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SHORT COMMUNICATION

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Viscosimetric study of polystyrene polymacromonomer dilute solutions

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Abstract The viscosimetric behaviour of poly(ω-norbornenyl polystyrene) polymacromonomers is studied in dilute solutions as a function of the degree of polymerisation and the branch molar mass. We emphasise the fact that the exact molar mass characterisation using scattering techniques is illusory, owing to a strong intermolecular contribution in the scattering distribution, as evidenced by neutron scattering. Two characteristic behaviours are evidenced in the viscosimetric dependence versus molar mass of the polymacromonomer and are attributed to their global conformation when they could be considered as spherically or cylindrically symmetric. Moreover for the branch of higher molar mass used an unexplained deviation appears between the two behaviours.

Key words Polymacromonomer · Molar mass · Conformation · Viscosity · Neutron

Introduction

It is now well established that the presence of ramifications or branches modifies notably the polymer chain conformation and especially the solution properties [1–3]. A certain number of investigations have focused on the study of these branched architectures and especially on the influence of the confinement on the branch conformation [4–9]. The confinement is obvious when the object considered is a star, in which case the presence of a central core from which a number of branches irradiate, not necessarily high, appreciably changes the density of segments when going from the centre of the star to its periphery [10].

A few years ago a new kind of polymer was synthesised: the polymacromonomers [11, 12]. These polymers have a regular distribution of branching points along their main backbone. They are made by the polymerisation of low-molar-mass chains: the macromonomers, terminated by a terminal reactive unsaturation. One gets a macromolecule whose backbone is made up of the macromonomer terminal function. All the repeating units of this main backbone give rise to branches that constitute a secondary skeleton [13–18].

The size of the branches can be varied at will, within a domain of molar masses ranging from some hundred to some thousands of grams per mole. The synthesis of the macromonomers may be realised by living anionic polymerisation, which results in narrowly distributed samples. When this condition is satisfied the objects may be considered as model compounds.

Because of the number of branches that constitute such polymacromonomers, the allowable space to each branch is limited, which results in their confinement. One easily conceives that this confinement will depend, for a given macromonomer, on its molar mass, the period of the main backbone (distance between two consecutive branches) and the respective size of the main and secondary skeletons.

For this last point, one can anticipate that the main skeleton would have a negligible dimension compared to that of the secondary one, if the polymerisation index, DP_n, of the polymacromonomer is small. Under such conditions the distribution of branches around the main skeleton should be rather radial, as in a star-shaped molecule, leading to a spherically symmetric distribution of the repeating units.

On the other hand, if the DP_n is large, one expects the main backbone to be more spacially extended than the branches. Under these conditions, the branch repeating units should be distributed around the main backbone with a tubular symmetry.

By changing the reactive unsaturation of the macromonomers one can modify the size of the backbone repeating units and change, to a certain extent, the period of branching. In this way the available volume per branch will be modified.

Such modifications in the spatial occupancy of the polymacromonomers should have an influence on their solution properties. The first physicochemical results we obtained, mainly using viscosimetry, are described here.

In short, the symmetry that develops within polymacromonomers and also the global shape of these objects are expected to depend on the following parameters:

- The size of the main backbone and therefore the DP_n of the polymacromonomer.
- The size of the branches.
- The distance between branches.
- The persistence length of the polymer forming the branches.

In a first approach we limited ourselves to the investigation of the viscosimetric behaviour of polystyrene polymacromonomers giving particular attention to the effect of two of the previously mentioned parameters, namely the DP_n of the polymacromonomers and the molar mass of their branches.

Experimental

Materials and characterisation

The polymacromonomers studied are poly(ω-norbornenyl polystyrene) (PNBPS), which were synthesised by ring-opening metathesis polymerisation of a polystyrene macromonomer whose chain end was fitted with norbornenyl unsaturation [19]. Three macromonomers, with different molar masess, were prepared. Starting from each of these macromonomers, several polymacromonomers of variable DP_n were obtained. The corresponding polymacromonomer and macromonomer characteristics are listed in Table 1. The theoretical DP_n of the polymacromonomers are those targeted when synthesising them. Obviously there may be a large discrepancy between these values and the true values of the DP_n obtained through the polymerisation. Only an accurate determination of the polymer molecular mass makes possible the knowledge of the value. This is a reason why some of the characterisation techniques that can be used give only approximate values of the molar mass. Size-exclusion chromatography (SEC), for the lack of a standard for this kind of architecture, cannot be calibrated rigourously; only the universal calibration technique could be used with the uncertainties correlated. Light scattering (LS), which is an absolute technique, is also questionable, as we shall see later.

