(3) The singlet–triplet mixing has been extensively studied by us in the CIDEP study of aqueous solutions of alcohols,[4] acids, and other compounds.[5]
(4) A. D. Trifunac and M. C. Thurnauer, *J. Chem. Phys.*, **62**, 4889 (1975).
(5) A. D. Trifunac, unpublished results.
(6) J. B. Pedersen and J. H. Freed, *J. Chem. Phys.*, **59**, 1869 (1973); J. H. Freed and J. B. Pedersen, *Adv. Magn. Reson.*, **8**, 2 (1975); J. B. Pedersen, *J. Chem. Phys.*, **59**, 2656 (1973).
(7) The second-order rate constant for radical reaction k_2' consists of two parts, k_2 and F, where k_2 is half of the second-order rate constant for new bimolecular collisions of radicals and F is the probability of reaction per collision. Both k_2 and F are affected by the ionic strength. We cannot separate these two effects. For detailed discussion see ref 6.
(8) P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, **73**, 4207, 4214 (1969)
(9) H. A. Schwarz, *J. Am. Chem. Soc.*, **77**, 4960 (1955).
(10) In the time-resolved study of $\cdot CH_2COO^-$ radical, smaller enhancement and reduced intensity of the central line in a 0.01 M solution of acetate was observed.[11]
(11) R. W. Fessenden, *J. Chem. Phys.*, **58**, 2489 (1973).
(12) At low malonate concentrations the absorption of the low-field line of malonate is changed to emission at longer times ($\gtrsim 3$ μs) after the pulse.
(13) When $T_1\beta \ll 1$, the radicals will lose their polarization before they collide with new radicals. However, when the larger concentration of radicals is produced ($n_0 \sim 10^{-3}$ M and $\beta \sim 10^6$) the above may no longer be true (see ref 6).
(14) We speculate that part of the polarization that we observe at 2–3 μs after the electron pulse may be created before uniform radical distribution is reached. With the higher dose we create more radicals, but the number of radicals that can participate in the polarization process (at short times) may be approximately constant, since they are contained in separated spurs. These ideas would accomodate Fessenden's results,[11] which were obtained at lower radical concentrations and later times (8–10 μs after the electron pulse), since the nonuniform radical concentration would affect only the early polarization production (at times <1 μs) which would disappear in several microseconds ($\sim 3T_1$).
(15) Recent instrument improvements allow us to obtain EPR spectra as close as 50–100 ns after the electron pulse.

Studies on the Formation of Topological Isomers by Statistical Methods

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Abstract: To improve the statistical synthesis of topological isomers, the factors which determine the amount of threading of linear chain molecules in macrocyclic rings were studied in detail. Polymeric rotaxanes were prepared by statistical threading of poly(ethylene glycols) in "crown polyethers". The compounds were mixed and heated, and the equilibrium was "frozen" by polymerization of the chains to polyurethanes by adding naphthalene-1,5-diisocyanate. The amount of threaded rings was determined after selective separation of the components on silica gel. The effects of the molar ratios of rings to chains, length of chain, radius of the ring, volume of the system, and temperature on the amount of threading were studied. Based on statistical consideration of ratio of reactants and volume of the system, and on geometrical factors, the following mathematical expression was derived to show the effect of these factors on the amount of threading: $N = k[m_e m_g(1 - e^{-n_e/\pi n_g})n_e n_g^{\beta}\theta]/V$ where N is the number of threadings, m_e and m_g are the number of moles of rings and chains respectively, n_e and n_g are the number of atoms in rings and chains, V is the total volume, and θ is the threading angle, which depends on the radius of the ring (r) and diameter of the chain end (d) and is determined by $\cos\theta = d/2r$. The constants β and k which suit the results are $\beta = 1.3$ and $k = 0.195$. There was good correlation between this mathematical model, the experimental results, and molecular models imitating the ring–chain threading system. The optimal conditions found for the threading system was utilized for the preparation of [2]-[ω,ω'-di(*O*-trityl)poly(ethylene glycol) 400]-[dibenzo-58.2-crown-19.4]rotaxane in relatively high yield (15%). Similar yield was obtained by polymerizing ethylene oxide by the di(potassium alkoxide) derivative of tetra(ethylene glycol) in the presence of "crown" polyether. Chromatographic and spectral evidence, as well as hydrolysis of the blocking trityl groups, was used to prove the structure of the rotaxane. The thermal decomposition of the rotaxane was investigated at 130–190 °C. The following equilibrium was found to exist: rotaxane $\rightleftharpoons$ ring + chain (k, k'), and the reaction constants were determined. The stability of the rotaxane was explained, taking into consideration the data obtained for the heat of decomposition (9.5 kcal/mol) and the activation energies of the decomposition and threading processes (15.9 and 3.4 kcal/mol, respectively). The higher activation energy needed for the decomposition was explained by the dipole–dipole interactions which exist between the ethylene oxide units in the threaded chain and those in the ring.

Since the first synthesis of a catenane by Wasserman[1] in 1960, only few topological isomers—catenanes and rotaxanes—have been prepared. Several approaches were developed, including the directed synthesis,[2] which needs many consecutive reaction steps, the statistical method,[1,3] which is relatively much simpler to perform but produces very low yields of the topological isomer, and the Möbius-strip method,[4] by which the formation of the desired product was demonstrated mass spectrometrically, although it has not yet been isolated. Variation of the statistical method taking advantage of orientation of polar reactants at interfaces was utilized for the synthesis of polycatenanes.[5]

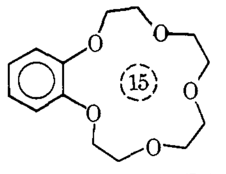
Besides Wasserman, the statistical threading of linear chain molecules in macrocyclic ring molecules was used by Harrison,[3] who synthesized several rotaxanes. The rings in these cases were built of 24–33 atoms, and the yields were between 0.0013–1.6%. Harrison investigated the stability of the various rotaxanes and the effect of ring size on their yields.

Frisch and Wasserman[6] proposed an expression for estimating the amount of threading of linear chain molecules through macrocyclic rings. The yield predicted for the synthesis of the catenane by Wasserman[1] was 4%, compared with the 1% yield which was found experimentally.

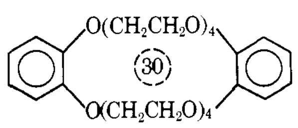
As a result of the difficulties in the preparation of topological isomers, very little is known about their physical properties. Particularly interesting are their colligative properties which are determined by the number of molecules. Until now, only one measurement has been reported,[7] which shows that a [3]-catenane having a "tight" structure behaves as if it was one molecule.

The present study was undertaken to achieve a fuller understanding of the statistical threading of linear molecules in macrocyclic rings, and to utilize the data thus obtained to improve the statistical synthesis of a rotaxane.

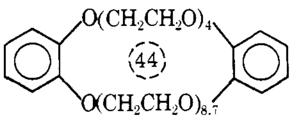
Statistical Threading of Linear Chains in Macrocyclic Rings. A "threading system" was developed with the purpose of investigating the factors which determine the amount of statistical random threading of chain molecules in macrocyclic rings. The chain molecules which were chosen were poly(ethylene glycol) chains having a degree of polymerization $\overline{DP}_n = 3, 4, 8.7$ (PEG 400), 13.2 (PEG 600), and 22.3 (PEG 1000), the last three being composed of a narrow distribution of poly(ethylene oxides).[8] These chain molecules were mixed in different ratios with ring molecules of "crown polyether" type, which were based on combinations of tetra(ethylene glycol) and poly(ethylene glycol) 400 (PEG 400), specifically dibenzo-30-crown-10 (I) (mixed with half-molar amount of dibenzo-15-crown-5, Ia), dibenzo-44.1-crown-14.7 (II), and dibenzo-58.2-crown-19.4 (III). The first number in the name of the "crown" polyether designates the average number of atoms which form the ring, and the second number indicates the average number of oxygen atoms in the ring.



