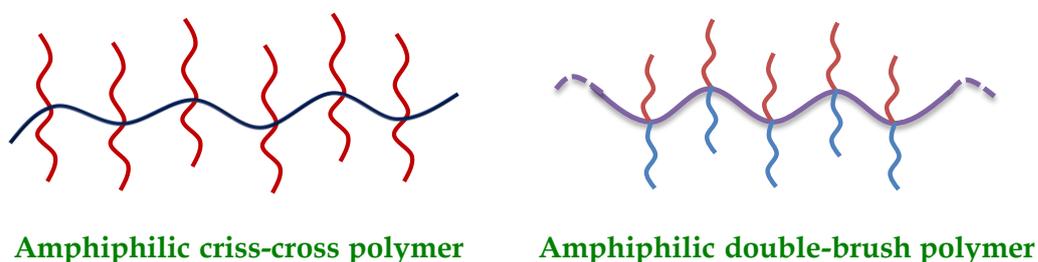


Amphiphilic polymers, wherein two or more immiscible polymeric segments are connected covalently, form an interesting class of macromolecules that can self-assemble in block selective solvents as well as in bulk, to exhibit a variety of elegant nano-structures. In this context, simple block copolymers have been studied extensively. Graft copolymers, on the other hand, are a unique class that contains polymeric pendant chains of one type attached to backbone of a second type. Depending on the grafting density, the graft polymers can be broadly classified into two categories; these are comb polymers, where the distance between the two grafting segments is large and brush polymers, where the pendant chains are grafted densely at every repeat unit. The most striking feature of these graft copolymers is that, with increase in the grafting density of the pendant segments, the backbone of the graft copolymers begins to adopt a stretched conformation. This unique property of graft copolymers impart interesting solution and bulk properties which cannot be achieved in simple linear polymers. In the present thesis, we first studied various aspects of the self-assembly behaviour of two novel types of amphiphilic graft copolymers, namely, criss-cross polymers and double-brush polymers, as depicted in scheme 1.



*Scheme 1. Schematic representation of the two types of amphiphilic graft polymers studied in this thesis.*

Controlling conformation of synthetic polymer chains, both in solution and in solid state, has been long term challenge as it confronts the entropy driven random coil conformation. For the past two decades there have been a significant efforts to control folding of polymeric chains via H-bonding interactions, bond angle constrains, solvophobic interactions, donor acceptor interactions, and so on. More recently, our group has demonstrated the immiscibility driven folding of periodically grafted amphiphilic copolymers (PGACs), wherein the immiscibility of the pendant and the backbone forces the polyethylene-like

backbone to adopt a folded zigzag conformation that is further stabilized by crystallization of one or both the segments.

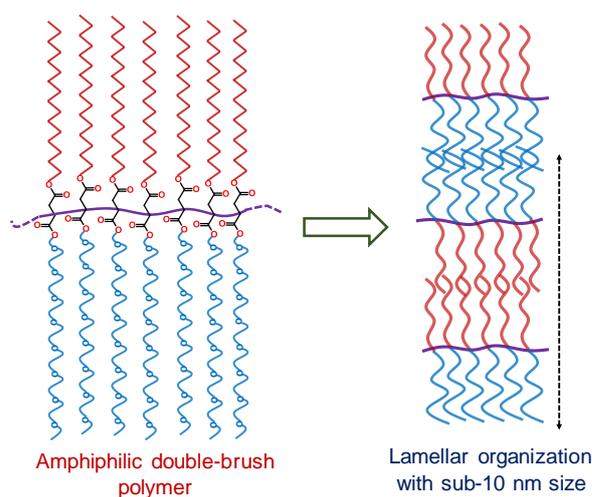
We first investigated the folding behaviour of an amphiphilic comb polymer, wherein two crystallizable hydrophobic alkyl chains are periodically grafted along a hydrophilic polyethylene glycol-like (PEG) backbone in a criss-cross orientation; implying that the alkyl chains lie across the backbone on either sides, as depicted in Scheme 2. The polymers were prepared by simple transesterification of dimethyl-2,5-didocosoxy terephthalate with PEG diols of different molecular weights; thus, permitting a variation of the periodicity of the grafting along the backbone. DSC, WAXS and variable temperature-IR studies confirmed that, in spite of the presence of intervening PEG segments, the pendant alkyl chains crystallize. This is a direct consequence of immiscibility driven self-segregation of pendant docosyl units via folding of the PEG backbone to generate a *Janus* folded polymeric chain, as depicted in scheme 2; here the periodicity of grafting acts as a “folding regulator”. Studies of model criss-cross amphiphiles helped confirm the hypothesized *Janus*-type chain folding. Interestingly, SAXS studies revealed that the folded chains further organize to generate a lamellar morphology with sub-10 nm domain spacings.



