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Interactions between Low-Density Polyethylene (LDPE) and Polypropylene (PP) during the Mild Cracking of Polyolefin Mixtures in a Closed-Batch Reactor

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ABSTRACT: Thermal decomposition behaviors of neat polypropylene (PP) and low-density polyethylene (LDPE) and LDPE/PP mixture with different ratios (30/70, 50/50, 70/30) are studied under nonisothermal conditions in closed-batch reactors. The presence of a synergistic effect is observed for mixture samples with a PP composition of ≥30 wt %. Different proportions of PP in LDPE/PP mixtures give different interaction effects. The 70/30 LDPE/PP mixture starts to give viscosity-reducing effect and can degrade at lower temperature; the 50/50 LDPE/PP mixture gives higher gaseous products yield, specifically, more methane, ethane and propane; and the 30/70 LDPE/PP mixture makes more aromatics formed in the liquid products. The synergetic effect of LDPE and PP is related not only to the mass fraction of PP, but also to the reaction time. The interactions mechanism are related to enhanced intermolecular hydrogen transfer between LDPE/its cracked products and PP/its cracked products, not only in the liquid phase but also in the gas phase, because of the long cracking time in closed-batch reactors, where PP/its cracked products provide more radicals and PE/its cracked products provide more secondary hydrogen for intermolecular hydrogen transfer, and the combination of these factors enhances the chain breakage. This study also indicates that LDPE/PP mixture increases the aromatics formation mainly by increasing olefinic content due to the more β-scission reactions in the LDPE/PP mixture mild cracking.

1. INTRODUCTION

High-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), and poly(vinyl chloride) (PVC) are the main plastics in municipal solid waste. The former three plastics (HDPE, LDPE, and PP) generally comprise a majority of the plastic waste.[1,2] Tertiary recycling, in which discarded plastic products are converted to value-added petrochemical or fuel feedstock, has received increasing attention in recent years. Pyrolysis or cracking of polyolefins, as well as their blends, in the absence of air or oxygen has been widely studied in recent years,[3–6] since thermal degradation is the simplest form of tertiary recycling of addition polymers.

Polyolefins are cracked through a complex free-radical mechanism[7] and yield waxes and oils, aromatics, and gaseous alkenes (ethene and propene, etc.).[8,9] However, the products of cracking and global kinetics present great differences, even under similar conditions, because of the branching of polyolefin molecules. Bockhorn et al.[10] showed that the products of PP degradation are more complex than those of PE degradation. Lee et al.[11] indicated that PE shows a higher degradation temperature than PP does, and a higher fraction of paraffin exists in the degradation product of PE. Westerhout et al.[12] sequenced the conversion rate of cracking as HDPE < LDPE < PP < PS.

Ballice[13] found that more volatile hydrocarbons would be produced with increasing PP in the co-pyrolysis of LDPE/PP. Albano et al.[14] stated that the acceleration could be far more noticeable in the degradation of HDPE/PP blends, when the concentration of PP is >20%. A higher yield of solid residue was observed by Williams et al.[15] in the decomposition of the plastic mixture, suggesting the significant interaction between the plastic components. Miranda et al.[16] indicated that the synergistic effect in the decomposition of PE/PP mixture could be explained as a intermolecular hydrogen transfer from the more stable polymer toward the radicals of less-stable polymers. Furthermore, the interaction due to intermolecular radical transfer by hydrogen abstraction often results in destabilization of the more-stable polymer and slight retardation of the less-stable polymer.[14,17] Waldman et al.[18] observed that the LDPE/iPP blend is thermally more stable than expected under inert atmosphere, where LDPE acts as a stabilizer of iPP by retarding the autocatalytic propagation of tertiary carbon radicals, probably by cross-linking. In addition, no obvious product-changing interaction between PE and PP was observed by Predel et al.[33] and Westerhout et al.[19]

Our former studies show that the effect of PP in HDPE/PP or HDPE/LDPE/PP mixtures may significantly decrease the cracking temperature and the viscosity of liquid product. It is clear that an understanding of the interaction between PE and PP is important in the cracking of polyolefin mixtures. In this work, our objective is to investigate the interactions between LDPE and PP in mild cracking of polyolefin mixtures, and to determine the existence of synergistic effects with different PP ratios, and particularly to focus on the enhanced intermolecular hydrogen transfer between PP/its cracked products and LDPE/

its cracked products occurring both in the liquid phase and the gaseous phase with longer reaction time, which is different from published information.

2. EXPERIMENTAL SECTION

2.1. Materials. Low-density polyethylene (LDPE, type LD100AC) and polypropylene (PP, type K7726) in the form of grains 2–4 mm in size, manufactured by SINOPEC Beijing YanShan Company (Beijing, PRC), were used as the experimental materials. Their main properties are presented in Table 1. *n*-Hexane was used as the solvent in this work, which was analytical reagent grade and made by Beijing Chemical Works.

Table 1. Typical Properties of Polyolefins Used in This Work

polyolefin	type	density (20 °C), kg m^{-3}	melt flow index, g (10 min)$^{-1}$
LDPE	LD100AC	0.9225	2
PP	K7726	0.905	27

n-Hexane is used as solvent to separate the insoluble in liquid products by vacuum filtration in order to observe the residue changes with reaction conditions and also to separate the insoluble in liquid products by vacuum filtration for FTIP analysis.

2.2. Mild Cracking System. The mild cracking of polyolefins was performed in a closed batch reactor under nitrogen atmosphere. The mild cracking system, supplied by Beijing Xinranda Company, consists of four main parts, a reactor system, a gas removal and collection system, a data acquisition and control system and a cooling system, as shown in Figure 1.

The reactor system consists of a 1000-mL stainless steel vessel externally heated by an electric ring furnace, and fitted with a purging gas inlet valve, two outlet valves for gas sampling, and liquid sampling or purging gas discharge, respectively. The reaction vessel is stirred using a stirrer with rotor blade attached to an inner magnetic drive rotor powered through an outer magnetic drive rotor.

The reactor is equipped with a pressure gauge to measure the internal pressure while the experiments are performed. The controller is used to control the reaction temperature and stirring apparatus. The software, developed by Beijing Xinranda Company, is used to complete the data acquisition. The cooling water coil is arranged in the vessel for quick cooling as the cracking experiment finished. High-purity nitrogen (>99.999%) and a mass flow controller (CS200), supplied by Beijing Sevenstar Electronics Co., Ltd., were used to complete the air purging. A gas chromatography (GC) device (Model GC-9130, supplied by J-H Instruments), fitted for thermal conductivity and flame ionization detection (GC-TCD/FID), is used to analyze the gaseous products.

2.3. Experimental Procedure and Conditions. Polyolefin samples with masses of ~200 g were used in each cracking experiment. The reactor was purged by nitrogen to prevent the presence of air in the reactor before the cracking experiment started. In the cracking experiments, the reactor system was heated at a rate of 3–5 °C min^{-1}.

The temperature of 400 °C (410 °C for LDPE at series D) was chosen as the upper limit of cracking temperature and the timing of cracking is started from 200 °C, in order to study the interaction between LDPE and PP under isothermal (400 °C) and nonisothermal conditions (200–400 °C) in a closed-batch reactor. The pressure of reactor was recorded, and the reactor was cooled by cooling water or air until the temperature inside the vessel reached room temperature, as cracking experiments finished. The gaseous and liquid products of mild cracking were carefully collected for further analysis. For all the experiments, the initial pressure is ordinary pressure (gauge pressure = 0.00 MPa).

Four series of experimental conditions, as shown in Table 2, were designed in order to study the interaction between LDPE and PP. In particular, series A was used to compare the thermal decomposition behaviors of LDPE/PP and PP in a shorter cracking time, while series D was used to compare the viscosity changes of liquid products from 50/50 LDPE/PP and LDPE decomposition with a longer cracking time range.

