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Vulcanisation of a binary mixture of long polymers

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Abstract. We consider a mixture of two polymers A and B which are compatible for certain values of the concentration and temperature. The polymerisation index of polymers A is N_A while that of polymers B is N_B ; both N_A and N_B are considered to be much greater than one. In the general case, three different types of cross-links between the chains can be introduced: $A-A$, $B-B$ and $A-B$. The cross-links can be chemical if, for example, we introduce certain amounts of vulcanising agents, or physical if, for instance, the monomers have the capability of forming hydrogen bonds when they touch. This last case leads to reversible gelation.

The mapping of the gelation problem into a percolation problem in the Bethe lattice—an approximation which is equivalent to that of Flory, Stockmayer and Gordon and coworkers—allows us to find, in a standard way, the critical surface, the gel fraction and the weight-average molecular weight of the finite molecules. In the case of physical cross-linking we plot, in addition, the gelation curves on a temperature–concentration diagram. We also discuss the phase separation and demixtion of the cross-linked system.

1. Introduction

Gelation and vulcanisation processes have been studied for a very long time (Flory 1941, 1953, Stockmayer 1943, 1944). Formation of chemical bonds between linear polymer molecules, commonly referred to as cross-linking, may lead to the formation of infinite networks. Flory (1941, 1953) considered this problem first, for a monodisperse polymer melt, while Stockmayer (1944) extended the treatment to a more realistic case with a distribution of chain lengths, but always considering the same polymer species. The approximation of neglecting intramolecular interactions ('loops') was seen to hold well for the gel point and the several average polymerisation degrees of these undiluted polymer melts. Gordon and coworkers (Gordon 1962, Gordon and Malcom 1966, Gordon and Ross-Murphy 1975 and references therein) reformulated the method in terms of the theory of branching ('cascade') processes by Good (1948, 1955, 1960) and were able to consider some of the effects introduced by intramolecular (cyclisation) reactions (Gordon and Scantlebury 1966). It is now recognised that the Flory–Stockmayer–Gordon theory is analogous to the percolation problem on the Bethe lattice (Stauffer 1976).

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We wish to consider here a percolation model for vulcanisation of long polymer chains, similar to the one proposed by Stauffer (1976) for gelation of monomeric units. The solution of the vulcanisation problem of a binary mixture of long polymers, which, to our knowledge, hasn't been solved explicitly, will suffice to show the method.

In § 2 we will consider explicitly the vulcanisation problem of a binary mixture of polymers. In § 2.1 we introduce, first, some definitions that will be used in the rest of the paper. In § 2.2 some percolation quantities will be considered. In § 2.3, the mapping of the vulcanisation problem into a percolation problem on the Bethe lattice will be made and the approximation discussed. In § 2.4 we will obtain the solution of the percolation problem in that lattice, including the critical surface, the gel fraction and the weight-average molecular weight of the finite molecules; we will see that by taking some suitable limits, we recover earlier results by Flory and Stockmayer. In § 3 we consider the case of physical cross-linking and plot the resulting gelation curves on a temperature-concentration diagram. Finally, in § 4, we discuss the phase separation of our cross-linked binary mixture.

2. The vulcanisation problem of a binary mixture of polymers

2.1. Some definitions

Let us consider a melt of two polymers *A* and *B* which are compatible for certain values of the concentration and temperature. Assuming that the monomers *A* and *B* have the same size†, each monomer *A* is then surrounded by *z* monomers *B* or/and *A* (including the two monomers *A* along the chemical sequence of the corresponding chain) and each monomer *B* is also surrounded by *z* other monomers. So, for simplicity, we may consider a three-dimensional infinite regular lattice of coordination number *z*, where each lattice site is occupied by a monomer *A* of a chain *A* or by a monomer *B* of a chain *B* (cf figure 1). The bonds of that lattice (not counting those between monomeric units followed one after the other along the chemical sequences) will serve as receptacles for the cross-linking agents *A*-*A*, *B*-*B* and *A*-*B*. We will introduce first some definitions:

$$\begin{aligned} n_A \text{ (} n_B \text{)} &= \text{number of chains } A \text{ (} B \text{) per site,} \\ N_A \text{ (} N_B \text{)} &= \text{number of monomers per chain } A \text{ (} B \text{)} \quad (N_A, N_B \gg 1), \\ M_A \text{ (} M_B \text{)} &= \text{molecular weight of monomeric units } A \text{ (} B \text{),} \\ C_A &= \text{concentration of monomers } A = n_A N_A, \end{aligned} \quad (1)$$

$$C_B = \text{concentration of monomers } B = n_B N_B, \quad (2)$$

with $C_A + C_B = 1$.

$$W_A = \text{weight fraction of polymers } A = \frac{n_A N_A M_A}{n_A N_A M_A + n_B N_B M_B}, \quad (3)$$

$$W_B = \text{weight fraction of polymers } B = \frac{n_B N_B M_B}{n_A N_A M_A + n_B N_B M_B}, \quad (4)$$

$$X_{AA} = \text{number of cross-links } A\text{-}A \text{ per site,}$$

† This is a simplifying assumption and not a restriction. The same results can be obtained with monomers *A* and *B* of different sizes.

X_{BB} = number of cross-links B - B per site,

X_{AB} = number of cross-links A - B per site,

X_{cross} = total number of cross-links per site = $X_{AA} + X_{BB} + X_{AB}$,

ρ_{AA} = fraction of monomers A that are cross-linked with monomers A
 $= 2X_{AA}/n_A N_A = 2X_{AA}/C_A$, (5)

ρ_{AB} = fraction of monomers A that are cross-linked with monomers B
 $= X_{AB}/n_A N_A = X_{AB}/C_A$, (6)

ρ_{BB} = fraction of monomers B that are cross-linked with monomers B
 $= 2X_{BB}/n_B N_B = 2X_{BB}/C_B$, (7)

ρ_{BA} = fraction of monomers B that are cross-linked with monomers A
 $= X_{AB}/n_B N_B = X_{AB}/C_B$, (8)

with

$\rho_{BA} = (C_A/C_B)\rho_{AB}$. (9)

$(z - 2)\phi_A$ = probable number of nearest-neighbour monomers A to a monomer A , not counting its two adjacent monomers along the chemical sequence of the chain. In the non-correlated case ($T = \infty$), we should have

$\lim_{T \rightarrow \infty} \phi_A = C_A$.

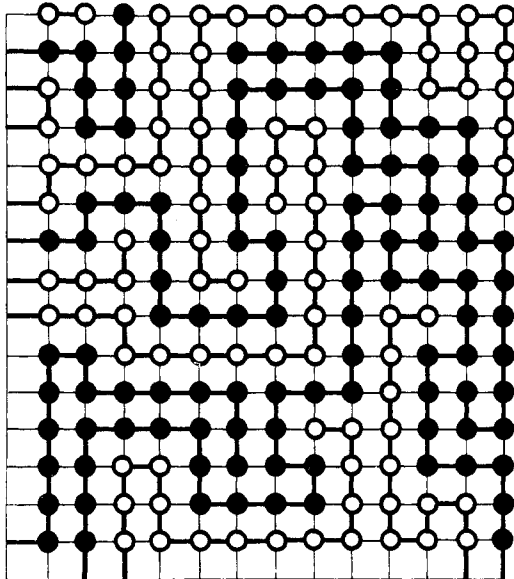


Figure 1. A two-dimensional representation of a melt of two polymers A (open circles) and B (full circles). The light bonds serve as receptacles for the existing cross-linking agents.

