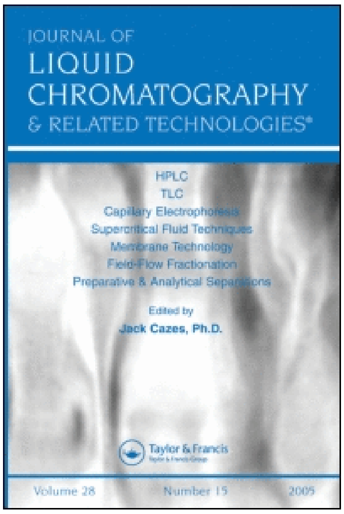

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CHARACTERIZATION OF POLYTHIIRANES USING MULTIDETECTION SIZE EXCLUSION CHROMATOGRAPHY

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ABSTRACT

Series of polythiiranes with pendant Oxyethylene groups have been characterised. Size Exclusion Chromatography (S.E.C.) analysis of polymers with such polar groups needs some precautions. Accurate measurement of dn/dc is used in order to check the amount of recovery of the injected samples. Polymers with short side chains are normally eluted, but an irreversible adsorption occurs for long side chains. There appears to be an intermediate situation for which adsorption is reversible and produces an important dependence of elution volume on injected concentration.

Using a combined Light Scattering, a Viscometric detector, and additional off-line Dynamic Light Scattering (D.L.S.) measurements, it was possible to study, more completely, the relationship between size and molecular weight for such polymers. When

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some of these polymers do not exhibit any adsorption phenomenon, universal calibration is observed and a constant correction factor is available, allowing the conversion of relative molecular weights into absolute molecular weights.

INTRODUCTION

Complete characterisation of solution properties of new polymer samples is normally becoming an easy task using multidetection S.E.C. combining detection by Differential Refractometer, Light Scattering, and Viscometer.[1] Actually, for totally new structures, it is necessary to be very careful and to check, separately, different aspects of the elution of the samples. Different situations can be observed, from pure size exclusion up to liquid adsorption. By proper choice of eluent composition and column package, it is possible to observe the interesting intermediate case of critical point of liquid adsorption for which both effects compensate and elution volume becomes independent of molecular weight.[2]

In this work we choose to keep on using a classical SEC package (Styrene/DVB gels) and eluent (THF), but the Oxyethylene side chains of the samples are of various lengths, allowing observation of a variety of elution behaviours. The first problem is to determine the amount of recovery of the sample after elution, which needs accurate dn/dc measurements. Then, it is useful to compare results at different injection concentrations, in order to check if a reversible adsorption occurs or pure size exclusion process takes place. When using multidetection facilities, it is necessary to be very careful with moderate molecular weights samples as, unavoidably, the signal/noise ratio is relatively low.

Additionally, in the case of abnormal retention due to adsorption processes, we can only extract the weight average molecular weight and no detailed information on molecular weight distribution can be obtained. To obtain other reliable information about the size of such polymers, off line Dynamic Light Scattering measurements appears to be very efficient. Finally, once complete characterisation is performed for series of samples, it becomes possible, for further routine analysis, to simply apply a correction factor to the Polystyrene equivalent Molecular Weights.

EXPERIMENTAL

Materials

All polymers were prepared by ring opening polymerisation of the corresponding macromonomers. The synthesis of the macromonomers and experimental conditions of polymerisation were described previously.[3]

Figure 1 presents the chemical structures of the macromonomers and of the different polymers studied.

Instrumentation and Experimental Protocol

S. E. C. was performed using THF as eluent (from Merck, “for Synthesis” grade). The commercial antioxidant was eliminated by distillation, and the eluent reservoir was kept under nitrogen to prevent further oxidation and water adsorption. For conventional S.E.C., an isocratic pump (Spectra Physics P100), an automatic injector (Waters Wisp 712), a Differential Refractometer (Waters R410), and a 60 cm length column (Polymer Lab mixed C) were used. Data collection and treatment were performed using software developed in our laboratory.

