Supramolecular Association of Acid-Terminated Poly(dimethylsiloxane)s. 2. Molecular Weight Distributions

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ABSTRACT: Association through hydrogen bonding of benzoic acid-terminated poly(dimethylsiloxane) **1** in low-polarity solvents has been studied by FTIR spectroscopy and viscosimetry. At high concentrations, chain extension leads to high viscosity values, whereas at low concentrations, intramolecular hydrogen bonding is responsible for the formation of low-viscosity cyclic species. A quantitative model based on Jacobson−Stockmayer theory and describing the competition between chain extension and macrocyclization is presented. On the basis of this model, the molecular weight distributions of ring and chain fractions has been calculated as a function of concentration in three different solvents. The length of the siloxane backbone has been shown to have a large influence on the cyclic weight fraction and on the average molecular weight.

1. Introduction

Self-assembly is a very powerful way of building large or complicated objects which would be impossible to synthesize directly by conventional covalent synthesis.[1] Of course, nature uses self-assembly comprehensively in most biological processes, and we are only beginning to unravel some of the rules enabling us to predict the results of associations. In this field, supramolecular polymers, which can be defined as arrays of small molecules held together by noncovalent interactions, offer potential advantages over covalent polymers due to the reversibility of their properties.[2] 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.

Even if we consider only hydrogen-bonded supramolecular polymers, numerous studies have been reported on widely different systems. Hydrogen-bond interactions between small molecules can form chains or tapes whose study is highly relevant for crystal engineering.[3] They can also lead to main chain and side chain liquid crystalline polymers.[4] If molecular packing is disturbed, hydrogen bonding can be responsible for the properties of low molecular mass gelators[5] which have been shown to change organic solvents into strong gels at concentrations as low as 1%. Compared to these condensed-state properties, solution properties of hydrogen-bonded supramolecular polymers[6−13] have been much less studied. This is due both to poor solubility and to characterization difficulties of the assemblies because their molecular weight changes with concentration, solvent, and temperature.

However, characterizing in detail the dependence of molecular weight of hydrogen-bonded supramolecular polymers on concentration, solvent polarity, and temperature is important for the development of potential applications. With this aim in mind, we have designed and synthesized[14,15] a model system: benzoic acid-terminated poly(dimethylsiloxane)s **1** (Figure 1), which are highly soluble in nonpolar solvents due to the siloxane backbone and in which the benzoic acid moieties form reasonably strong hydrogen-bonded dimers.

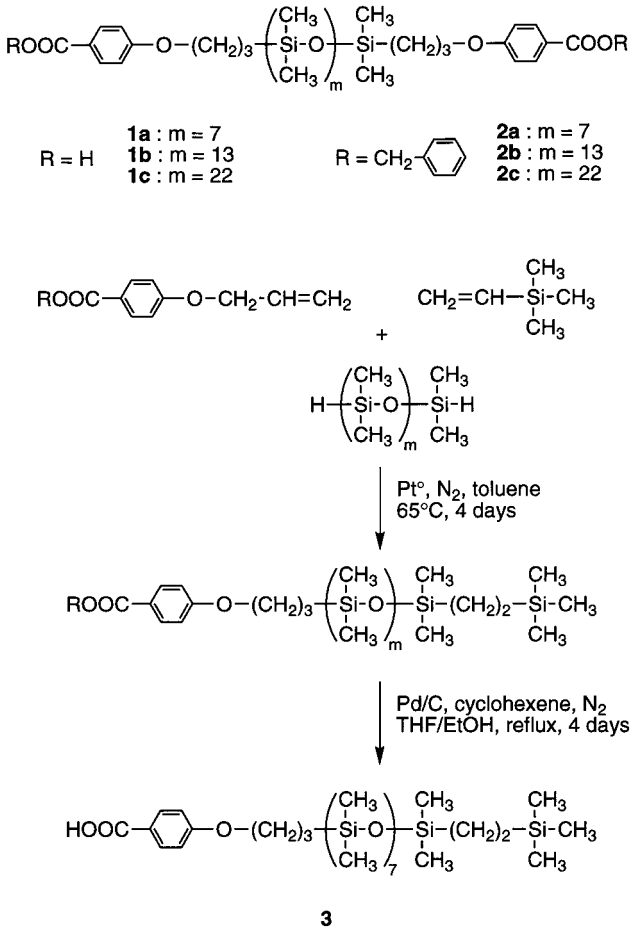

Figure 1. Structure of telechelic oligomers.

Poly(dimethylsiloxane)s **2** and **3** (Figure 1) were also synthesized and used as references because they contain 0 or 1 benzoic acid group, respectively. The present paper describes a qualitative and quantitative interpretation of properties of **1** in nonpolar solvents based on characterizations by FTIR spectroscopy and viscosimetry.

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2. Experimental Section

Synthesis. Synthesis of **1** and **2** has been reported previously.[14] Monofunctional oligomer **3** was synthesized analogously (Figure 1): 5.00 g (16×10^{-3} equiv of SiH) of α,ω-hydride-terminated PDMS (Hüls America Inc., $\overline{DP}_n = 8$, $I_p = 1.1$), 1.06 g (4×10^{-3} mol) of *p*-allyloxybenzylbenzoate,[14] 1.20 g (12×10^{-3} mol) of vinyltrimethylsilane (Aldrich), and 5 mL of toluene (distilled over sodium) were introduced in a round-bottom flask. After purging with nitrogen, 9 μL of platinum catalyst PC085 (platinum−cyclovinylmethylsiloxane complex from Hüls America Inc.) ([Pt]/[SiH] = 10^{-4}) was added, and the reaction mixture was heated at 65 °C for 4 days. The cohydrosilylation afforded a statistical mixture of three addition products (containing 0, 1, or 2 ester functions), which were separated by silica gel column chromatography with dichloromethane/hexane mixtures as eluents. Deprotection of the acid function and purification were performed as previously reported for **1**[14] (overall yield: 15%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.1 and 6.9 (2d, 4H, C_6H_4), δ 4.0 (t, 2H, O−CH_2), δ 1.9 (m, 2H, O−CH_2−CH_2), δ 0.7 (m, 2H, O−CH_2−CH_2−CH_2−Si), δ 0.4 (s, 4H, Si−CH_2−CH_2−Si), δ 0.1 (m, 46.6H, Si(CH_3)$_2$), δ 0.0 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 172.0 (*C*OOH), δ 163.5/132.2/121.4/114.1 (C_6H_4), δ 70.6 (O−*C*H_2), δ 23.1 (O−CH_2−*C*H_2), δ 14.0 (O−CH_2−CH_2−*C*H_2−Si), δ 10.1/7.9 (Si−*C*H_2−CH_2−Si), δ 1.0 (O−Si(*C*H_3)$_2$−O), δ 0.0/−0.7 (O−Si(*C*H_3)$_2$$CH_2$), δ −2.4 (Si(*C*$H_3$)$_3$). ^{29}Si NMR ($CDCl_3$, ppm): δ 8.7 (O−*Si*($CH_3$)$_2$−$CH_2$−$CH_2$−Si), δ 7.8 (($CH_2$)$_3$−*Si*($CH_3$)$_2$−O), δ 3.4 (*Si*($CH_3$)$_3$), δ −20.8/−21.7 (O−*Si*(CH_3)$_2$−O). Size exclusion chromatography was performed in tetrahydrofuran with a UV detection (see ref 14 for details) using a polystyrene calibration curve: $\overline{M}_n$ = 1000 g/mol, $I_p = 1.1$.

