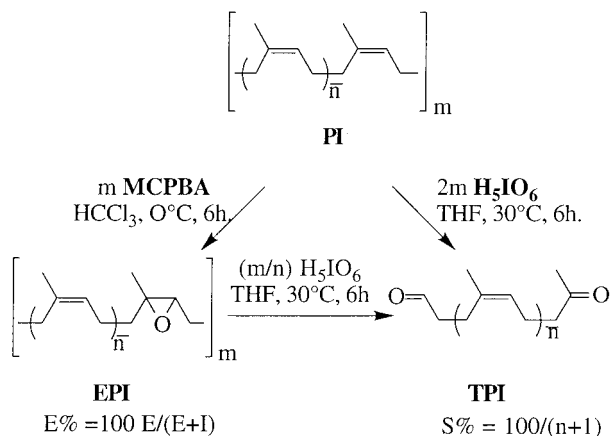
used as the solvent at a flow rate of 1 mL/min. The column set was calibrated with polystyrene (PS) standards, giving  $M_{n,PS}$ . <sup>1</sup>H-NMR spectra were recorded with a Bruker AC 400 Fourier transform spectrometer operating at 400.13 MHz. CDCl<sub>3</sub> was used as a solvent. Tetramethylsilane was used as an internal standard.

### Epoxidized polyisoprene (E<sub>7</sub>PI) preparation

PI was dissolved in chloroform, and the solution was introduced into a three-necked, round-bottom flask equipped with a dropping funnel and cooled in an ice bath. To the stirred solution, MCPBA dissolved in chloroform was added dropwise. An overall concentration of approximately 17 g L<sup>-1</sup> was employed with a varying monomer unit/MCPBA molar ratio (Table I). The reaction solution was stirred at 0°C for up to 6 h. A color test semiquantitative determination of residual peracid was performed, and if necessary, Na<sub>2</sub>SO<sub>3</sub> was added before the solution was washed with aqueous NaHCO<sub>3</sub> and dried over MgSO<sub>4</sub>. E<sub>7</sub>PI was recovered by precipitation into methanol and dried in vacuo. The composition of the epoxidized rubbers was determined from <sup>1</sup>H-NMR data with  $I_{2.67}/I_{5.11} = E/I$  (where E is an epoxidized unit and I is an isoprenic unit).

### H<sub>5</sub>IO<sub>6</sub> oxidation of E<sub>4</sub>PI and PI in THF

The polymer (2 g) was dissolved in THF (50 mL), and the solution was introduced into a three-necked, round-bottom flask equipped with a dropping funnel and a reflux condenser and was maintained at 30°C with a thermostatic bath. To the stirred solution, H<sub>5</sub>IO<sub>6</sub> (H<sub>5</sub>IO<sub>6</sub>/E molar ratio = 1/1 or H<sub>5</sub>IO<sub>6</sub>/I molar ratio = 0.08/1) dissolved in THF (5 mL) was added dropwise. The reaction solution was kept at 30°C. Samples (6 mL) of the reaction solution were withdrawn after 0.5, 1, 2, 4, and 6 h from the start of the reaction. Iodic acid was filtered, and the polyisoprene-cleaved product was precipitated into methanol (60 mL), dried in vacuo, and analyzed by <sup>1</sup>H-NMR and SEC. From the final reaction solution, insoluble iodic acid was removed by filtration, and the oligomeric products were precipitated into methanol (10/1, v/v)



