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RESEARCH ARTICLE

Review on Polymer Brush Synthesis Via Controlled Radical Polymerization Technique.

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Abstract

In this review, we discussed mainly on fabrication of polymer brushes by using controlled radical polymerization technique. Controlled radical polymerization (CRP) techniques provide enormous possibilities for synthesizing well-defined polymers with controlled architectures and molar masses, high graft density with well-distributed polymeric brushes. In fact, we also discussed the atom transfer radical (ATRP) and Reversible fragmentation chain transfer (RAFT) radical polymerization. Also, we had discussed the general characterization techniques of polymer brushes.

Review could be more useful for researchers in general to understand the polymer brush preparation and its characterization.

Introduction:-

Polymer brushes (PBs) can be defined as long-chain macromolecules that are attached with an anchor site to a surface.[1] An interesting class of smart macromolecular brushes consist of stimuli-responsive polymer brushes because their assemble and properties can be tuned in an accurate and predictable manner by using an external stimulus.[2] Such type of smart PBs have attracted substantial research interest in the latest years since they play an important role in a wide range of applications in several areas of materials science research and technology.[3-5] Physicochemical properties and shape of polymers usually show rapid and reversible changes in response to small changes in the environment (e.g., solvent, ionic strength, electrochemistry and pH).[6-9][5, 10]

In the past decade, the limitations of FRP have been overcome as several procedures for CRP have evolved based on an understanding and integration of chemistry developed over the past 60 years in the fields of organic chemistry, conventional radical polymerization, and living ionic polymerizations. Controlled radical polymerization (CRP) techniques provides enormous possibilities for synthesizing well-defined polymers with controlled architectures and molar masses.[8, 11-14]

For instance, reversible addition fragmentation chain transfer (RAFT) polymerization allows the use of acidic monomers and also the use of polar solvents like ethanol. Therefore, this technique is most widely employed method to prepare water soluble polymers.[1]However, the chain transfer agent (CTA) has to be carefully selected depending on the nature of the monomer.[12, 13, 15] Alternatively, transition metal-catalyzed controlled radical polymerization techniques provide good control over the polymerization of several monomers.[16]

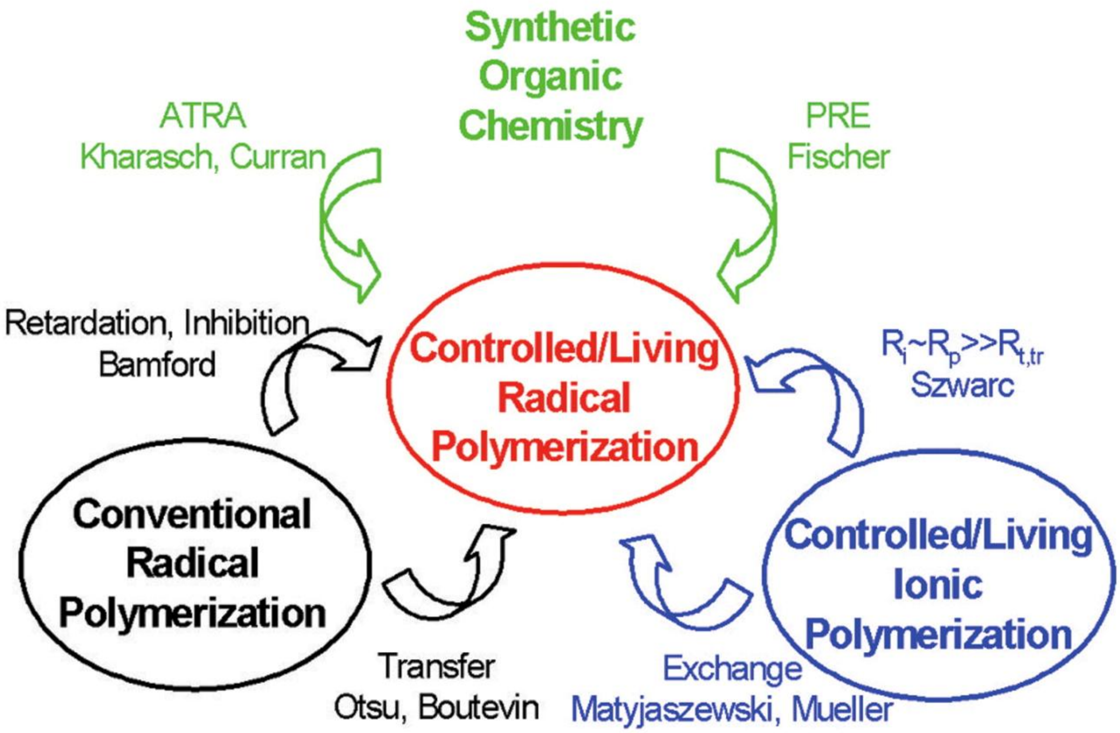


Figure 1. Development of CRP by integration of advances in several fields of chemistry.[14]

