

## A Semiempirical Derivation of Phase Domain Size in Interpenetrating Polymer Networks

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### Synopsis

In previous papers, interpenetrating polymer networks were shown to display a cellular structure. The phase domain size of polymer II was shown to depend inversely on the crosslink density of polymer I. The present paper presents a semiempirical derivation of equations which show quantitatively the dependence of the phase domain size of polymer II on the crosslinking density of polymer I, and also on the interfacial energy and the overall composition. If polymer II is linear, the dependence on the molecular weight of polymer II is also included. The values of the phase domain sizes so estimated are compared with experimental results. While theory and experiment yield good agreement, the semiempirical nature of the equations must be borne in mind.

### INTRODUCTION

Most of the interesting classes of polymer blends,<sup>1</sup> graft<sup>2</sup> and block<sup>3</sup> copolymers, and interpenetrating polymer networks (IPN's)<sup>4,5</sup> display some type of phase separation. For example, block copolymers that have dispersed spheres, cylinders, or alternating lamellar structures are well known, while solution-type graft copolymers exhibit a phase-within-a-phase-within-a-phase morphology. The cellular structure of sequentially synthesized IPN's has been well established.<sup>6-8</sup>

A typical cellular structure for an SBR/PS IPN is shown in Figure 1. In this transmission electron micrograph, the diene-containing phase has been stained with osmium tetroxide.

While each of these polymer/polymer systems exhibit characteristic morphologies, only in the case of the block copolymers has a serious effort been made to understand phase domain size and structure in terms of macromolecular parameters.<sup>9</sup> The object of this paper is to present a semiempirical approach toward correlating the phase domain size of IPN's and semi-IPN's of the first kind (polymer I crosslinked, polymer II linear) with crosslink density, composition, and interfacial tension. The resulting equations will be tested, employing data published elsewhere.<sup>8</sup>

### THEORY

A thermodynamic approach will be used to develop a theory for predicting the size of the IPN domains. The derivation is performed for a semi-IPN of the first kind but can be extended to the full IPN as a limiting case.

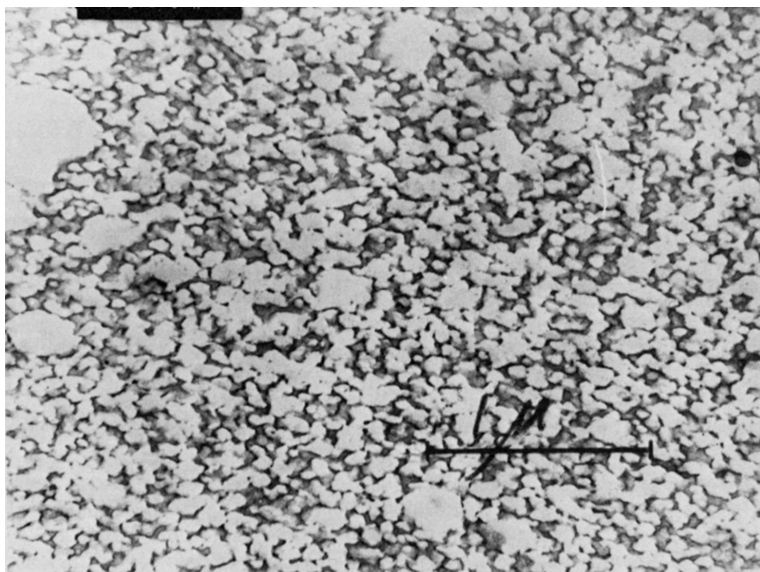


Fig. 1. Transmission electron micrograph of a styrene-butadiene rubber/polystyrene (SBR/PS) interpenetrating polymer network. The SBR portion is stained with osmium tetroxide. Sample from series No. 5, with 0.1% Dicum in the SBR.

In this simplified treatment, IPN morphology is evolved over the following hypothetical path, and the free-energy change over this route is developed. Initially, in state 1, polymer I and polymer II are completely separated. At an intermediate level, state 2, the polymer I network is uniformly swollen with polymer II, and the two polymers form a regular solution. Finally, in state 3, polymer II phase separates into spherical domains within the polymer I network, with no change in the volume of the system. It is assumed that, on a macroscopic scale, phase separation does not alter the state of swelling of the polymer I network. It is also presumed that thermodynamic equilibrium is achieved in each step, which represents a significant approximation in the case of IPN's.

