Supporting Information

Investigation of the substituent influence on dielectric properties for polyethylene derivatives

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General Information

Materials

Poly(ethylene-co-vinyl acetate) (EVA, VA=40 wt%=18 mol%, melt index @190 ºC=52 g/10 min), was purchased from Aladdin Co., Ltd. Shanghai, China. 1,1'-(azodicarbonyl)-dipiperidine (ADDP) was purchased from Innochem Co., Ltd., Beijing, China. All abovementioned chemicals were used as received without further purification.

Characterization and Instrumentation

Fourier transform infrared (FT-IR) spectrum were recorded on a Thermo Fisher Nicolet 6700 FTIR spectrometer. The measurement was carried out in the range of 4000–650 cm^{-1} with the number of scans per spectrum of 32 and the spectruml resolution of 4 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker Avance III 400 HD spectrometer operating at 400 MHz chloroform-d or 1,2-dichlorobenzene-d_4 solvents. Molecular weight and polydispersity (Đ) were measured by gel permeation chromatography (Agilent 1260 Infinity II) in THF (40 °C) mobile phase based on narrowly distributed polystyrene (PS) standard with a flow rate of 0.3 mL/min. Melting and glass transition behavior of the polymers were measured by differential scanning calorimetry (DSC) using a TA Q200 instrument. The samples were heated under nitrogen from 60 °C to 200 °C at a rate of 20 °C per minute and isothermal for 3 min, then cooled to –130 °C at a rate of 10 °C per minute, followed by heating to 200 °C at a rate of 10 °C per minute. The T_m and T_g were determined from the second heating run, and the crystallization temperature T_c was obtained from the cooling trace.

Experimental Procedures

Preparation of PE-OTol

For information on the raw materials and reagents used and the procedure for the synthesis of EVOH, please refer to the *General Information* and *Preparation of EVOH* sections in the Supplementary Information of reference 43 in the main text. PE derivative PE-OTol was prepared by using EVOH (1 mmol of functionality) and PPh3 (3 mmol) were dissolved in THF (20 mL), followed by adding *p*-cresol (3 mmol). After stirred for 15 min, ADDP (3 mmol) and BHT (50 mg) were added. The mixture was allowed to stir at 25 °C for 16 hours before precipitation and sonication in methanol for three times. PE-OTol were obtained after drying under vacuum with the isolated yield of 92%. ^{1}H NMR (400 MHz, CDCl3): δ 7.11-6.95 (br m, 2H), δ 6.82-6.66 (br m, 2H), δ 4.21-4.06 (br m, 1H), δ 2.27 (s, 3H), δ 1.76-1.52 (br m, 8H), δ 1.43-0.98 (br m, 34H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 156.7, 129.9, 129.6, 115.9, 77.0, 34.0, 29.7, 27.2, 25.4, 20.5; IR (neat): 2918 (s), 2850 (s), 1611 (m), 1507 (s), 1458 (m), 1233 (s), 816 (m), 718(m).

Table S1. Determined dielectric properties of the synthesized PE derivatives.

sample	ε' @10^{-2} Hz	ε' @10^{0} Hz	ε' @10^{3} Hz	ε' @10^{7} Hz	$\omega_p{}^a$ (Hz)	$\varepsilon''_p{}^b$
LLDPE	2.03	2.03	2.03	2.04	N.A.	N.A.
PE-Br	14.24	5.83	2.82	2.26	1.8×10^6	0.16
PE-I	129.47	24.80	4.35	2.61	1.8×10^6	0.31
PE-OPh	3.71	3.38	3.33	2.75	3.2×10^5	0.15
PE-OTol	2.21	1.97	1.93	1.59	8.7×10^4	0.10
PE-ONaph	3.60	2.89	2.64	2.57	N.A.	N.A.
PE-N$_3$	14.10	5.09	4.35	3.52	N.A.	N.A.
PE-Tr	5.07	4.80	2.98	2.37	5.6×10^1	0.50
PE-Naph	2.31	2.27	2.24	2.22	N.A.	N.A.
PE-pip	4.59	3.40	2.65	2.46	2.1×10^{-1}	N.A.
PE-NB	2.89	2.39	2.20	2.18	N.A.	N.A.

^{a} Corresponding frequency at the ε'' peak.
^{b} Peak value in the plot of ε'' versus frequency.