Unfortunately, these techniques, namely atom transfer radical polymerization (ATRP) and single electron transfer controlled radical polymerization (SET-LRP), are based on the oxidation reduction equilibrium of the transition metal and ligand complex which can be disturbed in the presence of acidic monomers. As a consequence, protected monomers have to be used during the polymerization.[12, 13, 16]

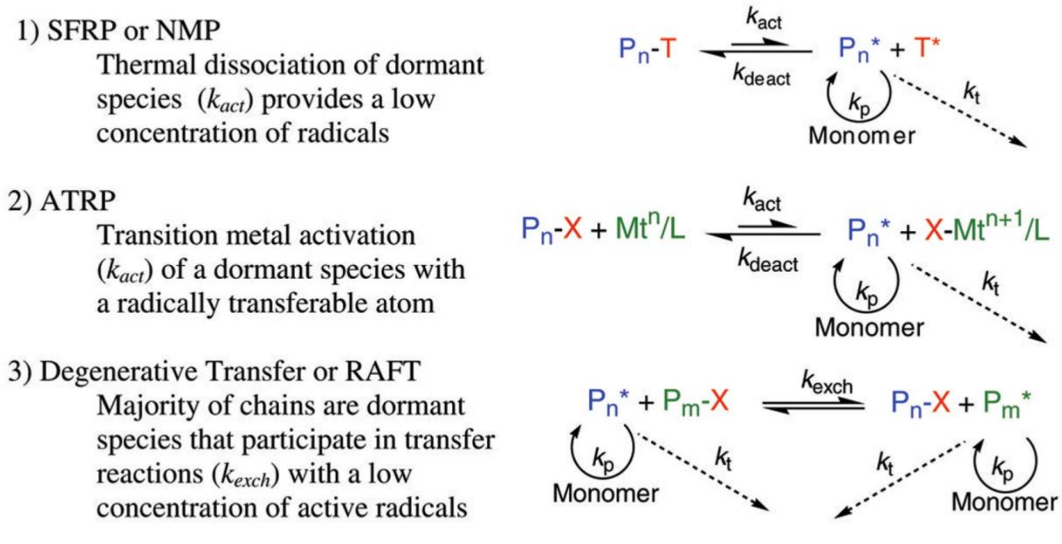


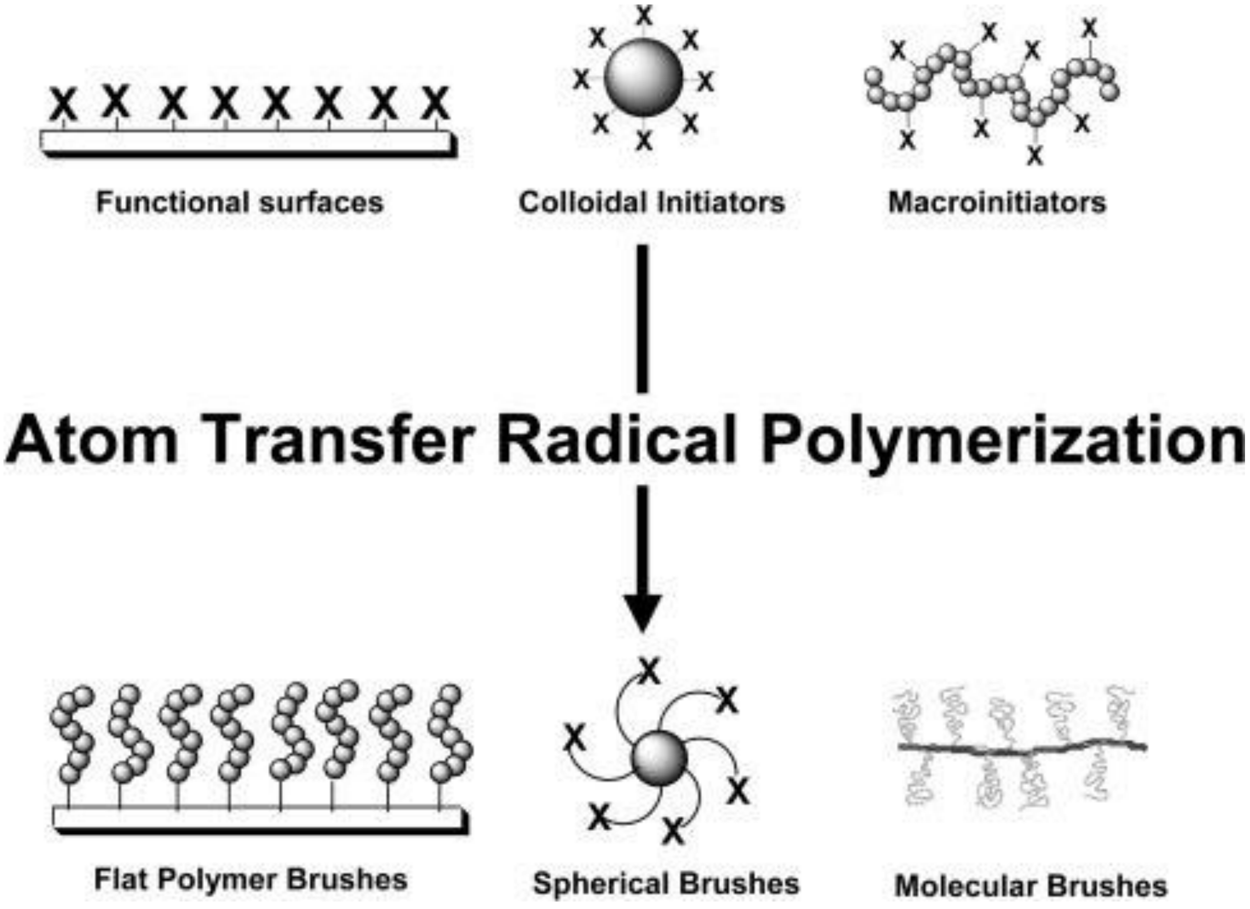
Figure 2. The three main CRP methods.

