Characterization of Structure of Comblike Polymer by Pyrolysis Gas Chromatography and Fourier Transform Infrared Spectroscopy

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ABSTRACT: The characterization of branching in comblike polymers using high-resolution pyrolysis gas chromatography (HRPGC) and Fourier transform infrared spectroscopy (FTIR) is investigated. The branching type can be identified from characteristic peaks of monomer and a group of dimers in pyrograms derived from α- and β-scission of branched atoms. By resolving the overlapping bands between 2800–3000 cm^{-1}, the relative absorbance of CH$_2$ can be used to calculate the average branch length L. This method is helpful in evaluating the property of drag-reduction agents. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 359–363, 2001

Key words: comblike polymer; branch; HRPGC; FTIR

INTRODUCTION

The length and distribution of branches have a substantial effect on the physical properties of polyethylene, such as density, rigidity, hardness, gas permeability, and crystallinity. Because of the commercial importance of these polymers, many workers have undertaken studies to investigate the short or long chain branch in polyethylene and its copolymers with other α-olefins containing 4–8 carbon atoms, which contain a few branches attached to the main chain. Infrared (IR) spectroscopy and ^{13}C-nuclear magnetic resonance (NMR) spectroscopy have been commonly applied to identify and quantify branch type,[1–3] and, recently, pyrolysis–hydrogenation gas chromatography (PHGC) has been proved to be an effective way to characterize short branch of polyolefins.[4,5]

During the late 1960s, polymer served as a draw-reduction agent in oil fields has gradually gained attention; the most commonly used draw-reduction agent is now known to be composed of poly-α-olefins, especially their copolymer whose comonomer containing different carbon atoms of 2–20, as well as some additives. Since the length and distribution of branches influence the drag-reduction property greatly, it is important to produce branches under controlled circumstances, analyzing their concentrations and distributions. In these branched polymers, the content of the branch is much higher than that in traditional branched polyethylene. Therefore, work is needed to investigate the possibility and method of characterization of these polymers.

In this work, various model poly-α-olefins and copolymers have been synthesized and analyzed by high-resolution pyrolysis gas chromatography (HRPGC) and infrared spectroscopy, the pyrolysis mechanism of which can be illustrated by HRPGC. The semiquantitative result of the branch can be obtained by IR.
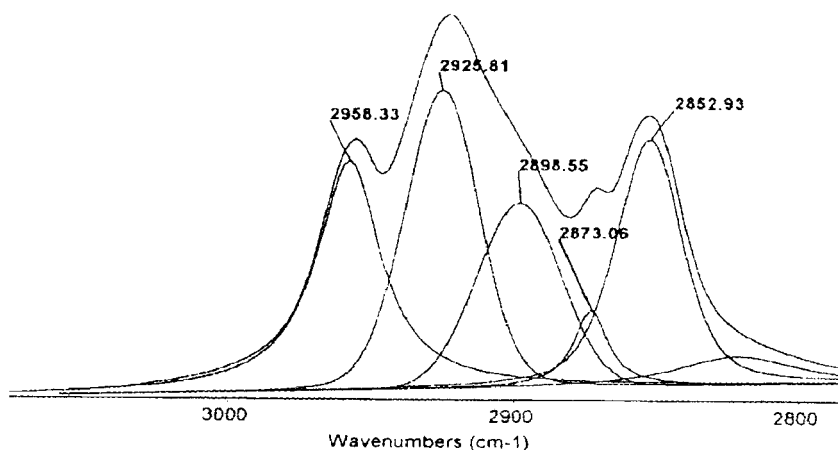
Figure 1 The peak–solve result in C–H vibration zone

