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Supramolecular association of acid terminated polydimethylsiloxanes. 3. Viscosimetric study

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Abstract

Due to dimerization through hydrogen bonding of chain ends, benzoic acid terminated polydimethylsiloxane **1** forms a supramolecular polymer in low polarity solvents. Viscosity measurements in dichloromethane, carbon tetrachloride and hexane have been performed. In order to analyze the results, a covalent model **6** of the supramolecular polymer has been synthesized and its viscosimetric parameters (Mark-Houwink and Huggins constants) have been measured. It is experimentally shown that, in dilute solution, the viscosity of a supramolecular polymer can be satisfactorily evaluated if viscosimetric parameters of a suitable covalent model are known.

Keywords: Supramolecular polymer; Hydrogen bond; Telechelic polydimethylsiloxanes; Capillary viscosimetry

1. Introduction

The concept of self-assembly is increasingly applied to the field of polymer science. Supramolecular polymers, which can be defined as arrays of small molecules held together by non-covalent interactions [1], offer potential advantages over covalent polymers due to the reversibility of their properties. The interactions used to build supramolecular polymers range from ionic and metal–ligand interactions to dispersive forces, but hydrogen bonding is particularly favored because of its fixed stoichiometry, directionality and simplicity.

One way to obtain a supramolecular polymer is to use telechelic polymers bearing self-complementary hydrogen bonding groups at the chain ends [2,3]. Unlike telechelic ionomers [4–6] and hydrophobically endcapped water soluble polymers [7–9] which form reversible networks due to the multiple aggregation of chain ends, telechelic polymers bearing dimerizable hydrogen bonding groups can form chain extended reversible polymers.

In order to understand the properties of these supramolecular polymers, it is of utmost importance to be able to measure their molecular weight, which is not a trivial task because the molecular weight of supramolecular assemblies depends on concentration, solvent polarity and temperature. So far, zero shear viscosity [3], capillary viscosimetry of solutions containing a chain stopper [10] and chain end titration by FTIR [11,12] have been used to estimate the molecular weight of hydrogen bonded supramolecular polymers.

In this paper, we investigate the relevance of capillary viscosimetry as a tool to characterize supramolecular polymers. Thus, the solution viscosity of benzoic acid terminated polydimethylsiloxane **1** [11,12] (Fig. 1) has been measured. The results have been interpreted by comparing them to the viscosity of a covalent model **6** of the supramolecular polymer **1** (Fig. 1).

2. Experimental

2.1. Synthesis

Synthesis of **1**, **2** and **3** has been reported previously [13], and **4** has been synthesized according to Ref. [14]. Polymer **6** of several molecular weights was synthesized according to Fig. 1. Typically, polymer **6f** was prepared as follows.

*Synthesis of polymer **6f**.* 1.92 g (3.08×10^{-3} mol of SiH) of α,ω-hydride terminated polydimethylsiloxane **5** (Rhône–Poulenc, $DP_n = 17$, $M_w/M_n = 1.4$), 0.41 g (1.56×10^{-3} mol) of 4,4′-bisallyloxybiphenyl **4** and 0.027 g (0.10×10^{-3} mol) of 4-allyloxybenzylbenzoate **3**

