Engineering soft nanostructured functional materials via orthogonal chemistry

Daniel Gromadzki

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Abstract Nanostructured amphiphilic block copolymers, graft copolymers, polymeric thermally responsive molecular brushes and polymer stars are only few examples of macromolecular architectures accessible either via controlled/living radical polymerization (CLRP) techniques or the combination of CLRP mechanisms with efficient post-polymerization routes including click chemistry. Precise control over the composition, molecular weight and functionalities is a prerequisite for soft polymeric materials to self-organize into ordered morphologies. This contribution describes novel orthogonal chemical routes for the synthesis of macromolecular architectures and self-assembly of functional soft polymeric materials. Emerging potential applications of well-defined block and graft copolymers are outlined as well.

Keywords Polymerization · Self-assembly · Nanostructured functional polymers

1 Introduction

Soft nanostructured polymeric materials can be generated via bottom up and top down approaches relying either on direct chemical synthesis and molecular self-assembly into desired conformation and morphology or externally controlled routes for achieving self-assembly (e.g. nanolithography), respectively (Xia and Whitesides 1998). Currently more sophisticated polymeric materials including block copolymers, brushes, stars, tadpole-shaped or hyperbranched copolymers with unprecedented control of molecular and architectural parameters are readily accessible thanks to impressive breakthrough in development of synthetic methodologies, namely controlled/living radical polymerization-CLRP- (Braunecker and Matyjaszewski 2007) and click chemistry (Kolb et al. 2001).

Block copolymers are fascinating macromolecules exhibiting ability to self-organize into ordered morphologies at the nanoscale via the process of microphase separation (Ruzette and Leibler 2005). Figure 1 shows some of block copolymer architectures accessible by macromolecular engineering.

Spontaneous self-assembly of diblock copolymers leads to formation of long-range ordered mesophases typically body-centered arrays of spheres, cylinders, bicontinuous-double-diamond and lamellae with a size ranging from few to hundred nanometers, depending upon composition (Φ) as shown in Fig. 2. The phase behavior of block copolymers is governed by

D. Gromadzki (✉)
Fundamentals of Advanced Materials Group,
Faculty of Aerospace Engineering,
Delft University of Technology,
Kluyverweg 1, 2629 HS Delft, The Netherlands
e-mail: D.Gromadzki@tudelft.nl

Fig. 1 Example of block copolymer architectures accessible via CLRP

incompatibility of building segments given by the product of the Flory–Huggins interaction parameter (χ) and degree of polymerization (N). In addition, the self-organization of block copolymers is influenced by processing parameters (casting conditions, solvent, temperature etc.). More importantly, the intrinsic molecular parameters like sequence of monomeric units (random, gradient) and molecular weight distribution (polydispersity) have a profound effect on block copolymer self-assembly. The latter parameter is of particular importance because all block copolymers prepared by CLRP schemes exhibit a certain

molecular weight distribution due to the fact that termination events during the course of CLRP are not completely eliminated. On the other hand, polydispersity resulting from imperfections inherent to particular CLRP routes can be beneficial in designing self-assembled nanostructures (order-order phase transitions and size of microphase separated domains).

Therefore, better understanding of the kinetics of the CLRP processes will allow controlling self-assembly in block copolymers. Notwithstanding the fact that the effect of polydispersity on molecular disorder has been recognized long ago, it was until recently that the first experimental results from CLRP-block copolymers could emerge (Lynd et al. 2008).

2 Working principle

Synthesis of block and graft copolymers with defined architecture can be achieved from almost any radically polymerizable monomer under facile conditions of CLRP in bulk, solution and in dispersed media. In addition, nearly 50% of all commercial synthetic polymers are prepared using radical chemistry which makes CLRP attractive for industrial applications. Among various CLRP systems introduced in the past

Fig. 2 Phase diagram for diblock copolymers representing typical mesophases: face centered cubic (FCC), body centered cubic (BCC), hexagonal (HEX), bicontinuous gyroid (GYR) and lamellar (LAM) phase. Reprinted with permission from <http://www.physics.nyu.edu/pine/research/nanocopoly.html>

