# Study of Propylene-1-butene-ethylene Terpolymer and Reactor Blend by TREF and $^{13}$C-NMR

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**ABSTRACT:** A terpolymer of propylene-1-butene-ethylene (TERPO) and a reactor mixture of TERPO with an ethylene-1-butene copolymer (BLEND) were completely characterized by TREF, $^{13}$C-NMR, DSC, and GPC, from which special equations for quantitative $^{13}$C-NMR were derived. TERPO was shown to be composed mainly of highly isotactic propene and similar amounts of ethylene and 1-butene. BLEND fractions were composed of variable amounts of TERPO and a random copolymer of ethylene-1-butene. The blend of TERPO and copolymer acts as two independent phases, each having its own elution temperatures dependent only on its crystallizability, itself only influenced by the comonomer content. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1880–1890, 2001

**Key words:** terpolymer; reactor blend; $^{13}$C-NMR; fractionation; TREF

## INTRODUCTION

TREF (temperature-rising elution fractionation) is a very powerful technique for studies of the compositional heterogeneity in polyolefins. This technique achieves fractionation on the basis of crystallizability, which has been shown to be influenced mainly by comonomer content, degree of tacticity, and sequence length. It has been shown[1] that elution temperature is only affected by molecular weights lower than 10,000 g/mol, a range that is inferior to that of standard polymers.

$^{13}$C-NMR is the best technique for studying polyolefin sequence distributions and tacticity. Sequence distributions are of particular impor-

tance in copolymers since crystallinity that results from long ethylene or propylene sequences affects the mechanical performance of the final product. $^{13}$C-NMR also provides insight into the number and nature of catalytic sites.[2] Studies of $^{13}$C-NMR of copolymers such as E/P and E/B have been widely reported[3,4]; however, there are few examples of $^{13}$C-NMR determination of terpolymers of ethylene-propylene-1-butene.[5,6]

The simultaneous use of $^{13}$C-NMR and TREF can be very informative, and it is essential for a good knowledge of heterogeneous materials. Several authors have used these techniques in conjunction by in order to study the copolymers of E/B,[7,8] E/P,[9] E/H,[10] E/S,[11] and E/C$_{18}$.[12]

Reactor blends are mixtures of polymers in a reactor, and some of them have previously been studied by TREF. Reactor blends of isotactic polypropylene (i-PP) and ethylene-propylene-rubber (EPR), known as "impact PP," have been studied by several authors.[13–16] It was concluded that

**Table I    Characteristics of Unfractioned Materials**

|  | $D^{23oC}$ (g/ml) | $T_m$ (°C) | $T_c$ (°C) | $M_w$ (g/mol) | $M_w/M_n$ | [E] (mol %) | [B] (mol %) | [P] (mol %) |
|---|---|---|---|---|---|---|---|---|
| TERPO | 0.899 | 131 | 93 | 290000 | 6.3 | 7.3 | 6.6 | 86.7 |
| BLEND | 0.917 | 125 | 110 | 157000 | 3.9 | 88.7 | 3.1 | 8.2 |

TREF facilitates the individual analysis of composition and molecular weight of the two phases of these blends. Wild[17] and Kelusky[18] used analytic TREF to quantify blend phases such as LLDPE–LDPE, EVA–LLDPE, HDPE–EPDM, and HDPE–PIB. A study by TREF of a commercial copolymer[19] showed it was a blend of a PP homopolymer, a P/E statistical copolymer, linear PE, a block P/E copolymer, and an isotactic polypropylene homopolymer.

The purpose of this work was to use TREF, ^{13}C-NMR, DSC and GPC to study two heterophasic materials: a terpolymer of propylene-1-butene-ethylene (TERPO) and a reactor mixture of TERPO with an ethylene-1-butene copolymer (BLEND). To identify the sequence distribution, it was necessary both to make a more accurate determination of the chemical shifts for terpolymers than that available in the literature and to develop a methodology to obtain ^{13}C-NMR quantitative results.

## EXPERIMENTAL

The heterophasic polymers used in this work were a terpolymer of propylene-1-butene-ethylene (TERPO) and a reactor mixture of TERPO with ethylene-1-butene copolymer (BLEND). The terpolymer concentration in the blend was approximately 15 mass %. The catalyst used was a fourth generation heterogeneous Ziegler–Natta TiCl$_3$/MgCl$_2$. The synthesis has been done in two gas-phase reactors: in the first reactor the terpolymer was synthesized, and in the second the copolymer was synthesized. Prepolymerization of propene and butene was done, representing about 1 mass % of the final product.

The ^{13}C-NMR spectra were obtained at 90–120°C depending on the fraction solubility. The equipment used was a Varian Inova 300 operating at 75 MHz. Sample solutions of the polymer were prepared in $o$-dichlorobenzene (ODCB) and benzene-d$_6$ (20% v/v) in 5-mm sample tubes. Deuterated solvent was used in order to provide an internal lock signal. The chemical shifts were referenced internally to the —(CH$_2$)$_n$— sequence, which was measured as 30 ppm from the Me$_4$Si. Spectra were measured using a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s.

p-TREF was used to obtain the fraction of the narrow short-chain branching distribution for further analysis by other techniques. A 2-g polymer sample was dissolved in 200 mL of ODCB at 140°C over 1 h (an antioxidant, such as BHT, was added to the solution to prevent oxidative degradation) and transferred to a steel column (100 × 20 mm ID) packed with inert material (silica) through which the ODCB could be pumped. The crystallization step was carried out at a rate of 2°C/h down to 25°C. The temperature was then increased discontinuously at a rate of 20°C/h in steps of 5°C up to 140°C. Each fraction was precipitated using an excess of methanol, filtered, dried at 80°C for 6 h, and weighed.

