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Polymer Vol. 36 No. 8, pp. 1639-1654, 1995

0032-3861/95/$10.00+0.00

Temperature rising elution fractionation of linear polyolefins

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(Received 8 July 1994; revised 24 August 1994)

Temperature rising elution fractionation (t.r.e.f.) is a technique for the fractionation and characterization of polymers with high crystallizability that has gained some popularity over the past few years, in particular for the copolymers of olefins. This review will cover the general aspects of t.r.e.f. and describe some of the most revealing applications published in the literature. In addition, recent measurements that have been carried out on the t.r.e.f./^{13}C n.m.r. spectroscopic characterization of polypropylenes synthesized using metallocene catalysts, as well as using classical heterogeneous Ziegler–Natta catalysts, are reported on herein.

(Keywords: t.r.e.f.; polyolefin fractionation; polyolefin characterization)

INTRODUCTION

In 1945 Stockmayer[1] derived the instantaneous bivariate distribution for chain length and composition for the synthesis of linear copolymers by chain-growth polymerization, a distribution function which is finding new applications even today. The special features of this distribution are shown in *Figures 1a* and *1b* for five different copolymers. The copolymers differ in their number-average molecular weights (M_ns) and average composition, but all have the product of their reactivity ratios ($r_1.r_2$) equal to 1, and are therefore random copolymers. All five copolymers have the most probable molecular-weight distribution. Regarding the composition distributions, the deviations from the average composition are larger for polymer chains having smaller lengths. This is quite intuitive, since one expects to observe more composition variability for shorter polymer chains when the synthesis is carried out at constant monomer concentrations. Stockmayer's distribution is a convenient way to quantify this intuitive concept.

What is important to stress is that copolymers, even when made under synthesis conditions where they have the most probable chain length distribution, are expected to show composition variations. This composition distribution affects the chain solubility significantly for polymers of high crystallizability and can be investigated by t.r.e.f. As we will see later, a single Stockmayer distribution is too simplified to describe most commercial polyolefins for which broader molecular weight and composition distributions exist.

Most commercial olefin copolymers are synthesized using heterogeneous Ziegler–Natta catalysts. It is generally accepted that these catalysts have multiple-site types, with each site type instantaneously producing polymer with different Stockmayer bivariate distributions[2]. Therefore, the chemical composition distribution of the accumulated copolymer can be considered as being an average of that produced by the individual site types. The simulated t.r.e.f. curve of a binary linear copolymer made by a five-site type catalyst can be obtained by superimposing the chemical composition distributions shown in *Figure 1b*. In this case, the simulated t.r.e.f. curve shows a remarkable resemblance to the experimental t.r.e.f. curves obtained for linear low-density polyethylene (LLDPE) (see *Figure 1c*). For these polymers, the use of t.r.e.f. is even more important to comprehensively measure their properties and fully understand the mechanisms of chain synthesis.

It is also important to recall that the macroscopic properties of polymers cannot be uniquely determined by average values. Determining, for example, the molecular weight averages of a polymer sample by light scattering or osmometry, or with a more crude estimation from melt flow index measurement, is usually not sufficient to uniquely define the state of the polymer sample, since polymers with the same average molecular weights can possess other properties that differ markedly. Even a knowledge of the full molecular-weight distribution for polypropylene may not be sufficient for many practical applications, due to stereoirregularities.

In the same way, determining the average compositions of copolymers or the average degrees of branching by *FT*i.r. or ^{13}C n.m.r. spectroscopy will not entirely define the polymer in question. The whole distribution of composition in addition to chain length is necessary in order to accomplish this task.

Temperature rising elution fractionation (t.r.e.f.) is currently the best technique for obtaining a composition distribution for polymers of high crystallizability.

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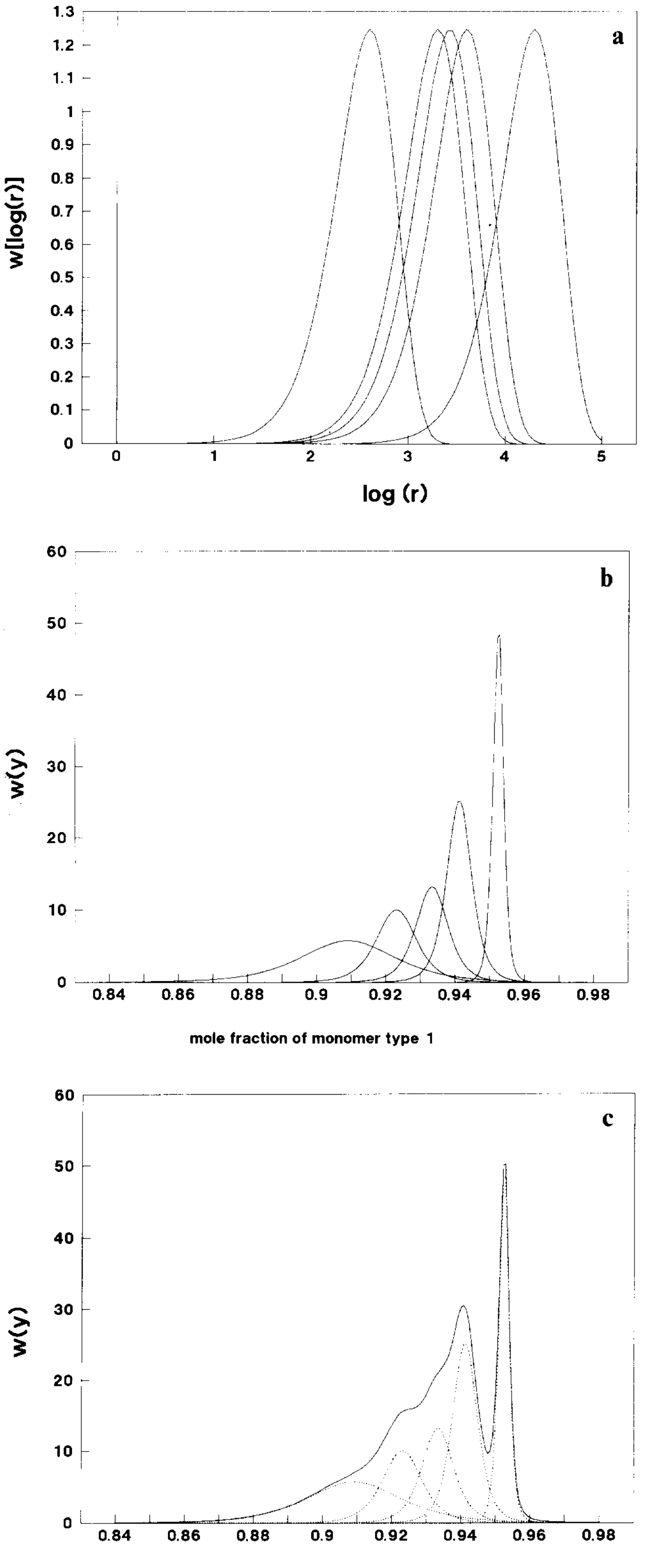

Figure 1 (a) Chain length distribution of five copolymers having different mean chain lengths. (b) Chemical composition distribution of five copolymers having different mean chain lengths. (c) Theoretical t.r.e.f. curve of LLDPE made by a five-site type catalyst

Detailed information about the molecular structure of polymers can be correlated to their macroscopic properties and therefore to their final applications. For instance, *Figure 2* shows the property relationships with density, molecular weight and melt index for polyethylene. Take impact strength as an example. According to this figure, this property decreases when the density of polyethylene increases. Therefore, by lowering the density of polyethylene, for example by copolymerizing ethylene with some other α-olefin, one can increase the impact strength.

However, this does not give us the complete description of the polymer, because besides its composition we also have to be aware of its molecular weight. *Figure 2* illustrates how the properties of polyethylene vary with molecular weight. In the particular case of impact strength, this property is inversely proportional to the molecular weight.

Since copolymers show distributions of both molecular weight and composition, and since not only the average values, but also the shape of these distributions, can have a marked influence on the polymer properties, only the determination of this bivariate distribution can lead to a more complete understanding of the polymer behaviour in end-use applications.

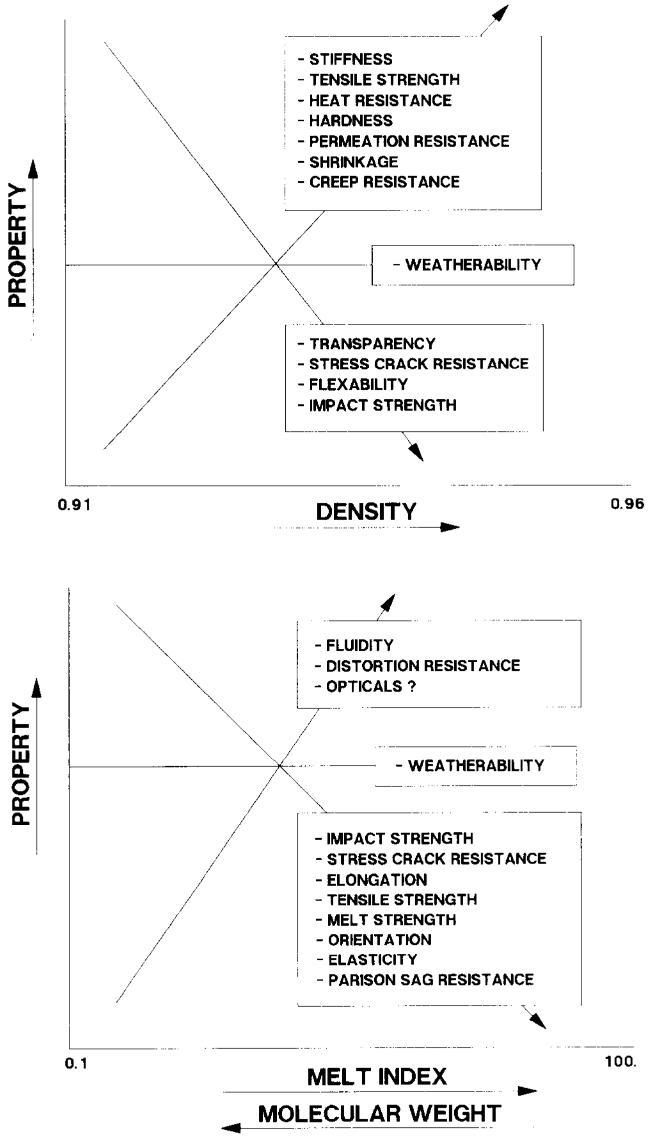

Figure 2 Property relationships with density, molecular weight and melt flow index for polyethylenes

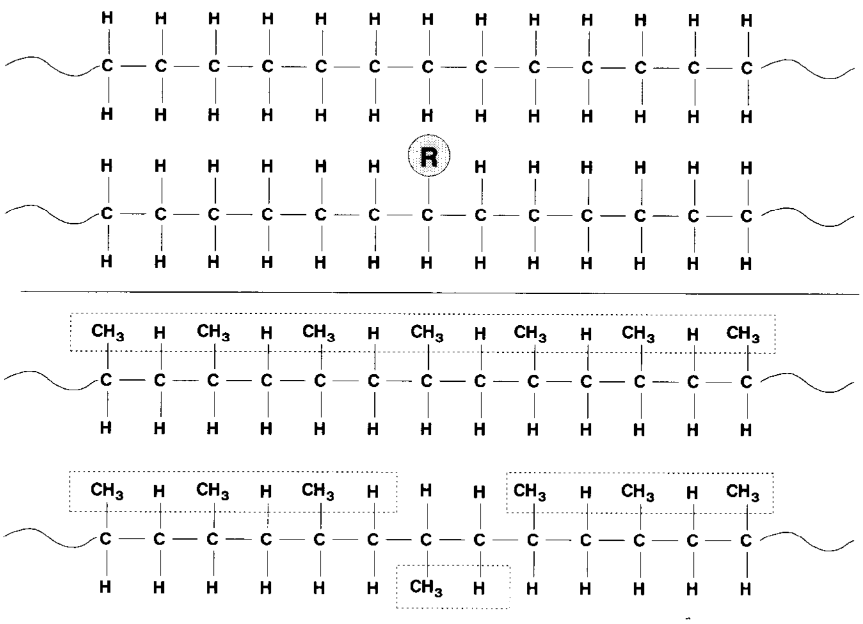

Figure 3 Effect of comonomers and stereoregularity in chain structure and crystallinity

We will review in this paper how t.r.e.f. can be applied to obtain the composition distribution of this bivariate distribution.

