Models for the Trapping of Cyclic Poly(dimethylsiloxane) (PDMS) Chains in PDMS Networks

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ABSTRACT: Two theoretical methods were developed to model the trapping of poly(dimethylsiloxane) (PDMS) rings present at the time of network formation by the end-linking of PDMS chains. Monte Carlo methods were first used to generate representative samples of cyclics having degrees of polymerization (DP) of 20, 40, 75, 120, and 200. Criteria were then developed to determine whether a particular ring would be topologically trapped by one or more network chains. The more realistic model yielded values for the percent trapped that were in excellent agreement with experiment over the entire DP range.

Introduction

In recent years, the study of cyclic oligomers and polymers has gained renewed interest in both experimental and theoretical investigations.[1] The wide range of systems studied has included structures as diverse as cyclic ethers, elemental sulfur, siloxanes of various types, styrene, peptides, and deoxyribonucleic acid. This increased interest is somewhat ironic in that what we now know to be (linear) polymers were originally believed by many to be cyclic species, a judgment based mainly on difficulties in detecting end groups.[2] One particular (and the most widely investigated) siloxane polymer in this regard, poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$], is the subject of the present investigation.

Siloxane polymers possess, under proper equilibrating conditions, a propensity to form rings containing as few as six skeletal bonds (degree of polymerization DP of three) to as many as several hundred bonds.[3] Recent advances in separation techniques have made it possible to collect relatively narrow molecular weight fractions of these PDMS ring species in gram quantities. The physical properties of these rings have been studied extensively, both in solution and in the bulk for a wide variety of thermodynamic and configuration-dependent properties including surface characteristics,[4] glass transition temperatures,[5] dipole moments,[6,7] radii of gyration,[8] diffusion coefficients,[9] and neutron and X-ray scattering functions.[10]

Recent experiments[11,12] on the topological trapping of such cyclic PDMS species present at the time of network formation have provided an experimental basis and an incentive for developing theoretical models for the trapping process. In these experiments, a given amount of a particular cyclic with a narrow distribution of molecular weight, and thus of ring size, was mixed with hydroxyl-terminated PDMS (M_n 18000 g/mol). The mixtures typically consisted of approximately 0.15 weight fraction cyclics and 0.85 weight fraction linear chains. The end-linking was carried out by using the stoichiometric amount of tetraethylorthosilicate (TEOS) [$Si(OC_2H_5)_4$] necessary to produce on curing as ideal a network as possible, i.e., with a minimal number of network defects such as dangling ends. The resulting cross-linked samples were subsequently extracted, and the amount of cyclic species topologically trapped was determined. A network simultaneously prepared with the identical polymer/TEOS mixture was used as a blank to determine the amount of uncross-linked, and thus extractable, linear polymeric material in the cross-linked linear PDMS/TEOS/cyclic sample.[11,12] A schematic of the topological trapping on the molecular level is shown in Figure 1. Ring A will be extractable with solvent, whereas rings B, C, and D are topologically trapped within the network structure and thus are unextractable. The experiment described was performed for a wide variety of PDMS rings ranging from 30 to 512 skeletal bonds. The fractions of cyclic species trapped ranged from zero (30 bonds, DP = 15) to 94 wt % (512 bonds, DP = 256), with the dependence being a sigmoid-shaped curve, as shown in Figure 2. The estimated experimental error in the percent trapped was ±5%.

The question these experiments posed theoretically was whether it was possible to duplicate the trapping efficiency behavior through use of a realistic model.[13] Such a model would employ cyclic chains generated by using available configurational statistics derived for linear PDMS. Included would be an appropriate treatment of the cross section of the threading linear chain species, which must pass through the ring prior to being cross-linked into a three-dimensional network in order that the ring be trapped topologically within it.

