

Processability and Structure of Dynamically Modified Linear Low-density Polyethylene with Different Branching Contents Using a High Peroxide Content

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Electronic Supplementary Information

Abstract Dynamic melt modification of polyethylene *via* the direct grafting of peroxide fragments shows promise for the development of processable functionalized materials. In this study, four linear low-density polyethylenes (LLDPEs) with comparable molecular weights but different short-chain branch (SCB) contents (ranging of 5–66 per 1000 carbon atoms) were modified *via* dynamic melt mixing using 2 wt% benzoyl peroxide at 145 °C and 50 r/min for 30 min. The influence of SCB content on the processability and structure of the resulting products was systematically investigated. All modified products exhibited good melt processability with melt flow rates (MFR) ranging from 0.46 g/10min to 1.07 g/10min. Products derived from low-SCB LLDPEs showed a lower MFR, higher cross-linking content, a larger number of long-chain branches, and a higher degree of benzoyl grafting. In contrast, those produced from high-SCB LLDPEs exhibited improved processability, reduced cross-linking, fewer long-chain branches, and lower benzoyl grafting levels. A detailed structural investigation of the soluble and insoluble fractions, which were separated using trichlorobenzene fractionation, was conducted to analyze the structural features of various modified products and demonstrate that the SCB content (*i.e.*, tertiary carbon density) significantly influences radical coupling during dynamic modification. Elevated tertiary carbon density, by introducing greater steric hindrance, suppresses radical coupling during dynamic modification, thereby reducing the efficiency of both crosslinking and peroxide fragment grafting. These findings provide new insights into the structure-reactivity relationships in peroxide-induced polyethylene modification and lay the foundation for tailoring material properties *via* dynamic processing.

Keywords Polyethylene; Peroxide; Short-chain branching; Dynamical modification; Processability

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INTRODUCTION

Polyethylene (PE) is one of the most cost-effective and widely used thermoplastic polymers owing to its excellent processability, chemical stability, electrical insulation, and mechanical properties.^[1–3] However, its fully saturated and non-polar molecular structure leads to inherently low surface energy and poor functionalization potential. This significantly limits their application in areas requiring surface adhesion, coating compatibility, or high-performance interfaces.^[4–6] Although the copolymerization of ethylene with polar monomers can impart polarity and introduce functionality, this approach is often constrained by complex synthesis and high cost.^[7,8] As a practical alternative, post-polymerization modification techniques offer a more viable route to functionalize PE, providing compatibility with ex-

isting PE resins while maintaining favorable bulk properties. Among these, peroxide-initiated grafting of polar monomers (*e.g.*, maleic anhydride, acrylic acid, glycidyl methacrylate) is widely used because of its operational simplicity, efficiency, and scalability.^[9–13]

In addition to serving as initiators for grafting polar functional monomers onto the PE chain, peroxides can act as functionalizing agents by directly grafting onto PE chains through free-radical mechanisms. The peroxide-mediated modification of PE involves a series of complex radical reactions. Upon thermal decomposition, peroxides generate reactive primary free radicals, which abstract hydrogen atoms from PE chains to form macromolecular radicals (PE·). These macroradicals can undergo coupling reactions, leading to crosslinking or, in some cases, the direct grafting of peroxide-derived fragments onto the polymer backbone.^[14–16] The coupling of PE· with primary radicals bearing polar or functional groups enables the chemical modification of PE using peroxides alone without additional functional

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monomers.^[15,16] However, at higher peroxide concentrations, the direct grafting reaction typically occurs with low probability, and undesirable crosslinking often dominates, impairing melt processability. To address this, Maillard *et al.*^[17–20] investigated the influence of the peroxide structure on the grafting efficiency. They found that alkyl peroxides (e.g., dicumyl peroxide (DCP) and di-*tert*-butyl peroxide) predominantly promoted crosslinking with limited grafting, whereas peroxyesters and peroxyketals favored grafting with reduced crosslinking. Based on these insights, they designed and synthesized specific asymmetric peroxides that decomposed into two distinct primary radicals: one prone to hydrogen abstraction (generating PE $\cdot$) and the other favoring grafting onto PE. These tailored peroxides enhanced direct grafting while suppressing crosslinking.^[17–19] However, such custom peroxides often require complex synthesis, and efficient grafting usually requires organic solvent systems, which limits their compatibility with established polymer-processing technologies and hinders their practical application.

In an earlier study, Masikni *et al.*^[21] reported the modification of an ethylene-octene copolymer with the commonly used DCP via dynamic melt mixing. In contrast to static conditions, which typically yield cross-linked and non-processable products, materials obtained by the “dynamical modification” retained significant processability. The authors proposed that the shear-induced formation of hyperbranched structures, rather than a permanent crosslinked network, accounted for this behavior. This study suggests that dynamic processing with peroxides can yield modified PE with retained processability. Inspired by this work, we recently employed dynamic melt mixing with 2.0 wt% benzoyl peroxide (BPO) to prepare low-density polyethylene (LDPE) materials exhibiting both good fluorescence and processability.^[22] Based on the proposed mechanism, the applied shear disrupts the initially formed crosslinked network, leading to a fragmented and processable structure, whereas BPO-derived fragments grafted onto LDPE chains impart fluorescence. These results demonstrated the potential of combining common peroxides with dynamic processing for PE modification. Nevertheless, the key factors determining the properties and structure of the resulting materials, such as the influence of the molecular architecture of PE, are far from being understood. Elucidating these factors is essential for developing a reliable and dynamically modified technique to produce high-performance PE with tailored functionality and processability.

During the radical reaction process of peroxides directly modifying PE, the competition between grafting and crosslinking reactions is closely related not only to the characteristics of the peroxide^[17–20] but also to the structure of the PE matrix resin^[23,24]. Our recent work found that LDPE could be

directly functionalized by peroxide.^[22] While the architecture of LDPE is complex, comprising both long and short branches, it is not an ideal candidate for clarifying structural variation. In contrast, linear low-density polyethylene (LLDPE) possesses a simpler linear chain topology with only short-chain branches (SCB),^[25–27] offering an ideal model system for systematically investigating the influence of branching on flow behavior and structural evolution. In this study, four LLDPEs with comparable molecular weights but different SCB content (5–66/1000C) were dynamically modified using 2 wt% BPO under identical dynamic melt mixing conditions, and the effect of the SCB content on the processability and structure of the resulting product was investigated. Our results revealed that the introduction of SCB increased the density of tertiary carbons that can participate in radical reactions, thereby inhibiting the formation of the crosslinking network and weakening the grafting efficiency. Within the range of SCB contents studied, higher branching led to markedly reduced crosslinking, improved melt flow, and lower grafting rate. Rheological characterization, combined with solvent fractionation, further revealed that these differences were primarily attributable to the SCB content. These findings deepen the understanding of structure-reactivity relationships in peroxide-mediated dynamic modification of PE and contribute to the development of advanced techniques to produce processable functionalized PE with tailored performance.

EXPERIMENTAL

Materials

The raw LLDPE materials used in this study are listed in Table 1. Benzoyl peroxide (BPO, 98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Solvent, 1,2,4-trichlorobenzene (TCB, 98%) was purchased from Honeywell B&J Specialty Chemicals Co., Ltd. (Charlotte, USA). Antioxidant, 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%), was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used as received without further purification.

For the convenience of later discussion, the LLDPE samples were named as “LLx”, where “x” represents the number of SCB as listed in Table 1. For example, the commercial LLDPE resin 2038.68G with an SCB of 5 was labeled LL5.