Table S2. The determined elemental composition in the blends of PE-Br/*LLDPE,* PE-I/*LLDPE,* and PE-OPh/*LLDPE. The PE derivatives content is 5.9 wt% for the blends*

sample	C /wt%	Br/ wt%	I /wt%	O /wt%	total /wt%
PE-Br/LLDPE	98.1±0.3	1.9±0.4	0.0	0.0	100.0
PE-I/LLDPE	98.0±0.6	0.0	2.0±0.6	0.0	100.0
PE-OPh/LLDPE	99.0±0.3	0.0	0.0	1.0±0.7	100.0

Table S3. Determined mechanical properties of the selected PE derivatives, their blends with the LLDPE matrix, and EVA/LLDPE blend. The PE derivative content is 5.9 wt% for all the blends.

sample	Young's modulus (MPa)	stress-at-break (MPa)	strain-at-break (%)	stress-at-yield (MPa)
LLDPE	36.1±1.5	9.2±1.3	496.5±262.9	8.7±0.6
PE-Br	3.8±0.5	8.4±0.7	1069.6±127.8	N.D.[a]
PE-I	1.9±0.2	3.7±0.1	429.7±84.0	N.D.
PE-OPh	2.9±0.8	11.5±2.5	531.3±85.0	N.D.
PE-Br/LLDPE	58.9±3.7	12.5±2.3	1066.8±308.2	9.3±0.1
PE-I/LLDPE	56.7±2.4	7.6±2.4	443.6±250.1	8.9±0.3
PE-OPh/LLDPE	54.2±1.5	13.0±1.6	1106.2±165.8	8.9±0.1
EVA/LLDPE	69.4±0.9	11.8±0.5	917.8±82.8	8.6±0.5

[a] *N.D. means not determined.*

Table S4. $T_{g,DMA}$ values of PE derivatives of PE-Br, PE-I, PE-OPh *and their blends, the LLDPE is used as reference material. The PE derivative content is 5.9 wt% for the blends.*

