SUPPORTING INFORMATION

Polyethylenes Functionalized with Ureidopyrimidone: Synthesis, Thermomechanical Properties and Shape Memory Behavior

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1. Measurement and Characterization

1.1 Nuclear Magnetic Resonance (NMR)

The ^{1}H NMR and ^{13}C NMR spectroscopy was carried out on a Bruker AVANCE 500 (500 MHz) spectrometer. The PHEE sample dissolved in DMSO-d_6 was measured at 25 °C; the PCOE-OH samples dissolved in toluene-d_8 was measured at 25 °C. For the PE-OHs, the samples were dissolved in toluene-d_8 and then measured at 80 °C. The values of ^{1}H NMR and ^{13}C NMR chemical shift are expressed with reference to the residual solvent peak at 2.50 ppm of the deuterium DMSO or 2.13 ppm of the deuterium toluene.

1.2 Size Exclusion Chromatography (SEC)

The molar mass of PHEE was measured on a Waters 1515 gel permeation chromatography (GPC) system equipped with three Waters RH columns (*i.e.*, RH1, RH3 and RH4) and a reflect index detector at 80 °C. N,N'-Dimethylformamide (DMF) containing 0.01 mol × L^{-1} lithium bromide (LiBr) was used as the eluent at a flow rate of 1.0 mL × min^{-1}. The molar mass values of PCOE-OHs were measured on a HLC-8320GPC instrument equipped with TSK gel GMHXL column (7.8 ID x 30 CM, 9 um) and a reflect index detector at 40 °C. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL × min^{-1}. The solutions were passed through a 0.22 μm PTFE filter prior to injection, and the molar mass values were expressed relative to polystyrene standards.

1.3 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectroscopy was carried out on a Perkin Elmer 1000 Spectrometer at room temperature. The solutions of PHEE and PCOE-OH dissolved in tetrahydrofuran were casted on the KBr windows. The films of PE-OH and PE-UPy were sufficiently thin so that Lambert-beer law was followed. The spectra were recorded at the resolution of 2 cm^{-1} with 64 scans.

1.4 Differential Scanning Calorimetry (DSC)

The DSC measurements were performed on a TA Instruments Q2000 equipped with a RCS 90 cooling system. About 8 ~ 10 mg of sample was put in an aluminum pan and then subjected to DSC measurements under a nitrogen atmosphere. All the samples were heated up to 150 ^{o}C and held at this temperature for 3 min and then quenched to -40 ^{o}C. The samples were heated from -40 to 160 °C at a heating rate of 20 °C × min^{-1} and then cooled at a cooling rate of 10 °C × min^{-1}.

1.5 Wide Angle X-ray Diffraction (WXRD)

The wide-angle X-ray diffraction (XRD) experiments were carried out on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα (λ = 0.154 nm) irradiation at 40 kV and 40 mA using a Ni filter. Data were recorded in the range of 2θ =5 ~ 40° at the scanning rate of 6.0 ^{o} × min^{-1}, respectively.

1.6 Rheological Measurements

The specimens for rheological measurements were prepared with disk-like flakes with the sizes of 25 mm in diameter and 1 mm in thickness. The tests were performed on a TA Instruments DHR-2 rheometer equipped with the parallel plates. The measurements were conducted with a frequency sweep from 0.01 to 100 Hz at 150 °C. The temperature scans were carried from 150 to 200 °C at the frequency of 1 Hz.

1.7 Tensile Tests

The tensile tests were performed on a WDW-2 electron universal testing machine equipped with a 2000 N load cell. Dumb bell-shaped specimens were machined with the dimension of 12 mm in length and 2 mm in width and 0.6 mm in thickness. The specimens were uniaxially stretched with the speed of 50 mm × min^{-1}. For each sample, at least five parallel tests were conducted and the parameters of mechanical properties were reported as the averages of five successful tests.