So, the probable number of nearest-neighbour monomers B to a monomer A is

$$(z-2)(1-\phi_A).$$

$(z-2)\phi_B$ = probable number of nearest-neighbour monomers B to a monomer B , not counting its two adjacent monomers along the chemical sequence of the chain. Also

$$\lim_{T \rightarrow \infty} \phi_B = C_B.$$

The probable number of nearest-neighbour monomers A to a monomer B is then

$$(z-2)(1-\phi_B).$$

The number of contacts (bonds) $A-A$ per site is given by

$$\frac{1}{2}n_A N_A (z-2)\phi_A, \quad (10)$$

while the number of contacts $B-B$ per site is

$$\frac{1}{2}n_B N_B (z-2)\phi_B, \quad (11)$$

and the number of contacts $A-B$ per site is

$$n_A N_A (z-2)(1-\phi_A) = n_B N_B (z-2)(1-\phi_B). \quad (12a)$$

The total number of contacts per site is then given by $\frac{1}{2}(z-2)$. From relation (12a) and definitions (1) and (2), we obtain

$$\phi_B = 1 - C_A \frac{(1-\phi_A)}{(1-C_A)}. \quad (12b)$$

The average number of $A-A$ possible bonds leaving a polymer A is

$$\sigma_{AA} + 1 = N_A (z-2)\phi_A \approx \sigma_{AA}, \quad (13)$$

the average number of $A-B$ possible bonds leaving a polymer A is

$$\sigma_{BA} + 1 = N_A (z-2)(1-\phi_A) \approx \sigma_{BA}, \quad (14)$$

with similar relations for σ_{BB} and σ_{AB} , where the index A is replaced by B and vice-versa.

Now we will make the usual assumption that the cross-linking process occurs at random. This means that, for a certain typical configuration of the chains, each contact (bond) $A-A$ is equally probable to be occupied by a cross-link $A-A$, with similar statements for contacts $B-B$ and $A-B$. So, the probability for an $A-A$ contact to be occupied by an $A-A$ cross-link is

$$p_1 = X_{AA} / [(n_A N_A (z-2)\phi_A) / 2] = \rho_{AA} / (z-2)\phi_A, \quad (15)$$

while the probability for a $B-B$ contact to be occupied by a $B-B$ crosslink is

$$p_2 = X_{BB} / [(n_B N_B (z-2)\phi_B) / 2] = \rho_{BB} / (z-2)\phi_B, \quad (16)$$

and the probability for an $A-B$ contact to be occupied by an $A-B$ cross-link is

$$\begin{aligned} p_3 &= X_{AB} / [n_A N_A (z-2)(1-\phi_A)] = \rho_{AB} / (z-2)(1-\phi_A) \\ &= X_{AB} / [n_B N_B (z-2)(1-\phi_B)] = \rho_{BA} / (z-2)(1-\phi_B). \end{aligned} \quad (17)$$

It is worth noting that, in the usual vulcanisation problem of chains, each monomeric unit carries only one functional group capable of cross-linking. This would mean, in our model, that if a bond emanating from a certain monomer is occupied by a cross-linking agent, the other bonds emanating from the same monomer cannot be occupied. However, as the critical thresholds are very low ($p_{1c}^{\max} = 1/\sigma_{AA} \ll 1$, $p_{2c}^{\max} = 1/\sigma_{BB} \ll 1$, $p_{3c}^{\max} = 1/(\sigma_{AB}\sigma_{BA})^{1/2} \ll 1$ as we will see below), and as we will be dealing with probabilities not far above the threshold, the occupancy of two bonds belonging to the same monomer is a very rare event. So, for a good range of values of the occupation probabilities (below and above the threshold), such that they are still much less than one, the results taking into account this complication in the model, are not expected to differ appreciably from those for which all the bonds of one type are equally probable to be occupied by a cross-linking agent of the corresponding type.

2.2. The percolation of the chains

As we can see, we have a bichromatic percolation problem of chains with three different types of bonds. Let

$$\begin{aligned}
 N_{s,t} &= \text{total number of clusters per site of } s \text{ chains } A \text{ and } t \text{ chains } B, \\
 N_s &= \text{total number of clusters per site of } s \text{ chains } A \text{ and} \\
 &\text{any number of chains } B = \sum'_{t=0}^{\infty} N_{s,t} \quad (s \geq 1),
 \end{aligned}$$

where the prime in the summation indicates that it doesn't include the infinite cluster.

$$\begin{aligned}
 N_t &= \text{total number of clusters per site of } t \text{ chains } B \text{ and any number of} \\
 &\text{chains } A = \sum'_{s=0}^{\infty} N_{s,t} \quad (t \geq 1).
 \end{aligned}$$

The probability that a chain *A* belongs to an infinite cluster is then given by

$$P^A(\mathbf{p}) = 1 - (1/n_A) \sum'_{s=1}^{\infty} sN_s = 1 - (1/n_A) \sum'_{s=1,t=0}^{\infty} sN_{s,t} \tag{18}$$

while the probability that a chain *B* belongs to an infinite cluster is

$$P^B(\mathbf{p}) = 1 - (1/n_B) \sum'_{t=1}^{\infty} tN_t = 1 - (1/n_B) \sum'_{s=0,t=1}^{\infty} tN_{s,t} \tag{19}$$

Let us define the percolation probability as the probability for any monomer to belong to an infinite cluster:

$$\begin{aligned}
 P(\mathbf{p}) &= C_A P^A(\mathbf{p}) + C_B P^B(\mathbf{p}) \\
 &= 1 - \sum'_{s+t \geq 1} (sN_A + tN_B) N_{s,t} \tag{20}
 \end{aligned}$$

and the gel weight-fraction as

$$\begin{aligned}
 G(\mathbf{p}) &= W_A P^A(\mathbf{p}) + W_B P^B(\mathbf{p}) \\
 &= 1 - \sum'_{s+t \geq 1} \frac{(sN_A M_A + tN_B M_B) N_{s,t}}{n_A N_A M_A + n_B N_B M_B} \tag{21}
 \end{aligned}$$

In order to calculate other quantities such as the weight-average molecular weight of the finite clusters, we will introduce the ghost site (Reynolds *et al* 1977, Marland and Stinchcombe 1977). Each monomer A is connected to the ghost site by M_A bonds and each monomer B is connected to the ghost site by M_B bonds[†]; each of these bonds can be occupied with probability h and empty with probability $1 - h$. As a result, each chain A is connected to the ghost site by $N_A M_A$ bonds and each chain B by $N_B M_B$ bonds. In this way, the probabilities for a chain (A or B) to belong to an infinite cluster become

$$P^A(\mathbf{p}, h) = 1 - (1/n_A) \sum_{s=1, t=0}^{\infty} s N_{s,t} (1-h)^{(sN_A M_A + tN_B M_B)}, \quad (22)$$

$$P^B(\mathbf{p}, h) = 1 - (1/n_B) \sum_{s=0, t=1}^{\infty} t N_{s,t} (1-h)^{(sN_A M_A + tN_B M_B)}. \quad (23)$$

So, the probability for a monomer to belong to an infinite cluster is now

$$\begin{aligned} P(\mathbf{p}, h) &= C_A P^A(\mathbf{p}, h) + C_B P^B(\mathbf{p}, h) \\ &= 1 - \sum_{s+t \geq 1}^{\infty} (sN_A + tN_B) N_{s,t} (1-h)^{(sN_A M_A + tN_B M_B)}, \end{aligned} \quad (24)$$

while the gel weight-fraction is

$$\begin{aligned} G(\mathbf{p}, h) &= W_A P^A(\mathbf{p}, h) + W_B P^B(\mathbf{p}, h) \\ &= 1 - \frac{\sum_{s+t \geq 1}^{\infty} (sN_A M_A + tN_B M_B) N_{s,t} (1-h)^{(sN_A M_A + tN_B M_B)}}{n_A N_A M_A + n_B N_B M_B}. \end{aligned} \quad (25)$$