FTIR Spectroscopy. Infrared spectra were recorded at room temperature on a Perkin-Elmer FTIR 1760 spectrometer in KBr cells of 0.01−5 cm path lengths. Hexane (SDS), carbon tetrachloride (SDS), and dichloromethane (SDS) stored on molecular sieves were used. A "background" spectrum of pure solvent was subtracted, and after deconvolution (using a Lorentzian band shape), the areas of the free carbonyl band (1740 cm^{-1}) and hydrogen-bonded carbonyl band (1690 cm^{-1}) were measured (see Supporting Information). Molar extinction coefficients of free (ϵ_f) and hydrogen-bonded (ϵ_b) carbonyl bands were determined graphically[16] for **1a, 1b**, **1c**, and **3** assuming that they all have the same molar extinction coefficients. The results are summarized in Table 1.

Table 1. Molar Extinction Coefficients of Free (ϵ_f) and Hydrogen-Bonded (ϵ_b) Carbonyl Bands for 1a, 1b, 1c, and 3 at Room Temperature

coefficient	CH_2Cl_2	CCl_4	hexane
ϵ_f (L mol^{-1} cm^{-2})	23 300 ± 2000	14 900 ± 2500	9400 ± 4400
ϵ_b (L mol^{-1} cm^{-2})	29 500 ± 2000	29 300 ± 1000	25 800 ± 500

Viscosimetry. Capillary viscosimetry was performed at 25 ± 0.1 °C with a Cannon-Manning semi-microviscometer. Solutions in hexane (SDS, stored on molecular sieves) were prepared 1 day before the measurements and filtered on Millex membranes (Φ = 0.45 μm).

Nonlinear Curve Fitting. The association constant *K* was determined by nonlinear least-squares curve fitting of FTIR data with Microsoft Excel software.[17]

3. Validation of the Model

3.1. Qualitative Description. Figure 2 shows the reduced specific viscosity (η_{sp}/c) of solutions of diacid **1b** and diester **2b** versus concentration (*c*) in hexane at 25 °C. In the concentration range examined ($2 < c < 60$ g/L), two regimes can be identified:

(i) At high concentrations ($c > 10$ g/L), the viscosity of diacid **1b** is much higher than the viscosity of diester **2b**. This difference can only be due to the association of the chain ends of **1b**. Indeed, FTIR spectroscopy shows (Figure 3) that most acid groups are dimerized (1690 cm^{-1}) and that only a very small fraction of acid groups are unassociated (1740 cm^{-1}). Two basically different forms of supramolecular architectures can be envisaged: if the only interaction involved is dimerization of the acid groups, then chain extension would occur and a supramolecular polymer would be obtained. On the other hand, if dimerization of the acid groups occurs together with aggregation of polar chain ends, then micellar structures would be obtained. On the basis of the fact that para-substituted benzoic acids are known to form dimers in solution,[18] we make the assumption that diacid **1b** forms only supramolecular polymers. We will show that the quantitative model based on this assumption is in full agreement with experimental results from FTIR spectroscopy (see below), static and dynamic light scattering,[19] and viscosimetry[20] of dilute solutions. We can thus consider that at concentrations higher than 10 g/L **1b** is a "reversible" polymer, the molecular weight of which is much higher than that of **2b**.

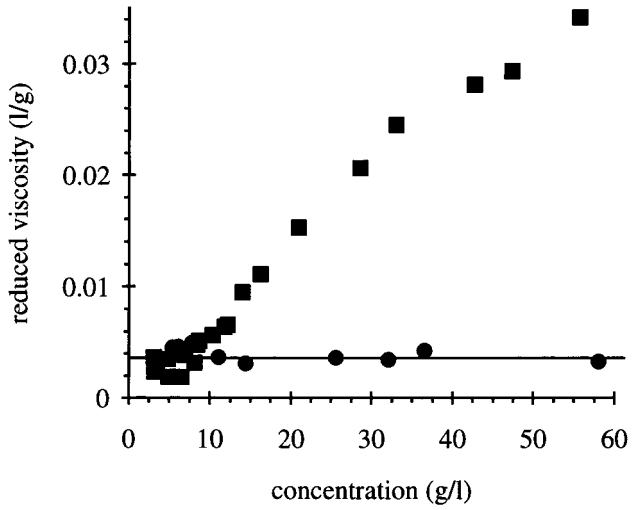


Figure 2. Reduced specific viscosity of diacid **1b** (■) and diester **2b** (●) measured in hexane at 25 °C.

