

Randomly cross-linked copolymers ethylene vinyl acetate and ethylene methyl acrylate. N.m.r. observation of dry and swollen states

A. Viallat* and J. P. Cohen-Addad

Laboratoire de Spectrométrie Physique Associé au CNRS, Université Joseph Fourier, BP87, 38402 St Martin d'Hères Cedex, France

and P. Cassagnau and A. Michel

Laboratoire des Matériaux Organiques à Propriétés Spécifiques, CNRS, BP24, 69390 Vernaison, France

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This work deals with the swelling properties of polyethylene gels prepared from long precursor ethylene/ethylene methyl acrylate (EMA) and ethylene/ethylene vinyl acetate (EVA) copolymers by random cross-linking between the EVA and EMA monomers repeated along the ethylene chains. An n.m.r. approach is proposed to characterize the statistical structure of dry and swollen gels. A power law relationship observed between the n.m.r. parameter and the swelling ratio suggests that the swollen gels obey a packing condition. The mechanisms of swelling of active statistical segments are investigated: a progressive change of chain segment conformation is evidenced upon swelling. A single master curve characterizing variations of chain statistics with the concentration is obtained for gels prepared at various cross-link densities.

INTRODUCTION

It is now well established that the presence of permanent cross-links or coupling points confers to polymer networks a complex statistical texture. The statistical units which structure the network correspond to correlation domains and define the gel mesh size. The collective behaviour of these meshes governs the mechanisms of deformation of gels submitted, for instance, to an elongational extension or to a swelling effect. Although the correlation domains which characterize polymer networks near the gel point are usually well described by the theory of percolation^{1,2}, applied in its critical³ or in its mean field Flory-Stockmayer version^{4,5}, no general framework of the description of more strongly cross-linked gels has been developed until now.

The main difficulty consists of identifying these correlation domains since they are not simply defined by two consecutive cross-links. They depend on the number and the statistical repetition of junction points along the polymer chains. The topological properties of gels and, therefore, their mechanisms of deformation strongly depend on the method of network preparation. For instance, the swelling behaviour of end-linked gels is different from the behaviour of randomly cross-linked vulcanizates: the swelling ratio of end-linked systems increases with the molecular weight of precursor chains^{6,7}, whereas, for vulcanizates⁸, it decreases with the molecular weight of precursor chains.

Correspondingly, the distribution of cross-links is different in the two networks. In the former system, the long precursor chains are retained in the final gel structure since the cross-linking sites are located at both chain extremities, and there is no dangling chain ends, while in the latter system the cross-linking sites are randomly distributed among all monomers and, therefore, no length characteristic of precursor chains is preserved in the final gel structure. Moreover, many dangling chain ends are present in the structure. This example shows that a better understanding of the physical behaviour of polymer gels necessitates a deep insight into the intimate statistical structure of networks.

This work concerns the swelling behaviour of well-defined networks made from copolymers ethylene/ethylene vinyl acetate (EVA) and ethylene/ethylene methyl acrylate (EMA) where the fraction and the average distribution of EVA and EMA sites along the chains are known. The random cross-linking reaction occurs between EVA and EMA sites. These gels exhibit features which are common to the two systems which have just been evoked: they are characterized by a random repetition of cross-links among the comonomer sites along the chain, as in the case of vulcanization. However, as in the case of end-linked gels, the short chain segments defined by two consecutive EVA or EMA sites along the precursor polymer chains are retained in the final gel structure.

The purpose of this work is to explore the statistical structure of these gels and to describe their mechanisms of swelling in good solvent. An n.m.r. approach is proposed, coupled with macroscopic swelling experiments, to investigate at a pertinent molecular space-scale

* To whom correspondence should be addressed

the mechanisms of chain segment deformation upon swelling.

The proposed n.m.r. approach relies on observation of the transverse magnetic relaxation of spins of protons attached to the chain segments. The topological constraints exerted on polymer chains by cross-links define chain segments with fixed extremities, whose rotational motions of monomeric units, hindered by the coupling points, are strongly non-isotropic. The transverse magnetization is sensitive to the non-isotropic orientations of skeletal bonds: it probes the state of deformation of network chain segments induced by the presence of constraints.

EXPERIMENTAL

Materials

EVA and EMA copolymers were supplied by Atochem. The respective amount of acetate and acrylate groups contained in these copolymers, x_A and x_B , is 28 wt% and the respective molecular weights for the EVA and EMA copolymers are respectively: $M_{w,A} = 53.5 \text{ kg mol}^{-1}$, $M_{n,A} = 19 \text{ kg mol}^{-1}$ and $M_{w,B} = 94.3 \text{ kg mol}^{-1}$, $M_{n,B} = 22 \text{ kg mol}^{-1}$.

The glass transition temperature, T_g , of the EVA/EMA miscible blend was measured by d.s.c. experiments; it was observed at 242 K. The EVA/EMA system exhibits a crystalline phase at room temperature. The melting point of the crystalline phase was observed at about 333 K. The amount of crystallinity was measured by n.m.r.; as expected, the stronger gels were less crystallized. All swelling and n.m.r. experiments were conducted above the melting temperature at 343 K and 373 K.

The number of acetate (or acrylate) sequences per ester unit is derived from the quantitative distribution of the ester centred triads. This distribution is obtained from ^{13}C n.m.r. spectra based on assignments reported by Randall⁹.

The quantitative distribution of acrylate units in EMA copolymers is obtained from ^{13}C n.m.r. spectra with the assignments reported by Bruch¹⁰.

The results are the following:

ethylene vinyl acetate copolymers; sequences EVE, EVV, VVV, respectively, in 95%, 5% and 0%;

ethylene methyl acrylate copolymers; sequences EAE, EAA, AAA, respectively, in 90.75%, 7.95% and 1.30%.

The average sequence length of ethylene sequences between two comonomer units EVA or EMA is, respectively, equal to 7.9 and 8.1 monomers.

The initial systems are therefore well-defined: comonomers are isolated from one another along the chains and the average distance separating adjacent comonomers in both EVA and EMA copolymers are similar.

Network formation

The reaction of ethylene vinyl acetate and ethylene methyl acrylate polymer blends with dibutyl tin oxide in a molten state leads to irreversible co-cross-linking of the copolymer chains¹¹.

