Gel formation in ionomers

Jean Francois Joanny
Department of Physics, University of California, Los Angeles, Ca. 90024, USA

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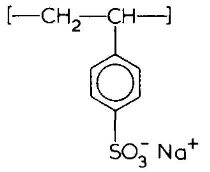
A theoretical study of the phase diagram of ionomer solutions in water is presented. These systems show two phase transitions: a demixing transition and a gelation. The demixing transition is studied using Flory's theory of polymer solutions. The gelation concentration always scales as the overlap concentration c^*; the dependence of the phase boundaries on temperature and on the fraction f of metallic groups along the chain is studied. At high temperatures, in a good solvent regime, c_{gel} is proportional to $f^{-8/5}$; at lower temperatures c_{gel} is proportional to f^{-1}.

INTRODUCTION

In the last few years, due to their increasing importance in industry, new techniques have been developed to synthesize rubbers. Some rubbers are now prepared by making a gel in solution and then expelling the solvent from the gel. The gel is usually constructed by making crosslinks between polymer chains. The crosslinking can be chemical as usual in gels, but it can also be physical[1–3]. The ionomer gels are a good example of the physically-crosslinked systems[4–7].

Ionomers are copolymers[8–11] where one constitutent is an organic monomer such as polystyrene and the other constituent is the same organic molecule carrying a metallic group (usually a sulphonate or carboxylate group) such as:



The fraction f and the distribution of the metallic groups along the chains may be chemically controlled.

When such polymer chains are diluted in a polar solvent, there is a dissociation of the polar group, and the chain is a polyelectrolyte carrying an average charge $-fe$ per monomer. The physical properties of polyelectrolytes have been extensively studied (see ref 12 and refs therein); the effective interaction between monomers is a repulsive Coulomb force and the chains are almost completely stretched.

However, if ionomer chains are diluted in a non-polar solvent such as benzene (the dielectric constant of which is $\epsilon \approx 1$) or if they are in a molten or solid phase, the metallic groups are not dissociated, and the polar groups are electric dipoles. The resulting physics is then completely different because of the attractive nature of the dipole–dipole interaction. Because of this attractive interaction, the dipoles have been experimentally recognized to make small clusters. In a solid or molten phase, clusters up to 150 dipoles have been observed[11]. In a non-polar solvent this association between dipoles serves as a crosslink which may lead to gelation[8]. In this paper, we are concerned with the conditions for the formation of this gel as functions of temperature and concentration.

The phase diagram of these ionomer solutions does not only involve gel formation. At sufficiently low temperatures the second virial coefficient between two chains may be negative. At low temperatures the solution then has a tendency to separate into two phases: one mostly composed of polymer, the other mostly of solvent. This demixing phase transition is similar to the Flory segregation of polymers in poor solvents[13,14]. There is a competition between the segregation and the gelation process. The order parameter for the segregation is the concentration, c, of monomers. The important property for gelation is the connectivity: two chains are connected if there is a physical link between them, i.e. if two dipoles, one from each chain, are bound together. A cluster is not associated with a concentration inhomogeneity; the concentration may be uniform and yet with existing clusters. The solution forms a gel when there is an infinite cluster. The formation of a gel can be detected by mechanical experiments; e.g. the bulk viscosity of the solution diverges at the gelation threshold. The physical gel has also to be distinguished from the network formed by entanglements when different chains begin to overlap (in the semidilute region[15]). There is another important difference between segregation and gelation: the gelation transition is not a thermodynamic transition and cannot be described by a free energy; it is rather related to percolation[20]. In the specific case of ionomers, the crosslinks are physical and can be destroyed by increasing the temperature, leading to a reversible gelation.

The section below is devoted to the process of association between dipoles, the two following sections study independently segregation and gelation, and in the last section, we attempt to describe the competition and the interferences between these two phase transitions.

INTERACTIONS BETWEEN DIPOLES: ASSOCIATION PHENOMENA

In solution in a non-polar solvent, the metal groups distributed along the ionomer chains interact with one another via a dipolar interaction and have a tendency to make clusters of two or more dipoles. This cluster formation is the electric analogue of the association of magnetic colloidal grains studied by de Gennes and Pincus[16] and Jordan[17].