Molecular-weight distributions for the whole resin and its fractions were determined on a Waters 150C gel permeation chromatograph (DV-RI detection) at 140°C in trichlorobenzene (TCB; HPLC grade with 0.05% BHT) at a flow rate of 1.0 mL/min. Dissolution was carried out at a concentration of 0.1% (w/v) at 170°C during 2 h or until complete dissolution. Calculations were made utilizing standard techniques (universal calibration curve using narrow polystyrene standards).
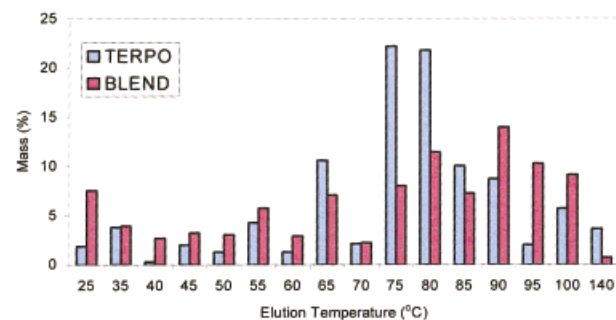


**Figure 1**    Mass distribution of the $p$-TREF fractions of TERPO and BLEND.

**Table II   Characteristics of TERPO and BLEND Fractions**

| Fraction (No.) | $T_e$ (°C) | TERPO | | | | BLEND | |
| | | $T_m$ (°C) | $T_c$ (°C) | $M_w$ (g/mol) | $M_w/M_n$ | $T_m$ (°C) | $T_c$ (°C) |
|---|---|---|---|---|---|---|---|
| 1 | 25 | 77 | 48 | | | 59 | 37 |
| 2 | 35 | 94 | 65 | 72600 | 4.6 | 73 | 52 |
| 3 | 40 | | | | | 74/103 | 39/59 |
| 4 | 45 | 102 | 71 | 77000 | 3.4 | 83/106 | 47/66 |
| 5 | 50 | 106 | 73 | | | 87/108 | 51/70 |
| 6 | 55 | 110 | 77 | | | 92/108 | 59/76 |
| 7 | 60 | 114 | 81 | | | 96/110 | 65/81 |
| 8 | 65 | 117 | 83 | 154000 | 3.8 | 100/112 | 72/86 |
| 9 | 70 | 120 | 88 | | | 104/114 | 72/90 |
| 10 | 75 | 124 | 89 | 248600 | 3.2 | 108/116 | 81/95 |
| 11 | 80 | 129 | 95 | | | 115/130 | 103 |
| 12 | 85 | 134 | 99 | 261900 | 3.7 | 121/135 | 109 |
| 13 | 90 | 137 | 102 | 266600 | 4.4 | 127 | 113 |
| 14 | 95 | 125/141 | 106 | | | 130 | 116 |
| 15 | 100 | 127/150/159 | 112 | | | 133 | 117 |
| 16 | 140 | 156 | 116 | | | 130/157 | 116 |
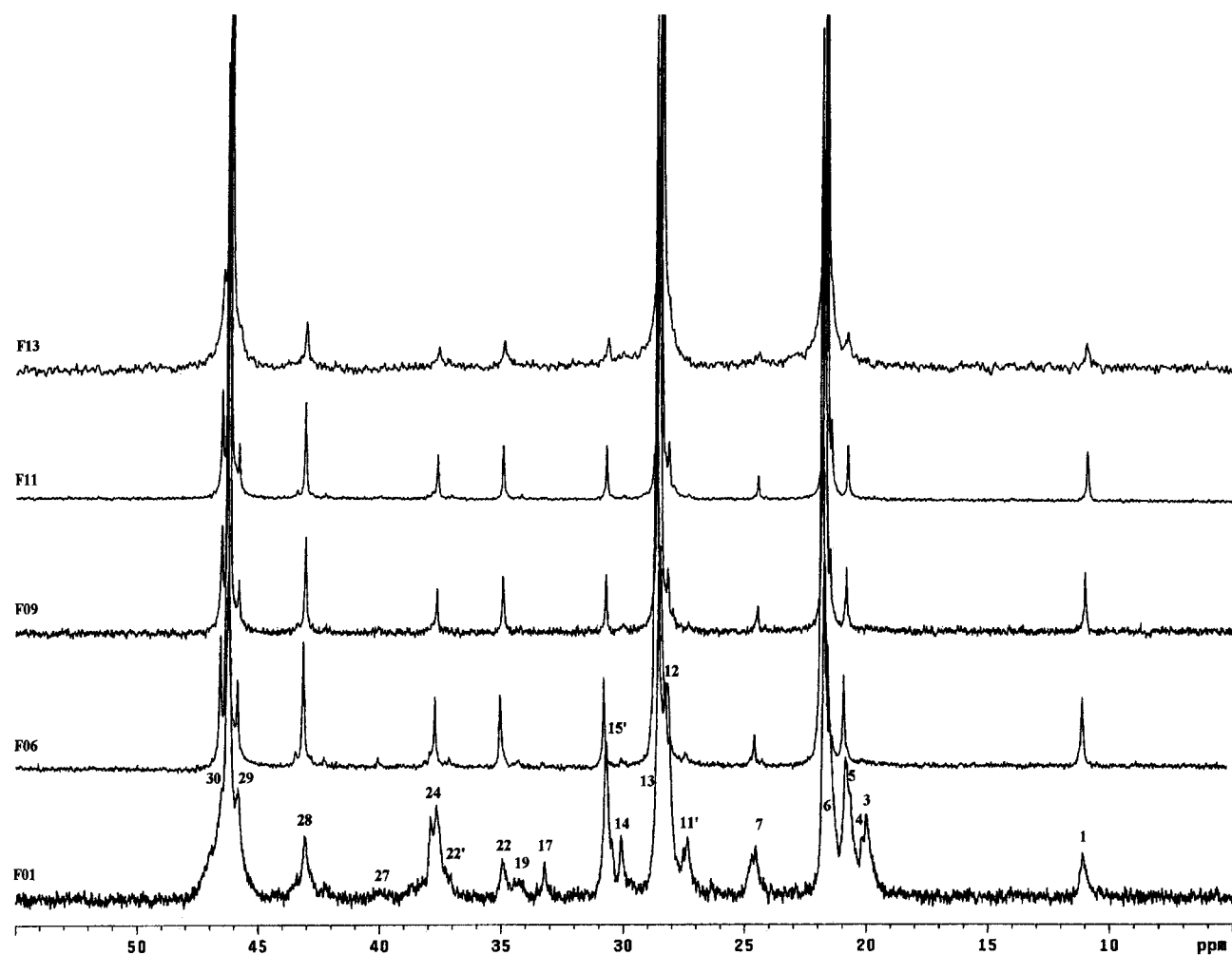


