

Electronic Supplementary Information (ESI)

for

Remote dibenzocycloheptyl substitution on a bis(arylmino)pyridyl-iron ethylene polymerization catalyst; enhanced thermal stability and unexpected effects on polymer properties

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SI-1 Experimental section

General considerations

All manipulations involving air- and moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Prior to use, toluene was refluxed over sodium and distilled for 24 h under a nitrogen atmosphere. Methylaluminoxane (MAO, 1.46 mol L⁻¹ solution in toluene) and modified methylaluminoxane (MMAO, 2.00 mol L⁻¹ in *n*-heptane) were purchased from Akzo Nobel Corp. High purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 100 °C in dichlorobenzene-*d*₂ (C₆D₄Cl₂) with TMS as an internal standard. 1D sequence inverse-gated decoupled ¹³C NMR spectra of the saturated polyethylenes given in the electronic supporting information (ESI2) were measured on JNM-ECZ400S/L1 instrument at 100 °C in dichlorobenzene-*d*₂ (C₆D₄Cl₂); the inverse gated single 90° pulse was employed and the recycle delay was set at 12 s (7*T₁). IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 micro-analyzer. Molecular weight and molecular weight distributions (*M*_w/*M*_n) of the polyethylenes were measured using a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as solvent. The melting points of the polyethylenes were measured from the fourth scanning run on a Perkin-Elmer TA-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere. In the procedure, a sample of about 5.0 mg was heated to 160 °C at a rate of 20 °C min⁻¹ and maintained for 2 min at 160 °C to remove the thermal history, then cooled at a rate of 20 °C min⁻¹ to -20 °C, and then heated to 160 °C at a rate of 10 °C min⁻¹. The bis(imino)pyridines, **L1** - **L4** along with Fe_{2,6-iPr2Ph} have been prepared according to literature procedures.^{1,2}

Synthesis of [2,6-{(2-R¹,4-(C₁₅H₁₃),6-R²C₆H₂)N=CMe}₂C₅H₃N]FeCl₂

(a) R¹ = R² = Me (**Fe1**). Under a nitrogen atmosphere, a solution of FeCl₂·4H₂O (0.08 g, 0.40 mmol) and **L1** (0.30 g, 0.40 mmol) in THF (20 mL) was stirred for 14 h at room temperature. The mixture was then concentrated under reduced pressure and diethyl ether added to initiate precipitation. The precipitate was collected by filtration, washed with an excess of diethyl ether (3 × 15 mL) and dried under reduced pressure to yield **Fe1** as a blue powder (0.28 g, 80%). FT-IR (cm⁻¹): 3016 (w), 2968 (w), 2928 (w), 1619 (m, ν_{C=N}), 1588 (m), 1478 (s), 1449 (m), 1373 (m), 1310 (w), 1263 (s), 1218 (s), 1132 (w), 1101 (w), 1042 (m), 983 (w), 947 (w), 881 (m), 813 (m), 764 (s), 696 (w). Anal. calcd for C₅₅H₅₁Cl₂FeN₃ (879.28): C, 75.00; H, 5.84; N, 4.77. Found: C, 74.85; H, 5.94; N, 4.75%.

(b) R¹ = R² = Et (**Fe2**). In a manner similar to that described for the synthesis of **Fe1** but with **L2** as the bis(imino)pyridine, **Fe2** was isolated as a blue powder (0.29 g, 78%). FT-IR (cm⁻¹): 3058 (w), 3014 (w), 2966 (m), 2932 (w), 2877 (m), 1618 (m, ν_{C=N}), 1586 (s), 1490 (m), 1454 (s), 1370 (s), 1333 (w), 1309 (w), 1267 (s), 1215 (s), 1160 (w), 1136 (w), 1100 (m), 1027 (m), 982 (w), 946 (w), 889 (m), 831 (w), 805 (m), 761 (s), 734 (m), 695 (w). Anal. calcd for C₅₉H₅₉Cl₂FeN₃ (935.34): C, 75.64; H, 6.35; N, 4.49. Found: C, 75.31; H, 6.58; N, 4.41%.

