

The Solid State ^{13}C NMR Study of Gamma Radiation of Ethylene-Octene Copolymer

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Abstract: Ethylene-octene copolymer (POE) samples exposed to γ -radiation under a series of absorbed doses have been investigated using thermal analysis, sol-gel analysis and solid state ^{13}C nuclear magnetic Resonance (NMR). The chemical shift of POE was assigned and peak evolution as a function of radiation dose was discussed. An obviously evolution is that the peak area of 33.6 ppm decreases as a function of the increase of radiation dose, and at the same time, the peak shape broadens gradually. This indicates that the chain scission occurred between α -C and branch chain C (methine) or between C1 (the sidegroup hexyl) and branch chain C (methane) after radiation. The chain scission is severer with the increase of absorbed dose. The ^{13}C NMR spectra of the corresponding gels confirmed the result. The variation in linewidth of the resonance at 33.6 ppm in samples of POE irradiated to different doses was attributed to information of chain, scission, new cross linking, and crystalline components.

Keywords: Ethylene-octene copolymer (POE), γ -radiation, solid-state ^{13}C NMR, Chain Scission.

1. INTRODUCTION

Ethylene-octene copolymer (POE) manufactured using a constrained geometry catalyst is provided with narrow molecular distribution and homogeneous comonomer distribution. The copolymer is widely used in blending polymers, packaging materials, biomedical materials [1-3] due to good tear resistance and long shelf life. Radiation is both an efficient and economical means for the production of new or modified polymer [4]. The effect of radiation on polyolefin has been widely reported, with the principal focus being on the change of structure and property after radiation [5,6]. Poongavalappil [7] researched on the influence of electron beam irradiation on the thermal, mechanical, and rheological properties of ethylene-octene copolymer with high comonomer content. Li [8] researched the influence of gamma irradiation conditions including atmosphere, absorbed dose and heat treatment of samples on the cross-linking of irradiated POE, and discussed the cross-linking reaction of irradiated POE. Roberto [2] researched the effect of gamma irradiation in an inert atmosphere on the chemical, physical and mechanical properties of POE of differing molecular weights and comonomer content. They found that the low molecular weight and low octane content copolymer showed chain scission

mainly. But they obtained the results from mechanical behaviour and did not characterize it from the structure. The effect of POE concentration and molecular weight on the POE mobility in the blends were also examined with ^1H solid state NMR [9]. The solid state ^{13}C NMR spectra can characterize efficiently the structure of insoluble polymers and mobility of macromolecules, as well as detecting any degradations of polymer. This makes solid state ^{13}C NMR widely applicable in monitoring the radiation-thermal degradation of polymers, aging of irradiated polymer and polymer motion [10-14]. In this paper, thermal analysis, sol-gel analysis and the solid state ^{13}C NMR spectra of POE under different absorbed doses are introduced to investigate the change of the chemical structure of irradiated POE. Carbon-13 spectra are referred to the chemical shift of α -C (33.6 ppm). Radiation modification of polymers results in the formation of a three-dimensional network structure through union of macro radicals generated. It is well known that irradiation of polymer causes the crosslinking of polymer chains and that the use of high irradiation doses may lead to the degradation process, the crosslinking sections can not be dissolved in solvents, so the gel contents used to be a parameter to characterize crosslinking degree. To further explore the radiation mechanism in POE, the results obtained by NMR are compared to those obtained by DSC and gel measurements. Chain scission and gel are discussed and an attempt is made to explain the mechanisms of radiation degradation and radiation crosslinking.

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2. EXPERIMENTATION

POE (ENGAGE 8150, M_w , 133,000; M_n , 68,000; 1-octene (mole%), 13.33, Degree of crystallinity (%), 10, was obtained from DOW Inc., USA). The plate samples used in this study were prepared by melt pressing of pellet samples (185 °C, 15 min). After compression molding, the plates were moved and allowed to cool at room temperature. The plate samples were subjected to gamma radiation in nitrogen atmosphere using Co-60 source (300k Ci, Shanghai University) at room temperature. Absorbed doses by the samples were 50, 100, 150, 200 and 250kGy respectively. For the extraction samples were cut in very small pieces, weighted and then placed in cooper wets of known mass. The cooper wets were tied up to ensure that the samples remain in cooper wets during the swelling process. The tied cooper wets containing samples were then put into the flasks with xylene at boiling temperature for 24 hours and then dried to a constant weight. Finally, the gel fraction was determined by weighing the mass. After the extraction process, the sol fraction (POE chains of low-molecular weight) was removed from the sample by diffusion in the solution, while the gel fraction remained in cooper wets. The gel amount was estimated by measuring the mass of the gel fraction (m_g) and the calculated loss of the samples mass was attributed to the sol fraction. The weight percentage of the gel (w_g) was obtained by $w_g = (m_g/m) \times 100\%$. Isothermal and subsequent melting behaviors were investigated using a Perkin Elmer, Inc., USA, and the temperature was calibrated with the indium