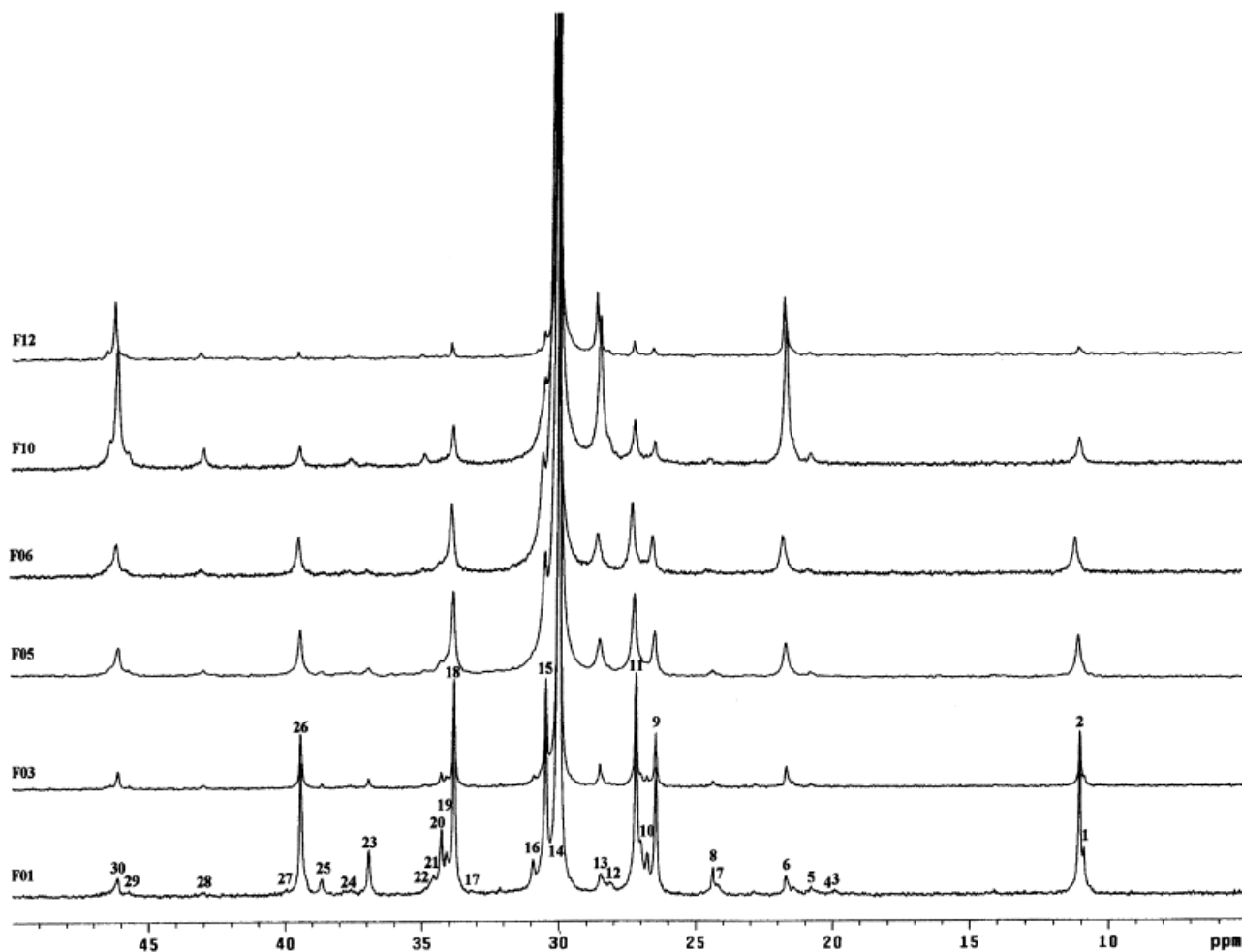**Figure 2**   $^{13}$C-NMR spectra of TERPO fractions 01, 06, 09, 11, and 13.

**Figure 3**   ¹³C-NMR spectra of BLEND fractions 01, 03, 05, 06, 10, and 12.

Thermal properties of the samples were determined on a DSC TA 2910 dynamic scanning calorimeter using standard procedures.

## RESULTS AND DISCUSSION

Table I shows the characteristics of the unfractionated materials. TERPO was composed mainly of propene (86.7 mol %) and roughly equal amounts of ethylene and 1-butene. BLEND was composed mainly of ethylene (88.7 mol %), with the remaining 11 mol % being 1-butene and propene. Considering that all propene in BLEND comes from the terpolymer (TERPO), the amount of terpolymer in BLEND would be of 8 mol % (or 12 mass %). This value is close to that given in the process data corresponding to a value of 15 mass % of TERPO in the final sample (BLEND). The heterogeneity of these materials is evident from

the broad polydispersities, specially that of the TERPO (6.3). The molecular-weight values of BLEND must be taken with caution because this material is a mixture of two phases with different compositions, a fact that may be a cause for error in GPC measurements in spite of the use of viscosimetric detection. The DSC thermogram of BLEND is similar to an ethylene-α-olefin thermogram and does not detect the presence of TERPO, probably because of the small amount of this terpolymer (8 mol %) in the total sample.

