Determination of the Molecular Architecture of Synthetic and Natural Rubber by the Use of Thermal Field-flow Fractionation and Multi-angle Laser Light Scattering[†]

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The processability of elastomers is largely governed by molecular architecture and hence the influence of molecular weight distribution, branching and gel content is of great interest. Analysis by conventional size exclusion chromatography (SEC) has limitations which may distort the molecular weight distribution. However, the combination of Thermal Field Flow Fractionation (ThFFF) and Multi-angle Laser Light Scattering (MALLS) has allowed absolute molar mass and size distribution to be obtained without the need for calibration, standards or assumptions. ThFFF is a separation technique that enables the physical structure and composition of complex macromolecules to be determined and relies on diffusive transport as the principal mechanism of separation. An open channel geometry minimises shear effects, making it possible to separate fragile, high molecular weight polymers, whilst the absence of a stationary phase means that adsorption effects can be ignored. Consequently, complex mixtures of polymer, micro-gel and macro-gel can be studied in a single run without the need for filtration. By combining all the information derived from ThFFF/ MALLS a more comprehensive molecular weight distribution, including levels of branching, can be determined. Light scattering profiles and absolute molecular weight distributions were determined by ThFFF/MALLS for a number of synthetic and natural rubbers and comparisons have been made with results obtained from conventional SEC. For example, the molecular weight distribution of natural rubber has been shown to extend up to 10^9 g/mol with approximately 20% of the rubber having a molecular weight greater than 10^7 g/mol. MALLS can also provide information on the size distribution of species and this is discussed further in relation to both synthetic and natural rubber.

It is well known that the rheological properties of rubber, like any polymer melt, are greatly affected by variations in molecular weight distribution and branching. Production techniques, for both synthetic and natural rubber, will influence molecular architecture; more so for synthetic rubber where deliberate modification creates material specific properties. Therefore, it is of great practical importance to understand how the fundamental

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structure of rubber molecules, including branching, effects processability and final product performance.

Certain elastomers have molecular weight distributions with tails that extend beyond 10^7 g/mol, *i.e.* above the exclusion limit of the majority of size exclusion chromatography (SEC) columns. Rubber in solution may also contain a significant gel component and this is routinely separated prior to injection onto a SEC column, making analysis of the true molecular weight distribution virtually impossible. Also many high molecular weight polymers are fragile and easily susceptible to shear degradation that may occur in SEC columns. Such degradation will cause a downward shift of molecular weight distribution from that of the original material, again making subsequent analysis unreliable.

Field-flow fractionation (FFF) is a series of separation techniques that has been applied to many macromolecular and colloidal systems. As with conventional SEC, FFF is a flow-elution method in which differential retention is achieved by application of an external field or gradient perpendicular to a narrow, ribbon-like flow channel. This technique was first developed by Prof. J. Calvin Giddings[1] and uses an open channel for separation, making it possible to separate macro-molecules and particles ranging in size from 5 nm (or 10^3 g/mol) to 100 μm.

Thermal Field-flow Fractionation (ThFFF)

ThFFF is a variety of FFF in which a temperature gradient is used as the field. The theory of ThFFF has been developed and refined by several workers[2-4] and is briefly reviewed here.

In ThFFF, separation is achieved by applying a temperature gradient (10^4 °C.cm^{-1}) across a thin (127 μm) ribbon-like channel through which a polymer solution flows *(Figure 1)*. The temperature gradient drives polymer molecules towards the cold or accumulation wall by the process of thermal diffusion. The concentration of molecules due to thermal diffusion is opposed by mass diffusion and at equilibrium a solute zone is formed whose concentration profile decreases exponentially from the cold wall. The fundamental mechanism of separation is provided by the velocity profile across the thin dimension of the channel; velocity is fastest in the centre and slowest at the two walls. Consequently, the distance between the cold wall and the solute zone governs the rate at which the zone travels through the channel. Polymers are separated because constituent molecules of different size attain equilibrium at different distances from the cold wall; smaller molecules sited further from the cold wall travel faster and are eluted first. Therefore the subsequent fractogram describes an elution sequence which proceeds from low to high molecular weight.