The combined detector used for multidetection experiments was described elsewhere.[4] The eluent is collected in a small reservoir, then transferred to a Light Scattering cell, and finally transferred to the viscometer. Miniaturised solenoid operated isolation valves permit these transfers. The LS cell is placed in an index matching liquid bath (filled with toluene) so as to eliminate reflectance at the glass/air interface. The incident light source is a 5 mW helium-neon laser emitting light at 633 nm. A set of 10 Miniaturised Photomultipliers (PM, Hamamastu, Japan, type R3811) allows simultaneous observation of the scattered light at fixed angles (θ = 15, 30, 45, 60, 75, 90, 105, 120, 135, and 150 degrees). A common power supply (Hamamastu, Japan, type CEE5) provides stable conditions for these PM.

A reference photodiode measures the intensity of the incident light. This allows the correction for fluctuations of the incident light intensity. In practice, however, these fluctuations are negligible. The signals from the ten PM, from the reference photodiode and from up to three other signals (chromatographic detectors, pump, etc.), are treated by individual amplifiers with zero and gain adjustments.

Data collection and transmission to a Personal Computer (PC) is performed by a multi-channel data processor (DAP 2400 from Microstar). The scattered light intensities collected during a given span time (usually 1 s) are stored after normalisation by the incident light intensity. The capillary viscometer is a suspended level type with a calibrated capillary tube (length 9 cm and diameter 0.44 mm). Two light barriers placed around the upper part allows automatic flow time measurement. These flow times are also stored on the PC. Very efficient temperature regulation and precise geometry conditions are required to allow stable time flow measurements. After each analysis, average LS intensities of each angle and fraction and flow time trough capillary are computed and stored. Then the molar mass, radius of gyration and intrinsic viscosity can be calculated using concentration values obtained from a DR detector.

Dynamic light scattering measurements were performed using a multi τ correlator (ALV 5000) and an Argon LASER (Spectra-Physics 2000)