We will now define the weight-average molecular weight of the finite molecules as

$$\begin{aligned} (MW)_w(\mathbf{p}) &= \frac{(\partial G / \partial h)_{h=0}}{(1-G)_{h=0}} = \frac{\sum_{s+t \geq 1}^{\infty} (sN_A M_A + tN_B M_B)^2 N_{s,t}}{\sum_{s+t \geq 1}^{\infty} (sN_A M_A + tN_B M_B) N_{s,t}} \\ &= \frac{W_A (\partial P^A / \partial h)_{h=0} + W_B (\partial P^B / \partial h)_{h=0}}{W_A (1-P^A)_{h=0} + W_B (1-P^B)_{h=0}}. \end{aligned} \quad (26)$$

2.3. The Bethe lattice approximation

Let us consider an infinite Bethe lattice with sites A (chains A) and sites B (chains B) as in figure 2. Every site A is surrounded by $\sigma_{AA} + 1$ sites A and $\sigma_{BA} + 1$ sites B , while every site B is surrounded by $\sigma_{BB} + 1$ sites B and $\sigma_{AB} + 1$ sites A . In this way, the functionality of the sites A is $\sigma_{AA} + \sigma_{BA} + 2 = N_A(z - 2) \gg 1$, while the functionality of the sites B is $\sigma_{BB} + \sigma_{AB} + 2 = N_B(z - 2) \gg 1$. In that lattice we are going to have three different types of bonds (A - A , B - B and A - B), which can be occupied with probabilities p_1 , p_2 and p_3 , respectively, and which will be denoted henceforth by p_1 , p_2 and p_3 . Also, each site A is connected to the ghost site by $N_A M_A$ bonds and each site B is connected to the ghost site by $N_B M_B$ bonds.

Any possible path—through chains and bonds—between two given chains in the original lattice is represented as a path between two corresponding sites in the Bethe

[†] The fact that M_A and M_B need not be integers can be handled by considering instead two integers \tilde{M}_A and \tilde{M}_B such that $(\tilde{M}_A)/(\tilde{M}_B)$ is approximately equal to $(M_A)/(M_B)$. Then, we only need to divide the expressions for the molecular weight by $(\tilde{M}_A)/(\tilde{M}_A) = (\tilde{M}_B)/(\tilde{M}_B)$, getting the same results as in the text.

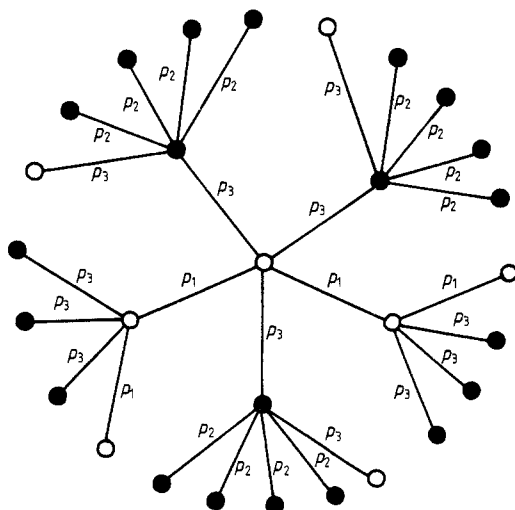


Figure 2. Bethe lattice with sites *A* (open circles) and sites *B* (full circles). In this example, every site *A* is surrounded by $\sigma_{AA} + 1 = 2$ sites *A* and $\sigma_{BA} + 1 = 3$ sites *B*, while every site *B* is surrounded by $\sigma_{BB} + 1 = 4$ sites *B* and $\sigma_{AB} + 1 = 2$ sites *A*. p_1 , p_2 and p_3 are the occupation probabilities of the bonds *A*-*A*, *B*-*B* and *A*-*B*, respectively.

lattice; one can see that all closed paths are taken into account by mapping each chain into more than one site in the Bethe lattice. However, the mere fact of the existence of closed paths in the original lattice, requires us to map every chain to an infinite number of sites in the Bethe lattice; in this way, all possible paths (closed and non-closed) are represented an infinite number of times. We can see that an infinite path in the real three-dimensional lattice corresponds to an infinite path in the Bethe lattice, but a closed (finite) path in the real lattice also corresponds to an infinite path in the Bethe lattice. So, the assumption is made that, for systems containing units of high functionality, the measure of the infinite paths in the Bethe lattice which corresponds to closed (finite) paths in the original lattice is negligible compared with that corresponding to infinite paths in the real lattice. This allows us to say *approximately* that the infinite Bethe lattice percolates when the real system percolates. However, the assumption is stated and *the issue is decided by the results obtained from that assumption*.

2.4. The solution of the percolation problem on the Bethe lattice.

We will solve the problem using a method introduced by Stinchcombe (1974) and extended by Turban (1979) to a case similar to ours. Let

- $R_1(h)$ = probability that a site *A* does not belong to an infinite cluster in a branch starting with a bond p_1 , given that such site is not connected to the ghost site.
- $R_2(h)$ = probability that a site *B* does not belong to an infinite cluster in a branch starting with a bond p_2 , given that such site is not connected to the ghost site.
- $R_3(h)$ = probability that a site *B* does not belong to an infinite cluster in a branch starting with a bond p_3 , given that such site is not connected to the ghost site.
- $R_4(h)$ = probability that a site *A* does not belong to an infinite cluster in a branch starting with a bond p_3 , given that such site is not connected to the ghost site.

It is not difficult to see that

$$1 - P^A(\mathbf{p}, h) = (1 - h)^{(N_A M_A)} R_1(h)^{(\sigma_{AA}+1)} R_4(h)^{(\sigma_{BA}+1)} \tag{27}$$

and

$$1 - P^B(\mathbf{p}, h) = (1 - h)^{(N_B M_B)} R_2(h)^{(\sigma_{BB}+1)} R_3(h)^{(\sigma_{AB}+1)}. \tag{28}$$

Also, we can have the following recurrence relations:

$$R_1(h) = 1 - p_1 + p_1(1 - h)^{(N_A M_A)} R_1(h)^{(\sigma_{AA})} R_4(h)^{(\sigma_{BA}+1)}, \tag{29a}$$

$$R_2(h) = 1 - p_2 + p_2(1 - h)^{(N_B M_B)} R_2(h)^{(\sigma_{BB})} R_3(h)^{(\sigma_{AB}+1)}, \tag{29b}$$

$$R_3(h) = 1 - p_3 + p_3(1 - h)^{(N_A M_A)} R_4(h)^{(\sigma_{BA})} R_1(h)^{(\sigma_{AA}+1)}, \tag{29c}$$

$$R_4(h) = 1 - p_3 + p_3(1 - h)^{(N_B M_B)} R_3(h)^{(\sigma_{AB})} R_2(h)^{(\sigma_{BB}+1)}. \tag{29d}$$

From equations (27), (28), (29a) and (29b), we obtain

$$P^A(\mathbf{p}, h) = 1 - [R_1(h)^2 - (1 - p_1)R_1(h)]/p_1 \tag{30}$$

and

$$P^B(\mathbf{p}, h) = 1 - [R_2(h)^2 - (1 - p_2)R_2(h)]/p_2. \tag{31}$$

So,

$$\frac{\partial P^A(\mathbf{p}, h)}{\partial h} = \frac{(1 - p_1 - 2R_1(h))}{p_1} \frac{\partial R_1}{\partial h} \tag{32}$$

and

$$\frac{\partial P^B(\mathbf{p}, h)}{\partial h} = \frac{(1 - p_2 - 2R_2(h))}{p_2} \frac{\partial R_2}{\partial h}. \tag{33}$$

