Supplementary Informations (ESI) for

A functional polymer with chemically switchable crystallinity

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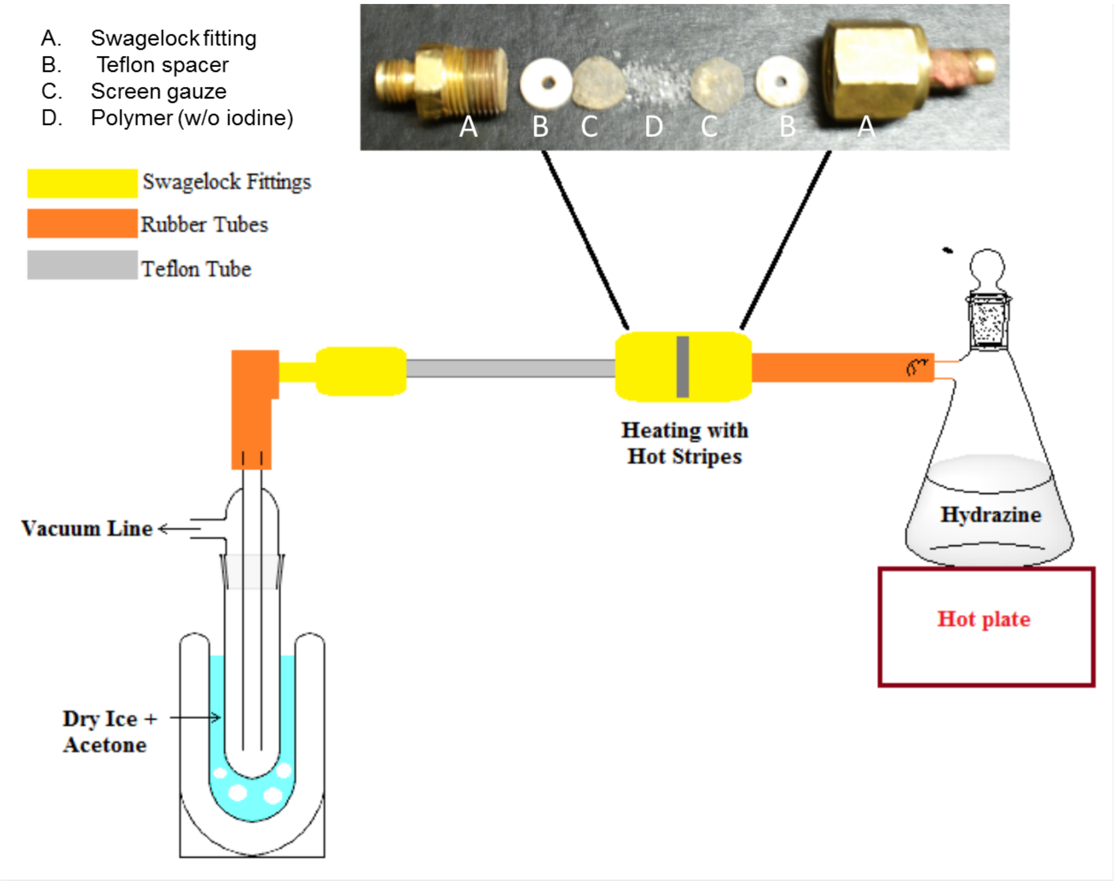
Experimental

1. Materials. All manipulations for the synthesis of catalysts were done under argon using standard Schlenk techniques. Ligand **1** (2-[bis(2-metoxyphenyl)-phosphanyl]-4-benzenesulfonic acid and ligand and catalyst **1** was prepared and characterized according to the literature (references 13 and 7). Solvents were purified over a mBraun solvent purification system. Diacetone acrylamide (DAAM) was purified by crystallization in ethyl acetate. The DAAM was dried under vacuum for 12 hrs. Hydrazine hydrate was used without any purification. Ozone was generated by a Welsbach Ozonator T-408 (Welsbach Corp.,Philadelphia, Pa.)

2. Synthetic procedures.

2.1 Typical procedure for DAAM copolymerization. In a drybox, a 400 mL Parr stainless steel reactor was loaded with 26.4 mg of catalyst **1** (4.4 x 10^{-5} mol), 20 g of DAAM and 180 ml of toluene containing 2 mg of 2,6-di-*tert*-butyl-4-methylphenol (BHT). The reactor was connected to a monitoring station outside the drybox, it was heated to the desired temperature, and the mixture stirred with a four-blade impeller at 800 rpm. After 15 hrs of reaction time at 75^{o}C under 300 psi of ethylene pressure, the reactor was cooled down to room temperature and slowly depressurized. The polymers were precipitated in four volumes of methanol, collected by centrifugation, washed with methanol by soxhlet extraction for 12 hrs and dried under vacuum.

Typical procedure for cross-linking (with hydrazine and iodione). The cross-linking agent (hydrazine hydrate) was boiled at 100^{o}C under a vacuum established by a rotary vane vacuum pump (Scheme 1). The vapors were then transported to a compressed ring containing the polymer (100 mg) and iodine (20 mg) (ID: 1cm). The ring was heated at 80 ^{o}C. After 5 hours of reaction, the apparatus was cooled down at room temperature. Iodine was neutralized by stirring the polymer in an aqueous solution of saturated potassium thiosulfate. The material was washed 4 times with acetone. Finally, the polymer was dried at 60 ^{o}C under vacuum for 12 hours.



Scheme 1. Apparatus for cross-linking DAAM-ethylene copolymer by hydrazine vapors

Typical conditions for ozonolysis.
The cross-linked polymer (50 mg) was suspended into 25 mL of CHCl3 for 12 hours and the mixture was cooled in an ice bath. Then O_3 was bubbled into the suspension for 30 minutes under stirring. The solvent was then evaporated under vacuum, and the residual solid was washed with acetone and dried in vacuum. Weight = 77 mg

3. Characterization

3.1 GPC

The molecular weight distributions were determined by gel permeation chromatography (GPC) using a Viscotek HT GPC equipped with triple detection operating at 160 ^{o}C. The eluent was 1,2,4-trichlorobenzene, and separation was performed on three PolymerLabs Mixed B(-LS) columns. The dn/dc of pure linear polyethylene was found to be 0.106 mL/g at this temperature. Owing to the fact that the copolymers have low incorporations in polar monomer, their dn/dc was approximated to the one of pure PE. The polymer was also analyzed by GPC-coupled with an IR4 detector from PolymerChar and set at 2915 cm^{-1} and 1739 cm^{-1}.