DEFINITION OF TEMPERATURE RISING ELUTION FRACTIONATION

T.r.e.f. can be concisely defined as a technique to fractionate semicrystalline polymers according to their solubility–temperature relationship and thus to their molecular structures. Two important parts of this definition must be stressed. First, t.r.e.f. only fractionates semicrystalline polymers. It is not applicable to amorphous polymers because t.r.e.f. is mainly sensitive to differences in polymer crystallinity/solubility. Secondly, the t.r.e.f. technique fractionates polymer chains according to the molecular structure that affects crystallinity/solubility. Distinct molecular structures of semicrystalline polymers are reflected in their different crystallinity/solubility, and t.r.e.f. is sensitive to these differences.

A complementary definition is as follows: t.r.e.f. is sensitive to and based on the relationship between molecular structure, chain crystallinity and dissolution temperature. Therefore, different molecular structures will be reflected in distinct crystallinities that will translate to dissimilar dissolution temperatures. T.r.e.f. operates in the reverse order, i.e. by making use of the differences in dissolution temperature that arise due to the dissimilar crystallinities of polymer chains we can infer their molecular structures.

Figure 3 illustrates those ideas. The upper chain is the homopolymer, namely high-density polyethylene (HDPE). It has a very high structural order and therefore crystallizes in the form of a hard and brittle polymer. However, if we substitute one of the hydrogens attached to the backbone by another chemical group (R), we disrupt the structural order of the original chain. Now this unit may not crystallize with the other regular chains, and therefore the crystallinity of the polymer will be lower than that of the original fully regular one. This is carried out commercially with polyethylenes in order to alter the macroscopic properties of the polymer, and the products are known as linear low-density polyethylene (LLDPE). The extraneous monomer unit or comonomer can be, for instance, 1-butene, 1-hexene or 1-octene.

In a similar way, when considering a homopolymer that can experience stereoisomerism, such as polypropylene, the crystallinity of the original chain can be altered by the introduction of a monomer in the inverse position, known as an atactic placement. This polymer will be less crystalline than the corresponding one where all of the methyl groups are on the same side of the chain. The lower part of *Figure 3* illustrates these ideas.

T.r.e.f. makes use of these differences in molecular structure to fractionate the polymer chains.

T.r.e.f. can be divided into two sequential stages, as illustrated in *Figure 4*, namely precipitation and elution. In the precipitation step, the polymer is dissolved in a good solvent and then put in contact with an inert support; the solvents commonly used are trichlorobenzene (TCB), *o*-dichlorobenzene (ODCB), xylene or α-chloronaphthalene. The usual supports are chromosorb P, glass beads, silica gel or stainless steel shots. The precipitation or crystallization is carried out under well controlled conditions by slowly decreasing the temperature. Polymer fractions that remain in solution are removed as the first fraction. Mirabella[3] proposed that the polymer coats the support in layers of different crystallinity, as shown in greatly exaggerated dimensions in the detail of *Figure 4*. The layers that are closer to the surface of the support were precipitated at higher temperatures and therefore are more crystalline than the external ones. This step can be performed in a stirred vessel (as shown in *Figure 4*) or directly in the t.r.e.f. column.

In the second step, the polymer layers are eluted from the support in the reverse order to that in which they were precipitated. Solvent flows through a column packed with the polymer-coated support while the temperature is slowly increased. If the column is connected to a mass concentration detector, a curve of the type depicted in *Figure 4* is obtained: less crystalline fractions elute first

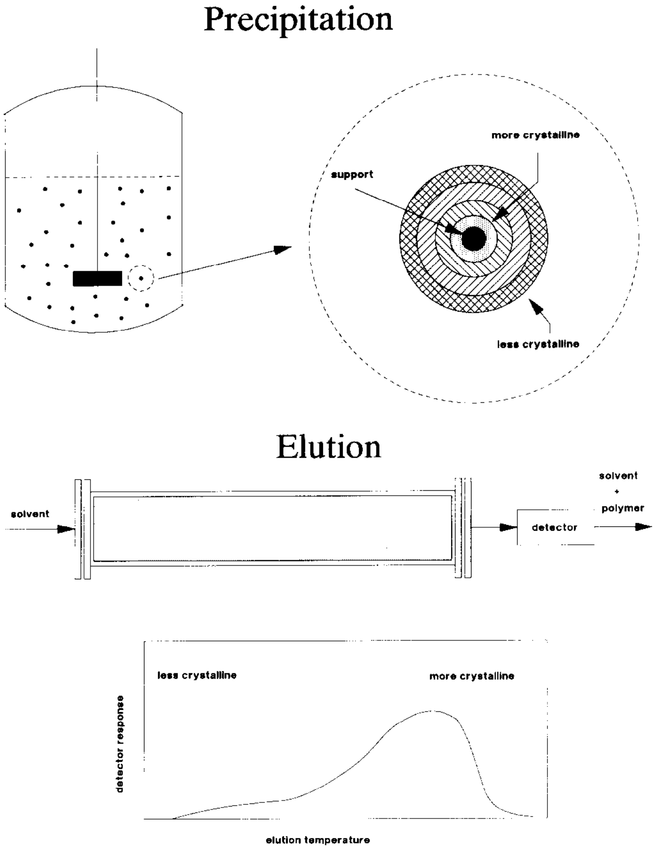

Figure 4 Schematic representation of temperature rising elution fractionation (t.r.e.f.)

at lower temperatures while more crystalline fractions are only eluted at higher temperatures at the end of the fractionation.

T.r.e.f. can be operated in two ways. Preparative t.r.e.f. is a separation technique in which polymer fractions are collected at predetermined temperature intervals. These fractions are then analysed off-line to determine their microstructures. Analytical t.r.e.f. is an analytical technique in which the eluted polymer is continuously monitored by an on-line detector as shown in the bottom part of *Figure 4*. In this case no further analysis of the fractions is normally carried out if a calibration curve that relates elution temperature to the investigated property, for example the degree of chain branching in LLDPE, was previously determined. Since standards of narrow-composition distribution for t.r.e.f. calibration are not easy to obtain, they generally have to be previously obtained by preparative t.r.e.f.

The basic features of preparative and analytical t.r.e.f. are shown in *Table 1*. Preparative t.r.e.f. requires larger columns in order to hold larger samples so that the fractions can be big enough to be analysed off-line. Analytical techniques such as ^{13}C n.m.r. and *FT*i.r. spectroscopy, d.s.c. and g.p.c. are commonly used on the fractions and can give a wealth of information about the polymer sample. Clearly, more information about the samples can be obtained by using preparative t.r.e.f. than analytical t.r.e.f. Preparative t.r.e.f. is, however, more time consuming than analytical t.r.e.f., not only in operation, but also in the time required for filtering, drying and analysing the fractions.

As a general recommendation, analytical t.r.e.f. should be used for routine work, such as qualitative comparison between different copolymers and quality control, while preparative t.r.e.f. is more useful for research and development investigations.

A characteristic calibration curve for the analytical t.r.e.f. of LLDPE reported by Wild *et al.*[4] is shown in *Figure 5*. The calibration standards were preparative fractions of polyethylene resins of similar melt flow index produced in an autoclave reactor at different temperatures (and therefore containing different short-chain branching (SCB) levels) and ethylene–butene copolymers. The points fall on a straight line, with some deviation at lower degrees of short-chain branching. Several, but not all, of the calibration curves for SCB *versus* elution temperature for LLDPE shown in the literature are linear. It is important that the polymer samples investigated by t.r.e.f. have the same microstructure as the standards used for calibration. There is no 'universal' calibration curve for t.r.e.f. Besides SCB, other factors affecting chain crystallinity, such as comonomer sequence length, are of fundamental importance in determining the elution temperature of the fractions.

Generic t.r.e.f. profiles of some common polyolefins are presented in *Figure 6*. Atactic polypropylene has a

Table 1 Comparisons between analytical and preparative t.r.e.f.

Preparative t.r.e.f.	Analytical t.r.e.f.
Fractions are collected at predetermined temperature intervals	Continuous operation
Information about molecular structure is obtained off-line by additional analytical techniques	Information about molecular structure is obtained on-line by means of a calibration curve
Requires larger columns and larger sample sizes	Requires smaller columns and smaller sample sizes
Time-consuming but can generate detailed information about polymer microstructure	Faster than preparative t.r.e.f. but generates less information about polymer microstructure.

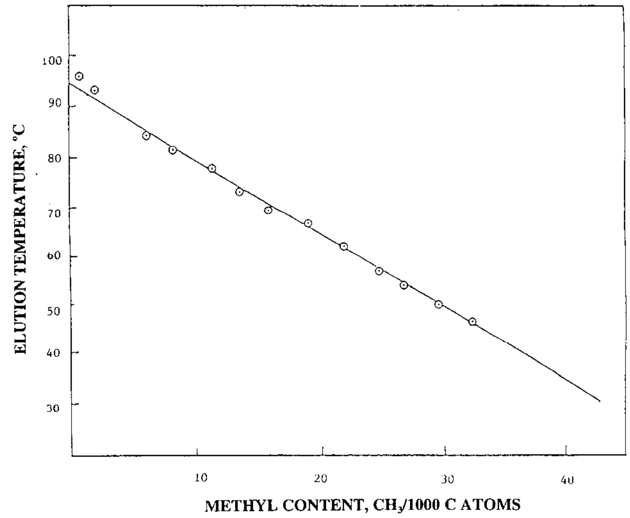

Figure 5 Analytical t.r.e.f. calibration curve for HDPE and LLDPE; calibration standards are fractions obtained by preparative t.r.e.f. of polyethylene resins of similar melt flow index produced in an autoclave reactor at different temperatures and LLDPE (ethylene/butene) (reproduced from ref. 4)

