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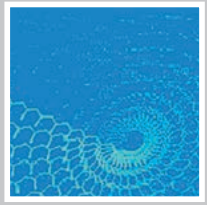

Polymer and Colloid Highlights

Division of Polymers, Colloids and Interfaces

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New Phosphine Reagents for the Living Polymerization of Aminobenzoic Acids and its Oligomers

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Polymerization reactions are typically categorized according to the mechanism as either *chain growth* or *step growth* processes. Typical examples of chain growth polymers are polyethylene, polypropylene and polystyrene. Step growth polymers are made from monomers carrying at least two functional groups A and B, which can react with each other. Examples of the latter are all polyesters, polyamides and polyurethanes. In step growth reactions all monomers, oligomers and polymer chains carry one of these reactive groups A or B at their chain end, and therefore all these species can react with another in a fairly uncontrolled manner. This leads to polymers with a high dispersity and makes the formation of block copolymers impossible.

About 20 years ago Yokozawa and his group showed that 4-amino benzoic acid esters could be N-H deprotonated by strong bases to yield electronically self-deactivated monomers that can only react with a suitable initiator group.[1,2] This mechanism forces the AB-type monomers to react one by one with the chain end of the original initiator molecules, and converts the reaction into a chain growth polymerization. In principle, any reaction conditions that prevent or slow down the bimolecular reactions between AB-type monomers with respect to their reaction with an initiator (A or B) should allow for a chain growth polymerization.

In a recent publication[3] we could show that the two new chlorophosphonium iodide reagents chlorotriphenylphosphonium iodide (PHOS1) and chlorotri(ortho)methoxyphenylphosphonium iodide (PHOS2) allow the activation of aromatic carboxylic acids by conversion into acid chlorides in the presence of aromatic primary or secondary amines. Because this reaction is extremely fast, aromatic amino acid monomers can be added slowly to a mixture of an amine initiator and the suitable phosphonium reagent (Fig. 1A, B). The monomer is immediately converted into the amino acid chloride but due to its low concentration any bimolecular step-growth side reactions are suppressed (Fig. 1C). The initiator, on the other hand, is present in much higher concentration. Therefore the most probable reaction is the one between the initiator amine and the monomer acid chloride. This step leads to elongation of the growing chain by one monomer unit while the terminal amine group is reinstalled (Fig. 1D). We demonstrated that this chain growth mechanisms does not rely on monomer self-deactivation, by confirming that oligomeric amino acids can also be polymerized in a living fashion.

Most notable is the fact that the new method allows the living synthesis of poly(*p*-phenylene terephthalamide) from which commercial Kevlar is made and living poly(5-amino-2,4-bisalkoxy benzoic acids). The latter represent polymeric foldamers that fold into hollow helices in non-polar solvents.

We believe that the ability to polymerize sequence defined aramid oligomers in a living fashion will impact several fields from fundamental polymer chemistry to materials engineering.

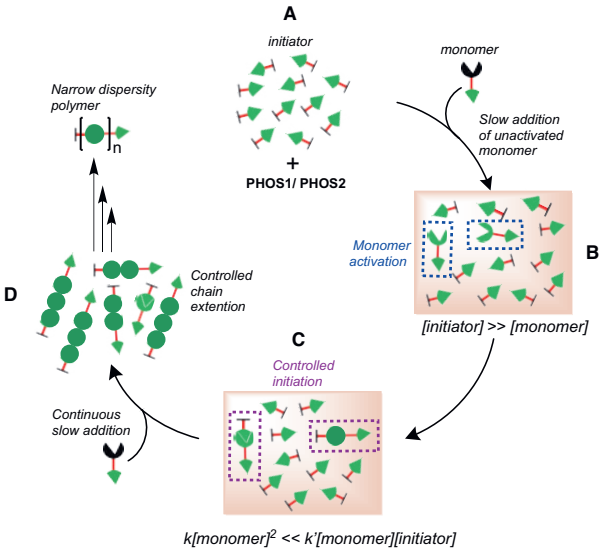

Fig. 1 Chain growth polymerization of AB-type monomers. Slow monomer addition, fast monomer activation and an initiator present at higher concentration allow for a chain-growth of aromatic amino acid monomers.

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