1.8 Shape Memory Tests

The one-way cyclic shape memory tests were performed on a DMTA-Q800 apparatus. First, the specimens were heated up to 150 °C with the speed of 3 °C × min^{-1} and then stretched at 150 °C at the loading rate of 4.0 KPa × min^{-1}. Keeping the load, the specimen was cooled to 50 °C at the rate of 3 °C × min^{-1} to fix the temporary shape. At 50 °C, the load was lifted and the specimen was heated up to 150 °C at the rate of 3 °C × min^{-1}. In all these steps, the change in strain was recorded as functions of temperature and stretching load. Shape fixity (F) was defined by eq. S1:

$$F = \frac{\varepsilon_f(N)}{\varepsilon_s} \times 100\% \quad \text{(S1)}$$

where ε_f is the strain of the fixed temporary shape after removing the stress, ε_s is the strain after the specimen was stretched and before the stress was removed, and N is the cycle number. Recovery (R) was defined by eq. S2:

$$R = \frac{\varepsilon_s - \varepsilon_r(N)}{\varepsilon_s - \varepsilon_r(N-1)} \times 100\% \quad \text{(S2)}$$

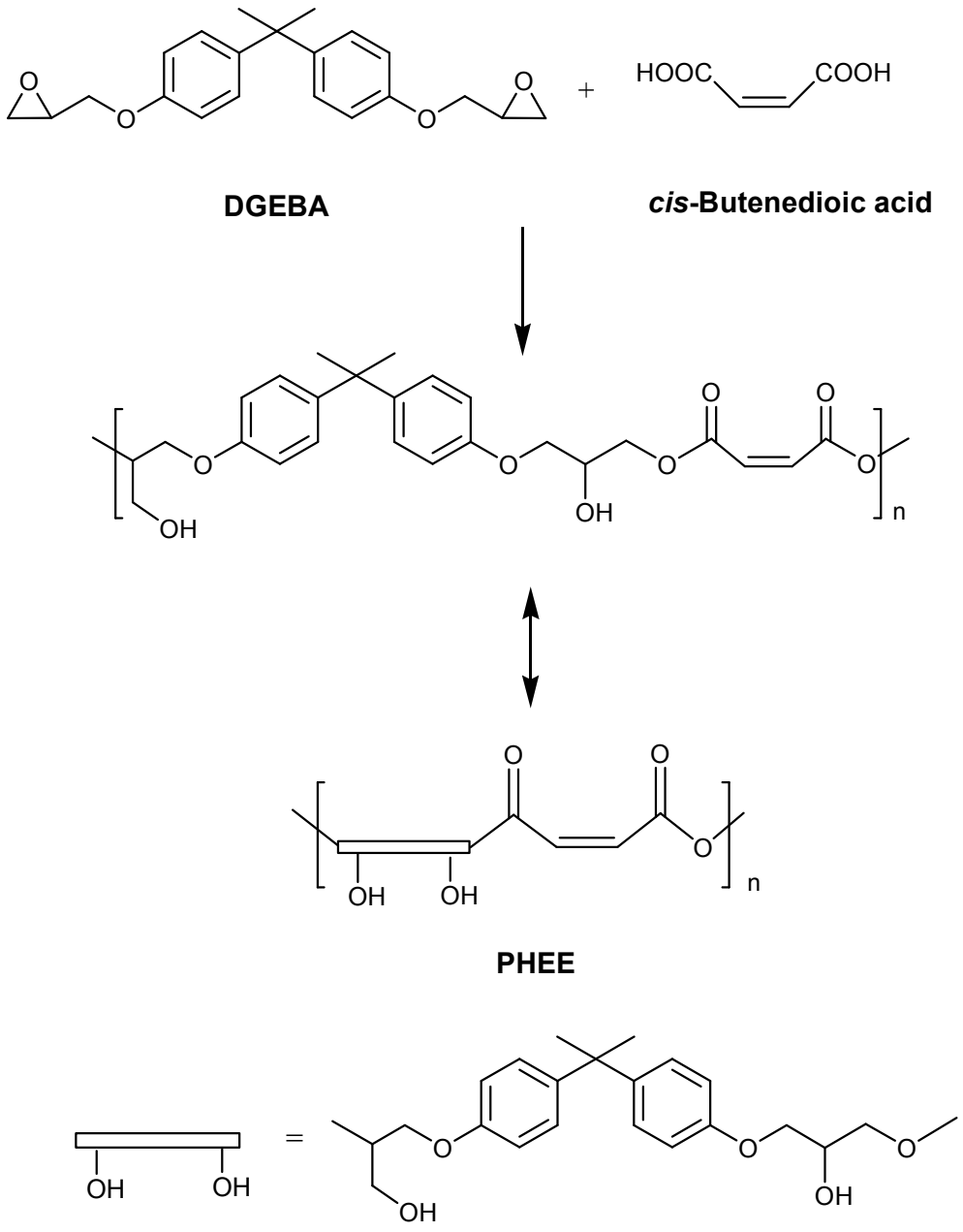
where ε_r is the residual strain of the specimen at the completion of the one-way shape memory cycle.