The LS measurements were performed using two different experimental setups; the first was a classical FICA photogoniometer, the second was the laser LS instrument WYATT DAWN. Both sets of results show a nonmonotonous variation of the scattered intensity as a function of angle; consequently we are outside the domain of the scattering vector where the Guinier or Zimm approximation is valid. Thus zero-angle extrapolation has to be performed, over two or three points at best, which implies a great inaccuracy in the experimental determination of the molar mass. The variation of the intensity scattered by a 2% NBPS

Table 1 Macromonomer and polymacromonomer specifications and intrinsic viscosties

$\overline{M}_n$ macromonomers[a]	$\overline{M}_n$ polymacromonomers[b]	$\overline{DP}_{n,exp.}$	$[\eta]$.100 (dl/g)
2700	2700	1	3.62
	5400	2	6.10
	52370	19	10.27
	179750	66	14.75
	213430	79	17.66
	455320	169	31.96
4800	4800	1	5.95
	9600	2	9.5
	64460	13	10.14
	130760	27	11.85
	225550	47	13.06
	567870	118	19.03
11000	11000	1	10.39
	22000	2	16.5
	58580	5	18.44
	64030	6	18.79
	153200	14	19.21
	250520	23	15.68
Polystyrene linear	9100	88	9.78
	18100	174	14.40
	37900	364	23.75
	96400	927	44.35
	190000	1827	71.21

[a] Molar mass obtained by size-exclusion chromatography ($gmol^{-1}$)
[b] Molar mass obtained by osmometry ($gmol^{-1}$)

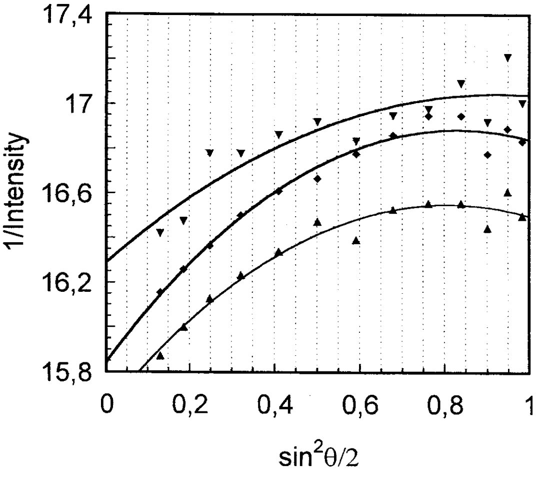

Fig. 1 Light scattered, measured using a WYATT DAWN instrument by successive fractions of ω-norbornenyl polystyrene (*NBPS*) polymacromonomer in a Zimm representation

polymacromonomer solution in tetrahydrofuranis shown in Fig. 1 in a Zimm representation obtained using the WYATT instrument. The theoretical DP_n of the polymacromonomers is 74 and the average molar mass of its branches is 4800 $gmol^{-1}$ adopted a more appropriate representation than that provided by the software of the instrument, which tends to flatten the ordinate axis and therefore leads to approximate, if not erroneous, molar masses.

The three curves in Fig. 1 represent intensities scattered by fractions following one another that are eluted by the SEC columns of the apparatus. This kind of scattered intensity distribution is not rare: it can be associated with various situations, namely

- The form factor $P(\vec{q})$, of monodisperse hard spheres, which has an oscillating behaviour.
- The occurrence in the solution of a preferential distance that is associated with interactions between solute objects.

In the case of the polymacromonomers in our study, and for the samples of high DP_n, only the second situation is conceivable. As Coulomb-type interactions cannot exist here, only excluded-volume-type interactions can be responsible for the evolution of the scattered intensity. This phenomenon is not really surprising: owing to the compactness, the high density that develops within these objects prevents their interpenetration and as the concentration increases leads to a preferential distance between them.

This interpretation is corroborated by the result shown in Fig. 2, which is a representation, in arbitrary units, of the light and neutron intensities scattered by the same solution, at small angles. The scattering vector windows, accessible through these two techniques, are complementary, which allows a better characterisation of the scattering function $S(\vec{q})$. One can observe in Fig. 2 the occurrence of a maximum in the scattered intensity distribution, outside the **q**-vector window accessible to LS, as the previous result would lead one to expect.

The possible alternatives to characterise DP_n rigorously are tonometry and osmometry. The first of these techniques could be applied with accuracy only for very low molar masses, less than 10^4 $gmol^{-1}$, the second one in the range 2×10^4–6×10^5 $gmol^{-1}$. Thus the molar mass domain accessible to the experience is restricted.

