

Recent Advancement in Comb-like Polymers: A Review

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ABSTRACT

'Comb-like polymers' are a special class of polymers. These are consisting of two types of chains, first one is the backbone chain and second is long side chains. The structure of such a polymer is very similar to hair comb. Usually, every monomer unit in the backbone has a long n-alkyl side chain. Comb like polymers have an intrinsic ability towards forming ordered structure. Now-a-days, these polymers find wide range of applications because of their excellent physico-chemical properties. Some applications are in preparation of polysoaps (polymeric disinfectants), as dispersing agent for ink and paints, textile industry, in surface modification of various materials, in making glass adherent film, absorber, etc. Herein, in this paper we present a review of comb-like polymers and their structure-properties and applications. The recent developments of comb-like polymers especially on nanostructured comb-like polymers are also discussed.

KEYWORDS: *Comb-like polymers, Nanostructured polymers, Long side chain, Branched polymers*

INTRODUCTION

Comb-like polymers are special branch of polymers. Such polymers may be prepared by the process of grafting in the main chain and are usually high molecular weight polymers^[1, 2]. These are usually synthesized by polymerizing vinyl monomers having long n-alkyl side chain. Day-by-day synthetic methodology is improving resulting in the designing and synthesis of

different types of comb-like polymers. The two main basic structure units of comb-like polymers are backbone chain and long side chain. Side chain parts are generally of aliphatic type. The attachment of backbone and side chain is associated with different chemical junctions viz. $-\text{CH}_2-$, $-\text{COO}-$, $-\text{CONH}-$ etc. The properties of comb-like polymers depend upon some important molecular parameters such as

attachment of functional groups, flexibility of backbone chain, functional group attached to the side chain, rigid state of backbone and length of side chain. Polymers having short side chain with backbone comes in class of linear polymers but when long side chain is fixed to the backbone it becomes a different class of polymer called "Comb-like polymers"^[3]. These polymers have different physico-chemical behavior than general linear polymers. Choosing long side chains having predetermined properties are useful for preparing desired comb-like polymers. Minimum four carbons in side chain are good for synthesis of comb like polymers. The monomers used are mainly higher homologues of poly(α -olefins)^[4], poly(n-alkyl acrylates)^[5], poly(vinyl-n-alkyl esters), poly(N-n-alkyl-acrylamide)s⁶, poly(vinyl-n-alkyl ethers), poly(n-acyl systems)⁷, poly(N-n-alkylmaleimide)s^[8], etc. Comb-like polymers have good thermal behavior, conformation variation, phase transitions, and side chain crystallization value^[9]. They are extensively used in various areas of human need, viz. as liquid crystalline polymers^[10], in textile industry¹¹, in paint industry^[12], for drug delivery^[13], as polymer surfactants^[14], in making glass adhering film^[15], in chemistry^[16], in proton conducting electrolyte^[17], as surface modifiers^[18], absorber^[19], in electronics^[20], as pour point depressant^[21], etc. Their fantastic structural design, characteristics and good applicability in different areas results in good demand for such polymers in present and coming years. Polymers of comb-type can be classified into five categories, viz. polymers consisting of: flexible main chains, semi-rigid main chains, rigid main chains, side chain liquid crystalline type, and side-chain supramolecular complexes^[22]. Structural composition and

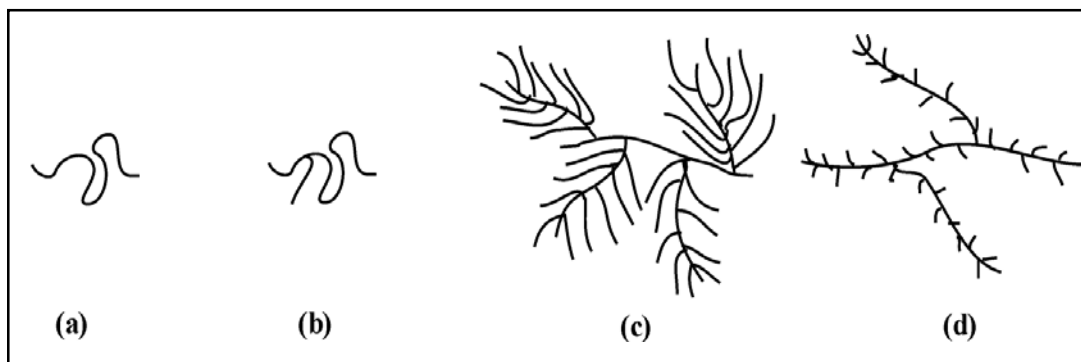
polymeric main and side chain attachment factor decides the method of preparation. Day by day promising applications of these types of polymers are increasing in different areas. We are discussing here different type of comb like polymers and their synthesis, structural characteristics and different areas of applications.

