ABC-Type Linear Triblock Terpolymers

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This entry aims to cover the most recent advances regarding the synthesis of linear ABC-type triblock terpolymers by RAFT polymerization, as well as their self-assembly properties in aqueous solutions. RAFT polymerization has received extensive attention, as it is a versatile technique, compatible with a great variety of functional monomers and reaction conditions, while providing exceptional and precise control over the final structure, with well-defined side-groups and post-polymerization engineering potential. Linear triblock terpolymers synthesis can lead to very interesting novel ideas, since there are countless combinations of stimuli/non-stimuli and hydrophilic/hydrophobic monomers that someone can use. One of their most interesting features is their ubiquitous ability to self-assemble in different nanostructures depending on their degree of polymerization (DP), block composition, solubilization protocol, internal and external stimuli.

ABC triblock terpolymers   RAFT polymerization

1. General Synthetic Strategies for ABC Triblock Copolymers by RAFT

Up to this point, RAFT polymerization has generated precise synthesis of ABC-type triblock terpolymers, incorporating a wide variety of monomers bearing side groups of choice, as well as controlled molecular weights and narrow molecular weight-distribution. Factors like the block sequence and the composition of the final macromolecules can influence the nanostructures formed in solutions.

Indeed, Altintas et al. [1] reported the synthesis of ABC triblock terpolymers bearing primary alkyl bromide on block A, protected alkyne on block B and protected hydroxyl pendant groups on block C. The authors proceeded in post polymerization functionalization of the terpolymer with Hamilton wedge (HW) for block A, benzene-1,3,5-tricarboxamide (BTA) for block B and cyanuric acid (CA) for block C. It should be mentioned that the dithioester groups of the RAFT agent were removed by radical-induced reduction after the fabrication of the initial triblock.

In the same manner, Germack and Wooley [2] have presented the synthesis of ABC and ACB triblock terpolymers composed of tert-butyl acrylate (tBA), isoprene (Ip) and styrene (St) blocks, which are susceptible to post-polymerization functionalization. The synthesis started by creating the macro-chain transfer agent (mCTA) by polymerizing tBA utilizing a synthesized S-1-dodecyl-S′-(r,r′-dimethyl-r′-acetic acid)trithiocarbonate CTA agent, which was used as the initial block for the synthesis of $P(tBA)_{53}$-b-$P(Ip)_{48}$-b-$P(St)_{71}$ and $P(tBA)_{53}$-b-$P(St)_{46}$-b-$P(Ip)_{133}$ terpolymers with controlled molecular weights. Both triblock terpolymers presented rather narrow

molecular weight distributions (1.3 and 1.5), depicting the ease-of-use and good control of the RAFT technique over the polymerization of all three monomers.

Mixtures of solvents can be also utilized in RAFT, as Ghamkhari et al. [3] have shown with the synthesis of poly (2-hydroxyethyl methacrylate)-b-poly(*N*-isopropyl acrylamide)-b-poly[(*N*-4-vinylbenzyl), *N*,*N*-diethylaminehydrochloride] (PHEMA-b-PNIPAM-b-PVEAH) in a water/methanol mixture, with the use of 4-cyano-4-[(phenylcarbothioyl) sulfanyl] pentanoic acid as CTA. The triblock terpolymers exhibit strong anti-yeast and anti-microbial properties against *S. aureus*, *B. cereus*, *C. albicans* and *E. coli*.

The degree of polymerization of each block in ABC terpolymers seems to play an important role in the final nanostructures according to Xu et al. [4]. The group published the preparation of epoxy-functionalized poly (glycerol monomethacrylate)-*b*-poly (2-hydroxypropyl methacrylate)-*b*-poly(glycidylmethacrylate), (PGMA-*b*-PHPMA-*b*-PGlyMA) triblock terpolymer vesicles, synt hesized by RAFT polymerization. More specifically, PGMA was polymerized in ethanol with 4-cyano-4-(ethylthiocarbonothioylthio) pentanoic acid as the CTA and the homopolymer was utilized as macro-CTA for the polymerization of PHEMA via enzyme-initiated aqueous RAFT dispersion polymerization in ambient conditions, resulting to vesicular structures. The PGMA-*b*-PHPMA vesicles were used as seeds for the polymerization of GlyMA via seeded RAFT emulsion polymerization at room temperature, as the GlyMA monomer is insoluble in water. It was demonstrated that as the molecular weight of the PGlyMA block increased, the vesicles were becoming rougher and that the PGMA-b-PHPMA-b-PGlyMA triblock terpolymer vesicles could be utilized as Pickering emulsifiers for hexane-in-water emulsions.

