

# Effect of Comonomer Composition on the Properties of Polyacrylonitrile Precursor and Resulting Carbon Fiber

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## SYNOPSIS

Since the itaconic acid (IA) comonomer is the potential initiator of cyclization, therefore the introduction of IA comonomer into polyacrylonitrile (PAN) precursor can depress the onset of exotherm (or cyclized temperature) and peak temperature. However, the more the IA content, the lower the conversion of acrylonitrile (AN) in the polymerization reaction. Although 2-ethylhexyl acrylate (2-EHA) comonomer in PAN precursor may prevent the cyclization propagation of nitrile groups during oxidation, PAN precursor with a few percent of 2-EHA comonomer has a more preferred orientation. As the content of 2-EHA comonomer further increases, the orientation of the resulting carbon fiber decreases correspondingly.

In this study, PAN precursor, with the composition of 98 mol % AN, 1.5 mol % 2-EHA, and 0.5 mol % IA, and its resulting carbon fiber have the best mechanical properties. From the results, it is shown that there is a good relationship between the tenacity and modulus of PAN precursor and those of its resulting carbon fiber.

## INTRODUCTION

Carbon fibers can be made from many materials; however, only three materials have gained industrial importance: rayon, pitch, and polyacrylonitrile (PAN). Rayon is injured by a relatively high carbon loss during carbonization; pitch-based carbon fibers give relatively poor tensile property, unless they are prepared from extremely purified mesophase pitch. At present, PAN appears to be the most widely used precursor for making high-performance carbon fiber.<sup>1-3</sup>

The quality of the ultimate carbon fibers depends largely on the quality of the precursor fibers.<sup>4</sup> Most PAN-based precursor fibers are made from copolymer<sup>5-8</sup> with acrylonitrile (AN) content of greater than 95 wt %. The introduction of a few percent of comonomer greatly enhances the internal mobility of polymer segments (or decreases the glass transition temperature,  $T_g$ <sup>9,10</sup>), depresses the onset of cyclized temperature during oxidation,<sup>11-15</sup> and

improves the spinnability.<sup>16</sup> As the contents of comonomers in AN copolymers increased, the crystallinity became lower and the crystallite size became small.<sup>17,18</sup> The tensile strength and modulus values of the resulting carbon fibers are functions of the crystalline content<sup>19</sup> and orientation<sup>20</sup> of the original PAN fiber.

Our studies showed that the introduction of 2-ethylhexyl acrylate (2-EHA) comonomer could cause the increase of crystal orientation of PAN precursor and improved mechanical properties, and the cyclized temperature of PAN precursor could be depressed by introducing itaconic acid (IA) comonomer. Until now, few papers have been concerned with the effect of comonomers in PAN fiber on the properties of PAN precursor and its resulting carbon fiber. Therefore, we have attempted to study how the properties of PAN precursor and its resulting carbon fiber are affected by different contents of comonomers.

## EXPERIMENTAL

The PAN homopolymer and copolymers used in this study were polymerized in the mixed solvent of ace-

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**Table I** The Composition and Molecular Weight of PAN Precursors

Sample Number	Intrinsic Viscosity (dL/g)	$\bar{M}_w \times 10^5$	Dispersity	Feed Composition AN : 2-EHA : IA (mol %)	Elemental Analysis C%, N%, H%
P0	1.67	3.70	1.82	100	—
P1	1.71	3.72	1.81	98 : 1.5 : 0.5	67.04, 23.91, 6.11
P2	1.68	3.68	1.78	96 : 3.5 : 0.5	67.61, 22.09, 6.22
P3	1.61	3.31	1.86	93 : 6.5 : 0.5	67.39, 21.48, 6.62

tone and dimethyl sulfoxide at 60°C with  $\alpha$ ,  $\alpha'$ -azobis (isobutyronitrile) as initiator under an inert atmosphere of nitrogen. The resulting polymerization solution was directly spun to form PAN precursor fiber using spinneret (1500 holes, 0.06 mm/hole, L/d = 1) through 10% DMSO coagulation bath at 5°C, then stretched in boiling water and dried. PAN precursor was stabilized at 250°C for 30 min, then at 270°C for 1 h in air, under 0.15 g/denier tension. The oxidized PAN fiber was carbonized to 1200°C under a high-purity nitrogen atmosphere.