EXPERIMENTAL

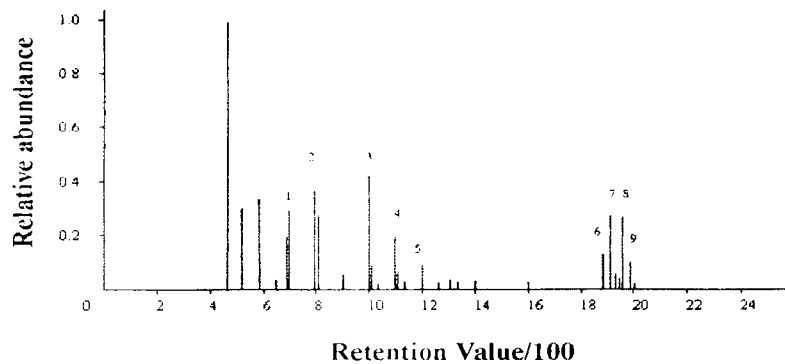### Materials

A series of samples was prepared by bulk polymerization with Ziegler–Natta catalysts at different temperatures and Ti/Al molar ratios. 1-octene, 1-decene and 1-dodecene were used as monomer to synthesize three kinds of polymers with side chain of 6C, 8C, and 10C, respectively. Also, a copolymer of these three monomers was
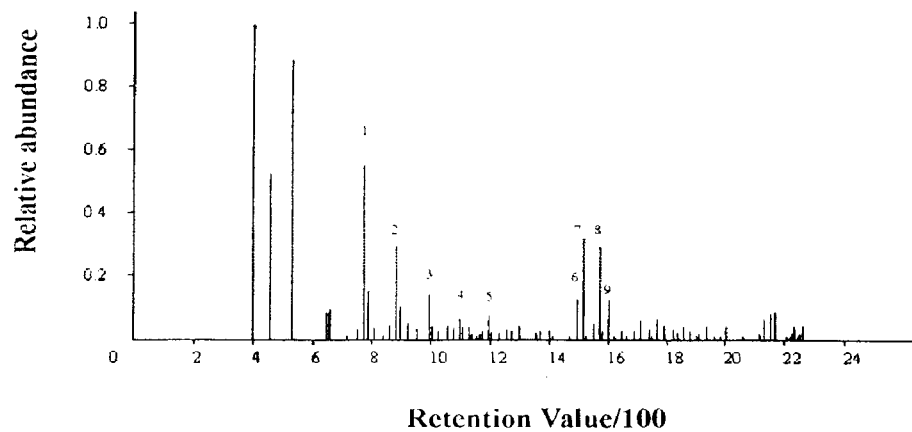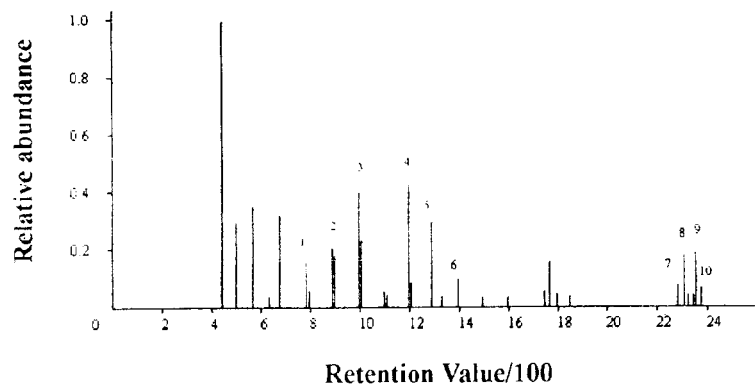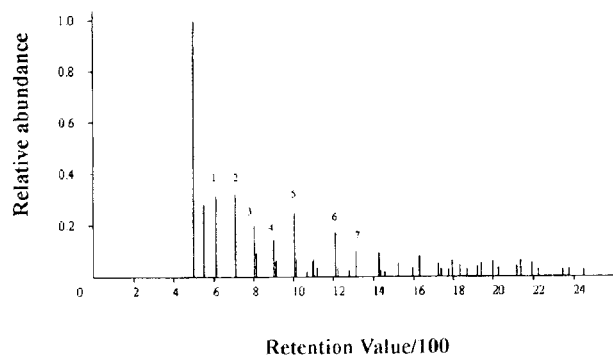

(a)

(b)

Figure 2 Pyrograms of (a) poly(1-octene), (b) poly(1-decene), (c) poly(1-dodecene), and (d) 1-octene-1-decene-1-dodecene terpolymer

