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Star shaped and hyperbranched aromatic polyesters

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Abstract: This review reports on synthesis of star-shaped and hyperbranched polyesters, poly(ester-amide/s and poly(ester-imide)s. Further more star-shaped polyesters having hyperbranched star arm and A-B-A triblock copolymers having hyperbranched A-blocks are included. All these structures were prepared by one-pot polycondensations of A-B or A_nB type monomers. Three different polycondensation methods were used and compared.

INTRODUCTION

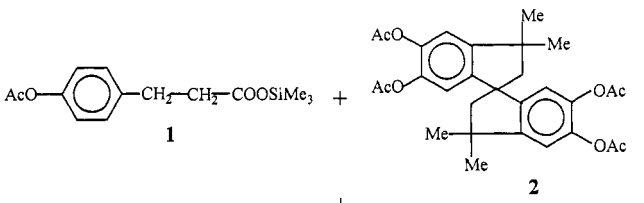
Technically produced polycondensates are usually based on A-A and B-B monomers (with A and B being functional groups which react selectively with each other) because of their low costs. However, A-B type monomers have a much greater synthetic potential which becomes particularly evident when copolycondensations with multifunctional comonomers are taken into account. For instance, copolycondensations of A-B and A_4 monomers will yield four arm star polymers, whereas the copolycondensation of A4 with A-A and/ or B-B monomers will yield crosslinked gels. An even more interesting aspect of the A-B monomers is their copolycondensation with A_nB type multifunctional monomers resulting in randomly branched (hyperbranched) copolymers. These are multifunctional, amorphous, soluble polymers which are not crosslinked regardless of the conversion provided the polycondensation is a clean process. The present contribution reports on star-shaped and hyperbranched polyesters prepared from aromatic monomers in an "one-pot-procedure".

Star-shaped polyesters:

Star-shaped polyesters having linear star arms were preferentially synthesised from 3-(4-hydroxyphenyl) propionic acid (HPPA) because this is a commercial, non-toxic monomer yielding biodegradable (ref. 1,2) and potentially liquid-crystalline (LC) copolyesters (ref. 3,4). This hydroxy acid was "activated" by acteylation of the phenolic group and by silylation of the CO_2H group(**1**). The tetraacetate of the commercial 5,5`, 6,6`-tetra hydroxy-3,3,3`,3`1-tetramethyl spirobisindane(**2**) served as star-center and (A_4 type) comonomer (eq. 1) The star-shaped homopolyesters of HPPA(**3**) were soluble up to an average length of 20 monomer units per star arm (ref. 5). Longer star arms induce high crystallinity and insolubility quite analogous to the linear-homopolyester. More or less thermotropic star-shaped copolyesters were obtained, when the activated HPPA was copolycondensed with activated 4-hydroxybenzoic acid (**4**) and 6-hydroxynaphthoic acid (**5**) (ref. 6). Increasing lengths of the star arms improved the stability and homogeneity of the mematic phase.

Hyperbranched polyesters:

The first example of hyperbranched polymers were invented by the evaluation in the form of amylopectin and glycogen. A first theoretical discussion of this type of branching and of polycondensations yielding hyperbranched polymers was published by Flory (ref. 7). A first successful synthetic approach was reported by the authors and his coworkers (ref. 8) based on the copolycondensation of 3-trimethylsiloxy benzoyl chloride (A-B) and 3,5-bistrimethylsiloxybenzoyl chloride (A_2B). The variation of their molar feed ratio allowed to vary the branching density over a broad range. Analogous copolyesters having different endgroups were prepared by copolycondensation of 3-acetoxybenzoic acid and 3,5-bisacetoxybenzoic acid (ref. 8). Other research groups developed this approach mainly in direction of the hyperbranched homopolyesters of 3,5-hydroxybenzoic acid (ref. 9,10) or 5-hydroxysioplthalic acid (ref. 11). More recently the author has elaborated a new approach based on acetylated hydroxy acid having silylated carboxylic groups (ref. 5,6,12-14). The silylation of the COOH groups reduces proton catalysed side reactions causing crosslinks.