Reference: Behl, M.; Lendlein A. *"Shape-memory Polymers" Mater. Today* **2007,** *10,* 20~28

1.9 Stress Relaxation Tests

The stress relaxation tests were carried out on a TA Instruments DMA Q800 system; the strain value was set as ε = 15 % at 170 °C.

SCHEMES



Scheme S1 Synthesis of PHEE (macro-CTA)

TABLES

Table S1 Thermal properties of PE-OH and PE-UPy samples

Samples*	ΔH_m (J×g^{-1})	ΔH_c (J×g^{-1})	Samples*	ΔH_m (J×g^{-1})	ΔH_c (J×g^{-1})
PE_5-OH	164.5	168.9	PE_{10}-UPy	164.1	171.2
PE_8-OH	162.5	168.1	PE_{15}-UPy	155.7	161.9
PE_{11}-OH	158.4	162.8	PE_{21}-UPy	152.9	157.1
PE_{14}-OH	148.8	154.2	PE_{26}-UPy	143.3	147.9
PE_{20}-OH	137.0	140.6	PE_{35}-UPy	123.6	127.9

*: The digits behind "PE" represent the weight percentage of HEE and/or HEE(UPy)

Table S2 Mechanical properties of PE and PE-OH samples

Samples*	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
Plain PE	26.7±2.2	866±125	287±30
PE_5-OH	28.3±2.3	760±120	329±26
PE_8-OH	27.0±2.1	650±103	376±21
PE_{11}-OH	26.0±2.4	552±72	347±31
PE_{14}-OH	20.6±2.5	450±81	363±43
PE_{20}-OH	19.0±1.9	257±78	318±29

*: The digits behind "PE" represent the weight percentage of HEE and/or HEE(UPy)

Table S3 Mechanical properties of PE and PE-UPy samples

Samples*	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
Plain PE	26.7±2.2	866±125	287±30
PE_{10}-UPy	31.7±2.1	580±105	435±33
PE_{15}-UPy	32.2±2.7	450±85	459±41
PE_{21}-UPy	26.0±2.3	83±20	470±23

PE_{26}-UPy	22.7±1.7	38±11	454±29
PE_{35}-UPy	22.0±2.0	15±8	405±39

*: The digits behind “PE” represent the weight percentage of HEE and/or EE(UPy)

Table S4 Shape fixity (*F*) of one-way shape memory cycle tests

Samples	Shape fixity (F) (%)				
	*N** =1	*N* = 2	*N* = 3	*N* = 4	*N* =5
PE_{10}-UPy	98.5	98.6	98.7	98.7	98.8
PE_{21}-UPy	97.3	97.6	97.7	97.7	97.8
PE_{35}-UPy	95.9	96.0	96.1	96.3	96.6

**N* stands for cycle number

Table S5 Shape recovery (*R*) of one-way shape memory cycle tests

Samples	Shape recovery (R) (%)				
	*N** =1	*N* = 2	*N* = 3	*N* = 4	*N* =5
PE_{10}-UPy	12.3	56.3	62.1	66.4	68.9
PE_{21}-UPy	29.8	74.4	80.4	82.8	84.9
PE_{35}-UPy	32.8	75.3	80.2	85.0	86.3

