Electronic Supplementary Information

Byproduct Free Curing of a Highly Insulating Polyethylene Copolymer Blend: An Alternative to Peroxide Crosslinking

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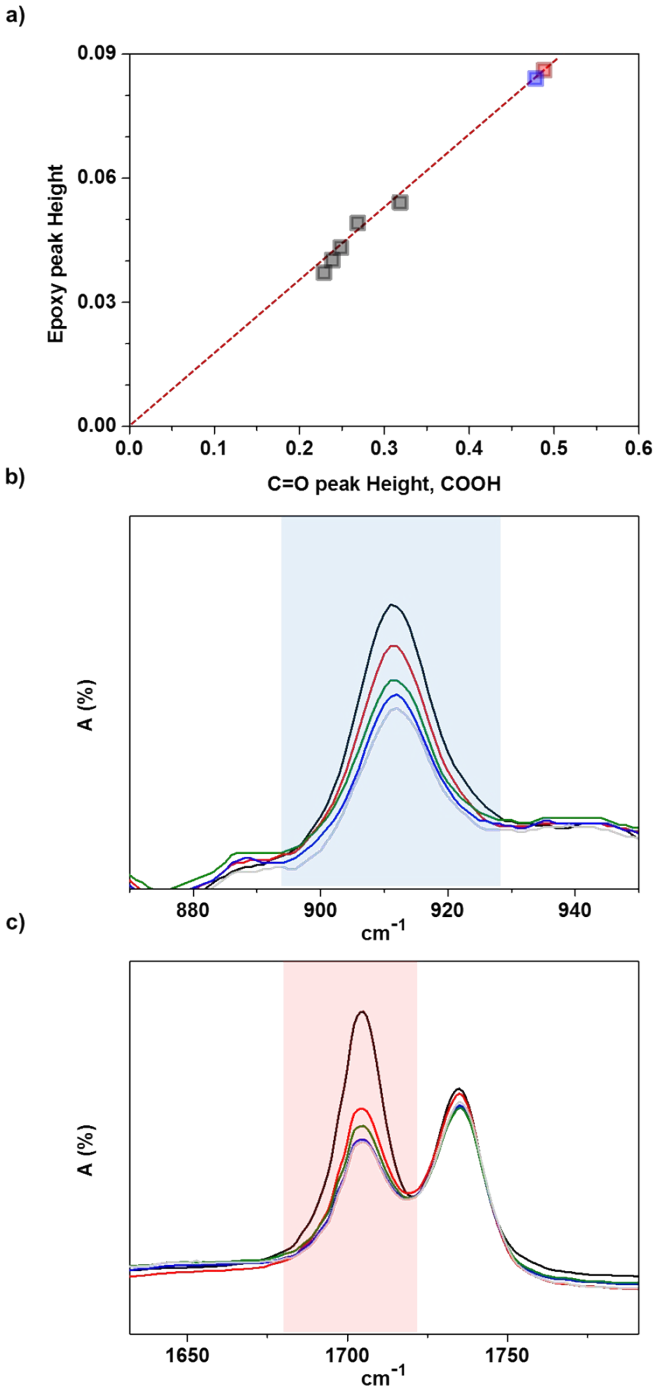

Fig. S1 **a)** Peak heights obtained from fitting of the epoxy 911 cm^{-1} peak signal and carboxylic acid C=O stretch peak at 1705 cm^{-1} (the 1734 cm^{-1} peak is the C=O stretch of the ester of GMA). From right to left, simulated p(E-*stat*-GMA):p(E-*stat*-AA) polymer blend where we predicted the peak heights based on the FTIR spectra of the individual polymers (red), extruded polymer blend (blue) and polymer blend cured at 2.5, 5, 7.5, 15 and 20 min. **b)** Epoxy 911 cm^{-1} peak signal and **c)** carboxylic acid C=O stretch peak at 1705 cm^{-1} obtained from ATR-FTIR spectra of the 1.7:1 p(E-*stat*-GMA):p(E-*stat*-AA) polymer blend, extruded (black line) and cured at 200 °C for different times (2.5-20 min).

