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Complex Formation between Cyclic Urethane and Zinc Chloride: Its Effect on Polyrotaxane Synthesis

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ABSTRACT

The complex formation between cyclic urethane based on diethylene glycol and hexamethylene diisocyanate and $ZnCl_2$ has been investigated by the NMR method. It has been established that coordination proceeds only through oxygen atoms of cyclic urethane. Its ability to aggregate into ordered clusterlike complexes under the influence of $ZnCl_2$ has been proved. The effect of clusterlike complexes on styrene polymerization in the presence of such complexes and pure cyclourethane, leading to polyrotaxane formation, has also been investigated. X-ray diffractograms of extracted reaction products show the maxima typical for both polystyrene and cyclic urethane. The analogous investigation of products obtained in the presence of the linear analogue of cyclic urethane and its complexes with $ZnCl_2$ prove that polystyrene and urethane are not chemically bonded. The number of cyclic molecules corresponding to one polymer chain in the polyrotaxanes obtained has been calculated. It was established that this number is notably increased when cyclourethane is preliminarily bonded into clusterlike complexes with $ZnCl_2$.

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INTRODUCTION

Compounds consisting of molecules which are not chemically bonded (catenans, rotaxanes, knots [1]) have recently been investigated [2-6]. These compounds are formed by mechanical entanglements. They were first discovered in some groups of the nuclein class [2-4]. Catenans and rotaxanes may also be synthesized by various statistical and directional methods [5, 6]. Polyrotaxanes are of great interest due to the peculiarities of their structure which result in specific and original properties [7-11].

The directional methods of polyrotaxanes synthesis [9, 10] permit an increase in the product yield and an increase in the content of macrocycles threaded on the polymer chain in comparison with the products of statistical synthesis [8].

In this paper we attempt to develop a new directional method for polyrotaxane synthesis. Our main idea is based on the possibility of obtaining ordered aggregates of macrocycles due to their complex formation with any complexing agent [12]. We believe the number of macrocycles penetrated by one growing polymer chain during polyrotaxane synthesis should be increased in this way. $ZnCl_2$ was used as the complexing agent. Earlier [13] it was shown that some oligomers can form clusterlike complexes with $TiCl_4$. The formation of similar clusterlike complexes between cyclic urethane and $ZnCl_2$ is expected in this case. We have chosen polystyrene as the penetrating polymer because styrene polymerization is well studied and polystyrene properties are defined rather well. Styrene, due to its low polymerization rate, is very convenient and permits a polymer with a high molecular mass to be obtained.

EXPERIMENTAL

The cyclic urethane with 34 atoms/cycle, consisting of two residues of diethylene glycol and two of hexamethylene diisocyanate, was used as the macrocycle in our experiments (Fig. 1). This macrocycle has various functional groups (ether, carboxyl atoms of axigen, nitrogen atoms) capable of forming complexes with metal salts (in particular with $ZnCl_2$) [14].

All the solvents and initial reagents were thoroughly purified and dried. Cyclic urethane (CU) was obtained in dichlorethane solution according to the method described in Ref. 15. To identify the urethane, IR spectroscopy and thin-layer chromatography were used. Linear diurethane (LDU) from oligodiol and hexamethylene diisocyanate was produced without solvents, the ratio of components during synthesis being 1:2. The water content in $ZnCl_2$ did not exceed 0.5%.