Having this fact in mind, Zhang et al. [5] have presented a very interesting idea to synthesize ABC triblock terpolymers structure with the use of acrylated nucleobase containing monomers via RAFT polymerization. In that work, the group prepared three poly(thymine acrylate)-*b*-poly(n-butyl acrylate)-*b*-poly(adenine acrylate) with different DPs, mediated by the 2-cyano-2-propyl dodecyl trithiocarbonate as CTA. The nucleobase terpolymers tend to form lamellar and cylindrical structures in the bulk phase, while present excellent thermal and mechanical properties, which originate from the strong hydrogen bonding between adenine and thymine molecules and could be regulated by simply modifying the DP of each block.

Differences in block position have been presented by Messerschmidt et al. [6] with an interesting approach of anchoring amphiphilic triblock copolymers onto textile surfaces enabling them to withstand dirt and present better cleaning properties. In this manner, the group proceeded with the synthesis of two triblock copolymers, consisting of a hydrophobic poly (tert-butylstyrene-co-n-hexyl acrylate) P(tBS-co-nHA) block, a poly(*N*-acryloxysuccinimide) (PNAS) block, used for anchoring, and a poly(*N*,*N*-dimethylacrylamide) (PDMA) hydrophilic block. The polymerization was mediated with the use of S-methoxycarbonylphenylmethyl dithiobenzoate (MCPBD) CTA due to its ease of synthesis and the controlled polymerization obtained for the particular monomers. The difference between the two terpolymers lies in the position of the anchor block, which is placed either in the middle, or at the end of the triblock terpolymer chains. The resulting terpolymer conformations on the surface of textiles lead to the extension of relevant hydrophilic or hydrophobic blocks, depending on the environmental conditions.

RAFT polymerization can be also used in combination with other techniques as shown by Chen et al. [7] who prepared poly(oligoamide 11)-*b*-poly(lauryl methacrylate)-*b*-poly(methyl methacrylate) (OPA11-*b*-PLMA-*b*-PMMA) nanostructures. The group initially created the macro-CTA by melt polycondensation of oligoamide 11 and functionalizing it with 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPADB), while PLMA and PMMA were prepared by RAFT polymerization. Structural studies have revealed a vesicle-nanoparticle network consisting of a PLMA core, OPA 11 and a PMMA corona.

Synthesis and self-assembly of the block copolymers at the same time can be also achieved in order to study different formations in function with the degree of polymerization, as shown by Marble et al. [8] The group prepared poly(glycerol monomethacrylate)-*b*-poly(2-hydroxypropyl methacrylate)-*b*-poly(benzyl methacrylate) (PGMA-*b*-PHPMA-*b*-PBzMA) triblock terpolymers via polymerization induced self-assembly (PISA) RAFT technique which was mediated by the use of 2-cyano 2-propyl benzodithioate (CPDB) as CTA. The resulting molecular weight dispersities were rather narrow for all the samples, depicting a controlled polymerization process. Lower DP of PBzMA block leads to large worm-like structures, while further polymerization up to a point creates uniform spheres. Additionally, the terpolymers present low-sheer emulsifying ability when droplets of n-dodecane are introduced into their aqueous solutions.

The polymerization of the third block in a non-selective solvent can lead to interesting self-assembled nanostructures, as presented by Samanta et al. [9] that have utilized a modified surfactant-free RAFT-mediated miniemulsion polymerization to synthesize poly[2-(methacryloyloxy)ethyl ammonium chloride]-*b*-poly(n-butyl acrylate)-*b*-poly(isobornyl acrylate) (PMTAC-*b*-PBA-*b*-PIBA) ABC triblock terpolymers. The PMTAC macro-CTA was synthesized in water containing silica nanoparticles, utilizing 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DTMPA), while the third block was polymerized in a miniemulsion, forming raspberry-like particles. These nanostructures proved to have anti-icing and antibacterial properties and could be applied onto cotton fabric, paper or even glass, enabling them to be functional materials for polymer coatings or multifunctional paints.