(c) $R^1 = R^2 = iPr$ (**Fe3**). In a manner similar to that described for the synthesis of **Fe1** but with **L3** as the bis(imino)pyridine, **Fe3** was isolated as a blue powder (0.30 g, 77%). FT-IR (cm^{-1}): 3401 (w), 3014 (w), 2965 (m), 2926 (w), 1618 (m, $\nu_{\text{C=N}}$), 1586 (s), 1474 (w), 1447 (s), 1369 (s), 1330 (w), 1309 (w), 1264 (s), 1216 (s), 1162 (w), 1129 (w), 1079 (m), 1042 (s), 981 (w), 946 (w), 879 (m), 811 (m), 763 (s), 695 (w). Anal. calcd for $\text{C}_{63}\text{H}_{67}\text{Cl}_2\text{FeN}_3$ (991.41): C, 76.20; H, 6.80; N, 4.23. Found: C, 76.36; H, 6.63; N, 4.26%.

(d) $R^1 = \text{Me}$, $R^2 = \text{Et}$ (**Fe4**). In a manner similar to that described for the synthesis of **Fe1** but with **L4** as the bis(imino)pyridine, **Fe4** was isolated as a blue powder (0.31 g, 85%). FT-IR (cm^{-1}): 3058 (w), 3015 (w), 2964 (w), 2927 (m), 2874 (w), 1695 (w), 1619 (w, $\nu_{\text{C=N}}$), 1586 (s), 1489 (w), 1447 (s), 1367 (s), 1310 (w), 1251 (s), 1212 (s), 1158 (w), 1135 (w), 1101 (w), 1027 (m), 983 (w), 946 (w), 881 (m), 807 (m), 751 (s), 692 (w). Anal. calcd for $\text{C}_{57}\text{H}_{55}\text{Cl}_2\text{FeN}_3$ (908.83): C, 75.33; H, 6.10; N, 4.62. Found: C, 75.56; H, 6.03; N, 4.86%.

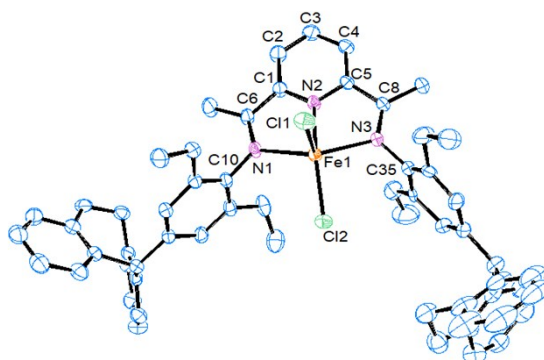
X-ray structure determinations

The single-crystal X-ray diffraction study of **Fe2** was conducted on a XtaLAB Synergy-R HyPix diffractometer with graphite monochromated Cu-K α ($\lambda = 1.54184 \text{ \AA}$) at 169.99(10) K, while for **Fe4** the study was performed on a dtrek-CrysAlisPro-abstract goniometer imported Rigaku diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173.00 K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. Using Olex2,³ the structures were solved with SHELXT program using Intrinsic Phasing⁴ and refined with the SHELXT refinement package using Least Squares minimization.⁵ Crystal data and processing parameters for **Fe2** and **Fe4** are summarized in Table S2.

Table S1. Selected bond lengths (\AA) and angles ($^\circ$) for **Fe2** and **Fe4**

Bond Lengths	Fe2	Fe4
Fe1-Cl2	2.2596(8)	2.2547(8)
Fe1-N1	2.206(2)	2.201(2)
Fe1-N2	2.080(2)	2.068(2)
Fe1-N3	2.199(2)	2.213(2)
Fe1-Cl1	2.3247(9)	2.3157(9)
Bond Angles		
Cl2-Fe1-Cl1	114.58(3)	119.43(3)
N1-Fe1-Cl2	102.84(7)	100.63(6)
N1-Fe1-N3	140.71(9)	143.81(9)
N1-Fe1-Cl1	99.53(7)	96.37(6)
N2-Fe1-Cl2	151.71(7)	145.43(7)
N2-Fe1-N1	73.35(8)	73.82(8)
N2-Fe1-N3	73.07(9)	73.95(8)
N2-Fe1-Cl1	93.59(7)	95.15(7)
N3-Fe1-Cl2	97.16(6)	96.59(6)
N3-Fe1-Cl1	102.35(7)	102.49(8)

(a) ORTEP drawing of **Fe2** with the thermal ellipsoids set at 30% probability. Hydrogen atoms have omitted for clarity.



