The Effect of Short-Chain Branching on the Thermolysis/Reactive Distillation of Polyethylene

W. C. MCCAFFREY,* D. G. COOPER, M. R. KAMAL

Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Canada H3A 2B2

ABSTRACT: Thermolysis, coupled with reactive distillation, was investigated as a process to convert waste olefin-based polymers into value-added products. The degradation of two types of polyethylene, linear low and high density, was investigated. The initial molecular structure of the polymer was found to have a large effect on the rate of molecular weight reduction. The linear low-density polyethylene started to produce volatile products earlier and at a faster rate than the high-density polyethylene. Preferential scission of the side branches from the linear low-density polymer backbone was shown to be one of the first steps of the degradation mechanism. Once the branches were stripped from the linear low-density polyethylene, the degradation products were similar to those produced from high-density polyethylene. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1415–1421, 1999

Key words: short-chain branching; thermolysis/reactive distillation; polyethylene

INTRODUCTION

Tertiary recycling of waste polymers into monomers, chemical feed stocks, fuel, or other value-added products is an attractive alternative to landfilling and incineration. Thermal or catalytic processes are commonly used to achieve this conversion, with each process yielding different types of products. Gasoline-type products with a high degree of branching and aromiticity can be generated by the thermocatalytic treatment of waste polyethylene.[1,2] High severity or ultrapyrolysis of waste polyethylene results in the production of short-chain olefins (C_1 to C_4) and some aromatics.[3] Low-temperature pyrolysis or thermolysis of waste polyethylene has been studied extensively,

and has been shown to yield three main fractions: a gas, a condensable fraction, and a waxy fraction.[4–6] The formation of the waxy fraction was later shown to be unavoidable in systems in which the volatile products were immediately removed from the reactor. Linear alkanes as large as C_{94} have been observed to vaporize without decomposition.[7] Thermolysis coupled with reactive distillation can convert waste polyethylene into condensable liquid products with high yields and suppress the production of the waxy fraction. The main products from thermolysis/reactive distillation are primarily α-olefins (43 mol %) and normal alkanes with an average chain length of approximately 14 carbons.[8] These products have the potential to be used as a feedstock for the production of synthetic lubricants or as monomers.[9]

The initial structure of the starting polymer has an important effect on the mechanism and rate of degradation.[10] Pyrolysis-Gas Chromatographic analysis is a useful tool to investigate sequence length and chain branching in polyethylene.[11,12] The kinetics of degradation of branched

polymers in the thermobalance were shown to be different than those for strictly linear polyethylene.[4] Pyrolysis of branched polyethylenes in a fluidized sand bed reactor showed that both the aromatic production and the rate of degradation increased with branching concentration.[13] An interesting characteristic of the lower temperature thermolysis/reactive distillation process is that the condensed products from the reaction are mainly straight-chain alkanes and alkenes, regardless of the structure of the polyethylene feed. Both linear low-density, a highly branched polymer, and high-density polyethylene, a linear polymer, produce the same types of condensable liquid products despite the difference in initial molecular structure of the two polymers.[14] As a result, analysis of the global weight loss and characterization of the liquid fraction were not sufficient to determine the degradation reaction mechanism. No previous studies have focused on characterizing the chemical changes that occur during the early stages of thermolysis. This study probes the mechanism further through the characterization of the polymer melt during reaction, by FTIR, and off-gas analysis.

MATERIALS AND METHODS

Polymers

All of the polymers that were used in this study were available commercially, and were used as received. The linear low-density polyethylene used in this study, SCLAIR 8111, was supplied in powder form by DuPont Canada Ltd. The number-average molecular weight was 17,000, and the polydispersity was 2.97. The high-density polyethylene, SCLAIR 2908, was also supplied in powdered form by DuPont Canada Ltd., and had a number-average molecular weight of 22,300 and a polydispersity of 3.33. Technical grade nitrogen was supplied by MEGGS.

Apparatus

The thermolysis/reactive distillation reaction system used for all of the experiments was a bench-scale apparatus, and was configured as described in detail previously.[14] The apparatus consisted of a 500-mL kettle-type reactor that was surrounded with a heating mantle and continuously purged with nitrogen. Volatile products were passed through a plain distillation column before collec-

tion. Experiments were conducted in a semibatch manner with a 200-g charge of polymer to the reactor and continuous collection of products. Prior to the start of heating, the reactor was purged with nitrogen for 30 min to remove oxygen.

