A Thorny Problem? Spinodal Decomposition in Polymer Blends

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Research into mixtures of polymers developed rapidly in the 20th century, soon after Staudinger's seminal paper on the long chain nature of the molecules. Interest was driven both by intellectual curiosity about whether, why, and how such very large molecules could mix and by prospects for new and useful materials, in analogy to metallic alloys and glasses. By 1968, when the first issue of *Macromolecules* appeared, there was already a considerable literature covering polymer thermodynamics and miscibility (e.g., Flory−Huggins lattice theory dates from the early 1940s), the occurrence of upper and lower critical solution phase behavior, the means of modifying mixture behavior, and detecting phase boundaries. The early issues of *Macromolecules* reflect this interest in polymer blends and mixtures from both a theoretical and a practical viewpoint, and what is striking is that the leading contributions to the literature at this time were from scientists employed by the large chemical companies which manufactured predominantly bulk polymers. The blend literature of this period includes many explorations of potential polymer pairs for study. Emerging as a "model" blend, polystyrene (PS) is partially miscible with poly(vinyl methyl ether) (PVME) exhibiting a lower critical solution temperature (LCST) behavior when solvent cast from (some) common solvents. Amorphous and commonly available PS and PVME demix at accessible temperatures (above both glass transition temperatures T_g but below the ceiling temperatures), and their properties such as refractive indices and T_gs are far enough apart to report on demixing experiments such as light scattering or calorimetry. Despite its unpromising material properties, PS/PVME rapidly became the "fruit fly" of polymer blends.[1−3]

In 1975, Nishi, Wang, and Kwei,[1] working at Bell Laboratories, published their much-cited paper with the first experimental study of spinodal decomposition and nucleation and growth in a polymer blend using NMR and light transmission, examining data against the three defining characteristics of spinodal decomposition: first, a "continuous but rapid growth of sinusoidal composition modulation of a certain wavelength", Λ; second, that "the diffusion coefficient must be [effectively] negative" (i.e., requiring *uphill* diffusion); and, third, a "uniform yet random and interconnected" morphology (a nonsufficient condition). The "spinodal decomposition" process was further confirmed by pulsed NMR data obtained from a blend isothermally annealed inside the unstable region for phase separation (recognized today as the spinodal region) where a continuous change in composition of the new phase occurred while its volume remained constant. One year prior to the foundation of *Macromolecules*, John W. Cahn had delivered the 1967 Institute
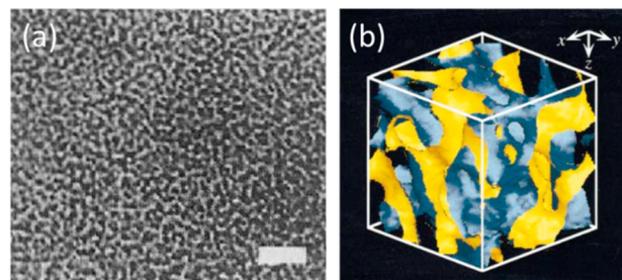
Figure 1. (a) Optical microscopy image of a demixed PS/PVME blend, of near-critical composition quenched into the unstable region (105 °C) after 300 s, reported by Nishi et al.;[1] the scale bar indicates 10 μm. Reproduced with permission from ref 1. (b) 3D image obtained by stacking of laser scanning confocal microscopy (LSCM) scans of a late-stage spinodal structure of a polybutadiene/poly(styrene-*ran*-butadiene), after Jinnai et al.;[7] the box size is 30 × 30 × 30 μm³. Reproduced with permission from ref 7. Copyright 1997 American Physical Society.