The presence of methyl acetate indicates that some redistributive transesterification occurs giving covalent cross-linking by the following reaction:



The kinetics of this cross-linking reaction has been assessed by thermogravimetric analysis coupled with gas chromatography, which allows the measurement of moles of methyl acetate evolved¹¹. From the kinetic equation, the evolved moles per volume of methyl acetate come from the formation of identical moles per volume of cross-linking junctions.

Therefore, the cross-link density of the EVA/EMA network is quantitatively determined from the value, p_A , of the extent of the reaction.

Network preparation

The EVA/EMA/Bu₂SnO blend was fixed at 48/48/4 wt%. This blend was mixed in a twin-screw extruder (Leistritz, LSM30-34). The temperatures were regulated from 130°C at the feed zone to 165°C at the die. The networks were formed in a molten state by curing between heating parallel plates at a temperature of 200°C. From different curing times at this temperature, EVA/EMA networks with various extents of cross-linking were obtained. The extent of the reaction was achieved from the kinetic curve which was validated in a previous study¹¹.

Measurements

The state of maximum swelling on the gels was induced by the osmotic pressure of xylene. The equilibrium swelling ratio was measured by gravimetry.

N.m.r. experiments were performed using a pulse spectrometer MSL 100 Brüker operating at 60 MHz. All relaxation functions were measured by using Carr–Purcell spin–echo sequences. Pseudosolid echoes have been described elsewhere. They are formed from the following appropriate pulse sequence:

$$\begin{aligned} &(\pi/2)_y - \tau/2 - (\pi)_y - \tau/2 - (\pi/2)_{-x} - \tau/2 - (\pi)_y \\ &- \tau/2 - (\pi)_{-y} - \tau/2 - (\pi)_{-y} - \tau/2 - (\pi)_y \end{aligned}$$

The swelling effect studied by n.m.r. was made by using deuterated xylene; swollen gels were placed in sealed n.m.r. tubes under a nitrogen environment.

PRINCIPLE OF THE N.M.R. APPROACH

The principle of the n.m.r. approach relies on observation of the transverse magnetic relaxation of spins of protons located on polymer chains. The relaxation process results from dipole–dipole interactions existing among nuclear spins. These interactions are significantly averaged in molten and dilute systems by the fast molecular diffusional motions of monomeric units. However, the conformational fluctuations of chain segments defined between two entanglements in melts or between two consecutive cross-links in gels exhibit a non-isotropic character due to the presence of topological constraints which are exerted on both ends of the segments. The resulting non-isotropic motions of skeletal bonds of these chain segments induce a non-zero average of dipolar interactions. The residual dipolar interaction governs the relaxation of the transverse magnetization of gels. It is sensitive to the reduction of entropy affecting the chain segments caused by the presence of cross-links. It provides structural information about the state of deformation of these segments. In melts, the topological constraints induced by entanglements are not permanent

and so, the existence of the residual dipolar interaction is directly associated with the lifetime of entanglements. In this case, the first average process of dipole-dipole interactions leading to the residual dipolar interaction is followed by a further progressive reduction of dipolar interaction when the chain segments progressively lose their orientational memory and vanish. In this case, n.m.r. observations reflect the molecular motions of disentangling chain segments.

Pseudosolid behaviour

Identification of the mechanisms of magnetization relaxation is necessary to determine the nature of the information provided by n.m.r. observations. This can be done easily by the observation of pseudosolid echoes

on the n.m.r. signal. Such echoes are formed only when relaxation of the transverse magnetic relaxation is governed by pure residual dipolar interactions. The spin echo function obeys specific properties¹². First, the intersection of two echo functions formed at $t = \tau_1$ and $t = \tau_2$ must occur at $t = \tau_1 + \tau_2$. Second, the tangent of the relaxation function and the echo function must be opposite at the starting point of the echo function. These properties are verified in the case of a gel at 100°C (*Figure 1b*). By contrast, these properties are not verified in the melt at 100°C where echoes are flat (*Figure 1a*). In this latter case, the relaxation rate of entanglements is high enough to induce a partial motional averaging effect of the residual spin interactions: in molten uncross-linked systems, the relaxation process of the proton

