DOI: 10.1002/masy.200751105

Molecular Topology Fractionation of Polystyrene Stars and Long Chain Branched Polyethylene Fractions

David M. Meunier,[*1] *Theodore M. Stokich Jr.,*[1] *David Gillespie,*[2] *Patrick B. Smith*[1]

Summary: Control of long chain branching (LCB) architecture is an area of considerable interest in materials science because LCB can have a dominating effect on polymer rheology and properties. Currently no analytical technique provides a quantitative description of the LCB topologies in these materials beyond a basic estimation of the average number of branch points per molecule. Neither the molecular weight of the branch, nor the shape of the branched molecule (e. g. star, comb, ''H'' or other) can be determined using current state of the art methodology such as size exclusion chromatography (SEC) with molecular weight sensitive detectors or nuclear magnetic resonance spectroscopy.

In our laboratory, we have developed a fractionation method that sorts polymer solutes based on LCB topology. The approach, which we term molecular topology fractionation (MTF), utilizes a separating medium comprising channels having dimensions similar in size to the dimensions of the macromolecules being analyzed. An applied flow field provides the driving force for the separation. Although the details of the separation mechanism are not well understood at this time, two possible mechanisms are being considered. In one, dissolved solute molecules are restricted by the channels such that the relaxation modes for reorientation determine the rate of transport. In the second, pinning (or entanglement) of molecules on the stationary phase determines the rate of transport. Both mechanisms result in the largest molecules eluting latest (opposite to the sequencing in SEC), and produce significant additional retardation for LCB chains above that of linear chains. This additional retardation leads to fractionation of an LCB distribution even if the hydrodynamic radii of the components are the same.

In this paper, an overview of the MTF experiment will be provided. MTF fractionation of PS stars is presented to demonstrate the separation of LCB chains from linear chains and LCB chains based on topology. The application of MTF for characterizing LCB polyolefin fractions will be shown. The paper will also include a brief discussion of the coupling of MTF and SEC in an on line two dimensional approach for determination of LCB distributions.

Keywords: branching distribution; characterization; entanglement; lightly cross-linked homogeneous ethylene octene copolymer; long chain branching; pinning; star polystyrene; topology fractionation

Introduction

Molecular topology fractionation[1] (MTF) is a relatively new dilute solution polymer separation technique developed within the Dow Chemical Company.[2] The development

---

[1] The Dow Chemical Company, Analytical Sciences, Midland, MI
E-mail: DMeunier@dow.com
[2] The Dow Chemical Company, Polyolefins Research, Freeport, TX

of MTF was driven by a need for better tools for characterizing long chain branching (LCB). Present state-of-the-art techniques such as 13C NMR[3] and size-exclusion chromatography (SEC) with molecular weight sensitive detectors[4] provide information about the average number of branches per molecule. Neither technique provides information about the molecular weights of the branches nor the shapes of the branched molecules. Additionally, for low levels of branching, both techniques are operating at relatively low signal to noise, making detection of low levels of LCB a challenge.

Long chain branching is introduced into polymers because it can have substantial impact on the rheological behavior of the system provided the branch lengths are significantly larger than the entanglement molecular weight.[5] Because their radii of gyration are smaller, LCB polymers shear thin to a greater extent than linear polymers of the same molecular weight. On the other end of the shear spectrum, LCB polymers offer higher zero shear viscosity than their linear counterparts. This is because LCB polymers entangle much more effectively than their linear counterparts. The enhanced entanglement of LCB polymers was the motivation for the present embodiment of MTF. The idea was to create an entangling environment within a chromatographic column through which LCB molecules and linear molecules would be forced to flow. It should be noted here that the term ‘‘entanglement’’ in the MTF experiment is interchangeable with the term ‘‘pinning’’. The original idea behind MTF column development was to create a series of posts on which LCB chains or linear chains could become pinned.

In the first successful demonstration of MTF, poly(styrene-co-divinylbenzene) monolithic columns, having macropores (channels) of average diameter on the order of 100–200 nm, were used in the separation.[1] In that work, MTF was characterized by a flow rate dependent reversal in elution order of linear PS molecular weight standards. Additionally, chains possessing LCB were shown to be retained longer than linear chains of the same hydrodynamic size.

It was recognized that a second mechanism may also be operative in the MTF separation. This second mechanism involves chain restriction followed by relaxation/reorientation. In this mechanism, dissolved solutes may become restricted by a fraction of the column macropores such that the relaxation times for reorientation determine the rate of transport. Either mechanism, pinning or relaxation/reorientation, is expected to be sensitive to topology; both may be operative in a real system.

In this work, new MTF columns are introduced. The columns were prepared via high pressure packing of sub-micron, nonporous silica (surface functionalized with PS) into stainless steel columns. The new columns were used to study the elution behavior of regular PS stars. In addition, the columns were used to perform high temperature MTF on relatively narrow fractions of lightly cross-linked homogeneous ethylene octene copolymers.

Experimental Part

Materials and Samples

The silica used to pack MTF columns was obtained from Admatechs Co. Ltd. (Aichi, Japan). The product identification number was SO-C2 lot BMI206. An SEM image of these particles is shown in Figure 1. In addition, particle size distribution data provided by the vendor revealed that the average particle diameter was 0.5 micrometers and the half-width of the distribution was ~0.3 micrometers.

Narrow molecular weight polystyrene (PS) standards were obtained from Polymer Laboratories (Amherst, MA) and were used as received. Polymer standard solutions for MTF studies were prepared individually with concentrations ranging from 0.5 to 1 mg/ml depending on the molecular weight, with lower molecular weight standards prepared at higher concentration and vice-versa. The tetrahydrofuran (THF) used for standard dissolution

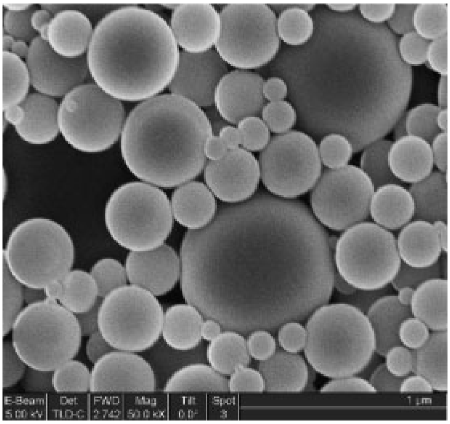

Figure 1.
SEM Image of non-functionalized Admatechs Silica. The silica was functionalized with PS and packed into a column by Mel Cabey of the Diazem Corporation.

was obtained directly from the LC reservoir so as to minimize the contributions from solvent mismatch peaks. Standard solutions were stored in the dark at ambient temperature when not in use. For SEC, standards were prepared as cocktails and the concentration of each standard in a cocktail was 0.5 mg/mL.