2. Stimuli-Responsive ABC Triblock Copolymers

The macromolecular architecture of ABC-type triblock terpolymers offers the possibility for incorporation of one or more than one stimuli-responsive block in the same polymer. Thermo and pH-responsive monomers have been utilized in the synthesis of a considerable number of triblock terpolymers using RAFT polymerization, since they present interesting functionalities in terms of self-assembly, that in turn make them interesting as potential drug/protein nanocarriers for targeted delivery with controlled-release ability.

Pal et al. [10] published the synthesis of the pH- and thermo- responsive poly (*N*-isopropylacrylamide-*b*-n-butyl acrylate-*b*-4-vinylpyridine), (PNIPAM-*b*-PBA-*b*-P4VP) triblock terpolymers in DMF, with cyanomethyl dodecyl trithiocarbonate as the CTA and azobisisobutyronitrile as the thermal initiator. The self-assembly properties of the terpolymers in aqueous solutions at pH = 3 and pH = 8 were also investigated. It was proven that the terpolymers form core–shell-corona micelles with P4VP cores, PBA shells and PNIPAM coronas at temperatures below the

LCST of PNIPAM and at pH > 4.7. When dissolved in chloroform, the PNIPAM-*b*-PBA-*b*-P4VP organize into globular morphologies with PNIPAM, PBA and P4VP as the inner, intermediate and outer layers, respectively.

The synthesis of a series of poly[2-(dimethylamino)ethyl methacrylate-b-lauryl methacrylate-b-(oligo ethylene glycol)methacrylate], (PDMAEMA-b-PLMA-b-POEGMA) triblock terpolymers via sequential RAFT polymerization was presented by Skandalis and Pispas [11], utilizing 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid as the CTA, starting from the preparation of PDMAEMA homopolymer which was later on used as the macro-CTA for the synthesis of the PDMAEMA-b-PLMA diblock copolymer. The diblock was used as the macro-CTA for the chain extension with OEGMA, resulting to the final triblock terpolymers (Scheme 1). A typical quaternization reaction with methyl iodide followed, in order to convert the tertiary amine groups of PDMAEMA into quaternary amine groups with permanent positive charges giving QPDMAEMA-b-PLMA-b-POEGMA cationic terpolymers. Both the amine and quaternized terpolymers self-assemble into spherical micelles with PLMA cores and (Q)PDMAEMA/POEGMA mixed coronas in water. The initial terpolymers do not present response to pH variations due to crowding effects in the micelle corona that originate from the presence of POEGMA blocks. The QPDMAEMA-b-PLMA-b-POEGMA micelles were utilized as non-viral vectors for complexation with DNA [12] and insulin [13], via electrostatic interactions, and the physicochemical properties of the complexes were studied in considerable detail as a function of components mixing ratio besides ionic strength of the aqueous solutions.
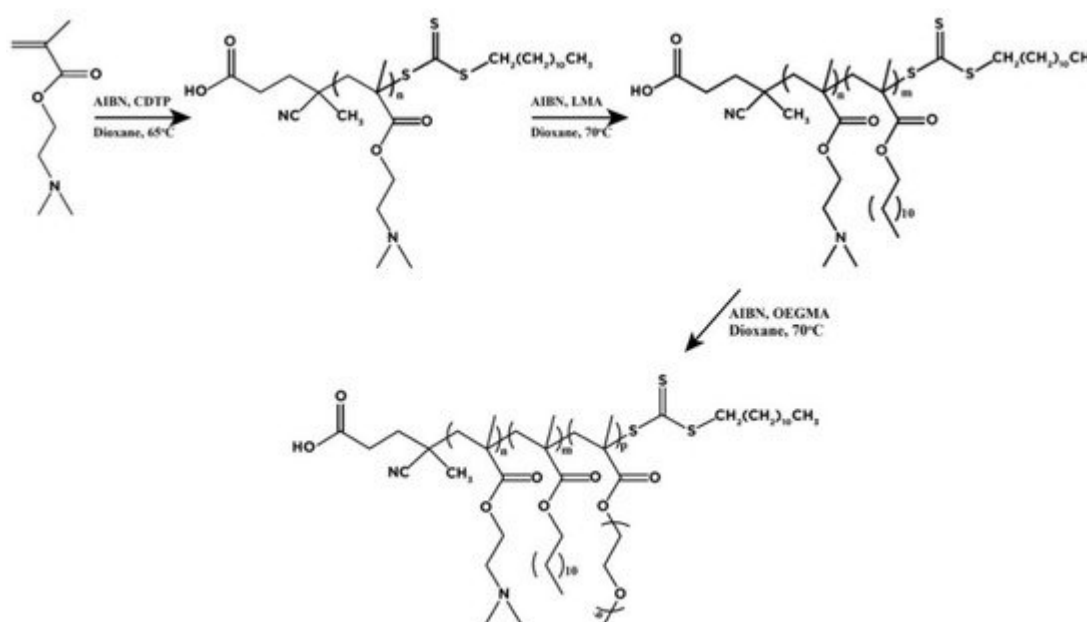
Scheme 1. Synthesis of PDMAEMA-b-PLMA-b-POEGMA triblock copolymers by sequential RAFT polymerization [11].