2. Different Polymer Architectures and Their Differences

On the basis of the chain structures, polymers are mainly classified as linear and branched polymers. The linear polymer architecture is the simplest form in all types of polymers in which a single chain is present having no branching or cross linking. When the linear polymer chain is folded in regular packed form it results in crystalline structure but when folded in random pattern crystallinity is lost. Some examples of this type polymer are polyacrylonitrile (PAN), polyvinyl chloride (PVC), high density polyethylene, nylon, teflon, polyester etc.^[23-24] Branched polymers are polymers with branches in the main chain. These branching occur by replacing some atoms from the backbone by side substituent or chains. Such side chains affect properties of the polymers like chain entanglement, sliding of chains on one another. Long side chains can increase toughness, polymer strength and glass transition temperature (T_g) which may be due to some increase in the number of entanglements on per chain. Such polymers show good compactness, and segment density.^[25] Scheme 1 shows different structures of linear and branched polymers. 'Comb-type polymers' is one of the most important classes of branched polymers. In this, side chains are connected to the backbone chain on one side

in a regular pattern and have distinguished structural characteristics containing by the main chain and pendant side chains.^[26] The comb polymer is said to be regular if the arms attached to the backbone are identical. They have selected functionality. Glycogen, starch, low density polyethene are common examples of branched polymers. Researchers synthesized polymers having controlled structural composition such as the length scale, stiffness of polymer backbone and side chain topology so that a polymer may give intelligent response. Scheme 2 and 3 shows various polymer architectures and their classification. Comb-like polymers have potential benefits over linear polymers due to having some special properties over other common polymers such as low tensile strength, low toxicity, biocompatibility, long circulation half life, low

density, high accumulation at target site, low melting and boiling point and high solubility.^[27] These properties are caused by their hierarchical type structures for example crystallization phase transition which is confined to nanoscale level, and conformational variations which depend on chain-length. Some important properties of linear and comb-like polymers are compared in Table 1. Branched polymers have low hydrodynamic volume and are denser than linear polymers of same molecular weight. Such polymers find applications in many areas and are very much advantageous over the linear polymers, such as in biomedical applications, food packaging, drug delivery, textile, waste treatment, proton conduction, chemistry, electronic fields, high performance functional material used in



Scheme 1. (a) linear Polymer chain (b) long-chain branched polymer (amylose-like), (c) short-chain branched polymer (amylopectin-like), (d) both short-chain and long-chain branched polymer (polyacrylate-or polyethylene-like)

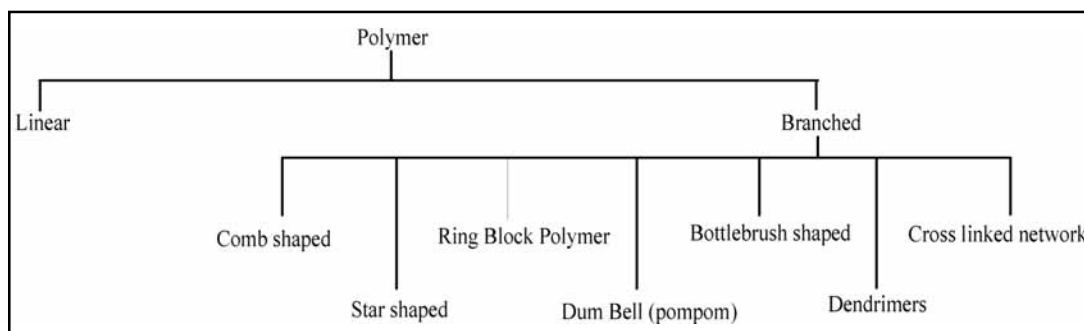
microchip cooling, microelectronic devices etc^[28-33].

Today, modern chemistry offers many synthetic tools towards synthesizing polymers having special architecture with advanced

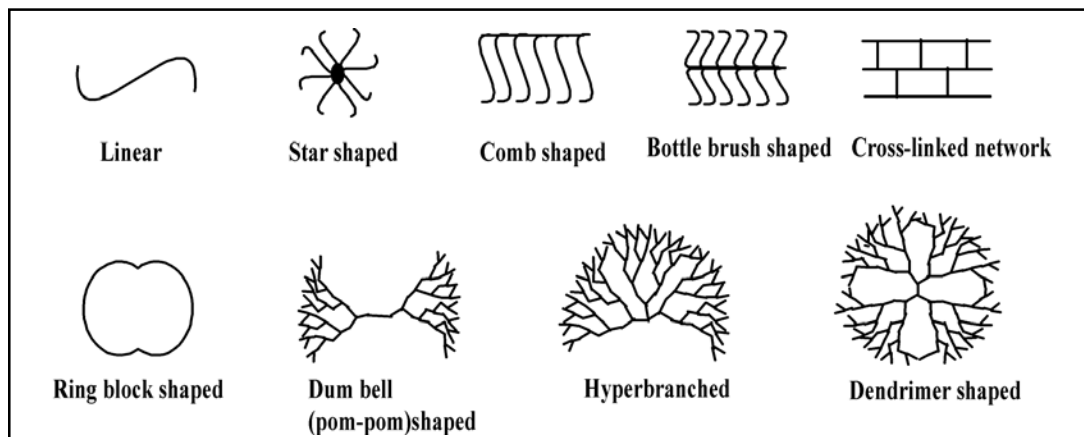
functionalities and novel topologies. For example, hyperbranched, block, comb, star, dendritic, dumb-bell, cyclic type polymers. These are widely detailed with molecular level design. Their excellent features and properties

TABLE 1. Comparison between some important properties of linear and comb like polymers

Properties	Linear Polymer	Comb-type Polymer
Crystallinity	Crystalline	Crystallinity depends on chain length
Viscosity	Highly viscous, tightly packed	Low viscosity, loosely packed
Molar mass distribution	No change occurs when molar mass increases	Increases when molar mass increases
Melting and Boiling point	High	Lower than liner polymer
Functionality	Lower with the molar mass	Higher with the molar mass
Packing ability and structure	Easily packed but less compact and less symmetrical	Difficult to pack but more compact and more symmetrical
Structure	Simple structure having pendant group	Complex structure having polymer chains