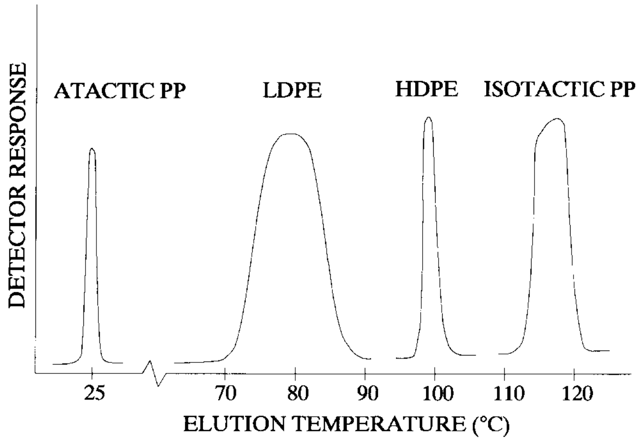

Figure 6 T.r.e.f. chromatograms of some polyolefins

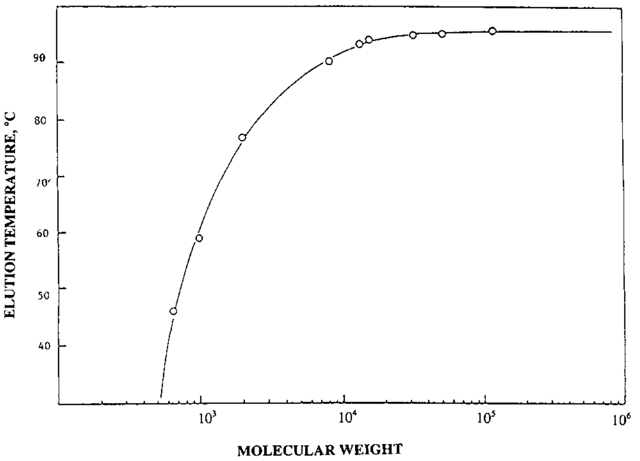

Figure 7 Influence of molecular weight on the elution temperature of narrow *MWD* linear polyethylene (HDPE) (reproduced from ref. 4)

disorganized molecular structure and therefore does not crystallize. It elutes as the first fraction since it is soluble even at room temperature in the solvents commonly used. The short- and long-chain branches of high-pressure, low-density polyethylene (HP-LDPE) also decrease its crystallinity, causing it to elute at lower temperatures. Since there will be a distribution of branching, the t.r.e.f. profile is broad. HDPE is a highly crystalline polymer and therefore elutes at a higher, narrower temperature range. Finally, highly isotactic polypropylene is also highly crystalline and since it is generally less soluble it elutes at temperatures which are even higher than polyethylene. Stereoregularity defects and monomer inversions can broaden its t.r.e.f. profile.

The most important step in the t.r.e.f. process is the sample crystallization. As mentioned before, during the crystallization step polymer chains of different crystallinity are separated. The elution step is simply the careful recovery of the already fractionated polymer. Therefore, one has to be very careful in order to avoid secondary effects such as cocrystallization and molecular weight influences during the precipitation step. This is accomplished by a slow cooling rate. Wild *et al.*[4] suggest an upper limit of 2°C h^{-1} for a variety of polyethylene types. This is evidently the limiting slow step of the technique. In the case of copolymers of polypropylene, for example, where it is necessary to cool the polymer solution from 140°C to room temperature it takes approximately $2\frac{1}{2}$ days to complete the precipitation step.

The effect of molecular weight on the fractionation of polyethylene was reported by Wild *et al.*[4] and is illustrated in *Figure 7*. Linear polyethylene samples (HDPE) of a narrow molecular-weight distribution (*MWD*) were used to produce this curve. The elution temperature is virtually molecular-weight independent for values larger than 10 000. For shorter chains, the effect of the non-crystallizable chain ends[5] becomes more pronounced and the elution temperature decreases. It seems, therefore, that for common commercial copolymers of high molecular weight, the influence of molecular weight on the fractionation is negligible.

Cocrystallization is another concern when one deals with t.r.e.f. If chains of different structure crystallize at the same time, then the usefulness of t.r.e.f. as a separation technique is severely reduced. However, if the precipitation step is carried out carefully, this does not seem to be the case. In *Figure 8*, the circles indicate a t.r.e.f. profile of a mixture of equal parts of 3 fractions of polyethylene obtained by preparative t.r.e.f., while the triangles represent the t.r.e.f. profiles of the same fractions obtained individually[4]. The first peak corresponds to a HDPE fraction having $M_w = 32\,000$ and the two other peaks represent LLDPE with methyl contents of 6.2 and 19.1 methyls per 1000 carbon atoms. There is a very good agreement between the two curves and at least for this case cocrystallization effects do not seem to be important.

Solvent type does not seem to play a significant role in t.r.e.f. as far as fractionation resolution is concerned. As can be seen in *Figure 9* for four different solvents, the calibration curves are almost parallel[6]. The better the solvent, then the lower the elution temperature for a polymer of a given molecular structure, as can be seen by comparing the dissolution temperatures of LLDPE and HDPE in TCB (best solvent) and α-chloronaphthalene (worst solvent). Notice that this is also in excellent agreement with Flory's theory of melt-point depression by solvents[5].

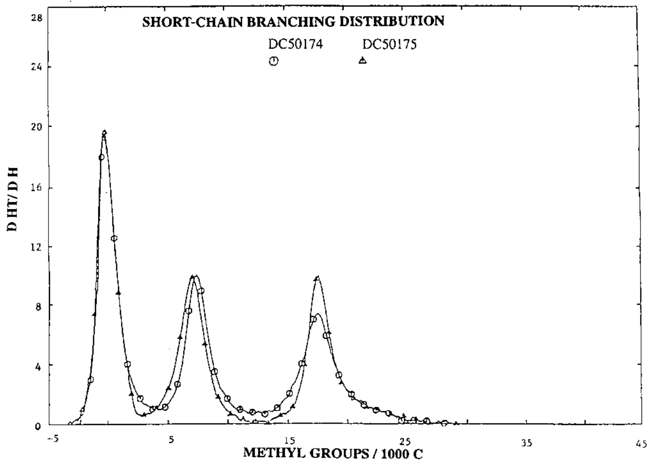

Figure 8 Influence of cocrystallization for polyethylene samples. The left-hand peak corresponds to HDPE having $M_w = 32\,000$, the intermediate peak to LLDPE having 6.2 methyls per 1000 carbon atoms and the right-hand peak to LLDPE having 19.1 methyls per 1000 carbon atoms (reproduced from ref. 4)

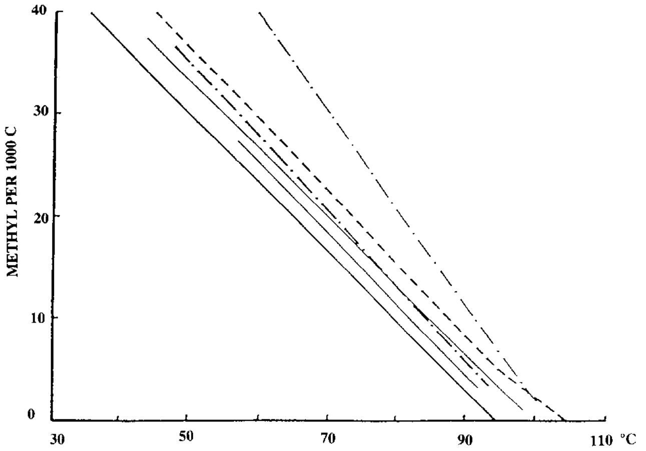

Figure 9 Effect of solvent type on t.r.e.f. calibration curves for HDPE and LLDPE: (——) trichlorobenzene; (——) xylene; (— · —) *o*-dichlorobenzene; (– – – –) α-chloronaphthalene (reproduced from ref. 6)

LITERATURE REVIEW

T.r.e.f. has been mainly applied for characterizing polyolefins, especially polyethylenes, polypropylenes and their copolymers. Some applications have also been reported for polymer blends which are particularly interesting for the evaluation of cocrystallization in the fractionation process. A very extensive and comprehensive review of t.r.e.f. applications was published by Wild[7].

Polyethylene

High-pressure low-density polyethylene (HP-LDPE) was the first polyolefin to be studied by a t.r.e.f. related technique. One of the earliest attempts to fractionate HP-LDPE according to its degree of chain branching in an apparatus based on increasing temperature fractionation was performed by Desreux and Spiegels[8]. Hawkins and Smith[9] applied this same technique to the, by that time, new HDPE produced by heterogeneous Ziegler–Natta catalysts. A linear relationship between the short-chain branching (SCB) and the elution temperature was obtained for four types of HDPE and one type of HP-LDPE.

In a somewhat different approach, Shirayama *et al.*[10] fractionated HP-LDPE according to molecular weight by the solvent gradient method. The fractions obtained were further fractionated according to their SCB by a temperature elution method. It was found that the SCB distribution was broader when the average molecular weights of the fractions were lower. Notice that this result is in good agreement with the Stockmayer bivariate distribution in which a broader composition distribution (or SCB distribution) is expected for chains with lower average molecular weights.

The acronym t.r.e.f. was first proposed by Wild and Ryle[11]. These authors showed how the principles of increasing temperature fractionation could be adapted to an analytical technique to determine the SCB of LLDPE. The suggested approach was to obtain fractions of a narrow SCB distribution having different SCB averages by using increasing temperature fractionation techniques (later called preparative t.r.e.f.) and then use them to determine a calibration curve of the SCB as a function of elution temperature for the analytical t.r.e.f. A linear relationship between SCB and elution temperature was obtained.

T.r.e.f. also proved to be useful in fractionating 'composite' HP-LDPE molecules synthesized by varying the operation conditions of different regions of an autoclave reactor[12]. A linear relationship between methyl group concentration and elution temperature was only observed for a sample of LLDPE (ethylene/1-butene copolymer).

Nakano and Goto[13] proposed a combination of analytical t.r.e.f. and g.p.c. in an automated composition fractionation/molecular-weight distribution measurement mode. The fractions were collected in a stepwise mode and directly injected into the gel permeation chromatograph. Four low-density polyethylene (0.921–0.924) and one HDPE (0.978) and their mixture were analysed to assess the usefulness of the system. The fractionation of one sample took ~ 10 h to complete. This analytical system is very attractive because it permits the determination of the complete bivariate distribution online. Care should be exercised, however, in the interpretation of the g.p.c. results, since this technique is sensitive to the radius of gyration of a polymer in solution which depends both on the molecular weight and the chemical composition of the polymer.

Probably the most substantial work to date defining the applicability and limitations of analytical t.r.e.f. was published by Wild *et al.*[4]. The HDPE and LLDPE standards for calibration of the analytical t.r.e.f. process were obtained from fractions from preparative t.r.e.f., which were then analysed by *FT*i.r. to determine the SCB. The calibration curve obtained for the degree of SCB *versus* elution temperature was linear, as presented in *Figure 5*. Molecular weight effects on the fractionation efficiency were tested by determining the elution temperature of linear polyethylenes with different molecular weight averages. It was found that the elution temperature was affected by this parameter only for molecular weights lower than 10 000 (see *Figure 7*). However, the chain ends are non-crystallizable units and therefore for small chains the solubility increases significantly. Profiles of fractions having different degree of SCB and of mixtures of these fractions almost overlapped, showing that cocrystallization effects were not important for the systems studied (*Figure 8*). As additional evidence, the SCB obtained by using the calibration curve and that for the whole copolymer obtained by using *FT*i.r. showed good agreement. HP-LDPE samples from autoclave and tubular reactors were also compared and their different structures were attributed to differences in reactor types and polymerization conditions. LLDPE and ethylene copolymers with vinyl acetate and ethyl acrylate were also fractionated with good efficiency.

