with $\delta W_0/\delta\vec{j}(s) = \beta l\vec{f}/3$ and $\vec{R} = (\beta L l/3)\vec{f}$. Then

$$(3\cos^2\theta_{\vec{u}(s)} - 1)\mathcal{L}^*(3|\vec{u}(s)|) = (3\cos^2\theta_{\vec{f}} - 1)\mathcal{L}^*\left(3\frac{\beta l\vec{f}}{3}\right) = (3\cos^2\theta_{\vec{R}} - 1)\mathcal{L}^*\left(3\frac{|\vec{R}|}{L}\right)$$

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NMR Approach to the Characterization of the Swelling Process of Polyethylene Networks

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ABSTRACT: Statistical properties of irregular polyethylene networks of different cross-link densities were probed by determining their gel fraction and equilibrium swelling ratio and by measuring the magnetic relaxation of protons. Experimental results were in agreement with the description of the vulcanization of linear chains within a percolation framework leading to a G^{-1} dependence of the equilibrium swelling ratio Q_m. A parametrized assay function was formed to fit the observed relaxation functions. The fit yielded the second and fourth moment behavior of the resonance line. Evidence for a two-step swelling behavior of the PE networks in the presence of a swelling agent (xylene) is given. The second moment of the relaxation functions observed in networks swollen at equilibrium was shown to be independent of the cross-link density. This result was assigned to the existence of a submolecule perceived from NMR with a size smaller than the average distance between cross-links in the polymer gel.

I. Introduction

This work deals with the statistical structure of randomly cross-linked networks obtained from the gelation process of long linear polymer chains. Vulcanization processes of linear chains in the bulk polymer may be pictured either by a classical branching process giving rise to treelike structures or by a percolation process on an infinite renormalized lattice generating on infinite cluster above the percolation threshold. Renormalization consists in taking the primary chain radius for the lattice parameter and the molecular weight Z for the functionality. For vulcanization in contrast with gelation of polyfunctional monomers, both descriptions are not in conflict but give coherent and complementary results.[1]

The swelling behavior of an irregular gel strongly depends on its functionality and cross-link density.[2] A picture of the swelling process must take into account the fractal dimension of the network and of the network strands in the dry state and in the presence of a solvent. A theoretical treatment within a percolation framework relating the equilibrium swelling to the gel fraction near the gelation threshold has recently been developed.[3]

Determining the statistical structural units is one of the major problems in describing the gel system. The gel behavior is sensitive to the average properties of these statistical domains. In a system of vulcanized chains, the coexistence of entanglements and cross-links is a further complication. Trapped entanglements are known to play a major part in the swelling process of cross-linked networks by acting as additional constraints.[4]

The investigation of quantum coherence properties of the transverse relaxation function has proved to be a convenient tool to probe the gel structure on a semilocal space scale.[5]

It has been shown that the fractal structure of chain segments statistically determined by two consecutive junctions whether they are temporary entanglements or covalent bridges can be investigated by the residual energy Δr of spin-spin interactions. This residual energy results from nonisotropic rotational diffusions of proton pairs attached to polymer chains. The NMR technique thus yields information on all hindrance effects exerted on chain segments.

The state of stretching of a given elementary chain may be reflected by the transverse magnetic relaxation function: it has been shown that the residual energy Δ_r of dipole-dipole interactions of proton spins attached to a chain of fixed end separation vector r_e is expressed as a function of both $|r_e|$ and the number of skeletal bonds Ne in the chain segments. For small extensions, Δ_r is known to be given by

$$\hbar\Delta_r \propto \hbar\Delta_G\frac{|r_e|^2}{\mathrm{Ne}^2a^2} \qquad (1)$$

where Δ_G is the dipole-dipole interaction observed in the glassy state and a is the monomer unit length.[6] The purpose of this paper is to get a picture of the swelling process of weakly cross-linked polyethylene networks as it is perceived in a macroscopic scale by equilibrium swelling ratio and in a microscopic scale by its magnetic relaxation response. We probed the statistical properties of chain segments in dry and swollen polyethylene networks covering a wide range of cross-link densities. It was necessary to include observations at intermediate swelling

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to get a comprehensive model of polymer gels. Our final aim is to determine the actual nature of statistical submolecules sensed by the transverse relaxation function.

II. Experimental Section

Samples. Networks were obtained by cross-linking high-density polyethylene (d = 0.953) of high molecular weight (M_w = 250 000) in the presence of a constant amount of a high-temperature three-functional cross-linking agent (Patent FR 2.521.573). Before cross-linking, the PE powder and the additives were compression molded to form a homogeneous bulk plate. Cross-link formation takes place in a nitrogen environment at 493 K. We arrived at different cross-link densities by quenching the samples from vulcanization temperature to liquid nitrogen temperature after various heating times.