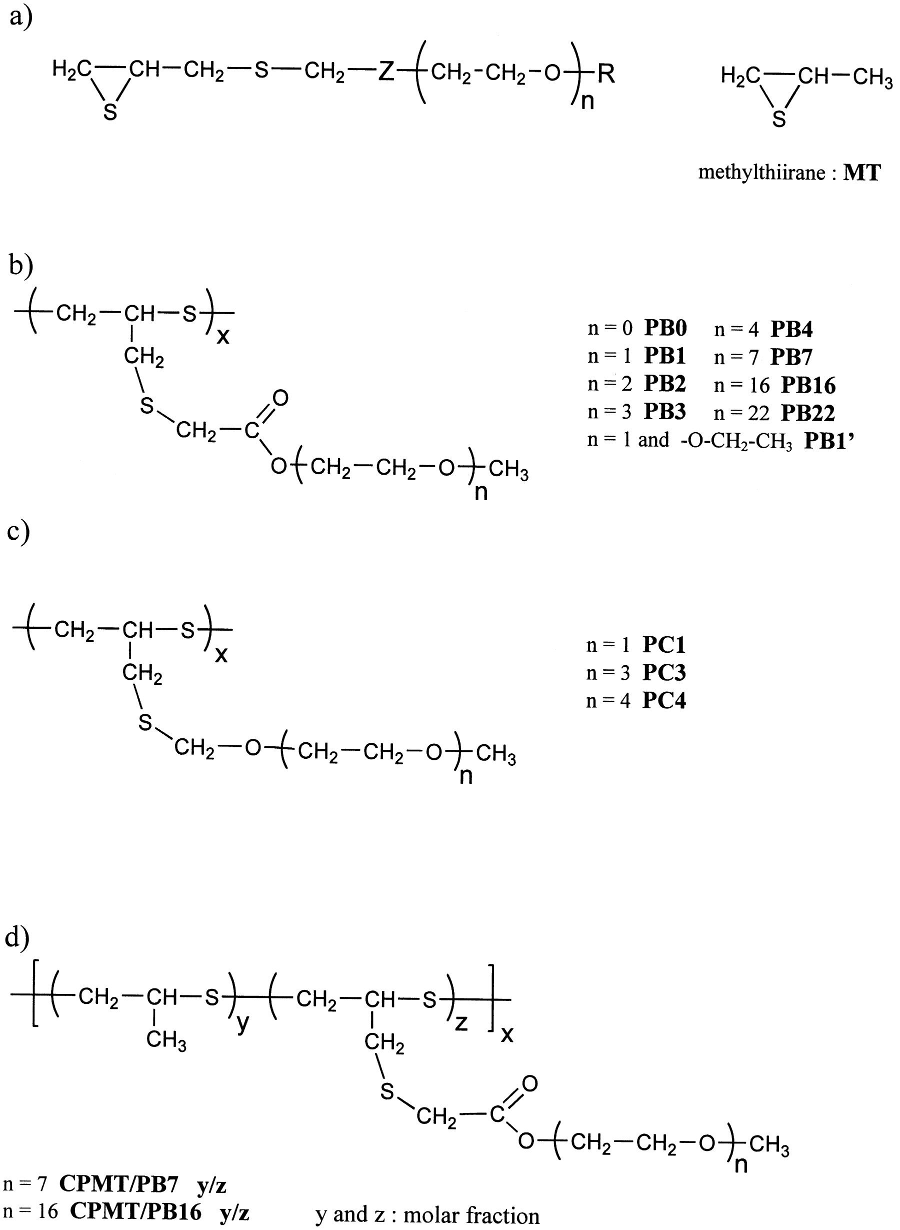

Figure 1. Chemical structure of POE-thiirane macromonomers and polymers: a. POE-thiirane macromonomers; b. POE-homopolythiiranes with an ester linkage; c. POE-homopolythiiranes with an ether linkage; d. methylthiirane/POE-thiirane copolymers.

RESULTS

Conventional S. E. C. Using Differential Refractometer Detector

As the chemical structure of the studied samples is far from classical, it is necessary to be especially careful about S. E. C. results validation. Reversible or irreversible adsorption phenomena are checked by measuring percentage of recovery and by studying influence of concentration and temperature.

Measurements of dn/dC Values and Percentage of Recovery

A chromatographic device with stable flow rate, reproducible injection volume, and sensitive differential refractometer is very convenient for measuring dn/dC values in a relative mode.

In this work, we simply replaced the chromatographic column by an empty tube (1 m length, 1.2 mm internal diameter) to prevent any risk of adsorption.

It is essential to use only fresh solutions prepared with the eluent flowing through the chromatographic apparatus. Indeed, when running a real S.E.C. experiment using a column, low molecular weight impurities are eluted later than the sample, and the sample peak is well separated. Without a column, any impurity would give a signal polluting that of the sample.

For each recorded point:

$$H_i = k\ dn/dC\ C_i \text{ with } C_i = \frac{m_i}{\Delta V}$$

ΔV being the elution volume increment between two adjacent points.

For the whole peak the area is:

$$A = \Sigma H_i = k\ dn\ /\ dC\ \Sigma C_1$$

$$= \frac{k.dn/dC}{\Delta V} \Sigma m_i$$

$$= \frac{k.dn/dC}{\Delta V} m_{inj}$$

k is a constant depending on the refractometer and data acquisition system. It is measured by injection of a known amount of a standard with a well known dn/dC. Here a polystyrene standard was used (dn/dC = 0.185 cm^3/g in THF at 633 nm). The dn/dC is then obtained by injection of a known amount of the studied sample.

In this way, only relative values of dn/dC are obtained. Indeed, for a given polymer/solvent system, the refractive index increment dn/dC slightly changes

Table 1. Measured Refractive Index Increments for Polythiiranes

Reference	OE Weight Fraction	dn/dC (cm^3/g)	Eluted Fraction (%)
PBO	0.00	0.153	100
PB1	0.20	0.133	100
PB2	0.33	0.117	100
PB3	0.44	0.109	100
PB4	0.50	0.105	100
PB7	0.63	0.094	100
PB16	0.78	0.076	27 - 75
PB22	0.84	0.074	0

with the wavelength.[5] The differential refractometer operates with a broad band optical source (in the near I.R. for R410 refractometer) and we simply admit that the ratio of sample dn/dC over standard dn/dC is independent of wavelength, even if each absolute dn/dC has a slight dependence with wavelength.

Results are summarised in Table 1.