The free-energy change for polymer II domain formation,  $G_d$ , is the sum of the free-energy changes from states 1 to 2 and from states 2 to 3:

$$\Delta G_d = \Delta G_{12} + \Delta G_{23} \quad (1)$$

The free-energy change from state 1 to state 2 is equal to the sum of the ordinary free energy of mixing,  $\Delta G_m$ , and the elastic free-energy change of the polymer I network which is uniformly swollen with polymer II,  $\Delta G_{el}$ :

$$\Delta G_{12} = \Delta G_m + \Delta G_{el} \quad (2)$$

The free-energy change from state 2 to state 3 is equal to the sum of the ordinary free energy of demixing,  $\Delta G_{dm}$ , and the surface free energy for domain formation,  $\Delta G_s$ :

$$\Delta G_{23} = \Delta G_{dm} + \Delta G_s \quad (3)$$

### Free Energy of Mixing

The term  $\Delta G_m$  in eq. (2) is represented by eq. (4), where  $\Delta H_m$  and  $\Delta S_m$  are the heat and entropy of mixing, respectively, and  $T$  is the absolute temperature at which mixing occurs:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (4)$$

The heat of mixing of nonpolar substances can be represented by a Van Laar-Hildebrand-Scatchard expression<sup>10</sup>:

$$\Delta H_m = V(\delta_1 - \delta_2)^2\phi_1\phi_2 \quad (5)$$

where  $\phi_1, \phi_2$  = volume fraction of polymers 1 and 2, respectively;  $\delta_1, \delta_2$  = solubility parameters of polymers 1 and 2, respectively; and  $V$  = total volume of mixture.

Using a lattice model, Flory<sup>11</sup> has developed an expression for the entropy of mixing between a solvent and polymer. Extending this development to the case of a mixture of two polymers, the entropy change can be approximated by

$$\Delta S_m = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (6)$$

where  $N_1, N_2$  = number of polymer 1 and 2 molecules, respectively; and  $k$  = Boltzmann's constant.

The ordinary free energy of mixing can now be expressed by the following equation:

$$\Delta G_m = V(\delta_1 - \delta_2)^2\phi_1\phi_2 + KT(N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (7)$$

### Elastic Free-Energy Change

The elastic free-energy change is primarily an entropy contribution arising from the uniform swelling of the polymer I network by polymer II. This can be expressed as

$$\Delta G_{el} = -T\Delta S_{el} \quad (8)$$

Flory has derived the entropy change for the isotropic swelling of a rubber network:<sup>11</sup>

$$\Delta S_{el} = -(k\nu_1/2)(3\alpha_1^2 - 3 - \ln \alpha_1^3) \quad (9)$$

where  $\nu_1$  = the effective number of polymer chains in network I; and  $\alpha_1$  = the ratio of perturbed to unperturbed chain dimensions for network I.

The chain expansion parameter,  $\alpha_1$ , can be expressed as

$$\alpha_1 = (r/r_0)_1 \quad (10)$$

where  $r_0$  and  $r$  are the root-mean-square (rms) end-to-end distances of the unperturbed and perturbed molecule, respectively, for polymer I. Also,  $r_0$  is equal to<sup>11</sup>

$$r_0 = KM^{1/2} \quad (11)$$

where  $K$  is a known constant for most polymers and  $M$  is the average molecular weight of the polymer. Combining eqs. (10) and (11) and substituting into eq. (9) with the assumptions that  $r$  equals  $r_1$ , the rms distance between crosslink sites

in polymer network I, and  $M$  equals  $M_{cl}$ , the number-average molecular weight between crosslink sites for the polymer I network, yields

$$\Delta S_{el} = - \left[ \frac{k\nu_1}{2} \right] \left[ \frac{3r_1^2}{K^2 M_{cl}} - 3 - \ln \left( \frac{r_1}{KM_{cl}^{1/2}} \right)^3 \right] \quad (12)$$

The elastic free-energy change from state 1 to state 2 is then

$$\Delta G_{el} = \left[ \frac{kT\nu_1}{2} \right] \left[ \frac{3r_1^2}{K^2 M_{cl}} - 3 - \ln \left( \frac{r_1}{KM_{cl}^{1/2}} \right)^3 \right] \quad (13)$$