2.4. Analysis Procedures. *2.4.1. Gaseous Product Analysis.* The gaseous product was analyzed by means of GC (Model GC-9130). A detailed separation of the gaseous mixture of C_1–C_6 saturated and unsaturated hydrocarbons, H_2, and CO_2 in one sample can be completed.

2.4.2. Liquid Product Analysis. The viscosity of liquid product was measured by viscometer (Model NDJ-5S) coupled with five rotors (Nos. 0–4). The measurement range of the viscometer can be 0–10^5 mPa s through a combination of rotor with rotation speed. The molecular structures of liquid fractions were determined by a FTIR spectrometer (Tensor 27) in the wavenumber range of 4000–400 cm^{-1}. ^{1}H NMR was recorded on 300 MHz Bruker spectrospin instruments. The samples of liquid products were diluted with CDCl$_3$. Elemental analysis was determined using an elemental analyzer, according to ASTM Standard D5291-96. Distillation was performed to divide the liquid products into light fractions (<330 °C) and heavy fractions (>330 °C) under ordinary pressure. The distillation apparatus includes a distilling flask (250 mL), a heater band, an electric heating and a condenser pipe. A gas chromatograph coupled to
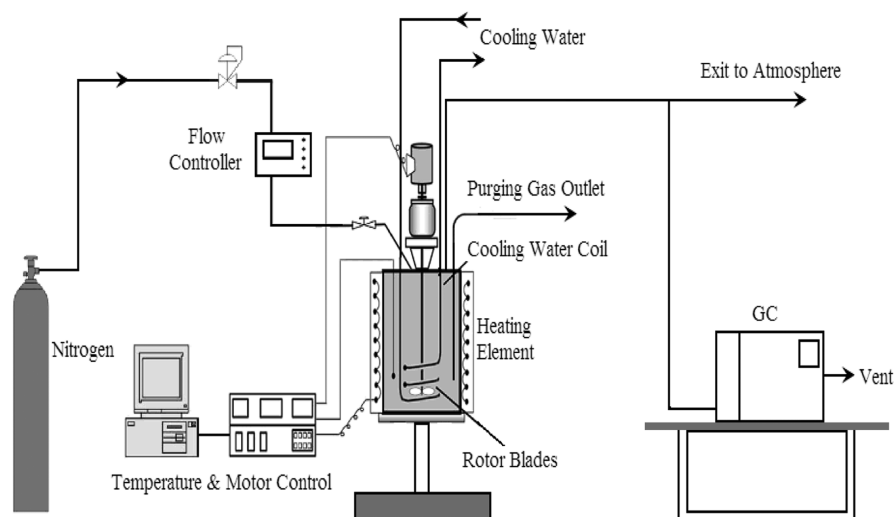

Figure 1. Schematic diagram of the mild cracking reactor system.

Table 2. Experimental Scheme and Experimental Conditions in This Study

	polyolefin sample	experimental conditions
		Series A
1	50/50 LDPE/PP	upper limit of cracking temperature: 400 °C
2	30/70 LDPE/PP	average heating rate:[a] 3−5 °C min^{−1}
3	PP	cracking time: 60 min from 200 °C
		cooling method: cooling to room temperature by cooling water
		Series B
1	LDPE	upper limit of cracking temperature: 400 °C
2	70/30 LDPE/PP	average heating rate:[a] 3−5 °C min^{−1}
3	50/50 LDPE/PP	cracking time: 80 min from 200 °C
4	30/70 LDPE/PP	cooling method: cooling to room temperature by air
5	PP	
		Series C
1	LDPE	upper limit of cracking temperature: 400 °C
2	70/30 LDPE/PP	average heating rate:[a] 3−5 °C min^{−1}
3	50/50 LDPE/PP	cracking time: 110 min from 200 °C
4	30/70 LDPE/PP	cooling method: cooling to room temperature by air
5	PP	
		Series D
1	LDPE	upper limit of cracking temperature: 400 °C for 50/50 LDPE/PP, 410 °C for LDPE
		average heating rate:[a] 3−5 °C min^{−1}
2	50/50 LDPE/PP	cracking time: 50−170 min from 200 °C
		cooling method: cooling to room temperature by air

[a]For each experiment, the heating rate was kept constant before the temperature was up to ~250 °C; then, it became distinguishing because of the different thermal cracking characteristics of plastics. So it was an average value for all nonisothermal time (from room temperature to the upper limit of the cracking temperature).

a mass spectrometer (GC-MS) (GCT Premier, Waters), using a DB-5 column (30 m × 0.25 mm I.D.), was employed to analyze the light fraction (<330 °C). Centrifugal separation was performed by the low-speed centrifuge made by Jintan Medical Instrument Factory. In every process, the centrifugal speed is 3500 rpm, and the time is 20 min.

2.4.3. Yield Calculation. After the reactor had cooled, the reactor was opened and liquid products were carefully discharged into a vessel and weighed. At the same time, the remains inside the reactor were wholly collected using paper and also weighed. The mass of liquid products was the sum of the two collections. The yield of liquid products was calculated by the ratio of the mass of liquid products and that of raw material, as shown in eq 1.

$$\text{yield of liquid products (\%)} = \frac{\text{mass of liquid products}}{\text{mass of raw material}} \times 100 \tag{1}$$

The yield of gaseous product could be calculated as the difference of 100% and the yield of liquid product:

$$\text{yield of gaseous products} = 100\% - \text{yield of liquid products} \tag{2}$$

2.4.4. Theoretical Noninteraction Pressure Calculation. The theoretical noninteraction pressure in mild cracking of LDPE/PP mixtures was calculated using eq 3:

$$\text{theoretical pressure} = \frac{m_{\text{LDPE}}P_{\text{LDPE}} + m_{\text{PP}}P_{\text{PP}}}{m_{\text{LDPE}} + m_{\text{PP}}} \tag{3}$$

where m_{LDPE} and m_{PP} are the mass percentages of PE and PP, respectively, in a PE/PP mixture. P_{LDPE} and P_{PP} are the respective

gauge pressures at the end of reaction when LDPE and PP are cracked alone.

2.4.5. Residue Analysis. The residue in this study refers to the *n*-hexane insoluble and sediment obtained from centrifugal separation. Vacuum filtration (250 mL) with Buchner funnel (80 mm) was used to filtrate the liquid by vacuum pump (Model 2XZ-2 type Rotary). Ashless filter paper is medium speed with a diameter of 7 cm. In each run, ~8 mL of liquid sample and 20 mL of solvent were poured into a triangle flask and mixed well by shaking, and then the solution was poured into the Buchner funnel completely to filtrate for ~2 min. Finally, the filter paper with residue was dried in the bake oven for 20 min at 100 °C. The sediment obtained from centrifugal separation was also dried in the bake oven for 20 min at 80 °C and weighed. The yield of residue was calculated by the ratio of the mass of residue and that of raw material, as shown in eq 4.

$$\text{yield of residue (\%)} = \frac{\text{mass of residue}}{\text{mass of liquid sample}} \times \text{liquid product yield} \times 100 \tag{4}$$

3. RESULTS AND DISCUSSION

3.1. Product Yields. Mild cracking of polyolefin samples (LDPE, 70/30 LDPE/PP, 50/50 LDPE/PP, 30/70 LDPE/PP, and PP) under experimental conditions of Series A, B, C, and D were performed to study the interaction of PP and LDPE. The temperature- and pressure-cracking time relationships under the experimental conditions of series C are shown in Figure 2. Table 3 presents mild cracking results of polyolefin samples under the experimental conditions of series A, B, C, and D. High similarity in the temperature−cracking time relationships are exhibited in Figure 2, although the heating rate in the cracking of LDPE is higher than that observed in the cracking of PP and LDPE/PP mixtures. However, the pressure−cracking time relationships are dependent on the ratio of PP in the LDPE/PP mixture. The pressure of the cracking system is approximately proportional to the amount of volatile products in an isothermal isochoric process, according to the gas equation of state. In other words, higher pressure is related to more-volatile products and, furthermore, more cracked chemical bonds.