Intrinsic viscosity (IV) measurements of PAN fibers were carried out in DMF with 0.5 LiBr wt % at 30°C by a Sohott-Gerate AVS 300 viscometer, equipped with a Ubbelohde solution viscometer. The average molecular weight and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) were determined by Waters model 440 gel-permeation chromatograph (eluting solvent: DMF containing 0.5 LiBr wt %; column:  $\mu$ -BONDAGEL E-Linear). The average molecular weights of various PAN precursors are shown in Table I.

The contents of carbon, nitrogen, and hydrogen in PAN precursor were determined by the well-known method of elemental analysis (Table I) using a Carlo Erba elemental analyzer.

Thermograms of PAN precursors were obtained using a Perkin-Elmer system 7/4 differential scanning calorimeter. Samples were heated under air purge at a heating rate of 20°C/min. A Rigaku X-ray diffractometer with CuK $\alpha$  radiation as the source was used to study the wide angle at 35 kV and 10 mA.

The crystallite size ( $L_c$ ) was calculated from the following equation<sup>21</sup>:

$$L_c = K\lambda / (B \cos \theta)$$

where  $\lambda$  is the wavelength of CuK $\alpha$  X-ray,  $B$  is the half-value width in the radian of the X-ray diffraction intensity ( $I$ ) vs.  $2\theta$  curve, and  $K$  is 0.89 (a constant).

The crystallinity index for PAN fiber was measured by Bell and Dumbleton's method.<sup>22</sup> Uchide et al.<sup>23</sup> have introduced an "aromatization index" ( $AI$  value):

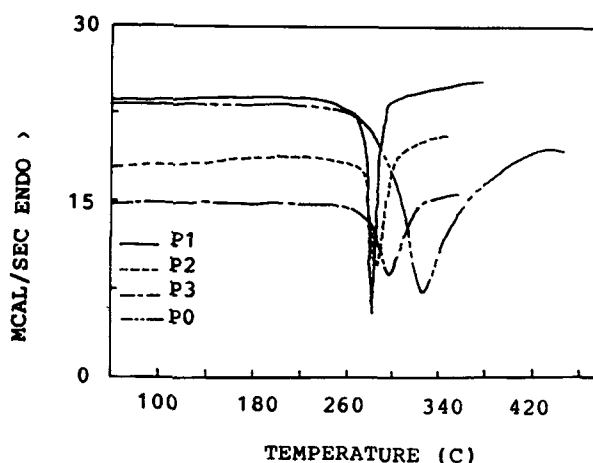
$$AI = I_A / (I_A + I_P)$$

where  $I_A$  is the intensity of the diffraction produced by aromatized structures at  $2\theta = 25^\circ$ , and  $I_P$  is the intensity at  $2\theta = 17^\circ$ .

Orientation was determined by Rigaku X-ray diffractometer using fiber specimen attachment by employing the following formula<sup>24</sup>:

$$H(\%) = [(360 - \sum Xi) / 360] \times 100\%$$

where  $H(\%)$  is the orientation and  $Xi$  is the half-width in degrees of the intensity distribution at  $2\theta = 17^\circ$  and  $25^\circ$  for PAN precursor and carbon fiber, respectively.



**Figure 1** DSC curves of PAN precursors with different comonomer composition: measured weight of sample, (P0) 3 mg; (P1–P3) 6 mg.

**Table II** DSC Characterization of PAN Precursors

Sample Number	Feed Composition AN : 2-EHA : IA (mol %)	Onset of Exotherm (°C)	Peak Temperature (°C)	Heat of Exotherm (cal/g)
P0	100 : 0 : 0	261	328	-464
P1	98 : 1.5 : 0.5	200	283	-129
P2	96 : 3.5 : 0.5	209	288	-107
P3	93 : 6.5 : 0.5	222	300	-92
P4	99.5 : 0 : 0.5	230	295	-371
P5	97 : 1.5 : 1.5	188	—	—
P6	95 : 1.5 : 3.5	184	—	—
P7	98.5 : 1.5 : 0	272	319	-257
P8	98.5 : 3.5 : 0	290	316	-127

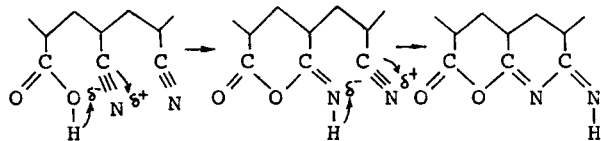
Mechanical properties of PAN and carbon fiber were measured by a Microcomputer Universal Material Tester (Hung Ta Co., Ltd) type 8104 at cross-head speed of 10 mm/min and 0.5 mm/min for PAN precursor and carbon fiber, respectively, with gauge length of 20 mm and load cell of 30 g. Pore size of PAN fiber and resulting carbon fiber was measured with Micromeritics Autopore II 9220 using pressure from 0 to 55,000 psia.