A three arm star PS sample was obtained from Polymer Source, Inc. (Dorval, Quebec, Canada). The star was made via anionic polymerization followed by coupling of the living anions with a trifunctional coupling agent as depicted in Figure 2. The vendor reported a weight-average molecular weight (M_W) of 1480 kg/mol for the arms of the star and 4760 kg/mol for the whole star sample. The reported whole polymer M_W does not make sense considering the sample was supposed to be a three arm star with some uniarm material present. The higher than theoretically possible M_W for the whole sample may suggest the presence of some high molecular weight impurities. Further, our characterization of the 3-arm star sample (see Results and Discussion Section) indicates that the uniarm material is actually substantially lower in molecular weight than the value supplied by the vendor.

Lightly cross-linked homogeneous ethylene octene copolymer samples were fractionated via a solvent non-solvent method to produce relatively narrow fractions for MTF. A preparative fractionation unit (PolymerChar, Valencia, Spain) was used to separate each whole polymer sample into narrow fractions with the resulting M_W's nominally from 20 to a maximum of 200–400 Kg/mole and polydispersities PDI's ranging from 1.3 to 1.5. For the whole polymer samples, short chain branch frequencies ranged from 17 to 32 short branches per thousand backbone carbon atoms, and short chain branching had minimal influence on MTF elution. Long chain branching frequencies (LCBf) of the unfractionated materials were determined by triple detector SEC[4] and ranged from

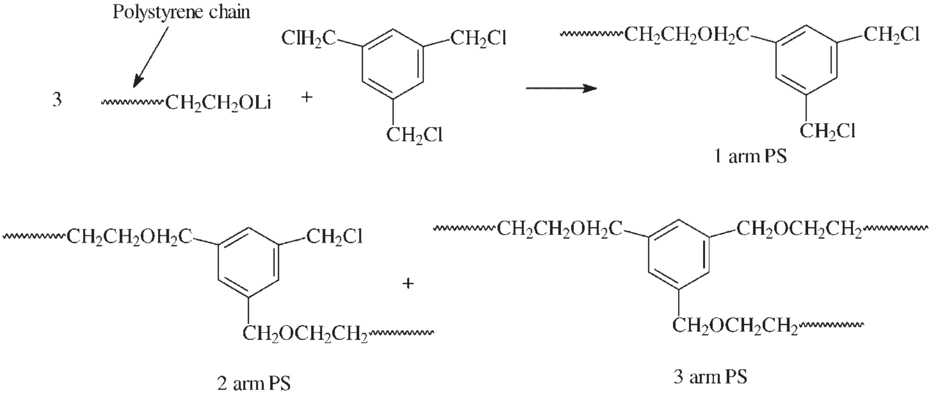

Figure 2.
Reaction Scheme used by Polymer Source Inc. to synthesize the 3-arm star sample.

0.005 to 0.7 long branches per thousand backbone carbon atoms. LCBfs were not determined for the fractions themselves. Because a fractionation was carried out, it is not clear that the average LCBfs still apply to each fraction in a series. It is expected that fractions from the LCBf = 0.005 sample would have a *very* small population of long chain branched molecules, while fractions from the LCBf = 0.70 sample would be expected to have a large population of multiply-branched LCB molecules, especially in the higher molecular weight fractions.

Equipment for MTF

The LC system used for MTF and SEC analyses consisted of a Waters Alliance 2695 pump/autosampler and a Viscotek model 302 multidetector array. The 2695 pump was used to deliver precise flowrates in the 0.01 to 0.05 mL/minute regime for MTF. HPLC grade THF (Omnisolv, HPLC Grade, EMD Chemicals) was used as the solvent and eluent. The eluent was continuously degassed. Injection volumes were 0.01 mL. The multi-detector array included UV absorbance, low angle (LALLS) and right angle laser light scattering, differential refractive index (DRI) and differential viscometer detectors. The detectors and columns were held at 50 °C for SEC. Column dimensions for MTF were 4.6 mm I. D. X 150 mm L and were packed with PS functionalized silica (made from SO-C2 described above).

A Waters Alliance Model GPCV2000 was used for high temperature MTF experiments. A flow of 0.01 ml/min was employed, and like the Waters 2695 pump used in ambient temperature experiments, the pump in the high temperature SEC was able to deliver this low flow rate both reliably and reproducibly. The carousel, injector and column regions were all controlled at 145 °C. Two detectors were used for the sample analysis: (1) A Polymer Char Model IR4 (Valencia, Spain) infrared concentration detector and (2) A Precision Detectors, Inc. (Franklin, MA) dual angle light scattering detector, Model 2040 PDI, with sensors at 15° and 90°. The pairing of these detectors provided the capability to observe the molecular weight distribution and produce an estimate of radius gyration across the elution profile of a sample.

The TCB eluent was continuously degassed by sparging the reservoir with helium and by the operation of the in-line system degasser. Injection volumes for these experiments were 0.01 mL. For high temperature MTF, concentrations were chosen to keep the product of intrinsic viscosity and concentration ($C \times [\eta]$) less than ~0.15. Samples were prepared directly in the autosampler vial by weighing an aliquot of the polyethylene fraction, adding the appropriate amount of solvent and shaking for 2 hours at 160 °C.