Sample	$T_{g,DMA}$ (°C)
LLDPE	-22.9
PE-Br	-18.7
PE-Br/LLDPE	-25.5, 46.3
PE-I	-18.1
PE-I/LLDPE	-31.6, 43.2
PE-OPh	-14.1
PE-OPh/LLDPE	-24.2, 29.8
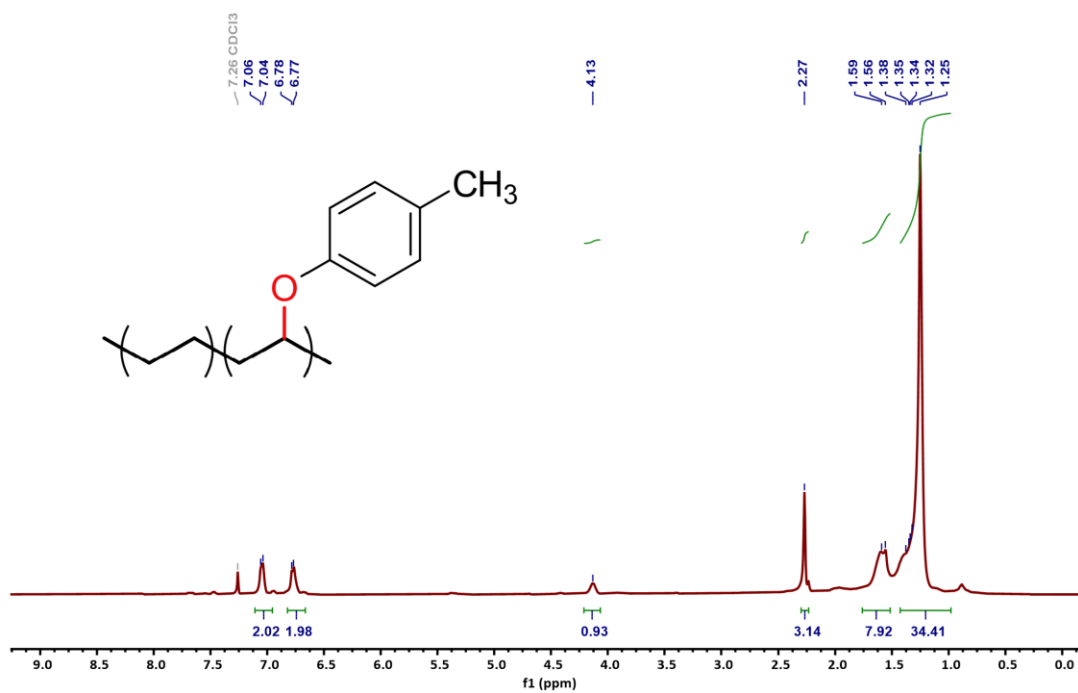
Figure S1. ^1H NMR spectra of the synthesized PE-OTol in CDCl₃.
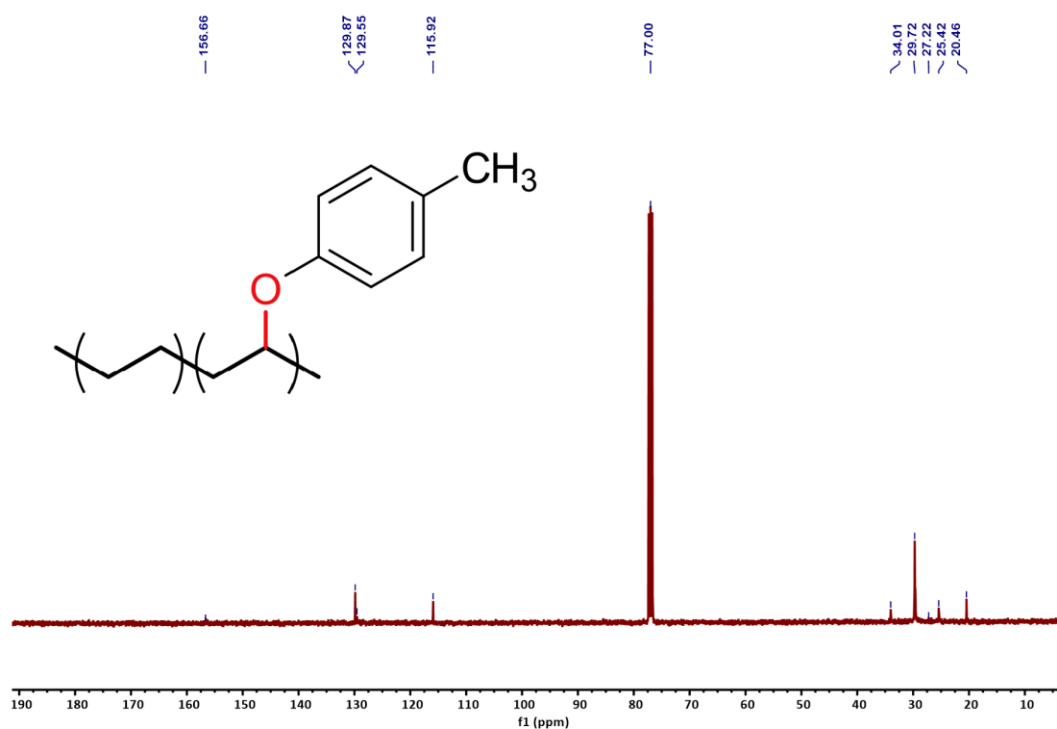
Figure S2. ^{13}C NMR spectra of the synthesized PE-OTol in CDCl₃.
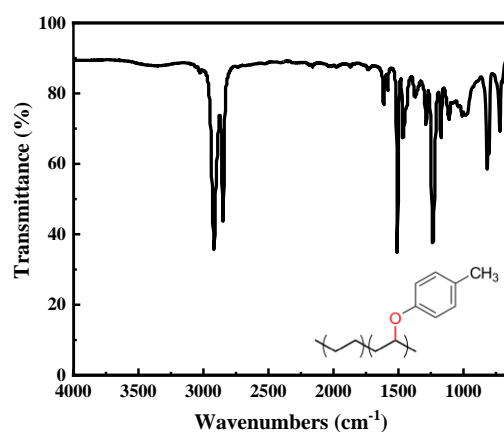
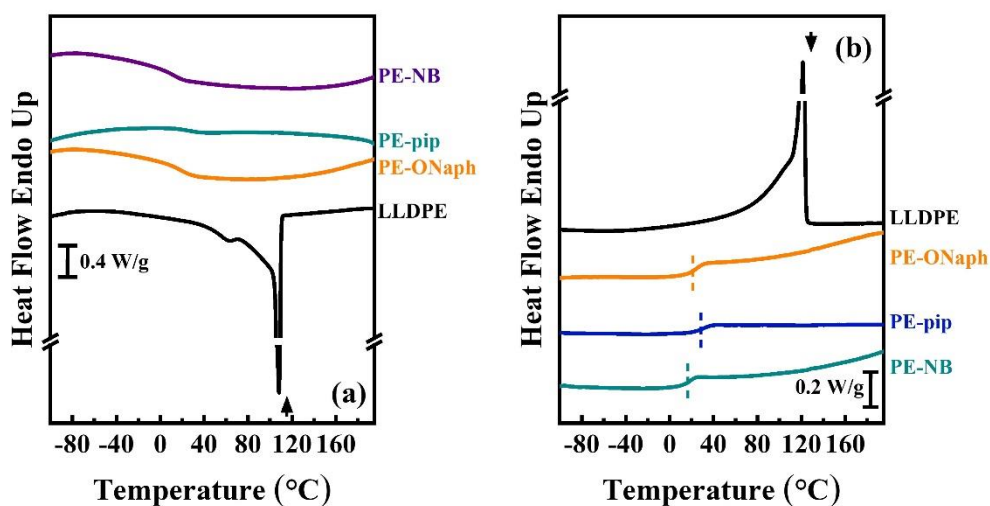*Figure S3. FTIR spectrum of the synthesized PE-OTol.*