## RESULTS AND DISCUSSION

### Thermal Properties of PAN Precursors

Figure 1 shows DSC curves of PAN precursors with different comonomer composition. The greater the content of AN in PAN copolymer, the higher the height of the exothermic peak in the DSC curve. It is believed that the exothermic peak is influenced by the ability of nitrile groups to react, and changes in the actual height of the exothermic peak are related to the number of nitrile groups able to react or to the ability of nitrile groups to react rapidly.<sup>25</sup>

Pure PAN fiber (sample P0 in Table II) has a higher onset of exotherm at approximately 261°C and a higher peak temperature at approximately 328°C. The introduction of a few percent of IA comonomer into PAN precursor (comparing sample P0 and sample P4) greatly lowers the onset of exotherm and peak temperature. This is because IA comonomer can initiate the cyclization of the CN group according to the following mechanism<sup>26</sup>:

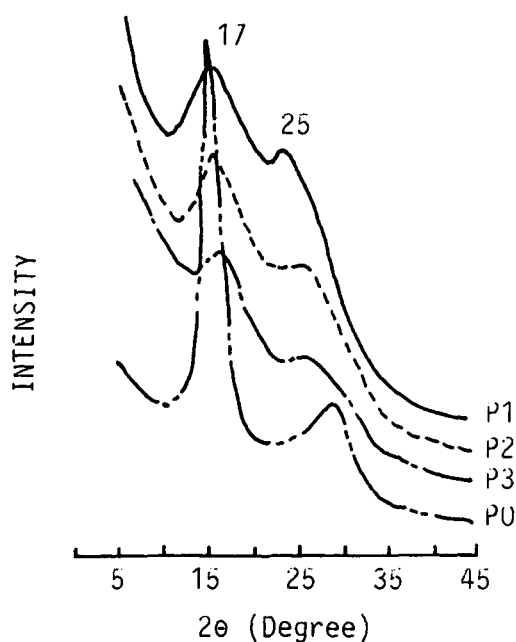


Therefore, the initial cyclized temperature (onset of exotherm) of PAN precursor can be decreased. When the content of 2-EHA comonomer in PAN precursor (comparing sample P0 and P7–P8 in Table II) increases, the onset of exotherm and peak temperature increases. This is attributed to that the 2-EHA comonomer can prevent the cyclization propagation of CN groups, but itself can participate in cyclization. In the AN:2-EHA:IA copolymers (sample P1–P3 in Table II), the increase of 2-EHA comonomer can result in the increase of initial cyclized temperature and peak temperature; therefore, it is desirable to control the 2-EHA content as little as possible. As the IA comonomer content is increased (comparing samples P1 and P5–P6 in Table II), the onset of the exotherm is decreased. However, as the content of the IA comonomer is slightly increased, the conversion of AN for the copolymerization markedly decreases, as shown in Table III. This indicates that as the content of IA comonomer increases the reaction rate of copolymerization decreases.

Figure 2 shows the X-ray diffraction patterns of oxidized PAN fiber that were used to measure aromatization indexes (*AI* value) that correspond to the degree of CN cyclization. Because of its higher

**Table III** Effect of IA Comonomer on the Conversion of AN

Feed Composition AN : 2-EHA : IA (mol %)	Reaction Time (h)	Conversion of AN (%)
98 : 1.5 : 0.5	8	75
97 : 1.5 : 1.5	8	50
95 : 1.5 : 3.5	8	20