The general retention equation for isoviscous and parabolic flow that describes the elution order for each component from the channel is:

$$R = \frac{t^o}{t_r} = \frac{V^o}{V_r} = 6\lambda \left[\coth \frac{1}{2\lambda} - 2\lambda \right] \qquad \dots 1$$

where R is the retention ratio, t_r and V_r are the elution time and volume for a given component, V^o is the channel void volume and t^o is the time for non-retained samples to elute. The retention parameter λ is defined as:

$$\lambda = \frac{l}{w} \qquad \dots 2$$

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where 1 is the solute thickness and w is the channel thickness. The retention parameter for ThFFF is given by:

$$\lambda = \frac{D}{D_T \, \Delta T} \qquad \ldots 3$$

where D is the ordinary diffusion coefficient, D_T is the thermal diffusion coefficient and ΔT is the difference in temperature between the hot and cold walls. D_T is virtually independent of chain length and branching, whereas D has a molecular weight *(M)* dependence of the following form for random coil polymers:

$$D = \Phi M^{-n} \qquad \ldots 4$$

which because of the lack of dependence of D_T upon M can be written as:

$$\log\left(\frac{D}{D_T}\right) = \log\lambda\Delta T = \log\Phi - n\log M \qquad \ldots 5$$

where Φ and n are *empirical constants.* Such an equation serves as the basis for calibrating elution volume (or time) to molecular weight.

Multi-angle Laser Light Scattering (MALLS)

MALLS is an analytical technique derived from classical methods for determining absolute molecular weight and size. Unlike traditional detectors, the MALLS photometer has eighteen discrete photo-detectors spaced around a flow cell in a special geometry, ensuring that measurements may be made simultaneously over a broad range of angles, typically $15°$ – $160°$, depending on solvent/glass refractive indices *(Figure 2)*. The unique electro-optical configuration, combined with use of a flow

cell, enables this detector to be coupled to a variety of separation systems, such as a ThFF Fractionator.

The intensity of scatter can be directly related to the molecular weight of polymer, and the root mean square radius of gyration according to *Equations 6* and *7*[7]:

$$\frac{K^*c}{R(\theta)} = \frac{1}{[M_w P(\theta)]} + 2A_2 c \qquad \ldots 6$$

where $R(\theta)$ is the excess Rayleigh light scattering factor, M_w is the weight average molar mass, $P(\theta)$ is the scattering function, A_2 is the second virial coefficient and

$$K^* = \frac{4\pi^2 \, n_o^2 (dn/dc)^2}{\lambda_o^4 N_A} \qquad \ldots 7$$

where n_o is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_o is the wavelength of laser light and N_A is Avogadro's number. The scattering function $P(\theta)$ is related to the radius of gyration *(R_g)* by the following relation:

$$P(\theta) = \left[1 + \frac{16\pi^2}{3\lambda^2} \, \langle R_g^2 \rangle \, \sin^2\left(\frac{\theta}{2}\right)\right] \qquad \ldots 8$$

To determine molecular weight for a given elution slice, the scattering is plotted as a *function of angle and extrapolated back to zero* angle. The intercept value is then used to determine the absolute molecular weight of each monodisperse slice, while the slope of the line gives an independent measure of root mean square radius of gyration *(Figure 3)*. Data for each slice are combined to produce a series of distribution plots for the sample as a whole,

