Macromolecules **1994,** *27,* 5032–5036

Gel-like Behavior of pH Dependent Latex Films

J. P. Cohen-Addad* **and C. Bogonuk**

Laboratoire de Spectrométrie Physique associé au CNRS, Université Joseph Fourier, Grenoble I, B.P. 87, 38402 St. Martin d'Hères Cedex, France

V. Granier

Rhône-Poulenc Recherches, 52 rue de la Haie-Coq, 93308 Aubervilliers Cedex, France

Received February 10, 1994; Revised Manuscript Received May 31, 1994[⊗]

ABSTRACT: Gel-like properties of soft latex particles, made of styrene–butyl acrylate statistical copolymers, were observed after forming thin films; polymer chains were not covalently linked to one another. Acrylic acid groups, inserted at random on chain skeletons of copolymers, were supposed to play the role of cross-links. The concentration of these carboxylic acid groups, hereafter called κ_{COOH}, was varied from 100 to 800 μmol/g; the pH of emulsions, prior to the formation of films, was given three values: 2.5, 5, and 7.5. Measurements of the gel fraction or of the swelling ratio of latex films were performed as a function of the κ_{COOH} variable to attempt to show that this concentration determines the state of gelation. The gel fraction was was shown to obey an experimental master curve which was empirically described as an exponential function of κ_{COOH}, and an estimate of the threshold of gelation was given by $\kappa^c_{COOH} = 20$ μmol/g, at a pH equal to 7.5; the threshold was lowered by raising the pH of the emulsions. Using toluene as a good solvent, the swelling ratio was also found to obey an empirical master curve represented as a function of the inverse of the ($\kappa_{COOH} - \kappa^c_{COOH}$) variable; the power law associated with this curve suggests that the state of maximum swelling corresponds to a set of closely packed coils.

I. Introduction

This work deals with properties of polymeric gels that are made without covalently linking polymer chains. Elements of these networks are held together physically by secondary forces resulting from hydrogen bonding and ionic interactions. The linkages are weak compared to covalently linked gels and can thus be broken by gentle physical changes. In this work, polymeric gels were thin films prepared from latex particles made of styrene and butyl acrylate statistical copolymers. The core of each latex particle is surrounded by a thin hydrophilic layer which consists of acrylic acid sequences copolymerized with core polymers. Physical properties were observed on latex systems obtained after drying a solution, cast as a film. Noncovalent cross-links are formed between carboxylic acid groups located on particles which come into contact. The nature of these cross-links depends on the pH which characterizes emulsions prior to the formation of films. At low pH ($\approx$2.5), hydrogen bonds are dominant but copolymers are expected to behave like ionomers when solutions are neutralized or partly neutralized by using a base.

The purpose of this work was to characterize the gel-like behavior of latex films. The characterization was focused on measurements of two physical quantities: the Q_m swelling ratio resulting from the effect of osmotic pressure induced by a good solvent and the G gel fraction. More precisely, it was attempted to determine the role played by the carboxylic acid concentration in the definition of the state of gelation of latex films.

Pioneer descriptions of polymeric gel formation proposed by Flory[1] and Stockmayer[2] have been based on the use of a Cayley tree (Bethe lattice); networks were supposed to grow without the existence of loops. Then, the cross-linking effect has been identified as a percolation process.[3,4] Starting from the p probability to connect two chains, let p_C denote the threshold of percolation. A variable of state of percolation is defined by $\epsilon = |p - p_C|/p_C$; ϵ is also considered as a variable of state of gelation of polymer networks. The percolation approach accounts implicitly for the presence of loops in network structures. Physical quantities such as the gel fraction (G), the swelling ratio (Q_m), and the modulus of elasticity (E) are predicted to depend on the single ϵ variable; however, the actual dependence of these quantities on ϵ is still unknown except for ϵ values very close to zero (critical domain). de Gennes has predicted that the Cayley tree approximation should give a satisfactory description of sol–gel transitions observed on long chains cross-linked at random.[3] In accordance with this prediction, it has been recently shown both experimentally and theoretically that the gelation variable of polybutadiene chains cross-linked at random by sulfur is determined by