standard. All Differential scanning calorimetry (DSC) experiments were performed under a nitrogen purge at a constant flow rate. Sample weights were between 2–3 mg. All irradiated and non-irradiated POE samples were dried at 80 °C under vacuum for 12 h before measurement. DSC experiments of isothermal crystallization and subsequent melting behaviors were performed as follows: the sample was heated to 120 °C at a rate of 50 °C/min and held at this temperature for 3 min to eliminate any previous thermal history, and then cooled. The crystallization of irradiated and non-irradiated POE samples was studied by a differential scanning calorimetry (DSC) (Perkin Elmer, Inc., USA) with a heating rate of 20 °C/min under nitrogen and a cooling rate of 20 °C/min.

The solid state ^{13}C NMR spectra were obtained using a MERCURY plus 400 (Varian, Inc.) spectrometer, with which the cross-polarization magic angle spinning (CP-MAS) technique was applied. Samples weighting 50-100 mg were packed into 4 mm rotors and spun about the magic angle at 4 kHz. Solid-state ^{13}C NMR spectra (10K scans) were measured using ^{13}C single-pulse excitation with ^1H high-power decoupling during detection. A recycle delay of 5 s, and 90° pulse durations of 4.5 μs were employed.

3. RESULTS AND DISCUSSION

3.1. Gel Test and Thermal Analysis

The degree of crosslinking of a polymer can be estimated by the mass percentage of its gel fraction.

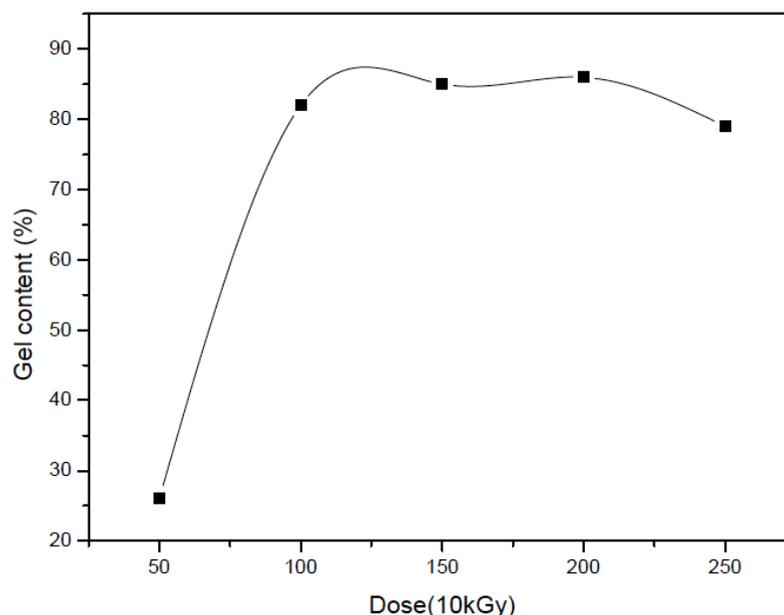


Figure 1: The effect absorbed dose on the gel fraction of POE.

