



A new method for investigation of short-chain branching distribution in polyethylene by combined use of FTIR and TREF

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Qualitative analysis of short-chain branches was carried out on High-Density Polyethylene by Fourier transform infrared spectroscopy. In this work, the copolymer was fractionated according to chemical composition by preparative temperature rising elution fractionation (TREF), and resulting fractions were submitted to FTIR analyses. Fourier self-deconvolution was used to resolve overlapping bands for ethyl, butyl, and isobutyl branches. An infrared spectrophotometer was calibrated for the quantitative determination of butene-1 in copolymers. In this procedure, using calibration derived from analysis 1, butane-ethylene copolymers of known composition (¹³C NMR analysis), the following measurements are performed. The FTIR and NMR data are in qualitative and quantitative agreement. The FTIR technique is less costly and faster than NMR spectroscopy. These results were explained by the existence of a heterogeneous distribution of comonomer molecules. This method eliminates every personal mistake and enables the FTIR technique to determining short chain branching distribution.

According to the results of TREF, low molecular weight fractions at lower temperature and higher molecular weight fractions were isolated at higher temperatures. Also, infrared spectroscopy measurements showed that this technique could separate fractions according to their degree of short chain branching. The low molecular weight segments had more short-chain branching than the higher molecular weight segments.

Keywords: High-Density Polyethylene, short-chain branches, fractionation, temperature rising elution fractionation, Fourier transform infrared.

Introduction

Bimodal HDPE resins benefit from their bimodality by having the strength and stiffness of HDPE, while retaining the high-stress-crack resistance and process ability of a unimodal medium density polyethylene¹.

To reach bimodal high-density polyethylene (HDPE) with broad to extensive molecular-mass distributions, the cascade process is used. The reactors are run in a cascade and at very different process conditions (Fig. 27, bottom in Ref. 2).

In this process, in the first reactor, high amounts of hydrogen are fed with ethylene. This process leads to the formation of low-molecular-mass polyethylene. The second reactor is loaded with much less hydrogen to form a high- or very high-molecular-mass polyethylene².

This process allows further essential product modifications, such as the incorporation of comonomers in the long

polymer chains within the second reactor. This product builds up a polymer alloy with a low-molecular-mass ethylene homo polymer and a high-molecular-mass ethylene-1-alkene copolymer in the solid-state consisting of crystalline regions (crystal lamella) and amorphous regions in between. The low-molecular-mass-homo polyethylene mainly forms the crystalline regions. The high-molecular-mass copolymers form the amorphous regions and act as tie molecules that connect the crystal lamella (Fig. 29 in Ref. 2).

These polymer-blend products as used for drinking-water, sewage, and gas pipe applications. Many investigators have pointed out that the amount and distribution of SCB are significant factors in determining the physical properties of bimodal HDPE resins³⁻⁹.

In order to study the structural heterogeneity of polyolefin, many analytical techniques have been employed. Tempera-

ture rising elution fractionation (TREF), a technique that fractionates semi-crystalline polymers according to their solubility-temperature relationship, has been widely used in the characterization of compositional heterogeneity of polyolefin^{10–12}.

The term “Temperature Rising Elution Fractionation” (TREF) was first applied by Shirayama *et al.* to describe the method used to fractionate low-density polyethylene (LDPE) based on the degree of short-chain branching (SCB)¹³. TREF can be applied in analytical or preparative modes (called A-TREF or P-TREF, respectively)^{14,15}. In a TREF, the eluted solution concentration is continuously monitored by the detector at gradually increased elution temperature. Information on the macromolecular structure is obtained online through the calibration curve. The technique requires smaller columns, smaller sample amounts, and shorter time than P-TREF but generates less information about the polymer microstructure. In P-TREF, a series of fractions are collected at predetermined temperature intervals, and more massive columns and sample amounts are generally used. In this technique, information on the macromolecular structure is obtained offline through further analysis via other techniques. The technique is time-consuming but can generate detailed information on the polymer microstructure¹⁶. The determination of Short Chain Branching Distribution (SCBD) in high-density polyethylene is essential for the relation between the degree of branching and its physical properties. The TREF provides a separation of the polymer into individual fractions based on intermolecular fractionation and chemical composition, which can be analyzed independently by DSC, FT-IR, and NMR. Solvent gradient fractionation (SGF) is suitable for fractionating polyolefin by molecular weight differences^{17–19}. Many publications stress the existence of a link between the way of distribution and the long-term (tens of years) properties. However, because of the meager amount of SCB present in the pipes produced, at the moment, only IR can give correct and quick answers. However, the result is the average SCB content²⁰. Infrared spectroscopic methods have shortcomings in measuring of short-chain branching content. The IR vibrational modes of the methyl group, only that corresponding to deformation near to 1376 cm^{-1} are of interest for a quantitative determination of the methyl group concentration in PE²¹. Since the 1376 cm^{-1} band cannot differentiate short-chain branches from end groups, at low branching levels, correction factors must be used to separate the two²².