The PDMS(linear)/PDMS(cyclic) system was particularly suitable for such an endeavor for two reasons. First, the experimental circumstance of having PDMS linear chain segments interacting with virtually identical cyclic PDMS segments minimizes any problems associated with microphase separation. Any possible separation brought about by slightly different Θ temperatures is minimized by the relatively low molecular weights of cyclic and linear species. This aspect, when coupled to the very high chain segment flexibility of siloxane chains, reinforces the validity of the assumption of an equilibrium distribution of chain segments which any model must have. Second, the large number of theoretical studies of PDMS chains, both linear and cyclic, provide a sufficient understanding of its configurational statistics necessary for applying Monte Carlo methods to the generation of representative sets of cyclic species. It also provides an excellent test of the applicability of statistical parameters, derived from Θ solution conditions, to the properties of the bulk amorphous state. This was predicted by Flory and has been verified to a large extent by theoretical agreement with experiment results for chain cyclization[14] and small-angle neutron scattering functions.[15,16]

Theoretical Models and the Method of Calculation of the Trapping Efficiency

Generation of Cyclic Chains. In order to study theoretically the average environment of the repeat units of a cyclic PDMS polymer chain, it was first necessary to generate a sufficient number of representative cyclic chains for a given degree of polymerization. Once this is accom-

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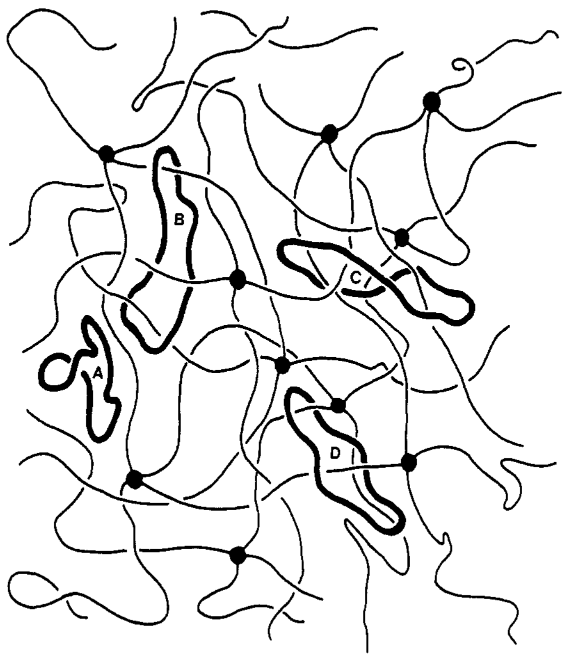

Figure 1. Schematic of the topological trapping of rings during network formation.

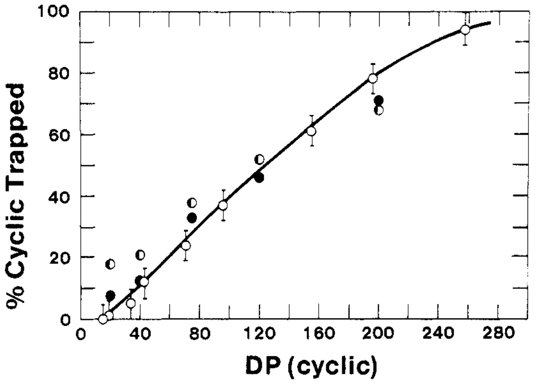

Figure 2. Experimental (○) and theoretical trapping efficiencies using model I (◐) and model II (●) for poly(dimethylsiloxane) (PDMS) rings trapped in a model PDMS network. The theoretical results are for a network chain cross-sectional radius of 3.5 Å.

plished, any model can be applied to them and subsequently the results properly averaged over the ensemble. This represents a standard technique for applying Monte Carlo methods to polymer systems.[17-19] Specifically, chain generation was accomplished by using conditional probability matrices derived by using the rotational isomeric state formalism.[18,19]

The chain statistics, chain geometry, and choice of rotational isomeric states were the same as used previously for PDMS and were all adopted for each DP of cyclic species. The chain statistics for PDMS are characterized by two statistical weight matrices within a second-order rotational isomeric states scheme.[20] These incorporate the first- and second-order statistical weight parameters representing the interactions dependent upon one or two consecutive backbone bond rotations, respectively. One matrix $\mathbf{U}'$ represents the interactions dependent upon rotations about the pair of backbone bonds spanning a silicon center, while another $\mathbf{U}''$ represents those interactions dependent upon the pair spanning an oxygen center. The matrices for PDMS are each of order 3, with the row and column indices corresponding to the rotational isomeric state conformations of the two bonds, which in this case are trans (t), gauche-plus (g$^+$), and gauche-minus (g$^-$). One first-order parameter σ and one second-order parameter ω are used, with energies $E(\sigma) = 0.85$ kcal/mol and $E(\omega) = 1.1$ kcal/mol.[20,21] For a temperature of 300 K, these energies yield values for σ and ω of 0.240 and 0.158, respectively. The form and resultant statistical weight matrices are given by