By taking the derivatives of the system (29), we obtain a linear system for $\partial R_i/\partial h$ ($i = 1, 2, 3, 4$), whose solution is straightforward, leading to

$$(\partial R_1/\partial h)_{h=0} = -p_1(Q/D) \tag{34}$$

and

$$(\partial R_2/\partial h)_{h=0} = -p_2(T/D), \tag{35}$$

where

$$\begin{aligned} Q = & N_A M_A R_1^{(\sigma_{AA})} R_4^{(\sigma_{BA}+1)} - p_2 N_A M_A \sigma_{BB} R_1^{(\alpha_{AA})} R_2^{(\sigma_{BB}-1)} R_3^{(\alpha_{AB}+1)} R_4^{(\sigma_{BA}+1)} \\ & + p_3 N_B M_B (\sigma_{BA} + 1) R_1^{(\sigma_{AA})} R_2^{(\sigma_{BB}+1)} R_3^{(\sigma_{AB})} R_4^{(\sigma_{BA})} \\ & + p_3^2 N_A M_A \sigma_{AB} R_1^{(2\sigma_{AA}+1)} R_2^{(\sigma_{BB}+1)} R_3^{(\sigma_{AB}-1)} R_4^{(2\sigma_{BA})} \\ & + p_2 p_3 N_B M_B (\sigma_{BA} + 1) R_1^{(\sigma_{AA})} R_2^{(2\sigma_{BB})} R_3^{(2\sigma_{AB}+1)} R_4^{(\sigma_{BA})} \\ & + p_2 p_3^2 N_A M_A (\sigma_{AB} + \sigma_{BB} + 1) R_1^{(2\sigma_{AA}+1)} R_2^{(2\sigma_{BB})} R_3^{(2\sigma_{AB})} R_4^{(2\sigma_{BA})}, \end{aligned} \tag{36}$$

$$\begin{aligned} T = & N_B M_B R_2^{(\sigma_{BB})} R_3^{(\sigma_{AB}+1)} - p_1 N_B M_B \sigma_{AA} R_1^{(\sigma_{AA}-1)} R_2^{(\sigma_{BB})} R_3^{(\sigma_{AB}+1)} R_4^{(\sigma_{BA}+1)} \\ & + p_3 N_A M_A (\sigma_{AB} + 1) R_1^{(\sigma_{AA}+1)} R_2^{(\sigma_{BB})} R_3^{(\alpha_{AB})} R_4^{(\sigma_{BA})} \\ & + p_3^2 N_B M_B \sigma_{BA} R_1^{(\sigma_{AA}+1)} R_2^{(2\sigma_{BB}+1)} R_3^{(2\sigma_{AB})} R_4^{(\sigma_{BA}-1)} \\ & + p_1 p_3 N_A M_A (\sigma_{AB} + 1) R_1^{(2\sigma_{AA})} R_2^{(\sigma_{BB})} R_3^{(\sigma_{AB})} R_4^{(2\sigma_{BA}+1)} \\ & + p_1 p_3^2 N_B M_B (\sigma_{BA} + \sigma_{AA} + 1) R_1^{(2\sigma_{AA})} R_2^{(2\sigma_{BB}+1)} R_3^{(2\sigma_{AB})} R_4^{(2\sigma_{BA})} \end{aligned} \tag{37}$$

and

$$D = (1 - p_1\sigma_{AA}R_1^{(\sigma_{AA}-1)}R_4^{(\sigma_{BA}+1)})(1 - p_2\sigma_{BB}R_2^{(\sigma_{BB}-1)}R_3^{(\sigma_{AB}+1)}) - p_3^2R_1^{(\sigma_{AA}+1)}R_2^{(\sigma_{BB}+1)}R_3^{(\sigma_{AB}-1)}R_4^{(\sigma_{BA}-1)}(\sigma_{AB} + p_2(\sigma_{BB} + \sigma_{AB} + 1) \times R_2^{(\sigma_{BB}-1)}R_3^{(\sigma_{AB}+1)})(\sigma_{BA} + p_1(\sigma_{AA} + \sigma_{BA} + 1)R_1^{(\sigma_{AA}-1)}R_4^{(\sigma_{BA}+1)}), \quad (38)$$

and where R_1, R_2, R_3 and R_4 satisfy equations (29) with $h = 0$.

Using equations (20), (21), (26), (30), (31), (32), (33), (34) and (35), we can obtain expressions for $P(\mathbf{p}), G(\mathbf{p})$ and $(MW)_w(\mathbf{p})$:

$$P(\mathbf{p}) = C_A \frac{p_1 + (1 - p_1)R_1 - R_1^2}{p_1} + C_B \frac{p_2 + (1 - p_2)R_2 - R_2^2}{p_2}, \quad (39)$$

$$G(\mathbf{p}) = W_A \frac{p_1 + (1 - p_1)R_1 - R_1^2}{p_1} + W_B \frac{p_2 + (1 - p_2)R_2 - R_2^2}{p_2} \quad (40)$$

and

$$(MW)_w(\mathbf{p}) = \frac{W_A p_1 p_2 (2R_1 + p_1 - 1)Q + W_B p_1 p_2 (2R_2 + p_2 - 1)T}{(W_A p_2 R_1 (R_1 + p_1 - 1) + W_B p_1 R_2 (R_2 + p_2 - 1))D}. \quad (41)$$

The expressions (39), (40) and (41), together with the definitions (36), (37), (38) and the recurrence relations (29) with $h = 0$, give the formal solution of the percolation problem of our binary mixture of chains in the Bethe lattice approximation. Below the percolation threshold $R_1 = R_2 = R_3 = R_4 = 1$, on physical grounds; this in turn means that $P(\mathbf{p})$ and $G(\mathbf{p})$ are zero. Above the percolation threshold, there is a non-trivial solution of the recurrence relations with the R 's generally less than one. The expression for the weight-average molecular weight below the threshold is explicitly given by

$$(MW)_w^<(\mathbf{p}) = \{W_A(1 + p_1)[N_A M_A - p_2 \sigma_{BB} N_A M_A + p_3(\sigma_{BA} + 1)N_B M_B + p_3^2 \sigma_{AB} N_A M_A + p_2 p_3(\sigma_{BA} + 1)N_B M_B + p_2 p_3^2(\sigma_{BB} + \sigma_{AB} + 1)N_A M_A] + W_B(1 + p_2)[N_B M_B - p_1 \sigma_{AA} N_B M_B + p_3(\sigma_{AB} + 1)N_A M_A + p_3^2 \sigma_{BA} N_B M_B + p_1 p_3(\sigma_{AB} + 1)N_A M_A + p_1 p_3^2(\sigma_{AA} + \sigma_{BA} + 1)N_B M_B]\} / \{(1 - p_1 \sigma_{AA}) \times (1 - p_2 \sigma_{BB}) - p_3^2[\sigma_{AB} + p_2(\sigma_{BB} + \sigma_{AB} + 1)][\sigma_{BA} + p_1(\sigma_{AA} + \sigma_{BA} + 1)]\}. \quad (42)$$