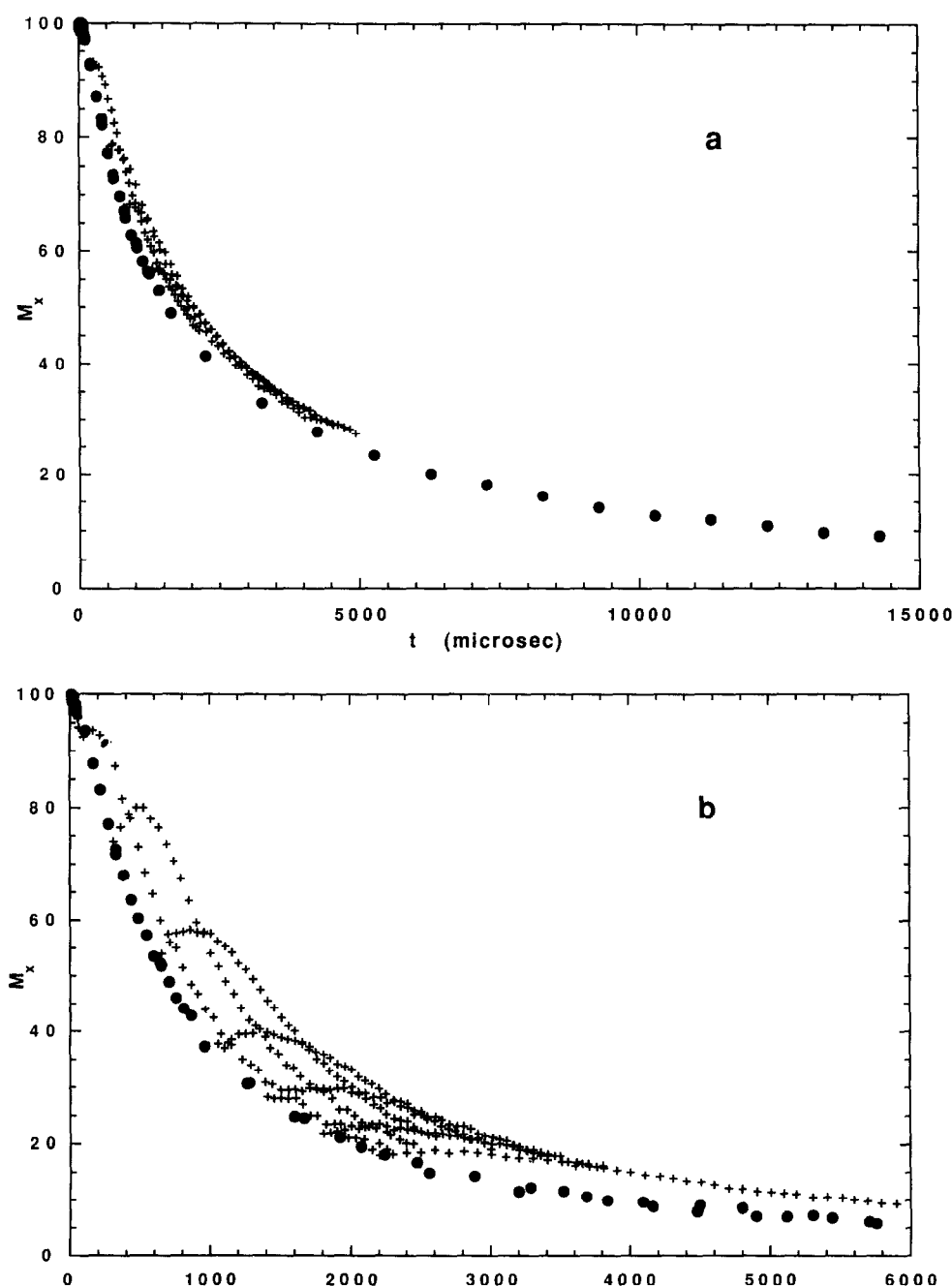


Figure 1 Relaxation functions (●) of uncross-linked (a) and cross-linked (b) systems at $T = 100^\circ\text{C}$. Pseudosolid echoes (+) are well-defined in (b) and flat in (a)

transverse magnetization reflects the molecular dynamics of chain segments.

Spin interactions in gel

The residual dipolar interaction induced by the existence of non-isotropic rotations of monomeric units entirely governs the mechanism of relaxation of the transverse magnetization of gels. The residual dipolar interaction of a chain segment *i* of contour length *L* defined by two adjacent coupling junctions is expressed as¹²

$$\langle H_D(r_L, L) \rangle = (3 \cos^2 \theta_L - 1) \frac{\langle r_L^2 \rangle}{\langle r_L^2 \rangle_0} a^2 \Lambda H_D^0 \quad (1)$$

where H_D^0 is the dipole–dipole interaction which should be observed along one chain segment in the glassy state, *a* is the skeleton bond length, $\langle r_L \rangle$ is the non-zero averaged end-to-end vector of the chain segment, θ_L is the angle between the end-to-end vector r_L and the steady magnetic field, $\langle r_L^2 \rangle_0$ is the mean square end-to-end distance of a segment; it is proportional to *L* for a Gaussian chain; Λ accounts for angular correlations among three neighbouring skeletal bonds of the segment *i*.

The relaxation function assigned to the chain segment *i* is

$$M_x(r_L, L)(t) = \text{Tr} \{ e^{i(H_D(r_L, L))t} M_x e^{-i(H_D(r_L, L))t} M_x \} / \text{Tr} \{ M_x^2 \} \quad (2)$$

The relaxation function of the whole sample is the average of $M_x(r_L, L)$ over all network chain segments. Each segment is characterized by its contour length *L* and its end-to-end vector r_L :

$$M_x(t) = \int G(r_L, L) M_x(r_L, L)(t) dr_L dL \quad (3)$$

where $G(r_L, L)$ is the distribution function of end-to-end vectors of chain segments constituting the gel. The possible distribution of contour lengths *L* of chain segments is accounted for by writing $G(r_L, L)$ as a product of a distribution over *L* and a distribution over end-to-end vectors of segments of given contour length *L*:

$$G(r_L, L) = D(r_L)P(L)$$

Spin response analysis

A specific method of analysis of relaxation curves has been recently developed¹² when the relaxation function is governed by pure residual spin–spin interactions. It provides information on the size of characteristic chain segments of the gels, i.e., of the mean contour length of chain segments, and on the moments of the distribution, $D(r_L)$, of end-to-end vectors of the chain segments.

The two following integrals are easily computed¹²:

$$\phi_1 = \int_0^\infty (\sqrt{t})^{-1} M_x(t) dt \quad (4)$$

$$\phi_3 = \int_0^\infty (\sqrt{t})^{-1} \frac{dM_x(t)}{dt} dt \quad (5)$$

where $M_x(t)$ is given by equation (3). Then, it is shown¹² that the ratio (ϕ_3/ϕ_1) is equal to χ_c , where χ_c is given by equation (6):

$$\chi_c \propto \frac{\Lambda}{a^3} \frac{m_3}{m_1} \langle r_L^2 \rangle_L^{-1} \propto \frac{\Lambda}{a^3} \frac{m_3}{m_1} L_m^{2\nu} \quad (6)$$

The average size of one chain segment is given by $\langle r_L^2 \rangle_L^{1/2} \propto (L_m/a)^\nu$, where the average $\langle r_L^2 \rangle_L$ is performed over all contour lengths, $\nu = 0.5$ for a Gaussian chain of 0.588 for a chain with excluded volume and L_m is the gel mean contour length (first moment of the distribution $P(L)$).

The product $\phi_1\phi_3$ is equal to π_c , where π_c is given by equation (7):

$$\pi_c \propto m_3 m_1 \quad (7)$$

where $m_i = \int_0^\infty D(r_L/\sigma_L)(r_L/\sigma_L)^i d(r_L/\sigma_L)$ are the moments of the normalized distribution $D(r_L/\sigma_L)$, where σ_L is the mean quadratic value of the end-to-end vector of a chain segment.

Therefore, the parameter π_c reflects changes of the shape of the distribution function of end-to-end vectors r_L , for instance from a Gaussian distribution to an excluded volume distribution, while the parameter χ_c is sensitive to the size of network chain segments, L_m ; χ_c plays the role of a relaxation rate.

DRY CROSS-LINKED SYSTEMS

Prior to investigation of the mechanisms of gel deformation induced by swelling, it is worth studying the physical state of networks characterized by various cross-link densities. The statistical structure of gels is investigated from the n.m.r. parameters χ_c and π_c in molten systems at 70°C and 100°C.