$$\mathbf{U}' = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} = \begin{bmatrix} 1 & 0.240 & 0.240 \\ 1 & 0.240 & 0 \\ 1 & 0 & 0.240 \end{bmatrix} \qquad (1a)$$

$$\mathbf{U}'' = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} = \begin{bmatrix} 1 & 0.240 & 0.240 \\ 1 & 0.240 & 0.038 \\ 1 & 0.038 & 0.240 \end{bmatrix} \qquad (1b)$$

The statistical weight matrices are then used in the generation of the set of a priori probabilities for all possible bond-pair conformations for the two types of backbone bond pairs.[21] It is also necessary to evaluate the a priori probabilities of the conformations accessible to a single backbone bond as well. The a priori probability of bonds $(i - 1)$ and (i) being in the conformations η and ξ, respectively, is given in a general form by

$$p(\eta,\xi;i - 1,i) = [\mathbf{U}_1\mathbf{U}_2\mathbf{U}_3...\mathbf{U}_{i-1}\hat{\mathbf{U}}_i\mathbf{U}_{i+1}...\mathbf{U}_{n-1}\mathbf{U}_n]/\mathbf{Z} \qquad (2)$$

where

$$\mathbf{U}_1 = [1\ 0\ ...\ 0]^{\mathrm{R}} \text{ (row)}$$
$$\mathbf{U}_n = [1\ 1\ ...\ 1]^{\mathrm{C}} \text{ (column)}$$

$$Z = \Pi_{i=1}^{n}\mathbf{U}_i$$

$$(i - 1)/i$$

$$\hat{\mathbf{U}}_i = \eta\begin{bmatrix} 0 & 0 & ... & 0 & 0 \\ \vdots & \vdots & ... & \vdots & \vdots \\ 0 & 0 & ... & u_{\eta\xi} & 0 \\ 0 & 0 & ... & 0 & 0 \\ 0 & 0 & ... & 0 & 0 \end{bmatrix}$$

The a priori probabilities for the conformations of a single backbone bond are obtained by retaining the appropriate column for bond (i) in the matrix $\hat{\mathbf{U}}_i$ rather than the single (η,ξ) element. It is assumed that the a priori conformational probability of a bond pair is independent of its location within the chain. This is an excellent assumption, except for the terminal or penultimate bonds of the chain. The resultant a priori probability matrix $\mathbf{P}$ for a single bond and matrices $\mathbf{P}'$ and $\mathbf{P}''$ representing bond pairs are then

$$\mathbf{P} = [0.734\ 0.132\ 0.132] \qquad (3a)$$

$$\mathbf{P}' = \begin{bmatrix} 0.517 & 0.109 & 0.109 \\ 0.109 & 0.023 & 0 \\ 0.109 & 0 & 0.023 \end{bmatrix} \qquad (3b)$$

$$\mathbf{P}'' = \begin{bmatrix} 0.522 & 0.107 & 0.107 \\ 0.107 & 0.022 & 0.004 \\ 0.107 & 0.004 & 0.022 \end{bmatrix} \qquad (3c)$$

The a priori probability matrix elements are used to evaluate the conditional probability matrix elements representing the two types of backbone bond pairs. A conditional probability is the probability that a particular bond (i) will be in the conformation ξ given that bond $(i - 1)$ is in the conformation η. The conditional probabilities $q(i - 1, i; \eta,\xi)$ were evaluated from

$$q(\eta,\xi;i - 1,i) = p(\eta,\xi;i - 1,i)/p(\eta;i - 1) \qquad (4)$$

using the elements of the a priori probability matrices given above. This procedure was performed for all possible conformations accessible to each of the backbone bond

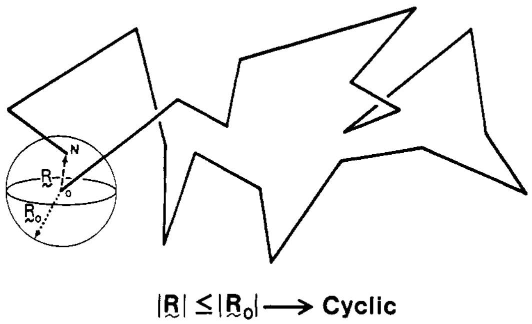

Figure 3. Schematic of the criterion for "cyclization" of a generated Monte Carlo chain.

