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# Use of FT-IR Spectrometry for On-Line Detection in Temperature Rising Elution Fractionation

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**Summary:** Temperature rising elution fractionation (TREF) has become a popular analytical technique that is able to determine the chemical composition distribution (CCD) of an ethylene/$\alpha$-olefin copolymer. An infrared (IR) detector is commonly used in TREF detection to measure the concentration of the polymer solution exiting the column as a function of elution temperature. The chemical composition of the eluting polymer at a given elution temperature can be predicted from the relationship between comonomer content and TREF elution temperature pre-established through $^{13}$C nuclear magnetic resonance (NMR) analysis of TREF fractions. In this article, a Fourier transform infrared (FT-IR) spectrometer has been coupled with a TREF instrument to provide a more powerful tool for characterizing complex olefin copolymers. The Partial Least Squares (PLS) technique is used when analyzing the FT-IR spectra of the eluting polymer solutions. The power of on-line FT-IR detection in TREF is demonstrated using a few complex copolymer systems, such as ethylene-octene copolymer, polystyrene grafted ethylene-vinyl acetate copolymer and ethylene-methyl acrylate copolymer.

**Keywords:** chemical composition distribution (CCD); fourier transform infrared (FT-IR) spectrometry; on-line FT-IR detection; polyolefins; temperature rising elution fractionation (TREF)

## Introduction

The polyolefins industry has had a long history of new product introductions through technological developments, and the pace of these developments has accelerated in the last a few decades. This has been a period of breakthrough discoveries, from advanced Ziegler-Natta (Z-N) catalyst technology, through metallocene catalysis. With each of these new technology developments, more control of the polymer structures was achieved by the product designers allowing new, high value products to be produced. For example, in the 1990s, metallocene catalysis technology allowed the control of polymer composition distributions.

Polymer characterization provides information about the molecular structure that builds a bridge between polymer properties and polymerization conditions. On the one hand, molecular structure determines polymer properties and end-use applications, and on the other hand, molecular structure can be controlled by polymerization conditions. A number of tools have been developed and widely used for polymer characterization. Examples of these techniques include but are not limited to: i) Vibrational spectroscopy (infrared absorption spectroscopy and Raman scattering) is one of the oldest and most powerful techniques for analyzing polymer composition and structure.[1] ii) The unique chemical selectivity and high flexibility of nuclear magnetic resonance (NMR) allows one to study structure, chain conformation and molecular dynamics in much detail and depth.[2] iii) Size-exclusion chromatography (SEC) has become a popular technique for determining polymer molar mass averages and molar mass distribution (MMD) since

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its inception in the 1960s.[3] iv) TREF[4] and crystallization analysis fractionation (CRYSTAF)[5,6] have been used to determine the chemical composition distribution (CCD). v) Cross-fractionation[7] is a combination of two or more fractionation techniques, each of which separates polymer chains according to a different microstructural characteristic, that can probe information on chain microstructure in greater detail than any single fractionation technique.

It is well-known that FT-IR spectroscopy is a powerful tool for material identification and has been used off-line for post-fractionation analysis, but there are few if any published papers describing the use of on-line FT-IR in combination with TREF. In this article, the author demonstrates the method of TREF coupled with an on-line FT-IR spectrometer developed recently for complex copolymer characterization. Chemical compositional distribution is described and its application is demonstrated using several types of copolymers.

## TREF

TREF has become a popular analytical technique that is able to determine the CCD of an ethylene/$\alpha$-olefin copolymer.[8] Figure 1 shows schematically an experimental set-up for TREF originally developed by Wild et al.[4] TREF involves two consecutive steps: crystallization and elution. In the crystallization step, polymer is crystallized from a dilute solution by slowly decreasing the temperature inside a column packed with an inert support to form a layer structure (Figure 2). Fractionation takes place during the crystallization step according to crystallizability. The materials with higher crystallizability crystallize first at higher temperatures to form the inner layers, followed by the materials with lower crystallizability at lower temperatures to form the outer layers. In the elution step, the polymer deposited on the support is eluted from the column with a continuous flow of solvent at increasing temperatures. The crystallized materials in the outer layers with lower crystallizability dissolve and elute first at lower temperatures, followed by the materials in the inner layers with higher crystallizability. An on-line detector measures the concentration of the polymer solution exiting the column. As a result, information can be obtained about polymer concentration as a function of TREF elution temperature (Figure 3). The chemical composition of the eluting polymer at a given elution temperature can be predicted from the relationship between comonomer content and TREF elution

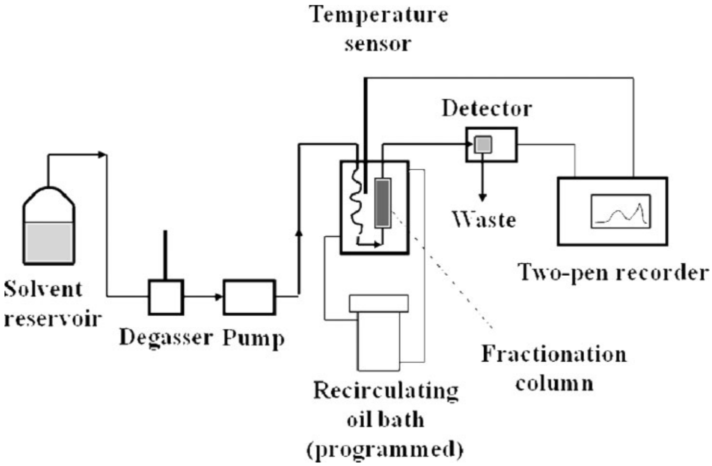


***Figure 1.***
Schematic diagram of analytical TREF.

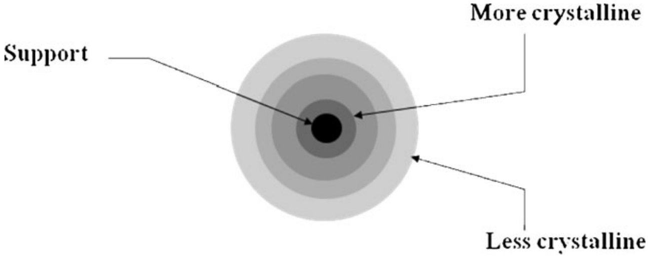


*Figure 2.*
Illustration of crystallized polymer layers.