State of gelation

The effect of variation of temperature on the relaxation functions is illustrated in *Figure 2*. Pseudosolid echoes are well defined at all temperatures. This discloses that the mechanisms of n.m.r. relaxation are governed by pure dipolar interactions. Therefore, the relaxation function of gels observed at high temperature can be characterized by the n.m.r. parameters χ_c and π_c . Variations of χ_c and π_c are represented in *Figures 3a* and *b* as a function of the cross-link density. Variations of χ_c are linear with the cross-link density at 70°C and 100°C. This shows that the effects of cross-linking upon the n.m.r. behaviour are additive. Enhancement of the orientational order of skeletal bonds results from the increase of density of internal constraints, which is linear with the cross-link concentration. Such a behaviour has already been observed on vulcanized polybutadiene chains¹³. The parameter π_c is constant: this independence with respect to the concentration of cross-links and to the temperature shows that the statistical law of distribution of end-to-end vectors between coupling junctions is invariant.

Values of $\chi_c(0)$ have been extrapolated at 70°C and 100°C. Each value of $\chi(0)$ is associated with the initial state of constraints in the system, which is enhanced by addition of topological constraints due to cross-linking process. This initial state of constraints was found to correspond to simply entangled polybutadiene chains in ref. 13. The entanglement network cannot be directly perceived by n.m.r. in an EVA/EMA molten system since its lifetime is short compared to the n.m.r. timescale as is shown by the badly defined shapes of pseudosolid echoes (*Figure 1*). However, this temporary entanglement network is indirectly perceived in gels since it is frozen by the presence of cross-links: it is characterized by the

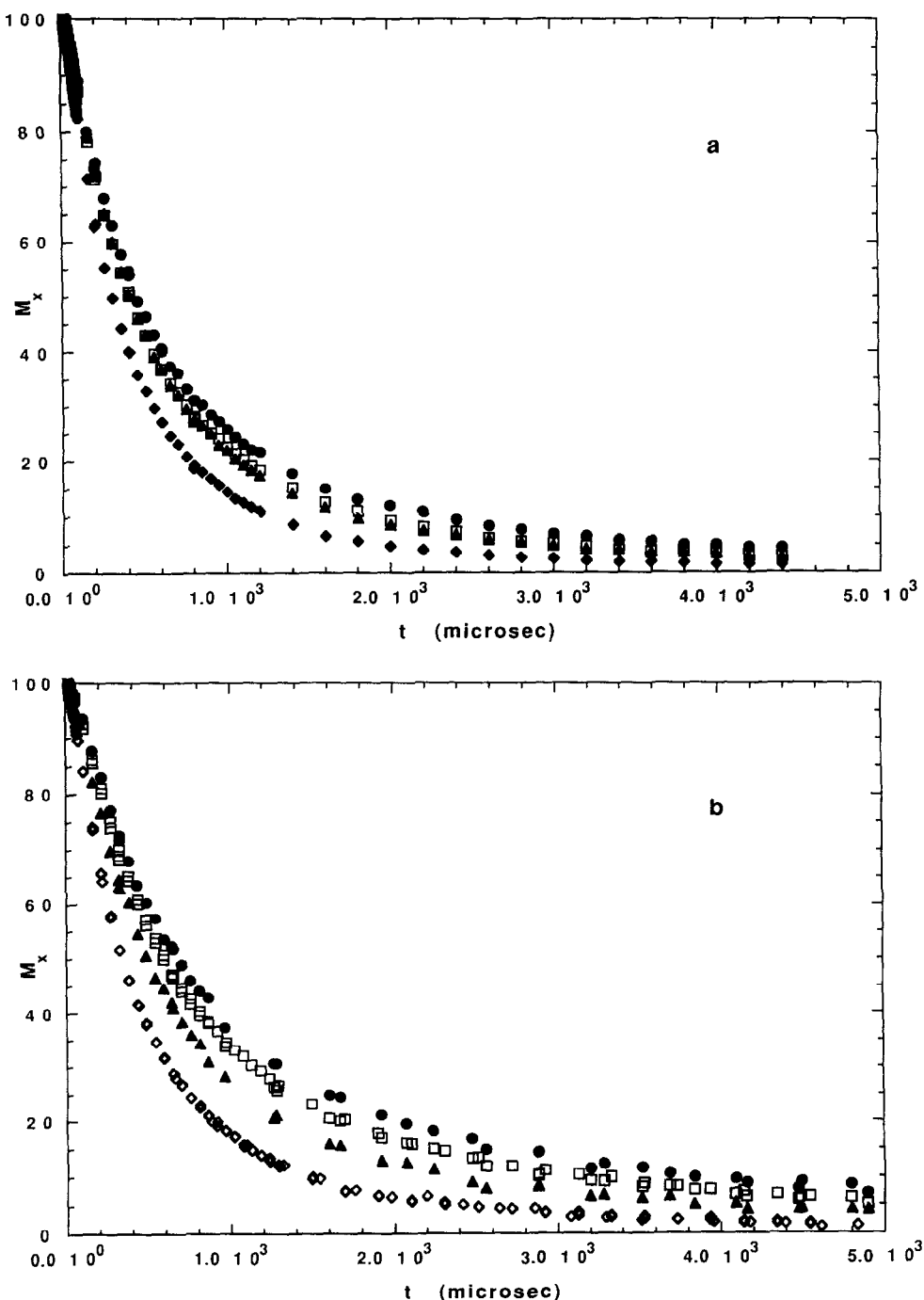


Figure 2 Relaxation functions of molten gels at (a) 70°C: ● $p_A = 0.0125$; □ $p_A = 0.022$; ▲ $p_A = 0.06$; ◆ $p_A = 0.175$; and at (b) 100°C: ● $p_A = 0.0125$; □ $p_A = 0.022$; ▲ $p_A = 0.06$; ◆ $p_A = 0.175$; + $p_A = 0$

density of constraints revealed by the extrapolated value of $\chi_c(0)$. The observed decrease of $\chi_c(0)$ upon raising the temperature is due to an increase of free volume with temperature which affects the term Λ : the increase of free volume enhances the local chain flexibility.

