

Materials. TiCl_3 .AA, AlEt_2Cl (10 wt% in toluene), 10-undecen-1-ol, chlorotrimethylsilane, triethylamine and calcium hydride were used as they were when received from Sigma-Aldrich. Toluene were dried via refluxing over sodium for 24 hours.

Protection of –OH monomer. 34.46g of 10-undecen-1-ol and 20.22g of triethylamine were dissolved into 500ml of THF, and then 21.72g of chlorotrimethylsilane were introduced slowly in room temperature. The white powders appeared immediately. The suspension was kept stirring at 60°C for 8 hours, and the white powders were filtered to remove. The yellow filtered liquor was distilled under vacuum, and the fraction at 60°C was redistilled over CaH_2 before use.

Synthesis of PE copolymers with Ziegler-Natta catalyst. In a typical reaction (PE-7, with 5.9 mol% of OH content), a dried Parr 450 ml stainless autoclave equipped with a mechanical stirrer was charged with 13 ml toluene and 12 ml protected monomer, TiCl_3 .AA (0.1g) and $\text{Al}(\text{Et})_2\text{Cl}$ (5ml, 10 wt% toluene) were injected after purging with ethylene gas. After 30 mins of reaction at 70°C under 40 psi pressure of ethylene gas, the polymer solution was quenched with methanol. The resulting product was washed with HCl/methanol (0.5M), methanol and THF each for 2 times, and then vacuum-dried at 60°C. About 4.9 g of PE-OH copolymer was obtained with a catalytic activity of 58.4 Kg of PE/mol·h. The structure of this PE-OH specimen was performed by ^1H -NMR spectra in Figure 1.

Polymer characterization. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer in 1,1,2,2-tetrachloroethane- d_2 at 110°C. The thermal properties of the polymers were measured by TA Instruments Q100 differential scanning calorimeter (DSC) with a heating and cooling rate of 10° C/min under nitrogen. The molecular weights of polymers were determined by intrinsic viscosity in decahydronaphthalene (decalin) dilute solution at 135 °C according to the polyethylene standard measurement. Thermogravimetric analysis (TGA) experiments were performed on a TGA Q600 (TA instruments) at the heating rate of 10°C/min under nitrogen atmosphere with the speed of 50 ml/min.

Thin film preparation and dielectric measurement. Vacuum-melting pressing was utilized at optimizing temperature and pressure (220°C and 24000 psi for PE) with the samples between Teflon sheets. The prepared films with the thickness around 50 μm were annealed in vacuum oven at 90°C for 8 hours. Gold (<0.1 μm thickness) was sputtered on both surfaces of the polymer films. The dielectric constant of this dry sample was measured by an HP multifrequency LCR meter in the frequency range of 100 Hz to 1M Hz at room temperature. For comparison, the same piece of film was merged into water for another 8 hours, and then the

surface water was carefully wiped out with paper towel. The dielectric constant test and TGA measurement were conducted to this wet film with same processes.

Table 1. Properties of PE and PE-OH copolymers

Run ^{*1}	[OH] ^{*2} mol%	M _v ^{*3} mol/g	T _m °C	T _c °C	ΔT ^{*4} °C	ΔH _m J/g	χ ^{*5} %	Dielectric Constant 1kHz	Dielectric Loss x10 ³ 25°C,1kHz
PE-0	0	2,410,000	134.41	118.51	15.90	142.1	48.49	2.29	0.49
PE-3	1.30	1,430,000	128.95	115.23	13.72	136.0	46.41	2.87	2.64
PE-4	2.25	1,120,000	128.46	113.52	14.92	114.6	39.11	3.06	4.77
PE-7	5.90	1,030,000	127.69	112.96	14.73	80.86	27.88	3.89	17.9

*1 Al(Et)₂Cl was as co-catalyst; the ratio of [Al(Et)₂Cl]/[TiCl₃.AA] is 5; polymerized at 70°C.

*2 Determined by ¹H-NMR.

*3 Determined by intrinsic viscosity in decalin at 135 °C with standard of polyethylene.(M_v=K[η]^σ, K=62x10⁻³mL/g, σ=0.7)

*4 ΔT was defines as the difference between T_m and T_c

*5 The crystallinity degree χ was determined by the ratio of ΔH_m to that of the perfect crystal of PE (293.0J/g).

