Capability of Thermal Field-Flow Fractionation for Analysis of Processed Natural Rubber

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Applicability of Thermal field flow fractionation (ThFFF) was investigated for the analysis of masticated natural rubber (NR) adhesives produced by a hot melt mastication process. An optimum ThFFF condition for NR analysis was found by using tetrahydrofuran (THF) as a solvent/carrier and a field-programming. Low flowrate (0.3 mL/min) was used to avoid stopping the flow for the sample relaxation. Measured molecular weight distribution was used to monitor degradation of rubber during the mastication process. Rubber samples collected at three different stages of the mastication process and were analyzed by ThFFF. It was found that in an anaerobic process rubber degradation occurs at the resin-mixing (compounding) zone as well as in the initial breakdown zone, while in an aerobic process most of degradation occurs at the initial breakdown zone. It was also found that E-beam radiation on NR causes a slight increase in the NR molecular weight due to the formation of a branched structure.

Introduction

A complete understanding of the behavior of pressure-sensitive adhesives requires knowledge of the molecular weight (MW) and molecular weight distribution (MWD) of the adhesives. This is particularly true in hot melt masticated adhesives because of the degradation that occurs during the mastication process. In contrast are solvent-coated adhesives which undergo very little degradation during processing. One of the limiting factors in the characterization of hot melt masticated natural rubber (NR) adhesives has been the lack of knowledge of MWD and the processing parameters which affect the breakdown of the rubber. This knowledge is important in understanding the NR mastication process, developing NR adhesives, and scaling-up of production equipments.

One of methods that has been used for determining MWD of hot melt masticated NR adhesives is the inherent viscosity (IV) measurements. This method has several drawbacks. First, the IV measurement gives only the information on average MW, not the overall profile of the MWD. Second, the IV measurement does not give meaningful results for the actual adhesives because of the large fraction (30-50%) of low molecular weight resin that is added into the adhesive. Thus the IV method can only be used on pure NR.

Thermal field-flow fractionation (ThFFF) is a chromatography-like separation technique that is applicable to separation and characterization of various lipophilic polymers[1-12] and particles in suspension.[13-18] One of routine applications of ThFFF is the determination of MWD (and thus average MW) of polymeric materials. The retention time in ThFFF increases with the D_T/D ratio, where D_T is the thermal diffusion coefficient and D the mass diffusion coefficient.[6] For homopolymers, retention in ThFFF is mostly governed by the mass diffusion coefficient, D.[19-21] The mass diffusion coefficient, D is given by[22]

$$D = \frac{RT}{6\pi\eta_o N_A}\left[\frac{10\pi N_A}{3[\eta]M_V}\right]^{1/3} \tag{1}$$

, where R is the universal gas constant, T temperature, η_o fluid viscosity, N_A Avogadro's number, M_V viscosity-average MW, and $[\eta]$ intrinsic viscosity. D decreases as MW increases, and thus in ThFFF the retention time increases as MW increases, resulting in a MW-based separation of polymers. ThFFF is particularly useful for analysis of ultrahigh MW polymers.[6,9,23,24] ThFFF is claimed to offer higher resolution than SEC,[10] particularly for polymers having MW higher than about a million.[6,12] The superior resolution of ThFFF for high-MW polymers results in a more accurate analysis.[25] One of unique features of ThFFF is the openness of the channel. The open channel geometry minimizes non-ideal phenomena such as shear degradation of the polymers and adsorption of polymers onto the channel surface.[6] It also allows the passage of microgel particles through the channel. ThFFF has been used for analysis of microgel-containing polymers.[25-32] Since the ThFFF channel is open, sample filtration is not required and non-ideal SEC phenomena such as adsorption and shear degradation are expected to be minimized in ThFFF. A potential of ThFFF for analysis of NR-related material has been shown earlier.[28] In this report, capability of ThFFF is evaluated as a technique for determining MWD of NR and NR-adhesives, and thus for monitoring of NR mastication process. Also, an experimental design was performed which evaluated the effect of process conditions on the MWD of NR adhesives. Effect of electron beam treatment on NR was also investigated.

Experimental Section

Thermal Field-Flow Fractionation (ThFFF) of NR.