*Scheme 2. Schematic representation of the amphiphilic criss-cross polymer and its immiscibility driven folding behaviour.*

Recently, there has been growing interests towards reducing the microphase separated nanostructures to sub-10 nm length scales for variety of potential applications. It is well known that, in case of block copolymers the microphase separation is governed by the degree of polymerization ( $N$ ) and the Flory-Huggins interaction parameter ( $\chi$ ); for microphase separation to occur the value of  $\chi N$  must reach the threshold value of 10.5. Therefore, such small length scales cannot be readily achieved by the simple reduction of the total molecular weight of the polymer. Recently, block copolymers with high  $\chi$  values have been studied which was found to compensate for the decrease in  $N$ .

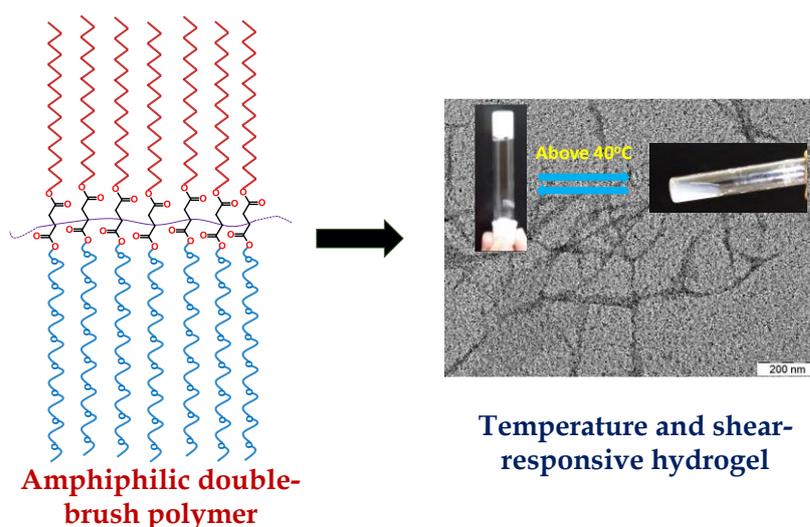
In this context, self-assembly of PGACs have proven to be a promising approach to reduce the domain sizes in microphase separated morphologies.<sup>1,2</sup> In order to explore alternate strategies, we designed a series of amphiphilic double-brush polymers, wherein two immiscible pendant chains are anchored at the same point on every repeat unit. Such polymers were prepared via micellar polymerization of hetero-functionalized itaconic acid based *surfmers* that contain a reactive double bond at the junction of the two immiscible segments. The important revelation of this work is that, despite of the relatively short pendant chains (namely, cetyl-PEG, cetyl-glycerol, cetyl-fluoroalkyl chains), the mutual incompatibility between the pendant segments appears to drive self-segregation along the polymeric backbone to generate *Janus* polymeric chains. DSC, WAXS and variable temperature-IR studies confirmed that either one or both the pendant chains crystallize, which acts as the key parameter to reinforce the microphase separated morphology, apparently breaching the lower  $\chi N$  limit. Furthermore, SAXS studies revealed the formation of lamellar morphologies with ultrasmall interlamellar spacing in the range of 4-6 nm (scheme 3); and, most importantly, the domain spacing matches almost exactly with the estimated length of the pendant segments. Thus, we have successfully shown that sub-10 nm domains can be generated using a fairly simple strategy that could be further exploited for some interesting potential applications.