Sample Preparation

The dynamically modified samples were prepared by reactive melt mixing of LLDPE with BPO using a Haake PolyLab OS torque rheometer (Thermo Fisher, USA) equipped with roller rotors. The preparation process was as follows: 50 g of LLDPE and 1 g of

Table 1 The information of the raw LLDPE.

Sample code	Product grade	Manufacturer	M_w^a (kg/mol)	M_n^a (kg/mol)	PDI ^a	SCB ^b	MFR ^c (g/10min)
LL5	2038.68G	Dow Chem.	90	15	6.0	5.0	1.0
LL18	LL0209AA	Dushanzi Petrochem. Co.	89	13	6.8	18.0	1.0
LL45	DFDA7042	Lanzhou Petrochem. Co.	87	13	6.7	45.0	1.2
LL66	DFDA9047	Lanzhou Petrochem. Co.	93	15	6.2	66.0	1.2

^a determined using high-temperature gel permeation chromatography (HT-GPC) (Fig. S1 in the electronic supplementary information, ESI), ^b CH₃/1000C determined by ¹³C-NMR (Fig. S2 in ESI), ^c determined according to GB/T 3682.1-2018 at 190 °C under a load of 2.16 kg.

BPO (2 wt%) were added to a mixing chamber preheated at 145 °C, followed by mixing at 50 r/min for 30 min. The resulting modified products were denoted as mLLx. For instance, the modified product derived from LLDPE grade 2038.68G with an SCB of 5 was labeled mLL5. All samples in the LLx and mLLx series were compression-molded into sheets of the desired thickness using a compression molding machine (Gotech, China) at 160 °C under a pressure of 20 MPa for 5 min.

Solvent fractionation was used to separate the bulk products into soluble and insoluble fractions. The insoluble fractions were obtained by placing the compression-molded films in a 1000-mesh stainless steel mesh and immersing them in a 160 °C TCB solution (containing the antioxidant 0.05 wt% BHT) for 3 h. The insoluble part was dried and used for rheological and gel swelling experiments. The soluble fraction was the portion remaining in the extraction solution, which was concentrated and characterized using HT-GPC.

Characterizations and Measurements

The melt mass flow rate (MFR) of all the samples was measured using an SS-3600F melt indexer (Sartec, China) according to the GB/T 3682.1-2018 standard. The testing was conducted at 190 °C under a 2.16 kg load.

¹H-NMR and ¹³C-NMR spectra were acquired on an NMR spectrometer (AVANCE III HD 500, Bruker, Switzerland) at 130 °C. Approximately 30 mg of each sample was dissolved in 0.5 mL deuterated 1,1,2,2-tetrachloroethane. The group attributes were analyzed based on ¹H-NMR spectrum, and the branch architecture of the raw materials was determined based on ¹³C-NMR spectrum.

The fluorescence emission spectra were measured using an FLS-1000 fluorescence spectrometer (Edinburgh Instruments, UK) at room temperature. The excitation and emission slit widths were both set to 1 nm, with an excitation wavelength of 290 nm.

The rheological properties of the samples were measured using a strain-controlled rheometer ARES-G2 (TA Instruments, USA) equipped with 25 mm parallel plates by monitoring the storage modulus (*G'*), loss modulus (*G''*), and complex viscosity (*|η**). Small-amplitude oscillatory shear tests were conducted at 180 °C with 1% strain, covering a frequency range of 0.01–100 rad/s (measured from high to low frequency). The gap between parallel plates was adjusted to 1 mm. Large-amplitude oscillatory-shear (LAOS) tests were performed on the sample at 0.6283 rad·s^{−1}, with strain amplitudes ranging from 1% to 1000%.

The content of the insoluble fraction and the calculation of crosslinking density were as follows. The mass of the dried insoluble fraction (*M*₁) and the initial mass of the untreated sample (*M*₂) were used to calculate the content of the insoluble fraction as *M*₁/*M*₂. The crosslink density, that is, the *M*_w between crosslink points (*M*_{c,swell}), of the insoluble fractions was determined by solvent-swelling experiments in *p*-xylene at 138 °C for 2 h. The *M*_{c,swell} was determined by the follow Flory-Rehner equation Eq. (1)^[28] and Eqs. (2) and (3):

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = \rho_p V_0 M_c^{*-1} \left(\frac{1}{V_r^3} - \frac{V_r}{2} \right) \quad (1)$$

To correct for the loose chain end present in the material, *M*_c^{*−1} was replaced with the following expression:

$$M_c^{*-1} = M_{c,swell}^{-1} (1 - 2M_{c,swell} \bar{M}_n^{-1}) \quad (2)$$

V_r is the volume fraction of polymer in the swollen gel:

$$V_r = 1 / \left[\left(\frac{M_s \rho_p}{M_p \rho_s} \right) + 1 \right] \quad (3)$$

where *M_p* is the weight of the dry gel, *M_s* is the weight of solvent absorbed by the gel, *ρ_p*=0.806 g/cm³ that is the density of the polymer; *ρ_s*=0.761 g/cm³ that is the density of the solvent, *χ*=0.31 that is the polymer-solvent interaction parameter for PE in *p*-xylene; *V*₀=139.3 cm³/mol that is molar volume for *p*-xylene; and *M_n* is the number-average molar mass of the uncrosslink polymer.^[29]

The molecular weight (*M_w*) and molecular weight distribution (PDI) of the samples were measured at 160 °C using a 1260 Infinity II high-temperature gel permeation chromatography (HT-GPC) system (Agilent, USA) equipped with three PLgel 10-mm mixed-BLS columns. TCB containing 0.05 wt% BHT as an antioxidant was employed as the eluent at a flow rate of 1.0 mL·min^{−1}. The system was coupled with a differential refractive index (RI) detector and infrared (IR) detector (Thermo Nicolet iS50, Thermo Fisher, USA). The SCB and SCB distributions were determined using HT GPC/IR. The infrared signals corresponding to CH₃ and CH₂ in the samples were recorded as a function of the GPC elution volume. The soluble fraction was dissolved in TCB containing 0.05 wt% BHT for 3 h at 160 °C to prepare a solution with a concentration of approximately 1 mg/mL and then filtered through a metal membrane before testing.

RESULTS AND DISCUSSION

Samples Preparation

The modified samples were prepared by dynamic melt-mixing of LLDPE resin with 2 wt% BPO at 145 °C for 30 min. Based on the decomposition kinetic data of BPO reported in the literature,^[30] the half-life of BPO at 145 °C can be extrapolated calculated as approximately 24 s. These processing conditions promote rapid radical generation for effective grafting and ensure complete BPO decomposition within the reaction time. Typical torque and temperature curves versus time of the preparation process are shown in Fig. 1. As illustrated in Fig. 1(a) and the enlarged view in Fig. 1(b), from the onset of mixing, the torque of all the samples rose rapidly to a peak, corresponding to the feeding peak. Unlike conventional polymer melt processing, in which the torque decreases and then remains stable, a secondary torque increase is observed, followed by a gradual decline. According to Masikni *et al.*^[21] and our recent research^[22], this second torque rise is related to branching and cross-linking reactions initiated by peroxide decomposition, which increases the melt viscosity. The maximum torque indicates that the polymer melt has reached the peak degree of crosslinking, and a higher maximum torque value corresponds to a higher degree of crosslinking. The scorch time is defined as the time to reach the maximum torque, where a shorter time implies a faster cross-linking rate. The subsequent decline in torque corresponds to shear-induced mechanical fragmentation of the crosslinked network, eventually reaching a steady-state torque that remains constant until the end of processing. The end-torque value reflects the stabilized melt viscosity under