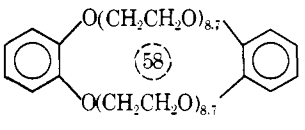
benzo-15-crown-5 (Ia)



dibenzo-30-crown-10 (I)



dibenzo-44.1-crown-14.7 (II)



dibenzo-58.2-crown-19.4 (III)

Mixing time of 0.5 h at 120 °C was found to be enough for establishing "threading equilibrium". The amount of threading of the chains in the ring molecules was determined by "freezing" the mixture. This was carried out by the addition of naphthalene-1,5-diisocyanate, which reacted with the poly(ethylene glycol) chain to yield high molecular weight polyurethanes. Although the naphthalene group is not bulky enough to prevent "falling off" of a threaded ring, nevertheless due to the polymeric nature of the product this de-threading would be significant only in the vicinity of the polymer chain end—a relatively small fraction. Cooling and keeping the product in the solid state minimizes this effect. Indeed, measurements done on a polymeric rotaxane at a time interval of 60 days did not show significant differences in the amount of threading.

A method was devised for determining the amount of threading. It consisted of adsorbing the reaction mixture on silica gel and extracting by alcohol the free macrocyclic polyether, which was determined quantitatively from its uv absorption, while the polyurethane and polyrotaxane molecules remained adsorbed. The part of the macrocyclic rings which could not be extracted consists of the rings that were threaded in polyrotaxane formation.

It may be argued that the fact that only part of the macrocyclic ring could be extracted from the silica gel does not mean that the other part has been necessarily incorporated in the polyrotaxane, and two other possibilities may be considered: the formation of some chemical complex or bond (without threading) between ring and chain molecules, and the mechanical entrapping of the rings by coils of the polymer chain.

A series of evidence rule out these possibilities: (a) When a macrocyclic polyether was mixed with a polyurethane, separately prepared, and adsorbed on silica gel, 96 ± 8% of the polyether was extracted, thus indicating that no complex is formed between these compounds. (b) Dissolving several samples of polyrotaxane in DMF at different concentrations did not release the expected amount of macrocyclic polyethers as would have been the case if there was random mechanical entrapping of the rings by the polymer coils. (c) A reaction of some sort between the ring and another constituent of the system is not likely, as a solution of a polymerized sample showed an increase in the amount of free crown compound from 36% to 82% after 60 days. (d) It is known[9,10] that on heating at 240 °C, polyurethanes undergo degradation in which CO_2 is liberated. Since the macrocyclic polyethers were found to be stable under these conditions (crown polyethers were reported[11] to be stable up to 380 °C), it would be expected that on heating the polyrotaxane, the polyurethane chains will degrade, leading to release of threaded macrocyclic rings. Indeed on heating a polyrotaxane mixture for 60–90 min, the amount of free macrocyclic ring substantially increased. It may thus be concluded that the polymerization of the chain–ring mixture indeed "freezes" the threading equilibrium of macrocyclic rings on the chain molecules.

Threading Equilibrium in the Chain–Ring System. The only data relating to the factors which determine the amount of threading in chain–ring systems were given by Harrison[3c] and showed a monotonic increase in the yield of rotaxane with increasing ring size up to a critical value, at which a sharp drop was found due to instability of the formed rotaxane.

In the system developed by us it was possible to measure the overall extent of threading (regardless of the stability of the rotaxane which can be formed), as well as many other parameters of the system.

Tables I and II show the effect of the molar ratio of chain to ring molecules and the effect of the length of the chains, for the various ring sizes, on the extent of threading. It is obvious that the total amount of threaded rings increases with increasing the molar ratio of rings to chains up to 1:1 (Table I). Maximum threading occurs with PEG 400-600, whereas shorter or longer chains give less threading (Table II). The effect of increasing the ring size is considerable and leads to an increase of threading especially on passing from the 30-atom (I) to the 44.1-atom ring (II).

The effect of total volume of the threading system was never measured, although intuitively one may assume that increase of volume would result in less threading. The effect of change of the volume of the reaction mixture due to changing the components' ratio is demonstrated in Tables I and II. In order to measure the effect of diluting the system by a neutral component, various amounts of hexachloroethane were added. As expected, the amount of threading decreased by about 50% when the total volume of the reaction mixture was doubled (Table III).

In order to permit analysis of the threading system on the basis of statistical and geometrical parameters, it was important to evaluate the significance of energy relations in the threading process. To obtain such information, the threading reaction was investigated at various temperatures, ranging from 100 to 207 °C. No significant effect of temperature on the extent of threading was observed (Table IV).

Molecular and Mathematical Models for the Threading System. Up to now, the only available experimental data concerning the effect of the various parameters in statistical threading were provided by Harrison,[3c] who examined only the effect of ring size. Even this work does not provide information about threading in large rings ($n \geqslant 33$) because the rotaxanes which they form are unstable.

Theoretically, a mathematical model for statistical threading was proposed by Frisch and Wasserman,[6] which is very sensitive to the value of bond length chosen.

The experimental data of the present work did not fit this model. The threading system is extremely complicated not only by statistical complexity, but also by geometrical factors, interactions between components, energy barriers, flexibility of molecules—all these play an important role in the formation of threading equilibrium. As a result of these considerations

Table I. Effect of Ring to Chain Molar Ratios on Extent of Threading[a]

Ring compd	Molar ratio, ring/chain	Molar ratio, threaded ring/chain	Rings threaded,[b] %
III	0.4	0.20 ± 0.10	50
III	1.0	0.63 ± 0.11	63
III	2.0	0.52 ± 0.25	26
III	4.0		/76 ±
/2	19		
II	0.5	0.30 ± 0.22	60
II	1.0	0.41 ± 0.18	41
II	2.0	0.52 ± 0.10	26
II	4.0	0.42 ± 0.12	11
I[c]	0.4	0.06 ± 0.04	15
I[c]	0.8	0.11 ± 0.10	14
I[c]	1.6	0.17 ± 0.14	11

[a] PEG 600 (average no. of atoms in chain = 40.6) (5 mmol) was mixed with the ring compounds and heated at 120 °C for 30 min. 1,5-Naphthalenediisocyanate (5.25 mmol) was added and heating continued for 30 min. [b] Out of total introduced. [c] Contains ⅓ of benzo-15-crown-5.

Table II. Effect of Chain Length on Extent of Threading[a]

Ring compd	Poly(ethylene glycol)	Av no. of atoms in chain	Rings threaded,[b] %
III	Tri-EG	10	10 ± 14
III	Tetra-EG	13	32 ± 10
III	PEG 400	27.1	52 ± 13
III	PEG 600	40.6	63 ± 11
III	PEG 1000	67.9	48 ± 10
II	Tri-EG	10	30 ± 9
II	Tetra-EG	13	22 ± 17
II	PEG 400	27.1	34 ± 14
II	PEG 600	40.6	41 ± 18
II	PEG 1000	67.9	30 ± 13
I[c]	Tri-EG	10	2 ± 2
I[c]	Tetra-EG	13	9 ± 3
I[c]	PEG 400	27.1	12 ± 8
I[c]	PEG 600	40.6	11 ± 10
I[c]	PEG 1000	67.9	12 ± 8

[a] Poly(ethylene glycol) (5 mmol) and ring compound (5 mmol) were mixed and heated at 120 °C for 30 min. 1,5-Naphthalenediisocyanate (5.25 mmol) was added and heating continued for 30 min. [b] Out of total introduced. [c] Contains ⅓ of benzo-15-crown-5.

we tried to develop a mathematical model for our specific system that will take into account the actual process of threading and the effect of the undoubtedly important ratio of the relative sizes of the chain end to be threaded and the ring. Thus optimalization of parameters could possibly be achieved for improving the statistical synthesis.