TERPO and BLEND were fractionated by preparative TREF (p-TREF), and the chemical composition distribution (CCD) is given in Figure 1. It is shown that 75.5% (w/w) of TERPO is eluted between 65°C (F08) and 90°C (F13). On the other hand, the BLEND CCD is broader: fractions 10–15 (elution temperatures between 75°C and 100 °C) form 60.2% of BLEND, the very soluble fractions, fractions 1–5 (elution temperatures of
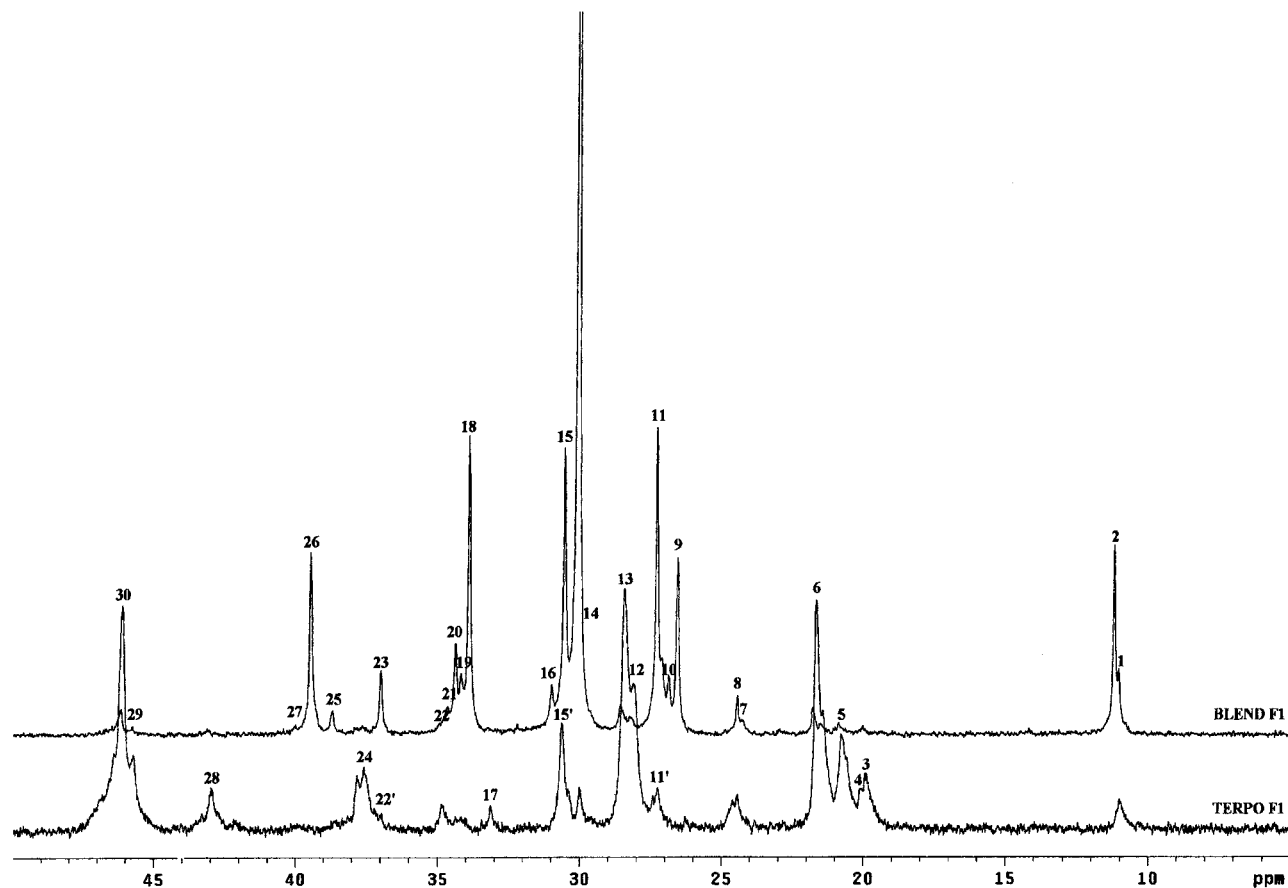
**Figure 4** $^{13}$C-NMR spectra of 01 fractions from TERPO and BLEND.

25–50 °C) form 20.5%, and another important set of fractions, fractions 6–9 (elution temperatures of 55–70 °C) form 18% of BLEND.

Table II shows the characteristics of the TREF fractions. It can be seen that the melting points increase with increasing elution temperature, an expected behavior because TREF separation was done by crystallizability. Table II also shows that some fractions (TERPO F14 and F15 and BLEND F03–F12) exhibited two or even three melting points, suggesting a heterogeneity of materials in these fractions. TERPO F14 seems to be formed by an ethylene modified by some branching ($T_m$ = 125°C) and by the terpolymer ($T_m$ = 141°C). TERPO F15 seems to have three species: a modified polyethylene ($T_m$ = 127°C), a terpolymer fraction ($T_m$ = 150°C), and a polypropylene homopolymer ($T_m$ = 159°C) probably resulting from the prepolymerization. The increase in polyethylene in fractions 14 and 15 was confirmed by IR analysis; unfortunately it was not possible to do the $^{13}$C-NMR of these fractions because of insufficiency of sample material. The existence of two

melting points in BLEND was expected and is a result of the mixture of terpolymer (TERPO) with the EB copolymer.

TERPO molecular weights also increase with elution temperature, but this is due largely to more highly branched polymers having lower molecular weights because of a higher ratio of termination and propagation reaction rates rather than an eventual separation of TREF accounting for the molecular weight. The lack of separation by molecular weight is shown by the broad molecular weight distribution of the fractions (close to 4). The BLEND GPC of the fractions was not done because of the difficulty of interpreting the results of material with a heterophasic character.

