

Supporting Information

Copolymerization of propylene with Si-containing α,ω -diolefin: How steric hindrance of diolefins affects long chain branch formation

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Experimental section

Materials

Anhydrous toluene was purified by Solvent Purification System (SPS, Mbraun). The dimethyl pyridylamido-hafnium catalyst and the Si-containing comonomers were synthesized according to the procedure reported before. All of monomers used for the polymerization were dried over CaH₂ for 72 h before distillation. Polymerization grade propylene (from Yanshan Petrochemical Corp.) was used as received. Other reagents were commercially available and used as received. All work involving air- and/or moisture-sensitive compounds were carried out in an MBraun glove box or under a nitrogen atmosphere by using standard Schlenk technique.

Synthesis of LCBPPs

The typical procedure for copolymerization is as follows: the copolymerization was carried out in a 150 mL Schlenk flask equipped with a mechanical stirrer. The flask was repeatedly evacuated and refilled with nitrogen, and finally filled with propylene gas (atmospheric pressure) from a Schlenk line. The prescribed amount of Si-containing monomers, triisobutyl aluminium (TIBA) and solvent were added to the Schlenk flask and stirred for 5 min. Subsequently, the polymerization reaction was started by adding the prescribed amount of catalyst and cocatalyst. The reaction mixture was stirred for prescribed time at 25 °C, and the reaction was terminated with the addition of a mixed solution of EtOH and HCl aqueous solution. The resultant copolymers were precipitated from ethanol, collected on a filter paper by filtration and then dried *in vacuo*.

Characterization

The molecular weight, molecular weight distributions and intrinsic viscosity were determined at 150 °C by a PL-GPC 220 type high temperature size exclusion chromatography equipped with a two-angle laser light scattering detector (TALLS), a viscosity detector, and a differential refractive index detector with 1,2,4-trichlorobenzene (TCB) as the solvent at a flow rate of 1.0 mL min⁻¹. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). All of the samples used for SEC analysis were purified by extraction with hot toluene to remove the polymer gel. The ¹H NMR and ¹³C NMR data of the polymers were obtained on a Bruker 400 MHz spectrometer at 135 °C with *o*-C₆D₄Cl₂ as a solvent. The contents of pendent vinyl group were roughly estimated by $(I_{5.0 \text{ ppm}} + I_{10 \text{ ppm}})/(I_{0.3 \text{ ppm}} + I_{5.0 \text{ ppm}} + I_{10 \text{ ppm}})$, where $I_{5.0 \text{ ppm}}$ and $I_{10 \text{ ppm}}$ is the total intensity of methyl groups of cyclic units. $I_{0.3 \text{ ppm}}$ is the total intensity of the methyl group of acyclic units. The melting temperatures (T_m s) were measured by a differential scanning calorimetry (DSC) TA Instruments Q2000. The data were collected with the heat/cool/heat cycle at a heating rate of 10 °C·min⁻¹ from 0 °C to 200°C under N₂ atmosphere. Rheological measurements were performed on a rheometer (TA, ARES-G2) at 180 °C. The parallel plates with a diameter of 25 mm and a gap height of 0.8 mm were used. The range of the frequency sweep was from 0.628 to 628 rad/s, and a strain of 1% was used, which was in the linear viscoelastic regime for all samples. Extensional viscosities were measured at strain rates varying from 0.05 to 5 s⁻¹. The rheometer oven was purged with dry nitrogen to avoid degradation of samples during measurements.