T.r.e.f. has also often been used to study the nature of polymerization catalysts. In a very interesting paper, Usami *et al.*[14] compared four LLDPE samples made by different processes with one HP-LDPE sample. These profiles are depicted in *Figure 10*. While the HP-LDPE sample presents a relatively narrow, low-elution-temperature range, all four LLDPE samples show considerably broader and bimodal t.r.e.f. profiles. All of the LLDPE samples were produced by different processes, therefore this behaviour could not be linked to reactor operation conditions. Since LLDPE samples

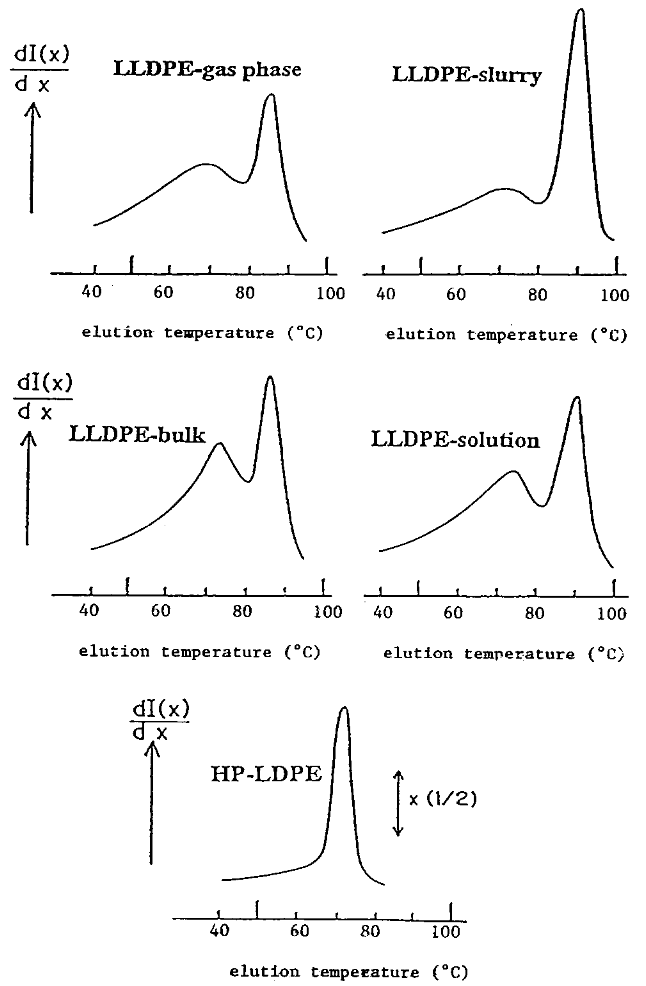

Figure 10 T.r.e.f. profiles of LLDPE and HP-LDPE (reproduced from ref. 14)

were produced by catalytic processes, it was proposed that there were at least two different types of active sites on the catalyst, one producing almost exclusively linear homopolymer polyethylene and the other LLDPE with a broad composition distribution. Recalling Stockmayer's bivariate distribution, this is equivalent to saying that each site type produces polymer that follows the Stockmayer distribution and the distribution for the bulk copolymer is in fact the superposition of these individual distributions. Apparently t.r.e.f. is able to partially separate the products of each one of the active site types. These polymers can be considered as a blend, at the molecular level, of different types of polymers made simultaneously on the same catalyst particle.

The d.s.c. curves of some of these LLDPE fractions[15] are shown in *Figure 11*. Curve F1 corresponds to the fraction obtained at the lowest temperature and F6 to that at the highest. As expected, the melting points increase from F1 to F6, according to the also increasing degree of molecular order of the fractions. Bimodal, broad t.r.e.f. curves for LLDPE and narrower, unimodal curves for HP-LDPE were also observed by Wild *et al.*[15] when comparing three different LLDPE samples and one HP-LDPE sample by using both analytical and preparative t.r.e.f. By cross-fractionation with size exclusion chromatography (s.e.c.) the authors concluded that the lower-molecular-weight species tended to be more branched, with this dependence being more important for HP-LDPE than for LLDPE.

Hazlit and Moldovan[16] and Hazlit[17] also proposed an automated analytical t.r.e.f. apparatus in order to speed up the fractionation when using a modified process-control g.c. analyser. It is claimed that this system can fractionate 8 samples of LLDPE in 24 h. Four independent t.r.e.f. columns are operated in parallel and data acquisition is by a microprocessor. To achieve faster analyser rates the reported cooling and heating rates are much higher than those usually considered adequate enough to avoid molecular-weight effects during the precipitation/fractionation process.

Mirabella and coworkers[3,18] used analytical t.r.e.f. to compare HDPE, HP-LDPE and LLDPE. The t.r.e.f. profiles of HDPE were unimodal and sharp, while those of HP-LDPE were unimodal and broad and those of LLDPE were trimodal. D.s.c. of the fractions from t.r.e.f. showed that the melting point and heat of fusion increased with elution temperature, i.e. with decreasing amount of SCB.

Schouterdan *et al.*[19] fractionated LLDPE by successive solution fractionation (molecular weight controlled), followed by analytical t.r.e.f. The fractionation curves of all molecular weight fractions were bimodal, except for the first one obtained. The d.s.c. curves of the various molecular weight fractions were also complex and multimodal. These authors concluded that the SCB is broader for the lower-molecular-weight fractions. Notice that this is again in agreement with Stockmayer's bivariate distribution in which the lower-molecular-weight

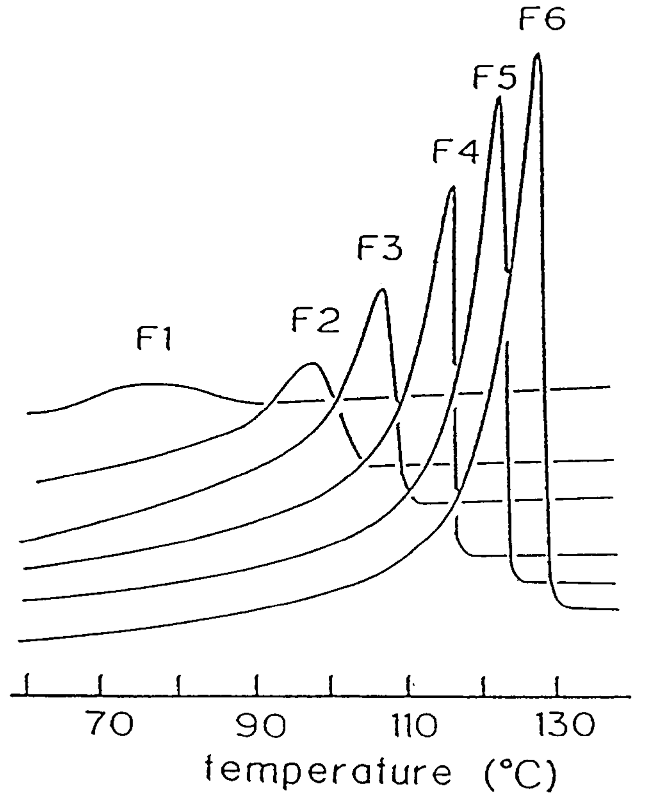

Figure 11 D.s.c. melting curves of LLDPE fractions produced by using the t.r.e.f. process (reproduced from ref. 15)

species show a broader composition distribution than the higher-molecular-weight materials.

Kulin *et al.*[20] compared t.r.e.f. with a liquid–liquid phase separation technique for the fractionation of HP-LDPE. The fractions were characterized by s.e.c., light scattering, viscosity, i.r. spectroscopy, d.s.c. and ^{13}C n.m.r. spectroscopy. It was concluded that the fractionation mechanism of the liquid–liquid method was regulated by molecular weight while t.r.e.f. was regulated by SCB. However, t.r.e.f. did not seem to fractionate well according to long-chain branching, supposedly because the long-chain branches behave essentially as main chains and therefore have little effect on chain crystallinity.

Vela-Estrada and Hamielec[21] reviewed a number of techniques for determining the bivariate distribution of semicrystalline and amorphous copolymers. For crystalline copolymers, the combination of t.r.e.f. and g.p.c. is suggested as the most efficient method. For amorphous copolymers, g.p.c. with adsorption h.p.l.c. has been successfully employed in some cases. Some results of the preparative t.r.e.f. of ethylene/1-octene copolymers were also shown.

Wilfong and Knight[22] used analytical t.r.e.f. to study the crystallization behaviour of ethylene/1-octene copolymers. Small-angle light scattering was used to determine spherulite size, and it was found that the latter decreased with increasing degree of branching.

Kakugo *et al.*[23] analysed ethylene/1-hexene copolymers using t.r.e.f. and determined a trimodal composition distribution. This was attributed to the presence of three types of catalyst sites, with the most common producing 1-hexene-rich random copolymer, the intermediate producing ethylene-rich random copolymer, while the least numerous gave a copolymer containing long sequences of ethylene. The influence of sequence-length distribution on t.r.e.f. fractionation was studied by Karbashewski *et al.*[24]. From the comparison of four LLDPE samples with different degrees of comonomer 'blockiness', it was concluded that a universal calibration curve relating the elution temperature to the degree of SCB cannot be obtained since t.r.e.f. is influenced by the comonomer sequence-length distribution of the copolymer.

Polypropylene

One of the first attempts to fractionate isotactic polypropylene by an increasing temperature fractionation technique was reported by Wijga *et al.*[25], where the method was compared to the fractionation of polypropylene by the elution gradient method (in which fractionation is carried out by increasing the fraction of solvent in a solvent/non-solvent mixture at constant temperature). The second method was concluded to be regulated mainly by molecular weight with the first technique being controlled by both molecular weight and stereoregularity of the polypropylene molecules.

Probably the first insight into the leading mechanism regulating the fractionation efficiency of t.r.e.f. was reported by Kamatah and Wild[26]. The fractional crystallization of polypropylene from dilute solution was found to be mainly dependent on stereoregularity and almost independent of molecular weight. The precipitations were carried out in a flask at constant temperature under certain conditions, i.e. *the molecules should certainly be able to precipitate out of solution according to their crystallizability under tantamount equilibrium conditions and without experiencing any physical hindrance from neighbouring molecules.* The refining of these ideas would lead to the development of t.r.e.f. in its modern form.

Mainly isotactic polypropylene produced by a $TiCl_4$/$MgCl_2$ catalyst, with and without electron donors, was fractionated by Kioka *et al.*[27] over a wide temperature range (−65 to 140°C). The samples produced without electron donors showed much broader distributions of molecular weight and isotacticity. The average molecular weight of the fractions increased with elution temperature, but not enough to suggest that the fractionation was influenced by molecular-weight effects. Melting point and isotacticity indexes also increased with elution temperature, indicating that the fractionation mechanism is controlled by stereoregularity.

Copolymers

Kakugo *et al.*[28] used preparative t.r.e.f. to investigate the active catalytic site centres during the formation of ethylene/propylene and propylene/1-butene copolymers. The fractions were analysed by ^{13}C n.m.r. spectroscopy and the authors concluded that the lower isospecific catalytic centres were more active toward ethylene but that its activity did not change as much for 1-butene.

Kakugo *et al.*[29] also fractionated random ethylene/propylene copolymers, made by three different catalytic systems, by preparative t.r.e.f. and solvent extraction. Using ^{13}C n.m.r. spectroscopy they found that their samples were a mixture of polyethylene, random copolymer and copolymer containing long sequences of ethylene.

Cheng and Kakugo[30] combined preparative t.r.e.f. with ^{13}C n.m.r. spectroscopy to characterize compositional heterogeneity in ethylene/propylene copolymers produced by a Ti-based heterogeneous Ziegler–Natta catalyst. The triad sequences of each fraction were determined by ^{13}C n.m.r. spectroscopy. Using these measurements, reaction probabilities and relative weight fractions were estimated for different multiple-site statistical models. A Bernoullian model containing 3–4 active-site types gave the best data representation.