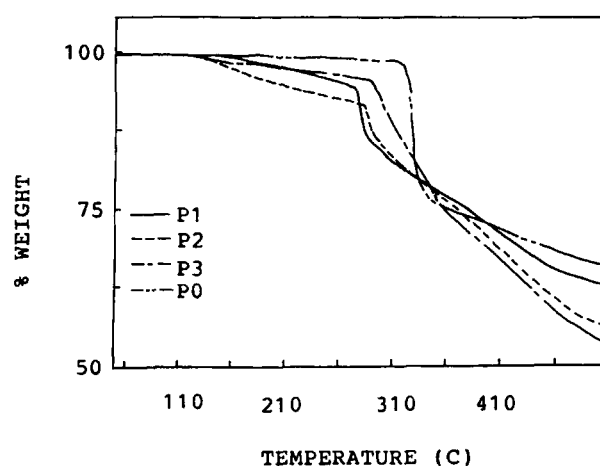
**Figure 2** X-ray diffraction patterns of oxidized PAN fibers.

initial cyclization temperature (onset of exotherm at approximately 261°C), pure PAN was not cyclized at all when heated to 250°C, i.e., the *AI* value is zero (sample P0 in Table IV). Because of the lowest onset of exotherm at approximately 200°C, sample P1 has the largest *AI* value. The decrease of initial cyclization temperature results in the increase of the *AI* value. This indicates that the larger the *AI* value, the faster is the cyclization of CN groups.

TGA analyses of PAN precursors with different composition are shown in Figure 3. The higher the AN content in the PAN fiber, the greater and quicker is the weight loss at the approximately peak temperature of the DSC curve, i.e., the slope of the weight loss curve is greater. This is because most of the CN groups are cyclized and decomposed rapidly.

**Table IV** Effect of Comonomer Composition on Aromatization Index

Sample Number	Oxidation Temperature (°C)	Onset of Exotherm (°C)	Aromatization Index (%)
P0	250	261	0
P1	250	200	46.0 ± 0.2
P2	250	209	40.4 ± 0.2
P3	250	222	37.7 ± 0.3

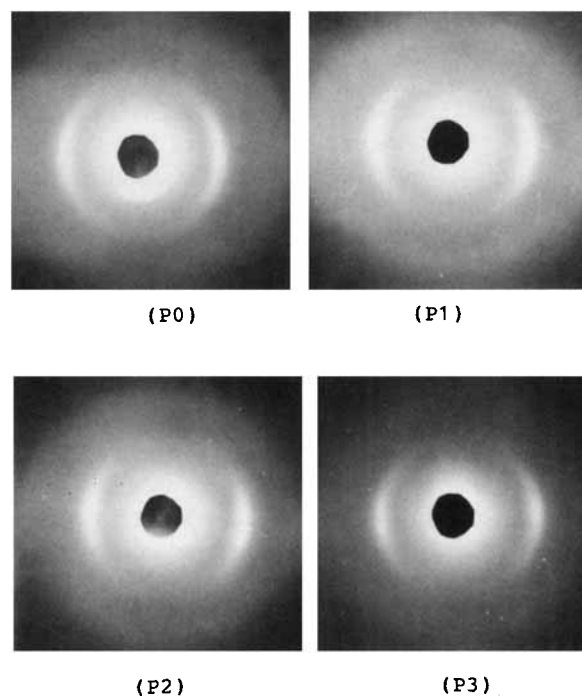


**Figure 3** TGA curves of PAN precursors with different comonomer composition.

But the total weight loss of PAN precursor with higher AN content is less, i.e., the yield of carbon fiber is higher.

#### Mechanical Properties of PAN Precursors

Figure 4 shows X-ray diffraction photographs of various PAN precursors. From the photographs, the



**Figure 4** X-ray diffraction photographs of various PAN precursors.

**Table V** The Mechanical Properties of Various PAN Precursors

Sample Number	Crystallite Size $L_c$ (Å)	Crystallinity Index	Orientation (%)	Modulus (g/d)	Tensile Strength (g/d)	Break Elongation (%)
P0	$30.4 \pm 0.1$	$0.74 \pm 0.02$	$73.2 \pm 0.2$	$78 \pm 4$	$3.6 \pm 0.4$	$22.4 \pm 0.5$
P1	$34.3 \pm 0.4$	$0.77 \pm 0.01$	$76.4 \pm 0.5$	$120 \pm 8$	$5.0 \pm 0.3$	$20.9 \pm 0.4$
P2	$29.4 \pm 0.3$	$0.76 \pm 0.01$	$78.3 \pm 0.3$	$80 \pm 2$	$4.2 \pm 0.4$	$19.9 \pm 0.4$
P3	$27.2 \pm 0.2$	$0.69 \pm 0.02$	$81.5 \pm 0.6$	$62 \pm 2$	$3.0 \pm 0.1$	$19.1 \pm 0.3$

length of the arc should be as small as possible for the optimum orientation of the molecular chain along the fiber axis and the width of the arc gives an indication of the crystal size.<sup>19</sup>