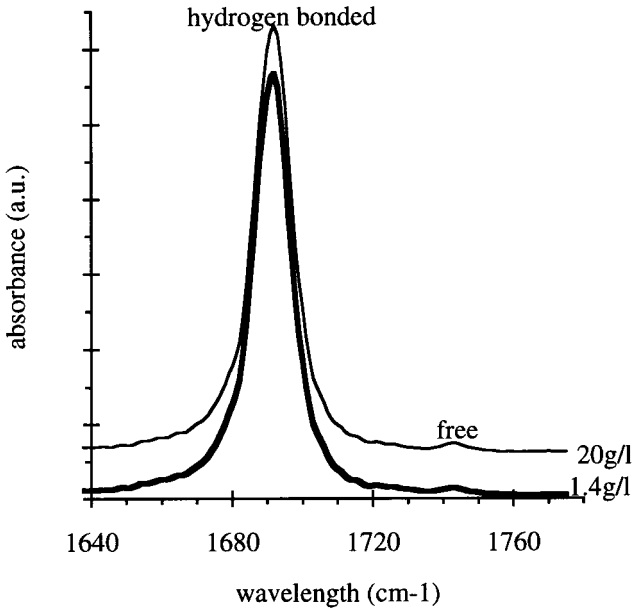


Figure 3. FTIR spectra of the carbonyl region of solutions of diacid **1b** in hexane at room temperature at 20 g/L (—) and 1.4 g/L (—) (path length: 0.14 and 0.5 mm, respectively).

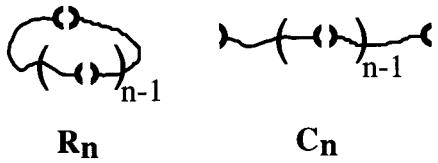
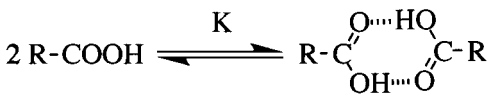


Figure 4. Schematic representation of supramolecular polymers.

(ii) At low concentrations ($c < 10$ g/L), the viscosities of diacid **1b** and diester **2b** are similar (Figure 2). Since Figure 3 shows that even at 1.4 g/L acid groups are still mainly dimerized, the low viscosity can only be explained if intramolecular association is taking place.[21] Ring formation in noncovalent reversible polymers has already been theoretically described[22] and demonstrated in the case of telechelic polystyrene chains coupled by acid−base interactions.[23]

To describe the association of diacid **1b**, we thus have to take into account two sets of species: linear chains C_n and rings R_n of degree of association n ($n \geq 1$) (Figure 4).

3.2. Quantitative Model. a. Chain Fraction. Let us first express the concentration of linear chains of degree of association n, $[C_n]$. Consider the dimerization equilibrium (1) of acid functions with K being the corresponding constant: $K = [A_b]/2[A_f]^2$ where $[A_f]$ and $[A_b]$ are the concentrations of free and bound acid functions, respectively.



(1)

If the association of acid groups is independent of the length of the chain, then the association constant of equilibrium (2) is $4K$ because of the difunctionality of C_1 and C_{n-1}.

$$C_1 + C_{n-1} \overset{4K}{\rightleftharpoons} C_n \tag{2}$$

Consequently, $[C_n] = 4K[C_1][C_{n-1}]$, and thus we find

$$[C_n] = (4K)^{n-1}[C_1]^n \quad (n \geq 1) \tag{3}$$

Relation 3 gives the whole distribution of linear chains as a function of K and $[C_1]$. This expression is of course equivalent to the classical Flory distribution valid in the case of polycondensation.[24]

b. Ring Fraction. Jacobson and Stockmayer have developed a theory of cyclization at equilibrium[25] which has been experimentally confirmed for several different systems.[26] On the basis of four assumptions—(i) all rings are strainless, (ii) the end-to-end distances of linear chains obey Gaussian statistics, (iii) the probability of ring formation is governed by the fraction of all conformations for which the ends coïncide, and (iv) the reactivity of each terminal functional group is independent of chain length—the equilibrium concentration of rings of degree of association n can be expressed as

$$[R_n] = B\frac{x^n}{n^{2.5}} \tag{4}$$

where x is the conversion in the chain fraction and B is a constant. With our notations

$$x = 1 - \frac{\sum_1^\infty [C_n]}{\sum_1^\infty n[C_n]} \tag{5}$$

Substituting eq 3 in eq 5 yields

$$x = 4K[C_1] \tag{6}$$

Consequently

$$[R_n] = B\frac{(4K[C_1])^n}{n^{2.5}} \tag{7}$$

Relation 7 gives the whole distribution of cyclics as a function of K, B, and $[C_1]$.

c. Mass Balance. The concentration of free chains $[C_1]$ is determined by the mass balance equation:

$$2\sum_1^\infty n[C_n] + 2\sum_1^\infty n[R_n] = [A_0] \tag{8}$$

where $[A_0]$ is the total acid concentration. Substituting eq 3 and eq 7 in eq 8 yields

$$\frac{[C_1]}{(1-4K[C_1])^2} + B\sum_1^\infty \frac{(4K[C_1])^n}{n^{1.5}} = \frac{[A_0]}{2} \tag{9}$$

If the two constants K and B are known, eq 9 can be solved numerically (see Appendix 2) to determine $[C_1]$. Then, using relations 3 and 7, the whole distributions of chains ($[C_n]$, $n \geq 1$) and rings ($[R_n]$, $n \geq 1$) are known.

3.3. Application of the Model to Diacid 1b in Dichloromethane. a. Determination of *K*. It is possible to determine independently the value of the dimerization constant K on a monofunctional oligomer such as **3** because in this case, no cyclization is possible. Combining the mass action law (eq 10) and the mass balance equation (eq 11) yields the fraction of free acid groups (eq 12) for a solution of **3** having a total acid concentration $[A_0]$.

$$K = [A_b]/2[A_f]^2 \tag{10}$$

$$[A_0] = [A_b] + [A_f] \tag{11}$$

$$\frac{[A_f]}{[A_0]} = \frac{\sqrt{1+8K[A_0]}-1}{4K[A_0]} \tag{12}$$

Figure 5 shows the fraction of free acid functions versus concentration for solutions of **3** in dichloromethane determined experimentally from FTIR measurements. Fitting eq 12 to the experimental points yields a value of $K = 260 \pm 50$ L/mol for the dimerization in dichloromethane. This value is compatible with literature values of benzoic acid dimerization in several nonpolar solvents.[16]

b. Determination of *B*. Figure 5 also shows the fraction of free acid functions versus concentration for solutions of diacid **1b** in dichloromethane. This free acid fraction is clearly lower than for monoacid **3**, which