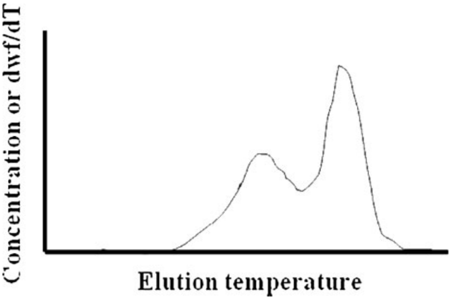


*Figure 3.*
TREF profile.

temperature (calibration curve) established through $^{13}$C NMR analysis of TREF fractions. The TREF profile shown in Figure 3 is good enough to be used for qualitative comparisons. With an appropriate calibration curve, the temperature axis can be converted to units of short-chain branching (SCB), and the converted TREF profile can be used to estimate the number- and weight-average SCB values as well as the the short-chain branching distributions (SCBD) which are analogous to molar mass averages and distributions.

## Detection in TREF

As already mentioned, an on-line detector is required in TREF for measuring the concentration of the polymer solution exiting from the column. In addition to the concentration detector, a molar mass sensitive detector (e.g. light scattering) is used in some cases to determine the polymer molar mass, and in other cases a viscometer is used to measure the viscosity of the polymer solution exiting from the column. An IR detector is commonly used as the concentration detector in TREF and the measurement is based on a single wavelength. For example, the wavelength is usually fixed at 3.4 μm for polyolefin analysis. The polymer concentration [C] can be calculated from the absorbance A according to Beer-Lambert law:

$$A = L \times \varepsilon \times [C]$$

where L is the optical path length of the FT-IR cell and $\varepsilon$ is the absorption coefficient at the given wavelength. An ethylene/$\alpha$-olefin copolymer is relatively simple and the IR detector works very well for determining its concentration, since the absorption coefficient of C-H stretching (i.e. at 3.4 μm) from the methylene in the comonomer unit is practically identical to those in the polymer backbone.

A complex copolymer produced by polymerization of monomers $m_a$ and $m_b$, to give poly ($m_a$-co-$m_b$), will next be considered. The IR spectrum of this copolymer is shown in Figure 4. The IR

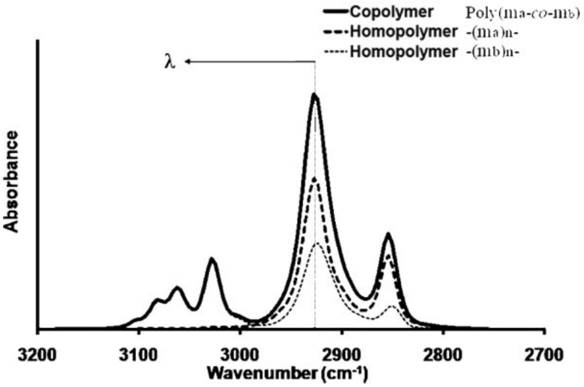


**Figure 4.**
IR spectrum of copolymer poly($m_a$-*co*-$m_b$).

absorbance ($A_{co}$) at any given wavelength can be considered as the sum of those ($A_{ma}$ and $A_{mb}$) from the monomer units $m_a$ and $m_b$, that is,

$$\begin{aligned} A_{co} &= A_{ma} + A_{mb} \\ &= L \times \varepsilon_a \times [C_a] + L \times \varepsilon_b \times [C_b] \end{aligned}$$

where L is the optical path length of the FT-IR cell, $\varepsilon_a$ and $\varepsilon_b$ are the absorption coefficients of the monomer units at the given wavelength, $[C_a]$ and $[C_b]$ are the concentrations of monomer units. This equation cannot be solved since the absorption coefficients are not the same for both monomer units ($\varepsilon_a \neq \varepsilon_b$). There are two unknowns ($[C_a]$ and $[C_b]$) but only one measured absorbance ($A_{co}$). Thus, the IR detector based on the measurement at single wavelength does not work in this case, and an alternative is required for measuring polymer concentration.

## FT-IR Detection

One method for solving the above problem is based on using FT-IR spectrometry for determination of polymer concentration in TREF. FT-IR spectrometry has been coupled with SEC for determining comonomer content as a function of molar mass in polyolefins.[9–11] On-line FT-IR detection combined with a viscometer has been used in SEC for characterization of complex copolymers.[12] Instead of the measurement at a single wavelength as in the IR detection, a spectrum can be obtained in the FT-IR detection. Calculation can now be performed using multiple wavelength bands and an advanced technique such as a dual-wavelength technique for a relatively simple two-component system or a multivariate calibration method for a more complex multi-component system.

Considering the previous example of IR spectrum of poly ($m_a$-co-$m_b$), this time the calculation is based on the absorbances at two wavelengths as shown in Figure 5. The following relationships exist according to Beer-Lambert law:

$$A_{1co} = L \times \varepsilon_{1a} \times [C_a] + L \times \varepsilon_{1b} \times [C_b]$$

$$A_{2co} = L \times \varepsilon_{2a} \times [C_a] + L \times \varepsilon_2 b \times [C_b]$$

where $[C_a]$ and $[C_b]$ are the concentrations of monomer units, and $A_{1co}$ and $A_{2co}$ are the absorbances at the given wavelengths $\lambda_1$ and $\lambda_2$, respectively. L is the optical path length of the FT-IR cell, $\varepsilon 1_a$ and $\varepsilon 1_b$, $\varepsilon 2_a$ and $\varepsilon 2_b$ are the absorption coefficients of the monomer units at the given wavelengths $\lambda_1$ and $\lambda_2$, respectively. Thus, the concentrations of monomer units can be calculated easily from the absorbances at the two wavelengths:

$$\begin{aligned} [C_a] = (\varepsilon_{2b} \times A_{1co} - \varepsilon_{1b} \times A_{2co})/(L \times \varepsilon_{1a} \\ \times \varepsilon_{2b} - L \times \varepsilon_{2a} \times \varepsilon_{1b}) \end{aligned}$$

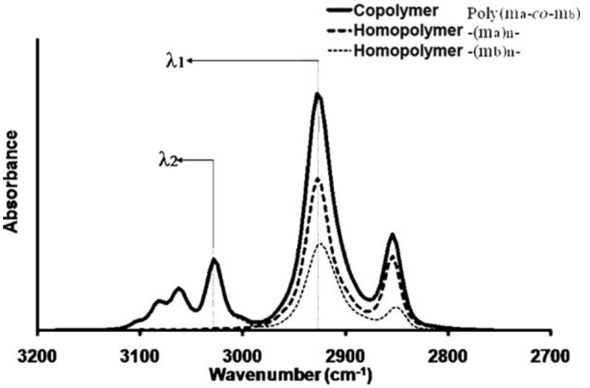


*Figure 5.*
Two-wavelength technique.

$$[C_b] = (\varepsilon_{2a} \times A_{1co} - \varepsilon_{1a} \times A_{2co})/(L \times \varepsilon_{1b} \times \varepsilon_{2a} - L \times \varepsilon_{2b} \times \varepsilon_{1a})$$

Then, the total polymer concentration can be calculated as:

$$[C] = [C_a] + [C_b]$$

and the chemical composition in terms of the weight percent of comonomer $m_b$ as:

$$m_b wt\% = 100 \times [C_b]/([C_a] + [C_b])$$

The dual wavelength technique therefore works well for two-component systems.