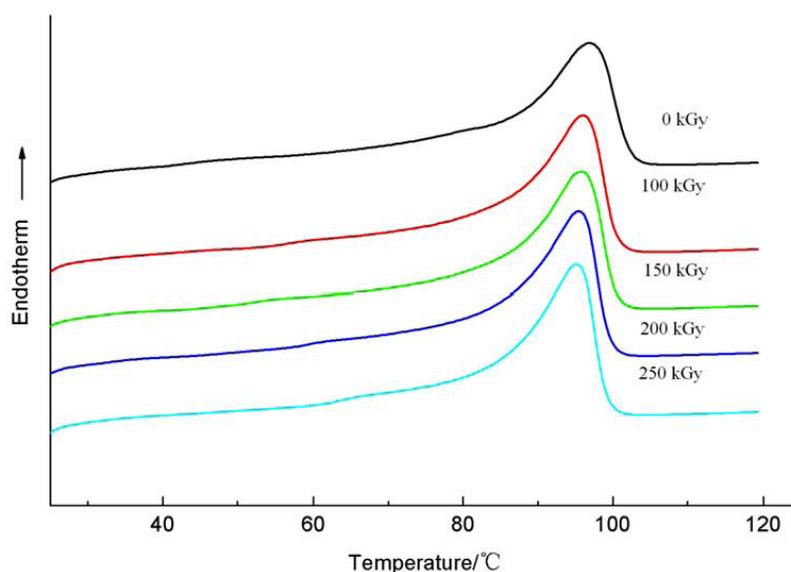


Figure 2: The DSC of POE before irradiation and after irradiation first heated at 20 °C/min.

Figure 1 shows the gel fraction of different systems at different absorbed dose under N_2 atmosphere. It is found that the gel fraction of copolymers increases markedly with the increase of dose below 100 kGy, which is due to increased crosslinking. With increasing absorbed dose, the generation of radicals is expected to increase and lead to more crosslinking. The gel fraction of POE samples irradiated at 200 kGy is higher than that of POE samples irradiated at 250 kGy, due to the degradation of polymer at higher dose. Moreover, the value of gel fraction of POE irradiated at 200 kGy is slightly higher than that of POE irradiated at 150 kGy. This is probably due to the mechanisms of degradation and crosslinking of POE.

From the basic radiation chemistry point of view, the quantitative determination of participation of crosslinking vs. degradation of chosen polymer is important. These acts relate to the partition of deposited ionizing energy between single- and multi-ionization spurs [15]. The crystallization curves of the irradiated POE samples and virgin POE samples were obtained by using DSC.

The DSC of heating and cooling curves illustrating the crystallization behavior of the irradiated POE samples and virgin POE samples are shown in Figures 2 and 3, respectively. Analyzing results are shown in Table 1.

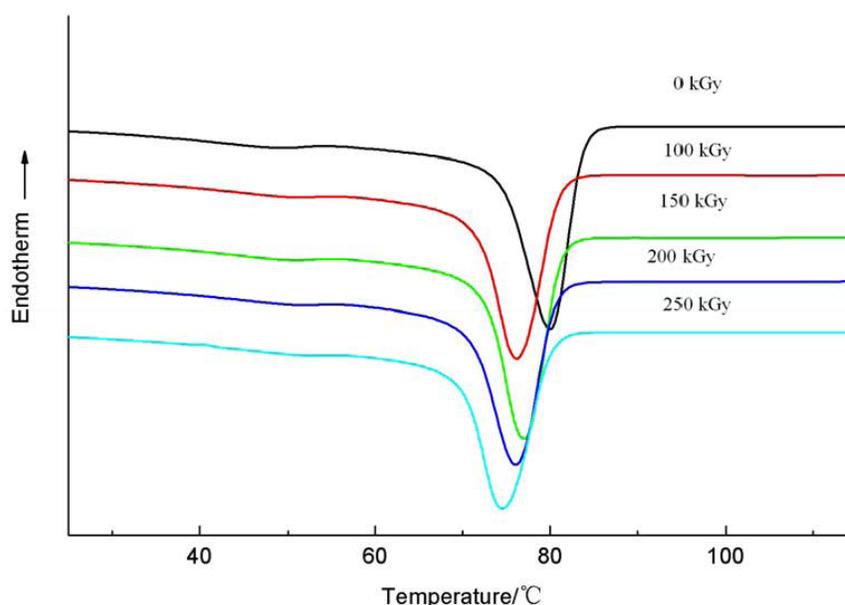


Figure 3: The DSC of POE before irradiation and after irradiation cooled at 20 °C/min.