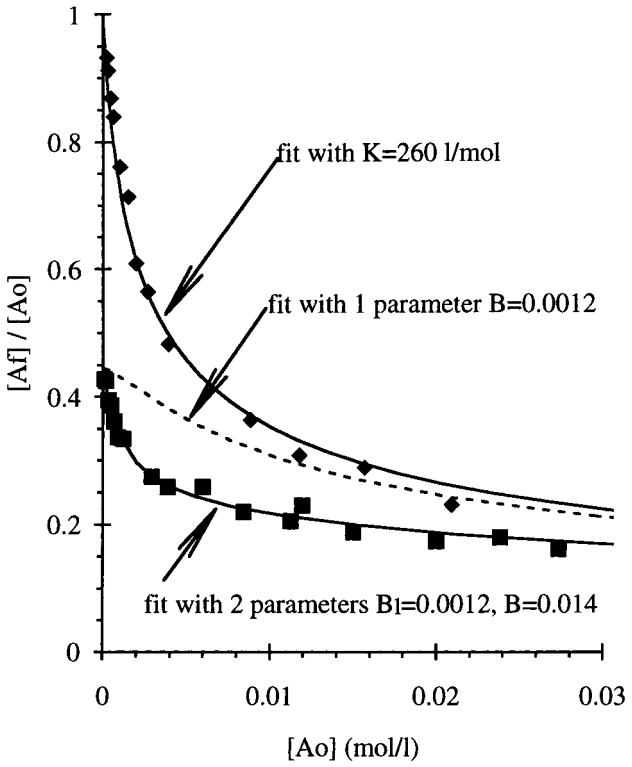


Figure 5. Fraction of free acid groups for diacid **1b** (■) and monoacid **3** (◆) versus concentration in dichloromethane at room temperature.

qualitatively confirms the presence of significant amounts of cyclics. In particular, at low total acid concentrations, the free acid fraction does not tend toward 1 but toward a lower value $L = 0.45$. This limit L is directly related to the cyclic fraction. Indeed, at high dilution, the only two species present are the cyclic monomer R_1 and the linear monomer C_1. Consequently,

$$L = \frac{[C_1]}{[R_1] + [C_1]} \tag{13}$$

and using eq 7 yields

$$L = \frac{1}{1 + 4KB} \tag{14}$$

and then $B = 1.2 \times 10^{-3}$ mol/L.

With the values of K and B thus determined, it is possible to calculate $[C_1]$ with eq 9 and the free acid fraction of diacid **1b** in dichloromethane with

$$\frac{[A_f]}{[A_0]} = \frac{2\sum_1^\infty [C_n]}{[A_0]} = \frac{2[C_1]}{(1 - 4K[C_1])[A_0]} \tag{15}$$

The result is plotted in Figure 5 (curve labeled "fit with 1 parameter $B = 0.0012$"). The trend shown by the theoretical curve is in qualitative agreement with experimental data, but the overall cyclic concentration is underestimated. This can be due to the fact that relation 4 has been established with the assumption that the chains follow Gaussian statistics,[25] which means that the chains have to be long enough for relation 4 to be valid. Such a discrepancy between Jacobson−Stockmayer theory and experimental data is usually observed for short cyclics.[26]

To take this point into account, we can use two cyclization constants: the first one (B_1) for the monomer which does not obey Gaussian statistics and the second one (B) for all other species which are supposed to obey Gaussian statistics.[27] Relation 7 should then be replaced by

$$[R_1] = 4KB_1[C_1] \quad \text{and} \quad [R_n] = B\frac{(4K[C_1])^n}{n^{2.5}}, \quad n > 1 \tag{7′}$$

and eq 9 by

$$\frac{[C_1]}{(1 - 4K[C_1])^2} + 4KB_1[C_1] + B\sum_2^\infty \frac{(4K[C_1])^n}{n^{1.5}} = \frac{[A_0]}{2} \tag{9′}$$

Values of the constants B_1 and B are adjusted so that experimental and calculated values of free acid fraction are in agreement (see Appendix 1). The best fit was obtained with $B_1 = 1.2 \times 10^{-3}$ mol/L and $B = 14 \times 10^{-3}$ mol/L. Then eq 9′ is solved to calculate $[C_1]$ as a function of $[A_0]$ (see Appendix 2), and finally, the free acid fraction is calculated according to eq 15. It can be seen (Figure 5) that the fit is excellent over the whole concentration range. This result implies that it is possible to consider that the cyclization of n-mers (for $n \geq 2$) follows Gaussian statistics, but the cyclization of the monomer is significantly hindered because $B/B_1 = 12$.

To test this last point, diacids with shorter (**1a**) or longer (**1c**) siloxane backbones were characterized. Indeed, if cyclization of monomer **1b** is significantly hindered, then cyclic monomer formation in the case of shorter diacid **1a** must be even more hindered, but cyclic monomer formation in the case of longer diacid **1c** must be less hindered.

3.4. Influence of the Number of Siloxy Units. a. Diacid 1a. Figure 6 shows the experimentally determined fraction of free acid groups versus concentration for solutions of **1a** in dichloromethane. Using the same association constant ($K = 260$ L/mol), these points were fitted as previously (see Appendix 1), and the result is also plotted in Figure 6. An excellent fit is again obtained with the following cyclization constants: $B_1 = 0.15 \times 10^{-3}$ mol/L and $B = 7 \times 10^{-3}$ mol/L. In this case, $B/B_1 = 44$, which means that cyclic monomer (R_1) formation is highly hindered. Its formation likely involves a large strain. This conclusion is coherent with the very high fraction of free acid groups obtained at low concentrations ($L = 0.85$), which means that the cyclic monomer R_1 is less stable than the linear monomer C_1.

b. Diacid 1c. The results for the longer diacid **1c** are also shown in Figure 6. Again, using the same association constant ($K = 260$ L/mol), it is possible to obtain an excellent fit with cyclization constants $B_1 = 1.4 \times 10^{-3}$ mol/L and $B = 4 \times 10^{-3}$ mol/L. In this case, $B/B_1 = 3$, which means that the cyclic monomer is indeed less hindered than in the case of diacid **1b**.