MTF Columns and Functionalized Packing Material

The polydisperse silica obtained from Admatechs was functionalized with PS by Mel Cabey of the Diazem Corporation (Midland, MI). Columns for MTF were packed with this PS functionalized silica by Diazem. The packing procedure consisted of slurrying the particles in a proprietary mixture of solvents and pressure packing them into the column at 6,000 PSI. Pressure was held at 6,000 PSI for 8 hours. The column outlet frit was constructed as follows. A nominal 0.5 micrometer frit was placed in the column outlet. Next, a short (e. g. a few millimeters) layer of 2 micrometer non-porous silica was packed next to the outlet frit. Finally, the column was filled with the packing particles. The column was then flushed overnight with THF or TCB before MTF experiments commenced.

SEC Experiments

SEC was carried out using the same liquid chromatography hardware as was used for MTF in order to define the polydispersity of the 3-arm star test sample as precisely as possible. A set of four mixed-B columns from Polymer Laboratories (Amherst, MA) was chosen for the separation. A flowrate of 1.0 ml/minute and an injection volume of

0.05 ml were used. Both conventional SEC results (relative to linear PS) and absolute molecular weight results (from LALLS) were determined. Data were reduced using OmniSEC software from Viscotek.

The cross-linked polyethylene whole polymers and fractions were characterized by triple detector high temperature SEC. The system consisted of a PL-220 with light scattering (PDI 2040 as described above), differential viscometry (Viscotek 4 capillary bridge design), and concentration detectors (IR4 and DRI). The column set consisted of 3 mixed-B columns from Polymer Laboratories. Sample concentrations were 1 to 2 mg/ml and injection volume was 0.100 ml. Data were reduced using custom written software.

Results and Discussion

SEC Characterization of the 3-Arm Star Sample

SEC and SEC-LALLS-DV were used to determine the molecular weight distribution (MWD) of the 3-arm star in order to compliment and aid in the analysis of MTF results. The linear PS equivalent MWD is shown in Figure 3. It is readily apparent that there are at least three components in this sample, even though they are not well resolved. Based upon calibration with linear polystyrene standards, these three components have apparent peak molecular weights of approximately 1,250, 2,500, and 3,500 kg/mole, as annotated on the distribution. It is arguable that there is a fourth component at apparent molecular weight above 3,500 kg/mole because the shape of the distribution in that regime appears slightly non-Gaussian. But if there were material eluting in that region, its molecular weight would not be known from this analysis.

The linear PS equivalent M_W and number-average molecular weight (M_N) of the 3-arm star determined from the distribution shown in Figure 3 were, 3,260 and 2,700 kg/mol, respectively. The M_W value from LALLS was, 3,760 kg/mol. The fact that the absolute M_W was larger than the linear equivalent M_W is consistent with the presence of branched molecules in the distribution. The Mark – Houwink plot from SEC-LALLS-DV, shown in Figure 4, also provides strong evidence for the presence of branched species in the distribution.

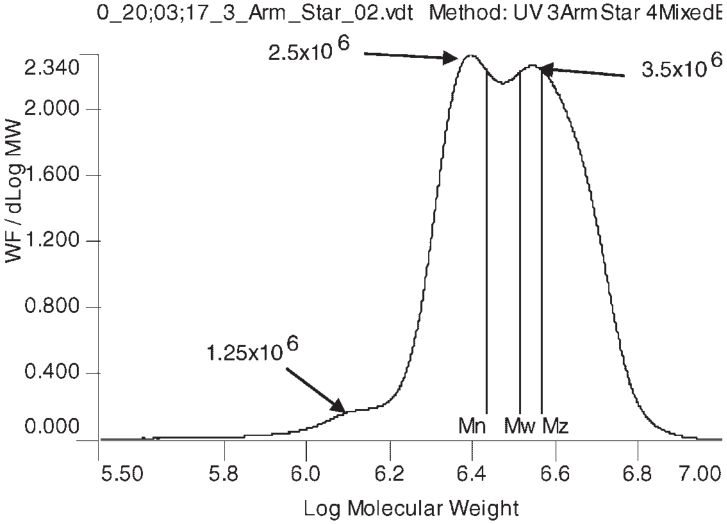

Figure 3.
Linear PS apparent molecular weight distribution of the 3-arm star sample as determined by SEC. The numbers next to the arrows represent the linear PS equivalent molecular weight at the apices of the individual peaks.

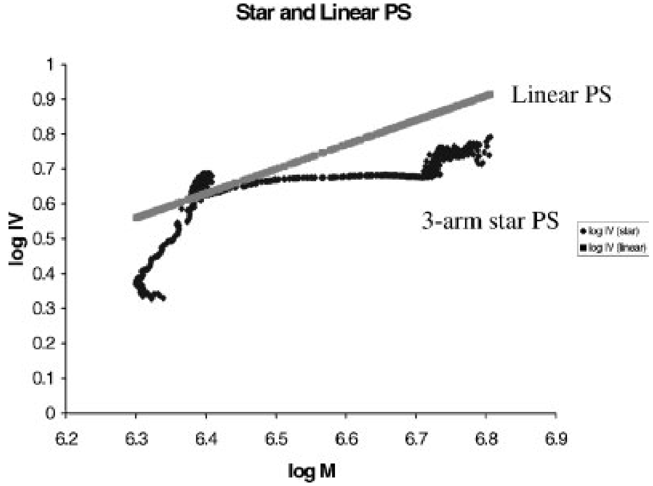

Figure 4.
Mark – Houwink plots of linear PS and star PS.

In summary, SEC characterization of the 3-arm PS star indicated that it was not a pure component, but rather consisted of a mixture of single arm, two-arm, and 3-arm species. Secondly, the molecular weights were lower than reported by the vendor for both the arms and the whole polymer sample. Arm molecular weights of ~1,250 kg/mol were found in this study, versus 1,480 kg/mol reported by the vendor. A whole polymer M_W value of 3,760 kg/mol was found here, versus 4,760 kg/mol reported by the vendor. Considering the distribution shown in Figure 3 (~5% uniarm, ~45% two arm and assuming the balance of material is 3-arm), it is not possible to rationalize the M_W value determined in this study, nor by the vendor. The only way to rationalize either reported M_W is to consider the presence of higher molecular weight species in the sample (e. g. 4-arm stars or higher).

