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Review

Recent advances in ATRP methods in relation to the synthesis of copolymer coating materials

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ABSTRACT

Atom transfer radical polymerization (ATRP) is currently one of the most often used synthetic polymerization methods to prepare well-defined copolymers with complex architecture. This review covers some fundamentals of ATRP, presents new ATRP initiating processes with ppm amounts of copper catalysts and various reducing agents together with recent developed electrochemically controlled ATRP, as well as discusses ATRP enables to precise control over macromolecular structure, order, and functionality. Moreover, this review briefly describes some of the copolymer coating materials that can now be prepared e.g., protective coatings with increased hydrophobicity, functional bioactive surfaces and functional biomaterials, as well as highlights some of the commercialization efforts currently underway. The research activities in the last decade indicate that ATRP has become an essential tool for the design and synthesis of advanced, noble and novel copolymer coatings.

Contents

1. Introduction

Recent needs in a range of protective coatings permanently connected with natural materials such as wood and paper or with ceramics and metal articles force the search for new polymeric materials. However raw material limited possibilities and environmental issues are directing the attention of researchers for improving polymerization methods of the well-known and widely applied such as vinyl monomers, as well as raw materials useful for producing condensation polymers and additive polymers e.g. PU. In recent years, these needs have been additionally enhanced by the need to develop new synthetic biomaterials well cooperating with the tissues of the human body. In our opinion, new polymerization methods discovered in recent years allow for the production of polymers with controlled macromolecular structure and they are outgoing opposite these very specific applications of polymer coatings. In addition less important is to use the new monomers, and much more important is obtaining during the polymerization step of even known vinyl monomers and acrylic new structures of such macromolecules. Latest methods in this regard, already well developed from the side of preparative and theoretical explaining kinetics and mechanism of their progress, but still poorly used in

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Notations

AA	acrylic acid
AFM	atomic force microscopy
AGET	activators generated by electron transfer
ARGET	activators regenerated by electron transfer
ATRP	atom transfer radical polymerization
BIBB	2-bromoisobutyryl bromide
Bpy	2,2′-bipyridine
CM	cellulose membranes
CMU	Carnegie Mellon University
CRP	controlled radical polymerization
CuBr	copper (I) bromide
CuBr$_2$	copper (II) bromide
CuCl	copper (I) chloride
CuCl$_2$	copper (II) chloride
DI	dispersity
DMAEMA	2-dimethylaminoethyl methacrylate
DMMSA	2-(methacryloyloxyethyl) ethyl-dimethyl-(3-sulfopropyl)-ammonium
DMVSA	*N*,*N*-dimethyl-*N*-(*p*-vinylbenyl)-*N*-(3-sulfopropyl) ammonium
DP	degree of polymerization
eATRP	electrochemically mediated ATRP
EBIB	ethyl 2-bromoisobutyrate
EGDMA	ethylene glycol dimethacrylate
GMA	glycidyl methacrylate
HEMA	2-hydroxyethyl methacrylate
ICAR	initiation for continuous activators regeneration
LCST	lower critical solution temperature
LRP	living radical polymerization
MDI	4,4″-methylene diphenyl diisocyanate
ME	2-mercaptoethanol
Me$_6$-TREN	hexamethylated tris(2-aminoethyl)amine
MIP	molecularly imprinted polymer
MPC	2-methacryloyloxyethyl phosphorylcholine
MUBIB	ω-mercaptoundecyl bromoisobutyrate
MW	molecular weight
MWD	molecular weight distribution
NI	normal initiation
NIP	nonimprinted polymer
NIPAM	*N*-isopropylacrylamide
OEG	oligo(ethylene glycol)
OEGMA	oligo(ethylene glycol) methacrylate
PBA	poly(*n*-butylacrylate)
PDA	poly(dopamine)
PDMS	poly(dimethylsiloxane)
PEG	poly(ethylene glycol)
PMDETA	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethlyenetriamine
PMMA	poly(methyl methacrylate)
PES	polyethersulfone
PPCPA	poly(pentachlorophenyl acrylate)
PPPGMA	poly(poly(propylene glycol methacrylate))
PS	polystyrene
PSf	polysulfone
PTMO	poly(oxytetramethylene) glycol
PTX	paclitaxel
PU	polyurethane
PVDF	poly(vinylidene fluoride)
PVP	poly(*N*-vinylpyrrolidone)
RA	reducing agent
SAM	self-assembled monolayer
SEM	scanning electron microscope
SET-LRP	single-electron transfer living radical polymerization
SI-ATRP	surface-initiated ATRP
SR	reverse initiation
SR&NI	simultaneous reverse and normal initiation
SS	stainless steel
TEA	triethylamine
QA	quaternary ammonium
VBA	vinylbenzoic acid

materials engineering are methods known under the general name of atom transfer radical polymerization (ATRP). Therefore in the presented publication we would like to draw attention to the latest developments in this field and to indicate the directions of applications of polymers with a very specific structure, not known before a few years in the engineering of protective coatings.

This article reviews recent advances in the preparation of copolymer coating materials using ATRP for biomedical and other applications. The modification of polymer surfaces, hydrophobic in most of the cases, is required for multiple applications. For instance, low surface energy polymeric materials do not adhere well to other materials and need of further modification/surface treatment to improve adhesion.

ATRP is one of the most powerful and versatile CRP processes used for the synthesis of functional copolymers with well-defined architectures, controlled molecular weights, and tunable sequences. It enables precise control over MW, MWD, and functionality [1–4]. Block copolymers are an interesting class of materials that possess different properties compared to those of each individual homopolymer segments they are composed of. As block length is playing a major role on the properties of the block copolymers, effective control of the block lengths is important and this can easily be achieved using different CRP methods [5]. Most of the desirable properties of narrow MWD block copolymers (synthesized by living polymerization or ATRP) originate from their ability to form well-defined nanostructures with different morphologies of tunable periodicity or size, and this provides the primary driving force for the intensive interest in field of coating applications over the polydisperse copolymers (random or alternative) synthesized by conventional radical polymerization. Narrow MWD block copolymers (controlled) are more useful for coating application rather than polydisperse random copolymers synthesized by conventional radical polymerization. It results from it, that in regular arrangements, in which arranging structures results from intermolecular interactions, exists a possibility of the simpler crystallization as a result of stronger intermolecular interactions.

Recent advances in the synthesis of block copolymers have focused on techniques that either enable the preparation of completely new materials or represent a substantial improvement with respect to the existing methods in terms of scalability, environmental friendliness, or scope. One observable trend is to design experimental setups which allow for the automated and optimized synthesis of polymers and block copolymers. Another ongoing topic involves attempts to reduce the environmental impact of existing polymer syntheses. In ATRP reactions, the metal catalyst (most often Cu, as well as Fe, Ru, Ni, etc.) loading could be decreased down to ppm levels through the use of a suitable additive for catalyst regeneration, for example in ARGET process [6,7].

2. The most important mechanisms of the growth of polymer chains used in ATRP methods

ATRP is one of the most rapidly developing areas of polymer science, allowing to obtain effective control over molecular weights, narrow molecular weight distributions, functionalities,

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