

# Swelling of polybutadiene as latex particles and cast films by styrene and acrylonitrile monomers

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During emulsion polymerization, the diene structure of butadiene leads to the formation of a network by crosslinking on the residual double bonds. Investigation of the swelling of polybutadiene particles and films cast from latexes, by styrene and acrylonitrile, was carried out in order to get more information on polymer structure and behaviour in the presence of monomers. A thermodynamic approach has permitted us to determine several parameters, such as the average number of butadiene units between two crosslinking points, which represents the crosslink density and was compared with data from simulation of butadiene emulsion polymerization. Swelling by monomer mixtures of various compositions has shown a preferential solvation of styrene as a function of comonomer composition. Comonomer composition in the particles is important in the final structure of an acrylonitrile-butadiene-styrene particle prepared by emulsion polymerization of styrene-acrylonitrile on a polybutadiene seed. Diffusion coefficients of monomers were determined after a kinetic study.

(Keywords: swelling; polybutadiene; latex; film)

## INTRODUCTION

Study on the swelling of polybutadiene films cast from latexes and of particles by monomers with different polarities (styrene (S) and acrylonitrile (AN)) is one approach that allows one to get information about polybutadiene structure and solvent-polymer compatibility. Studies have already been carried out by Dimonie *et al.*<sup>1</sup> on swelling of polystyrene particles by an azeotropic S-AN mixture. Locatelli and Riess<sup>2</sup> have already shown the influence of the S-AN mixture composition on the preferential solvation of S in polybutadiene gel solution.

The aim of this work is to examine the effect of several thermodynamic parameters according to the Flory equations: the polybutadiene crosslink density, the particle size and the monomer mixture composition on the swelling equilibrium. This is expected to provide information on the grafting reaction of S-AN on polybutadiene seed with a view to further preparing structured latex particles of acrylonitrile-butadiene-styrene (ABS).

In the case of polybutadiene, batch emulsion polymerization leads to particles that are more or less crosslinked. The number of butadiene units between two crosslinking points and the amount of insoluble macromolecules are dependent upon the monomer conversion, i.e. upon the relative amounts of monomer and polymer within the reaction medium.

Experiments have shown that polybutadiene latexes may contain the same percentage of insoluble macromolecules but exhibit a different swelling behaviour, which is achievable by stopping the homopolymerization of butadiene at various conversions (Figure 1).

Thus, it is quite important to study the influence of crosslink density on the thermodynamic swelling equilibrium. The behaviour of each monomer (pure or in mixtures of various compositions) has been investigated. Particularly, it has appeared interesting to examine the effect of temperature on swelling and to determine the diffusion coefficients of S and AN into polybutadiene films.

## EXPERIMENTAL

### *Polybutadiene latex synthesis*

Three latexes referred to as A, B and C, with different crosslink densities, were used in this study. They were obtained by stopping the emulsion polymerization of butadiene at various conversions.

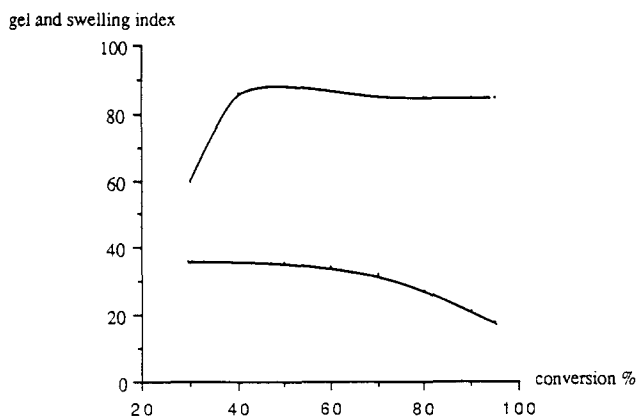
1,3-Butadiene (purity over 99%) was purified from its stabilizer (*p*-*t*-butylcatechol) with NaOH. The homopolymerization was carried out in a batch process, in the presence of a chain transfer agent, *t*-dodecylmercaptan (TDM), at 70°C in a steel reactor able to support pressures around 10 to 12 atm. The emulsifier was dodecanoic acid (for biochemistry; purity over 99%) and pH was about 9.5. Kinetics was followed by determination of solid content, from which conversion degree *versus* time was obtained.

Since the three latexes were obtained at various conversions, their particle sizes are obviously different. A large particle size latex G was prepared by seeded polymerization.

### *Latex characterization*

The characteristics are given in Table 1. Solid contents and conversion degrees were determined using the gravimetric method. Particle sizes were estimated by

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**Figure 1** Gel and swelling index (grams of toluene absorbed per gram of flocculated polybutadiene) as a function of butadiene conversion during the homopolymerization

**Table 1** Characteristics of latexes and polymers used for swelling experiments

Characteristics	A	B	C	G
Conversion (%)	77	90	100	90
Solid content (%)	27	31	34	38
Average diam. (nm)	79	92	99	490
Gel index (%)	80	89	92	95
Swelling index (g/g)	24	18	13	6

quasielastic light scattering measurements (Coulter Nano-sizer apparatus). The gel percentage represents the amount of insoluble macromolecules contained in 100 g of polymer. Thus, a small quantity of each latex was first treated with a solution of NaCl and then with a solution of acetic acid in order to flocculate the polymer. After filtration on a metal grid, the polymers were dried under vacuum. A known quantity of each polymer (mass  $M_1$ ) was put in a small basket made with calibrated metal grid (200 mesh) and left in contact with toluene (purity over 99%) for 2 days. It is expected that soluble macromolecules were extracted. The insoluble part (mass  $M_2$ ) was dried under vacuum and the gel index is given as  $100M_2/M_1$ .

