



# Spinodal nanostructures in polymer blends: On the validity of the Cahn-Hilliard length scale prediction<sup>☆</sup>

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## ABSTRACT

Spinodal decomposition of partially miscible polymer blends has the potential to generate well-defined polymeric nanostructured materials, with precise control of length scale and connectivity, and applications ranging from membranes and scaffolds to photovoltaics. In this review, we briefly summarize the theoretical basis for describing spinodal decomposition in binary polymer blends, and the parameters that determine the accessible demixing length scales and the timescales over which they develop. We then examine experimentally the validity of the classical Cahn-Hilliard (CH) theory prediction for the initial spinodal length scale,  $\Lambda \equiv 2\pi/\sqrt{-G''/(4k)}$  where  $G''$  is the second derivative of the free energy of mixing with respect to composition, and  $k$  is the 'square gradient' parameter, accounting for changes in free energy arising from concentration gradients. Benefitting from the perspective of over 40 years of neutron and light scattering data, and noting (remaining) misconceptions in the literature when analyzing phase separation, we examine a large collection of  $\Lambda$  measurements, and independent  $-G''(T)$  and  $k$  experimental estimates. Overall, we find the CH prediction for  $\Lambda$  to be remarkably accurate for all blends and self-consistent conditions examined. We then summarize design considerations for generating polymeric materials via spinodal decomposition, bound by thermodynamics of available polymer systems, coarsening kinetics governed by rheology, as well as by engineering constraints. The fulfillment of the potential of this approach in the development of real functional materials demands, however, improved thermodynamic theories for polymer blends, able to quantitatively predict  $G''(T)$  and  $k$  in terms of molecular structure and interactions.

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## Contents

1. Introduction	2
1.1. Bicontinuous polymeric materials	2
1.2. Introducing the characteristic spinodal length scale $\Lambda$	3
2. Thermodynamics of polymer mixtures	4
2.1. Mixing free energy and phase diagrams	4
2.2. Flory-Huggins theory for binary polymer blends	5
2.3. Scattering experiments to determine $G''$ and $\chi$	5
3. Spinodal decomposition in polymer blends	6
3.1. Main results from Cahn-Hilliard theory	6
3.2. Thermal fluctuations and the Cahn-Hilliard-Cook development	6
3.3. The concentration gradient parameter $k$	7
3.4. The mobility term $M$	8
3.5. Intermediate and late stages of phase separation	9

<sup>☆</sup> Dedicated to the memory of John W. Cahn (1928–2016).

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3.6.	Cahn-Hilliard self-consistency checks.....	9
3.7.	Demixing in off-critical mixtures.....	11
4.	Comparison with self-consistent experimental data.....	11
4.1.	Data required for comparison with predictions for the spinodal length scale $\Lambda$ .....	11
4.2.	The need for contrast and common artefacts.....	12
4.3.	Experimental observation of early stage spinodal decomposition.....	13
4.4.	How well do $G''$ and $k$ data predict spinodal phase sizes $\Lambda$ ?.....	15
4.5.	Comparison between $\Lambda$ and $R_g$ .....	16
5.	Practical limits for controlled spinodal decomposition of real polymer mixtures.....	16
5.1.	Range of $G''$ and $\chi$ values for partially miscible blends.....	16
5.2.	Further theoretical expressions for the free energy of mixing in polymer blends.....	19
5.3.	Practical approaches for achieving and controlling deep quenches.....	19
6.	Summary and outlook.....	19
	Acknowledgments.....	20
	References.....	20