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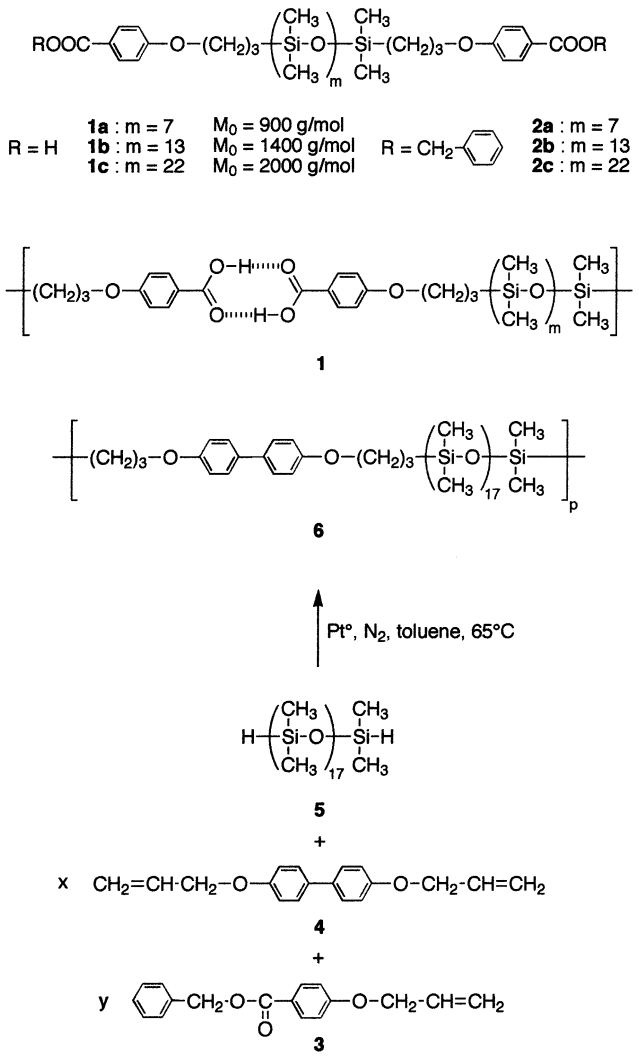

Fig. 1. Structure of telechelic oligomers **1** and **2** and polymer **6**.

were introduced in a flask. After purging with nitrogen, 2 μl of platinum catalyst PC085 (platinum–cyclovinylmethylsiloxane complex from ABCR) ([Pt]/[SiH] = 10^{-4}) in 5 ml of toluene (distilled over sodium) were added and the reaction mixture was heated at 65°C overnight. Disappearance of the SiH band at 2125 cm^{-1} was checked by FTIR. The polymer was recovered by precipitation in acetonitrile. Yield and molecular weight (measured by size exclusion chromatography in tetrahydrofuran with UV and refractive index detections using a polystyrene calibration curve) are reported in Table 1. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 7.5 and 6.9 (2d, 4H, C_6H_4), δ 3.9 (t, 2H, O–CH_2), δ 1.9 (m, 2H, O–CH_2–CH_2), δ 0.7 (m, 2H, CH_2–Si), δ 0.1 (m, 54H, Si–CH_3).

Polymers **6a**–**6e** were synthesized using the same procedure as for **6f** with the proportions of reagents reported in Table 1.

Table 1
Characteristics of polymers **6a**–**6f**

Polymer	[**4**]/[**5**]	[**3**]/[**5**]	M_w[a] (g/mol)	M_w/M_n[a]	Yield (%)
6a	0.50	0.50	6600	1.7	70
6b	1.00	0.75	9300	1.4	80
6c	1.00	0.39	14,100	1.7	75
6d	1.00	0.20	18,100	1.7	85
6e	0.83	0	26,200	1.9	90
6f	1.01	0.065	35,200	1.5	85

[a] Measured by size exclusion chromatography in tetrahydrofuran, using a polystyrene calibration curve.

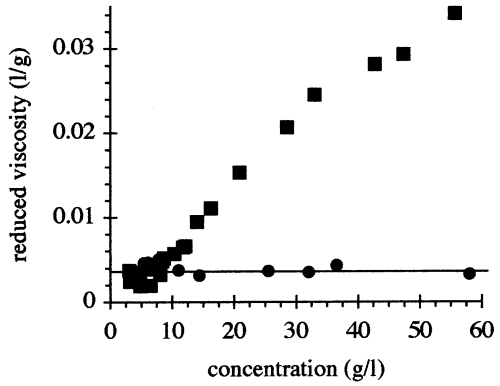

Fig. 2. Reduced viscosity of diacid **1b** (■) and diester **2b** (●) measured by capillary viscosimetry in hexane at 25°C.

2.2. Viscosimetry

Capillary viscosimetry was performed at 25 ± 0.1°C with a Cannon–Manning semi-micro viscometer. Solutions in hexane (SDS, stored on molecular sieves) were prepared one day before the measurements and filtered on Millex membranes ($\Phi = 0.45$ μm).