With the same experiment, it was possible to estimate the swelling index  $M/P$  (mass of monomer absorbed per gram of polymer) which provides information on the crosslink density, according to Flory *et al.*<sup>3,4</sup>. If  $M_3$  is the weight of the sample swollen by toluene, the swelling index  $M/P$  is  $(M_3 - M_1)/M_1$ .

#### Film preparation

Hydroquinone (purity over 99%) was added to the samples of latex before film preparation in order to prevent the action of temperature and u.v. light on residual double bonds with formation of free radicals. Films were prepared by letting latexes 'dry' on Teflon supports at room temperature (to prevent bubble formation) for 2 weeks.

#### Swelling measurements

Swelling of polybutadiene particles was determined from light scattering measurements. The latex was diluted at a concentration suitable for the light scattering measurements. After swelling, dilution would have changed the thermodynamic equilibrium. Pure monomer

was added in large quantity in order to saturate water in monomer and to reach maximum swelling. Styrene (99%, stabilized with 0.005% of a hydroquinone derivative) and acrylonitrile (99%, stabilized by 40 ppm of monomethyl ether) were used such as they were. This was easy in the case of styrene but acrylonitrile is very soluble in water and makes the latex flocculate.

The gravimetric method was used in the case of films. The swelling equilibrium is reached when the weight of the swollen sample is constant. Using different films prepared from the same latex and letting them swell for various times in flasks filled with the monomers in excess, it was possible to follow the kinetics of the phenomenon. The study lasted for 24 h.

Mixtures of S-AN in various proportions were used to swell the films. At the swelling equilibrium and subsequent weighing, swollen samples were placed for 24 h in 25 cm<sup>3</sup> of DMF (dimethylformamide, 98%) which is a common solvent of S and AN. The two monomers were extracted. In order to estimate the contribution of each monomer in swelling, the concentrations of the solutions of S and AN (extracted from the films) in DMF were determined by vapour-phase chromatography (v.p.c.) using a flame ionization detector (f.i.d.). Calibration curves were made using S-DMF and AN-DMF solutions of known concentrations.

The extraction of styrene and acrylonitrile by DMF from the films was considered as total because, after a second treatment of the same film by DMF, v.p.c. did not allow detection of any trace of monomer in the second solvent solution.

To show the influence of temperature on swelling equilibrium and kinetics, measurements were done at 20, 45 and 65°C in a thermostated bath.

#### THERMODYNAMIC ASPECTS: RESULTS AND DISCUSSION

If solvent is in excess, absorption equilibrium is reached when the chemical potential of diluent in the swollen network is equal to the chemical potential of the pure solvent in excess outside the network.

According to Flory and Huggins theory<sup>3</sup>, the chemical potential of the solvent in a high-molecular-weight polymer is:

$$\Delta\mu' = \mu' - \mu_0 = RT[\ln \Phi_m + (1 - 1/\bar{x})(1 - \Phi_m) + \chi(1 - \Phi_m)^2]$$

where  $\Phi_m$  is the volume fraction of monomer in the swollen polymer system,  $\bar{x}$  is the number-average degree of polymerization and  $\chi$  is the interaction parameter between the solvent and the polymer.

The elastic deformation of the network during swelling also causes a change in the free energy of the system. From Flory-Rehner theory<sup>3-5</sup>, this contribution is:

$$\Delta\mu'' = \mu'' - \mu_0 = RT[(1 - \Phi_m)^{1/3} - (1 - \Phi_m)/2]/L_{ret}$$

$L_{ret}$  is the average number of monomer units connecting two crosslinking points.

Gibbs and Thomson have introduced a potential due to the increase of the particle surface during swelling and:

$$\Delta\mu''' = \mu''' - \mu_0 = 2V\gamma/r$$

$V$  is the partial molar volume of the solvent,  $\gamma$  the interfacial free energy of the polymer and  $r$  the radius of

**Table 2** Simulation and experiments on crosslink density and swelling of films ( $M/P$  (f) (g/g)) and particles ( $M/P$  (p) (g/g)) by styrene.  $D_i$  (nm) is the initial diameter of the particles and  $D_{sw}$  (nm) is that of the swollen particle.  $M/P$  (ps) is the simulated swelling of particles;  $L_{ret}$  (s) and  $L_{ret}$  (ex) are the simulated and experimental average number of butadiene units between two crosslinks

Polymer	$D_i$	$D_{sw}$	$M/P$ (f)	$M/P$ (p)	$M/P$ (ps)	$L_{ret}$ (s)	$L_{ret}$ (ex)
A	79	103	22	1.1	0.80	1960	2134
B	92	119	16	1.1	0.85	1265	1276
C	99	126	12	1.0	0.90	1000	836
G	490	718	5.5	1.9	2.00	—	184

the swollen particle. In the polymer phase, the total change in the free energy of the solvent is the sum of the three terms:

$$\begin{aligned} \Delta\mu = RT \{ & \ln \Phi_m + (1 - 1/\bar{x})(1 - \Phi_m) + \chi(1 - \Phi_m)^2 \\ & \text{(solution)} \\ & + [(1 - \Phi_m)^{1/3} - (1 - \Phi_m)/2]/L_{ret} \} \\ & \text{(crosslinking)} \\ & + 2V\gamma/r \quad \text{(interfacial tension)} \end{aligned}$$