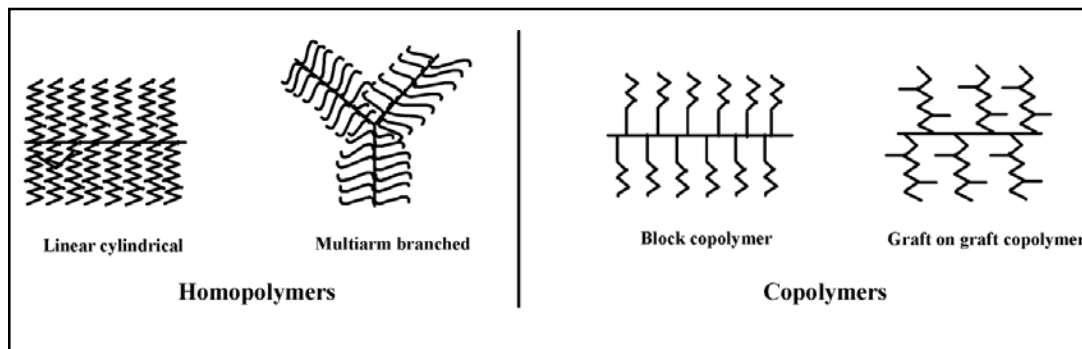


Scheme 2. Flow chart diagram of various types of polymer architectures



Scheme 3. Different types of polymer structures

of such polymers are advantageous and productive for the preparation of many structure controllable materials.^[34-36] Scheme 4 shows some structural composition of homo and



Scheme 4. Different structural compositions of Comb-like polymers

copolymers of important bottle brush like comb polymer structure.

3. Different Forms of Comb Like Polymers

Comb-like polymers may have crystalline form, amorphous form and/or supermolecular form.

3.1 Amorphous form of comb like polymers

Amorphous form of comb-like polymers can be characterized by short range order in the arrangement of polymeric chains. They are synthesized either by the reciprocal action of attached long side chains or from intermolecular interaction of backbone chain. From the study of results of X-ray results obtained from amorphous poly(α -olefins), it was found that when side chain length increases the reflection in the region of low angles of scattering also increases.

In amorphous state folded polymeric chain compose parallel macromolecules which form mass of chain which are arranged in ordered macromolecule aggregates. The lengthy side chain structure in amorphous form is identified

by layered order of the alkyl side chains and which are packed in hexagonal form. The parallel type of packing of adjacent side chain is always energy wise favorable. Ordered aggregates of macromolecule clusters are synthesized by placing parallel macromolecules as folded polymer chains. X-ray diffraction, electron microscopy, optical diffractometry etc are some modern experimental techniques for studying the amorphous phase of comb like polymers. The higher toughness of the attachment bridges that causes higher distortion in the conformation of the long side chain macromolecules over the sections next to the backbone chain (as compared to polyvinylethers (PVE), polyamide (PA) etc.) inhibits the main chains from coming to each other but when spacing are near about equal to the side chain length, they come together^[37, 38]. So, it may be concluded that layered ordering arrangement of side methylene chain characterizes the long side chain structure in the amorphous state. At a proper length of side chain, crystallization appears

when structural elements are constituted by ordered regions of amorphous polymers.

3.2 Crystalline form of comb like polymers

Rehberg and Fisher in 1944 firstly mentioned the ability of crystallization of long side chain. They studied that crystallization property of comb like polymers is dependent on relation between glass transition temperature (T_g) value and side chain length of the comb like polymer^[39]. When length of side chain increases upto a critical length, at first the T_g value drop then rises in a systematic manner. This relation is also followed by some long side chain containing comb-like polymer such as poly(vinyl ethers and esters), poly(*n*-alkyl)styrenes and poly-acylstyrenes), cellulose esters, poly(*n*-alkyl acrylamides), poly(2-*n*-alkyl- 1,3-butadienes), etc^[40, 41]. Turner and Jones gave modern concept for crystallization on the basis of the long side chain architecture. They studied it by X-ray diffraction method. Turner et al disagree by the concept given by Rehberg and fisher that crystallization property depends only on long side chain. Researchers concluded after their studies on comb like polymers that if the length of side chain is short (3-4 carbon atoms) close packing and crystallization depends on both backbone and side chain of macromolecules having helical conformation and isotactic configuration, but when the length of side chain exceed than 4-8 carbon atom due to high energy of side chain interaction the crystallization property of the polymer only depends on side chain and is not affected by backbone of comb like polymer^[42]. In this condition layered structure is formed and crystallization increases effectively. Researchers studied two forms of polymers

differing by long spacing value, packing arrangement for long side chain macromolecules. The crystallization is done in one and two layer form. Polymers having lengthy side chain viz. polyacrylate (PA), polymethacrylate (PMA), poly vinyl-ethers and polyesters can crystallize in only hexagonal form. For the nature of layer packing, long side chains are characterized by two types of spacing i.e. d_1 and d_2 , whose value linearly increases with the rise of carbon number in side chain. Thus, a wide range of composition of packing of side chains cause crystallization on long side chain copolymers, that is to say a relatively small defect in the packing of long side chains caused by introduction of "foreign" units. The flexibility degree of backbone and connection bridge and also the ability of desired conformational changes labeled by the rapid crystallization of the side chain, will decide the number of methylene group taking part in process of crystallization^[43]. Many of studies are done on interplanar spacing for hydrocarbons having long chain and their derivatives for crystalline structure. Pattern of packing comparatively of branching is studied by X-ray diffraction. It was found that in isotactic polyhexene-1-polyoctadecene-1 series, when side chain is of 4-5 carbons, crystallization occurs below 0°C. Polyhexene-1 is orthorhombic or monoclinic, polyheptene-1 is mono or triclinic structured. Polyoctene has amorphous structure and it fails form crystals even at too low temperature. If side chain is seven carbon structured both backbone and side chain participating in crystallization of poly(α -olefine). X-ray studies confirmed the long spacing value between side chains. It increases with the increase in length of side chain. These

side chains are arranged in two types of forms in polyethylene. First one is triclinic packing in which side branches are placed at right angle to the backbone. Here backbone is helical structured and side chains are placed in long spacing. Second one is orthorhombic. In this form crystallinity is at higher degree but long spacing value is shorter. Backbone is tertiary or quaternary helix and inclination of side chain is 130° to the main chain. Isotactic poly(α olefins) having smaller side chains cannot form such crystal structure^[44].