Polyisoprene
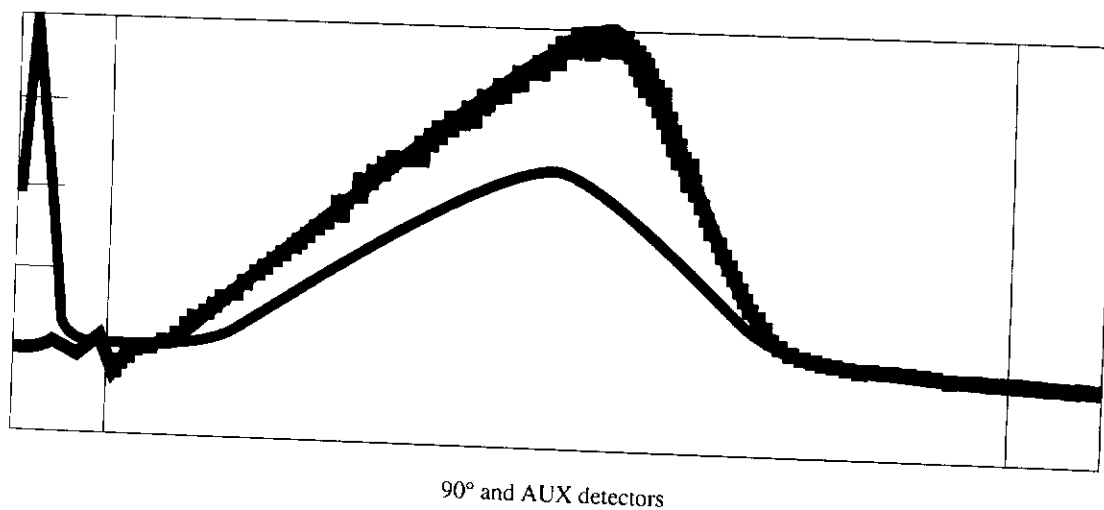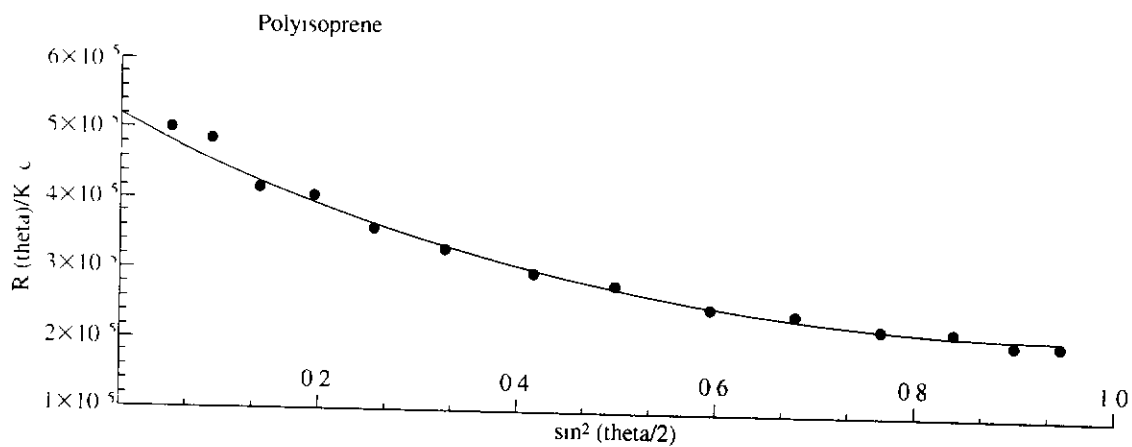
Peak, Slice   1,3080
Volume   8 778 mL
Fit degree   2
Conc   (2 087 ± 0 001) e-5 g/mL
Mw   (5 167 ± 0 091) e+5 g/mol
Radius   69 4 ± 2 2 nm

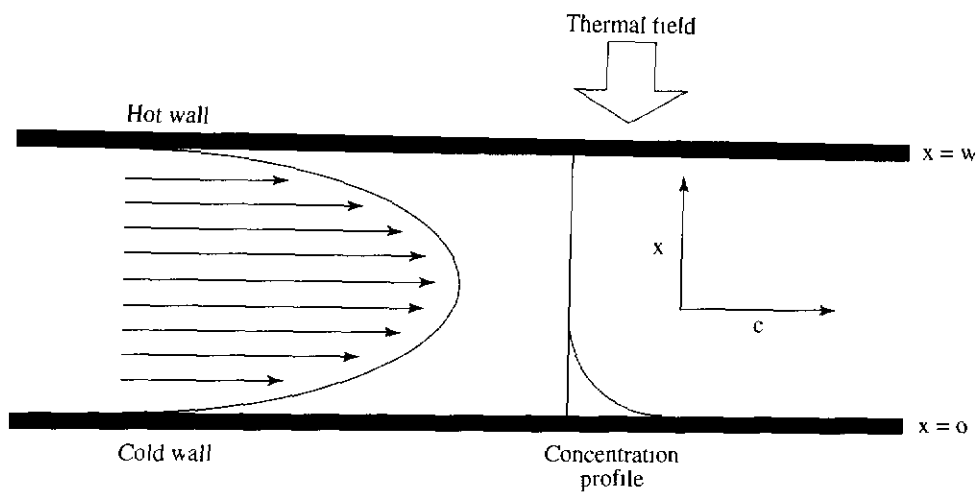*Figure 3 Typical Debye plot obtained from the MALLS software*