Two monomers carrying dipoles $\vec{p}_1$ and $\vec{p}_2$ have an energy

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of interaction u_{12} depending on their distance apart, r:

$$u_{12} = \frac{1}{4\pi\epsilon r^3}\left[\mathbf{p}_1\cdot\mathbf{p}_2 - \frac{3}{r^2}(\mathbf{p}_1\cdot\mathbf{r})(\mathbf{p}_2\cdot\mathbf{r})\right] \qquad (1)$$

In order to characterize this interaction, it is useful to introduce a dimensionless coupling constant λ. If a is the size of a monomer and p the value of the dipole moment*:

$$\lambda = \frac{p^2}{4\pi\epsilon a^3 T} \qquad (2)$$

When λ is large, the most probable configuration for the dipoles is to be parallel to $\vec{r}$ and the attraction is much larger than the thermal agitation. This can lead to an association between dipoles. If λ is small the thermal agitation dominates and there is no association. At room temperature, for usual atomic dipoles (in a non-polar solvent $\epsilon \simeq 1$) $\lambda \sim 10$–100 and we are thus in the strong coupling limit.

Even in extremely dilute solution there are some contacts between dipoles; two dipoles are in contact if their distance is smaller than a few a. For simplification we shall assume that when two dipoles are in contact, there are only two possibilities; either they stick and form a dimer or they remain free and move independently. The energy gain u when two dipoles stick together is given y equation (1) with r equal to a few a:

$$u = -T\alpha\lambda \qquad (3)$$

where α is a constant of order unity.

The probability p_1 for any two dipoles in contact to form a dimer is then:

$$p_1 = \frac{e^{-u/T}}{1+e^{-u/T}}\,F(u/T) \qquad (4)$$

The first factor is just a Boltzman law, the second factor $[F(u/T)]$ is the probability that there is actually a bound state between the molecules (e.g. ref 27). The function $F(u/T)$ is given by:

$$F\left(\frac{u}{T}\right) = \frac{\Gamma(3/2,-u/T)}{\Gamma(3/2)} \qquad (5)$$

where $\Gamma(n,x)$ is the incomplete Γ function. At zero temperature p_1 is equal to 1; when the temperature becomes very large p_1 behaves like $(u/T)^{3/2}$ and goes to zero. The probability for two monomers to form a dimer is then:

$$p_2 = f^2 p_1 \qquad (6)$$

As we are dealing with dilute solutions, the probability of contact between more than two dipoles is extemely low, and we may neglect the formation of oligomers of more than two dipoles.

Another important parameter to characterize the dipolar interaction is the second virial coefficient which governs the segregation process. This virial coefficient has been calculated by Jordan[17]:

$$A_2 = -\pi a^3 \frac{e^{2\lambda}}{9\lambda^3} \quad (\lambda > 1) \qquad (7)$$

The second virial coefficient is negative (attractive force) and an increasing function of temperature. The attractive forces between dipoles also have an important effect on the configurational properties of isolated ionomer chains and many lead to a collapse. The Flory free energy for an isolated ionomer chain of N monomers and radius R is[13]:

$$\frac{F}{T} = \frac{3}{2}\frac{R^2}{Na^2} + \frac{1}{2}(v+f^2A_2)\frac{N^2}{R^3} + \frac{1}{6}w^2\frac{N^3}{R^6} \qquad (8)$$

where v is the excluded volume parameter and $w^2 \approx a^6$, the third virial coefficient between monomers. A collapse thus occurs when*:

$$(v+f^2A_2)\frac{N^{1/2}}{a^3} < -1 \qquad (9)$$

We will assume that the fraction of dipoles is small enough to avoid a collapse at high temperatures. If the number of dipoles is too large, the polymer and the solvent would be incompatible because of the hydrophilic nature of the ionic groups[8].