Comonomer content and sequence distribution of the samples were studied by $^{13}$C-NMR. Characterization of ethylene-propylene-1-butene terpolymers has been done by other authors.[5,6] This work found some regions, characterized as 19.9–21.5, 33.9–34.9, and 45.9–46.9 ppm, were improved and also identified some resonances that had been absent in a previous work. $^{13}$C-NMR

**Table III   TERPO Experimental and Theoretical Chemical Shifts and Triad and Carbon Assignments**

| Signal (No.) | Chem. Shifts Exp. (ppm) | Chem. Shifts Calc. (ppm) | Triads | Carbon | No. of C |
|---|---|---|---|---|---|
| 1 | 11.07 | 11.36 | BBB | $1B_2$ | 1 |
| | | | BBP + PBB | $1B_2$ | 2 |
| | | | PBP | $1B_2$ | 1 |
| | | | EBB + BBE | $1B_2$ | 2 |
| 3 | 19.97 | 20.61 | PPP(rr) | $1B_1$ | 1 |
| 4 | ~20.00 | 19.63 | EPE | $1B_1$ | 1 |
| 5 | 20.85 | 20.12 | EPP + PPE | $1B_1$ | 2 |
| | | 20.61 | PPP(mr) | $1B_1$ | 1 |
| 6 | 21.76 | 20.61 | PPP(mm) | $1B_1$ | 1 |
| | | | BPP + PPB | $1B_1$ | 2 |
| | | | BPB | $1B_1$ | 1 |
| 7 | 24.49 | 24.58 | PEP | $\beta\beta B_1$ | 1 |
| 11′ | 27.36 | 27.27 | PEE + EEP | $\beta\delta B_1$ | 2 |
| 12 | 28.00 | 27.66 | BBB | $2B_2$ | 1 |
| | | | BBP + PBB | $2B_2$ | 2 |
| | | | PBP | $2B_2$ | 1 |
| 13 | 28.56 | 28.38 | PPP | $brB_1$ | 1 |
| | | | BPP + PPB | $brB_1$ | 2 |
| | | | BPB | $brB_1$ | 1 |
| 14 | 30.02 | 29.96 | EEE | $\delta\delta B_1$ | 2 |
| 15′ | 30.72 | 30.46 | PEE(P) + PEE(P) | $\gamma\gamma B_1$ | 1 |
| | | 30.45 | PPE + EPP | $brB_1$ | 2 |
| 17 | 33.19 | 32.52 | EPE | $brB_1$ | 1 |
| 19 | 34.15 | 34.47 | EBB + BBE | $\alpha\delta B_2$ | 2 |
| 22 | 34.99 | 34.98 | BBB | $BrB_2$ | 1 |
| | | | BBP + PBB | $BrB_2$ | 2 |
| | | | PBP | $BrB_2$ | 1 |
| 22′ | 37.10 | 36.91 | EPE | $\alpha\delta B_1$ | 1 |
| | | | PEE + EEP | $\alpha\delta B_1$ | 1 |
| 24 | 37.66 | 37.41 | PEP | $\alpha\gamma B_1$ | 1 |
| | | | (P)EPP + PPE(P) | $\alpha\gamma B_1$ | 1 |
| 27 | 40.003 | 38.98 | BBB | $\alpha\alpha B_2$ | 2 |
| | | | BBP + PBB | $\alpha\alpha B_2$ | 1 |
| 28 | 43.07 | 41.67 | BBP + PBB | $\alpha\alpha B_1 B_2$ | 2 |
| | | | PBP | $\alpha\alpha B_1 B_2$ | 2 |
| | | | BPP + PPB | $\alpha\alpha B_1 B_2$ | 2 |
| | | | BPB | $\alpha\alpha B_1 B_2$ | 1 |
| 29 | 45.80 | 44.11 | (P)EPP + PPE(P) | $\alpha\alpha B_1$ | 2 |
| | | | (E)PPP(E) | $\alpha\alpha B_1$ | 2 |
| 30 | 46.20 | 44.36 | BPP + PPB | $\alpha\alpha B_1$ | 2 |
| | 46.51 | | (P)PPP(P) | $\alpha\alpha B_1$ | 2 |

assignments were based on previous assignments of EB, EP, and PB copolymer spectra and on theoretical chemical shifts calculated by Linderman and Adams,[20] as well as on comparisons between both materials. As TERPO is composed mainly of propene and low amounts of ethylene and 1-butene, it is reasonable to expect it will exhibit BP and EP sequences with either an absence of or in the presence of very low amounts of

EB sequences. By the same reasoning, BLEND was expected to exhibit an absence of BP sequences. This helped in identifying the resonances.

The nomenclature of Usami and Takayama[21] is used in this work. Branches are named as xBn where n is the length of the branch and x is the carbon number beginning with the methyl group, designated "1." For the backbone carbons, Greek letters showing the positions of the nearest ter-