ThFFF system was a Polymer Fractionator model T100 purchased from FFFractionation, LLC. (Salt Lake City, Utah, USA). The ThFFF channel has the thickness of 0.0127 cm, breadth of 2 cm, and length of 45.6 cm. HPLC-grade tetrahydrofuran (THF) from JT Baker Inc. (Phillipsburg, NJ, USA) was used as the solvent/carrier. The effluent was monitored by a Varex Mark IIA evaporative light scattering detector (ELSD). The ELSD settings were tube temperature = 75 °C, N_2 flow = 45 mm, and range = 0.2. A power programming[33] was employed for all ThFFF analysis of NR materials, where the temperature gradient ΔT was gradually decreased from the initial value of 90 °C ("initial ΔT") down to the final value of 3 °C ("hold ΔT") during a run. Other programming parameters were $t_1 = 6$ min and $t_a = -3$ min. ThFFF experiments require stopping the flow for the sample to reach an equilibrium under the given field strength (stop-flow operation). By using low flowrate, the stop-flow step can be avoided as the sample can reach an equilibrium before it migrates far down the channel. All ThFFF runs were made without stopping the flow (non-stopflow method) at the flow rate of 0.3 mL/min.

NR solutions were prepared at the concentration of approximately 0.2% (w/v) in THF and were injected using a Rheodyne injector equipped with a 20 μL loop without prior filtration. Molecular weight of NR was determined using a calibration curve constructed with a series of narrow polystyrene standards. NR is known to have a similar chemical structure as polyisoprene. Due to the difference in chemical structure between the sample (NR) and the calibration standard (polystyrene), the reported NR molecular weights are not absolute but polystyrene-equivalent molecular weights.

Materials. Two natural rubber samples were used in this study. They are "CV60" and a ribbed smoked sheet ("RSS1") obtained from Cargill company (New York, NY, USA). The compounded natural rubbers (rubber adhesives) were obtained by processing the NR through a thermo-mechanical degradation process, where the natural rubber is mechanically broken down, and then mixed with a tackifier resin in an extruder.

Thermo-Mechanical Mastication of Natural Rubber. Thermo-mechanical mastication is a process to break the NR and then mix the NR with tackifying resin to make pressure-sensitive adhesives. As seen in Figure 1, the mastication process consists of two zones: (1) initial rubber breakdown zone and (2) the resin-mixing (or compounding) zone. The NR fed into the process is mechanically broken down at the first zone, and then mixed with tackifying resin at the second zone to produce the final compounded NR adhesive. The mastication process can be performed with (aerobic) and without (anaerobic) the air injected into the process. The injection of the air usually results in more breakdown of NR.

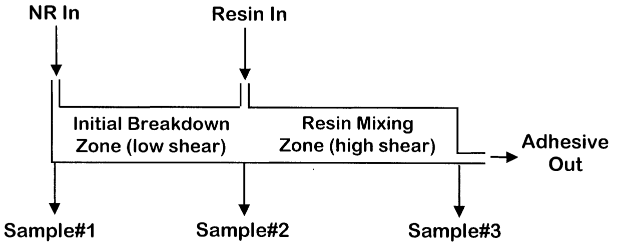

Figure 1. A schematic diagram of the thermo-mechanical mastication process of natural rubber.

Results and Discussion

Determination of Average MW of NR Adhesives Using ThFFF. Various experimental parameters affect D and D_T, and thus the retention in ThFFF. The external field strength (temperature drop across the channel, ΔT) is one of the most important parameters in ThFFF. Generally D_T/D increases as the field strength increases, and thus the retention time increases. Under a constant field strength, D_T/D increases as the molecular weight of the sample increases. For samples having broad molecular weight distributions such as NR, the field-programming could be useful as it prevent excessive retention of ultrahigh MW components. Through a systematic approach, an optimum ThFFF condition was found for analysis of NR materials by using a power-programming[33] as described in the experimental section.