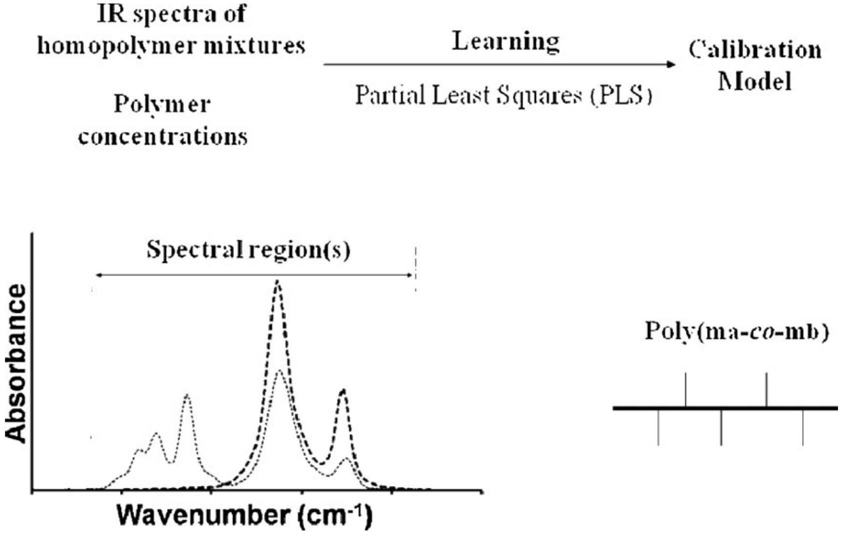
The multivariate calibration method, for example partial least squares (PLS), is required for analyzing the IR spectra of more complex multi-component systems. PLS regression is an extension of a multiple linear regression model. A theoretical basis for PLS algorithm has been described by Kowalski and coworkers.[13] A tutorial on the PLS algorithm has also been described in the literature.[14] Moreover, partial least squares regression has become a standard tool in chemometrics for modeling linear relations between multivariate measurements.[15] It has been successfully applied to quantitative spectroscopy analyses,[16,17] and commercial PLS software is available from FT-IR instrument suppliers (e.g. OPUS QUANT, Bruker; TQ Analyst, ThermoNicolet). OPUS QUANT, the PLS software provided by Bruker, was used in this study for quantitative FT-IR spectral analyses. The process of building a calibration model is demonstrated in Scheme 1.

Generally speaking, a sufficiently large number of standards are made to represent the copolymer system by mixing the solutions of the two homopolymers. The IR spectra of the standard solutions are inputted into the QUANT software along with the polymer concentrations. There are several methods available in the software for spectral reprocessing, including the first and second derivatives of the spectra as well as straight line subtraction of the spectra in given frequency ranges. Two methods can be used for validation: Test Set and Cross Validation. Test Set Validation is usually used if the number of standards is large. In this case the spectra of the standards are defined into two independent sets, one for calibrating the system and the other for validating the model. Both sets consist of about the same number of spectra. On the other hand, Cross Validation can be used if the number of standards is limited. The concentrations of the unknown copolymer solutions can be predicted from the established PLS calibration model based on their IR spectra.

## Experimental Part

### Chemicals

The antioxidant, 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%), used in this study was



**Scheme 1.**
Process of building PLS calibration model.

purchased from Aldrich and the solvents 1,2,4-trichlorobenzene (TCB, EM Science, Omnisolve grade) as well as tetrachloroethylene (TCE, EM Science, Omnisolve grade) from VWR. The ethylene/$\alpha$-octene copolymer I was a commercial resin and ethylene/$\alpha$-octene copolymer II was an experimental sample. The ethylene homopolymer (SRM1484a, Mw = 119600 g/mol, Mw/Mn = 1.19) was obtained from National Institute of Standards and Technology as well as the low molar mass hydrocarbon (eicosane, $C_{20}$) from Aldrich. The ethylene-vinyl acetate copolymer (EVA) was provided by Equistar and the narrow MMD polystyrene (PS) sample (PS47500, Mw = 47500 g/mol, Mw/Mn = 1.06) from Pressure Chemical Company. The polystyrene grafted ethylene-vinyl acetate copolymers (PS-*graft*-EVAs) and the copolymers of ethylene-methyl acrylate (EMA) were experimental samples.

### Instrumental Set Up

As shown in Figure 6, the CRYSTAF-TREF 200+ from Polymer ChAR was used for crystallization and fractionation. It was coupled with the FT-IR flow through cell (FT-IR Interface) from Polymer Laboratories (1 mm optical path length, 70 μl in volume, $CaF_2$ windows) via heated transfer lines. The FT-IR flow through cell was mounted on a base plate in the sample compartment of FT-IR spectrophotometer (Bruker TENSOR 27). One computer was used to control the crystallization and elution and the other for FT-IR data acquisition.

### Static FT-IR measurements

For FT-IR flow cell calibration, sample solutions were prepared by dissolving an appropriate amount of polymers in approximately 20 mL of solvent at a given temperature (at 105 °C in TCE or at 140 °C in TCB). Both the solvents and the samples were weighed to the nearest 0.1 mg. The concentrations of polymer solutions in mg/cm$^3$ were calculated using the densities of the solvent (i.e. TCE 1.4796 g/cm$^3$ at 105 °C or TCB 1.3257 g/cm$^3$ at 140 °C). The polymer solutions were transferred with a syringe to the FT-IR flow through cell that was pre-heated to 105 °C or 140 °C and the corresponding FT-IR spectra were obtained by scanning after a 1-minute equilibration time. FT-IR spectra were acquired on the Bruker TENSOR 27 FT-IR spectrophotometer equipped with OPUS operating software. The sample