$$\epsilon = \frac{2\gamma_c^s \bar{M}_w}{\bar{x} M_s} - 1 \tag{1}$$

γ_c^s is the concentration of sulfur (w/w), $\bar{x}$ is the average number of sulfur atoms per cross-link, and M_s is the atomic mass of sulfur.[5] The functionality of polybutadiene chains is the N number of monomeric units, and the percolation threshold is given by $p_C = N^{-1}$, according to Flory model. Equation 1 applies to small amounts of sulfur ($\lesssim$0.015 g/g); physical quantities such as the modulus of elasticity, the swelling ratio, and the magnetic relaxation of protons, measured on vulcanized chains, have been shown to depend on ϵ defined by eq 1. The average number of cross-links per chain is roughly given by $(\epsilon + 1)/2$.

II. Principle of the Analysis

In this work, copolymers forming latex particles were expected to behave like vulcanized chains where hydrogen bonds and ionic interactions play the role of cross-links. This behavior was assumed to extend to latex films, too. All samples were observed above the glass transition temperature. This was measured from DSC; it was equal to 5 °C for all samples. Let κ_{COOH} denote the concentration of carboxylic acid groups; the analysis of experimental

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

0024-9297/94/2227-5032$04.50/0

results is based on the assumption that there exists a variable of gelation; this is supposed to be expressed as

$$\epsilon = \gamma(\mathrm{pH})\kappa_{\mathrm{COOH}} - 1 \tag{2}$$

where the γ parameter is pH dependent. The $\gamma(\mathrm{pH})$ parameter was introduced to account for the possible variation of the number of active cross-links when the pH is increased from 2.5 to 7.5. Considering a given solvent, the strength of cross-links formed by ions, at pH $\approx$ 7.5, is probably higher than that of cross-links formed by hydrogen bonds, at pH $\approx$ 2.5. In other words, it is considered that the effective number of cross-links is not equal to $\kappa_{\mathrm{COOH}}^{\mathrm{c}}$ but to a pH dependent fraction of this quantity. The percolation threshold is given by $\kappa_{\mathrm{COOH}}^{\mathrm{C}} = 1/\gamma(\mathrm{pH})$; physical quantities such as the gel fraction or the swelling ratio are supposed to be functions of the ϵ variable

$$G = \mathcal{G}[\epsilon]$$

and

$$Q_{\mathrm{m}} = \mathcal{Q}[\epsilon]$$

Experimental curves which represent the gel fraction measured as a function of κ_{COOH}, for different pH values, must obey a property of superposition. More precisely, considering $\gamma(\mathrm{pH}_1)$ and $\gamma(\mathrm{pH}_2)$ corresponding to two pH values, it must be shown that the experimental curve ($\mathcal{A}_2$) associated with $\mathcal{G}[\gamma(\mathrm{pH}_2)\kappa_{\mathrm{COOH}} - 1]$ can be superposed on the curve ($\mathcal{A}_1$) associated with $\mathcal{G}[\gamma(\mathrm{pH}_1)\kappa_{\mathrm{COOH}} - 1]$, provided a constant factor equal to $\gamma(\mathrm{pH}_1)/\gamma(\mathrm{pH}_2)$ is applied to the scale of concentrations of carboxylic acid groups of the $\mathcal{A}_2$ curve. The same analysis must apply to the swelling ratio, considering the same $\gamma(\mathrm{pH}_1)/\gamma(\mathrm{pH}_2)$ scale factor. The $\gamma(\mathrm{pH})\kappa_{\mathrm{COOH}}$ product is considered an estimate of the mean number of cross-links per chain in latex films.