### Free Energy of Demixing

Returning to eq. (3),  $\Delta G_{dm}$  is equal to

$$\Delta G_{dm} = \Delta H_{dm} - T\Delta S_{dm} \quad (14)$$

where  $\Delta H_{dm}$  and  $\Delta S_{dm}$  are the heat and entropy of demixing, respectively. The heat of demixing can be approximated by a negative heat of mixing which is the opposite of eq. (5):

$$\Delta H_{dm} = -\Delta H_m = -V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (15)$$

The entropy of demixing is the entropy change between states 2 and 3. At state 2,  $\Delta S$  is equal to eq. (6), or

$$\Delta S_2 = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (16)$$

From statistical mechanics, the entropy of a system in a specified state can be defined in terms of the number of possible arrangements of the "particles" composing the system which are consonant with the state of the system.<sup>12</sup> Each possible arrangement is called a complexion of the system, and the entropy is defined by eq. (17), first developed by Boltzmann, where  $\Omega$  equals the number of complexions:

$$\Delta S = k \ln \Omega \quad (17)$$

In the final state, the two polymers are considered to be completely phase separated. Polymer I forms the continuous phase, and polymer II forms the discontinuous phase.  $N_d$  domains of polymer II are formed, with a total of  $N_2$  polymer II molecules occupying the domains. If a particular polymer II molecule is able to enter any of the  $N_d$  domains during phase separation, the number of complexions is

$$\Omega = (N_d)^{N_2} \quad (18)$$

For state 3,  $\Delta S$  can now be expressed as

$$\Delta S_3 = k \ln (N_d)^{N_2} = kN_2 \ln N_d \quad (19)$$

(The entropy of polymer I, a pure phase, may be considered zero.) By subtracting eq. (16) from eq. (19), the entropy of demixing is obtained:

$$\Delta S_{dm} = \Delta S_3 - \Delta S_2 = k(N_2 \ln N_d + N_1 \ln \phi_1 + N_2 \ln \phi) \quad (20)$$

Substituting eqs. (15) and (20) into eq. (14) yields the ordinary free energy of demixing:

$$\Delta G_{dm} = -V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 - kT(N_2 \ln N_d + N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad (21)$$

### Surface Free Energy for Domain Formation

A special problem to be considered involves interfacial free energy. The surface free energy for polymer II domain formation is equal to

$$\Delta G_s = \gamma A_s \quad (22)$$

where  $\gamma$  is the interfacial energy and  $A_s$  is the surface area of interaction between polymer I and polymer II. If the polymer II domains are assumed to be spherical, the surface area is equal to

$$A_s = N_d \pi D_2^2 \quad (23)$$

where  $D_2$  is the average polymer II domain diameter. Substituting eq. (23) into (22) yields

$$G_s = \pi \gamma N_d D_2^2 \quad (24)$$

### Free-Energy Change for Domain Formation

The free-energy change for polymer II domain formation is obtained by adding eq. (7), (13), (21), and (24):

$$\Delta G_d = \pi \gamma N_d D_2^2 - k T N_2 \ln N_d + \left[ \frac{k T \nu_1}{2} \right] \left[ \frac{3 r_1^2}{K^2 M_{cl}} - 3 - \ln \left( \frac{r_1}{K M_{cl}^{1/2}} \right)^3 \right] \quad (25)$$

Since all the polymer II is assumed to be located in the domains, the volume of polymer II is

$$V_2 = N_d \pi D_2^3 / 6 \quad (26)$$

and the number of polymer II domains is

$$N_d = \frac{6 V_2}{\pi D_2^3} \quad (27)$$

From the electron microscopy results presented earlier, the polymer II (PS) domain size is clearly a function of the degree of crosslinking of the polymer I (SBR) network. Although the exact relationship may be complex, for simplicity assume that the domain size is a linear function of the rms end-to-end distance between crosslink sites of the polymer I network, expressed by eq. (28) where  $C$  is a proportionality constant relating the physical distance between the crosslink sites of polymer I and the domain dimensions of polymer II (see Fig. 2):

$$D_2 = C r_1 \quad (28)$$

Equation (25) now can be rewritten in the form

$$\Delta G_d = \frac{6 \gamma V_2}{D_2} - R T \bar{N}_2 \ln \left( \frac{6 V_2}{\pi D_2^3} \right) + \left[ \frac{R T \nu_1}{2} \right] \left[ \frac{3 D_2^2}{C^2 K^2 M_{cl}} - 3 - \ln \left( \frac{D_2}{C K M_{cl}^{1/2}} \right)^3 \right] \quad (29)$$

where  $\bar{N}_2$  is the number of moles of polymer II and  $\nu_1$  is the effective number of moles of crosslinked chains in the polymer I network.