Another class of copolymers of great commercial importance which has been studied by t.r.e.f. is that comprising the high-impact copolymers of propylene and ethylene. These copolymers are produced by using at least two reactors in series. Only propylene is fed to the first reactor, where it forms isotactic polypropylene. The effluent of the first reactor is then fed to the second reactor along with a mixture of propylene and ethylene. In this way, the effluent of the second reactor contains a mixture, at the molecular level, of polypropylene and propylene/ethylene copolymer. The copolymer portion is rubbery and helps to dissipate stress, making the brittle polypropylene more resistant to impact. Much speculation about the nature of this copolymer can be found in the literature, and t.r.e.f. is probably the most efficient way to solve this puzzle.

Mirabella[31,32] was the first to fractionate this polymer by using t.r.e.f., and a characteristic profile is shown in *Figure 12*. As can be seen, different zones can be clearly identified. The rubbery propylene/ethylene copolymer fractions are soluble at room temperature (zone 1). At somewhat higher temperatures, fractions of crystallizable ethylene/propylene copolymer are present (zone 2). Unexpectedly, at even higher temperatures, a fraction of

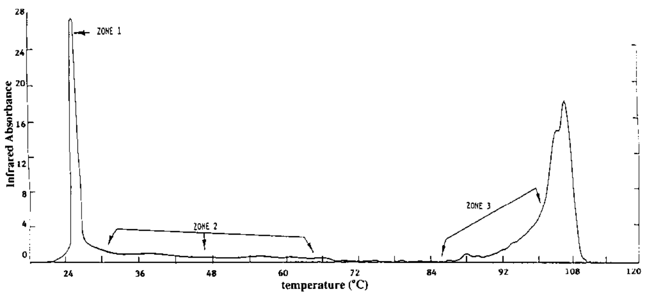

Figure 12 T.r.e.f. profile of a propylene/ethylene high-impact copolymer (reproduced from ref. 32)

ethylene-rich copolymer can be recovered (zone 3). Finally, isotactic polypropylene formed in the first reactor is recovered at the end of the fractionation. Similar results were also reported by Usami *et al.*[33].

In a recent paper, Mirabella[34] proposed a method to determine the ethylene concentration distribution in random copolymers of ethylene and propylene with fractions of ethylene varying from 1 to 5 wt%. A calibration curve for analytical t.r.e.f. was obtained from the analysis of preparative t.r.e.f. fractions. It was found that the content of ethylene in the copolymer correlated adequately with the weight-average elution temperature of the analytical t.r.e.f. chromatograms of the fractions from preparative t.r.e.f. The t.r.e.f. curves of several commercial ethylene/propylene random copolymers were shown to be broad and significantly different in shape. Unfortunately, no information about the catalyst type or the reactor operation conditions of the copolymer samples analysed by t.r.e.f. was presented in this work.

Polymer blends

T.r.e.f. was also applied to the study of polymer blends, and the results are particularly interesting in the evaluation of cocrystallization effects. Kelusky *et al.*[35] reported profiles of individual HP-LDPE and LLDPE, as well as their 50/50 blend (shown in *Figure 13*). Solid lines indicate the actual t.r.e.f. profile while the dotted lines identify the summation of the individual t.r.e.f. curves. Notice how the blend profile adjusts very well to the individual profiles, even in this case where there is considerable superposition of the individual profiles.

Similarly, profiles of ethylene/vinylacetate copolymer (EVA) and LLDPE and their 50/50 blend are depicted in *Figure 14*. Again, blend and individual profiles agree quite well[35].

PRESENT EXPERIMENTAL INVESTIGATION

The t.r.e.f. apparatus used at The McMaster Institute of Polymer Production Technology (MIPPT) is shown in *Figures 15* and *16*. It can be run in both preparative and in analytical modes.

The precipitation step is carried out independently of the elution step in the glass kettle illustrated in *Figure 15*. This is inserted in an oil bath equipped with a programmable temperature controller. The kettle is provided with a nitrogen inlet, a condenser in the vent outlet, a digital thermometer and a mechanical stirrer.

The solvent, polymer sample, support and stabilizer are added to the glass kettle in the desired proportions, with nitrogen being fed continuously to the glass kettle in order to minimize sample oxidation. The stirrer is turned on and the temperature is then increased rapidly to a level at which all polymer chains are soluble; the system is then maintained at that temperature for 2 h. The mixture is then slowly cooled to room temperature at a constant rate of cooling of no more than 2°C min^{-1}. The polymer coated support is then transferred to the t.r.e.f. column.

The elution apparatus is shown in *Figure 16*. The t.r.e.f. column is positioned inside a programmable oven. Fresh solvent is fed to the column by a l.c. pump through a 4-port switching valve. The column effluent can be directly collected outside the oven in the case of preparative fractionation or is sent to an on-line i.r. detector in the case of analytical t.r.e.f.

In the case of preparative t.r.e.f., the temperature is increased at predetermined intervals and the polymer solution is collected until no more precipitation of polymer is observed upon adding methanol. In the case of analytical t.r.e.f. the temperature is raised continuously and the amount of eluted polymer is monitored by the i.r. detector.

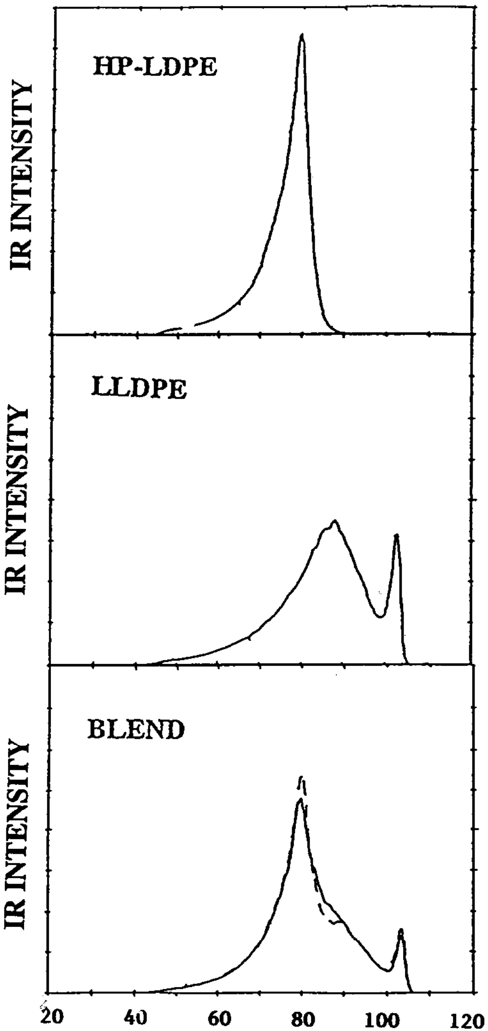

Figure 13 T.r.e.f. profiles showing the effect of cocrystallization of HP-LDPE/LLDPE blends (reproduced from ref. 35)

The samples that will be shown next were all fractionated by using t.r.e.f. in the preparative mode. The operational conditions used and some of the characteristics of our t.r.e.f. apparatus are shown in *Table 2*. The t.r.e.f. column dimensions and operational conditions for analytical and preparative modes reported in the literature are shown in *Tables 3* and *4*, respectively.

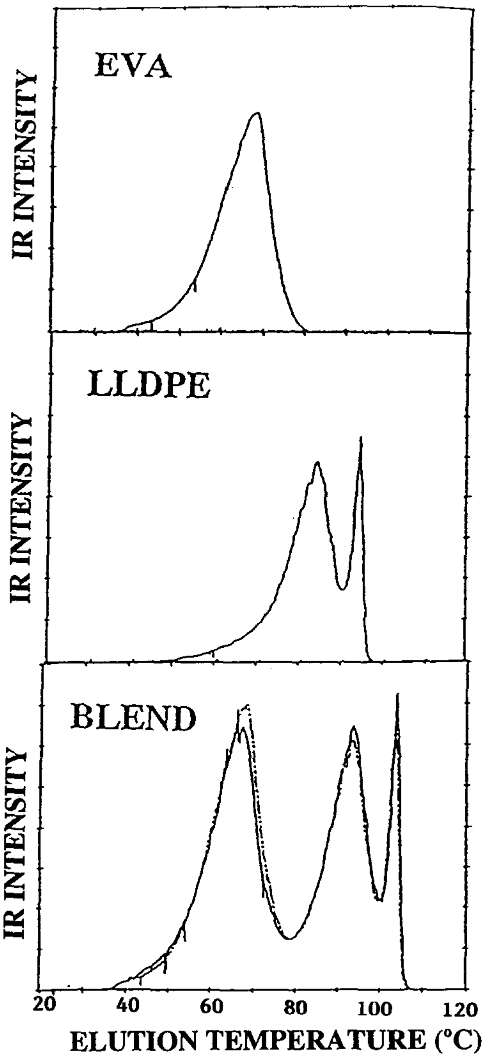

Figure 14 T.r.e.f. profiles showing the effect of cocrystallization of EVA/LLDPE blends (reproduced from ref. 35)

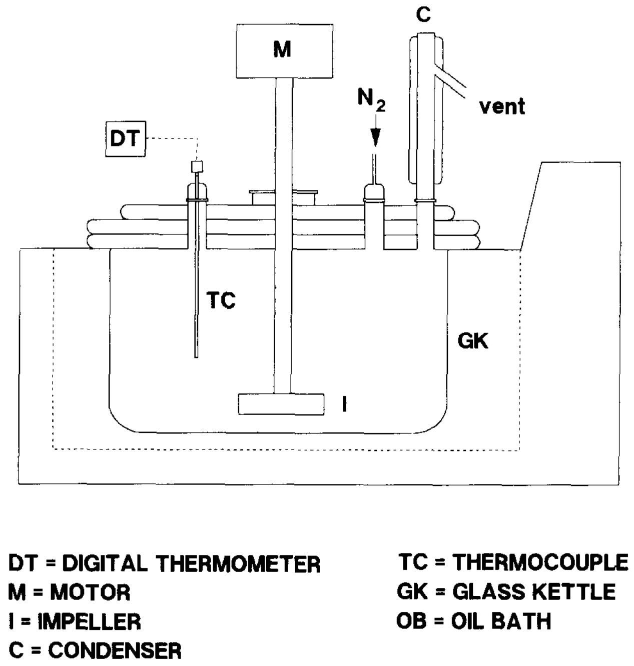

Figure 15 Precipitation stage of the MIPPT t.r.e.f. apparatus

Table 2 Characteristics and operational conditions of the MIPPT t.r.e.f. apparatus

Precipitation stage	
Type of support	Chromosorb P (250–177μ)
Polymer concentration	0.004 g ml^{-1}
Solvent type	Trichlorobenzene
Antioxidant type	Irganox 1010
Antioxidant concentration	0.002 g ml^{-1}
Temperature range	140°C–room temperature
Cooling rate	1.8°C h^{-1}
Stirring speed	80 rpm
Nitrogen pressure	13.8 kPa (2 psi)
Elution stage	
Column size	30 cm x 5 cm i.d.
Solvent type	Trichlorobenzene
Temperature range	Room temperature–140°C
Solvent flow rate	4.0 ml min^{-1}
Size of fractions	Fractions are collected until polymer stops precipitating from solution when methanol is added

