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Characterization of functionalized styrene–butadiene rubber by flow field-flow fractionation/light scattering in organic solvent

Dae Young Bang [a], Da Young Shin [a], Seunghwa Lee [b], Myeong Hee Moon [a,*]

[a] *Department of Chemistry, Yonsei University, Seoul 120-749, South Korea*
[b] *R&D Center, Korea Kumho Petrochemical Co. Ltd., Daejeon 305-348, South Korea*

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Abstract

Flow field-flow fractionation (FlFFF) using an organic solvent as mobile phase has been effectively utilized for the separation and characterization of functionalized styrene–butadiene rubbers (SBR) that are polymerized and followed by coupling reaction in solution. Separation of broad molecular weight SBR was accomplished by an asymmetrical FlFFF channel in THF under field programming and the molecular weight distribution (MWD) of the SBR sample was determined by on-line measurement of light scattering. In this study, FlFFF has been utilized to characterize high-MW functionalized SBR from the low-MW non-functionalized molecules which were used for coupling reaction to produce high-MW functionalized SBRs, and to determine the coupling number of the functionalized SBRs depending on the type of the coupling reagents. The resulting MWD of the SBR samples prepared by the different coupling reagents ($SnCl_4$ and a polydimethylsiloxane compound) were compared.

Keywords: Flow field-flow fractionation; Organic-solvent flow FFF; Light scattering; Molecular weight distribution; Styrene–butadiene rubber; Functionalized SBR

1. Introduction

Flow field-flow fractionation (FlFFF), an universal separation method among the FFF family, is a versatile technique to characterize a wide-size range of macromolecules. FlFFF has been applied for the separation of proteins, water soluble polymers, emulsions, inorganic nano-materials, colloids, cells, bacteria, and etc [1–6]. Since separation in FlFFF takes place in unobstructed channel spaces such as a flat rectangular channel or a hollow fiber membrane, FlFFF has a superior advantage of handling macromolecules with minimized risk of interaction between samples and a separation device like packed chromatographic column [1,2,7–10]. The versatility and wide applicability of FlFFF largely come from its capability of flexible field control since the field strength can be varied by changing the rate of crossflow for a rectangular channel system or radial flow in case of hollow fiber. The choice of the carrier liquid can be varied from aqueous solutions to organic solvents depending on the sample nature.

However, most FlFFF studies have been done by utilizing typical FlFFF channel systems for samples dispersed in aqueous solutions. One of the main difficulties in employing organic solvents as a carrier liquid for FlFFF was the proper selection of a solvent-resistant membrane [11]. In literature, very few studies have been reported on the use of organic solvents in FlFFF to deal with organic soluble polymers. The first trials were made by Brimhall et al. [12] and Caldwell et al. [13] using cellulose nitrate membrane for the separation of polystyrene samples. Later, regenerated cellulose membrane under various solvents were examined by Kirkland and Dilks [14], Giddings and co-workers [15] and Wijnhoven et al. [11]. Polyimide/PET membrane was also evaluated for organic-solvent FlFFF by Miller and Giddings [16]. Recently, Kok and co-workers [17] reported the possible use of a polyacrylonitrile (PAN) hollow fiber (HF) as an HF FlFFF channel for organic solvents, and they demonstrated its utility for the fractionation of PS standards.

In this study, FlFFF in organic solvents is applied first for the separation and size characterization of synthetic and modified styrene–butadiene rubber (SBR) samples using a regenerated cellulose membrane. Compared to the earlier studies on the feasibility of FlFFF in organic solvents by using mostly PS standards, this study demonstrates the capability of FlFFF to

* Corresponding author. Tel.: +82 2 2123 5634; fax: +82 2 364 7050.
E-mail address: mhmoon@yonsei.ac.kr (M.H. Moon).