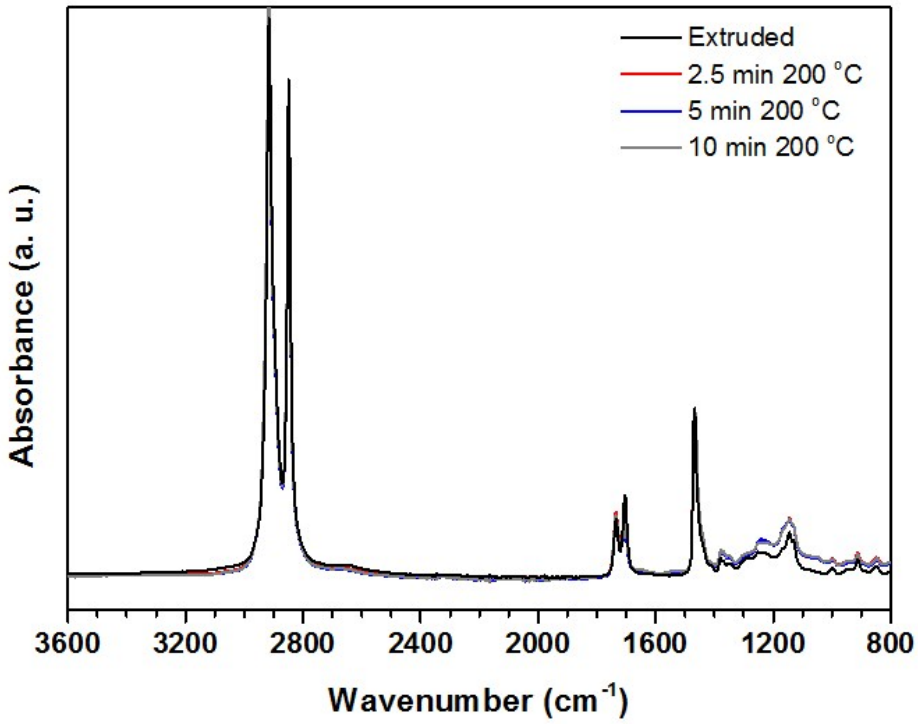

Fig. S2 ATR-FTIR spectrum of p(E-*stat*-GMA):p(E-*stat*-AA) polymer blend at stochiometric ratios crosslinked at 200 °C for 2.5, 5 and 10 min. Analysis of the spectra indicates that the main side reactions of the hydroxyl group can be ruled out, as evidenced by the absence of water absorption band in the region between 3500-3700 cm^{-1}, associated with symmetric and asymmetric stretching of O-H groups.