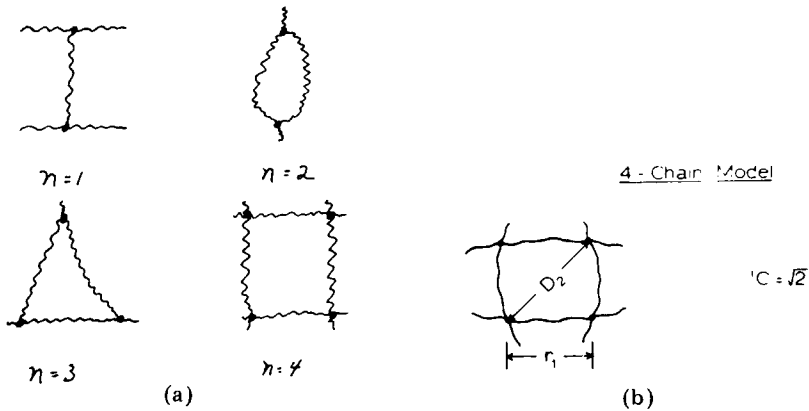


Fig. 2. Molecular models for evaluating  $C$ . (a) Schematic diagram of some simple crosslink clusters, useful for estimating the parameter  $n$ , and hence  $C$ , in eqs. (28) and (34). (b) The four-chain model, showing the relationship between  $r_1$  and  $D_2$ .

In order to determine the domain diameter which gives the minimum free energy change, the first derivative of eq. (29),  $d(\Delta G_d)/dD_2$ , is equated to zero and solved implicitly for  $D_2$ . This procedure yields

$$\frac{\nu_1 D_2^3}{C^2 K^2 M_{cl}} + \left( \bar{N}_2 - \frac{\nu_1}{2} \right) D_2 = \frac{2\gamma V_2}{RT} \quad (30)$$

The number of moles of polymer II is equal to

$$\bar{N}_2 = W_2/M_2 \quad (31)$$

where  $W_2$  and  $M_2$  are the weight and molecular weight, respectively. The number-average molecular weight between crosslink sites for polymer I,  $M_{cl}$ , can be related to the crosslink density  $\nu_1$  by the following equation:<sup>11</sup>

$$\frac{1}{M_{cl}} = \frac{\nu_1 \bar{v}_1}{V_1} + \frac{2}{M_1} \quad (32)$$

where  $V_1$ ,  $\bar{v}_1$ , and  $M_1$  are the volume, specific volume, and primary molecular weight, respectively, of polymer I. The last term on the right side of eq. (32) arises from the need to correct for dangling end chains in lightly crosslinked materials. Assuming a density of 1.0 g/cm<sup>3</sup> for both polymers so that the weights are equivalent to the volumes along with the relationship

$$W_1 + W_2 = 1 \quad (33)$$

and substituting eqs. (31) to (33) into eq. (30), the equation for the polymer II domain diameter is obtained:

$$\left( \frac{\nu_1 D_2^3}{C^2 K^2} \right) \left( \frac{\nu_1}{1 - W_2} + \frac{2}{M_1} \right) + \left( \frac{W_2}{M_2} - \frac{\nu_1}{2} \right) D_2 = \frac{2\gamma W_2}{RT} \quad (34)$$

Finally, the constant  $C$  from eq. (28) is evaluated in the following manner. Several models may be used to evaluate the constant  $C$ , where the domains are pictured as surrounded by a crosslink cluster containing  $n$  chains (see Fig. 2). The  $n = 1$  model predicts  $C = 1$ . The four-chain model predicts  $C = \sqrt{2}$ . In reality, all possible chain combinations leading back to the point of origin have to be considered, and a weighted sum from  $n = 1$  to  $n = \infty$  should be used. For

simplicity,  $n$  will be taken as 4, yielding  $C = \sqrt{2}$ , which assumes that the polymer II domains are surrounded by an average of four polymer I chain segments.