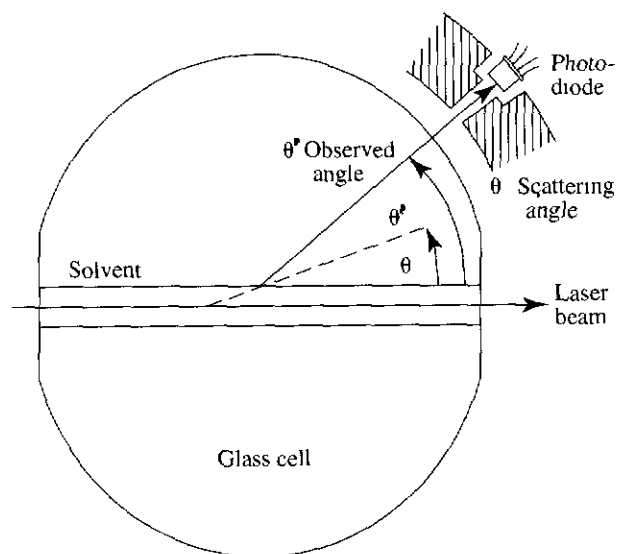Figure 1   Principles of ThFFF separation

Figure 2   Scattering geometry of MALLS flow cell

providing absolute size distributions and absolute molecular weight. By defining the relationship between size and molecular weight, essential parameters can be derived, including molecular conformation and the extent of long-chain branching.

EXPERIMENTAL

The rubbers used in this study were *Cariflex IR305* (Shell), *Natsyn 2200* (Goodyear), Natural rubber (SMR L) and BR (Europrene Neo-*cis* BR40, 98% *cis*-1,4 poly(butadiene), Enichem). Samples were dissolved in HPLC grade cyclohexane (Sigma-Aldrich Chemical Company), which was also used as carrier solvent in the ThFFF channel. Samples (1.0 – 2.0 mg/ml) were introduced into the channel *via* an injection valve fitted with a 20 µL loop.

The ThFFF system was a Polymer Fractionator Model T100 manufactured by FFFractionation Inc, (Salt Lake, Utah, USA). The channel comprised of two nickel plated copper bars with highly polished surfaces separated by a Teflon coated polyimide spacer, 46 cm long (tip-to-tip), 2 cm wide and 127 µm thick. The lower bar was cooled with circulating water and the upper bar heated by two 1.5 kW heater elements. The channel was pressurised to approximately 100 p.s.i. to elevate the boiling point of the carrier solvent. ΔT, the initial temperature gradient across the channel, was set between 50°C and 80°C, depending on the rubber, and programmed to decay over a given period of time. This so-called, 'power programming' enabled separation of low molecular weight species from the void peak at a high initial ΔT. Then the programme slowly released the thermal field allowing high molecular weight polymer to move towards the centre of the channel and

into faster moving fluid elements. Consequently, complete fractionation was achieved in a reasonable time (up to one hour). A Waters 515 HPLC pump was used for solvent delivery. The channel effluent was detected by a DuPont 2310 variable wavelength ultra-violet detector (at 215 nm) and a Wyatt DAWN DSP multi-angle laser light scattering detector at 633 nm. The measured flow rate of the mobile phase through the system was 0.171 ml/min.

The SEC analyses were performed on a set of Polymer Laboratories Mixed-B columns using THF at a flow rate of 0.75 ml/min and a temperature of 40°C; nominal concentration was about 5 mg/ml in all cases. The detector utilised UV light at 215 nm. The instrument was calibrated with polystyrene standards.

RESULTS/DISCUSSION

Figure 4 shows the size exclusion chromatograms obtained from filtered solutions of *Cariflex IR305* and *Natsyn 2200*. The molecular weight distributions are essentially similar with a peak molecular weight of 500 000.