**Table IV    BLEND Experimental and Theoretical Chemical Shifts and Triad and Carbon Assignments**

| Signal (No.) | Chem. Shifts Exp. (ppm) | Chem. Shifts Calc. (ppm) | Triads | Carbon | No. of C |
|---|---|---|---|---|---|
| 1 | 10.98 | 11.36 | EBB + BBE | $1B_2$ | 2 |
|  |  |  | BBB | $1B_2$ | 1 |
|  |  |  | BBP + PBB | $1B_2$ | 2 |
|  |  |  | PBP | $1B_2$ | 1 |
| 2 | 11.13 | 11.36 | EBE | $1B_2$ | 1 |
| 3 | 19.97 | 20.61 | PPP(rr) | $1B_1$ | 1 |
| 5 | 20.83 | 20.61 | PPP(mr) | $1B_1$ | 1 |
|  |  |  | PPE + EPP | $1B_1$ | 2 |
| 6 | 21.75 | 20.61 | PPP(mm) | $1B_1$ | 1 |
|  |  |  | PPB + BPP | $1B_1$ | 2 |
|  |  |  | BPB | $1B_1$ | 1 |
| 7 | 24.41 | 24.58 | PEP | $\beta\beta B_1$ | 1 |
| 8 | 24.49 | 25.08 | BEB | $\beta\beta B_2$ | 1 |
| 9 | 26.51 | 27.16 | EBE | $2B_2$ | 1 |
| 10 | 26.82 | 27.41 | EBB + BBE | $2B_2$ | 2 |
| 11 | 27.24 | 27.52 | EEB + BEE | $\beta\delta B_2$ | 2 |
| 12 | 28.19 | 27.66 | BBB | $2B_2$ | 1 |
|  |  |  | BBP + PBB | $2B_2$ | 2 |
|  |  |  | PBP | $2B_2$ | 1 |
| 13 | 28.52 | 28.38 | PPP | $brB_1$ | 1 |
|  |  |  | PPB + BPP | $brB_1$ | 2 |
|  |  |  | BPB | $brB_1$ | 1 |
| 14 | 30.04 | 29.96 | EEE | $\delta\delta B_2 + \delta\delta B_1$ | 2 |
| 15 | 30.52 | 30.21 | EEB + BEE | $\gamma\delta B_2$ | 2 |
|  |  | 30.45 | PPE + EPP | $brB_1$ | 2 |
| 16 | 30.97 | 30.46 | BEEB | $\gamma\gamma B_2$ | 1 |
| 17 | 33.19 | 32.52 | EPE | $brB_1$ | 1 |
| 18 | 33.86 | 34.22 | EEB + BEE | $\alpha\delta B_2$ | 1 |
|  |  |  | EBE | $\alpha\delta B_2$ | 1 |
| 19 | 34.15 | 34.47 | EBB + BBE | $\alpha\delta B_2$ | 2 |
| 20 | 34.34 | 34.47 | (E)BEB | $\alpha\gamma B_2$ | 2 |
| 21 | 34.5 | 34.72 | (B)BEB | $\alpha\gamma B_2$ | 2 |
| 22 | 34.99 | 34.98 | PBP | $brB_2$ | 1 |
|  |  |  | BBB | $brB_2$ | 1 |
|  |  |  | BBP + PBB | $brB_2$ | 2 |
| 23 | 36.97 | 37.05 | BBE + BBE | $brB_2$ | 2 |
| 24 | 37.66 | 37.41 | PEP | $\alpha\gamma B_1$ | 1 |
|  |  |  | (P)EPP + PPE(P) | $\alpha\gamma B_1$ | 1 |
| 25 | 38.70 | 38.48 | EBB + BBE | $\alpha\alpha B_2$ | 1 |
| 26 | 39.47 | 39.12 | EBE | $brB_2$ | 1 |
| 27 | 40.00 | 38.98 | BBB | $\alpha\alpha B_2$ | 2 |
|  |  |  | BBP + PBB | $\alpha\alpha B_2$ | 1 |
| 28 | 43.07 | 41.67 | BBP + PBB | $\alpha\alpha B_1B_2$ | 2 |
|  |  |  | PBP | $\alpha\alpha B_1B_2$ | 2 |
|  |  |  | BPP + PPB | $\alpha\alpha B_1B_2$ | 2 |
|  |  |  | BPB | $\alpha\alpha B_1B_2$ | 1 |
| 29 | 45.80 | 44.11 | (P)EPP + PPE(P) | $\alpha\alpha B_1$ | 1 |
|  |  |  | (E)PPP(E) | $\alpha\alpha B_1$ | 1 |
| 30 | 46.20 | 44.36 | PPB + BPP | $\alpha\alpha B_1$ | 2 |
|  | 46.51 |  | (P)PPP(P) | $\alpha\alpha B_1$ | 1 |

**Table V   Equations for Quantitative Analysis of TERPO Sequences**

$[EEE] = I_{14}/2$

$[EEP + PEE] = I_{11'}$

$[PEP] = I_7$

$[EEB + BEE] = 2(I_{18} - I_{26})$

$[BEB] = I_8$

$[EPE] = I_{17}$

$[EPP + PPE] = 2(I_{24} - I_7)$

$[PPP] + [BPP + PPB] = (I_{29} + I_{30}) - 2(I_{24} - I_7)$

$[BPB] = I_{12} + I_{13} - I_{22} - [(I_{29} + I_{30}) - 2(I_{24} - I_7)]$

$[PBP] = I_{22} - I_{27}$

$[BBB] + [BBP + PBB] = I_{27}$

$[EBE] = I_{26}$

$[EBB + BBE] = I_{19}$

$[E] = I_{14}/2 + I_{11'} + I_7 + 2I_{18} - 2I_{26} + I_8$

$[P] = I_{17} + I_{12} + I_{13} - I_{22} - 2I_{24} + 2I_7$

$[B] = I_{22} + I_{26} + I_{19}$

tiary carbon neighbors and "br" are used instead of $x$ for the methylenes and the branch points, respectively.

Figure 2 shows TERPO ^{13}C-NMR spectra for some fractions, Figure 3 shows the BLEND ^{13}C-NMR spectra, and Figure 4 shows the spectra for TERPO and BLEND for the most branched fractions of each type (TERPOF01 and BLENDF01).

^{13}C-NMR chemical shifts and carbon and sequence assignments of TERPO and BLEND are shown in Tables III and IV, respectively.

For quantitative analysis of sequences and comonomer content it was necessary for the spectra be taken under specific conditions. The procedure described by Traficante[22] was adopted. Using an integral accuracy of 90% instead of 100% increases the S/N by 31%. The use of a pulse angle of 74° instead of 90° permits the pulse delay to be reduced from 5 $T_1$ to 2 $T_1$ with an integral accuracy of 90%. The $T_1$ values for most carbons in these samples are less than 2.0 s, and therefore, a delay time of only 4 s is sufficient. The Nuclear Overhauser Enhancement (NOE) is generally as-

sumed to be complete and identical for all carbons in the polymers. Based on these considerations, we were able to obtain quantitative spectra in shorter times.

Equations developed to determined sequences and comonomer contents are presented in Table V for TERPO and in Table VI for BLEND. These equations describe the sequence concentrations obtained from normalized integrals ($I_n$), where $n$ is the signal number, as shown in Figures 3 and 4. These equations are not the same for the two materials because some of the signals shown by TERPO are not present in BLEND and vice versa and also because some of the resonances isolated in one are superposed in the other, complicating the integral determination.