**N* stands for cycle number

FIGURES

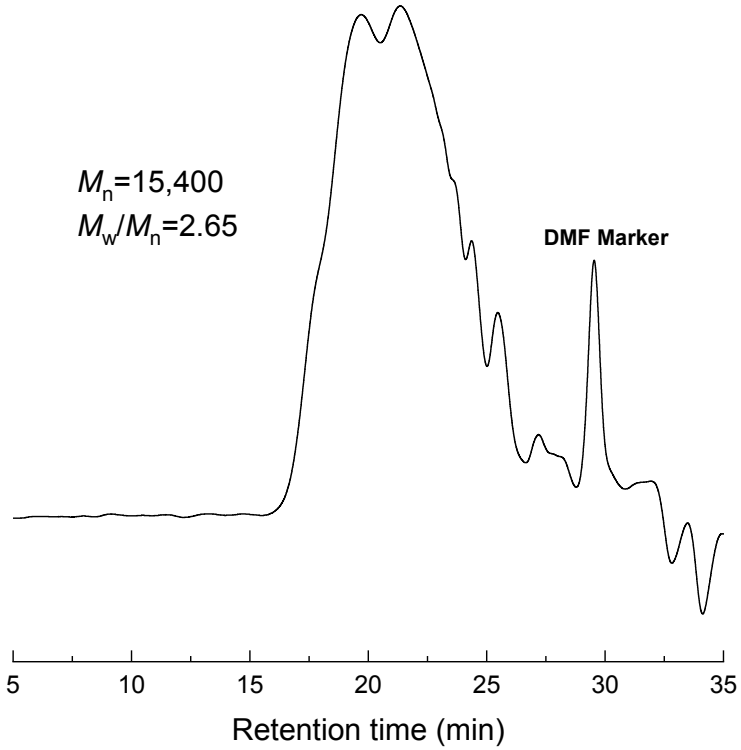


Figure S1 SEC curve of PHEE (macro-CTA)