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separate SBR samples in THF. MW determination was made using an on-line light scattering detector (dual angles) coupled to the asymmetrical FlFFF (AFlFFF) channel. Characterization of synthetic or natural rubbers has been up to now mostly done by using thermal FFF (ThFFF) [18–23] with multiangle light scattering [19,20]. Since FFF methods do not require sample filtration which may sometimes exclude gel-like particles in natural rubber sample, ThFFF demonstrated its capability to analyze the gel contents of natural rubber [22]. In addition, FFF provides a capability of separating a wide MW range of polymers without utilizing several columns connected in series and without a risk of sample interaction with the packing materials in size exclusion chromatography (SEC). FlFFF is well suited for the separation of sample materials larger than 10,000 Da. In order to separate SBR samples with a broad MWD, the field programming technique was successfully applied to reduce the retention time of high MW components. The SBR samples examined in this study were commercial products which were prepared by an anionic solution polymerization method and were functionalized with metal halides or polydimethysiloxane compound to prepare large MW elastomers that are being used in tires. It is shown that AFlFFF coupled on-line with light scattering (LS), AFlFFF/LS, can be powerfully utilized for the monitoring the difference of MWDs and the coupling number according to the preparations.

2. Experimental

2.1. Reagents

Polystyrene standards were 96.4, 117, 427, and 1090 kDa obtained from Tosoh Corp. (Tokyo, Japan). The three functionalized SBR samples were obtained from the R&D Center of Korea Kumho Petrochemical Co. Ltd. (Daejeon, Korea), and they were synthesized by solution polymerization process. Each sample was prepared at different styrene contents and with different coupling reagents. The styrene content, the Mooney viscosity values, and d*n*/d*c* values of the three samples provided by the manufacturer are listed in Table 1. Each sample was dissolved in THF at a concentration of 20 μg/μL. For FlFFF separation, THF was used as a carrier liquid. For the optimization of flow rate conditions, 1 μL (20 μg) of linear polystyrene standard was injected. In the case of SBR samples, 10 μL (200 μg) of each sample solution was injected.

2.2. FlFFF/LS

The FlFFF channel was the model AF1000 Focus Asymmetric Flow FFF system equipped with a channel cartridge for organic solvents from Postnova Analytics (Lansberg, Germany). The channel space had a tip-to-tip length of 28.0 cm, a thickness of 250 μm, and an initial breadth of 2.0 cm with a final breadth of 1.0 cm in a trapezoidal shape. Both ends of the channel space were cut in a triangular shape. At the accumulation wall of the AFFFF channel, regenerated cellulose having a MW cutoff of 10 kDa from Postnova was placed.

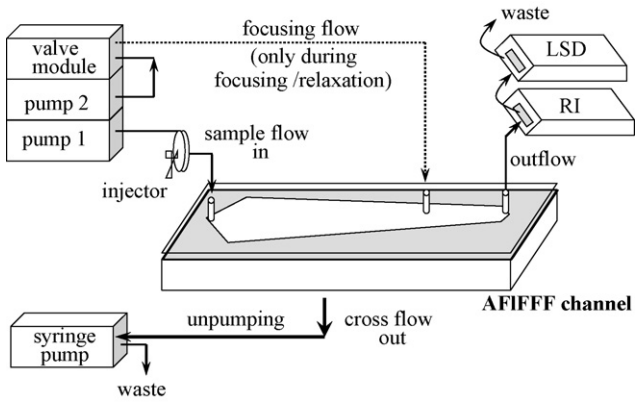

Fig. 1. Schematic diagram of the AFlFFF/RI/LS channel system.

Sample injection was made with a Model 7725i loop injector from Rheodyne (Cotati, CA, USA). Sample solution was delivered to the inlet of the AF1000 channel at 0.4 mL/min by a Model PN 1122 HPLC pump (called as the tip pump) from Postnova, while the focusing flow was introduced into the channel at 2.9 mL/min through the focusing flow inlet that was placed 10.0 cm upstream the channel outlet. The configuration of the AFlFFF channel and the flow connections are depicted in Fig. 1. During the focusing/relaxation procedure, most of the incoming flow exited through the accumulation wall as crossflow (2.5 mL/min) and part of the flow (0.8 mL/min) exited through the channel outlet toward the LS detector. This was to make the detector continuously flushed. The flow rate leading to the detector during the focusing process was set at the same value of outflow rate used for AFlFFF separation of SBR samples. For the efficient control of crossflow rate, a Model PN1610 syringe pump from Postnova was located at the crossflow outlet at the unpumping mode. The unpumping of the crossflow was helpful to accurately control the crossflow rate and outflow rate. After 3.5 min of focusing/relaxation, the focusing flow pump was stopped, and the tip pump flow rate was raised to a flow rate which was the sum of the crossflow and outflow rates. Control of all pumps and valves were made automatically by the software NovaFFF AF1000 Control from Postnova. For field programming (or crossflow programming), crossflow rate was decreased during the run according to a multiple-stage linear