Tables VII and VIII show TERPO and BLEND percentage of sequences and monomer content of the fractions obtained by these equations. Table VII shows the increase of propene and the decrease of ethylene and 1-butene with elution temperature and the absence of sequences EB (the detection of [EBB+BBE] in some soluble fractions

**Table VI   Equations for Quantitative Analysis of BLEND Sequences**

$[EEE] = I_{14}/2$

$[EEP + PEE] = 2I_{17}$ $[PEP] = I_7$

$[EEB + BEE] = I_{11}$

$[BEB] = I_8$

$[EPE] = I_{17}$

$[EPP + PPE] = 2(I_{24} - I_7)$

$[PPP] + [BPP + PPB] + [BPB] = I_3 + I_5 + I_6 - 2(I_{24} - I_7)$

$[PBP] = I_{12} - I_{27}$

$[BBB] + [BBP + PBB] = I_{27}$

$[EBE] = I_{26}$

$[EBB + BBE] = (I_{23} + 2I_{25})/2$

$[E] = I_{14}/2 + I_{11} + 2I_{17} + I_7 + I_8$

$[P] = I_{17} + I_3 + I_5 + I_6$

$[B] = I_{26} + I_{23}/2 + I_{25} + I_{12}$

**Table VII   TERPO Percentage of Sequences and Monomer Content Obtained by $^{13}$C-NMR**

| Sequence (mol %) | TERPO (mol %) | F01 (mol %) | F06 (mol %) | F08 (mol %) | F09 (mol %) | F10 (mol %) | F11 (mol %) | F12 (mol %) | F13 (mol %) |
|---|---|---|---|---|---|---|---|---|---|
| [EEE] | 1.4 | 2.3 | 1.3 | 0.4 | 2.1 | 0.4 | 0.4 | 0.8 | 0.3 |
| [EEP + PEE] | 2.0 | 6.1 | 1.9 | 2.8 | 0.9 | 2.0 | 1.2 | 0 | 0 |
| [PEP] | 3.9 | 8.4 | 4.3 | 4.4 | 4.4 | 3.8 | 2.7 | 2.5 | 1.7 |
| [BEE + EEB] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| [BEB] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| [EBE] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| [EBB + BBE] | 0 | 2.0 | 1.3 | 0.7 | 1.3 | 0.9 | 0.6 | 0 | 0 |
| [PBP] | 6.0 | 2.3 | 6.2 | 6.9 | 6.5 | 5.9 | 4.9 | 4.8 | 4.3 |
| [BBB] + [BBP + PBB] | 0 | 2.2 | 0.9 | 0.9 | 0.8 | 0.8 | 0.4 | 0 | 0 |
| [EPE] | 0 | 3.0 | 0.5 | 0.2 | 0 | 0 | 0 | 0 | 0 |
| [EPP + PPE] | 6.0 | 18.0 | 6.4 | 5.6 | 5.6 | 4.2 | 4.3 | 3.8 | 3.8 |
| [PPP] + [BPP + PPB] | 67.2 | 42.0 | 69.6 | 71.0 | 68.7 | 76.7 | 79.5 | 84.5 | 85.0 |
| [BPB] | 13.4 | 13.6 | 7.8 | 7.0 | 10.0 | 5.4 | 6.0 | 3.6 | 5.0 |
| [E] | 7.3 | 16.85 | 7.4 | 7.7 | 7.3 | 6.3 | 4.3 | 3.4 | 2.0 |
| [B] | 6.0 | 6.6 | 8.4 | 8.5 | 8.5 | 7.6 | 5.9 | 4.8 | 4.3 |
| [P] | 86.7 | 76.6 | 84.2 | 83.8 | 84.2 | 86.2 | 89.8 | 91.9 | 93.8 |

was negligible). The percentages of triads of Table VII were used to calculate the number-average sequence length of ethylene ($n_E$) and 1-butene ($n_B$) between sequences of propene in TERPO. The equations employed are those used by Randall[23]:

$$n_E = [E]/1/2[EP] \qquad n_B = [B]/1/2[BP]$$

$$[EP] = [EPE] + 1/2\,[EPP + PPE]$$
$$+ [PEP] + 1/2\,[EEP + PEE]$$

$$[PB] = [BPB] + 1/2[BPP + PPB]$$
$$+ [PBP] + 1/2[BBP + PBB]$$

The results presented in Table IX show that there are 1.1–1.9 sequences of ethylene between se-

**Table VIII   BLEND Percentage of Sequences and Monomer Content Obtained by $^{13}$C-NMR**

| Sequence | BLEND (mol %) | F01 (mol %) | F03 (mol %) | F05 (mol %) | F06 (mol %) | F10 (mol %) | F12 (mol %) |
|---|---|---|---|---|---|---|---|
| [EEE] | 81.7 | 44.1 | 65.6 | 68.6 | 73.3 | 65.6 | 82.7 |
| [EEP + PEE] | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| [PEP] | 0 | 1.1 | 0 | 0 | 0 | 0 | 0 |
| [BEE + EEB] | 6.7 | 25.7 | 17.2 | 14.8 | 12.2 | 6.6 | 1.7 |
| [BEB] | 0.4 | 2.8 | 1.4 | 1.0 | 0.5 | 0.5 | 0.2 |
| [EBE] | 3.1 | 14.1 | 9.0 | 7.1 | 5.9 | 2.7 | 0.8 |
| [EBB + BBE] | 0 | 4.4 | 1.5 | 1.7 | 0.3 | 0.6 | 0 |
| [PBP] | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 |
| [BBB] + [BBP + PBB] | 0 | 0.6 | 0 | 0 | 0 | 0 | 0 |
| [EPE] | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| [EPP + PPE] | 0 | 0.3 | 0 | 0 | 1.1 | 0 | 0 |
| [PPP] + [BPP + PPB] + [BPB] | 8.2 | 5.5 | 5.3 | 6.8 | 6.7 | 24.1 | 14.5 |
| [E] (mol %) | 88.7 | 73.6 | 84.1 | 84.4 | 86.0 | 72.7 | 84.7 |
| [B] (mol %) | 3.1 | 20.6 | 10.5 | 8.8 | 6.2 | 3.3 | 0.8 |
| [P] (mol %) | 8.2 | 5.7 | 5.3 | 6.8 | 7.8 | 24.1 | 14.5 |