At swelling equilibrium,  $\Delta\mu = 0$ . In this work, the standard potential is assumed to be that of the pure monomer, i.e.  $\mu_0 = 0$ . So:

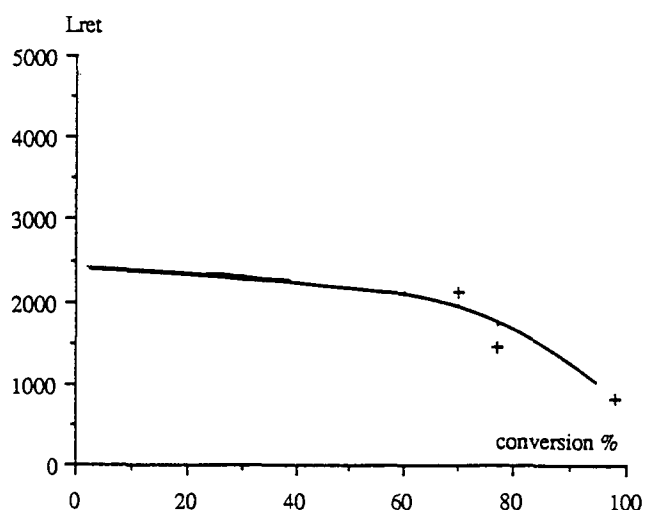
$$RT \{ \ln \Phi_m + (1 - 1/\bar{x})(1 - \Phi_m) + \chi(1 - \Phi_m)^2 + [(1 - \Phi_m)^{1/3} - (1 - \Phi_m)/2]/L_{ret} \} + 2V\gamma/r = 0$$

$\Delta\mu''$  and  $\Delta\mu'''$  are always positive as  $(1 - 1/\bar{x})(1 - \Phi_m)$  and usually  $\chi(1 - \Phi_m)^2$ . Their contribution must balance that of the negative term  $\ln \Phi_m$ . The larger their values, the smaller is the solvent fraction  $\Phi_m$ .

#### Swelling of polybutadiene particles and films by pure monomers

*Swelling by pure styrene.* Swelling experiments on films have allowed us to determine the number of monomer units between two crosslinking points. Experimental and simulated results are plotted in Table 2. The interaction parameter between styrene and polybutadiene is assumed to be about 0.44. By simulation on a computer theoretical data of the emulsion homopolymerization of butadiene by a batch process can be obtained<sup>6</sup>. The approach requires knowledge of two important parameters: the ratio  $K_{p1-2}/K_p$  (where  $K_{p1-2}$  is the reaction rate constant of the 1-2 residual double bond of a monomer unit and  $K_p$  that of the propagation rate) and the swelling of particle by the monomer. The swelling is a function of several parameters: the particle size, the interaction parameter and the crosslinking. The computing allows one to simulate different useful functions such as the kinetic chain length, the average number of monomer units between two crosslinks, the weight distribution of macroradicals with 0, 1, 2, ... crosslinks just before termination (one basic assumption is that termination mainly occurs by transfer or disproportionation) and the proportion of soluble macromolecules without any crosslink. In this work, the most important information given by the simulation is the weight distribution of the macromolecules with different number of crosslinks (Figure 4) and the average number of monomer units between two crosslinks. The number of monomer units between two crosslinks is then a function of the monomer conversion.

The simulation, which takes into account the molecular-weight distribution of growing chains, shows that,



**Figure 2** Determination of  $L_{ret}$  by simulation of the homopolymerization of butadiene and by experiments of swelling by styrene

at any conversion, there are always chains with no crosslinks and chains with at least one crosslink. This is the reason why crosslinked polymer appears at very low conversion and, even at high conversion, uncrosslinked macromolecules do exist.

On Figure 2 are shown simulated data obtained from simulation of the homopolymerization of butadiene and experimental data from swelling of films by styrene. There is good agreement between the two kinds of data for the determination of the average number of monomer units between two crosslinks. At 60% monomer conversion decreasing occurs. This conversion corresponds to the disappearance of the droplets as predicted by experimental curves giving the change in the butadiene gas pressure in the reactor.

On Figure 3, simulation and experiments give more or less the same results for gel index ( $GI$ ) at conversion of butadiene above 30%. For lower conversions, the difference in the experimental and simulated data comes from the definition of an insoluble macromolecule: for the simulation, a macromolecule is insoluble when it has at least two crosslinks. But that does not mean that this macromolecule is a part of a large enough polymer network not to be extracted in the experimental conditions.

It is important to note the difference between the gel index, which gives information about the amount of insoluble macromolecules, and the swelling index, which is representative of the crosslink density: a polymer can present a high gel index but can swell largely in a solvent.