Additional complications result because the molar absorptivity of the methyl deformation band varies with short-chain branch length^{23–25} and branch ends²⁶.

Investigation of the physical and mechanical properties of polyethylene performed by Hubert *et al.*³, SCB was determined based on the terminal methyl group in IR, whereas at low concentrations, the difference between the terminal methyl group and the side branch was not possible. The study of the distribution of short-chain branching in low-density polyethylene carried out by Kenzo *et al.* Also the determination of the SCB is in terms of methyl group absorption in IR, which for the samples with molecular weights below 20,000, determination of side branches requires the use of toxic solvents and high temperatures. Satoru Hosoda¹⁷ to determine short chain branching using IR and methyl group adsorption, he used a correction factor formula, which requires the measurement of a number of molecular parameters.

Although FTIR spectroscopy is a relatively fast and straight forward approach, we have undertaken a study to investigate the use of this technique for the qualitative analysis of short-chain branching in polyethylene. The first quantitative method was reported in 1950²⁷, which subsequently evolved into an ASTM standard method²⁸. This research, describes the FTIR technique then estimates a rapid, accurate, and new test scheme that utilizes the TREF method to fractionate polyethylene and the SCB of fractions.

Experimental

A. Material:

PE-100 (ethylene/1-butene copolymer) was an industrial-grade of HDPE (CRP-100, synthesized based on a Ziegler-Natta (Z-N) catalyst, Jam Petrochemical Company, Iran) which was kindly supplied in granular form.

The material used in this study is a type of 1-olefin comonomer from the high-density polymers group, which is an ethylene/1-butene copolymer with a short-chain branch of ethyl, prepared by two reactors with hexane solvent. The density of this polymer is 0.948 and exhibits excellent mechanical properties.

B. Characterization method:

B.1. Preparative temperature rising elution fractionation (P-TREF):

The direct relationship between the crystallization and dissolution temperature with the length of the regular se-

quences within the chain is the basis of the TREF. Thus, if the chains of a polymer can be precipitated or dissolved according to the concentration of the short-chain branches, the desired polymer can be effectively fractionated, and each component analyzed carefully.

P-TREF consisted of a cylindrical column 7 cm in diameter and 40 cm in height. This column was packed with seeds of an average diameter of 0.07 cm and submerged in an oil bath with a programmable thermostat that controlled the temperature of the bath. Fractionations were carried out on about 2 g of sample dissolved in 200 cm³ of xylene at 130°C to make a solution with a concentration of approximately 1 wt%). Ingra NOx 1010 was used as a stabilizer to prevent sample decomposition at high temperatures. Solutions were loaded directly on to the top of a TREF column of packed finely divided silica sand. In each run, a polymer solution heated at 130°C for 2 h and then cooled to room temperature (25°C) slowly at a rate of 2°C/h to crystallize the polymer chains on the seeds. The column was slow cooled overnight to room temperature. After the dissolution of polymer chains by a stream of pure solvent (xylene), the fractions in solvent steam were precipitated. After separation, the prepared fractions were tested by subsequent tests including FTIR

B.2. Fourier transform infrared spectroscopy:

In this paper, the infrared spectroscopic technique has been used to identify ethylene/1-butene copolymer using absorption bands of short-chain branches and comparison with reference spectra.