**Scheme 2** Idealized reaction scheme for the synthesis of TPI.

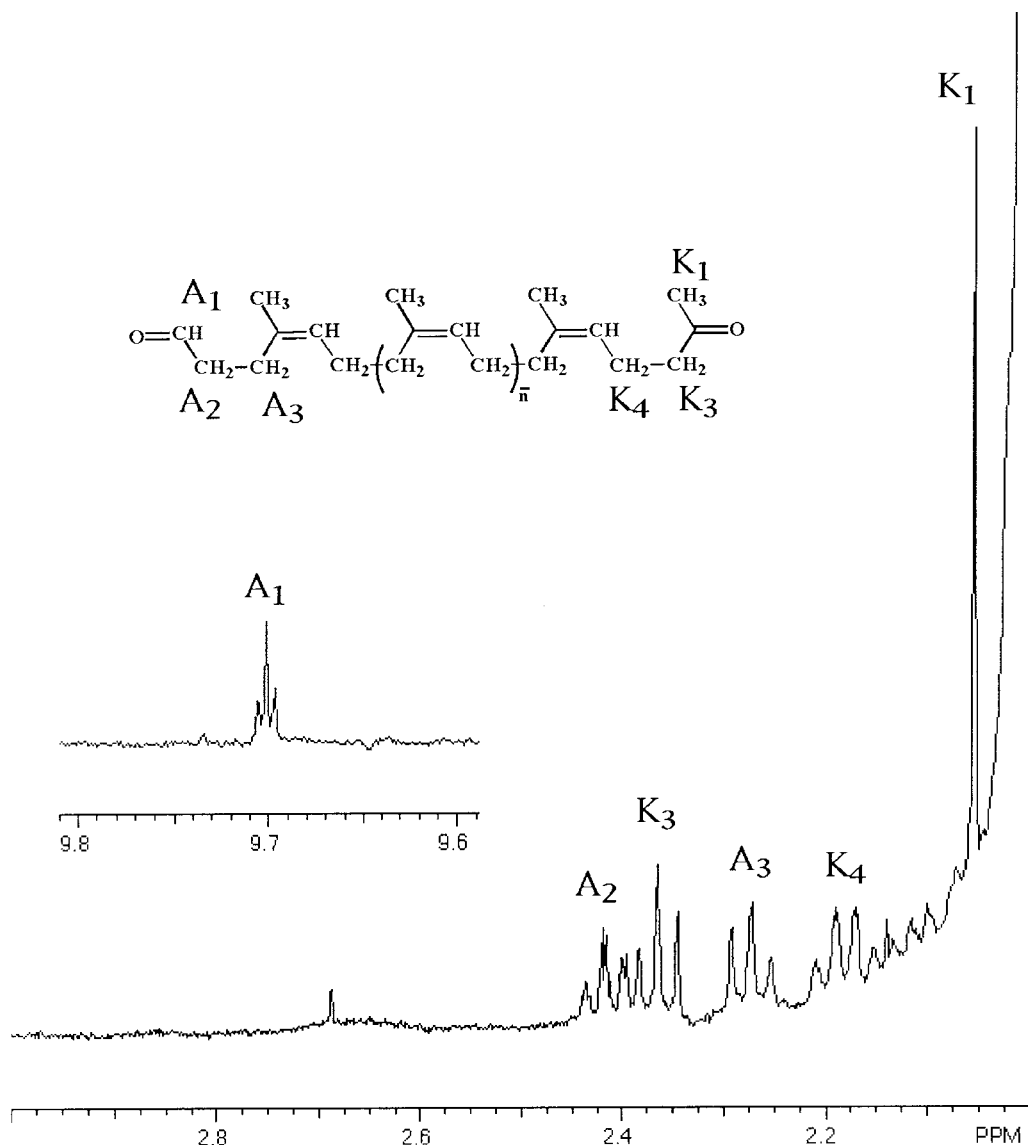


Figure 1  $^1\text{H-NMR}$  spectrum of TPI derived from a  $\text{H}_5\text{IO}_6$  reaction with  $\text{E}_4\text{PI}$  in THF.

and recovered by dissolution into methylene chloride and evaporation of the solvent.