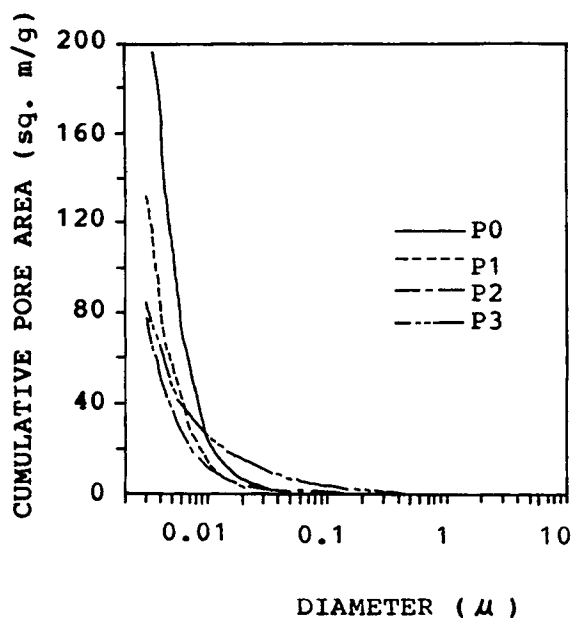
PAN precursor with 1.5 mol % 2-EHA comonomer and 0.5 mol % IA comonomer (sample P1 in Table V) has the highest Young's modulus and tensile strength among the samples studied; this is due to it having the highest crystallinity, the largest crystalline size, and smaller size of pores (Fig. 5) in PAN precursor. As the content of 2-EHA comonomer (samples P2-P3 in Table V) further increases, the tensile strength and modulus of PAN precursor decreases. This is because poly(2-EHA) is an amorphous polymer; therefore, PAN precursor with higher 2-EHA content (Table VI) has a lower degree of crystallinity and smaller crystalline size, but has more preferred orientation. From the above results, the introduction of a few percent of 2-EHA co-

monomer into PAN precursor can improve the mechanical properties of PAN precursor; therefore, PAN copolymer shows better mechanical properties than those of pure PAN precursor.

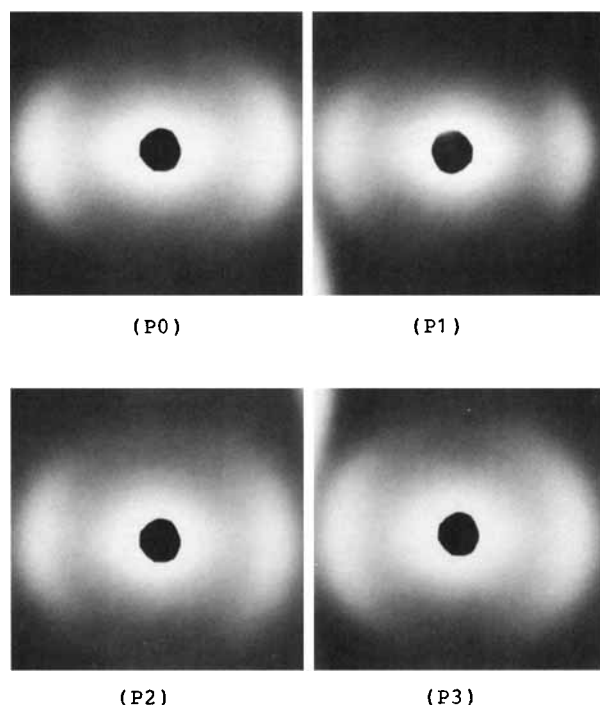
### Mechanical Properties of Resulting Carbon Fibers

Generally, the better the orientation of precursor fiber, the more preferred the orientation of its resulting carbon fiber.<sup>20</sup> Figure 6 shows X-ray diffraction photographs of resulting carbon fibers. When Figure 6 is compared with Figure 4, it is interesting to note the change of orientation from PAN precursor to its carbon fiber. As the content of 2-EHA comonomer increases, the orientation of PAN precursor increases (samples P1-P3 in Table V), but the orientation of its resulting carbon fiber unexpectedly decreases (samples P1-P3 in Table VII). This is affected by the amorphous phase of PAN precursor.