Therefore one should be cautious when considering results for the behaviour of polymacromonomers whose molar mass is not determined using these techniques.

The experimental characteristics of our polymacromonomers are listed in Table 1. The mean molar mass, M_n, which gives the DP_n was determined using osmometry and tonometry techniques in their respective domain of sensitivity.

Viscosimetric measurements

Viscosity measurements were realised using a Ubbelohde-type flow capillary viscosimeter. We determined the limiting viscosity indices, or intrinsic viscosities, by extrapolation to zero concentration of the reduced and inherent viscosities. Mother solutions, as well as the solvent of dilution, were carefully filtered on a Millipore filter. The concentrations of mother solutions were chosen so as to obtain times of flow approximately 30% longer than that of the solvent. The extrapolated intrinsic viscosities are plotted against the approximate molar masses of the polymacromonomers in Fig. 3. The viscosity variation of a linear polystyrene, according to the Mark–Houwink law (see later), determined on polystyrene standards on the same equipment is also plotted in this graph.

$$[\eta] = 13.29 \times 10^{-3} M^{0.703}. \qquad (1)$$

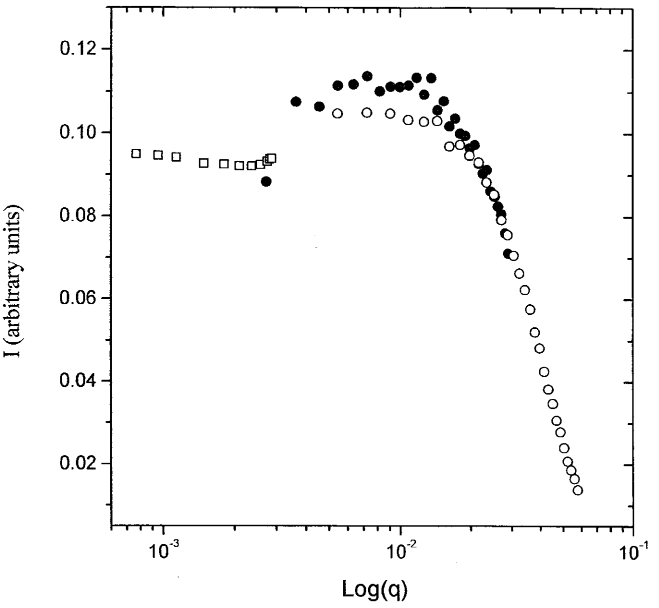

Fig. 2 Light (□) and neutron (●, ○) intensities scattered by a 2% solution of NBPS in toluene (deuterated toluene for small-angle neutron scattering), two different resolutions have been used for neutron scattering

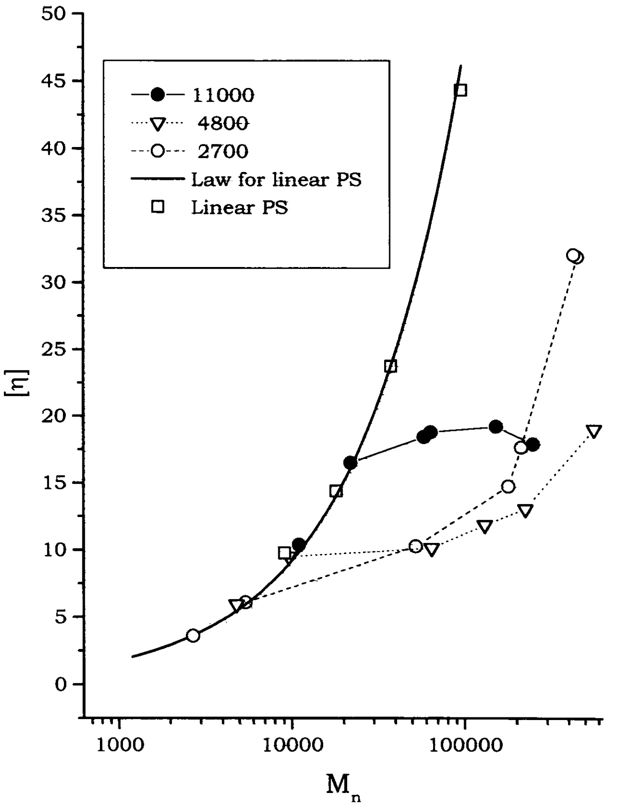

Fig. 3 Intrinsic viscosities of NBPS polymacromonomer as a function of molar mass for different branch molar masses (○, 2700 $gmol^{-1}$, ▲, 4800 $gmol^{-1}$, □, 11000 $gmol^{-1}$)

The intrinsic viscosities obtained are plotted as a function of the DP_n of the polymacromonomer in Fig. 4. This representation was made with the view of finding out a possible dependence on the size of the main backbone.