(b) ORTEP drawing of **Fe4** with the thermal ellipsoids set at 30% probability. Hydrogen atoms have omitted for clarity.



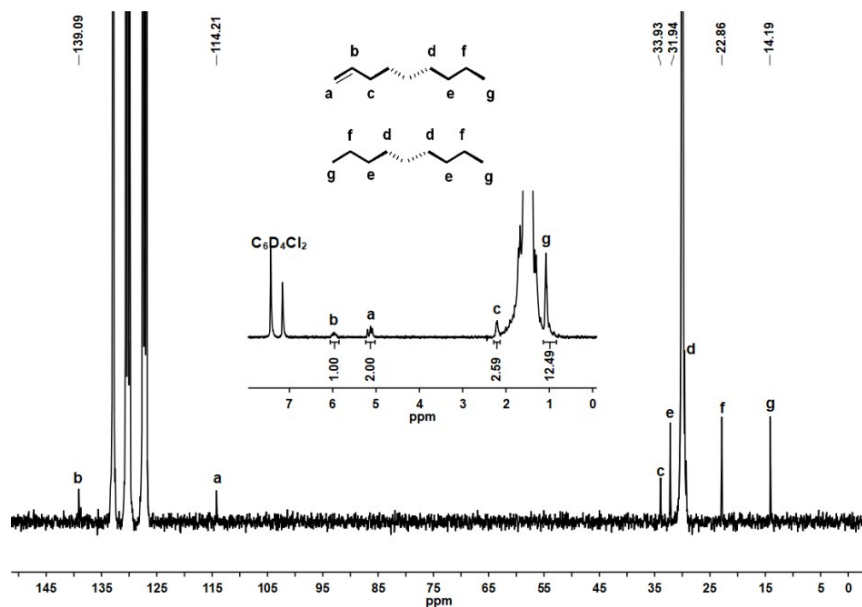
Table S2. Crystal data and structure refinement for **Fe2** and **Fe4**

Identification code	Fe2	Fe4
Empirical formula	C ₅₉ H ₅₉ Cl ₂ FeN ₃	C ₅₇ H ₅₅ Cl ₂ FeN ₃
Formula weight	936.84	908.79
Temperature/K	169.99(11)	173.1500
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /c
a/Å	48.0435(5)	21.6551(4)
b/Å	12.54440(10)	17.1174(3)
c/Å	16.9753(2)	16.8958(3)
α/°	90	90
β/°	90.6180(10)	102.716(2)
γ/°	90	90
Volume/Å ³	10230.02(18)	6109.3(2)
Z	8	4
ρ _{calc} /cm ³	1.217	0.988
μ/mm ⁻¹	3.624	0.366

$F(000)$	3952.0	1912.0
Crystal size/mm ³	0.194 × 0.131 × 0.071	0.231 × 0.103 × 0.036
Radiation	CuK α ($\lambda = 1.54184$)	MoK α ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	7.284 to 150.822	3.062 to 63.078
Index ranges	$-59 \leq h \leq 59$	$-30 \leq h \leq 30$,
	$-8 \leq k \leq 15$	$-24 \leq k \leq 23$,
	$-21 \leq l \leq 21$	$-23 \leq l \leq 23$
Reflections collected	31816	100995
Independent reflections	10039 [$R_{\text{int}} = 0.0293$, $R_{\text{sigma}} = 0.0298$]	18760 [$R_{\text{int}} = 0.0786$, $R_{\text{sigma}} = 0.0771$]
Data/restraints/parameters	10039/881/899	18760/27/595
Goodness-of-fit on F^2	1.059	1.029
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0597$ $wR_2 = 0.1736$	$R_1 = 0.0783$, $wR_2 = 0.1812$
Final R indexes [all data]	$R_1 = 0.0722$ $wR_2 = 0.1919$	$R_1 = 0.1300$, $wR_2 = 0.2040$
Largest diff. peak/hole / e \AA^{-3}	0.76/-0.33	0.56/-0.34