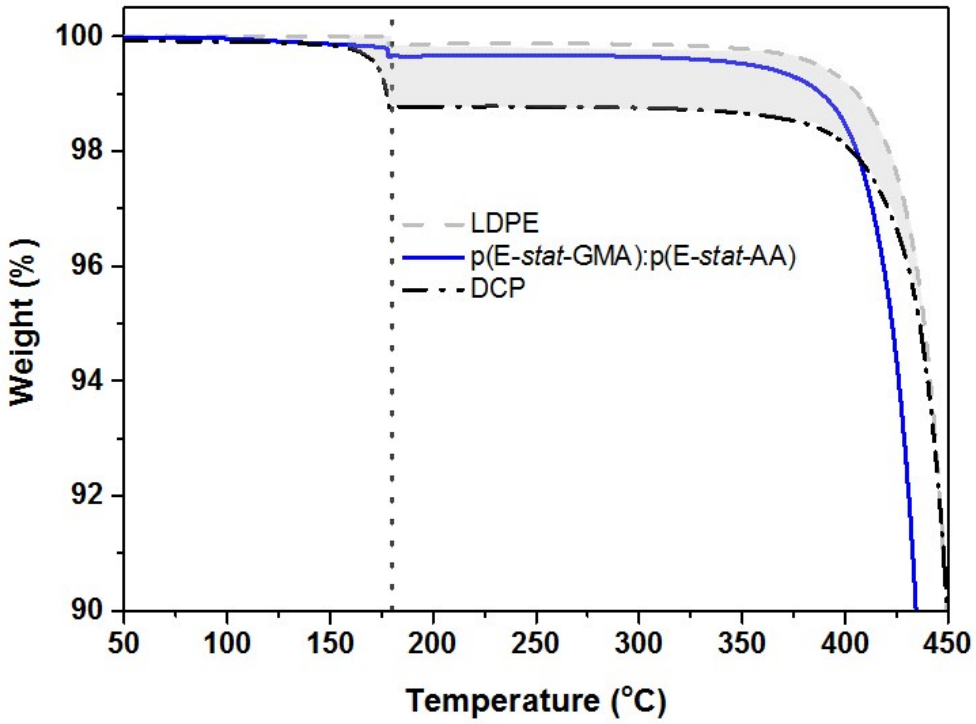

Fig. S3 TGA thermograms of neat LDPE, LDPE crosslinked with 2 % wt dicumyl peroxide (DCP) and p(E-*stat*-GMA):p(E-*stat*-AA) blend cured at 180 °C for 15 min. The shaded area highlights the weight loss of volatile byproducts that arise from DCP decomposition.

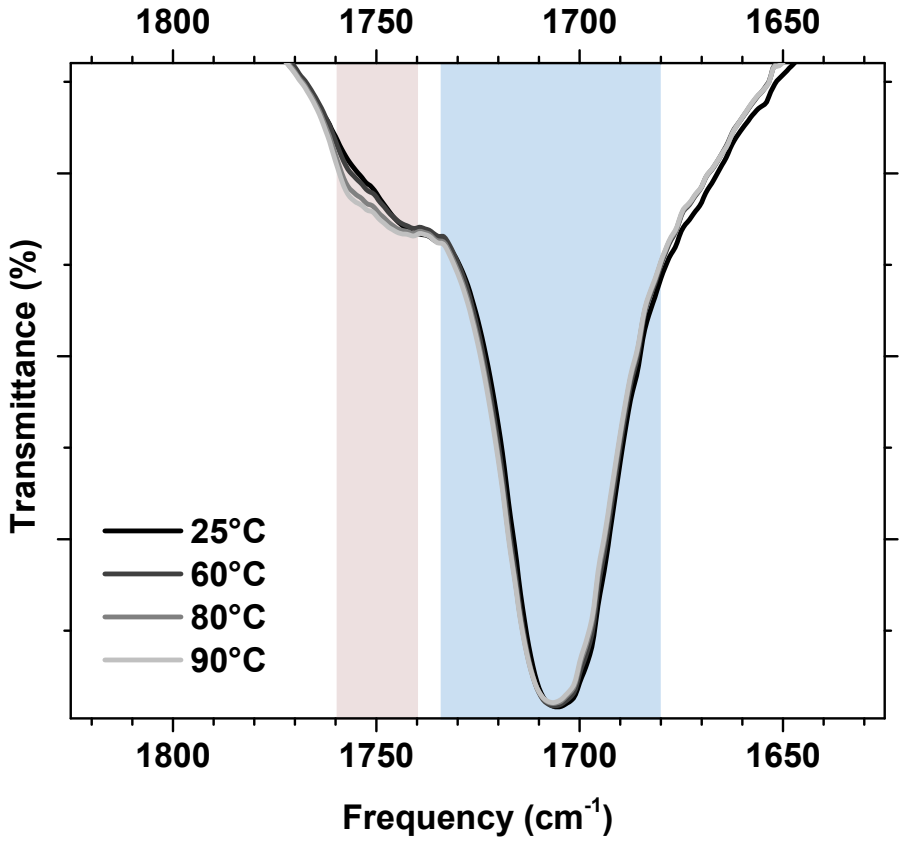

Fig. S4 FTIR spectra of p(E-*stat*-AA) taken in transmission mode. A step-wise increase in temperature from room temperature to 90 °C produces a slight decrease in the transmittance around 1750 cm^{-1} (red region), associated with the C=O stretch in the free acid. For the C=O stretch in the dimerized acid centered around 1705 cm^{-1} (blue region) no significant change in the transmittance can be detected. Hence, even at temperatures close to Tm the vast majority of the carboxylic groups are dimerized. Spectra taken at 25, 60, 80 and 90 °C.

