Vulcanization and critical exponents

M. Daoud

Vulcanization and critical exponents

M. Daoud (*)

Boston University, Department of Physics, Boston, Mass. 02215, U.S.A.

Résumé. — Nous étudions un problème particulier de vulcanisation de chaînes en solutions semi-diluées où on a ajouté une concentration ρ d'agent vulcanisateur. Ce problème est équivalent à la percolation d'éléments ayant une fonctionnalité f dépendant à la fois de la longueur N des chaînes initiales et de la concentration C en monomères. Notre approche nous permet de tenir compte des effets de volume exclu et de concentration en monomères. Nous montrons que les exposants critiques de percolation peuvent être observés dans certaines conditions. Alors que la théorie de Flory prévoit une région critique extrêmement étroite pour la vulcanisation du liquide polymérique, et qu'on n'observe dans ce cas que les exposants de champ moyen, nous montrons que la largeur de la région critique, ainsi que le point de gel, dépendent fortement de la concentration. Ceci nous permet d'envisager la concentration C^* de recouvrement d'un autre point de vue. Nous discutons également le gonflement des gels ainsi obtenus.

Abstract. — We consider a particular case of vulcanization of polymer chains in a semi dilute solution where a concentration ρ of vulcanizing agent has been added. This problem is equivalent to the percolation of elements having a functionality f depending both on the length N of the initial chains and on the monomer concentration C. Our approach allows us to take into account excluded volume effects as well as monomer concentration effects. We show that the critical percolation exponents can be observed under certain conditions. Whereas Flory's theory for vulcanization in the melt predicts a very small critical region and only mean field exponents can be observed in this case, we show that the width of the critical region, as well as the gel point, depend strongly on concentration. This allows us to consider the overlap concentration C^* from a different point of view. We also discuss the swelling of these gels.

Introduction. — Gelation and vulcanization problems have been studied for a very long time both theoretically [1]-[3] and experimentally [2], [3]. Only connectivity properties were considered, linked to the existence of a gel phase above a threshold (gel point). Not all the solvent effects were taken into account by these approaches. Thus the problem, as it was studied, was purely geometrical [2]. On the other hand, polymer solutions have also been studied extensively these last few years [5]-[10] and it was shown that solvent effects are very important for the conformation of the chains [9]-[11]. But there was no satisfactory theoretical connection between these two problems, although it was known through swelling properties, for instance, that solvent effects may have dramatic effects on gels. However, very significant progress has been made very recently [11], [12].

We wish to consider here a special case of gelation, namely the gelation of chains, or vulcanization :

We start with a polymer solution where a very small amount ρ of a vulcanizing agent is added. Under the influence of this agent, the polymer chains cross-link. Above a threshold ρ_c, there is an infinite branched chain (gel). The purpose of the paper is mainly to show that critical exponents can be observed under certain conditions in the vicinity of the threshold. Flory [2] considered this problem first, for chains in the melt. De Gennes [13] showed recently that in this case, the observed exponents should be classical. This is due to the narrowness of the critical region, and was related to the length N of the chains. In the following, we are going to analyse the preceding problem in a different way, and to extend it to the case of semi dilute solutions. Let us emphasize that the problem which we are considering here is the gelation of chains. So we suppose that the number of cross-links of a chain with the others is small. The changes in our approach when this number increases are briefly discussed in the conclusion.

Let us end with a word of caution. The properties we are discussing in the semi dilute case are valid for short time scales. The experimental situation we

(*) On leave of absence from C.E.N. Saclay.

have in mind is the following : we suppose that the agent is photoactive. Then the mixture made of the polymer solution and the cross-linking agent is flashed for a very short time, during which the cross-linking process occurs. We suppose that there is no further cross-link.

1. Vulcanization in the melt.

— Let us first consider the case of a polymer melt. This has been studied by Flory [2] and de Gennes [13] who showed that only mean field exponents should be observed. Let us consider this from a slightly different point of view. We know that in the melt all the monomers are in contact, leading to a mean field value for the radius of gyration, for instance.

$$R^2 \sim N l^2 \tag{1}$$

where l is the statistical length.