PHASE SEPARATION – SEGREGATION

At low temperatures, the second virial coefficient between chains is negative and leads to a separation of the solution into two phases[13,14]. However, ionomers are copolymers and one cannot exclude a microphase separation with formation of regions containing only dipoles and regions containing no dipoles. If the ionic groups are at the ends of the chain, one can, for instance, imagine the formation of micelles. A very powerful theoretical tool for the study of both segregation and microphase separation has turned out to be linear response theory[14,18]. In the following, for simplicity, we restrict ourselves to the study of ionomers with dipoles distributed at random along the chain; in this particular case we shall see that there is no microdomain formation.

Let us consider the solution at a thermodynamic equilibrium with a monomer concentration c. On each chain we label each monomer by a number i starting from one end. We introduce the concentration c_i of monomers labelled by

$$i \quad \sum_{i=1}^{N} c_i = c$$

We also define a variable u_i on each monomer which is 1 if the monomer carries a metallic group and 0 otherwise. If the metallic groups are distributed randomly, the mean value $\langle u_i\rangle$ averaged over all the chains is f, and u_i and u_j $(i \neq j)$ are independent variables:

$$\langle u_i\rangle = f$$

$$\langle u_i u_j\rangle = \langle u_i\rangle\langle u_j\rangle = f^2 \qquad (10)$$

We now displace the equilibrium by introducing a small fictitious potential $\delta\phi$ acting on all the monomers. This potential induces a change δc_i in the equilibrium concentra-

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* We choose a temperature unit where the Boltzmann constant is 1.

* For Gaussian chains ($R = N^{1/2}a$) the attractive interaction given by the second term of equation (8) is greater than T.

tions and a restoring potential $\delta\phi_{i,\mathrm{int}}$ on all the monomers.

In momentum space, the concentration shift $\delta c_i(q)$ for a given momentum q is proportional to the total potential acting on the monomers:

$$\delta c_i(q) = \sum_j \chi_{ij}(q)\,[\delta\phi(q) + \delta\phi_{j,\mathrm{int}}(q)] \tag{11}$$

χ_{ij} is the linear response between monomers i and j for an ideal isolated chain:

$$\chi_{ij} = -\frac{c}{TN}\exp-\left(\frac{q^2a^2}{6}\,|i-j|\right) \tag{12}$$

In the restoring potential $\delta\phi_{j,\mathrm{int}}$ there are two contributions, one coming from the excluded volume interactions acting on all monomers and one coming from the dipolar interaction. If we write the Flory excluded volume free energy in the usual way:

$$\frac{F}{T} = \frac{1}{2}vc^2 + \frac{1}{6}w^2c^3 \tag{13}$$

(v is the excluded volume parameter, an increasing function of temperature vanishing at a temperature θ, w^2 the third virial coefficient roughly independent of temperature) the contribution to $\delta\phi_{j,\mathrm{int}}$ is:

$$(v + w^2c)\,\delta c$$

$$\delta c = \sum_i \delta c_i \tag{14}$$

The dipolar contribution to the internal potential $\delta\phi_{j,\mathrm{int}}$ is:

$$u_j \sum_k u_k\,\delta c_k\,g(q) \tag{15}$$

$g(q)$ is the direct pair correlation function for the dipolar potential equation (1):

$$g(q) = \int \mathrm{d}^3\vec{r}\;\mathrm{e}^{i\vec{q}\vec{r}}\left[1 - \mathrm{e}^{-[u_{12}(r)/T]}\right] \tag{16}$$

It has been calculated by De Gennes and Pincus[16] and can be approximated after averaging over dipolar orientations by:

$$g(q) = A_2\,[1 - b(q^2a^2)] \tag{17}$$

where b is a number of order unity. Introducing equations (14) and (15) into equation (11), and averaging over the chain configurations, we obtain the RPA equations:

$$\delta c_i(q) = \sum_j \chi_{ij}\,[\delta\phi(q) + (v + w^2c)\,\delta c(q)$$

$$+ \sum_k \langle u_j u_k\rangle \delta c_k(q) g(q)] \tag{18}$$

If we introduce the linear response function χ of the solution:

$$\delta c = \chi\delta\phi \tag{19}$$

equation (18) yields:

$$\chi = \frac{-1}{(v + w^2c) + f^2g(q) + \dfrac{1}{\chi_0(q)}} \tag{20}$$

where we have introduced the notation

$$\chi_0 = -\sum_{ij}\chi_{ij}$$

which is the response function of an ideal chain first calculated by Debye:

$$\chi_0(x) = \frac{2}{x}\left[1 + \frac{e^{-x} - 1}{x}\right]\frac{cN}{T} \tag{21}$$

$$x = \frac{Nq^2a^2}{6}$$

$g(q)$ and $1/\chi_0$ are increasing functions of q. The response function χ is thus maximum for $q = 0$. There are no divergences of χ for non-zero q vector which would be characteristic of a microdomain formation. Thus there is no microdomain formation as previously suggested[18].