MTF Separation of the 3-Arm Star Sample

The 3-arm star sample was injected onto an MTF column packed with the PS functionalized silica. The flowrate was 10 μl/minute, thus providing the MTF elution order reversal for molecular weights exceeding the critical molecular weight.[1] The resulting MTF fractogram, as detected by 90° light scattering is shown in Figure 5. Because the detector only responds to polymeric species, the fractogram reveals the presence of a least 4 different polymeric modes in the sample. Based on the SEC data obtained for this sample, one would have expected at least three modes in the distribution, but there was no clear evidence of a fourth mode in the SEC data.

Interpretation of the MTF fractogram of the 3-arm star sample presented a challenge. However, the combination of LALLS detection and UV detection enabled estimates of the M_W values across the MTF profile. Additionally, the MTF elution times of the species present in the 3-arm star were compared to those of linear PS standards. The ratio of LALLS detector response to the concentration detector response increased progressively from mode 1 to mode 4. In fact, the progression of the ratio followed a 1×, 2×, 3× and 4× order upon moving from mode 1 to mode 4, respectively. Thus, the elution order observed in Figure 5 is consistent with that expected for MTF[1], and the progression of molecular weight is consistent with that expected for a star sample constructed via coupling of discreet arms. However, although the 4th mode may have been anticipated from the SEC and LALLS data,

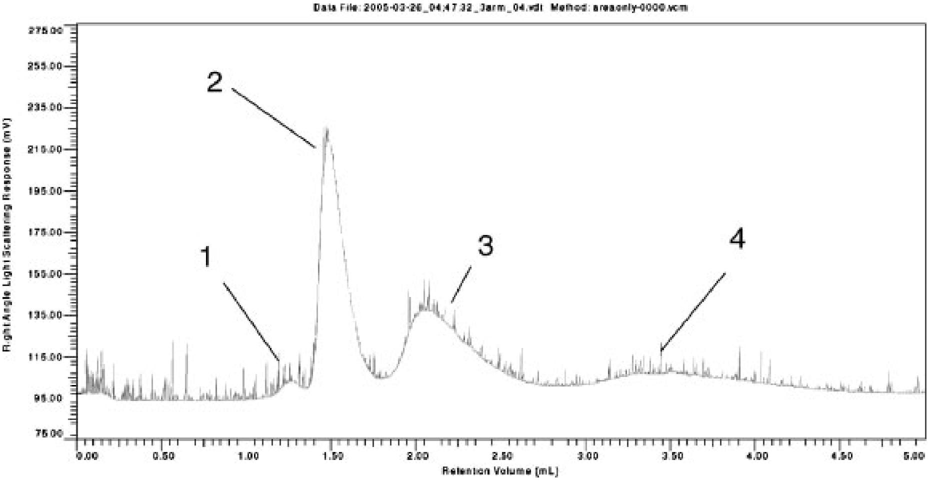

Figure 5.

MTF fractogram of 3-arm star sample as detected by 90° light scattering. The assignments of the four modes observed in the fractogram are discussed in the text. The modes are numbered 1 through 4 with 1 being the earliest eluter and 4 being the latest eluter.

its presence is now clearly revealed in the MTF experiment. Formation of the 4-arm star is discussed below.

Considering the SEC data, it would appear that a small amount of uniarm material and a relatively large amount of two-arm material was present in the sample. Both uniarm and two-arm material are linear species, and as such, their MTF elution behavior should match that of linear PS standards. A comparison of the relative peak elution volumes (or times) of linear PS standards and the peaks of the 4 modes in the 3-arm star sample is shown in Figure 6. The molecular weights of the first two modes were taken from the SEC data and assigned based on the known elution order of MTF. As can be observed, the elution volumes of the first two modes are consistent with those of linear PS standards, and thus, these two modes appear to represent the uniarm and 2-arm species present in the sample. It is clear that the latter two modes were retained far longer than the corresponding linear chains and, the LALLS/UV ratios suggest that the molecular weights of these modes are 3 and 4 times the molecular weight of mode 1, respectively.

The light scattering detector used in these studies employed detection angles of 7 degrees and 90 degrees. Although it is possible to estimate the radius of gyration (R_G) from two angle light scattering data, the expected R_G values for a multi-arm species having arm molecular weights of 1,250 kg/mol exceed the values that can be determined reliably from two angle data.[6] Calculations of the 7 degree particle scattering form factor, P(7), for PS stars[7] having arm molecular weights of 1,250 kg/mol suggest that M_W values obtained from 7 degree light scattering data should provide reasonably accurate molecular weights of the potential species present in the fractogram.

To improve the signal to noise ratio for both the concentration detector response and the light scattering response, the injected mass of the 3-arm star sample was increased by a factor of five over the standard conditions. The improved signal to noise enabled a reasonable estimate of the absolute M_W values across the MTF elution profile of modes 3 and 4. This analysis revealed that the third mode included molecular weights ranging from ~3,100 kg/mol to 3,900 kg/mol. A 3-arm