## 1. Introduction

### 1.1. Bicontinuous polymeric materials

Polymeric materials with bicontinuous structures are desirable for a range of practical applications, which derive their function and performance from large interfacial areas and phase connectivity. For example, in the recent application area of organic photovoltaic cells, the electron donor and acceptor phases in a bulk heterojunction (BHJ) design must demix at a scale commensurate with the exciton diffusion length (approximately 10 nm) and interpenetrate to provide continuous pathways for charge transport. Fig. 1(a–c) depicts conjugated polymer:fullerene nanostructures readily achieved by spontaneous phase separation following solvent evaporation, yielding phase sizes of the order of 20 nm [1–3], recently reviewed by Kramer and co-workers [4]. The solvent (or mixture of solvents) evaporation and film formation pathways [3], as well as polymer and/or fullerene crystallization, often occurring upon further thermal annealing [2], are all known to play a key role in this highly non-equilibrium process. All-polymer active layers [5,6], where both donor and acceptor are polymeric, are also increasingly common in organic solar cells. Polymeric membranes for various separation processes have similar requirements for a bicontinuous morphology with a well-defined length scale, and are generally fabricated via a solvent-mediated demixing, and phase inversion approach, resulting in significant spatial gradients (depicted in Fig. 1d [7]) intrinsic to this directional solidification process [8,9]. Russell [10] and co-workers have investigated the solvent induced phase separation of immiscible polymer pair (polystyrene and poly(styrene-*r*-2-vinyl pyridine)), with a modest degree of immiscibility. Upon spin coating from toluene, and rapid quenching, films with bicontinuous structures and characteristic sizes as small as approximately 80 nm were obtained. As noted by the authors “such a size is unusual for macrophase separated polymer blends”, approaching those of block copolymer templates. The self-assembly of block-copolymers in the melt [11], as well as the formation of polymer microemulsions [12], by combining immiscible homopolymers and a diblock copolymer ‘compatibilizer’ can also yield bicontinuous structures at equilibrium conditions, although requiring precise synthesis and assembly over a narrow interaction and composition parameter space. Reactive blending, for instance the synthesis of random graft copolymer chains by mixing polymers with complementary reactive groups at high temperature [13], also results in bicontinuous structures at the nanoscale, albeit necessitating functionalized precursors. Another reactive blending approach relies on the polymerization or crosslinking of a monomer within a polymeric mixture, such that phase separation ensues upon increasing molecular mass, and

kinetic arrest takes place due to vitrification or network formation. Examples are provided in Fig. 1f for a thermally-driven [14] and in Fig. 1g for a light-driven [15,16] spinodal decomposition process, although at larger length scales than previously discussed. Evidently, a range of equilibrium (e.g., block-copolymer assembly) and non-equilibrium (e.g., solvent-induced demixing) approaches can be employed to achieve bicontinuous morphologies

One route to two-phase structures that has long been discussed in the literature, but is not included in the examples shown in Fig. 1, is the thermally induced spinodal decomposition of a partially miscible polymer mixture. In this process, demixing takes place as a blend is quenched within the unstable region of its phase diagram, yielding an initial bicontinuous structure with a well-defined length scale  $\Lambda$  that subsequently coarsens over time, driven by a reduction of interfacial area and thus free energy. For practical applications, this unstable state is then kinetically arrested by chemical or physical means, for instance by cooling the mixture below its glass transition temperature  $T_g$ . At least conceptually, this approach is potentially the simplest and most versatile route to generating bicontinuous polymer structures of sub-micron length scales.

In the last four decades or so, many detailed experimental observations of phase separation via spinodal decomposition in polymer blends have been reported and compared to various theoretical descriptions of demixing and coarsening. In particular, the Cahn-Hilliard [18] (and Cahn-Hilliard-Cook [19]) theory provides remarkably simple predictions for the initial demixing length scale, the growth kinetics of concentration fluctuations, and the time window for which this linear approximation to the diffusion equation is expected to hold. Perhaps surprisingly, a number of questions remain about how well the theory describes data and, importantly, guides the design and fabrication of nanostructured materials. We refer the interested reader to a number of excellent reviews discussing the theoretical approaches to describing spinodal decomposition, for instance by Binder [20], Hashimoto [21], Han and Akcasu [22]. Despite the extensive literature on both experimental and theoretical aspects of spinodal decomposition there are still widespread misconceptions, evident in recent literature, about the spatial and temporal scale of the process, and the controlling material parameters. In short, two sets of blend data are required for the design of spinodal structures: (i) the thermodynamics of mixing which provides the driving force for phase separation and (ii) the rheology or mobility of the blend which, alongside the former, governs the rate of response. After a brief overview in the next section, these concepts are detailed in Sections 2 and 3 to follow.

In this review, we seek to examine the *intersection* of theory and experiment from a pragmatic perspective. Our aims are as follows:

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