Figure S4. DSC traces of PE-ONaph, PE-pip, and PE-NB during (a) cooling and (b) second

heating. The determined T_g is indicated by a dash line. A reference for comparison is provided

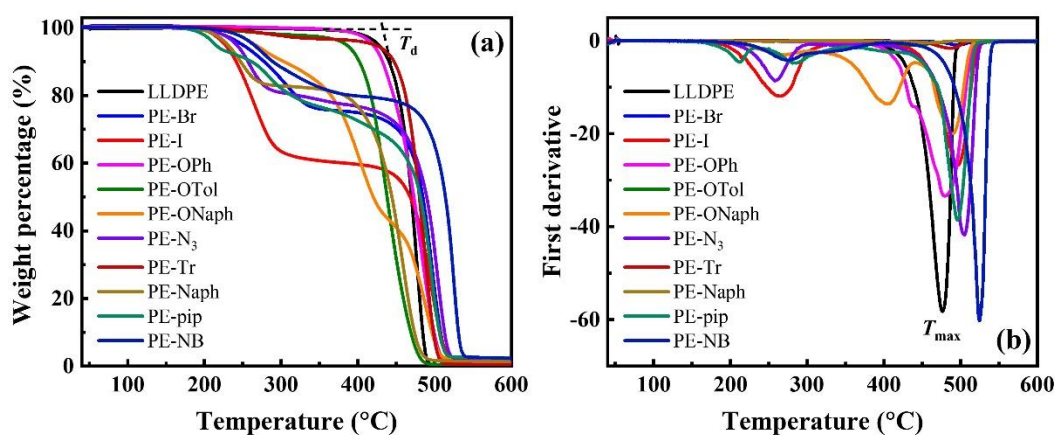*with LLDPE featuring saturated C-H bonds (black line). No evident T_c and T_m is detected in*

the plots.