For classical FFF, molecular size increases across the distribution and *Figure 5* shows a typical plot of radius of gyration *versus* elution volume. The concentration profile is overlaid to show how molecular size varies from 30 nm to 130 nm across the distribution. The fractogram illustrates the expected separation mechanism by which the smallest molecules are eluted first, the converse of SEC. *Figure 6* shows the differential molecular weight and size distribution derived from the previous fractogram *(Figure 5)*. The slope of the double logarithmic plot of radius of gyration *versus*
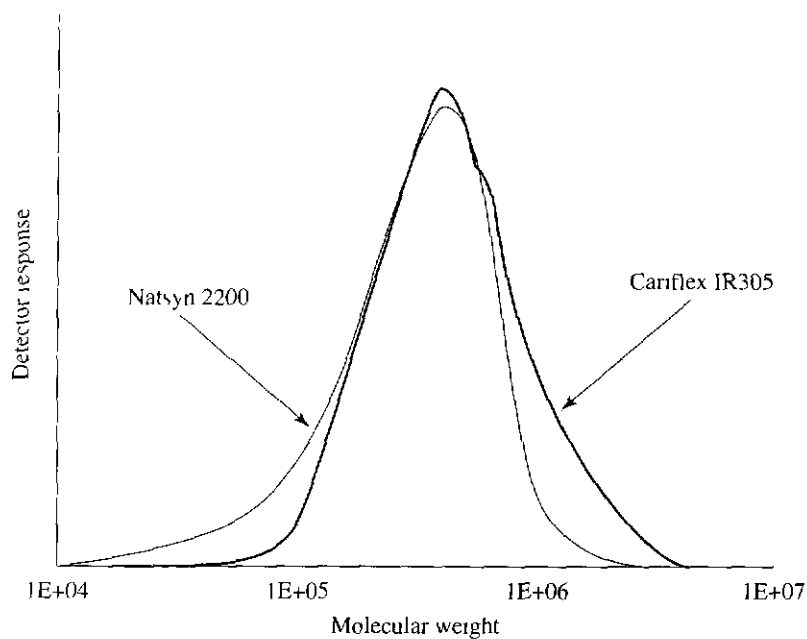
Figure 4. Molecular weight distribution of Natsyn 2200 *and* Cariflex IR305 *obtained by SEC*
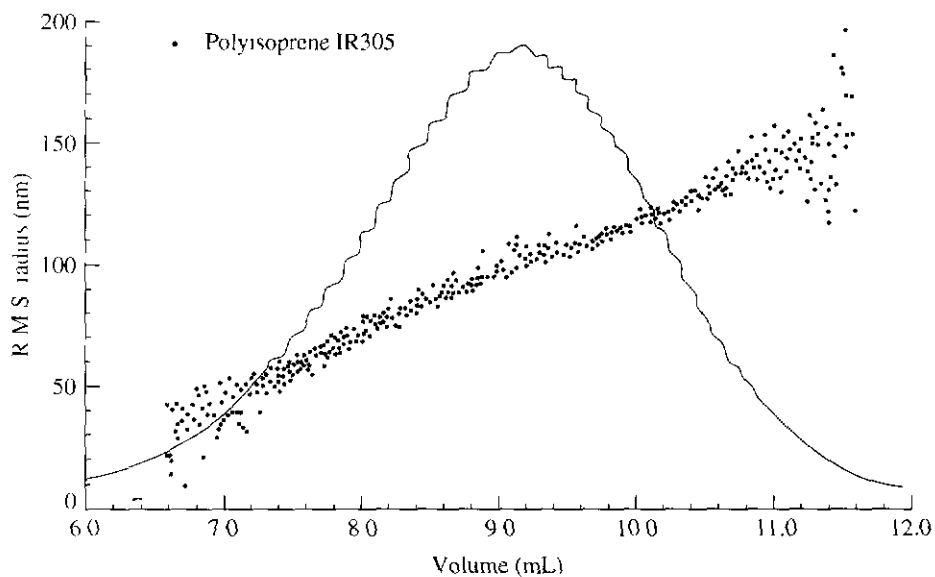

Figure 5 Fractogram showing the size based separation of IR305
The UV concentration profile is also shown.

molecular weight indicates the type of molecular conformation that polymer chains adopt in solution[8][9]. Random, linear polymer coils, in good solvents, have slopes in the range 0 5 – 0 6 Branched molecules may have slopes smaller than a value typical of a random coil, making the change of slope a measure of the extent of long-chain branching. The slope calculated from data shown *(Figure 6)* was approximately 0 5 This would indicate that IR305 was comprised essentially of linear molecules throughout the molecular weight distribution Analysis of the polyisoprene, *Natsyn 2200*, yielded results *(Figure 7)* in which the molecular weight distribution was much broader than IR305, extending to a value of 10^7 g/mol and where the slope of radius of gyration *versus* molecular weight changed from approximately 0 5 to 0.3 at about 5×10^5 g/mol It seems reasonable to assign the limiting line with a slope of 0 3 to branched species and the one with a slope of 0 5 to linear polymer chains. Interpretation of such results would suggest that polymer below a molecular weight of 5×10^5 g/mol is linear and that above is branched, with the extent of branching increasing with increasing molecular weight. *Natsyn 2200* contained an appreciable gel content (25% w/v in THF) which, because of filtration prior to injection, would not be analysed *via* conventional SEC Conversely, all the elastomer was injected onto the ThFFF channel and so a more comprehensive analysis of the molecular weight distribution and conformation emerged by the combination of ThFFF/MALLS Such an analysis also throws light on how molecular conformation is dependant on the stereo-specific catalyst systems used for the synthesis of these two polyisoprenes[10], *i e* Zeiger-Natta type catalysis for *Natsyn 2200* and lithium-anionic catalysis for IR305