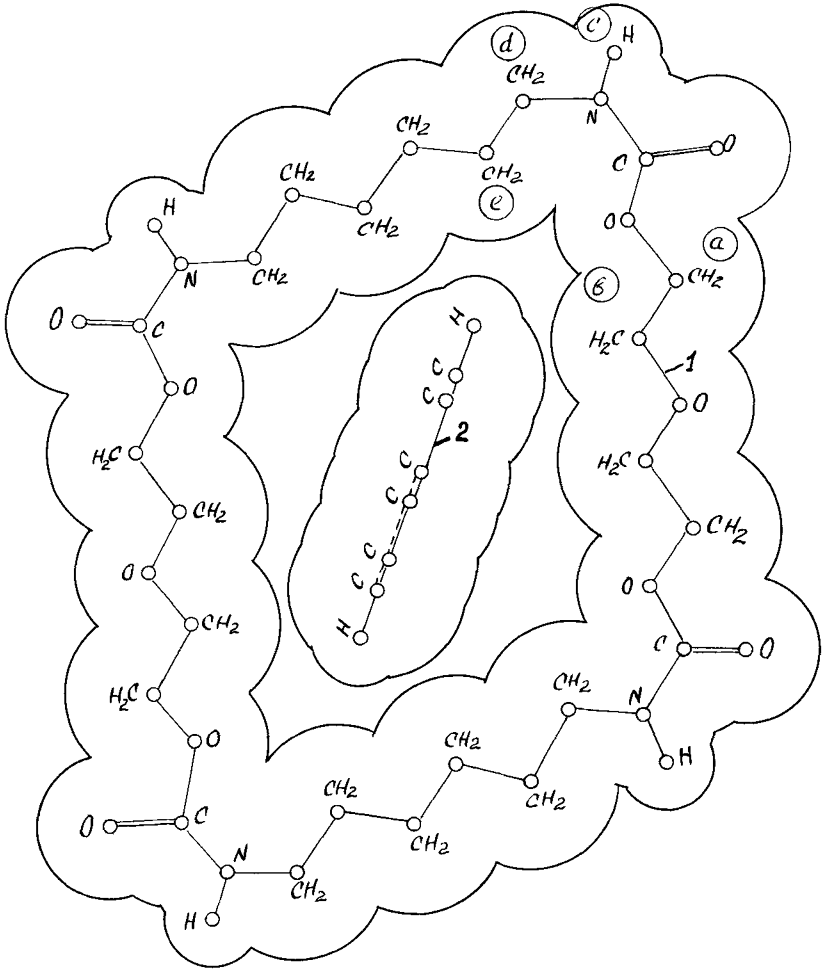

FIG. 1. Scheme of polyrotaxane formation: 1 is the cross section of the CU molecule in the ring plane; 2 is the cross section of the PS molecule in the plane perpendicular to the macromolecule axis.

The polymerization of styrene was performed without initiator for 3-4 months in vacuumized ampules.

The synthesis of polyrotaxane was realized in the following way. Styrene was polymerized in the presence of both free CU and its complexes with $ZnCl_2$ [12]. Pure CU and the CU-$ZnCl_2$ complex in dimethylsulfoxide (DMSO) were placed in glass ampules. Then the solvent was removed in vacuo. Styrene was condensed into the ampules, and they were degassed and sealed off. It should be noted that no initiator was introduced into the reaction mixture. Polymerization was initiated by traces of oxygen in the system. The reaction proceeded very slowly (3-4 months), and as a result the polystyrene molecular mass reached 10^5-10^6. Due to this the long polymer chains, penetrating macrocycles, prevent the cycles from "sliding off." The reaction products obtained were thoroughly extracted by ethanol in order to remove $ZnCl_2$. To remove the free PS and unbound CU, the samples were extracted by benzene and DMSO, respectively. The molecular mass of pure polystyrene in the case of statistically produced polyrotaxane was 10^6 and for polyrotaxane synthesized in the presence of $ZnCl_2$ it was 10^5. The molecular masses of PS were determined by viscometry in toluene solutions.

The complex formation between CU and $ZnCl_2$ was investigated by NMR spectra and the viscometry method. NMR spectra were obtained for polymers dissolved in deuterated DMSO by using a BS-467 spectrometer with an operating frequency of 60 MHz. Hexamethyldisiloxane (HMDS) was taken as the internal standard. Deuterated DMSO was selected as a solvent because it dissolves ligand rather well, although it complicates the quantitative analysis of the complex formation due to specific interaction with urethane and coordination with $ZnCl_2$.

A DRON-2 diffractometer was used for x-ray wide-angle scattering investigations at room temperature. Copper anode radiation filtered through nickel foil was used. Intensity curves were taken in the range of an automatic step-scanning detector. The experimental intensity values were normalized to equal intensity of the primary beam and the unit optical path, taking into account the adsorption of the radiation used [16].