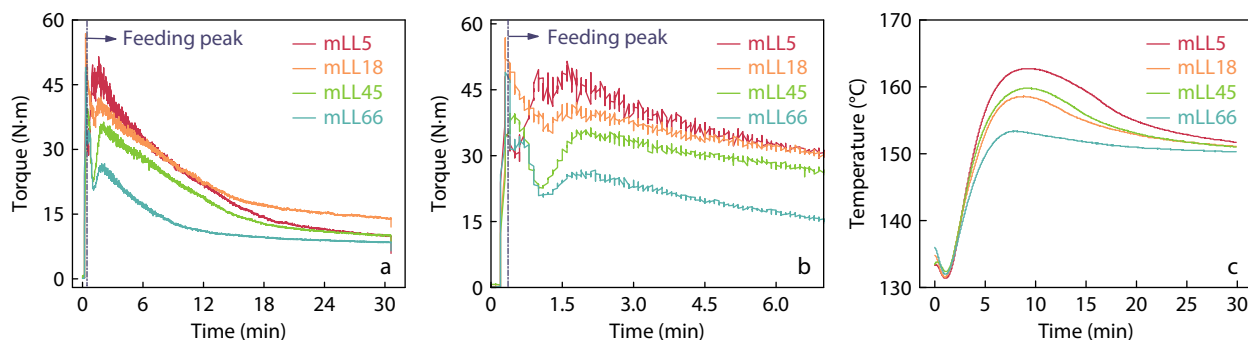


Fig. 1 (a) The mixing torque, (b) enlarged view in 0–7.5 min, and (c) mixing temperature for four samples.

dynamic shear, with a lower value indicating a greater processability of the final product. The average values of the maximum torque (excluding the feed peak), end-torque values, and scorch time (defined as the time to reach maximum torque) are listed in Table 2. Among all samples, mLL5 exhibited the highest maximum torque, highest end-torque, and shortest scorch time. As the SCB content increased, both the maximum and end torque values gradually decreased, while the scorch time increased. This behavior is consistent with prior findings under static conditions, which reported a decrease in crosslinking efficiency with increasing SCB.^[31] This trend suggests that a high SCB content reduces the extent of branching and cross-linking during the dynamic modification of LLDPE.

Table 2 The torque values and scorch time for different samples.

Sample	Max-torque value (N·m)	End-torque value (N·m)	Scorch time (min)
mLL5	51.9±0.3	13.2±0.2	1.6±0.1
mLL18	41.9±0.5	12.3±0.2	1.8±0.1
mLL45	35.9±0.4	9.5±0.3	2.0±0.2
mLL66	26.7±0.3	8.4±0.1	2.1±0.2

The temperature curves during processing are shown in Fig. 1(c). Starting from mixing, the temperature decreases owing to heat absorption for PE melting, then rises rapidly, and subsequently declines gradually. Among all the samples, mLL5 exhibited the fastest heating rate and highest melt temperature, which was attributed to increased viscous dissipation from its higher crosslink density. As the SCB content increased, the melt temperature decreases due to reduced internal friction caused by lower crosslinking. The combined torque and temperature profiles indicate that variations in the SCB content led to different extents of branching, crosslinking, and network fragmentation during dynamic mixing, ultimately producing products with distinct structural characteristics.

The Melt Processability and Structural Characteristics of Bulk Samples

The melt processability of the product was evaluated using melt flow rate (MFR). The MFR value is inversely proportional to the apparent shear viscosity of the melt, where a higher MFR indicates a lower apparent viscosity, and thus, better processability. The MFR values were listed in Table 3, with values of 0.46, 0.59, 0.81, and 1.07 g/10min for mLL5, mLL18, mLL45, and mLL66, respectively. With the addition of a high BPO content, the MFR of the product was measurable, suggesting that they still possessed a certain degree of melt processability. As shown in Fig. 2(A), the MFR of the modified sample gradually increases. This continuous increase indicates that a higher SCB content generally leads to improved MFR. Overall, these results demonstrate that the melt processability of the bulk products is strongly influenced by the SCB content.

Because melt processability is closely associated with molecular architecture, the structural characteristics of the modified products were further investigated. In a recent study,^[22] we found that the fluorescence exhibited by modified LDPE is related to the grafting of radicals generated by BPO decomposition. Here, we measured the fluorescence intensity of four modified LLDPEs products. As shown in Fig. 2(B), all four modified LLDPE samples exhibited relatively strong fluorescence, indicating that BPO fragment radicals were grafted onto the LLDPE chains. Furthermore, the fluorescence intensity decreased with increasing SCB content, from 7.20×10^6 a.u. for the low-SCB sample (mLL5) to 6.31×10^6 a.u. for mLL18, 5.68×10^6 a.u. for mLL45, and 3.84×10^6 a.u. for the high-SCB sample (mLL66). In this dynamic modification system, fluorescence arises from the spatial conjugation of grafted benzoyl groups, which is significantly influenced by complex local chemical environment factors. Therefore, although the fluorescence intensity cannot be used to quantify the absolute number of grafted groups, these results indicate that grafted benzoyl groups decreased in the higher-SCB LLDPE.

Table 3 The MFR, fluorescence properties and grafting densities of samples.

Sample code	MFR (g/10min)	Fluorescence intensities ($\times 10^6$ a.u.)	Grafting density on secondary carbon ^a (grafts/1000C)	Grafting density on tertiary carbon ^a (grafts/1000C)
mLL5	0.46±0.02	7.20±0.11	2.3	1.0
mLL18	0.59±0.02	6.31±0.09	2.0	1.2
mLL45	0.81±0.01	5.68±0.18	1.8	1.3
mLL66	1.07±0.07	3.84±0.16	1.6	1.3

^a Determined by ¹H-NMR (Fig. S3 in ESI).

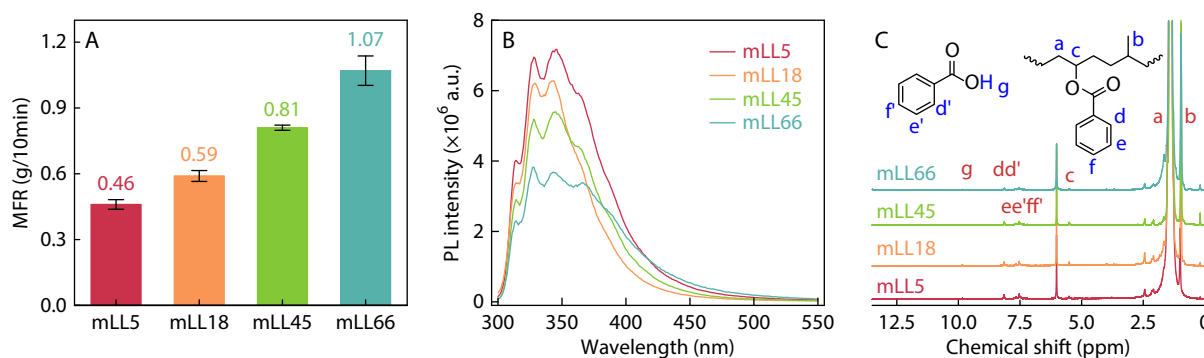


Fig. 2 (A) MFR, (B) fluorescence spectra and (C) $^1\text{H-NMR}$ spectra of the four samples.

