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Scattering perspectives on nanostructural inhomogeneity in polymer network gels

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ABSTRACT

Scattering methods based on spatial and temporal contrast fluctuations in polymer-network gels, which originate from polymer-segmental density fluctuations, reveal rich insight into different types and levels of nanostructural inhomogeneity in these soft materials. Complementary contrasting as provided by light, neutron, and X-ray scattering allows such information to be obtained on nano- to micrometer length scales. On top of that, complementary use of static and dynamic scattering methods allows the interplay and effect of these inhomogeneities to be unraveled. This article interrelates a multitude of studies on the application of scattering techniques for analytical assessment of structural inhomogeneity in polymer-network gels conducted since the 1970s.

Contents

1. Introduction

Polymer-network gels consist of three-dimensionally crosslinked chain molecules swollen with a solvent [1]. They can be formed by different methods, most typically based on uncontrolled chain-growth polymerization abetted by in-situ crosslinking, as shown in Fig. 1a, or on better controlled random or regular interconnection of pre-polymerized building blocks, as shown in Fig. 1b and c. Depending on the conditions during these different ways of formation, and depending on the conditions during the subsequent state of observation, polymer-network gels exhibit diverse and complex nanoscopic architectures [2,3]. Commonly, the polymer-network mesh topology on scales of 1–10 nm is not uniform and regular, as idealized in Fig. 1c, but polydisperse and irregular, as sketched in Fig. 1b. On top of that, many swollen polymer networks display a further level of spatial inhomogeneity on scales of 10–100 nm and beyond, as sketched in Fig. 1a. This structural complexity markedly affects the optical clarity, mechanical strength, and permeability of polymer gels, which is of central relevance for their performance in popular applications such as those as superabsorbers [4], soft contact lenses [5,6], carriers of bioactive agents [7,8], and matrixes in the analytical sciences [9–13]. As a result, polymer-network inhomogeneity has been a vibrant field of research since the 1970s [14]. This article reviews a core part of this extensive research, with a focus on the analytical assessment of structural inhomogeneity in polymer-network gels by scattering techniques. Such work experienced increasing popularity since its first remarkable notion four decades ago and then climaxed in the early 2000s, as

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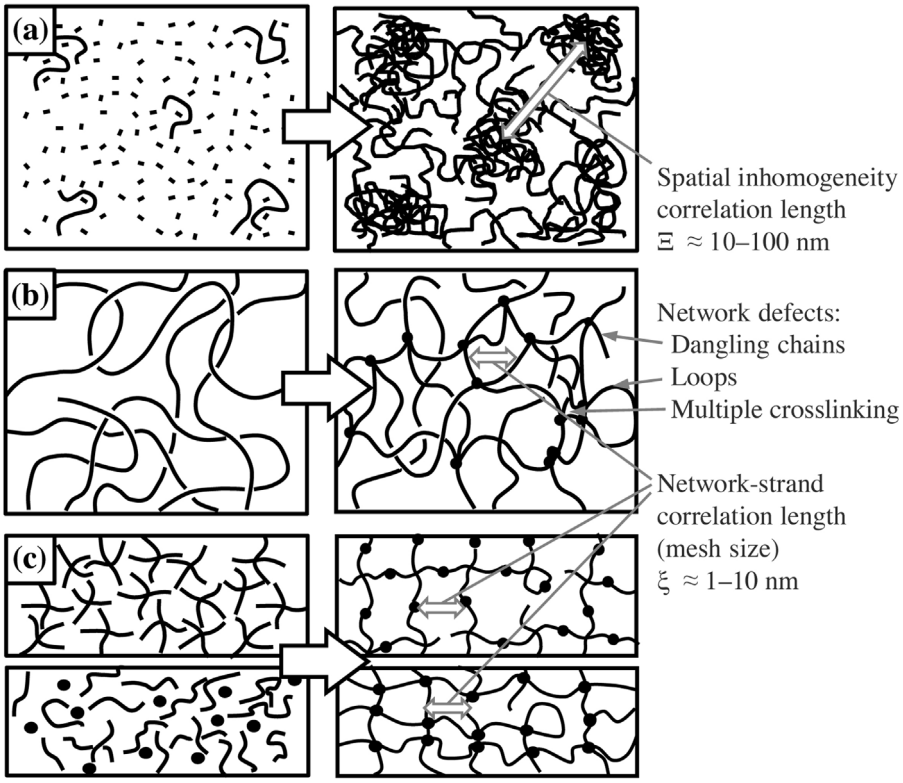

