멤브레인(Membrane Journal)
Vol.7, No.2, July, 1997, 49-56

총 설

고분자 용액에서의 Coarsening 현상

송 승 원

(주)유공 대덕기술원
(1997년 5월 30일 접수)

Coarsening Phenomena in Polymer-Solvent Systems—A Review

Seung-Won Song

Taedok Institute of Technology, Yukong Limited 140-1, Wonchon-Dong, Yusung-Gu, Taejon 305-370, Korea
(*Received May 30, 1997*)

Abstract: In order to understand the formation of polymeric membranes or microcellular foams, phase separation phenomena in polymer solutions should be understood. The present review examines the progress made in the understanding of these phenomena, with emphasis on selected polymer-solvent systems. In the case of polymer-solvent systems, coarsening is of particular importance as it may come to dominate or overshadow spinodal decomposition effects within the first minute or few minutes of phase separation. In this article, some of the most important theoretical models of late stage of phase separation are reviewed, and recent experimental studies on coarsening in polymer-solvent systems are studied.

1. Introduction

Phase separation phenomena in polymer-solvent systems can be brought about by variations in temperature, pressure, and composition of the polymer solutions. Phase separation in polymer-solvent systems can be classified into two major categories: solid-liquid phase separation and liquid-liquid phase separation [1]. Solid-liquid phase separation results from vitrification or crystallization of one or all of the chemically different equilibrium liquid phases, and liquid-liquid phase separation results from the thermodynamic instability of a polymer-solvent system. While the mechanism of solid-liquid phase separation is generally the classic one of nucleation and growth, the mechanism of liquid-liquid phase separation depends on the state of the thermodynamic stability of the system. In one region, nucleation and growth predominates; in another, spinodal decomposition is the phase separation mechanism.

Liquid-liquid phase separation in polymer solutions has been used for many years in the preparation of microporous materials. The characteristic morphology of the phase-separating polymer solutions resulting from a nucleation and growth mechanism is either a poorly interconnected, stringy, beady structure which is mechanically fragile or a well interconnected structure with highly nonuniform pore sizes. The nucleation and growth mechanism occurs in the metastable region. In contrast, spinodal decomposition occurring in the unstable region results in a well interconnected, mechanically strong struc-

ture with highly uniform pore sizes[2-5].

2. Liquid-Liquid Phase Separation

The thermodynamic criteria for solubility in a two component polymer-solvent system can be expressed in terms of the Gibbs free energy of mixing, $\triangle G_m$, and its second derivative with respect to polymer volume fraction, ϕ, at a fixed temperature T and pressure P [6, 7]:

$$\triangle G_m < 0 \quad (1)$$

$$\left(\frac{\partial^2 \triangle G_m}{\partial \phi^2}\right)_{T,P} > 0 \quad (2)$$

If either criterion is not met, the solution may separate into two phases in equilibrium. As shown in Fig. 1, when the locus of minima, for which the chemical potentials of each component are equal in both phases, is plotted in the form of a temperature-composition phase diagram, the resulting curve is referred to as the binodal. The limit of metastability, where $\partial^2 \triangle G_m / \partial \phi^2 = 0$, is called the spinodal. Inside the spinodal, separation takes place by a continuous and spontaneous procedure occurring by a diffusional flux against a concentration gradient (uphill diffusion, i.e., the second derivative of Gibbs free energy of mixing, $\partial^2 \triangle G_m / \partial \phi^2$, is negative).

In the unstable region, any small fluctuations in composition will lower the free energy and continue to grow. This procedure is called spinodal decomposition[8]. In the metastable region(the second derivative of Gibbs free energy of mixing is greater than zero) small fluctuations tend to decay, and hence phase separation can only proceed by overcoming a barrier with a large composition fluctuation. The process requiring an increase in the free energy to form initial fragments(nuclei) is referred to as nucleation. After a nucleus reaches a critical size, the system decomposes from the homogeneous region into the heterogeneous region with a decrease in free energy, and the nuclei grow in extent without changing composition, which is termed growth. This phase separation mechanism is called nucleation and growth [9].