Figure 8 shows the dependence of radius of gyration on elution volume for *cis*-BR40 and the size-volume relation does not exactly follow the trend expected This relationship can be explained with the occurrence of large gel species (500 nm – 600 nm) which eluted in the first 0 5 mL, after which normal separation took place Increasing the physical size of the rubber molecule brings another mechanism of fractionation (Steric FFF) into play at a point defined as steric inversion At this point of separation forces are larger and diffusion, which is strongly suppressed, no longer plays a major role in retention Large particles are driven to the accumulation wall by the thermal field and are stopped by the physical barrier of the wall Thus equilibrium elevation of the particle depends upon its size Larger particles project further into the flow than their smaller counterparts and so they are literally 'bowled along' more rapidly. Consequently, large particles elute before small particles, opposite to that expected *via* classical fractionation It is also likely that large particles co-eluted with low molecular weight species at the beginning of ThFFF separation. If so, the measured radius of gyration was an average value obtained for a particular elution slice and would mean that the actual size of gel particles was much larger, possibly greater than 1 μm

Characterisation of natural rubber (SMR L) also revealed how steric inversion affects the molecular weight profile at the initial portion of the distribution *(Figure 9)*, where a mixture of species were co-eluted. The high molecular weight material eluting at the end of the separation has a molecular weight more than an order of magnitude greater than would be calculated from conventional SEC Combination of these two effects will increase the measured molecular weight of natural
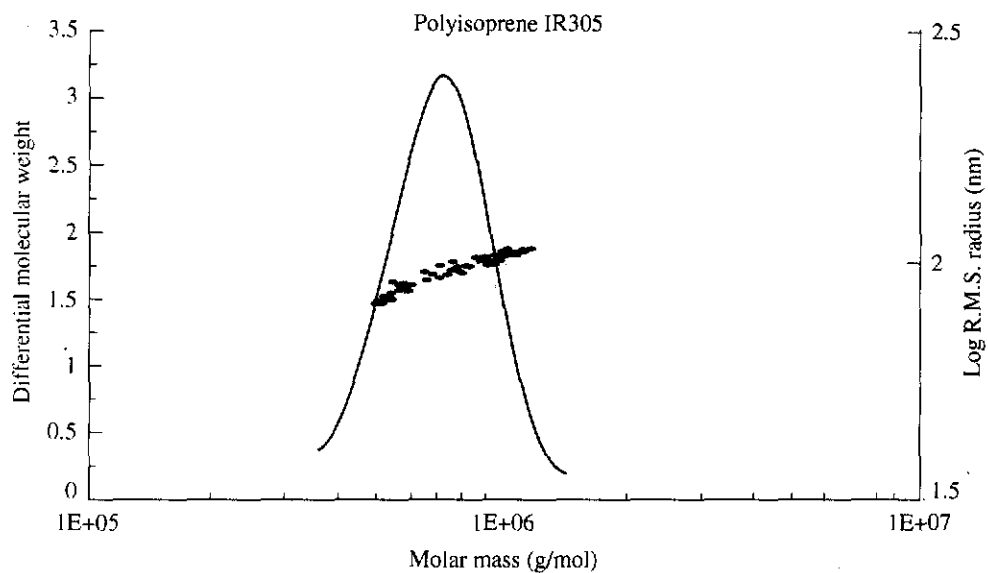
Figure 6. Differential molecular weight and radius of gyration as a function of molar mass for Cariflex IR305.
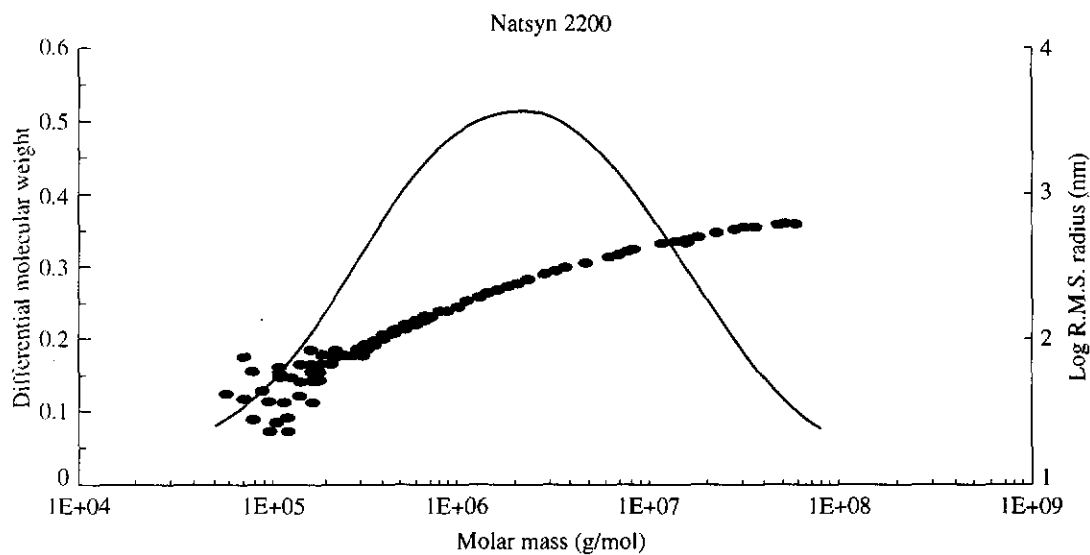