For FTIR measurement samples were prepared by hot pressing polymer and their fractions between polyester sheets in a mold, at temperatures in the range of 185–200°C, depending on the melting point of the polymer. Samples were pressed for approximately 60–120 s at 10 bar, immediately released the pressure, removed from the pressed and air-cooled to room temperature. In our study, it is desirable to have a film thickness of 0.02–0.05 cm to avoid interference fringes problems. The thicknesses used were the mean of the five measurements.

Infrared spectrophotometer (Bruker-Tensor27) is capable of making the spectrometric measurements that purged with dry nitrogen with a DTGS detector. Typically 32 scans were signal-averaged at 4 cm⁻¹ nominal resolution. Position measurements and band areas were obtained using Nicolet SX software.

The infrared spectrum of the sample versus an air background was obtained between 4500–400 cm⁻¹. The quantitative analysis carried out by performing the calculations described in the following. Interactive subtraction of the reference HDPE spectrum (Fig. 1(a)) from the sample spectrum is performed (Fig. 1 (b))²⁹. Since the use of Ziegler-Natta catalysts almost completely inhibits the occurrence of intra and intermolecular reactions, the presence of short-chain branches was supposed to be a result of the 1-butene comonomer contents.

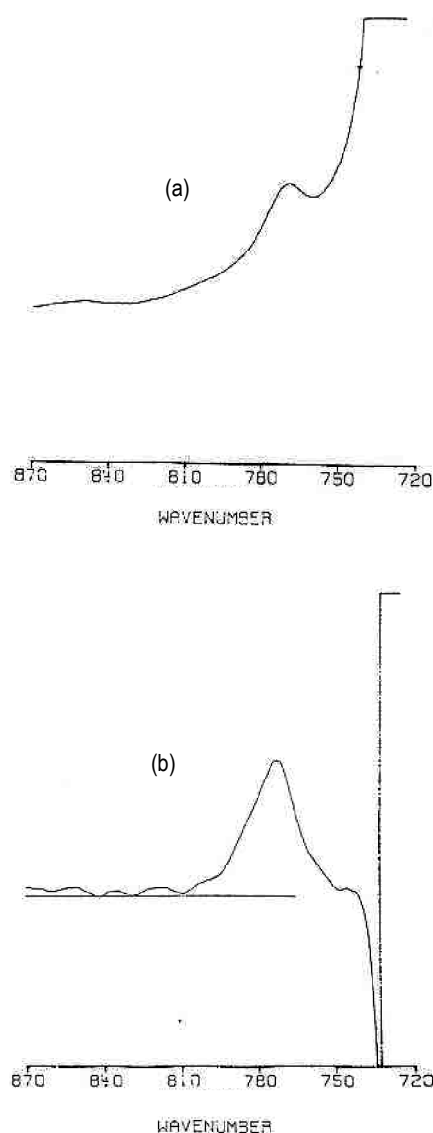


Fig. 1. (a) Spectral range 872–720 cm⁻¹ before subtraction and (b) after subtraction (Horizontal baseline is reported).

Results and discussion

Previous studies on HDPE have investigated the effect of short-chain branching distribution on crystallization rate and mechanical properties. The result of this study showed that placement of the branches on longer molecules reduces the rate of crystallization at high crystallization temperatures, and that SCB on the high-molecular-weight components increases their resistance to crack growth⁴.

Comparison to bimodal and multimodal polyethylene has shown that polycrystalline resins have a very high molecular weight and an extensive, MW distribution. These multimodal resins have a uniform SCB distribution, are highly resistant to crack growth, and have higher toughness than other polyethylene. These results are due to the unusually high MW properties of these products, which make them suitable for PE-100 pipe compared to bimodal resins⁷.

Combined analysis of Size Exclusion Chromatography and infrared spectroscopy short chain branching distribution across molecular weight distribution (MWD) in ethylene/1-olefin copolymers has been investigated. An essential feature of this method is to determine the SCB level in the range of $\pm 0.5/1000\text{C}$ in resins containing ethyl or butyl branch. Using this method, SCB versus MWD profiles can detect changes due to catalyst or process even in HDPE samples⁸.

In another study, an ethylene/1-hexene copolymer synthesized using a metallocene catalyst was analyzed using a cross-fractionation technique. The polymer was first fractionated by solvent gradient fractionation, and the fractions were separated according to short-chain branching differences by temperature gradient fractionation¹⁸.