Our former studies showed that the effect of PP on the cracking of HDPE/PP mixture is insignificant when the mass fraction of PP in HDPE/PP mixture is <20 wt %, and the effect of PP becomes notable when the mass fraction of PP increases to 40 wt % or more. Figure 2 indicates that the effect of PP becomes notable even when the mass fraction of PP increases to 30 wt % or more. The similarity on the pressure−cracking time relationships of 50/50 and 30/70 LDPE/PP mixtures and that of PP also indicates the similar degradation rate of 50/50 LDPE/PP, 30/70 LDPE/PP, and PP under such conditions.

The final gauge pressure in the cracking experiment of 70/30 LDPE/PP mixture is higher than the corresponding theoretical noninteraction pressure, and higher than that of neat LDPE and PP as well, showing more volatile products produced in the mild cracking of LDPE/PP mixture due to the synergetic effect of LDPE and PP. Such observations are in accordance with the results determined by Chowlu et al.[20] However, as shown in Table 3, the gauge pressure in the cracking experiment of 30/70 LDPE/PP mixture is lower than that of PP under the experimental condition of series A, which shows also that the synergetic effect of LDPE and PP is related not only to the mass fraction of PP in LDPE/PP mixture, but also to the cracking time.
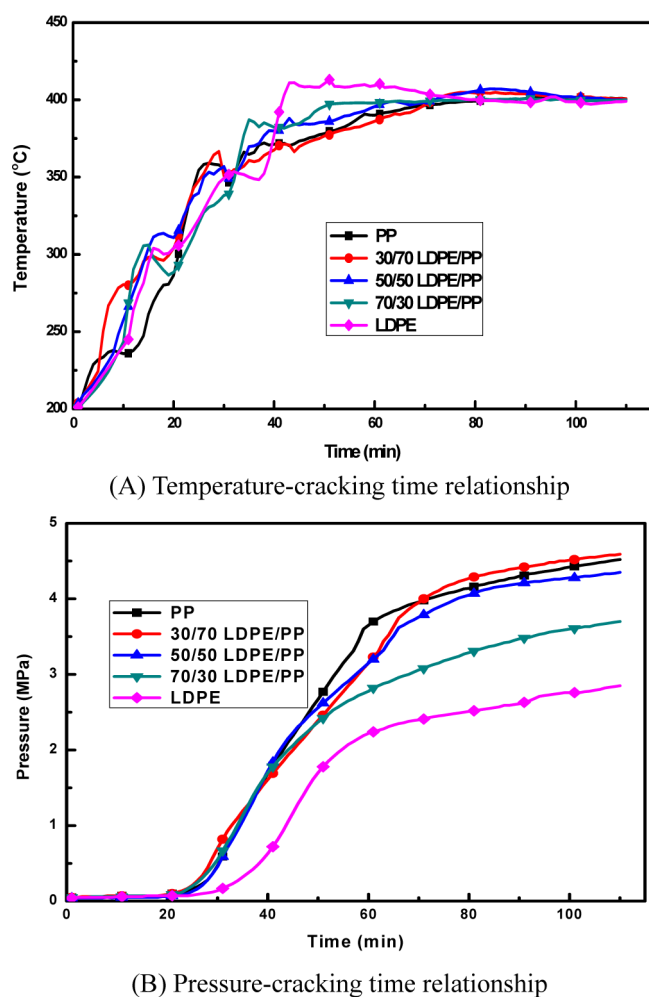
(A) Temperature—cracking time relationship

(B) Pressure—cracking time relationship

Figure 2. Temperature—cracking time and pressure—cracking time relationships in mild cracking of polyolefin samples under the experimental condition of series C.

As shown in Table 3, mild cracking of LDPE will produce a highly viscous dark yellow or brown waxy liquid product under the experimental conditions of series B or C, the yield of which could reach 95 wt % or more. While mild cracking of PP will receive low viscosity black or dark brown liquid product, with yield more than 93 wt %. The final gauge pressure in cracking of PP is much higher than that of LDPE. This result is consistent with the discussion in the literature,[10,21] indicating more volatile products produced and more C−C bonds cracked in mild cracking of PP. Most of the mild cracking of LDPE/PP mixture will produce low-viscosity black liquid product, with a yield of 91−93.7 wt % or more. The viscosity-reducing effect of PP on the liquid product can visibly be observed, when the mass fraction of PP is higher than 30 wt % in the LDPE/PP mixture. The effect of PP on increasing the yield of gaseous product can also be observed in mild cracking of 50/50 and 30/70 LDPE/PP mixtures under the same experimental conditions.

In addition, the experimental conditions of series D gives a range of cracking time of 50−170 min. Mild cracking of LDPE will produce solid or highly viscous yellow or brown waxy liquid product at cracking times of 50−110 min. On the other hand, the viscosity-reducing effect of PP on the liquid product can visibly be observed at cracking times of 50−70 min with the viscosity decreasing from 63 mPa s to 2.3 mPa s. Also, at a longer cracking time such as 170 min, the viscosity of liquid

product from the mild cracking of LDPE is still higher than that of liquid product from mild cracking of 50/50 LDPE/PP. On the other hand, for the mild cracking of LDPE, the gaseous product yield increases from 4.94 wt % to 7.46 wt %, but for the mild cracking of 50/50 LDPE/PP, the gaseous product yield increases from 4.89 wt % to 10.42 wt %. These results show that there is less C−C bond breaking for the mild cracking of LDPE than that for mild cracking of 50/50 LDPE/PP.

Miranda et al.[16] indicated that the synergistic effect during the decomposition of PE/PP mixture could be explained by a hydrogen transfer from the more-stable polymer toward the radicals of the less-stable polymers, and intermolecular hydrogen transfer seemed to be the predominant reaction between components of the polymer mixtures. In addition, the interaction effect due to intermolecular radical transfer by hydrogen abstraction often results in slightly retarded, less-stable polymer weight loss and more-stable polymer destabilized.[10,16] The synergistic effect in this work is quite complex and is possibly related not only to the intermolecular radical transfer by hydrogen abstraction, but also to the complex secondary reactions of the cracked products of LDPE/PP mixtures, because the reactions occurred in both liquid and gas phases and suffered a long cracking time.

It is a fact that the yields of all liquid products are >90 wt % in this work, except for 50/50 LDPE/PP with long cracking time, and the yields of gaseous products are <10 wt %. On the other hand, the yield of liquid products is subject to a quick decrease at higher cracking temperatures. Moreover, the viscosity of liquid products has decreased greatly, compared to the high viscosity of PP or PE.[22] Such results indicate that more viscosity reduction and the acquisition of more liquid products can be achieved simultaneously in mild cracking of polyolefins by optimizing the combination of cracking time and cracking temperature, which is important for the unitization of liquid products in subsequent processes.

3.2. Analysis of Gaseous Product. Table 4 shows the yields of gaseous products obtained from mild cracking of LDPE, PP, and LDPE/PP under the experimental conditions of series A, B, and C. As observed from Table 4, the yields of alkenes exhibit great differences under the experimental conditions of series A, B, and C. Propene becomes the main component in gaseous product by mild cracking of PP or LDPE/PP mixture, and its mass fraction will increase as the mass fraction of PP in the LDPE/PP mixture increases. However, the yield of gaseous product is not sensitive to the increase in cracking time. The mass fraction of ethene in the gaseous product is relatively small for all cracking experiments (~0.2 wt % of the feed). The yields of alkanes are relatively small and become higher as the cracking time increases. The mass fraction of PP in LDPE/PP mixture also is related to the mass fraction of alkanes in gaseous product, indicating that the interaction between PP and LDPE can affect the distribution of alkanes.