III. Experimental Section

Materials. Emulsions. Samples were made from aqueous dispersions of polymer latex particles which are spherical droplets with diameters ranging from 1000 to 1200 Å. They consist of a hydrophobic core and a hydrophilic shell. The manner of synthesis has been already reported elsewhere.[6] Contents of monomeric units in systems obtained after polymerization were $(40 - x)$% styrene, 60% butyl acrylate, and x % carboxylic acid. The pH of the emulsion was near 2.5. Furthermore, some of the emulsions were neutralized using two different bases (NaOH or NH_4OH) to adjust pH values to 5 or 7.5.

Film Formation. Films were made by dehydration of the aqueous dispersions according to the following procedure. Dispersions were first degassed under a moderate vacuum, and then, concentrated emulsions were spread on a silicone mould to form a thin layer (2 mm). Liquid films were then dried in an oven, in the presence of water vapor; the drying temperature was 30 °C. After 48 h, films were removed from the molds. A list of characteristic parameters of the latex films is given in Table 1.

Gel Fraction. The G gel fraction of the sample was defined as the ratio of the weight of the dry extracted gel to the weight of the original sample. The sol was extracted in toluene, at room temperature, for 7 days, and the solvent was renewed 5 times. Samples were thoroughly dried over 15 days, under vacuum, after removing the sol fraction.

Equilibrium Swelling. The Q_{m} swelling ratio of each sample was defined as the ratio of the volume of the swollen gel over the volume of the dry gel obtained after extraction. It was determined at the end of the extraction performed in toluene, using a weighing method; Q_{m} was calculated from the densities of the solvent and the polymer equal to 0.87 and 1.06, respectively.

Table 1

label	% X	κ_{COOH} (μmol/g)
SBA-2.5	3.3	458
	2.5	347
	0.5	69
SBA-5-NaOH	3.3	458
SBA-5-NH_4OH	3.3	458
SBA-7.5-NaOH	6	833
	4.5	625
	3.3	458
	2.5	347
	1.5	208
	0.5	69.5
SBA-7.5-NH_4OH	3.3	458
	2.5	347
	1.5	208
	0.5	69.5

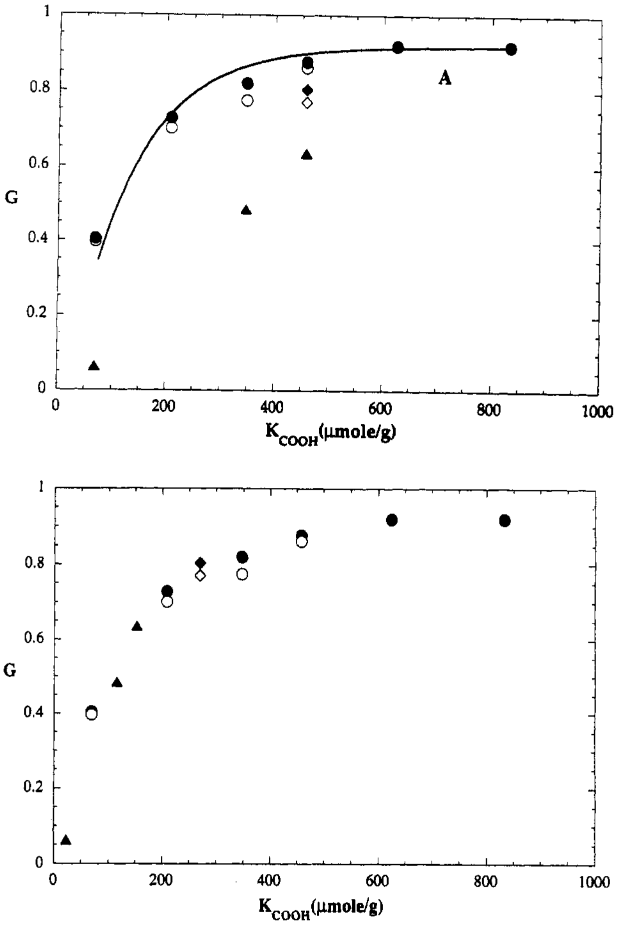

Figure 1. Gel fraction as a function of the carboxylic acid group concentration and the pH of emulsions. (A, top) Key: (●) pH = 7.5 (neutralizing agent: NaOH); (○) pH = 7.5 (neutralizing agent: NH_4OH); (◆) pH = 5 (neutralizing agent: NaOH); (◇) pH = 5 (neutralizing agent: NH_4OH); (▲) pH = 2.5 (neutralizing agent: NaOH). (B, bottom) The empirical A curve, drawn at pH = 7.5, was used as a reference. Scale factors equal to 1.7 for pH = 5 and 3 for pH = 2.5 were used to shift experimental points to the A curve.