Table 1
Styrene/vinyl ratio and Mooney viscosity value of each functionalized SBR sample used in this study

Sample i.d.	Coupling agent	Styrene content (%)	Vinyl content of butadiene (%)	Mooney viscosity	d*n*/d*c*
SOL5150	$SnCl_4$	10	45	75	0.131
SOL5280	$SnCl_4$	20	70	80	0.135
SOL5270S	PSi-86[a]	21	70	45	0.137

[a] US Patented 6,566,480: α,ω-bis[2-(trichlorosilyl)ethyl]polydimethylsiloxane.

decay program. Eluted components were sequentially monitored by a Static PN3000 dual angle light scattering detector (15° and 90°) from Postnova, at a wavelength of 680 nm, and by an RI750F refractive index detector from Young-Lin Co. (Seoul, Korea). For the normalization of the LS detector signals, a PS standard of 96.4 kDa was used. Data collection, and calculation of MWD from light scattering signals were processed by the software Discovery 32, from Postnova.

2.3. Size exclusion chromatography (SEC)

SBR samples were analyzed by SEC. A series of four SEC columns of different pore sizes (5–13 μm) and a guard column were utilized: Models of G6000HXL, G5000HXL, G4000HHR, G3000HHR, and Guard H from Tosoh Corp. (Tokyo, Japan). SBR samples were analyzed at 1.0 mL/min under THF at a column temperature of 40 °C. Injection volume of each sample was 200 μL with a sample concentration of 2.5 mg/mL. An HPLC system (VP series) from Shimadzu (Kyoto, Japan) was utilized. Detection was made with the Triple Detector Array™ with low angle light scattering detector (7°), the model TDA302 from Viscotek (Houston, TX, USA). Calibration of the detector was made with the 117 K PS standard.

3. Results and discussion

Performance of the FlFFF system for organic solvents was tested in THF with the separation of polystyrene standard mixtures having MW values of 96, 427, and 1090 kDa. Fig. 2 shows an FlFFF fractogram of programmed-field separation of PS mixture, represented with both the RI and the 90° scattered signals. The separation was achieved with an injection of 20 μg of the mixture (6.7 μg of each PS standard), and flow rate conditions were 0.4 mL/min for the sample loading flow rate, 0.8 mL/min for the outflow rate, 2.5 mL/min for the initial crossflow rate which decayed linearly at two stages: crossflow rate began decaying after 0.5 min, then decreased to 2.0 mL/min during 10 min, and further decreased to 0.5 mL/min during 5 min, and then maintained at 0.5 mL/min until the end of separation. While the PS sample mixtures were introduced at 0.4 mL/min through the channel inlet, the focusing flow for focusing/relaxation of the injected samples was simultaneously delivered to the channel through the focusing inlet (see Fig. 1) at 2.9 mL/min. This is a necessary step to provide sample equilibrium in AFlFFF. Focusing/relaxation was kept for 3.5 min and, after then, the focusing flow was stopped, and the channel inlet flow rate was raised to 3.3 mL/min. During the focusing/relaxation, part of focusing flow which was introduced to the channel through the focusing inlet exited to the detector at the flow rate value which was required for separation (0.8 mL/min) so that a continuous flow passage was maintained at the detector. This keeps the detector baseline from the abrupt change that normally occurs during flow conversion at the end of the focusing/relaxation step. Fig. 2 shows a complete separation of PS standards from 96 to 1090 kDa under the above field programming condition which was further optimized for the separation of modified SBR molecules. The LS signal intensity recorded at 90° is significantly different from that of the RI signal intensity since light scattering depends on both molecular weight and concentration whereas the refractive index detection relies only on the concentration of the sample. The delay time (0.80 min) between the two detectors was corrected for the LS signals.