The CV60 NR was first processed by an anaerobic mastication process. The CV60 NR fed into the mastication process ("CV60-1"), the NR collected after the initial breakdown zone ("CV60-2"), and the compounded NR collected at the end of the mastication process ("CV60-3") were characterized using ThFFF. ThFFF fractograms are shown in Figure 2. Comparing with the fractogram obtained by injecting the resin alone, the tall peak of the compounded CV60-3 NR eluting at about 6.5 minute was identified as that of the low molecular weight tackifying resin that was added into

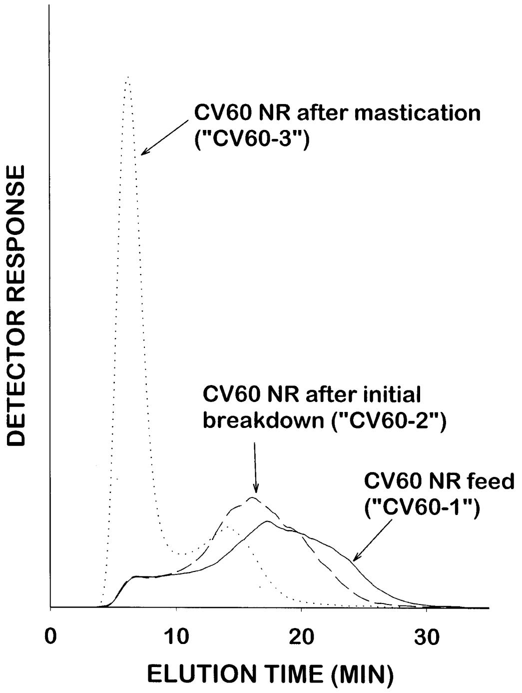

Figure 2. ThFFF fractograms of CV60 NR collected at three different stages of an anaerobic mastication process.

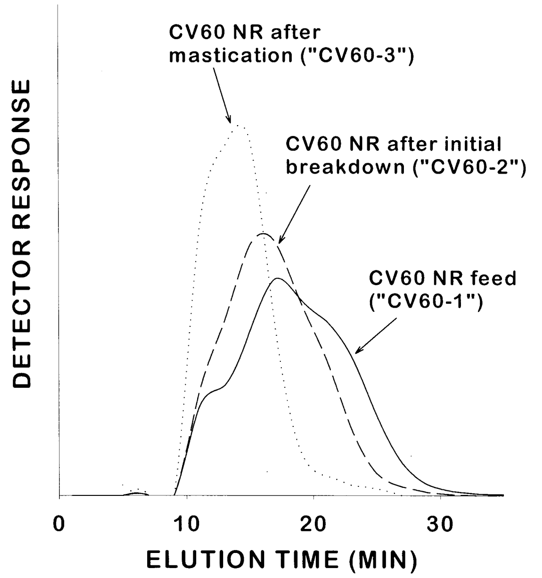

Figure 3. ThFFF fractograms of CV60 NR collected at three different stages of an anaerobic mastication process with the low molecular weight resin peak removed.

the process right after the initial breakdown zone. Only the rubber fraction of the adhesive is of interest to us as it determines the mechanical properties of the adhesive. The low molecular weight resin peak was mathematically removed from the fractogram of the CV60-3, and the results are shown in Figure 3, where the areas of all three peaks are normalized. The average retention time of the rubber decreases as the mastication process proceeds, indicating the breakdown (degradation) of the rubber occurs during the mastication process. The polystyrene-equivalent weight-average molecular weights (M_w) of the rubber fractions determined by ThFFF are shown in Table 1. The average MW of the rubber decreases as the mastication process proceeds as expected. It is however somewhat surprising to see that the rubber breakdown occurs not only at the initial breakdown zone but also at the resin mixing zone.

One may question whether the presence of the resin in CV60-3 might affect ThFFF behavior of the rubber molecules. Figure 4 shows the ThFFF fractograms of CV60-2 (CV-60 NR collected after the initial breakdown zone) and a mixture of the CV60-2 and the tackifier resin. The mixture was prepared by adding the tackifier resin into a solution of the CV60-2. The early-eluting resin peak was removed from the fractograms again. No significant difference was found between the fractograms of CV60-2 and the CV60-2/resin mixture. The weight-average molecular weight was 2.0 × 10^5 and 1.9 × 10^5 for CV60-2 and the mixture, respectively. This result confirms that the presence of the tackifying resin does not affect the behavior of the NR molecules in ThFFF, and that the NR breakdown occurs throughout the whole mastication process.