3.2 FTIR

The solid polymers FTIR spectra were recorded on a Nicolet 6700 Spectrometer equipped with Smart ATR accessory (ThermoSci).

3.4.1 Liquid-state NMR

All the NMR spectra were recorded on a Varian Inova 600 MHz. NMR spectra of the polymers with DAAM were recorded in tetrachloroethane-d_2 (TCE) at 85^{o}C and 115^{o}C. For ^{13}C spectra (10000 scans), an ungated decoupling sequence with a pulse angle of 20^o and a delay of 10s between two scans was used in order to ensure quantitative measurements.

3.4.2 Solid-state NMR

All ^{13}C spectra were recorded on a Varian Inova 600 MHz spectrometer using a 4 mm double resonance MAS probe and a spinning frequency of 12.5 kHz. Direct pulse spectra were initiated by a 3.33 µs pulse followed by a rotor-synchronized Hahn echo to reduce the probe signal. All cross-polarization spectra (including WISE) were initiated by a 1 ms long Hartmann-Hahn period with RF fields of 75 kHz on ^{13}C and 97.5 kHz on ^{1}H (15% ramp). For all spectra TPPM-15 ^{1}H decoupling was used during the 20 ms-long acquisition time and the spectral width was 75 kHz. Recycle delays were 20 s for the direct pulse spectra and 10 s for the cross-polarization spectra. T_2 measurements were performed by varying the interpulse delay in a Hahn echo between 80 and 9600 µs, T_1's using an inversion recovery sequence and delays between 0.1 and 100 s. WISE spectra were recorded at a spinning frequency of 5 kHz using 64 increments in the indirect dimension and a ^{1}H spectral width of 250 kHz.

3.5 DSC

Differential scanning calorimetry measurements (DSC) of solid samples were performed on a DSC823e equipped with an FRS5 sample cell, a sample robot, a Julabo FT400 intracooler and an HRS7 sensor from Mettler Toledo. Samples were heated from 20^{o}C to 140^{o}C at a rate of 10^{o}C/minute and data were analyzed with STAR software. All reported values are for samples which have first been heated past their melting point and slowly cooled from the melt at a rate of 0.3 ^{o}C/minute, except for the crosslinked PE (stage B in Scheme 1 of article), for which the melting point was only observed for the first heating cycle (prior cooling). This sample does not crystallize after being melted.

The content of crystallinity was obtained from the enthalpy of melting, which was normalized by the heat of melting of a 100% crystalline PE sample (294 J/g).

Copolymers of ethylene and DAAM

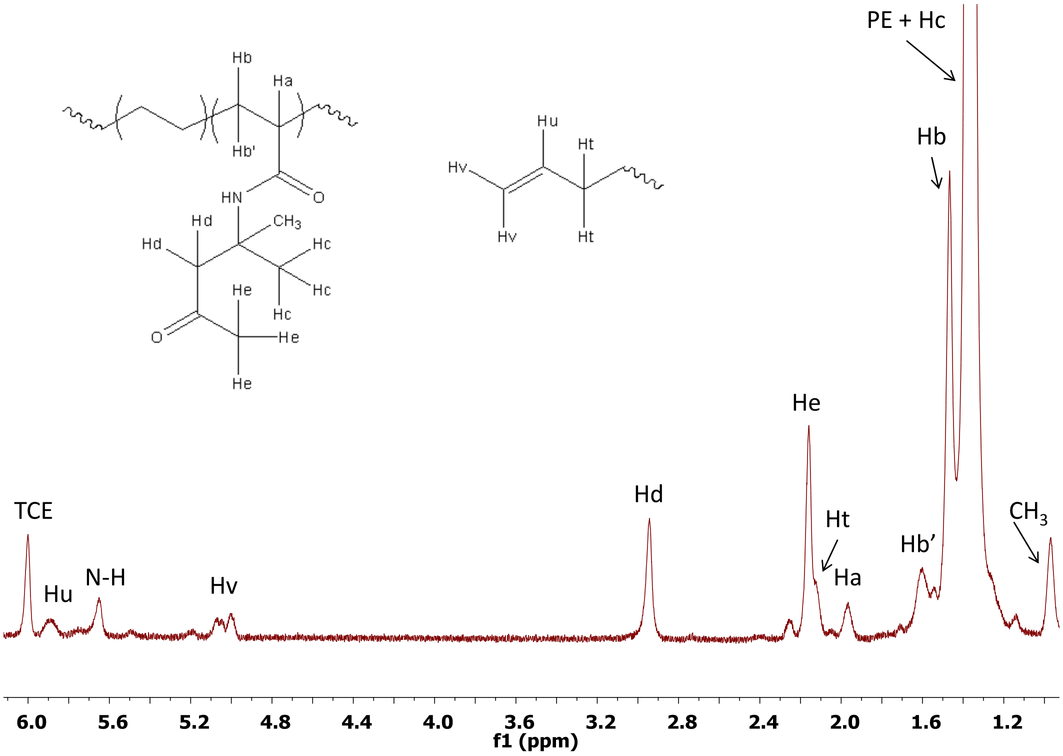


Figure 1a. ^{1}H NMR of poly(E-co-DAAM) with 1.7 mol% of DAAM using catalyst **2**. ($C_2D_2Cl_4$, T = 115 °C).

^{1}H NMR (600 MHz, T = 115 °C, TCE-d_2, δ): 5.9 (m, 1H, CH2=C**H-**, end group), 5.65 (m, 1H, N-**H**, amide), 5.0-5.1 (m, 2H, C**H**$_2$=CH-, end group), 2.95 (m, 2H, C=OC**H**$_2$C), 2.15 (m, 3H, C**H**$_3$C=OCH$_2$), 2.1 (m, 2H, CH$_2$=CH-C**H**$_2$-, end group), 1.95 (m, 1H, CH$_2$C**H**C=ONH), 1.6 (m, 1H, C**H**$_2$CHC=ONH), 1.45 (m(m, 1H, C**H**$_2$CHC=ONH), 1.35 (m, 4H, C**H**$_2$-CH$_2$, main chain PE + m, 6H, NHC(C**H**$_3$)$_2$), 0.95 (m, 3H, -C**H$_3$**, end chain)