Synthetic strategies for preparing polymer thin films made up of polymer brushes use the “grafting-from” and “graft to” techniques.[17] The grafting from strategy normally yields a higher graft density of polymers with controllable coverage on the surface than "graft to" approach.[18] In the grafting-from approach, an initiator bound to the substrate enables an easy control on the thickness and density of the polymer brushes using a wide range of polymeric techniques such as living ring-opening metathesis polymerization (ROMP),[19] anionic polymerization or controlled radical polymerization (CRP) i.e. nitroxide-mediated polymerization (NMP),[16] atom-transfer radical polymerization (ATRP)[20] and reversible addition fragmentation chain transfer polymerization (RAFT).[11, 21]

Atom Transfer Radical Polymerization and Brush Synthesis:-

An attractive feature of ATRP and other controlled/living radical processes is the ability to simultaneously grow chains from multifunctional cores, or surfaces (Scheme 1). An advantage of ATRP systems is the facile functionaliza- tion of target substrates using commercially available a-haloesters, or benzyl halides, circumventing the multi- step synthesis necessary for functional alkoxyamines and dithioesters. ATRP initiator groups have been successfully coated onto both organic and inorganic materials, with either flat or curved surfaces. From this approach, polymer brushes of varying composition and dimensions have been prepared by surface-initiated growth from macroscopic wafers or particles, (sub) micron-sized colloids and polymer backbones.

Ideally, in using efficient multifunctional initiators for ATRP, the number of functional initiating sites translates into stars or brushes possessing the exact number of tethered polymer chains. However, termination reactions at either low or high conversion may alter the functionality and molar mass distribution of tethered chains. An additional consideration in using multifunctional initiators is that termination can occur either by intermolecular coupling of growing radicals or in an intramolecular fashion by neighboring surface-immobilized chains.



Scheme 1. Examples of polymer brushes synthesized by ATRP using ‘‘grafting from’’ approach from various functional substrates, such as flat wafers, particles, colloids and polymers (X-halogen). [20]

Reversible addition-fragmentation chain transfer (RAFT):-

The “livingness” of this polymerization process can be ascertained from a linear first-order kinetic plot, accompanied by a linear increase in polymer molecular weight with conversion, with the value of the number-average degree of polymerization (DP_n) determined by the ratio of reacted monomer to initially introduced initiator (i.e., $DP_n = D[M]/[RX]_0$).[12, 13, 22]

RAFT polymerization begins when radicals are generated by decomposition of a peroxide or azo type free radical initiator. The initiating radical species reacts with the monomer and in what has been termed as the pre-equilibrium, the radicals on the ends of the propagating chains quickly attack the reactive C=S bonds of the CTA to produce a carbon centered intermediate radical. This species may undergo a β-scission reaction which can either yield the reactants back, or release the R group as a radical fragment and leave the polymeric chain capped with the dithioester. The R radical released is free to initiate new chains by attacking monomer or they may attack back on the dithioester capped chain.[12]