Table 1: DSC Analysis of Copolymers

Dose (kGy)	T _m (°C)	T _c (°C)
0	96.83	79.887
100	96.50	76.20
150	96.15	77.21
200	95.50	76.21
250	95.15	74.54

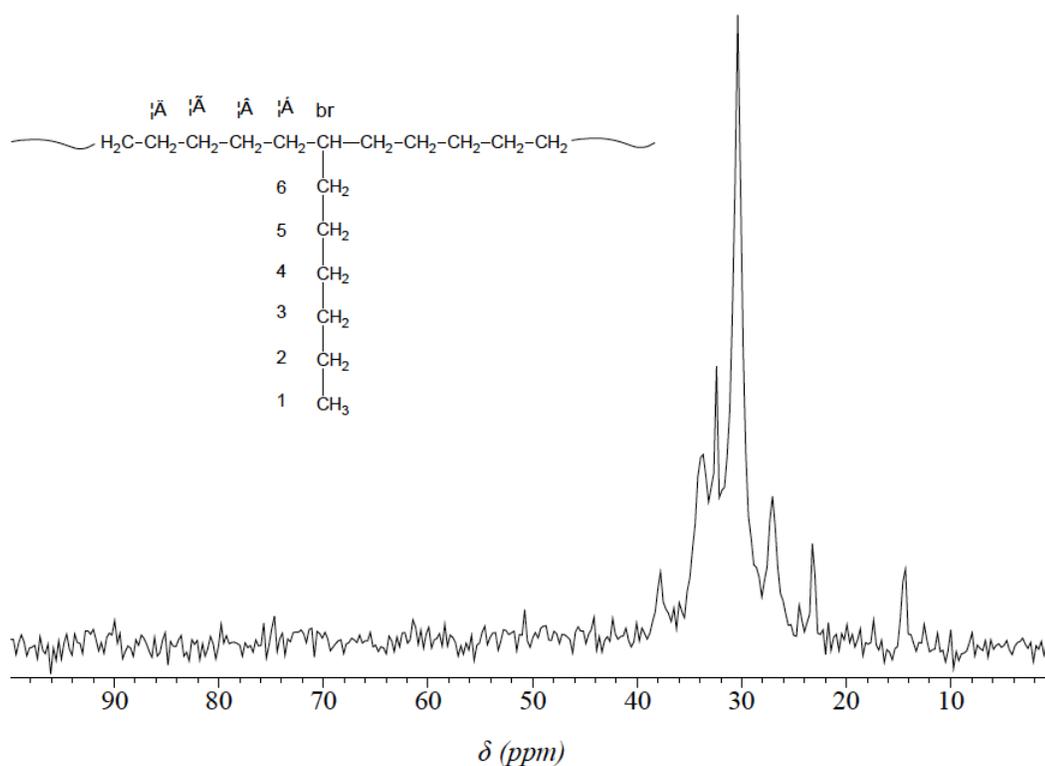
For POE samples, the T_m and T_c decrease slightly after irradiation. This is probably related to the crystalline state of copolymers. The results indicate that

the crystalline state of irradiated POE become imperfect with radiation dose.

3.2. Chemical Shift Assignments

The solid state ^{13}C NMR spectrums of unirradiated POE are shown in Figure 4, the main spectral assignments of the sample are carried out on the basis of published results obtained for polymer in solution [16] and calculated value obtained from Grant and Paul Empirical Rules [12].

All chemical shifts together with corresponding chemical structure are gathered in Table 2. There are seven major peaks and the major ones are identical to the solution-state spectrum of POE.

**Figure 4:** The solid state ^{13}C NMR spectrum of unirradiated POE.**Table 2: Chemical Shifts Assignments for Unirradiated POE**

Chemical shift (ppm)	Calculate value(ppm)	Assignment
37.6	35.7	CH, Branch chain C
33.6	35.0	C ₆ , α-C
32.3	32.3	C ₃
30.2	30.2, 30.6	Isolated CH ₂ , γ, δ-C, C ₄
26.9	28.0	C ₅ , β-C
23.0	22.8	C ₂ (-CH ₂ CH ₃)
14.3	13.7	CH ₃ chain end