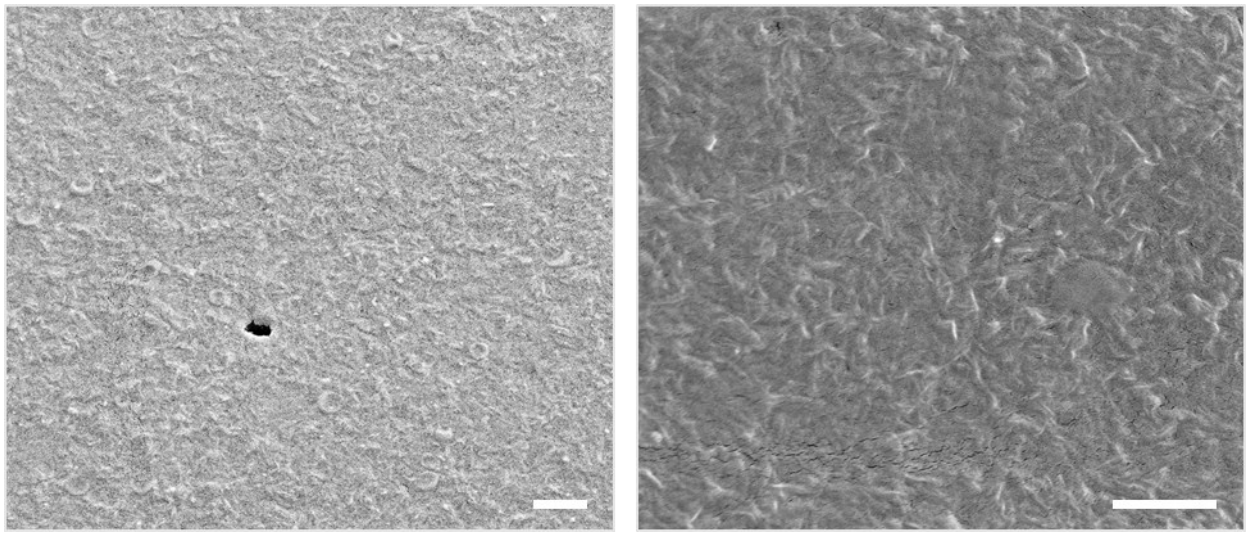

Fig. S5 SEM micrographs of a 1.7:1 stoichiometric p(E-*stat*-GMA):p(E-*stat*-AA)blend. No phase separation of the blend components can be detected. Scale bar equal to 1 μm.

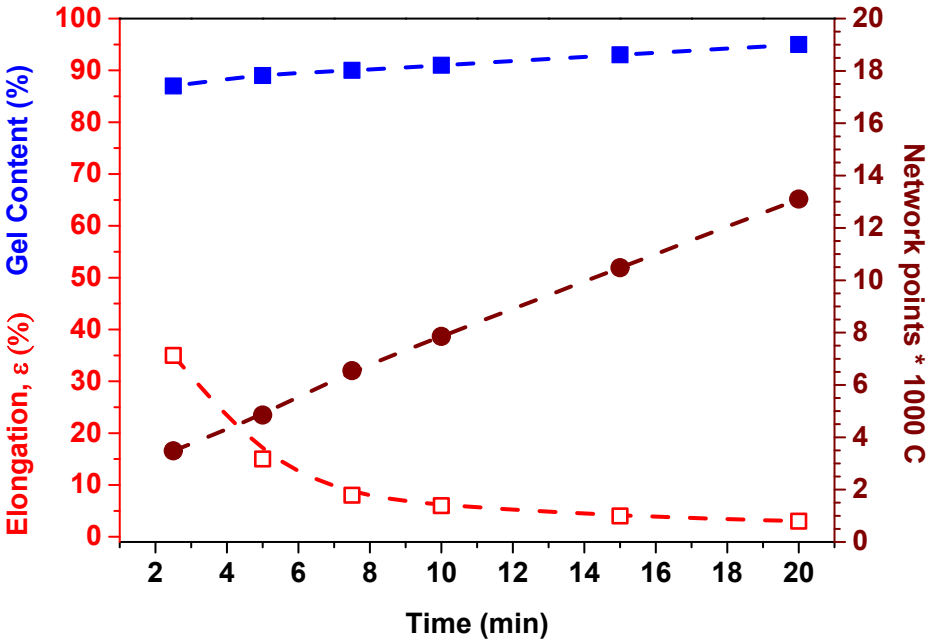

Fig. S6 Effect of time on Hot set Elongation (□), Network point formation*1000 C atoms (● from hot set) and Gel content (■) for a 1.7:1 stoichiometric p(E-*stat*-GMA):p(E-*stat*-AA) formulation cross- linked at 200°C.

