Dynamic scaling and fractal behaviour of spinodal phase separation in polymer mixtures of poly(methyl methacrylate) with poly(styrene-*co*-acrylonitrile)

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Dynamic scaling and fractal behaviour of spinodal phase separation is studied in a binary polymer mixture of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN). In the later stages of spinodal phase separation, a simple dynamic scaling law was found for the scattering function $S(q, t)$: $S(q, t) \sim q_m^{-3}\tilde{S}(q/q_m)$. The possibility of using fractal theory to describe the complex morphology of spinodal phase separation is discussed. In phase separation, morphology exhibits strong self-similarity. The two-dimensional image obtained by optical microscopy can be analysed within the framework of fractal concepts. The results give a fractal dimension of 1.64. This implies that the fractal structure may be the reason for the dynamic scaling behaviour of the structure function.

(Keywords: phase separation; scaling; light scattering; fractal)

INTRODUCTION

The spinodal phase separation of polymer blends in the liquid state is currently attracting a lot of interest from both academic and industrial institutions. Many investigations have been carried out and good results have been obtained[1]. In spite of this, our understanding of spinodal phase separation is far from complete.

In the very early stages of spinodal phase separation, growth of the amplitude of the dominant concentration fluctuations primarily takes place with no change in size as Cahn's theory[2] predicts. In the intermediate stage, however, both the size and amplitude of the concentration fluctuations increase, and in the late stage, the structure of the microphase change shows self-similarity, i.e. the structural change with time only involves increase in size.

The self-similarity in the microdomain structure in the late stage demands a scaling law for the structure function $S(q, t)$:

$$S(q, t) \sim q_m^{-d}\tilde{S}(q/q_m) \qquad (1)$$

where $\tilde{S}(q/q_m)$ is a universal function independent of time t. Such a scaling relation was found to hold for the results of a computer simulation using a kinetic Ising model by Marro *et al.*[3] and also in actual phase separation processes in polymer mixtures[4–6].

By various thermal treatments (i.e. heating or cooling) a single-phase polymer mixture will become an inhomogeneous two-phase mixture. When the volume fraction of one phase is less than the other, the minor phase exists as isolated particles. For such irregular and ramified domains, we can describe the geometry approximately by fractal theory because the unmixing structures show self-similarity[7].

The fractal geometry of the clusters can be expressed in terms of the mass scaling exponent, the fractal dimension[7], D

$$M(L) \sim L^D \qquad (2)$$

where $M(L)$ is the amount of mass inside a sphere of radius L. In general D is always less than or equal to the spatial dimensionality d, because of the 'open' character of the fractal structure. The most easily understood and determined fractal dimension is the density–density scaling function $\rho(L)$

$$\rho(L) \sim L^{D-d} \qquad (3)$$

In this paper, we attempt to test the dynamic scaling and fractal behaviour of spinodal phase separation for poly(methyl methacrylate) (PMMA) with poly(styrene-*co*-acrylonitrile) (SAN) mixtures. Although dynamic scaling has been tested for polymeric systems[5,6,8], what happens to the morphology and how it occurs have not been studied. Our paper deals with these problems and discusses the relationship between dynamic scaling of the structure function and the fractal behaviour of the morphology of spinodal phase separation.