SWOLLEN GELS

An n.m.r. approach, coupled with swelling measurements, is proposed to describe the states of maximum and intermediate swelling induced by the osmotic pressure of a good solvent. The state of swelling of each gel is characterized at 70°C by its swelling ratio, Q , and by the n.m.r. parameters χ_c and π_c computed from

the transverse magnetization of the swollen gel. Although the n.m.r. relaxation functions of swollen gels are characterized by a long decay (up to 50 ms), they are governed by pure residual spin-spin interaction: pseudosolid echoes are well defined.

The quantities Q_m and χ_m , measured at the maximum swelling as well as the gel fraction, G , must be a function of the same variable of gelation, τ , discussed below.

Variable of gelation

The formation of a system of randomly cross-linked chains is usually described by a process of percolation. The variable of gelation, τ , is then proportional to the

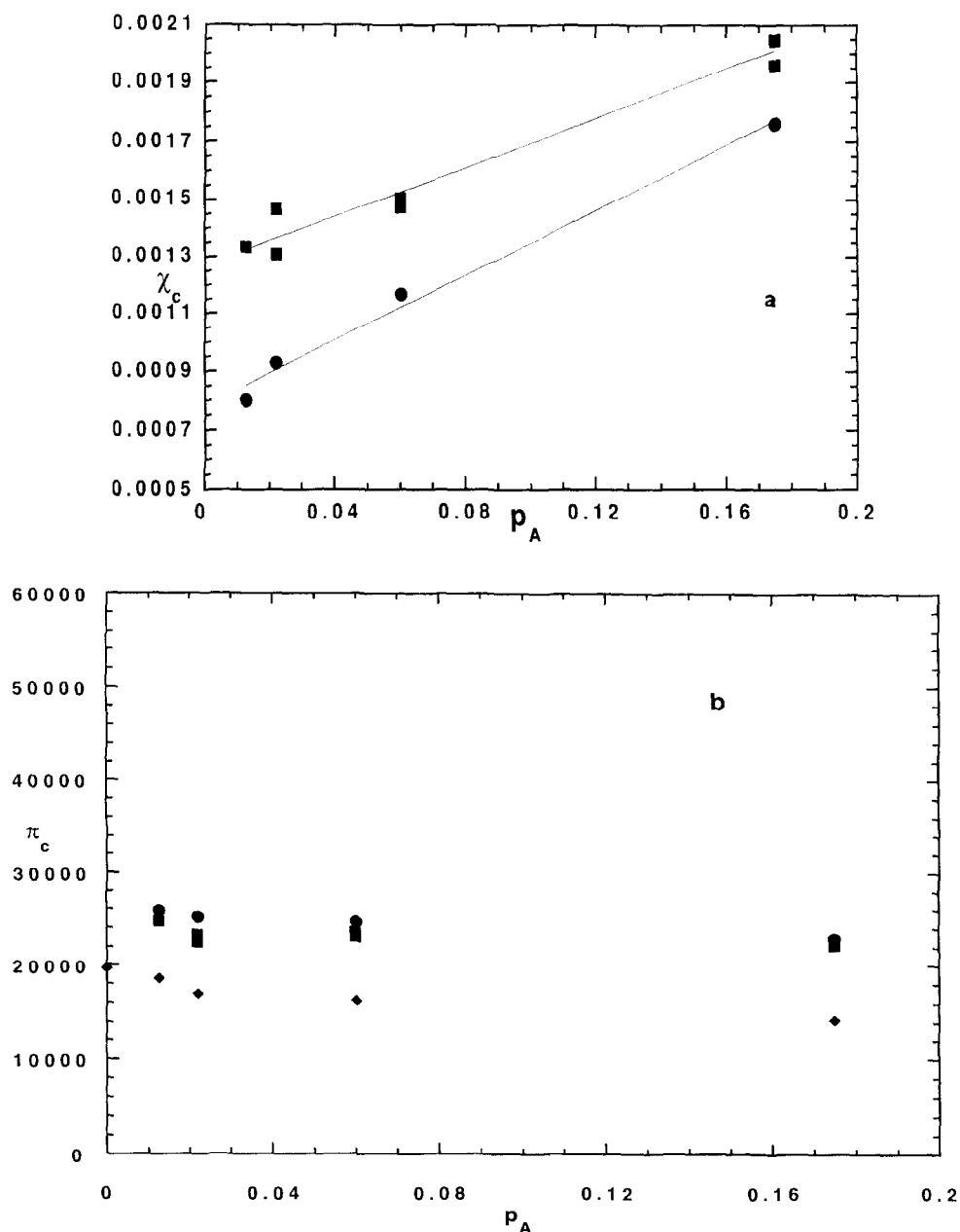


Figure 3 (a) Variations of χ_c as a function of p_A , and (b) variations of π_c as a function of p_A : ■ $T = 70^\circ\text{C}$; ● $T = 100^\circ\text{C}$; ◆ $T = 25^\circ\text{C}$

variable of percolation, $p - p_c$, where p is the probability of attaching one chain to another and p_c is the value of p at the threshold of gelation; in the gels studied here, p can be identified with the extent of the reaction p_A . Following the Flory approach⁴, the value of p_c can be roughly estimated from the value of p for which the average number, $\langle n \rangle$, of cross-links expected on a chain which belongs to a cluster becomes greater than 1. This number $\langle n \rangle$ is obtained from experimental values (molecular weight, amount of EVA and EMA units along the chains and stoichiometry); it is found to be of the order of $290p_A$, so that $p_c \approx 0.0035$. The variable of gelation, τ , is therefore predicted to be proportional to the factor $(p_A - 0.0035)$.

The gel fraction, G , is the order parameter for sol-gel transition³. It is currently taken to describe the cross-linking and the swelling process^{14,15}. Experimental values of G are reported in Table 1. Although G is obviously a function of τ , it is not directly related to the statistical

unit which gives rise to the swelling process since the gel fractions of strongly cross-linked systems are equal to 1 although their swelling ratios differ from one to another.

The maximum swelling ratio, Q_m , and the n.m.r. parameter, χ_m , observed on swollen gels are both functions of p_A (Figures 4a and b). The limiting values of p_A corresponding to the threshold of percolation ($Q_m^{-1} = 0$ and $\chi_m = 0$) are of the order of the estimated value of p_c , 0.0035.