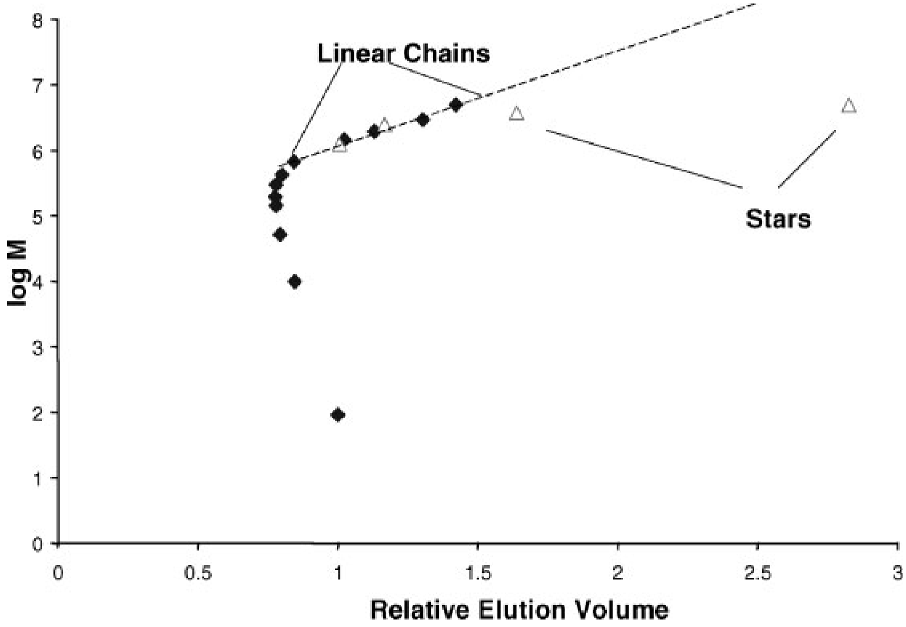

Figure 6.
Relative peak elution volume (or peak elution time) of linear PS standards (solid diamonds) and the four modes observed in the PS star fractogram (open triangles) shown in Figure 5.

star would be expected to have a molecular weight of ~3,750 kg/mol based on the molecular weight of the uniarm species. Thus, the third mode appears to represent the 3-arm star material. Finally, the fourth mode includes molecular weights ranging from ~4,500 kg/mol to ~7,000 kg/mol. Near the apex of the fourth mode, the M_W is ~5,000 kg/mol. The expected Mw of a 4-arm star is 5,000 kg/mol. The fourth mode would appear to be, predominantly, 4-arm star material. The higher molecular weights detected near the tail of the distribution most likely stem from low signal to noise in both the concentration detector and light scattering detector traces due to the very low concentration of material present.

Based on the reaction scheme used to make the star sample, one would not immediately expect the formation of a 4-arm star. However, in the synthesis of star polymers, it has been observed that molecules having more arms than the functionality of the coupling agent are often produced. The chemistry responsible for this observation is known as the lithium-halide exchange reaction.[8] In the case of the chemistry used to make this 3-arm star sample, synthesis of species having more than 3 arms is entirely possible.

Interpretation of the MTF fractogram has revealed some interesting characteristics of the MTF separation mode. First, long chain branched molecules are retained substantially longer than linear molecules of the same molecular weight. Referring to Figure 6, one can see that a 4-arm star is retained nearly a factor of two longer than a linear molecule of the same molecular weight (the highest molecular weight linear standard in the figure is approximately the same molecular weight as the 4-arm star). Additionally, the 3-arm stars are also retained much longer than linear molecules of the same molecular weight by about a factor of 1.4. Secondly, the 3-arm star and 4-arm star co-eluted in SEC, but these species are clearly separated in the MTF mode. Thus, MTF would not only appear to separate long chain branched molecules from linear molecules, but appears to separate long chain branched molecules having similar hydrodynamic volumes and differing long chain branching topology.

Sample recovery from the MTF column was also studied. For linear chains, quantitative recoveries were obtained over the molecular weight range of 10 kg/mol to 5,000 kg/mol. For the 3-arm star sample, recoveries on the order of 60% were typical. Because recoveries were quantitative for linear chains, it is assumed that the lack of recovery was due to incomplete elution of the star branched molecules. Even though recovery was below 100%, it is still clear that MTF separates based on topology. The estimate of peak M_W came from ratioing the light scattering detector signal to the concentration detector signal. The accuracy of the estimate, and hence the interpretation of the fractogram, does not require complete elution of the sample. Recent data acquired at the University of Amsterdam[9] with a similar column, revealed near quantitative elution (recovery >95%) of the same 3-arm star sample studied here. Longer run times were required to achieve the near quantitative recovery. Run time has no influence on MTF resolution. Flow rate and macropore dimensions within the column are the two largest factors influencing resolution. The fact that longer run times were required to achieve near quantitative recovery suggest that even higher order stars (more than 4 arms) were present in the sample, and more time would be needed to elute these.

MTF of Polyethylene Fractions

The molecular weight range of the polyethylene fractions relative to the MTF reversal molecular weight is an important consideration. Figure 7, for example, shows an overlay of all the MTF peak elution times for the complete set of polyethylene fractions (full range of M_W's and LCBf's), superimposed with those of the linear polystyrene standards. For the linear polystyrene standards, the M_W's have been plotted after scaling them down by a factor of 0.43 in order to adjust for the difference in the hydrodynamic volume relative to linear polyethylene. After accounting for hydrodynamic size differences, the superpositions are good as was observed previously for the PS, polybutadiene pair.[1] However, the M_W's for most fractions lie too close to the reversal or critical molecular weight, M_C, for it to be differentiated based on branching (all points in the set lie on one curve). For each LCBf, at least one fraction lies above M_C, by about a factor of two, as M_C for polyethylene would appear to be on the order of ~100 Kg/mole. Even these fractions cannot be distinguished by their peak elution times.

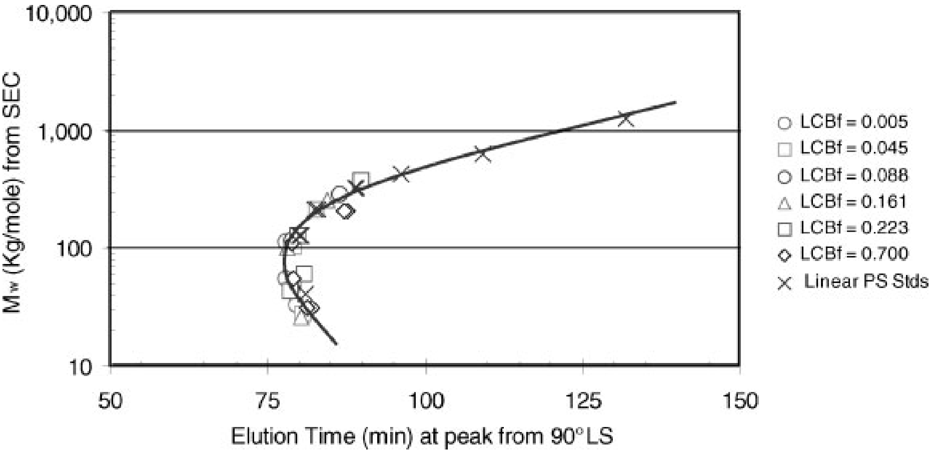

Figure 7.
MTF reversal curve comparing peak elution times of linear PS standards with those from lightly cross-linked homogeneous ethylene octene copolymer fractions.