Table 3 Analytical t.r.e.f. operational conditions and specifications

Column	Support	Polymer concentration	Solvent	Cooling rate (°C h^{-1})	Heating rate (°C h^{-1})	Solvent flow rate (ml min^{-1})	Ref.
SS 10 x 0.4″	Chromosorb P	0.007 g ml^{-1}	TCB	1.5	20	2	3, 18, 31, 32
SS 15 x 5″	–	0.5%	TCB	1.5	8.0	4	4
SS 15 x 5″	–	0.004 g ml^{-1}	TCB	1.5	8.0	6	11
SS 6 x 0.3″	Glass beads (GCC 110)	0.01 g ml^{-1}	ODCB	–	–	1	13
SS 6 x 0.3″	Glass beads (GCC 110)	0.4%	ODCB	–	–	1	14
–	Glass pearls (800 μm)	1%	TCB	–	–	–	19
–	Silica gel	–	ACNT[a]	–	–	–	35
SS 1/8″ i.d.	SS shot	0.6%	TCB	6–600[b]	–	–	16

[a] α-Chloronaphthalene

[b] Hazlit[17] uses different cooling rates for different temperature intervals: 600°C h^{-1} from 122 to 106°C, 6°C h^{-1} from 105 to 50°C, and 18°C h^{-1} from 50°C to room temperature

Table 4 Preparative t.r.e.f. operational conditions and specifications

Column	Support	Polymer concentration (%)	Solvent	Cooling rate (°C h^{-1})	Heating rate (°C h^{-1})	Solvent flow rate (ml min^{-1})	Ref.
SS 15 × 5″	Chromosorb P	–	Xylene	2	8	20	4, 11
–	Chromosorb P	1	Xylene	1	4	20	12
–	Chromosorb P	1	Xylene	1	9.6	20	20
12 × 2″	Chromosorb P	–	TCB	6	60	–	21
SS 18 × 3″	Sea sand (35–48 mesh)	–	Xylene	–	–	–	23, 28, 29, 30
SS 20 × 4″	Chromosorb P	0.5	TCB	1.8	3.6	40	22

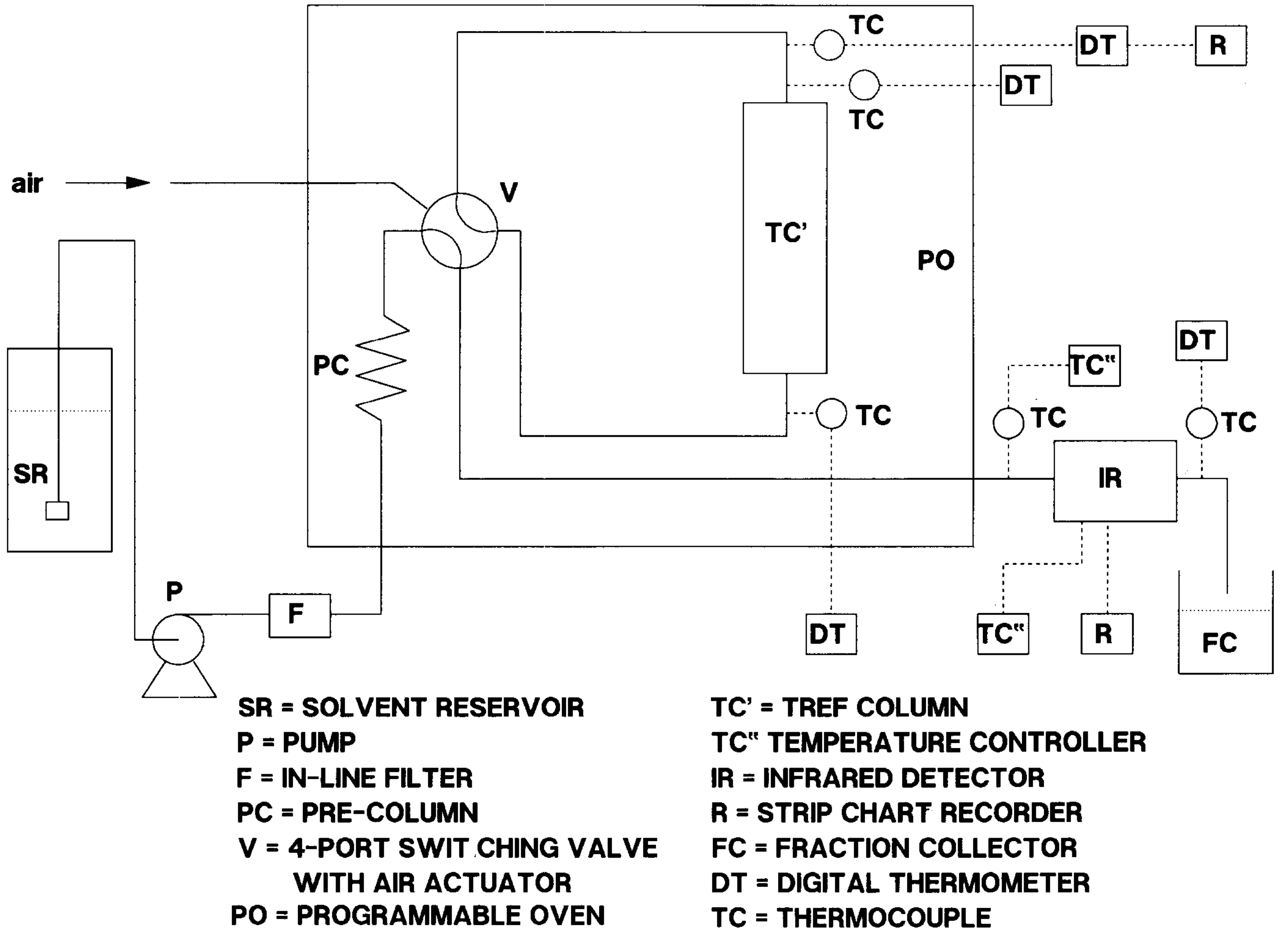

Figure 16 Elution stage of the MIPPT t.r.e.f. apparatus

Propylene/ethylene high-impact copolymers

A commercial propylene/ethylene high-impact copolymer produced in a heterogeneous Ziegler–Natta industrial process is our first example of t.r.e.f. preparative fractionation. The distribution of the fractions as a function of elution temperature is shown is *Figure 17*. Homopolymer polypropylene is obtained in the higher-temperature fractions while ethylene/propylene copolymer is obtained in the lower-temperature fractions.

The d.c.s. curves of some of the fractions are shown in *Figure 18*. There is a consistent change towards sharper melting curves and higher melting temperatures as one goes from fractions obtained at lower temperatures to those obtained at higher temperatures.

Structural information about the polymer chains can be obtained by analysing the ^{13}C n.m.r. spectra of the fractions. *Figure 19* shows the ^{13}C n.m.r. spectrum with peak assignments[36] of the fraction collected between 60 and 80°C. The letters P, S and T indicate primary (methyl), secondary (methylene) and tertiary (methine) carbon atoms, respectively. The greek letters refer to the location of the nearest primary carbons in each side of the chain, as suggested by Carman and Wilkes[37]. Therefore, a $S_{\alpha\alpha}$ carbon is a secondary carbon which is

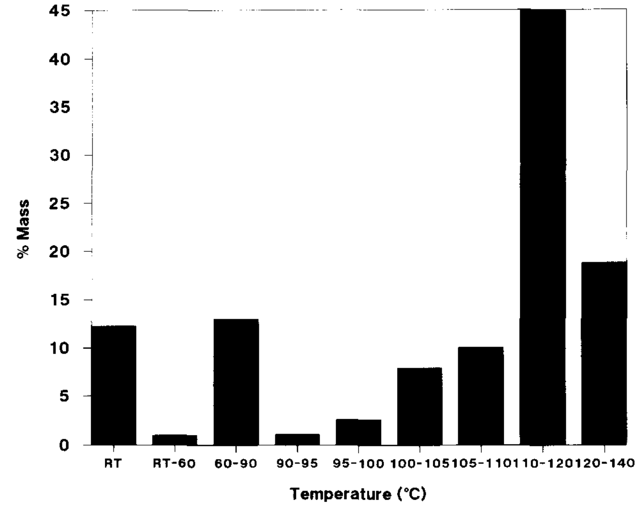

Figure 17 Preparative t.r.e.f. profile of an ethylene/propylene high-impact copolymer

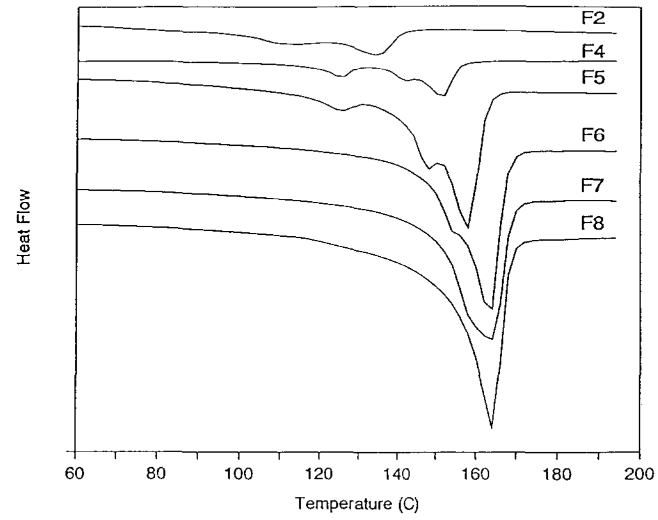

Figure 18 D.s.c. curves of fractions of a propylene/ethylene high-impact copolymer, obtained at various elution temperatures in the t.r.e.f. process: F2, 60–80; F4, 95–100; F5, 100–105; F6, 105–110; F7, 110–120; F8, 120–140°C

adjacent to two primary carbon atoms, a $S_{\alpha\beta}$ carbon is a secondary carbon which is adjacent to a primary carbon atom and is one carbon atom away from a primary carbon, and so on, until we reach a $S_{\delta\delta}$ carbon which is three carbon atoms away from a primary carbon atom on both sides of the chain. The ^{13}C n.m.r. spectral resolution can only distinguish up to $\delta\delta$ carbon atoms, with longer separations also being treated as $\delta\delta$ carbon atoms. The chain microstructures detected in the ^{13}C n.m.r. spectrum of the ethylene/propylene copolymer are shown in *Figures 20* and *21*. As can be seen, the spectra describe an ethylene/propylene copolymer without monomer inversions.

In *Figure 22* the ^{13}C n.m.r. spectra of six fractions of copolymer are compared. The peaks associated with ethylene units decrease rapidly from the fraction obtained between 60 and 80°C to the one obtained between 100 and 105°C.