Product Composition

Liquid samples were characterized by gas chromatography, a Hewlett Packard 5890 Series II with a flame ionization detector (FID), and a 30 m × 0.53-mm thin-film HP1 capillary column. Gas samples were characterized using a 30 m × 0.53-mm thick film column, DB1 from Chromatographic Specialists. The peaks were identified by comparison of the retention times with those of known standards. An indirect measurement of the CH_2:CH_3 ratio was determined by Fourier Transform Infrared Spectroscopy, FTIR, Nicolet Magna FTIR, and a diffuse reflectance sample holder. To analyze the nonvolatile products from HDPE and LLDPE by FTIR, a diffuse reflectance technique was utilized. Hard samples were abraded with sandpaper, which was then placed in the sample compartment. The small amount of sample that adhered to the sandpaper was sufficient to provide a spectrum. By comparing the sample with a blank piece of sandpaper, the nonvolatile residue could be analyzed. The major limitation of this technique was that only samples hard enough to be abraded by the sandpaper could be analyzed. This limitation could be relaxed somewhat for the slightly softer samples by freezing the sample and the paper prior to sanding. Any waxy sample that did not smear on the sandpaper, or that was not melted by the heat of the IR laser beam, could be analyzed by this technique.

RESULTS

Yield of Liquid Products

The total yields of product fractions from both HDPE and LLDPE from thermolysis/reactive distillation at 440°C after 120 min of reaction are presented in Table I. Yields of the liquid fraction for both polymers vs. reaction time are shown in Figure 1. The reaction time includes the time to heat the polymer melt from ambient to reaction temperature. The total heat-up time for the reactor was 20 min to 350°C and 35 min to reach a

Table I   Product Yields from Thermolysis/Reactive Distillation of Polyethylene

Polyethylene Type	% Yield		
	Gas	Liquid	Residue
HDPE	10.4	77.5	12.4
LLDPE	7.6	85.8	6.6

Reaction temperature: 440°C.

temperature of 440°C. A significant production of condensable liquid product started at approximately 40 min for LLDPE and at approximately 50 min for HDPE.

Analysis of Gas Products

To follow the production of the various noncondensable gaseous components during the reaction, instantaneous samples of the exit gas stream from the condenser were taken at intervals throughout the experiments via a gas-tight syringe. Gas samples were then immediately injected into the gas chromatograph. A distribution of aliphatic products was observed, which ranged from C_1 to C_9. The peaks were identified by comparing the retention times with those from a mixed standard gas. All of the chromatograms that were collected were similar to that presented in Figure 2. Data collected from both LLDPE and HDPE at times of 30 and 120 min are summarized in Figures 3 and 4, respectively. Notably, for

Figure 2   Gas chromatogram of the noncondensable fraction obtained from LLDPE at 30 min.

LLDPE at 30 min, there was a predominance of ethane when compared to the other chain-length species. At 120 min, the distribution of aliphatics for both LLDPE and HPDE appeared normal, with an average chain length of three carbon atoms.

Analysis of Residue

Analysis of the nonvolatile reaction products from linear low-density polyethylene was difficult because the samples tended to be solid. It was possible to obtain good FTIR spectra (e.g., Fig. 5). Small samples were removed from the reactor during the course of an experiment, cooled, and then analyzed. The absorbance spectrum obtained from a sample of nonvolatile residue from the thermolysis of LLDPE can, typically, be divided into three broad bands: C—H stretching from 2800 to 3300 cm^{-1}; C—H bending from 1350 to 1470 cm^{-1}; and C—H rocking at 650 to 1000 cm^{-1} (Fig. 5). The region that was found to be the most useful in this study was the absorbance associated with the C—H bending. LLDPE can be characterized qualitatively using the methyl deformation band at approximately 1378 cm^{-1}. In this region, however, it is not possible to easily

Figure 1   Cumulative yield of the condensable liquid product from the thermolysis of (a) HDPE, and (b) LLDPE at 440°C.