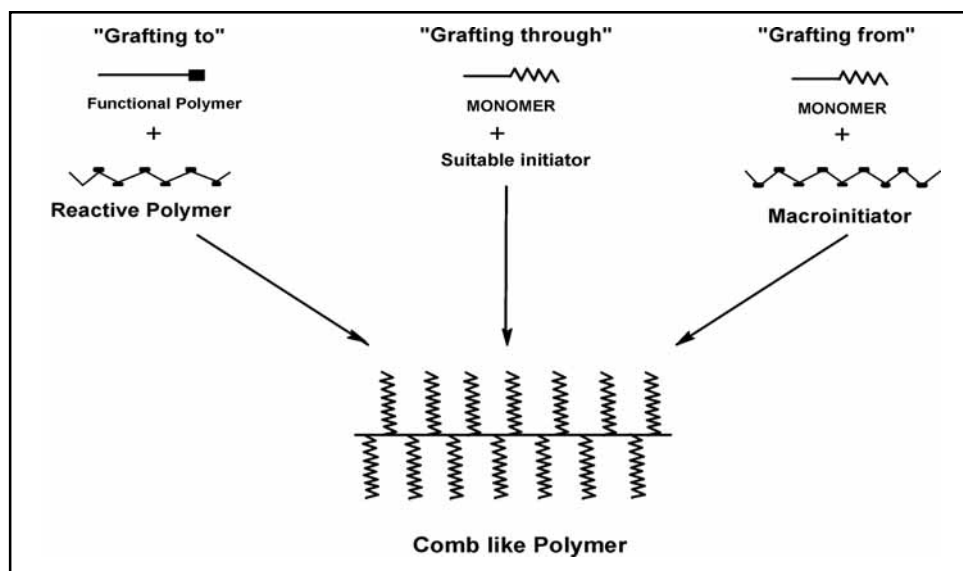
3.3 Supermolecular form of comb like polymers

Supermolecular form of comb like polymers is generally prepared by amorphous polyvinyl esters and poly(*n*-alkyl acrylates) having long side chains^[45]. Atactic and isotactic polymers both form "Spherulites". Polymer and copolymer having long side chain which can crystallize in absence of hexagonal packing of side chain of comb like

polymers are determined by globular structure and not by spherulites or fibrillar structure. Generally the supermolecular form depends on the length of side chain and not on the structure of backbone of comb like polymers. This occurs due to the growth in energy in side chain interaction. The physical state is rubber at room temperature and can form striped structure. It was found that if the length of side chain is with 3-4 carbons having isotactic configuration, both backbone and side chain is participating but when side chain length is upto 4-8 carbons, hindered crystallization occurs. This will disrupt the close packing in amorphous form having layer structure. Again increase in carbon number in side chain favor good crystallization in polymers having supermolecular form^[46-48].

4. Synthesis of Comb-like Polymers

Several synthetic methodologies are studied to prepare different variety of comb-like



Scheme 5. Methods of preparation for comb like polymers by "Grafting through" and "Grafting from" methods

polymers. The general methods are grafting through, grafting to, and grafting from. The method of preparation is selected on the architecture and properties of the monomer involved and desired comb-like polymer. The basic methods of preparation are shown below in scheme 5. The detailed discussion of such synthetic methodologies is observed in literature^[49] and is beyond the scope of the review.

“Grafting Through” Method is generally suitable for polymerization of low molecular weight monomer and macromonomer^[50-59]. In this case the side branches are independently synthesized. Branches are end-functionalized having a polymerizable end group mostly an olefinic end group. In “Grafting-onto” Method an end functional polymer chain can be grafted on a macromolecular backbone having reactive sites. The evaluation of the mean distance in between two sequential grafts with the backbone can be done by “Grafting to” method^[60-64]. The “grafting from” method is useful for preparing comb like polymers having well defined brush type structures. This process is done by starting the polymerization of side chain on the backbone polymer having initiating sites as active centers eg. by using organometallic compounds for metalation of the C-H bond. Many of interesting newly developed topological structured comb-like polymers have been developed by using blend of grafting from and controlled radical polymerization method^[65, 66].