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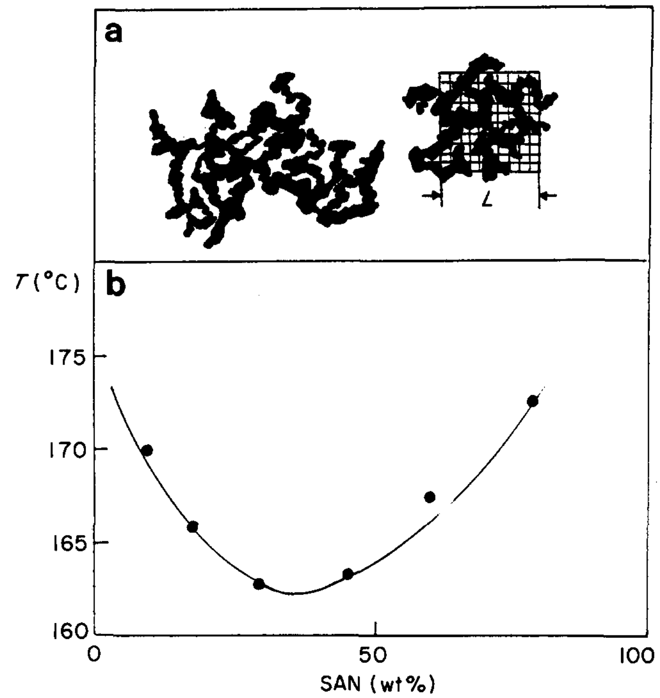

Figure 1 (a) Schematic diagram for the density calculation. (b) Phase diagram of PMMA/SAN blends

EXPERIMENTAL

SAN ($\bar{M}_m = 1.3 \times 10^5$, $\bar{M}_m/\bar{M}_n = 2.45$, 30 mol% acrylonitrile) was obtained from Aldrich, USA. PMMA ($\bar{M}_m = 1.98 \times 10^5$, $\bar{M}_m/\bar{M}_n = 2.5$) was also obtained commercially. Blends were prepared by solution casting a common solvent (1,2-dichloroethane). The solution was cast onto a cover glass for light scattering measurements and optical microscopy. The solvent was allowed to evaporate slowly at 30°C and the blends were dried under vacuum at 50°C for 72 h.

A 2 mW He–Ne laser light source with a wavelength of 632.8 nm was used. The series of spinodal phase separation experiments were made by jump-up from 25°C to a two-phase region for various temperatures. A temperature controller with an accuracy of ±0.1°C was utilized.

The morphology of the thin films was studied by optical microscopy. A thin layer of the blend cast on a slide was introduced into a transparent programmable heating stage at 184.0°C (*Figure 1*)[9].

Calculation of fractal dimension

The fractal dimension for two-dimensional ramified domains of spinodal phase separation can be obtained from micrographs using the following method. A square network (*Figure 1a*, lattice size = 1.0 mm) was used to cover the ramified domain. The number of occupied lattices of a given ramified domain lying within the square were counted. The number was divided by the Euclidean area, L^2, to give the density, $\rho(L)$. Because of the random choice of the centre sites for the square, we take an average density over many centre sites for a given size square.

RESULTS AND DISCUSSION

Typical time-evolution scattering curves for PMMA/SAN (65/35 w/w) are depicted in *Figure 2* at 170°C. When the blend undergoes phase separation, a clear scattering maximum develops at a particular angle. As phase separation proceeds, this scattering maximum moves to lower scattering angles associated with phase growth, while the scattered intensity increases with phase separation time t.

The scaled structure factor $F(X)$ is defined as:

$$F(X) = q_m^3 I(q/q_m) \tag{4}$$

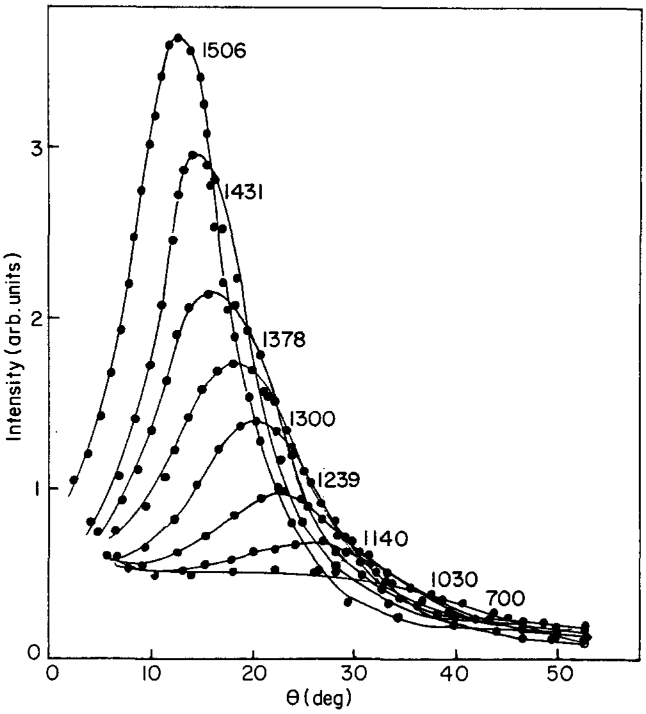

Figure 2 Time-evolution of scattered intensity obtained from PMMA/SAN (65/35 w/w) at 170°C. The time (in minutes) is indicated on each curve

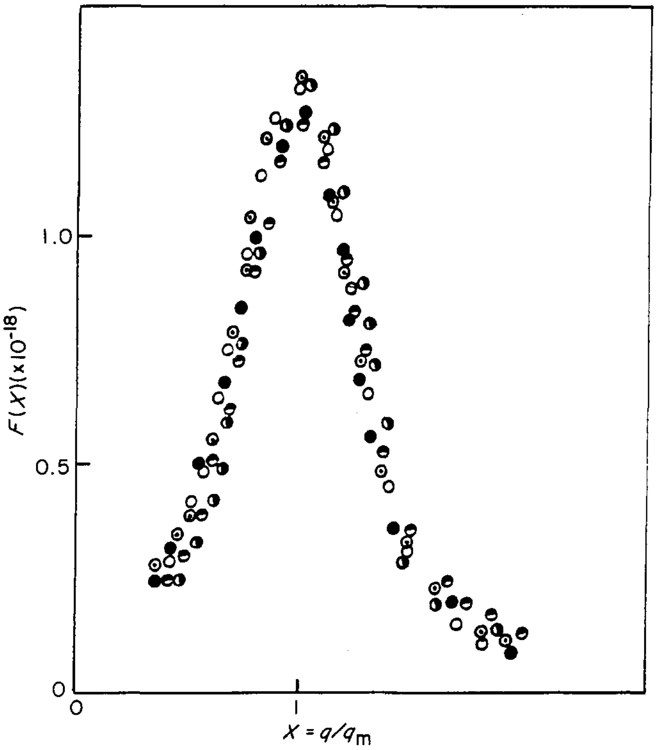

Figure 3 Self-similarity tests for PMMA/SAN (65/35 w/w) at 170°C. Time (min): (⊙) 1403; (○) 1434; (◑) 1481; (●) 1506; (○) 1543

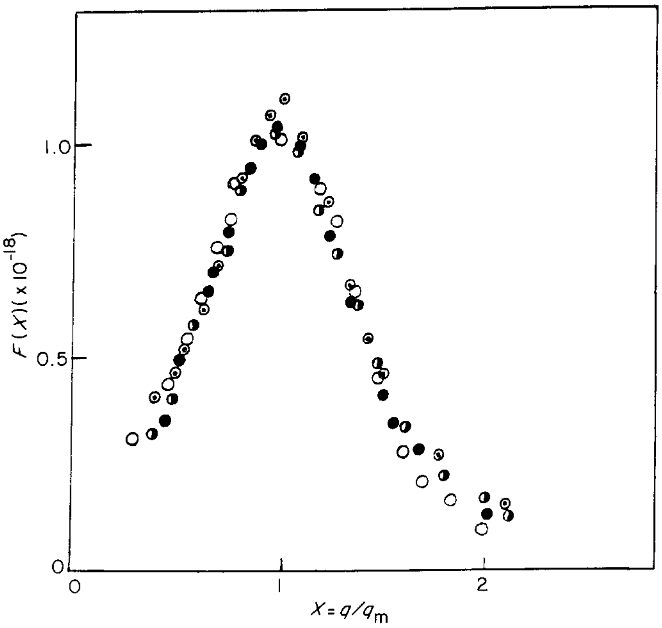

Figure 4 Self-similarity tests for PMMA/SAN (65/35 w/w) at 184°C. Time (min): (⊙) 222; (●) 241; (◑) 275; (○) 300