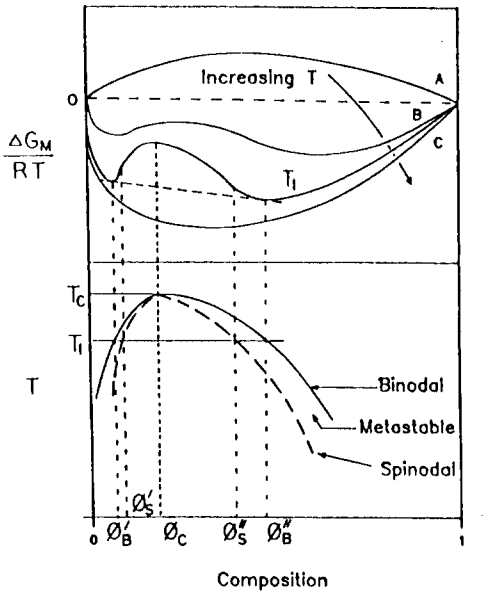

Fig. 1. Gibbs free energy of mixing as a function of polymer volume fraction showing partial miscibility. Note minima ϕ_B' and ϕ_B'' of common tangent, inflection points ϕ_S' and ϕ_S', critical point ϕ_c', and influence of temperature for a system possessing an upper critical solution temperature (UCST).

3. Late Stage of Spinodal Decomposition

The microstructure of the two-phase system will continue to evolve even after the early stage development of structure, in response to its tendency to reduce the surface energy associated with interfacial area. This process, called coarsening, often results in a reduction in the number of droplets and an increase in their size[10-13]. The coarsening process is of both fundamental and practical interest in materials science and has been the subject of significant theoretical and experimental studies.

3. 1. Coarsening Mechanisms

Three different mechanisms have been described as being responsible for coarsening in the late stag-

es of phase separation: Ostwald ripening, coalescence, and the hydrodynamic flow mechanism. In the first, Ostwald ripening, the total energy of the two-phase system composed of a dispersed second phase in a matrix can be decreased *via* an increase in the size of the second phase and thus a decrease in total interfacial area. Coarsening occurs by the gradual dissolution of the smaller droplets and gradual growth of the larger droplets by diffusion of the dispersed phase through the matrix phase. Such a process is called Ostwald ripening, after the physical chemist W. Ostwald, who first described the process. In the coalescence mechanism, coarsening occurs by two or more droplets impinging on each other by translational diffusion and forming a single droplet. The third mechanism of coarsening is the hydrodynamic flow mechanism. According to Siggia [12], in the cylindrical part of the bicontinuous structure, the gradient of pressure along an axis of the cylinder causes a flow of inner fluid from a narrow to a wide region, which results in coarsening of domains. As the basis of the hydrodynamic flow mechanism is an interfacial instability, phases of different size, and therefore different radii of curvature, have different pressures, which in turn cause flow[14].

3.2. Dynamics of Coarsening

Siggia[12], who considered theoretically a general two-component system undergoing phase separation, took into account both diffusive coalescence/Ostwald ripening and hydrodynamic flow effects in order to explain the accelerated growth rate beyond the initial stage. He also indicated that the coarsening rate will accelerate further at a second crossover determined by the acceleration due to gravity and the density difference of the two coexisting phases. He estimated that the domain growth proceeds in three stages:

(i) intermediate stage (including coalescence)

$$d \sim \left(\frac{k_B T}{\eta}\right)^{\frac{1}{3}} t^{\frac{1}{3}} \quad \xi \ll d \leq \left(\frac{k_B T}{\sigma}\right)^{\frac{1}{2}} \tag{3}$$

(ii) flow stage

$$d \sim \left(\frac{\sigma}{\eta}\right) t \quad \left(\frac{k_B T}{\sigma}\right)^{\frac{1}{2}} \leq d \leq \left(\frac{\sigma}{g \triangle p}\right)^{\frac{1}{2}} \tag{4}$$

(iii) gravity-dominated stage

$$d \geq \left(\frac{\sigma}{g \triangle \rho}\right)^{\frac{1}{2}} \tag{5}$$

where g is the gravitational constant and $\triangle \rho$ is the density difference between the two phases. After the flow stage, the coarsening rate accelerates further due to gravity and the density difference of the two coexisting phases; in this last stage, coarsening does not follow a power law, and macroscopic layering is achieved.