*Scheme 3. Schematic representation of the self-assembly of amphiphilic double-brush polymer.*

The amphiphilic double-brush polymer which contains hydrophobic cetyl groups and hydrophilic PEG chains exhibited an interesting behaviour, namely polymerization-induced

gelation, when the concentration of the monomer exceeded 2.5 wt%. TEM images confirmed the presence of elongated fibrillar network possibly formed from cylindrical micellar aggregates, as shown in scheme 4; DSC and WAXS studies confirmed that the gel is formed via the collocation and crystallization of the pendant cetyl chains in water. Interestingly, heating the hydrogel beyond the DSC melting temperature ( $\sim 40$  °C) transformed it into a sol, while cooling it restored the gel; variable temperature rheological measurements helped confirm this thermally reversible gel-to-sol transition. These findings, apart from confirming that the gelation occurs because of crystallization of the cetyl chains, also opens up the possibility of encapsulating hydrophobic therapeutics by a simple heating-cooling process; since the transition temperature is fairly low, these systems could be of interest for the encapsulation of some temperature-sensitive drugs. These hydrogels also exhibit a shear-induced transformation from a gel-to-sol at shear stress of  $\sim 30$  Pa, which makes it very attractive as an injectable hydrogel matrix.



*Scheme 4. Formation of hydrogel upon polymerization-induced self-assembly of amphiphilic double-brush polymer.*

Study of surface functionalized polymeric nanoparticles has gained momentum, especially in the context of biomedical applications, electronics and photonics, etc. Among different techniques that are used to prepare such nanoparticles, emulsion polymerization has been studied extensively as it provides good control over the particle size distribution and utilizes benign reaction conditions. Furthermore, the hydrophilic moieties present in the emulsifier

used for the emulsion polymerization would decorate the surface of the particle; thus, providing ample opportunities to tailor the surface of the polymeric nanoparticles.

In this context, various hetero-functionalized amphiphilic itaconates were investigated as non-ionic *surfmers*; the nature of the hydrophilic segment was varied from PEG, glycerol or even dopamine, while the hydrophobic segments were either cetyl or octyl chains. These *surfmers* were utilized for the emulsion polymerization of styrene to generate PEGylated PS, glycerol coated and dopamine coated “sticky” PS latexes, respectively, as depicted in scheme 5. Furthermore, using a fluorinated *surfmer*, containing fluoro-alkyl chain and cetyl chains as the two immiscible segments, the preparation of PS nanoparticles having a fluororous-rich surface was also explored. NMR, GPC and DSC studies confirmed the copolymerization of the *surfmers* with styrene and thereby confirmed the covalent surface functionalization of the latexes. DLS and SEM images showed the formation of uniform sized spherical particles in most of the cases. Interestingly, dopamine coated particles exhibited the anticipated adhesive property towards a variety of substrates. The PEGylated and fluorinated polystyrene copolymers were also examined for their ability to serve as coatings to modify the wetting behaviour of surfaces.