3. Results and discussion

3.1. Expression for the reduced viscosity

Fig. 2 shows the reduced viscosity (η_{sp}/c) of solutions of diacid **1b** and diester **2b** versus concentration (c) in hexane at 25°C.[1] We have previously shown [11,12] that at high concentrations ($c > 10$ g/l), the high viscosity of diacid **1b** is due to the formation of large linear (C_n) and cyclic (R_n) supramolecular chains (Fig. 3), and that at low concentrations ($c < 10$ g/l), the solution is mainly composed of cyclic monomer (R_1). Thanks to the previously established model based on infrared spectroscopic data [11,12], it is possible to calculate the concentrations of all species present in solution

[1] The Newtonian behavior of a 50 g/l solution of diacid **1b** in dodecane was established for shear rates between 1 and 100 s^{-1}, and a reduced viscosity of 0.025 l/g was found which is nearly identical to the value measured by capillary viscosimetry at the same concentration in hexane (Fig. 2).

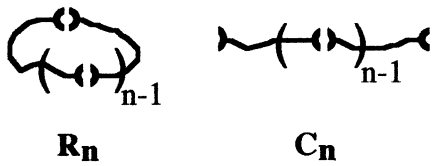

Fig. 3. Schematic representation of supramolecular polymers.

($[C_n]$, $[R_n]$) for any concentration c of diacid **1**:

$$[C_n] = (4K)^{n-1}[C_1]^n \quad (n \geq 1) \tag{1}$$

$$[R_n] = B\frac{(4K[C_1])^n}{n^{2.5}} \quad (n > 1), \qquad [R_1] = 4KB_1[C_1] \tag{2}$$

where K is the association constant corresponding to the dimerization of acid groups, B_1 is the cyclization constant associated to cyclic monomer, B is the cyclization constant associated to all other cyclics and $[C_1]$ is determined by solving the mass balance equation:

$$\frac{[C_1]}{(1-4K[C_1])^2} + 4KB_1[C_1] + B\sum_2^\infty \frac{(4K[C_1])^n}{n^{1.5}} = \frac{c}{M_0} \tag{3}$$

where M_0 is the molecular weight of diacid (Fig. 1).

With the knowledge of the whole molecular weight distributions, the viscosity of the solution can be calculated if we assume that Mark-Houwink and Huggins relationships can be applied. The validity of these relationships in the case of supramolecular polymers is not obvious because of the dynamic nature of the chains. The effect of reversible chain-scission reactions on rheological properties of supramolecular polymers has been theoretically investigated only in the case of entangled polymer solutions [15]. It is our aim to see if the use of Mark-Houwink and Huggins relationships affords a good description of low concentration experimental results. Thus, we assume that the intrinsic viscosity of the linear chains and rings, respectively, are:

$$[\eta]_C = K_C(\overline{M_{wC}})^{a_C} \text{ and } [\eta]_R = K_R(\overline{M_{wR}})^{a_R} \tag{4}$$

where K_C, K_R, a_C and a_R are constants, and $\overline{M_{wC}}$ and $\overline{M_{wR}}$ are the weight average molecular weights of the chain and ring fractions, respectively. It can be further assumed that $K_R \approx 0.6K_C$ and $a_R = a_C = a$, because in the case of covalent polymers, the viscosity of cyclic macromolecules has been shown to be proportional to the viscosity of linear chains of the same length, and the ratio $[\eta]_R/[\eta]_C$ is close to 0.6 [16]. The calculation of $\overline{M_{wC}}$ and $\overline{M_{wR}}$ is given in Appendix A.

Then, the intrinsic viscosity of the whole solution is:

$$[\eta] = w_C[\eta]_C + w_R[\eta]_R \tag{5}$$

where the weight fractions of the chains and rings (w_C and w_R, respectively), are given by:

$$w_C = \frac{\sum_1^\infty n[C_n]}{[C_0]} = \frac{[C_1]/[C_0]}{(1-4K[C_1])^2} \text{ and } w_R = 1 - w_C \tag{6}$$

with $[C_0] = c/M_0$, the total molar concentration of diacid.

Substituting Eqs. (4) and (6) in Eq. (5) yields:

$$[\eta] = \frac{[C_1]/[C_0]}{(1-4K[C_1])^2}K_C(\overline{M_{wC}})^a + \left(1 - \frac{[C_1]/[C_0]}{(1-4K[C_1])^2}\right)0.6K_C(\overline{M_{wR}})^a \tag{7}$$

Finally, the reduced viscosity of the solution is given by:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \tag{8}$$

where k_H is the Huggins constant.