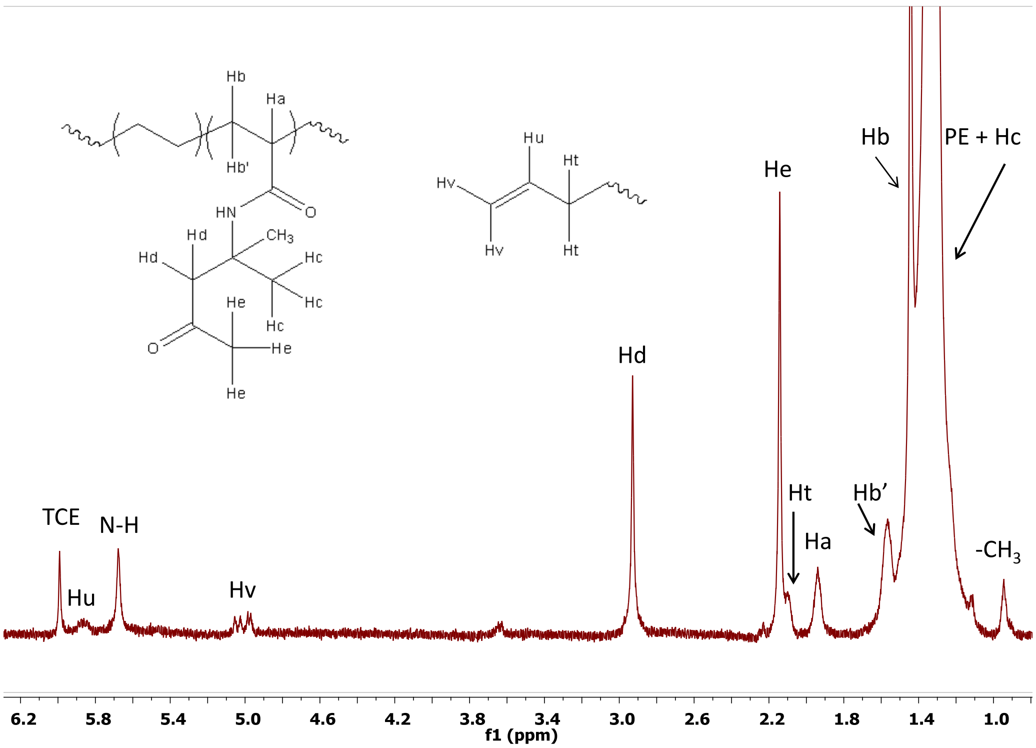


Figure 1b. ^{1}H NMR of poly(E-co-DAAM) with 2.8 mol% of DAAM using catalyst **1**. ($C_2D_2Cl_4$, T = 115 ^{o}C).

^{1}H NMR (600 MHz, T = 115 ^{o}C, TCE-d_2, δ): 5.9 (m, 1H, CH2=C**H**-, end group), 5.65 (m, 1H, N-**H**, amide), 5.0-5.1 (m, 2H, C$\mathbf{H}_2$=CH-, end group), 2.95 (m, 2H, C=OC$\mathbf{H}_2$C), 2.15 (m, 3H, C$\mathbf{H}_3$C=OCH_2), 2.1 (m, 2H, CH_2=CH-C$\mathbf{H}_2$-, end group), 1.95 (m, 1H, CH_2C**H**C=ONH), 1.6 (m, 1H, C$\mathbf{H}_2$CHC=ONH), 1.45 (m(m, 1H, C$\mathbf{H}_2$CHC=ONH), 1.35 (m, 4H, C$\mathbf{H}_2$-CH_2, main chain PE + m, 6H, NHC(C$\mathbf{H}_3$)$_2$), 0.95 (m, 3H, -C$\mathbf{H}_3$, end chain)

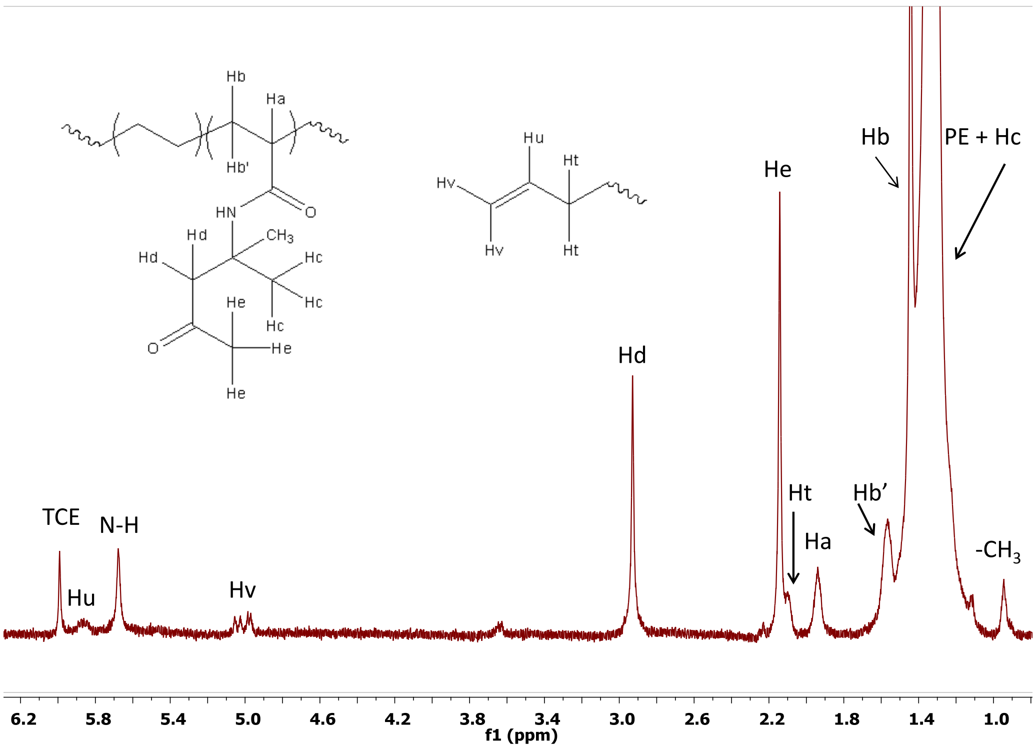


Figure 1c. ^{1}H NMR of poly(E-co-DAAM) with 5.6 mol% of DAAM using catalyst 1. ($C_2D_2Cl_4$, T = 115 ^oC).