It is also noteworthy that, in the case of polybutadiene, as the crosslinking occurs during the polymerization, the network is not homogeneous. On Figure 3, it appears that, even at high conversion, linear macromolecules are

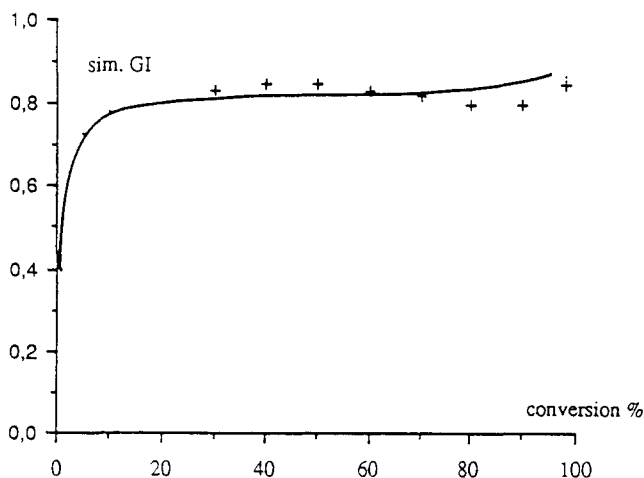


Figure 3 Experimental (+) and simulated gel index as a function of monomer conversion

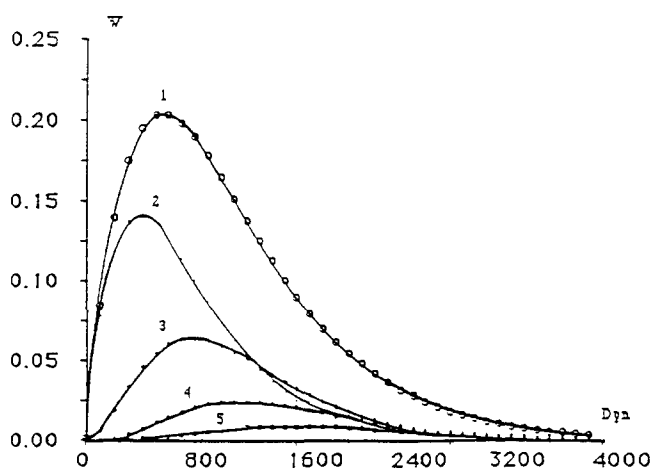


Figure 4 Simulated mass distribution of macromolecules as a function of their polymerization degree  $DP_n$ : as no crosslinking occurs during polymerization (curve 1); as crosslinking occurs—mass fraction ( $W$ ) of macromolecules with no (curve 2), one (curve 3), two (curve 4) and three (curve 5) crosslinking points

generated. So, there are linear chains in the network. These chains, which have a broad distribution from simulation (Figure 4), will surely have a contribution in the swelling. This fact was confirmed by experiment, which shows that, for high conversion, there is never more than 90–95% of insoluble macromolecules.

The polybutadiene films (Table 2) behave as predicted by Flory equations: the denser the network, the less important is the swelling.

The swelling of polybutadiene particles by styrene has shown the importance of the radius. Maximum swelling of particles is really much smaller. It appears (Table 2) that, for particles smaller than 100 nm, the relative increase of the diameter is about 30%. The influence of crosslinking is not so effective as in the case of films. It is shown that the effect of radius is larger than the effect of the crosslink density. The relative increase of diameter of large particles (490 nm) is experimentally about 46% with a maximum swelling of 1.9 g/g: even if large particles are more crosslinked, their size allows a larger swelling. This phenomenon has been predicted by simulation of swelling using Flory's equations. Figure 5 gives the simulated diameter increase as a function of crosslink density and initial diameter of the particle. If the initial

diameter  $D_i$  is about 100 nm, the average number of butadiene units between two crosslinks  $L_{ret}$  does not influence the swelling even when  $L_{ret}$  is about  $10^5$ . For a particle whose  $D_i$  is larger than 100 nm,  $L_{ret}$  has an effect on the swelling: the larger  $D_i$ , the more important is the effect of  $L_{ret}$  on the swelling.

Figure 6 shows the change in the relative diameter increase versus  $D_i$  and  $L_{ret}$ . For a constant  $L_{ret}$ , the more important  $D_i$ , the higher is the relative increase of  $D_i$ .

From the two figures (Figures 5 and 6), there is a good agreement between simulation and experiment.

*Swelling by pure acrylonitrile.* Working with films and using the experimental values of  $L_{ret}$  obtained by swelling in toluene, it was possible to determine the thermodynamic interaction parameter  $\chi$  between pure acrylonitrile and polybutadiene. For each polymer, the maximum swelling is about 0.2 g of monomer per gram of polymer. The amount of monomer absorbed is not dependent on the density of the network. The interaction parameter was estimated to be 1.29. This value, much greater than 0.5, shows the low compatibility between the polar monomer and the polymer.

Scott<sup>7</sup> established a diagram giving the change in the maximum swelling as a function of the solvent-polymer interaction parameter and the average molecular weight

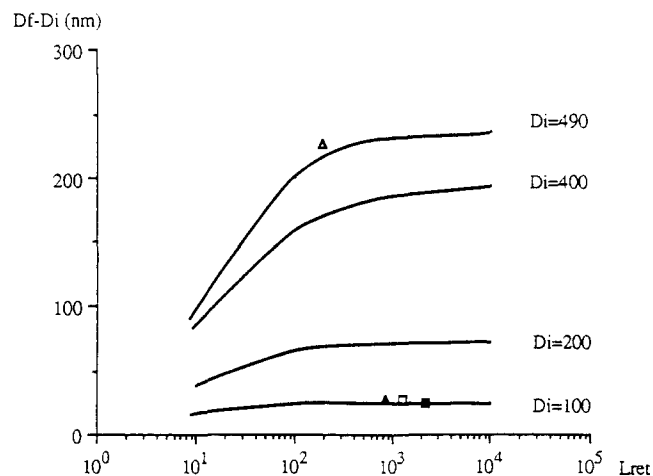


Figure 5 Simulated and experimental ( $\Delta$ ) increase ( $D_f - D_i$ ) of particle diameter at swelling equilibrium by styrene versus crosslink density ( $L_{ret}$ ) and initial diameter  $D_i$ . \*  $D_i = \blacksquare$ , 79;  $\square$ , 92;  $\blacktriangle$ , 99;  $\triangle$ , 490