$^1\text{H-NMR}$ spectroscopy is a powerful technique that enables the accurate quantification of grafted groups and even the identification of grafting sites. We further employed $^1\text{H-NMR}$ spectroscopy (Fig. 2C) to characterize BPO-derived fragments grafted onto the PE backbone. The numbers of grafted carbon atoms at different positions, as calculated from the spectra, are listed in Table 3. Grafts located on secondary carbons were quantified directly from proton resonance at 5.45 ppm, whereas the number of grafts on tertiary carbons was obtained by subtracting the secondary carbon grafts from the total graft count. For the low-SCB sample mLL5, the number of secondary carbon grafts was the highest (2.3/1000C), while the number of tertiary carbon grafts was the lowest (1.0/1000C). With increasing SCB content, secondary carbon grafting decreased, whereas tertiary carbon grafting increased slightly. Overall, the total graft count declined. For the high-SCB sample mLL66, the secondary carbon grafts dropped to 1.6/1000C, and the tertiary carbon grafts rose to 1.3/1000C. A comparison between the fluorescence intensity and grafting densities revealed a consistent decreasing trend with increasing SCB content across the modified product. Based on these results, it can be concluded that a higher SCB content leads to a lower grafting ratio, likely because the high concentration of SCB in LLDPE inhibits the grafting reaction.

After characterizing the grafting structure of the modified product, we investigated its bulk rheological behavior to assess how these molecular structural changes affected the structural characteristics. Small-amplitude oscillations enable probing of material responses across different time scales by varying the deformation frequency. The measured viscoelastic response reflected multiple relaxation processes within the experimental frequency window. In particular, the low-frequency region reveals microstructures undergoing slow relaxation, while it is profoundly influenced by a variety of molecular chain structures, such as molecular weight, distribution, branching, and crosslinking. The rheological properties of four raw LLDPE resins (LL5, LL18, LL45, and LL66) were examined. The storage modulus (G') and loss modulus (G'') of these resins were nearly identical across the measured frequency range, indicating a similar melt viscoelastic behavior prior to modification (Fig. S4 in ESI). Subsequently, the rheological responses of four modified products (mLL5, mLL18, mLL45, and mLL66) were compared. Fig. 3(a) displays the G' as a function of the angular frequency (ω). All modified samples exhibited substantially enhanced G' values relative to un-

modified resins, confirming the occurrence of peroxide-induced crosslinking and branching. However, the four modified LLDPEs exhibited distinct variations in the low-frequency region. mLL5 and mLL18 showed a significant increase in G' , suggesting the presence of structures with long-chain branching or gel networks. These structures introduce additional entanglements and restrict chain mobility, thereby impeding segmental relaxation and increasing G' . A slight exception is observed between mLL5 and mLL18, where the latter shows a higher G' in the low-frequency range, which may be attributed not only to long-chain branching or the gel networks, but also to other chain structural factors. In contrast, mLL45 and mLL66 exhibit typical end-relaxation behavior similar to that of linear polymers: the G' values decrease slightly, and the upturn in the low-frequency region becomes less pronounced. This trend indicates that lower-SCB LLDPEs are more prone to form long-chain branches or crosslinked structures under dynamic processing, whereas higher-SCB LLDPEs tend to yield more linear or weakly branched architectures with lower moduli. Similarly, G'' increases markedly compared with the raw materials (Fig. 3b), and within the tested frequency range, G'' decreased as the SCB content of the raw materials increased. The variation in the complex viscosity $|\eta^*|$ with shear frequency ω is shown in Fig. 3(c). All samples exhibited shear-thinning behavior, with the viscosity decreasing as the frequency increased. At high frequencies, the $|\eta^*|$ values converged for all samples, whereas in the low-frequency region, the low-SCB sample exhibited the highest viscosity. In higher-SCB LLDPE, the complex viscosity gradually declined, reflecting a reduced degree of network formation.

To further reveal the differences in the internal structure of the modified products, we drew the van Gurp–Palmen (vGP) plots. This diagram provides an intuitive view of the molecular structure, especially the long-branched structures. These plots depict the phase angle (δ) versus the magnitude of the complex modulus and are effective in revealing chain branching and topological differences. Branching structures shift the vGP curve toward lower δ values; a smaller δ and reduced area under the curve indicate greater chain branching.^[32] As shown in Fig. 3(d), sample mLL66 had the highest δ value, reflecting minimal branching, whereas mLL18 had the lowest δ value, indicating extensive chain branching. The vGP plots for mLL5 and mLL18 also exhibited clear inflection points, further confirming the existence of branched or network struc-

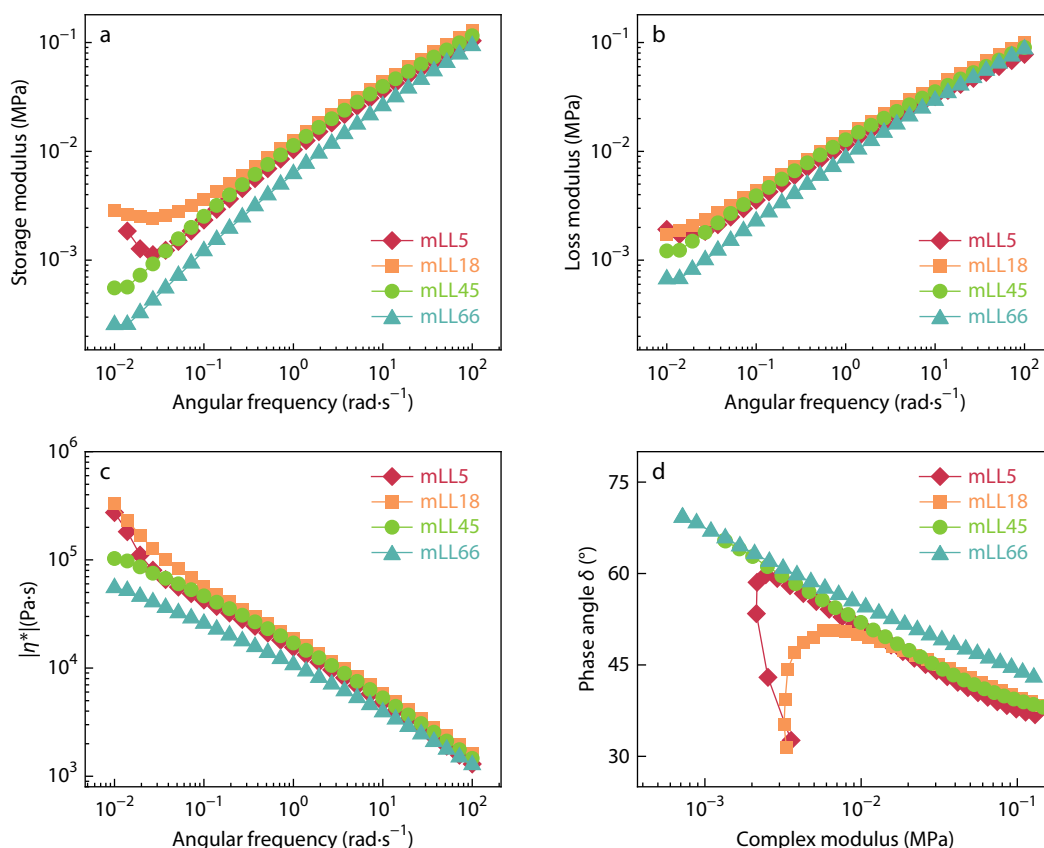


Fig. 3 Viscoelastic behavior at 180 °C of samples with different degrees of branching. Frequency dependence of (a) storage modulus (G'), (b) loss modulus (G'') and (c) complex viscosity ($|\eta^*|$). (d) The Van gurp-palmen diagram.

tures. In summary, rheological analyses confirm that dynamic melt modification introduces varying degrees of branching and crosslinking depending on the SCB content of the base LLDPE. LLDPEs with low SCB form more complex structures, resulting in higher modulus and viscosity, whereas those with high SCB exhibit lower crosslinking and branching degrees, leading to reduced viscoelastic responses.