of Metals Lecture "Spinodal Decomposition",[4] providing a masterful account of the previous decade of theoretical breakthroughs by Cahn and Hilliard[5,6] and others. By contrast with metal alloys and glasses, polymers avoided the added complexity of elastic strains and offered much slower demixing time scales compared to simple liquids, which could effectively be tuned by molecular weight. Nishi et al. immediately appreciated the significance of the *uphill* diffusion proposed by Cahn−Hilliard, whereby the diffusional flux takes place *against* a concentration gradient. They succinctly explain that this can be accounted for "by including in the diffusion equation higher order terms which reflect the thermodynamic contributions of gradient energy terms". Cahn had described the evolution of local mixture concentration ϕ following a sudden jump into the unstable (or spinodal) region by

$$\partial\phi/\partial t = MG''\nabla^2\phi - 2Mk\nabla^4\phi + \text{nonlinear terms} \quad (1)$$

where M is a diffusional mobility and k captures the additional free energy penalty due to concentration gradients. Within the spinodal, the second derivative of the free energy of mixing ΔG_m with respect to composition $G'' \equiv \partial^2\Delta G_m/\partial\phi^2$ is

negative, and thus the effective diffusion constant $D \equiv MG''$ is also negative.

The origins of the term "spinodal" take us to 19th century thermodynamics in The Netherlands[11] and the van der Waals equation of state of a "real gas" (Figure 2a). While the free
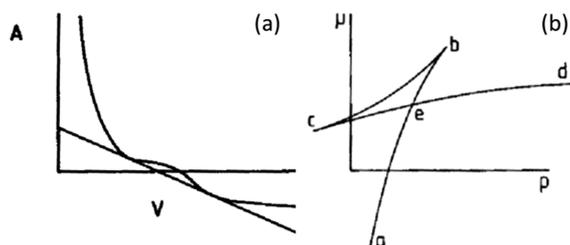
Figure 2. (a) Isothermal Helmholtz energy A as a function of volume, showing the double-tangent defining the metastable region (corresponding to the coexisting vapor and liquid phases in van der Waals "real gas" equation of state) and the two inflection points. (b) Chemical potential μ showing two cusps, b and c, as a function of pressure p. This word "spinodal" derives from the latin *spina*, for thorn or prickle, as well as backbone. Adapted with permission from ref 11. Copyright 2002 Royal Netherlands Academy of Arts and Sciences.

energy varies smoothly with composition, the chemical potential changes abruptly at the inflection points, doubling back on itself, leading to the structure schematically shown in Figure 2b. This structure was likened to a thorn or prickle, for which the Latin name is *spina*—hence spinodal. Interestingly, van der Waals was the inaugural professor of physics at the newly formed University of Amsterdam. His counterpart in chemistry was van't Hoff, on whose osmotic law Staudinger based his own viscosity law.[12]

There was no immediate follow-up to Nishi et al.[1] in the experimental literature, but theoreticians, notably de Gennes,[8] Pincus,[9] and Binder,[10] developed mean-field theoretical descriptions of spinodal decomposition in polymer blends, taking into account the connectivity of macromolecules and Flory–Huggins thermodynamics as well as thermal noise effects. In 1983, two experimental papers[2,3] appeared in the same issue of *Macromolecules*, investigating phase separation, mainly spinodal decomposition, in fruit-fly PS/PVME using light scattering. Binder refers to a proof copy of ref 2 in his seminal paper.[10] Snyder et al.,[2] using both angular dependent and forward light scattering, measured the growth rate of the concentration fluctuations during phase separation, obtaining the apparent diffusion coefficient, D_{app}, from which the spinodal boundary could be determined. They demonstrated that the Cahn–Hilliard linearized theory quantitatively applied to the early stages of spinodal decomposition in polymer blends. The characteristic centrosymmetric spinodal scattering pattern is shown in Figure 3a. (On a personal note, one of us met Hal Snyder and Paul Meakin at conferences in the mid-1980s and was kindly given a stunning spinodal decomposition video, which has made its way from Betamax, VHS, and CD to the present and is still "in use"; while optical microscopy cannot capture the early stages of demixing, the video clearly identifies ripening processes of evaporation–condensation, Brownian coalescence, and "tubular necking".)