5. Structures and Properties of Comb-like Polymers

The study of structure and properties of comb-like polymers highlights the crystallization, phase transition, and other physiochemical

properties. The liquid crystalline properties can be set according to need by changing comb-like polymer backbone and side chain structure and spacing between them^[67]. Some of the properties are discussed below:

5.1 Crystallization and Thermal Behavior

Crystallization process and thermal behavior of comb-like polymers depends on structural architecture in main chain and different side chain lengths. Crystallization properties depend on packing structure of both main and side chains and number of units in branching. Many comb-like polymers having rigid rod-like backbone can be prepared by making fine graft in molecular chain backbone. Addition of side chains gives crystallization and thermal behavior which can be modified by changing the length of side chain. Long flexible alkyl chain attached as side chain can also induce the thermotropic phase transition behavior with crystallized structure. It has been found through several studies that stiffer the backbone of comb polymer higher the number of methylene group required to produce crystallization. Different experiments were conducted on poly(vinyl esters), poly(*N-n*-alkyl-acrylamides) and poly(*n*-alkyl acrylates), for studying the crystallization behavior in which the length of side chain varying in range 12 to 22. Flexible backbone requires minimum number of carbon in side chain to show crystallinity and thermal properties as compared to rigid and semirigid backbone. Ordered arrangement of polymeric molecular chain and variation in numbers of monomer in backbone and side chain define different types of advanced structure and properties of comb like polymers^[68-70]. Y. Lin et al studied microphase structure, morphology and linear rheology of PVSt-g-(PS-*b*-PE) (PVSt:

poly(4-(vinylphenyl)-1-butene, PS: polystyrene and PE: polyethylene) comb-like copolymer which are strongly affected by volume fraction of the backbone. Increase from 10.9% upto 54.5% in volume fraction of PS portion, microphase separated structure of the polymer changes in poor-order lamellar structure from poor-order spherical structure. The melt peak(T_m) starts from 104°C with complete melting at 110°C which shows that PE part is crystalline. The primary crystallization peak temperature (T_c) gradually decreases with increase in the amount of PS. DSC results also shows that secondary crystallization becomes stronger^[71].

Lin *et al.* also studied on similar composition in which PS volume was increased from 42.7% to 76.9%. Thus the microphase separated structure changes to cylindrical structure from lamellar phase structure. They observed that PVSt4.9-g-(PS/PE-3) has cylindrical microdomains but PVSt1.7-g-(PS/PE-1) and PVSt4.9-g-(PS/PE-2) shows lamellar microdomains. This shows that the crystallization value of side chain PE in PVSt4.9-g-(PS/PE-3) is confined to separate disperse phase and continuous PS phase.^[72]

X. Zhu *et al.* reviewed the response of degree of branching on physical and chemical properties of hyperbranched polymers (HBPs).^[73] Yan and coworkers synthesized a series of polyethers with different degree of branching from the cationic polymerization of 3-ethyl(methyl)-3-(hydroxymethyl)oxetane (PEHO). The DSC melting curves result that the linear PEHO is partially crystalline and hyperbranched PEHO is amorphous by nature. With the decreasing DB, the increase in

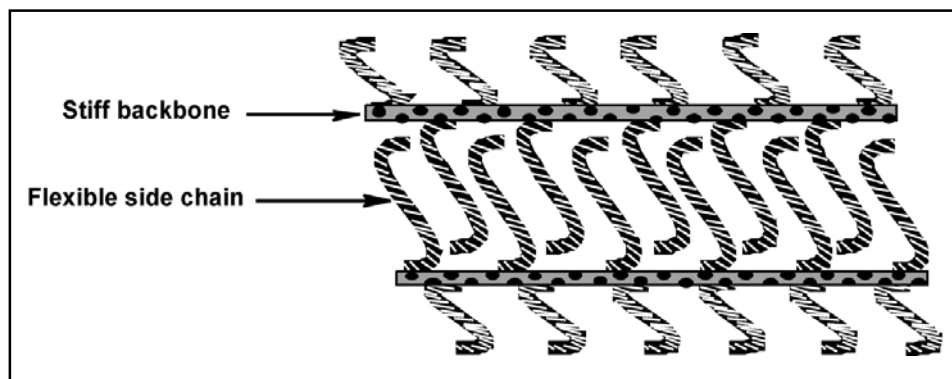
crystallinity of polyethers appears. By changing the branch-length of polymers, the biocompatibility and several other properties were altered.^[74]

Takayanagi *et al.* studied the structure and properties comb-like polymers of N-substituted PPTA having different side-chain substituents. The alkyl side chain with PPTA comb-like polymers definitely improves the solubility and reduces the melt-processing temperature. Moreover, the side-chain crystallization behavior strongly appears when the number of carbon atoms present in the side chain is more than 14.^[75] Shi *et al.* systematically studied the packing and crystallization behaviour of side-chain of the PBA(n)Cs series of comb polymers having the number of C-atoms ranging from 10 to 18. The crystallizability of side chains continuously improves with the increasing length of the side chain. The minimum number of carbon atoms for crystallization was 14. Longer side chains needed to realize side chain crystallization.^[76, 77] The amorphous state changes to melt state by change in branch chain length. The T_g of PSVS-g-PS copolymers is higher than the other. This combination might result from decrease in movement of chain segment. This is due to the restriction of surrounded side chain. This phenomenon is observed because of the chain end effect of polystyrene units having the excess free volume around the chain ends. The number of the chain end per unit molecular weight decreases with the increase of side chain length. However, when the side chain is the same, the T_g is similar among the graft copolymers with different graft densities.^[78]

5.2 Ordered Packing Structure and Phase Transition

Many researchers have found that the comb-like polymers have hexagonal crystalline structure. This structure is due to the crystalline property which depends upon number of carbon atom present in the side chain of comb-like polymers. Critical crystalline thickness in side chain is responsible for generating ordered packing structure in comb-like polymer. Alternate amorphous and crystalline layered structures in comb-like polymers were studied. In that structures backbone is amorphous and side chain is crystalline in nature in which the crystalline side chain is surrounded by amorphous main chain^[79-81]. In scheme 6 the packing structure of stiff backbone is shown

with flexible side alkyl chain. The backbone of comb-like polymer also affects the conformational state and relaxation process of comb polymer with the packing structure property^[82]. The ordered packing and phase transition is very much dependent on the length of side chain. Different phase behavior, chain relaxation and conformational variation are also depending upon attachment of side chain. Study on PEI(n)Cs and CS(n)Cs comb-like polymers are very much in ordered phase which are monoclinic and orthorhombic crystal structure due to the increased length of side chain. The conformation variation behavior and phase transition also exhibit a difference from stiff rod polymers. By adopting much larger segment of CH₂, the flexible backbone can do conformation adjustment entering in the crystal lattice in comparison to rigid ones.