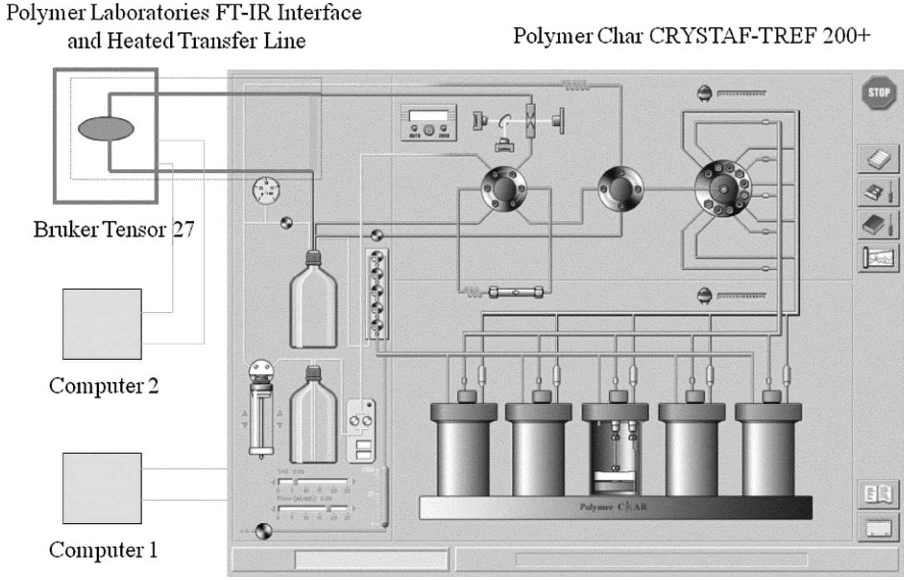


***Figure 6.***
Instrumental set up.

and detector compartments of the spectrophotometer were continuously purged with dried nitrogen gas. The spectra were acquired in the absorbance mode and were background corrected against pure solvent. All spectra were measured at 8 cm$^{-1}$ resolution with 32 scans.

### TREF-FT-IR Analysis

A polymer sample (40 to 150 mg) was introduced into the reactor vessel of the Polymer ChAR TREF unit. The reactor vessel was filled with 20 ml TCE or TCB, heated to the desired dissolution temperature (105 °C in TCE or 140 °C in TCB) for 2 to 8 hours. The solution was allowed to equilibrate at a given stabilization temperature (90 °C in TCE or 120 °C in TCB) for 30 to 45 minutes. The solution (0.5 to 1.0 ml) was then loaded into the TREF column filled with glass beads, and allowed to crystallize with a temperature drop from the stabilization temperature to 30 °C (0.1 or 0.2 °C/minute). After equilibrating at 30 °C for 30 minutes, the crystallized sample was eluted with TCE (0.5 mL/minute) or TCB (0.75 mL/minute) with a temperature ramp from 30 °C to the stabilization temperature (0.25 or 0.5 °C/minute). The TREF column was cleaned at the end of the run for 20 minutes at the dissolution temperature. The eluting polymer solution was monitored using the Bruker Tensor 27 FT-IR spectrometer.

All FT-IR spectra were acquired using OPUS process software. Background spectra of the solvent were obtained prior to each run. All spectra were measured at 8 cm$^{-1}$ resolution with 64 scans (one spectrum in ~ every 20 seconds). Spectra from individual time slices were analyzed in "real-time" for component concentrations using the chemometric technique (i.e. PLS). The concentration data were acquired using OPUS process software. These data were processed using Excel and OMNIC software to provide the average chemical compositions and chemical composition distributions.

## Results and Discussion

### Ethylene/$\alpha$-Octene Copolymers

As already mentioned, the IR detector works well for ethylene/$\alpha$-olefin copolymers regarding the polymer concentration measurement in TREF. However, establishing the correlation between the TREF elution temperature and the polymer chemical composition (i.e. comonomer content) is a very time- and labour-consuming process. It includes collecting the TREF fractions and doing the post-fractionation analyses typically by NMR. The use of on-line FT-IR detection in TREF provides a fast means to measure the comonomer content in ''real-time''.

The FT-IR determination of the comonomer content for ethylene/$\alpha$-olefin copolymers in TCB solution relies on methyl and methylene absorption bands between 3000 and $2800\,cm^{-1}$. In this region of the spectrum, the solvent (TCB) has a minimal amount of interfering absorption. The IR spectral aspects of ethylene/$\alpha$-olefin copolymers in this region have been well addressed and the spectral deconvolution has been reported by DesLauriers et al.[10] Similar to DesLauriers' work, Figure 7 shows the FT-IR spectrum of the linear polyethylene (SRM1484a) in solution and the peaks fitted using GRAMS AI software (baseline function: linear; peak function: Gaussian + Lorentzian). Since this sample is a homopolymer with $Mn = 100500$ g/mol, its spectrum can be viewed as representing absorptions that solely arise from backbone methylene units. It has been reported that methyl chain-ends on polymers with $Mn > 9000$ g/mol contribute little to the visible complexity of the spectrum.[10] The two strong bands at 2855 and $2926\,cm^{-1}$ correspond to symmetrical and asymmetrical C-H stretching vibrations of methylene ($CH_2$) groups, respectively.[18] In addition to these two bands, the shoulder at $\sim 2900\,cm^{-1}$ is a combination absorption possibly arising from $CH_2$ deformation bands as suggested by DesLauriers et al [10] with the support from the solid state FT-IR analysis of PE.[19] The respective symmetrical and asymmetrical vibrations for methyl groups[18] at 2874 and $2957\,cm^{-1}$ are illustrated in the FT-IR spectrum of eicosane (Figure 8). When methyl moieties appear as chain ends to chain branches, spectral profiles are similar to those found for straight-chain hydrocarbons, i.e. five main peaks as fitted using GRAMS AI software (baseline function: linear; peak function: Gaussian + Lorentzian).

For building the calibration model using the PLS method, seventy-four standards were made by mixing the solutions of the homopolymer with the solutions of the low molecular weight hydrocarbon. Some single site catalyst (SSC) resins were also taken as standards. The infrared spectra of standard solutions were inputted into the QUANT software along with the polymer concentrations and methyl concentrations. Second derivatives of the spectra in given frequency ranges and cross validation were used in the calculations. The PLS regression method is a ''full spectrum method''. However, in some cases spectral noise in

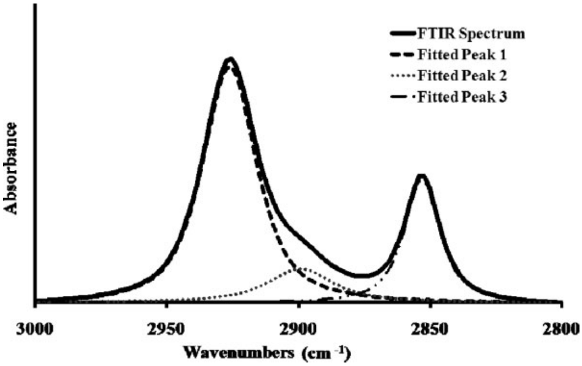


*Figure 7.*
Expanded IR spectrum of PE homopolymer.