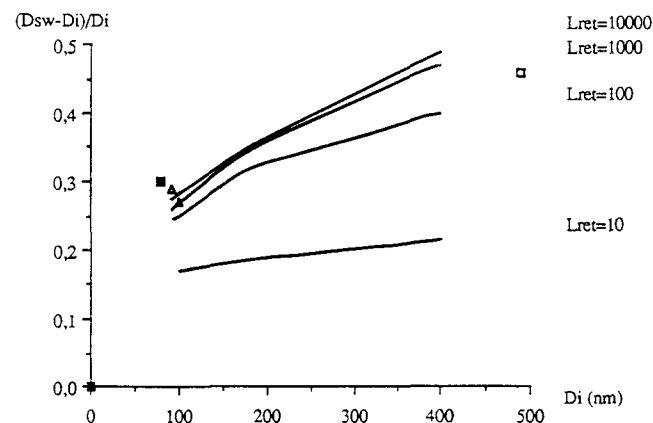


Figure 6 Experiments and simulation of swelling of polybutadiene particles by styrene as a function of the initial diameter and network density.  $L_{ret} = \blacksquare$ , 184;  $\square$ , 184;  $\blacktriangle$ , 836;  $\triangle$ , 1276;  $\blacksquare$ , 2134

between crosslinks. According to this diagram, using experimental  $L_{ret}$  and experimental maximum swellings,  $\chi_{AN/PB}$  would be about 1.2–1.3. This value is not different to that determined in this study. Experiments on particles were not successful. Acrylonitrile, indeed, makes the latex flocculate rapidly. The change of the radius is so low that it cannot be detected with usual light scattering apparatus.

#### Influence of composition of S-AN mixture on equilibrium swelling at 20°C

In the case of a mixture of two monomers ( $i$  and  $j$ ) in the presence of a polymer particle, the chemical potential of each monomer in the monomer phase ( $m$ ) is assumed to be:

$$\mu_i^m = \mu_i^{m0} + RT[\ln \Phi_i + (1 - V_i/V_j)\Phi_j + \chi_{ij}\Phi_j^2] \quad (1)$$

where  $\Phi_i$  and  $\Phi_j$  are the volume fractions of each monomer,  $V_i$  and  $V_j$  are their partial molar volumes and  $\chi_{ij}$  is the thermodynamic interaction parameter.  $\mu^0$  is assumed to be equal to 0.

In the polymer phase ( $p$ ), similar equations can be written<sup>4</sup>:

$$\begin{aligned} \mu_i^p = \mu_i^{p0} + RT[\ln \Phi_i + (1 - \Phi_i) - \Phi_j m_i/m_j - \Phi_p m_i/m_p \\ + (\chi_{ij}\Phi_j + \chi_{ip}\Phi_p)(\Phi_j + \Phi_p) \\ - \chi_{jp} m_i/m_j \Phi_j \Phi_p] + 2V_{ij}^p/r \end{aligned}$$

If swelling polybutadiene particles with pure styrene causes a radius change large enough to be detected, the phenomenon with acrylonitrile is different. Using mixed monomers to swell the polymer, it is expected that the change in radius will be a function of the monomer concentration in the initial mixture. So, for mixtures more or less rich in acrylonitrile, swelling would have to be very small. The experiments were preferably carried out with polybutadiene films.

**Swelling of films.** Results plotted on Figures 7 and 8 show the importance of the mixture composition on the contribution of each monomer. In every case, for each polymer and for each monomer mixture composition, the amount of acrylonitrile absorbed in a polybutadiene film is smaller than the amount of styrene. This phenomenon can be explained thermodynamically.

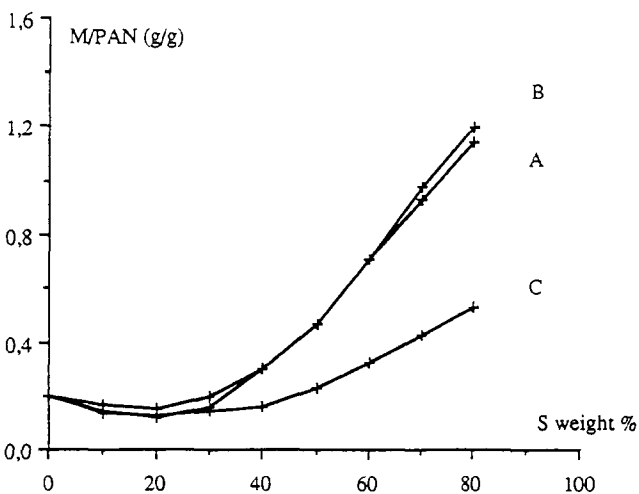


Figure 7 Maximum swelling  $M/P$  (g/g) of acrylonitrile in polybutadiene films versus initial composition of swelling mixture S-AN