Table 1. Weight-average MW of anaerobically masticated CV60 NR

Sample	$M_w{}^a$
CV60 NR feed	3.1 × 10^5
CV60 NR after initial breakdown zone	2.0 × 10^5
CV60 NR after mastication	8.9 × 10^4

[a] Polystyrene-equivalent molecular weight

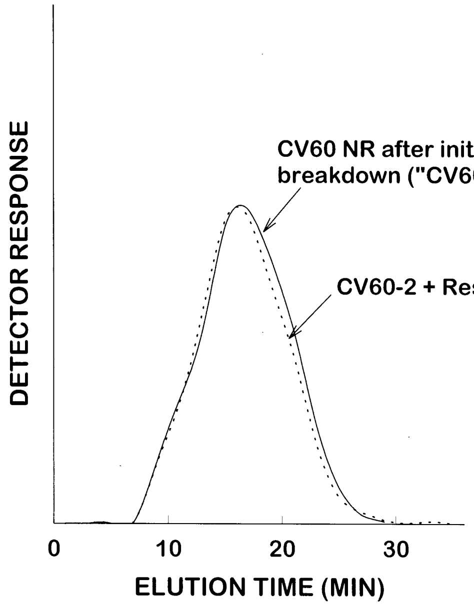

Figure 4. ThFFF fractograms of CV60-2 and a mixture of CV60-2 + resin with the resin peak removed.

Another NR sample, "RSS1" collected at three different stages of an aerobic mastication process were characterized using ThFFF at the same experimental conditions. The "RSS1" NR is the raw material and is known to have higher molecular weight than the CV60. This time air was injected into the mastication process to promote the NR degradation. Figure 5 shows the ThFFF fractograms of the RSS1 fed into

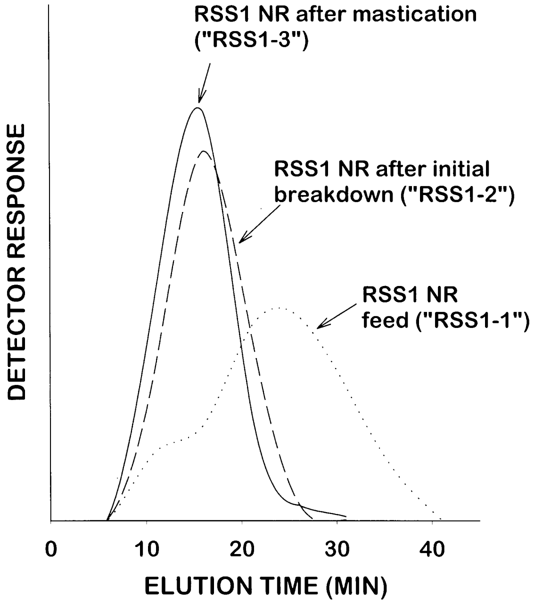

Figure 5. ThFFF fractogram of RSS1 NR collected at three different stages of an aerobic mastication process with the resin peak removed.

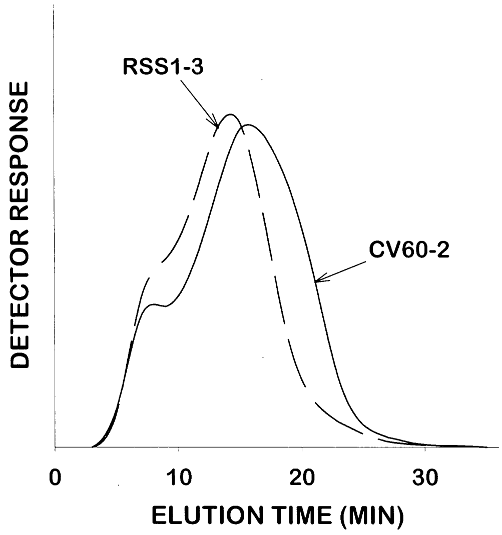

Figure 6. ThFFF fractograms of CV60-4 and RSS1-4 NR prior to being E-beam irradiated.

the process (“RSS1-1”), RSS1 collected after the initial breakdown zone (“RSS1-2”), and the final compounded rubber (“RSS1-3”). The early-eluting resin peak is again removed from the fractogram of the “RSS-3”. It is noted that, unlike for the CV60, most of the degradation of RSS1 NR occurs in the initial breakdown zone. The amount of breakdown occurred in the resin mixing zone is relatively small.