Results for the three diacids are summarized in Table 2. They show that the shorter the siloxane chain (m), the more hindered cyclic monomer formation (B/B_1 is larger). Table 2 also shows that the influence of m on B is not simple because B increases in the order **1c** ($m =$

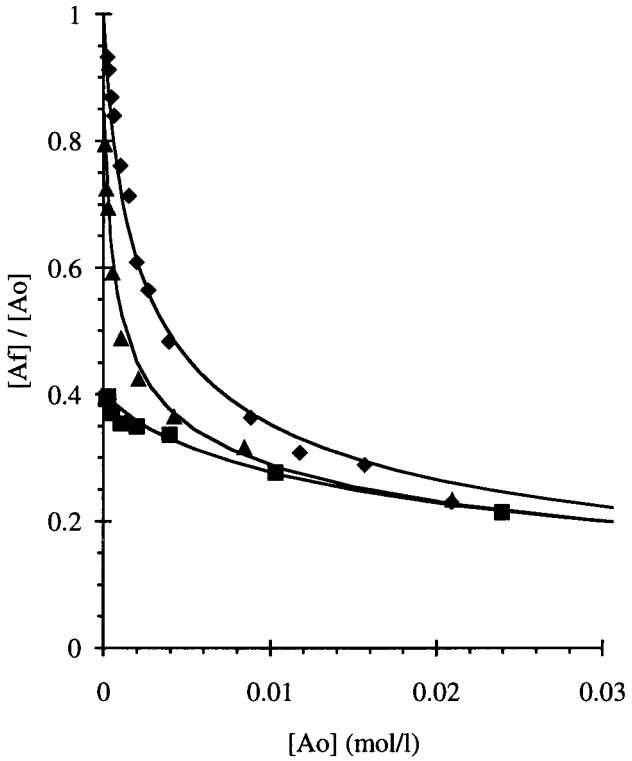


Figure 6. Fraction of free acid groups for diacids **1a** (▲), **1c** (■), and monoacid **3** (◆) versus concentration in dichloromethane at room temperature.

Table 2. Association Constant (*K*) and Cyclization Constants (B_1 and B) for Diacids in Dichloromethane

diacid	m	K (L/mol)	B_1 (10^{-3}mol/L)	B (10^{-3}mol/L)	B/B_1
1a	7	260 ± 50	0.15 ± 0.05	7 ± 2	44 ± 20
1b	13	260 ± 50	1.2 ± 0.2	14 ± 2	12 ± 4
1c	22	260 ± 50	1.4 ± 0.2	4 ± 2	3 ± 2

22) < **1a** (m = 7) < **1b** (m = 13). This behavior can be explained by the fact that B depends on two parameters: ν (the number of chain atoms in **1**) and b (which measures the average stiffness of **1**) through relation 16.[25]

$$B = \left(\frac{3}{2\pi\nu}\right)^{3/2} \frac{1}{2b^3} \qquad (16)$$

In the present case, increasing m increases ν but decreases b because the siloxane spacer is more flexible than the propyleneoxybenzoic acid chain ends. As a consequence, B can either increase or decrease when m increases.

Next, the influence of solvent was investigated to further test our model.

3.5. Influence of the Solvent. Several studies of the equilibrium cyclization of poly(dimethylsiloxane)[28] have shown that the nature of the solvent has a small influence on values of cyclization constants. Changing from a thermodynamically good solvent to a Θ solvent has been shown to affect the cyclization constant by a factor of 1.5 only.[28]

In our case, the three solvents investigated are good solvents, so to a first approximation, we can consider that cyclization constants are the same.

a. Carbon Tetrachloride. Fraction of free acid groups for **3** and **1b** in carbon tetrachloride was measured by FTIR at different concentrations (Figure 7). The association constant was determined to be K = 4300 ± 1300 L/mol by fitting the data of monoacid **3**. Then, based on the cyclization constants previously determined in dichloromethane, a theoretical curve for diacid **1b** in carbon tetrachloride was plotted (Figure 7). The good agreement with experimental data is gratifying, because in this case (**1b** in carbon tetrachloride), no fitting parameter is used.[29]

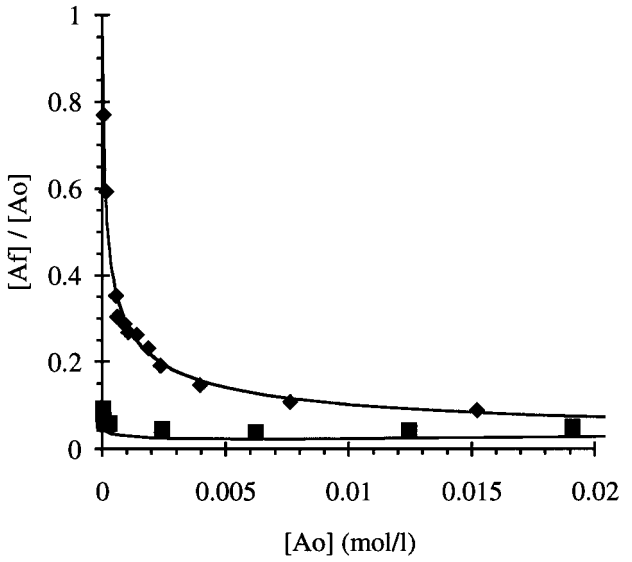


Figure 7. Fraction of free acid groups for diacid **1b** (■) and monoacid **3** (◆) versus concentration in carbon tetrachloride at room temperature.

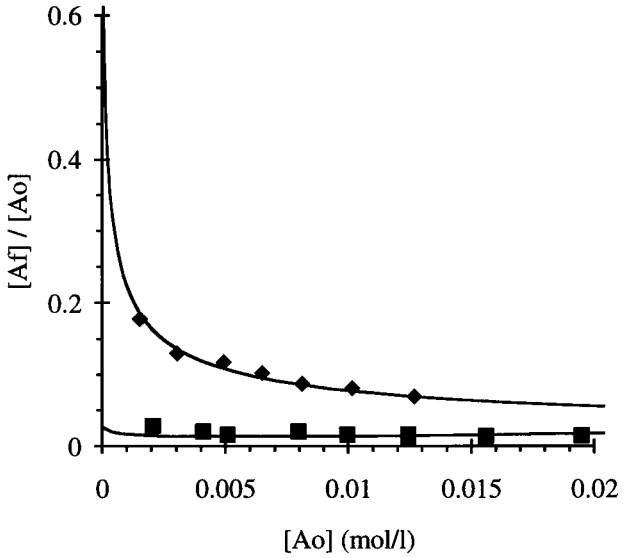


Figure 8. Fraction of free acid groups for diacid **1b** (■) and monoacid **3** (◆) versus concentration in hexane at room temperature.

b. Hexane. The fraction of free acid groups for **3** and **1b** in hexane was measured by FTIR at different concentrations (Figure 8). Again, the association constant was determined by fitting the data of monoacid **3**: K = 7700 ± 5000 L/mol. Then, the same cyclization constants as in dichloromethane and carbon tetrachloride were used to draw a theoretical curve for diacid **1b** in hexane (Figure 8). The agreement with experiment is also very good in this case.