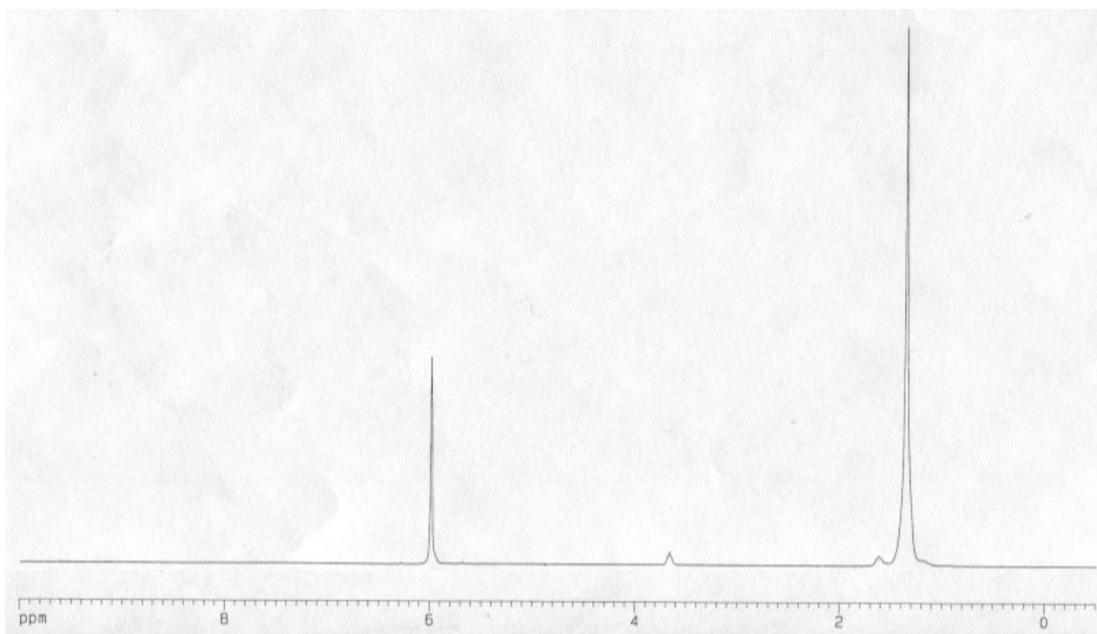


Figure 1, $^1\text{H-NMR}$ spectra of PE-7 ($[\text{OH}]=5.90$ mol%).