The dithioester capped state comprises the dormant species in a RAFT reaction. It is critical to note the general form and function of the dormant dithioester adduct is the same as that of the original CTA, dormant polymer chain takes place of the R group.This species is referred to as a macro chain-transfer agent (macro-CTA). [13, 14, 23] The preequilibrium continues until all initiator is consumed and all R groups are released as radicals to initiate more chains. At this point, main equilibrium begins and is governed by the same mechanism of radical attack on the C=S bond followed by β-scission of the resulting intermediate radical. However, in the main equilibrium stage this process takes place solely between propagating chains and macro CTAs, resulting in a rapid exchange of the dithioester cap. This rapid exchange ensures each chain has the same probability of growth and minimizes termination reactions leading to the living characteristics observed.

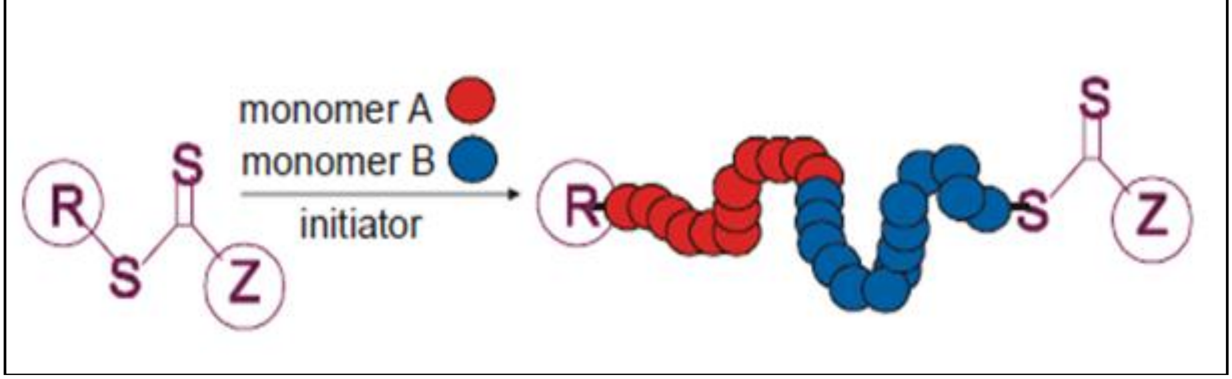


Figure 3. (a) Mechanism of RAFT and (B) flow chart RAFT addition.

RAFT polymerization[11] has been successfully applied to grow well-controlled brushes on substrates to alter the surface properties of the materials. This polymerization technique has also been used to obtain inorganic particles with controlled polymer hair size including gold, silica/silicon as well as glass surfaces.[18, 23-25] The RAFT agent can be immobilized on the substrate, then initiator and monomer are added together to start the radical polymerization or radicals can be generated on the surface itself by covalent attachment of an initiator and RAFT agent is added in a second stage, while monomer is introduced in the reaction mixture at the very latest stage.[20] Two methods are available for immobilization, the RAFT agent can either be attached via its R-group (anchoring side) or Z-group, the macroiniziator site, where reaction propagates (for a better understanding of the RAFT method a graphical representation of this approach can be found in in Figure 3).

Growing polymer brushes with schematic diagram:-

RAFT agents can be immobilized on the surfaceor radicals can be generated on the surface by covalent attachment of a Raft agent while the RAFT agent has been added to the solution.[25-28]

“Grafting from” methods using RAFT-initiator-immobilized or vinyl zed surfaces to grow polymers from surfaces with conventional radical polymerizations can yield functional polymer brushes, although it is difficult to regulate grafted polymer chain lengths under these reaction conditions.To overcome these problems, polymer brushes prepared by the “grafting from” method were proposed using controlled living radical polymerization [30-34]that more readily provides polymer chains with predetermined molecular weights and narrow polydispersities, controlling reaction times at appropriate monomer concentrations and temperature. Graft thickness for grafted surfaces is obtained by varying concentration of monomer feeding ratio with time.