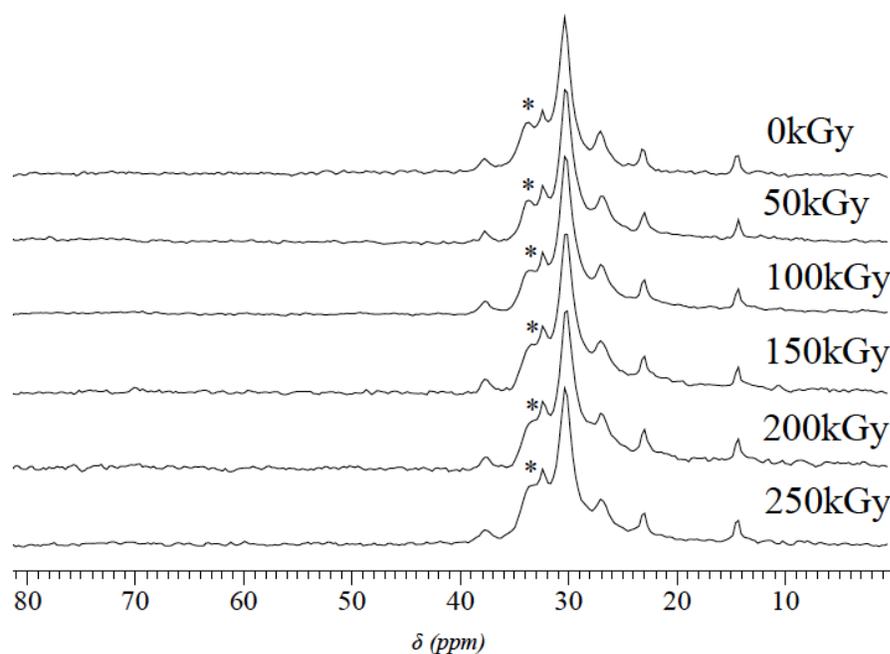


Figure 5: Solid-state ^{13}C NMR spectra of POE following irradiation to a series of doses in air at room temperature, line broadening $\text{LB}=30$.

3.3. Peak Evolution as A Function of Radiation Dose

Figure 5 shows the spectra obtained from POE samples. There is no evident change in the chemical shifts comprising with the unirradiated POE. An obviously evolution is that the peak area of 33.6 ppm decreases as a function of the increase of radiation dose, and at the same time, the peak shape broadens gradually. This indicates that the chain scission occurred between $\alpha\text{-C}$ and branch chain C (methine) or between C1 (the sidegroup hexyl) and branch chain C (methane) after radiation. The chain scission is severer with the increase of absorbed dose. It can be explained in terms of the chemical structure of POE and Charlesby-Pinner basic assumptions about radiation of polymer [17]. According to the assumptions, it is considered that the reactions of crosslinking and scission are independent of each other, radiation scission of POE occurs at random and the degree of crosslinking and fracture are proportional to the radiation dose. On the other hand, based on the chemical structure, the bond between methine and methene is prone to break down under high energy gamma radiation, which will produce the steady 3° carbon free radical and promote the chain scission. As a result, the content of $\alpha\text{-C}$ or C1 decreases with the increase of absorbed dose.

Irradiated POE is a semi-crosslinking polymer. Usually, crosslinking and scission signals ordinary

show different chemical shifts. Then, secession may also influence total line shape and width. The solid-state ^{13}C NMR spectra of irradiated POE and corresponding gel are shown in Figure 6. After radiation, there will both form non-soluble crosslinking net structure and fracture polymer fragments. And after extraction, crosslinking net structure will be only left. Comparing the spectra of irradiated POE with corresponding gel, it can be found that the area under the 33.6 ppm peak of the gel extract shows a significant decrease after extraction whether under 100kGy or 250kGy. It indicated that the chain scission between branch chain C and C1 took place, and on the basis of Charlesby-Pinner basic assumptions the chain scission between branch chain C and $\alpha\text{-C}$ also occurred numerously. From Figures 6b and 6d, the peak of 33.6 ppm becomes flat at dose of 100kGy, but becomes small peak at dose of 250kGy. It may be concerned with the radio-degradation of POE.

In addition, comparing Figures 6a with 6b or Figures 6c with 6d, the peak intensity at 32.3 ppm enhance relatively to the methyl peak, it may be explained with the formation of new crosslinking structure.