Figure S5. TGA results of the PE derivatives: (a) plots of weight percentage versus temperature and (b) their first derivative curves. LLDPE (block line) is used as the basis of comparison.
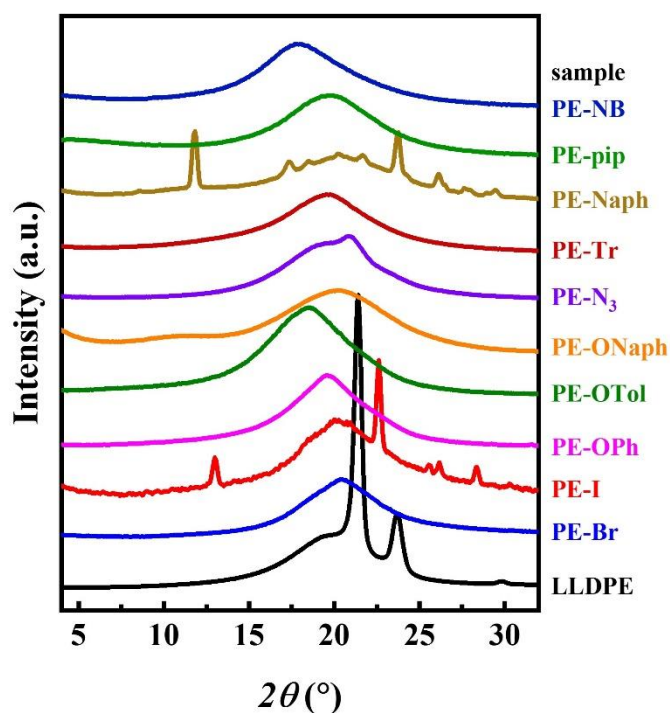
Figure S6. Comparison of the 1-D WAXD curves of the obtained PE derivatives. The curves have been vertically shifted to avoid overlap.
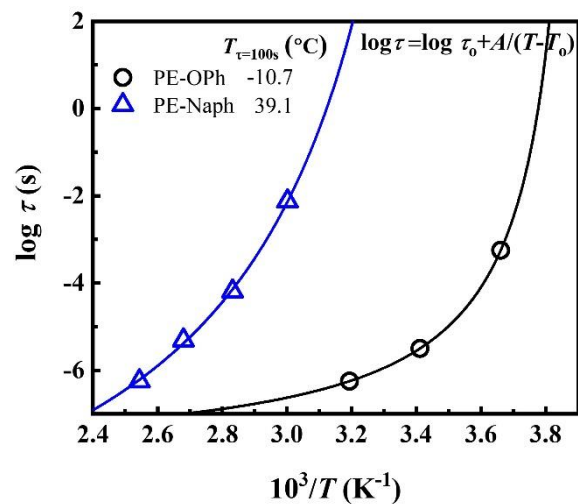
Figure S7. Semi-log plots of relaxation time versus temperature inverse for PE-OPh and PE-Naph. Slid lines are the fitting results by Vogel-Fulcher-Tammann (VFT) equation, which is inserted in the figure. The temperature corresponding to a relaxation time of 100 s was extrapolated from the fitted line, and determined as the characteristic temperature $T_{\tau=100s}$ (indicated in the figure).
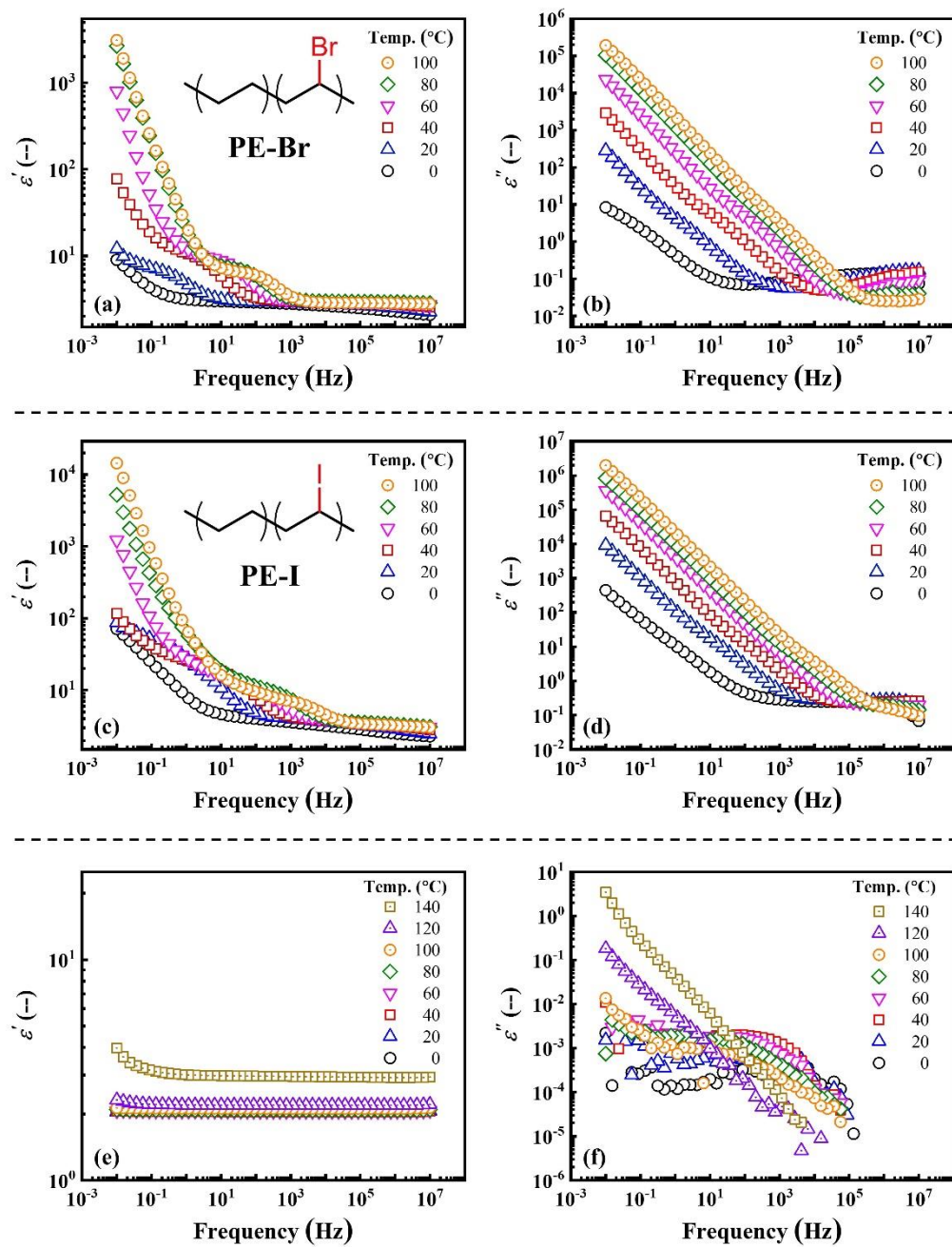
Figure S8. Temperature dependence of the measured dielectric properties of PE derivatives