Large-amplitude oscillatory shear measurements were employed to further characterize the molecular structure of the modified LLDPE, large-amplitude oscillatory shear (LAOS) measurements were employed. According to Wilhelm *et al.*,^[33,34] LAOS is sensitive to polymer architectural features, with prior studies highlighting its responsiveness to LCB variations. We evaluated the changes in the LCB before and after dynamic modification and defined an LCB factor, denoted as D_{LCB} , which was calculated using the following equation:

$$D_{LCB} = \frac{A_B}{A_L \cdot a} - 1 \quad (4)$$

where parameter A reflects the polymer's nonlinearity at infinite amplitude, which is independent of the molecular weight distribution but is influenced by the molecular weight and topology. The subscript B in parameter A indicates a branched sample, while L denotes a linear sample. Parameter a is a vertical shift factor that eliminates the influence of molecular weight and allows a direct comparison of the long-chain branching topology. (Details of the calculation procedures are provided in Fig. S5, and Table S1 in ESI). To simplify comparisons before and after

modification, the D_{LCB} value for the raw LLDPEs (LL5, LL18, LL45, and LL66), which is inherently a linear sample, was set to 0. The change in the LCB content upon modification, ΔD_{LCB} was used to evaluate the structural variation. As shown in Table 4, all modified samples exhibited positive ΔD_{LCB} values, confirming that the introduction of BPO led to an increase in LCB. From mLL5 to mLL66, ΔD_{LCB} values decreased sequentially to 0.91, 0.82, 0.44, and 0.28, respectively. This indicates that low-SCB LLDPEs generate more LCBs during dynamic modification, whereas higher-SCB LLDPE generate fewer LCBs. This is likely due to the greater susceptibility of high-SCB chains to scission under thermal and mechanical stresses during melt processing, which counteracts the formation of long-chain branched structures.

To further visualize these LCB variations, a polar coordinate plot of σ_3/σ_1 versus Φ_3 (phase angle) was employed, as shown in Fig. 4. In these plots, the size of the arc radius provides a direct visual measure of nonlinearity, where a larger radius signifies a greater number of LCB. All the modified mLLx sam-

Table 4 The rheological long-chain branching characterization of before and after modified PE.

Sample code	D_{LCB}	Sample code	D_{LCB}	ΔD_{LCB}
LL5	0	mLL5	0.91	0.91
LL18	0	mLL18	0.82	0.82
LL45	0	mLL45	0.44	0.44
LL66	0	mLL66	0.28	0.28

ples exhibited larger arc radii than their unmodified counterparts, corroborating the enhanced LCB formation observed in the LAOS analysis. Notably, the arc radius shows an inverse correlation with the SCB content of raw LLDPE: mLL5 exhibits the largest radius, whereas mLL66 displays the smallest radius. This trend confirms that a higher SCB content suppresses nonlinear viscoelasticity in the product. Intriguingly, despite uniform initiator concentrations and comparable macromolecular radical densities, the LCB differences imply that shear-mediated stress localization near BPO-derived branch/crosslink points preferentially degrades the LCB in high-SCB systems during processing. Given these pronounced rheological differences, especially in the LCB characteristics, a more detailed and fraction-specific structural analysis was conducted.

Rheological analyses indicated that the structural characteristics of the modified LLDPEs strongly depend on the SCB content of the base resin. A lower SCB content promotes the formation of long-chain branches and network structures, resulting in higher moduli and complex viscosities, whereas a higher SCB content leads to fewer branches and weaker networks, producing lower viscoelastic responses. These structural variations are directly related to melt processability, with

more branched networks corresponding to reduced flowability and less branched structures maintaining better melt processability.

Characterization Product by Solvent Fractionation

To perform a detailed structural analysis of the modified LLDPE samples, a solvent fractionation method inspired by the solution fractionation procedure used in HT-GPC testing was performed. In this approach, the fraction passing through the filter membrane was defined as the soluble fraction, while the portion retained by the membrane was defined as the insoluble fraction. To carry out the separation, a 1000-mesh stainless-steel mesh was chosen for solvent extraction, ensuring that the soluble portion obtained could be reliably compared with the molecular weight distribution measured by GPC. The solvent extraction was performed in TCB at 160 °C for 3 h, and the soluble fraction exhibited an M_w nearly identical to that measured directly by GPC, as shown in Fig. S6 (in ESI). This confirms that the separation method preserves the composition of the soluble phase and allows for complete characterization of all product fractions.

Insoluble fractions

The proportion of the insoluble fractions was determined by weighing the dried insoluble components obtained after sol-

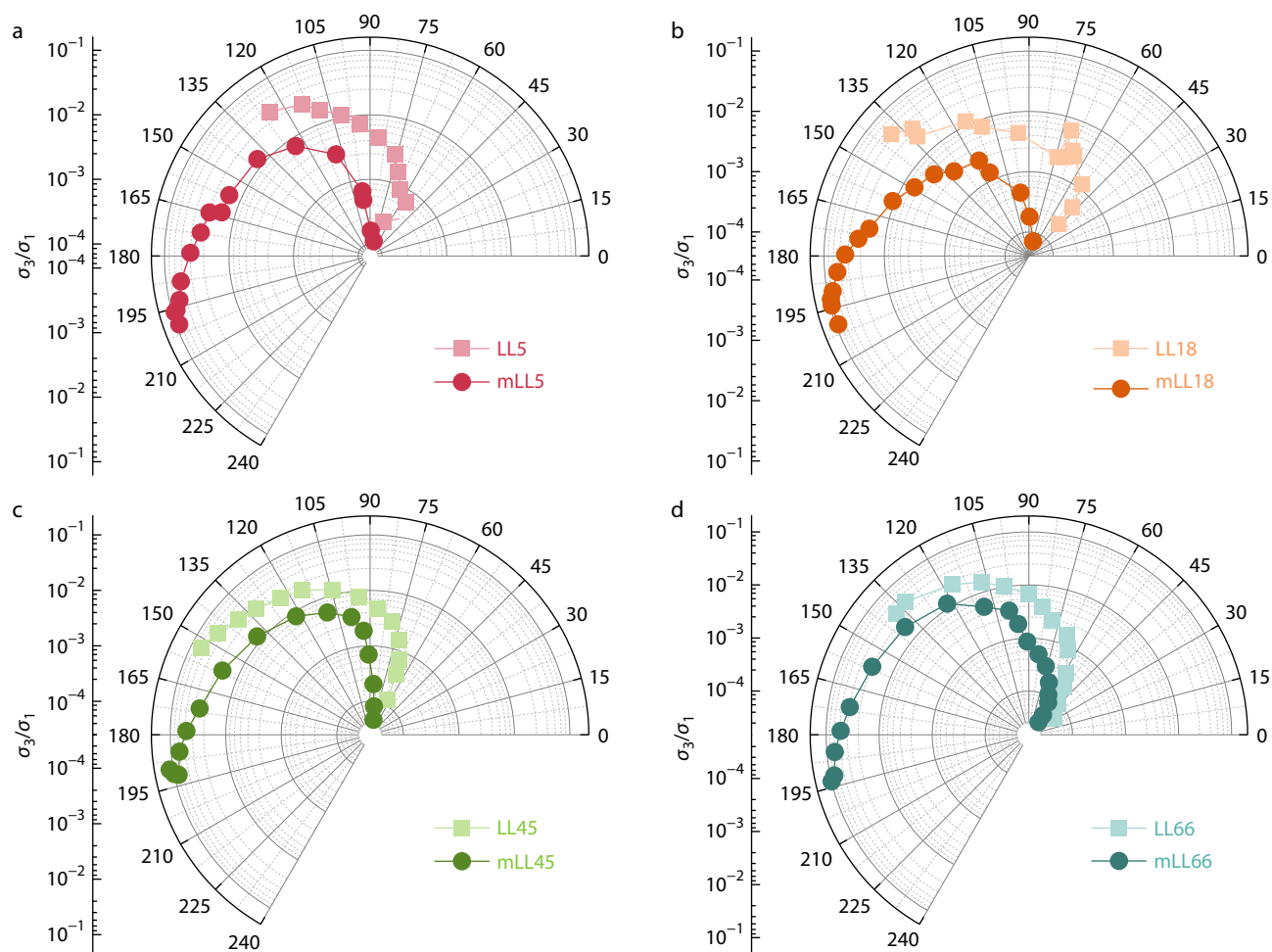


Fig. 4 The relative third stress intensity (σ_3/σ_1) as a function of the phase angle (Φ_3) for (a) LL5 and mLL5, (b) LL18 and mLL18, (c) LL45 and mLL45, and (d) LL66 and mLL66 samples.