3.4. Line Width

Figure 7 shows the variation of linewidth versus the absorbed doses for each of the measured resonances. When polyolefin is subject to radiation leading to crosslinking, the mobility of main chain will become

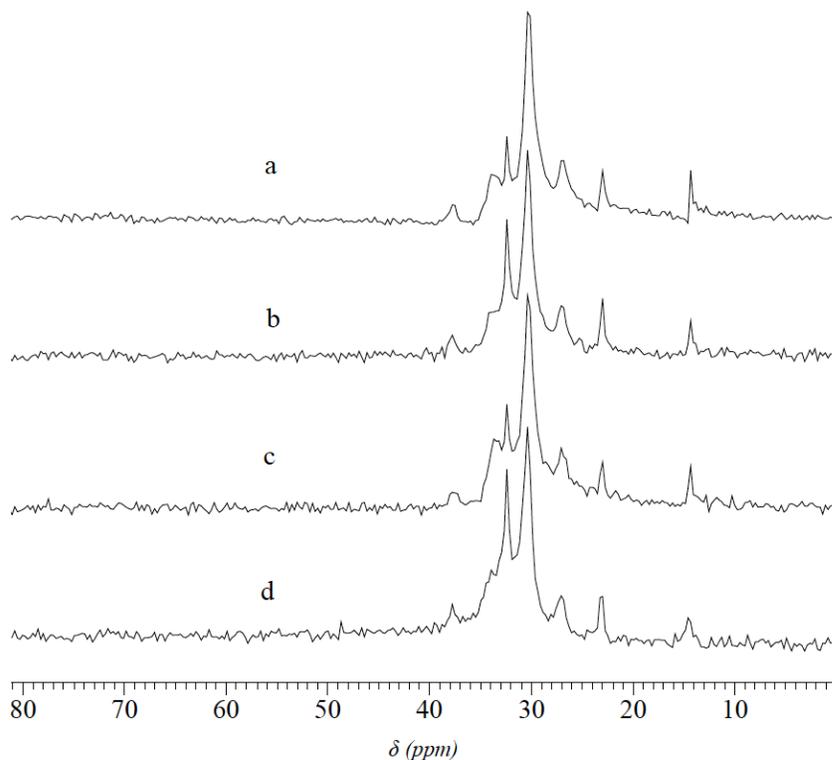


Figure 6: Solid-state ^{13}C NMR spectra of irradiated POE and the extracted gel under corresponding absorbed dose. **a**, irradiated POE, 100kGy; **b**, extracted gel, 100kGy; **c**, irradiated POE, 250kGy; **d**, extracted gel, 250kGy.

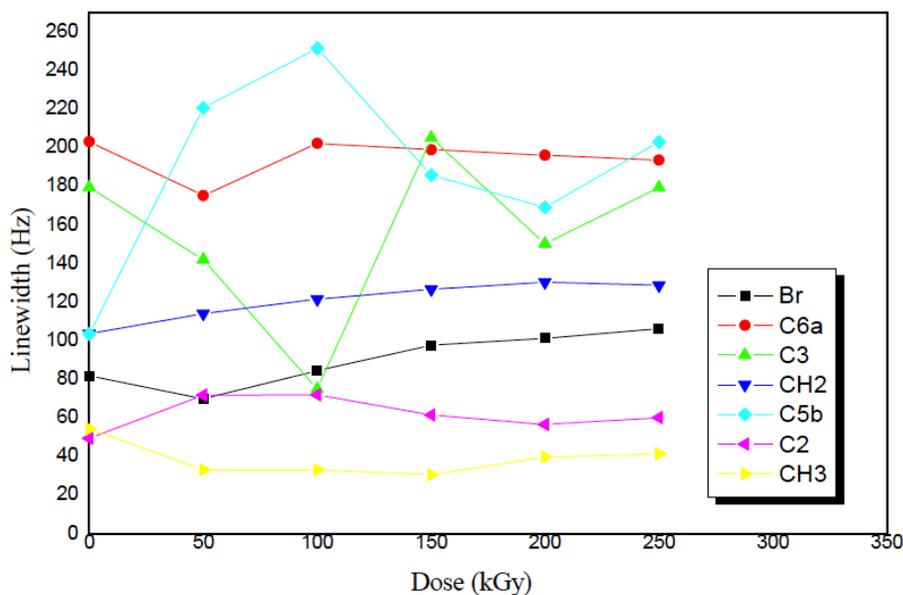


Figure 7: The variety of linewidth versus the absorbed doses.