The critical surface is obtained as follows: assuming that we are above but very near the threshold, we may write

$$R_1 = 1 - \eta_1, \quad R_2 = 1 - \eta_2, \quad (43a, b)$$

$$R_3 = 1 - \eta_3, \quad R_4 = 1 - \eta_4, \quad (43c, d)$$

where the η 's are positive infinitesimals. On introducing the above equations into the relations (29) with $h = 0$, and keeping only first-order terms in $\eta_1, \eta_2, \eta_3, \eta_4, \epsilon_1, \epsilon_2$ and ϵ_3 ($\epsilon_i = p_i - p_{ic}$), we get the set

$$(1 - p_{1c} \sigma_{AA})\eta_1 - p_{1c}(\sigma_{BA} + 1)\eta_4 = 0, \quad (44a)$$

$$(1 - p_{2c} \sigma_{BB})\eta_2 - p_{2c}(\sigma_{AB} + 1)\eta_3 = 0, \quad (44b)$$

$$-p_{3c}(\sigma_{AA} + 1)\eta_1 + \eta_3 - p_{3c} \sigma_{BA} \eta_4 = 0, \quad (44c)$$

$$-p_{3c}(\sigma_{BB} + 1)\eta_2 - p_{3c} \sigma_{AB} \eta_3 + \eta_4 = 0, \quad (44d)$$

which has a non-trivial solution only when

$$(1 - p_{1c}\sigma_{AA})(1 - p_{2c}\sigma_{BB}) - p_{3c}^2[\sigma_{AB} + p_{2c}(\sigma_{BB} + \sigma_{AB} + 1)][\sigma_{BA} + p_{1c}(\sigma_{AA} + \sigma_{BA} + 1)] = 0, \quad (45)$$

which defines the critical surface. A look at the weight-average molecular weight below the threshold (equation (42)) shows that the critical surface could have been guessed directly: the critical surface is characterised by the divergence of $(MW)_w(\mathbf{p})$, which is obtained when the denominator is zero since the numerator remains regular.

In order to proceed further we need to recognise that the maximum value of p_{1c} (when $p_{2c} = p_{3c} = 0$) is $1/\sigma_{AA} \approx 1/(N_A(z-2)\phi_A) \ll 1$. Similarly, the maximum values of p_{2c} and p_{3c} are

$$p_{2c}^{\max} = 1/\sigma_{BB} \approx 1/(N_B(z-2)\phi_B) \ll 1$$

and

$$p_{3c}^{\max} = 1/(\sigma_{AB}\sigma_{BA})^{1/2} \approx 1/\{(z-2)[N_A N_B(1-\phi_A)(1-\phi_B)]^{1/2}\} \ll 1.$$

The critical surface then reduces to

$$(1 - p_{1c}\sigma_{AA})(1 - p_{2c}\sigma_{BB}) - p_{3c}^2\sigma_{AB}\sigma_{BA} \approx 0. \quad (46)$$

As we are interested in the percolation quantities not far above the threshold (when we expect the approximation involving the loops not to be so strong), we can restrict ourselves to the case when p_1, p_2 and p_3 are very small compared with unity. In this case the expressions for the weight-average molecular weight reduce to

$$\begin{aligned} (MW)_w(\mathbf{p}) = & \{W_A p_1 p_2 (2R_1 - 1)(N_A M_A R_1^{(\sigma_{AA})} R_4^{(\sigma_{BA}+1)} - p_2 \sigma_{BB} N_A M_A \\ & \times R_1^{(\sigma_{AA})} R_2^{(\sigma_{BB}-1)} R_3^{(\sigma_{AB}+1)} R_4^{(\sigma_{BA}+1)} + p_3 \sigma_{BA} N_B M_B R_1^{(\sigma_{AA})} R_2^{(\sigma_{BB}+1)} \\ & \times R_3^{(\sigma_{AB})} R_4^{(\sigma_{BA})}) + W_B p_1 p_2 (2R_2 - 1)(N_B M_B R_2^{(\sigma_{BB})} R_3^{(\sigma_{AB}+1)} \\ & - p_1 \sigma_{AA} N_B M_B R_1^{(\sigma_{AA}-1)} R_2^{(\sigma_{BB})} R_3^{(\sigma_{AB}+1)} R_4^{(\sigma_{BA}+1)} + p_3 \sigma_{AB} N_A M_A \\ & \times R_1^{(\sigma_{AA}+1)} R_2^{(\sigma_{BB})} R_3^{(\sigma_{AB})} R_4^{(\sigma_{BA})})\} / \{ [W_A p_2 R_1 (R_1 + p_1 - 1) \\ & + W_B p_1 R_2 (R_2 + p_2 - 1)] + [(1 - p_1 \sigma_{AA} R_1^{(\sigma_{AA}-1)} R_4^{(\sigma_{BA}+1)}) \\ & \times (1 - p_2 \sigma_{BB} R_2^{(\sigma_{BB}-1)} R_3^{(\sigma_{AB}+1)}) - p_3^2 \sigma_{AB} \sigma_{BA} R_1^{(\sigma_{AA}+1)} R_2^{(\sigma_{BB}+1)} \\ & \times R_3^{(\sigma_{AB}-1)} R_4^{(\sigma_{BA}-1)}] \} \end{aligned} \quad (47)$$

and

$$\begin{aligned} (MW)_w^<(\mathbf{p}) = & [W_A(N_A M_A - p_2 \sigma_{BB} N_A M_A + p_3 \sigma_{BA} N_B M_B) + W_B(N_B M_B - p_1 \sigma_{AA} \\ & \times N_B M_B + p_3 \sigma_{AB} N_A M_A)] / [(1 - p_1 \sigma_{AA})(1 - p_2 \sigma_{BB}) - p_3^2 \sigma_{AB} \sigma_{BA}]. \end{aligned} \quad (48)$$

To get the η 's we need to keep second-order terms in the expansion of the equations (29). In this way we find

$$(1 - p_{1c}\sigma_{AA})\eta_1 - p_{1c}\sigma_{BA}\eta_4 = u, \quad (49a)$$

$$(1 - p_{2c}\sigma_{BB})\eta_2 - p_{2c}\sigma_{AB}\eta_3 = v, \quad (49b)$$

$$\eta_3 - p_{3c}\sigma_{AA}\eta_1 - p_{3c}\sigma_{BA}\eta_4 = x \quad (49c)$$

and

$$\eta_4 - p_{3c}\sigma_{BB}\eta_2 - p_{3c}\sigma_{AB}\eta_3 = y, \quad (49d)$$

where

$$\begin{aligned} u &= \sigma_{AA}\varepsilon_1\eta_1 + \sigma_{BA}\varepsilon_1\eta_4 - \frac{1}{2}p_{1c}\sigma_{AA}^2\eta_1^2 - p_{1c}\sigma_{AA}\sigma_{BA}\eta_1\eta_4 - \frac{1}{2}p_{1c}\sigma_{BA}^2\eta_4^2 \\ &= \varepsilon_1\eta_1/p_{1c} - \eta_1^2/2p_{1c}, \end{aligned} \quad (50)$$

$$\begin{aligned} v &= \sigma_{BB}\varepsilon_2\eta_2 + \sigma_{AB}\varepsilon_2\eta_3 - \frac{1}{2}p_{2c}\sigma_{BB}^2\eta_2^2 - p_{2c}\sigma_{BB}\sigma_{AB}\eta_2\eta_3 - \frac{1}{2}p_{2c}\sigma_{AB}^2\eta_3^2 \\ &= \frac{p_{3c}\sigma_{AB}\varepsilon_2\eta_1}{p_{1c}(1-p_{2c}\sigma_{BB})} - \frac{p_{2c}p_{3c}^2\sigma_{AB}^2\eta_1^2}{2p_{1c}^2(1-p_{2c}\sigma_{BB})^2}, \end{aligned} \quad (51)$$

$$\begin{aligned} x &= \sigma_{BA}\varepsilon_3\eta_4 + \sigma_{AA}\varepsilon_3\eta_1 - \frac{1}{2}p_{3c}\sigma_{BA}^2\eta_4^2 - p_{3c}\sigma_{BA}\sigma_{AA}\eta_1\eta_4 - \frac{1}{2}p_{3c}\sigma_{AA}^2\eta_1^2 \\ &= \varepsilon_3\eta_1/p_{1c} - p_{3c}\eta_1^2/2p_{1c}^2 \end{aligned} \quad (52)$$

and

$$\begin{aligned} y &= \sigma_{AB}\varepsilon_3\eta_3 + \sigma_{BB}\varepsilon_3\eta_2 - \frac{1}{2}p_{3c}\sigma_{AB}^2\eta_3^2 - p_{3c}\sigma_{AB}\sigma_{BB}\eta_2\eta_3 - \frac{1}{2}p_{3c}\sigma_{BB}^2\eta_2^2 \\ &= \frac{p_{3c}\sigma_{AB}\varepsilon_3\eta_1}{p_{1c}(1-p_{2c}\sigma_{BB})} - \frac{p_{3c}^2\sigma_{AB}^2\eta_1^2}{2p_{1c}^2(1-p_{2c}\sigma_{BB})^2}. \end{aligned} \quad (53)$$