Table 3 sums up the values of the parameters used. Since the association constants (K) are determined from independent data relative to monoacid **3**, we can see that only two adjustable parameters (B_1 and B) are

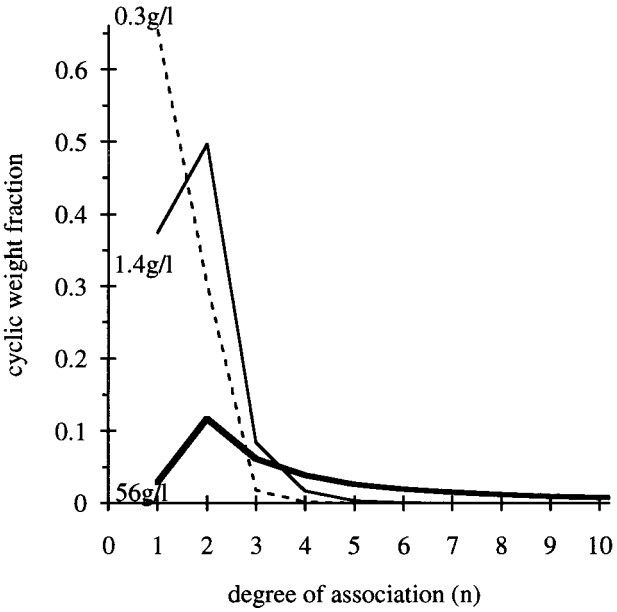


Figure 9. Calculated molecular weight distribution of the cyclic fraction of diacid **1b** for several concentrations (0.3 g/L, - - -; 1.4 g/L, —; 56 g/L, **—**) in hexane at room temperature.

Table 3. Association Constant (*K*) and Cyclization Constants (B_1 and *B*) for Diacid 1b in Several Solvents

solvent	*K* (L/mol)	B_1 (10^{-3}mol/L)	*B* (10^{-3}mol/L)
CH_2Cl_2	260 ± 50	1.2 ± 0.2	14 ± 2
CCl_4	4300 ± 1300	1.2 ± 0.2	14 ± 2
hexane	7700 ± 5000	1.2 ± 0.2	14 ± 2

necessary to correctly describe three different curves corresponding to diacid **1b** in dichloromethane, carbon tetrachloride, and hexane.

4. Molecular Weight Distributions Derived from the Model

In this last part, we now use the experimentally determined parameters *K*, *B*, and B_1 to calculate the molecular weight distributions of cyclic and linear chains in order to vizualise the effect of concentration, structure of the monomer, and polarity of the solvent.

4.1. Molecular Weight Distributions of Diacid 1b in Hexane. Figure 9 shows the distribution of cyclics for several concentrations of **1b** in hexane. As expected, at very low concentrations ($c \leq 0.3$ g/L), the main species are cyclic monomers R_1. However, in the concentration range $1.4 \leq c \leq 56$ g/L, the cyclic dimers R_2 have the largest weight fraction: the main species are not R_1 because of ring strain. Figure 9 also shows that, whatever the overall concentration, the content of cyclics of degree of association higher than 10 is very low.

In the case of linear chains (Figure 10), the increase in concentration induces an increase of both the overall weight fraction (the area under the curve increases) and the average degree of association (the maximum of the curve shifts to the right).

4.2. Influence of the Length of the Diacid. It has been shown in the previous section that the cyclization constants B_1 (for monomers) and *B* (for *n*-mers) depend strongly on the number of dimethylsiloxy units of the diacids **1a, 1b**, and **1c**. The consequence on the cyclic weight fraction in hexane is shown in Figure 11. In general, reducing the length of the monomer is expected

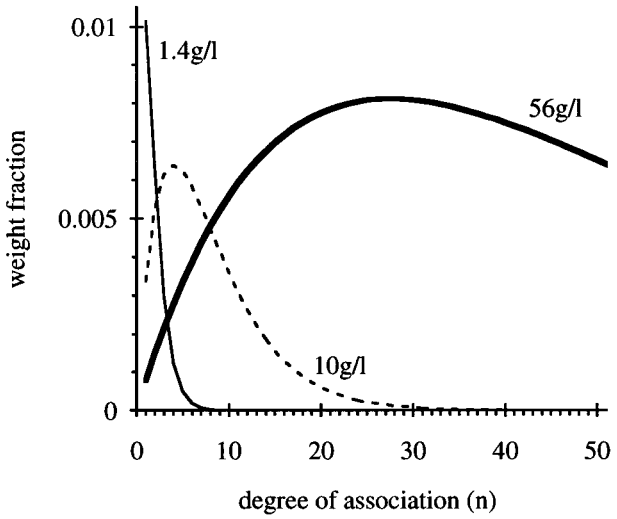


Figure 10. Calculated molecular weight distribution of the linear fraction of diacid **1b** for several concentrations (1.4 g/L, —; 10 g/L, - - -; 56 g/L, **—**) in hexane at room temperature.

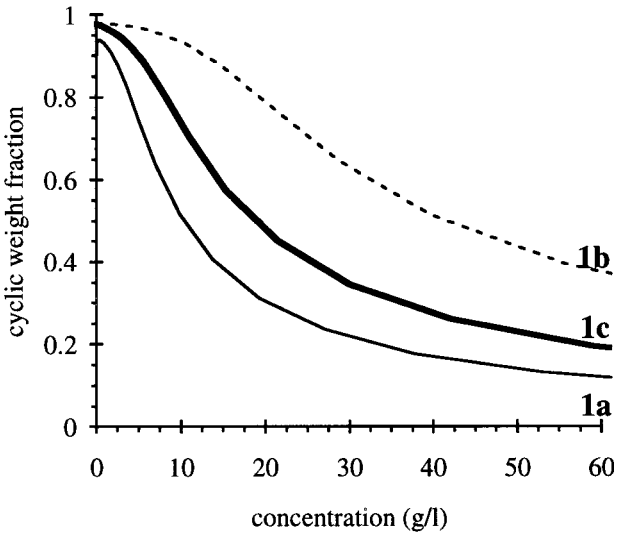


Figure 11. Calculated cyclic weight fraction versus concentration of diacids **1a** (—), **1b** (- - -), and **1c** (**—**) in hexane at room temperature.

to increase the cyclic content because of the increase in the probability of ring closure. Indeed, diacid **1b** has a higher cyclic content than **1c**, but reducing further the length of the monomer from **1b** to **1a** actually decreases the cyclic content because of the higher strain in cyclic monomers R_1.