The amount of ethylene in the t.r.e.f. fractions can be estimated from the ^{13}C n.m.r. peak intensities by using the relationships suggested by Cheng[36]. If we call E and P the total amounts of ethylene and propylene, respectively, in the copolymer, then:

$$s=\sum_{i,j} S_{i,j}=k(2E+P) \qquad (1)$$

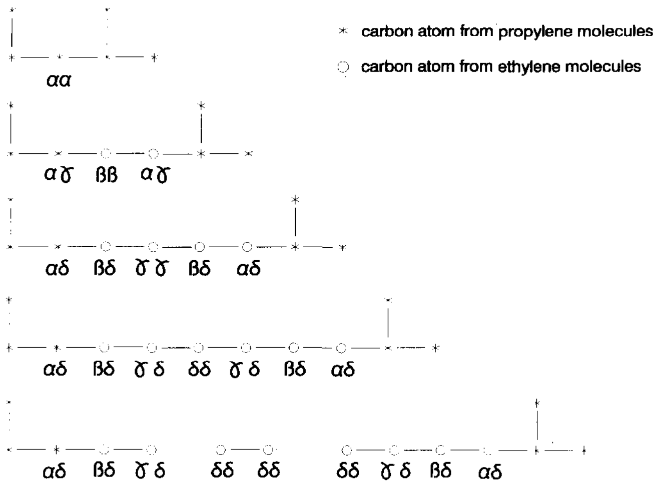

Figure 20 Methylene carbons in propylene/ethylene copolymers without monomer inversions

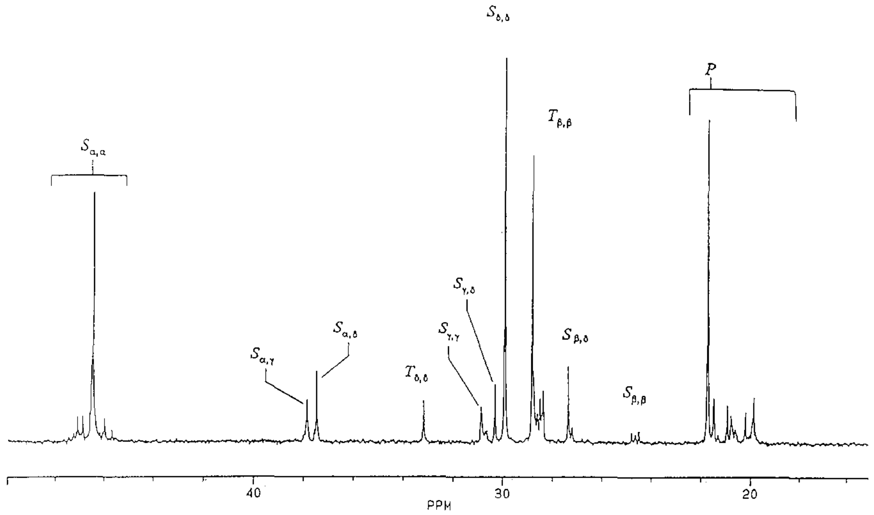

Figure 19 ^{13}C n.m.r. spectral peak assignments of a propylene/ethylene high-impact copolymer

where *i,j* can be α, β, γ, or δ and *k* is the n.m.r. signal proportionality constant. *E* is multiplied by 2 because there are two secondary carbons in one ethylene monomer unit.

In the same way, for primary and tertiary carbons, we obtain the following:

$$p=\sum_{i,j} P_{i,j}=t=\sum_{i,j} T_{i,j}=kP \qquad (2)$$

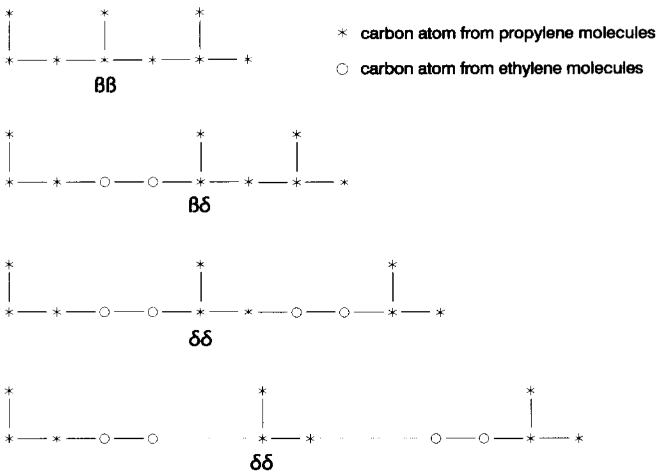

Figure 21 Methyl and methine carbons in propylene/ethylene copolymers without monomer inversions

Combining equations (1) and (2) one easily obtains the following relationships for the mole fractions of ethylene and propylene as follows:

$$\frac{E}{E+P}=\frac{s-t}{s+t}=\frac{s-p}{s+p} \qquad (3)$$

$$\frac{P}{E+P}=\frac{2t}{s+t}=\frac{2p}{s+p} \qquad (4)$$

Alternative computational schemes have been published in the literature[36,38]. For quantitative spectra, these different computational schemes must give consistent results.

The amount of ethylene in the three first fractions, as calculated by equations (3) and (4), is 42.0, 23.9 and 3.3%, respectively (temperature range 60–105°C). No peaks related to ethylene can be detected for the other three fractions. The main factor regulating the fractionation at higher temperatures is the stereoregularity of the polypropylene chains. By analysis of the methyl area of the spectra the following triad distribution was found:

Temperature (°C)	mm	mr	rr
105–110	97.86	1.54	0.61
110–120	99.04	0.96	–
120–140	100	–	–

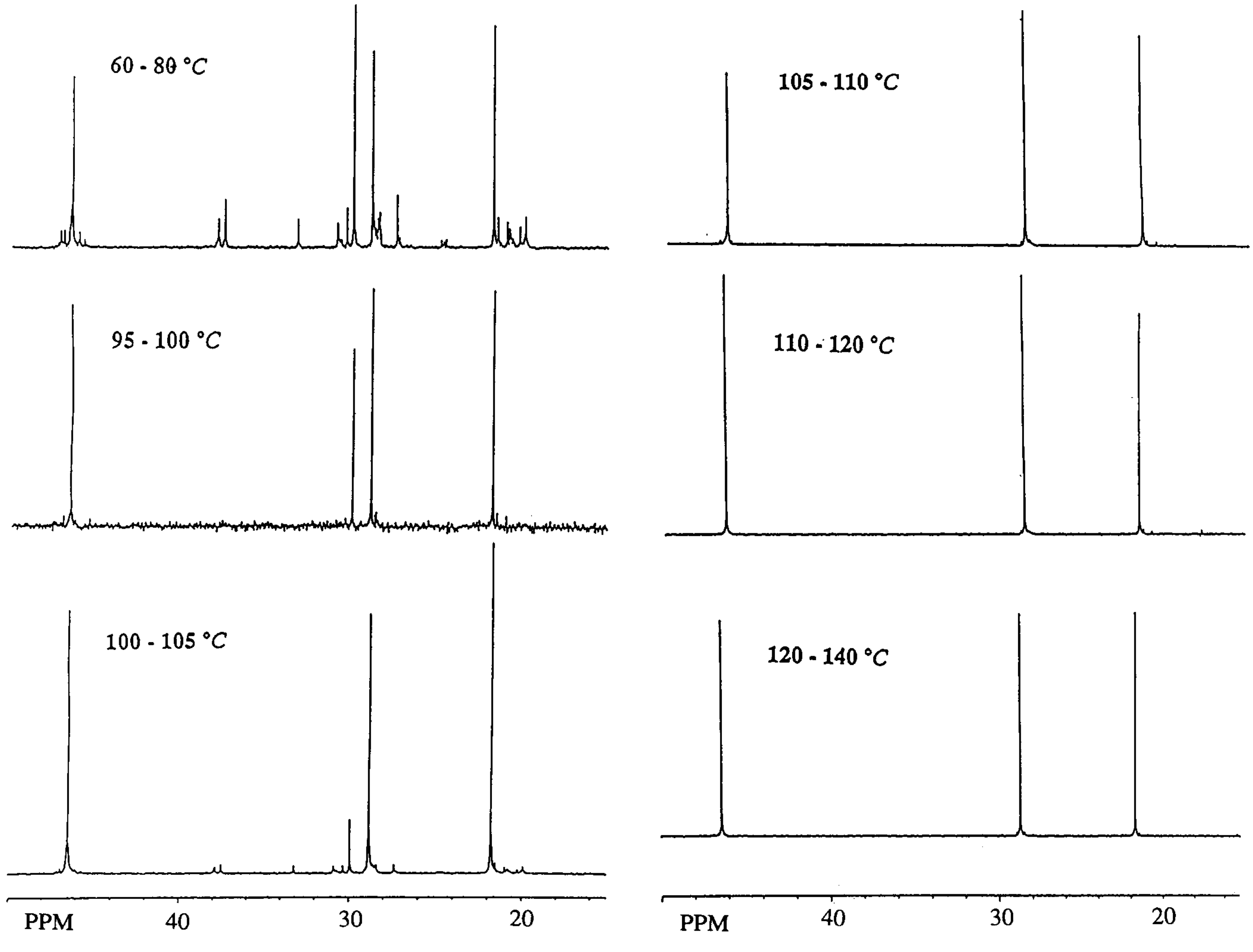

Figure 22 ^{13}C n.m.r. spectra of fractions of a propylene/ethylene high-impact copolymer produced by using the t.r.e.f. process

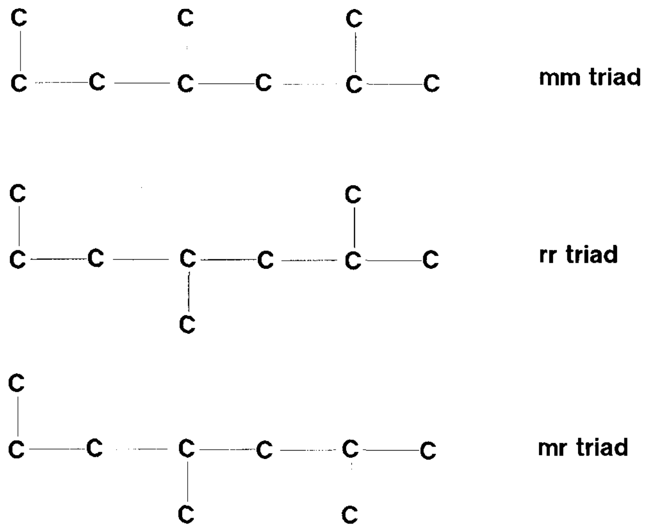

Figure 23 Meso and racemic placements in polypropylene

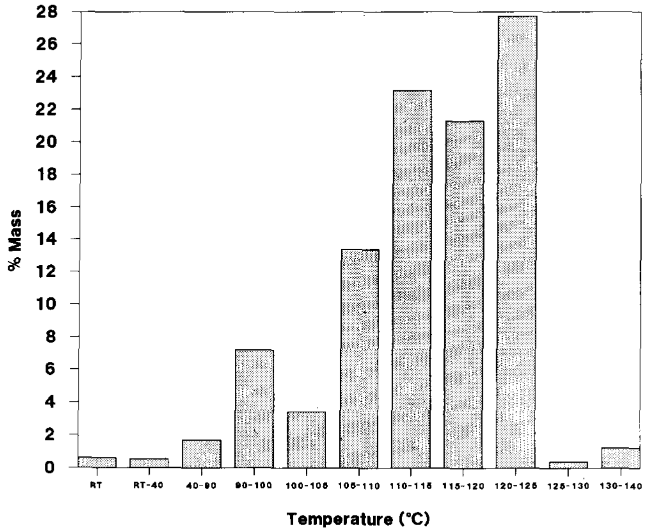

Figure 24 Preparative t.r.e.f. profile of polypropylene made by a heterogeneous $TiCl_3$/diethylaluminium chloride Ziegler–Natta catalyst

where m refers to a meso (isotactic) placement and r to a racemic (syndiotactic) placement, as illustrated in *Figure 23*.

Polypropylene made by heterogeneous Ziegler–Natta catalyst

Figure 24 shows the t.r.e.f. profile of a polypropylene made in our laboratories using a commercial unsupported heterogeneous Ziegler–Natta catalyst in a semi-batch slurry reactor. As can be seen, although most of the polymer is recovered between 100 and 125°C, some fractions can be collected either above or below this temperature range. Since there is only one monomer unit, the fractionation is solely controlled by the stereo- and regioregularity of the chains.