The reaction mechanism of polyolefin degradation is highly variable and depends on the type of polymer and the nature of reaction conditions.[23] McCaffrey et al.[24] observed that the intramolecular hydrogen transfer followed by β-scission is an important mechanism for the production of short-chain olefins. Ueno et al.[7] conducted a quantitative analysis of random and chain-end scissions in the thermal degradation of polyethylene, showing that the ratio of random and chain-end scissions at lower temperature are 87.8% and 11.2%, respectively. Bockhorn et al.[10] reported that the intramolecular hydrogen transfer

Table 3. Mild Cracking Results of Polyolefin Samples under the Experimental Conditions of Series A, B, C, and D

polyolefin sample/cracking tome after 200 °C, min	gauge pressure, MPa		yield, wt %		liquid product	
	final	room temperature (20 °C)	gaseous	liquid	μ (20 °C), mPa s	color
Series A						
50/50 LDPE/PP	3.70	0.43	6.32	93.68	4.0	brown
30/70 LDPE/PP	3.46	0.32	4.44	95.56	5.8	dark yellow
PP	3.88	0.28	4.82	95.18	2.2	dark yellow
Series B						
LDPE	2.30	0.36	4.52	95.48	67	dark yellow
70/30 LDPE/PP	3.37	0.42	6.30	93.70	4.6	dark brown
50/50 LDPE/PP	4.22	0.52	8.60	91.40	1.5	black
30/70 LDPE/PP	4.44	0.45	7.38	92.62	1.2	black
PP	4.18	0.29	5.82	93.81	1.4	dark brown
Series C						
LDPE	2.75	0.48	5.00	95.00	41.6	brown
70/30 LDPE/PP	3.78	0.52	6.64	93.36	2.8	black
50/50 LDPE/PP	4.32	0.60	8.09	91.91	3.2	black
30/70 LDPE/PP	4.66	0.55	8.98	91.02	1.5	black
PP	4.54	0.37	6.92	93.08	2.8	black
Series D						
LDPE/50	1.67	0.31		solid		light yellow
LDPE/60	2.17	0.35	4.94	95.06	160	yellow
LDPE/70	2.46	0.42	5.00	95.00	87	brown
LDPE/110	2.97	0.50	6.23	93.77	5.8	dark brown
LDPE/130	3.16	0.58	6.44	93.56	3.4	black
LDPE/150	3.37	0.58	6.86	93.14	3.3	black
LDPE/170	3.54	0.59	7.46	92.54	2.5	black
50/50 LDPE/PP/50	2.89	0.33	4.89	95.11	63.0	dark green
50/50 LDPE/PP/60	3.55	0.45	6.23	93.77	4.0	dark brown
50/50 LDPE/PP/70	3.96	0.51	7.16	92.84	2.3	dark brown
50/50 LDPE/PP/110	4.45	0.63	9.51	90.49	1.4	black
50/50 LDPE/PP/130	4.64	0.68	10.35	89.65	1.3	black
50/50 LDPE/PP/150	4.72	0.68	10.41	89.59	1.3	black
50/50 LDPE/PP/170	4.78	0.70	10.42	89.58	1.3	black

Table 4. Yields of Gaseous Products Obtained from Mild Cracking of LDPE, PP, and LDPE/PP under the Experimental Conditions of Series A, B, and C

polyolefin sample	yields of main gaseous products (wt % of feed)					
	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6
Series A						
50/50 LDPE/PP	0.048	1.11	1.42	0.20	0.91	1.46
30/70 LDPE/PP	0.022	0.64	0.86	0.12	0.48	1.34
PP	0.021	0.77	0.89	0.11	0.37	1.87
Series B						
LDPE	0.052	0.65	1.20	0.17	1.10	0.62
70/30 LDPE/PP	0.053	1.10	1.59	0.17	1.14	1.01
50/50 LDPE/PP	0.061	1.57	2.07	0.21	1.37	1.57
30/70 LDPE/PP	0.050	1.53	1.93	0.18	1.22	1.88
PP	0.025	0.98	1.23	0.12	0.62	2.13
Series C						
LDPE	0.056	0.75	1.28	0.15	1.01	0.51
70/30 LDPE/PP	0.066	1.39	1.73	0.17	1.07	0.80
50/50 LDPE/PP	0.058	1.52	1.86	0.17	1.13	1.08
30/70 LDPE/PP	0.067	1.63	1.87	0.15	1.21	1.46
PP	0.036	1.36	1.47	0.12	0.77	1.96

followed by β-scission occurred, and the β-scission of primary radicals leading to ethene is not evident at lower temperatures in the degradation of HDPE. Tertiary radicals will be formed via rearrangement reactions of primary and secondary radicals and subsequent β-scission lead to volatile alkenes and the chain carrier for PP degradation.

It is not surprising that the yield of propene is the highest in mild cracking of neat PP, while the yield of ethene is the lowest for all runs. Propene is mainly produced by β-scission of primary and secondary radicals initiated by the random scission of polypropylene and ethene is produced by β-scission of primary radicals initiated by the random scission of polyethylene. The probability of producing secondary radical by β-scission is higher than that of producing primary radical before transforming to the tertiary radical, because of the higher stability of the secondary radical. Such a presumption is consistent with the experimental observations that a higher yield of propene is obtained with shorter cracking time, and it is less enhanced with extending the cracking time to another 50 min. On the other hand, the influence of LDPE in the mild cracking of the LDPE/PP mixture is negligible, because the propene production involves β-scission but not intermolecular hydrogen transfer.

Higher yields of gaseous alkanes are obtained in the mild cracking of the LDPE/PP mixture. The production of gaseous alkanes are related to the intermolecular hydrogen transfer. Furthermore, it can also be concluded that more secondary H atoms exist in the cracking product of LDPE, while more primary H atoms in the cracking product of PP, based on the observation that LDPE cracked into more *n*-alkanes[25,26] and PP cracked into more *iso*-alkenes or *iso*-alkanes.[10,21] It can be

considered that the presence of LDPE increases the probability of intermolecular hydrogen transfer, resulting in the production of more gaseous alkanes, while heavy hydrocarbon formation by radical recombination is probably inhibited, which will be further discussed in section 3.4.

3.3. Analysis of Liquid Product. *3.3.1. NMR Spectroscopy Analyses.* The detailed ^{1}H NMR analyses of the liquid products, sediment, and hexane insolubles derived from the mild cracking of LDPE, PP, and the LDPE/PP mixture are given in Table 5. Because the aromatic content is relatively

Table 5. Parameters Obtained from ^{1}H NMR Spectra of Liquid Products, Sediment, and Hexane Insolubles Derived from the Mild Cracking of LDPE, PP, and the LDPE/PP Mixture under the Experimental Conditions of Series B

polyolefin sample	sample for NMR	% H[a]		
		aromatics	olefinics	paraffinics
LDPE	liquid product	0	0.14 (±0.01)	99.86 (±0.01)
70/30 LDPE/PP		0.95 (±0.05)	0.92 (±0.05)	98.13 (±0.09)
50/50 LDPE/PP		1.09 (±0.13)	0.74 (±0.27)	98.17 (±0.37)
30/70 LDPE/PP		3.34 (±0.47)	5.01 (±0.13)	91.65 (±0.34)
PP		0.65 (±0.57)	2.43 (±0.51)	96.91 (±0.36)
LDPE	sediment	0.65 (±0.57)	0.98 (±0.01)	98.36 (±0.56)
70/30 LDPE/PP		1.62 (±0.56)	1.29 (±0.56)	97.09 (±0.00)
50/50 LDPE/PP		3.46 (±0.52)	2.20 (±0.52)	94.35 (±0.89)
30/70 LDPE/PP		3.45 (±0.53)	2.51 (±0.54)	94.05 (±0.51)
PP		0.65 (±0.56)	1.63 (±0.56)	97.72 (±0.55)
LDPE	hexane insolubles	5.35 (±1.69)	5.07 (±0.50)	89.57 (±1.66)
70/30 LDPE/PP		9.98 (±1.47)	6.66 (±0.73)	83.36 (±1.86)
50/50 LDPE/PP		28.09 (±0.85)	15.73 (±0.85)	56.19 (±0.83)
30/70 LDPE/PP		24.15 (±1.79)	12.06 (±1.34)	63.79 (±3.10)
PP		18.82 (±0.45)	10.59 (±0.67)	70.59 (±0.29)

[a]For each feed (LDPE, PP and LDPE/PP), two replicated experiments have been performed under the same experimental conditions, and for each liquid product, sediment, or hexane insoluble, two replicated tests have been carried out.

lower compared with the aliphatic content in this study, so liquid products, sediment and hexane insolubles are all used as sample for NMR in order to precisely compare the alkene/aromatics content changes in mild cracking of LDPE, PP and the LDPE/PP mixture under series B conditions.