Fig. 1. Polymer-network architectures as obtained by three different approaches of gelation, each illustrated in one of the figure panels. (a) Formation of an irregular and spatially inhomogeneous polymer-network gel by uncontrolled chain-growth crosslinking copolymerization of monomers and crosslinkers, thereby causing static spatial variation of the polymer-segmental and crosslinking density on scales of 10–100 nm. (b) Formation of a just locally inhomogeneous polymer-network gel by random crosslinking of side-functionalized chains in a semidilute solution, thereby forming polydisperse network meshes on scales of 1–10 nm but no additional spatial inhomogeneity on larger scales as those illustrated in panel a. (c) Formation of a potentially regular and homogeneous polymer-network gel by cross-coupling of complementarily functionalized star-polymer building blocks (upper half-panel) or end-linking of suitably capped chains to functional linkers (lower half-panel). [2,3], Copyright 2014 and 2015. Adopted with permission from Wiley-VCH.

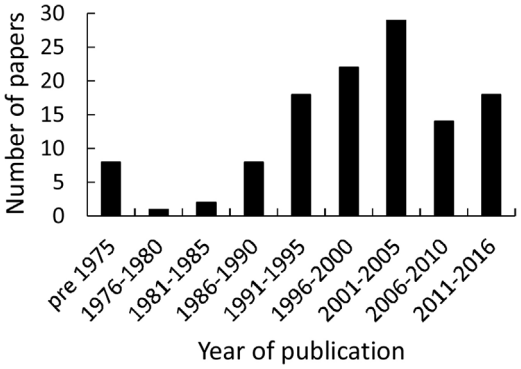

Fig. 2. Publication record of the original research papers reviewed in this article (excluding references to other review articles or books).

visualized in Fig. 2, when research on polymer networks and gels attracted remarkable fundamental interest. In the following half decade, the publication activity first decreased, but since about 2010, there is re-growing interest, as also seen in Fig. 2. This is due to two developments. First, the field has witnessed seminal breakthroughs in the attempt of preparing defect-free model-type polymer networks based on controlled polymerization and on click chemistry; these model networks both serve as a material basis to (re-)address a plethora of fundamental polymer-physical questions, and as a class of highly tough and resilient gels. Second, in quite a contrast to these model-network gels, there is increasing interest in multi-scale hierarchical structural complexity in soft matter, including inhomogeneous and porous gels, which have promise to serve as membranes in energy conversion devices and in laboratory analytics. This article aims to bridge these early insight-oriented and recent application-oriented developments in view of consistently and comprehensively cross-relating the existing picture of polymer-network structural inhomogeneity as gained by scattering methods.

2. Norms and nomenclature

Polymer-network inhomogeneity in a gel manifests itself in various forms spanning multiple length scales, as indicated in Fig. 1. To account for this diversity, several schemes of classification have been introduced.

Norisuye, Shibayama, and co-authors differentiated between two types of inhomogeneities in polymer-network gels. One is imparted during the gelation process by the “freezing-in” of thermal concentration fluctuations at the gelpoint, which are particularly strong if the gelling system is close to its phase-boundary spinodal line [15–17]. The static polymer-network inhomogeneity resulting from this process has been referred to as “frozen concentration fluctuation” [15,17–23], “frozen blobs” [24], “frozen inhomogeneity” [16,25], and “frozen elastic constraints” [26], and it is a central motif in a closely related theory on gel polymer-network structures introduced by Panyukov and Rabin [27–30]. On top of these frozen concentration fluctuations, a further type of inhomogeneity manifests itself in the form of a non-random irregular distribution of the crosslinking junctions in a gel, as sketched in Fig. 1a, which was detected in light-scattering studies by Norisuye, Shibayama, and co-workers [17].