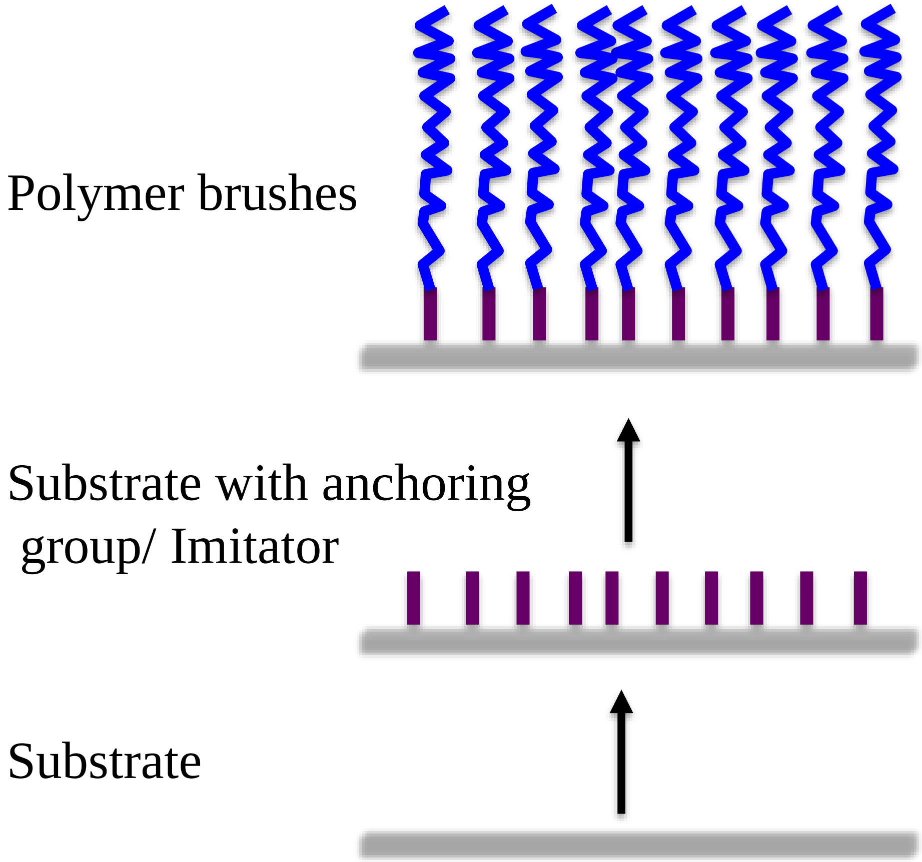


Figure 4. Concept for the synthesis of covalently attached polymer monolayers via radical graft polymerization (“grafting from” technique) using immobilized initiators.

Characterization of polymer brushes:-

The characterization of polymer brushes can be a challenging task since many of theanalytical tools in polymer science are solution-based techniques. Table 1 provides anoverview of the different techniques that have been used to characterize polymer brushes. For a broad variety of polymer brush properties, Table 1 lists the analytical methods that are available to study that particular property. Instead of discussing the technical details of all the analytical techniques, this section will highlight how some of the most prominent properties of a polymer brush can be studied with the analytical tools that are currently available.

Property	**Methods**													
	SPM	Optical and electron microscopy	Electrochemistry	Ellipsometry	Infrared spectroscopy	Contact angle measurement	SPR	TOF-SIMS	QCM(-D)	XPS	XRR	TGA	GPC	NEXAFS
Chemical composition and structure					x	x		[26, 27]		x				[28]
Thickness	[29, 30]	[31]		x							[10, 32]	[33]		
Molecular weightmolecular weight distribution	[34, 35]												[36]	
Brush density	x			x								[42]	x	
Topography and surface structure	x	[37, 38]				x		[39]		[40, 41]	[10, 32]			
Stiffness	x							x						
Conformation and swelling	[43, 44]		[45, 46]	[47, 48]	x	x	[43, 49]		[50, 51]					[52]
Polymerization kinetics	x			x					[53, 54]					
Electronic and electrochemical properties			[55]											

Table 1. Overview of analytical techniques that are available for the characterization of polymer brushes.SPM: scanning probe microscopy; SPR: surface plasmon resonance; TOF-SIMS: time-of-flight secondary ion mass spectroscopy; QCM(-D): quartz crystal microbalance (with dissipation monitoring); XPS: X-ray photoelectron spectroscopy; XRR: X-ray reflectivity; TGA: thermogravimetric analysis; NR: neutron reflectivity; GPC: gel permeation chromatography; NEXAFS: near edge X-ray absorption fine structure analysis.

Conclusions:-

In this review, we presented the polymer brushes synthesis by control radical polymerization method. In particular, we explain the advantages of the ATRP and RAFT initiated polymerization. This could more useful information for the investigator to understand for the preparation of polymer brushes.

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