Discussion

The intrinsic viscosity behaviours, observed in Figs. 3 and 4, are typical of polymacromonomers and may be more generally of highly grafted polymers. In the whole domain of molar mass investigated, the viscosity is lower than that of the linear polymer of the same mass. This confirms clearly that polymacromonomers are much more compact than equivalent linear polymers. Moreover, it may be noticed that the evolution of the viscosity as a function of the molar mass is also very different. One can actually discriminate between two distinct domains of variation that are observed whatever the molar mass of the branches.

For small DP_n, or molar masses, the intrinsic viscosity remains almost constant regardless of the polymacromonomer size. For example, the samples that carry branches of 4800 $gmol^{-1}$ exhibit only a viscosity increase of less than 20%, while their global molar mass varied more than 1 order of magnitude (10^4–2×10^5 $gmol^{-1}$). The viscosity is multiplied by a factor of 7 for a linear polymer in the same range of molar mass. Although the viscosity rise is slightly more important for the two other families of polymacromonomers, one can, as a first approximation, consider the intrinsic viscosity as being almost constant in this region. As one would expect, the viscosity increases from one family to the other with the size of branches.

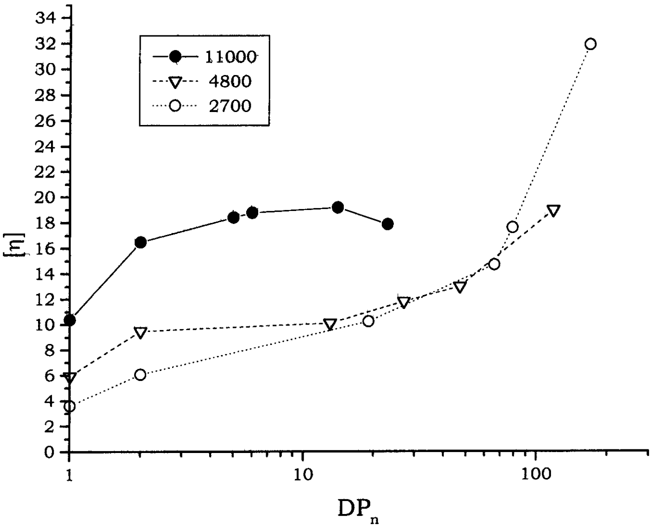

Fig. 4 Intrinsic viscosities of NBPS polymacromonomer as a function of DP_n for different branch molar mass (○, 2700 $gmol^{-1}$, ▲, 4800 $gmol^{-1}$, □, 11000 $gmol^{-1}$)

As the molar mass of the polymacromonomer increases, the viscosity gradually increases and tends to be parallel with the variation observed for linear chains. This evolution of the intrinsic viscosity with the molar mass of the objects was reported by Tsukahara and coworkers [20, 21], for poly(ω-methacryloyloxyethyl polystyrene) (PMMAPS) polymacromonomers, whose structure, except the period, is the same as that of NBPS. It is to be noted that, in general, Tsukahara polymacromonomers exhibit a higher polymolecularity than ours.

The existence of two regimes in the viscosity versus DP_n plot for polymacromonomers can be easily explained. If one refers to the Einstein theory of viscosity, it is known that the viscosity of a solution of compact spheres is given by the following relationship:

$$[\eta] = 2.5\Phi_s, \tag{2}$$

where Φ_s is the volume fraction of spheres in the solution. This relationship can also be written

$$[\eta] = 2.5\frac{N_A}{\rho}. \tag{3}$$

N_A is the Avogadro number and ρ the sphere density. It is evident that in the case of a compact sphere ρ is a constant and the viscosity $[\eta]$ does not change whatever the sphere radius and, therefore, whatever its mass. One can then write

$$[\eta] = KM^0. \tag{4}$$

The intrinsic viscosity laws for other models, such as ellipsoids and rods, have also been determined. For rods, the expression for the intrinsic viscosity is molar-mass dependent according to

$$[\eta] = K\frac{M^2}{\ln M}, \tag{5}$$

where M is the molar mass of the rod.

As M becomes larger the following approximation can be made:

$$[\eta] \cong KM^2. \tag{6}$$

In the two limiting cases of spheres and rods, the relationships obtained look like that of the Mark–Houwink law, but with different molar-mass exponents, namely 0 and 2.