The general expression for dn/dC homopolymers (ester series) is

$$(dn/dC)_{sample} = (dn/dC)_{OE}\ \omega_{OE} + (dn/dC)_{PB0}\ \omega_{PB0}$$

$$(dn/dC)_{sample} = (dn/dC)_{PB0} - [(dn/dC)_{PB0} - (dn/dC)_{OE}]\ \omega_{OE}$$

with ω_{OE} and ω_{PB0} weight fractions of OE and PB0 parts ($\omega_{OE} + \omega_{PB0} = 1$).

In this way, after linear regression, we obtain: (dn/dC)sample = 0.151 - 0.093 ωoεand (dn/dC)OE= 0.058 cm^3/g. This is not far from the dn/dC value for a simple POE sample ((dn/dC) = 0.069 ± 0.002 cm^3/g), the difference being related to end chain effect.

The same behaviour is observed for homopolymers of the PC series with

$$(dn/dC)_{sample} = 0.146 - 0.090\ \omega_{OE}$$

For copolymers **CPMT/PB** we obtain in the same way:

$$(dn/dC)_{sample} = 0.174 - 0.077\ \omega_{MB7}$$

and $(dn/dC)_{sample} = 0.174 - 0.098\ \omega_{MB16}$

with ω_{MB7} and ω_{MB16} weight fractions of **MB7** and **MB16** macromonomers parts.

After determination of dn/dC values, the measurement of the percentage of recovery after elution through S.E.C. column is immediate. The mass of eluted sample is:

$$m = \frac{A\Delta V}{k\,dn/dc}$$

and is compared with the mass of injected sample.

For polymers with short or moderate length side chains (one to seven OE units), the whole sample is eluted, whereas for longer POE side chains, a strong and irreversible adsorption was observed. Nevertheless, we can't exclude for short POE side chains, a completely reversible adsorption.

Influence of Concentration

The **PB7** situation is special; the total recovery is noticed, but a strong tailing effect on peak shape and an important concentration dependence of peak position is observed. That seems to indicate a reversible adsorption.

In order to study, precisely, this chromatographic behaviour, we have injected this sample at different concentrations between 1 and 20 mg/mL. Results are shown in Figure 2.

These data have been analysed assuming a classical Langmuir isotherm for which there is a equilibrium between adsorption and desorption of a monolayer of solute on the pore surface.

Let us note θ the fraction of surface covered by adsorbed solute in contact with a mobile phase containing solute at concentration C.

Equality of adsorption and desorption rates means:

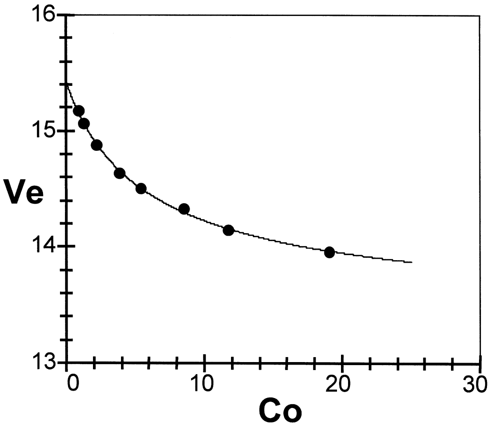

Figure 2. Elution volume versus injected concentration for PB7 samples. The solid line represents calculations from the present work.

$$k_a C (1- \theta) = k_d \theta \qquad (1)$$

In a classical way, elution is governed by the capacity factor k', ratio of the solute adsorbed on the stationary phase, to solute dissolved in the stagnant phase inside the pores. Here k' is proportional to θ/C ratio and when $C \rightarrow 0$, $k' \rightarrow k'_{max}$ $\propto k_a/k_d$ If we introduce $C_{0.5}$ conncentration for which half of the surface is covered, meaning $k' = k'_{max}/2$, equation (1) can be rewritten in a more convenient way:

$$k' = \frac{k'_{max}}{1 + C/C_{0.5}}$$

With this definition and if k' is stable during elution:

$$V_e = V_0 + K\ V_P\ (1 + k')$$

That explains, qualitatively, peak retardation when $C \rightarrow 0$ as $k' \rightarrow k'_{max}$ in this case.

That explains also, the strong peak retardation: in the peak front, C is low and peak front moves slowly and is constantly awaiting the main part of the peak. On the contrary peak, the tail moves slower and slower as concentration is lowering.