As seen from Table IV, the energy factors in this system seem to be insignificant. This can be explained in the light of the relative sizes of the chain ends and of the radius of the rings. Furthermore, due to the chemical similarity between the crown polyethers and poly(ethylene glycols), the chain ends (with which the threading process begins) show no preferred interaction with any element in the system.

The present system, in which the threading is therefore determined by probability and geometrical factors only, is easily imitated by molecular models, which were constructed in the proper dimensional proportions using spherical balls so that the ratio between the length of the chains and the diameter of the rings and that between the radii of the rings and the chain ends were kept in scale, in good approximation.

A number of chain and ring models were thoroughly mixed, and the number of threadings was counted. The results obtained were very similar to the experimental results (Figure 1-3). Figure 4 describes the results obtained for the threading with the molecular models.

Table III. Effect of Dilution on Extent of Threading[a]

Molar ratio, hexachloroethane/PEG 600	Total system volume[b]/reactants volume	% threading
0	1.00	63 ± 11
1	1.06	58 ± 10
2	1.13	43 ± 17
4	1.24	37 ± 17
8	1.50	34 ± 5
16	2.00	28 ± 9

[a] Ring compound, III, was mixed with an equal amount (5 mmol) of PEG 600, and hexachloroethane was added. The mixture was heated at 120 °C in an ampule to prevent sublimation of hexachloroethane. The ampule was opened in order to add naphthalene-1,5-diisocyanate (5.25 mmol). [b] Calculated from the densities of hexachloroethane (2.09) and the average measured density for the other two components (0.9).

Table IV. Effect of Temperature on the Extent of Threading[a]

Temp, °C	100	120	150	207
Rings threaded, %	65 ± 19	63 ± 11	58 ± 15	69 ± 20

[a] The system was composed of III (0.005 mol) and PEG 600 (0.005 mol). The polymerization to rotaxanic polyurethane was carried out for 30 min at the equilibrium temperature, except for the experiment carried out at 207 °C, where after 10 min the reaction mixture was cooled down to 150 °C to prevent thermal decomposition.

Statistical Model for the Threading System. Threading of a chain molecule into a ring molecule can possibly occur only in case that a chain end is positioned at the "soap bubble film" of the ring. If r is the radius of the extended ring, then each ring which has an element at a distance smaller than $2r$ from a chain end has several orientations that fulfill this requirement. The number of chain ends that would be inside a sphere with a radius of $2r$, which is described around an element of a given ring is given by $[m_g N_A (4\pi/3)(2r)^3]/V$, where m_g is the number of moles of glycol chain molecules, N_A is the Avogadro number, and V is the volume of the system. The total number of chain ends (N) that are in the "threading space" of all the ring molecules (m_e mol) would be:

$$N = \frac{m_g m_e N_A{}^2 (4\pi/3)(2r)^3}{V} = k_1 \frac{m_g m_e r^3}{V} \qquad (1)$$

However, not all the chain ends encompassed in the hypothetical sphere are in the proper orientation for threading. A simple calculation shows that the fraction of the chain ends with the correct orientation amounts to ⅛, and therefore eq 1 remains unchanged, except for the numerical value of k_1, which would be replaced by k_2.

In deriving eq 1, the chain end was taken as a point. But since actually it has dimensions, it may hypothetically be described as an end of a rod which is to be threaded through a ring. Maximum threading is expected when the plane of the ring is perpendicular to that of the chain. When this plane is deviated, there will be a certain critical angle (θ) which depends on the diameter of the rod (d) and on the radius of the ring (r) beyond which threading will not be possible. Only a fraction, given by $2\theta/\pi$, of all the chain ends that are in the plane of the rings can, therefore, satisfy the threading conditions. Angle θ is calculated from $\cos\theta = d/2r$. The diameter of the poly(ethylene glycol) chains (d) was taken as 4.5 Å, which is that of the CH_2 group

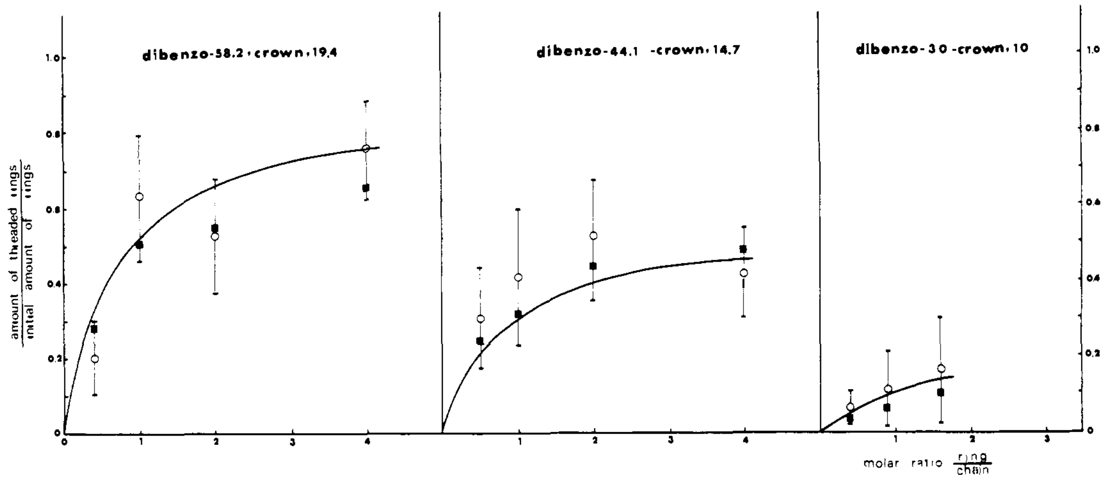


Figure 1. Dependence of the extent of threading on the ring/chain molar ratio. (○) experimental value ± standard deviation (■) value from molecular models. The curve is that calculated from the mathematical model. PEG 600 (0.005 mol) was used.

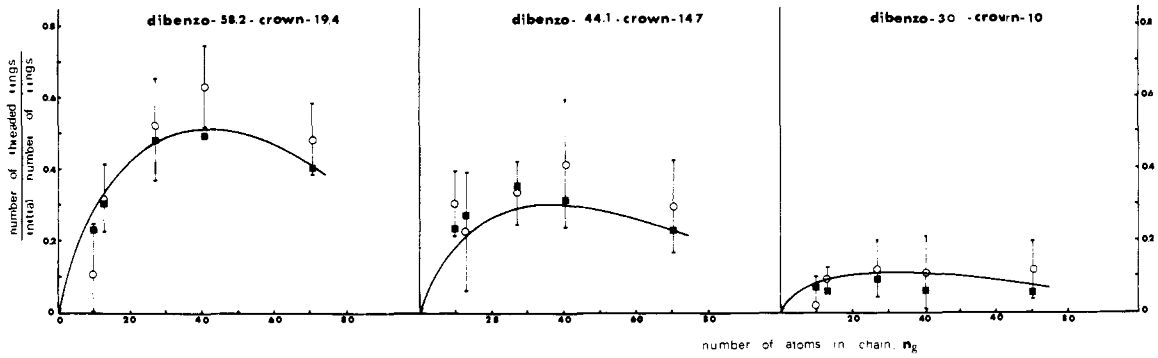


Figure 2. Dependence of the extent of threading on the chain length. (○) experimental value ± standard deviation (■) value from molecular models. The curve is that calculated from the mathematical model; macrocyclic polyether (0.005 mol) and poly(ethylene glycol) (0.005 mol) were used.