Binder and coworkers[15, 16] suggested a dynamic scaling law for the late-stage of spinodal decomposition, and Furukawa[17-21] formulated an asymptotic scaling function indicating that there is only one length scale in the phase separating system, and physical quantities depend on time only through this length scale. The scaling law is a more general form of coarsening theory, and the asymptotic behavior of the characteristic length is depicted by

$$d \propto t^{a} \tag{6}$$

with the exponent "a" depending on the microscopic mechanism of particle growth.

The crossover behavior in the coarsening process was first observed in the systems of critically quenched low molecular weight fluid mixtures[22-25]. Later, Hashimoto and coworkers[26, 27] and Bates and Wiltzius[28] indicated for the polymer blends that "a" depends on time t over a broad time scale, with a crossover between coarsening processes which is consistent with the idea put forth by Siggia[12].

It has been noted that the entire process of spinodal decomposition can be divided into three stages, namely, early, intermediate, and late stages

[26, 27]. In the early stage, the behavior was found to be approximated by Cahn-Hilliard theory, and the growth in amplitude of dominant concentration fluctuations takes place without change in wave number or size. In the intermediate stage, both the amplitude and size of the concentration fluctuation increase but do not reach the equilibrium values. In the late stage, the amplitude of the fluctuation reaches its equilibrium value, and the fluctuation grows in size. Fig. 2 shows the spatial concentration fluctuation of one component at three different stage of unmixing. Later, Bates and Wiltzius[28] divided the late stage into the transition stage and the final stage for their four-stage model. As the composition fluctuation amplitude approaches the equilibrium values, the spinodal decomposition process enters the transition stage, characterized by a decreasing interfacial thickness ($\triangle(t)$ in Fig. 2) and an increasing length scale (wavelength). Once the interfacial profile is equilibrated, a crossover to the final stage occurs. In the final stage of spinodal decomposition, the wavelength is expected to increase while maintaining a self-similar two-phase morphology.

Time-resolved scattering techniques have been used to determine the coarsening dynamics. The time evolution of the concentration fluctuations in the unmixing process can be scaled with a single length parameter, $\xi(t)$ [26], and this correlation length, which corresponds to the wavelength $\lambda(t)$ of the periodic structure, can be determined from the scattering vector $q_m(t)$ giving rise to maximum scattering intensity:

$$\xi(t) = \lambda(t)/2\pi = 1/q_m(t) \tag{7}$$

The magnitude of the scattering wave vector q is defined as

$$q = (4\pi/\lambda_0)\sin(\theta/2) \tag{8}$$

where λ_0 and θ are, respectively, the wavelength of x-ray, neutron, or light in the medium and the scattering angle in the medium. The time evolution of the characteristic length of the structure is expected to follow a power law so that the maximum intensity of scattering profile, I_m, and the magnitude of the scattering vector, q_m, obey scaling laws:

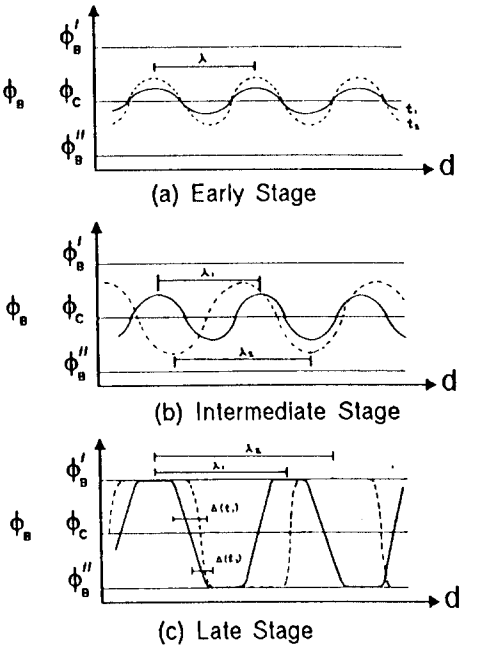

Fig. 2. Schematic representation of spatial concentration fluctuation of one component in the critical mixture at three different stages of spinodal decomposition: (a) early stage; (b) intermediate stage; (c) late stage. In each diagram, the dashed curves represent the composition profile at a later time (t_2) than that given by the solid curves (t_1). ϕ_B' and ϕ_B'' correspond to the equilibrium composition in each phase.

$$q_m(t) \sim t^{\alpha} \tag{9}$$

$$I_m(t) \sim t^{\beta} \tag{10}$$

It should be noted that the exponents α and β themselves appear to be time dependent, reflecting the crossovers among various coarsening mechanisms [27]. As wave number is inversely related to interdomain separation and thus cell size, the exponent from time-resolved light scattering should be

equal in magnitude but opposite in sign to those obtained for growth in cell size.