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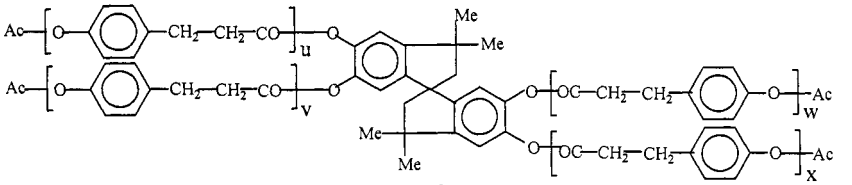

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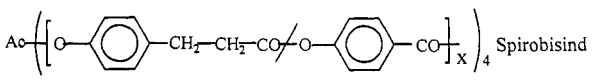

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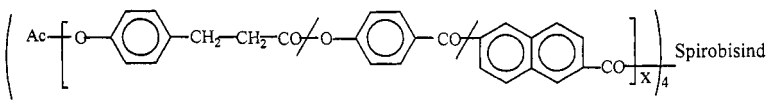

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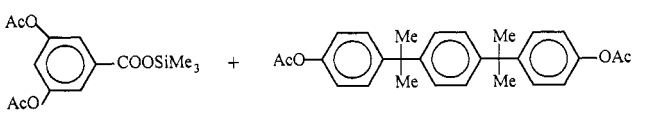

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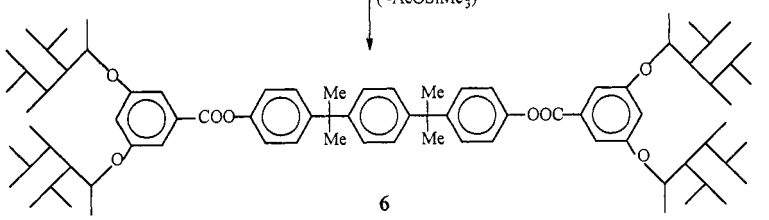

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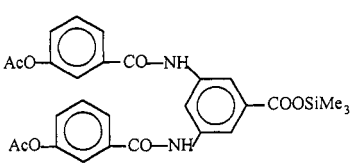

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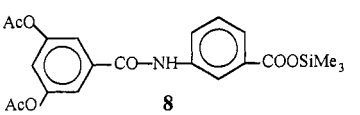

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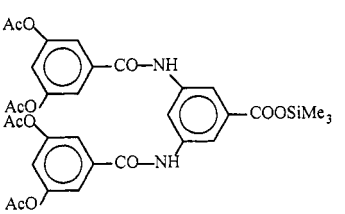

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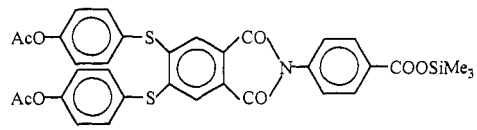
Using this new approach star-shaped polyesters having hyperbranched star-arms(**6**) were prepared by direct copolycondensations of activated 3,5-dihydroxybenzoic acid and A_2 or A_4 type star-center comonomers (eq. 2) (ref. 12). Using telechelic oligo (ether-ketone)s having two acetate endgroups as B_2 comonomer A-B-A-triblock copolymers with hyperbranched A-blocks were obtained (ref. 15,16). On the basis of the same polycondensation methods three classes of hyperbranched poly (ester-amide)s were prepared from monomer based on 3-aminobenzoic acid and 3,5-diaminobenzoic acid (**7-9**) (ref. 17-19). Further more first syntheses of hyperbranched poly (ester-imide)s were performed based on the monomer **10** which was prepared in four step synthesis from 4,5-dichlorophthalic acid (ref. 20). The ongoing research concentrates on hyperbranched homo and copolymers of gallic acid which is a natural rather non-toxic monomer. Depending on the comonomers the gallic acid was either activated in the form of structure **11** (ref. 21) or **12** (ref. 22).



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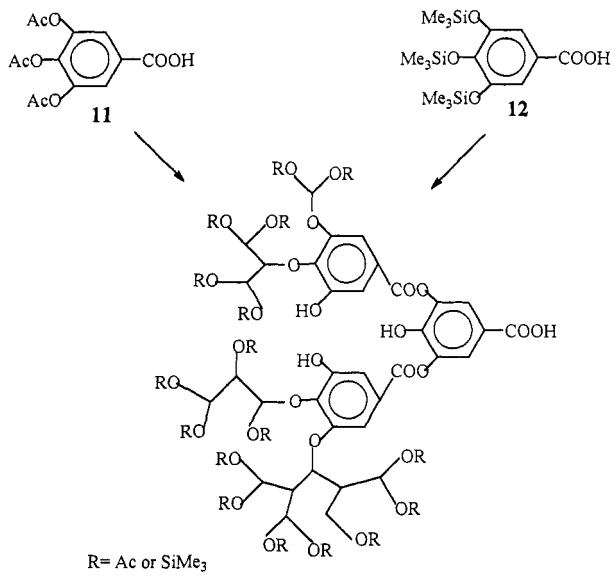

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