SI-2 Method used to determine the molar ratio of unsaturated to saturated linear polymer chains present in polyethylene produced using **Fe1/MAO** at 70 °C/10 atm

(a) ^{13}C NMR and ^1H NMR spectra of a polyethylene sample obtained using **Fe1/MAO**: the run temperature was 70 °C and the ethylene pressure was 10 atm (entry 12, Table 2). The labels a – g indicate the proton and carbon assignments on the polymer backbone in the ^1H NMR and ^{13}C NMR spectra, respectively.

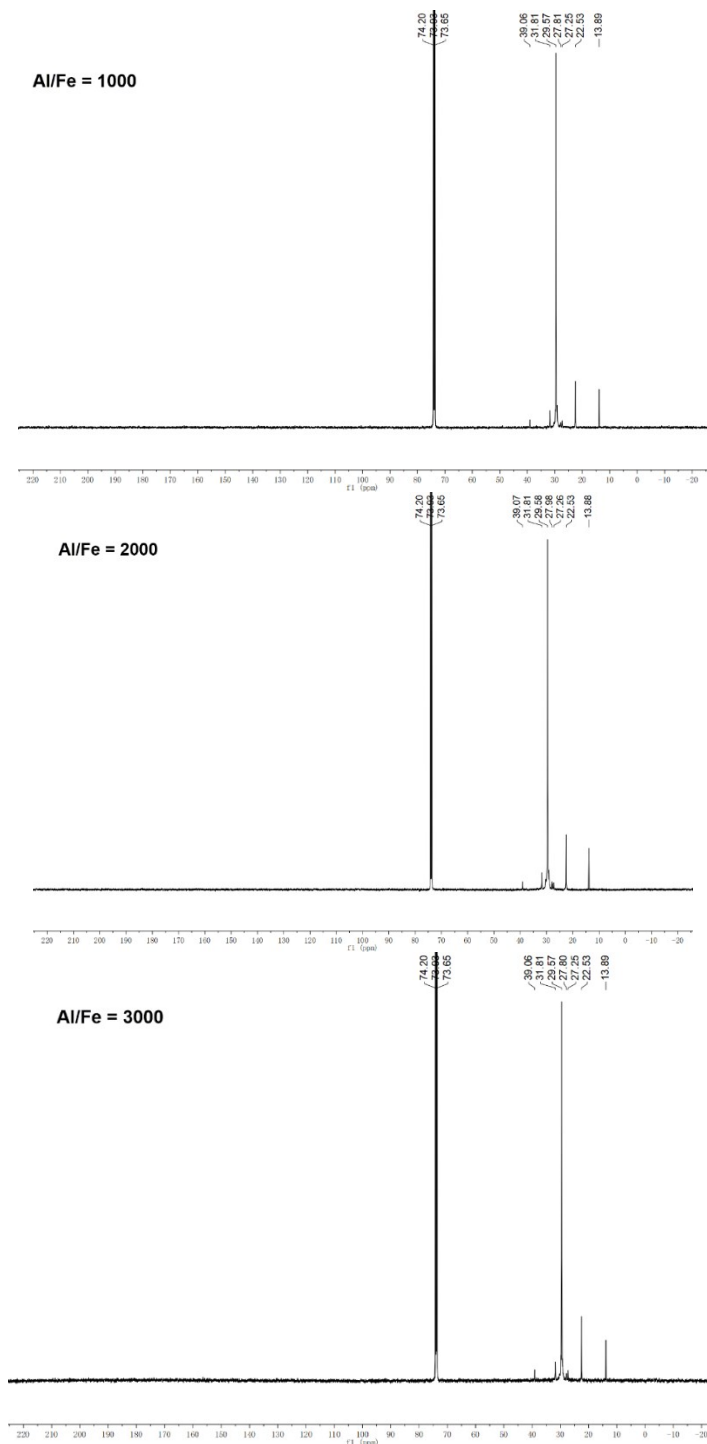


(b) *Method*: According to the literature,⁶ the most upfield peak “g” in the ^1H NMR spectrum of polyethylene can be assigned to a terminal methyl group, this