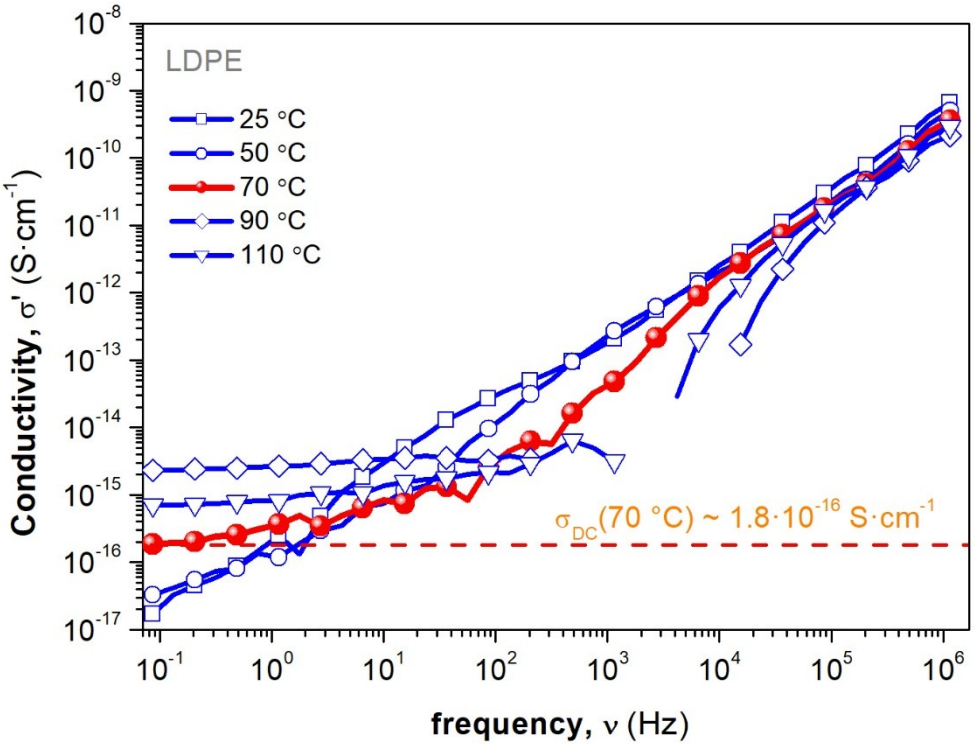

Fig. S7 Conductivity measured at different temperatures, ranging from 30 to 130 °C in 20 °C steps, for reference LDPE.