The same group reported on the synthesis of poly (n-butyl acrylate-*b*-N isopropylacrylamide-*b*-2-(dimethylamino) ethyl acrylate), (PnBA-*b*-PNIPAM-*b*-PDMAEA) double-responsive (temperature and pH) triblock terpolymers [14]. The PDMAEA amine groups were quaternized with CH$_3$I to give triblock terpolymers with permanent positive charges. The effect of pH and temperature variations on the self-assembly properties of both the amine and quaternized terpolymers in aqueous solutions were investigated. It was observed that the PnBA-*b*-PNIPAM-*b*-

PDMAEA terpolymers form spherical micelles with a tendency for intermicellar aggregation, even at room temperature conditions, while the spherical micelles of the quaternized terpolymers show lower or no tendency for aggregation (depending on the PDMAEA ratio), due to their higher solubility in water.

Temperature and pH- responsive triblock terpolymers composed of poly(ethylene oxide)-b-poly(*N*-isopropylacrylamide)-b-poly(acrylic acid), (PnBA-b-PNIPAM-b-PAA) by sequential RAFT polymerization in dioxane were presented by Papagiannopoulos et al. [15], using 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid as the CTA. The self-assembly behavior as well as the response to temperature alterations of the terpolymers in aqueous solutions were investigated using scattering methods. Moreover, the group studied the effect of the addition of lysozyme, a positively charged protein, in the aqueous polymer solutions Electrostatic interactions with the oppositely charged PAA block at pH 7 were observed. The results demonstrate the formation of aggregates at room temperature, that transform into dense objects above the LCST of PNIPAM. The addition of lysozyme amplified the inter-aggregate interactions and led to significant increase in the size and scattering intensity, which becomes even more pronounced as solution temperature increases.

Giaouzi et al. [16] worked on the synthesis and self-assembly in H_2O of poly(2-(dimethylamino)ethyl acrylate)-*b*-poly(*N*-isopropylacrylamide)-*b*-poly(oligo ethylene glycol methyl ether acrylate), (PDMAEA-*b*-PNIPAM-*b*-POEGA) triple hydrophilic and double-responsive (temperature and pH) triblock terpolymers. The synthesis was achieved by three-step RAFT polymerization in dioxane, involving 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid as the CTA. The group also performed post-polymerization functionalization on the tertiary amine pendant groups of the PDMAEA polyelectrolyte block with iodomethane and 1-iodohexane (via quaternization reactions), as well as with 1,3-propanesultone (via sulfobetainization reaction). The self-assembly studies on the parent terpolymers revealed the formation of aggregates, which become more compact above the phase-transition temperature of PNIPAM, due to thermally induced aggregation and changes in the solvation state of the PNIPAM block. The quaternized triblocks form larger aggregates than the initial triblock through the whole temperature range and it was observed that the phase-transition temperature varies depending on the length of the hydrocarbon chain of the quaternizing agent. On the other hand, the zwitterionic terpolymers exhibit the opposite behavior and their aggregates show an increase in size as temperature increases.