IV. Gel Behavior

IV.1. Gel Fraction. Gel fractions measured as a function of the carboxylic acid concentration are reported in Figure 1, for two pH values of the emulsions (7.5 and 2.5); free chains were extracted by using toluene. At a pH equal to 7.5, there is no effect resulting from the nature of the base used to neutralize the emulsions; an empirical curve was drawn through the experimental points (A

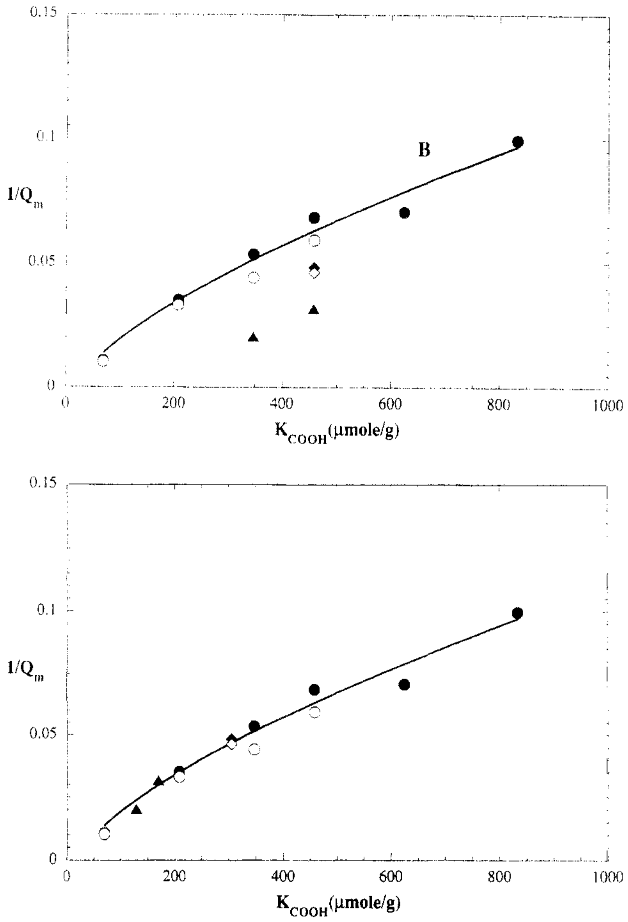

Figure 2. Inverse of the swelling ratio as a function of the carboxylic acid concentration and the pH of emulsions. (A, top) The key to points is the same in Figure 1A. (B, bottom) The empirical B curve, drawn at pH = 7.5, was used as a reference. Scale factors equal to 1.5 for pH = 5 and 2.7 for pH = 2.5 were used to shift experimental points to the B curve.

curve). Three experimental values of the gel fraction were obtained at a pH equal to 2.5; then, a reduction factor equal to 3 was applied to the carboxylic acid concentration scale to shift these experimental points to the A curve, drawn for a pH equal to 7.5. The effect of the scale reduction is shown in Figure 1B. The two experimental points corresponding to a pH equal to 5 are also reported in Figure 1A; they were shifted to the A curve by using a reduction factor equal to 1.7.

IV.2. Swelling Ratio. A similar analysis was applied to the inverse of the swelling ratio induced by the osmotic pressure of toluene. Experimental points are reported in Figure 2A where a slight effect of the nature of the neutralizing agent is perceived at a pH equal to 7.5. An empirical curve was drawn through the experimental points corresponding to a pH equal to 7.5 (B curve); then, the two experimental points corresponding to a pH equal to 2.5 were shifted to the B curve using a reduction factor of the scale of carboxylic acid concentration equal to 2.7. The effect of the scale reduction is shown in Figure 2B. The two experimental points corresponding to a pH equal to 5 were also shifted to the empirical B curve, by using a reduction factor equal to 1.5.