1H NMR (600 MHz, T = 115 ^oC, TCE-d_2, δ): 5.9 (m, 1H, CH2=C**H**-, end group), 5.65 (m, 1H, N-**H**, amide), 5.0-5.1 (m, 2H, $C\mathbf{H}_2$=CH-, end group), 2.95 (m, 2H, C=O$C\mathbf{H}_2$C), 2.15 (m, 3H, $C\mathbf{H}_3$C=OCH_2), 2.1 (m, 2H, CH_2=CH-$C\mathbf{H}_2$-, end group), 1.95 (m, 1H, CH_2C**H**C=ONH), 1.6 (m, 1H, $C\mathbf{H}_2$CHC=ONH), 1.45 (m(m, 1H, $C\mathbf{H}_2$CHC=ONH), 1.35 (m, 4H, $C\mathbf{H}_2$-CH_2, main chain PE + m, 6H, NHC($C\mathbf{H}_3)_2$), 0.95 (m, 3H, -$C\mathbf{H}_\mathbf{3}$, end chain)

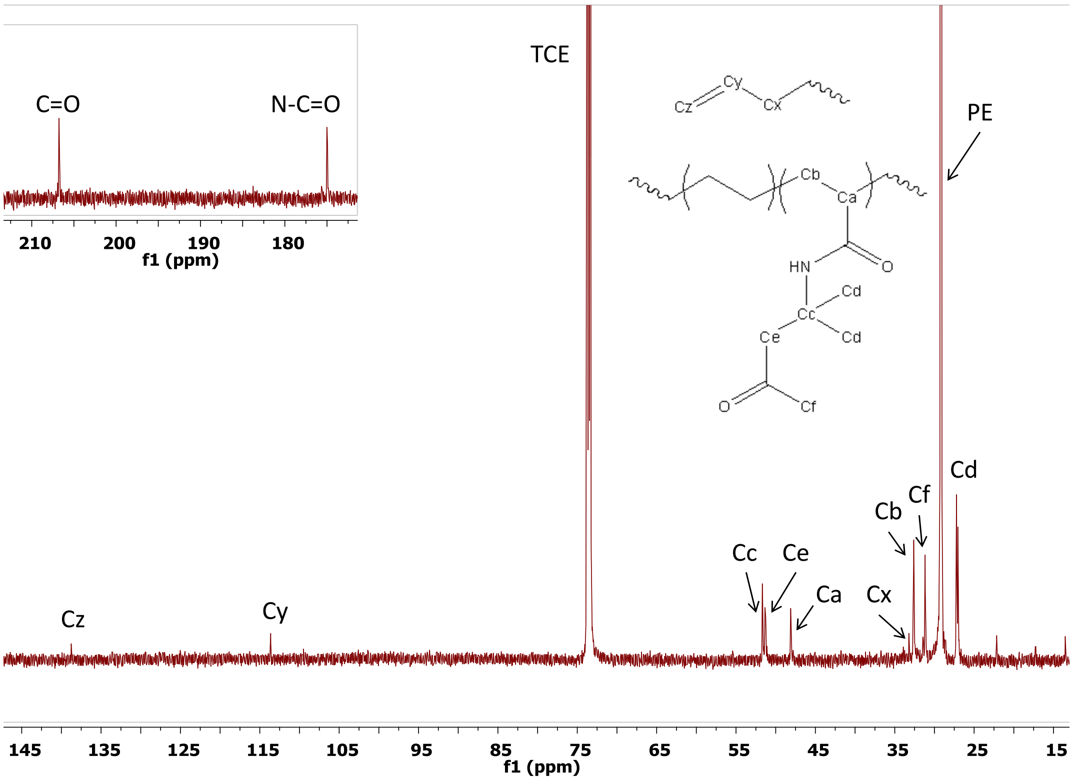


Figure 2a. ^{13}C NMR of poly(E-co-DAAM) with 5.6 mol% of DAAM using catalyst 2. ($C_2D_2Cl_4$, T = 90 ^{o}C).

13C NMR (100 MHz, T = 85 ^{o}C, TCE-d_2, δ): 207.0 (m, 1C, $CH_2\mathbf{C}{=}OCH_3$), 174.9 (m, 1C, $CH_2CH\mathbf{C}{=}ONH$), 138.1 (m, 1C, $\mathbf{C}H_2{=}CH\text{-}CH_2$), 113.5 (m, 1C, $CH_2{=}\mathbf{C}H\text{-}CH_2$), 52.0 (m, 1C, $NH\mathbf{C}(CH_3)_2$), 51.5 (m, 1C,$CH_3C{=}O\mathbf{C}H_2$), 47.6 (m, 1C, $CH_2\mathbf{C}HC{=}ONH$), 32.7 (m, 1C, $CH_2{=}CH\text{-}\mathbf{C}H_2$), 32.5 (m, 1C, $\mathbf{C}H_2CHC{=}ONH$), 32.0 (m, 1C, $CH_2C{=}O\mathbf{C}H_3$), 28.0 (m, 2C, main chain PE), 27.2 (m, 2C, $NHC(\mathbf{C}H_3)_2$)