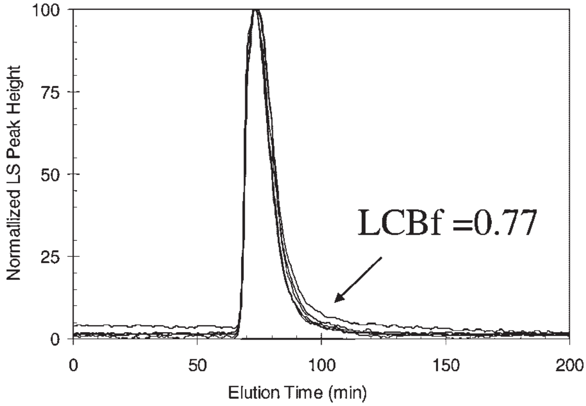

Figure 8.
MTF Fractograms of lightly cross-linked homogeneous ethylene octene copolymer fractions. All fractions had M_W values near M_C. LCBf of parent polymers from which these fractions were acquired varied from 0.005 to 0.77 per 1000 backbone carbons. Details concerning the fractions can be found in Table 1. Detection was by laser light scattering at a detection angle of 15°.

In previous work,[1] long chain branched samples had to exceed M_C before any additional retention was observed. The same observation was made in this study. Figure 8 provides an overlay of the MTF fractograms for polyolefin fractions having M_W values of $\sim$100 kg/mol and spanning the entire range of LCBf (i. e. virtually at the M_C for this column). With the exception of a slight amount of tailing observed for the fraction coming from the highest LCBf polymer, the fractograms in Figure 8 are virtually identical. There are a couple of reasons for this. First, the fractions are too close to M_C and too close in M_W (see Table 1) to be differentiated by their peak elution times, and second, except for the highest LCBf fraction, Mark – Houwink plots from triple detector SEC indicated there was little LCB detected in the parent polymer samples near 100 kg/mol.

MTF fractograms of the highest M_W polyethylene fractions are compared in Figure 9. Details concerning the molecular weights and polydispersities of these fractions and the LCBf's of the parent polymers are provided in Table 1. Although the M_W values from SEC differ slightly among the fractions, the polydispersities, and hence the breadths of the size distributions, are all very similar. Additionally, the M_W values for these fractions all exceed M_C by more than a factor of two. The main differentiating feature among these fractions is the long chain branch frequency. For the fraction coming from the sample having the lowest

Table 1.
SEC and LCB data for polyethylene fractions.

LCBf (branches/1000 C)[a]	M_W (kg/mol) from SEC[b]	Polydispersity (M_W/M_N)[b]
0.005	220/115	1.4–1.4
0.045	215/119	1.5–1.3
0.088	229/103	1.5–1.4
0.161	254/102	1.5–1.3
0.223	383/127	1.7–1.5
0.7	209/109	1.5–1.4

[a] Values from parent polymer from which fractions were acquired.
[b] Values from SEC based on linear HDPE, first value represents M_w of highest molecular weight fraction, while second value represents M_w of fraction closest to M_C.

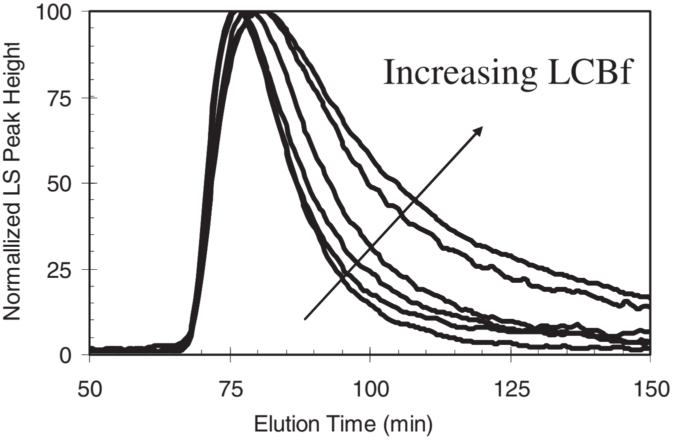

Figure 9.
MTF Fractograms of lightly cross-linked homogeneous ethylene octene copolymer fractions. All fractions had M_W values nearly two times M_C. LCBf of parent polymers from which these fractions were acquired varied from 0.005 to 0.7 per 1000 backbone carbons. Details concerning the fractions can be found in Table 1. Detection was by laser light scattering at a detection angle of 15°.

LCBf, about one chain in ten contains a long chain branch site. At the other extreme, for the fraction coming from the sample having the highest LCBf, there are about 10 branch sites per molecule.

As is evident in Figure 9, MTF is able to fractionate these higher molecular weight samples. MTF provides six distinct distributions for these samples and the main structural parameter that distinguishes these samples is the LCBf. Therefore, when there is a LCB distribution within the sample whose M_W exceeds M_C, MTF can fractionate it.

The fractionation of the polyolefin samples by MTF yields fractograms that look different from those observed for the polystyrene star. However, considering the types of branching present in the stars versus the PE fractions, one would expect the fractograms to look different. In the case of the PS star, the M_W values of the 3-arm and 4-arm material exceeded M_C, by more than a factor of 10. Additionally, the PS stars consisted of nearly discreet components, as they were made via anionic polymerization followed by coupling. On the other hand, these PE fractions come from randomly branched polymers. Thus, in each fraction, there is a distribution in number of branches and lengths of branches.

The other feature to note in Figure 9 is that not all species in these fractions appear to be MTF-effective. This is evident because the peak in the distribution is not sensitive to the LCBf. This is most likely due to the fact that a significant portion of the material in these fractions consists of linear chains. However, the breadth of the fractogram and degree of tailing both increase with increasing levels of LCB. Yet to be determined is whether the "MTF-effective" branches (i. e. those having the longest retention times) are also those that have a dominating effect on zero shear viscosity.