**Table IX   Average Sequence Length Distribution in TERPO**

| Fraction No. | PE (mol %) | PB (mol %) | $n_E$ | $n_B$ |
|---|---|---|---|---|
| TERPO | 7.9 | 12.0 | 1.8 | 1.0 |
| F01 | 23.45 | 6.8 | 1.4 | 1.9 |
| F06 | 8.95 | 13.3 | 1.6 | 1.3 |
| F08 | 8.8 | 14.7 | 1.7 | 1.2 |
| F09 | 7.65 | 13.8 | 1.9 | 1.2 |
| F10 | 6.9 | 12.6 | 1.8 | 1.2 |
| F11 | 5.45 | 10.2 | 1.6 | 1.2 |
| F12 | 4.4 | 9.6 | 1.5 | 1.0 |
| F13 | 3.6 | 8.6 | 1.1 | 1.0 |

**Table X   Tacticity of Propene Sequences in TERPO**

| Fraction | $mm$ | $mr$ | $rr$ | $m$ | $r$ |
|---|---|---|---|---|---|
| F01 | 0.78 | 0.10 | 0.12 | 0.83 | 0.17 |
| F06 | 0.88 | 0.12 | 0 | 0.94 | 0.06 |
| F08 | 0.995 | 0.005 | 0 | 0.997 | 0.003 |
| F09 | 0.976 | 0.024 | 0 | 0.988 | 0.012 |
| F10 | 0.982 | 0.018 | 0 | 0.991 | 0.009 |
| F11 | 0.995 | 0.005 | 0 | 0.997 | 0.003 |
| F12 | 0.988 | 0.012 | 0 | 0.994 | 0.006 |
| F13 | 0.93 | 0.07 | 0 | 0.965 | 0.035 |

quences of propene, this is also demonstrated by the predominance of [PEP] sequences (Table VII). For the first fraction $n_B$ is close to 1 except (F01), where there are nearly 2 units of 1-butene between propene sequences. The amount of ethylene and 1-butene decreases with the elution temperature, which is proportional to the decreasing crystallinity. This means the presence of ethylene and 1-butene in this polymer disturbs crystallinity, acting as defects in the crystalline lattice. Crystallinity in these materials is derived from de propene sequences that increase with elution temperature. It is possible to make an approximate calculation of tacticity of propene sequences using the relation

$$mm = I_6 - [BPP+PPB] - [BPB]$$

as it is impossible to obtain the triad [BPP+PPB] isolated. We had to do the following supposition: [BPP+PPB] = 2[PBP], which is true for a predominant propene copolymer:

$$mr = I_5 - [EPP+PPE]$$

$$rr = I_3$$

Triads can be substituted by the integrals using the relationships shown in Table V. Results for the propene sequences tacticity can be seen in Table X. Propene sequences are highly isotactic except for the first fractions from F01 to F06, which are probably formed by sites that are less specific.

Table VIII shows an increase of ethylene with elution temperature except in fraction 10, where there was a decrease. On the other hand, there is an important increase in the amount of propene in the same fraction, decreasing in fraction 12. This behavior coincides with the elution of TERPO, which is important in fractions 10 and 11 [with elution temperatures of 75°C and 80 °C, respectively (Fig. 1)]. Sequences of EP and PB are largely absent in BLEND; their existence is derived only from TERPO. EB sequences are very important in the first fractions, decreasing with the 1-butene content and with an increase of elution temperature. The average sequence length for 1-butene (Table XI) is close to 1 for all the fractions, meaning that 1-butene is randomly distributed in the copolymer ethylene-1-butene. The existence of almost equal amounts of [PPP] + [BPP+PPB] + [BPB] rather than [P] (Table VIII) means that all propene comes from PPP sequences, the same as saying it is a homopolymer.

BLEND is formed by a random copolymer of ethylene-1-butene, the most important product in the most soluble fractions (from fractions 1 to 5), and by a homopolymer of propene. The most crystalline fractions are formed by a copolymer of ethylene-1-butene with a very small amount of

**Table XI   Average Sequence Length Distribution in BLEND**

| Fraction No. | EB (mol %) | $n_E$ | $n_B$ |
|---|---|---|---|
| BLEND | 6.85 | 25.9 | 0.9 |
| F01 | 31.95 | 4.6 | 1.3 |
| F03 | 19.75 | 8.5 | 1.1 |
| F05 | 16.35 | 10.3 | 1.1 |
| F06 | 12.65 | 13.6 | 1.0 |
| F10 | 6.8 | 21.4 | 1.0 |
| F12 | 1.85 | 91.6 | 0.9 |

butene and a homopolymer of propene. The homopolymer is derived from TERPO, so it is not really a homopolymer since the amount of PB and PE sequences present in TERPO are too insufficient to be detected.

## CONCLUSIONS

A terpolymer of propylene-1-butene-ethylene was completely characterized by $^{13}$C-NMR, both qualitatively and quantitatively. The crystallizability in TERPO is due exclusively to the isotactic microstructure of propene, ethylene and 1-butene acting as defects in the crystalline lattice, thereby decreasing crystallinity. Fractionation of the terpolymer was controlled mainly by the amount of comonomers (ethylene and 1-butene) in each fraction, with the percentage of stereoregularity having a secondary influence.

TERPO and the ethylene-1-butene copolymer in BLEND act as two independent phases, each with its own elution temperature dependent only on its crystallizability, which in turn is influenced exclusively by the comonomer content.

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