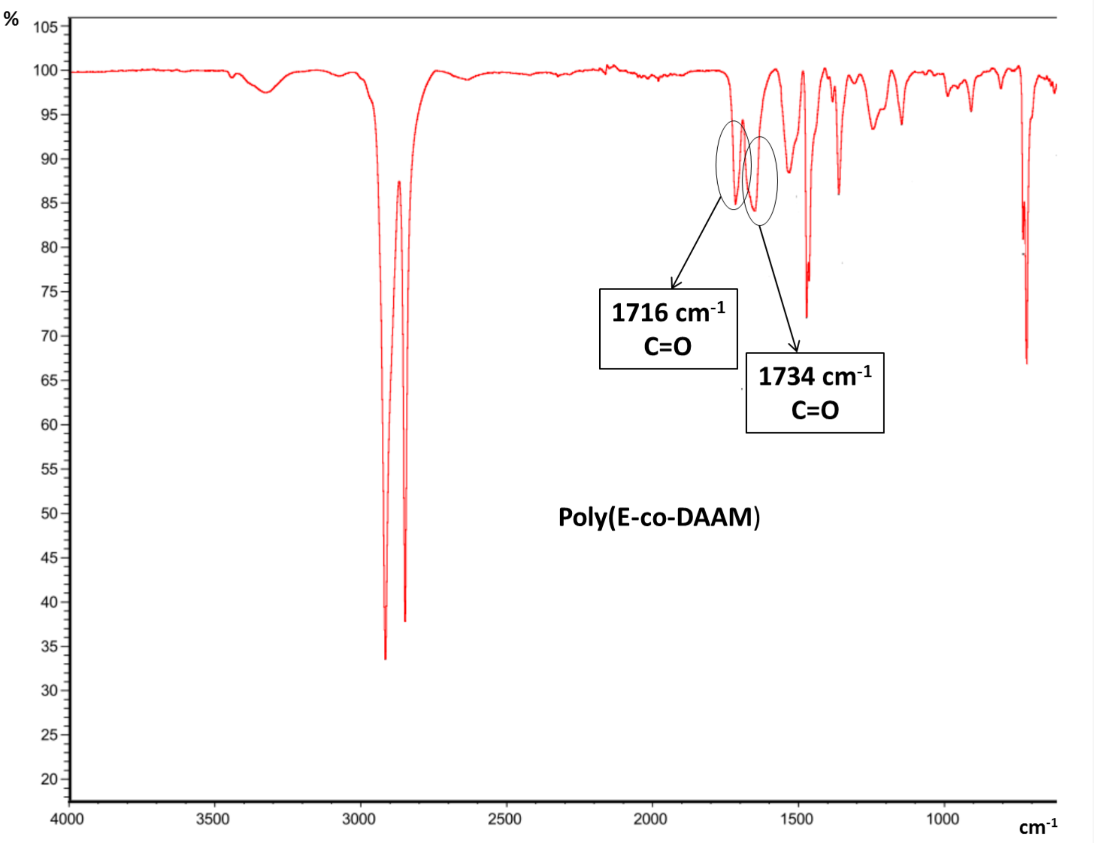
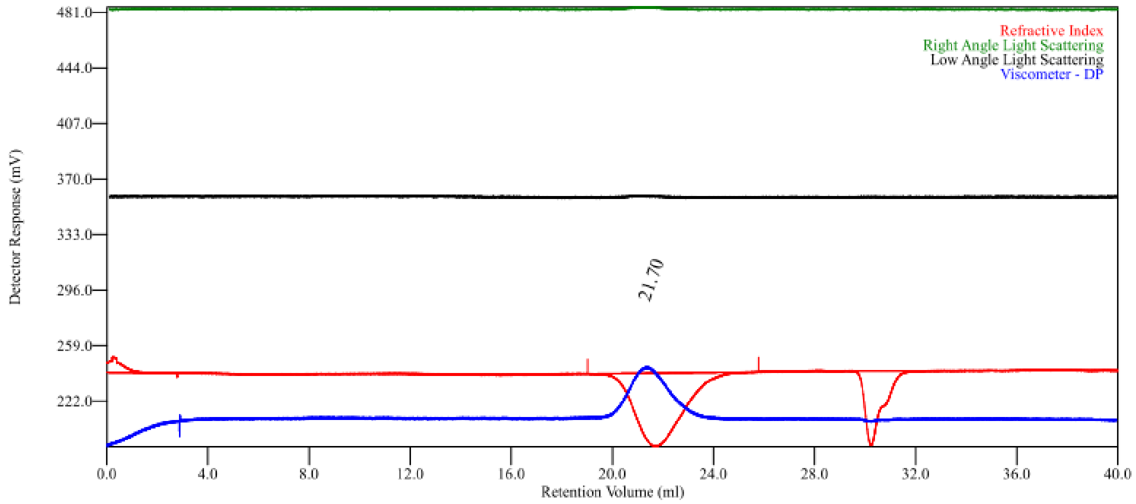


Figure 3a. FTIR (ATR) of poly(ethylene-co-DAAM) with 1.7 mol% of DAAM using catalyst 2.

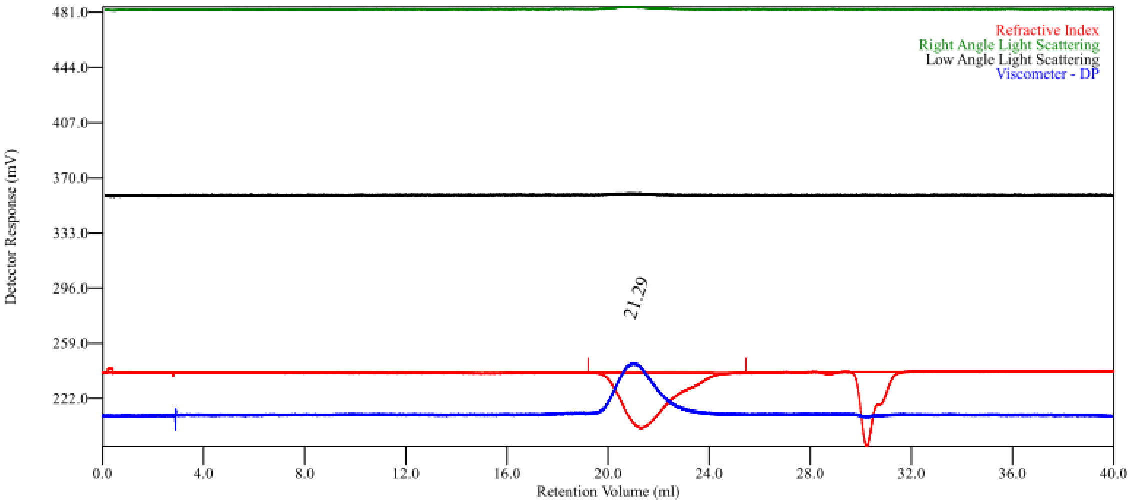
Assignations are based on: X. Zhang et al. J. Appl. Polym. Sci. **2012**, 123, 1822-1832

IR (ATR): *v* = 2915.2 cm^{-1} (m, CH_2, stretch), 2848.1 cm^{-1} (m, CH_2, stretch), 1716.3 cm^{-1} (m, C=O), 1734.4 cm^{-1}, 1472.5 cm^{-1} (s, CH_2, scissor), 1462.1 cm^{-1} (m, CH_2, scissor)



Multi-Detectors-Results		
Peak RV	ml	21.697
Mn	Daltons	2.669
Mw	Daltons	5.415
Mz	Daltons	8.320
Mp	Daltons	5.417
Mw/Mn		2.029
IV	dl/g	0.1753
Rh	nm	2.364
Rg	nm	No Calc
Wt Fr	Peak	1.000
Mark-Houwink a		0.682
Mark-Houwink logK		-3.284
Branches		0.000
Branch Freq.		0.000
RI Area	mvml	104.17
UV Area	mvml	0.00
RALS Area	mvml	1.85
LALS Area	mvml	0.53
IVDP Area	mvml	63.07