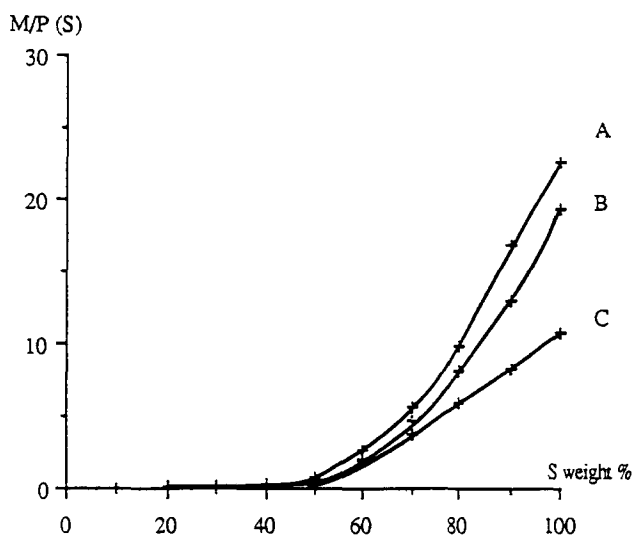


Figure 8 Maximum swelling of styrene in polybutadiene films as a function of initial composition of swelling mixture S-AN

According to Flory's equations, the interaction parameter between acrylonitrile and polybutadiene was found to be about 1.29. This value is much higher than  $\chi_{S/PB}$  which was assumed to be about 0.44.

Using mixtures of S-AN at 20°C to swell the films, it was noted that the quantity of absorbed acrylonitrile is increased in the presence of styrene: from 0.2 g/g for pure acrylonitrile to 1.2 g/g for a mixture containing 80 wt% styrene. The richer the mixture in styrene, the more important is the phenomenon. The opposite behaviour is observed for styrene, whose swelling capability decreases in the presence of acrylonitrile. According to equation (1), there are two parameters which could be a function of the mixture composition: the molar volumes (which should be considered as partial molar volumes) and the interaction parameter between the two solvents.

Up to 40–50 wt% styrene in the mixture, the swelling is constant. The influence of the composition swelling mixture is effective above 40–50 wt%.

#### Influence of increasing the temperature

The study was carried out with pure monomers and with a mixture with 70 wt% styrene. The experimental results are given in Tables 3 and 4.

In the case of pure monomers, the maximum swelling is not significantly affected by increasing the temperature, which shows that the thermodynamic parameters are not very sensitive to temperature.

With the monomer mixing (70 wt% S), maximum swelling becomes higher when the temperature increases, particularly when  $T$  is above 45°C (Table 4). This behaviour is different when compared with pure monomers. One assumption is that thermodynamic parameters of the mixture can vary with temperature. We can think that temperature affects the 'crossed' interaction parameter between the mixture and the polymer, as well as the interaction parameter between the two monomers. Recent theories<sup>8,9</sup> introduce the free volume and expansion coefficient concepts.

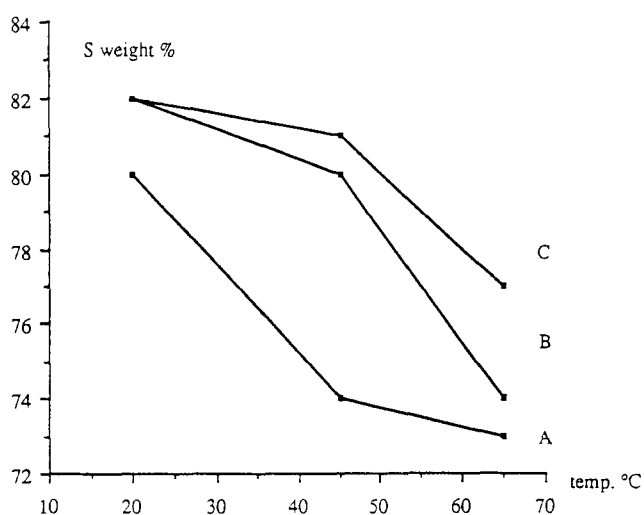
It is possible to determine, by solvent extraction and gas chromatography analysis, the composition of the comonomer mixture in the film at swelling equilibrium versus temperature. The results are plotted on Figure 9. The initial composition of the swelling mixture was about

**Table 3** Influence of temperature on thermodynamic equilibrium of swelling by pure monomers

Monomer film	M/P(pure AN) (g/g)			M/P(pure S) (g/g)		
	A	B	C	A	B	C
20°C	0.22	0.20	0.20	22	16	11
45°C	0.23	0.21	0.21	23	15	14
65°C	0.25	0.25	0.27	25	15	14

**Table 4** Influence of temperature on swelling by a mixture of weight composition 70/30

Monomer film	M/P(pure AN) (g/g)			M/P(pure S) (g/g)		
	A	B	C	A	B	C
20°C	1.46	1.08	0.96	5.80	4.80	3.45
45°C	1.90	1.20	1.03	6.20	4.80	3.04
65°C	2.99	1.73	1.46	8.05	4.97	5.00

**Figure 9** Change in weight composition of the mixture in the film (at swelling equilibrium) versus temperature

70 wt% styrene. At maximum swelling, the composition in the film is different: in the film, the mixture composition is always richer in styrene. It is observed that there is a decrease of the styrene concentration when temperature becomes higher. For the less dense film (A), the composition of the mixture in the film is not too different from the initial monomer feed. This could be regarded as a preferential solvation effect as already observed<sup>1,2</sup>.