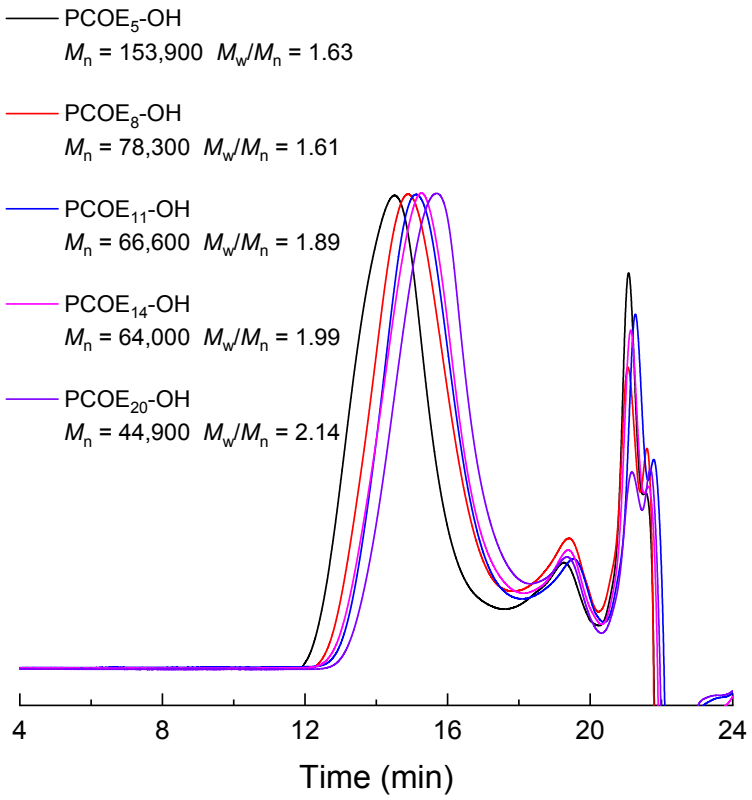
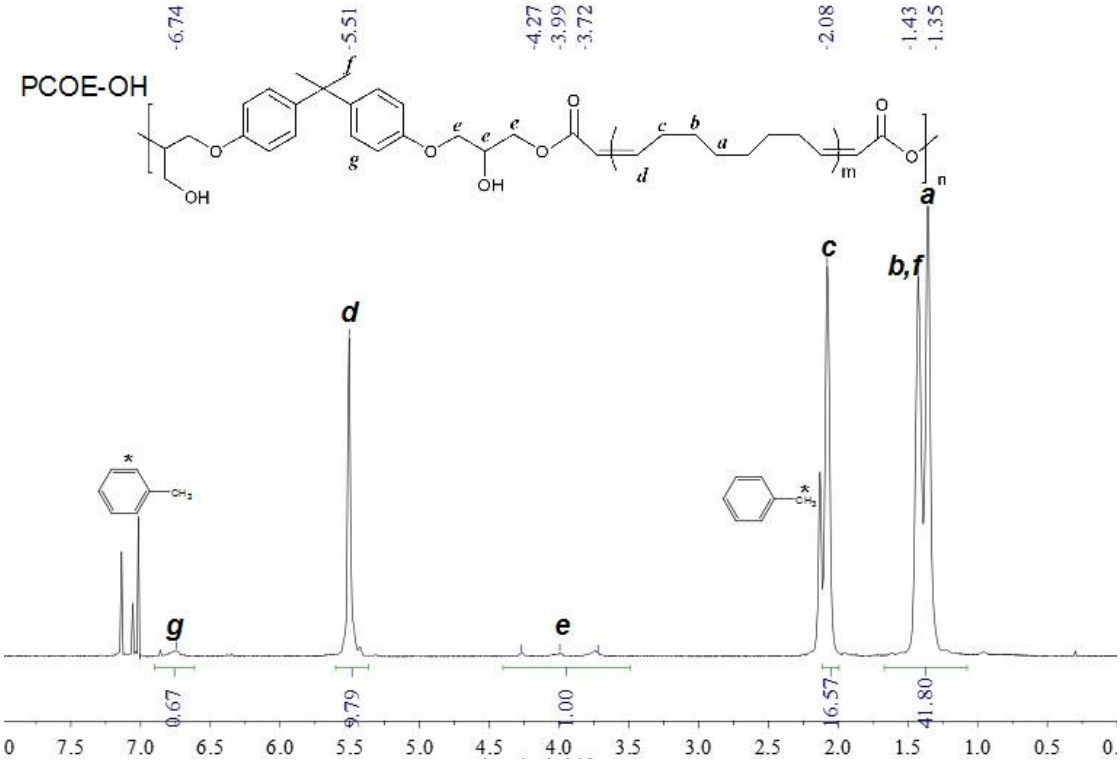