Equation (34) can be simplified if eqs. (10), (11), (28), and (35) below are used to replace the parameters  $C$ ,  $K$ ,  $r_1$ , and  $\alpha_1$ . Since both polymers are considered to have a density of unity,  $\alpha_1^3$  may be expressed as

$$\alpha_1^3 = \frac{W_1 + W_2}{W_1} \quad (35)$$

After the appropriate substitutions and algebraic manipulations, the modified equation for the polymer II domain diameter is

$$D_2 = \frac{2\gamma W_2}{RT\nu_1 \left[ \left( \frac{1}{1 - W_2} \right)^{2/3} + \frac{W_2}{\nu_1 M_2} - \frac{1}{2} \right]} \quad (36)$$

which contains no arbitrary constants.

The crux of the problem in the derivations of eqs. (34) and (36) is related to the variation of the end-to-end distance between crosslink junctions for polymer I ( $r_1$ ) within the sample after phase separation of polymer II occurs. The implicit and perhaps somewhat incorrect assumption in both equations is that an average value

$$r_1 = \alpha_1 r_{10} \quad (37)$$

can be substituted, whereas the polymer I chains surrounding the polymer II phase domain are likely to be more highly extended than predicted by eq. (37). (It may be that the sum of the end-to-end distances within the sample,  $R = \sum_i r_{1i}$ , remains the same before and after phase separation, but the distribution changes.)

TABLE I  
Experimental and Theoretical PS Domain Size in IPN's

Series no.	Type	Comp. of IPN, % SBR/% PS	Experimental	Domain size, $\mu\text{m}$			
				Form I (eq. 34)			Form II (eq. 36)
				$\gamma = 1$	$\gamma = 3$	$\gamma = 10$	$\gamma = 1$
3	Semi-1	20/80	0.15	0.081	0.125	0.192	0.171
12	Semi-1	21/79	0.15	0.080	0.122	0.188	0.16
6	Semi-1	22/78	0.055	0.032	0.046	0.069	0.044
14	Semi-1	18/82	0.060	0.035	0.050	0.075	0.047
4	IPN	22/78	0.11	0.089	0.128	0.190	0.57
13	IPN	20/80	0.11	0.093	0.133	0.198	0.59
5	IPN	21/79	0.065	0.034	0.048	0.071	0.053
15	IPN	19/81	0.060	0.036	0.050	0.074	0.054
5	IPN	11/89	0.105	0.117	0.168	0.250	0.42
5	IPN	24/76	0.10	0.086	0.123	0.183	0.66

### Comparison of Theory to Experiment

Table I shows experimental values for the phase domain diameter obtained in an earlier paper<sup>8</sup> for the SBR/PS IPN's and semi-I compositions. Also shown are values calculated from eqs. (34) and (36).

From equilibrium swelling measurements, the crosslink density of SBR (polymer I) as a function of Dicum concentration has been determined by means of the Flory-Rehner equation,<sup>11</sup> and average values are listed in Table II. The number-average molecular weight of the SBR copolymer was taken as  $M_1 = 9.6 \times 10^4$ . A value of  $K = 8.2 \times 10^{-9}$  has been selected from literature data<sup>13</sup> for pure PB and is considered to be adequate for SBR since the copolymers consist primarily of butadiene segments. The interfacial energy for many polymer pairs<sup>14,15</sup> lies between 1 and 10 dynes/cm, and  $\gamma = 3$  dynes/cm has been calculated for the PB/PS system.<sup>16</sup> Therefore,  $\gamma$  equal to 1, 3, and 10 dynes/cm is used to study the effect of interfacial energy on domain size.

Equation (34), which assumes the four-chain model resulting in  $C = \sqrt{2}$  (or a statistical average of all possible chain models, approximated by the four-chain model), yields nearly correct values for domain size in all cases (see Table I). When eq. (34) is simplified to eq. (36), the parameters  $C$  and  $K$  are eliminated, and no arbitrary constants remain. Also, the equation is linear in terms of  $D_2$  and simpler to interpret. The values for domain size obtained from eq. (36) fit the semi-1 compositions well when  $\gamma = 1$  dyne/cm but poorly for the full IPN's. however, it should be pointed out that the main derivation was performed originally for the semi-1 case.

TABLE II  
Values of  $M_c$  for SBR Networks

% Dicum in SBR	$M_c \times 10^{-5}$
0.10	0.226
0.20	2.38

It may be concluded that the phase domain size of polymer II is inversely proportional to the crosslink level of polymer I. The compositional variation is more complex. While reasonable agreement between theory and experiment is shown in the above, the semiempirical nature of the equations must be emphasized. It is planned to give the equations a more severe test in the near future.

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