Fig. 3 Mechanism of atom transfer radical polymerization

nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible-addition fragmentation chain transfer polymerization (RAFT) are the most commonly used techniques (Braunecker and Matyjaszewski 2007). The key feature of all CLRP processes is based on establishment of a dynamic equilibrium between propagating radicals and various dormant species. For instance, in ATRP polymerization a copper (I) complex, $\text{CuX}/2\text{L}$ ($\text{X} = \text{Cl}$ or Br , and $\text{L} = 2,2'$ -bipyridine [bipy] or a 4,4'-disubstituted-2,2'-bipyridine) activates reversibly the dormant polymer chains via a halogen atom transfer reaction (Fig. 3). It is the dynamic equilibrium between growing radicals and dormant species which is responsible for controlled behavior of ATRP and a synthesis of well-defined macromolecules with a degree of polymerization set by the ratio of the concentrations of converted monomer $[\text{M}]$ to the introduced initiator $[\text{I}]_0$, ($DP = \Delta[\text{M}]/[\text{I}]_0$).

The discovery of CLRP techniques in the past decade has set tremendous impact on contemporary polymer science. Each technique has its advantages and limitations. For instance, until recently NMP was applicable mostly for the synthesis of styrene and styrene-like derivatives. ATRP and RAFT are able to polymerize wider range of monomers although direct polymerization of acidic monomers to afford well-

defined polyelectrolytes or block copolymers containing acidic segments is very difficult since most CLRP mediating agents are sensitive to acidic conditions. This can be circumvented by selective post-functionalization of one block of a copolymer prepared by living polymerization, for example, using efficient azide-nitrile click chemistry (Gromadzki et al. 2008a, b).

Very often synthesis of a desired architecture cannot be accomplished using a single mechanism but the combination of various CLRP mechanisms must be attempted. This is especially true for the preparation of comb-like copolymers. Figure 4 illustrates synthesis of comb-like copolymers with various grafting density via the “grafting from” process. The first step involves preparation of polymeric backbone (macroinitiator) by copolymerization of monomers at a given polymerization feed in order to adjust concentration of initiating sites (black dots) while the second step is actually the grafting process of a functional monomer building side chains. Since both syntheses of macroinitiator and side chains have been conducted under CLRP conditions, the resulting well-defined comb polymer is an excellent model system to gain insight into fundamental questions in soft matter in general and in polymer physics in particular, namely the correlation between molecular structure, conformation and macroscopic properties.

One of the main goals of the Marie Curie Research and Training Network *Self-Organization under Confinement* (MCRTN-SOCON) network was to shed light on the properties of comb-like copolymers in solution, bulk and at surfaces (Claesson et al. 2010). A range of diverse comb copolymers have been prepared either by conventional radical polymerization involving the macromonomer route or by using

Fig. 4 Synthesis of comb-like copolymers via controlled/living radical polymerization

various novel synthetic pathways, i.e. “grafting from” ATRP (Krivorotova et al. 2010a, b), “grafting through” RAFT (Krivorotova et al. 2010a, b), NMP combined with “grafting from” iniferter or “grafting onto” strategy Gromadzki et al. (2008a, b, 2010) and azide-alkyne click chemistry (Kulbokaite et al. 2009). Most of the polymers synthesized exhibit a high level of tunability because they are responsive to changes in temperature, pH, salt and humidity, electric field enabling tailoring of the properties or solution behavior to a desired range.

3 Application fields

Block and graft copolymers are of immense technological importance. Many commercial applications of block copolymers are already known, such as thermoplastic elastomers which can be used as adhesives, sealants, breathable cloths, gels and coatings etc. (Holden et al. 2004).

Photonic gels and high-density data storage media are another field of block copolymers application as active components of display or telecommunication devices for controlling and processing light (Kang et al. 2007). The position of a stop band has been adjusted either by changing the refractive index or the domain spacing of the crystal structure by addition of homopolymer or using external stimuli (swelling, salt, electric field). However, the microdomain spacing in ordered block copolymers nanostructure can be tuned simply by changing polydispersity (Lynd et al. 2008). This additional tool inherent to CLRP has not yet been addressed in the design of photonic gels and other soft materials but it is likely to attract attention of researchers in the near future.

Amphiphilic block copolymers composed of hydrophobic and hydrophilic segments are known to form micelles in aqueous milieu with hydrophobic core and hydrophilic shell as represented schematically in Fig. 5. Such assemblies with mesoscopic size range have witnessed much attention in pharmaceutical and biomedical field as carrier systems in targeted drug delivery (Kataoka et al. 1993). Size and surface properties of polymeric micelles are crucial in achieving high efficiency in drug delivery. Again, robust orthogonal chemical strategies will be central to development of novel colloidal drug delivery carriers (Iha et al. 2009). For instance, most

Fig. 5 Spherical multimolecular diblock copolymer micelle

of the polymers prepared by ATRP are terminated with halogen end-groups which after appropriate transformations can be used for conjugation of active molecules via click chemistry. This allows fine-tuning of the material properties both at molecular level and on the self-assembled nanostructure surface.