Scheme 6. Stiff backbone with flexible side chains in a packing model

When side chain length is increased, PEI(n)Cs can easily form a regular crystalline structure (n greater than 20) than that of less length of chain (n less 18). The flexible form shows a complicated phase transition as compared to rigid rod polymeric backbone^[83-84]

5.3 Properties

The comb-like polymers with their special topology and architecture exhibits fascinating properties specially when using rigid, semirigid, conjugated and flexible polymers. The value of melting point is high for flexible backbone and

flexible long side chain. With the increase in length of side chain the comb like polymer move from amorphous to crystalline form^[85, 86]. The physical and chemical properties of comb structured polymers are highly dependent on chemical properties of monomers involved, number of monomers and polarity of backbone and side chain.

The stereoregularity of backbones and length of side chain decide the crystallinity of comb-like polymers. The syndiotactic form gives highly packed side chain as compared to isotactic comb-like polymers. Comb-like polymers with strong polar groups shows poor solubility. The solvent which is good for side chain of hydrophobic type is always poor for backbone of hydrophilic type in comb like polymer. The hierarchical functionalized architecture of comb like polymers depends on both the side and molecular chains ordered arrangement and properties. They have thermal energy storage capacity due to having crystallizable alkyl side chains and are useful for making high performance materials due to low melting processibility character. The nematic, smectic and cholesteric mesophases are shown by side chain with rigid groups containing comb like polymers. Researchers have made different types of nanomorphologies of comb-like polymers by changing temperature, solvent and surrounding template etc. These morphologies are cylindrical, spherical, flower, lamellar, hexagonal and hyperbranched micellar morphologies. By fluctuating chain number volume fraction, side chain numbers and interaction between monomers of main chain and side chain, nine morphologies (stable) are described. The management of block numbers, repulsion

between chemically connected different functional groups, chain flexibility and the volume fraction made body centered cubic structure, lamellar phases, hexagonal cylinder, hexagonally modulated lamellae and gyroid structure in comb like polymers. Different studies are made on π -conjugated polymers which are also useful in application of sensors, organic photovoltaics, thin film devices and thin film transistors(organic). Various morphologies, such as environment sensitive nature, micelles formation nature, efficient charge transport performance, gas separation and proton conductive membrane are also reported⁸⁷⁻⁹⁰. Researchers reported some novel performance by comb-like polymers by introducing selected predetermined units on the main chain of polymer. By introducing some flow improver additives comb-like polymers can be used as pour point depressant for oil. The crystalline structure is also helpful in this application. Some examples are long chain acrylic esters copolymers, poly(n-alkyl(meth)acrylate), acrylic acid and poly(n-behenyl oleate-co-maleic anhydride)dimethyl ricinolate.

6. Nano-structural Comb-like Polymers

Nanotechnology is a modern concept, which provides an opportunity to work at very minute level towards synthesizing nanostructures having new molecular organization. In last couple of decades, the field of nanotechnology has grown enormously and has been applied for many areas of human need. Polymeric materials prepared with nanometer-range dimensions are called nanostructured polymeric materials. These materials have high surface-to-volume ratio, exciting bulk and surface properties, size coupled properties,

small size of the building blocks (in nanometer scale), unique physicochemical properties etc. Nanostructured polymers are synthesized by two approaches, *viz.* bottom-up and top-down approach. These nanostructured polymers have great potential of applications in various fields such as for drug delivery, gene delivery, biomedical field, tissue engineering, biosensors, thermoplastic elastomers, coatings, dispersants, surfactants, as optoelectronic etc ^[91-93].

K. Ishizu *et al.* have reviewed nanostructural polymers having various macromolecular architectures. They gave special consideration to rod like, hyperbranched macromolecules and brush polymers. Comb shaped copolymers are formed by free radical copolymerization of binary macromolecules^[94]. H. Deng *et al.*, have synthesized theranostic gold nanomicelles. It has been prepared from comb like polymers which are biocompatible by nature. It is used for the process of thermo-chemotherapy and multifunctional imaging. The gold micelles are prepared by assembling 6 nm size nanoparticles of gold. It shows great absorbance in the near-infrared region. It is good for multimodal type bioimaging and very effective in vivo photothermal treatment and chemotherapy^[95]. Some newly synthesized nanostructured comb polymers are very beneficial in the area of modern industrial applications. Recent studies and synthesis of permanent anti-static additives or breathable membranes makes these polymers having outstanding balances of antagonistic working ability. Polyamide-g-polyolefin (PA-g-PO) has property of exclusive balance between low modulus produced at room temperature and high level thermo-mechanical resistance.

