



ELSEVIER



Controlled architecture for improved macromolecular memory within polymer networks

Stephen A DiPasquale and Mark E Byrne

This brief review analyzes recent developments in the field of living/controlled polymerization and the potential of this technique for creating imprinted polymers with highly structured architecture with macromolecular memory. As a result, it is possible to engineer polymers at the molecular level with increased homogeneity relating to enhanced template binding and transport. Only recently has living/controlled polymerization been exploited to decrease heterogeneity and substantially improve the efficiency of the imprinting process for both highly and weakly crosslinked imprinted polymers. Living polymerization can be utilized to create imprinted networks that are vastly more efficient than similar polymers produced using conventional free radical polymerization, and these improvements increase the role that macromolecular memory can play in the design and engineering of new drug delivery and sensing platforms.

Address

Biomimetic & Biohybrid Materials, Biomedical Devices, & Drug Delivery Laboratories, Department of Biomedical Engineering, Rowan University, Glassboro, NJ 08028, USA

Corresponding author: Byrne, Mark E (byrnem@rowan.edu)

Current Opinion in Biotechnology 2016, 40:170–176

This review comes from a themed issue on **Tissue, cell and pathway engineering**

Edited by **April Kloxin** and **Kyongbum Lee**

<http://dx.doi.org/10.1016/j.copbio.2016.06.001>

0958-1669/© 2016 Elsevier Ltd. All rights reserved.

Introduction

Macromolecular memory within polymer networks is a new method for control of network architecture [1–3]. This technique has promise in the creation of nanostructured biomaterials for use as carriers in drug delivery and biosensing substrates via the creation of gels with controlled transport and binding properties. Macromolecular imprinting techniques introduce memory within the network architecture leading to increased affinity and capacity as well as decreased transport of a template molecule [3–7]. The technique is based on specific non-covalent interactions between the template molecule and one or more monomers to form template–monomer complexes as the polymer network is forming. Molecular imprinting

has traditionally been associated with highly crosslinked polymer networks due to the decreased flexibility of the polymer chains. The lower flexibility aided the creation of template affinity due to the retention of the shape specificity of the polymer chain functionality forming the template complexation site [8,9]. However, recently it has been shown to work effectively even in weakly crosslinked networks with flexible polymer chains [10,11]. The key in weakly crosslinked polymers is to strengthen the interaction of the template with the polymer chains by using complementary chemistry within an appropriately sized flexible architecture rather than relying on rigidity. Thus, imprinting in weakly crosslinked networks is favored by heteropolymer systems with multiple monomer–template interactions. While the use of heteropolymers to induce stronger template complexation is beneficial for better memory creation, it leads to heterogeneity in the polymer network.

Conventional free radical polymerization (FRP) processes have been the predominant reaction used in this field. Only recently have other formation strategies such as living/controlled polymerization been used for more control over network structures and a better understanding of structure–property relationships. The one drawback to conventional free radical polymerization is the lack of control over chain propagation and termination due to the very high reactivity of the radical species. This results in the formation of polymer networks with heterogeneous structures with imperfections like primary and secondary cycles; and pendant, unreacted double bonds [12,13]. Living polymerization can be exploited to decrease heterogeneity and substantially improve the efficiency of the imprinting process for both highly and weakly crosslinked imprinted polymers [14]. Our group has been leaders in this area and this paper briefly describes the benefits of using living/controlled polymerization (LRP) in the development of imprinted polymers. Understanding the role living/controlled polymerization plays in the creation of imprinted crosslinked polymer networks is a new direction in the field.

Structural evolution of networks

Structural evolution of polymer networks created using traditional free radical polymerization has been studied [12,13,15,16] and the mismatch between rapid chain growth and slow chain relaxation of the forming polymer has been understood to result in structural heterogeneity and high degree of randomness. As the polymerization occurs and the conversion increases, the bimolecular