Finally, the use of MTF fractograms to derive a long chain branching distribution for a given hydrodynamic volume slice (e. g. from SEC) can be visualized with the aid of Figure 10. In this figure, an overlay of all three detector responses is provided for the highest LCBf fraction studied. The traces in the figure are actually the fitted results from exponentially modified Gaussian fits of the experimental data.[10] The agreement between the fitted data and experimental data was excellent. Figure 10 provides additional insight into the MTF separation. First, it

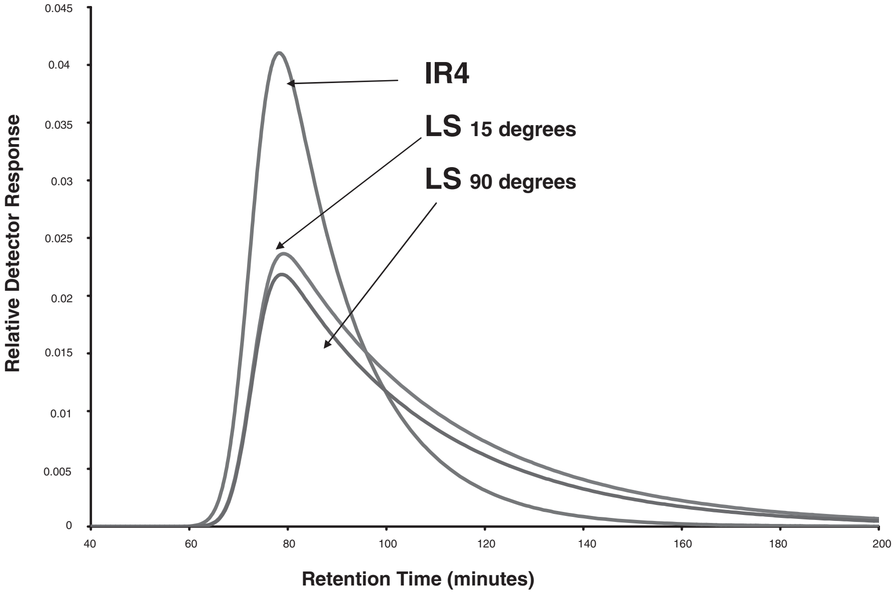

Figure 10.

Exponentially modified Gaussian fits of experimental MTF fractograms obtained for the most highly branched homogeneous ethylene octene copolymer fraction. Shown are the concentration detector (IR4), 15° and 90° light scattering traces.

can be noted that the ratio of 15° light scattering response to 90° remains roughly constant across the fractogram. This means that the R_G's of the chains eluting across the fractogram are roughly constant. Roughly constant R_G across the distribution is not surprising considering the fraction had a relatively narrow size distribution (i. e. SEC $M_W/M_N \sim 1.4$). Secondly, the ratio of 15° light scattering to IR4 (concentration) is not constant across the fractogram, but rather, it increases with increasing retention times. Thus, in MTF, chains having the same R_G's but different molecular weights are being separated, and retention increases with increasing molecular weight. At constant R_G, increasing molecular weight stems from increasing levels of branching. Thus, in MTF, chains containing the highest levels of branching are retained the longest.

In SEC, molecules are separated by hydrodynamic size, and for a sample containing LCB, this means branched chains and linear chains of the same hydrodynamic size co-elute. Among these co-eluting species, chains containing more branching will be of higher molecular weight than those containing little or no branching. In Figure 10, it was shown that MTF separates chains of the same size according to molecular weight, which means MTF separates chains according to the amount of branching present. Thus, the coupling of SEC and MTF with light scattering detection (two or more angles) would enable the determination of a branching distribution for each SEC fraction. The approach would proceed as follows: Across the MTF elution profile from each SEC fraction, both M_W and R_G are obtained from light scattering. For many linear polymers, including polyethylene, the relationship between R_G and M_W has been determined from multi-angle light scattering.[11] Alternatively, one can use the Flory-Fox equation to estimate the linear chain radii of gyration, $R_{G,L}$ for a given M_W.[12] The radii of gyration of the branched species, $R_{G,B}$, are determined from the angular dependence of their light scattering as these species elute from the MTF column. Thus, with knowledge of both $R_{G,B}$ and $R_{G,L}$, one can determine the branching index, g, across the entire MTF elution profile. The Zimm-Stockmayer model can then be used to predict the number of branch sites per chain across the MTF elution profile from g.[13] This process can be repeated for each size fraction from SEC. The distribution information potentially gleaned from the SEC-MTF-light scattering experiment cannot be obtained by any other technique at present. For example, SEC with molecular weight sensitive detectors provides only an average number of branch sites at each hydrodynamic size interval.

Particle Size Dependence of M_C

All MTF results presented to this point were obtained using columns packed with functionalized, polydisperse silica having an average particle diameter of 0.5 μm. To learn more about the particle size dependence of MTF, additional columns were packed with 0.81 and 0.75 μm silica. These silicas, obtained from Bangs Laboratories (Fishers, IN), had very narrow size distributions in contrast to the 0.5 μm material. The nominal sizes of these materials were 0.97 and 0.8 μm, respectively. The sizes reported above were estimated from SEM images. These columns were also packed by Mel Cabey, Diazem Corporation (Midland, MI) and the silica was not functionalized prior to packing.

The dependence of M_C on packing particle size is shown in Figure 11. It is clear that the critical molecular weight falls off monotonically with decreasing particle size. However, the correlation does not appear to be linear, but with only three data points, it is difficult to estimate the functional form of the relationship with any certainty. The decrease in M_C with decreasing particle size is consistent with previous MTF work performed using monolithic columns.[1] While the exact details of the MTF separation mechanism are not understood, it is clear that there is a certain critical solute size that has to be reached before the MTF mechanism is operative.