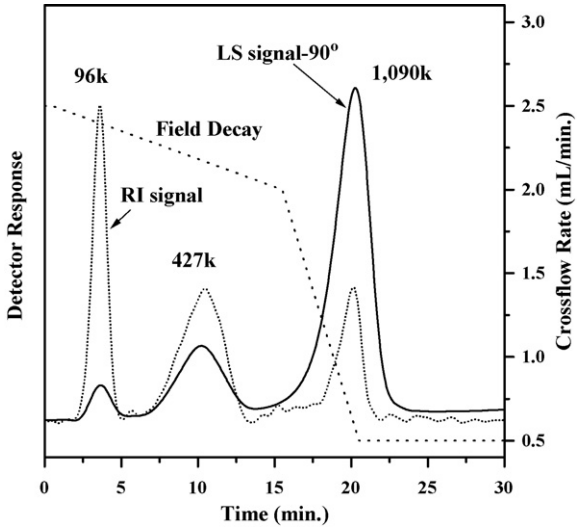

Fig. 2. Field-programmed separation of PS standard mixtures (96, 427, and 1090 kDa) by AFlFFF system in THF with RI and LS-90° detection The flow rate conditions were 0.8 mL/min for outflow rate and 2.5 mL/min for initial crossflow rate. Details of field programming (crossflow rate programming) is explained in the text.

The run condition used in Fig. 2 was applied for the examination of the functionalized SBR samples which were prepared by coupling reaction of the anionic SBR molecule with metal halide or polydimethylsiloxane compounds in order to produce large molecular weight SBRs. The functionalized rubber molecules are known to provide a better dispersion with fillers (such as carbon black or silica), and the resulting elastomers exhibit improved mechanical properties [24,25]. AFlFFF in this study has been employed to determine the sample MWD, and to study the coupling pattern of functionalized SBR materials depending on the coupling agents. Fig. 3 shows the FlFFF fractograms of the functionalized SBR sample SOL5150 (200 μg of each injection) which was coupled with $SnCl_4$, plotted with LS signals at 90°. Sample recovery was calculated to be 84.34 ± 1.25% ($n = 3$) by comparing peak area values of each DRI peak with the measured peak area value obtained without applying crossflow rate to make sample unretained. The FlFFF fractogram of the SOL5150 sample in Fig. 3 shows a bimodal distribution pattern in which the first small peak represents for the elution of the free SBR molecules (non-functionalized) and the second eluting tall peak represents the functionalized SBR molecules by tin chloride used for the sample preparation. The light scattering signal recorded at both 15 and 90° along with the RI signal were processed to calculate the MW value at each experimental retention time, and the resulting MW values were plotted as open circles in Fig. 3. The results showed that the functionalized SBR molecules were up to $\sim 4 \times 10^6$ Da. The weight-average MW value (M_w) of each peak of the SOL5150 sample was calculated as $4.73(\pm 0.12) \times 10^5$ for the free SBR molecules and

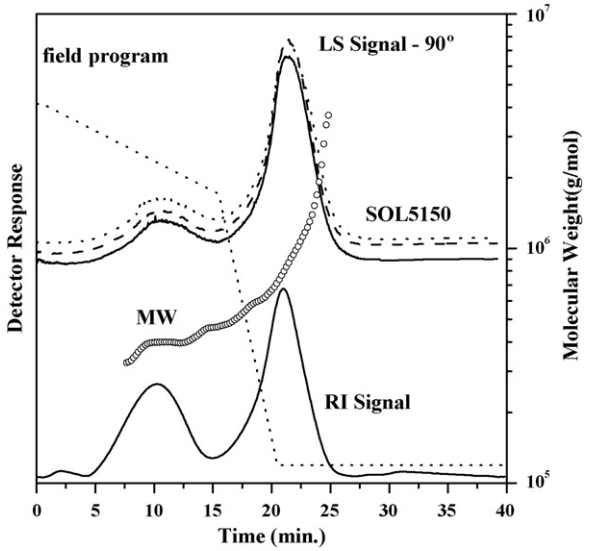

Fig. 3. AFlFFF fractograms (represented with LS-90° and RI signals) of a functionalized SBR sample (SOL5150) which was coupled with $SnCl_4$ along with calculated MW values at each retention time slice. Flow rate conditions and the same carrier solvent (THF) were the same as used in Fig. 2.