PE-Br (top), PE-I (middle), and LLDPE (bottom), including the log-log plots of ε' ((a), (c),

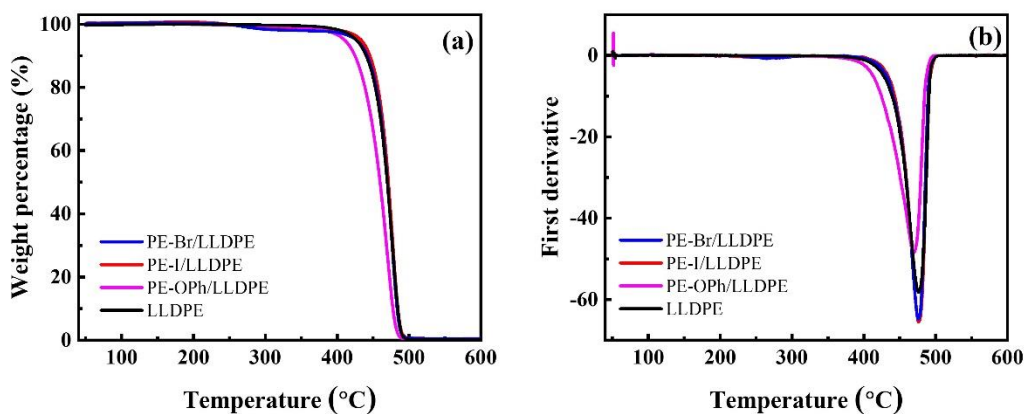*and (e)) and ε'' ((b), (d), and (f)) versus frequency, respectively.*

Figure S9. TGA results of the blends of PE derivatives with LLDPE matrix: PE-Br/LLDPE,

PE-I/LLDPE, and PE-OPh/LLDPE. The LLDPE is used a reference material. The PE

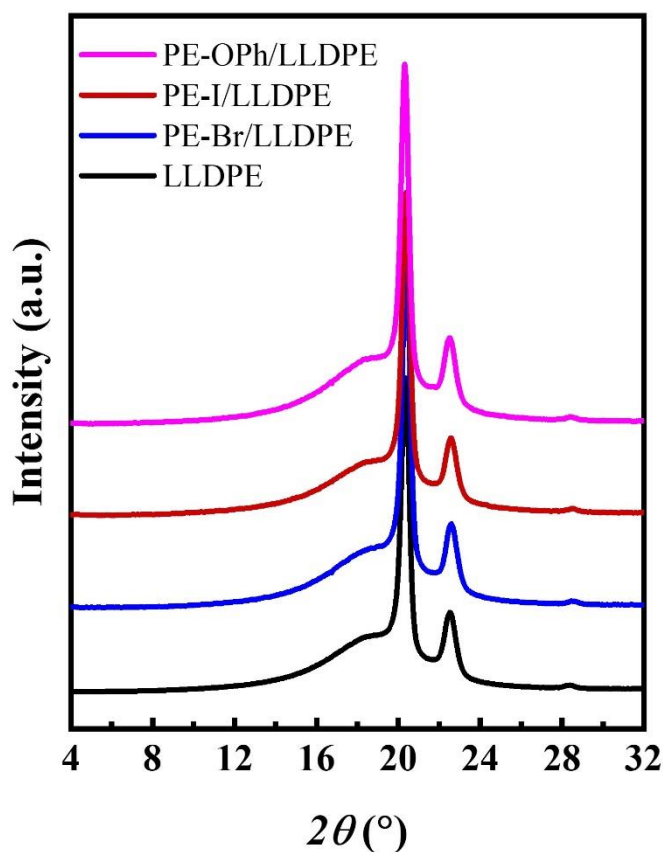*derivative content is 5.9 wt% for all the three blends.*