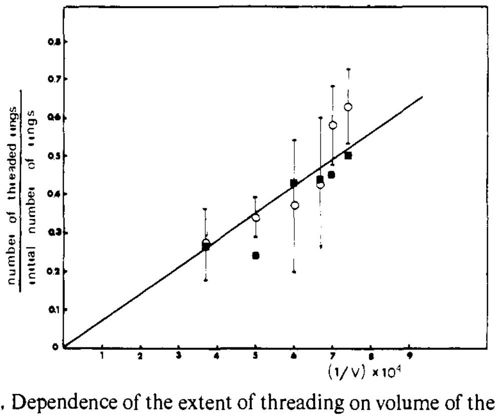


Figure 3. Dependence of the extent of threading on volume of the system. (○) experimental value ± standard deviation (■) value from molecular models. The curve is that calculated from the mathematical model. Equimolar amounts of dibenzo-58.2-crown-19.4 and PEG 600 (0.005 mol) with varying amounts of hexachloroethane were used.

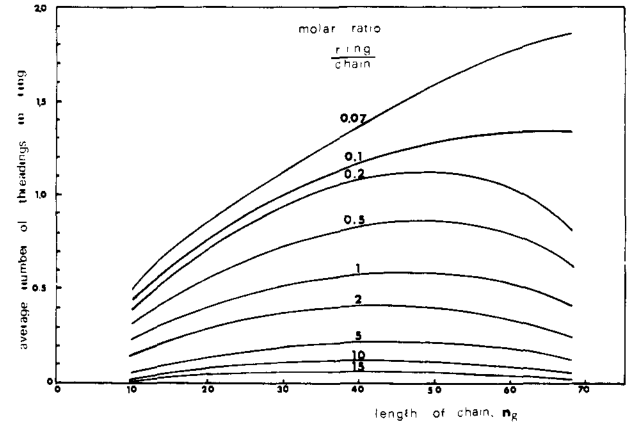


Figure 4. Dependence of the extent of threading on the ring/chain molar ratio and on the chain length (measurements with molecular models). Rings having 57–58 atoms were used.

near the terminal OH (which latter is somewhat smaller). It should be noted that for the extreme case, when $\theta = 0$ ($\cos\theta = 1$), the smallest ring radius that can still allow threading is 2.25 Å, which is that of a 20-21-atom ring built from C–C and C–O bonds. This ring size is very similar to the accepted[6,12] minimal value for threading (20–22 atoms). The number of threadings in our system would be expressed by

$$N = k_3 \frac{m_g m_e r^3 \theta}{V} \tag{2}$$

Equation 2 takes into consideration the possibility of threading a number of chains through a given ring. Besides, the possibility of threading of several rings on one chain must be considered, naturally depending on the length of the chain. The tendency of the polymer chain to form a random coil must be hindered by the presence of a threaded ring. Therefore, if n_g is the number of atoms in the backbone of a chain molecule, the effective length would be some value between the end-to-end distance of the extended chain[13] which is proportional to n_g, and the end-to-end distance of the randomly coiled chain which is proportional to $n_g^{1/2}$. (For the sake of simplicity, all atoms in the chain are considered equal.) The number of possible threaded rings per chain increases with this effective length, which would be n_g^{α}, where $\frac{1}{2} < \alpha < 1$.

In the same way, when the chain is longer, the already threaded ring is more effectively prevented from "falling off" the chain. Similarly, this "de-threading" is expected to be easier when the area of the ring is larger. Thus, we arbitrarily modified eq 2 to the following:

$$N = k_3 \frac{m_e m_g r^3 \theta}{V} \frac{n_g^{\alpha+\alpha'}}{r^2} = k_3 \frac{m_e m_g r \theta n_g^{\beta}}{V} \quad (3)$$

where $1 < \alpha' < 0.5$ and $\beta = \alpha + \alpha'$.

Another factor which was incorporated into the mathematical model is related to the dynamics of the threading: the ratio between the ring diameter (d_e) and the number of atoms in the chain molecule (n_g). If we describe the threading as a process where the center of gravity of the chain moves toward the cross section of the ring, then two extreme cases are possible. When $d_e \gg n_g$, almost all the cases in which the center of the chain moves toward the ring will result in threading. On the other hand when $n_g \gg d_e$, threading will occur only in the few cases where the ring is near the chain end and in the right angle. This limitation was found from the molecular models to be very important. A factor of the type of $1 - e^{-d_e/n_g}$, or similarly $1 - \exp(-n_e/\pi n_g)$, expresses quite closely this limiting behavior.

Thus if we replace the ring radius (r) by its number of atoms (n_e), the expression for the estimation of the number of threadings in the system of poly(ethylene glycol) chains and macrocyclic crown compounds would be:

$$N = k_3 \frac{m_e m_g (1 - e^{-n_e/\pi n_g}) n_e n_g^{\beta} \theta}{V} \quad (4)$$

where $1 < \beta < 2$.

Almost all the parameters in eq 4 are measurable, and the only one that needs calculation is the threading angle, θ. Its calculation was based on the bond distances[14] in the molecules and on an assumption of an extended zig-zag structure of the ring.[15] The radius of the circle described by the atoms' nuclei was found, and a value of 1.7 Å was substracted as the mean of the radii of the atoms and groups. Thus θ was found to be 0.92, 1.23, and 1.32 rad for dibenzo-30-crown-10, dibenzo-44.1-crown-14.7, and dibenzo-58.2-crown-19.4, respectively. As the rings have a similar structure if they are not extended, their projection area would assumably be proportional to their extended area.

Correlation Between the Mathematical Model and the Experimental Results. A good correlation was found between the experimental results, the molecular models' threadings, and the mathematical model for values of $k = 0.195$ and $\beta = 1.3$ (Figures 1-3).

It may be concluded that the amount of threadings that exists in our system is much larger than was found in any previous system. This is especially true for the larger rings (44 and 58 atoms). The size of the ring affects the threading more than any other parameter. Each ring size has an optimal chain length for maximum threading. It is easily calculated from eq 4 that this length, for a molar ratio of 1:1, is 2.5-3 times the ring diameter.

In cases where the chain length is very long, $n_g \gg n_e$ and the molar ratio of ring to chain is 1:1, the amount of threading diminishes with increasing the chain length, according to eq 4. This could be due to the fact that the overall volume is increased without a parallel increase in the number of chains. Secondly, threading would occur only as a result of movement of the chain end toward the ring, while movement of the chain as a whole would not necessarily result in threading.

For very large rings, the amount of threadings increases by increasing the length of the chain (which can in this case behreaded through more rings) and by increasing the amount of the chains.

In a large excess of either component, the threaded fraction of the minor constituent will reach a limit which depends on the geometrical parameters. It follows that beyond a certain limit of concentration, the fraction of threaded rings will decrease on increasing the amount of a component in the system. This may be explained by the fact that for a sufficient excess of one component, each molecule of the other component "sees" from all sides only other molecules, and increasing the amount of the last ones would not result in more threadings.