Figure 12 shows that the average molecular weight of linear chains increases much more with concentration than in the case of cyclics. Moreover, the influence of the length of the diacid on molecular weight of the supramolecular chains is not trivial: below 50 g/L, the order is **1b** < **1a** < **1c**. This result is the consequence of the competition between different factors. The increase in the number of dimethylsiloxy units has several effects: First, it obviously increases the weight of the repeat unit and thus the weight of the supramolecular chains. Second, it decreases the molar concentration of associating groups for a given weight concentration, so that the degree of association is reduced because of the mass action law. Finally, it has an effect on the cyclization constants and thus on the cyclic weight fraction. An increase in cyclic content lowers the concentration in the chain fraction, and again because of

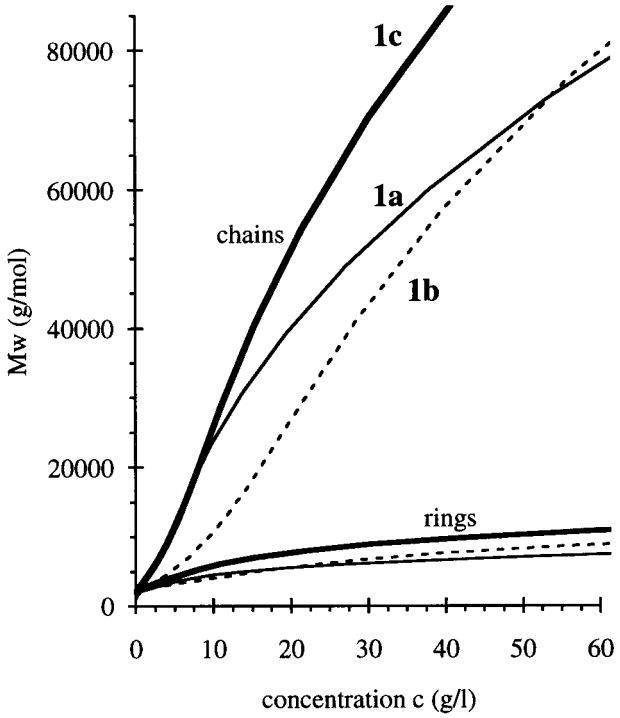


Figure 12. Calculated weight-average molecular weight of the cyclic and linear fractions of diacids **1a** (—), **1b** (- - -), and **1c** (—) versus concentration in hexane at room temperature.

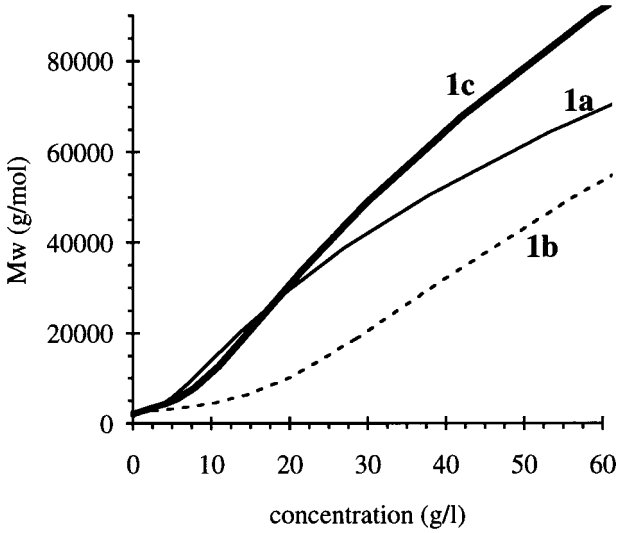


Figure 13. Calculated weight-average molecular weight (linear + cyclic fractions) of diacids **1a** (—), **1b** (- - -), and **1c** (—) versus concentration in hexane at room temperature.

mass action, it decreases the degree of association of the linear chains. The delicate balance between these different effects is illustrated by the fact that, unlike in hexane, in dichloromethane the order for the molecular weight of linear chains is changed to **1a** < **1b** < **1c** (data not shown).

If we consider now the average molecular weight of the whole system consisting of chains and cyclics (Figure 13), we see that, if c > 20 g/L, $\overline{M}_W$ increases in the order **1b** < **1a** < **1c**, but if $c \approx 10$ g/L, the order is changed to **1b** < **1c** < **1a**. This last point again reveals the large influence of cyclization.

4.3. Influence of the Solvent. Figure 14 shows the cyclic weight fraction for diacid **1b** in several solvents: the lowest cyclic content is present in the most polar

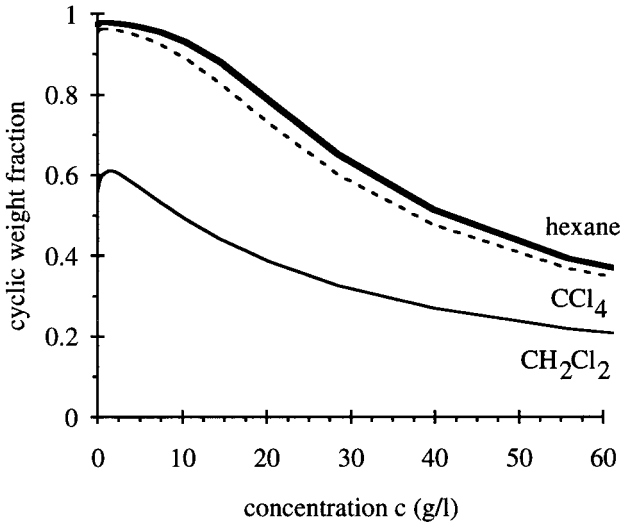


Figure 14. Calculated cyclic weight fraction versus concentration of diacid **1b** in hexane (—), carbon tetrachloride (- - -), and dichloromethane (—) at room temperature.

solvent (dichloromethane). The reason is that increasing the polarity of the solvent reduces the association constant of the acid group and thus transforms some associated acid groups into free acid groups. This transformation in the case of cyclics necessarily produces some linear chains.