Our starting point is a remark made by de Gennes [13] that in the problem of chain percolation, there is an elementary length which is the radius of a chain. So what we are going to do is to reduce the chain percolation problem to a polyfunctional condensation [14]. This is achieved by two scale-transformations :

1) on the lengths

$$r \rightarrow r' = \frac{r}{R} \tag{2a}$$

2) on the arc lengths

$$n \rightarrow n' = \frac{n}{N}. \tag{2b}$$

Thus a chain is replaced by its centre of mass, (or by a renormalized monomer). So, in the renormalized problem, we have points at each site ; each point has a functionality $f = N$, and each bond has a probability ρ of being present. As N is very large, we expect mean field theory to be valid. The threshold is

$$\rho_c \sim N^{-1} \tag{3}$$

which is Flory's result [2]. (So we check that ρ is very small indeed.) Different characteristic quantities [14] can be calculated in the renormalized problem. The corresponding expression in the initial chain percolation problem is obtained by using relations (2a) and (2b). Let $\delta\rho$ be a small quantity. The mean radius of a branched molecule is

$$\xi_p \sim \left(\frac{\delta\rho}{\rho_c}\right)^{-\nu_{\underline{p}}} N^{1/2} \tag{4}$$

which is de Gennes' result [13]. The mean size of a branched molecule, which is the number of monomers in this molecule, is

$$Z \sim \left(\frac{\delta\rho}{\rho_c}\right)^{-\gamma_{\underline{p}}} N. \tag{5}$$

The mean number of molecules per site (i.e. branched polymer concentration) is

$$N \sim \left(\frac{\delta\rho}{\rho_c}\right)^{2-\alpha_{\underline{p}}} N^{-3/2}. \tag{6}$$

The gel fraction, which is the probability that a monomer belongs to the infinite molecule is

$$\Theta \sim \left(\frac{\delta\rho}{\rho_c}\right)^{\beta_{\underline{p}}} \tag{7}$$

(Θ is the number of monomers belonging to the infinite molecule divided by the total number of monomers, so it is scale invariant). Here, $\alpha_{\underline{p}}$, $\beta_{\underline{p}}$, $\gamma_{\underline{p}}$, $\nu_{\underline{p}}$ are exponents in the percolation problem. Their numerical values depend on the value of $\delta\rho$ relative to the critical region.

For our purpose here, we only need the mean field values ($\alpha_{\underline{p}} = -1$, $\beta_{\underline{p}} = \gamma_{\underline{p}} = 1$ $\nu_{\underline{p}} = \frac{1}{2}$) in order to determine the width of the critical region by a Ginzburg argument. To do this, we evaluate the relative fluctuation $x = \langle \delta v^2 \rangle / \langle v \rangle^2$ of the number of connected monomers in a volume $\xi_{\underline{p}}^d$.

This relative fluctuation x is easily shown to be [13]

$$x \sim Z\Theta^{-2} \xi_{\underline{p}}^{-d} C^{-1} \tag{8}$$

where C is the monomer concentration. Here $C \sim l^{-d}$. In the mean field region, the fluctuations are negligible ($x \ll 1$). By using (4) to (8) and the mean field values for the exponents, we easily find for the mean field region ($x \ll 1$) :

$$\frac{\delta\rho}{\rho_c} > N^{-1/3} \qquad (d = 3). \tag{9}$$

So the critical region is defined by

$$\delta\rho \ll \delta\rho^*$$

$$\frac{\delta\rho^*}{\rho_c} \sim N^{-1/3} \tag{10}$$

which shows that the critical region is very narrow for usual polymer chains (note that $\rho_c \sim N^{-1} \ll 1$). We are going to see that this is no longer true in semi dilute solutions.

2. Semi dilute solution.

— In the melt, all the monomers were equally reactive because each was surrounded by other monomers in contact with it. This situation is no longer valid in semi dilute solutions : a given chain no longer has N contacts with the other chains (including contacts with itself) but a smaller number, depending on the monomer concentration C. This is very important because only monomers in contact can make cross-links. The situation before the cross-linking process may be described as follows.

(A more detailed discussion of semi dilute solutions can be found in refs. [9] and [10]) :

— For small distances, solvent effects, i.e. excluded volume effects, are present. The chain behaves as if it were alone. This is what we called a *blob*. If we suppose that it contains g statistical elements and has a radius ξ,

$$\xi \sim g^{3/5} \sim C^{-3/4} \qquad (11)$$

ξ can be seen as the mean distance between two successive contacts of a chain.