pairs, and the results were collected in the corresponding pair of conditional probability matrices $\mathbf{Q}'$ and $\mathbf{Q}''$:

$$\mathbf{Q}' = \begin{bmatrix} 0.703 & 0.148 & 0.148 \\ 0.826 & 0.174 & 0 \\ 0.826 & 0 & 0.174 \end{bmatrix} \tag{5a}$$

$$\mathbf{Q}'' = \begin{bmatrix} 0.710 & 0.145 & 0.145 \\ 0.808 & 0.166 & 0.026 \\ 0.808 & 0.026 & 0.166 \end{bmatrix} \tag{5b}$$

It should be noted that whereas the nine elements in each of the **P** matrices sum to unity, it is the separate rows in the **Q** matrices that do so. This stems from the definitions of a priori and conditional probabilities since any pair of bonds must be in one of the possible sets of rotational isomeric states, whereas given the conformation of one bond, its successor must be in one of the conformational states available to it.

The final step was the actual generation of a Monte Carlo chain using the derived conditional probability matrices. The first bond of a chain was assumed to be in the trans conformation. A random number was generated and compared with the elements in the corresponding row in the proper conditional probability matrix for the first two bonds of the chain. Where it fell in the cumulative sum of the elements of that row determined what the conformation was of the second bond of the chain. The procedure was repeated for successive bonds of the chain, alternating between the two conditional probability matrices until a chain of the desired DP was determined. The row in the matrix repesenting bond (i) was determined by the conformation of the last generated bond ($i - 1$).

Once a chain of a given DP was generated by this method, its end-to-end distance was evaluated by established matrix techniques,[21] and if it was less than a certain value $|R_0|$, the chain was considered a cyclic and all of its coordinates put into a file for subsequent use. This criterion for cyclization is depicted in Figure 3. The procedure was repeated until enough cyclic chains were generated. A previous study on the theoretical dipole moments of cyclic PDMS chains indicated that a range $0 < |R_0| < 3.0$ Å is reasonable.[6] This criterion for cyclization was used for DP = 20, 40, and 75; however, it was relaxed to a cutoff of 4.5 Å for DP = 120 and 200 chains to improve the generation efficiency.

For a given cutoff radius, the number of chains meeting the cyclization criterion diminishes as the −2.5 power of the degree of polymerization. The time needed to evaluate the end-to-end distance is proportional to DP, thus the overall efficiency in terms of cyclics generated per unit time scales as the −3.5 power of DP. This limited the maximum DP for which a sufficient number of cyclics could be studied in a reasonable time. For example, only 48 DP = 200 cyclics were generated in over an hour of CPU time on a mainframe IBM computer, requiring over 400 000 linear chains to be generated. Increasing the cutoff distance by a factor of 1.5 increases the efficiency by a factor of 3.4 as it scales as the cube of this factor, i.e., the volume in which the closure condition is assumed to be met.

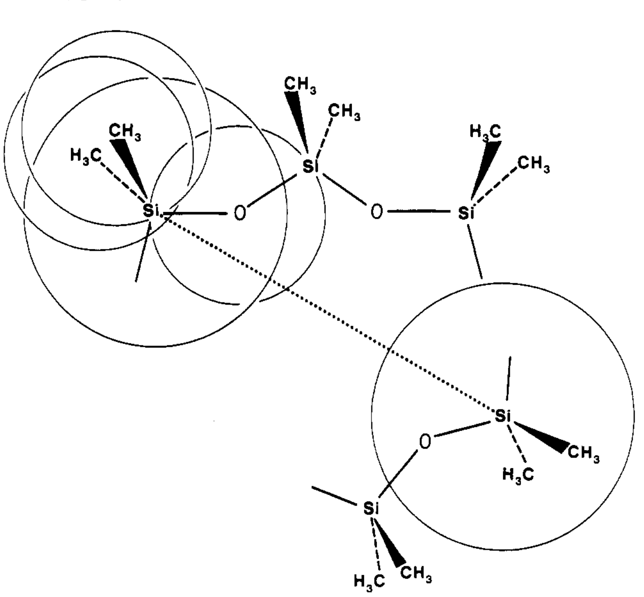

Figure 4. Schematic of the model I criterion for deciding whether a cyclic has a repeat unit free of conflicts, thus permitting the cyclic to be trapped.