Figure 7. Differential molecular weight and radius of gyration as a function of molar mass for Natsyn 2200.
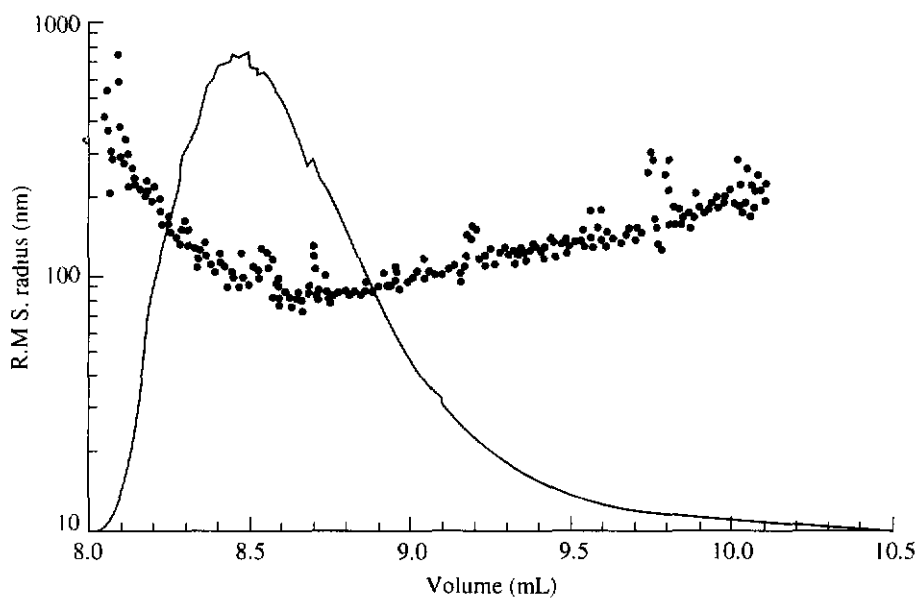
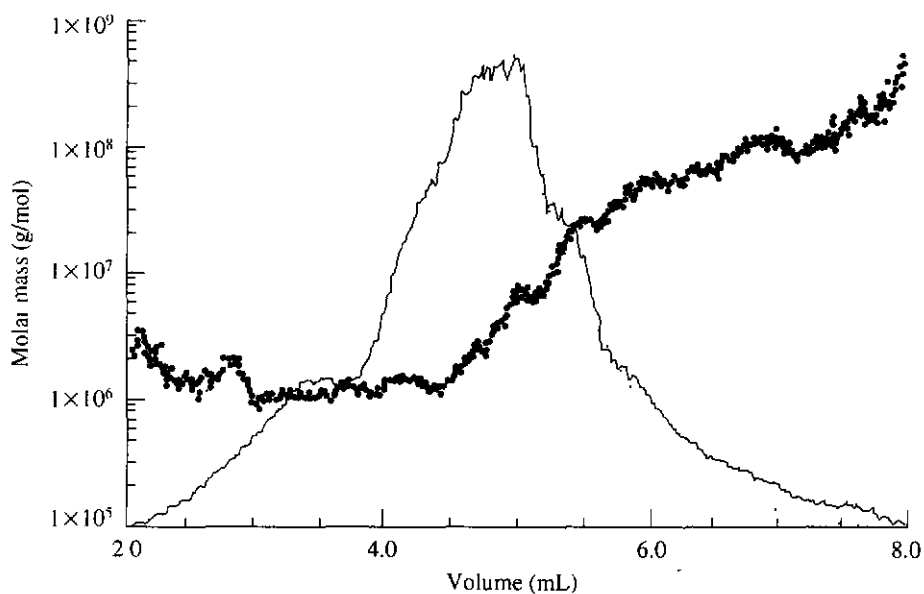*Figure 8. Fractogram of* cis-BR40 *showing the size distribution through the light scattering profile.*