— For larger distances, due to the contacts between chains, the excluded volume effect is screened. This may be seen in the following way : if we take the blob as a statistical element, the semi dilute solution looks like the melt. In particular, the radius of gyration is

$$R^2 \sim \frac{N}{g}\xi^2$$
$$\sim NC^{-1/4} . \qquad (12)$$

This is a hint which shows us how to attack the vulcanization problem : in the semi dilute case, a transformation amounting to taking the blob as a statistical element reduces the problem to the usual case of melts as considered in section 1.

This transformation can be written : for distances

$$r \to r' = \frac{r}{\xi} \sim rc^{3/4} \qquad (13a)$$

for arc lengths

$$n \to n' \simeq \frac{n}{g} \sim nc^{5/4} . \qquad (13b)$$

In this transformation, the length N of a chain becomes

$$N \to N' = \frac{N}{g} \sim NC^{5/4} . \qquad (14)$$

Because all the monomers are not equally reactive, ρ remains unchanged in the transformation [16]. (This transformation does not change the probability that two *blobs* cross-link.) Notice that in the transformed problem, the renormalized monomers (i.e. the blobs) are equally reactive.

The problem has now been reduced to that which we studied in section 1. In terms of the variables r' and n' the results are the same as in section 1. Let us just quote those we need (in terms of r and n) for our purpose of applying the Ginzburg criterion :

$$\rho_c \sim (NC^{5/4})^{-1} \sim \left(\frac{c^*}{c}\right)^{5/4} \qquad (15)$$

where we have introduced the overlap concentration c^* separating the semi dilute from the dilute regimes.

Note that ρ_c goes to a constant of order unity as c goes to c^* (see Fig. 1). The threshold can be written in a scaled form :

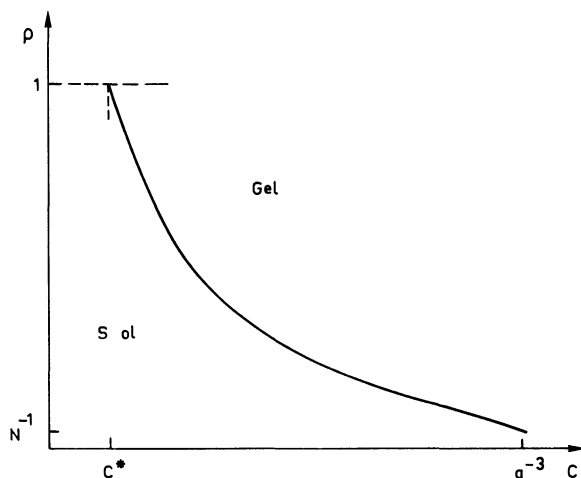$$\rho_c = f\left(\frac{c}{c^*}\right) \qquad (16)$$

Fig. 1. — Phase diagram between the sol phase for low values of the concentration C and the vulcanized (gel) phase. The critical region is very narrow (of under N^{-1}) for the concentrated solutions and becomes longer and longer as concentration is decreased. When C goes to C^*, ρ goes to some constant value, independent of N and C, smaller than, but of order unity.

with

$$f(x) \sim \begin{cases} x^{-5/4} & \text{if} \quad x \gg 1 \\ 1 & \text{if} \quad x \to 1 \end{cases} \qquad (17)$$

in the same way

$$Z \sim \left(\frac{\delta\rho}{\rho_c}\right)^{-\gamma_p} N \qquad (18a)$$

$$\Theta \sim \left(\frac{\delta\rho}{\rho_c}\right)^{\beta_p} \qquad (18b)$$

$$\xi_p \sim \left(\frac{\delta\rho}{\rho_c}\right)^{-\nu_p} N^{1/2} c^{-1/8} . \qquad (18c)$$

Here again, let us emphasize that these results are valid only when *chain* percolation is considered : we suppose that the number of cross-links per chain is finite (and small), which is usually the case near the threshold. In order to determine the width of the critical regions, two arguments may be given :

(*a*) Let us first consider the problem in the coordinates of the centre of mass. In these coordinates, the problem reduces to the polycondensation of f functional units. Now, f is the number of contacts of a chain with the others. So the effective coordination number is

$$f \sim NC^{5/4} . \qquad (19)$$

This number is very large in the melt, but decreases very strongly when the monomer concentration is decreased. So we expect the critical region to become wider.