Effect of Electron-Beam (E-beam) Irradiation on Molecular Weight of NR. It has been suspected that one may be able to build molecular weight of NR by irradiating an E-beam. An effort was made to understand the effect of E-beam irradiation on the MW of NR. Two samples of NR used in this experiment are CV60 NR taken after the initial breakdown zone of an anaerobic process (“CV60-4”) and RSS1 NR compounded through an entire aerobic process (“RSS1-4”). Both rubbers were solvated in toluene, coated onto a polyester sheet at 10.5 grains, and were E-beamed (@175 kV) at four different dosages (0.5, 1, 2, and 3 Mrad). The rubber was then peeled off the polyester sheet and was dissolved in THF. The solutions were then characterized by ThFFF. Figure 6 shows the fractograms of CV60-4 and RSS1-4 NR prior to being irradiated by E-beam. CV60-4 is retained more than the RSS1-4, indicating the average MW of CV60-4 is higher than that of the RSS1-4. Figure 7 and 8 show the fractograms of the RSS1-4 and CV60-4 that are E-beamed at various dosages. For both samples, the retention increases slightly as the E-beam dosage increases, suggesting slight increase in average MW with the dosage. The weight-average MW (M_w) of the samples determined by ThFFF are summarized in Table 2. As expected from Figures 7 and 8, the average MW slightly increases as the E-beam dosage increases before the onset of gelation. Both RSS1-4 and CV60-4 formed insoluble gel when irradiated at 2 and 3 Mrads, thus were unable to be run in ThFFF. This suggests that E-beam irradiation on NR results in the formation of crosslinks. Prior to gelation, the NR does indeed 'build' molecular weight slightly. This increase in molecular weight, however, is due to the formation of a branched structure. The original NR is known to have a fairly linear molecular structure. This result suggests that it is not possible to build the molecular weight of NR using E-beam radiation

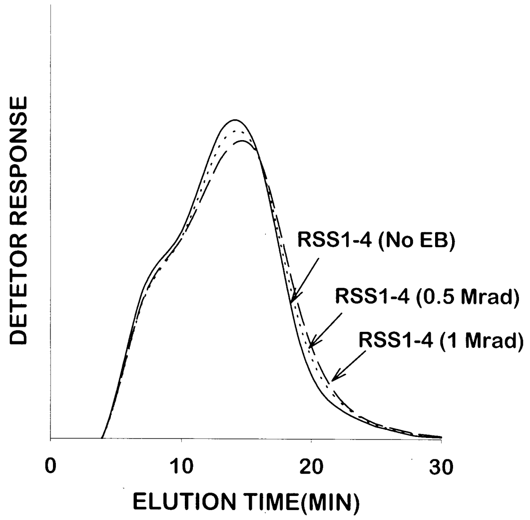

Figure 7. ThFFF fractograms of RSS1-4 NR E-beamed at different dosages.

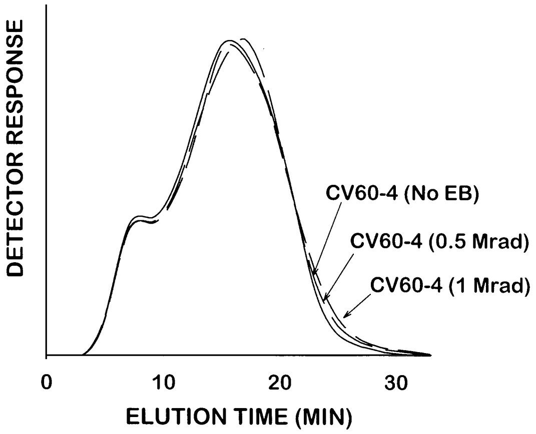

Figure 8. ThFFF fractograms of CV60-4 NR E-beamed at different dosages.