Calculation of long chain branching density

The branching parameters g and g' could be calculated by the ratio of $\langle R_g^2 \rangle$ or $[\eta]$ of a branched polymer to that of a linear polymer with same molecular weight:

$$g = \frac{\langle R_g^2 \rangle_{branch}}{\langle R_g^2 \rangle_{linear}} \quad (1)$$

$$g' = \frac{[\eta]_{branch}}{[\eta]_{linear}} \quad (2)$$

The g' values of the copolymers are less than 1 (Table 2), confirming the presence of LCBs in polypropylene backbone. The relationship of g and g' can be expressed as:

$$g' = g^\varepsilon \quad (3)$$

where ε is an exponential factor and its value depends on branch type, experimental conditions and molecular weight. We took $\varepsilon = 0.75$ in the present work according to the previous reports. For polydisperse polymers with four functional points, the branching parameter g can be correlated to the branching points m along the molecule by the equation:

$$g = \left[\left(1 + \frac{m}{6} \right)^{0.5} + \frac{4m}{3\pi} \right]^{-0.5} \quad (4)$$

From the number of branching points m , the number of LCBD per 10000 carbons can be determined for each fraction as:

$$\text{LCBD} = \frac{m}{M} \times 10000 \times M_M \quad (5)$$

where M_M is the molecular weight of the repeat units and M is the molecular weight of the branched polymer. The weight average LCBD for each polymer was calculated and the result was summarized in Table 2.

Table S1. The reactivity ratio data for propylene/diallylsilane

Monomer	Conc.(mM/L)	X	Incorp.(%)	Y	G	F
DMS	1.83	47.05	1.60	61.50	46.28	35.99
	3.66	23.52	3.25	29.77	22.73	18.59
	7.31	11.76	6.04	15.56	11.00	8.89
	14.62	5.88	11.0	8.09	5.15	4.27
	29.25	2.94	20.5	3.88	2.18	2.23
MPS	5.88	14.63	3.17	30.55	14.15	7.00
	11.76	7.31	6.22	15.08	6.83	3.55
	23.52	3.66	11.83	7.45	3.17	1.79
	47.04	1.83	19.02	4.26	1.40	0.79
	94.08	0.91	30.48	2.28	0.51	0.37
DPS	5.48	15.69	0.99	100.0	15.54	2.46
	10.96	7.85	2.01	48.75	7.69	1.26
	21.92	3.92	3.69	26.10	3.77	0.59
	43.84	1.96	7.53	12.28	1.80	0.31
MVS	3.125	27.52	1.90	51.63	26.98	14.67
	6.25	13.76	3.72	25.9	13.23	7.32
	12.5	6.88	6.86	13.6	6.37	3.49
	18.75	4.59	10.57	8.46	4.04	2.49
	25.0	3.44	13.37	6.48	2.91	1.83

Table S2. Calculation of LCBDs for the copolymer according to Zimm-Stockmayer method

Sample	M_w ($\times 10^4$ kg/mol)	$[\eta]_{\text{linear}}$ (dL/g)	$[\eta]_{\text{branch}}$ (dL/g)	g'	g	m	branch den
1	16.6	1.16	1.14	0.98	0.98		0
2	16.9	1.17	1.13	0.96	0.95	0.2	0.17
3	25.0	1.56	1.32	0.84	0.80	1.1	0.62
4	33.6	1.93	1.37	0.71	0.63	2.9	1.21
5	56.0	2.80	1.44	0.52	0.41	8.5	2.13
6	40.5	2.21	1.56	0.71	0.63	3.1	1.07
7	20.6	1.36	1.29	0.95	0.94	0.3	0.20
8	48.6	2.52	1.62	0.64	0.55	3.6	1.04
9	18.3	1.24	1.21	0.97	0.97	0.2	0.15
10	19.4	1.30	1.22	0.94	0.92	0.3	0.22
11	30.3	1.79	1.27	0.71	0.63	3.2	1.48
12	40.5	2.21	1.42	0.64	0.56	5.5	1.90
13	25.4	1.58	1.42	0.90	0.87	0.6	0.33
14	33.5	1.93	1.26	0.65	0.57	4.5	1.88
15	16.6	1.16	1.14	0.98	0.98		0
16	21.7	1.41	1.31	0.93	0.91	0.4	0.26
17	27.8	1.68	1.43	0.85	0.81	0.9	0.45
18	15.3	1.09	1.08	0.99	0.99		0
19	35.8	2.02	1.32	0.65	0.57	4.2	1.64
20	49.4	2.55	1.34	0.53	0.42	7.2	2.05
21	60.2	2.95	1.46	0.50	0.39	10.5	2.43
22	69.1	3.26	1.51	0.46	0.36	14.8	2.90
23	26.6	1.63	1.49	0.91	0.89	0.5	0.26
24	50.9	2.61	1.22	0.47	0.37	13.0	3.58