Table 1

p_A	G	Q_m (70°C)	Q_m (25°C)	Crystalline fraction
0.0125	0.78	17.6	5.1	0.29
0.0220	0.89	8.9	4.5	0.29
0.0600	0.94	5.2	4.4	0.14
0.1750	0.98	3.8	3.8	0.07
0				0.25

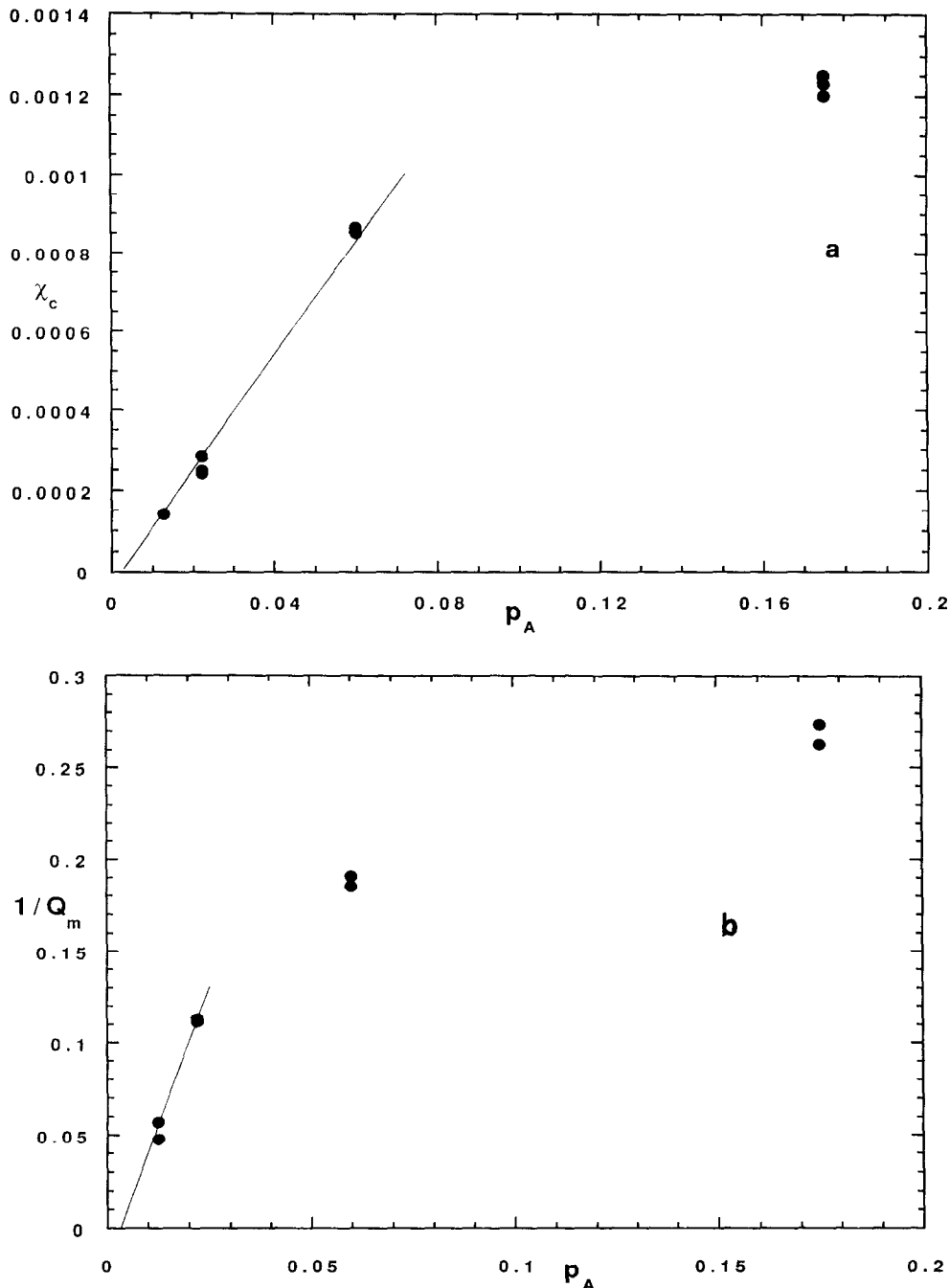


Figure 4 (a) Variations of χ_c measured on gels swollen at equilibrium as a function of p_A . (b) Variations of the inverse of the maximum swelling versus p_A ; $T = 70^\circ\text{C}$

Equilibrium swelling: a packing condition

The coupled n.m.r. and swelling approach is used to describe the state of maximum swelling. According to the c^* theorem proposed by de Gennes¹, a fully swollen gel can be pictured as a close packing of elementary chain segments of size L , disengaged from one another. The swelling ratio is expressed as

$$Q_m \propto \frac{\int_0^\infty L^{3\nu} P(L) dL}{\int_0^\infty LP(L) dL} \quad (8)$$

The numerator is the volume of the swollen gel and the denominator is the volume of the dry gel.

The swelling ratio is written from equation (8) as a

function of the mean value L_m :

$$Q_m \propto \frac{L_m^{3\nu}}{L_m} \propto L_m^{3\nu-1} \quad (9)$$

The n.m.r. parameter χ_m is expressed from equation (6)

$$\chi_m \propto L_m^{-2\nu} \quad (10)$$

It is thus predicted to depend on the swelling ratio according to the power law

$$\chi_m \propto Q_m^{-\frac{2\nu}{3\nu-1}} \quad (11)$$

A power law is experimentally observed as shown in Figure 5: the parameter χ_m varies linearly with Q_m^{-2} over a significant range of values of χ_m and Q_m . This result indicates that ν is equal to 0.5, revealing a Gaussian