methyl group comprises methyl chain ends for both saturated (*n*-propyl/*n*-propyl) and unsaturated (vinyl/*n*-propyl) polyethylenes. Hence, the integration of this methyl peak (12.49 in spectrum above and Figure 8 in manuscript) should be split into two parts (3 for the vinyl-terminated PE and 9.49 for the saturated PE). This means for 1 mole of unsaturated PE chain (3/3), there should be 9.49/6 (as two chain-end CH_3 groups) moles of saturated PE chain.

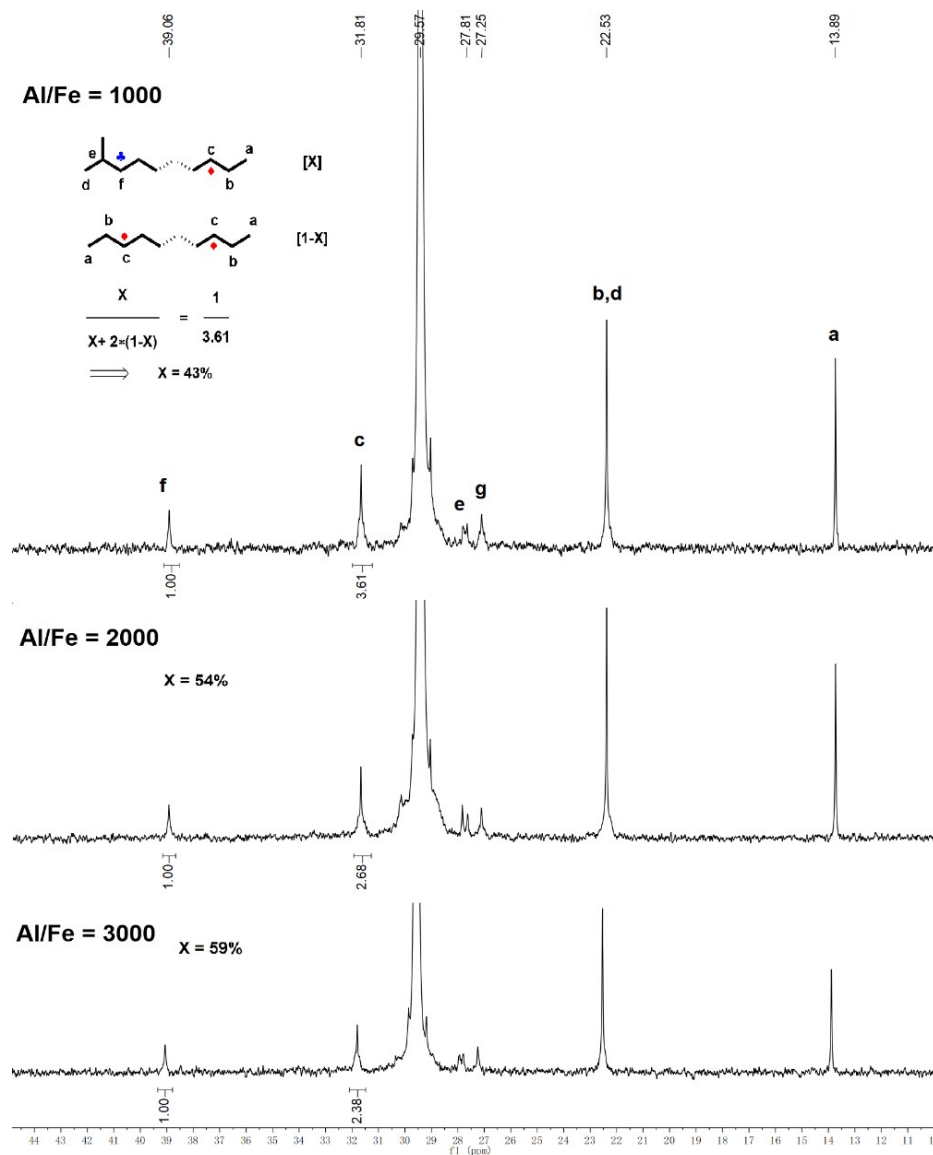
Therefore, the molar ratio of saturated PE to unsaturated PE is $(9.49/6):1 = 1.58:1$ and hence the % content of vinyl-terminated PE is: $1/(1+1.58) \times 100 = \mathbf{38.7\%}$.