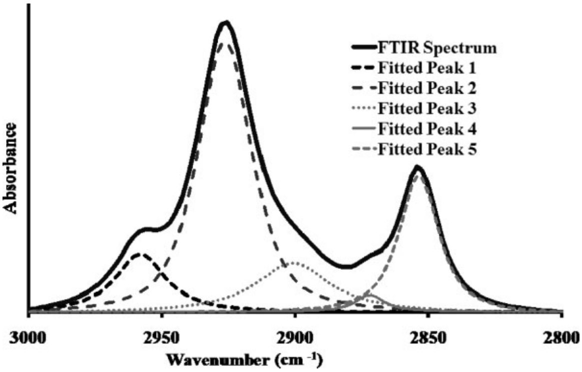


***Figure 8.***
Expanded IR spectrum of eicosane.

the samples may cause the PLS algorithm to interpret these features, which can degrade the model. In these cases it is better to narrow down a spectrum to a few absorption bands. The absorption band between 2800 and 3000 $\mathrm{cm}^{-1}$, in which there is least spectral noise, was chosen for building the calibration model in this study. Figure 9 shows calibrations for polymer concentration and methyl concentration.

Based on the FT-IR spectrum of the eluting polymer solution, the methyl content ($[CH_3]$) and polymer concentration ($[C]$) can be predicted from the above PLS calibration model and branch frequency (BrF) can be calculated using this equation:

$$\mathrm{Brf} = (14000 \times [\mathrm{CH_3}])/(15 \times [\mathrm{C}] - 14 \times n \times [\mathrm{CH_3}])$$

where $n$ depends on the type of the comonomer ($n = 5$ for octene).

It is known that both cooling and heating rates have impacts on the TREF chemical composition distribution (CCD) profile of a Z-N ethylene/$\alpha$-hexene LLDPE copolymer.[20] Experimental results have demonstrated that the selection and pairing of cooling and heating rates play a critical role in determining the CCD profile of the resin. Said differently, it was shown through numerous examples that very different CCD profiles ranging from seemingly "homogeneous" to "heterogeneous" behavior could be observed for the same resin using different cooling/heating rate combinations. Thus it is clear that a proper understanding and choice of both the cooling and heating rates is necessary to adequately discern molecular architecture information and also provides reason for caution in comparing data for different resins obtained under different conditions.

After examining several cooling/heating/flow rate combinations, the TREF-FT-IR run conditions were set as follows in the present work: cooling rate 0.20 °C /minute, heating rate 0.25 °C/minute, flow rate 0.75 mL/minute, and sample volume 1.0 mL. It was found that the sample concentration had no significant impact on the TREF-FT-IR profiles of the ethylene/$\alpha$-octene copolymers investigated in this work and there was a huge flexibility in sample concentration. In principle, TREF usually prefers a low sample concentration and FT-IR detection often requires a high sample concentration. In reality, the sample concentration can be determined based on the nature of the sample to be analyzed. For example, a higher sample concentration can be used for the broad composition distribution samples and a lower sample concentration for the narrow composition distribution samples. Typical sample concentration used in this work for TREF-FT-IR analysis is 40 to 150 mg of polymer in 20 mL TCB.

The TREF-FT-IR data of the random ethylene/$\alpha$-octene copolymer is shown in

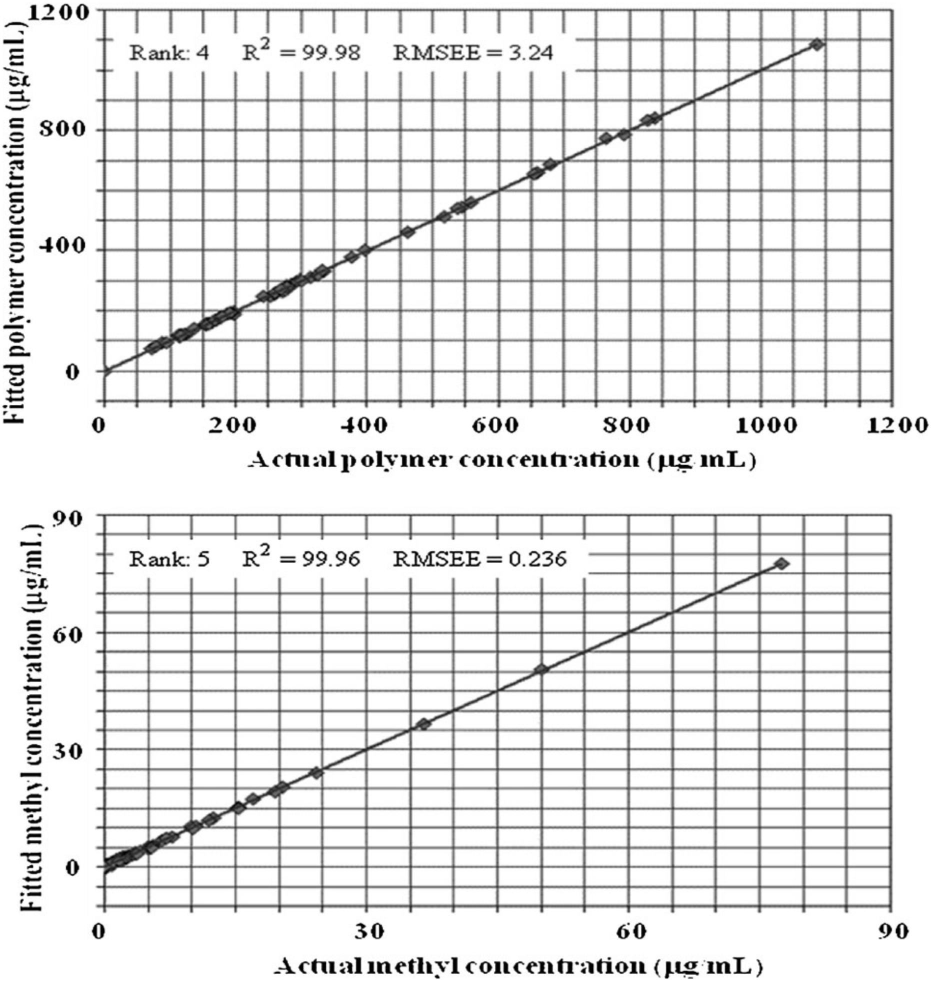


***Figure 9.***
PLS calibration model for ethylene/$\alpha$-octene copolymer.

Figure 10. The "dWf/dT" curve is the differential mass profile (versus TREF temperature). The "Accumulative Wt Fraction" curve is calculated based on the mass profile. The composition line is the measured comonomer content as a function of TREF elution temperature.