There have been numerous experimental studies and significant advances in our understanding of the late stage of spinodal decomposition. Many experimental investigations in the field of fluid mixtures, metallic alloys, inorganic glasses, polymer-polymer mixtures and polymer solutions have been analyzed with the concept of spinodal decomposition [21, 29-32]. Snyder and Meakin [33] suggested that when time and length are properly scaled, superposition of experimental phase separation data from metallic alloys, inorganic glasses, small molecule systems, and polymer blends may be obtained, indicating that the general form of phase separation dynamics is insensitive to the molecular details of the system. (Note that, more recently, several studies[28, 34] have indicated that polymer systems may have a non-universal scaling behavior in the intermediate stage, i.e., a strong dependence of phase separation dynamics on the quench depth was observed.)

Chou and Goldburg[24] defined a reduced time τ as follows:

$$\tau = t/t_c \tag{11}$$

where t_c is the characteristic time of the system defined as

$$t_c = \xi^2/D \tag{12}$$

A reduced wave number $Q_m(\tau)$ is defined by Hashimoto et al. [27] as

$$Q_m(\tau) = q_m(\tau)/q_m(\tau = 0) \tag{13}$$

In several experimental studies, when the reduced wave number Q_m is plotted against the reduced time τ, one observes that the data for several different quench temperatures fall on a universal curve, thus indicating that the domain growth law is independent of the quench depth[33, 35]. However, Bates and Wiltzius[28] suggested a quench depth dependent growth law from their experiments on isotopic polymer blends. They found a trend with temperature which is not anticipated by the universal scaling theory in the intermediate stage. This behavior was described by Bates and Wiltzius as being "inexplicable" from the simple scaling laws, and they suggested that further theoretical and experimental studies were required. (Note that Brown and Chakrabarti[34] have since then investigated the nature of the quench depth dependence of the power law exponent.) The number of spinodal decomposition and coarsening studies involving polymer-polymer mixtures has increased dramatically since the mid-1970s, while, surprisingly, relatively few studies of the coarsening process in polymer solution systems have been reported. In the case of polymer-solvent systems, coarsening is of particular importance as it may come to dominate or overshadow spinodal decomposition effects within the first minute or few minutes of phase separation.

4. Experimental Studies in Polymer-Solvent Systems

In 1982, Nojima et al. reported on coarsening of polystyrene (PS)-diisodecyl phthalate solutions ($M_w = 1.1 \times 10^5$) by *in situ* microscopic observation[36]. They observed droplets of one phase dispersed in a matrix of a second phase, with the average droplet diameter growing with time according to a power law with an exponent of 0.30 ($\pm$0.09) for the time frame less than 1000min. Although they could not distinguish between the Ostwald ripening and coalescence mechanisms, they suggested that the coarsening process was the result of coalescence. The possibility of crossover effects suggested by Siggia[12] was not discussed in this study and were not observed.

In the following year, Kuwahara and coworkers reported on coarsening in an isodensity system consisting of poly(dimethyl siloxane) and diethyl carbonate($M_w = 8.0 \times 10^4$) [37]. Using light scattering, they observed a coarsening stage after the early stage of spinodal decomposition in which the domain size grew in time with an exponent of 0.4 for

the time scale less than 10 min. They concluded that the scaling laws can be applied to a polymer solution in which two components greatly differ in molecular size. More recently, Kuwahara and Kubota [38] studied exactly the same system using a time-resolved light scattering technique and observed a 1/3 power law dependence of the reduced wave vector up to coarsening time scales of 10 min, but the flow stage of coarsening was not studied.