vent fractionation. The insoluble content was $15.82\% \pm 2.04\%$ for mLL5 and $6.66\% \pm 1.10\%$ for mLL18, while the gel content dropped to $1.32\% \pm 0.41\%$ for mLL45 and became negligible for mLL66. This trend indicates that low-SCB LLDPE retains more crosslinked networks generated during dynamic modification, whereas higher-SCB samples are more prone to shear-induced fragmentation, which suppresses the formation and stability of such networks. To further characterize the structural properties of the insoluble components, their rheological behaviors and crosslink densities were investigated. The rheological behavior of the insoluble fractions is shown in Fig. 5 and the corresponding detailed data are listed in Table 5.

In the linear viscoelastic region ($\gamma < 1\%$), Fig. 5(a) shows that the low-SCB sample mLL5 exhibited the highest storage modulus (244 kPa), whereas the higher-SCB sample mLL66 showed the lowest (134 kPa), indicating denser and stronger networks in low-SCB systems. Fig. 5(b) reveals that the low-frequency storage modulus follows the order $mLL5 > mLL18 > mLL45 > mLL66$, reflecting greater elasticity in low-SCB networks. Fig. 5(c) shows that the $\tan\delta$ values for all insoluble components were below 1, indicating elasticity-dominated behavior; mLL66 consistently displayed the highest $\tan\delta$, while mLL5 showed the lowest, again suggesting that low-SCB networks are more elastic and structurally stable.

Gel swelling experiments enabled the calculation of the molecular weight between the cross-linking points ($M_{c,swell}$), as listed in Table 5. Moreover, the ratio of cross-linking and chain-breaking reactions (p/q) during the dynamic process can be calculated from the $M_{c,swell}$ between cross-linking points and the initial M_w . The M_c of mLL5, mLL18, mLL45 and mLL66 were 59.1, 61.5, 65.7 and 75.2 kg/mol, which corresponded to the cross-linking density (ν) of 21.6, 16.9, 13.7 to 11.8, respectively. This change in structural parameters was accompanied by a decrease in insoluble fraction from 15.8% (mLL5) to 0% (mLL66), demonstrating that the high-SCB LLDPE achieves a lower and looser network construction

through dynamic mixing. Meanwhile, the p/q ratio (the ratio of cross-linking to chain breaking) decreased gradually with the increase in SCB from 2.12 for mLL5 to 0.97 for mLL66, indicating that the relative importance of the chain-breaking reaction was gradually increased during melt processing. These changes can be attributed to the differences in SCB content affecting the crosslinking reaction. Low-SCB LLDPE, with a higher chain regularity, promotes dense network formation, resulting in a higher modulus and crosslink density. In contrast, high-SCB LLDPE shows lower regularity and greater steric hindrance, leading to reduced modulus and crosslink density. The p/q ratio decreased with increasing SCB content, indicating that the chain scission was influenced by the SCB level. As the SCB content increased, the proportion of long branches in the bulk product decreased, suggesting more shear-induced breakage of the loosely crosslinked networks.

In summary, the structural analysis of the insoluble fractions via rheology and gel swelling experiments indicated that high-SCB LLDPE formed looser and fewer networks with lower crosslink density, whereas low-SCB LLDPE developed denser and more elastic networks, exhibiting higher crosslink density during dynamic modification.

Soluble fractions

The soluble components were analyzed by high-temperature GPC to determine the M_w and M_w/M_n , and the SCB distribution was determined by GPC-IR. While GPC-IR provides a reliable semi-quantitative measure of SCB, its accuracy can be influenced by detector calibration and the assumption of a uniform detector response across different chain architectures. In Fig. 6, the horizontal axis represents the logarithmic value of the molecular weight ($\lg M_w$), left vertical axis represents the normalized weight distribution, and right vertical axis represents the SCB distribution. The specific M_w , M_w/M_n , and SCB data for all the samples are listed in Table 6. The original LLDPE samples (LL5, LL18, LL45, and LL66) exhibit similar M_w (about 90 kg/mol) and

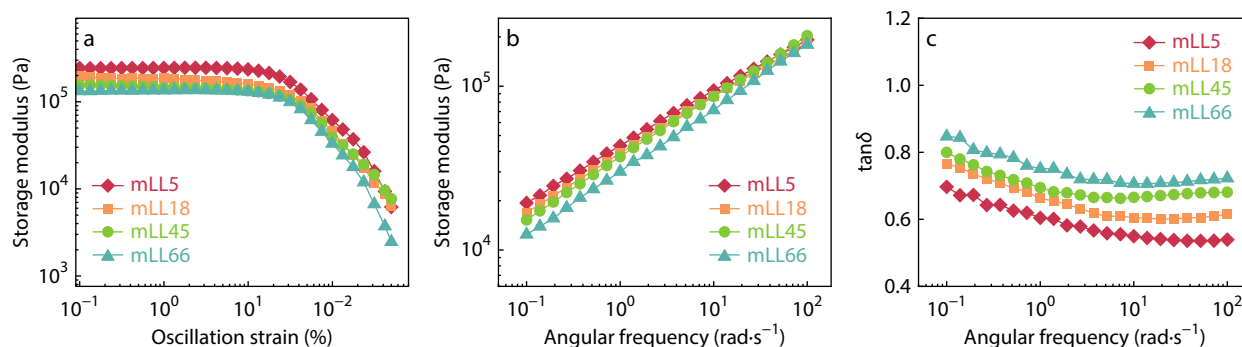


Fig. 5 Rheological behavior of insoluble components. Strain dependence of (a) storage modulus (G'). Frequency dependence of (b) storage modulus (G') and (c) $\tan\delta$.

Table 5 Molecular characterization of the insoluble fraction of the modified PE sample.

Sample code	Insoluble content ^a (%)	$G'_{plateau}$ (kPa)	$\bar{M}_{c,swell}$ ^b (kg/mol)	Crosslinking density (ν)	p/q
mLL5	15.82 ± 2.04	244	59.1	21.6	2.12
mLL18	6.66 ± 1.10	191	61.5	16.9	2.07
mLL45	1.32 ± 0.41	152	65.7	13.7	1.04
mLL66	0.08 ± 0.04	134	75.2	11.8	0.97

^a Determined by extraction; ^b Determined by swelling measurement.