In TREF analysis, it is known that the chemical composition of the eluting polymer at a given elution temperature can be predicted from the TREF calibration curve that correlates the TREF elution temperatures to comonomer contents. This calibration curve usually results from larger-scale preparative TREF analyses where fractions having varying short-chain branch (SCB) frequencies are then analyzed spectroscopically, typically by NMR or IR spectroscopy, to provide a measurement of the SCB frequency. Although several schemes have been proposed for the development of a universal calibration curve,[21,22] the existence of such universal curves is now widely discounted. It has been reported that the SCB length had an impact on the TREF calibration,[23] and experimental results indicated that the calibration curves shifted to lower TREF elution temperatures as the length of the SCB increased from methyl to butyl and hexyl. Others factors that might

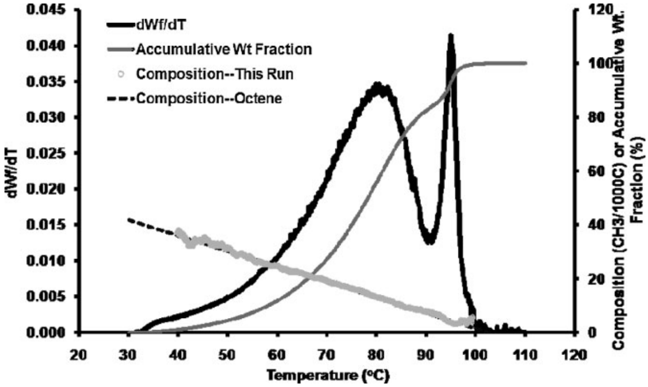


***Figure 10.***
TREF-FT-IR profile of random ethylene/$\alpha$-octene copolymer.

contribute to this shift included chain microstructural differences from variations in catalyst structure and pocess conditions. Thus, the branch type must be known in advance in order to calculate the SCB distributions and that unique calibration curves exist for copolymers made using different $\alpha$-olefin comonomers.

The power of using FT-IR in TREF detection is the on-line measurement of comonomer content. This is extremely important for characterization of complex olefin copolymers, such as olefin block copolymer (OBC) produced by chain shuttling polymerization,[24] since it provides a fast means to measure the comonomer content in ''real-time'' as compared with the very time- and labour-consuming off-line analyses of preparative TREF fractions spectroscopically by NMR or IR. As shown in Figure 11, the measured octene contents of the OBC copolymer by on-line FT-IR were significantly higher than those of the traditional random copolymer at the specific TREF elution temperatures. This agrees well with the previous observation by Shan and Hazlitt.[25]

### Polystyrene Grafted Ethylene-Vinyl Acetate Copolymers

PS-graft-EVA is an interpolymer of polyethylene and styrene copolymer. It was produced by polymerizing the styrene using free radical polymerization in the presence of EVA. As discussed in a previous section,

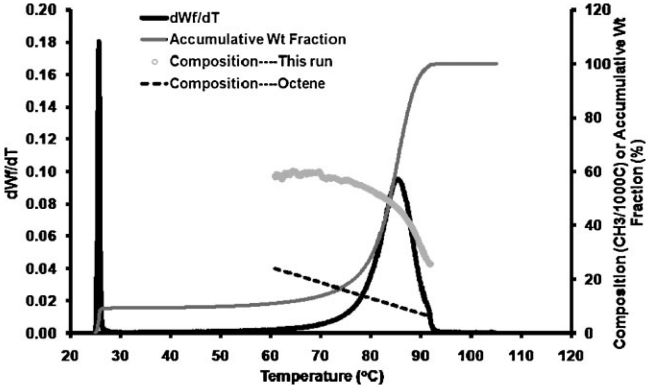


***Figure 11.***
TREF-FT-IR profile of block ethylene/$\alpha$-octene copolymer.

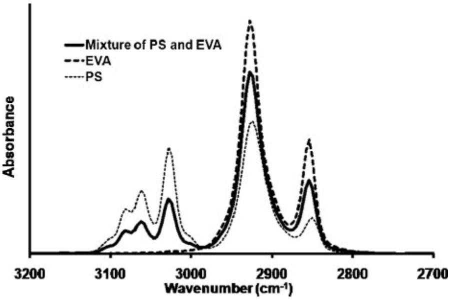


*Figure 12.*
Expanded IR spectra of PS, EVA and their mixture.

the concentration of this type of polymer in TREF analysis cannot be measured by the IR detector. The on-line FT-IR detection can be used to solve this problem.

Figure 12 shows the expanded FT-IR spectra of PS, EVA and their mixture, dissolved in TCE. When PS chains appear as the branches that are grafted to the EVA chains, spectral profiles of the PS-graft-EVAs are practically identical to those of physical mixtures of PS and EVA having the same chemical compositions in terms of polystyrene weight percent. The determination of polymer concentration and composition relies on absorption bands between 3200 and 2700 $\mathrm{cm}^{-1}$. For building the calibration model using the PLS method, eighty standards were made to represent the EVA-graft-PS copolymer system by mixing the solutions of the PS sample with the solutions of the EVA. The infrared spectra of standard solutions were inputted into the QUANT software along with the PS and EVA concentrations. The spectra were then divided into two independent sets, one for calibrating the system and the other for validating the model. Both sets consisted of about the same number of spectra. Straight Line Subtraction of the spectra in the spectral range of 2 720 to 3 135 $\mathrm{cm}^{-1}$ and test set validation were used in the calculations.

In TREF-FT-IR analysis, the eluting polymer solution is monitored using the Bruker Tensor 27 FT-IR spectrometer. Applying the above PLS calibration model to the FT-IR spectra allows for determining the concentration and composition (i.e., the weight fraction of polystyrene) of the eluting polymer at each TREF temperature. That is, the PS and EVA concentrations ([PS] and [EVA]) are predicted from the PLS calibration model. The total polymer concentration [C] can be calculated by

$$[\mathrm{C}] = [\mathrm{PS}] + [\mathrm{EVA}]$$

as well as the polymer composition (i.e., the weight fraction of polystyrene) by

$$\mathrm{PS\,wt\%} = 100 \times [\mathrm{PS}]/[\mathrm{C}]$$

In the present work, the TREF-FT-IR run conditions for analyzing PS-graft-EVA samples were as follows: cooling rate 0.10 °C/minute, heating rate 0.5 °C/minute, flow rate 0.5 mL/minute, and sample volume 1.0 mL. At the beginning of the elution, the sample was eluted with TCE at 30 °C for 20 minutes. The material eluted at this stage is defined as ‘‘Soluble Fraction @ 30C’’ (soluble material). Then, the crystallized sample was eluted with TCE with a temperature ramp from 30 °C to 90 °C. The material eluted at this stage is defined as ‘‘Insoluble @ 30C’’ (insoluble material).