The synthesis of thermo- and pH-responsive triblocks composed of poly(ethylene glycol)-*b*-poly(2-(2-methoxyethoxy) ethyl methacrylate-co-*N*-hydroxymethyl acrylamide)-*b*-poly(2-(diethylamino) ethyl methacrylate), (mPEG-*b*-P(MEO$_2$MA-*co*-HMAM)-b-PDEAEMA) was investigated by Liu et al. [17]. In order to achieve that, they synthesized a PEG containing macro-RAFT agent which was utilized for the synthesis of the P(MEO$_2$MA-*co*-HMAM) random middle block. Following this, the mPEG-*b*-P(MEO$_2$MA-*co*-HMAM) diblock was used as macro-CTA for the chain extension of DMAEMA in dioxane, resulting to the final ABC triblocks. The terpolymers form core–shell micelles when inserted in aqueous solutions of neutral pH, with mixed P(MEO$_2$MA-*co*-HMAM) and PEG shells, and PDEAEMA cores. In acidic pH, the terpolymers form micelles with P(MEO$_2$MA-*co*-HMAM) cores and mixed PDEAEMA/PEG coronas.

Mahmoodzadeh et al. [18] prepared poly(acrylic acid)-*b*-poly(*N*-isopropylacrylamide)-*b*-poly(ε-caprolactone)-SH(PAA-*b*-PNIPAM-*b*-PCL-SH) ABC triblock copolymers by combining ring-opening (ROP) and RAFT polymerization. The group started with the synthesis of bis(2-hydroxyethyl) disulfide, which was used as an initiator for the ring opening of ε-caprolactone in order to prepare the (PCL-S)$_2$ precursor block. For the next step, 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid was utilized for the preparation of the (PCL-S)$_2$ macro-CTA, which was used for the sequential polymerization of the remaining PNIPAM and PAA blocks. The final step comprises of the side-group modification to produce thiol-end capped PAA-*b*-PNIPAM-*b*-PCL-SH triblock terpolymers. Self-assembly studies in aqueous solutions show a temperature and pH responsive behavior that results in nanostructures of different size.

Guragain et al. [19] studied the effect of solution pH on the polymerization of poly (ethylene oxide-b-(2-dimethylamino) ethyl methacrylate-b-(2-hydroxypropyl methacrylate)) via visible light-mediated RAFT polymerization. For that purpose, 2-dodecylthiocarbonothioylthio-2-methylpropionate was used as the CTA and tris(2,2′-bipyridyl) dichlororuthenium(II) hexa- hydrate Ru(bpy) (3Cl$_2$·6H$_2$O) as the radical initiator. Self-assembly studies have shown that different morphologies and structures can be obtained by regulating the solution pH and the degree of polymerization (DP) of the PHPMA hydrophobic block.

The self-assembly properties of double thermo-responsive triblock terpolymers were studied by Ye et al. [20] who presented the synthesis of poly(di(ethylene glycol)ethyl ether acrylate)-b-poly(*N*,*N*-dimethylacrylamide)-b-poly(*N*-vinylcaprolactam) (PDEGA-b-PDMA-b-PVCL). The terpolymers were synthesized by a typical RAFT polymerization procedure with 2-ethylsulfanylthiocarbonylsulfanylpropionic acid methyl ester as the CTA in a water-ethanol solution mixture. The thermal phase transitions of the terpolymers were studied and it was revealed that they exhibit two LCST transitions due to the existence of both PDEGA and PVCL blocks in their macromolecular chain. Micelles with PDEGA cores and PVCL/PDMA outer layers are formed when the LCST of PDEGA is reached. Above the LCST of PVCL aggregates of micelles are formed that shrink in size as temperature increases further and PVCL dehydrates.