Reduction factors corresponding to the gel fraction and the inverse of the swelling ratio are reported as a pH function in Table 2.

To prove the existence of a single gelation variable, the inverse of the swelling ratio measured from all latex systems that were studied was represented as a function of the gel fraction. Experimental points were found to exhibit a monotonous variation whatever the pH or the nature of the neutralizing agent (Figure 3). The representation of all experimental points according to a single curve shows that there is one general G function which relates the gel fraction to the ϵ variable of gelation; similarly, there is also one general Q function which relates Q_m to ϵ. Therefore, $1/Q_m$ can be written as

Table 2

pH	$S(G)$	$S(1/Q_m)$
2.5	3 ± 0.3	2.7 ± 0.3
5	1.7 ± 0.4	1.5 ± 0.3
7.5	1	1

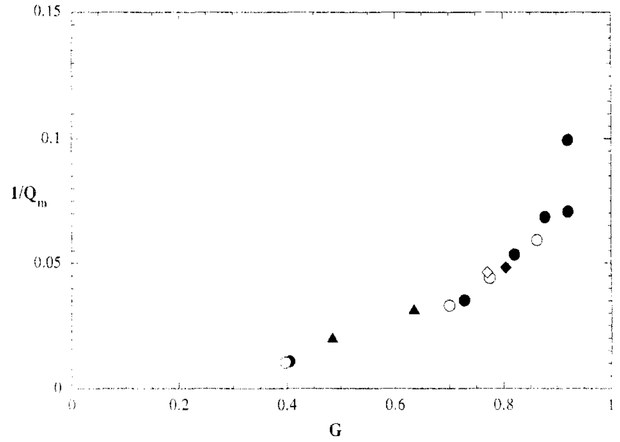

Figure 3. Empirical representation of the gel fraction as an exponential function of $\kappa_{COOH} - \kappa^C_{COOH}$; $\kappa^C_{COOH} \approx 20$ μmol/g.

$$1/Q_m = 1/\mathcal{Q}[\mathcal{G}^{-1}(G)] \qquad (3)$$

where $\mathcal{G}^{-1}$ is the inverse function of $\mathcal{G}$.

The strong increase of $1/Q_m$ observed when G varies from 0.7 to 0.9 corresponds to a narrowing of the mesh size of network structures while most polymer chains are linked to one another.

IV.3. Threshold of Gelation. An estimate of the threshold of gelation, corresponding to a pH value equal to 7.5, was derived from the empirical master curve drawn in Figure 2B: the κ^C_{COOH} threshold concentration was found to be equal to 20 μmol/g. Then, considering the scale factors used to build this experimental master curve, estimates of the threshold of gelation were found to be 12 and 8 μmol/g, for pH values equal to 5 and 2.5, respectively.

IV.4. Approximate Distribution of Finite Clusters. Starting from the approximate value of the threshold of gelation at pH = 7.5, experimental variations of the gel fraction can be empirically represented as the difference between unity and an exponential function of $\kappa_{COOH} - \kappa^C_{COOH}$; the fit is illustrated in Figure 4. The gel fraction is written as

$$G = 0.92(1 - \exp[-\mu(\kappa_{COOH} - \kappa^C_{COOH})]) \qquad (4)$$

with $\mu = 8.6 \times 10^{-3}$ (μmol/g)$^{-1}$ and $\mu/\gamma(\mathrm{pH}) = 0.17$, for a pH equal to 7.5. The highest value of G is 0.92 instead of unity because of the presence of impurities left in the samples after evaporating water to prepare the latex films; these impurities are weighed before the extraction and