## RESULTS AND DISCUSSION

### $\text{H}_5\text{IO}_6$ oxidolysis of weak epoxides in $\text{EPI}$

The partial epoxidation of PI was achieved with MCPBA at  $0^\circ\text{C}$ . The composition in isoprenic units (I) and epoxidized units (E) of the resulting  $\text{E}_r\text{PI}$  was determined from  $^1\text{H-NMR}$  data. The E/(I + E) molar percentages (E%) were 1, 2, and 4 in  $\text{E}_1\text{PI}$ ,  $\text{E}_2\text{P}$ , and  $\text{E}_4\text{PI}$ , respectively (Table I), corresponding to MCPBA/I molar percentages of 1, 2, and 4 respectively. Clearly, the previously reported fast and selective epoxidation<sup>10</sup> was checked.

The scission of the epoxide groups of  $\text{E}_4\text{PI}$  with  $\text{H}_5\text{IO}_6$  was first tested with the reaction performed in

$\text{CHCl}_3$  and in THF.  $^1\text{H-NMR}$  analysis allowed us to check the expected chain end in the resulting telechelic *cis*-1,4-polyisoprene (TPI).

As shown in Figure 1, in addition to the signals  $\text{A}_1$  and  $\text{K}_1$  of aldehyde and methylketone, respectively, the chain ends are also characterized by the signals  $\text{A}_2$  and  $\text{A}_3$  of the methylene groups in the neighborhood of the aldehyde group and by  $\text{K}_3$  and  $\text{K}_4$  of the methylene groups in the neighborhood of the methylketone group. Therefore, it was possible with NMR analysis to monitor the epoxide conversion and to observe that, after 24 h of reaction in chloroform at  $50^\circ\text{C}$ , residual epoxide (2%) was detected in the resulting TPI, whereas after the same time in THF at  $30^\circ\text{C}$ , no more epoxide was detected. The reason for these results could be the difference in the solubility of  $\text{H}_5\text{IO}_6$  in the two solvents. On this

TABLE II  
Molecular Weights of TPI and S% for Periodic Acid  
Oxidolysis of EPI in THF at 30°C

| Run            | E% in EPI | $M_{nPI}$ | $I_p$ | $DP_n$ | S%  |
|----------------|-----------|-----------|-------|--------|-----|
| 0 <sup>a</sup> | 4         | 4230      | 2.4   | 61     | 1.6 |
| 1              | 4         | 3320      | 1.9   | 47     | 2.1 |
| 2              | 2         | 5140      | 1.9   | 74     | 1.3 |
| 3              | 1         | 7760      | 2.0   | 113    | 0.9 |

<sup>a</sup> Run performed in chloroform at 50°C.

basis, the scission of the epoxide groups of E<sub>2</sub>PI and E<sub>1</sub>PI was performed in THF. Before the addition of H<sub>5</sub>IO<sub>6</sub>, the THF solution of EPI contained a gel fraction, which disappeared as soon as H<sub>5</sub>IO<sub>6</sub> was added.

The correlation of the molecular weight decrease with the degree of epoxidation was monitored by SEC. The PS standardized molecular weight ( $M_{PS}$ ; SEC analysis) was corrected by the Benoit factor  $B$  according to  $M_{PI} = B \times M_{PS}$  ( $B = 0.67$  was previously determined for PI<sup>11</sup>), and the number-average degree of polymerization ( $DP_n$ ) was obtained from the corrected  $M_n$  ( $M_{nPI}$ ). Therefore, it was possible to calculate the degree of scission (S%) from  $DP_n$  by the following relation:  $S\% = 100/(DP_n + 1)$ . According to the reaction scheme and a 100% yield, S% was expected to be identical in value to the degree of epoxidation, E%. Moreover, a random distribution of epoxidized units along the polymer chain led us to expect  $I_p$  of the resulting oligomer to be 2.