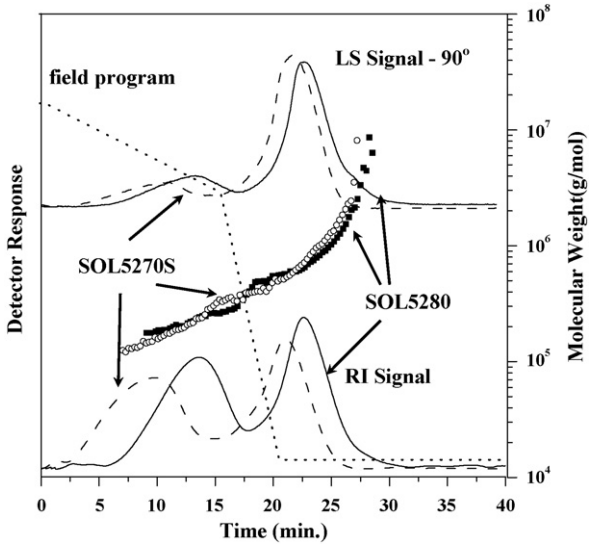

Fig. 4. Superimposed fractograms of the two functionalized SBR samples (SOL5280: coupled with $SnCl_4$ and SOL5270S: with polydimethylsiloxane compound) obtained by AFlFFF. Run condition was the same as used in Fig. 3.

$1.19(\pm0.03) \times 10^6$ for the functionalized ones, listed in Table 2. The calculation of each M_w value was made by the valley point of the bimodal peak. The calculated average MW values show that each tin metal ion binds with approximately 2.5 SBR molecules in average, which is known to be the coupling number.

The other functionalized SBR samples, SOL5280 and SOL5270S, were run at the same flow rate condition utilized in Fig. 3, and the FlFFF fractograms are superimposed in Fig. 4. The two functionalized SBR samples were originally prepared by using different coupling agents: $SnCl_4$ for the SOL5280 sample and α,ω-bis[2-(trichlorosilyl)ethyl]polydimethylsiloxane (PSi-86: US patent 6,566,480) for the SOL5270S sample. The FlFFF fractogram (solid line) and the corresponding MW values (filled squares) represent the data for the SOL5280 sample prepared by the similar method used for Fig. 3. The superimposed fractogram shown with broken lines in Fig. 4 represents data for the SOL5270S sample along with MW values by open circles. Apparently the elution pattern of each sample seems to be similar. However, the peak of the remaining SBR molecules (the first peak of the broken line) of the polydimethylsiloxane-functionalized SBR sample appears to shift toward retention time scales that are shorter (smaller molecular weight) than that of the $SnCl_4$-functionalized sample (SOL5280). Moreover, the second eluting peak of the functionalized molecules does not show tailing. Nonetheless, the tail at the end of elution of the SOL5280 implies that there are a considerable amount of large MW functionalized molecules, being that crossflow rate at this retention time region is already reduced to the lowest flow rate (0.5 mL/min). The MW values plotted in Fig. 4 for the two samples appear to overlap well each other through the entire retention times. This observation shows that separation of SBR molecules by FlFFF was well achieved by an increasing order of MW as retention time increased. To compare the MW distribution pattern of the functionalized SBR samples, the differential MWD curves in logarithmic scale are superimposed in Fig. 5. The broken line (SOL5150) curve and the dotted line curve (SOL5280) showed two different distributions although they were prepared with the same coupling agent, $SnCl_4$. These two samples were polymerized at different conditions prior to the coupling reaction. The styrene and vinyl content of the SOL5280 sample was known to be

Table 2
Calculated values of weight average and number average molecular weight of SBR samples

Sample i.d.		Free SBR's		Functionalized SBR's	
		$\overline{M_w}$	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_n}$
SOL5150	FFF	$4.73(\pm0.12) \times 10^5$	$4.55(\pm0.11) \times 10^5$	$1.19(\pm0.03) \times 10^6$	$9.95(\pm0.08) \times 10^5$
	SEC	$1.56(\pm0.02) \times 10^5$	$1.54(\pm0.04) \times 10^5$	$6.55(\pm0.07) \times 10^5$	$5.26(\pm0.04) \times 10^5$
SOL5280	FFF	$5.21(\pm0.15) \times 10^5$	$4.89(\pm0.21) \times 10^5$	$1.55(\pm0.05) \times 10^6$	$1.25(\pm0.17) \times 10^6$
	SEC	$1.89(\pm0.01) \times 10^5$	$1.85(\pm0.01) \times 10^5$	$8.39(\pm0.08) \times 10^5$	$6.89(\pm0.02) \times 10^5$
SOL5270S	FFF	$2.64(\pm0.01) \times 10^5$	$2.18(\pm0.14) \times 10^5$	$1.08(\pm0.06) \times 10^6$	$9.77(\pm0.05) \times 10^5$
	SEC	1.57×10^5	1.44×10^5	8.85×10^5	7.01×10^5