Table S3 Microstructure Characterization of linear PP and LCBPPs

Run	M_w^a ($\times 10^4$)	PDI ^a	g'^b	LCBD ^c	η_0^d [KPa·s]	n^e	Incorp. ^f (%)	Cyclic ^f (%)	Vinyl ^f (%)	LCB Selectivity (%)	T_m^g (°C)
1	16.6	1.9	0.98	0	0.63	0.88	–				159.3
2	16.9	1.9	0.96	0.17	2.60	0.76	–				157.3
3	25.0	2.1	0.84	0.62	2.68	0.71	–				156.6
4	33.6	2.0	0.71	1.21	3.90	0.65	1.2				151.2
5	56.0	2.8	0.52	2.13	12.8	0.53	3.5	95.3	n.o. ^h		147.2
6	40.5	2.1	0.71	1.07	4.25	0.68	6.9	92.4	3.2	4.4	140.8
7	20.6	1.2	0.95	0.20	0.70	0.82	–				150.5
8	48.6	2.2	0.64	1.04	11.6	0.59	–				152.1
9	18.3	1.7	0.97	0.15	2.20	0.87	–				156.2
10	19.4	1.7	0.94	0.22	2.65	0.82	–				157.0
11	30.3	1.8	0.71	1.48	3.30	0.74	1.3				155.4
12	40.5	2.5	0.64	1.90	10.0	0.61	3.2	91.2	5.2	3.6	150.7
13	25.4	1.8	0.90	0.33	3.50	0.67	6.9	90.5	6.2	3.3	145.7
14	33.5	3.4	0.65	1.88	13.5	0.55	10.8	89.2	6.9	3.9	129.8
15	16.6	1.8	0.98	0	1.20	0.89	–				155.7
16	21.7	1.9	0.93	0.26	5.74	0.83	1.9				150.9
17	27.8	1.9	0.85	0.45	9.60	0.75	3.1	85.7	11.6	2.7	143.5
18	15.3	1.8	0.99	0	0.62	0.88	3.2	84.4	12.8	2.8	143.4
19	35.8	2.0	0.65	1.64	3.62	0.64	–				155.2
20	49.4	2.5	0.53	2.05	6.48	0.52	1.2				154.2
21	60.2	3.0	0.50	2.43	9.65	0.43	3.2	n.o.	49.4		150.5
22	69.1	3.0	0.46	2.90	24.3	0.39	9.1	n.o.	64.3		137.8
23	26.6	1.9	0.90	0.26	–	–	6.1	97.0	n.o.		–
24	50.9	4.4	0.48	3.58	–	–	–	92.5	1.9	5.6	–

^a Weight-average molecular weights (M_w s) and polydispersity indices were determined by high temperature SEC with light scattering detector at 150 °C in 1,2,4-trichlorobenzene. ^bWeight average branching factor, $g'=[\eta]_{\text{branch}}/[\eta]_{\text{linear}}$. ^c long chain branching density per 10,000 carbon. ^d zero shear viscosity at 180°C. ^e Power-law exponent ($\eta^* = m\omega^{n-1}$) determined by small-dynamic oscillatory shear measurement. ^f Comonomer incorporation (mol%) and the cyclization selectivity were established by ¹H NMR spectra. ^g Determined by DSC. ^h n.o.=not observed.