SI-3 Method used to determine the molar ratio (X) of linear polymer chains containing isobutyl/*n*-propyl end groups to chains containing *n*-propyl/*n*-propyl end groups.

(a) 1D sequence inverse-gated decoupled ^{13}C NMR spectra of the saturated polyethylenes obtained using **FeI**/MMAO at Al:Fe molar ratios of 1000:1, 2000:1 and 3000:1; the run temperature was 20 °C and the ethylene pressure 1 atm (entries 8, 2 and 11, Table 3).



(b) Upfield regions of these 1D sequence inverse-gated decoupled ^{13}C NMR spectra and their analysis with regard to the relative integrals for peaks 'f' and 'c'.

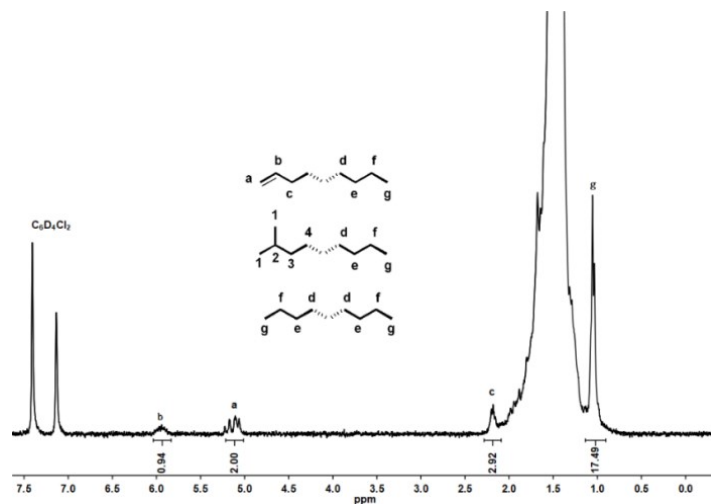


Method: Analysis of these ^{13}C NMR spectra of fully saturated polymers,⁷⁻¹⁰ obtained using **Fe1**/MMAO at three different Al:Fe molar ratios, revealed two types of end group compositions: isobutyl/*n*-propyl and *n*-propyl/*n*-propyl, and these are present in non-equal amounts. To quantify the relative amounts of these types of polymer chain, the molar ratio, X , has been determined. A representative calculation is given above for the molar ratio at 1000:1 where $X = 43\%$.

Remarks: On increasing the amount of MMAO from 1000:1, 2000:1 to 3000:1, the value of X increased from 43% to 59%. As would be expected when MAO was employed as the activator, the saturated polymer contains solely *n*-propyl/*n*-propyl end groups (see Figure 3 in manuscript), on account of the absence of aluminum isobutyl species in MAO.

SI-4 Method used to determine the molar ratio of unsaturated to saturated linear polymer chains present in polyethylene produced using **Fe1**/MMAO at 70 °C/10 atm

(a) ^1H NMR spectrum of the polyethylene sample obtained using **Fe1**/MMAO: the run temperature was 70 °C and the ethylene pressure 10 atm (entry 11, Table 4). The labels a – g indicate the proton assignments on the polymer backbone.



(b) *Method*: A similar calculation to that described in **SI-2** was performed based on integral data obtained from the ^1H NMR spectrum. Due to the very small amounts of isobutyl end groups present in this polyethylene, this was ignored when calculating the molar ratio.

Therefore, the molar ratio of saturated PE to unsaturated PE is $(14.49/6):1 = 2.42:1$ and hence the % content of vinyl-terminated PE is: $1/(1+2.42) \times 100 = \mathbf{29.3\%}$.

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