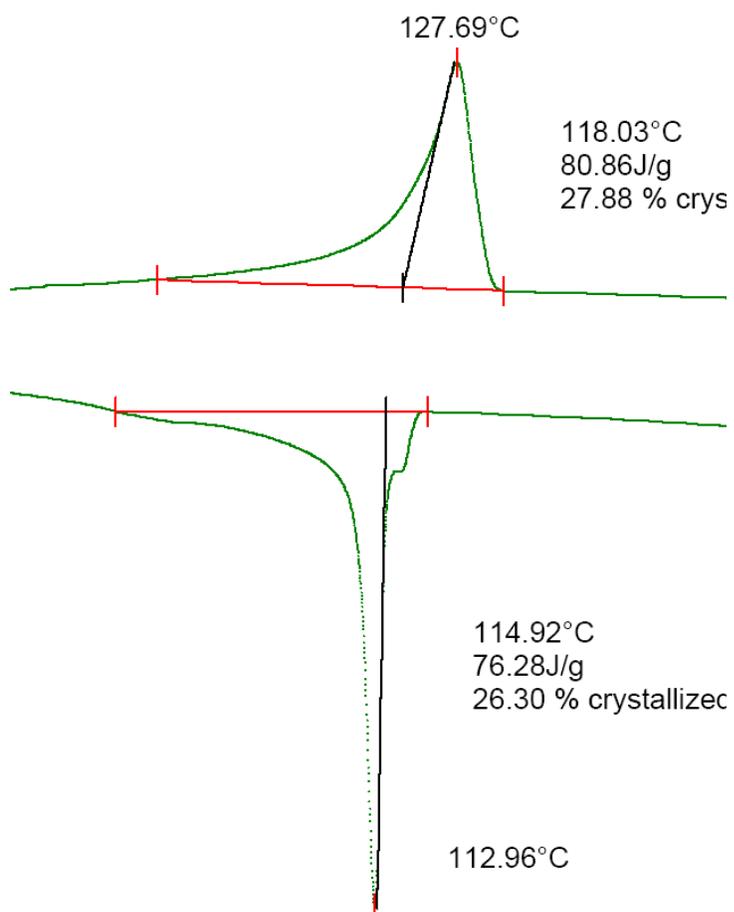


Figure 2, DSC curves of PE-7.

Figure 3. Comparison of TGA curve (with 1st derivative curve) of (left) dry and (right) wet PE-7.

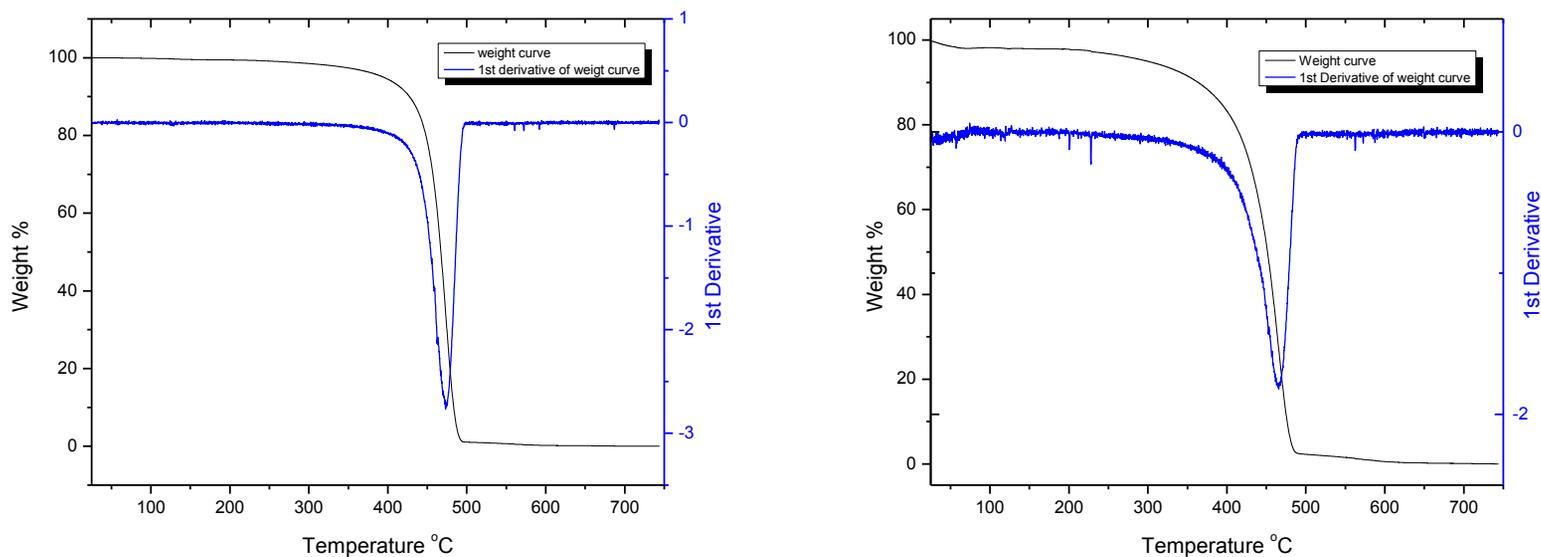


Table 2. TGA results of PE-7 sample (dry and wet conditions).

PE-7	Wt loss ^{*2}	
	25-105° C	105-250° C
dry ^{*1}	0.18%	0.67%
wet	1.81%	1.42%

^{*1} The dry sample was heated at 90° C in vacuum oven for 8 hours, and the wet sample (from the same polymer film) was merged in water for 8 hours, then drying in air (wiping off the surface water and without heating).

^{*2} Weight loss was calculated from TGA curves.

Figure 4, Dielectric constant and loss curves of dry sample (left) and wet sample (right) of PE-7.