Table 2. The Weight-Average MW’s (Mw) of NR irradiated with E-beam radiation at different dosages

Rubber	E-beam dose (Mrad)	M_w[a]
CV60	0	1.6×10^5
	0.5	1.7×10^5
	1	1.8×10^5
	2	gelation
	3	gelation
RSS1	0	1.0×10^5
	0.5	1.1×10^5
	1	1.2×10^5
	2	gelation
	3	gelation

[a] Polystyrene-equivalent molecular weight

Table 3. Design for CV60 NR Breakdown Experiment

Lot No.	Barrel Temp. °C	Screw Speed (rpm)	Resin Conc. (lb/hr)
1	107	300	70
2	"	"	100
3	"	400	70
4	"	"	100
5	135	300	70
6	"	"	100
7	"	400	70
8	"	"	100

and reform a linear polymer.

Effect of Processing Conditions and Formulation on M_w of CV60 NR. A 2^3 factorial experimental design (three variables at two different conditions) was employed to determine the effect of processing (mastication) condition and formulation on the molecular weight CV60 NR. The mastication of CV60 NR was run on a twin screw extruder. Three variables in the experimental design were (1) resin-mixing barrel temperature at 107 or 135 °C, (2) screw speed at 300 or 400 rpm, and (3) resin loading at 70 or 100 lb/hr. The CV60 NR feed rate was kept constant at 5 lb/hr. The temperature in the breakdown zone was kept constant at 135 °C. 1 pphr Irganox 1010 antioxidant was added to all lots. The formulation and conditions for all of the lots is summarized in Table 3.

The weight-average MW's determined by ThFFF are shown in Table 4. M_w of the feed CV60 NR was 3.8×10^5. Although the differences in M_w for different processing conditions are not very significant, the highest molecular weight among adhesives was measured for the lot 1 adhesive. This lot was processed with the low extruder temperature which should minimize thermal degradation. Lot 1 also had the lowest screw speed which should also minimize the shear degradation. It in interesting to see that the lot 1 also had the lowest resin level. Initially it was suspected that the lower resin content would lead to lower M_w due to the adhesive having a higher viscosity which would result in more shear degradation. An explanation of the resulting high molecular weight could be that the resin mixes into the rubber faster in low concentrations than in higher concentrations. At higher resin levels the resin has a tendency to melt and lubricate the screw rather than mix. In a high shear mixing zone this lubrication may not be enough to prevent the shear degradation of the large rubber particles.

Table 4. Weight-average MW's of CV60 NR determined by ThFFF for processing and formulation experiment

Lot No.	Rubber $M_w{}^a$ (g/mol)	Adhesive $M_w{}^b$ (g/mol)
1	3.4×10^5	1.6×10^5
2	3.0×10^5	1.3×10^5
3	2.7×10^5	1.3×10^5
4	2.7×10^5	1.3×10^5
5	3.0×10^5	1.5×10^5
6	2.8×10^5	1.4×10^5
7	2.6×10^5	1.3×10^5
8	2.7×10^5	1.4×10^5

[a,b]Polystyrene-equivalent molecular weight

Conclusions

Thermal Field Flow Fractionation (ThFFF) was evaluated as a tool for determining molecular weight (MW) and its distribution of masticated natural rubber (NR), and thus for monitoring of NR mastication process. It was found that, in an anaerobic process, NR breakdown occurs not only at the initial breakdown zone but also at the resin mixing zone. In an aerobic process, however, most of NR degradation occurs in the initial breakdown zone and the amount of breakdown occurred in the resin mixing zone is relatively small. It was also found that it is not possible to build the molecular weight of NR using E-beam radiation and reform a linear polymer.

ThFFF provides advantages over existing inherent viscosity (IV) measurement method for the analysis of rubber adhesives. The IV measurement provides no information on the MWD profile, and it does not give meaningful results for actual adhesives because of large fraction of resin (low molecular weight additive) added into the mastication process. ThFFF separates NR molecules according to the molecular weight, and provides elution profile that is directly related with the molecular weight distribution of NR sample. ThFFF also allows samples to be analyzed without pre-filtration.