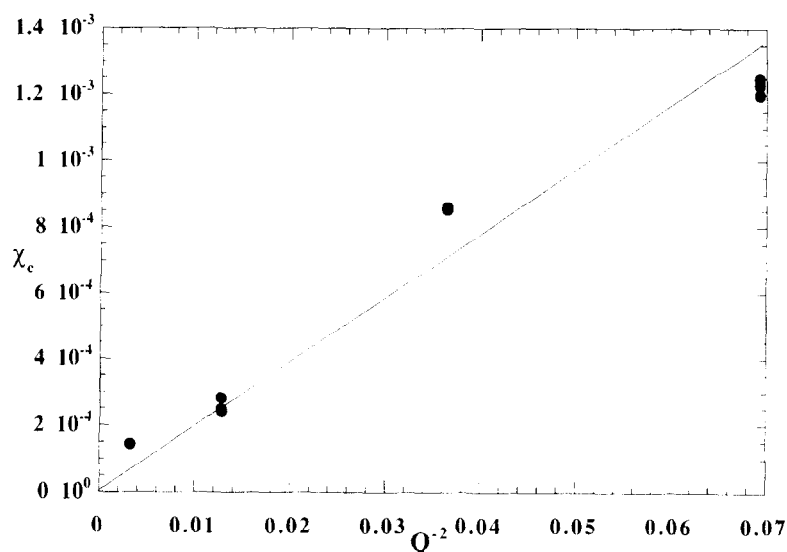


Figure 5 Variations of χ_c versus the variable Q^{-2} for gels swollen at equilibrium at various cross-link densities: $T = 70^\circ\text{C}$

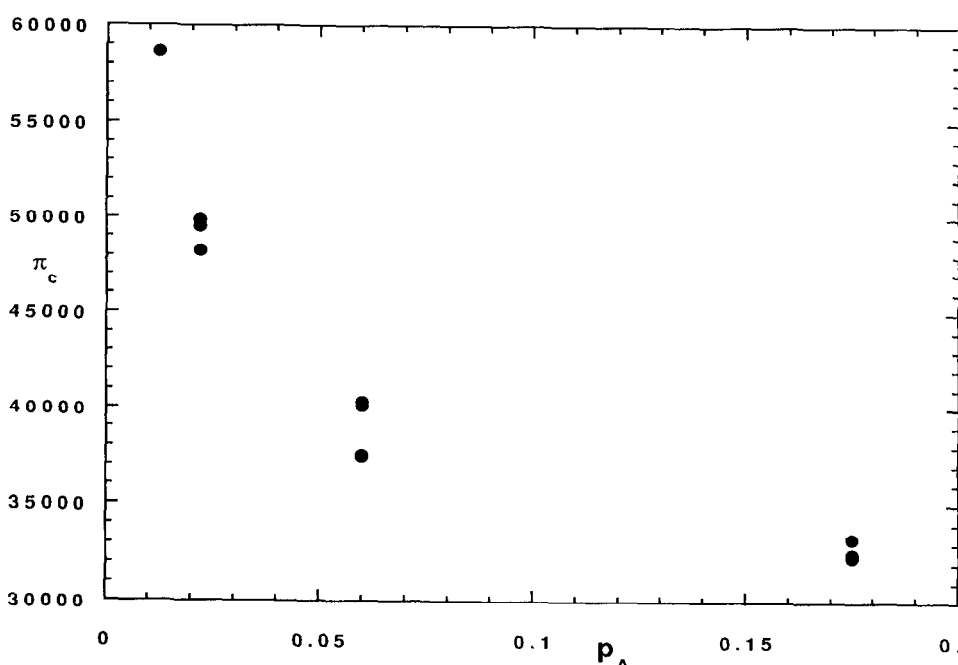


Figure 6 Variations of π_c measured at 70°C on gels at their maximum swelling state as a function of p_A

statistic of chain segments. This law of variation has been reported recently for vulcanized polybutadiene chains¹³. It is considered that the numerous dangling chain ends within the gel induce a screening of excluded volume interactions of active chain segments.

This approach shows that a relationship is clearly established between the macroscopic deformation applied to the gel and associated local deformations of structural chain segments. The observation of this relationship does not necessitate the exact identification of these active segments perceived at a molecular space-scale by n.m.r.

The parameter π_m , measured in fully swollen EVA/EMA gels, is reduced when the variable of gelation is increased (Figure 6). This result indicates that the width of the law of distribution of end-to-end vectors of an active segment narrows when the cross-link density increases, in gels swollen at equilibrium.

States of intermediate swelling

States of intermediate swelling are obtained by adding given amounts of solvent to gel samples. Variations of the n.m.r. parameters χ_c and π_c are reported as a function of Q in Figures 7a and b. A fast decrease of χ_c is observed when Q increases from 1 to 2. Then, χ_c slowly decreases and reaches the value obtained for the corresponding fully swollen systems. By considering that the ratio m_1/m_3 is roughly independent of the degree of swelling, equation (6) indicates that the value of L is expected to strongly increase at the beginning of the process of swelling, when Q increases from 1 to 2.

It has been noted that the parameter χ_c was sensitive to the reduction of entropy of a chain segment due to the presence of coupling points, whatever their nature. It is considered that although chain segment extremities remain constrained in swollen gels, the entropy of a