A. Fractionation results:

The TREF fractions collected at different elution temperatures with enough amounts can be applied in the various analyses. 10 fractions were obtained in TREF fractionation, and a typical analysis of fractional weight with elution temperature is given in Table 1.

This result indicates that, by remaining the system for a more extended period, the molecule's solubilization was favored in the subsequent temperatures. It is found that the low-temperature fraction corresponded to the low average molecular weight segment, and the high-temperature fraction corresponded to the high average molecular weight segment.

Table 1. Fractionation of the PE-100 copolymer

Fraction	Elution temp. (°C)	Weight of fraction (gr)	Weight (%)	$\Delta W/\Delta T$	Cumulative (%)
1	65–75	0.11612	6.152444	0.094653	6.152444
2	75–80	0.15537	8.232047	0.823205	14.38449
3	80–85	0.12698	6.727845	1.345569	21.11234
4	85–88	0.22348	11.84075	2.368151	32.95309
5	88–91	0.17170	9.097267	3.032422	42.05036
6	91–94	0.61963	32.83017	10.94339	74.88052
7	94–97	0.37793	20.02405	6.674685	94.90458
8	97–102	0.06092	3.227755	1.075918	98.13233
9	102–115	0.01380	0.731172	0.146234	98.8635
10	115	0.02145	1.136496	0.087423	100

Weight of samples used: 1.946 g.

The fractions weight distribution curve is shown in Fig. 2. Copolymer molecules being extracted for the most part at approximately 91–94°C.

B. Branching analysis by FTIR:

FTIR is easily applied for obtaining an accurate difference spectrum and is widely used as a rapid analytical tool for peak position. The use of the ethyl deformation band for qualitative analyses of short-chain branching was undertaken. An absorbance attributable to ethyl branches has been previously identified at 770 cm^{-1} ^{30,31}. All Montel laboratories using the subtraction of the reference HDPE spectrum from the sample spectrum will use polymer calibration standards that have been certified by the Ferrara R & D-ARC laboratory. Table 2 displays the values for established reference calibration standards²⁹.

C. Calibration:

Calibration is obtained by analyzing 1-butene-ethylene copolymers of known composition (¹³C NMR analysis) shown in Table 2²⁹.

Hence, the ratio A_{769}/S is derived for each standard, thus a relationship between $C_4\%$ wt. moreover, A_{769}/S has been established as reported in the following equation:

$$C_4\% \text{ wt} = b(A_{769}/S) + c(A_{769}/S)^2 \quad (1)$$

where the numerical coefficient values have been derived by interpolation according to the least square method. For example, the coefficient values determined by "G. Natta" Research Center are the following (Fig. 3):

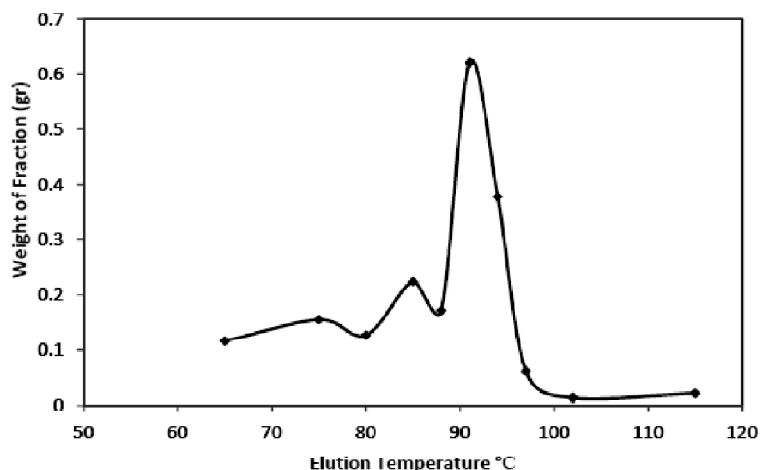


Fig. 2. Weight fraction distribution of PE-100.