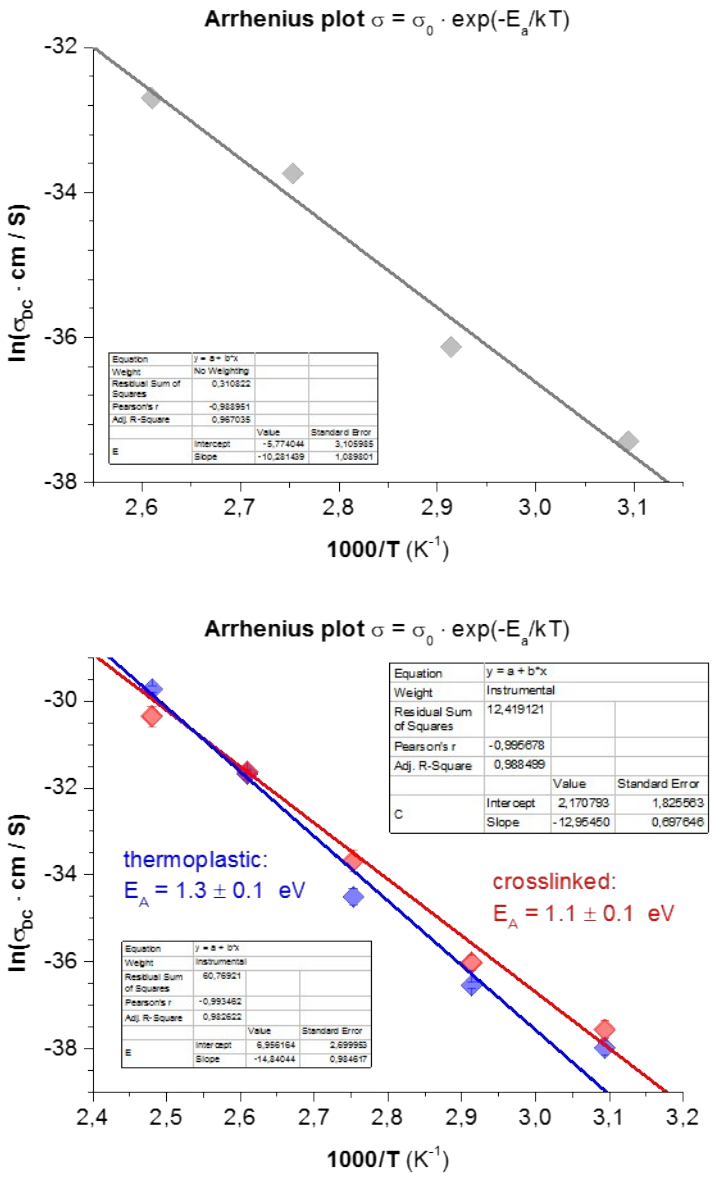

Fig. S8 Arrhenius plot for reference LDPE (top), as well as the thermoplastic and crosslinked copolymer blend (bottom).