MW values of free (the first peak) and functionalized SBR molecules (the second peak) in each sample were calculated separately. Each value is the average of the three replicate measurements (except the SEC results of SOL5270S). SEC results are provided by the manufacturer.

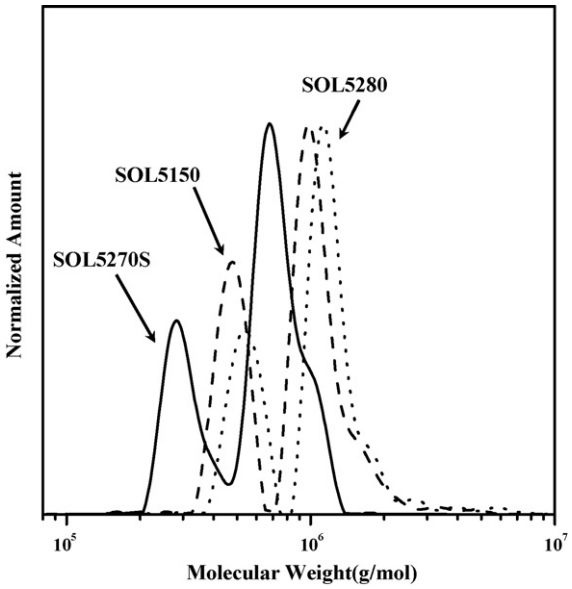

Fig. 5. Superimposed molecular weight distribution curves (area normalized) for the three functionalized SBR samples from the fractograms shown in Figs. 3 and 4.

20 and 70% as listed in Table 1, respectively. These contents are larger than those for the SOL5150 sample (10 and 45%, respectively). The MWD curve of the SBR sample with higher styrene-vinyl content appears to be shifted toward the larger MW scale than the sample with lower styrene content. However, when α,ω-bis[2-(trichlorosilyl)ethyl]polydimethylsiloxane was used as the coupling agent, the MW distribution curve of SOL5270S shifted toward the smaller MW scale than that of the SOL5280 sample, even though the styrene/vinyl contents of the two samples were similar as listed in Table 1. Moreover, the coupling number for the polydimethylsiloxane-modified SBR sample was calculated as 4.1 by simply dividing the average MW ($1.08(\pm0.06) \times 10^6$ Da) which corresponds to the peak of functionalized molecules by $2.64(\pm0.01) \times 10^5$ Da listed in Table 2, which is the average MW value of the non-functionalized ones while the coupling number for the SOL5280 was 3.0. It was reported that the use of the polydimethylsiloxane compound as a coupling agent for SBR showed a better dispersion of inorganic fillers than $SiCl_4$ or $SnCl_4$-functionalized SBR products, due to the hydrogen bonding between polydimethylsiloxane chain in functionalized SBR and inorganic filler particles such as silica [26,27]. Moreover, it is known that vulcanized polydimethylsiloxane-modified SBR showed improved mechanical and dynamic properties as elastomers. In Table 2, the weight average MW (M_w) and number average MW (Mn) values of the three SBR samples obtained by FlFFF are compared with those by SEC results. Since the SEC analysis was carried out with the four serial connection of columns followed by the detection of low angle laser light scattering with viscometric measurement, the average MW values of SEC results may vary from those by FlFFF with dual angle light scattering detection. While the average MW values of functionalized SBR molecules from SEC results were different from those obtained by FlFFF, the difference between the two methods showed a trend that SEC provided relatively smaller values than those of FlFFF.