(b) This can be made more precise by applying the Ginzburg criterion. Let us use relations (18)

$$(\gamma_{\underline{p}} = \beta_{\underline{p}} = 1, \nu_{\underline{p}} = \tfrac{1}{2}) .$$

Together with (9), for $d = 3$, we get for the mean field region :

$$\left(\frac{\delta\rho}{\rho_c}\right)^{3/2} N^{-1/2} c^{-5/8} \ll 1 .$$

Leading, for the critical region, to

$$\begin{aligned}\delta\rho &\ll \delta\rho^* \\ \frac{\delta\rho^*}{\rho_c} &\sim \left(\frac{c^*}{c}\right)^{5/12}\end{aligned} \Bigg\} . \tag{20}$$

Relation (20) shows very clearly that although the width of the critical region is very narrow in the bulk, where relation (10) is recovered, it depends strongly on concentration. In particular, when c goes to c^*, the critical region becomes very important (note that in this case, ρ_c goes to 1). As a result, the critical percolation exponents may be observed in the vulcanization of chains if the concentration of the solution is adequately chosen.

Let us remark that excluded volume effects, only, have been taken into account in this section. We know that the temperature effects also are present. These are complicated by the presence of elastic forces in the gel as is briefly discussed in the following section. A more detailed analysis of these effects will be given elsewhere.

3. **Swelling of the gel.** — An interesting aspect of the preceding approach is that it allows us to discuss the swelling of the gels. Let us start with a gel with a given concentration ρ, just above the threshold ρ_c, and let us vary the monomer concentration by adding some solvent. Figure 2 shows the initial conformation of the gel :

● For small scales ($r \ll \xi$), the chain behaves as if it were alone. This is the blob.

● For larger scales, contacts with other chains screen out the excluded volume interaction, and the behaviour of the chain is random.

● At still larger scales, we find the permanent network structure. This last structure depends mainly on the value of ρ. As the cross-links are permanent, their distribution cannot change when the concentration is decreased. The change in the structure can take place only via local rearrangement of the chains, if possible. When we decrease c, the size ξ of the blob increases (see eq. (11)) and so do both the radius of gyration of a chain and $\xi_{\underline{p}}$. This corresponds to the
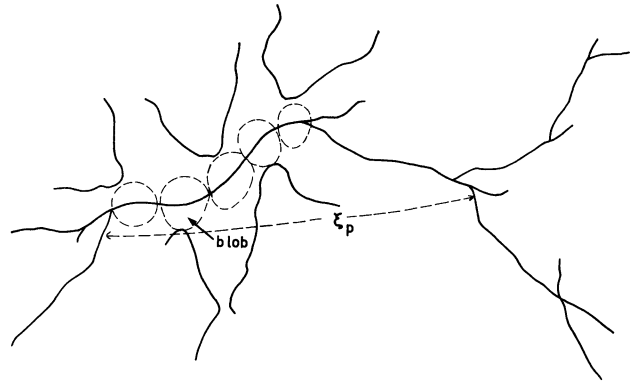

Fig. 2. — A representation of the vulcanized state :
● for small distances (blob) the behaviour is that of a single chain ;
● at longer distances, inside a chain the behaviour is random ;
● for large scales the permanent network structure is present.

swelling of the network. The process can take place as long as the equilibrium number of contacts between chains is larger than the number of cross-links. Near the threshold, there is almost one permanent cross-link per chain. So if we want to decrease the concentration below c^*, elastic forces due to the presence of permanent cross-links will restore the equilibrium concentration corresponding to a number of contacts equal to the number of cross-links. This may also be understood through our transformation in section 1 and 2. In a concentrated solution, the probability of having a junction is a function of $\rho N c^{5/4}$ only [18] :

$$p = g(\rho N c^{5/4}) \tag{21}$$

where $g(r)$ is some function. The condition which is imposed here is $p = $ const. ($> p_c$) when the concentration c is decreased, in order to keep this condition satisfied, the system changes the effective value of ρ.

$$\rho_{\text{eff}} N C^{5/4} = p .$$

(This corresponds to an enhanced probability of finding a cross-linking agent at the contact points when the system is diluted.)