Figure 3 Distribution in chain length of the gas product from (a) HDPE and (b) LLDPE at 30 min. The datum at each carbon number includes both the alkane and the alkene.

differentiate absorption associated with short-chain branching from end groups.[15,16] Methylene groups have a characteristic infrared absorption at approximately 1470 cm^{-1}. The variation in the ratios of the peak area at 1470 cm^{-1} (CH$_2$) to 1378 cm^{-1} (CH$_3$) of the nonvolatile residue with time for reactions of HDPE and LLDPE as determined by FTIR are presented in Figures 6 and 7, respectively. The data at time zero were obtained from diffuse reflectance FTIR analysis of the virgin HDPE and LLDPE polymers.

DISCUSSION

In previous publications we have reported that thermolysis coupled with reactive distillation of linear low-density polyethylene produced high yields of liquid hydrocarbons ranging from C$_6$ to C$_{30}$ with an average chain length of 13.6 carbons.[8] Interestingly, while the liquid yield from HDPE was lower than from LLDPE, as seen in Table I, the gas yield was higher. The rate of production of these condensable hydrocarbons was consider-

ably higher for the thermolysis of LLDPE than for HDPE (Fig. 1). The LLDPE used in this study was a copolymer of ethylene and butene, and had a high concentration of ethyl branches. HDPE, conversely, is essentially a linear polymer. Other researchers have observed similar effects when comparing the rates of degradation of low-density polyethylene (LDPE) and strictly linear polymers. Differences in the rates of degradation of different types of polyethylene were attributed to the variability in the amount of branching and the degree of crystallinity.[4,17] Crystallinity, which is influenced by the length of linear sequences in the polymer backbone, was shown to enhance the stability of the polyethylene. Less crystalline, or more highly branched polymers, were observed to be less stable to degradation.

Although the rate of liquid production was higher for the thermolysis of LLDPE than for HDPE, as shown in Figure 1, the compositions of the liquid products from the two polymers were essentially identical.[8] This is consistent with the

Figure 4 Distribution in chain length of the gas product from (a) HDPE and (b) LLDEP at 120 min. The datum at each carbon number includes both the alkane and the alkene.

Figure 5 Diffuse reflectance FTIR spectrum of the residue obtained from LLDPE at 440°C.

observation that the volatile degradation products from low- and linear low-density polyethylene were primarily linear alkanes and alkenes.[18] At first, this is surprising because the starting polymer was highly branched. Cleavage probabilities, however, in carbon–carbon bonds are dramatically altered by the presence of tertiary carbons. Figure 8 shows the sites of equal reactivity in a LLDPE molecule. Bonds α to the tertiary carbon have a higher probability of scission, and thus branched polymers have a higher rate of

Figure 6 Change in the ratio of absorbance at 1470 cm^{-1} to the absorbance at 1378^{-1} of the residue from the thermolysis of HDPE at 440°C. This is equivalant to the ratio of —CH_2— to —CH_3 functional groups.

Figure 7 Change in the ratio of absorbance at 1470 cm^{-1} to the absorbance at 1378 cm^{-1} of the residue from the thermolysis of LLDPE at 440°C. This is equivalent to the ratio of —CH_2— to —CH_3 functional groups.

initiation. The probability of β-cleavage has been shown experimentally to be approximately equal to α-cleavage.[11] Bonds that have a position σ to the tertiary carbon are considered to have a reduced probability of scission. Scission at the branch points at the α position is the only possible mechanism to produce linear reaction products. This is further supported because free radical-induced rearrangements are relatively rare. Unlike carbenium ion reactions, hydrogen and alkyl branches cannot undergo 1,2-migration in free radical reactions. Therefore, from these observations, it is proposed that the mechanism of thermolysis is a combination of random C—C bond scission and a preferential removal of the branches via α-scission.