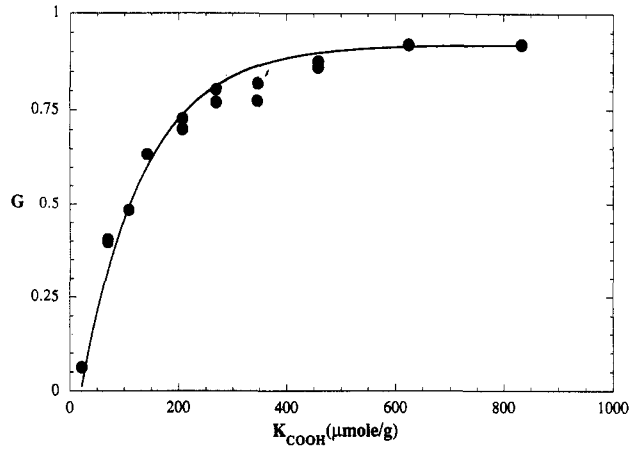

Figure 4. Inverse of the swelling ratio as a function of the gel factor. The key to the points is the same as that of Figure 1A.

then removed by the extraction. Using the ϵ variable, the gel fraction is also expressed as

$$G = 0.92(1 - \exp[-0.17\{\epsilon\}]) \tag{5}$$

Let n_0 denote the total number of chains filling the latex particles and $\mathcal{P}(n,\epsilon)$ the distribution function of clusters formed from n chains; then, $\mathcal{P}(n,\epsilon)$ and $\mathcal{G}(\epsilon)$ obey the relationship

$$\sum_n n\mathcal{P}(n,\epsilon) = n_0(1 - G(\epsilon)) \tag{6}$$

The right hand side of eq 6 yields the number of chains involved in the formation of the clusters. This number is probably not an exponential function of ϵ; therefore, eq 4 must be considered only as a convenient empirical description of the gel fraction. However, according to Lubensky and McKane, the cluster number, expressed away from p_C, can be written as

$$\mathcal{P}(n,\epsilon) \propto n^{1/9} \exp(-cn^{2/3}) \tag{7}$$

where c depends on the gelation variable;[7] using the above expression, it can be numerically shown that the sum defined by eq 6 is conveniently represented by an exponential function

$$\sum_n n\mathcal{P}(n,\epsilon) \propto \exp(-1.15c) \tag{8}$$

for $c \geq 2$.

Taking eq 5 into consideration, the above sum is identified as an exponential function of the ϵ variable by assuming that c is simply equal to 0.15 ϵ. It is supposed that eq 7 gives probably a reasonable approximate expression of the $\mathcal{P}(n,\epsilon)$ cluster number; however, it cannot be asserted that the empirical equation (4), which results from a numerical fit, demonstrates that expression 7 is valid.

IV.5. C^* Theorem. The C^* theorem was used to attempt to give a more quantitative description of gel properties of latex particles. This theorem, proposed by de Gennes, states that a polymeric gel swollen at equilibrium can be pictured as a set of closely packed coils held together by cross-links; consequently, the Q_m^{-1} concentration of a swollen network structure must be proportional to the C^* overlap concentration of free chains in solution.[3] Therefore, the swelling ratio is expected to be a power function of the mean chain segment determined by two consecutive cross-links; let N_c denote the mean number of skeletal bonds in such a segment. Then,

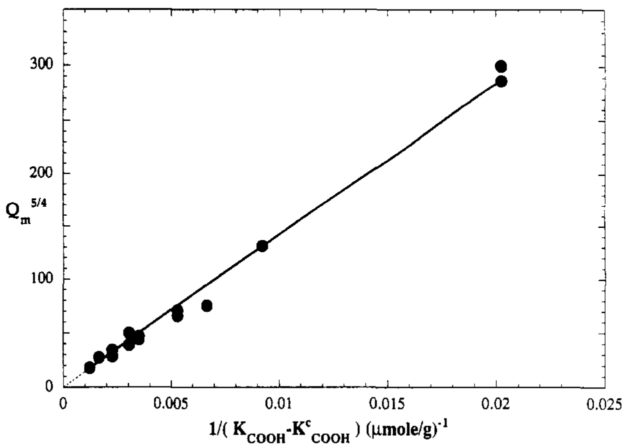

Figure 5. Variation of the 5/4 power of the swelling ratio as a function of the inverse of the carboxylic acid concentration. Experimental points are reported from Figure 2B.

$$Q_m = qN_c^{4/5} \tag{9}$$

q depends on the connectivity of packed coils; it is of order unity.

