Unusual Features of Ring-Opening Polymerisation

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Ring-opening polymerisation is a mean to transform stepwise polymerisation reactions into chain reactions, the cyclic monomers being prepared by intramolecular condensation of open chain bifunctional monomers [1,2]. The ring-opening polymerisation is initiated most conveniently with ionic initiators which may be of macromolecular structure. Thus, block- - and graft copolymers are obtained.

To synthesize well-defined architectures the elementary reactions of the ring-opening polymerisation have to be known in detail since there are various unusual features.

Six-membered cyclic carbonates, in particular 2,2-dimethyltrimethylene carbonate (DTC), are polymerised anionically and the copolymerisation of different cyclic carbonates results in random copolymers [3-14].

The copolymerisation of cyclic carbonates with ε-caprolactone (ECL) yields block copolymers with a tapered structure between the two blocks showing a compositional gradient from DTC-rich to ECL-rich segments [6,10,15,16].

While in both cases the active species is an alcoholate, the active species in the anionic ring-opening polymerisation of pivalolactone (PVL) is a carboxylate; thus, copolymerisation with DTC yields block copolymers since the carboxylate once formed is unable to attack the cyclic carbonate [16,17].

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In the copolymerisation of DTC with L-lactide (LLA) the latter monomer is polymerised with preference; whenever a cyclic carbonate unit is added, however, the newly formed alcoholate group attacks at the carbonyl carbon of a polylactide chain to produce a mixed diad [16,18]. The copolymerisation of DTC with ε-caprolactam results in alternating polyester urethanes due to the fact that the cyclic carbonate is polymerised preferentially and the nucleophilically activated ε-caprolactam then attacks at the carbonyl carbon of the polycarbonate chain to form an acylated ε-caprolactam which is ring-opened by an alcoholate chain end ([9].

In a very similar fashion the copolymerisation of DTC with tetramethylene urea occurs with $MgBu_2$ as a catalyst in the melt at 140 °C or in 1,1 '-dimethyltrimethylene urea solution at 120 °C. The result is a polyurethane and the mechanism very much resembles that described for the insertion of a nucleophilically activated s-caprolactam into the polycarbonate chain [20, 21].

Trimethylene urethane, in the contrast to the examples described above, is polymerised cationically with methyl triflate as the initiator at 100 °C in the melt. The polymerisation follows first order kinetics and a linear molecular weight/conversion dependence is observed as long as the melt is homogeneous. Strong deviations occur, however, when the polymer precipitates.

The mechanism follows an activated chain end pathway; in the initiation step the carbonyl carbon is methylated and an immonium ion is formed which in a-position to the urethane oxygen is attacked by the carbonyl oxygen of another monomer. In the same way, the activated chain end is nucleophilically attacked by an acetate anion to form an acetate end group or by triphenylphosphane to form a triphenyl phosphonium end group.

Instead, the activated chain end may be attacked by the NH-group of the monomer as the nucleophile. This, however, leads to the formation of a protonated monomer which is rather the reason for a termination reaction than for a transfer reaction.

In a similar way the cyclic tetramethyl urethane may be polymerised (at 67 °C in the melt) to yield the respective polyurethane [22-24].

This unusual series of polyurethanes, without mirror planes in the chain, shows a clearly alternating behaviour of the melting points, very similar to that of the corresponding polyamides. The alternating character is much stronger, however, and the melting points are lower than those of the respective polyamides. It should be mentioned, however, that the high and low melting point of neighbouring polymers is exclusively due to the even and odd number of methylene groups, respectively [23-25].

When living polytetrahydrofuran is used as a mono- or bifunctional initiator block copolymers AB or ABA are obtained. First, the polytetrahydrofuran chain is endcapped with one cyclic urethane moiety and after removal of tetrahydrofuran the polymerisation of the urethane occurs in the melt [26, 27].

The polymerisation of 2,2-dimethyltrimethylene urethane is thermodynamically disfavoured. The polymer, however, can be prepared by polycondensation of the diurethane formed from 3-hydroxy-2,2-dimethyltrimethylene isocyanate and the phenyl urethane ofthis isocyanate.

The polymerisation of cyclic esteramides, in particular of cyclic depsipeptides [29-32] has been investigated in great detail. A fourteen-membered cyclic esteramide is serratomolide, known as an antibiotic. This cycle, however, is extremely stable due to its conformation and intramolecular hydrogen bridges. It resists ring-opening polymerisation.

Therefore, we investigated the ring-opening polymerisation of the eleven-membered cyclic esteramides constituted of s-caprolactam and propiolactone or pivalolactone. The preparation of the monomers is achieved by acylation of s-caprolactam and subsequent ring-closure to form the cyclol and eventually the cyclic esteramide [33]. The unsubstituted esteramide is polymerised in the presence of $BuzSn(OMe)_2$ as the initiator following two pathways, i.e. the insertion into the Sn-OMe bond via an activated ester and the reaction via a nucleophilically activated monomer. Gel permeation chromatography indicates the presence of two different homologous series of oligomers, one with cyclic endgroups and one with methyl ester end groups. Still, the degree ofpolymerisation increases linearly with conversion [34].

The dimethylated cyclic esteramide with a large number of anionic and insertion type initiators follows the route of an activated monomer, an N-N peptidyl shift and a ring enlargement mechanism. The polymer structure is proven by means of NMR spectroscopy

and the homologous series of cyclic oligomers shows clearly larger elution volumes than the open-chain analogues [35, 36].

Ring-opening polymerisation thus is a versatile method to produce new structures and allows for the preparation of new block copolymers when macromolecular initiators are used.

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