M_w/M_n (about 6.0). After dynamic modification, the low-SCB samples (mLL5 and mLL18) showed significantly reduced M_w , an increased fraction of low- M_w species (10^2 – 10^4 g/mol), and broadened M_w/M_n . In contrast, the high-SCB samples (mLL45 and mLL66) displayed slightly increased M_w , with higher proportions of large molecular species (10^5 – 10^6 g/mol) and relatively smaller changes in M_w/M_n . The M_z/M_w ratio was used to assess the relative contents of the high- M_w fractions in the polymer. As shown in Table 6, the M_z/M_w of mLL5 and mLL18 decreased slightly compared to those of LL5 and LL18, whereas the M_z/M_w of mLL45 and mLL66 increased significantly. These results suggest that the soluble fraction of the high-SCB samples contained a greater proportion of high M_w species resulting from crosslinking/branching, while the soluble fraction of the low-SCB samples was enriched in lower M_w components resulting from network fragments.

The SCB distributions of the original and modified samples were also compared. As shown in the scatterplot in Fig. 6, the SCB in all LLx was primarily distributed within the M_w range of 10^3 – 10^6 . In Figs. 6(a) and 6(b), for low-SCB samples, such as

LL5 (SCB=5.4) and LL18 (SCB=17.4), dynamic modification resulted in slightly reduced SCB values (e.g., mLL5=4.3 and mLL18=16.3), particularly in the high- M_w region. This may be attributed to crosslinking reactions during dynamic mixing, where high-molecular-weight chains are more prone to crosslinking and form networks that are insoluble, thereby reducing their contribution to the average SCB in the soluble fraction. For the high-SCB samples (mLL45 and mLL66 in Figs. 6c and 6d), the high- M_w region of the soluble fraction exhibited SCB levels markedly exceeding those of the corresponding unmodified polymers. Higher SCB LLDPE provides more chain scission sites during BPO-initiated modification, leading to the formation of short-branched or lightly cross-linked structures. These structures may subsequently undergo chain scission, producing soluble fragments enriched with new SCB, thereby increasing SCB content in the high- M_w region of the soluble phase.

According to the molecular weight, distribution, and short branching results in soluble fractions, the structural changes during dynamic mixing are strongly influenced by the initial

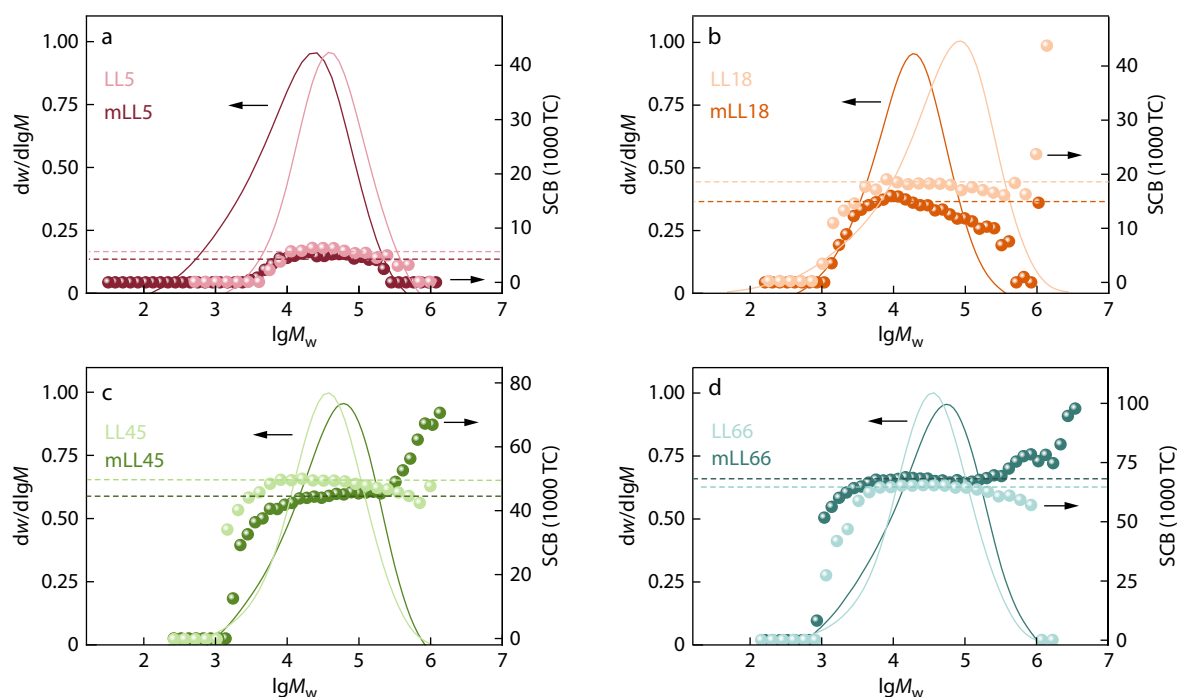


Fig. 6 Comparison of molecular weight distribution and SCB distribution of (a) LL5 and mLL5, (b) LL18 and mLL18, (c) LL45 and mLL45 and (d) LL66 and mLL66.

Table 6 Molecular characterization of the soluble fraction of the raw PE and modified PE.

Sample code	M_w^a (kg/mol)	M_n^a (kg/mol)	M_w/M_n^a	M_z/M_w^a	Average SCB ^b
LL5	90.0	15.0	6.0	4.4	5.4
mLL5	48.0	6.4	7.4	4.2	4.3
LL18	89.0	13.1	6.8	4.4	17.4
mLL18	35.0	6.2	5.7	4.1	16.3
LL45	87.0	12.9	6.7	4.6	48.6
mLL45	91.0	12.0	7.6	5.4	45.6
LL66	93.0	15.0	6.2	4.2	66.8
mLL66	98.0	15.8	6.2	6.8	69.9

^a Determined by HT-GPC; ^b Determined by HT-GPC-IR.

branching architecture of LLDPE. For low-SCB samples, dynamic mixing causes a decrease in M_w , broadening of M_w/M_n , and reduced SCB in the soluble fraction, likely due to the entrapment of high- M_w branched structures in the gel phase after the modification process. For higher-SCB samples, the soluble fractions tend to contain more high- M_w species, likely due to the presence of highly branched PE chains with a low degree of crosslinking and the release of long chains resulting from the fragmentation of the cross-linked networks.

The solvent fractionation results provided a comprehensive picture of the structural changes in dynamically modified LLDPE. The insoluble fractions indicate that low-SCB samples form denser crosslinked networks with higher moduli, while high-SCB samples generate looser and more fragmented networks due to enhanced chain scission. This difference in the network content and density led to significant differences in the M_w retained in the soluble fraction. Specifically, in the low-SCB samples, the modified PE showed a decreased M_w , resulting in a higher proportion of low- M_w components. This arises because the high crosslinking degree and dense network structure formed in the low-SCB LLDPE trap high- M_w chains in the insoluble fraction. These dense networks are difficult to break, leading only to the fragmentation of peripheral networks, thus generating low- M_w components. In the high-SCB samples, the modified PE showed an increased M_w . This was attributed to the low crosslinking degree, and a loose network structure was formed in the high-SCB LLDPE. Some lightly crosslinked, highly branched, and high- M_w chains can remain in the soluble fraction. Furthermore, the loose network was easily disrupted during shear processing, leading to the reformation of some high- M_w chains. These structural differences, dictated by the initial SCB content, directly influence the macroscopic behavior of the product: low-SCB LLDPE exhibits higher elasticity and lower processability, whereas high-SCB LLDPE shows reduced elasticity and enhanced flowability.