## KINETIC ASPECTS: RESULTS AND DISCUSSION

### Determination of diffusion coefficient

To study the swelling kinetics, the diffusion coefficients of pure monomers and mixtures were determined according to Beati's method<sup>10</sup> (see 'Experimental' section). The coefficients were estimated at different temperatures and for the different polymers, measuring the weight change of films immersed in liquid phase versus immersion time.

**Table 5** Diffusion coefficients  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ) at 20°C of pure monomers in polybutadiene films

Films	A	B	C
$D$ of AN ( $\times 10^{-7}$ )	9.45	6.45	4.06
$D$ of S ( $\times 10^{-7}$ )	1.55	1.67	3.22

For short times, Fick's equation is<sup>11</sup>:

$$\frac{M_t}{M} = \frac{4}{\pi^{1/2}} \left( \frac{Dt}{4L^2} \right)^{1/2}$$

$M_t$  is the mass of monomer taken up at time  $t$ ,  $M$  is the mass of monomer at equilibrium,  $2L$  is the thickness of the film and  $D$  is the diffusion coefficient:

$$D = \pi r^2 / 16$$

where  $r$  is the slope of  $M_t/M$  diagrams versus  $(t/s)^{1/2}$  and  $D$  is expressed in  $\text{cm}^2 \text{s}^{-1}$ .

### Kinetics of swelling by pure monomers at 20°C

Results are given in Table 5. In every polymer, the acrylonitrile diffusion coefficient is always higher than that of styrene. This could be explained comparing molar volumes of the two solvents. The molar volume is about  $66 \text{ cm}^3$  for acrylonitrile and  $115 \text{ cm}^3$  for styrene. The swelling kinetics is sensitive to crosslink density. The denser the network, the slower acrylonitrile diffuses. The reverse is observed in the case of styrene. This discrepancy in the behaviours can be explained as proposed by Zosel<sup>12</sup>. In fact, when the latex particles are crosslinked enough, the film cast from the latex shows bad cohesion. Crosslinking decreases the probability of existence of linear macromolecules that can diffuse during coalescence from one particle to another, allowing cohesion. So, as styrene is a good 'solvent' of polybutadiene and if the film is not really cohesive, the osmotic pressure due to styrene can dislocate the film. Preferential ways appear for the solvent and the diffusion rate seems to be higher.

Since acrylonitrile is not a good solvent of polybutadiene (the interaction parameter is about 1.29), the osmotic pressure is not important enough and the diffusion rate varies, as expected, with the density of the network.

Swelling by a monomer mixture: effect of the composition

Results of these experiments are plotted on Figures 10 and 11. It appears that the diffusion coefficients of the mixed monomers exhibit a minimum for the equimolar concentration (S/AN = 65/35 by weight). When the initial concentration of acrylonitrile in the mixture is higher than 35 wt% the mixture behaves as pure acrylonitrile and its diffusion coefficient decreases in denser network. But, when the mixture contains more than 65 wt% styrene, its behaviour is that of pure styrene: the smaller the distance between two crosslinking points in the film the higher is the coefficient of diffusion.

Influence of temperature on diffusion coefficient of S and AN from a 70/30 mixture

As shown on Figures 12 and 13, the diffusion coefficients of each monomer are markedly affected by the presence of the second monomer. Acrylonitrile coefficient in the mixture is lower than that of pure acrylonitrile. The increase is effective for temperatures above 45°C.

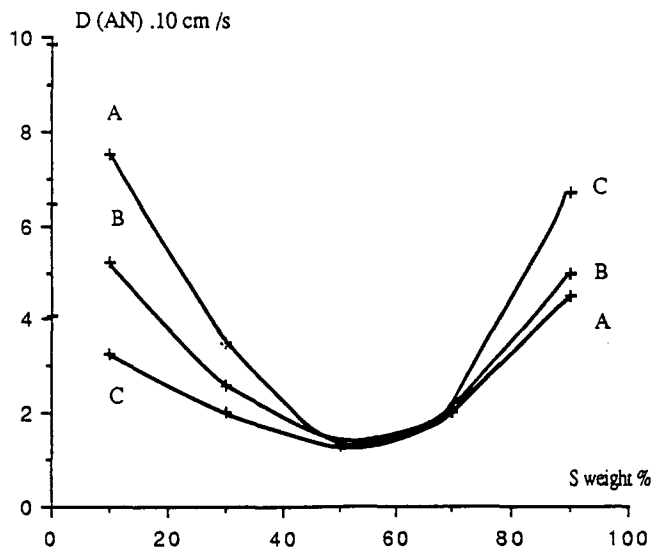


Figure 10 Diffusion coefficient of acrylonitrile (AN) from S-AN mixtures of various initial composition

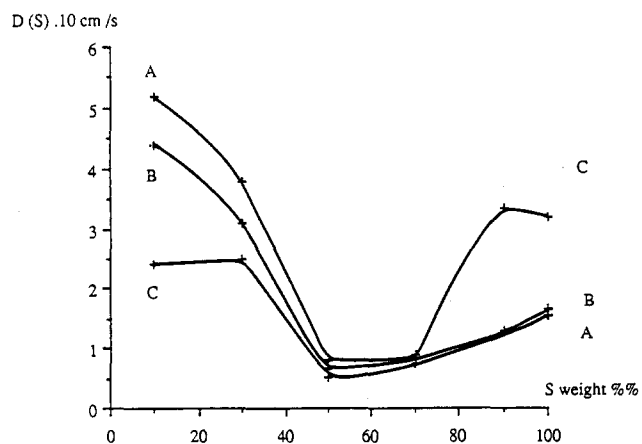


Figure 11 Diffusion coefficient of styrene in polybutadiene films from S-AN mixtures of various initial composition