Gel Fraction and Equilibrium Swelling. Polyethylene being a semicrystalline polymer at room temperature, gel extraction and equilibrium swelling measurements have to be carried out above the melting temperature T_m = 413 K. Xylene was chosen as solvent and swelling took place in an excess of boiling xylene at 413 K. to determine the gel fraction G, the soluble part of the network was washed out for 3 × 24 h, the solvent being renewed twice. Then the gel was carefully dried by heating under vacuum. The gel fraction was determined as the ratio of the weight of the dry extracted network to the weight of the initial cross-linked sample. Deterioration of the sample due to oxidation was considered as irrelevant as the addition of an antioxidation agent (2,6-di-*tert*-butyl-4-methylphenol) did not modify the measured gel fraction, significantly.

The degree of swelling in relation to the initial reaction bath is defined as the ratio of the volume of the swollen network to the initial volume of the unextracted network and is denoted by q. We denote Q as the degree of swelling of the dry extracted network. Equilibrium swelling degrees are called q_m and Q_m, respectively. The following relationship holds

$$q_m = GQ_m$$

The determination of swelling ratio at 413 K is a delicate task. A weighing method was used and the ratio of specific densities of solvent to polymer was measured at room temperature and considered to be independent of temperature. Except for very weak cross-link densities (G < 10%), the reproducibility of gel fraction and equilibrium swelling measurements was good and the precision was about 5–10%.

For NMR measurements, samples were swollen with deuteriated *p*-xylene and the swelling ratio was determined as before. The sample and solvent were sealed under a nitrogen environment at atmospheric pressure in short NMR tubes. Measurements could thus be performed without difficulty up to 420 K.

NMR Measurements. NMR measurements were carried out on a pulsed Bruker CXP spectrometer, operating at 60 MHz. All relaxation curves were drawn at 418 K.

Transverse magnetic relaxation functions were obtained by using a Carr–Purcell sequence to overcome usual inhomogeneity problems present in polymer systems. The pseudosolid spin–echo was obtained from the following four-pulse sequence:[7]

$$(\pi|y)-\tau/2-(\pi|y)-\tau/2-(\pi/2|x)-\tau_u/2-(\pi|y)-\tau_1/2$$

$(\alpha|y)$ denoting a rotation of angle α around the y axis. The $(\pi|y)$ pulses serve to focus the transverse magnetization at time τ to apply the specific $(\pi/2|x)$ pulse and at time $\tau + \tau_1$ to measure the spin–echo amplitude.

III. NMR Characterization of Dry Polyethylene Networks

The NMR characterization of partly cross-linked samples in their reaction bath relies on the following assumption that has been checked in a previous paper:[8] the transverse magnetic relaxation function $M_x(t)$ is a linear combination of two basic functions, $R_m(t)$ and $R_g(t)$.

$$M_x(t) = (1 - c_g)R_m(t) + c_gR_g(t)$$

$R_m(t)$ is associated with a rapidly fluctuating phase and coincides with the relaxation function of the PE melt. $R_g(t)$ corresponds to a stiffened phase and describes the relaxation function of a completely cross-linked sample. $R_g(t)$ is a rapidly decreasing function whereas $R_m(t)$ is a slowly decreasing function with a long tail. The weight factor c_g could be determined unambiguously by comparing tail amplitudes of $M_x(t)$ functions, and $R_g(t)$ was shown to be a constant function with c_g for c_g higher than 0.10. For very small c_g values $R_g(t)$ decays slightly more slowly.

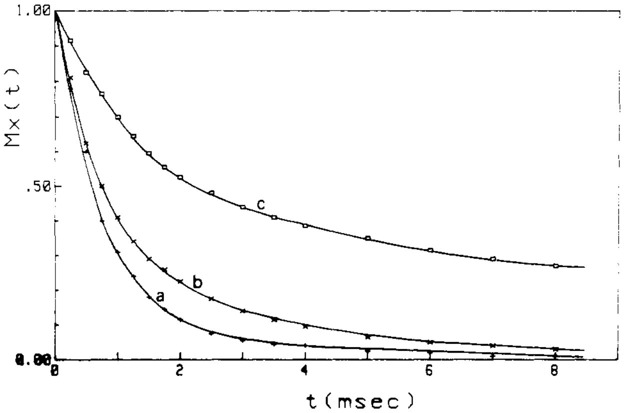

Figure 1. Two basic transverse magnetic relaxation functions $R_g(t)$ (curve a (+)) and $R_m(t)$ (curve c (□)) obtained from a linear analysis of relaxation functions $M_x(t)$ of partly cross-linked PE samples according to the formula $M_x(t) = (1 - C_g)R_m(t) + C_gR_g(t)$. Curve b (×) represents the transverse relaxation function observed after removing all free chains from partly cross-linked samples (T = 418 K).

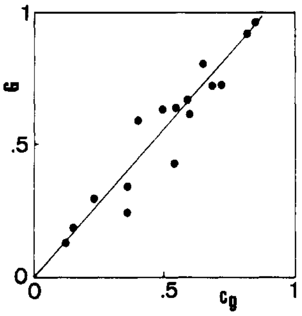

Figure 2. Gel fraction G of partly cross-linked samples is represented as a function of the weight factor C_g derived from the relaxation functions of partly cross-linked samples.