Figure 13 shows the TREF-FT-IR profile of the polystyrene sample. Polystyrene is soluble in TCE at room temperature thus no material was detected above 30 °C during the elution stage. As can be seen from the TREF-FT-IR profile shown in Figure 14, the EVA contains about 13% soluble material. The TREF-FT-IR profile of the mixture of polystyrene and EVA is shown in Figure 15. As expected, there was no polystyrene detected in the insoluble fraction, i.e. ‘‘PSwt in (Insoluble @ 30C)’’ = 0%. This is the key point for the determination of grafts in polystyrene grafted EVA. The free polystyrene is soluble in TCE at room temperature and elutes below 30 °C. Thus any polystyrene detected in the insoluble material (i.e. above 30 °C) must be those grafted on the EVA chains. Figure 16 shows an example for the TREF-FT-IR profile of polystyrene grafted EVA. The data reported are the soluble fraction at 30 °C

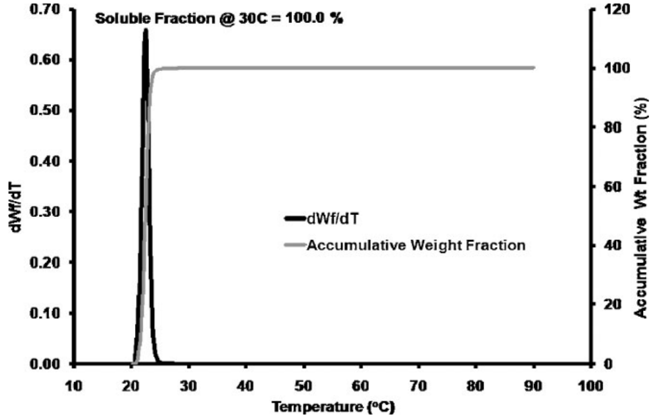


***Figure 13.***
TREF-FT-IR profile of polystyrene.

(“Soluble Fraction @ 30C”) and polystyrene content (“$PS_{wt}$ in Total”), the graft level (“$PS_{wt}$ in (Insoluble @ 30C)”) as well as the grafting efficiency (“$STY_{grafted}$/$STY_{total}$”).

Grafting efficiency (GE) is defined as the mass of grafted monomers divided by the total mass of polymerized monomers. It is well known that grafting of styrene to polybutadiene rubber has played an important role in the production of high impact polystyrene (HIPS) and has had a profound effect on HIPS properties. It decreased the interfacial tension between the polystyrene and polybutadiene rubber phase and prevented particle disintegration by acting as a surfactant or emulsifier. A high GE at the beginning of the reaction promoted an early phase inversion and the rubber particle size became smaller. However, if the grafting level is too high or overgrafting happens, the rubber morphology could be changed to an undesirable type.[26]

The grafting efficiency is an important parameter for the materials obtained by the polymerization of styrene in the presence of EVA since it affects the polymer morphology and thus material properties. As shown in Figure 17, the two samples have about the same composition in terms of polystyrene content but different grafting efficiencies, such that more phase separation

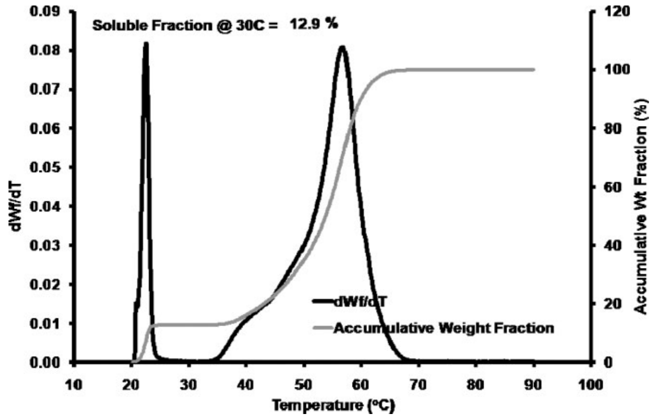


***Figure 14.***
TREF-FT-IR profile of EVA.

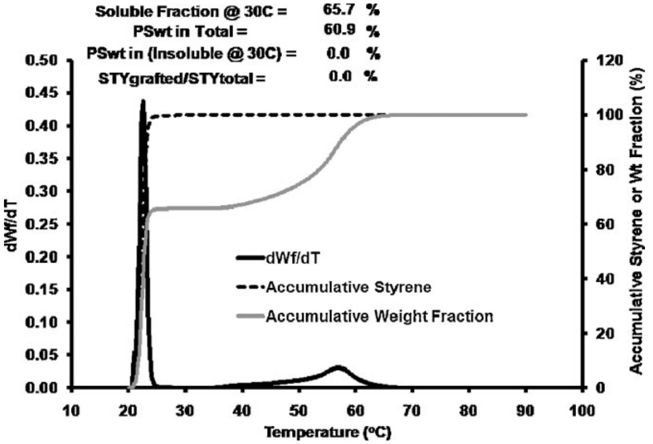


***Figure 15.***
TREF-FT-IR profile of PS and EVA mixture.

between the polystyrene and EVA domains was observed as expected for the material with less grafting efficiency by atomic force microscopy (AFM).

**Ethylene-Methyl Acrylate Copolymers**

Physical properties of olefin-based polymers, such as toughness and adhesion, can be improved via the incorporation of polar monomers,[27] such as methyl acrylate. Most manufacturing processes for preparing polar olefin polymers employ high-pressure polymerization. The formation of short chain branches (SCBs) has long been known to occur in the high-pressure olefin polymerization.[28] Much less formation of SCBs was observed in the preparation of polar olefin copolymers when the polymerization was performed in a controlled manner.[29]

As with ethylene/$\alpha$-olefin copolymers, the use of on-line FT-IR detection in TREF provides a fast means to measure the chemical composition in ‘‘real-time’’, avoiding the time- and labour-consuming process of collecting the TREF fractions and the post-fractionation analyses typically by NMR. In TREF-FT-IR analysis of ethylene-methyl acrylate (EMA) copolymers, both SCB and methyl acrylate can be