The second-order quantities u , v , x and y are not independent but satisfy the relation

$$\begin{aligned} 0 &= p_{2c}p_{3c}\sigma_{AA}\sigma_{AB}u + (1-p_{1c}\sigma_{AA} - p_{3c}^2\sigma_{AB}\sigma_{BA})v \\ &\quad + p_{2c}\sigma_{AB}(1-p_{1c}\sigma_{AA})x + p_{2c}p_{3c}\sigma_{AB}\sigma_{BA}y. \end{aligned} \quad (54)$$

A substitution of the expressions (50)–(53) in (54) leads to the relation

$$\begin{aligned} \eta_1 &= \frac{1}{F}[2p_{1c}\sigma_{AA}(1-p_{2c}\sigma_{BB})^2\varepsilon_1 + 2p_{1c}p_{3c}^2\sigma_{BB}\sigma_{AB}\sigma_{BA}\varepsilon_2 \\ &\quad + 4p_{1c}p_{3c}\sigma_{AB}\sigma_{BA}(1-p_{2c}\sigma_{BB})\varepsilon_3], \end{aligned} \quad (55)$$

where $F \equiv (1-p_{2c}\sigma_{BB})^2 + p_{3c}\sigma_{AB}(1-p_{1c}\sigma_{AA})$. By using equations (49) again, we get

$$\begin{aligned} \eta_2 &= (1/F)[2p_{2c}p_{3c}\sigma_{AA}\sigma_{AB}(1-p_{2c}\sigma_{BB})\varepsilon_1 \\ &\quad + 2p_{2c}p_{3c}\sigma_{BB}\sigma_{AB}(1-p_{1c}\sigma_{AA})\varepsilon_2 + 4p_{2c}p_{3c}^2\sigma_{AB}^2\sigma_{BA}\varepsilon_3], \end{aligned} \quad (56)$$

$$\eta_3 = (1/F)[2p_{3c}\sigma_{AA}(1-p_{2c}\sigma_{BB})^2\varepsilon_1 + 2p_{3c}^3\sigma_{BB}\sigma_{AB}\sigma_{BA}\varepsilon_2 + 4p_{3c}^2\sigma_{AB}\sigma_{BA}(1-p_{2c}\sigma_{BB})\varepsilon_3], \quad (57)$$

$$\eta_4 = (1/F)[2p_{3c}^2\sigma_{AA}\sigma_{AB}(1-p_{2c}\sigma_{BB})\varepsilon_1 + 2p_{3c}^2\sigma_{BB}\sigma_{AB}(1-p_{1c}\sigma_{AA})\varepsilon_2 + 4p_{3c}^3\sigma_{AB}^2\sigma_{BA}\varepsilon_3]. \quad (58)$$

Now, the expression (48) for $(MW)_w^<(\mathbf{p})$, very near the threshold, can be written as

$$\begin{aligned} (MW)_w^<(\boldsymbol{\varepsilon}) &= -[W_A(N_A M_A - p_{2c}\sigma_{BB}N_A M_A + p_{3c}\sigma_{BA}N_B M_B) + W_B(N_B M_B \\ &\quad - p_{1c}\sigma_{AA}N_B M_B + p_{3c}\sigma_{AB}N_A M_A)]/[(1-p_{2c}\sigma_{BB})\sigma_{AA}\varepsilon_1 \\ &\quad + (1-p_{1c}\sigma_{AA})\sigma_{BB}\varepsilon_2 + 2p_{3c}\varepsilon_3\sigma_{AB}\sigma_{BA}], \end{aligned} \quad (59)$$

while, by using (55), (56), (57) and (58), the expression (47) for $(MW)_w(\mathbf{p})$, above but very near the threshold, becomes

$$(MW)_w^>(\boldsymbol{\varepsilon}) = (MW)_w^<(-\boldsymbol{\varepsilon}). \quad (60)$$

We know that below the threshold $P^<(\mathbf{p}) = G^<(\mathbf{p}) = 0$. Above but very near the

threshold, the expression (40) for $G(\mathbf{p})$ can be written as

$$\begin{aligned} G^>(\boldsymbol{\varepsilon}) &= W_A \frac{\eta_1(1+p_{1c})}{p_{1c}} + W_B \frac{\eta_2(1+p_{2c})}{p_{2c}} \approx W_A \frac{\eta_1}{p_{1c}} + W_B \frac{\eta_2}{p_{2c}} \\ &= \left(\frac{2W_A}{F}(1-p_{2c}\sigma_{BB})^2 + \frac{2W_B}{H}p_{3c}^2\sigma_{AB}\sigma_{BA} \right) \varepsilon_1\sigma_{AA} \\ &\quad + \left(\frac{2W_A}{F}p_{3c}^2\sigma_{AB}\sigma_{BA} + \frac{2W_B}{H}(1-p_{1c}\sigma_{AA})^2 \right) \varepsilon_2\sigma_{BB} \\ &\quad + \left(\frac{4W_A}{H}p_{3c}^2\sigma_{AB}\sigma_{BA}^2 + \frac{4W_B}{F}p_{3c}^2\sigma_{AB}^2\sigma_{BA} \right) \varepsilon_3, \end{aligned} \quad (61)$$

where $H = (1-p_{1c}\sigma_{AA})^2 + p_{3c}\sigma_{BA}(1-p_{2c}\sigma_{BB})$. The expression (39) for $P^>(\boldsymbol{\varepsilon})$ may be obtained from this last relation by the substitutions $W_A \rightarrow C_A$ and $W_B \rightarrow C_B$.

Finally, we will use the relations (9), (13)–(17) in order to find the threshold, $P^>(\boldsymbol{\varepsilon})$, $G^>(\boldsymbol{\varepsilon})$, $(MW)_w^<(\mathbf{p})$, $(MW)_w^<(\boldsymbol{\varepsilon})$ and $(MW)_w^>(\boldsymbol{\varepsilon})$ as a function of measurable quantities. In this way, we obtain:

$$(1-\rho_{AAc}N_A)(1-\rho_{BBc}N_B) - (C_A/C_B)\rho_{ABc}^2N_A N_B = 0, \quad (62)$$

$$\begin{aligned} G^>(\Delta\mathbf{p}) &= [(2W_A/F)(1-\rho_{BBc}N_B)^2 + (2W_B/H)(C_A/C_B)\rho_{ABc}^2N_A N_B]N_A\Delta\rho_{AA} \\ &\quad + [(2W_A/F)(C_A/C_B)\rho_{ABc}^2N_A N_B + (2W_B/H)(1-\rho_{AAc}N_A)^2]N_B\Delta\rho_{BB} \\ &\quad + [(4W_A/H)(C_A/C_B)\rho_{ABc}^2N_A^2N_B \\ &\quad + (4W_B/F)(C_A/C_B)^2\rho_{ABc}^2N_A N_B^2]\Delta\rho_{AB}, \end{aligned} \quad (63)$$