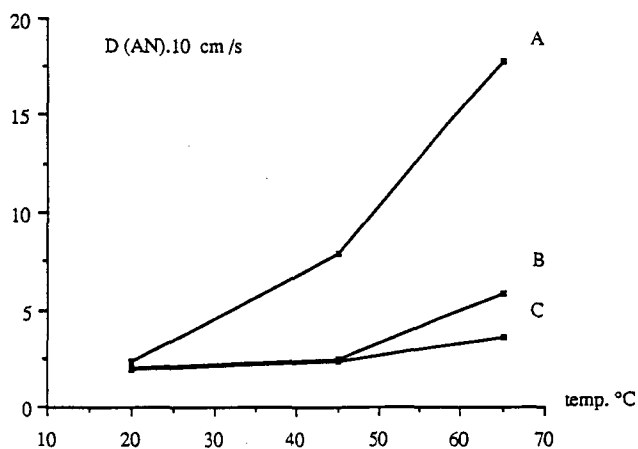


Figure 12 Diffusion coefficient of AN from initial mixture 70 wt% S in polybutadiene films as a function of temperature

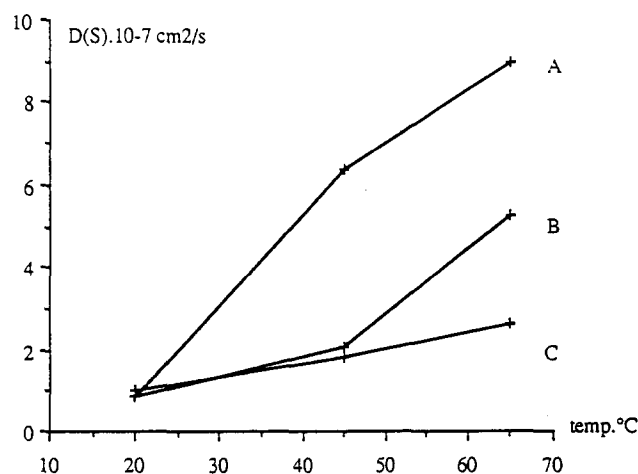


Figure 13 Diffusion coefficient of S from initial mixture 70 wt% S in polybutadiene films as a function of temperature

CONCLUSIONS

Swelling of polybutadiene (PB) films by pure acrylonitrile (AN) and styrene (S) or by S-AN mixtures of various compositions have allowed information about thermodynamic and kinetic aspects of the phenomenon to be obtained. Study of the thermodynamic parameters,  $M/P$  (maximum swelling) and  $\chi$  (interaction parameter), has shown that pure monomers behave in a different way than when they are in a mixture.

Using data from experiments on swelling of films by pure styrene, it was possible to determine the number of butadiene units between two crosslinking points,  $L_{ret}$ . The results were compared with data from simulation of butadiene homopolymerization by a batch process and a good agreement was found between simulation and experiments. From the swelling of films by pure acrylonitrile, the interaction parameter  $\chi_{AN/PB}$  was found about 1.29. This value is much higher than the parameter  $\chi_{S/PB}$  (0.44), explaining that the swelling of AN is always much lower than that of S.

Data from experiments on swelling of particles by pure styrene have shown the influence of the radius on the thermodynamic equilibrium, as predicted by Flory. For particles smaller than 100 nm diameter, the maximum swelling is affected much more by the radius than by the crosslink density. The phenomenon is the opposite for

larger particles. These experimental observations were confirmed by simulation.

In the case of the mixture, the concentration of each monomer has an influence on the behaviour of the other. The higher the AN concentration in the mixture, the lower is the maximum swelling by S. The opposite effect is observed for AN swelling. The interaction parameters between the two solvents could be a function of the composition of the initial mixture.

The kinetics of swelling was studied by determining the diffusion coefficients of pure and mixed solvents. According to its smaller molar volume, pure acrylonitrile diffuses faster than styrene in every polybutadiene. The network density does not have the same influence on AN and S swellings. The diffusion rate of AN in the film is decreasing when the crosslinking is denser. This is not the case with styrene, whose diffusion coefficient increases in a denser network. The coalescence process of crosslinking latexes can be considered as the reason for this behaviour.

The diffusion coefficients of mixed monomers are functions of the mixture composition. They are lower than those of the pure monomers. The equimolecular mixture, S/AN 65/35 wt%, seems to be particular. For this composition, the diffusion coefficients of S and AN are smaller. For lower concentrations of styrene, the system behaves as pure acrylonitrile and similarly as pure styrene for higher concentrations of styrene.

Experiments at different temperatures have shown that the diffusion coefficients of the mixed monomers are increasing when the temperature becomes higher.

Taking into account the effect of osmotic pressure due to styrene in the films, it is not a good approach to use

the experimental diffusion coefficients of S for diffusion into particles of mixtures with more than 60 wt% S.

During the polymerization of S-AN on a seed of polybutadiene, a composition drift of the copolymer appears. First, it is due to the difference of the reactivity ratios. On the other hand, it is due to the change in the comonomer composition because of the partition in the different phases (AN is very much more soluble in water than S, and S swells the polybutadiene much more than AN).

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