To obtain values for k'_{max} and $C_{0.5}$ it is necessary to take into account the change of concentration during peak elution. We have only studied the motion of peak top and admit that there is a linear decrease of concentration from C_0 injected concentration to C_S concentration at peak top is. So L being the column length, l the peak position;

$$C = C_0 - 1\frac{(C - C_0)}{L}$$

At this peak position:

$$k' = \frac{k'_{max}}{1 + C/C_{0.5}} \qquad v = v_1 \frac{V_0 + K\ V_p}{V_0 + K\ V_p\,(1 + k')}$$

v being the linear velocity of the solute and v_1 the linear velocity of same solute without adsorption.

As v is not constant, elution time t_e is obtained by integration

$$t_e = \int_0^L \frac{dl}{v}$$

After proper substitution:

$$t_e = t_1 \left(1 + \frac{K\ V_p}{V_0 + K\ V_p} \frac{k'_{max}\, C_{0.5}}{C_{0.5} - C_S} \ln \left(\frac{C_{0.5} + C_0}{C_{0.5} + C_S} \right) \right)$$

For our column set, we observe that $C_S = 0.08.C_0$. Experimental results are fitted with that expression on Figure 2 and the best fit is obtained with $C_{0.5}$=3 mg.mL^{-1} and k'$_{max}$=0.15. So, for the PB7 sample, we are in a rare situation where we observe a reversible adsorption of polymer corresponding to a simple Langmuir isotherm. For shorter POE sequences, adsorption is negligible and for longer POE sequences, adsorption becomes more and more irreversible, indicating a strong co-operative effect upon adsorption of such sequences. Similar behaviour is not observed for pure low M_w POE, confirming the importance of the co-operative effect.

Influence of Temperature

For samples totally recovered at ambient temperature, no change in elution volume is observed by warming the column at 30°C or 40°C, when taking into account the normal change in elution time due to the change of eluent density inside the warmed column. For the PB7 sample, some reversible adsorption still remains, even at 40°C. For long POE chain samples, irreversible adsorption still occurs in the same conditions. So these temperature changes are not sufficient to modify the elution behaviour of these systems.

Complementary Characterization

SEC with a simple concentration detector is a relative characterisation method. Combination of SEC measurements and other physico-chemical methods is necessary when absolute information is required. In that work, we used a multidetection device with the DR detector for concentration measurements and a combined detector on line with SEC, which allows measurement simultaneously with scattered light at 10 angles and viscosity.

The normal way, when combining DR and LS detection, is to establish the true calibration curve assuming each fraction is isomolecular. Nevertheless, as our samples have a relatively narrow distribution, the number of data points is not sufficient to obtain interesting calibration curves. Additionally, when adsorption occurs, spectacular discrepancies appear as for the PB7 sample. For that reason, we have decided to focus on the discussion of average values. In Table 2, we summarise SEC results for different polymer series obtained by varying the monomer to initiator molar ratio (M/I). The number and weight average molecular weights (Mn(PS) and Mw(PS)) are obtained by simple detection and using PS calibration curves, the absolute weight average molecular weight are obtained by LS (M_w (LS)), and the intrinsic viscosity ([η]).

These results allow us to calculate the viscometric radius R_η (radius of the sphere with same product [η]M);

Table 2. Polythiiranes: Monomer/Inititor Ratio, Molecular Weights (Polystyrene Calibration and Light Scattering Data), Intrinsic Viscosities, Mark-Houwink Prefactor, Viscosimetric Radii, and Stokes Radii