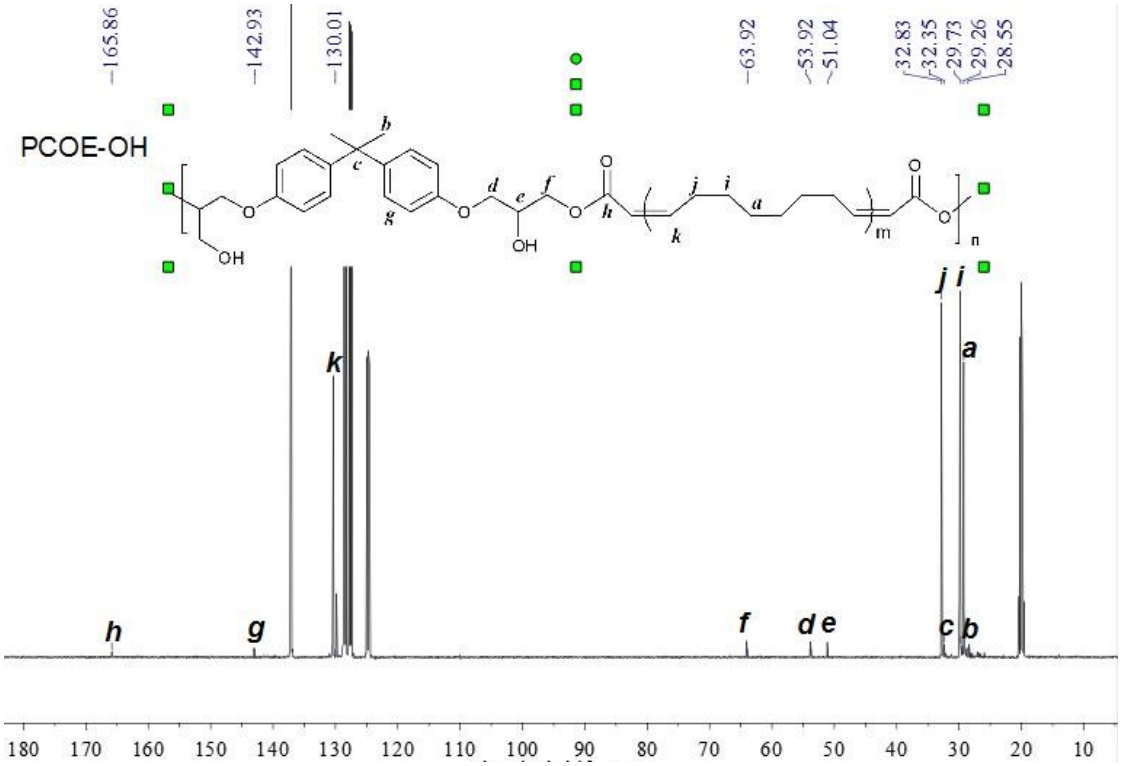
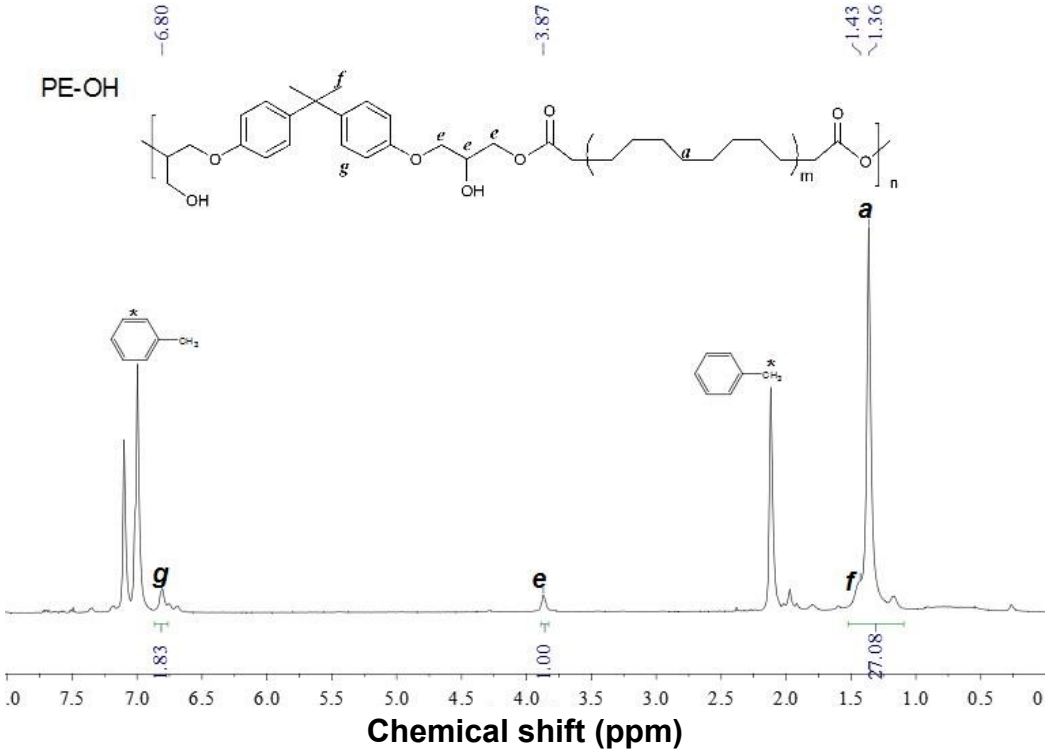