Branched polymers are an industrially relevant class of polymers and find numerous applications as compatibilizers, lubricants, viscosity and impact modifiers. Stimuli-responsive densely grafted brushes (macromolecular cylindrical brushes) synthesized within the SOCON network hold great promise for such diverse applications like biomedicine (smart drug delivery carrier), biotechnology (purification of proteins), electronic (as medium in lithium-ion battery) and last but not least in surface technology (lubrication and anti-fouling modifiers).

4 Training of young researchers

Dr. Daniel Gromadzki pursued his PhD in the field of macromolecular chemistry within the Institute of Macromolecular Chemistry of the Czech Academy of Sciences and Charles University in Prague, Czech Republic. His first Marie Curie Fellowship under Marie Curie Initial Research and Training Site at the Institute of Macromolecular Chemistry in Prague gave him the opportunity to engage into an interdisciplinary and international research team working both on synthesis and structural characterization of nanostructured block copolymers intended for application as membranes for fuel cells. Interaction with synthetic chemists and polymer physicists allowed him to acquire skills in design of macromolecular architectures by modern methods of polymerization and to work with unique techniques to characterize structural properties of polymers.

Table 1 Mobility of Marie Curie fellow Dr. Gromadzki

Year	Institute	Topics and skills acquired
2001	BASF AG, Ludwigshafen, Germany	Water-borne coatings, dispersions, foams
2001	Department of Environmental Engineering, Technical University of Szczecin, Poland	Catalysis
2002	Department of Colloid Chemistry, Max-Planck Institute of Colloids and Interfaces, Golm, Germany	Water-soluble polymers, polymer modification
2003	Department of Polymer Engineering, Faculty of Applied Natural Sciences, University of Bayreuth, Germany	Block copolymers, polymer blends
2004	Department of Technology of Elastomers and Chemical Fibres, Technical University of Szczecin, Poland	Polycondensation, hydrogels, biodegradable polyesters
2004–2010	Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic	Amphiphilic block copolymers, controlled radical polymerization, click chemistry
2005–2007	Department of Polymer Chemistry, Vilnius University, Vilnius, Lithuania	Controlled radical polymerization, click chemistry, comb copolymers, molecular brushes
2009	Polymeric GmbH, Berlin, Germany	Suspension polymerization, polymeric adsorbents, surface modification
2010	Fundamentals of Advanced Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, Delft, The Netherlands	High performance engineering plastics from green building blocks, fibres, self-healing polymers, macromolecular engineering

Upon receiving a second Marie Curie Fellowship within the MCRTN-SOCON, he moved to the Department of Polymer Chemistry at Vilnius University. This 6th European Framework Programme funded 13 teams in 9 countries within 4-year project, which was very productive and successful in terms of output and cooperation. For more information about MCRTN-SOCON the reader is referred to a special issue in *Adv Colloid Interface Sci* 155: 1–58, exclusively devoted to SOCON consortium. The aim of the MCRTN-SOCON was to understand the link between surface properties, bulk properties, films, and macroscopic colloidal systems. The particular focus was on mixed surfactant systems, surfactant–polymer systems, and on comb polymers (Stubenrauch 2010). The expertise of the Vilnius group focuses on the synthesis of novel polymers characterized by controlled composition and charge density including meth(acrylate) comb copolymers, molecular brushes and poly(ethylene glycol)-grafted chitosan. The research and educational program including goals and objectives, complementary skills and research management were set in a personal career development plan individually tailored for each Early Stage Researcher (ESR) or Experienced Researcher (ER) fellow of the SOCON network. The experience that Dr. Gromadzki gained during his

Marie Curie Fellowships and career mobility (Table 1) was extraordinarily helpful for his professional life as well as for his personal development. Marie Curie once said—“After all, science is essentially international, and it is only through lack of the historical sense that national qualities have been attributed to it”. Indeed, SOCON network was a prominent example of the international effort for advancement of science and cross-border collaboration.

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Weblinks

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