Figure S10. Comparison of the 1-D WAXD curves of the blends of PE-Br/LLDPE, PE-

I/LLDPE, PE-OPh/LLDPE, and the LLDPE matrix. The PE derivative content is 5.9 wt% for
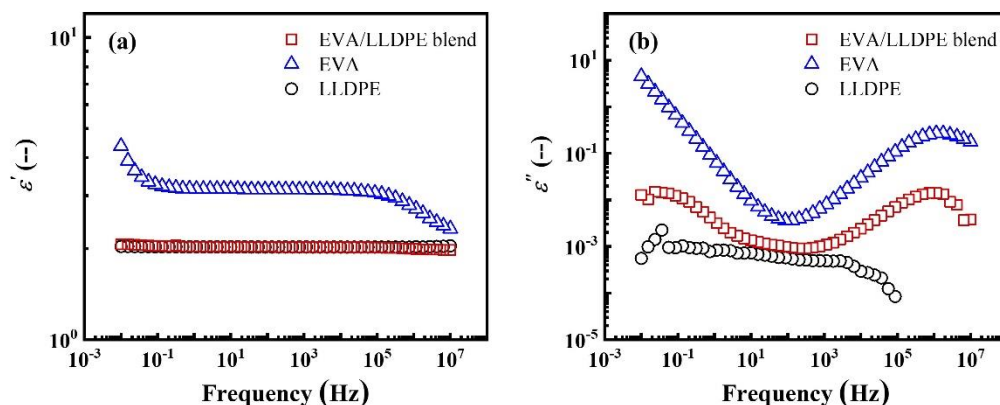
all the three blends.

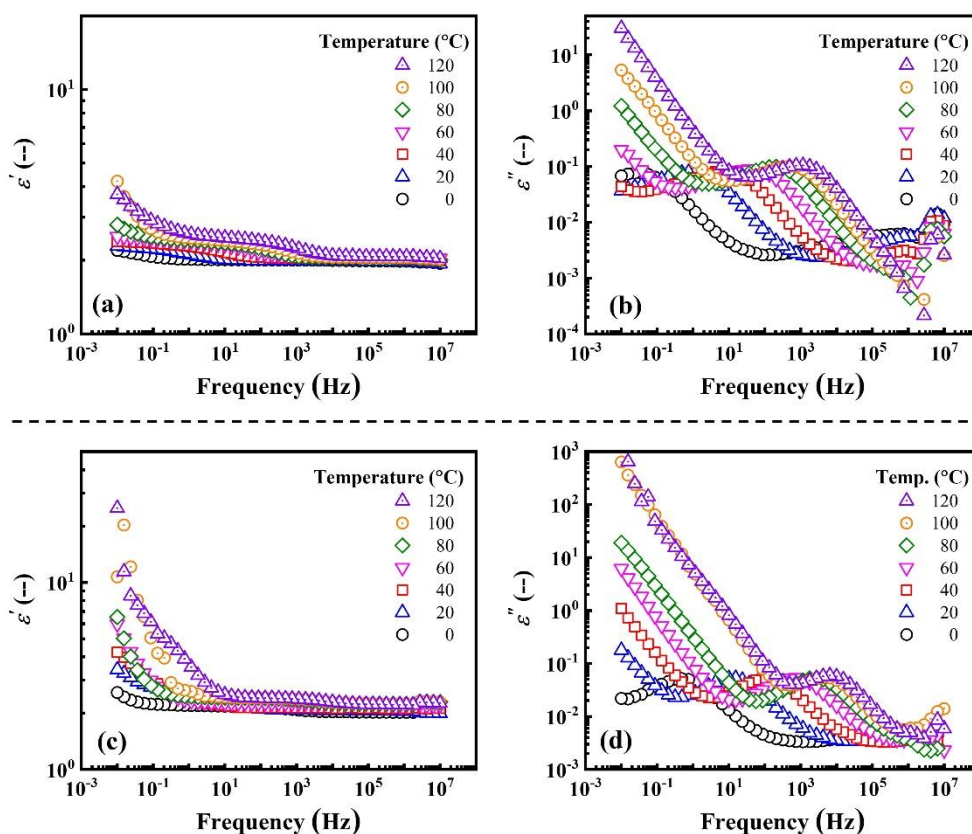*Figure S11. The obtained (a) ε' and (b) ε" of the reactant EVA used in this work and its blends with LLDPE, the content of EVA is 5.9 wt%.*