Linear Chain Cross Section and van der Waals Radii. The only additional cyclic parameters required were the van der Waals radii of the chain constituents, i.e., the Si and O atoms and the CH_3 group. The values chosen for the quantities were 2.25, 1.74, and 2.10 Å, respectively. These correspond to the values employed in the widely used molecular mechanics package MM2P.

The only other necessary parameter was the cross section of the linear PDMS chain, which must thread through the cyclic species prior to cross-linking in order that the cyclic be trapped. The diameter can be estimated from the wide-angle X-ray scattering results for PDMS, from which a characteristic inter-chain distance of approximately 7.99 Å is obtained.[22] This may be viewed as corresponding to a chain radius of 4.0 Å. An alternate and equally justifiable method to determine this quantity is through the use of the bulk density. With the assumption that the chain repeat unit is cylindrical and of length 2.69 Å (which represents the average length of a repeat unit in a PDMS chain of maximum length),[23] the chain radius can be estimated to be 3.88 Å, in excellent agreement with the X-ray analysis. In the two models to be discussed and for which results will be presented, values of the chain radius in the range 3.5–4.0 Å were investigated.

Theoretical Models for Topological Trapping. Two models were developed for determining the fraction of cyclic species trapped as a function of ring size and will be referred to as model I and model II. For model I, the procedure was as follows. Each repeat unit of the cyclic was treated in turn as a possible location for threading. To prevent discarding of all configurations, the six repeat units on either side of it had to be ignored. This represents a serious flaw in the model and will be addressed further below. Each Si, O, and CH_3 center in that repeat unit was checked to determine whether the distance between it and other relevant centers in the cyclic was greater than the sum of their respective van der Waals radii plus the threading chain diameter which was taken to have a value of 7.0 Å. This criterion is shown schematically in Figure 4. If this criterion is met for *all* distances treated in the calculation, the particular repeat unit was considered to

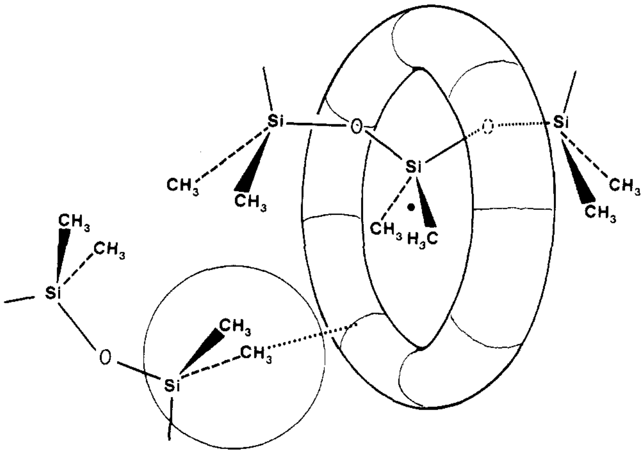

Figure 5. Schematic of the model II criterion for deciding whether a cyclic has a repeat unit free of conflicts, thus permitting the cyclic to be trapped.

be exposed. This procedure was repeated for each repeat unit in all the generated cyclic chains, and the results presented as the fraction of chains which had a given number of exposed repeat units. The weight fraction of chains trapped was then the fraction of chains which possessed one or more exposed repeat units.

It is a central assumption of both models that a chain which can be threaded will be; i.e., if a pathway is available for a chain having a specified chain diameter to pass unobstructed by one or more repeat units of a cyclic, then the linear chain will do so and upon cross-linking trap that cyclic. This assumption is both necessary and justified on the grounds that the total segment density will tend toward the bulk amorphous density from which the chain diameter was determined, and only one threading is necessary to trap a cyclic species. One complication could be penetration of a cyclic by only a loop from a linear chain. Whether this cyclic would be trapped would depend, of course, on whether the loop is itself penetrated by at least one other chain. In any case, this assumption must be added to the equally reasonable assumption that the statistics characteristic of linear PDMS chains are applicable to cyclic PDMS species, and thus the set of generated cyclic conformations is representative of the cyclics in the bulk.