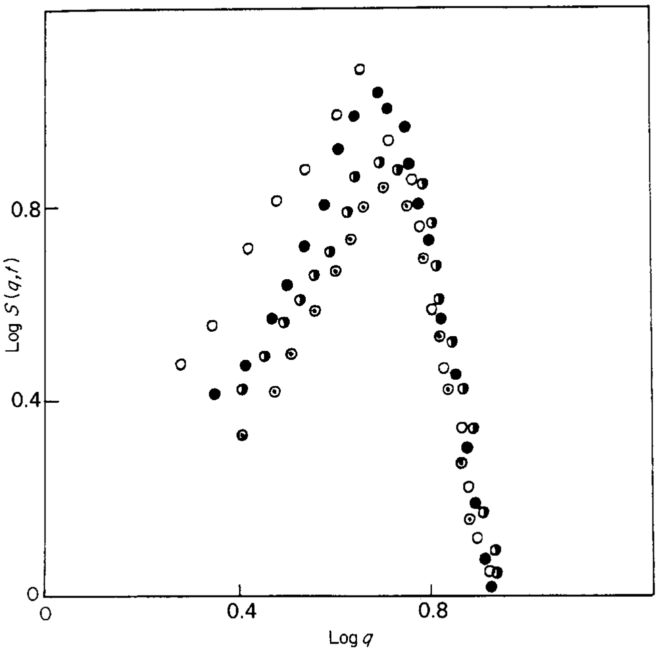

Figure 5 Asymptotic behaviour of the structure factor for PMMA/SAN (65/35 w/w) at 170°C. Time (min): (⊙) 1340; (◑) 1403; (●) 1481; (○) 1543

where $X = q/q_m$. As can be seen in *Figures 3* and *4* reasonably superimposed master curves were obtained for all temperature jumps in the late stage of spinodal phase separation, suggesting that dynamic self-similarity is preserved throughout the phase separation process.

Furukawa predicted the universal scaling function[10]:

$$\tilde{S}(X) \sim X^2/(y/2 + X^{2+y}) \tag{5}$$

where $X = q/q_m$ and y is defined as:

$$y = \begin{cases} d+1 & \text{for the non-critical mixture} \\ 2d & \text{for the critical mixture} \end{cases} \tag{6}$$

The asymptotic behaviour of the experimental and theoretical scaled structure factors at small and large X are compared in *Figures 5* and *6* for various temperatures. The results showed, at $X < 1$, $\tilde{S}(X)$ is approximately proportional to X^2, and, at $X > 1$, $\tilde{S}(X)$ is approximately proportional to X^{-6}. This result suggests that the spinodal phase separation of 35 wt% SAN is reminiscent of the behaviour of critical mixtures. The above results showed that in the late stages of the spinodal phase separation the growth of the phase separation domains satisfies the dynamic scaling hypothesis with the single length parameter $q_m(t)^{-1}$. Hence the domains grow with dynamic self-similarity.

What happens to this morphology in the later stages of spinodal phase separation? To answer this question, the change in the morphology of spinodal phase separation for PMMA/SAN (65/35 w/w) was studied using phase contrast optical microscopy. Upon introduction deep into the unstable region, phase separation was induced and the resulting morphological change was recorded over a period of time. *Figure 7* shows the phase structure