Figure S2 SEC curves of PCOE-OHs with various content of HEE


PCOE-OH
-6.74
-5.51
-4.27
-3.99
-3.72
-2.08
-1.43
-1.35
a
b,f
c
d
e
g
0.67
9.79
1.00
16.57
41.80
Chemical shift (ppm)


PCOE-OH
165.86
142.93
130.01
63.92
53.92
51.04
32.83
32.35
29.73
29.26
28.55
j i
a
k
h
g
f
d e
c b
Chemical shift (ppm)



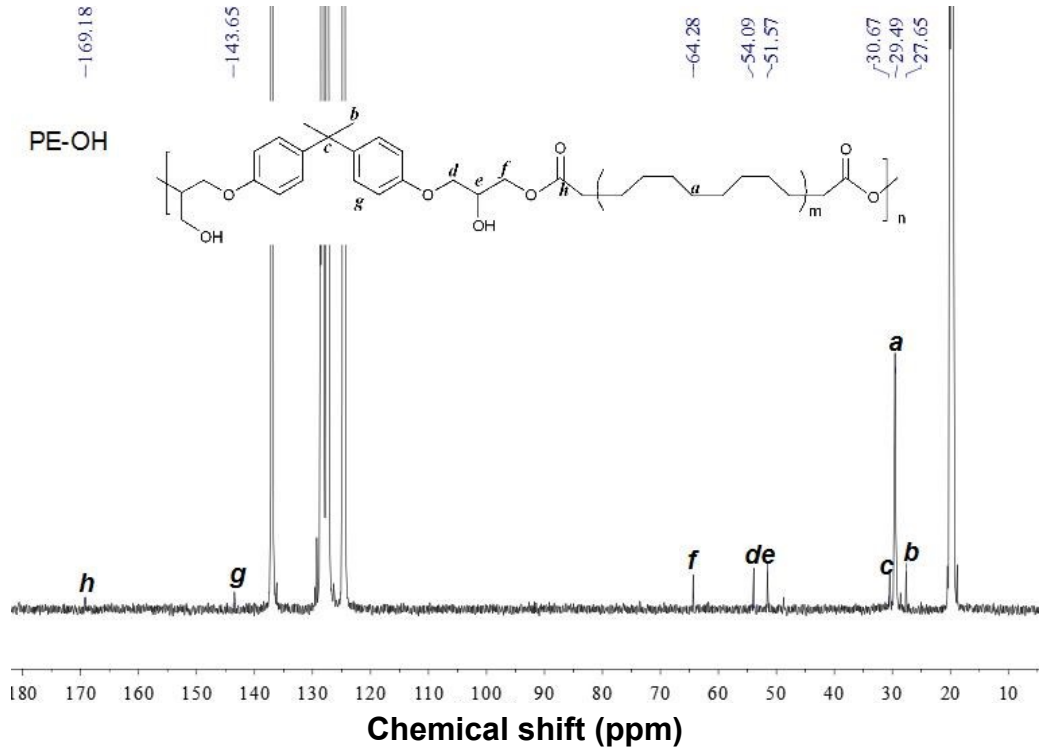


Figure S3 ^{1}H NMR and ^{13}C NMR spectra of PCOE-OH and PE-OH in toluene-d_8. The spectra of PCOE-OH were measured at 25 °C whereas those of PE-OH at 80 °C.