Polymer	M/I	M_n(PS) (10^3 g.mol^{-1})	M_w(PS) (10^3 g.mol^{-1})	M_w(LS) (10^3 g.mol^{-1})	[η] (cm^3.g^{-1})	K_η ($\times 10^2$)	R_η (nm)	R_S (nm)
PB1	500	76	145	211	38.6	9.2	10.9	10.3
	250	56	87	129	35.4	11.8	9.0	7.7
PC1	400	76	144	192	-	-	-	9.8
	100	43	88	128	28.2	9.5	8.3	7.7
PB3	400	20	44	66	11.7	6.2	5.0	5.7
	133	24	62	110	15.7	5.8	6.5	6.6
PC3	400	28	41	96	-	-	-	-
	200	26	39	62	14.1	7.7	5.2	5.6
	50	25	33	51	14.6	9.2	4.9	4.5
PB4	400	20	74	117	16.3	8.3	6.7	7.2
	100	17	62	93	14.8	8.3	6.0	6.2
	50	15	65	96	-	-	-	-
PC4	200	37	138	205	36.0	8.3	10.5	9.0
	100	28	95	142	27.6	8.3	8.5	7.3
	66	24	61	120	22.7	8.3	7.6	7.0
	28	4	8	15	5.7	8.3	2.4	2.6
PB7	400	3	9	195	23.4	5.9	9.0	8.9
	100	4	10	135	13.5	4.4	6.6	7.8
	100	8	12	117	-	-	-	-
	33	9	12	56	-	-	-	-

$$R_\eta = \left(\frac{3[\eta]M}{10\pi M}\right)^{1/3}$$

Additional off line measurements have been performed by Dynamic Light Scattering in THF at 20°C, in order to obtain Stokes radius R_S of each sample (radius of the sphere with same average diffusion coefficient).

$$R_S = \frac{KT}{6\pi}\eta 0 D_T$$

DISCUSSION

Mark-Houwink Relationship

Data for [η] are shown in Figure 3, and results obtained for PB4 and PC4 series allow us to establish the MH relationship:

$$[\eta] = 8.3\ 10^{-3}\ M_W^{0.68}$$

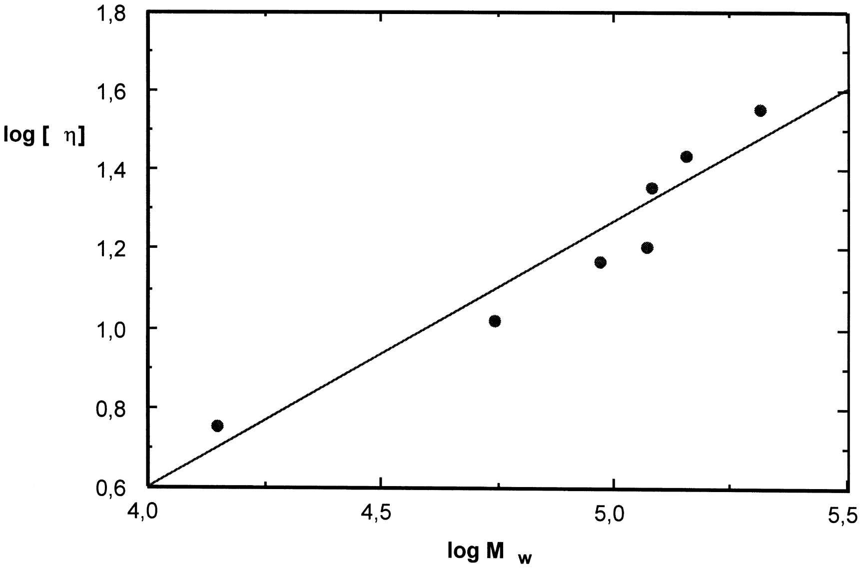

Figure 3. Mark-Houwink relationship for PB4 and PC4 polymers (data from Table 3).

For other series, the number of samples available is not large enough to establish MH relationship.

The exponent 0.67 is slightly lower than the one observed for flexible coils in good solvents, but similar values have been reported for other comb shape polymers.[6] For other series, assuming that the exponent is not changed, we can estimate the value of the constant Kη for $[\eta] = K\eta\ _{MW}{}^{0.67}$ These values are given in Table 2.

Additionally, we observe that K_η is lower when the length of OE side chains increases; the polymers becoming more and more branched and compact.

Relationship Between R_S and M_W

In that case, as shown in Figure 4, a correct correlation is obtained for all samples between R_S and M_W: $R_S = 1.5\ 10^{-2}\,M_W{}^{0.53}$. Here, the exponent is clearly lower than the value 0.6 normally observed for flexible coils in good solvents and that may be related with the relatively high thickness of the chain.