Krishnamurthy and Bansil [39] investigated coarsening in PS-cyclohexane solutions($M_w = 3.0 \times 10^5$) undergoing phase separation which they indicated was initiated by nucleation and growth rather than spinodal decomposition. Although they ignored the strong effects of gravitational sedimentation in their dilute polymer solutions(4 and 10% (w/v) of 3.0×10^5 M_w), they concluded from photographic observation that the decrease in number density of polymer-rich droplets over a rather long time period (up to 130 min) could be attributed to the coalescence of polymer-rich droplets. The Ostwald ripening and hydrodynamic flow mechanisms were not considered in their study. Later Lal and Bansil, studying the same PS-cyclohexane systems (1% (w/v) for 2.8×10^6 M_w and 7% (w/v) for 2.3×10^5 M_w) using time-resolved small angle light scattering, found a growth rate exponent between 0.4 and 0.5 and suggested that hydrodynamic flow effects are important in the coarsening of their dilute polymer solutions. However, they ignored the gravitational layering effect which was observed by Aubert [14] even in the very early stage of phase separation (less than 3 min).

In contrast to the studies made by observation in the solution state, coarsening in polymer solutions may also be characterized through the properties of microporous membranes made from phase separated polymer solutions. Tsai and Torkelson[3, 4] qualitatively investigated coarsening effects for the poly(methyl methacrylate)-sulfolane system and less viscous poly(methyl methacrylate)-tert butyl alcohol system($M_w = 9.3 \times 10^4$). They reported that a lacy structure, which is a characteristic morphology for membranes produced by thermally induced phase separation *via* spinodal decomposition, could also develop over substantial coarsening times for nucleation and growth initiated phase separation. They suggested that flow properties could play a vital role during the later stage of phase separation. They also found via mercury intrusion porosimetry measurements that for the poly(methyl methacrylate)-sulfolane system the coarsening time dependence of the average pore size followed a power law with an exponent of approximately 1/3 during the first 100 min of phase separation at 13℃ below the cloud point temperature[40].

In a more extensive study, Aubert[14] investigated coarsening in the PS-cyclohexane system($M_w = 2.2 \times 10^6$) using scanning electron microscopy and BET(Brunauer, Emmett, and Teller) surface area measurements. He showed that the growth rate of pore size follows a power law in time with an exponent in the range 0.18~0.31 and that the structures remained highly interconnected throughout the coarsening experiments. In contrast to other studies which investigated solution coarsening by *in situ* techniques and indicated that coarsening occurred by coalescence and/or the hydrodynamic flow mechanism, Aubert concluded that the Ostwald ripening mechanism was consistent with his observations. He also argued that the reason for not observing the hydrodynamic flow mechanism is because the high viscosity in the polymer-rich phase may make the hydrodynamic flow process very slow, while the diffusion process which occurs in the dilute phase associated with Ostwald ripening is relatively fast. However, due to the very rapid effects of gravitational sedimentation, the non-isodensity/low-viscosity PS-cyclohexane system may not be an appropriate choice for basic investigations of the coarsening process in polymer-solvent systems.

The evolution of coarsening in polymer solutions from a mechanism with growth rate kinetics consistent with Ostwald ripening or coalescence to one consistent with hydrodynamic flow was confirmed experimentally by Song and Torkelson[5, 32]. The

phase separation of *isopycnic/low-viscosity* polystyrene-diethyl malonate solutions and *non-isopycnic/high-viscosity* polystyrene-cyclohexanol solutions was studied by investigating the microstructure of polymer membranes made from them. At relatively short coarsening times, the coarsening rate of the cell size can be expressed as a power-law in time with the exponent increasing with increasing quench depth; for deep quenches, the growth rate has an exponent of 1/3 in agreement with the classic theories for coarsening by Ostwald ripening or coalescence. At longer coarsening times, there was a crossover to a much faster growth rate yielding an exponent of 1.0 independent of phase separation temperature, consistent with the hydrodynamic flow mechanism of coarsening. This crossover effect has been believed to be a universal phenomenon in three-dimensional coarsening of phase-separating systems and has been previously observed in low molecular weight fluid mixtures, inorganic glasses, metallic alloys, and polymer blend systems.

5. Conclusion

Even though polymeric membranes have been the subject of extensive research in various fields including chemical engineering and polymer science, most work has been related to the separation and permeation characteristics of membranes. Since membrane transport properties correlate directly with their morphology and the microstructure is strongly influenced by the different preparation variables, the ability to analyze quantitatively the conditions controlling the structure formation is of great practical importance. Recently, many studies have added significantly to our understanding of membrane formation by using thermally induced phase separation process in which membrane is formed via the removal of thermal energy rather than by the slower exchange of nonsolvent for solvent, and membrane formation is now well received as the elaborate technology, not the art.

