Trends in polymer science

Stratification, stimuli-responsiveness, self-healing, and signaling in polymer networks

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ABSTRACT

The design, development, and manufacturing of new materials continue to be an ongoing challenge for scientists and engineers. Because of similarities to biological systems having self-repairable properties, polymer networks are of particular importance and interest, and if designed properly, may provide an unprecedented opportunity for mimicking biological systems. This can be accomplished through the formation of nanostructured stimuli-responsive networks that individually or collectively respond to internal or external stimuli. This article outlines selected recent developments and future trends that will formulate foundation for the development of stratified heterogeneous stimuli-responsive polymer networks capable of reorganizing, self-healing, or signaling. The primary focus is on the physico-chemical attributes of multi-component polymer networks with localized glass transition temperatures capable of stratification and exhibiting stimuli-responsiveness or recognition attributes.

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1. Introduction

While the variation of nature responses to external and internal stimuli involves complex remodeling phenomena of reversible or irreversible processes, one common feature of biological systems is the formation of multi-layered directionally stratified structures that are often compartmentalized. Interactions via signaling and responsiveness within or outside these compartmentalized structures make biological systems unique with an extraordinary ability of healing wounds autonomously. For example, plants heal mechanical damages using suberin, tannins, or other phenols, which are activated to prevent further lesions [1,2], whereas lipids play a vital role in signaling, where membrane trafficking and biogenesis are controlled. These chemicals signal the wound formation by increasing the concentration levels of a given species in the damaged area and facilitate leakage and delivery of healing materials [1,3].

Along the same lines, nitric oxide (NO) acts as an essential regulatory molecule by signaling cascades of events that share plant hormones and send chemical messengers during damage formation [4–6]. In certain mammalian systems nitric oxide is also found to send an electrical impulse to trigger and activate phospholipid signaling to polarize the cell migration [5]. Although chemically different, the repairing of mechanical damage of a human skin is initiated by the outer flow of blood cells which are demobilized by the crosslinking of fibrin, thus leading to self-repairing [7]. Re-epithelialisation of human skin initiated by the lateral migration of stationary keratinocytes to the damaged area and the platelets of inflammatory cells signal the wound as soon as they are in contact with the exposed collagen, and trigger the platelets to release a healing substance to the wound [8]. While these few of many examples illustrate the complexity of chemical reactions involved in biological self-repair processes, a common feature and requirement for self-healing is the formation of stratified structures, localized heterogeneity, and stimuli-responsiveness of molecular entities.

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2. Stratification and heterogeneity

Due to similarities with biological systems the formation of stratified polymer networks has been of significant interest [9], whereby numerous research activities showed the importance of stratification on materials' properties, particularly in polymeric coatings. For example, when methyl methacrylate (MMA), n-butyl acrylate (n-BA), and heptadeca-fluorodecylmethacrylate (FMA) monomers were copolymerized in an aqueous phase in the presence of bio-active dispersing agents such as phospholipids (PLs), non-spherical particle morphologies were obtained [10]. These particles upon coalescence stratify to form unique film morphologies where the pFMA phase stratifies near the film–air (F–A) interface lowering static and kinetic coefficients of friction, whereas p(MMA/nBA) component resides near the substrate, allowing particle coalescence and enhanced adhesion. There are other examples where PLs resulted in the formation of hollow spherical particles [11] or tubules [12].