The aspects of model II were similar to those of model I, except for the criterion for determining whether a given repeat unit was exposed. In model I, the internuclear distances in the cyclic were determined to see whether they were greater than the sum of the requisite van der Waals radii and the diameter chosen for the threading chain. In model II, a torus was centered around each repeat unit in the cyclic and *all* centers checked to see if they in any way impinged within the enclosed volume of the torus. This is shown schematically in Figure 5. The torus is an expeditious means for sensing the environment of a specified repeat unit to gauge whether a pathway is open to a linear chain, which could potentially follow a path represented by a segment of the torus and thus thread through the ring. The torus was centered at the midpoint of the triangle defined by the Si and two CH_3 centers, with the plane of the torus perpendicular to the segment connecting the two backbone oxygen centers on either side of the Si center. Also, the torus was allowed to "breathe" in its major axis from 7.0 to 9.0 Å to try to accommodate itself so as to avoid all contacts with all constituent atoms/groups of the cyclic under consideration. The radius of the torus was given a fixed value of either 3.5 or 4.0 Å. Model II avoided the need to exclude a significant fraction of the cyclic chain from the calculation of possible conflicts and for this reason represents a significant improvement over model I.

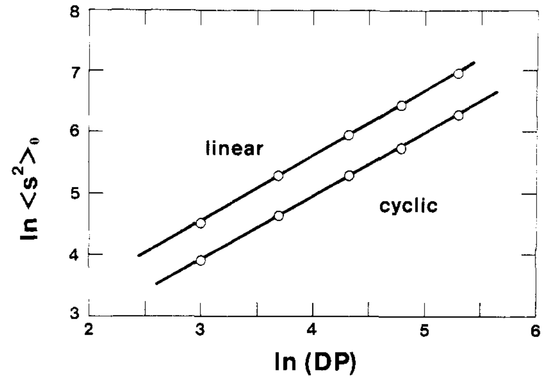

Figure 6. Plot of ln $\langle s^2\rangle_0$ for linear and cyclic PDMS chains as a function of ln (DP).

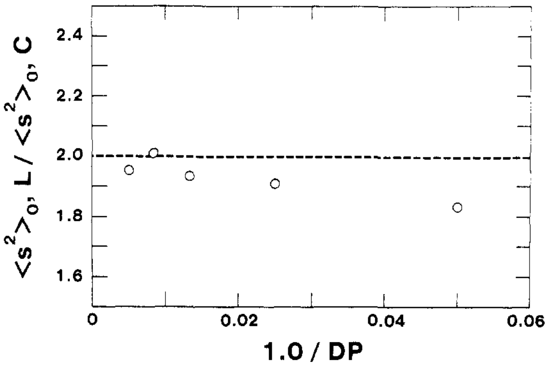

Figure 7. Plot of the ratio $\langle s^2\rangle_0$(linear)/$\langle s^2\rangle_0$(cyclic) for PDMS chains as a function of inverse DP.

Table I
Experimental and Theoretical (Model I) Trapping Efficiencies

exptl		theoretical			
			no.	% trapped (T)	
DP	% trapped (T)	DP	of cyclics generated	uncorrected	corrected[a]
15	0.0				
19	1.0				
		20	300	18.0	15.3
34	5.0				
		40	200	21.0	17.9
43	12.0				
71	24.0				
		75	200	38.0	32.3
96	37.0				
		120	200	52.0	44.2
155	61.0				
196	78.0				
		200	130	68.0	57.8
258	94.0				

[a] % T(corrected) = 0.85% T(uncorrected).

Results and Discussion

The quality of the sets of cyclic conformations that were generated by the procedure described above was tested by evaluating the average radius of gyration for each ring size. Also calculated were the radii of gyration of linear chains of the same degree of polymerization as the cyclics, using established matrix methods.[21] The values of ln $\langle s^2\rangle_0$ for rings and linears as a function of ln (DP) are shown graphically in Figure 6, and the ratio $\langle s^2\rangle_0$(linear)/$\langle s^2\rangle_0$(cyclics) vs 1/DP is shown in Figure 7. These calculations extend to much higher DP the results already in the literature for PDMS.[8] The linear relationships depicted in Figure 6 were thus verified for higher DP, as was the as-