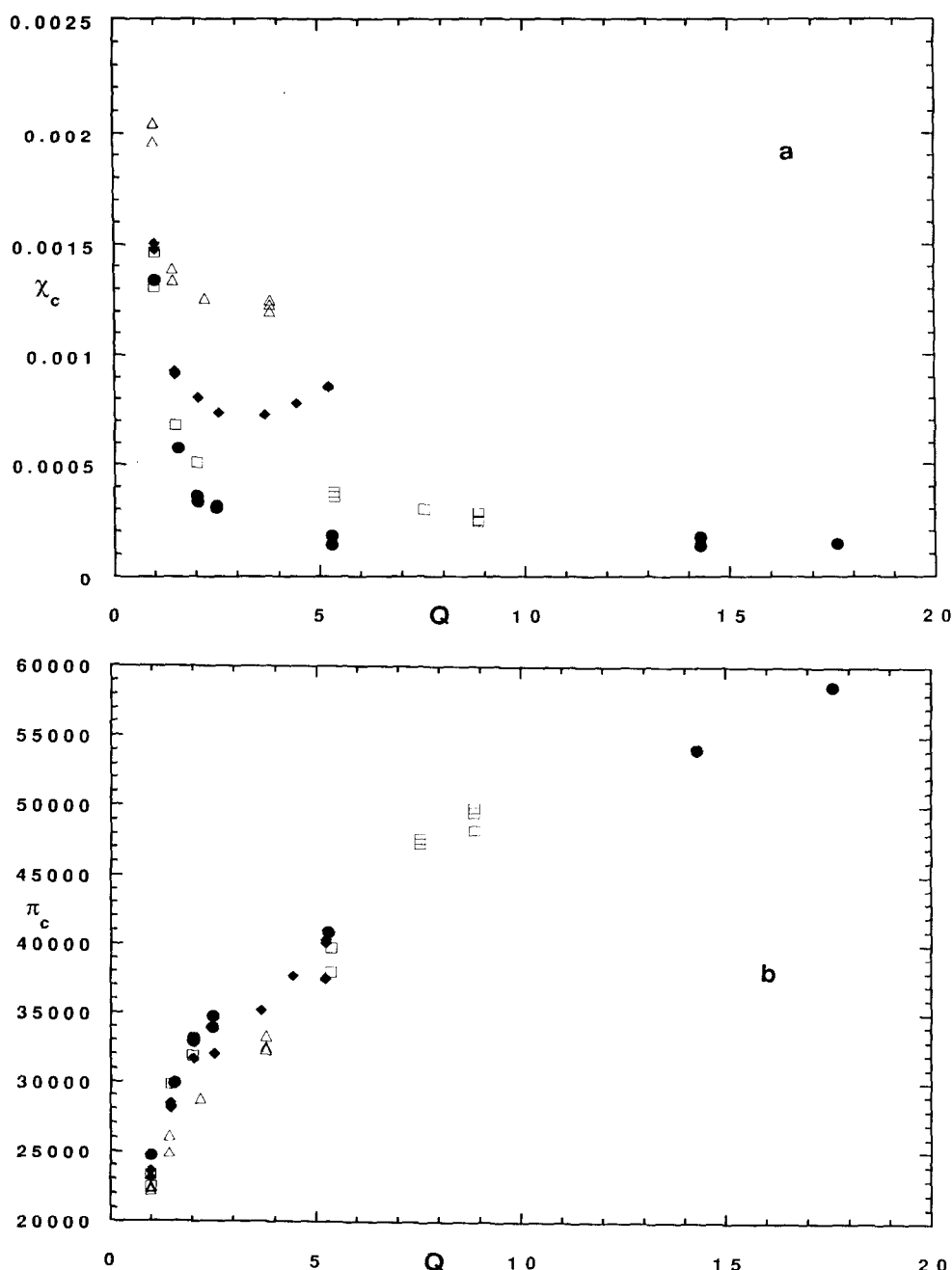


Figure 7 Variations of (a) χ_c and (b) π_c measured at 70°C on gels at intermediate degrees of swelling as a function of the swelling ratio Q : Δ $p_A = 0.175$, \blacklozenge $p_A = 0.06$, \square $p_A = 0.022$, \bullet $p_A = 0.0125$

segment increases upon dilution. This effect can be pictured as a disinterspersion of polymer chain segments upon dilution. It reflects the increase of the number of degrees of freedom of rotational motions with dilution, these motions remaining non-isotropic.

The parameter π_c is found to be an interesting variable to describe the mechanisms of segmental deformation upon swelling. It increases continuously with Q . A single master curve is obtained, for all cross-link densities of partially swollen gels. The parameter π_c reflects the shape of the distribution function of end-to-end vectors of a given contour length (equation (7)). Variations of π_c with Q disclose a broadening of the distribution function upon swelling. Two main phenomena may be evoked to explain this change of the distribution function. First, it can be considered that a chain segment becomes progressively less constrained by neighbouring segments

upon dilution: the number of possible chain conformations increases and the distribution function broadens. Second, a progressive change of statistics of active chain segments is observed upon solvent addition. This change of chain statistics detected from the variations of π_c with the concentration can be described by the picture of thermal blobs proposed by de Gennes¹. Each chain segment can be roughly pictured as a Gaussian packing of small domains, or blobs, which obey an excluded volume statistics; the dimension of the chain segment, R , is known to obey the scaling law:

$$R \propto L^{1/2} g^{1/10} a \propto L^{1/2} Q^{1/8} \quad (12)$$

where g is the contour length of the blob and g scales as $g \propto Q^{5/4}$. The blob size increases upon solvent addition so that the distribution function of end-to-end vectors of chain segments is progressively modified upon solvent

addition and depends only on the concentration. However, since even at the maximal swelling ratio the structural chain segment obeys Gaussian statistics, the blob size, characterized by g , is smaller than the chain segment dimension, L .

Finally, it should be noted that the overall dimension of one chain segment is expected, from equation (12), to slowly increase with Q . This prediction may explain the very slow decrease of χ_c , which varies like $1/R^2$, observed experimentally upon increasing Q after the end of the step of disinterspersion ($Q > 2$).

CONCLUSION

The purpose of this work was to progress into the description of the statistical properties of cross-linked polymer chains when the gelation conditions are far from the threshold of percolation. Polymer networks were obtained from the cross-linking process of long polymer chains where the reactive sites were statistically reparted along the chain backbone.

N.m.r. observation of the transverse magnetization of protons attached to monomers is sensitive to the anisotropy of rotational motions of skeletal bonds, induced by the presence of internal topological constraints: permanent cross-links or temporary entanglements. In the dry gels, the effect of constraints induced by the permanent cross-links was simply additive to the effect of constraints induced by entanglements. The permanent cross-links were found to freeze the temporary entanglement network. A standardized n.m.r. approach of swollen gels, relying on simple assumptions about the statistics of chain segments, gave evidence for the deformation of active chain segments upon swelling. A power law was obtained, which relied on the structural properties of the gel at the molecular scale, observed by n.m.r., to the macroscopic gel deformation induced by a swelling effect. This law showed that chain segments swollen at equilibrium are closely packed and obey a Gaussian statistics.

This approach does not require the precise identification of the active chain segments which give rise to the effect of swelling. It is important to be able to distinguish precisely whether active segments can be identified with segments comprised of two adjacent cross-links as is observed for end-linked gels, and in this case the size of

one segment depends on the cross-link density only, or whether they reflect the actual mesh size of the gel, and in this case the size of one segment depends on the number of cross-links per chain (function of the cross-link density and the degree of polymerization of the initial chains), as is observed in polybutadiene vulcanizates. The study of various EVA/EMA gels, prepared from initial chains whose copolymerization ratio and cross-link density are varied, is in progress. This study should lead to identification of the pertinent variable of the state of gelation and to determination of the structural elementary chain segment.

The n.m.r. study of intermediate swelling disclosed the progressive change of statistics of active chain segments. This change was found to be dependent on the concentration only.

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