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References

1. Lee, S. *J. Microcol. Sep.* **1997**, *9*(4), 281.
2. Thompson, G. H.; Myers, M. N.; Giddings, J. C. *Sep. Sci.* **1967**, *2*(6), 797.
3. Thompson, G. H.; Myers, M. N.; Giddings, J. C. *Anal. Chem.* **1969**, *41*, 1219.
4. Janca, J.; Kleparnik, K. *Sep. Sci. Technol.* **1981**, *16*(6), 657.
5. Brimhall, S. L.; Myers, M. N.; Caldwell, K. D.; Giddings, J. C. *Sep. Sci. Technol.* **1981**, *16*(6), 671.
6. Gao, Y. S.; Caldwell, K. D.; Myers, M. N.; Giddings, J. C. *Macromol.* **1985**, *18*, 1272.
7. Kirkland, J. J.; Yau, W. W. *Macromol.* **1985**, *18*, 2305.
8. Brimhall, S. L.; Myers, M. N.; Caldwell, K. D.; Giddings, J. C. *J. Polym. Sci.: Polym. Phys. Ed.* **1981**, *16*(6), 671.
9. Gunderson, J. J.; Giddings, J. C. *Macromol.* **1986**, *19*, 2618.
10. Gunderson, J. J.; Giddings, J. C. *Anal. Chim. Acta* **1986**, *189*, 1.
11. Kirkland, J. J.; Rementer, S. W.; Yau, W. W. *Anal. Chem.* **1988**, *60*, 610.
12. Lee, S. *Chromatography of Polymers*; Provder, T., Ed.; ACS Symp. Series No. 521, American Chemical Society: Washington, DC, 1993; pp 7-88.

13. Liu, G.; Giddings, J. C. *Anal. Chem.* **1991**, *63*, 299.
14. Jeon, S. J.; Schimpf, M. E.; Nyborg, A. *Anal. Chem.* **1997**, *67*, 3442.
15. Shiundu, P. M.; Remsen, E. E.; Giddings, J. C. *J. Appl. Polym. Sci.* **1996**, *60*, 1695.
16. Shiundu, P.; Giddings, J. C. *J. Chromatogr. A* **1995**, *715*, 117.
17. Ratanathanawongs, S. K.; Shiundu, P. M.; Giddings, J. C. *Coll. Surf. A* **1995**, *105*, 243.
18. Shiundu, P. M.; Liu, G.; Giddings, J. C. *Anal. Chem.* **1995**, *67*, 2705.
19. Giddings, J. C.; Caldwell, K. D.; Myers, M. N. *Macromol.* **1976**, *9*(1), 106.
20. Schimpf, M. E.; Giddings, J. C. *Macromol.* **1987**, *20*, 1516.
21. Schimpf, M. E.; Giddings, J. C. *J Polym. Sci.: Part B: Polym. Phys.* **1989**, *27*, 1317.
22. Rudin, A.; Johnston, H. K. *Polymer Letters* **1971**, *9*, 55.
23. Giddings, J. C.; Li, S.; Williams, P. S.; Schimpf, M. E. *Makromol. Chem., Rapid Commun*. **1988**, *9*, 817.
24. Lee, S. *Polym. Mater. Sci. Eng.* **1991**, *65*, 19.
25. Lee, S. *Chromatographic Characterization of Polymers: Hyphenated and Multidimensional Techniques*; Advances in Chemistry Ser. No. 247, Provder, T., Barth, H., Urban, M., Eds.; ACS: Washington, DC, 1995; pp 93.
26. Lee, S. *Tr. Polym. Sci.* **1993**, *1*(10), 303.
27. Li, X.; Giddings, J. C.; Kosman, J. J.; Rosenhamer, D. G.; Davidson, L. G. *3rd International Symposium on Field-Flow Fractionation*; October 5-7, Park City, Utah, 1992.
28. Lee, S.; Molnar, A. *Macromolecules* **1995**, *28*(18), 6354.
29. Fulton, W. S.; Groves, S. A. *J. Nat. Rub. Res.* **1997**, *12*(3), 154.
30. Weidner, S.; Kuhn, G.; Decker, R.; Roessner, D.; Friedrich, J. *J. Polym. Sci. A, Polym. Chem.* **1998**, *36*(10), 1639.
31. Shiundu, P. M.; Remsen, E. E.; Giddings, J. C. *J. Appl. Polym. Sci.* **1996**, *60*(10), 1695.
32. Antoniettei, M.; Briel, A.; Tank, C. *Acta Polym.* **1995**, *46*(3), 254.
33. Williams, P. S.; Giddings, J. C. *Anal. Chem.* **1987**, *59*, 2038.