Preparation of Rotaxane from a Crown Polyether and Poly(ethylene glycol)

Analysis of the statistical threading system indicated that maximal yield of a rotaxane would possibly be obtained by mixing dibenzo-58.2-crown-19.4 and poly(ethylene glycol) 600 in equimolar quantities.

As a bulky blocking group we chose the trityl group mainly because of the possibility of attaching it to the chain end with almost no dilution of the threading system. Trityl derivatives of poly(ethylene glycols) were previously[16] synthesized in benzene solution, but we found that 60% yield could be obtained by reacting triphenylchloromethane with the poly(ethylene oxide) in the presence of only an equivalent amount of pyridine at 100 °C.

To prepare the rotaxane the chain and ring molecules were mixed and heated at 120 °C for 30 min. Triphenylchloromethane was introduced, followed by the required amount of pyridine, and heating was continued to complete the reaction. Separation of the rotaxane from the reaction mixture proved to be very difficult. Many chromatographic methods were tried but no conclusive results were obtained. This difficulty seemed to be due to the similarity between the structure of the various components of the system. To circumvent this, poly(ethylene glycol) 600 was replaced by poly(ethylene glycol) 400 in order to change more significantly the balance between aromatic nuclei and ethylene oxide units in the reactants and product molecules. Indeed, on the basis of solubility differences, the reaction mixture was separated by partition chromatography on silica gel by elution with petroleum ether (40-60 °C), CCl_4, and $CHCl_3$. Three fractions were separated. The first one contained the "blocked" chain, ω,ω'-di(O-trityl)poly(ethylene glycol) 400 (IV), the third one contained the crown ring III, while the middle one showed characteristics which could be explained only by its being an equimolar combination of both these compounds.

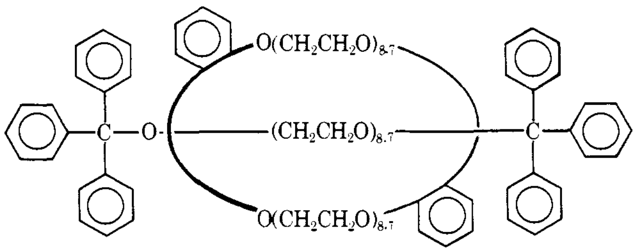
Evidence for Rotaxane Structure. The fraction which was isolated as a rotaxane showed ir, uv, and NMR spectra, as well as elementary analysis of an equimolar mixture of IV and III. It could possibly be therefore [2]-[IV-III]rotaxane (after Schill's nomenclature[2]). We tried to obtain direct mass spectral evidence for the rotaxanic structure, but no molecular ion could be detected due to the relatively high molecular weight of the compounds and the thermal instability of the trityl bonds.[17-19]

Hence we needed a series of "circumstantial evidence" for the existence of a rotaxane. To prove that the isolated rotaxane was not simply a mixture which was not properly separated, it was repassed through a chromatography column identical with that on which it was previously isolated; almost all the starting material was recovered in the middle fraction, as before. On the other hand a mixture of III and IV under these chromatographic conditions, yielded the components in the first and third fractions, and not in the middle one. TLC on silica gel, developed by ethanol (7):methanol (3) mixture, showed again the same behavior. Thus the isolated fraction is not a simple mixture of the components.

Likewise, no spectral evidence could be detected to indicate any chemically bonded combination of the components. In fact, on short boiling in 80% acetic acid, the rotaxane was completely hydrolyzed to produce triphenylcarbinol, PEG 400, and unchanged III, the identity of which was proved spectroscopically, by elementary analysis, and by TLC.

A densitometric follow-up of the thermal decomposition of the rotaxane showed, as expected, that the rate increased on raising the temperature from 130 to 190 °C. At the latter temperature, the decomposition became even greater due to the occurrence of thermal fission of the trityl groups. TLC of a rotaxane which was kept 6 months at room temperature showed a certain amount of decomposition to its components.

It may thus be concluded that the fraction isolated is indeed the desired topological isomer V. The yield of the isolated rotaxane was 15%.



V

Preparation of a Rotaxane by Addition Polymerization in the Presence of a Macrocyclic Ring

Having prepared the rotaxane V with a preformed poly(ethylene oxide) chain, we attempted to find out whether the polymerization of ethylene oxide to PEG chains in situ, in the presence of the macrocyclic polyethers, would affect the statistical behavior of the system.

To obtain the polymeric rotaxane it was necessary to polymerize ethylene oxide to a poly(ethylene glycol) having reactive end groups which can be capped by bulky trityl groups. Anionic polymerization of ethylene oxide leading to a "living" polymer having alkoxide anions as end groups was therefore used. Since potassium naphthalene was found to attack the macrocyclic polyether, dibenzo-58.2-crown-19.4, polymerization was initiated by the dipotassium derivative of tetra(ethylene glycol). The "crown polyether" served as the solvent, and ethylene oxide was introduced into the mixture. The polymerization was terminated after a week by adding triphenylchloromethane, thus achieving simultaneously termination and attachment of blocking groups to the chain ends. After initial separation by adsorption chromatography, a mixture was obtained containing crown polyether, ω,ω'-di(*O*-trityl)poly(ethylene glycol) and the rotaxane VI.

The final isolation of the rotaxane in this case was much more difficult than in the case of rotaxane V prepared from PEG 400. This is probably due to the fact that in the present synthesis the average molecular weight of the unthreaded and threaded PEG chain, as measured by NMR, was 700. This increase in the PEG content in the ω,ω'-di(*O*-trityl)poly(ethylene glycol) affects considerably its solubility and behavior in partition chromatography and makes it more similar to that of the "crown" ring compound which is built up of two PEG 400 chains. After trying many different methods, partition chromatography on silica gel–water was found to be quite effective in separating the mixture, although the fractionation was not so sharp.

Since the rotaxane was thermally unstable, as found previously, and did not show a molecular ion in the mass spectrum, proof for its structure was obtained from a series of indirect evidences. The uv, ir, and NMR spectra gave results identical with those obtained from equimolar mixtures of the rotaxane components.

Thermal decomposition of the rotaxane after 15 h at 150 °C was followed by partition chromatography. Since the separation was not sharp, an accurate result could not be obtained; however, it was estimated that 60% of the rotaxane decomposed into its components.

The rotaxane and its components were chromatographed on Poragel 60A. As expected the rotaxane (calculated mean molecular weight 2130) was eluted before its components (calculated molecular weights 950 and 1180 for the ring and chain, respectively). A similar chromatogram of a mixture of the rotaxane's subunits showed the absence of rotaxane.

Evidence for the absence of a chemical bond between the chain and ring molecules was obtained from hydrolysis of the blocking trityl groups by boiling dilute acetic acid. Spectroscopic and chromatographic analysis of the hydrolysate showed the expected triphenylmethanol, poly(ethylene glycol) 700, and unchanged macrocyclic "crown" polyether.

In the light of these results and by analogy with the rotaxane V, we conclude that a rotaxane was formed by the polymerization of ethylene oxide in the presence of macrocyclic rings. The yield was 11.2%, and though it is somewhat lower than that of the rotaxane formed with PEG 400, it shows that addition polymerization of a monomer in the presence of macrocyclic rings yields comparable results to those obtained in the threading of a preformed polymer of similar molecular weight, at least where the polymerization process is slow and permits reaching the equilibrium of the threading system.