Table 2. Reference calibration standards		
Polymer type	Sample name	Sample composition %C4 weight
Ethylene/1-butene	C24/2	3.3
Ethylene/1-butene	C24/4	6.6
Ethylene/1-butene	C24/6	8.5
Ethylene/1-butene	C24/9	11.7
Ethylene/1-butene	C24/11	13.5
Ethylene/1-butene	C24/16	16.5

$$B = 1.546 \quad C = -0.0160$$

Each laboratory should determine its calibration curve. Calibration must be checked at least once a month with at least three standard samples of different composition levels.

Since the occurrence of branches in HDPE, due to chain transfer reactions, is supposed to be inhibited by the catalyst, these ethyl bands can be attributed to the 1-butene groups. Consequently, these bands can be used to measure

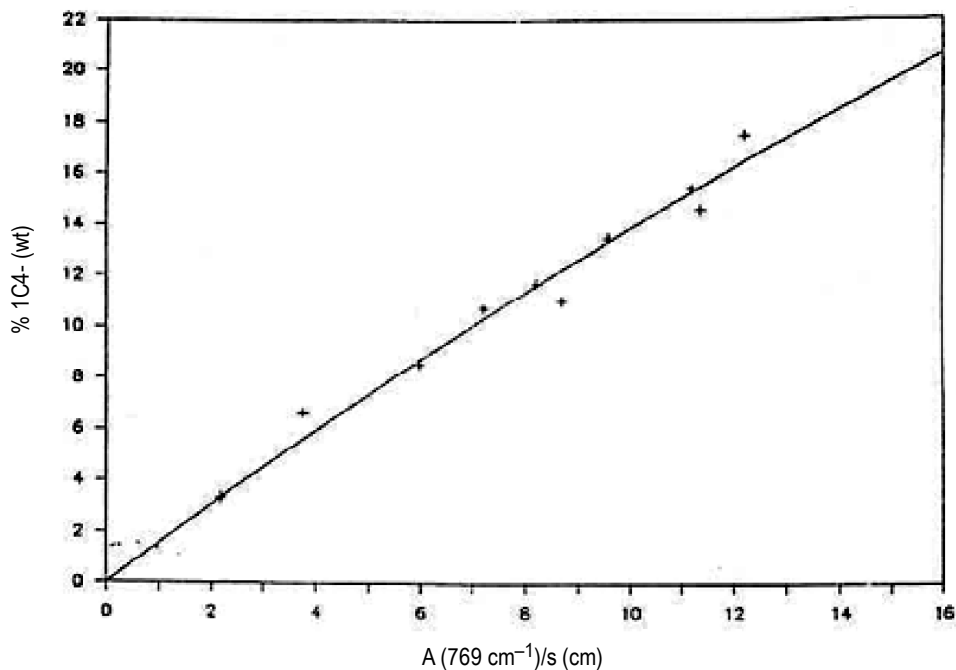


Fig. 3. Calibration curve for 1-butene content.