Figure 4a: GPC (HT) of poly(ethylene-co-DAAM) with 5.5 mol% using catalyst 2



Multi-Detectors-Results		
Peak RV	ml	21.287
Mn	Daltons	6.824
Mw	Daltons	9.829
Mz	Daltons	14.483
Mp	Daltons	9.756
Mw/Mn		1.426
IV	dl/g	0.1889
Rh	nm	2.991
Rg	nm	No Calc
Wt Fr	Peak	1.000
Mark-Houwink a		0.682
Mark-Houwink logK		-3.454
Branches		0.000
Branch Freq.		0.000
RI Area	mvml	81.83
UV Area	mvml	0.00
RALS Area	mvml	2.57
LALS Area	mvml	1.43
IVDP Area	mvml	60.69

Figure 4b: GPC (HT) of poly(ethylene-co-DAAM) 1.7 mol% using catalyst 2

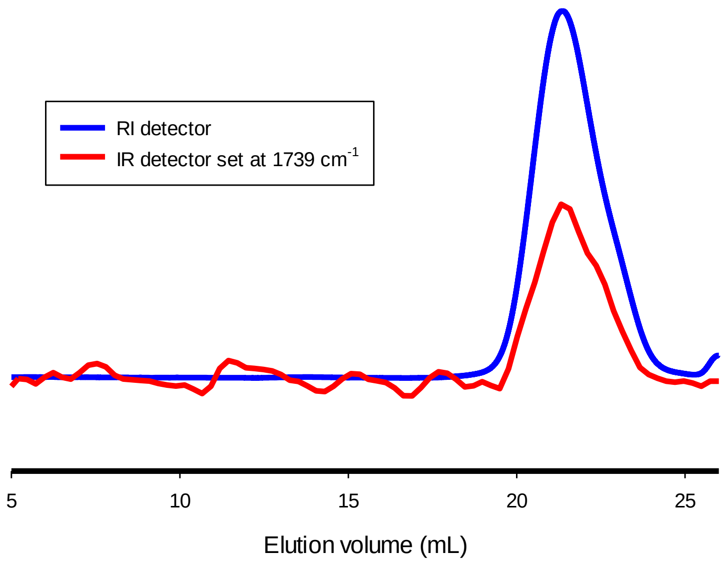


Figure 4c: GPC (HT) with FTIR detector of poly(ethylene-co-DAAM) 1.7 mol% using catalyst **2.**

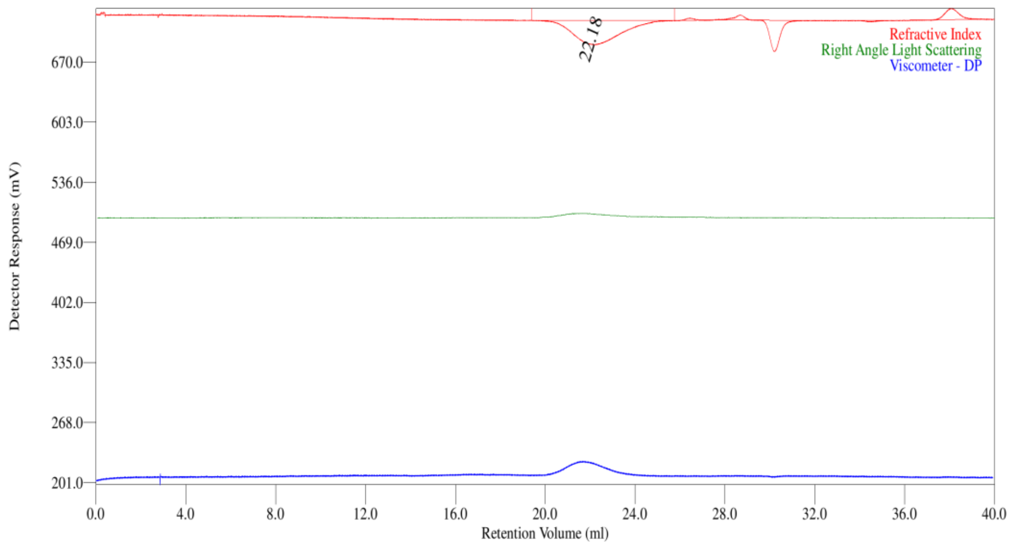


Figure 4d: GPC (HT) of poly(ethylene-co-DAAM) after crosslinking and O_3 treatment

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	22.183
Mn - (Daltons)	7,739
Mw - (Daltons)	9,817
Mz - (Daltons)	14,436
Mp - (Daltons)	8,134
Mw / Mn	1.268
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0623
Rh - (nm)	2.054
Wt Fr (Peak)	1.000
Mark-Houwink a	0.629
Mark-Houwink logK	-3.828
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	64.57
UV Area - (mvml)	0.00
RALS Area - (mvml)	10.73
LALS Area - (mvml)	0.00
IVDP Area - (mvml)	31.89

Cross-linked polymer of ethylene and DAAM

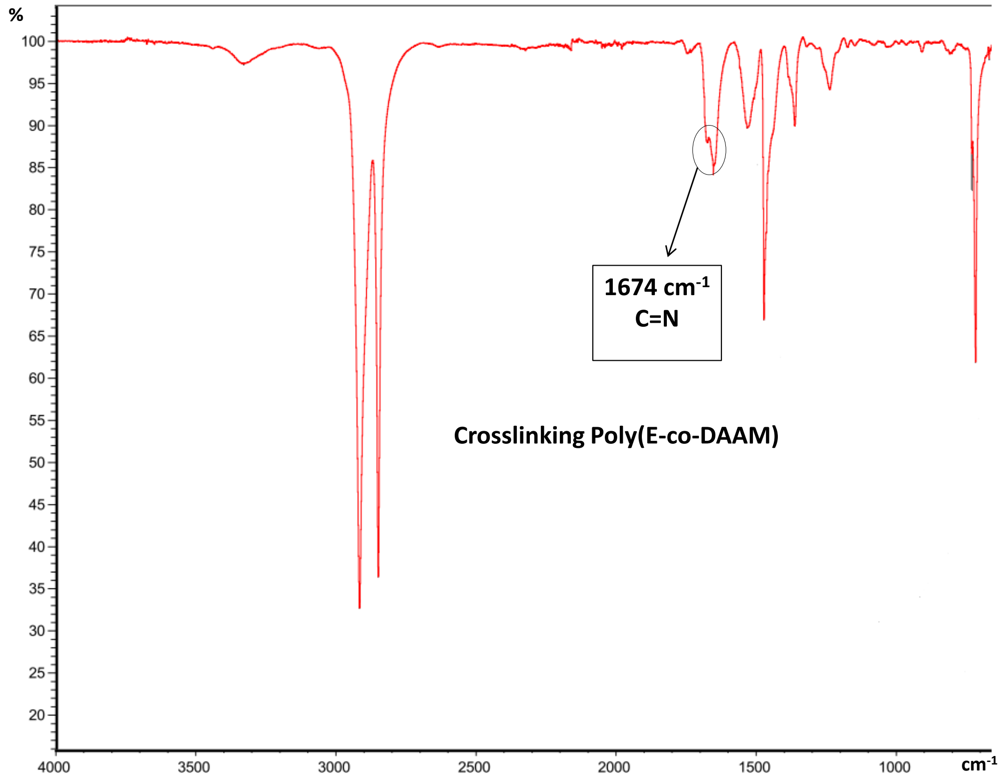


Figure 5a. FTIR (ATR) of cross-linked poly(ethylene-co-DAAM) with 1.7 mol% of DAAM using catalyst **2**.