Relationship Between R_η and R_S

With a MH exponent a = 0.67, the viscometric radius depends on mass with the power (1+0.67)/3 = 0.56 which is close to the exponent of the power law relating to Stokes radius (0.53) molecular weight. As a consequence, the ratio between the two radii has to be fairly stable as shown in Figure 5. For a coiled polymer in good solvent, the theoretical ratio is 0.75 (7). Here we obtain a slightly higher value, 0.83, which is not surprising as Stokes radius is a z average and viscometric radius is a weight average.

Universal Calibration Behaviour for Polythiiranes

Of course universal calibration can be used only in the case of pure steric exclusion chromatography and does not apply when adsorption occurs simultaneously. As the exponent of MH relationship (0.67) is very close to the one of PS in THF (0.70), a very convenient approximation is to assert that there is a constant ratio between M_{PS} and $M_{Polythiirane}$ eluted at the same volume.[8] Then, for the whole sample, the following relationship applies: $M_w(LS) = B.\ M_w(PS)$

Figure 6 shows that, even if there is some scatter, a relatively stable value, B=1.5, is observed for all the samples with short OE moieties. For the PB7 samples, no significant B values are obtained due to the important adsorption process.

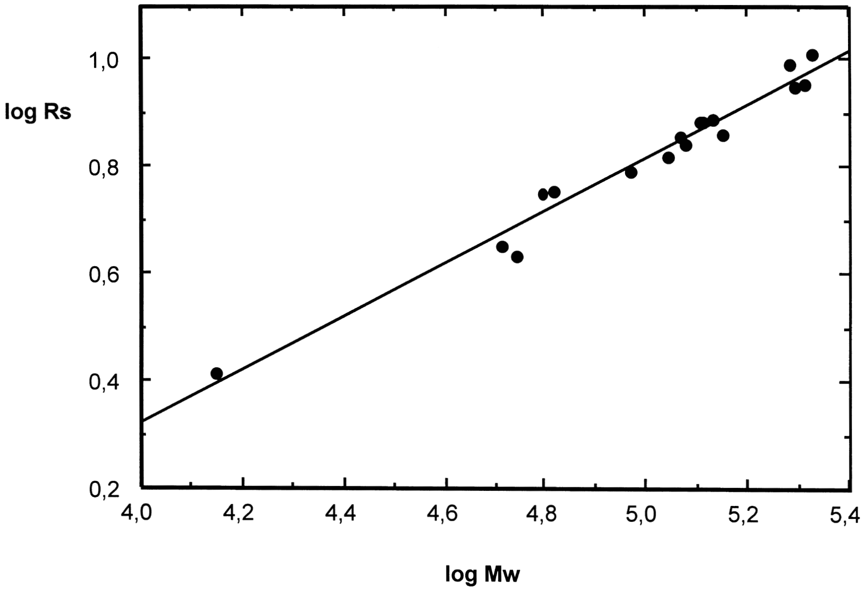

Figure 4. Stokes radius logarithm versus molecular weight logarithm (data from Table 3).

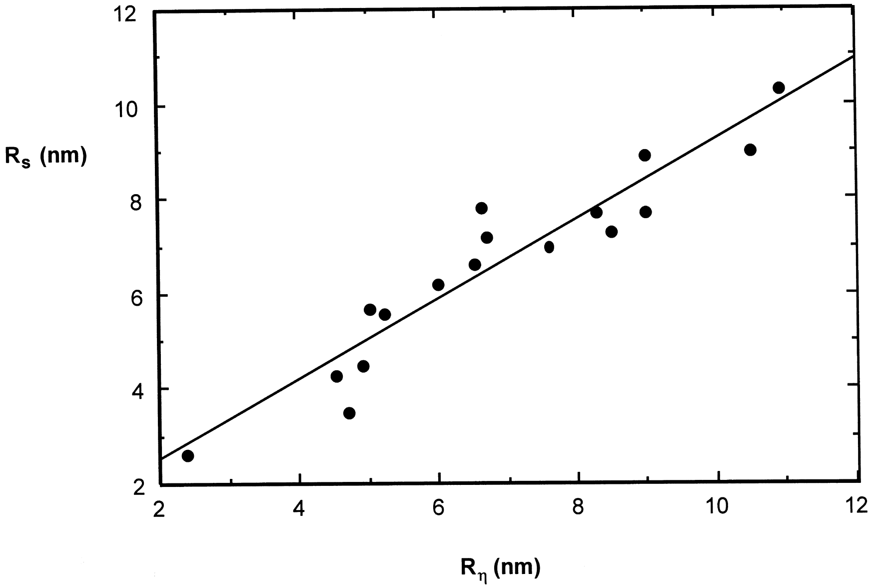

Figure 5. Dependence of Stokes radius with viscosimetric radius (data from Table 2).

