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Ring-opening polymerization by various ionic processes

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SUMMARY: The ring-opening polymerization of cyclic carbonates, lactones, ester amides, urethanes and ureas as well as selected copolymerization reactions yield a variety of new polymers with well-defined architecture. The investigation of the mechanism of ring-opening polymerization reactions with anionic, insertion and cationic initiators shows a number of peculiarities beside activated chain-end and activated monomer mechanisms such as transfer and termination reactions, ring-expansion polymerization as well as the thermodynamic una bility of polymerization in special cases.

Introduction

For physical investigations as well as for several applications a well-defined architecture of polymers is desirable. Thus, living polymerization reactions have gained great importance and have been realised to a high degree for anionic, cationic, radical, and metal complex initiated polymerizations. Ring-opening polymerization may also follow at least a quasi-living path, in particular when back-biting and trans-reactions are absent. Besides, it offers the unique possibility to obtain block-copolymers by linking structures which usually are obtained by chain growth reactions with those which commonly are obtained by step growth reactions. This is realised when a macromolecular initiator is employed for the ring-opening polymerization of suitable monomers.

Ring-opening polymerization of cyclic carbonates

Six-membered cyclic carbonates are polymerised with variety of anionic initators the alcoholate group being the active species. Random co-polymers are obtained when different six-membered cyclic carbonates are employed. Co-polymerization with ε-caprolactone yields

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blockcopolymers with a tapered structure inbetween the two blocks dimethyltrimethylene-carbonate (DTC) being polymerised first. In the co-polymerziation with pivalolactone (PVL) block-copolymers are obtained since whenever PVL forms the terminal unit the active group is a carboxylate group which is unable to open the carbonate ring1). In the co-polymerization of DTC with L-lactide (LLA), polylactide (PLLA) is formed first. Whenever a DTC unit is added to the active end it attacks the carbonyl carbon of a LLA unit to form an LLA-DTC-LLA triade. With the progress of polymerization an increasing amount of mixed diades is formed2).

The co-polymerization of DTC with ε-amino caprolactam (ECLam) follows a peculiar mechanism. While DTC is polymerised an ECLam anion is formed which attacks the carbonyl group of a carbonate unit to form an acylated ε-caprolactam endgroup which reacts in a ring-opening fashion with the alcoholate endgroup of another polymer chain to result in a polyester urethane unit. With $MgBu_2$ the reaction is fast and the polyester urethane is observed already after 5 min. With $Al(OsecBu)_3$ the reaction is slow and the ester amide is only observed after 5 h. It would be conceivable that an ECLam anion would attack the carbonyl carbon of an ester group as well as of a urethane group to result in a polyester amide or a polyester urea; urea groups, however, were not observed; amide groups are observed to a very small amount3).

Ring-opening polymerization of cyclic urethanes

Trimethylene urethane is obtained from amino propanol and diphenyl carbonate with $Bu_2Sn(OCH_3)_2$ as a catalyst at 140 °C. After distillation and crystallisation the urethane is obtained in a yield of 61 %.

With anionic initiators and Et_2Zn and other insertion catalysts in the bulk a polymer with urea and carbonate units is observed resulting from head-to-head and til-to-til reactions. In a similar way, the polycondensation of an open chain dimeric hydroxy urethane $HO(CH_2)_3NH-CO-O(CH_2)_3NHCO-OC_6H_5$ are observed due to transurethanisation reactions. Cationic initiators, however, such as BF_3-ether, triflic acid, or triflate result in a uniform polyurethane in high yield with M_n = 30.000. The reaction follows first-order kinetics in the beginning of the reaction which is homogeneous. At higher conversions the melt becomes heterogeneous and aberrations from first-order kinetics occur. Correspondingly, the number average molecular weight of the polymer increases linearly with conversion as long as the reaction is homogeneous.

With triflate the initiation is achieved by methylation of the carbonyl oxygen resulting in an immonium cation which attacks the carbonyl oxygen of a monomer with O-alkyl-cleavage. The propagation follows an activated chain-end mechanism. The terminal cyclic immonium group may also react with other nucleophiles than the monomer, e.g., acetate or triphenyl phosphane to form the resepective endgroups.

In the course of the reaction beside chain growth chain transfer and termination occur when instead of the carbonyl oxygen the nitrogene of a monomer is attacked by the living end. Then the chain is terminated by formation of an alkylated cyclic urethane endgroup and a protonated monomer which after reaction with trimethylene urethane forms a carbamate group that is decarboxylated to form an amino group being immediately protonated. Thus the transfer step is followed by a termination reaction4)5).

Instead of low molecular weight initiators mono- and bifunctionally grown polytetrahydrofuran may be used as an initiator. When reacted with the cyclic urethane a protonated imminocarbonate endgroup is formed which after evaporation of excess tetrahydrofuran initiates the polymerization of the cyclic urethane. Thus AB and ABA blockcopolymers are obtained6).

In a very similar way the cyclic tetramethylene urethane is polymerised. The polymerization, however, occurs already at 60 °C in the bulk which is well below of the ceiling temperature of tetrahydrofuran. Thus this monomer is even more suitable for the formation of the respective blockcopolymers.