hard. The ^{13}C linewidth is well suitable for evaluating segmental motions above T_g . The ^{13}C line shows a maximum broadening. The broadening width is typically \sim kHz order. This broadening is oftentimes utilized for judge of mobility. Usually, polymer shows extremely narrowing of 10-100 Hz at much higher temperature than T_g . These values are due to mainly

inherent structural disorders in the solid state, and magnetic field fluctuation. It can be found that the mobility of groups before radiation is that methyl \sim C2> methine $>$ isolated CH_2 , γ , δ -C, C4=C5, β -C>C3> C6, α -C. It reflects the information of structure of POE basically. After radiation the linewidth of methine and isolated CH_2 , γ , δ -C, C4 increases smoothly with

radiation dose. In this work, furthermore, chain, scission, new cross linking, and crystalline components also contribute to the line widths. In these complicated situations, it is difficult to judge mobility gradient of polymers from ^{13}C line widths. The information of chain, scission, new cross linking, and crystalline components is reflected by the linewidth.

We guess this increase corresponds to the formation of cross-linking structure, which limits the relaxation of polymer chains. The linewidth of methyl decreases first and then increases, this maybe explained with the chain scission at first and then the crystallinity of polymer fragments increases with the increase of polymer degradation. The linewidth of C6, $\alpha\text{-C}$ decreases first and then kept invariant, which maybe explained with the chain scission. In addition, the linewidth of C5, $\beta\text{-C}$ and C3 have a fluctuation, it may be explained with steady 3° carbon free radical couple with the free radicals and the new produced junction impeding the motion of C5, $\beta\text{-C}$, but the linewidth of C3 may be due to the sidegroup chain scission.

4. CONCLUSION

By researching the solid state ^{13}C NMR spectra of irradiated POE under a series of absorbed doses, an obviously chain scission was found in the $\alpha\text{-C}$ and C1. And the ^{13}C NMR spectra of the corresponding gels confirm the result. These results prove that the solid state ^{13}C NMR is useful discerning to some extent the differences in the molecular mobility of the crosslink polymer and exploring the microstructure of polymeric materials and the relationship between microstructure and macro-characteristics of polymers. This will be helpful to study future the reaction mechanisms under the gamma radiation. In addition, investigating the linewidths of irradiated POE under different doses, the information of chain, scission, new cross linking, and crystalline components is reflected by the linewidth.