The divergence of χ at 0 wavevector indicates a separation of the solution into two phases, the curve of the plane c–T where χ shows a divergence being the spinodal line of this phase separation. Its equation is:

$$(v + f^2A_2) + \frac{1}{Nc} + w^2c = 0 \tag{22}$$

This equation for the spinodal curve could be derived from a usual Flory free energy:

$$\frac{F}{T} = \frac{c}{N}\log c + \frac{1}{2}\tilde{v}c^2 + \frac{1}{6}w^2c^3 \tag{23}$$

where $\tilde{v}$ would be a renormalized excluded volume parameter taking into account the dipolar interaction: $\tilde{v} = \tilde{v} + f^2A_2$. The only effect of the dipolar interaction, when the dipoles are distributed at random is thus to renormalize the excluded volume parameter.

GEL FORMATION AT HIGH TEMPERATURE

We turn now to the higher temperature region where the interactions between different chains are not important but where the interaction between two single dipoles carrying metallic groups is large enough to allow the formation of two or more monomers. This aggregation, which is not a thermodynamic process leads to the formation of a gel.

The first theory of gels proposed by Flory[19], discusses in a mean field approximation the formation of infinite polymer trees, completely ignoring the formation of loops. More recently the sol–gel transition has been related to the critical properties of the percolation theory[20,21]. This model has recently been improved by Coniglio and coworkers who proposed a site–bond percolation theory of gelation.

Our approach, which is more phenomenological, starts from the usual continuum model for semi-dilute solutions. We show subsequently that this model can be described in terms of site–bond percolation with an approximate lattice.

We thus start from an ionomer solution above the θ point (to avoid segregation, we need $\tilde{v} > 0$). At a concentration c below the overlap concentration c^*, the number of contacts between monomers of different chains is very small, and there is no formation of clusters. The gelation transition thus occurs in the so-called semi-dilute regime. In this regime, the chains overlap and form a network where the knots are not links but entanglements. A very simple description of this network can be made in terms of blobs[24]. The solution behaves like a melt of subunits of size ξ called blobs; inside each blob (on a length scale smaller than ξ) we see a single chain behaviour (excluded volume or Gaussian, depending on temperature); at larger length scales we see a melt behaviour where the chains are essentially ideal. If each blob contains g monomers ($g = N$ for $c = c^*$), the number of blobs per chain is:

$$n = \frac{N}{g} \quad (n = 1 \text{ for } c = c^*) \tag{24}$$

Each blob is in contact with one or a few other blobs of other chains. The total number of contacts between one fixed chain and all the others is proportional to the number of blobs per chain, n.

Let us now consider two particular chains in contact: they occupy a volume $R^d (R = n^{1/2}\xi$, in a d-dimensional space). The concentration of blobs of one chain is:

$$c_1 = \frac{n}{R^d} \tag{25}$$

So each blob of the other chain is in contact with $c_1 \xi^d$ blobs of this chain, and the total number of contacts between the two chains is:

$$\gamma = n c_1 \xi^d = n^{2-d/2} \tag{26}$$

The number of chains in contact with a particular chain is:

$$z = \frac{n}{\gamma} = n^{[(d/2)-1]} \tag{27}$$

Two chains in contact make a cluster if and only if at least one of their γ contacts is a physical link between two dipoles. The probability for two chains in contact to make a cluster is:

$$p = 1 - (1 - p_2)^{\gamma} \tag{28}$$

As in all the problems connected with bond percolation, we expect a gel formation when the total number of chains linked to a fixed one is of order 1.5 in three dimensions (e.g. see ref 25).