Table II
Experimental and Theoretical (Model II) Trapping Efficiencies

exptl		theoretical			
			no. of cyclics	% trapped	
DP	% trapped	DP	generate	3.5-Å torus	4.0-Å torus
15	0.0				
19	1.0				
		20	300	7.5	5.5
34	5.0				
		40	200	12.5	7.0
43	12.0				
71	24.0				
		75	200	33.0	20.0
96	37.0				
		120	200	46.0	31.0
155	61.0				
196	78.0				
		200	130	71.0	51.0
258	94.0				

ymptotic approach to a ratio of 2.0 in the limit of large rings, as predicted theoretically[24] and observed experimentally.[25,26] It was also verified within the error of the Monte-Carlo procedure and number of cyclics used in the calculation, as seen in Figure 7. This strongly indicated that the generated samples were truly representative cyclic PDMS chains.

Experimental values for the trapping efficiencies and theoretical values calculated by using models I and II are given in Tables I and II, respectively, with specific results from both models along with the experimental results shown graphically in Figure 2. Focusing on model I initially, it is apparent from comparing the experimental results in the second column of Table I with the theoretical results in column five that a straightforward calculation with a 3.5-Å threading chain radius significantly overestimated the % trapped (T) for ring sizes of DP = 20 and 40. This is a direct consequence of the need to neglect six repeat units on either side of the one being tested. Model I also underestimated the % T for the largest rings, but to a lesser degree than the overestimation. The final column of Table I scales the values in the previous column by a factor of 0.85, the weight fraction of linear chains. This represents an attempt to correct for the experimental concentration of cyclic species at the time of network formation, since the cyclics could be viewed as competing for exposed repeat units. This correction is open to question; moreover, even if it is made, the improvement is negligible. Such competition could be tested experimentally by varying the fraction of cyclics of a given size present at the time of network formation and comparing the results with theoretical predictions. The number of cyclic chains used in the calculation of the DP = 200 trapping efficiency was less than that used for small cyclics, as shown in the first column of Tables I and II; thus, the accuracy of the theoretically trapped fraction is less for the highest ring size.

The results of the calculations using model II are given in Table II for torus radii of 3.5 and 4.0 Å. The results for a radius of 3.5 Å were of particular interest in that all five values are within the 5% error range of the experimental results coupled with a similar inherent error in the theoretical trapping efficiencies. This is particularly rewarding since model II is the more realistic model and comparison of the last two columns of Table II indicates that a torus radius between 3.5 and 4.0 Å would improve the agreement for the four smallest ring sizes but create a larger discrepancy between theory and experiment for the DP = 200 rings. It should be noted again that the theoretical results are based on only 130 cyclics for DP = 200. An intermediate torus radius would be close to the diameter evaluated from either the X-ray results (4.0 Å) or from the PDMS density (3.88 Å).

In conclusion, a suitable model has been developed for the trapping of cyclic species present at the time of network formation. It predicts that the fraction of cyclics trapped should depend on the fraction of exposed repeat units characteristic of the cyclic species and the cross section of the threading chains. In the models used, the fraction trapped should be independent of the molecular weight of the linear chains and their polydispersity. This prediction is born out by further experimental results on trapping in PDMS networks that are bimodal.[12] It should also be independent of the method of cross-linking. Model II may even allow for the calculation of the fraction trapped in samples cross-linked in a good solvent, through the use of cyclic chains generated so as to have a particular degree of excluded volume. One significant difficulty with pursuing such a set of calculations is the increased attrition of cyclic chain generation upon applying the additional constraint of volume exclusion. A more fundamental concern is the applicability of the statistical parameters for PDMS in a good solvent. A similar problem arises in using this model to interpret results of trapping experiments in which the cyclic and linear chains are significantly different, such as recent work on the trapping of PDMS cyclics in poly(2,6-dimethyl-1,4-phenylene oxide) networks.[27] The chains in such a system are not under Θ[28] conditions. Also, the additional problem of microphase separation mentioned earlier can occur, thus partially segregating the cyclic and linear chains and diminishing access of the linear chains to the cyclic species.

The excellent agreement between the experimental and theoretical results for PDMS cyclics trapped in PDMS networks adds further support to the assumptions made in this study, in particular the validity of using statistical parameters derived from Θ solution conditions[21,28] in the study of polymers in the bulk amorphous state.