where now, $F = (1-\rho_{BBc}N_B)^2 + (C_A/C_B)\rho_{ABc}N_B(1-\rho_{AAc}N_A)$, $H = (1-\rho_{AAc}N_A)^2 + \rho_{ABc}N_A(1-\rho_{BBc}N_B)$, and where $\Delta\rho_{AA} = \rho_{AA} - \rho_{AAc}$, $\Delta\rho_{BB} = \rho_{BB} - \rho_{BBc}$ and $\Delta\rho_{AB} = \rho_{AB} - \rho_{ABc}$. The expression for $P^>(\Delta\mathbf{p})$ is obtained from this last relation by making the substitutions $W_A \rightarrow C_A$ and $W_B \rightarrow C_B$. The relations (48), (59) and (60), for the weight-average molecular weight of the finite molecules, now become

$$\begin{aligned} (MW)_w^<(\mathbf{p}) &= \{W_A N_A M_A [1 - \rho_{BB}N_B + \rho_{AB}N_B(M_B/M_A)] \\ &\quad + W_B N_B M_B [1 - \rho_{AA}N_A + \rho_{AB}N_A(W_A/W_B)]\} / \{ (1 \\ &\quad - \rho_{AA}N_A)(1 - \rho_{BB}N_B) - \rho_{AB}^2 N_A N_B (C_A/C_B) \}, \end{aligned} \quad (64)$$

$$\begin{aligned} (MW)_w^<(\Delta\mathbf{p}) &= -\{W_A N_A M_A [1 - \rho_{BBc}N_B + \rho_{ABc}N_B(M_B/M_A)] \\ &\quad + W_B N_B M_B [1 - \rho_{AAc}N_A + \rho_{ABc}N_A(W_A/W_B)]\} / \{ (1 - \rho_{BBc}N_B) \\ &\quad \times N_A \Delta\rho_{AA} + (1 - \rho_{AAc}N_A)N_B \Delta\rho_{BB} + 2(C_A/C_B)\rho_{ABc}\Delta\rho_{AB}N_A N_B \} \end{aligned} \quad (65)$$

and

$$(MW)_w^>(\Delta\mathbf{p}) = (MW)_w^<(-\Delta\mathbf{p}). \quad (66)$$

As we can see, all these results are independent of the correlations existing in the system. The expressions (63), (65) and (66) indicate that the exponents β_p and γ_p , describing the behaviour near the threshold, are both equal to the mean-field value one, which is a consequence of our Bethe lattice approximation.

We now consider some particular cases:

(i) *One polymer system with two different lengths.*

In this case $M_A = M_B = M$, and W_A and W_B coincide with C_A and C_B , respectively.

Also, we have only one type of cross-linking agent. This in turn means that X_{AA} , X_{BB} and X_{AB} are not arbitrary but satisfy the relations

$$\frac{X_{AA}}{X_{\text{cross}}} = \frac{\text{number of contacts } A-A \text{ per site}}{\text{total number of contacts per site}},$$

$$\frac{X_{BB}}{X_{\text{cross}}} = \frac{\text{number of contacts } B-B \text{ per site}}{\text{total number of contacts per site}},$$

$$\frac{X_{AB}}{X_{\text{cross}}} = \frac{\text{number of contacts } A-B \text{ per site}}{\text{total number of contacts per site}}.$$

So, on using expressions (10), (11) and (12a), we obtain the relations

$$X_{AA} = \frac{1}{2}C_A\phi_A\rho = \frac{1}{2}C_A^2\rho, \quad (67)$$

$$X_{BB} = \frac{1}{2}C_B\phi_B\rho = \frac{1}{2}C_B^2\rho, \quad (68)$$

$$X_{AB} = C_A(1 - \phi_A)\rho = C_AC_B\rho, \quad (69)$$

because the system is not correlated in this case. Here ρ is the fraction of monomers that are cross-linked. Introducing these last relations into (5), (6), (7) and (8) leads to

$$\rho_{AA} = C_A\rho, \quad \rho_{BB} = C_B\rho, \quad (70), (71)$$

$$\rho_{AB} = C_B\rho, \quad \rho_{BA} = C_A\rho. \quad (72), (73)$$

The expression (62) for the threshold becomes

$$1 - \rho_c(C_A N_A + C_B N_B) = 0, \quad (74)$$

which coincides with an expression derived first by Stockmayer (1944), up to our approximation of long chains. The expression (64) for $(MW)_w^<(\rho)$ is now

$$(MW)_w^<(\rho) = M \frac{C_A N_A + C_B N_B}{1 - \rho(C_A N_A + C_B N_B)}, \quad (75)$$

which is Stockmayer's expression, up to the same approximation. Finally, the equation (63) for $G^>(\Delta\rho)$, above but very near the threshold, can be written as

$$G^>(\Delta\rho) = 2 \frac{(C_A N_A + C_B N_B)^3}{C_A N_A^2 + C_B N_B^2} \Delta\rho; \quad (76)$$

an expression that can be derived from a formula first quoted by Flory (1953, p 380).

(ii) *One monodisperse polymer system*

In this case $N_A = N_B = N$ also, and the relation (74) gives

$$1 - \rho_c N = 0, \quad (77)$$

and we recover a well known formula by Flory (1941, 1953). Also, in this case,

$$(MW)_w^<(\rho) = MN/(1 - \rho N) \quad (78)$$

and

$$G^>(\Delta\rho) = 2N\Delta\rho. \quad (79)$$

It is interesting to note that the same results can be obtained from equations (62), (63) and (64) by making $W_A = 1$, $N_A = N$, $M_A = M$, $\rho_{AA} = \rho$, $\rho_{AB} = \rho_{BB} = 0$, as it should be.

3. Physical cross-linking and the gelation curves

An interesting example of physical cross-linking concerns some polymeric systems, such as swine skin gelatin, where the monomers are capable of forming hydrogen bonds when they touch (Tanaka *et al* 1979, Ruiz-Azuara *et al* 1980, Coniglio *et al* 1979, Gonzalez and Muto 1980). For the case of a binary mixture of such polymer systems, one has to introduce, besides the Van der Waals interactions U_{AA} , U_{BB} and U_{AB} between nearest-neighbour monomeric units, the hydrogen bonding directional interactions E_{AA} , E_{BB} and E_{AB} . In this way, the energy of a bond $A-A$ is

$$-\varepsilon_{AA} = \begin{cases} -U_{AA} \text{ (Van der Waals) with weight } g_{AA} \\ -E_{AA} \text{ (bonding energy) with weight } 1 - g_{AA}, \end{cases}$$

the energy of a bond $B-B$ is

$$-\varepsilon_{BB} = \begin{cases} -U_{BB} \text{ (Van der Waals) with weight } g_{BB} \\ -E_{BB} \text{ (bonding energy) with weight } 1 - g_{BB}, \end{cases}$$

and the energy of a bond $A-B$ is

$$-\varepsilon_{AB} = \begin{cases} -U_{AB} \text{ (Van der Waals) with weight } g_{AB} \\ -E_{AB} \text{ (bonding energy) with weight } 1 - g_{AB}. \end{cases}$$