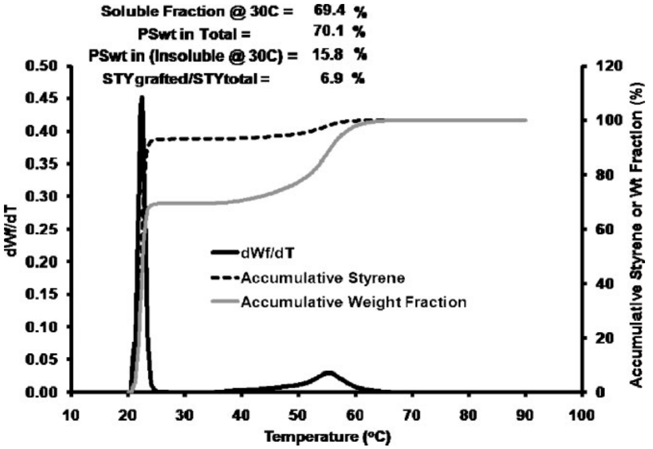


***Figure 16.***
TREF-FT-IR profile of PS-graft-EVA.

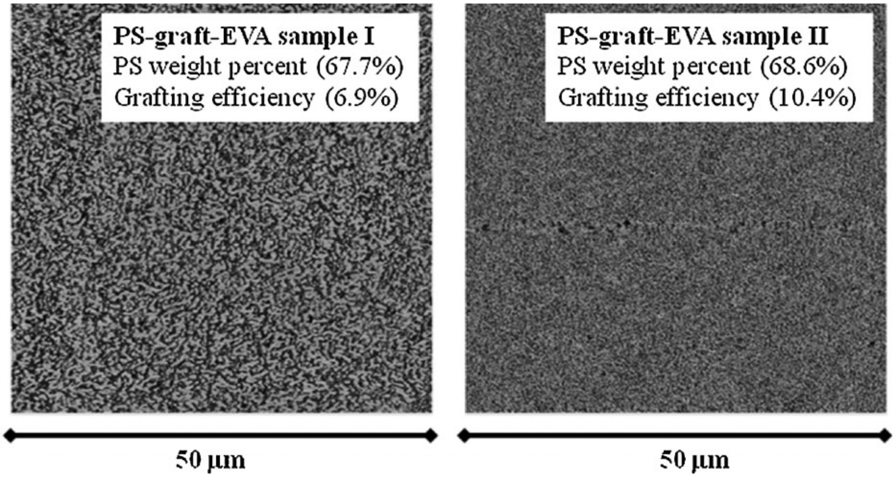


***Figure 17.***
AFM images of PS-graft-EVA.

quantified by the FT-IR detection. The determination of polymer concentration and composition relies on absorption bands between 3000 and 2800 $cm^{-1}$. For building the calibration model using the PLS method, fifty-six standards were made by mixing the solutions of EMA copolymers with known composition in terms of methyl acrylate weight percent and SCB content as determined by NMR, the polyethylene homopolymer as well as the low molar mass hydrocarbon. The IR spectra of the standard solutions were inputted into the QUANT software along with the concentrations of total polymer, methyl acrylate units and methyl end groups in SCBs. Second derivatives of the spectra in given frequency ranges and cross validation were used in the calculations.

The TREF-FT-IR run conditions for analyzing EMA copolymers were the same as for the ethylene/$\alpha$-octene copolymers: cooling rate 0.20 °C/minute, heating rate 0.25 °C/minute, flow rate 0.75 mL/minute, and sample volume 1.0 mL. The eluting polymer solution was monitored using the Bruker Tensor 27 FT-IR spectrometer. Applying the above PLS calibration model to the FT-IR spectra allows for determining the concentrations of each component in the eluting polymer at each TREF temperature. That is, [C], [MA] and $[CH_3]$ for total polymer and methyl acrylate units as well as SCB methyl end groups, respectively. The polymer compositions in terms of the weight percents of methyl acrylate as well as SCB methyl end groups can be calculated by

$$\mathrm{MA\,wt\%} = 100 \times [\mathrm{MA}]/[\mathrm{C}]$$

and

$$\mathrm{CH3\,wt\%} = 100 \times [\mathrm{CH_3}]/[\mathrm{C}]$$

respectively. Examples of TREF-FT-IR profiles are shown in Figures 18 and 19. In addition to methyl acrylate, SCB were detected in both samples.

## Conclusion

TREF is a popular analytical technique that is able to determine the chemical composition distribution of copolymers. A conventional IR detector is commonly used as the concentration detector in TREF and the measurement is based on a single wavelength. This works well for the simple copolymer systems such as ethylene/$\alpha$-olefin copolymers. However, the conventional IR detector does not work for complex copolymer systems, and an alter-

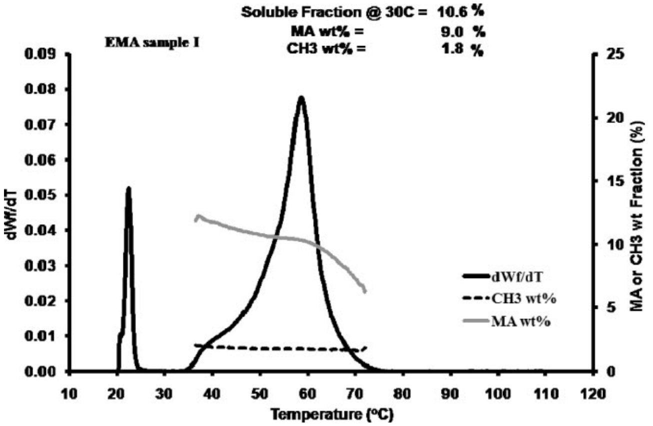


*Figure 18.*
TREF-FT-IR profile of EMA sample I.

native detection method is required for measuring the polymer concentration. In order to solve this problem, the use of FT-IR detection in TREF has been investigated in this work. The dual wavelength technique works well for two-component copolymer systems whereas the multivariate calibration method is required for analyzing the IR spectra of more complex multi-component copolymer systems. By applying the partial least squares technique, the power of FT-IR in TREF detection has been demonstrated using three copolymer systems: ethylene/$\alpha$-octene copolymers, polystyrene grafted ethylene-vinyl acetate and ethylene-methyl acrylate copolymers. In addition to polymer concentration, polymer composition (i.e. comonomer content) can be measured by on-line FT-IR detection. This eliminates very time- and labour-consuming TREF fraction collection as well as the post-fractionation compositional analyses by NMR and brings a benefit to the TREF analyses especially for the complex olefin copolymers such as ethylene/$\alpha$-olefin block copolymers and ethylene-methyl acrylate copolymers. Also, TREF-FT-IR analysis of polystyrene grafted ethylene-vinyl acetate provides an experimental means of measuring the

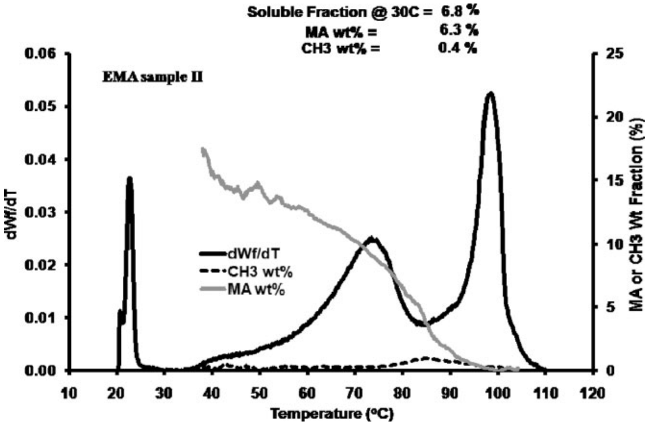


*Figure 19.*
TREF-FT-IR profile of EMA sample II.

grafting efficiency that is an important parameter affecting the polymer morphology and thus material properties.

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