Some examples are poly(oxyethylene glycol)-g-polyolefin (PEG-g-PO), poly(methyl methacrylate)-g-polyolefin (PMMA-g-PO).^[96] V. M. Weiss *et al* prepared structured polygonal shaped nanoparticles using comb shaped polymers. These comb shaped polymers are phase separated. Differently ordered nanostructures are synthesized by different degree of esterification of the OH groups of poly(glycerol adipate). A perfect lamellar arrangement is prepared for polymers with a high degree of esterification. This structure leads to spherical nanoparticles having internal onion type structure.^[97] A responsive nanostructure has been synthesized for triggered release of drug and cytotoxicity which is comb type poly(L-cysteine) derivatives having many different side groups. This research established facile method for the synthesis of graft polypeptides of comb like (by using the thiol-ene type click chemistry and photochemistry) and also gives an assuring platform for cancer therapy and on-demand nanomedicine^[98].

More recently, the preparation of polymer-modified graphene oxide (amphiphilic type) and its estimation in the making of nanocomposites of polystyrene have been studied. The method of surface initiated atom transfer radical polymerization (SI-ATRP) results in the formation of modified polymer. It is achieved from graphene oxide and successive sulphonation of the synthesized brush-type polymer. The lower glass transition temperature and upgraded thermomechanical properties are the attractive features of amphiphilic polymer-modified graphene surfactant containing nanocomposite films. It performed as multifunctional additive for polymer

nanocomposites^[99]. Yangbin *et al.*, explained that supramolecular nanochannels in comb polymers are useful to enhance anhydrous proton transport. They reported the synthesis, design and characterization of macromolecules and observed nanoscale type organizations of conduction of proton supramolecular nanochannels which are the main considerations in achieving efficient transportation of anhydrous protons^[100]. Irvine *et al.* experimented to clarify the design and properties of thin films that are made up of amphiphilic comb like polymers. It shows Arg-Gly-Asp (RGD) peptides nanoscale clusters useful for adhesion of cell on biomaterials in controlled manner. Poly (methylmethacrylate) is the backbone and side chains are of poly(ethylene oxide). By tethering process peptides placed on ends of side chain made clusters of nanoscale peptide¹⁰¹. For effective anion(hydroxide) transport process, comb like nanostructured poly(2, 6-dimethyl-1, 4-phenylene oxide) (PPO) polymers have been reported which has quaternary ammonium groups and it organizes in well-defined micro-morphology. These structures show unexpected improvement in conductivity and also resistivity from water as compared with non-comb shaped type PPOs¹⁰². Venkataraman *et al.* studied the effects of polymeric nanostructure shapes on the process of drug delivery. Different shapes of nanostructured polymers are possible through the top down and bottom up approaches. Its major thrust area is toxicity and cellular uptake^[103]. Today's, drug delivery process is largely based on the application of spherical nanostructures. Research conducted towards implications of other shapes will give better next generation carriers. Y. Chen *et al.*, have

reviewed different approaches to synthesize polymers of various shapes and importance of these shapes in drug delivery and future perspective of it^[104].

7. Some Newly Developed Comb-like Polymers and their Applications

From the last decade, comb like polymers are extensively studied to synthesize advance polymers having different types of properties for various applications. D. Yang *et al.* studied on understanding the surface properties and rheology of a comb like poly (acrylic-acid)/ poly(ethylene oxide) (PAA/PEO) copolymer in salinity condition. This polymer is very beneficial in petroleum and mining industry. Researchers show that absorption of polymer on silica surface is enhanced at larger salinity. This occurs due to the suppression on the electrical double layer. It is useful in preparing and processing polymer additives contained complex colloidal suspensions. Various applications of this polymer are in construction materials, tailings management, drilling mud and enhanced oil recovery^[105]. Xu *et al.* proposed a mechanism of improvement of flow of crude oil by addition of comb like polymer having long alkyl pendent. This comb polymer inhibits regular organization of paraffin crystal by putting in the paraffin molecules and prevents the network formation in the wax. This automatically improves the flow ability of the crude oil^[106]. Andrew Goodwin *et al.*, have reported anionic polymerization techniques which provide great control over molecular weights of backbone chain and side chain, spacing between branch, branch point's number of and branch point functionality. These properties give well defined grafted materials. This method allows for preparation of highly

complex tailored copolymer materials for different types of applications e.g. high impact plastics, thermoplastic elastomers, additives, pressure sensitive adhesives and foams^[107]. X. Jing *et.al.* recently studied carboxylic group containing novel comb-like copolymers including polycaprolactone. It was firstly working as CaCO₃ particles dispersant in polypropylene (PP). The process of dispersion was improved in the presence of comb like copolymer. This is due to the large repulsive

force produced due to effect of steric hindrance. They studied that the crystallization behavior, thermal stabilities and mechanical properties are affected by the coating amount of comb-like copolymer. The temperature of crystallization, crystallinity and also the rate of crystallization of composite made up of PP/CaCO₃ by coating of single layer comb-like copolymer. They have also excellent thermal stability, mechanical properties, including tensile strength, impact strength, Young's

TABLE 2. Some newly developed comb like polymers and their applications

Some newly developed comb like polymers	Applications	References
Si-doped flexible self-supporting comb-like polyethylene glycol copolymer (Si-PEG)	Polymer electrolyte for solid-state lithium-ion battery	114
Novel amphiphilic comb-like terpolymers	used to disperse solid particles in many different fields	115
Membrane-anchoring, comb-like pseudopeptides	for intracellular delivery	116
Side chain crystallizable polymers	useful in various medical application. viz. in stents	117
Thermo-responsive comb polymers as thickeners	for high temperature aqueous fluids	118
Jeffamine based polymers	highly conductive polymer electrolytes and cathode binder materials for battery application	119
Comb like polyacrylic acid-Grafted fatty alcohols	Thermal energy storage application	120
Multidentate comb-shaped polypeptides bearing trithiocarbonate functionality	valuable polypeptide-based quantum dots with hydrophilic character and biocompatibility for cellular imaging	121
Mixed micelles prepared by co-assembling expression in comb-like and grafting copolymers	Gene carriers for efficient gene delivery and endothelial cells	122
Comb like poly(ionic liquid-co-styrene)	Applications in graphene dispersion and CO ₂ separation	123
Bioresorbable polypeptide-based comb-polymers	for improving the stability and pharmacokinetics of proteins in vivo	124
Worm-like mesoporous TiO ₂ thin films templated using comb copolymer	for dye-sensitized solar cells with polymer electrolyte	125