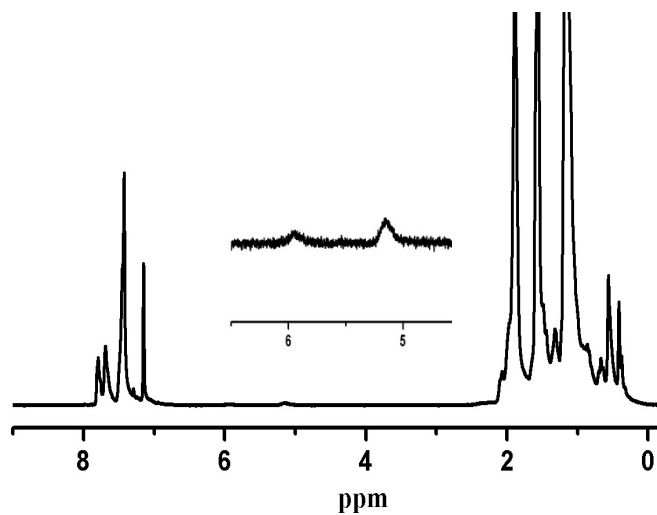


Fig. S1 The ^1H NMR spectrum of poly(propylene-*co*-DPS) with 8.5 mM/L feed concentration.

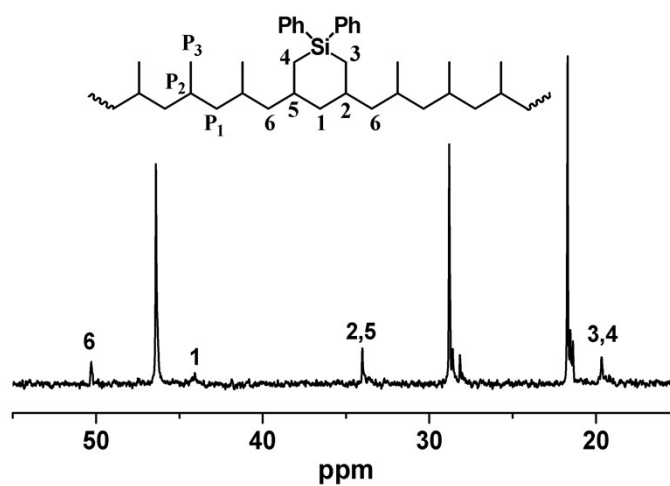


Fig. S2 The ^{13}C NMR spectrum of poly(propylene-*co*-DPS) with 8.5 mM/L feed concentration.

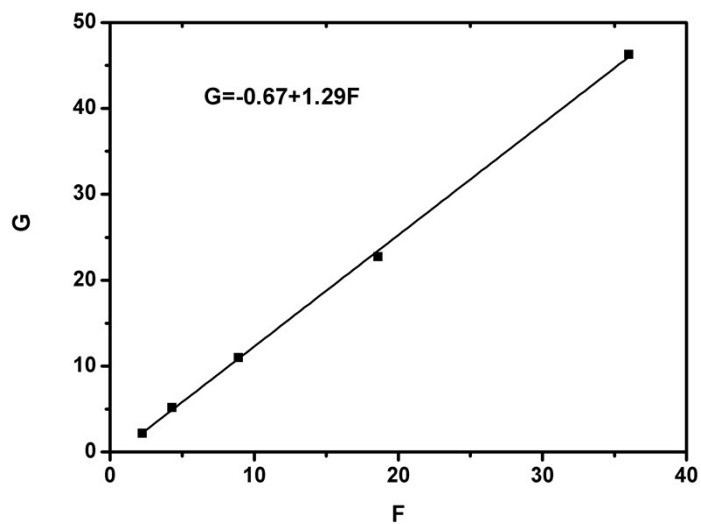


Fig. S3 The Fineman-Ross plot for propylene/DMS.