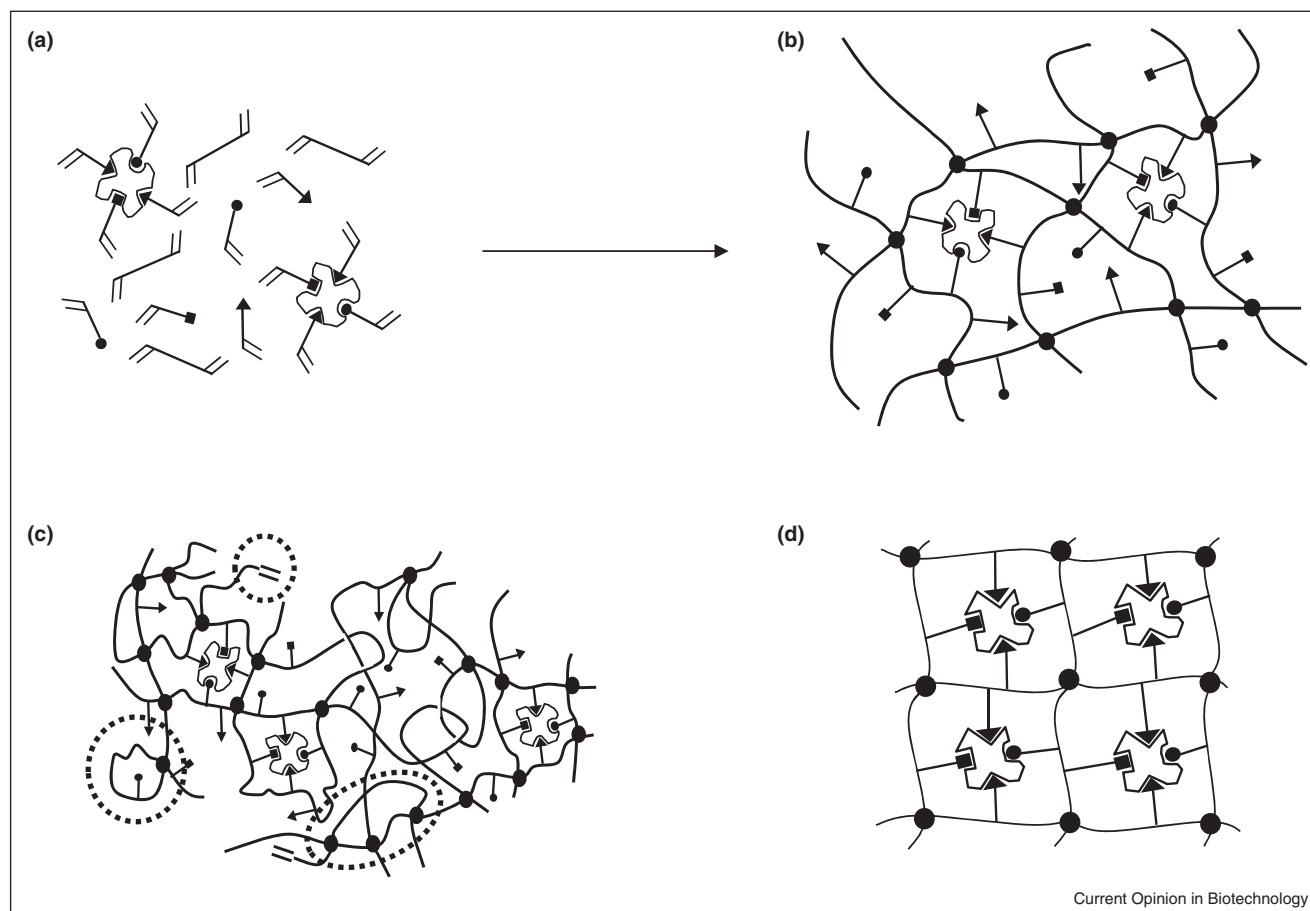
termination reaction between two polymer chains becomes difficult because of diffusional limitations introduced by the difference in rates described above. This results in an auto-acceleration of the reaction (Trommsdorff effect), during which an overabundance of carbon radicals results in explosive chain growth and the formation of localized heterogeneous regions that exhibit a high degree of crosslinking. Comparatively, living/controlled polymerization is a much slower reaction, making it thermodynamically favorable for the formation of a more homogeneous polymer network. Figure 1 provides a graphical analysis of the homogeneity that can be achieved when an imprinted polymer is produced using living/controlled radical polymerization compared to traditional free radical polymerization. LRP replaces the bimolecular termination between polymer chains with a macroradical-iniferter termination reaction which prevents or delays auto-acceleration. It is still not completely

clear how living/controlled reactions affect the creation of crosslinked polymer networks, however, recent work has attempted to understand this phenomenon [17–20]. Much of the current knowledge of LRP comes from kinetic analysis of polymerization reactions of non-crosslinked polymer chains that exhibit less polydispersity and a much narrower polymer chain length distribution than polymers synthesized using conventional FRP [16].

Using living/controlled polymerization to control imprinted network structure architecture

The use of living/controlled polymerization in order to create block copolymers as well as graft polymer chains and brushes onto existing polymer networks has been the primary focus of past work involving LRP [21–25]. This includes grafting of films to dormant polymer layers. However, the use of LRP to create imprinted networks

Figure 1



Macromolecular memory in crosslinked polymers. **(a)** Complexes formed between functional monomer and template within the pre-polymer formulation. Triangles, squares, and circles represent functionality that exists on functional monomers that non-covalently interact with corresponding sites on the template molecule. **(b)** Formation of a polymer network via free radical polymerization imprinted with macromolecular memory sites that bind the template molecule. **(c)** An imperfect imprinted network synthesized using conventional radical polymerization. Dashed circles highlight the highly heterogeneous nature of polymers created using conventional radical polymerization. **(d)** A polymer network with a high degree of homogeneity produced using living/controlled radical polymerization.

Download English Version:

<https://daneshyari.com/en/article/6487490>

Download Persian Version:

<https://daneshyari.com/article/6487490>

[Daneshyari.com](https://daneshyari.com)