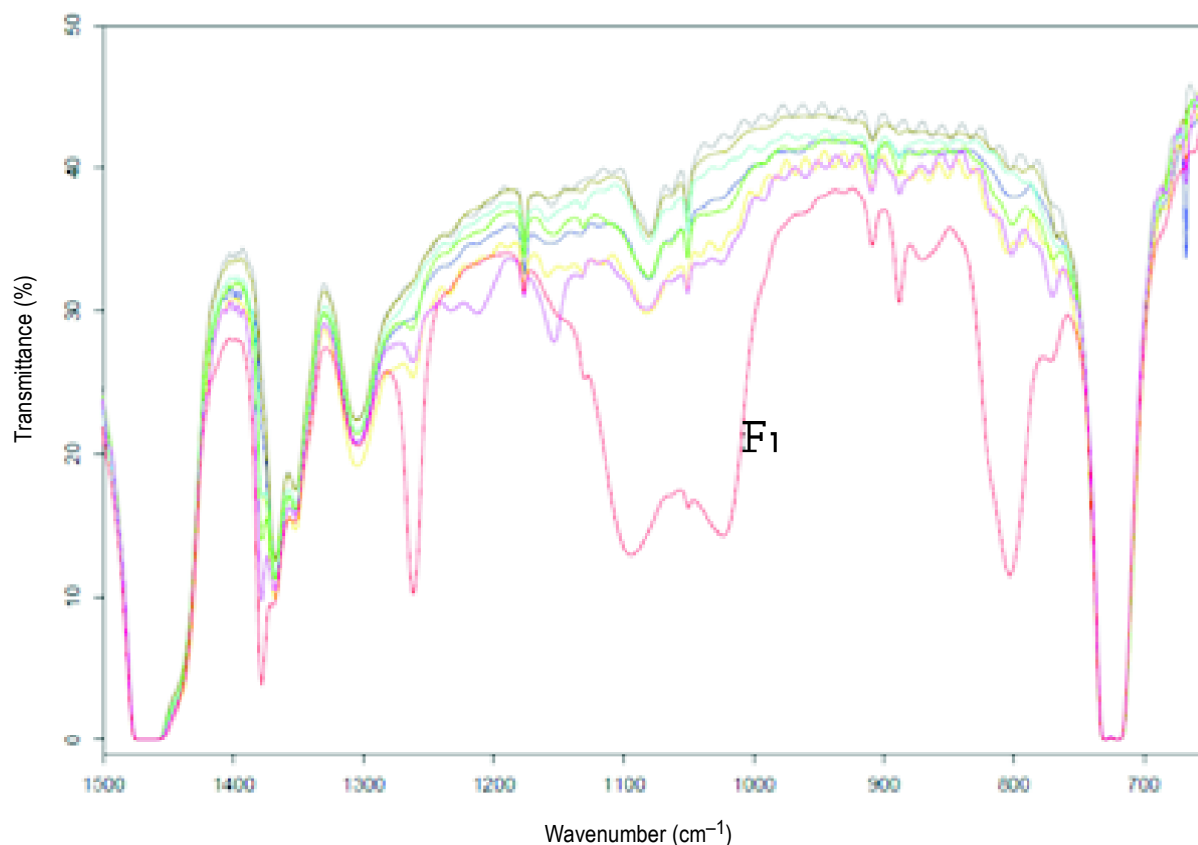


Fig. 4. A comparison of FTIR spectroscopy from the fractions obtained copolymer.

the SCB content in the copolymer. The spectra from the fractions are illustrated in Fig. 4. The SCB content that results from 1-butene groups was then determined from the absorbance of the ethyl band at 770 cm^{-1} . The quantitative analysis of the 1-butene content of fractions obtained from TREF is calculated from eq. (1) by Nicolet SX software²⁹.

The results given in Table 3, show that a well-defined

Table 3. The SCB content in each fraction of PE-100

Fraction	Absorbing species	Thickness of film (mm)	% SCB
1	Ethyl branches	0.0223	–
2	Ethyl branches	0.0203	4.46
3	Ethyl branches	0.0222	3.68
4	Ethyl branches	0.0231	3.72
5	Ethyl branches	0.0223	4.86
6	Ethyl branches	0.0216	3.71
7	Ethyl branches	0.0210	4.37
8	Ethyl branches	0.0212	3.58
9	Ethyl branches	–	–
10	Ethyl branches	–	–

rocking band is observed in each case, and a band-specific for ethyl branches appears at 770 cm^{-1} . This simple approach allows the identification of the SCB content. The spectra of the series of fractions except the fractions 9 and 10, which was of little value for analysis, show one band, in the region $769\text{ to }771\text{ cm}^{-1}$. As can be seen from Table 1 and Table 3 (fractions 2, 4 and fractions 4, 6), the high weight fractions contain less short-chain branches than the low weight fractions. As shown in Fig. 4, due to the incomplete separation of fraction 1 and the existence of an unknown peak, the software is not able to measure the content of the SCB.

Conclusions

Considering the variety of comonomers used in polyethylene and the effect of the short-chain branching has on the physical and mechanical properties of the product polymer, the use of a method dedicated to a particular comonomer and determining the comonomer value with high accuracy is a great advantage. The equation used in this work based on

the ASTM gives us high accuracy of the SCB value from the IR spectrum.

A combination of the two techniques, TREF and FTIR, can rapidly and efficiently analyze α -olefin copolymer type. The method proposed in this work for a systematic decomposition of bands offers a new optional way for the determination of the degree of SCB in HDPE with the advantage of less experimental difficulties and uncertainties inherent in the compensation methods. The present method eliminates, also, any subjective error of the operator, which occurs when obtaining the compensated spectra. The methods described in this report make FTIR spectroscopy much more potent for the characterization of short-chain branching in polyethylene and provide a rapid, inexpensive alternative to NMR spectroscopy for these analyses.