References

1. O. Olabisi, L. M. Robeson, and M. T. Shaw, "Polymer-Polymer Miscibility", Academic Press, NY, NY (1979).
2. R. M. Hikmet, S. Callister, and A. Keller, Polymer, **29**, 1378 (1988).
3. F.-J. Tsai and J. M. Torkelson, Macromolecules, **23**, 775 (1990).
4. F.-J. Tsai and J. M. Torkelson, Macromolecules, **23**, 4983 (1990).
5. S.-W. Song and J. M. Torkelson, J. of Membrane Sci., **98**, 209 (1995).
6. M. Kurata, "Thermodynamics of Polymer Solution", Trans. H. Fujita, Harwood Academic Publishers, Chur, Switzerland (1982).
7. K. Kamide, "Thermodynamics of Polymer Solutions: Phase Equilibria and Critical Phenomena", Elsevier, Amsterdam, The Netherlands (1990).
8. J. W. Cahn, Trans. AIME, **242**, 166 (1968).
9. K. Kamide, H. Iijima, and S. Matsuda, Polymer J., **25**, 1113 (1993).
10. I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids, **19**, 35 (1961).
11. C. Wagner, Z. Elektrochem., **65**, 581 (1961).
12. E. D. Siggia, Phys. Rev. A, **20**, 595 (1979).
13. P. W. Voorhees, Annu. Rev. Mater. Sci., **22**, 197 (1992).
14. J. H. Aubert, Macromolecules, **23**, 1446 (1990).
15. K. Binder and D. Stauffer, Phys. Rev. Lett., **33**, 1006 (1974).
16. K. Binder, Phys. Rev. B, **15**, 4425 (1977).
17. H. Furukawa, Phys. Lett., **62A**, 377 (1977).
18. H. Furukawa, Prog. Theor. Phys., **59**, 1072 (1978).
19. H. Furukawa, Phys. Rev. Lett., **43**, 136 (1979).
20. H. Furukawa, Phys. Rev. A, **23**, 1535 (1981).
21. H. Furukawa, Adv. Phys., **34**, 703 (1985).
22. N.-C. Wong and C. M. Knobler, J. Chem. Phys., **69**, 725 (1978).
23. W. I. Goldburg, C.-H. Shaw, J. S. Huang, and M. S. Pilant, J. Chem. Phys., **68**, 484 (1978).
24. Y. C. Chou and W. I. Goldburg, Phys. Rev. A,

20, 2105 (1979).
25. Y. C. Chou and W. I. Goldburg, Phys. Rev. A, **23**, 858 (1981).
26. T. Hashimoto, M. Itakura, and H. Hasegawa, J. Chem. Phys., **85**, 6118 (1986).
27. T. Hashimoto, M. Itakura, and N. Shimidzu, J. Chem. Phys., **85**, 6773 (1986).
28. F. S. Bates and P. Wiltzius, J. Chem. Phys., **91**, 3258 (1989).
29. T. Nose, Phase Transitions, **8**, 245 (1987).
30. S. Komura, Phase Transitions, **12**, 3 (1988).
31. K. Binder, Chap. 7 in "Phase Transformations in Materials", Ed. P. Haasen, Materials Science and Technology: A Comprehensive Treatment, VCH, Weinheim, FRG (1991).
32. S.-W. Song and J. M. Torkelson, Macromolecules, **27**, 6389 (1994).
33. H. L. Snyder and P. Meakin, J. Chem. Phys., **79**, 5588 (1983).
34. G. Brown and A. Chakrabarti. J. Chem. Phys., **98**, 2451 (1993).
35. T. Hashimoto, Phase Transitions, **12**, 47 (1988).
36. S. Nojima, K. Shiroshita, and T. Nose, Polym. J., **14**, 289 (1982).
37. N. Kuwahara, K. Hamano, N. Aoyama, and T. Nomura, Phys. Rev. A, **27**, 1724 (1983).
38. N. Kuwahara and K. Kubota, Phys. Rev. A, **45**, 7385 (1992).
39. S. Krishnamurthy and R. Bansil, Phys. Rev. Lett., **50**, 2010 (1983).
40. F.-J. Tsai, Ph.D. Dissertation, Northwestern University, Evanston, IL (1990).