In the same volume of *Macromolecules*, submitted one month apart, Hashimoto et al.[3] also investigated the spinodal decomposition of PS/PVME by light scattering, highlighting that "the scattering technique is *obviously* much more powerful [than NMR] in that one can obtain the relaxation rate $R(q)$ for
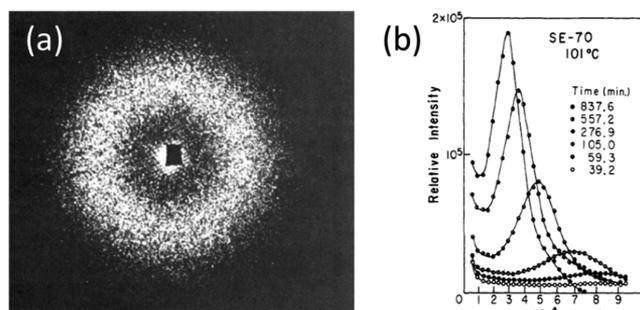
Figure 3. (a) Light scattering pattern of a demixed PS/PVME blend, reported by Snyder et al.[2] Reproduced with permission from ref 2. (b) Evolution of the (radially averaged) scattering intensity with time following the spinodal decomposition of a near-critical PS/PVME quenched ≈2 °C inside the unstable region, reported by Hashimoto et al.[3] The initial dominant length scale of the structure $\Lambda = 2\pi/q^*$, where q^* is the peak position, falls generally outside the window observed in light scattering (typically ≳300–600 nm). Reproduced with permission from ref 3.

each Fourier component q of the spatial composition fluctuations". For instance, measurement of the fastest growth rate $R(q^*) = MG''^2/8k$ readily quantifies the thermodynamic driving "force" G''. The authors fully appreciated the brevity of the "early stage" of spinodal decomposition and estimated the corresponding time scale to be $\tau \approx 4k/MG''^2$ from deviations from simple exponential growth of the amplitude of composition fluctuations. This narrow time window provided key guidance to ensure self-consistency of the experimental analyses that others have followed—or sometimes not!

A key Cahn–Hilliard prediction is a simple relationship between the initial size of the spinodal structure Λ, corresponding to the wavelength of fastest growing fluctuation, and the thermodynamics of the blend, G'':

$$\Lambda \approx \frac{2\pi}{q^*} = \frac{2\pi}{\sqrt{-G''/4k}} \tag{2}$$

It had been suggested by theory[10] that Λ in phase separating polymer blends could reach of order of "molecular dimensions". This scale was too small for light scattering experiments, as noted by Hashimoto et al.[3] and illustrated in Figure 3b. The increase in light scattering intensity is accompanied by a shift of the scattering peak toward lower q values, indicative of coarsening of the demixed compositional pattern. In 1985, the first small-angle X-ray and neutron scattering (SAXS/SANS) experiments on spinodal decomposition in a polymer mixture were reported,[13] employing solution chlorinated polyethylene and deuterated poly(methyl methacrylate) and finding $\Lambda \approx 30$–70 nm depending on quench depth, considerably below the light scattering range. While both techniques are well suited to the wavelength of concentration fluctuations, on both sides of the phase boundaries, SANS also requires access to reactor or spallation neutron sources and the deuteration of one of the component; scattering contrast is generally limited in SAXS. There is a rather limited number of partially miscible polymer pairs with a thermally accessible spinodal curve and where one of the components is available in a deuterated form. As a result, to date, comprehensive SAXS/SANS data remain relatively scarce.

In order to test the prediction of eq 2 across distinct systems, values of the relevant G'' and k are required. In the early 1970s,

de Gennes introduced the random phase approximation (RPA)[14] to interpret SANS (and SAXS) data from polymer blends in the one-phase region, allowing parameters such as the chain dimensions and interaction strength (the Flory χ parameter, or equivalent G'') to be readily estimated. Warner et al.[15] and Shibayama et al.[16] used this approach on a number of respectively low and high molecular weight blends. The SANS forward scattered intensity, $S(q{\to}0)$, directly yields G'', and k can be computed from experimental data via the RPA. In principle, therefore, all parameters needed to test eq 2 were available experimentally by SANS. However, while G'' is positive and readily measurable in the one-phase region, it becomes negative in the unstable region, and therefore the structure factor $S(q)$ becomes a "virtual" construct. The question then arose as to whether G'' from the one-phase region can be extrapolated through the spinodal temperature (where G'' vanishes). Since the mean-field approximation breaks down in the vicinity of the spinodal, the validity of such extrapolation was not obvious, until Schwahn et al.[17] showed that this temperature range was relatively narrow (a few degrees, for a typical dPS/PVME system). Higgins et al.[18] and Schwahn et al.[19] then compared experimentally measured G'' values in the one-phase region, using the RPA, with G'' values obtained in the two-phase region from a Cahn−Hilliard analysis of spinodal kinetics, finding a reasonable correlation with temperature *across* the spinodal line.