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References

1. L. L. Böhm, *Trends in Polymer Science*, 1996, **4**, 408.
2. L. L. Böhm, *Angew. Chem. Int. Ed.*, 2003, **42**, 5010.
3. L. Hubert, L. David, R. Séguéla, G. Vigier, C. Degoulet and Y. Germain, *Polymer*, 2001, **42**, 8425.
4. R. K. Krishnaswamy, Q. Yang, L. Fernandez-Ballester and J. A. Kornfield, *Macromolecules*, 2008, **41**, 1693.
5. L. L. Böhm, H. F. Enderle and M. Fleissner, *Adv. Mater.*, 1992, **4**, 234.
6. J. Cazenave, R. Séguéla, B. Sixou and Y. Germain, *Polymer*, 2006, **47**, 3904.
7. P. J. DesLauriers, M. P. Mcdaniel, D. C. Rohlfiing, R. K. Krishnaswamy, S. J. Secora, E. A. Benham, P. L. Maeger, A. R. Wolfe, A. M. Sukhadia and B. B. Beaulieu, *Polym. Eng. Sci.*, 2005, **45**, 1203.
8. P. J. DesLauriers, D. C. Rohlfiing and E. T. Hsieh, *Polymer*, 2002, **43**, 159.
9. A. Krumme, A. Lehtinen and A. Viikna, *Eur. Polym. J.*, 2004, **40**, 359.
10. J. B. P. Soares and A. E. Hamielec, *Polymer*, 1995, **36**, 1639.
11. J. Xu and L. Feng, *Eur. Polym. J.*, 2000, **36**, 867.
12. Y. Feng and J. N. Hay, *Polymer*, 1998, **39**, 6589.
13. K. Shirayama, T. Okada and S. I. Kita, *J. Polym. Sci., Part B: Polym. Phys.*, 1965, **3**, 907.
14. L. Wild, *Adv. Polym. Sci.*, 1990, **98**, 1.
15. S. Anantawaraskul, J. B. P. Soares and P. M. Wood Adams, *Adv. Polym. Sci.*, 2005, **182**, 1.
16. X. Yan-hu, B. Shu-qin and J. Xiang-ling, *Chinese Journal of Polymer Science*, 2015, **33**, 1000.
17. S. Hosoda, *Polym. J.*, 1988, **20**, 383.
18. E. T. Hsieh, *J. Macromol. Sci. Phys., B*, 1997, **36**, 615.
19. P. Schouterden, G. Groeninckx, B. Van der Heijden and F. Jansen, *Polymer*, 1987, **28**, 2099.
20. A. Krumme, M. Basiura, T. Pijpers, G. Vanden Poel, L. C. Heinz, R. Brill and V. B. F. Mathot, *Materials Science*, 2011, **17**, 260.
21. S. L. Agcarwal and O. J. Sweeting, *Chem. Rev.*, 1957, **57**, 665.
22. C. Baker and W. Maddams, *Makromol. Chem.*, 1976, **177**, 437.
23. W. Maddams, D. Morris and H. Willis, *Polym. Commun.*, 1989, **30**, 180.
24. C. Baker, W. Maddams, G. Park and B. Robertson, *Makromol. Chem.*, 1973, **165**, 321.
25. T. Usami and S. Takayama, *Polym. J.*, 1984, **16**, 731.
26. L. Lindeman, *J. Adams, Anal. Chem.*, 1971, **43**, 1245.
27. L. Cross, R. Richards and H. Willis, *Discuss. Faraday Soc.*, 1950, **9**, 235.
28. American Society for Testing Materials Designation D2238, 2012.
29. Montell Test Method, Method no.: MTM 15718E, Montell POLYOLEFINS; Revision: Feb. 1997, Issue: June: 1980. Determination of 1-butene content in 1-butene-ethylene copolymers.
30. F. Rugg, J. Smith and L. Waterman, *J. Polym. Sci.*, 1953, **11**, 1.
31. A. Willbourn, *J. Polym. Sci.*, 1959, **34**, 569.