The process can take place as long as ρ_{eff} is less than unity, leading to a minimum concentration proportional to c^*. (For this concentration, the probability of finding a cross-linking agent at a contact point is unity, because of the permanent nature of the cross-links.)

$$C_{\text{equ}} \alpha c^* \sim N^{-4/5} . \tag{22}$$

At this point let us remark that this approach is valid only if we consider the gelation of *chains*. In concentrated solutions, it holds only for low values of ρ ($\rho \sim N^{-1}$ in the melt). If ρ is increased drastically, we can eventually reach the percolation of blobs. Then the scale changes (eqs. (2)) are not expected to be useful and the whole approach breaks down. This might allow us to distinguish between light gels (per-

colation of *chains*) and strong gels (percolation of blobs). The difference between the two cases vanishes near c^* but seems to be very strong in concentrated solutions. Among others, we see that the swelling properties are not the same : a strong gel is not expected to swell as dramatically as a light gel. The local motions of the chains in a strong gel also seem much more restricted than in a light gel.

4. Conclusion. — We have considered the vulcanization of chains in semi dilute solutions. We have shown that critical percolation exponents can be observed in these solutions, whereas they are not if vulcanization is performed in the melt. This is due to the fact that by an appropriate transformation, this problem is equivalent to the polycondensation of f-functional units. The functionality f is the number of contacts of a chain with the others, (including contacts with itself). Whereas, in the melt $f = N$, leading to a very narrow critical region, in a semi dilute solution, $f = NC^{5/4}$ decreases very strongly. A widening of the critical region results, and critical exponents can be observed.

A more precise definition of c^* may be obtained in this way. If the vulcanization agent can react only with polymer chains, and if we consider the vulcanization problem with $\rho = 1$, starting from dilute solutions, c^* is the vulcanization threshold. For instance the viscosity of the solution diverges at c^* [17]. This provides a more precise definition of c^* than the usual cross over definition and this approach also allows us to discuss the swelling of gels. We argued that the gel swells to an equilibrium concentration proportional to c^*.

The whole approach is valid only if we consider gelation of chains. This leads us to distinguish between *light* gels, which we have considered here, and *strong* gels, corresponding to the gelation of *blobs*. The difference between them vanishes at c^* but becomes very sharp in concentrated solutions when the density ρ of cross-linking agent has to be much greater (about N times in the gel) to get the latter case. In particular, the swelling and dynamic properties should not be the same for both.

References

[1] STOCKMAYER, W. H., *J. Chem. Phys.* **11** (1943) 45.
[2] FLORY, P. J., *Principles of Polymer Chemistry* (Cornell U.P.) 1953.
[3] GORDON, M., *R.G.C.P. Plastiques* **4** (1967) 111.
[4] STAUFFER, D., *J. Chem. Soc. (Faraday Trans. II)* **72** (1976) 1354.
[5] DE GENNES, P. G., *Phys. Lett.* **38A** (1972) 339.
[6] DES CLOIZEAUX, J., *J. Physique* **36** (1975) 281.
[7] DAOUD, M., JANNINK, G., *J. Physique* **37** (1976) 973.
[8] MOORE, M. A., *J. Physique* **38** (1977) 265.
[9] FARNOUX, B., *Ann. Phys.* **1** (1976) 73.
[10] COTTON, J. P. *et al.*, *J. Chem. Phys.* **65** (1976) 1101.
[11] LUBENSKY, T. C., ISAACSON, J., *Phys. Rev. Lett.* **41** (1978) 829.
[12] CONIGLIO, A., STANLEY, H. E., KLEIN, W., to be published.
[13] DE GENNES, P. G., *J. Physique Lett.* **38** (1977) L-355.

[14] DAOUD, M. *et al.*, *Macromolecules* **8** (1975) 804.
[15] For an introduction to percolation problems, see for instance SHANTE, V. K. S., KIRKPATRICK, S., *Adv. Phys.* **20** (1971) 325. KIRKPATRICK, S., *Rev. Mod. Phys.* **45** (1973) 574.
[16] Here ρ is defined as a number per unit volume. This agrees with Flory's definition in the melt. In the transformation however, one has to keep only the effective agents. The number n of agents inside a blob is transformed into $n' = n/\xi^3$ and ρ remains constant.
[17] DE GENNES, P. G., *C. R. Hebd. Séan. Acad. Sci.* Paris **286B** (1978) 131.
[18] Another way is to say that the effective functionality f is a function of concentration $f = Nc^{5/4}$. As we have a gel, f has to be more than a certain constant, which also leads to a minimum concentration proportional to c^*.