An Unusual Transition from Point-like to Fibrillar Crystals in Injection-Molded Polyethylene Articles Induced by Lightly Cross-linking and Melt Penetration

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Characterizations of lightly Cross-linked Structures Obtained by Electron-irradiation Technology Rheological Behavior

The rheological behavior was tested using a stress-controlled dynamic rheometer (AR2000ex, TA instruments, USA) in parallel plate geometry at 190 oC. The gap between two plate was 1 mm. All the tests were performed under nitrogen atmosphere to prevent thermo-oxidative degradation. Dynamic frequency sweep between 0.01 and 100 Hz was carried out at a strain of 1%. The relaxation spectrums were obtained using a non-linear regression regularization method (NLREG) on the computer.

The relationship of storage modulus (G') versus frequency of samples with differnet irradiation doses were shown in Fig. S1. The storage modulus of 3Mrad was slightly higher than that of 2Mrad sample, which also higher than that of 0Mrad sample. And the slope of storage modulus at low frequency regime, G' of 0Mrad sample showed no deviation from the liquid-like behavior, of which frequency dependency was : $G' \sim \omega^{1.38}$, as the increasing of irradiation dose, the G' of 3Mrad sample showed solid-like behavior, of which relaxation exponents was 1.07 close to plateau like at low frequency region, which demonstrated that the networks in 3Mrad are more stable and stronger than those in 0Mrad. Although these relaxation exponents are less than the theory value ($G' \sim \omega^{2}$, liquid-like hehavior; $G' \sim \omega^{1}$, solid-like hehavior), it is accepted for large molecular weight distribution obtained by commercial way.

The continuous relaxation time spectrums of samples with different irradiation doses were shown in Fig. S2. The relaxation spectrums can be calculated from the storage modulus (G') using a non-linear regression regularization method (NLREG) put forward by Honerkamp and Weese [1] on the computer. The peak values of the relaxation time spectrum are called experimental relaxation times. The peak relaxation time increased intensively with increasing the irradiation dose, from about 0.005 s in 0Mrad to 0.5 s in 2Mrad sample, finally to about 4s in 3Mrad sample, the increasing magnification is about 800 times, which indicated that more stronger and stable networks introduced by electron-irradiation can enhance the relaxation time substantially.

Successive Self-nucleation and Annealing (SSA)

Successive self-nucleation and annealing (SSA) technique is based on the sequential application of self-nucleation and annealing steps to the polymer, which can be used to characterize different PE grades [2], cross-linked PE [3], and functionalized LLDPE and ULDPE [4]. The method is executed and described schematically in Fig. S3. The protocol is below:

(1) The samples were first melted at 200 oC for 10 min to erase the thermal history.

(2) The samples were cooled at 10 oC/min to 40 oC to the build an initial 'standard' thermal history.

(3) Heating scan at 10 oC/min up to a selected self-seeding and annealing temperature (Ts=134 oC), where the samples were isothermally kept for 5 min.

(4) Cooling scan at 10 oC/min was performed to 40 oC.

(5) Repeat the step (3), only the Ts was 5 oC lower than last stage, which can let some of unmelted crystals aneal during 5 min. The chosen Ts range was 134-119 oC for all samples.

(6) The melting behavior was recorded with a heating rate of 10 oC /min when thermal condition was over.

The melting curves of all samples using SSA methods were shown in Fig. S4. Only one melting endotherm peak was shown in the 0Mrad sample (see Fig. S4), which was also an evidence of linear structure of HDPE without any detectable branches. Two endotherm peaks were appeared in 2Mrad sample, high temperature peak representing original linear long chains and an unclear low temperature shoulder indicating shorter chains seperated by chemical branching points, which indicated that low content of chemical entangle points with shorter chains were formed after electron-irradiation. Finally, we can obviously see a temperature shoulder besides of high temperature peak emerged in 3Mrad sample, which demonstrated that more and more chemical entangle points with shorter chains were formed in 3M sample, and these chemical entangle points acted as permanent points due to they cannot slip and disentangle at high temperature compared with the transient points in buck melt. Combined the SSA technique and rheological behavior of all samples, we can confirm that some permanent entangle points in cross-linked structures were introduced into 2Mrad and 3Mrad systems successfully, and more stable and stronger networks are in 3Mrad rather than in 2Mrad system.