Properties of the Rotaxane V. The rotaxane V is a viscous brown liquid, similar to other rotaxanes that were synthesized.[2,3,19,20] The refractive index of the rotaxane was very close to that of an equimolar mixture of its components both at 20 °C (1.5228 compared with 1.5237) and at 60 °C (1.5082 compared with 1.5104). Its solubility was between that of its components. Thus while IV is soluble in hot hexane and III is insoluble in hot hexane and soluble to a small degree in hot cyclohexane, the rotaxane is completely soluble in hot cyclohexane and has a small solubility in hot hexane.

The colligative properties of the rotaxane were interesting. In contrast to the reported case[20] where a [3]-catenane was found by VPO (vapor-pressure osmometry) to behave like a regular molecule, in our case, the molecular weight of the rotaxane, as cryoscopically measured by camphor and by CBr$_4$, was in all cases close to the mean of the molecular weights of the components and not to their sum. A similar result was obtained by vapor-pressure osmometry, which represents, again, a colligative property. On the other hand, the molecular complex as a whole (in this case, rotaxane VI) behaves as it is expected to in gel permeation chromatography, that is, it has a higher molecular weight than its components. This may be due to the fact that in our case the relatively large size of the ring compound and of the chain permit large freedom of movement of the components in the rotaxane. This may also explain the fact that the NMR spectrum of the rotaxane did not show any change in the temperature range of +25 to −30 °C, contrary to the reported case of a rotaxane having a 32-atom ring, where some effect of the rotaxane structure on the NMR was found due to interaction between the two components.[3c]

Thermal Stability of the Rotaxane V. Harrison reported[3] data on the thermal stability of trityl-terminated rotaxanes with rings having up to 34 carbon atoms. In our system the diameter of the extended ring is about twice that of the effective diameter of the trityl group. This causes instability of the rotaxane but also enables rethreading.

The rotaxane was heated in the range 130–190 °C, and its decomposition was followed up by TLC (Figure 5). Due to the distribution of lengths in the ring and chain molecules, the apparent thermodynamic data is the average result of the various species in the mixtures. It is clear that up to 170 °C the

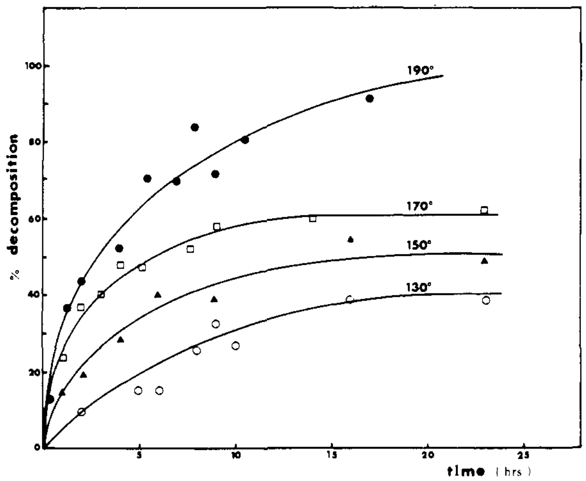


Figure 5. Thermal decomposition of rotaxane in bulk.

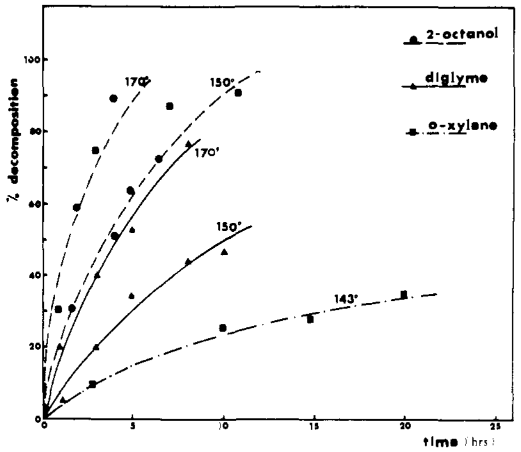


Figure 6. Thermal decomposition of rotaxane in solution (fits to the data).

Table V. Rate Constants of Thermal Decomposition of Rotaxane[a]

Temp, °C	Solvent	% rotaxane decomposed at equilibrium	Equilibrium constant $K = k/k'$, mol l.$^{-1}$	Rate constant decomposition k, s$^{-1} \times 10^4$	Rate constant of threading k', l. mol^{-1} s$^{-1} \times 10^4$
130	Bulk	40	0.133	0.112	0.84
150	Bulk	52	0.282	0.206	0.73
170	Bulk	61	0.477	0.485	1.02
150	Diglyme			0.189	
170	Diglyme			0.477	
150	2-Octanol			0.530	
170	2-Octanol			1.200	
143	Xylene			0.059	

[a] Rotaxane (150 mg) was heated for 1.5 h, and the amount of the free polycyclic ether liberated was determined.

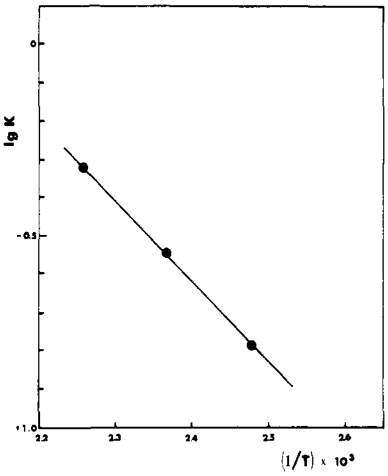


Figure 7. Dependence of the equilibrium constant, K, of the thermal decomposition of the rotaxane on temperature.

system is reaching an equilibrium:

$$\text{rotaxane} \underset{k'}{\overset{k}{\rightleftharpoons}} \text{ring} + \text{chain}$$

Such an equilibrium was suggested also by Harrison,[3c] and a similar equilibrium was described by Wang and Schwartz.[21] In polar solvents such as diglyme and 2-octanol at the same temperature (5% concentration of rotaxane), the decomposition of the rotaxane (Figure 6) follows a first-order reaction:

$$\text{rotaxane} \xrightarrow{k} \text{ring} + \text{chain}$$

This is clear because the probability of rethreading will be about 20 times smaller in the solvent than its absence, as shown before. It is seen that the rate of decomposition was about the same without solvent and in diglyme (Table V). This can be expected in the light of the chemical similarity between diglyme and rotaxane components, and the solvent, therefore, does not alter the interactions between the components. The situation is different with 2-octanol. where the decomposition is faster. This can be due to weakening of the intramolecular interactions as a result of hydrogen bonding between the rotaxane components and the solvent. Xylene as a nonpolar solvent had an opposite effect of slowing down the decomposition, as it may cause strengthening of the ring-chain interactions, as well as contraction of the rotaxane molecules.

The rotaxane is surprisingly stable in the light of the relative dimensions of the ring and the blocking group. A possible explanation may be provided by assuming that the poly(ethylene oxide) sections of the ring (and chain) molecules assume a "meander" conformation rather than a zig-zag one,[15,22] the former being generally accepted[23] as the more stable conformation. The diameter of III will thus be about 9.2 Å, compared with 18.6 Å for the zig-zag conformation, a size that may block the trityl group.