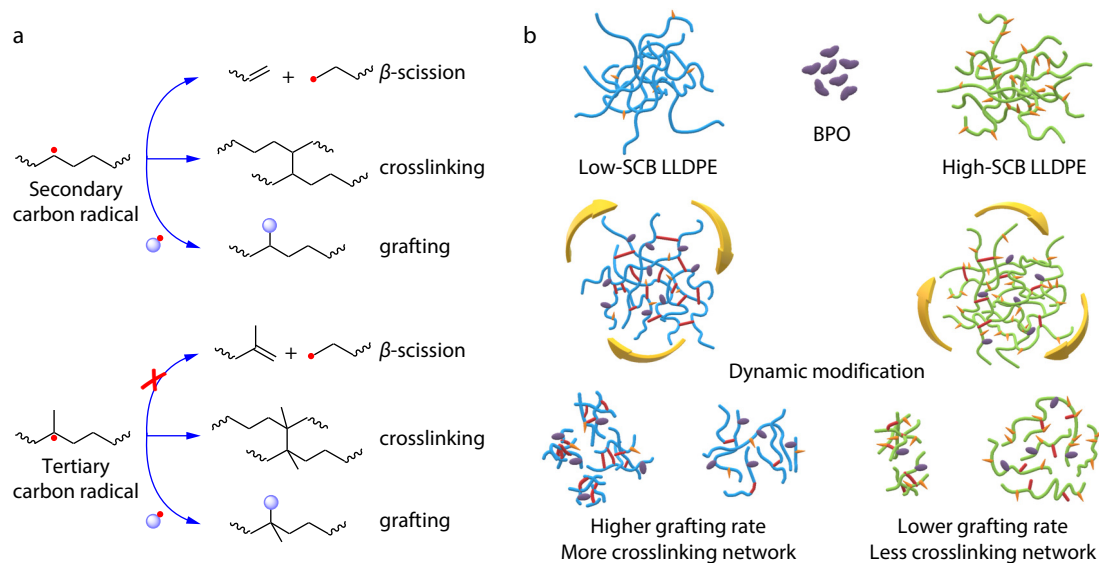
Possible Mechanism for Different Product Structures

Based on structural analyses of LLDPE products with different

SCB contents after dynamic modification, we propose a mechanistic explanation for the effect of SCB on the resulting product architecture.

As illustrated in Scheme 1(a), the BPO-initiated radical reaction begins with peroxide decomposition, generating benzoyloxy radicals, which abstract hydrogen atoms from the polymer backbone to form macroradicals. Secondary carbon radicals, which experience lower steric hindrance, readily undergo radical coupling, grafting, crosslinking, and β -scission reactions. In contrast, tertiary carbon radicals are more sterically hindered, less reactive toward coupling, grafting, and crosslinking, and rarely undergo β -scission reactions. In the early stages of dynamic mixing, high peroxide concentrations induce extensive radical reactions. For low-SCB LLDPE, the polymer backbone is largely composed of secondary carbons, leading to the predominant formation of secondary radicals. These radicals readily undergo β -scission, producing vinyl groups that enhance chain coupling and facilitate the generation of cross-linked or LCB structures. The high chain regularity and low steric hindrance promoted both efficient crosslinking and benzoyl fragment grafting, yielding a dense, uniform network with higher fluorescence intensity. For higher-SCB LLDPE, tertiary carbon radicals become more common because of the increased number of methyl-substituted carbons. These radicals rarely undergo β -scission and their steric hindrance reduces the efficiency of crosslinking and grafting. Consequently, the resulting network was looser and less uniform, and the level of benzoyl grafting decreased.

During dynamic modification, once the peroxide is largely consumed, the crosslinking reactions approach completion, and the subsequent structural evolution is mainly governed by chain scission under shear. As shown in Scheme 1(b), in low-SCB LLDPE, the high chain regularity and low steric hindrance favor the formation of dense, uniform networks that distribute stress more evenly; therefore, shear mainly induces partial network degradation and limited long-chain branching. In contrast, high-SCB LLDPE, with abundant short branches and high steric hindrance, developed looser and less uni-



Scheme 1 (a) The reaction pathways of macromolecular free radicals and (b) the product structures schematic diagram.

form networks. These irregular structures act as stress concentration sites, making the chains more prone to rupture, which leads to the breakdown of crosslinked domains and the release of soluble fragments with higher molecular weights and branching.

Finally, the structural and macroscopic properties of the modified LLDPEs exhibited a clear dependence on SCB content. In low-SCB LLDPE, the polymer backbone is dominated by secondary carbons with low steric hindrance. These reactive sites favor β -scission and radical coupling, leading to efficient crosslinking, benzoyl grafting, and generation of long-chain branches. The resulting network was dense and relatively uniform, with a higher degree of functionalization and stronger structural integrity. In high-SCB LLDPE, the increased fraction of tertiary carbons introduces steric hindrance that reduces radical coupling and grafting efficiency and interferes with the formation of compact networks. The networks formed are looser and more irregular, containing fewer long-chain branches and lower levels of grafting. These structural differences directly influence the macroscopic processability of modified products. Low-SCB samples, with their compact networks and abundant long-chain branches, exhibit a higher storage modulus and reduced melt flow rate. High-SCB samples have looser networks and fewer long-chain branches, higher soluble content, reduced gel density, and improved melt processability. Overall, the SCB content acts as a key structural parameter that modulates radical formation, crosslinking, and grafting during dynamic modification, ultimately influencing the molecular architecture and processability of the LLDPE.

CONCLUSIONS

In this study, we systematically investigated the effect of the SCB content on the structure and properties of LLDPEs modified via dynamic melt mixing with BPO. All the modified samples maintained good melt processability; however, clear differences emerged depending on the SCB levels. Low-SCB LLDPEs produce materials with lower melt flow rates, higher crosslink density, abundant long-chain branches, and more effective benzoyl grafting. In contrast, high-SCB LLDPEs yield products with enhanced melt processability but reduced crosslinking, fewer long-chain branches, and lower grafting efficiency. Fractionation analysis further confirmed that the tertiary carbon density critically affects radical coupling, as increased steric hindrance suppresses both crosslinking and peroxide fragment grafting. Overall, these findings highlight that the SCB content is a key structural parameter governing radical reaction pathways during peroxide modification. Importantly, this work provides practical insights for industrial applications, including functional films, tie layers, and adhesives, where precise control over network architecture and processability directly impacts performance and processability.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3466-8>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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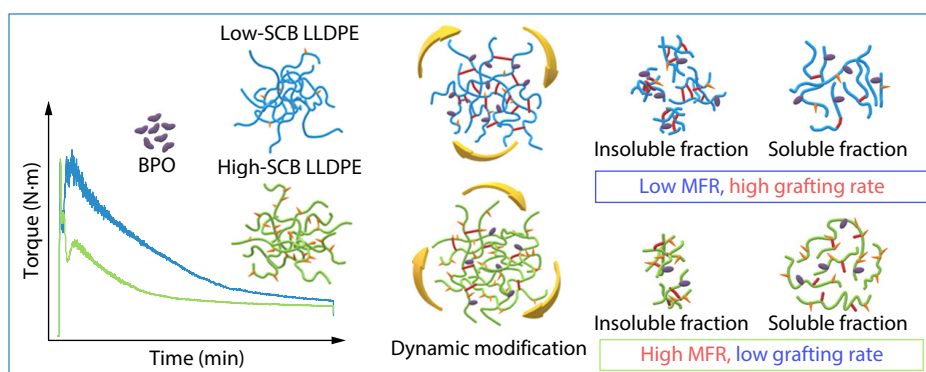
Graphical Abstract

Processability and Structure of Dynamically Modified Linear Low-density Polyethylene with Different Branching Contents Using a High Peroxide Content

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Processability and structure of dynamically modified four linear low-density polyethylenes (LLDPEs) with different branch contents using peroxide were investigated. It was found that, all samples were processable, and higher short-chain branch content led to better flowability, less cross-linked fractions, and lower grafting ratio of peroxide radicals onto the chains.



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