Figure S12. Variable-temperature dielectric results of (a)(b) PE-Br/LLDPE and (c)(d) PE-I/LLDPE, including the ε' ((a) and (c)) and ε" ((b) and (d)). The PE derivative content is 5.9 wt% for all the three blends.
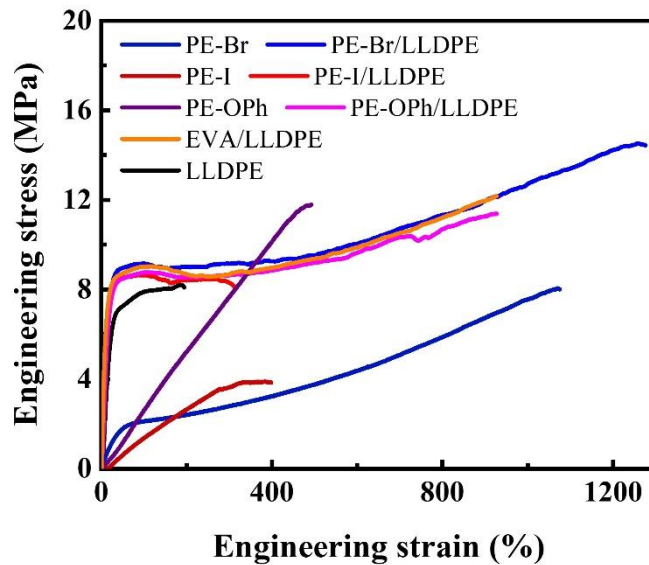
Figure S13. Representative engineering stress-strain curves for the selected PE derivatives, their blends with LLDPE matrix, and the EVA/LLDPE blends. The contents of PE derivatives and EVA in the blends are 5.9 wt%.
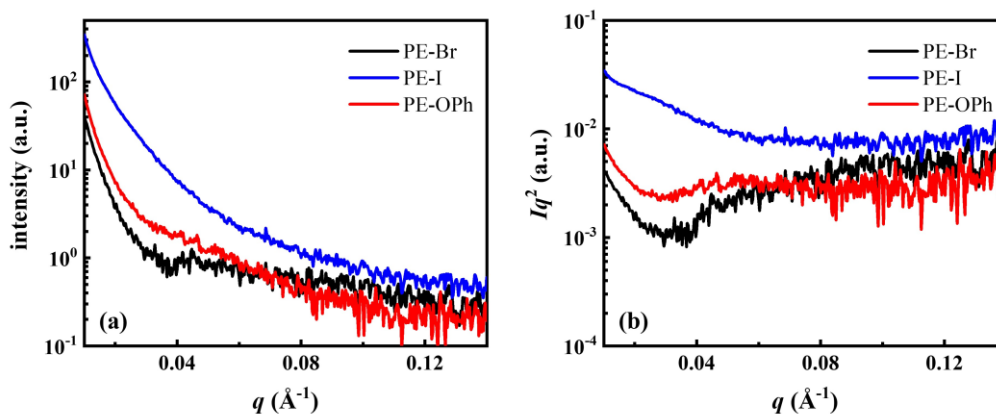

Figure S14. The obtained (a) 1-D SAXS and (b) Iq^2-q plots of PE derivatives of PE-Br, PE-I, and PE-OPh quenched from 200 ℃ by a liquid nitrogen bath. From the profiles, it seems that some weak signals could be detected in quenched PE-Br and PE-OPh. However, it could not be distinguished the microphase separation signals from that of crystallization, because a melting peak was observed in the DSC first heating curve.
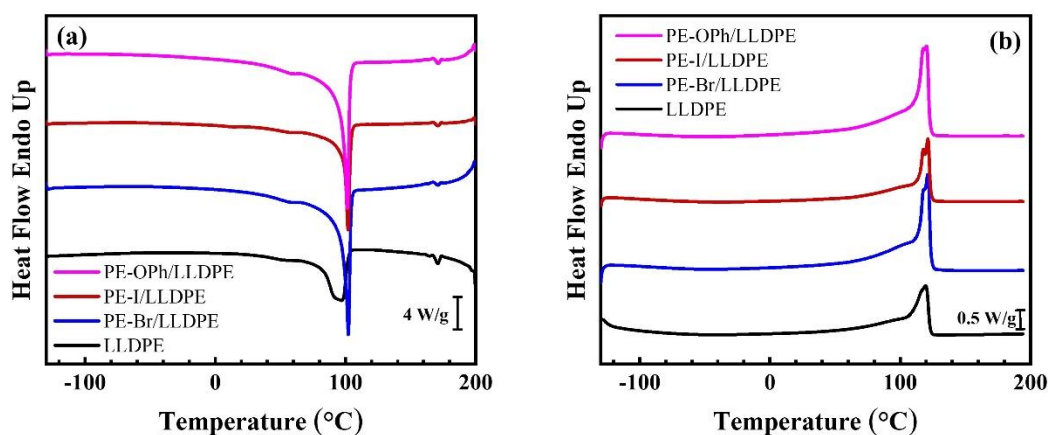
Figure S15. The (a) cooling and (b) second heating DSC traces of PE-Br/LLDPE, PE-I/LLDPE, and PE-OPh/LLDPE. The applied thermal protocol is that firstly heating from 60 °C to 200 °C at a rate of 20 °C/min and isothermal for 3 min to eliminate the thermal history. Then, cooled from 200 °C to -130 °C at a rate of ca. 50 °C/min. The final step is heated from -130 °C to 200 °C at a rate of 10 °C/min. Despite rapid cooling using a liquid nitrogen cooling system, crystallization peaks were still observed in the cooling curves, suggesting the rate was not fast enough to inhibit crystallization. In the second heating traces, no T_g was determined for any of the samples.