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REFERENCES

- [1] Bensason S, Nazarenko S, Chum S, Hiltner A, Baer E. Elastomeric blends of homogeneous ethylene-octene copolymers. *Polymer* 1997; 38: 3913-19. [http://dx.doi.org/10.1016/S0032-3861\(96\)00963-9](http://dx.doi.org/10.1016/S0032-3861(96)00963-9)
- [2] Roberto SB, Erin AM, Martinez-Pardo ME, Daniel LZ. Effect of gamma irradiation on ethylene-octene copolymers produced by constrained geometry catalyst. *Nucl Instrum Methods Phys Res Sect B* 1991; 151: 174-80. [http://dx.doi.org/10.1016/S0168-583X\(99\)00143-3](http://dx.doi.org/10.1016/S0168-583X(99)00143-3)
- [3] Hill DJT, Preston CML, Whittaker AK. NMR study of the gamma radiolysis of poly(dimethyl siloxane) under vacuum at 303K. *Polymer* 2002; 43: 1051-59. [http://dx.doi.org/10.1016/S0032-3861\(01\)00711-X](http://dx.doi.org/10.1016/S0032-3861(01)00711-X)
- [4] Adolphe C. XIth international meeting on radiation processing Avignon 25-30 March 2001 (Polymer irradiation: past-present and future). *Radiat Phys Chem* 2002; 63: 207-209. [http://dx.doi.org/10.1016/S0969-806X\(01\)00621-1](http://dx.doi.org/10.1016/S0969-806X(01)00621-1)
- [5] Reinholds I, Kalkis V, Zicans J, Meri RM, Bockovs I, Grigalovica A, Muizemnieks G. Mechanical and thermomechanical properties of radiation modified poly(ethylene-octene)/Ni-Zn ferrite nanocomposites. *IOP Conference Series: Materials Science and Engineering*. IOP Publishing 2013; 49(1): 012048. <http://dx.doi.org/10.1088/1757-899X/49/1/012048>
- [6] Hui S, Mushtaq S, Chaki TK, Chattopadhyay S. Effect of Controlled Electron Beam Irradiation on the Rheological Properties of Nanosilica-Filled LDPE-EVA Based Thermoplastic Elastomer. *J Appl Polym Sci* 2011; 119: 2153-66. <http://dx.doi.org/10.1002/app.32941>
- [7] Poongavalappil S, Svoboda P, Theravalappil R, Svobodova D, Danek M, Zatloukal M. Study on the influence of electron beam irradiation on the thermal, mechanical and rheological properties of ethylene-octene copolymer with high comonomer content. *J Appl Polym Sci* 2013; 128: 3026-33. <http://dx.doi.org/10.1002/app.38479>
- [8] Li JQ, Peng J, Qiao JL, Jin DB, Wei GS. Effect of gamma irradiation on ethylene-octene copolymers. *Radiat Phys Chem* 2002; 63: 501-504. [http://dx.doi.org/10.1016/S0969-806X\(01\)00633-8](http://dx.doi.org/10.1016/S0969-806X(01)00633-8)
- [9] Singla S, Beckham HW. Miscible Blends of Cyclic Poly(oxyethylene) in Linear Polystyrene. *Macromolecules* 2008; 41: 9784-92. <http://dx.doi.org/10.1021/ma800327c>
- [10] Roger AA, Mathew C, Kenneth TG, Roger L. Clough, Todd MA. Morphology changes during radiation-thermal degradation of polyethylene and an EPDM copolymer by ^{13}C NMR spectroscopy. *Polym Degrad Stab* 2001; 73: 355-62. [http://dx.doi.org/10.1016/S0141-3910\(01\)00097-0](http://dx.doi.org/10.1016/S0141-3910(01)00097-0)
- [11] Palmas P, Colsenet R, Lemarie L, Sebban M. Ageing of EPDM elastomers exposed to γ -radiation studied by ^1H broadband and ^{13}C high-resolution solid-state NMR. *Polymer* 2003; 44: 4889-97. [http://dx.doi.org/10.1016/S0032-3861\(03\)00476-2](http://dx.doi.org/10.1016/S0032-3861(03)00476-2)
- [12] David MG, Edward GP. Carbon-13 Magnetic Resonance II Chemical Shift Data for Alkanes. *J Am Chem Soc* 1964; 86: 2984-90. <http://dx.doi.org/10.1021/ja01069a004>
- [13] Perera MCS, Rowen CC. Radiation degradation of MG rubber studied by dynamic mechanical analysis and solid state NMR. *Polymer* 2000; 41: 323-34. [http://dx.doi.org/10.1016/S0032-3861\(99\)00087-7](http://dx.doi.org/10.1016/S0032-3861(99)00087-7)
- [14] Masaru M, Bin YZ, Xu CY, Ma L, Takahiko N, Takenori S. Relaxation mechanism in several kinds of polyethylene estimated by dynamic mechanical measurements, positron annihilation, X-ray and ^{13}C solid-state NMR. *Polymer* 2003; 44: 4325-40. [http://dx.doi.org/10.1016/S0032-3861\(03\)00352-5](http://dx.doi.org/10.1016/S0032-3861(03)00352-5)
- [15] Bik J, Gluszewski W, Rzymiski WM, Zagorski ZP. EB radiation crosslinking of elastomers. *Radiat Phys Chem* 2003; 67: 421-23. [http://dx.doi.org/10.1016/S0969-806X\(03\)00078-1](http://dx.doi.org/10.1016/S0969-806X(03)00078-1)

[16] Pooter MD, Smith PB, Dohrer KK, *et al.* Determination of the composition of common linear low density polyethylene copolymers by ¹³C-NMR spectroscopy. *J Appl Polym Sci* 1991; 42: 399-408.
<http://dx.doi.org/10.1002/app.1991.070420212>

[17] Charlesby A, Pinner SH. Analysis of the Solubility Behaviour of Irradiated Polyethylene and Other Polymers. *Proc Roy Soc* 1959; 249: 367-72.
<http://dx.doi.org/10.1098/rspa.1959.0030>

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