(c)

(d)

Figure 2 (*Continued from the previous page*)

synthesized, with a mole ratio of C8:C10:C12 = 2:3:5. According to this initial ratio, we obtained a theoretical average branch length of 8.60. As there should be a branch every two carbon atoms in the backbone, they are called comblike polymers. After polymerization, all the samples were dissolved in heptane and then precipitated by ethanol, the polymer was filtered and washed to

Table I   Possible Fragmentation Products from Poly-α-olefins

Peak No.	Pyrolysates Formed Through Scission in Poly-α-olefins							
	Poly (1-octene)		Poly (1-decene)		Poly (1-dodecene)		Terpolymer	
	RI	Assignments	RI	Assignments	RI	Assignments	RI	Assignments
1	800	n-Octene	700	n-Heptene	800	n-Octene	614	n-Hexene
2	895	n-Nonene	802	n-Octene	900	n-Nonene	709	n-Heptene
3	1000	n-Decene	1005	n-Decene	1001	n-Decene	805	n-Octene
4	1100	n-Undecene	1097	n-Undecene	1202	n-Dodecene	903	n-Nonene
5	1194	n-Dodecene	1201	n-Dodecene	1294	n-Tridecene	1003	n-Decene
6	1494	n-Pentadecene	1891	n-Nonadecene	1400	n-Tetradecene	1210	n-Dodecene
7	1509	n-Pentadecane	1911	n-Nonadecane	2285	n-Tricosene	1311	n-Tridecene
8	1569	Hexadecene[a]	1966	Eicosene[a]	2306	n-Tricosane		
9	1598	Hexadecene[a]	1988	Eicosene[a]	2357	Tetracocene[a]		
10					2377	Tetracocene[a]		

[a] All these pyrolysates have branches, but their structure was not yet certain.

Table II   Relative Absorbance of Standard Polymers

| Sample No.	Poly(1-octene)	Poly(1-decene)	Poly(1-dodecene)	Terpolymer
1	0.978	1.621	1.982	1.670
2	1.112	1.431	1.789	1.576
3	1.077	1.328	—	1.462
4	1.018	—	—	1.614
5	0.901	—	—	1.617
6	1.058	—	—	—
Average:	1.024	1.460	1.885	1.588
Standard deviation:	0.076	0.149	0.136	0.078

remove catalyst residual and unreacted monomer and dried. P1, P2, P3, P4, and P5 are commercial draw-reduction agents, and were also purified as mentioned above to get the main polymer components.

Fourier Transform Infrared Spectroscopy

A Nicolet 560 FTIR spectrometer was used to collect transmission spectra of samples, with resolution of 4 cm^{-1}. Films of samples were directly placed on the holder; spectra were acquired by collecting and averaging 32 scans. In the region of 3000–2850 cm^{-1} peaks, which were assigned to the C—H stretch vibration, peak fitting was used to resolve overlapping bands. There were five peaks in this region: 2958 and 2873 cm^{-1}, assigned to CH_3; 2925 and 2853 cm^{-1}, assigned to CH_2; and 2898 cm^{-1}, assigned to CH (Fig. 1).

High-Resolution Pyrolysis Gas Chromatography

A PYR-2A pyrolyzer was directly attached to a gas chromatography (Shimadzu GC-7A) with a fused-silica capillary column (25 m × 0.25-mm i.d.) coated with OV-101 and FID. The sample
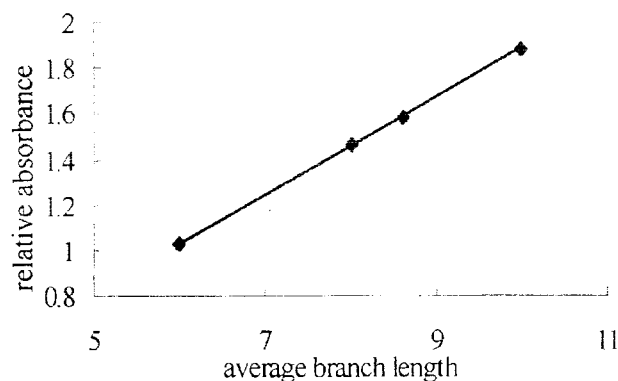
Figure 3   Calibration for average branch length

was pyrolyzed at 600°C, and the column temperature was programmed from 50°C (held for 1 min) to 220°C at a rate of 8°C/min. Here nitrogen was used as carrier gas at a flow rate of 50 mL/min. The peak assignment of pyrograms was carried out by the HRPGC expert system of polymers[6] developed in our group, combined with PGC-MS.