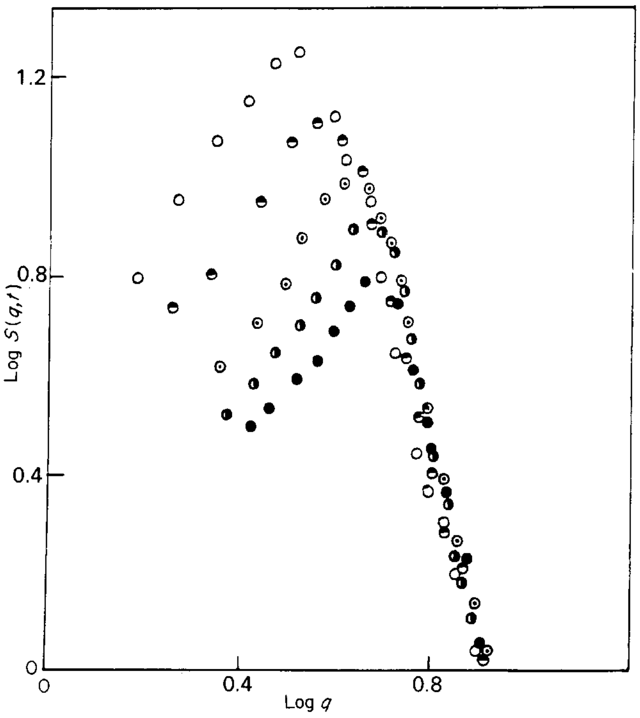

Figure 6 Asymptotic behaviour of the structure factor for PMMA/SAN (65/35 w/w) at 184°C. Time (min): (●) 186; (◑) 205; (⊙) 222; (○) 244; (○) 300

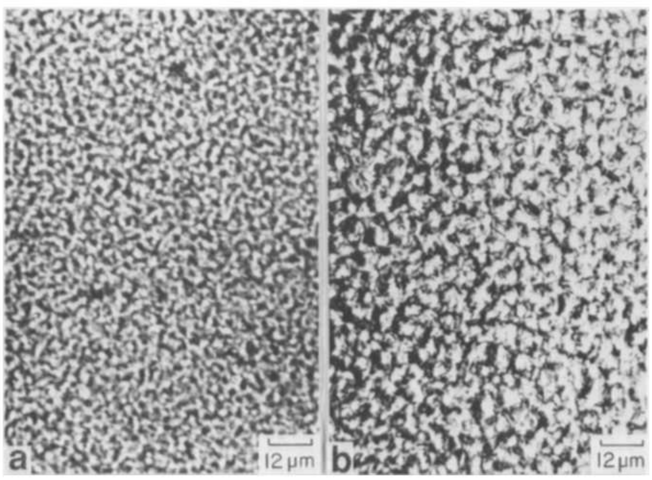

Figure 7 Micrographs of the morphology observed during spinodal phase separation: (a) 175 min; (b) 260 min