In a comparison of TPis prepared from EPI in chloroform and in THF, the results listed in Table II (runs 0 and 1) showed that, as expected from the NMR analysis, the reaction in THF led to lower molecular weight and higher S%. Moreover, the decrease in E% in EPI is clearly correlated to a decrease in S% and to an increase in the molecular weight of the resulting TPI. Moreover, the dispersity index of the TPI was nearly 2. This argues for a random distribution of the epoxidized units along the polymer chain. Despite the absence of residual epoxide in the TPI, S% remained lower than E%. Besides the approximations in the measurement of the molecular weight by SEC, these excessively high S% values could have resulted from the loss of the smallest oligomers during the workup for the isolation of the samples. Indeed, this phenomenon is more important for the higher E% values and, consequently, for the TPI with the lowest molecular weight (run 1).

### H<sub>5</sub>IO<sub>6</sub> oxidolysis of double bonds in PI

The conditions for the reaction of H<sub>5</sub>IO<sub>6</sub> with PI were selected with reference to the conditions for the reaction of H<sub>5</sub>IO<sub>6</sub> with EPI but with double weight ratios of H<sub>5</sub>IO<sub>6</sub> versus the polymer. Figure 2 shows typical

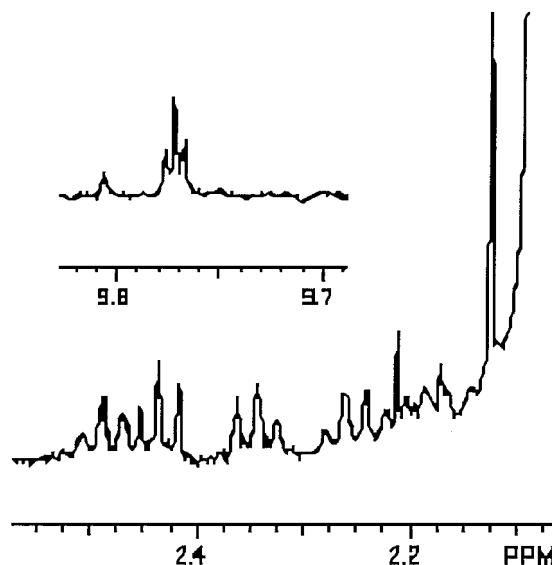


Figure 2 <sup>1</sup>H-NMR spectrum of TPI derived from a H<sub>5</sub>IO<sub>6</sub> reaction with PI in THF.

<sup>1</sup>H-NMR signals for the aldehydic and ketonic chain ends characterizing the same kind of TPis as those obtained by the selective cleavage of epoxide in EPI. Therefore, it is clear that H<sub>5</sub>IO<sub>6</sub> is a good reagent for the scission of double bonds in THF.

Table III shows the changes in S% in PI and in the molecular weight in the resulting I-cleavage-based TPI with the H<sub>5</sub>IO<sub>6</sub>/I molar percentage (PA%). In this case,  $M_{nPI}$  and S% were correlated to PA%, but probably as a result of the loss of very low molecular weight oligomers during the workup, S% was much lower in value than PA%. However, comparing these results with those obtained by the cleavage of EPI, we can see that, with twice as little H<sub>5</sub>IO<sub>6</sub> for the oxidolysis of EPI than for the oxidolysis of PI, the values are of the same order of magnitude. Therefore, it appears that 2 equiv of H<sub>5</sub>IO<sub>6</sub> is needed for the cleavage of a double bond. It seems reasonable to propose that the cleavage is the result of a two-step mechanism. In the first step, H<sub>5</sub>IO<sub>6</sub> reacts with a double bond to give an epoxide or  $\alpha$ -glycol:

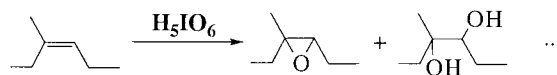
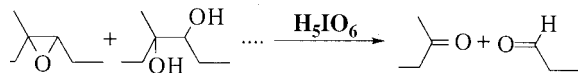