Figure 25 shows the d.s.c. curves of the first six fractions produced by the t.r.e.f. process. The pattern already observed for the high-impact copolymer is repeated here, with melting points increasing with elution temperature. *Figure 26* shows the ^{13}C n.m.r. spectra of some of these

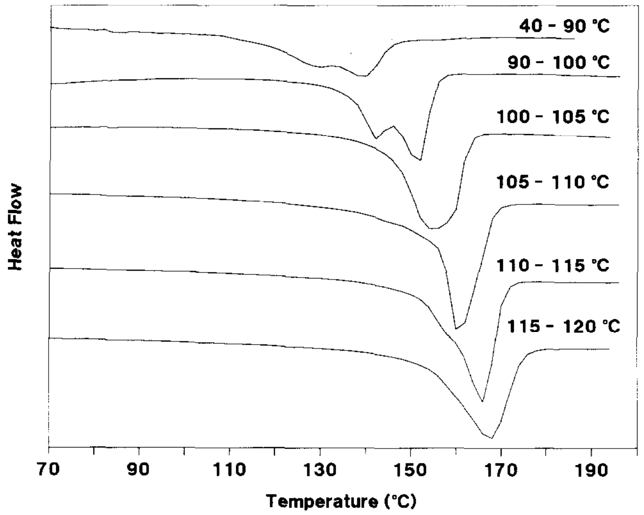

Figure 25 D.s.c. curves of fractions obtained by t.r.e.f. of polypropylene made by a $TiCl_3$/diethylaluminium chloride heterogeneous Ziegler–Natta catalyst

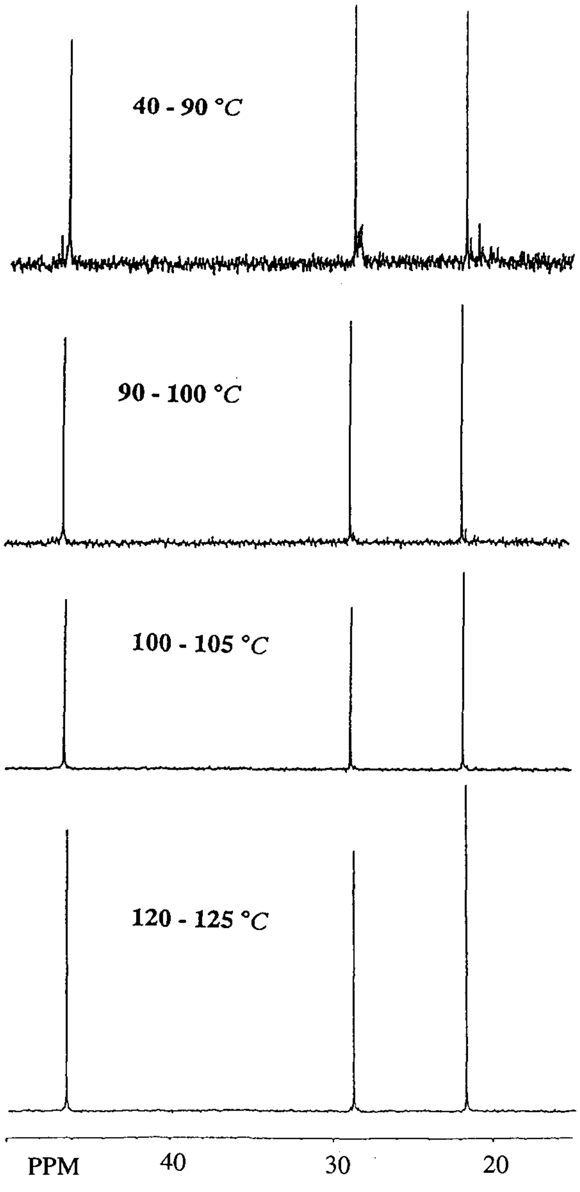

Figure 26 ^{13}C n.m.r. spectra of fractions obtained by t.r.e.f. of polypropylene made by a heterogeneous $TiCl_3$/diethylaluminium chloride Ziegler–Natta catalyst

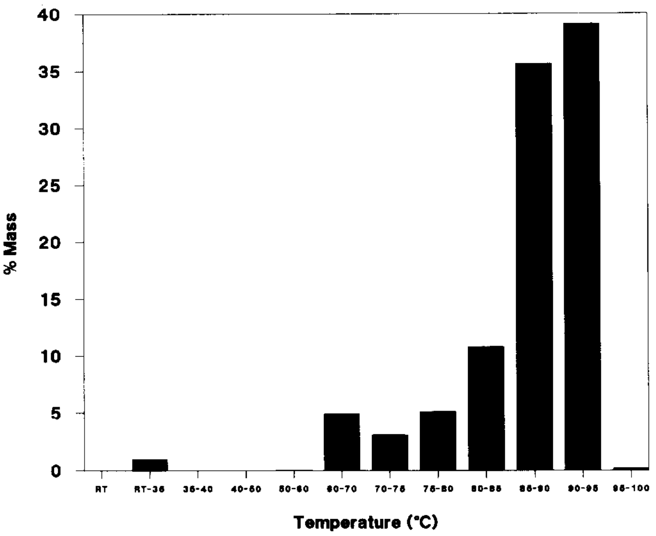

Figure 27 Preparative t.r.e.f. profile of polypropylene made by a homogeneous bis(indenyl)zirconium dichloride catalyst[39]

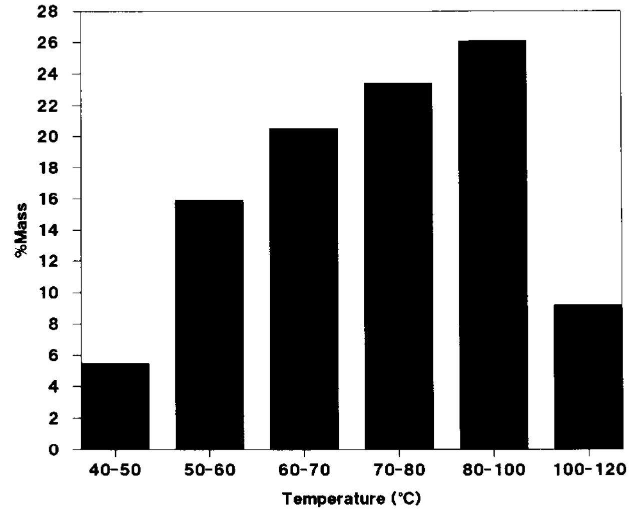

Figure 28 Preparative t.r.e.f. profile of LLDPE (ethylene/1-octene)

fractions. The degree of stereoregularity of the fractions clearly increases with elution temperature.

Polypropylene made by a metallocene catalyst

The industrial production of polyolefins by metallocene catalysts is a promising and growing field. Polyolefins made by these catalysts have narrower molecular weight and composition distributions than the ones produced by conventional heterogeneous Ziegler–Natta catalysts. T.r.e.f. is a suitable technique to help understand the novel properties of these new polymers.

The t.r.e.f. profile of a polypropylene made by a metallocene catalyst is presented in *Figure 27*. This sample was synthesized using the bis(indenyl) zirconium dichloride/methyl aluminoxane system[39]. It differs significantly from the t.r.e.f. profile of the conventional polypropylene shown in *Figure 24*. The lower elution temperatures of the metallocene polypropylene are probably due to chain defects such as atactic placements and monomer inversions (head-to-head and tail-to-tail placements).

Linear low-density polyethylene (LLDPE)

LLDPE is probably the polyolefin that has been most thoroughly studied by t.r.e.f. A t.r.e.f. profile of a commercial LLDPE (ethylene/1-octene) is shown in *Figure 28*.

The d.s.c. peak temperature of the fractions produced by t.r.e.f. as a function of elution temperature is presented in *Figure 29*. There is an almost linear relationship between the elution temperature and the peak temperature. In addition, the degree of short-chain branching (SCB) of the fractions was determined by ^{13}C n.m.r. spectroscopy and is shown as a function of the elution temperature in *Figure 30*. There is an inverse relationship between the degree of SCB and the elution temperature, since the crystallinity of the polyethylene molecules decreases with increasing degree of branching.

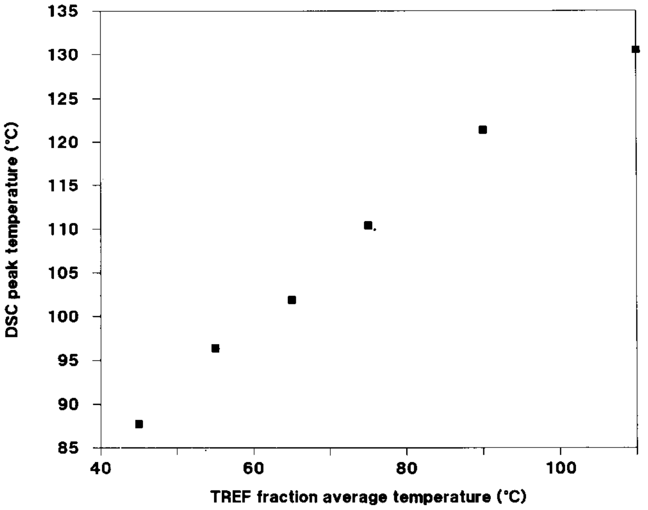

Figure 29 D.s.c. peak temperatures of fractions of LLDPE (ethylene/1-octene) obtained by t.r.e.f.

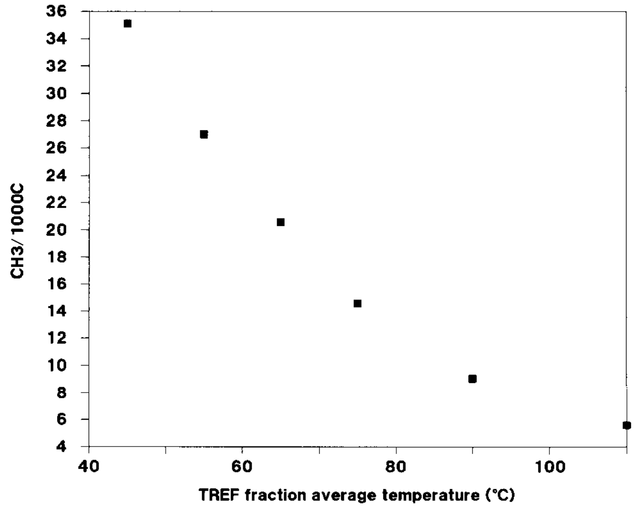

Figure 30 Relationship between SCB and fraction average temperature of samples of LLDPE (ethylene/1-octene) obtained by t.r.e.f.

CONCLUSIONS

T.r.e.f. is a powerful technique for fractionating and characterizing semicrystalline polymers. When t.r.e.f. is properly executed, it is regulated by the crystallinity of the polymer samples and is effectively independent of molecular weight and cocrystallization influences.

Preparative t.r.e.f. is a time-consuming procedure but when combined with various complementary analytical techniques can provide very detailed information about polymer microstructure.

The information obtained by analytical t.r.e.f. is more limited than that available from the preparative technique and its use depends on the determination of a reliable calibration curve. However, its much faster operation makes it more attractive for industrial applications, such as quality control, than preparative t.r.e.f.

The Stockmayer bivariate distribution is a useful technique for the interpretation of individual t.r.e.f. curves or for the cross-fractionation of polymer samples by using t.r.e.f.–s.e.c. techniques.

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