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Polymerization and co-polymerization of cyclic urethanes and ureas

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SUMMARY: The ionic ring-opening polymerization is a chain reaction which is initiated by low molecular weight as well as ''living'' high molecular weight ionic species to obtain block copolymers in the latter case. Thus, ring-opening polymerization is combined with vinyl polymerization and hence block copolymers are obtained which consist of vinyl polymer blocks and polymer blocks which generally are obtained by stepwise polymerization reactions, such as polycondensation and polyaddition polymerization.

The ring-opening polymerization of cyclic carbonates, lactones, cyclic depsipeptides, and lactames which in conjunction with cyclic carbonates leads to alternating polyesterurethanes as well as the ring-opening polymerisation of cyclic urethanes and ureas is of great interest to obtain completely new polymer systems. In this presentation in particular the ionic ring-opening polymerization of cyclic urethanes and ureas is presented and the mechanism of the polymerization reactions is discussed in detail.

Introduction

A great challenge of macromolecular chemistry is the synthesis of well-defined architectures of macromolecules. Living or controlled chain polymerization reactions are particularly suitable to reach the goal, while polymers obtained by step reactions, such as polycondensation and polyaddition polymerizations generally are less well-defined. If, however, the condensation reaction is applied to obtain cyclic monomers these are often eligible to a controlled ring-opening polymerization when suitable catalysts are used and end/back-biting reactions and transreactions are avoided; moreover, living polymer systems can be applied as initiators and block copolymers are obtained which otherwise cannot be synthesized.

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The ring-opening copolymerization itself presents a number of peculiarities; thus, the copolymerization of dimethyltrimethylene carbonate (DTC) with ε-caprolactone results in block copolymers with tapered structures between the blocks1); with pivalolactone blockcopolymers without tapured structures are obtained2); and with L-lactide (LLA) the polylactide formed in the beginning of the reaction is readily transferred to an alternating copolymer. Whenever a DTC unit is added to the living end of a polylactide chain the alcoholate will add to a carbonyl carbon of another polylactide chain under clevage forming a new living polylactide chain end and a polymer with an LLA-DTC-LLA triade3).

Another peculiar mechanism is observed when DTC is copolymerized with ε-caprolactame4). In the first place the polycarbonate is formed. The lactam enters the reaction when the active site of a polymer chain end is transferred to ε-caprolactame which then adds to the carbonyl carbon of another chain resulting in a polycarbonate chain with an activated caprolactame end and a living polycarbonate chain which attacks the activated ε-caprolactame unit to form an ester-urethane unit. This reaction is rather slow with $Al(OBu)_3$ as an initiator and fast with $MgBu_2$ as an initiator. Eventually, an alternating polyester-urethane is obtained which within NMR detection limits is free of urea units.

Ring-opening Polymerization of cyclic urethanes

Trimethylene urethane is obtained by the reaction of amino propanol with diphenyl carbonate in the presence of $Bu_2Sn(OCH_3)_2$ at 140 °C with a yield of 61 % after distillation and crystallisation.

The polymerization in the bulk with anionic and insertion initiators yields polymers with urea and carbonate units as well as the polycondensation of a dimeric urethane with hydroxy and phenyl urethane endgroups5).

On the other hand, the cationic ring-opening polymerization with $BF_3 \bullet O(C_2H_5)_2$ or

CF_3 SO_2R(R=OH, OCH_3) as initiator in the melt yields polyurethanes of uniform structure. The kinetics follow first order and the molecular weight increases linearly with conversion as long as the melt is homogeneous.

The initiation comprises methylation of the carbonyl oxygen and O-alkyl clevage upon nucleophilic attack of the respective methylene carbon by the carbonyl oxygen of a monomer molecule. Alternatively, the methylated monomer may react with the acetate anion or with triphenylphosphane as a nucleophile.

Side reactions observed in particular in the heterogeneous regime of the polymerization are transfer and termination reactions. When the living chain end is attacked by the nitrogen instead of the carbonyl oxygen atom of a monomer this results in a transfer reaction; the resulting active species is a protonated monomer which upon reaction with a monomer molecule results in a species with an active group and, after decarboxylation, an amine group being a terminating group.

Instead of a low molecular weight cationic initiator living tetrahydrofurane obtained with triflate or triflic anhydride as initiator may be used. In solution one monomer unit is added as an endgroup (endcapping). After removal of the solvent the polymerization occurs in the melt and di- and triblockcopolymers are obtained.

Dimethyltrimethylene urethane (DTU) is obtained by reaction of the amino alcohol with diphenyl carbonate. Polymerization of the monomer, however, cannot be achieved6). The polymer obtained by polycondensation reaction rather is readily degraded in the presence of $Bu_2Sn(oct)_2$ at 120 °C to form a homologous series of cyclic oligomers.

Consequently, the linear monourethane with one OH endgroup and one phenylurethane endgroup yields the cyclic monomer. The corresponding diurethane, however, yields the polymer. In the early stages of the polymerization linear oligomers are observed with - as expected - the even members of the homologous series. When the diurethane is copolycondensated with the monourethane unexpectedly beside the even members also the odd members of the homologous series are observed, though in smaller amount.

A cyclic diurethane is observed by reaction of the diamine with the respective bischloroformiate under Ruggl-Ziegler dilution conditions. The polymerization of the cyclic diurethane is achieved with $Bu_2Sn(OCH_3)_2$ or $Al(OiPr)_3$ both in solution and in the melt; as end groups the methyl group and the isopropyl group are obtained by NMR-spectroscopy, respectively7).

Polymerization of cyclic ureas

The polymerization of 5- and 7-membered cyclic ureas was reported already in 1958 by Hall with NaH as initiator in the melt; the polymers were not fully characterised, though.

While the 6-membered urea, dimethyltrimethylene urea, is not polymerized, tetramethylene urea is polymerized in the melt and ethylene urea in solution, both with strong basis.

Even more interesting is the copolymerization of tetramethylene urea with DTC both in the melt and in solution (N, N-dimethylpropylene urea, DMPU). In solution, within increasing monomer concentration the molecular weight of the polymer increases, the concentration of DTC in the copolymer being slightly enhanced over the concentration of tetramethylene urea units8).

The mechanism of the polymerization is similar to that of DTC and ε-caprolactame. This is clearly shown when tetramethylene urea is added to living poly DTC. The active site is transferred to the monomeric urea which then attacks the carbonyl group of a polycarbonate chain under clevage; the alkyloxycarbonylated cyclic urea endgroup then is ring-opened by a living polycarbonate end. In this way two urethane groups are formed.

In the contrast, tetramethylene urea is copolymerized with ethylene carbonate in the melt with $MgBu_2$ as initiator yielding an alternating copolymer right from the beginning as proved by NMR-spectroscopy. The mechanism of this reaction only can be envisaged in such a way that heterodimers are formed in the first place which then form the polymer via a step growth mechanism.

Conclusion

The ring-opening polymerization of cyclic monomers adds an important tool to the methods of preparation of well-defined macromolecular architectures. In particular, it allows the crossover from polymers obtained by chain reactions to those generally obtained by step growth reactions. The copolymerization of cyclic monomers is characterised by a large variety of unusual reactions and interesting polymers such as alternating poly(ester-urethane)s and polyurethanes comprising ethylene carbonate units.

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