To follow the reduction in the degree of branching, the nonvolatile residue was analyzed. From the theory of random degradation it would be expected that the molecular weight would be reduced significantly before appreciable weight loss

Figure 8 Bonds adjacent to ethyl branches that are susceptible to random cleavage. Relative degree of reactivity is: $\alpha \simeq \beta > \sigma$.

was detectable.[19] To follow the effects of thermolysis on the structure of the polymer, changes in the composition of the melt were followed by measuring the overall $CH_2 : CH_3$. For linear polyethylene such as HDPE, the $CH_2 : CH_3$ ratio should be proportional to the molecular weight of the polymer.[20] Through FTIR analysis of samples of the polymer melt taken during an experiment, the ratio of $CH_2 : CH_3$ was observed to behave as expected and to decrease with reaction time (Fig. 6). This observation is consistent with other observations of molecular weight reduction reported for the degradation of polyethylene, as followed by intrinsic viscosity.[18]

Experiments using LLDPE were also analyzed using the same analytical method as was used for the HDPE. One of the difficulties in using FTIR for LLDPE is that end groups and branches both have adsorption in the range of 1378 cm^{-1}. This was not expected to be a problem, however, because it had been reported that the scission of short branches from the backbone could be considered negligible.[11]

In the experiments conducted with LLDPE, the ratio of $CH_2 : CH_3$ did not decrease, as would have been predicted from the experiments with HPDE. Although the ratio for HDPE was observed to steadily decrease, the ratio for LLDPE initially increased to a maximum before decreasing (Fig. 7). It is important to point out that the majority of these structural changes were occurring in the polyethylene prior to significant weight loss. The observed increase in the $CH_2 : CH_3$ ratio could be caused by preferential scission of side chains from the polymer backbone. The side chains in the LLDPE, which were used for the experiments, were ethyl groups. If the initial mechanism of degradation was scission of the side branches, one CH_3 and one CH_2 group would be removed from the polymer for each scission. Because there were many more CH_2 than CH_3 functional groups, the loss of one of each group would cause the $CH_2 : CH_3$ ratio to increase. This observation of side-branch scission should also have significant implications for the melt processing of polyethylene, because changes in the $CH_2 : CH_3$ ratio were observed even during the heat up of the reactor. Degradation during repeated melt processing and extrusion is a major concern for the plastics recycling industry.[21,22]

If the branches were preferentially removed, then traces of the branches should be measurable in the off-gas from the reactor. In fact, this effect was observed during the early stages of the thermolysis of LLDPE [Fig. 3(b)]. At 30 min of reaction, a significantly larger amount of ethane was measure in the off-gas from LLDPE than from HDPE thermolysis (Fig. 3). Again, it should be noted that the light gas fraction was measured well before any significant weight loss was measured from the polymer melt.

The cleavage of two-carbon atom branches from the polymer backbone appears to be primarily characteristic of large-scale experiments. Although the cleavage of the side chains from the polymer backbone has been reported for long branches, it was considered negligible for short-chain branches.[11] However, this observation was based on pyrolysis GC experiments that used extremely small sample sizes, on the order of micrograms of polymer. The discrepancy may also be attributed to the differences between residence times in the two reactors. Pyrolysis GC involves a very short residence time when compared to conventional thermolysis.[23]

Although the branches are being stripped from the backbone of the polymer, a slower process of random scission also takes place. Such a process is similar to the one responsible for molecular weight reduction of the linear HDPE. Thus, for branched polyethylene, there are two competing mechanisms: the stripping of branches causes the $CH_2 : CH_3$ ratio to increase, and the random scission of the backbone, which would cause the ratio to decrease. An inspection of the bond dissociation energies confirms that random bond scission (87 kcal/mol) would be slower than the removal of an alkyl branch (80 kcal/mol).[24]

The maximum in the $CH_2 : CH_3$ ratio observed for the experiments with linear low-density polyethylene at 440°C occurs because there is a finite number of branches in the initial polymer charge to the reactor. The effect of stripping the branches on the $CH_2 : CH_3$ ratio decreases with time, as all of the branches would eventually be removed. As predicted, when the off-gas was analyzed after a long reaction time (after reacting for 120 min) no difference was observable between the distributions of the gaseous products obtained from the linear polymer [Fig. 3(a)], and those obtained from the branched polymer [Fig. 4(b)]. Because the slower random scission and eventually the faster free radical transfer processes continue well after all of the branches are removed, the $CH_2 : CH_3$ ratio would eventually decrease.

Small but significant amounts of internal olefins and 1,1-disubstituted olefins were detected in the liquid produced from the thermolysis of

Figure 9   Reactive bonds in the position β to a radical on a tertiary carbon.