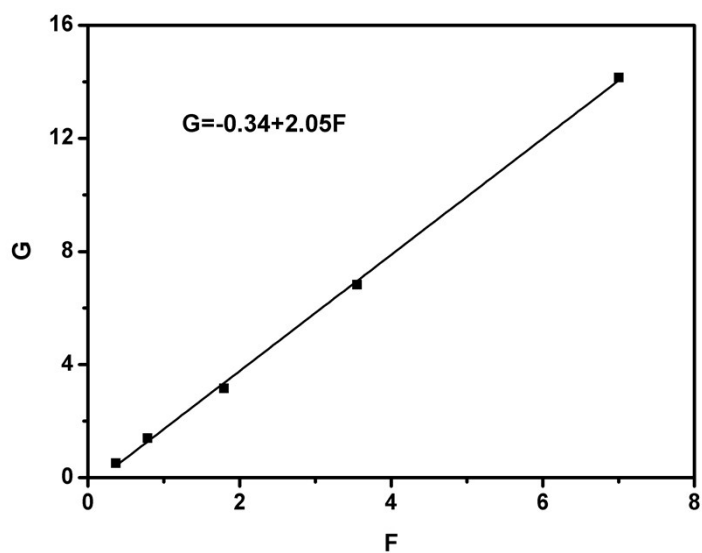


Fig. S4 The Fineman-Ross plot for propylene/MPS.

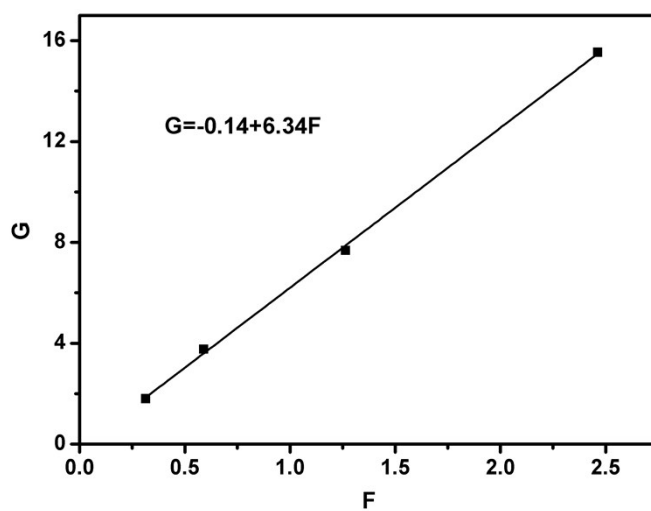


Fig. S5 The Fineman-Ross plot for propylene/DPS.

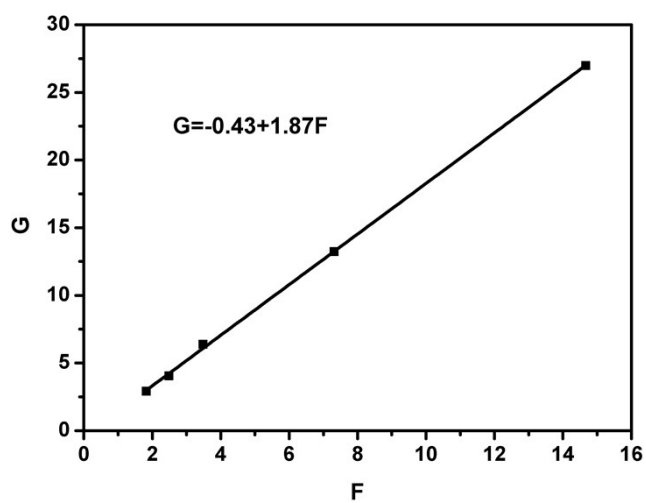


Fig. S6 The Fineman-Ross plot for propylene/MVS.

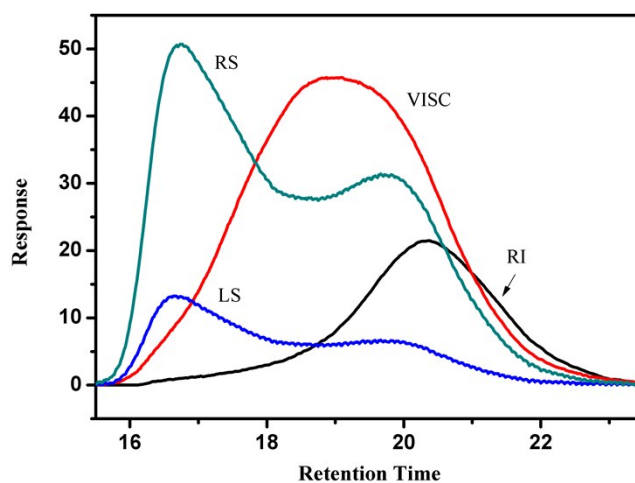


Fig. S7 The typical elution curves of the LCBPPs by SEC with triple detectors.