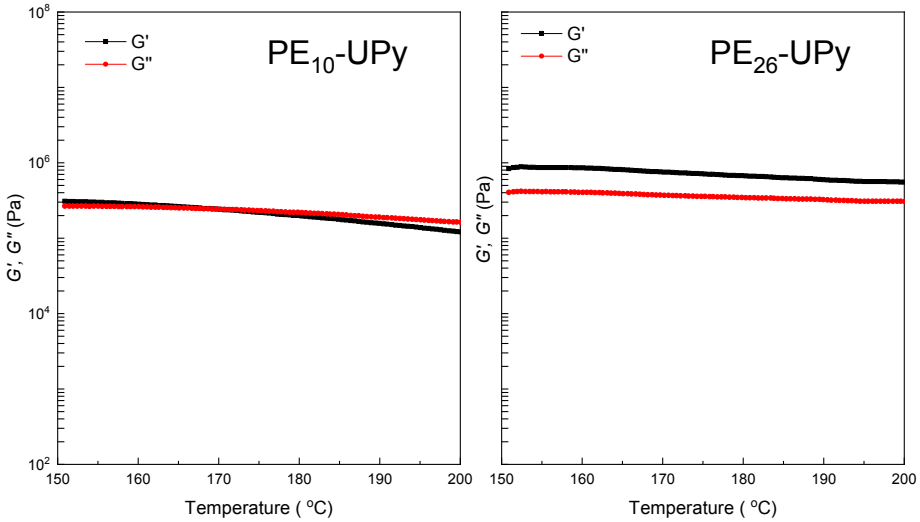


Figure S4 Plots of G′ and G″ as a function of temperature in the rheological measurements for PE_{10}-UPy and PE_{26}-UPy at 1 Hz

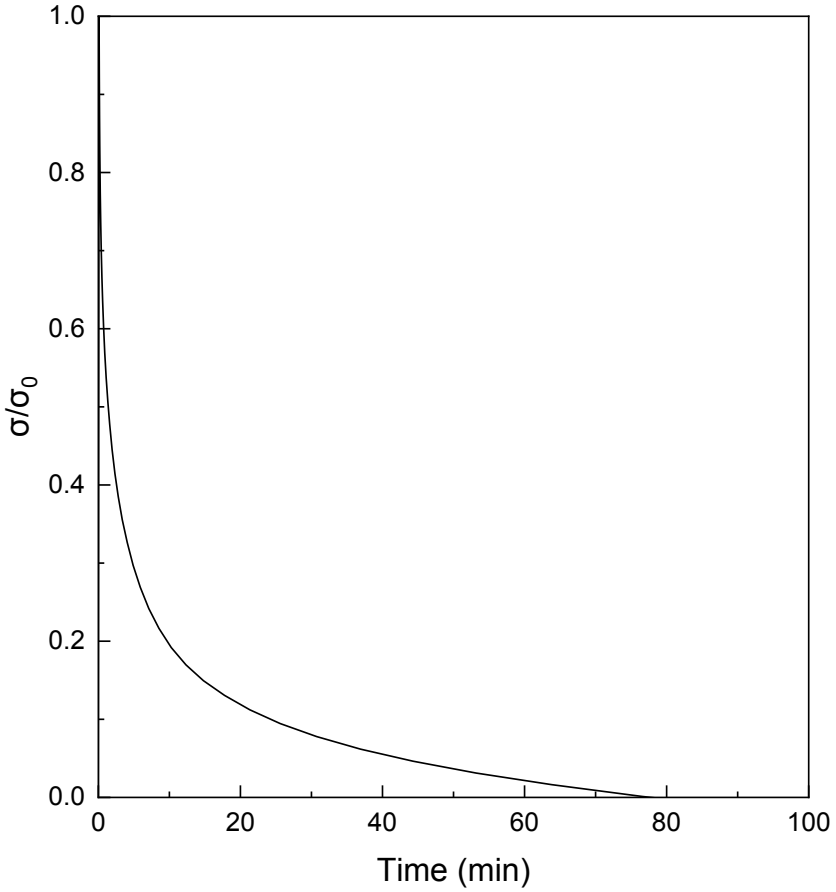


Figure S5 Stress relaxation curve of PE_{35}-UPy at 170 °C