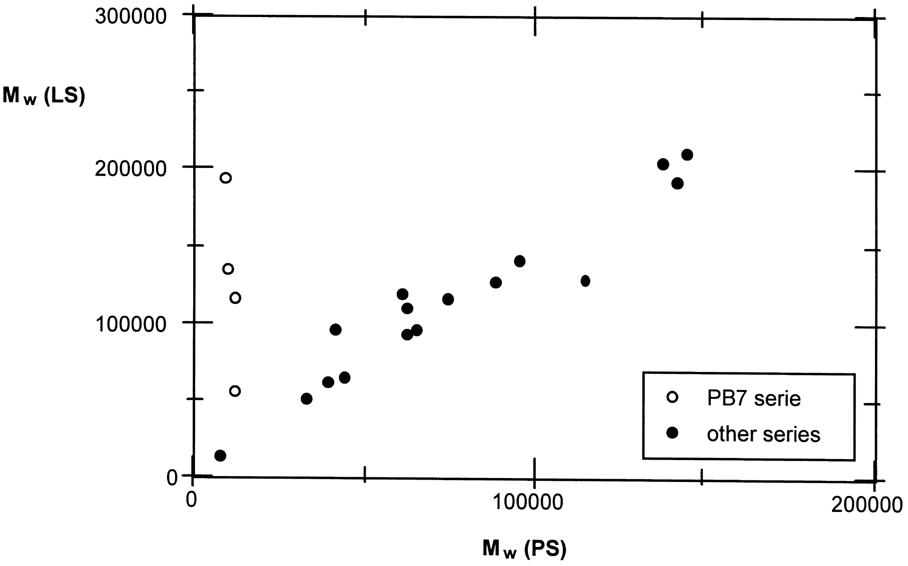

Figure 6. Comparison between molecular weights obtained by SEC/LS and Polystyrene calibration.

Thus, for further routine characterisation of polythiiranes with short OE moieties, it is possible to simply obtain absolute M_w and M_n values by correcting equivalent PS values using that B factor.

CONCLUSION

Polythiiranes, from functionalized macromonomers, is a new class of interesting polymers which present some difficulties for characterisation. Samples with long OE moieties (n>7) are irreversibly adsorbed on classical Styrene DVB columns when THF is used as eluent. There is an intermediate situation for n=7, where a reversible adsorption is combined with the size exclusion process. In this case, elution behaviour is well described using a Langmuir isotherm model. For shorter OE moieties, the elution takes place according to a pure size exclusion process. Coupling light scattering and viscometry on line with SEC and off line Dynamic Light Scattering achieved a complete description of the behaviour of dilute solutions of these samples in THF. A stable ratio, B= 1.5, between absolute Mw and equivalent PS Mw is observed.

Table 3.

Polymer	M/I	$M_n = 1.5\ M_n(PS)$ (10^3 g.mol^{-1})	M_0 (monomer unit)	DPn
PB1	500	114	210	540
	250	84	210	400
PC1	400	114	182	630
	100	64	182	350
PB3	400	30	310	100
	133	36	310	116
PC3	400	42	280	150
	200	39	280	140
	50	37	280	130
PB4	400	30	354	85
	100	25	354	72
	50	23	354	64
PC4	200	55	314	177
	100	42	314	134
	66	36	314	115
	28	6	314	19

For polymerisation kinetic interpretation, the most important parameter is Mn. Therefore, the best values are obtained by applying this B factor to equivalent PS Mn values. As a consequence, it appears that for the studied samples, there is only a rough correlation between M/I ratio and DPn values (Table 3). That seems to indicate that propagation rate is higher than initiation rate and, especially for low M/I values, all the initiator is not consumed at the end of the polymerisation.

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