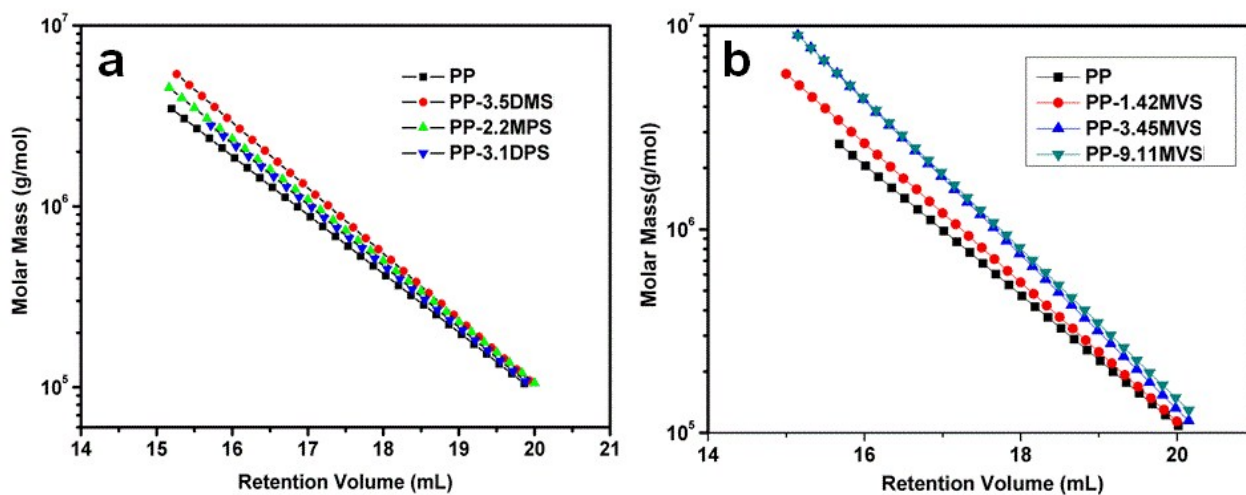


Fig. S8 Molecular weight vs retention time of linear PP and LCBPPs.

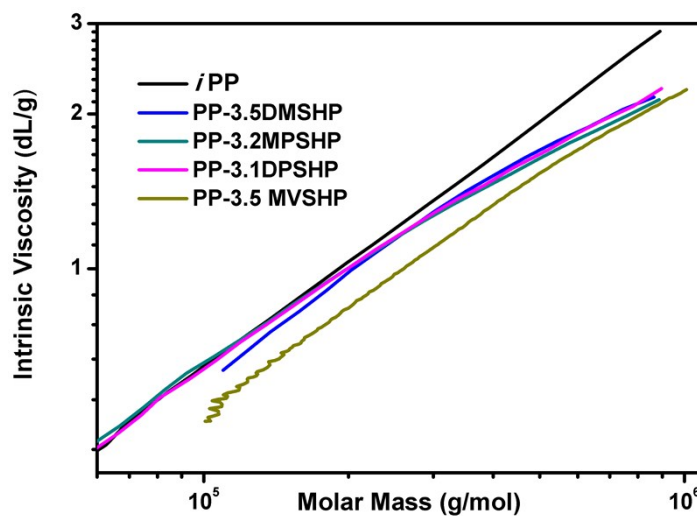


Fig. S9 Mark-Houwink plots of linear PP and some representative LCBPPs.