LLDPE.[8] Although scission of the bond α to the tertiary carbon is considered to be the initial mechanism for the degradation of branched polyethylene, other possibilities exist. Radicals will preferentially abstract the hydrogen on the tertiary carbon. A radical on the tertiary carbon weakens the bonds in the β position leading to a higher frequency of scission of these bonds (Fig. 9). This may explain the higher concentration of methane produced from LLDPE than from HDPE after 30 min of reaction (Fig. 3).

CONCLUSION

Significant changes occurred in the structure of LLDPE and HPDE during thermal treatment, well before any weight loss was detectable. Due to a higher concentration of tertiary carbons, LLDPE is much less stable to initial degradation than the more linear polymer. The major mode of reaction was the scission of branches from the polymer backbone. After stripping of the branches, the mechanism for LLDPE was the same for HDPE. This has significant implications for the processing of LLDPE, especially during secondary type recycling. For a tertiary recycling process, such as thermolysis coupled with reactive distillation, the thermolysis process can handle mixtures of the various types of polyethylenes without adversely impacting the overall quality of liquid reaction products, because branched polyethylene yields the same types of products as linear polyethylenes. Although crosslinked polyethylene was not evaluated in this study, it should yield similar results, because its behavior is comparable to that observed for the branched polyethylene.

REFERENCES

1. Songip, A. R.; Masuda, T.; Kuwahara, H.; Hashimoto, K. Energy Fuels 1994, 8, 136.
2. Shabtai, J.; Xiao, X.; Zmierczak, W. Energy Fuels 1997, 11, 76.
3. Lovett, S.; Berruti, F.; Behie, L. A. Ind Eng Chem Res 1997, 36, 4436.
4. Wall, L. A.; Madorsky, S. L.; Brown, D. W.; Straus, D.; Shima, R. J Am Chem Soc 1954, 76, 3430.
5. Madorsky, S. L.; Straus, S.; Thompson, D.; Williamson, L. J Polym Sci 1949, IV, 639.
6. Jellinek, H. H. G. J Polym Sci 1949, IV, 13.
7. Wall, L. A.; Flynn, J. H.; Straus, S. J Phys Chem 1970, 74, 3237.
8. McCaffrey, W. C.; Kamal, M. R.; Cooper, D. G. Polym Degrad Stabil 1995, 47, 133.
9. Deak, Gy.; Bartha, L. J Synth Lubr 1991, 8, 221.
10. Madorsky, S. L.; Straus, S. J Res Natl Bur Stand 1954, 53, 361.
11. Seeger, M.; Barrall, E. M. J Polym Sci Polym Chem Ed 1975, 13, 1515.
12. Michajlov, L.; Cantow, H.-J.; Zugenmaier, P. Polymer 1971, 12, 70.
13. Conesa, J.A.; Font, R.; Marcilla, A. Energy Fuels 1997, 11, 126.
14. McCaffrey, W. C.; Kamal, M. R.; Cooper, D. G. Polym Degrad Stabil 1998, to appear.
15. Blitz, J. P.; McFaddin, D. C. J Appl Polym Sci 1994, 51, 13.
16. Slowinski, E. J.; Walter, H.; Miller, R. L. J Polym Sci 1956, XIX, 353.
17. Igarashi, S.; Kambe, H. Bull Chem Soc Jpn 1963, 37, 176.
18. Oakes, W. G.; Richards, R. B. J Chem Soc 1949, 2929.
19. Simha, R.; Wall, L. A.; Bram, J. J Chem Phys 1958, 28, 894.
20. Lissac, P.; Berticat, P.; Phan-Quang-Tho, X. J Macromol Sci Chem 1971, A5, 901.
21. Hinsken, H.; Moss, S.; Pauquet, J.-R., Zweifel, H. Polym Degrad Stabil 1991, 34, 279.
22. El'darov, E. G.; Gol'dberg, V. M.; Zaikov, G. E. Polym Degrad Stabil 1986, 16, 291.
23. Lehrle, R. S.; Robb, J. C. J Gas Chromatography 1967, 89.
24. Benson, S. W. J Chem Educ 1965, 42, 502.