The energies E are generally one order of magnitude greater than the energies U . A pair of nearest-neighbour monomers is hydrogen bonded (cross-linked) when the interaction energy is $-E$. The probability that a pair of nearest-neighbour monomers $i-j$ ($i, j = A, B$) is hydrogen bonded (Coniglio *et al* 1979, Gonzalez and Muto 1980) is

$$p_{ij}(T) = (1 - g_{ij}) e^{(\beta E_{ij})} / [g_{ij} e^{(\beta U_{ij})} + (1 - g_{ij}) e^{(\beta E_{ij})}], \quad (80)$$

where $\beta = 1/kT$ and k is the Boltzmann constant. In this way, the numbers of cross-links $A-A$, $B-B$ and $A-B$ per site are not arbitrarily introduced from outside but they are fixed by the parameters $E - U$ and g , the concentration and temperature. On using expressions (10), (11) and (12a), these numbers are calculated as

$$X_{AA} = \frac{1}{2} C_A (z - 2) \phi_A p_{AA}(T), \quad (81)$$

$$X_{BB} = \frac{1}{2} C_B (z - 2) \phi_B p_{BB}(T), \quad (82)$$

$$\begin{aligned} X_{AB} &= C_A (z - 2) (1 - \phi_A) p_{AB}(T) \\ &= C_B (z - 2) (1 - \phi_B) p_{AB}(T). \end{aligned} \quad (83)$$

The fraction of cross-linked monomers (equations (5)–(8)) are then given by

$$\rho_{AA} = (z - 2) \phi_A p_{AA}(T) \approx (z - 2) C_A p_{AA}(T), \quad (84)$$

$$\rho_{AB} = (z - 2) (1 - \phi_A) p_{AB}(T) \approx (z - 2) (1 - C_A) p_{AB}(T), \quad (85)$$

$$\rho_{BB} = (z - 2) \phi_B p_{BB}(T) \approx (z - 2) (1 - C_A) p_{BB}(T), \quad (86)$$

$$\rho_{BA} = (z - 2) (1 - \phi_B) p_{AB}(T) \approx (z - 2) C_A p_{AB}(T), \quad (87)$$

where we have assumed, in the last equality, that the correlations in the system are weak. In this way, the equation for the gel point transforms into

$$[1 - (z - 2)C_A N_A p_{AA}(T)][1 - (z - 2)(1 - C_A)N_B p_{BB}(T)] - (z - 2)^2 C_A (1 - C_A) N_A N_B p_{AB}^2(T) = 0, \quad (88)$$

which is the desired relation between concentration and temperature. In figure 3 we

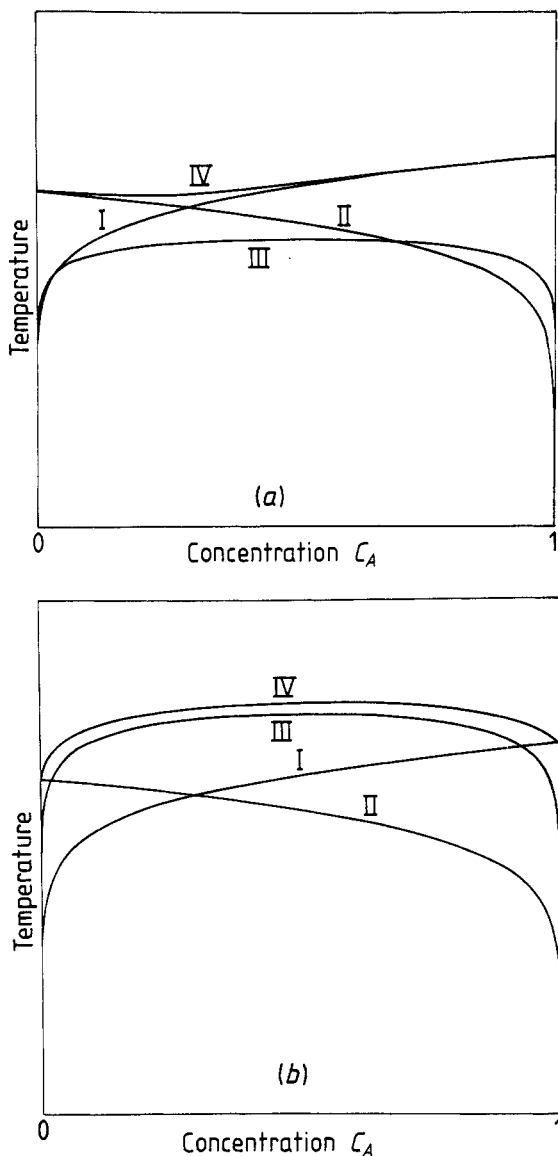


Figure 3. The gelation curves separating the gel phase (below) from the sol phase (above). In I, only crosslinks $A-A$ are present, in II, only crosslinks $B-B$ are present, in III, only crosslinks $A-B$ are present, and in IV, all three types of crosslinks are present. In (a) the parameters have been chosen such that $p_{AB}(T) < p_{AA}(T) \sim p_{BB}(T)$, while in (b) we have the inequality reversed.

have plotted the gelation curves, on a temperature–concentration diagram, for two sets of values of the parameters. In (a) we have chosen the parameters such that $p_{AB}(T) < p_{AA}(T) \sim p_{BB}(T)$, while in (b) we have the inequality reversed. In each of the figures we plotted the curves for which we have: (I) The onset of formation of an infinite molecule as if it were formed by cross-links $A-A$ only (the curve is obtained by making p_{BB} and p_{AB} equal to zero in equation (88)), (II) the onset of formation of the infinite molecule made by cross-links $B-B$ only (p_{AA} and p_{AB} equal to zero), (III) the onset of formation of the infinite molecule made by cross-links $A-B$ only (p_{AA} and p_{BB} equal to zero), and (IV) the onset of formation of the infinite molecule made by all types of cross-links (the full equation (88)). As a general feature, the curve IV is always above the other three curves, which means that it is always easier to have an infinite network made of all three types of cross-links at a given concentration. The curves I and II are well known in the studies of gelation in solvents by means of hydrogen bonds between the monomeric units composing the polymers (Tanaka *et al* 1979, Coniglio *et al* 1979, Ruiz-Azuara *et al* 1981, Gonzalez and Muto 1980). In our case of a binary mixture, the polymer not capable of forming hydrogen bonds (polymer B in curve I and polymer A in curve II) acts as a solvent as far as the gelation problem is concerned.

4. The phase separation

In the preceding discussion, we implicitly assumed a complete mixing of the species. We expect this hypothesis to hold for high temperatures. When we lower the temperature, however, this good miscibility breaks down and a segregation effect appears, as usual in two-component systems. Two different cases are to be considered, depending on the nature of the links between the chains.

(i) *Chemical cross-links* can be considered as ‘quenched’ cross-links at usual temperatures. In this case, the experimental procedure is important: cross-linking the system and then lowering the temperature does not lead to the same result as doing the same operation in the reverse order. The cooling down of the cross-linked system has been studied very recently by de Gennes (1979): Due to the presence of cross-links, the phase separation cannot occur well above the gel point, though there appear microdomains of A (B) rich phases. The size of these microdomains depends on the distance to the gel point. For more details the reader is referred to this reference.

(ii) *Physical cross-links*, on the other hand, can be considered as ‘annealed’ cross-links. They have a finite lifetime, and their number is fixed by monomer concentration and temperature. In this case we expect the phase separation to occur in the thermodynamic limit (note, however, that the equilibrium state may be reached in a very long time). Then, we expect the phase diagram to exhibit, besides the gelation curve discussed above (figure 3), a phase separation curve, and to be able to see the gelation curve at equilibrium, only outside the phase separation curve. The demixion problem can be described by the usual Flory–Huggins theory (Flory 1953, Huggins 1942a,b, Joanny 1978), with the parameters U_{ij} ($i, j = A$ or B) replaced by $U_{ij}(1 - p_{ij}(T)) + E_{ij}p_{ij}(T)$. Depending on the values we choose for the different parameters, the relative position of the gelation and phase separation curves may vary considerably. Let us mention here the possibility of getting a higher order critical point when the gelation curve goes through the critical point of the phase separation curve (Coniglio and Lubensky 1980). Then, for this point, we have two lengths (the correlation length for the fluctuations in the concentration and the connectedness length of the gelation problem) which simultaneously become infinite.

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