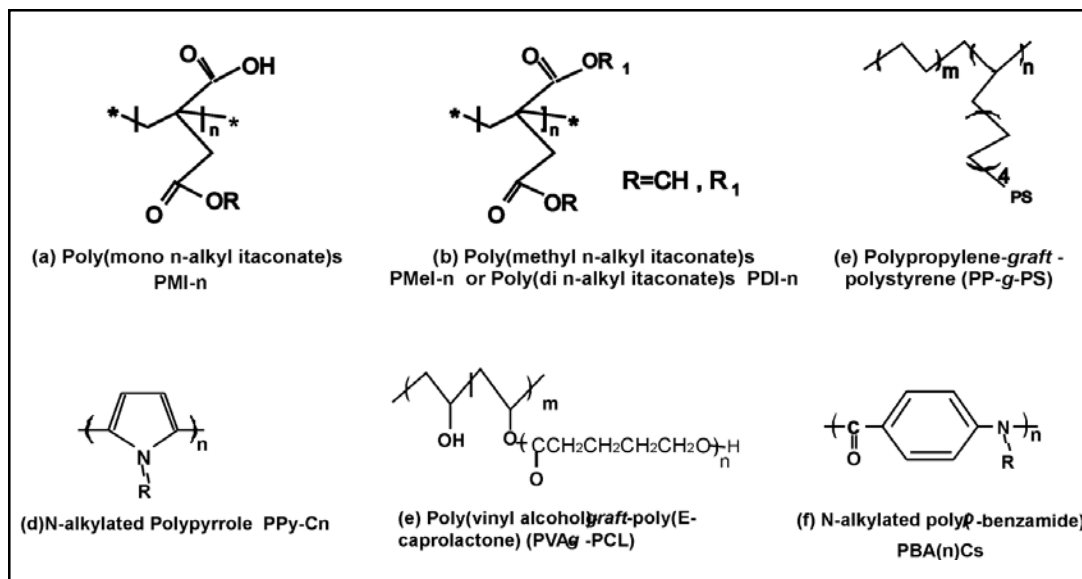


Fig. 1. Different types of comb like polymers

modulus and flexural modulus. This is due to the good dispersion property of CaCO_3 particles in the PP matrix^[108]. A number of comb like stereoregular cyclolinear-methylsiloxane copolymers which show the self-assembling behaviour have been prepared and studied. For the prepared macromolecular materials, the chiral mesogenic unit used as a side group, namely (S)-(-)-4-[1-ethoxycarbonyl ethoxy carbonyl]phenyl-4'-[11-tetramethyldisiloxyl undecenyloxy]-biphenyl-4'-carboxylate. The mesomorphic behavior is assured by it^[109]. C. R. L. Barron *et.al.* synthesized various poly (ethylene-co-acrylic acid)-cb-atactic polypropylene (EAA-cb-aPP) copolymers of comb block type by putting a commercial EAA copolymer that is grafted by PP-OH macromonomers. It is prepared by the free radical process having high-pressure. Therefore, the EAA-cb-aPP copolymers can be categorized as hyperbranched polymers.

This is due to having 11 wt% of EAA units in the polymer. This copolymer contains noticeable quantity of branches of long chain. The amorphous a PP a semi-crystalline EAA domain. In melt state it shows strong, textured and phase segregated, unexpected nucleatic effect (facilitate crystallization) properties. They postulate that from the interfacial anchoring of the aPP side chains in the aPP homopolymer domains, SH enhancement may arise. This would give outcome as added opposition for the EAA backbone to stretch under uniaxial load^[110]. Conjugated comb like polymers have excellent electrical, electrochemical and optical properties. Some long chain containing comb like polymers are synthesized having good property of stability and solubility such as polypyrroles, polythiophenes, polyanilines etc.^[111-113] Some more recently synthesized comb like polymers and their applications are listed in table 2.

8. CONCLUSIONS

Recent development in comb-like polymers is giving a new dimension to their application because such polymers are helpful in fine controlling on their aggregated structure, nanostructure and architectures by providing improved synthetic methodology. The change in polymeric backbones and alkyl side chain highly affects the chain structure, manner of packing, and hierarchical architecture of the comb polymers. In this review paper, we have discussed different aspects of comb-like polymers and their structural differences with linear and branched polymers, their structural forms and properties, the methods for synthesizing comb-like polymers having controlled microstructures, nanostructures and tailorable properties, and applications. Comb like polymers find applications in the preparation of many structural functional devices viz. microelectronics energy-storage devices and nanoporous membranes etc. Such polymers are widely used in excellent application areas such as drug delivery, proton conductor in preparation of polysoaps (polymeric disinfectants), dispersing agent for inks and paints, textile industries, surface modification of various materials, in making glass adherent film, absorber, etc. Comb like polymers are smart polymers due to their special architecture with adjustable mechanical and thermal properties. The special structure of such polymers results in better mechanical and thermal properties of polymers.

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Received: 10-05-2019

Accepted: 04-06-2019