While isotopic polymer blends, i.e., mixtures of otherwise identical hydrogenous and deuterated polymers, could have been expected to form "ideal" mixtures, at high enough molecular weights (where the entropy of mixing becomes almost negligible) tiny differences between the species becomes sufficient to drive phase separation upon cooling, through an upper critical solution temperature (UCST). Bates and co-workers (e.g., ref 20) reported experimental observations of spinodal decomposition for isotopic blends using light scattering (enabled by a small, but sufficient, refractive index contrast and large sample volumes), yielding minute values of G'' and thus a large initial Λ, ranging up to 800 nm.

After a slow start in the 1980s, the polymer literature contains a steady flow of publications (about 60−150 per year) focusing on spinodal decomposition in polymer blends, with many directed to applications in multiphase materials (such as membranes, photovoltaics, etc.), although some reporting theoretical and simulation developments. The field has been expertly reviewed by Hashimoto[21] and Akcasu and Han.[22] Recently, we assembled all data[23] (Figure 4) we could find in the literature reporting both G'' and Λ and satisfying the self-consistency requirements of the early stages of decomposition, building upon the criteria described above.[1−3] While details of the spinodal process still leave theoretical questions to be answered (e.g., strict mean field validity or the effect of hydrodynamics), overall eq 2 is remarkably robust.

Ever since the publication in *Macromolecules* by Nishi et al.[1] some 45 years ago, polymer scientists have been fascinated by the concept of uphill diffusion and the potential for functional, new materials with bicontinuous phases obtained from homogeneous blends (and solutions). There remain thorny questions for spinodal decomposition, including dynamic and compositional asymmetries; the impact of chain architecture and topology as well as supramolecular assembly; demixing in the vicinity of stability lines; the nonlinearity of the overall demixing process and loss of connectivity; the effect of external fields such as flow; and the coupling with numerous
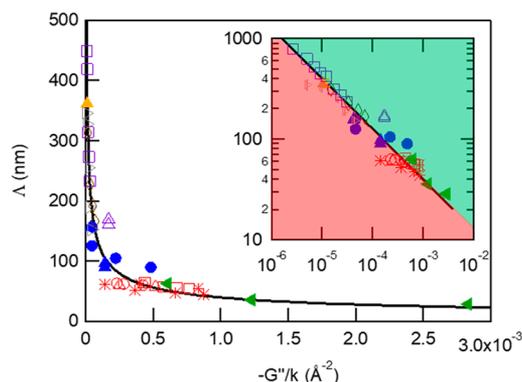
Figure 4. Compilation of the experimental data of the initial spinodal length scale Λ [nm] of multiple polymer blends, plotted following eq 2, shown as a solid line. The open and closed symbols correspond to data extracted from UCST and LCST blends, respectively (detailed in ref 23 and updated here (red ∗) with PαMSAN/dPMMA of varying tacticity[24]).

manufacturing processes such as thin film casting and membrane formation. A full treatment of fluctuation effects or the influence of hydrodynamics on the dynamics of phase separation is yet to come, and emerging theoretical concepts and experimental methods remain to be explored. However, the three featured papers[1−3] in this editorial lay sound foundations for the nano- and microscale design of new polymer materials based on the fundamental knowledge of molecular and thermodynamic properties of polymeric constituents. Spinodal decomposition and its thorny questions have given the polymer community plenty to explore, and still do. Citing one of the many epigrams of the French novelist Alphonse Karr, "we can complain because rose bushes have thorns, or rejoice because thorns have roses."

    Julia S. Higgins
    João T. Cabral ◉ orcid.org/0000-0002-2590-225X

■ AUTHOR INFORMATION

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.macromol.0c00581

Notes
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