The synthesis of polystyrene-b-poly(*N*,*N*-dimethacrylamide)-b-poly(4-vinylpyridine) (PS-b-PDMA-b-P4VP) by the solvent-exchange protocol using seeded RAFT polymerization in water/ethanol 1:1 mixture has been reported by Huo et al. [21]. The group has synthesized 4-cyano-4-(ethylsulfanylthiocarbonyl)sulfanyl pentanoic acid (ECT) CTA to provide a controlled polymerization process and take advantage of its trithiocarbonate (TTC) terminal group. The authors observed the formation of well-defined corona-shell nanoparticles in this solvent mixture, while transferring the samples to pure deionized water forces the hydrophobic P4VP block to retract in the core, leaving PDMA as the corona. They also successfully regulated the nanoparticle structure from corona-core micelles to multicompartment nanoparticles by just increasing the degree of polymerization of P4VP block.

Manipulation of the final self-organized structures of ABCs in an aqueous solution by initially modifying the degree of polymerization of the PNIPAM block and regulating the solution temperature above the PNIPAM LCST was reported by Qu et al. [22] They synthesized poly(styrene)-*b*-poly(*N*,*N*-dimethylacrylamide)-*b*-poly(*N*-isopropylacrylamide) (PS-*b*-PDMA-*b*-PNIPAM) ABC triblock terpolymers in a 1:1 mixture of acetone/n-hexane, with

the use of 4-cyano-4-(ethylsulfanylthiocarbonyl)sulfanyl pentanoic acid (ECT) as CTA. In this manner, shorter PNIPAM chains produce nanorods, while longer chains lead to nanospheres. At temperatures lower than the LCST, the structure resembles a micelle with PS as the core and PDMA-PNIPAM extended chains as the corona. By increasing the solution temperature above PNIPAM LCST, its chains collapse and turn towards the PS core, leaving the PDMA chains on the outer rim as the new corona.

3. Triblock Terpolymers Self-Assembly Properties in Solvent Exchange Protocols

Since each block of an ABC triblock terpolymer may by soluble in a different solvent, the solvent-exchange protocol can be utilized in order to enable tailoring of the self-assembly properties and the nanostructure formation in aqueous solutions.

Li et al. [23] developed α-norbornenyl polystyrene-b-poly(methyl acrylate)-b-poly(tert-butyl acrylate), (NB-PS-b-PMA-b-PtBA), ABC-type triblocks via sequential RAFT polymerization, using a norbornene-functionalized CTA. The NB-PS-b-PMA-b-PtBA terpolymers were used as triblock macromonomer for the preparation of PNB-g-(PS-b-PMA-b-PtBA) polymer brushes by ring opening metathesis polymerization (ROMP). Finally, the PtBA block was converted to PAA. The self-assembly behavior of the NB-PS-b-PMA-b-PtBA linear terpolymers and the PNB-g-(PS-b-PMA-b-PtBA) brushes were compared. When transitioned from DMF to water, the ABC-type triblocks form globular structures, while the brushes exhibited cylindrical morphologies.

Muslim et al. [24] presented the synthesis of poly(t-butyl acrylate)-*b*-poly(styrene)-*b*-poly(2-vinyl pyridine) (PtBA-*b*-PS-*b*-P2VP) triblock terpolymers and the manipulation of their self-assembly properties in solutions. The polymerization was mediated by the S-ethyl-S-(a, a-dimethyl-a′-acetic acid)trithiocarbonate (EDMAT), which was prepared in house. Molecular weight polydispersity was kept low at every step, with a final value of 1.22, depicting the controlled nature of the followed RAFT polymerization scheme. Self-assembly studies were conducted by refluxing the THF solution of the triblock terpolymers into different solutions of methanol and distilled water of pH 3. Spherical nanoparticles were formed in the case of methanol, while "core-compartmentalized" micelles were produced in water, with the particle diameter size range was from 22 to 46 nm.

Fernandez-Alvarez et al. [25] presented the synthesis of (poly(acrylic acid)-b-poly(4-hydroxystyrene)-b-poly[1-(4-(1-methyl-1,2-dicarba-closo- dodecaborane-2-yl methyl)-phenyl)ethylene] (PAA-b-PHS-b-PSC) triblock terpolymers with carborane pendant groups. The polymerization was mediated by 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid CTA and 2,2′-azo-bis-isobutyronitrile (AIBN) as the initiator. Self-assembly studies have shown that a transfer from a water/THF mixture to water leads to a structural transition from spherical to cylindrical micelles, while also presenting pH and photophysical properties, responding to pH and fluoride anions.

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