Dale's principle of "horror vacui" [24] may provide another explanation for the stability of the rotaxane. The same driving force for inclusion of solvent molecules in the hole of a macrocyclic ring[25] (which may be so strong as to cause chemical instability of the ring when trapped molecule is forced out[25a]) may be even stronger in our case, where dipole-dipole interactions between the ring and chain are expected to stabilize the rotaxane. Besides, the crown ring is very flexible and has a strong tendency to assume a suitable conformation for maximum dipole interactions, as shown by the versatility of ion-crown complexes.[10,26]

Support for this assumption was obtained from measuring the heat of the reaction: rotaxane $\rightleftharpoons$ ring + chain (k, k'). ΔH, obtained by plotting log K (Table V) vs. $1/T$ (Figure 7), was equal to 9.5 kcal/mol (based on average molecular weight of the rotaxane), which is the order of magnitude of the energy of the dipole interactions between the poly(ethylene oxide) segments.

The activation energies measured for the decomposition reaction were 15.9 ± 1.5 kcal/mol and for the threading process 3.4 ± 1.5 kcal/mol. The low activation energy required for the threading process is due to the fact that the process is dominated by geometrical and statistical, and not energetical, factors. The activation energy of the decomposition is of the order that is necessary to break electrostatic interactions.

Experimental Section

Materials and Apparatus. Uv spectra (in ethanol) were taken on a Unicam SP 800 spectrometer, ir spectra (in KBr) on a Perkin-Elmer Model 457 instrument, NMR spectra on Varian T60 and HA-100 instruments, and mass spectra on an Atlas MAT CH4 instrument. TLC was carried out on silica gel GF 254 (Merck) and visualized by uv lamp and iodine vapor adsorption. Quantitative measurements on TLC were carried out at 254 mμ using a Photovolt TLC densitometer, Model 350. Molecular weights were determined by the Rast method[27] using camphor aand carbon tetrabromide. DMF was distilled over P_2O_5. Poly(ethylene glycols) (Fluka) were dried by azeotropic distillation with benzene.

The "crown" polyethers, dibenzo-30-crown-10 (I), dibenzo-44.1-crown-14.7 (II), and dibenzo-58.2-crown-19.4 (III) were prepared according to Pedersen.[28] In the preparation of I, benzo-15-crown-5 was also formed. A larger proportion of the former was obtained by rapid addition of the second portion of β,β'-bis(β-chloroethoxy)diethyl ether to the reaction mixture. The resultant "crown" polyether mixture contained 65% of I as verified by molecular weight determinations and uv absorptions, where λ_{max} and ϵ_{max} differ. All the three "crown" polyethers were purified by column chromatography, and they gave the expected elementary analysis, ir, NMR, and molecular weights (Rast).

Anal. Calcd for $C_{28}H_{40}O_{10}$ (I): C, 62.69; H, 7.46; mol wt 536. Found: C, 62.82; H, 7.57, mol wt (camphor) 446 ± 20, indicating it to be a mixture with Ia (mol wt 268).

Anal. Calcd for $C_{37.4}H_{58.8}O_{14.7}$ (II): C, 60.42; H, 7.91; mol wt 743. Found: C, 60.49; H, 8.11; mol wt 770 ± 52.

Anal. Calcd for $C_{46.8}H_{77.6}O_{19.4}$ (III): C, 59.14; H, 8.17; mol wt 949.6. Found: C, 59.35; H, 8.19; mol wt (camphor) 972 ± 71, (CBr_4) 965 ± 42.

Polymeric Rotaxanes from Macrocyclic Polyether and Polyurethane Derived from 1,5-Naphthalenediisocyanate and Poly(ethylene glycol). Polyurethanes were prepared from naphthalene-1,5-diisocyanate and the glycols, triethylene glycol, polyethylene 400, 600, and 1000, in the presence of the crown polyethers I, II, and III.

The crown polyether was mixed at the required ratio with poly(ethylene glycol) and heated at 120 °C for 30 min. Solid naphthalene-1,5-diisocyanate (5% molar excess based on the glycol) was added with stirring, and after 30 min, the mixture was heated to 150 °C for 30 min. The polyurethanes were obtained as solid rubber-like or gelatinous materials, the latter being more soluble. They were obtained on increasing the amount of crown ether used in the reaction. Ir 1110 (C-O-C), 1725 cm^{-1} (-NHCOO-), NCO absorption at 2277 cm^{-1} absent; NMR (CF_3COOH) δ 6.82 (s, catechol protons), 3.62 (s, $-CH_2O-$), 7.1–7.8 (m, naphthalene); uv (ethanol) 275 (crown polyether), 251, 256, 262 mμ (polyurethane).

Determination of Threaded Crown Polyether in Polymeric Rotaxane. A 50–100-mg sample of the reaction mixture was dissolved in DMF (2 ml), and 5–10 μl of the solution was adsorbed on a TLC plate, coated with silica gel G (not activated). After drying the silica gel was extracted by absolute ethanol, and the amount of the crown polyether extracted was determined quantitatively by uv spectroscopy. Control measurements on pure crown compound at various concentrations showed that 89 ± 5% of the compound can be extracted back from the TLC by ethanol, and this value was taken into account in the calculations.

Thermal Degradation of Polyrotaxane. Polyrotaxane (150–200 mg) was sealed under vacuum in an ampule and heated at 240 °C for 60–90 min. The product was analyzed for free crown polyether.

Threading Experiments with Molecular Models. Molecular models, linear chains or rings, were constructed from wooden beads, each one taken as representing a $-CH_2CH_2O-$ group, threaded on a nylon string with small spaces between them to ensure flexibility of the model. Thirty of these models were manually mixed in various directions for 5 min. The threaded rings were counted (including "half-count" for the case where the chain end was situated in the ring cross section). For each case 8–10 measurements were taken, and the standard deviation was usually ±15 – 25%.

ω,ω'-Di(*O*-trityl)poly(ethylene Glycol) 400 (IV). Triphenylchloromethane (2.8 g, 0.01 mol) and pyridine (0.79 g, 0.01 mol) were added to poly(ethylene glycol) (0.005 mol) at 100 °C. The reaction mixture was stirred for 12 h under nitrogen, cooled, and diluted with CCl_4. The solution was filtered, and the solvent was distilled off in vacuo. The residue was partitioned on a column of alumina (activity I) by elution with petroleum ether 40–60 °C, followed by CCl_4 and chloroform. The desired product was obtained as a viscous liquid, $n^{20}D = 1.5613$, in the chloroform extract in 60% yield: uv (ethanol) λ_{max} 255 mμ (ϵ 2230), 261 (2500), 267 (1900), 272 (1250); ir 1105 (C–O–C), 1500, 1600 (aromatic C–H), 765 (C_6H_5) no OH absorption at 3350 cm^{-1}; NMR ($CDCl_3$) δ 3.62 (s, $-CH_2O-$), 3.16 (m, $-CH_2-OCPh_3$), 7.19 (m, C_6H_5), the integration ratios being as required. Other ω,ω'-di(*O*-trityl)poly(ethylene glycols) were similarly prepared.

Anal. Calcd for $C_{55.4}H_{64.8}O_{9.7}$: C, 75.14; H, 7.31; mol wt 885. Found: C, 75.21; H, 7.29; mol wt 905 ± 64 (camphor), 866 ± 57 (CBr_4).