The gelation curve is thus given by:

$$zp \cong 1.5 \tag{29}$$

To make equation (28) more explicit we can distinguish two limits.

(a) If p_2 is close to one (all the contacts are links), the gelation threshold is $z = 1$ or using equation (27), $c = c^*$. We recover a result first found by De Gennes[24].

(b) If, as in the special case of ionomers, p_2 is much smaller than 1, equation (28) reduces to:

$$p_2 = \frac{1}{n} \tag{30}$$

(In a melt $g = 1$, $n = N$ and equation (30) gives the well-known threshold for vulcanization[26] $p_2 = 1/N$.)

The gel concentration c_{gel} still scales like the overlap concentration c^*. However, p_2 being very small, the ratio c_{gel}/c^*, although independent of N, is much larger than one, and the gelation occurs in the semi-dilute régime. The gelation has nothing to do with concentration inhomogeneities. It is just related to the nature of the knots of the semi-dilute solution pseudo-gel. When enough links are actual physical crosslinks, the pseudo-gel (network) becomes a true gel.

We can explicitly calculate c_{gel} from equation (30) for two cases.

(i) For excluded volume blobs[15] the overlap concentration is $c^* \approx N^{-4/5}$ and the correlation length is $\xi \sim c^{-3/4}$. Thus:

$$n = \left(\frac{c}{c^*}\right)^{5/4} \tag{31}$$

and

$$c_{\text{gel}} = c^* f^{-8/5} \left[\frac{e^{-u/T}}{1 + e^{-u/T}} F\left(\frac{u}{T}\right)\right]^{-4/5} \tag{32}$$

(ii) For Gaussian blobs, $c^* \sim N^{-1/2}$, $\xi \sim 1/c$ and c_{gel} is given by:

$$c_{\text{gel}} = c^* \frac{1}{f} \left[\frac{e^{-u/T}}{1 + e^{-u/T}} F\left(\frac{u}{T}\right)\right]^{-1/2} \tag{33}$$

At high temperature excluded volume effects should be important; at lower temperatures, near the θ temperature the chain should be Gaussian. Experimentally, the dependence of c_{gel} on f should then change from a $1/f$ law to a $1/f^{8/5}$ law by increasing the temperature.

The gelation line is not the only interesting quantity in the gel formation. Indeed, most physical quantities (e.g. size of the clusters, viscosity of the solution, etc.) have singular behavours at the gelation threshold. This behaviour should be calculated in terms of percolation critical exponents[20,21]. However, the number of chains which can be linked with one chain z is much larger than one (see equation 27 with $n \gg 1$). If this quantity z (which is the equivalent of the coordination number in a lattice model) is much larger than one, the mean field theory for percola-

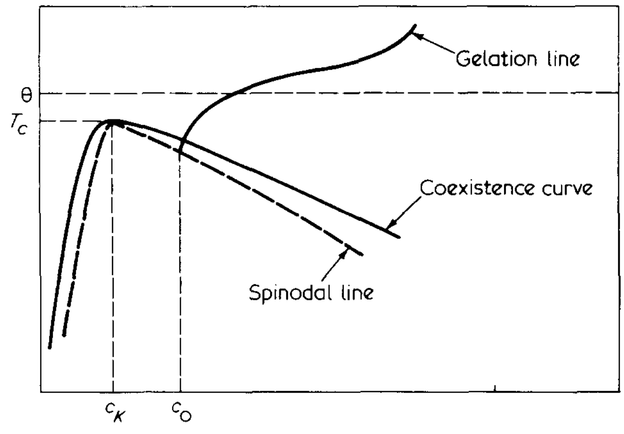

Figure 1 Temperature concentration phase diagram for ionomer solutions. T_c is the critical temperature, c_K the critical concentration and c_0 the point where the gelation line and the coexistence curve meet

tion gives correct results even close to the gelation threshold[26]. (This property is well known for thermal phase transitions like superconductivity and means that if the number of interacting neighbours is big, the fluctuations are small. The critical properties of percolation can be mapped on the critical properties of a Pott's model[27].) Since the property which plays the role of fluctuations in the percolation problem is loop formation, this means that in the study of the critical properties loops can be neglected and that the basic clusters are polymers trees.