In this work, the mean number of cross-links per chain which is involved in the gelation variable is also interpreted as the inverse of the mean segmental spacing between two cross-links along one chain; accordingly, the $(\gamma(\mathrm{pH})\kappa_{COOH} - 1)$ variable should be proportional to N_W/N_c (N_W is the weight average of the number of skeletal bonds in one chain). Correspondingly, the $Q_m^{5/4}$ function should be represented as a linear function of $(\kappa_{COOH} - \kappa^{C}_{COOH}{}^{-1})$

$$Q_m^{5/4} = \frac{q^{5/4} N_w \kappa^{C}_{COOH}}{\kappa_{COOH} - \kappa^{C}_{COOH}} \tag{10}$$

The experimental curve, corresponding to Figure 2B, is reported in Figure 5; it can be drawn as a straight line which goes through zero. Such a result shows that the N_W weight average is probably nearly constant for all latex systems; the relevant variable of gelation is the carboxylic acid concentration which determines the number of cross-links.

Furthermore, the lowering of the threshold of gelation, observed when the pH of neutralization of emulsions is raised, means that the corresponding number of physical cross-links, involved in gel properties, is smaller at a low pH (hydrogen bonding) than at a pH equal to 7.5 (ionic interactions). The efficiency of carboxylic acids to form cross-links depends on the pH of emulsion, prior to the formation of films. The presence of counterions induces interactions stronger than hydrogen bonds.

Finally, it may be worth emphasizing that the use of tetrahydrofuran was found to dissociate partly latex films and particles; this polar solvent was supposed to sever physical bonds formed within particles.

V. Conclusion

In this study of gel properties of latex films, polymer chains are not covalently linked to one another and the concentration of physical interactions which play the role of cross-links is not uniform within particles. Nevertheless, two features characterize the behavior of these polymeric systems. On the one hand, the state of gelation is determined by the concentration of carboxylic acid groups copolymerized with chains and the gelation threshold is shifted toward lower concentrations when the pH of emulsions, adjusted prior to the formation of films, is raised from 2.5 to 7.5. The interpretation of this result is based on the assumption that the number of physical cross-links is higher at a pH equal to 7.5 than at a pH equal to 2.5 (hydrogen bonding). On the other hand, the gel fraction and the swelling ratio are shown to be general functions of the concentration of carboxylic acid groups; one of them is derived from an approximate expression of the distribution function of cluster sizes, above the gelation threshold, while the other one is given by the C^* theorem. Several years ago, the gel behavior of vulcanized long chains was predicted to be described in a satisfactory way, by using a mean field approach.[3] This prediction resulted from an estimate of the width of the critical domain around the threshold of gelation; the width is determined by $Z^{-1/3}$; Z is the index of polymerization. Because of the narrowness of the critical domain, most properties of vulcanized chains can be described by considering a Cayley tree; this analysis applies also to properties observed in this study.

References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3091.

(2) Stockmayer, W. *J. Chem. Phys.* **1943**, *11*, 45.

(3) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, New York, 1979.

(4) Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis Ltd.: London, 1987.

(5) Cohen-Addad, J. P.; Soyez, E. *Macromolecules* **1992**, *25*, 6855.

(6) Joanicot, M.; Wong, K.; Maquet, J.; Chevalier, Y.; Pichot, C.; Graillat, C.; Lindner, P.; Rias, L.; Cabane, B. *Prog. Colloid Polym. Sci.* **1990**, *81*, 175.

(7) Lubensky, T. L.; McKane, A. J. *J. Phys. A* **1981**, *14*, L157.