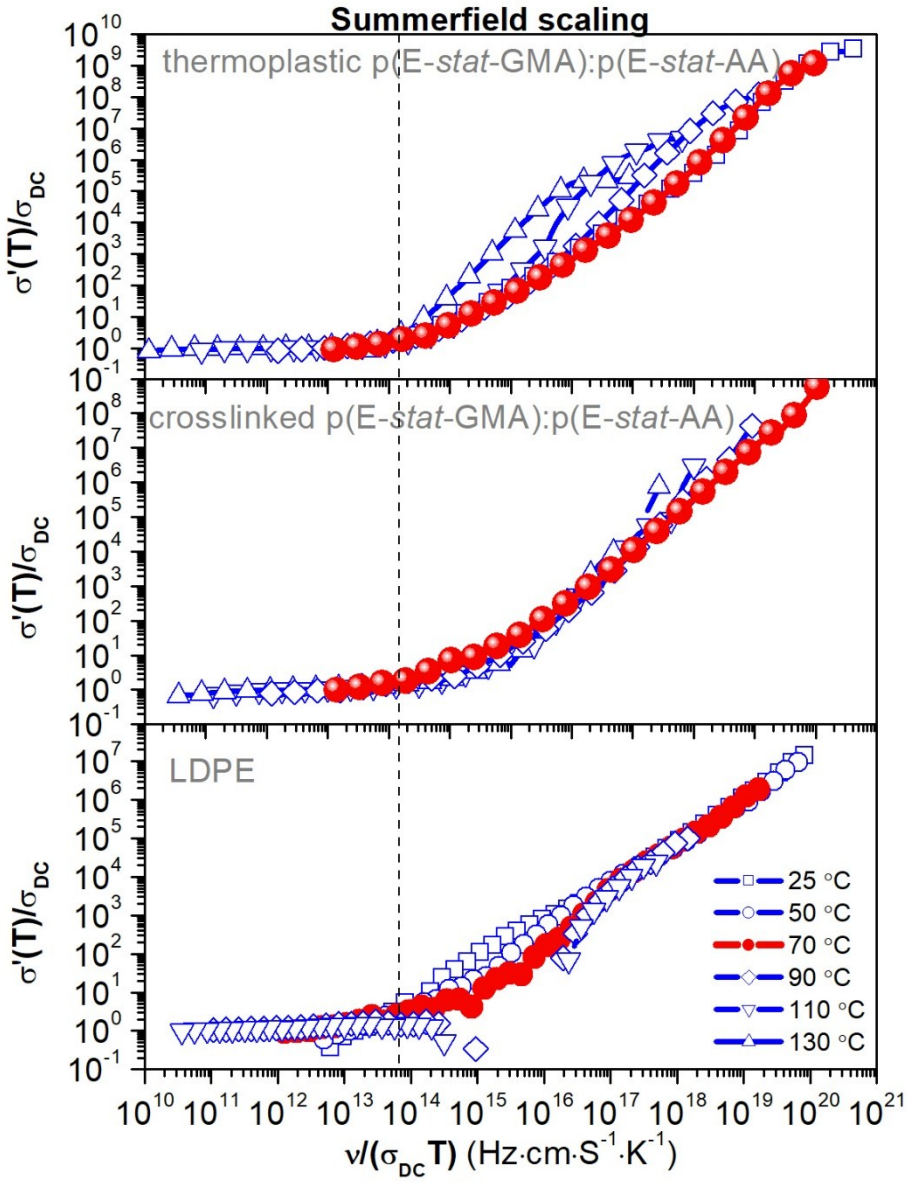

Fig. S9 We attempted to construct BDS master curves by using the Summerfield scaling. The dashed line indicates the crossover frequency of the thermoplastic blend. For both the thermoplastic and crosslinked blend we find that the data are congruent up to 70 °C but deviate from each other at higher temperatures (i.e. 90 to 130 °C). Just as for pure LDPE, the deviation is more pronounced in the case of the thermoplastic blend. This can be attributed to gradual melting of LDPE crystallites (cf. Figure 4: onset of melting considerably below T_m).

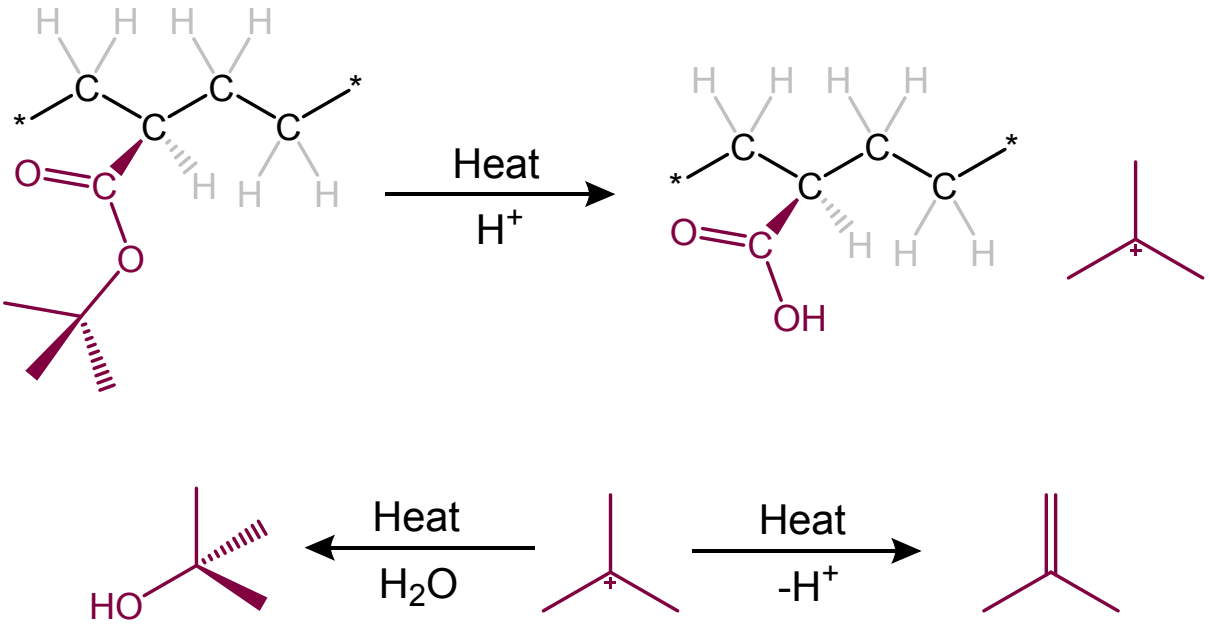

Fig. S10 Deprotection of p(E-*stat*-TBA) at temperature T > 200 °C: tert-butyl acrylate in presence of H^+ released from acrylic acid units releases a tert-butyl cation, which predominantly will react with moisture to give tert-butyl alcohol.