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Abstract

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Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak,
S. V. Vinogradova,
M. G. Vinogradov

A New Method for Obtaining Macrocyclic Compounds from Linear Polymers

As has been shown in a large number of examples, heterochain polymers obtained by equilibrium polycondensation, i.e., under conditions in which exchange reactions occur between the units of the polymer, always contain a small amount —no more than 1-2% of the weight of the polymer—of cyclic oligomers. Thus, from polyhexamethylene adipamide (nylon 66), a macrocyclic monomer and dimer were isolated ([1]); from poly-ϵ-caproamide, a dimer, trimer, etc., up to a nonamer ([2]); from the polymer of ω-aminoundecanoic acid (rilsan), a monomer and dimer ([3]); from polyethylene terephthalate, a trimer, tetramer, and pentamer ([4]); from poly-1,4-cyclohexylenedimethylene terephthalate, a trimer ([5]); and from a polyurethane based on hexamethylene diisocyanate and butanediol, a monomer and dimer ([6]).

If a linear polymer capable of undergoing destruction with the formation of macrocycles is heated under conditions in which the latter can be removed by distillation or sublimation as they form, the equilibrium polymer cycle will be shifted toward the formation of cyclic products. The method of thermal destruction of polymers was used by Carothers ([7]) for the synthesis of macrocyclic esters, anhydrides, and formals, and by Baker and Ollis ([8]) for the preparation of cyclic salicylides. Recently this same method was applied by Kluiber and Lewis ([9]) to the synthesis of cyclic intracomplex compounds of various aliphatic bis-(β-diketones) with beryllium.

We have found a new method for obtaining macrocyclic compounds, consisting in heating dilute solutions of polymers under conditions in which exchange reactions can occur between the units of the polymer macromolecules.

As is known, the probability of shifting the equilibrium

$$\text{linear heterochain polymer} \overset{\text{destruction}}{\underset{\text{polymerization}}{\rightleftarrows}} \text{heterocycle}$$

toward cycle formation will increase as the system is diluted, since the rate of the bimolecular reaction of polymerization of the cycles will thereby decrease,

Fig. 1

Figure 1: Fig. 1

whereas the rate of destruction of polymer molecules, which is a monomolecular reaction, does not depend on the concentration of the polymer in solution.

Obviously, at a sufficiently low solution concentration the equilibrium can be shifted substantially toward low-molecular cyclic products. The size of the cycles formed in dilute solutions will apparently be determined by both thermodynamic and energetic factors. From the thermodynamic standpoint, the size of the cycles should be the smallest, since the entropy of the system will then be greatest. At the same time, energetically the formation of the least strained cycles is most favorable, and consequently their size will also depend on the structure of the starting polymer.

In studying the properties of intracomplex polymers obtained by polycoordination of beryllium acetylacetonate and bis-(β-diketones) of the general

formula:

$$CH_3 - CO - CH_2 - CO - R - CO - CH_2 - CO - CH_3,$$

where

$$R = -\text{benzene ring}-O-\text{benzene ring}-, \quad -\text{benzene ring}-CH_2 - CH_2-\text{benzene ring}-, \quad -(CH_2)_8-$$

(I) (II) (III)

it was found that exchange reactions between the units of the macromolecules of these polymers, analogous to the reaction by which they are obtained, proceed[10] extremely readily. For example, the process of averaging polymer molecules by length between two fractions of polymer I having different molecular weights, at 70° in dimethylformamide, is completed after 6 hours, while at a temperature of about 100° equilibrium is reached within several minutes. It could therefore be assumed that, in dilute solutions, intracomplex polymers should readily undergo destruction on heating, with formation of cyclic products.