RESULTS AND DISCUSSION

As mentioned in the Introduction, our main task was to study the mechanism of polyrotaxane formation in the presence of complex-forming agents. We assumed that the formation of clusterlike complexes between the cyclic compound and the complexing agent would contribute an increase in the number of cyclic molecules penetrated by polymer chains due to the formation of clusterlike aggregates. Therefore, as a first step we investigated the conditions of complex formation between CU and $ZnCl_2$ by using NMR spectroscopy.

The full NMR spectrum of CU consists of five signals (Fig. 2). Their reference was selected according to published data [17]. The signals $\delta_1 = 2.36$ and $\delta_2 = 3.30$ are inherent to the solvent. The ratio

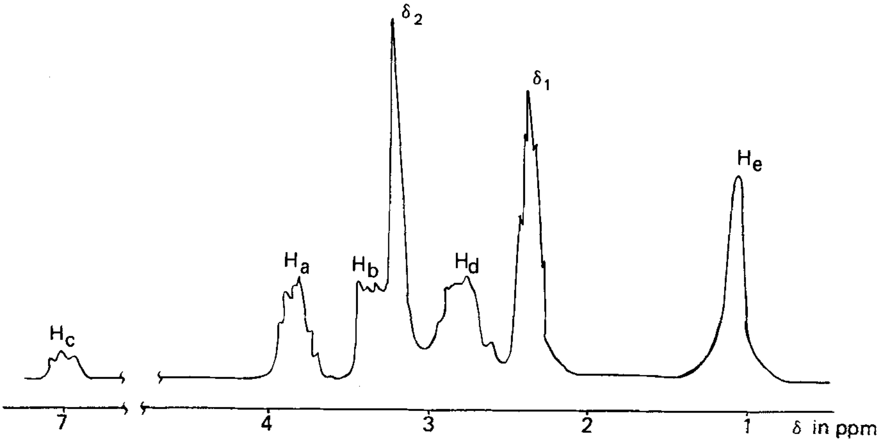

FIG. 2. NMR spectra of CU in DMSO.

of the number of each type of proton, as established from the integral spectra, is in a good agreement with the chemical formula of CU:

$$H_a:H_b:H_c:H_d:H_e = 2:2:1:2:4$$

When $ZnCl_2$ is added to CU, the signals are shifted to the region of weak fields. This effect may be explained by the decreasing electron density on the donor molecule of the ligand. As a result, the diamagnetic component of the shielding constant is diminished, leading to increasing chemical shift. The values of the chemical shifts (δ) of the proton of CU and their displacements (Δδ) depend on the change in $ZnCl_2$ concentration and are given in Table 1. As can be seen, the maximum changes of chemical shifts characterize the signals corresponding to the protons of the methylene groups, which are close to the groups $-CH_2-O-$ (H_b) and $-CH-O-CO-$ (H_a). The δΔ values decrease with increasing distance between the corresponding protons and the ether groups.

The invariability of δ for protons of nitrogen atoms in urethane groups H_c and for protons of groups H_d and H_e at a low concentration of $ZnCl_2$ is probably caused by insignificant changes in both the electron density of these parts of the ligand molecule and its conformation. Only after reaching some excess salt concentration as compared to the CU concentration do these changes become important enough for the shift of signals to be meaningful.

TABLE 1. Chemical Shifts of CU Signals and the Shifts Depending on $ZnCl_2$ Concentration in Solution

No.	$\frac{C_{ZnCl_2}}{C_{CU}}$	δH_a	$\Delta\delta H_a$	δH_b	$\Delta\delta H_b$	δH_c	$\Delta\delta H_c$	δH_d	$\Delta\delta H_d$	δH_e	$\Delta\delta H_e$
1	CU	3.93	-	3.38	-	7.02	-	2.83	-	1.14	-
2	0.33:1	3.94	0.01	3.39	0.01	7.02	0	2.83	0	1.14	0
3	0.5:1	3.94	0.01	3.40	0.02	7.02	0	2.83	0	1.14	0
4	0.75:1	3.95	0.02	3.41	0.03	7.02	0	2.83	0	1.14	0
5	1:1	3.96	0.03	3.41	0.03	7.02	0	2.84	0.01	1.14	0
6	1.5:1	3.96	0.03	3.42	0.04	7.02	0	2.84	0.01	1.14	0
7	2:1	3.96	0.04	3.43	0.05	7.02	0	2.84	0.01	1.15	0.01
8	3:1	3.97	0.04	3.43	0.05	7.02	0	2.85	0.02	1.14	0
9	4:1	3.97	0.04	3.44	0.06	7.03	0.01	2.85	0.02	1.15	0.01
10	5:1	3.97	0.04			7.03	0.01	2.86	0.03	1.15	0.01
11	6.65:1	3.97	0.04			7.03	0.01	2.86	0.03	1.15	0.01