This effect of solvent is remarkably different from the effect of solvent in ring−chain equilibration in the case of covalent polymers. For covalent polymers, the solvent has a limited influence on the cyclization constant, and the conversion of the reaction is usually high, so that, whatever the solvent, there is a concentration below which only cyclics are formed.[25] Here, the solvent imposes the conversion through the association constant so that if the association is not strong enough, linear chains are present even at infinite dilution.

The influence of the polarity of the solvent is also particularly striking on the average molecular weight of the linear chains (Figure 15). At 50 g/L, $\overline{M}_W$ for the linear chains is 5 times larger in hexane than in dichloromethane. The influence on the average molecular weight of cyclics is more limited.

5. Conclusion

We have shown that diacids **1** can be considered to form linear and cyclic supramolecular polymers in solution. A quantitative model based on Jacobson−Stockmayer cyclization theory is proposed. This model faithfully describes the variation of the free acid fraction with concentration in three different solvents.

The application of this model makes it possible to precisely describe the molecular weight distributions of cyclic and linear supramolecular polymers in solution. In particular, the structure of the associating molecules is shown to influence significantly and in a complex manner the average molecular weight of the supramolecular polymers through the content of cyclics. The polarity of the solvent is also responsible for large changes in ring fraction and molecular weight of supramolecular polymers.

Concerning the ring−chain equilibrium, it is worthwhile stressing the difference of behavior between these supramolecular polymers and classical covalent poly-

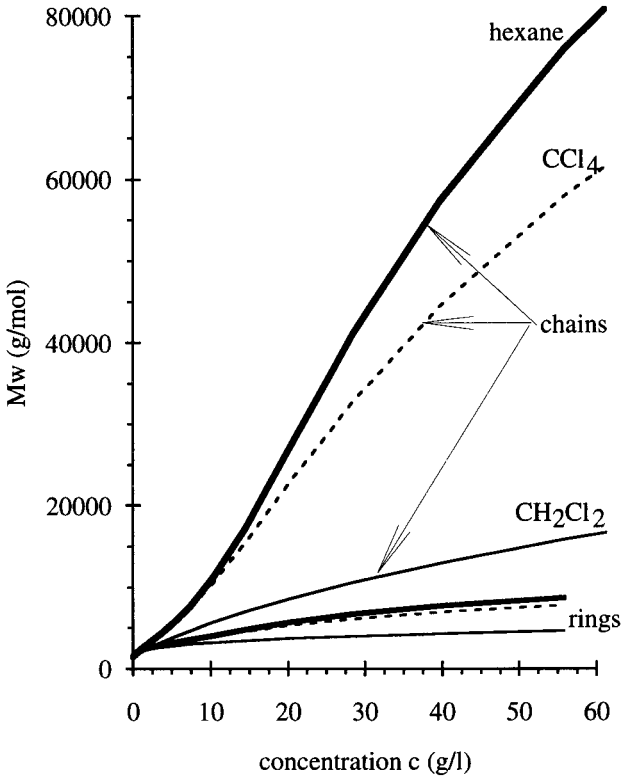


Figure 15. Calculated weight-average molecular weight of the cyclic and linear fractions of diacid **1b** versus concentration in hexane (—), carbon tetrachloride (- - -), and dichloromethane (—) at room temperature.

mers. In the former case, selection of the solvent and of the concentration fixes the cyclic fraction and the molecular weight, whereas in the latter case, chain-end conversion in the linear fraction can be fixed independently of solvent nature and concentration.

This work shows that the precise description of the behavior of supramolecular polymers in solution requires the knowledge not only of the association constant but also of the cyclization constant of the system.

Appendix 1. Adjustment of the Parameters B_1 and B

For each solution of diacid **1** in dichloromethane, the concentration of the linear monomer $[C_1]$ can be calculated through relation 15 because $[A_f]/[A_0]$ is measured and K is known. Then B_1 and B are adjusted (by nonlinear least-squares curve fitting) to minimize expression 17, where the summation is made over experimental data points.

$$\Sigma\left(\frac{[C_1]}{(1-4K[C_1])^2}+4KB_1[C_1]+B\sum_2^{\infty}\frac{(4K[C_1])^n}{n^{1.5}}-\frac{[A_0]}{2}\right)^2 \quad (17)$$

Alternatively, B_1 can be determined by extrapolation to zero concentration in Figure 5 (see section 3.3), and only B is determined by nonlinear curve fitting to minimize expression 17. The results obtained by both methods are the same.

Appendix 2. Solution of Eqs 9 and 9′

Equation 9′ can be expressed as

$$\frac{[C_1]}{(1-4K[C_1])^2}+4K(B_1-B)[C_1]+B\varphi(4K[C_1])-\frac{[A_0]}{2}=0 \quad (18)$$

with

$$\varphi(4K[C_1])=\sum_1^{\infty}\frac{(4K[C_1])^n}{n^{1.5}} \quad (19)$$

Of course, eq 9 is obtained if $B_1 = B$. With fixed values for K, B, B_1, and $[A_0]$ parameters, it is straightforward to solve eq 18 numerically (for instance with the Solver function provided in Microsoft Excel software) as long as the series 19 can be evaluated. For low values of $4K[C_1]$ ($4K[C_1] < 0.4$), this series is 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 another expression has to be used.[30] Truesdell et al.[30] showed that expressions 19 and 20 are equivalent:

$$\varphi(4K[C_1])=\Gamma(-0.5)\sqrt{-\ln(4K[C_1])}+\sum_{n=0}^{\infty}\zeta(1.5-n)\frac{(\log(4K[C_1]))^n}{n!} \quad (20)$$

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:[31] $\Gamma(-0.5) = -3.5449$, and values for $\zeta(1.5 - n)$, $n = 0-10$, are provided in Table 4.

Table 4. Values of the Riemann Zeta Function

n	$\zeta(1.5-n)$	n	$\zeta(1.5-n)$	n	$\zeta(1.5-n)$
0	2.6120	4	0.008 517	8	0.002 747
1	−1.4600	5	0.004 441	9	0.003 269
2	−0.2079	6	−0.003 092	10	−0.004 416
3	−0.02549	7	−0.002 671		

Expression 20 converges rapidly if $4K[C_1] \geq 0.4$, so that summing the first 10 terms is a very good approximation.

Supporting Information Available: Areas of the free and hydrogen-bonded carbonyl bands of **1a**, **1b**, **1c**, and **3** measured by FTIR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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