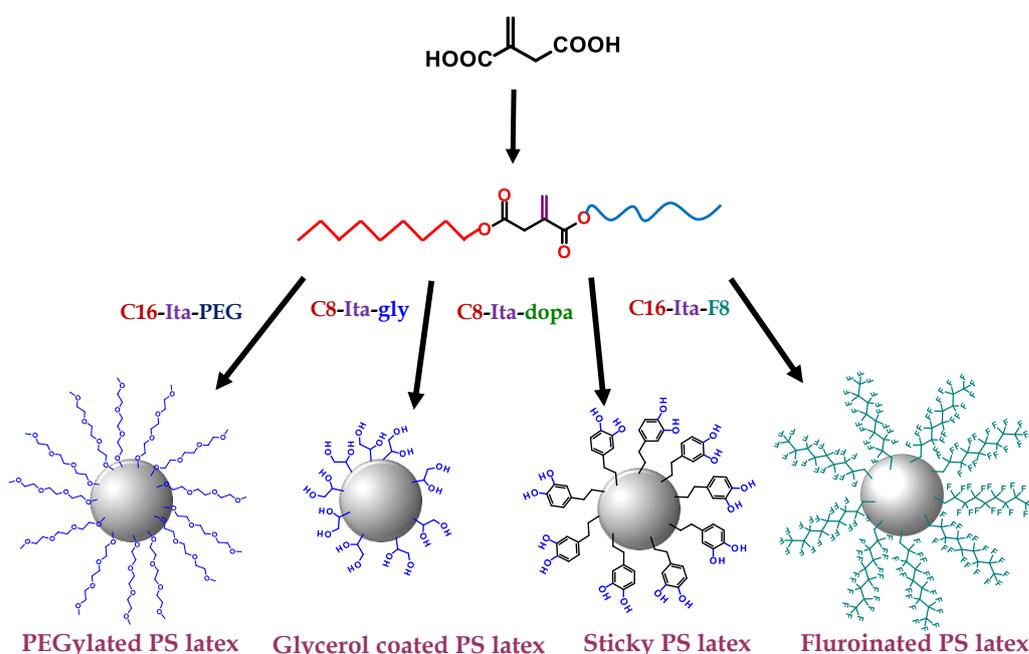
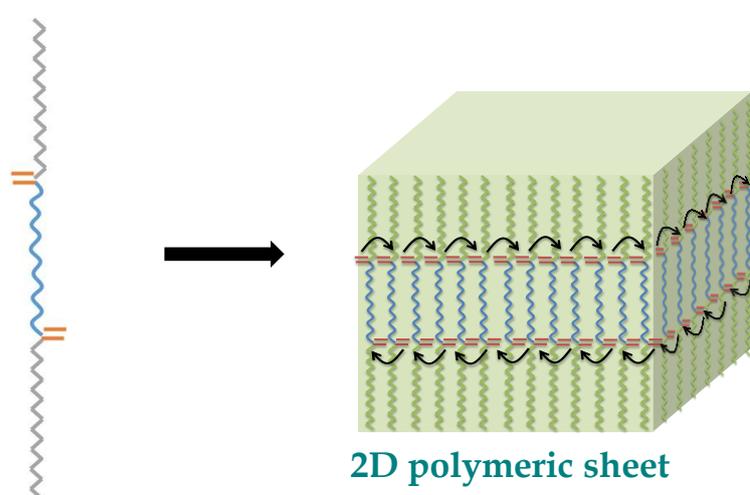


Figure 5. Schematic depiction of the formation of functionalized PS latexes using hetero-functionalized itaconate based surfmers.

In a more ambitious attempt, the potential for microphase separation of itaconate-based amphiphiles was explored as a basis for the preparation of cross-linked 2-D polymers; to accomplish this, ABA-type bola-amphiphilic systems were examined, wherein polymerizable units were placed at the two junctions of the A and B segments. It was anticipated that, upon self-segregation, such ABA-type amphiphiles would organize in a lamellar morphology with alternate A and B domains; here the double bonds, which are present at the junction of two immiscible segments, would collocate at two different planes. Therefore, upon polymerization, it can generate 2D nano-sheets. Evidently, in order to facilitate the polymerization, the double bonds in the self-assembled structure must have enough mobility. In this context, various cross-linkable bola-amphiphiles carrying terminal fluorocarbon segments with central hydrocarbon units, and those with central mesogenic biphenyl unit and terminal hydrocarbon segments, were examined; although polymerization was shown to occur, exfoliation to separate out the layers were unsuccessful. This was attributed to the inability to retain the layered morphology while at the same time maintain adequate mobility at the interfacial planes where polymerization was expected to occur; therefore, either polymerization did not occur or, if it did, a randomly cross-linked polymer was formed. In a final successful attempt, the polymerization was carried out in a vesicular dispersion of a suitably designed bola-amphiphile carrying two terminal PEG units and a central hydrocarbon segment; here, the polymerization occurred apparently forming a 2-dimensionally cross-linked layer, but one that is wrapped into a sphere.



*Figure 6. Schematic representation of polymerization of self-assembled structure of ABA-type amphiphile to generate 2D polymers.*