Fig. 1. Destruction of polymer I in solutions of different concentration at 130° (solvent—chlorobenzene)

As our study showed, all the indicated polymers in dilute solutions at low temperatures, even at room temperature, undergo destruction, while in concentrated solutions under the same conditions, or upon heating in the solid state at higher

Fig. 2

Figure 2: Fig. 2

temperatures, they again recover their initial properties. This phenomenon of reversible destruction of intracomplex polymers occurred in all the solvents we tested, including such inert ones as benzene, chlorobenzene, and diphenyl. Table 1 gives values of the logarithmic viscosity of polymers successively heated for 6 hours at 100° first in a 25% solution (solvent–chlorobenzene), then in a 0.5% solution, and then again in a 25% solution.

Fig. 2. Dependence of the yield of cyclic complex IV on the concentration of a solution of polymer III in chlorobenzene at 150°

The destruction products were isolated from the solution by evaporating the solvent at room temperature with the aid of a fan. The molecular weight of polymer I after destruction in a 0.5% solution, determined cryoscopically in nitrobenzene, was 1100, which corresponds approximately to a trimer; and the molecular weight of polymer II after destruction proved to be 560, which corresponds approximately to a dimer.

A study of the destruction of the polymers investigated in solutions of different concentration showed that, for each polymer, depending on its structure and molecular weight, there exists a concentration above which its molecular weight after heating of the solution remains unchanged. For example, as can be seen from Fig. 1, for polymer I with logarithmic viscosity $\eta_{\ln} = 0.43$, this concentration in chlorobenzene is $\sim 15\%$. For beryllium polysebacylacetonate (polymer III) with $\eta_{\ln} = 0.75$, it is $\sim 70\%$ in the same solvent.

Since the reversible change in molecular weight of intracomplex polymers in solutions is not accompanied by a change in the number of terminal enol groups at the chain ends, determined by titration by

Fritts' hypothesis ([11]); the cause of this phenomenon can lie only in the formation, from linear macromolecules capable of polymerization, of cyclic oligomers consisting of the same elementary units as the polymer molecules. This process may be represented schematically as follows:

$$\cdots - A - B - A - B - A - B - A - B \quad \rightleftarrows \quad A - B - A \cdots A - B - A - B - A$$
$$\cdots - B - A - B - A - B - A - B - A \quad \rightleftarrows \quad B - A - B \cdots B - A - B - A - B$$

etc.

As shown in the above-mentioned work ([9]), as a result of the thermal destruction of poly(beryllium sebacylacetonate) at 200° in vacuum, cyclic monomeric complex IV is formed.

(structure of complex IV)

(IV)

It could be expected that this compound would also be present in the products of destruction of poly(beryllium sebacylacetonate) in organic solvents. To verify this assumption, the products of destruction of polymer III in chlorobenzene were extracted with methanol, and the residue obtained after evaporation of the methanol at room temperature was heated in a sublimation apparatus at 75° and a vacuum of 10^{-3}–10^{-4} mm Hg. The substance sublimed under these conditions was the cyclic monomeric complex of sebacylacetonate with beryllium, IV, identical in its properties to the product obtained upon thermal destruction of polymer III. On melting, this monomeric complex was converted into a polymer with $\eta_{ln} = 0.55$. Figure 2 shows the dependence of the yield of cyclic monomer IV on the concentration of polymer III in chlorobenzene after heating the solution in sealed ampoules in a nitrogen atmosphere at 150° until equilibrium was established. At a solution concentration of 0.2%, the yield of pure monomer was 46%.

Table 1

Reversible destruction of intracomplex polymers in solution (solvent—chlorobenzene)

Polymer	η_{ln} (dl/g) of polymers in chlorobenzene as a result of their subsequent heating in solutions	η_{ln} (dl/g) of polymers in chlorobenzene as a result of their subsequent heating in solutions	η_{ln} (dl/g) of polymers in chlorobenzene as a result of their subsequent heating in solutions
Polymer	$C_{soln} = 25\%$	$C_{soln} = 0.5\%$	$C_{soln} = 25\%$
I	0.40	0.05	0.40
II	0.44	0.03	0.40
III	0.42	0.04	0.44

The degree of conversion of intracomplex polymers into cyclic oligomers also depends on the nature of the solvent and decreases with decreasing temperature.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.