4. Conclusion

This study demonstrated the applicability of FlFFF in organic solvent and on-line light scattering detection for the characterization of functionalized SBR samples. FlFFF separation of the functionalized SBR sample obtained by coupling reaction with metal halide or a polydimethylsiloxane compound showed clear differences among their molecular weight distribution curves. It also showed that the coupling number can be readily calculated since free and functionalized molecules were clearly separated by FlFFF. One of the advantages using FlFFF can minimize an unexpected loss of information which is often induced by a pre-filtration process of the sample solution prior to analysis. This gives more potential to FlFFF for characterizing the gel content of polymeric materials, especially in the case of natural rubbers. However, it must be underlined there is a consideration that a fully compatible membrane is required for applying FlFFF with any organic solvent to the analysis of various polymeric materials.

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References

[1] J.C. Giddings, Anal. Chem. 53 (1981) 1170A.
[2] J.C. Giddings, Science 260 (1993) 1456.
[3] B. Hecker, P.D. Fawell, A. Jefferson, J.B. Farrow, J. Chromatogr. A 837 (1999) 139.
[4] M. Andersson, B. Wittgren, H. Schagerlof, D. Momcilovic, K.-G. Wahlund, Biomacromolecules 5 (2003) 97.
[5] H. Thielking, W.-M. Kulicke, J. Microcol. Sep. 10 (1998) 51.
[6] P. Reschiglian, A. Zattoni, B. Roda, S. Casolari, M.H. Moon, J. Lee, J. Jung, K. Rodmalm, G. Cenacchi, Anal. Chem. 74 (2002) 4895.
[7] I. Park, K.-J. Paeng, Y. Yoon, J.-H. Song, M.H. Moon, J. Chromatogr. B 780 (2002) 415.
[8] D. Kang, M.H. Moon, Anal. Chem. 76 (2004) 3851.
[9] D. Kang, M.H. Moon, Anal. Chem. 77 (2005) 4207.
[10] H. Lee, H. Kim, M.H. Moon, J. Chromatogr. A 1089 (2005) 203.
[11] J.E.G.J. Wijnhoven, M.R. van Bommel, H. Poppe, W.Th. Kok, Chromatographia 42 (1996) 409.
[12] S.L. Brimhall, M.N. Myers, K.D. Caldwell, J.C. Giddings, Polym. Mater. Sci. Eng. 50 (1984) 48.
[13] L.D. Caldwell, S.L. Brimhall, Y. Gao, J.C. Giddins, J. Appl. Polym. Sci. 36 (1988) 703.
[14] J.J. Kirkland, C.H. Dilks Jr., Anal. Chem. 64 (1992) 2836.
[15] M.E. Miller, H. Lee, X. Li, R. Szentirmay, J.C. Giddings, Polym. Prepr. 35 (1994) 764.
[16] M.E. Miller, J.C. Giddings, J. Microcolumn Sep. 10 (1998) 75.

[17] M. van Bruijnsvoort, W.Th. Kok, R. Tijssen, Anal. Chem. 73 (2001) 4736.
[18] L. Lewandowski, M.S. Sibbald, E. Johnson, M.P. Mallamaci, Rubber Chem. Technol. 73 (2000) 731.
[19] M. Sibbald, L. Lewandowski, M.P. Mallamaci, E. Johnson, Macromol. Symp. 155 (2000) 213.
[20] W.S. Fulton, S.A. Groves, Nat. Rubber Res. 12 (1997) 154.
[21] S. Lee, C.H. Eum, A.R. Plepys, Bull. Korean Chem. Soc. 21 (2000) 69.
[22] S. Lee, A. Molnar, Macromolecules 28 (1995) 6354.
[23] P.M. Shiundu, E.E. Remsen, J.C. Giddings, J. Appl. Polym. Sci. 60 (1996) 1695.
[24] C.C. Chang, A.F. Halasa, J.W. Miller Jr., W.L. Hsu, Polym. Int. 33 (1994) 151.
[25] H.L. Hsieh, R.P. Quirk, Anionic Polymerization; Principles an Practical Applications, Marcel Dekker, New York, 1996.
[26] M. Hayashi, S. Mabe, K. Inagaki, Y. Nakatsuji, A. Imai, Polym. Reprints 43 (2002) 1083.
[27] V.A. Escobar, M. Barrios, M. Garcia-Ramirez, Int. J. Polymer. Mater. 52 (2003) 985.