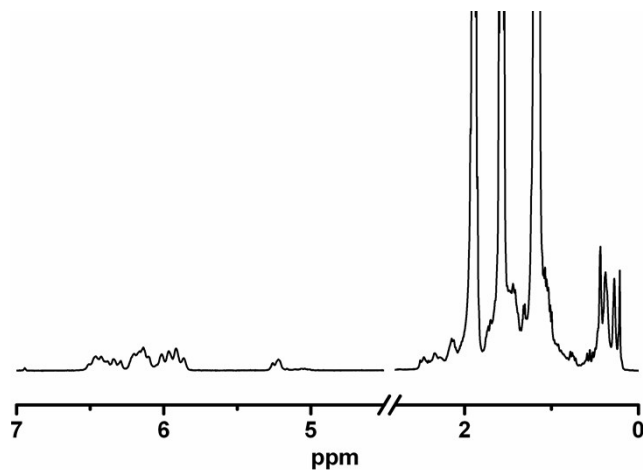


Fig. S10 The ^1H NMR spectrum of poly(propylene-*co*-MVS).

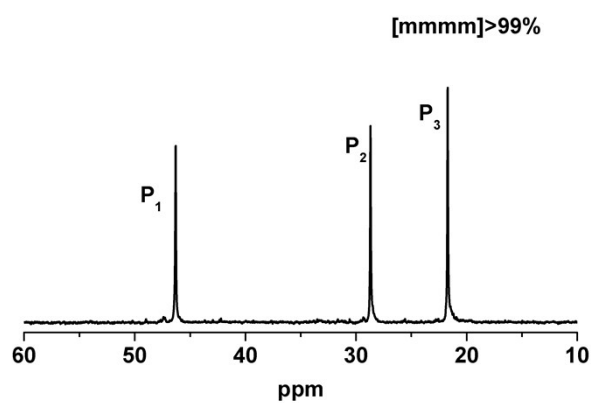


Fig. S11 ^{13}C NMR spectrum of poly(propylene-*co*-MVS).

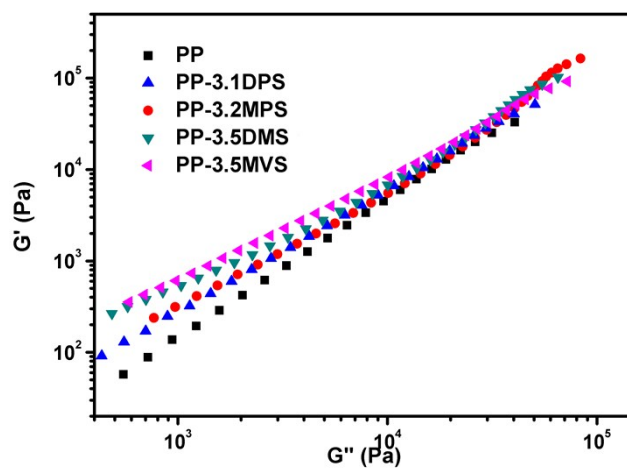


Fig. S12 Storage modulus vs loss modulus for linear *i*PP and LCBPPs.

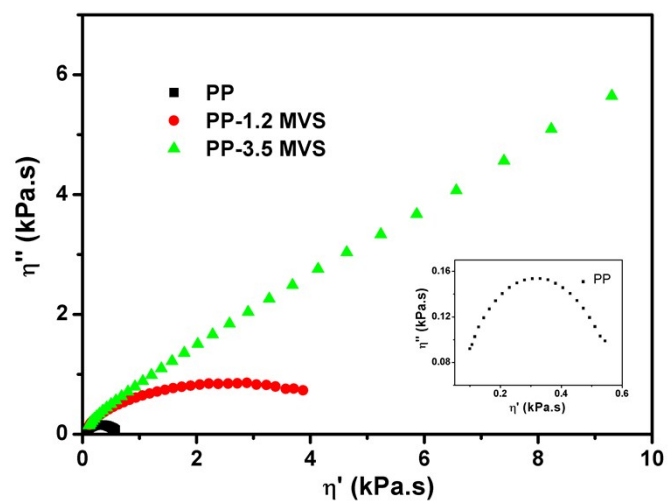


Fig. S13 Cole-Cole plots for linear PP and LCBPPs.