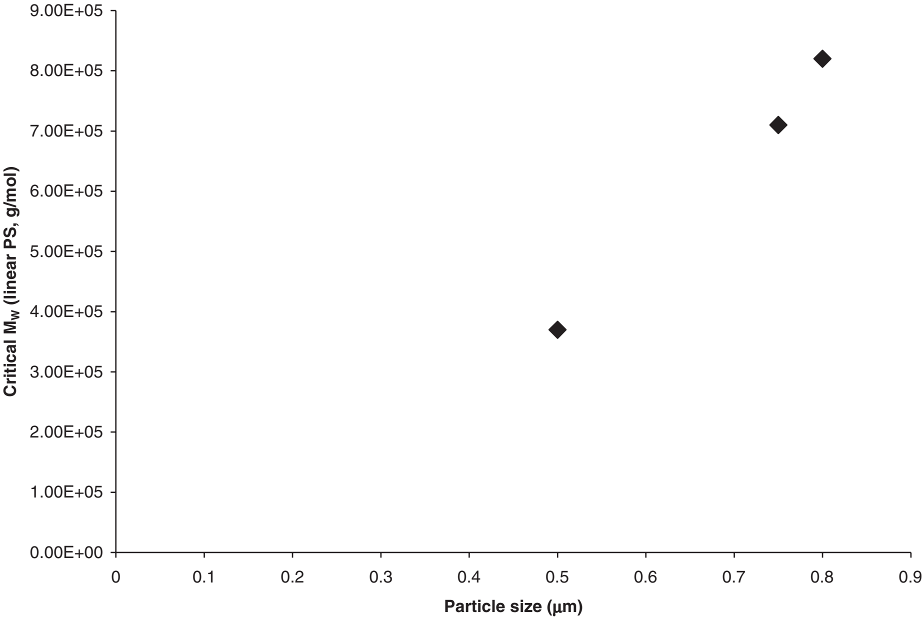

Figure 11.
Dependence of critical molecular weight (M_C) on packing particle size.

This critical size, expressed here as M_C (linear PS), decreases with particle size (i. e. macropore channel dimension). The functional form of the relationship between M_C and particle size may offer insight regarding the separation mechanism, but further work is needed to establish the relationship between M_C and particle size.

Conclusions

In a detailed analysis of a 3-arm star PS sample, it was shown that MTF can separate LCB chains from linear chains, and can separate LCB chains of differing topologies. The example shown in this paper included near baseline MTF resolution of at least 4 components present in a nominal 3-arm star sample. Despite having the same hydrodynamic volume, the 3-arm star was separated from the 4-arm star by MTF. Multidetector SEC results, knowledge of the synthesis chemistry and on-line low angle laser light scattering detection was used to interpret the MTF fractogram of the PS star sample. The clean MTF separation of star components synthesized via coupling of discreet arms will enable experimental validation of the Zimm-Stockmayer model for predicting the sizes of branched polymer chains.[13]

In a second application, polyolefin samples having similar hydrodynamic size distributions (i. e. similar breadth in SEC chromatogram) were fractionated differently by MTF with the major differentiating feature being the LCBf of the parent polyolefin polymer. For fractions exceeding M_C, MTF was shown to produce increasingly broader fractograms with increasing branching frequency.

Further interpretation of the polyolefin MTF fractograms with two angle light scattering detection revealed little change in R_G across the fractogram, but significant increases in M_W across the fractogram, especially for the highest branch frequency samples. At roughly constant R_G, branched chains are higher in molecular weight than linear chains. Thus, retention in MTF increased with increasing levels of branching. The fractionation provided by MTF combined with the structural information attainable with on line multiangle light scattering detection will potentially enable determination of a long chain branching distribution for each hydrodynamic size slice or fraction. Coupling of MTF and SEC in an automated on line fashion would facilitate determination of long chain branching distributions across the molecular weight distribution of a sample. Present state-of-the-art technologies such as SEC with molecular weight sensitive detectors or 13C NMR provide only an average number of branches per chain. Thus, the determination of branching distributions across the molecular weight distribution would provide structural information that is not attainable at present.

In this paper, new columns for MTF were introduced. The columns were packed with submicron polydisperse silica that had been surface treated with PS. MTF elution order reversal was observed for PS standards and PE fractions injected onto these new columns. Additionally, M_C was found to be dependent on packing particle size. Thus, MTF elution order reversal was not unique to the previously studied monolithic columns,[1] but rather, appears to be a general phenomenon attainable when the interstitial channels (i. e. macropores) in a column are of the appropriate dimensions, and when the flow rate is reduced.

Although the mechanism of MTF is not completely understood, two potential mechanisms are pinning (or entanglement) and polymer restriction followed by relaxation. Both may be operative in a MTF experiment. Both are expected to be sensitive to long chain branching topology.

[1] D. M. Meunier, P. B. Smith, S. A. Baker, *Macromolecules* **2005**, *38*, 5313–5320.

[2] P. B. Smith, D. M. Meunier, S. A. Baker, R. K. Prud'homme, International Patent Application, Publication Number WO 03/098208 A1, November 27, **2003**.

[3] *NMR and Macromolecules*, J. C. Jr, Ed., American Chemical Society, Washington, D.C. **1984**, Chapter 9.

[4] Wood-Adams, P. M. Randall, J. M. Dealy, A. W. deGroot, O. D. Redwine, Macromolecules. **2000**, *33*, 7489–7499.

[5] C. W. Macosko, *Rheology, Principles, Applications and Measurements*, Wiley-VCH New York **1994**, page 505.

[6] K. Terao, J. W. Mays, *Eur. Polym. J.* **2004**, *40*, 1623–1627.

[7] H. Benoit, *J. Polym. Sci.* **1953**, *11*, 507–510.

[8] T. Altares, Jr., D. P. Wyman, V. R. Allen, K. Meyersen, *J. Polym. Sci: Part A* **1965**, *3*, 4131–4151.

[9] Personal communication with Rob Edam, University of Amsterdam, June, 2006.

[10] E. Grushka, *Anal. Chem.* **1972**, *44*, 1733.

[11] P. Tackx, J. C. J. F. Tackx, *Polymer* **1998**, *39*, 3109–3113.

[12] P. J. Flory, T. G. Fox, *J. Am. Chem. Soc.* **1950**, *73*, 1904.

[13] B. H. Zimm, W. H. Stockmayer, *J. Chem. Phys.* **1949**, *17*, 1301–1314.