TABLE III  
Molecular Weights of TPI and S% for Periodic Acid  
Oxidolysis of PI in THF at 30°C and with Varying (PA%)

| Run | PA% | $M_{nPI}$ | $I_p$ | $DP_n$ | S%   |
|-----|-----|-----------|-------|--------|------|
| 1   | 8   | 4135      | 1.74  | 59     | 1.66 |
| 2   | 4   | 5673      | 1.74  | 82     | 1.21 |
| 3   | 2   | 9032      | 2.02  | 131    | 0.76 |

In the second step, the epoxide or  $\alpha$ -glycol is cleaved by reacting with a second equivalent of  $H_5IO_6$ :



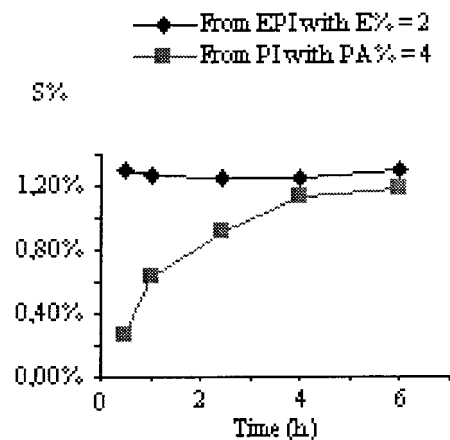
However, neither epoxide nor  $\alpha$ -glycol was detected in the resulting polymers. Therefore, this two-step process implies that the second step is much faster than the first.

### Comparison of the kinetics in the oxidolysis of epoxides and in the oxidolysis of double bonds

For the scissions of EPI and PI, the reaction progress was followed by the withdrawal of reaction aliquots (6 mL) and by the characterization of the oligomers by  $^1H$ -NMR and SEC. In both cases,  $^1H$ -NMR showed that, during the entire reaction, in addition to the *cis*-1,4 unit of the polymer chain, ketonic and aldehydic groups of the chain ends were characterized. Moreover, and especially for the oxidolysis of PI, the relative intensities of the corresponding signals increased with time.

$M_{nPI}$  values from SEC were used to calculate S%. The values of S% for some value of E% during EPI oxidolysis and for  $PA\% = 2E\%$  during PI oxidolysis were compared. Results listed in Table IV show that, for the maximum value of S%, 1 h was enough in the first case, whereas the second case required at least 4 h.

Figure 3 shows a typical graphical representation of S% versus time for  $E\% = 2$  in the oxidolysis of EPI and



**Figure 3** S% versus time in the reaction of  $H_5IO_6$  with epoxidized *cis*-1,4 polyisoprene EPI and *cis*-1,4 polyisoprene PI.

for  $PA\% = 4$  in the oxidolysis of PI. It is clear from this example that the  $H_5IO_6$  cleavage of epoxide is nearly instantaneous, whereas the  $H_5IO_6$  cleavage of double bonds is a slow reaction process. These results argue for the two-step mechanism in the cleavage of double bonds. Indeed, the instantaneous cleavage of epoxide allows us to propose controlling the kinetics by the slow conversion of double bonds into epoxides or glycols and to explain the absence of epoxide or glycol in the resulting oligomers.

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**TABLE IV**  
S% Versus Time for Oxidolysis of EPI with Varying (E%) and of PI with Varying (PA%)

| Time (h) | S%         |            |            |            |            |
|----------|------------|------------|------------|------------|------------|
|          | EPI E% = 4 | PI PA% = 8 | EPI E% = 2 | EPI E% = 1 | PI PA% = 2 |
| 0.5      | 2.5        | —          | 1.3        | 0.8        | —          |
| 1        | 4.1        | —          | 1.3        | 0.9        | 0.6        |
| 2        | 4.6        | 1.3        | 1.3        | 0.8        | 0.7        |
| 4        | 3.8        | 1.8        | 1.3        | 0.8        | 0.7        |
| 6        | 2.1        | 1.7        | 1.3        | 0.9        | 0.8        |