Each of the ^{1}H NMR spectra contains the dominant aliphatic peaks. The integrated area of ^{1}H NMR spectra illustrates the presence of −CH$_3$, >CH$_2$, and >CH− functional groups in the aliphatic region between 0.00 and 4.00 ppm. The olefinic hydrogen corresponds to the region between 4.00 and 6.00 ppm. The aromatic structures present in the liquid portion

clearly indicated by the peaks in the region between 6.00 and 8.00 ppm. As shown in Table 5, under the experimental conditions of series B, almost 100% of H atoms are aliphatic in the liquid products and sediment obtained from LDPE cracking, indicating the seldom occurrence of secondary reactions. Liquid products, sediment, and hexane insolubles obtained from 50/50 LDPE/PP and 30/70 LDPE/PP cracking give a higher content of aromatic H atoms, suggesting more secondary reactions occurred, because of the interactions between LDPE and PP in the LDPE/PP mixture.

It is also observed that liquid products, sediment, and hexane insolubles obtained from LDPE/PP mixture mild cracking give a higher content of olefinic H atoms than LDPE mild cracking, and in particularly, liquid products, sediment, and hexane insolubles obtained from 50/50 LDPE/PP and 30/70 LDPE/PP mild cracking also produce an olefinic H atom content, close to or higher than PP mild cracking, indicating that there are more mid-chain β-scission of radicals in the case of LDPE/PP mixture mild cracking. In addition, note that the alkene is unstable in the mild cracking with longer time and is likely to form heavy compounds such as aromatics by secondary reactions.

In addition, the interactions mechanism probably is related to the intermolecular hydrogen transfer, and, furthermore, it is probable that the LDPE/PP mixture increases the alkene content by enhancing β-scission, while the higher alkene content accelerates aromatics formation by unimolecular cyclation reactions, followed by dehydrogenation or Diels−Alder reactions, which require further study in the future.

3.3.2. FTIR Analysis. The composition and structure of liquid products were characterized using the Fourier transform infrared (FTIR) spectroscopy. Figure 3 shows the FTIR spectra of liquid products obtained via the mild cracking of LDPE, PP, and the LDPE/PP mixture under the experimental conditions of series C. The FTIR spectra of hexane insolubles obtained via the mild cracking of LDPE, PP, and LDPE/PP mixtures under the experimental conditions of series C are presented in Figure 4.
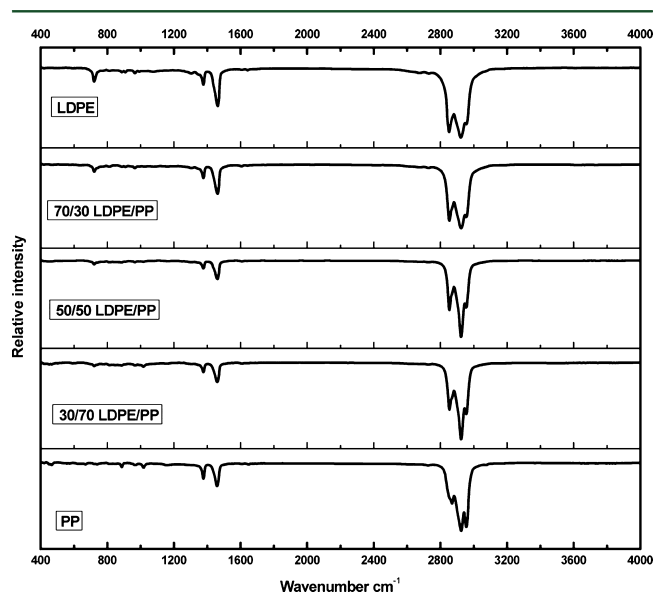

Figure 3. FTIR spectra of liquid product by mild cracking of LDPE, PP, and LDPE/PP mixtures under the experimental condition of series C.
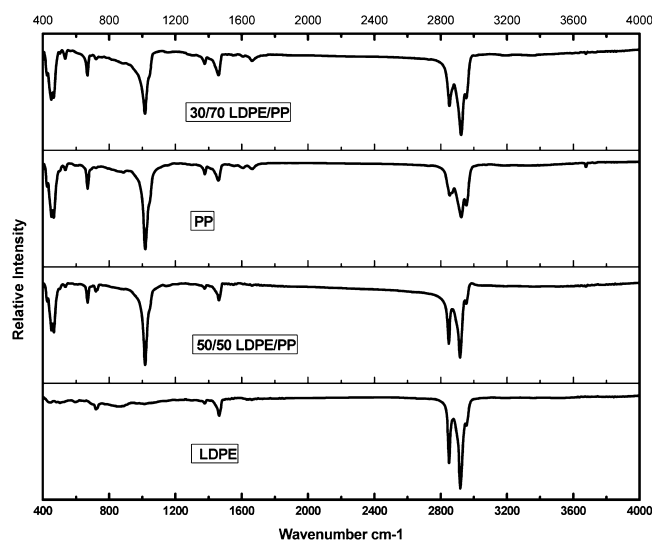
Figure 4. Fourier transform infrared (FTIR) spectra of hexane insolubles obtained via the mild cracking of LDPE, PP, and LDPE/PP mixtures under the experimental conditions of series C.

As shown in Figure 3, the peaks that appear in the range of 3000−2800 cm^{-1} indicate the existence of C−CH$_3$ (2960 cm^{-1}) and >CH$_2$ (2921 cm^{-1} and 2851 cm^{-1}) groups, referred to the aliphatic hydrocarbons in liquid products. The peaks in the range of 1350−1500 cm^{-1} confirm the existence of the aliphatic groups, the peak at 1377 cm^{-1} is the characteristic absorption of C−CH$_3$ group,[27] and the peak at 1460 cm^{-1} of >CH$_2$ group. The similarity of peaks at 2921 cm^{-1} and at 2851 cm^{-1} in these spectra confirms the aliphatic characteristic of liquid products. However, the peaks at 2960 cm^{-1} and 1377 cm^{-1} are more pronounced in the PP cracked products, which indicate that more isomeric hydrocarbons exist. The peaks at 1641 cm^{-1} and in the range of 850−1000 cm^{-1} confirm the existence of olefinic groups. In particular, the peaks at 909 cm^{-1} and 992 cm^{-1} correspond to the R−CH=CH$_2$ group.[28]

The peaks at 1015 cm^{-1} and 668 cm^{-1}, corresponding to the aromatic in-plane bending and C−H aromatic bending, appear

in the hexane insolubles formed via the mild cracking of PP and LDPE/PP mixtures, as shown in Figure 4, but do not appear in those formed via the mild cracking of LDPE. Such results show that less aromatics content exists in liquid products of mild cracking of neat LDPE, and the hexane insolubles contain mainly long-chain aliphatic hydrocarbons. Some aromatics, mainly polycyclic aromatic hydrocarbons, however, exist in hexane insolubles formed via the mild cracking of LDPE/PP mixtures, because of the interaction between LDPE and PP.

Figures 3 and 4 indicate that the FTIR spectra of cracked fractions obtained via the mild cracking of LDPE, PP, and LDPE/PP mixtures are similar, because of the high similarity of their polymeric structures and mechanism of thermal degradations. It is noted that the liquid products for all runs are dominated by the presence of alkanes and alkenes, which is consistent with the results by other workers,[29,30] although some aromatics content are found in hexane insolubles formed via the mild cracking of HDPE/PP.