In the contrast, the cyclic dimethyltrimethylene urethane is not polymerised in a ring-opening fashion. The respective polymer rather is readily depolymerised to form the cyclic oligomers and eventually the cyclic monomer. On the other hand, the polymer is not observed by polycondensation of the monomeric hydroxy urethane $HO\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}NH\text{-}CO\text{-}O\text{-}$

C_6H_5 which yields exclusively the cyclic monomer but by polycondensation of the dimeric hydroxy urethane $H[O\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}NH\text{-}CO\text{-}O]_2C_6H_5$. It should be mentioned however, that the copolycondensation of the linear mono- and diurethane is possible yielding not only the even but also the odd members of the homologous series7).

Cyclic diurethanes consisting of a tetramethylene diamine unit and a neopentylglycolbischloroformiate unit are readily polymerised with $Ti(OiPr)_4$ as well as with $Bu_2Sn(OMe)_2$ yielding polymers with an isopropyl endgroup and a methyl endgroup, respectively8).

Ring-opening polymerization of cyclic ureas

Five- and seven-membered cyclic ureas and their polymerization with NaH in the melt were reported already in the fifties. The seven-membered cycle is readily polymerised in the melt at 210 °C as well as in DMF-solution with sBuLi as initiator at 140 °C. Dimethylene urea is polymerised with NaH at 140 °C in the melt following an activated monomer mechanism.

Tetramethylene urea is as well co-polymerised with DTC and $MgBu_2$ as an initiator both in the melt at 140 °C or in N,N'-dimethyl propylene urea (DMPU) at 120 °C. With increasing monomer concentration the molecular weight increases. From the ^1H-NMR spectrum of the co-polymers it is seen that DTC is polymerised with slight preference and the ^{13}C-NMR spectrum gives a clear indication of the tetrades formed. Thus, while DTC diades are decreasing DTC/urea diades are increasing and urethane diades are increasing to a low level. A very similar picture is obtained when living polyDTC is reacted with tetramethylene urea. This provokes a mechanism which is similar to that discussed in the co-polymerization of DTC and ECLam: a carbonyl carbon of the carbonate group is attacked by the cyclic urea-anion; the acylated urea endgroup then reacts with an alcoholate endgroup in ring-opening fashion to form a urethane group9).

Surprisingly, tetramethylene urea is also copolymerised with ethylene carbonate to form a polyurethane which is clearly demonstrated by the ^1H-NMR spectrum. The cyclic tetramethylene urea anion reacts with dimethylene carbonate to form the acylated urea which then yields the alternating copolymer$^{10)}$.

Ring-opening polymerization of cyclic ester amides

The most well known cyclic ester amides are cyclodepsipeptides which are obtained by reaction of α-hydroxy carboxylic esters with sodium salts of α-amino acids and subsequent cyclisation reaction$^{11)}$. The polymerization generally is achieved with $Sn(oct)_2$ or $Sn(acca)_2$ in the melt$^{12)}$. Beside cyclic depsipeptides dimeric cyclic ester amides consisting of two α-amino acids and two β-hydroxy acids in an alternating fashion are of some interest because of their antibiotic character (serratomolide). They are obtained from β-hydroxy acyl piperazines or just by cyclodimerisation reactions of the respective hydroxy acids or amino acid chlorides.

The chemistry ressembles that of an amide bond which when activated undergoes an N→O shift under ring enlargement when steric conditions are fulfilled. The fourteen-membered cyclic ester amides, however, do not undergo ring-opening polymerization with both $Ti(OiPr)_4$ and $Bu_2Sn(OMe)_2$ because of the high stability of the cyclic (mp 230-260 °C), the rigid and strainfree ring conformation stabilized by trans annular H-bonds.

In the contrast to the fourteen-membered dimeric cyclic ester amide the eleven-membered ester amide consisting of a β-hydroxy carboxylic acid and an ε-amino carboxylic acid was considered to be a suitable monomer. It is synthesized from an acroylated or a β-bromo or a β-benzyloxy acylated ε-caprolactam via ring expansion reaction$^{13)}$. With $Bu_2Sn(OMe)_2$ in DMF solution (120 h, 100 °C) ring-opening polymerization with 100 % conversion is achieved. With increasing monomer/initiator ratio the molecular weight increases. GPC clearly shows the presence of two types of oligomers indicating two competing initiation mechanisms. No cyclic oligomers are found. The molecular weight increases lineary with conversion.

NMR indicates a fully alternating structure and two kinds of endgroups, i.e., a methyl ester endgroup and an acylated monomer endgroup in both cases the second endgroup being an alcohol endgroup. This corroborates the presence of two competing initiation mechanisms, i.e. the insertion of a catalyst into an acyl-O-bond and an activated monomer mechanism.

In the contrast to N-(3-hydroxypropionyl)-ε-amino caproic acid lactone the polymerization of N(3-hydroxypivaloyl)-ε-amino caproic acid lactone with naphthalene potassium, Bu_2Mg, $Al(OsecBu)_3$ and others as initiators follows exclusively a ring-expansion mechanism. After deprotonation of the monomer an equilibrium is achieved between the salt of the lactam and the salt of the cyclol. Then the anion performs a nucleophilic ring-opening of the monomer resulting - after protonation - in the key intermediate which intramolecularly forms the cyclol and after isomerisation the cyclic dilactame (cyclic dimeric ester amide). The molecular weight/conversion relation depends very much on the type of initiator used. The ^{13}C-NMR spectrum clearly shows the alternating structure of the polymer and GPC proves the cyclic nature of the oligomers as compared with those obtained via polycondensation of respective monomers which result in linear oligomers and polymers$^{14)}$.

Conclusion

The ring-opening polymerisation of different monomers is characterised by a broad variety of unusual reactions opening a wide field in new polymers and in particular copolymers with well-defined architecture.

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