Other essential features to achieve self-healing characteristics include localized heterogeneities as well as stimuli-responsiveness of the network components. While the majority of polymer studies focus on solution stimuli-responsive properties, the main challenge is the development of mechanically stable solids. In order for macromolecular segments to respond to external or internal stimuli it is necessary to provide adequate spatial conditions which are relatively easily attainable in solutions, where Brownian motion of solvent molecules requires relatively low energy for macromolecular segments to be displaced by solvent molecules. In contrast, in a solid phase, the challenge is to design a polymer network that upon stimuli, is capable of rearranging macromolecular segments while maintaining solid state properties. In order to design self-healing polymeric systems the major shift from a thermodynamic equilibrium free energy minimum approach to kinetic regimes of higher order organizational states is needed with facile transitions between two or more local metastable free energy minima of different structural features in energetically favorable positions. Fig. 1 schematically illustrates three cases of energy minima: (A) an equilibrium state with the minimum which, in order to "go" to another equilibrium state, requires a significant amount of energy; (B) two equivalent energy states which require substantially smaller amounts of energy, thus allowing oscillations between states 1 and 2, but the stability of the entire network is in jeopardy, and (C) a combination between (A) and (B). When the system is at the lowest energy state equilibrium (A), it will not exhibit stimuli-responsive characteristics, but retain its stability. In contrast, when two or more energy minima exist, such as shown in Fig. 1B, a relatively small amount of energy is required to transition from one state to another ($1 \rightarrow 2$ or $2 \rightarrow 1$), and such a system is expected to exhibit reversible stimuli-responsive characteristics. The presence of a combination of the three minima at different levels is illustrated in Fig. 1C, and the energy difference between ΔE_{eq} and ΔE_{sr} will determine the amount of energy required for stimuli-responsiveness. Self-assembled molecules called rotaxanes [13,14] are an example of molecular switches oscillating between the two states, thus creating an opportunity for the development of molecular-based computers, if placed into a network allowing these oscillations with a minimum energy that provides mechanical network integrity.

The presence of oscillating low energy minima at larger length scales may be accomplished by providing adequate spatial arrangements necessary for a system to undergo transition from one state to another, and rearrange in response to internal or external stimuli. For polymeric materials with local micro- and nano-level variations of glass transition temperatures (T_g), more free volume will be available in the areas of the lower T_g regions, thus providing energetically and spatially favorable conditions for rearrangements. In the design of such systems, controllable levels of organizations are achieved for creating conditions allowing an orchestrated heterogeneous network formation. For that reason one needs to manipulate structural features across a few lengths scales and recognize the fact that chemical entities within the space and concentration gradients will control localized free volume changes, and thus the localized T_g. There are documented indicators of this phenomenon. For example, bulk poly(methyl methacrylate) (PMMA) exhibits the T_g at 393 K, but a 25-nm-thick layer at the free surface of a 1000-nm-thick PMMA films show T_g values reduced by 5–6 K. For the same 25-nm-thick layer at the substrate of a 1000-nm-thick film the increase of T_g by 12 K was observed [15]. However, the T_g of a 25-nm-thick layer located 100 nm from either the film–substrate or the film–air interfaces in an 800-nm-thick multi-layer film is identical to the T_g bulk PMMA. Thus, spatial perturbations of the T_g values may occur over nano- or subnano-length scales, and although interfacial effects may alter glassy-state structural relaxation rates in the interfacial regions, heterogeneities at these scale lengths or even smaller are essential for creating compart-
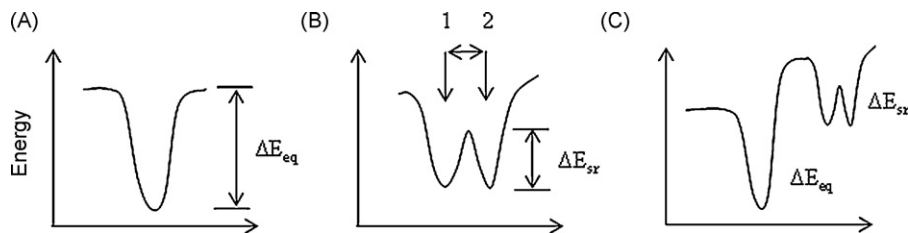

Fig. 1. Energetic states of a polymer system in equilibrium: (A) one stable energy minimum ΔE_{eq} of a functional system (significant energy would be required to "go" to another state); (B) two equal energy wells will require the same amount of energy $\Delta E_{sr} = E_1 - E_2$ to jump from state 1 to state 2; (C) combination of a stable equilibrium state (A) and two metastable states (B), where $\Delta E_{eq} > \Delta E_{sr}$.