Figure 9. Molecular mass versus elution volume for SMR L. Solid line denotes light scattering profile and dotted line denotes UV concentration profile.

rubber from a few million to many tens of millions. The dependence of the radius of gyration on molecular weight is shown in *Figure 10* and size data below a molecular weight of 10^6 g/mol may be affected by possible co-elution. Nevertheless, the slope of the plot from 10^6 g/mol to 3×10^7 g/mol is 0.3 and can be attributed to star-shaped or branched molecules. The slope of radius of gyration *versus* molecular weight depends on the segmental density of polymer species. Above 3×10^7 g/mol the slope tends to zero, an indication of the presence of microgel particles which are much denser than polymer coils.

A recent and only characterisation[11] of natural rubber by ThFFF relied solely upon synthetic linear polyisoprene standards for calibration to derive an apparent molecular weight distribution. It was recognised that the amount of information obtained by this method was limited and so there was a perceived need for an absolute measure of molecular weight, such as that now obtained by a ThFFF/MALLS system.

CONCLUSION

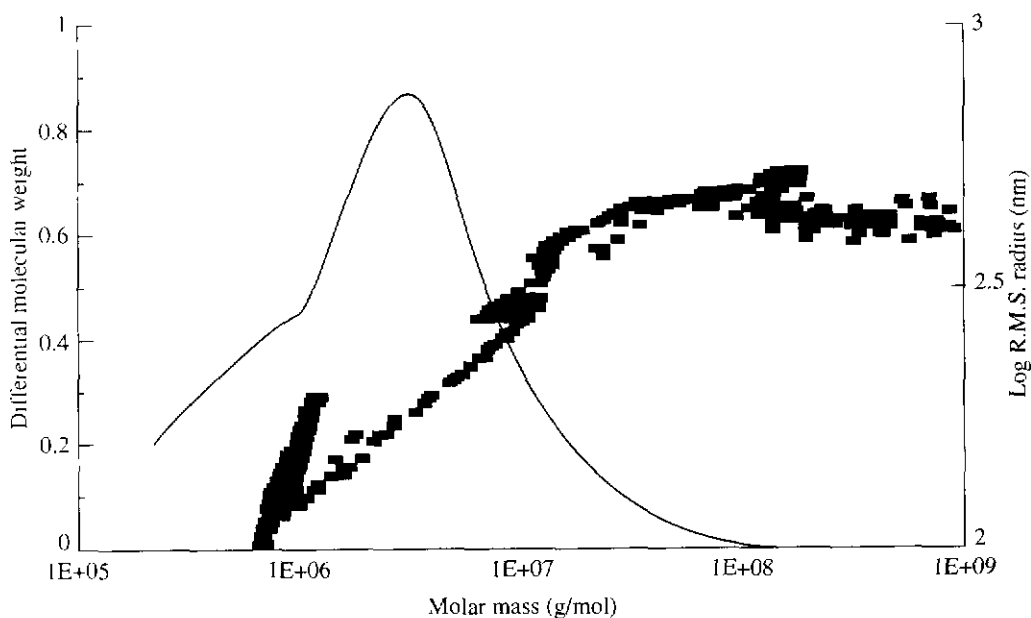This paper has demonstrated how complex mixtures of linear, branched and gel species

Figure 10. Differential molecular weight and radius of gyration as a function of molar mass for SMR L.

found in many elastomers can be studied without filtration. The novel combination of two powerful techniques, ThFFF and MALLS, has provided a system with distinct advantages over conventional SEC. The synergy between the two techniques provides a measure of absolute molecular weight and radius of gyration from which parameters such as long chain-branching can be derived.

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