Consequently, the reduced viscosity can be calculated with Eqs. (7) and (8) as long as the three constants K_C, a and k_H are known.

3.2. Estimation of viscosimetric parameters K_C, a and k_H

In order to estimate values for K_C, a and k_H from independent data, we used a covalent model **6** of the supramolecular polymer **1** (Fig. 1). Of course, **6** is a crude model, but its chain is made of polydimethylsiloxy blocks separated by short rigid groups, as in the case of supramolecular chains of **1**. Polycondensates **6a**–**6f** were synthesized by hydrosilylation of two monomers and a chain stopper (Fig. 1) in various proportions: their molecular weights are listed in Table 1. Then, the viscosity of solutions of polymers **6a**–**6f** in dichloromethane, carbon tetrachloride and hexane were measured, and the results in dichloromethane are reported in Fig. 4. Linear regression analysis of these data afforded values for Huggins constant k_H and

Table 2
Intrinsic viscosity and Huggins constant of polymers **6a**–**6f**

Polymer	Dichloromethane		Carbon tetrachloride		Hexane	
	$10^3[\eta]$ (l/g)	k_H	$10^3[\eta]$ (l/g)	k_H	$10^3[\eta]$ (l/g)	k_H
6a	7.5	0.42	7.3	0.42	5.3	1.77
6b	8.4	0.63	9.1	0.34	7.1	0.71
6c	11.5	0.53	12.5	0.31	10.7	0.29
6d	–	–	–	–	12.4	0.65
6e	17.6	0.46	18.8	0.30	17.1	0.23
6f	22.9	0.38	23.3	0.50	19.7	0.37

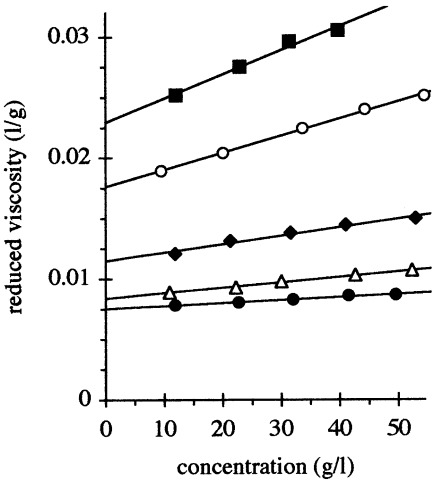

Fig. 4. Reduced viscosity of polymers **6a** (●), **6b** (△), **6c** (◆), **6e** (○) and **6f** (■) measured in dichloromethane at 25°C.

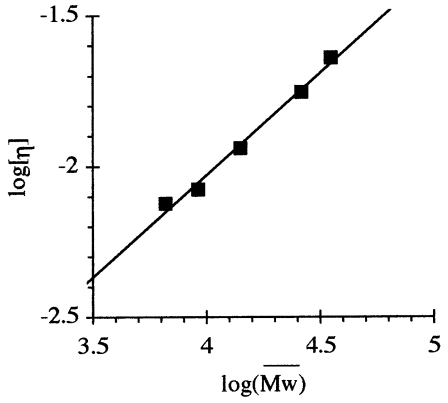

Fig. 5. Mark-Houwink plot for polymer **6** in dichloromethane at 25°C.

intrinsic viscosities (Table 2). Average values of $k_H = 0.5$ in dichloromethane and of $k_H = 0.4$ in carbon tetrachloride and hexane were obtained: these values are in the range of classical values for polymer solutions. Intrinsic viscosities were then used to derive Mark-Houwink constants K_C and a. The plot corresponding to data in dichloromethane is shown in Fig. 5 and the values obtained are displayed in Table 3. Values close to 0.7 (in dichloromethane and carbon tetrachloride) and 0.8 (in hexane) were obtained for the exponent (a), which are again in the range of classical values for solutions of polymers in a good solvent.

Table 3
Mark-Houwink parameters of polymers **6a–6f**

Solvent	a	K_C[a]	k_H
Dichloromethane	0.68	1.8×10^{-5}	0.5
Carbon tetrachloride	0.69	1.7×10^{-5}	0.4
Hexane	0.79	5.2×10^{-6}	0.4

[a] Units of K_C are determined by those of $[\eta]$ (l/g).