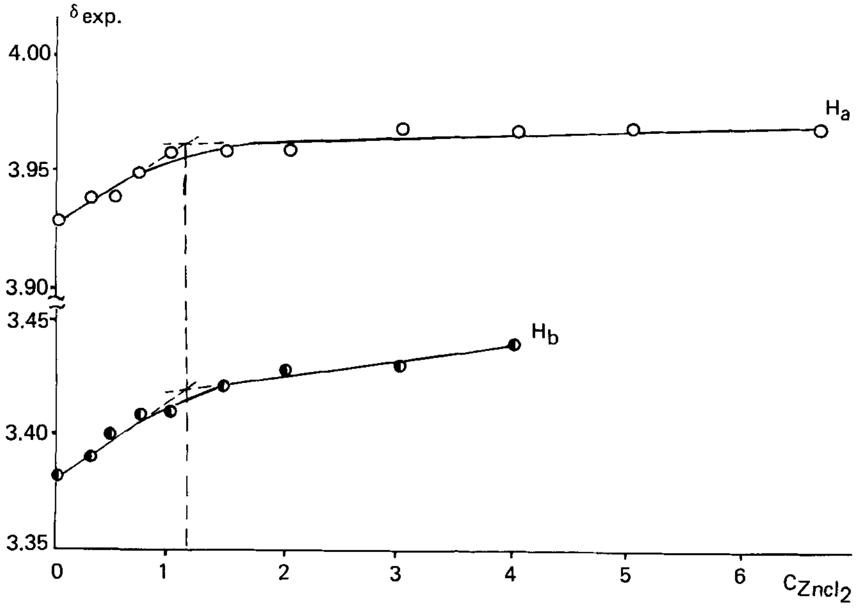

FIG. 3. The dependence of chemical shifts on the variation of $ZnCl_2$ concentration in solution (C_{CU} = 49 mol/m³).

The data obtained testify to the preferable participation of Cu oxygen atoms in complex formation with zinc. The absence of $ZnCl_2$ interaction with the nitrogen atoms of CU is probably explained both by lesser electron donor ability of nitrogen atoms compared to oxygen atoms [18] and by the interaction between the H atoms of NH groups and DMSO that leads to H bonding [19].

To determine the stoichiometric composition of the complexes, we used the method of molar ratios [14, 20]. The composition of the complexes may be defined by the inflection points of δ_{exp} - C_{ZnCl_2}/C_{CU}. The ratio valid for such points is C_{ZnCl_2}/C_{CU} = p/g where p and g are the stoichiometric coefficients in the equation

$$gCU + pZnCl_2 \rightleftharpoons [(ZnCl_2)_p(CU)_g]$$

In order to obtain these dependences we have used data on the changes of chemical shifts of H_a and H_b protons. The curves in Fig. 3 show the effect of $ZnCl_2$ concentration on chemical shifts of these protons. There, the inflection point corresponds to complexes of stoichiometric composition 1:1. For this stoichiometry one can suppose the existence of complexes where the ratio CU:$ZnCl_2$ is 1:1, 2:2, 3:3, etc.

The viscometric data show the growth in specific viscosity of a 0.074-M solution of complexes with a stoichiometric composition of 1:1 in DMSO ($\eta_{sp} = 0.3$) in comparison with the specific viscosity of a 0.074-M solution of pure CU ($\eta_{sp} = 0.2$). It is difficult to explain the increase of η_{sp} by the simple addition of the small compact molecules of $ZnCl_2$ to CU molecules with the formation of simple complexes. The data obtained are evidence for the formation of large, clusterlike aggregates of macrocycles.