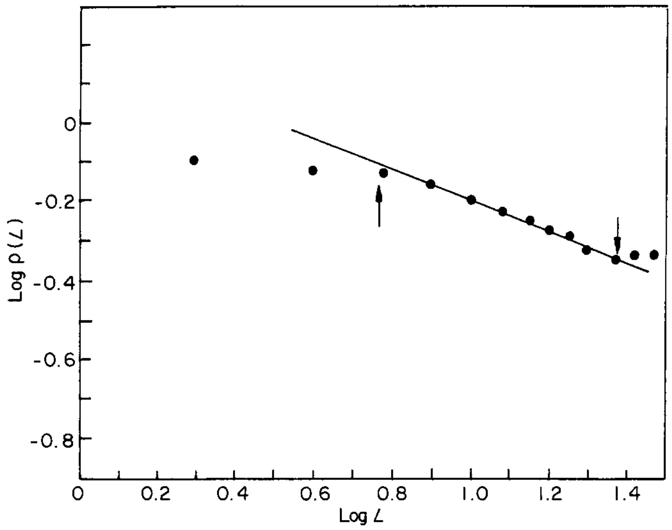

Figure 8 Plot of log $\rho(L)$ *versus* log L from *Figure 7a*

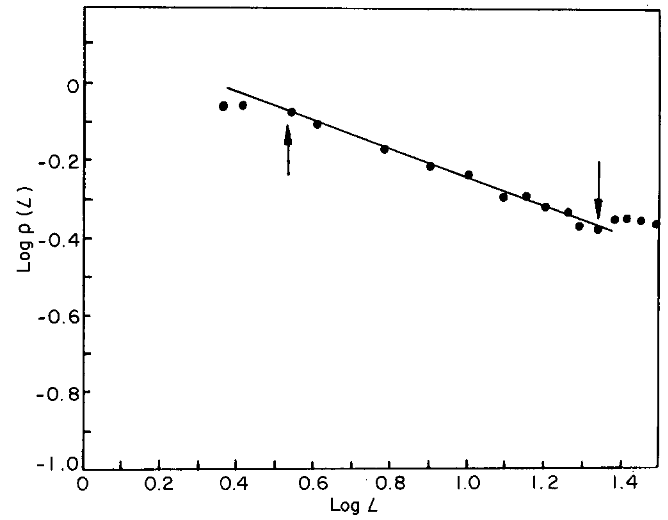

Figure 9 Plot of log $\rho(L)$ *versus* log L from *Figure 7b*

at 175 and 260 min, respectively, and clearly shows that phase structure increases with time.

The fractal dimension for two-dimensional ramified domains in the typical morphology of spinodal phase separation was obtained from *Figure 7*. As shown in *Figures 8* and *9* for 175 and 260 min, respectively, the density is scale-dependent and follows a power law that corresponds to a fractal dimension of ~ 1.64. In the later stages of spinodal phase separation the fractal dimensions do not change. The results show clearly that the ramified domains have self-similarity fractal character. These fractal dimensions are less than that of the two-dimensional percolation cluster (1.9) and larger than that of the two-dimensional percolation backbone $(1.6)^7$.

The results of light scattering and fractal analysis showed that the phase structure of spinodal phase separation has self-similarity. From *Figures 8* and *9*, we see that the self-similarity is in a certain range. From *Figures 3* and *4*, the results show that the self-similarity does not occur for small and larger X. Both results are unanimous. This implies that the fractal structure of spinodal phase separation may be the reason for the dynamic scaling behaviour of the structure function.

Recently, Binder[11] indicated that the percolation phenomenon of spinodal phase separation does not seem to show up in the structure function $S(X)$. The fractal behaviour cannot be observed by light scattering measurements of phase separation in polymer blends. Because the self-similarity of a cluster is limited, the structure function $S(X)$ scattering from a fractal object is expected to behave as

$$S(X) \sim X^{-D} \tag{7}$$

over some range of wave number X.

From the above results, it is clearly shown that the irregular morphology of spinodal phase separation in polymer blends may be described by fractal concepts. This may lead to a means of understanding the spinodal phase separation processes. Although a lot of work has been done in this field, the geometrical description of the growing objects and the dynamic growth laws of spinodal phase separation are not fully understood, and further work is still required.

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REFERENCES

1 Nose, T. *Phase Transition* 1987, **8**, 245
2 Cahn, J. W. and Hilliard, J. E. *J. Chem. Phys.* 1958, **28**, 258
3 Marro, J., Lebowitz, J. L. and Kalos, M. H. *Phys. Rev. Lett.* 1979, **43**, 282
4 Hasimoto, T., Itakura, M. and Shimidzu, N. *J. Chem. Phys.* 1986, **85**, 6773
5 Hashimoto, T., Itakura, M. and Hasegawa, H. *J. Chem. Phys.* 1986, **85**, 6118
6 Ohyama, Y., Kinoshita, S., Takahashi, M. and Nose, T. *Rep. Prog. Polym. Phys. Jpn* 1984, **27**, 503
7 Mandelbrot, B. B. 'The Fractal Geometry of Nature', Freeman, New York, 1982
8 Takenaka, M., Izumitani, T. and Hashimoto, T. *J. Chem. Phys.* 1990, **92**, 4566
9 Song, M., Liang, H. and Jiang, B. *Chinese Polym. Acta* 1990, **2**, 176
10 Furukawa, H. *Adv. Phys.* 1985, **34**, 703
11 Binder, J. *Physica* 1986, **140A**, 35