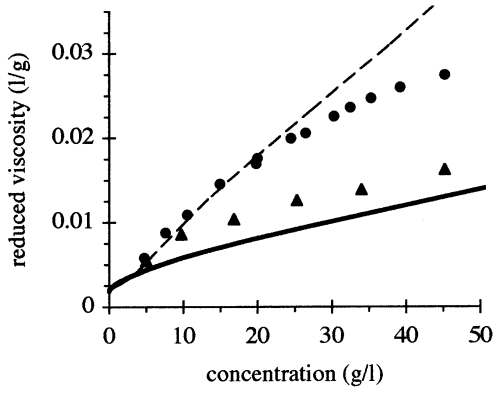

Fig. 6. Reduced viscosity of diacid **1a** measured (▲) and calculated (—) in dichloromethane and measured (●) and calculated (- - -) in carbon tetrachloride at 25°C.

3.3. Comparison of calculated and measured viscosities

Fig. 6 shows that the solutions of diacid **1a** in carbon tetrachloride are more viscous than solutions in dichloromethane: this is expected because hydrogen bonding is stronger in carbon tetrachloride due to its lower polarity. Fig. 6 also shows the curves calculated according to Eqs. (7) and (8) with viscosimetric parameters (K_C, a, k_H) of model polymer **6** (Table 3) and association parameters (K, B_1, B) determined by FTIR [11,12]. The agreement between viscosity measurements and calculated curves is very good, considering that several approximations were made and that no fitting parameter was used. This result seems to show that polymer **6** is a good model for the viscosimetric properties of supramolecular polymer **1a** in dichloromethane and carbon tetrachloride.

The same investigation was performed in the case of diacid **1b**: Fig. 7 shows that solutions of diacid **1b** in dichloromethane are less viscous than solutions in carbon tetrachloride and hexane, and that the latter two solutions display similar viscosities. The curves calculated according to Eqs. (7) and (8) are also plotted on Fig. 7, and the agreement with viscosity data appears to be less satisfactory than

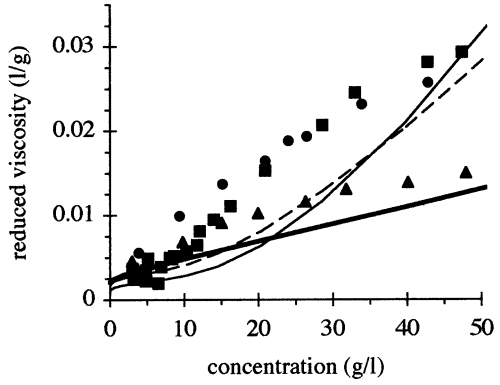

Fig. 7. Reduced viscosity of diacid **1b** measured (▲) and calculated (—) in dichloromethane, measured (●) and calculated (- - -) in carbon tetrachloride and measured (■) and calculated (—) in hexane at 25°C.

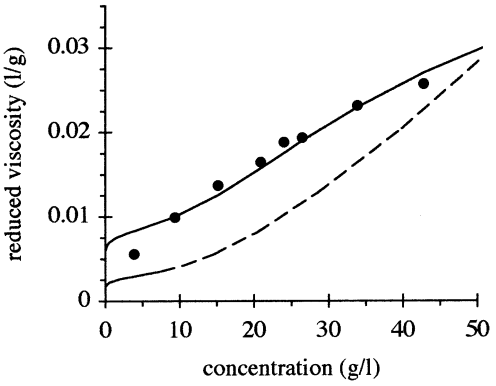

Fig. 8. Reduced viscosity of diacid **1b** measured (●) in carbon tetrachloride at 25°C, calculated with viscosimetric parameters of polymer **6** (- - -) and fitted by adjusting the viscosimetric parameters (—).

on Fig. 6. However, it is interesting to see that the relative position of the curves is correct: the calculated viscosities of the solutions of **1b** in hexane and carbon tetrachloride are very similar and significantly larger than in dichloromethane.

Another approach to the analysis of these viscosity measurements would be to consider the viscosimetric parameters (K_C, a, k_H) as adjustable parameters. For example, in the case of diacid **1b** in carbon tetrachloride, non-linear least square curve fitting yields an excellent fit (Fig. 8) with the following parameter values ($K_C = 3.7 \times 10^{-4}$, $a = 0.43$, $k_H = 0$). Of course, the quality of the fit is not a proof that the model is sound because too many adjustable parameters are used. Moreover, the values of the parameters obtained ($a = 0.43$ and $k_H = 0$) are not physically reasonable. Consequently, we prefer to use the viscosimetric parameters of model polymer **6** which afford a reasonable agreement between calculations and experiments without any fitting parameters.