Suppose the coordination number of Zn is 4, then the complex must be of a tetrahedric form. Our supposition is admissable because the coordination number of Zn may exceed 4 only in its complexes with strong electron donors [21], whereas the CU investigated does not belong to this category. Hence, the stoichiometric composition 1:1 may correspond to the following complexes:

$$nCU + nZnCl_2 \rightleftharpoons (ZnCl_2.CU)_n$$

with n equal to 1, 2, 3, etc. Therefore, we can suppose the existence of complexes where linear aggregates of CU molecules are interconnected by Zn ions. The latter may coordinate atoms of ether, ester, or carboxyl oxygen of two neighboring CU molecules. There, the angles between O. . .Zn. . .O bonds are approximately 109°, the planes of CU molecules being disposed at the same angle relative to each other.

Thus, based on the results obtained, we can assume the existence of ordered clusterlike complexes (Fig. 4).

From this point of view we have investigated the effect of these clusterlike complexes on polyrotaxane synthesis.

The curves of x-ray scattering intensities for products obtained after styrene polymerization in the presence of both CU and CU-$ZnCl_2$ complexes, as well as curves for pure CU, are presented in Fig. 5. The curves for polymers obtained in the presence of pure CU (Curve 3) and complex (Curve 1) have maxima which are characteristic both of PS and CU. Wide-angle x-ray scattering curves for pure PS (Curve 4) and CU (Curve 5) show that the intensities of the corresponding discrete peaks on Curves 1 and 3 correlate with the intensities of CU maxima (Curve 5) as 0.4:1 and 0.2:1, respectively. Based on these data we proposed that the volume fraction of the phase possessing a CU structure is 0.4 with $ZnCl_2$ present and 0.2 without $ZnCl_2$. To test this supposition, the values of the intensities of scattering for pure CU multiplied by 0.4 were subtracted from the values given on Curve 1. The result of subtraction (Curve 2) coincides with the values of

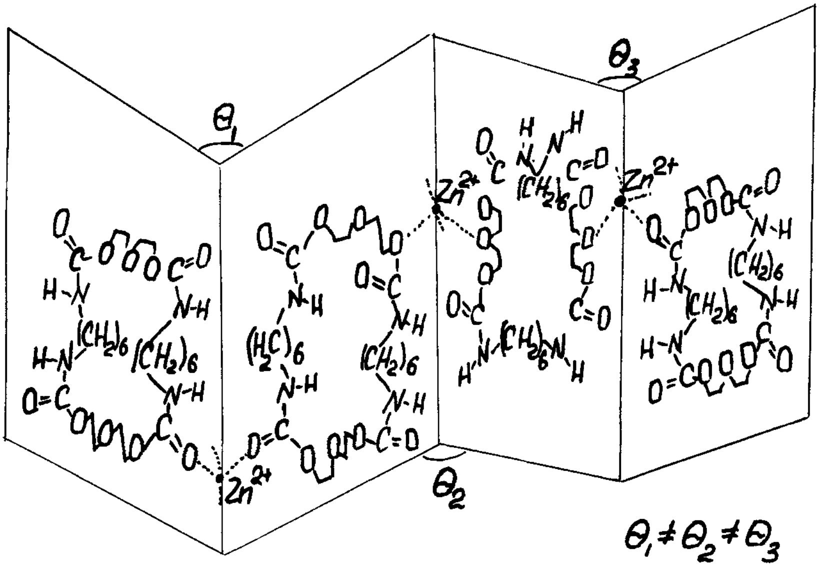

FIG. 4. Structural scheme of clusterlike complexes between CU and $ZnCl_2$.

scattering by pure PS multiplied by 0.6 (dashed line). Hence, the product resulting from styrene polymerization in the presence of CU complexes with $ZnCl_2$ contains 40% CU and 60% PS, while the system without the complexing agent has 20% CU and 80% PS.

The results obtained prove that while styrene polymerizes with CU dissolved in it, pure PS cannot be fully extracted from the products that are formed. It should be noted that the amount of CU in the reaction product is considerably increased when CU has been preliminarily coordinated in the complex.