[2]-[ω,ω'-Di(*O*-trityl)poly(ethylene glycol) 400]-[dibenzo-58.2-crown-19.4] rotaxane (V). Crown III (1.9 g, 0.002 mol) was mixed and heated under nitrogen with poly(ethylene glycol) 400, (0.8 g, 0.002 mol) at 120 °C for 30 min. Solid triphenylchloromethane (1.1 g, 0.004 mol) was added, followed by pyridine (0.35, 0.0044 mol). Heating was continued for 15 h. The mixture was cooled, dissolved in CCl_4 (30 ml), and filtered from pyridine hydrochloride. The solvent was evaporated, the residue was diluted with CCl_4 (2 ml) and adsorbed on a column of silica gel (Hopkins and Williams, M.F.C.) saturated with water (50% w/w). Elution with petroleum ether 40–60 °C led to the separation of triphenylmethanol and ω,ω'-di(*O*-trityl)poly(ethylene glycol) 400 (1.1 g). After that a middle fraction (0.2 g) was eluted with a 1:1 mixture of petroleum ether 40–60 °C and CCl_4, the pure rotaxane (0.56 g, 15%) was eluted with CCl_4. Elution with chloroform led to recovery of unreacted III.

Anal. Calcd for $C_{102.2}H_{142.4}O_{29.1}$: C, 66.86; H, 7.76; mol wt 1834. Found: C, 66.72; H, 7.94; mol wt 912 ± 72 (camphor), 880 ± 41 (CBr_4), 860 ± 55 (vapor-pressure osmometry).

Hydrolysis of the *O*-Trityl Groups of Rotaxane V. A solution of rotaxane (121 mg) in 80% acetic acid was boiled for 10 min and evaporated to dryness in vacuo. The residue was taken up in chloroform and water. The aqueous fraction was distilled off leaving 22 mg (84%) of a viscous colorless liquid, which was identified from ir and NMR as poly(ethylene glycol) 400. The chloroform fraction was concentrated to a small volume and separated on a column of silica gel (Hopkins and Williams) containing 50% water. Elution with petroleum ether 40–60 °C yielded triphenylmethanol (30 mg, 90%), identified from uv, ir, and NMR spectra as well as melting point and mixed melting point (160 °C) with an authentic sample. Elution with chloroform–methanol (4:1), drying of the eluate, and evaporation yielded the crown polyether III, (44 mg, 70%) identified from uv, ir, and NMR as well as elemental analysis.

Anal. Calcd for $C_{46.8}H_{77.6}O_{19.4}$ (III): C, 59.14; H, 8.17. Found: C, 59.09; H. 8.09.

Dipotassium Alkoxide Derivative of Tetra(ethylene glycol). Tetra(ethylene glycol) (Fluka) (2.5 g, 0.0125 mol) was cooled in an acetone–dry ice mixture, and a solution of potassium naphthalene 1.8 N in dry THF was added dropwise under nitrogen until a stable color of the mixture was obtained.[29] The initiator solution was used without further purification.

Rotaxane VI. III (3.0 g, 3.13 mmol) was added under nitrogen to the alkoxide initiator solution. The THF was evaporated in vacuo by gentle heating to 50 °C for 10 min. The mixture was stirred and cooled in an acetone–dry ice bath, and ethylene oxide (3.0 g) (Matheson) was introduced at the rate of 0.25 g/min. The reaction mixture was kept for 3 h in the acetone–dry ice bath, 6 h in a salt–ice bath, followed by 6 days at room temperature. Termination was done by adding a solution of triphenylchloromethane in dry benzene (50% excess) and mixing for 2 h. The benzene was driven off in vacuo, and the residue was dissolved in chloroform (150 ml) and extracted with water to remove free poly(ethylene glycol). The chloroform was evaporated, and the residual oil was extracted with petroleum ether 40–60 °C to separate the naphthalene and dihydronaphthalene. The residue was taken up in CCl_4 and passed through a column made from a nylon sleeve packed with alumina (activity I). The elution was done with petroleum ether 40–60 °C. A yellow band (triphenylchloromethane and triphenylmethanol) which moved in the front[30] was cut, and the rest of the adsorbent was extracted by methanol. Further separation was done on silica gel (Hopkins and Williams) containing 50% water, eluting with petroleum ether 40–60 °C, CCl_4, benzene, chloroform, and methanol, in that order. The fractions obtained were examined by NMR. The rotaxane was concentrated mainly in the benzene fraction, with an additional amount in the chloroform fraction. From the former fraction the rotaxane (0.74 g, 11.2%) was isolated: uv (ethanol λ_{max} 252 mμ (ϵ 1010), 256 (1150), 262 (1200), 275 (3520); ir (Nujol) 1595, 1500, 1255, 1105, 765, 745 cm^{-1}. No OH absorption was found at 3300-3500; NMR ($CDCl_3$) δ 3.17 (m, 4 H, CH_2OCPh_3), 3.58 (s, 112 H, $-CH_2-O-$), 3.78 (m, 8 H, $-CH_2CH_2OAr$), 4.10 (m, 8 H, $-CH_2OAr$), 6.81 (s, 8 H, catechol protons), 7.19 (m, 30 H, Ph_3C-).

Anal. Calcd for $C_{115.2}H_{160.4}O_{33.6}$: C, 65.66; H, 7.89. Found: C, 65.61; H, 7.70.

The CCl_4 fraction contained ω,ω'-di(*O*-trityl)poly(ethylene glycol): NMR (CCl_4) δ 3.17 (m, 4 H, $-CH_2OPh_3$), 3.58 (s, 58 H, $-CH_2O-$), 7.21 (m, 30 H, Ph_3C-); $\overline{DP}$ of PEG chain from NMR 15.5 (mol wt 700).

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Synthesis of a Catenane by a Statistical Double-Stage Method

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Abstract: A novel two-stage statistical synthesis of catenanes was developed based on converting a rotaxane to a catenane. In the first stage, [2]-ω,ω'-bis-*O*-[*p*-(α-bromotolyl)diphenylmethyl]poly(ethylene glycol) 400-[dibenzo-58.2-crown-19.4]rotaxane was synthesized by the statistical method by mixing the "crown" polyether with poly(ethylene glycol) 400 to produce a threading equilibrium mixture at maximum concentration and blocking the hydroxyl end groups with bromomethyltrityl groups. In the second stage the rotaxane was cyclized through the α-bromotolyl end groups in very dilute solution in DMF with zinc/copper couple to yield the catenane [2]-{*cyclo*-[1,2-diphenylethane-*p,p'*-di(α-benzhydryl)poly(ethylene glycol) 400]}-[dibenzo-58.2-crown-19.4] in 14% yield. Besides the catenane, a fraction of oligorotaxane having a $\overline{DP}$ of 3 was formed by linear condensation polymerization.

The statistical method for preparing topological isomers gives very low yields of catenane.[1,2] It presents two contradictory requirements: very high concentration of chain and ring molecules to permit maximum threading and, at the same time, very low concentrations for the cyclization of the chain to produce a macrocyclic ring.

Previously[3] we reported the statistical synthesis in relatively high yield (15%) of [2]-[ω,ω'-di(*O*-trityl)poly(ethylene glycol) 400]-[dibenzo-58.2-crown-19.4]rotaxane, where the ring is a macrocyclic crown polyether based on poly(ethylene glycol) 400. In the present work we made use of the relative stability of a similar rotaxane to cyclize its linear chain through its two blocking groups, under conditions of high dilution to yield a catenane.

Results and Discussion

A rotaxane III, having terminal functional groups for cyclization, was prepared by mixing poly(ethylene glycol) 400 with the macrocyclic "crown" polyether,[3] dibenzo-58.2-crown-19.4 (I), in equimolar amounts. The mixture was heated at 120 °C for 30 min to affect threading equilibration, followed by reacting the glycol chain ends with the blocking group, *p*-(α-bromotolyl)diphenylbromomethane (II), which has been synthesized for this purpose.