RESULTS AND DISCUSSION

Pyrolysis Mechanism

The pyrograms of poly(1-octene), poly(1-decene), poly(1-dodecene), and 1-octene-1-decene-1-dodecene terpolymer [Fig. 2(a– d)] were obtained by HRPGC. The retention value was expressed with retention index (RI), which can be calculated using Kovat's equation with the conference peaks of pyrolysates of HDPE–a series of n-alkenes.[7] The carbon number of pyrolysate was about equal to the RI value divided by 100. According to the RI value and the result of PGC-MS, there are characteristic dimers of every homopolymer [Fig. 2(a–c)]. In homopolymers, the peaks of monomers are the locally strongest except the small molecules with low boiling point. There are four characteristic peaks in the dimer group; the former two are n-alkylene and n-alkylane with carbon atoms of $2n-1$, and the latter two are branched alkylene with carbon atoms of $2n$. Because 1-octene-1-decene-1-dodecene terpolymer [Fig. 2(d)] was synthesized by three monomers, we were able to find three characteristic monomer peaks. The detailed assignments of main peaks listed in Table I. Using this rule in commercial drag-reduction agents, P1 may very well be composed of 1-nonene and 1-dodecene, with pyrolysates of 17C and 23C, the character of dimers of 1-nonene and 1-dodecene, respectively. The structure of P2 is very

Table III   Average Branch Length of Commercial Drag-Reduction Agent

	P1	P2	P3	P4	P5
Average branch length, L	6.6	7.0	7.5	8.2	6.1
Carbon number of monomer	8–9	~ 9	9–10	10–11	8–9
Drag reduction, %	20.6	28.5	36.0	33.2	—

much like that of P1; the difference may come from the relative content of two monomers, as may be true of P3 as well. P4 is quite different from P1–P3, composed mainly of 1-decene, while P5 is quite like a copolymer of these three monomers.

Density and Length of Branches

By resolving the overlapping bands between 2850–3000 cm^{-1}, the absorbance of each functional group can be measured. The great average molecular weight M_n, which was obtained from the viscometry, is ~1,000,000. Thus, we have good reason to neglect CH$_3$ at two ends of the molecule; at the same time, the longer the branches, the more the relative absorbance of CH$_2$ to CH$_3$, and the ratio of CH$_2$ to CH$_3$ can represent average length of branch L, which corresponds to the carbon number in branch. By calculating the relative absorbance of CH$_2$ (2853 cm^{-1}) to CH$_3$ (2958 cm^{-1}) in poly-α-olefins and terpolymers (Table II), is a calibration line shown in Figure 3. With this calibration line, it is possible to quantitative analyze L of some commercial drag-reduction agents, also, it is possible to choose proper monomer to improve its property. The result is shown in Table III, which is consistent with that of PGC analysis. It shows that drag-reduction agent synthesized by a monomer of C$_{9-11}$ will exhibit good property. It also can be proved by the result that the commercial drag-reduction agents are really copolymers of α-olefins.

CONCLUSIONS

The application of FTIR spectroscopy and HRPGC facilitates analysis of the type and average branch length in comblike polymers. In pyrograms of these polymers, there are characteristic peaks of monomer and dimers, the result of α- and β-scission of polymer chain. The average branch length of comblike polymers can be calculated from the calibration line. The method proposed in this report gives a powerful tool to characterize the structure of branched polymer, which influences the property of drag-reduction agent greatly, also it may be helpful in choosing drag-reduction agents.

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