In order to test whether CU is chemically bonded with the growing PS chains or not, we have investigated styrene polymerization in the presence of the linear analogue of CU. We have used linear diurethane (LDU) obtained from HMDI and the monoethyl ether of ethylene glycol. Polymerization was performed both in the presence of pure LDU and its complexes with $ZnCl_2$. The reaction product was also investigated by the x-ray method. The diffractogram of the product obtained by polymerization of styrene in the presence of pure LDU after removing PS is shown as Curve 7. The curve for the product obtained in the presence of complexes LDU with $ZnCl_2$ after removing PS and $ZnCl_2$ is identical to Curve 7 and is not given here. Note that Curve 7 repro-

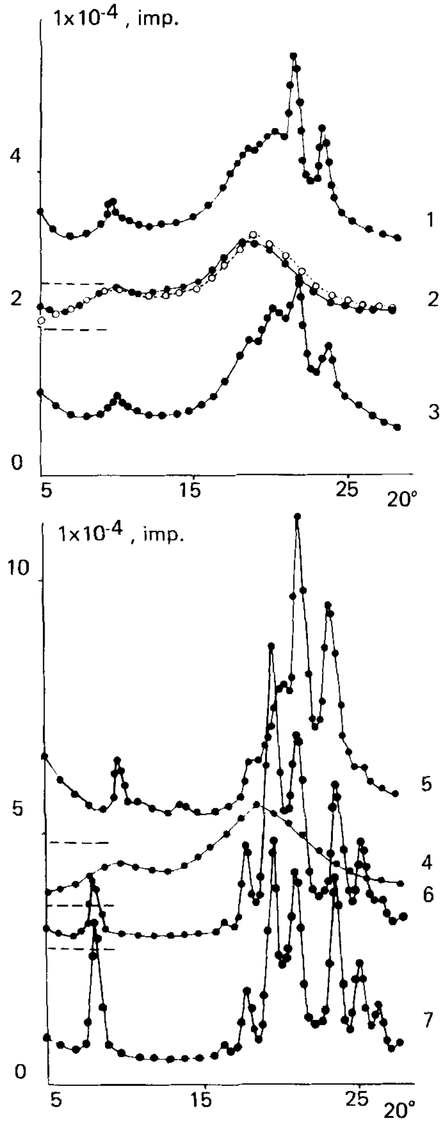

FIG. 5. Diffractograms of initial compounds and reaction products: 1 is the intensity curve for polyrotaxane obtained in the presence of $ZnCl_2$; 2 is the result of the subtraction from Curve 1 of the intensity of scattering by the phase characterized by a pure CU structure (the profile of scattering produced by a corresponding quantity of PS is shown by the dotted line); 3 is the intensity curve for polyrotaxane obtained in the absence of $ZnCl_2$; 4, 5, and 6 are diffractograms of PS, CU, and LDU, respectively; 7 is the diffractogram of the product resulting after PS removal from the system which was formed by styrene polymerization in the presence of LDU.

duces the peculiarities of the LDU scattering curve (Curve 6) rather well. From this fact the conclusion is drawn that PS and LDU are not bonded chemically while when styrene is polymerized in the presence of LDU (independent on the presence or absence of $ZnCl_2$ in the system). Based on these data, we believe that CU is also not bonded chemically with PS. All the results testify to the formation of a polymer with the polyrotaxane structure in the presence of CU.

The polyrotaxanes obtained are formed by CU molecules penetrated by polystyrene chains. CU molecules with atom groups approximated by van der Waals radii are shown on Fig. 1. As is seen, the cross section of the styrene monomer unit in PS is freely disposed in the CU cavity. The Steward-Brigleb construction model has also shown that the monomer unit of the PS molecule may be easily disposed in the cavity of CU. Hence, there is no steric hindrance for the penetration of CU molecules by PS chains during polymerization.

As mentioned above, the amount of CU in polyrotaxane obtained in the presence of free CU is less than in the presence of complexes with $ZnCl_2$. From these data and from the densities of PS and CU, we have calculated the quantity of styrene monomer units in the chain corresponding to one urethane cycle. Approximately 18 to 19 monomer units correspond to one macrocycle in polyrotaxane created by the statistical method of synthesis and 6 to 7 monomer units when $ZnCl_2$ is used.

Thus, the data present evidence of the increasing number of cyclic molecules on the polystyrene chain in polyrotaxane synthesis if the macrocycles were ordered into clusterlike complexes beforehand.

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