IR (ATR): ν = 2915.2 cm^{-1} (m, CH_2, stretch), 2848.1 cm^{-1} (m, CH_2, stretch), 1674.0 cm^{-1} (m, C=N), 1734.4 cm^{-1}, 1472.5 cm^{-1} (s, CH_2, scissor), 1462.1 cm^{-1} (m, CH_2, scissor)

Cross-linked polymer of ethylene and DAAM after ozonolysis

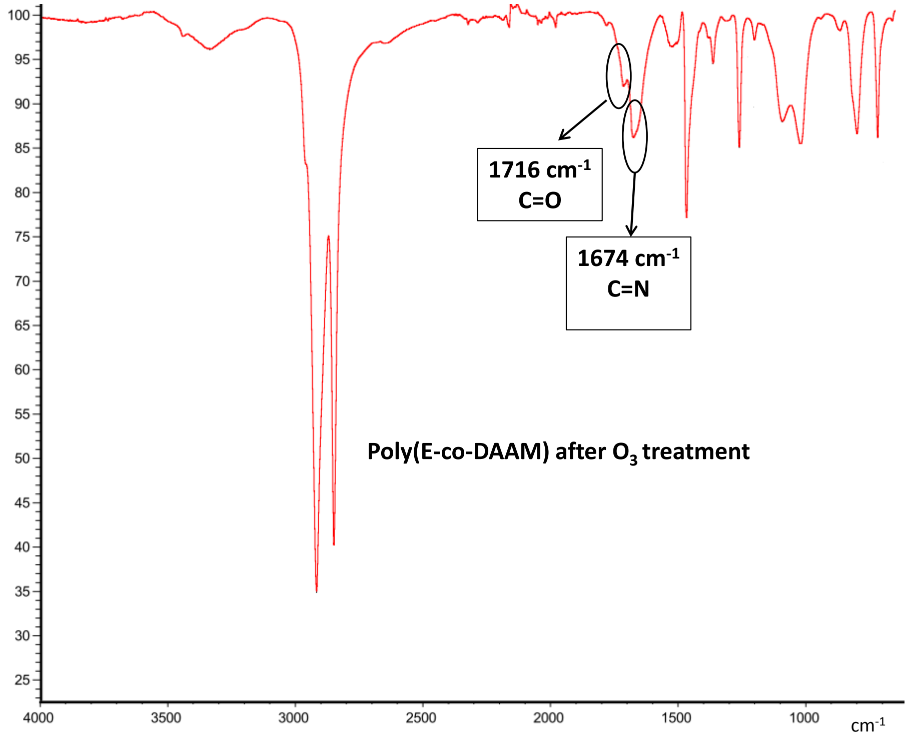


Figure 6a. FTIR (ATR) of poly(ethylene-co-DAAM crosslinking) after bubbling with O_3 with 1.7 mol% of DAAM using catalyst 2.

IR (ATR): ν = 3333.9 cm^{-1} (m, PE chain scission), 2915.2 cm^{-1} (m, CH_2, stretch), 2848.1 cm^{-1} (m, CH_2, stretch), 1674.0 cm^{-1} (m, C=N), 1716.3 cm^{-1} (m, C=O) 1734.4 cm^{-1}, 1472.5 cm^{-1} (s, CH_2, scissor), 1462.1 cm^{-1} (m, CH_2, scissor), 1092-1020 cm^{-1} (m, PE chain scission)

Evolution of the melting points of linear copolymers of ethylene with polar monomers

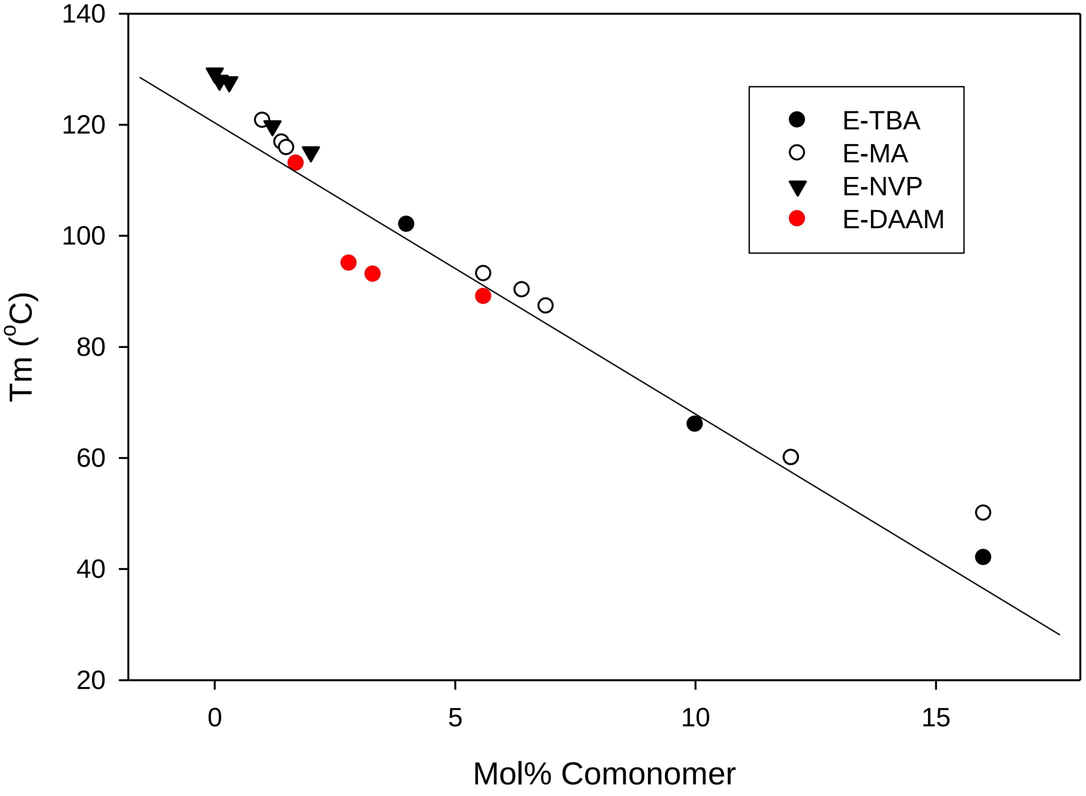


Figure 7: Melting temperatures (^oC) of various polymers containing different polar monomers (%mol) using Pd based catalysts. TBA : *tert*-butyl acrylate, MA : methyl acrylate, NVP : N-vinyl pyrrolidinone.