Gel Content

The gel content of 0Mrad, 2Mrad and 3Mrad samples was tested based on ASTMD 2765 [5]. All the samples were washed with

xylene as the solvent at 145 oC for 12h, and antioxygen 1010 was added 0.1 % to prevent the degradation of polymer. All samples were performed as the same situation that nothing was left after washing. So the gel fractions of all samples were 0 %, which indicated that the content of cross-linked structures is too low to be detected. But we still use concept of cross-linked structure in this work resulted from it is universal known that light eletron beam can make PE cross-linked, even the content is so low that hardly any gel content.

Gel Permeation Chromatography

All the samples were washed by 1,2,4-trichlorobenzene at 135 oC to gain the molecular weights and molecular weight distribution. The results were shown in Fig. S5. The molecular weight increased slightly with increasing dose of irradiation, Mn increased from 2.9×10^4 in 0Mrad to 3.2×10^4 in 2Mrad, finally to 3.4×10^4 in 3Mrad sample, and Mw increased from 8.3×10^4 in 0Mrad to 9.5×10^4 in 2Mrad, finally to 1.0×10^5 in 3Mrad sample.

Reference

1 J. Honerkamp and J. Weese, *Rheologica Acta*, 1993, **32**, 65-73.

2 A. Müller, Z. Hernandez, M. Arnal and J. Sánchez, *Polymer bulletin*, 1997, **39**, 465-472.

3 M. Arnal, V. Balsamo, G. Ronca, A. Sánchez, A. Müller, E. Canizales and C. U. de Navarro, *Journal of thermal analysis and calorimetry*, 2000, **59**, 451-470.

4 L. Marquez, I. Rivero and A. J. Müller, *Macromolecular Chemistry and Physics*, 1999, **200**, 330-337.

5 H. Khonakdar, S. Jafari, U. Wagenknecht and D. Jehnichen, *Radiation Physics and Chemistry*, 2006, **75**, 78-86.

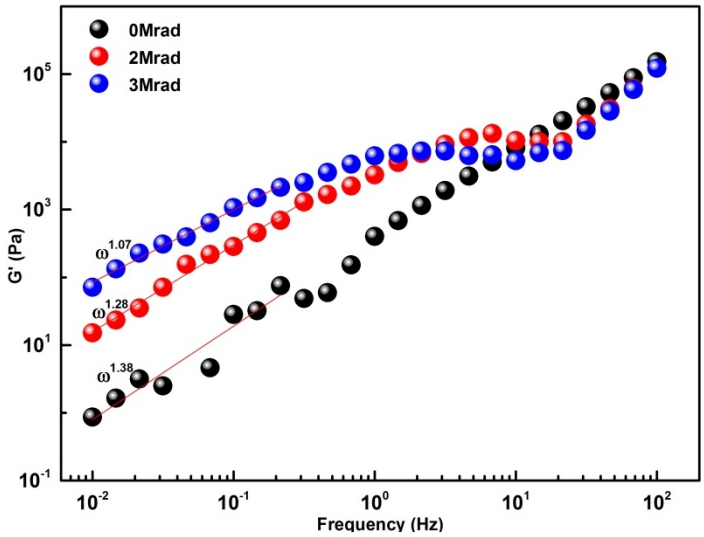

Fig. S1 The storage modulus versus frequency of samples with different irradiation doses.

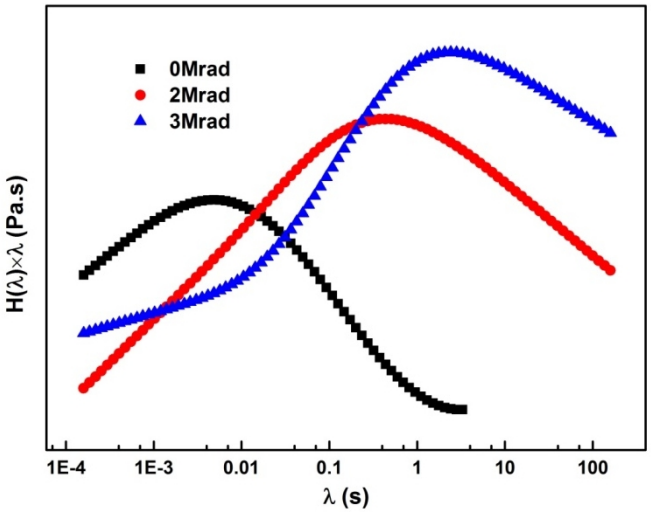

Fig. S2 Relaxation time of samples with different irradiation doses.