Let us now try to describe the formation of the gel by a generalized lattice model. At each site of the lattice, we put a polymer chain. The distance between two nearest neighbour chains is the radius R of the chains. (The radius of the chains varies with concentration, but this is not relevant for percolation properties.) In our description of the gelation process, the number of nearest neighbours of one chain (number of chains which can be linked to a given one) changes with the concentration. We can thus follow Stanley and introduce a lattice where the coordination number ζ is the maximum number of nearest neighbours a chain can have, $\zeta = N^{1/2}$ (see equation 27 with $g = 1$). As explained by Stanley the gelation is the result of two percolation problems on this lattice: (A) a site percolation, (B) a bond percolation between nearest neighbour sites; this percolation being relevant if we are above the percolation threshold for the site percolation. In terms of polymer solutions the site percolation (A) describes just the formation of the semi-dilute polymer solution. For site percolation, we know[25] that at the threshold, the fraction of space occupied by the sites is of order one. The site percolation threshold is thus $c \approx c^*$. Above this threshold we have an infinite cluster (the semi-dilute network) and we can study the bond percolation problem (B) which we called connectivity before. The threshold given by $\vec{\zeta}_p = 1$ where $\vec{\zeta}$ is the effective number of nearest neighbours in the infinite cluster ($\vec{\zeta} = z$) and p the probability of having a bond between two sites.

PHASE DIAGRAM OF THE IONOMER SOLUTION

In the two previous sections we have studied independently the two phase transitions of the ionomer transition. We can summarize the results on a phase diagram. The demixing transition is characterized by a usual coexistence curve which could be calculated from the free energy (equation 13). However, this coexistence curve is not very different from the spinodal line calculated in equation (12).

The critical concentration is $c_K \approx c^*$. In the limit of infinite temperatures the gelation line goes to infinity as $c_{gel}/c^* \approx (T/u)^{6/5}$ (see equation 32). The two curves (gelation line and coexistence curve) meet at a certain concentration $c = c_0$†. However, in the vicinity of $c = c_0$ the two transitions may not be treated independently. The objects of the segregation are no longer chains but clusters of chains, and the fluctuations of concentration due to the spinodal line may create regions where the concentration is large and favours the formation of clusters. We now give a qualitative argument tending to show that the two curves meet in the vicinity of the critical point.

(1) Suppose that c_0 is smaller than c_K. Before the segregation we have the formation of big clusters of S chains. The Flory free energy for these chains is then:

$$\frac{F}{T} = \frac{c}{NS}\log c + \frac{1}{2}\tilde{v}c^2 + \frac{1}{6}w^2c^2 \qquad (34)$$

(It is the same as equation 13 except that the translational term $(c/NS)\log c$ is reduced, because the clusters all include NS monomers.) The critical concentration for the solution is now $1/NS^{1/2}$. This concentration goes to zero as the concentration gets closer and closer to c_0 (the number of chains per cluster becomes infinite), and so segregation occurs before we reach the concentration c_0. This implies $c_K < c_0$.

(2) Suppose c_0 is larger than c_K and that the solution is at critical temperature T_c. If we start from zero concentration and increase the concentration, when we approach the critical concentration c_K, the fluctuations become important, we can have regions of size ξ_T (the thermal correlation length, characteristic length of thermal fluctuations) such that the concentration is above c_0. This leads to the formation of clusters of size ξ_T which become infinite at $c = c_K$.

If the two curves meet at the critical point, this point as noticed by Stanley is of a very special type: there are two characteristic lengths, the thermal length ξ_T and the percolation length $\xi_p = R(c - c_{gel}/c_{gel})^{-\nu_p}$ which is the correlation length of pairs of dipoles. These two lengths should become equal and diverge with a renormalized exponent which is neither the percolation exponent nor the Ising exponent of the thermal transition.

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† When the equilibrium concentration of the dense phase of the demixing transition is higher than c_0, it is above the gelation threshold; the dense phase is actually a gel.

‡ If c_0 is close to c^*, near c_0, $n = 1$, and the mean field theory is not a good description of percolation; the percolation correlation length diverges at c_0 with an exponent $\nu_p \neq 1/2$

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