The modulus and tensile strength of the carbon fiber produced from sample P1 (Table VII) are better than that from a pure PAN precursor (sample P0).<sup>27</sup> This is because the resulting carbon fiber produced from sample P1 has more preferred orientation, larger crystalline size, and smaller size of pores (Fig. 7). From comparing Table VII with Table V, it is believed that since PAN precursor pos-

**Figure 5** Pore-size distributions in PAN precursors.**Table VI** Effect of 2-EHA Comonomer on the Crystal of PAN Precursors

Feed Composition AN : 2-EHA (mol %)	Crystallite Size $L_c$ (Å)	Crystallinity Index	Orientation
98.5 : 1.5	$41.4 \pm 0.3$	$0.76 \pm 0.01$	$78.2 \pm 0.5$
96.5 : 3.5	$37.3 \pm 0.4$	$0.75 \pm 0.01$	$82.4 \pm 0.6$

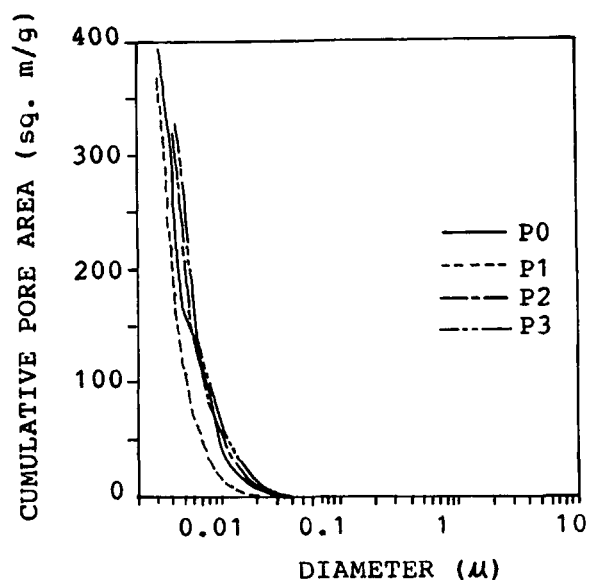


**Figure 6** X-ray diffraction photographs of the resulting carbon fibers.

esses good mechanical properties its resulting carbon fiber also shows good mechanical properties. This indicates that there is a relatively good relationship between the tensile strength and modulus of a precursor and those of its resulting carbon fiber.<sup>9,19</sup>

## CONCLUSIONS

The introduction of 0.5 mol % itaconic acid comonomer into PAN precursor can greatly depress



**Figure 7** Pore-size distributions in various resulting carbon fibers.

the initial cyclization temperature. As the amount of IA comonomer is increased, the reaction rate of copolymerization decreases. The introduction of 1.5 mol % 2-EHA into PAN precursor can improve both the orientation and mechanical properties of PAN precursor and its resulting carbon fiber. The results show that there is a good relationship between the modulus and tenacity of PAN precursor and those of its resulting carbon fiber.

From the above results, we believe that the sequence order of IA and 2-EHA comonomers in the polymer chain can considerably affect the thermal (like cyclized temperature) and mechanical properties of PAN precursor and the size of side group of acrylate comonomers can affect the orientation of PAN precursor and its resulting carbon fiber. Therefore, we will continue the study of these two topics.

**Table VII** The Mechanical Properties of Resulting Carbon Fibers

Sample Number	Crystallite Size $L_c$ (Å)	Orientation (%)	Modulus (g/d)	Tensile Strength (g/d)	Break Elongation (%)
P0	$10.2 \pm 0.1$	$75.5 \pm 0.2$	$850 \pm 14$	$5.8 \pm 0.4$	$0.7 \pm 0.1$
P1	$10.8 \pm 0.2$	$76.3 \pm 0.3$	$1539 \pm 81$	$15.3 \pm 2$	$1.2 \pm 0.2$
P3	$10.8 \pm 0.2$	$72.4 \pm 0.5$	$1048 \pm 66$	$10.3 \pm 1.5$	$0.9 \pm 0.1$
P3	$9.4 \pm 0.1$	$69.3 \pm 0.2$	$764 \pm 20$	$5.2 \pm 0.5$	$0.5 \pm 0.1$

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