The same investigation was performed in the case of diacid **1c**: Fig. 9 shows that the solutions of diacid **1c** in carbon tetrachloride and hexane have similar viscosities. As

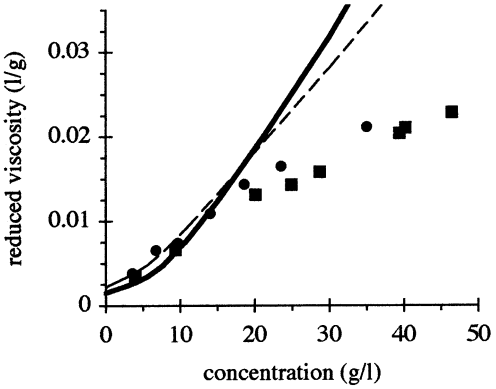

Fig. 9. Reduced viscosity of diacid **1c** measured (●) and calculated (- - -) in carbon tetrachloride and measured (■) and calculated (—) in hexane at 25°C.

before, the curves calculated according to Eqs. (7) and (8) do not agree perfectly with viscosity measurements of **1c**, but the model reproduces correctly the fact that viscosities in carbon tetrachloride and hexane are nearly identical.

3.4. Relative influence of association constant and viscosimetric parameters on viscosity

There is a large difference of viscosity between solutions of **1a** in carbon tetrachloride and in dichloromethane (Fig. 6). Since changing the solvent modifies both the association constant of the chain ends and the viscosimetric parameters, it is of interest to compare the magnitude of these two effects. The good agreement between calculated and measured viscosities in the case of diacid **1a** enables us to use our model to answer this question. Fig. 10 shows three different curves calculated using the same association constant ($K = 4300$ l/mol which is the value in carbon tetrachloride) but different viscosimetric parameters corresponding to the three solvents used: dichloromethane ($K_C = 1.8 \times 10^{-5}$, $a = 0.68$, $k_H = 0.5$), carbon tetrachloride ($K_C = 1.7 \times 10^{-5}$, $a = 0.69$, $k_H = 0.4$) and hexane ($K_C = 5.2 \times 10^{-6}$, $a = 0.79$, $k_H = 0.4$). These three curves are very similar, showing that for the three solvents considered, the change in viscosimetric parameters is not the main effect when the solvent is changed. Fig. 10 also shows two curves calculated with the same viscosimetric parameters (those corresponding to dichloromethane) but different association constants corresponding to dichloromethane ($K = 260$ l/mol) and carbon tetrachloride ($K = 4300$ l/mol). These two curves are significantly different, proving that the association constant is the main parameter influencing the viscosity of diacid **1a**.

Thus, a ratio of 16 between the association constants is responsible for the large difference of viscosities between

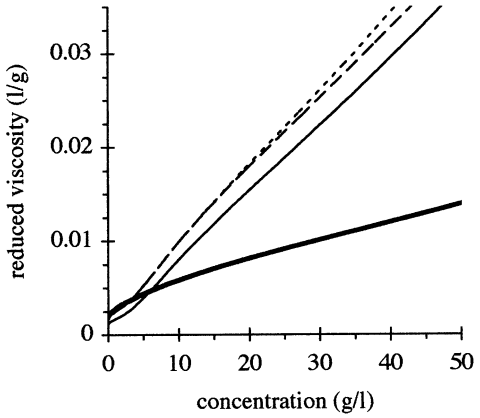

Fig. 10. Reduced viscosity calculated for diacid **1a** with different parameter values: K = 4300 1/mol and viscosimetric parameters in dichloromethane: $K_c = 1.8\ 10^{-5}$, a = 0.68, $k_H = 0.5$ (.....); K = 4300 1/mol and viscosimetric parameters in carbon tetrachloride: $K_c = 1.7\ 10^{-5}$, a = 0.69, k_H = 0.4 (---); K = 4300 1/mol and viscosimetric parameters in hexane: $K_c = 5.2\ 10^{-6}$, a = 0.79, k_H = 0.4(—); K = 2601/mol and viscosimetric parameters in dichloromethane: K = $1.8\ 10^{-5}$, a = 0.68, k_H = 0.5 (—).

solutions of **1a** or **1b** in dichloromethane ($K = 260$ l/mol) and carbon tetrachloride ($K = 4300$ l/mol). On the other hand, both direct measurements and calculations show (Figs. 7 and 9) that a ratio of 2 is not enough to significantly alter the viscosity of **1b** or **1c** ($K = 4300$ l/mol in carbon tetrachloride compared to $K = 7700$ l/mol in hexane).