The weak increase in the polymacromonomer intrinsic viscosity, in the domain of the small DP_n, indicates that in solution these objects adopt the global shape of a compact sphere. As the DP_n increases, the main backbone grows, forcing the object to take gradually a more elongated form, which causes an increase in the viscosity. The molar-mass exponent in the viscosity law then increases; however, it is to be noted that the exponent does not tend towards the limit of 2, as expected for polymacromonomers of high molar mass, but rather to the values found for linear chains. The variation of viscosity tends to be parallel to that of a linear chain and the exponent of *M*, in the Mark–Houwink law for polymacromonomers of higher molar mass, is slightly less than that of linear polystyrene. One can therefore view these objects as flexible cylinders, with a vermiform conformation and a global statistic close to that of a coil. The term vermiform is used in the case where a large transverse dimension exists instead of "wormlike" since this latter term corresponds already to a well-defined and different concept in polymer science.

It is easy to imagine that these objects gradually change, from a spherical symmetry to a transverse cylindrical one, as the size of the main backbone increases; however, this change of shape, even if it is gradual, does not always result in a monotonous variation of the intrinsic viscosity. Indeed, one observes in Figs. 3 and 4 a downward trend for $[\eta]$, between the domain of almost constant viscosity and that where it grows regularly, at least for one family of polymacromonomers with branches whose molar masses are 11000 gmol^{-1}. The decrease in $[\eta]$ is more pronounced when the molar mass of the branch is increased.

This decrease in the viscosity is quite surprising and it does not seem to be an experimental artifact. Indeed, if we plot the Tsukahara viscosimetric data in a graph (Fig. 5) the same kind of behaviour is suggested.

The effect appears for a molar mass of branches around 12000 gmol^{-1} for the PMMAPS, while in the case of the PNBPS it occurs for masses of around 5000 gmol^{-1}. The main difference between the two types of polymacromonomers, apart from their different chemical structure, is that the period of the main backbone of PNBPS is twice that of PMMAPS.

In this study, devoted to the solution properties of polymacromonomers, we have shown that their intrinsic viscosity exhibits a peculiar behaviour that was found to depend on both the number of branches they are made of and their molar mass. The hypothesis of a progressive transformation from a spherical symmetry to a cylindrical one as a function of the $\mathrm{DP_n}$ seems to be verified. The compactness of spherically symmetric objects increases with decreasing molar mass of the side branch, but at the same time a tubular symmetric conformation is developed as the overall $\mathrm{DP_n}$ increases. It is to be noted that polymacromonomers with higher $\mathrm{DP_n}$ do not behave as typical rods or rigid cylinders, but rather as flexible cylinders, i.e. like linear chains with a large transverse section.

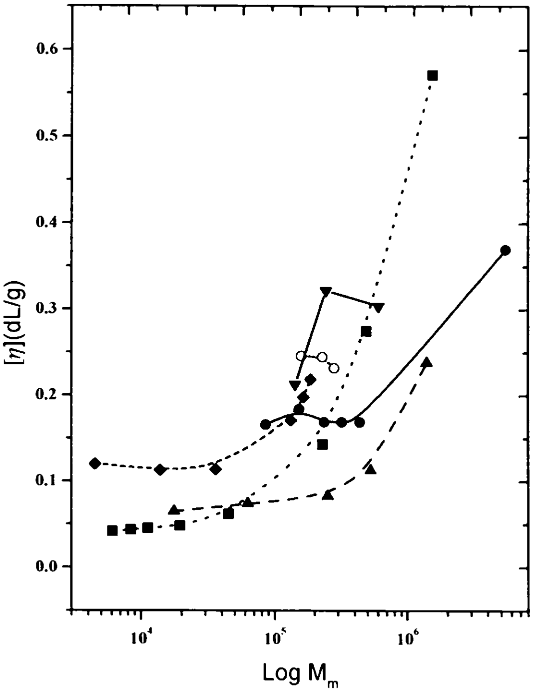

Fig. 5 Tsukahara viscosimetric data (■ MA-PSt800, ▲ MA-PSt2900, ■ MA-PSt5500, ● MA-PSt12400, ○ MA-PSt14000, ▼ MA-PSt27000)

Between the behaviour corresponding to the models of a sphere and a flexible cylinder, a significant decrease in the viscosity can be observed, which mirrors a shrinkage of the apparent hydrodynamic volume of these objects in solutions. We have no well-defined arguments for the interpretation of this phenomenon. We believe that it is linked to the polymacromonomer shape change according to the mean $\mathrm{DP_n}$. Accurate characterisations are now being carried out using various techniques to try to solve this problem.

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