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Para-Linked, Aromatic, Thermotropic Polyesters with Low Mesophase Temperatures

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ABSTRACT: The solubility, thermal, and optical properties of completely aromatic, para-linked, 2,2′-disubstituted biphenyl and substituted phenyl polyesters are reported. The results show that these moieties enhance solubility, e.g., methylene chloride and tetrachloroethane are typical solvents, and lower mesophase transition temperatures to less than 200 °C in most examples. Oriented and unoriented films of the soluble polymers are completely amorphous as evidenced by X-ray diffraction. Scattering of visible radiation by unoriented films can be attributed to voids as shown by scanning electron micrographs. Film samples which are oriented to 70–80%, measured by IR dichroism, are almost completely nonscattering and exhibit birefringence values of 0.65. These unusual properties may be attributed to a decrease in intermolecular forces caused by the trifluoromethyl-substituted phenyls and noncoplanar biphenyls.

Introduction

In recent papers[1] we described the unique optical and solution properties of 2,2′-disubstituted biphenyl polyamides for optical applications. Most of these polymers are colorless and very soluble in a variety of solvents such as tetramethylurea (TMU) and *N*-methylpyrrolidone (NMP) without LiCl. Many polymers composed of the 2,2′-bis(trifluoromethyl)biphenyl moiety are soluble in acetone or tetrahydrofuran, and one of these polymers is soluble up to 50% (w/v). Highly oriented polymer films are nonscattering, almost completely amorphous, and highly birefringent. This lack of crystallinity and unique solubility is probably due to weak intermolecular forces attributable to little or no H-bonding, random distribution of enantiomeric biphenyls, and the size and nature of the biphenyl substituents. The unusually high birefringence is a consequence of the rodlike conformation of the backbone and high electron density.

Unfortunately, none of these modified rodlike polyamides exhibit a melting point or a thermotropic liquid-crystalline transition, and consequently, oriented films can only be obtained by casting and stretching or extruding from polymer solutions. Since high molecular orientation is required for high birefringence, the orientation generated by extrusion and drawing of the extrudate must be locked-in by rapid extraction or evaporation of solvent. Although the development of this technique was partially successful, it was very difficult to obtain films exhibiting high birefringence, optical clarity, and flatness.

Because of these limitations, an investigation of rodlike polyesters was begun. The major advantage exhibited by these materials is liquid crystallinity and potential melt processability.

The first reported observations of thermotropic liquid-crystalline behavior in polymers were made by Roviello and Sirigu[2] and independently by Kuhfuss and Jackson.[3] The materials described in the latter study were copolymers of poly(ethylene terephthalate) and *p*-hydroxybenzoic acid; the solid to liquid crystal transition temperatures were in the 300–350 °C range. However, because optical devices such as polarizing beam splitters and nonabsorbing polarizers require birefringence values in excess of 0.4, it was decided to restrict the molecular structures of the polymers of this investigation to aromatic, para-linked repeat units such as poly(*p*-hydroxybenzoate) or the analogous poly(1,4-phenylene terephthalate) without flexible spacers. Unfortunately both of these polymers are highly crystalline and do not melt up to 500 °C. Subsequent developments in the field showed that the degree of crystallinity could be reduced and the crystalline to nematic transition temperatures could be lowered to the 200–400 °C range by disrupting the geometric regularity of the backbone. Three very effective molecular modifications were devised to accomplish this: a linear offset, e.g., 2,6-naphthyl,[4] lateral substituents,[5] and monomers of different length. It should be noted, however, that none of these modifications, either individually or in combination, with one possible exception,[6] completely eliminated crystallinity in rodlike polyesters.

In this report we describe the results of an investigation of the effect of 2,2′-disubstituted biphenyls and trifluoromethyl-substituted phenyls on solubility, transition temperatures, and morphology of para-linked, aromatic polyesters.

Experimental Section

Monomer Synthesis. The hydroquinones used were obtained from Aldrich Chemical Co. Hydroquinone was recrystallized from toluene. Methylhydroquinone was twice recrystallized from toluene. The diacetate of chlorohydroquinone was first prepared and purified by column chromatography before deacetylation and sublimation.

The diacid chlorides of terephthalic and 2,6-dinaphthoic acids were synthesized by standard procedures[4] and recrystallized from hexane and hexane/CH_2Cl_2, respectively, before use. The syn-