4. Conclusion

Supramolecular polymers **1a**, **1b** and **1c** have been characterized by capillary viscosimetry in several solvents. We have shown that deriving Mark-Houwink parameters from a fit of reduced viscosity versus concentration is not a satisfactory procedure because too many fitting parameters are involved. That is why a covalent model, presenting a structural similarity to the supramolecular polymers, has been synthesized and characterized. This covalent polymer proves to be a good model for supramolecular polymer **1a** but not for **1b** and **1c**.

Acknowledgements

The authors are grateful to G. Ducouret for low shear viscosity measurements.

Appendix A

Expression for the weight average molecular weight of the linear chain fraction.

By definition

$$\overline{M_{wC}} = M_0 \frac{\sum_{n=1}^{\infty} n^2[C_n]}{\sum_{n=1}^{\infty} n[C_n]} \tag{9}$$

Substituting Eq. (1) yields:

$$\overline{M_{wC}} = M_0 \frac{1 + 4K[C_1]}{1 - 4K[C_1]} \tag{10}$$

Expression for the weight average molecular weight of the cyclic chain fraction.

By definition

$$\overline{M_{wR}} = M_0 \frac{\sum_{n=1}^{\infty} n^2[R_n]}{\sum_{n=1}^{\infty} n[R_n]} \tag{11}$$

Substituting Eq. (2) yields:

$$\overline{M_{wR}} = M_0 \frac{B\psi(4K[C_1]) - 4K(B - B_1)[C_1]}{B\varphi(4K[C_1]) - 4K(B - B_1)[C_1]} \tag{12}$$

Table 4
Values of the Riemann Zeta function

n	$\zeta(1.5-n)$
0	2.6120
1	−1.4600
2	−0.2079
3	−0.02549
4	0.008517
5	0.004441
6	−0.003092
7	−0.002671
8	0.002747
9	0.003269
10	−0.004416
11	−0.006672

with

$$\psi(4K[C_1]) = \sum_{1}^{\infty} \frac{(4K[C_1])^n}{n^{0.5}} \tag{13}$$

and

$$\varphi(4K[C_1]) = \sum_{1}^{\infty} \frac{(4K[C_1])^n}{n^{1.5}} \tag{14}$$

For low values of $4K[C_1]$ ($4K[C_1] < 0.4$), Eqs. (13) and (14) are rapidly convergent, so that summing the first 10 terms is a very good approximation. However, for values of $4K[C_1]$ close to 1, this is not the case and other expressions have to be used [17]. Truesdell et al. [17] showed that equivalent expressions for Eqs. (13) and (14) are:

$$\psi(4K[C_1]) = \frac{\Gamma(0.5)}{\sqrt{-\ln(4K[C_1])}} + \sum_{n=0}^{\infty} \zeta(0.5 - n) \frac{(\ln(4K[C_1]))^n}{n!} \tag{15}$$

and

$$\varphi(4K[C_1]) = \Gamma(-0.5)\sqrt{-\ln(4K[C_1])} + \sum_{n=0}^{\infty} \zeta(1.5 - n) \frac{(\ln(4K[C_1]))^n}{n!} \tag{16}$$

where $\Gamma(z)$ and $\zeta(z)$ are the Gamma function and the Riemann Zeta function, respectively. Their numerical values can be found in the literature [18]: $\Gamma(0.5) = 1.7725$, $\Gamma(-0.5) = -3.5449$ and values for $\zeta(0.5 - n)$ and $\zeta(1.5 - n)$, $n = 1$–10 are provided in Table 4. Eqs. (15) and (16) converge rapidly if $4K[C_1] \geq 0.4$, so that summing the first 10 terms is a very good approximation.

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