3.3.3. GC-MS Analysis. The chromatograms of liquid fractions (<330 °C) obtained from LDPE and 50/50 LDPE/PP mild cracking under the experimental conditions of series C are shown in Figure 5.

As shown in Figure 5, LDPE mild cracking mainly produces *n*-alkanes and the alkanes with 16 to 22 C atoms were also detected in the liquid products (<330 °C), while PP mild cracking favors *i*-alkanes or *i*-alkenes, which agree with the polyethylene and polypropylene structure and fit the results observed by others.[10,25,31] Moreover, 50/50 LDPE/PP mild cracking also produces *n*-alkanes and *i*-alkanes/*i*-alkenes, but the *n*-alkanes with more than 17 C atoms were not detected and the *n*-alkanes with 10−16 C atoms were formed only in very small amounts, indicating that the presence of PP can enhance the cracking of C−C bonds to produce more short-chain alkanes (such as heptane).

The analytical results from GC-MS show that the mild cracking of LDPE, PP, and 30/70 LDPE/PP in this study produces some aromatic compounds. In particular, except for a few aromatics (such as 1,4-diphenyl acetate), all the aromatic compounds identified in the liquid fraction derived from 30/70
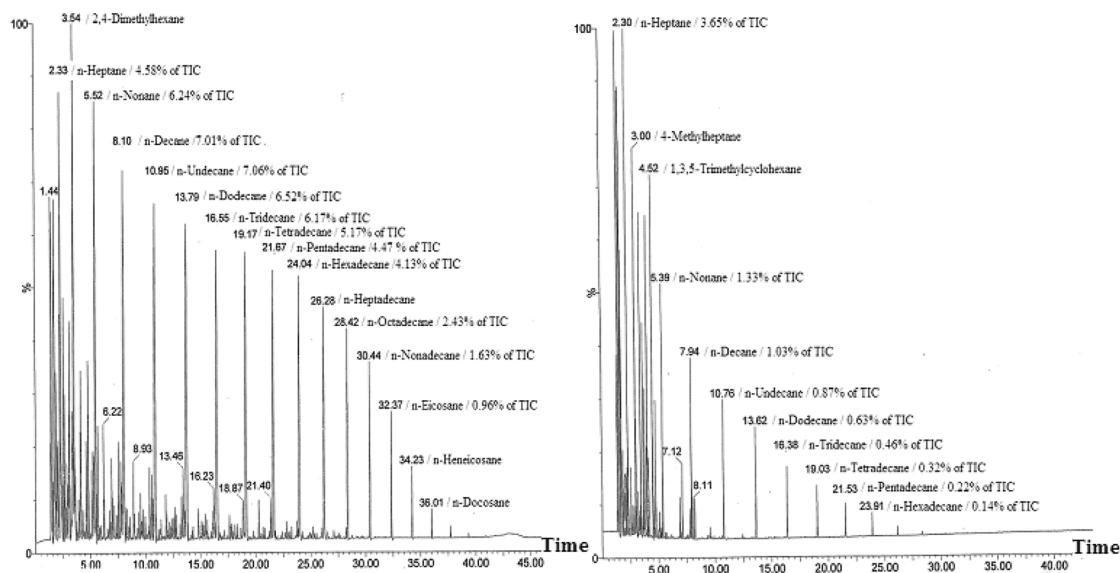

Figure 5. Gas chromatogram of the liquid fractions (<330 °C) obtained from LDPE (left) and 50/50 LDPE/PP (right) mild cracking under the experimental conditions of series C.

LDPE/PP mild cracking were also present in the light fraction derived from LDPE or PP mild cracking, showing that LDPE/PP mixture increases the alkene content and then accelerates the formation of aromatics by unimolecular cyclation reactions, followed by dehydrogenation or Diels—Alder reactions, which is in accordance with the foregoing conclusion.

3.3.4. Elemental Analysis. Table 6 shows the elemental analysis of the liquid products/heavy fractions (boiling point

Table 6. Elemental Analysis of the Liquid Products/Fractions (Boiling Point >330°C)/Sediment Obtained Via the Mild Cracking of PP, LDPE, and the LDPE/PP Mixture under the Experimental Conditions of Series C

polyolefin sample	sample for elemental analysis	C/H ratio	n_H/n_C
LDPE	liquid products	6.08 (±0.04)	1.97 (±0.01)
50/50 LDPE/PP	liquid products	6.21 (±0.02)	1.93 (±0.01)
30/70 LDPE/PP	liquid products	6.25 (±0.05)	1.92 (±0.01)
PP	liquid products	6.06 (±0.06)	1.97 (±0.02)
LDPE	sediment	5.88 (±0.14)	2.04 (±0.05)
50/50 LDPE/PP	sediment	6.24 (±0.04)	1.92 (±0.01)
30/70 LDPE/PP	sediment	6.36 (±0.03)	1.89 (±0.01)
PP	sediment	6.15 (±0.02)	1.95 (±0.01)
LDPE	>330 °C heavy fractions	5.98 (±0.03)	2.00 (±0.01)
30/70 LDPE/PP	>330 °C heavy fractions	6.83 (±0.05)	1.76 (±0.01)
PP	>330 °C heavy fractions	6.43 (±0.06)	1.87 (±0.02)

>330 °C)/sediment obtained via the mild cracking of PP, LDPE, and the LDPE/PP mixture under the experimental conditions of series C.

The H/C molar ratio of liquid products obtained via the mild cracking of neat LDPE under the experimental conditions of series C is quite similar to that of polyolefins, as shown in Table 6, implying that the aliphatic hydrocarbons are main components of liquid products. However, the H/C ratio of liquid products obtained via the mild cracking of 50/50 LDPE/PP and 30/70 LDPE/PP becomes lower than that of neat

LDPE or PP, which is in accordance with the results shown in section 3.2 (higher yields of gaseous alkanes in mild cracking of LDPE/PP mixture means higher H/C molar ratios of gaseous products), indicating that some aromatics appeared in the liquid products because of the secondary reactions. In addition, the H/C ratio of heavy fractions (boiling point >330 °C)/sediment is approximately equal to that of liquid products in the case of the mild cracking of neat LDPE, showing that LDPE decomposes into a wide distribution of aliphatic alkanes and alkenes by random scission. However, in the mild cracking of PP, 30/70 LDPE/PP, or 50/50 LDPE/PP under the experimental conditions of series C, the H/C ratio of heavy fractions or sediment is lower than that of liquid products, suggesting the appearance of aromatics in heavy fractions or sediment.

3.3.5. Residue Analysis. In this study, the residue consists of hexane insolubles and the sediment obtained from centrifugal separation. The results for the hexane insolubles and sediment obtained from centrifugal separation are shown in Table 7, and the sediment obtained via the mild cracking of PP, LDPE, and the LDPE/PP mixture under the experimental conditions of series D are shown in Figure 6.