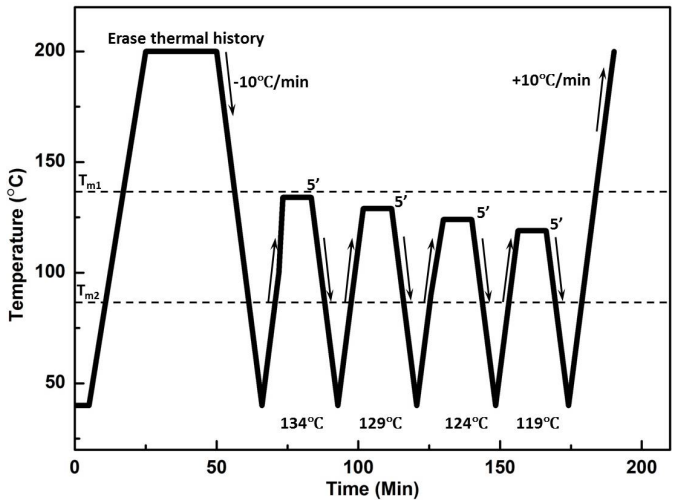

Fig. S3 Basic schematic picture of the experimental protocol of the SSA technique as described in DSC.

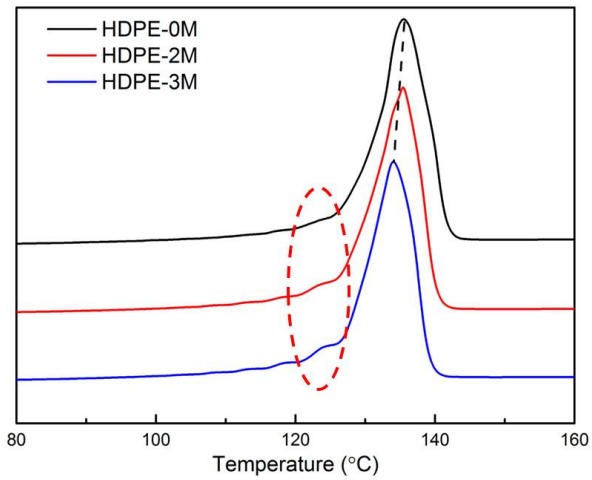

Fig. S4 DSC heating scans at 10 oC of samles with different irradiation doses using SSA methods.

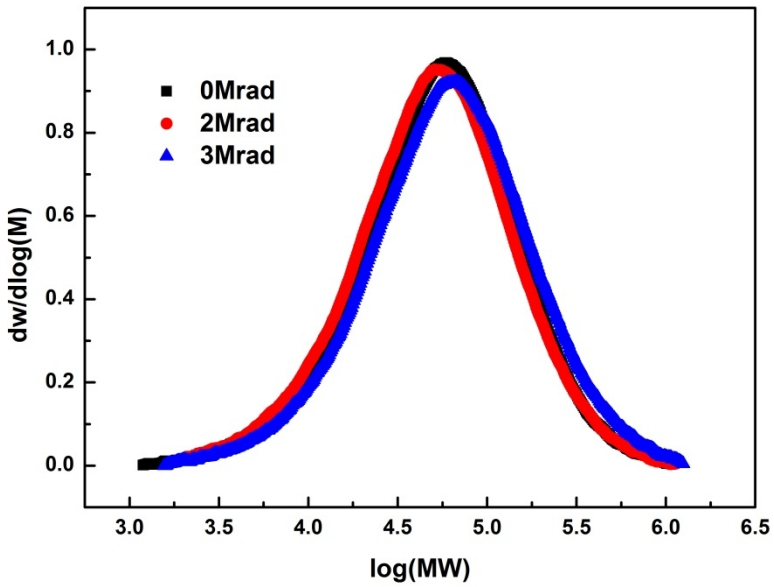

Fig. S5 GPC curves showing molecular weights and distributions of samples with different irradiation doses.