Copolymers E-TBA : V. A. Kryuchkov, J.-C. Daigle, K. M. Skupov, J. P. Claverie and F. M. Winnik, *J. Am. Chem. Soc.*, 2010, **132**, 15573.
Copolymers E-MA : K. M. Skupov, P. R. Marella, M. Simard, G. P. A. Yap, N. Allen, D. Conner, B. L. Goodall and J. P. Claverie, *Macromol. Rapid Comm.*, 2007, **28**, 2033 and K. M. Skupov, L. Piche and J. P. Claverie, *Macromolecules*, 2008, **41**, 2309.
Copolymers E-NVP : K. M. Skupov, J. Hobbs, P. Marella, D. Conner, S. Golisz, B. L. Goodall and J. P. Claverie, *Macromolecules*, 2009, **42**, 6953.

Heat stability of the non cross-linked and cross-linked polymers

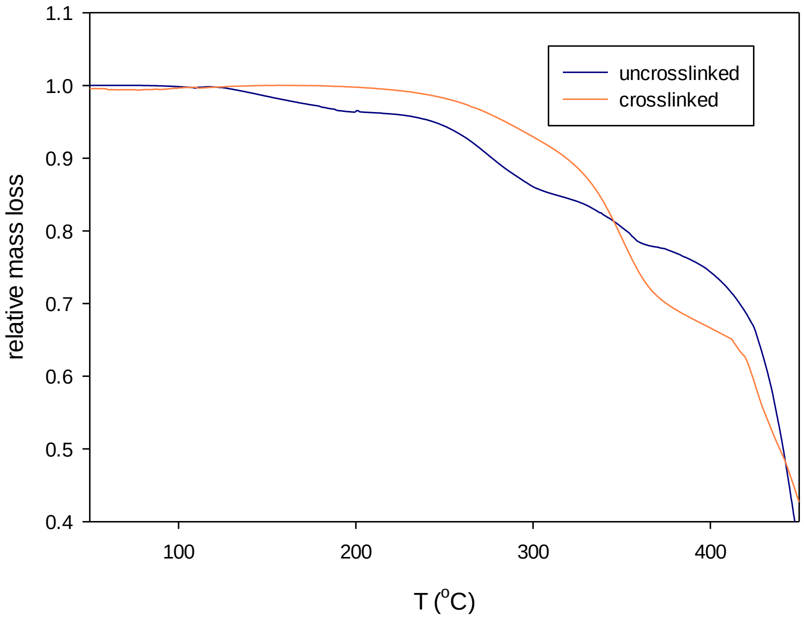


Figure 8: TGA traces of both polymers before and after cross-linking (1.7 mol%).

Crystallinity recovery after O_3 treatment

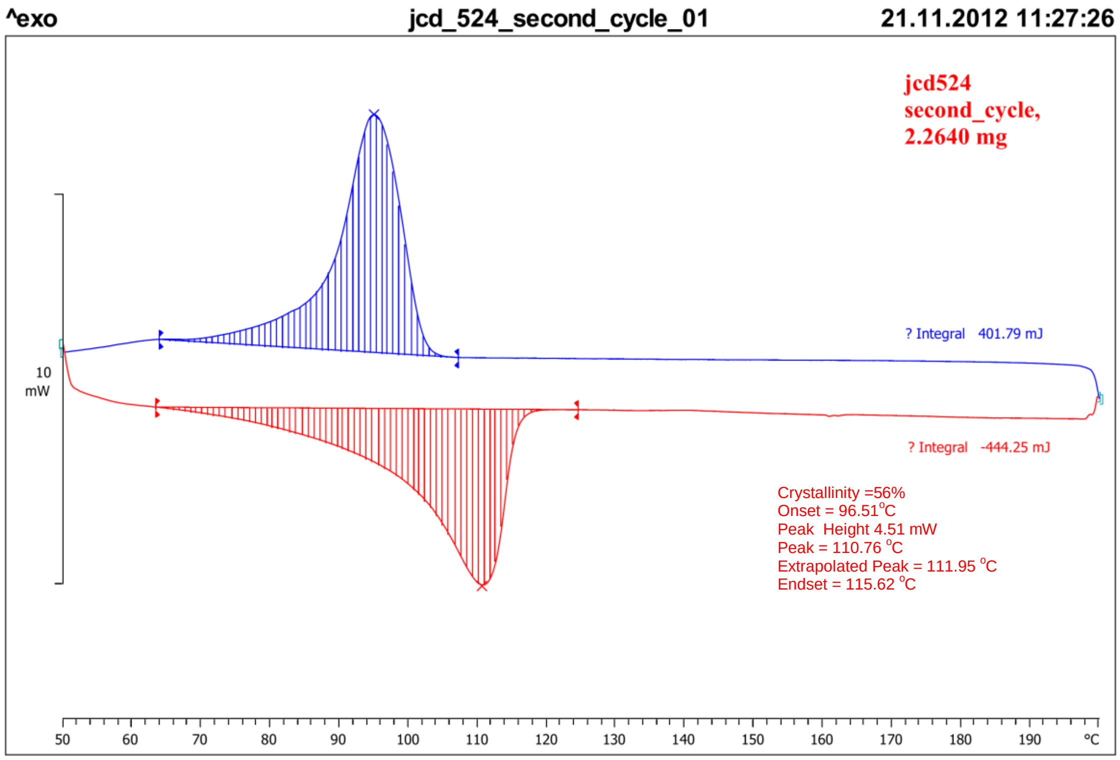


Figure 9: DSC spectrum (10 °C/min) of polymer after ozone treatment and after heating 4h at 140°C and 2h at 160oC then cooled at a rate of 0.3°C/min (second treatment).