As observed from Table 7, under the experimental conditions of series A, the hexane insolubles from the mild cracking of the 50/50 LDPE/PP, 30/70 LDPE/PP, and PP are all light yellow. In addition, under the experimental conditions of series B, the hexane insolubles from the mild cracking of the 50/50 LDPE/PP and 30/70 LDPE/PP become black, while those from the mild cracking of the PP and LDPE are still light yellow and that from the mild cracking of 70/30 LDPE/PP gives a deep yellow color. Moreover, under the experimental conditions of series C, the hexane insolubles from the mild cracking of the 50/50 LDPE/PP and 30/70 LDPE/PP are black, while the hexane insoluble from the mild cracking of the LDPE is yellow and that obtained from the mild cracking of PP becomes dark gray. And the dark gray is probably related to the higher content of methyl (as shown in Figure 4) in the hexane insolubles obtained from PP cracking. Meanwhile, the yield of hexane insolubles from the mild cracking of the LDPE decreases as the cracking time increases (from series B to series C), and the yield of hexane insolubles from the mild cracking of the LDPE/PP mixture and PP decreases from series A to series B and little

Table 7. Residue Analysis of the Liquid Products by Vacuum Filtration and Centrifugal Separation

| polyolefin sample	series	Properties of Hexane Insolubles		Properties of Sediment	
		wt %	color	wt %	color at 80 °C
50/50 LDPE/PP	A	1.52 (±0.06)	light yellow	12.64	yellow liquid
30/70 LDPE/PP	A	1.83 (±0.08)	light yellow	15.49	yellow liquid
PP	A	1.13 (±0.03)	light yellow	9.54	yellow liquid
LDPE	B	3.19 (±0.06)	light yellow	29.03	brown liquid
70/30 LDPE/PP	B	0.71 (±0.05)	yellow	10.59	dark brown liquid
50/50 LDPE/PP	B	0.48 (±0.04)	black	4.16	black solid—liquid mixture
30/70 LDPE/PP	B	0.32 (±0.03)	black	2.96	black solid—liquid mixture
PP	B	0.23 (±0.02)	light yellow	3.34	dark brown solid—liquid mixture
LDPE	C	1.62 (±0.06)	yellow	19.85	brown liquid
70/30 LDPE/PP	C	0.56 (±0.01)	black	4.90	black solid—liquid mixture
50/50 LDPE/PP	C	0.41 (±0.03)	black	4.24	black solid
30/70 LDPE/PP	C	0.54 (±0.02)	black	2.28	black solid
PP	C	0.44 (±0.01)	dark gray	2.17	black solid
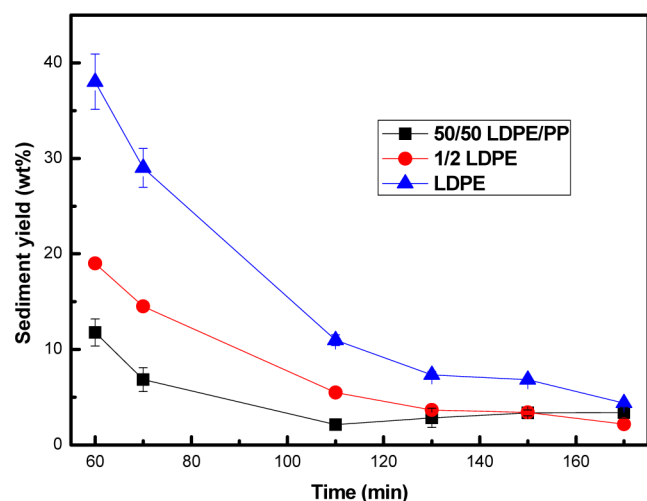
Figure 6. Sediment yields obtained via the mild cracking of LDPE and 50/50 LDPE/PP mild cracking under the experimental conditions of series D (1/2 LDPE is the half of the value sediment yields obtained via the mild cracking of LDPE).

change is observed from series B to series C. Therefore, it should be noted that, with increasing reaction time (LDPE for series B and C, LDPE/PP and PP for series A and B), there is a decrease in the yield of hexane insolubles, but it becomes darker for LDPE (from light yellow to yellow) and for LDPE/PP (from light yellow to yellow or black), which may mean that there is a concentration of heavier compounds.

All these indicate that, with the increasing reaction time (especially from series A to series B), there are some interactions of LDPE and PP that are responsible for the formation of the black residue (Table 5 shows that the hexane insolubles from the mild cracking of the 50/50 LDPE/PP and 30/70 LDPE/PP under the experimental conditions of series B contain higher aromatics), and, furthermore, these interactions are related to the enhanced intermolecular hydrogen transfer

and some complex secondary reactions, which is also consistent with the former conclusions.

As observed from Table 7, under the experimental conditions of series B and C, the sediment (yellow material) yields from the mild cracking of the LDPE are much higher than those from the mild cracking of the LDPE/PP mixture and PP. In addition, further sediment for LDPE mild cracking are liquid at 80 °C, showing that there are mainly the long-chain hydrocarbons. As shown from Figure 6, under the experimental conditions of series D (from 70 to 130 min), the sediment yields from the mild cracking of the 50/50 LDPE/PP are much lower than those from the mild cracking of the LDPE and also lower than half of those obtained from the mild cracking of the LDPE, indicating that a great reduction in molecular weight occurs, because of the interaction between LDPE and PP. Furthermore, the sediment yields from the mild cracking of the LDPE decrease as the cracking time increases, while the sediment yields from the mild cracking of the 50/50 LDPE/PP first decrease and then increase as the cracking time increases; these results indicate that (i) the liquid products from the mild cracking of the LDPE still consist of some long-chain aliphatic hydrocarbons and (ii) there are some secondary reactions responsible for the formation of heavier compounds in the longer cracking time (from 110 min to 170 min) in the case of the mild cracking of 50/50 LDPE/PP.

3.4. On the Interaction between PP and LDPE. The degradation mechanism of PE and PP are radical chain mechanisms,[32] which includes chain initiation, chain propagation, and chain termination, and the rate-determining step is the initiation.[10] Chain initiation occurs by C–C homolytic chain scission in the polymer backbone to form primary radicals (R_p) (for LDPE or PP) or secondary radicals (R_s) (for PP) at random positions.[33] In the propagation steps, radicals have several competitive fates: intermolecular hydrogen transfer to form alkane and secondary or ternary radicals, β-scission of radicals to form ethene or propene and smaller radicals, and intramolecular hydrogen transfer to form secondary or ternary radicals. Levine et al.[34] indicated that intermolecular hydrogen

A---chain initiation
B---β-scission
C---intramolecular hydrogen transfer
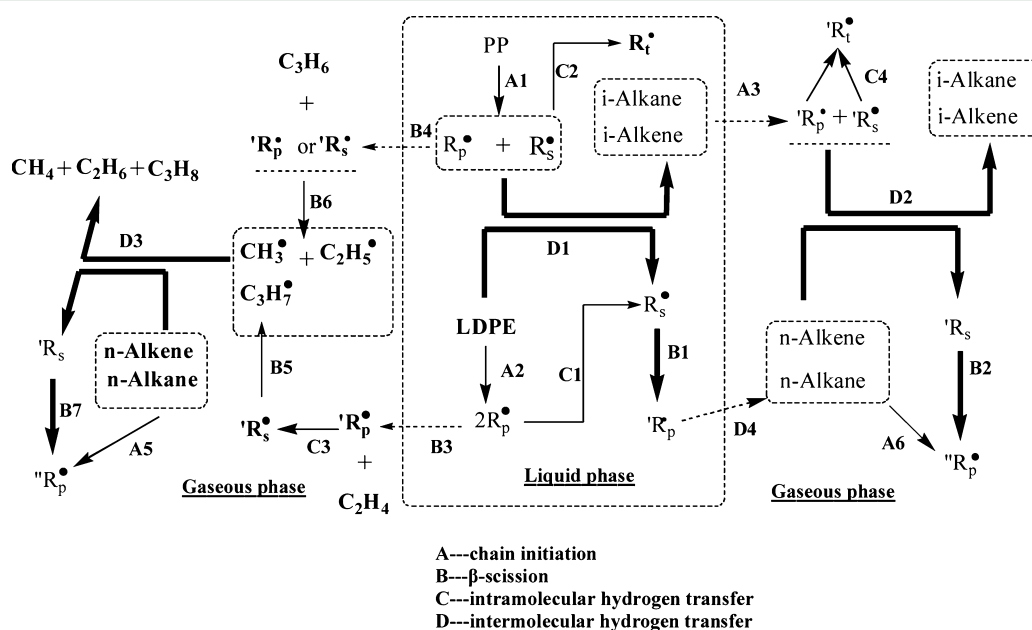D---intermolecular hydrogen transfer

Figure 7. Proposed interaction scheme by enhanced intermolecular hydrogen transfer.

transfer is a more dominant reaction than intramolecular hydrogen shift for end-chain radicals in HDPE pyrolysis. For PP degradation, because of the low alkane concentration, in contrast to the polyethylene degradation, transfer reactions seem to play a minor role.[10]

In this study, the LDPE/PP mixture is mildly cracked for a longer time in a closed-batch reactor, so the interaction between PP and LDPE involving the intermolecular hydrogen transfer relates not only to the chain initiation, but also to the chain propagation process. Furthermore, this interaction occurs not only in the liquid phase, but also in the gaseous phase. That is to say, the intermolecular hydrogen transfer is greatly enhanced in this study. Figure 7 shows the interaction mechanistic model proposed, which considers only the main reactions (chain initiation, intermolecular hydrogen transfer, intramolecular hydrogen transfer, and β-scission) in order to evaluate the interaction between PP and LDPE.

Many studies show that the apparent energy of activation for PP thermal cracking is lower than that for PE thermal cracking.[10,16] Therefore, the thermal degradation of PP starts at relatively low temperatures, compared to that of LDPE. As shown in Figure 7, at lower temperatures (such as 400 °C in this study), there are more radicals from the thermal degradation of PP (feature A1 in Figure 7) than from the thermal degradation of PE (feature A2 in Figure 7) in the initiation process. The decomposition of PP provides LDPE with more radicals (R_p or R_s), and after intermolecular hydrogen transfer from the LDPE and a β-scission, respectively (features D1 and B1 in Figure 7), the reaction path of the decomposition of LDPE is taken. Therefore, chain transfer reactions with R_p or R_s can enhance the initiation reaction of LDPE degradation—the homolytic chain scission with its high apparent activation energy.

When the radicals (R_p or R_s) from thermal degradation of PP abstract hydrogen from LDPE or their cracked products (D1, D2, and so on in Figure 7), they can form i-alkanes or i-alkenes, while LDPE and their cracked products degrade to form shorter-chain n-alkanes/n-alkenes by β-scission, followed by intermolecular hydrogen transfer (for example, see features B1 and D4 in Figure 7). The C—C bond energy of i-alkanes/i-alkenes is often lower than that of C—C bond of n-alkanes/n-alkenes with the same carbon number, which leads to a more likely probability for bond breakage for i-alkanes/i-alkenes (such as feature A3 in Figure 7). At the same time, the hydrogen on the different carbon is captured in the following rank/order (from easy to difficult): tertiary carbon > secondary carbon > primary carbon. Contrast to PP/its cracked products (mainly i-alkanes or i-alkenes), LDPE/its cracked products (mainly n-alkanes or n-alkenes) provides more secondary hydrogen and makes the intermolecular hydrogen transfer easier (see features D2 and D3 in Figure 7). Therefore, it is considered that, in the mild cracking of the LDPE/PP mixture, with longer cracking time, PP/its cracked products provide a greater probability for bond breaking/more radicals, while PE/its cracked products provide more secondary hydrogen, and the combination of these two factors enhance the intermolecular hydrogen transfer. As shown in Figure 7, sufficient intermolecular hydrogen transfer (feature D3 in Figure 7) enhances the formation of methane/ethane/propane from corresponding radicals in the mild cracking of the LDPE/PP mixture, which is accordance with the results given in section 3.2.

In addition, intermolecular hydrogen transfer (see features D1 and D2 in Figure 7) often results in alkanes/alkenes and new secondary radicals. Subsequent β-scission (features B1 and B2 in Figure 7) of the secondary radical further leads to alkene and primary radical. Therefore, enhanced intermolecular hydrogen transfer contributes to more alkene formation and enhanced molecular weight reduction, which are in agreement with the results given in sections 3.3.1, 3.3.3, and 3.3.5.

There are also many studies involving the kinetics of the decomposition of polyolefins, and some kinetic mechanisms of neat PP, PE, or their mixture pyrolysis have been proposed in recent years.[35,36] Figure 8 shows two kinetic schemes proposed
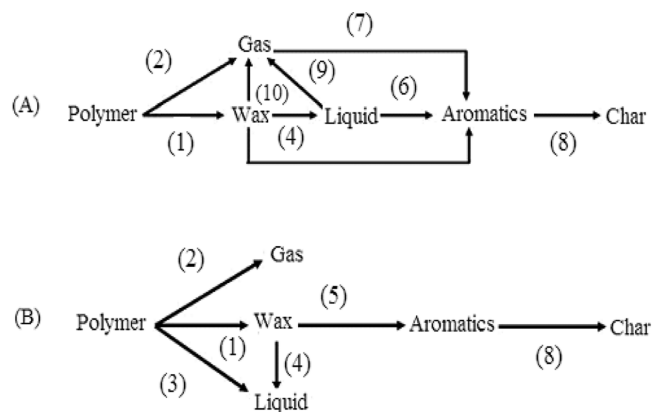

Figure 8. Proposed kinetic scheme by (A) Onwudili et al.[25] and (B) Elordi et al.[36]

by Onwudili et al.[25] (Figure 8A) and Elordi et al.[37] (Figure 8B). These mechanisms proposed are in agreement with the deductions from our former study and also are used to analyze the interaction between PP and LDPE in this study.

In this work, the polyolefins were mildly cracked in a closed-batch reactor with long reaction time, where the reactions occurred not only in the liquid phase but also in the gaseous phase. According to the conclusions obtained from the former part and other studies,[16] the presence of PP in the LDPE/PP can increase the LDPE degradation, which increases the speed of reactions (1) and (4) in Figure 8, which leads to low-viscosity liquid products at lower temperature and is useful for the polymer pyrolysis or cracking. When the mass ratio of PP is ≥50%, more alkane gas (such as methane, ethane, and propane) are also produced, because of intermolecular hydrogen transfer between LDPE and PP, and that accelerates reactions (2), (9), or (10) in Figure 8. Furthermore, when the mass ratio of PP is equal to 70%, more aromatics are formed in the liquid products, by unimolecular cyclation reactions followed by dehydrogenation, or by Diels—Alder reactions, which increases reaction (5) or (6) in Figure 8, and then reaction (8) in Figure 8 can also be improved, which are disadvantageous for the mild cracking.

4. CONCLUSIONS

This work has investigated the interactions of LDPE and PP during mild cracking of polyolefin mixtures. The results indicate that a significant interaction can be observed when the mass fraction of PP is more than 30 wt %. Furthermore, different proportions of PP in the LDPE/PP mixture give different interaction effects. The 70/30 LDPE/PP mixture starts to give a viscosity-reducing effect and can degrade at lower temper-

ature; the 50/50 LDPE/PP mixture gives higher yields of gaseous products (specifically, higher methane, ethane, and propane yields); and the 70/30 LDPE/PP forms more aromatics in the liquid products. The synergetic effect of LDPE and PP is related not only to the mass fraction of PP, but also to the reaction time.

The interactions mechanism are related to intermolecular hydrogen transfer between LDPE/its cracked products and PP/its cracking products, and such intermolecular hydrogen transfer occurs not only in the liquid phase but also in the gaseous phase, because of the long cracking time in the closed-batch reactor, where (i) PP/its cracked products provide more radicals, (ii) PE/its cracked products provide more secondary hydrogen for intermolecular hydrogen transfer, and (iii) the combination of these two factors enhances the chain breakage. That is to say, the intermolecular hydrogen transfer is greatly enhanced in this study. This study also indicates that the LDPE/PP mixture increases the formation of aromatics mainly by increasing olefinic content, because of the greater number of β-scission reactions in the mild cracking of the LDPE/PP mixture. The synergistic effect in this work is quite complex and is related not only to the intermolecular radical transfer by hydrogen abstraction but also to the complex secondary reactions. Intermolecular hydrogen transfer increases the amount of gaseous products and enhances the chain breakage, while complex secondary reactions of the cracked products from LDPE/PP increase the aromatics and then char. Hence, utilization of the mixed polyolefin without a need for further separation is desirable in the practical polyolefin recovery and recycling. The effect of PP in the LDPE/PP mixture may decrease the cracking temperature and the viscosity of liquid product significantly; at the same time, it is possible to reduce the disadvantaged interactions by reducing the reaction time.

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The authors declare no competing financial interest.

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