The relaxation functions of completely extracted networks did not depend on the initial cross-link density and were found to be very similar to $R_g(t)$ functions. Figure 1 shows the two basic functions $R_g(t)$ and $R_m(t)$ and the relaxation function of a dry extracted network. The weight factor c_g is drawn as a function of gel fraction in Figure 2.

It was proved by the pseudosolid spin–echo technique that the $R_m(t)$ function is associated with chain segments that fluctuate within the time scale determined by the residual dipolar energy whereas the $R_g(t)$ function describes a system of frozen end-to-end vectors.

IV. Gel Fraction and Equilibrium Swelling

Observation. Gel fraction and equilibrium swelling measurements were performed on the randomly cross-linked PE networks, covering a broad range of cross-link densities. Swelling degrees Q_m and q_m as a function of G are drawn in Figure 3. As may be expected, the equilibrium swelling ratio Q_m of extracted networks decreases with increasing cross-link density. The swelling ratio q_m of the partly cross-linked precursory bulk polymer levels off for weakly cross-linked networks at a value of about q_m = 11. The swelling ratio q_m decreases for gel fractions higher than 0.6, corresponding to c_g > 0.75. This inde-

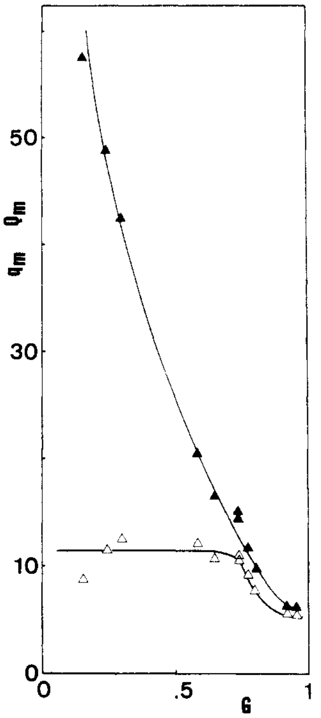

Figure 3. Swelling behavior of partly cross-linked PE networks characterized by their gel fraction G: (▲) equilibrium degree of swelling Q_m of the dry extracted network; (△) equilibrium degree of swelling q_m of the unextracted network.

pendence of q_m on cross-link density for low cross-link densities, which corresponds to Q_m being proportional to G^{-1}, is worth further comment.

Discussion. The above experimental result may be derived within a percolation framework.[3]

In order to calculate the equilibrium swelling ratio, one makes the following basic assumptions, corroborated by further results of this paper: Swelling the partly cross-linked sample is a two-step process and is due to (i) a disinterpenetration of the intertwined meshes of the network and (ii) a swelling of the average mesh size.

When no topological constraints hinder the complete separation of n interpenetrated meshes, swelling equilibrium degree q_m of the partly cross-linked sample is given by

$$q_m = n\gamma^3 \tag{2}$$

where γ is an isotropic stretching factor of the network and n is the number of intertwined networks.

Considering mean-field exponents, Daoud recently derived that the maximum swelling degree q_m, given by formula 2, proves to be independent of G.

We further assume that in the presence of topological constraints as entanglements, the maximum value q_m is reduced by a factor r due to incomplete disinterpenetration and is consequently given by

$$q_m = rn\gamma^3 \tag{3}$$

Near the gelation threshold, for very loose systems, it seems plausible that r is independent of cross-link density. We actually found a behavior in good agreement with the proposed scaling laws.

Turning back to Figure 3, at higher G values, we observe a breakdown of this behavior and a cross-over to a cross-link density range where q_m rapidly decreases with G. A possible explanation is that the structure becomes less and less able to disinterpenetrate and r is no longer independent of n but is a decreasing function of n. We then expect a decrease of q_m with cross-link density.

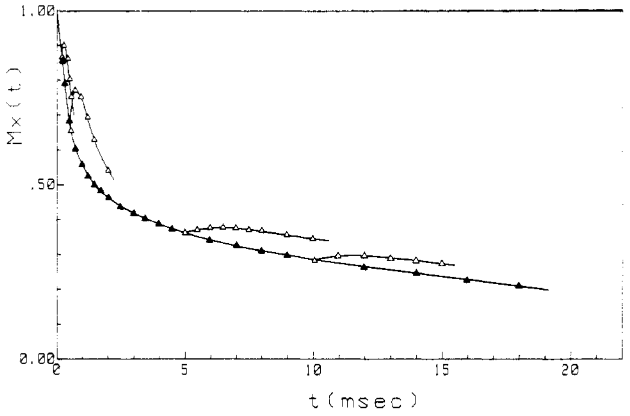

Figure 4. Transverse magnetic relaxation functions (▲) and pseudosolid spin–echoes (△) formed from several times τ observed in a network swollen at equilibrium at T = 418 K. The equilibrium swelling ratio Q_m is 7.2.

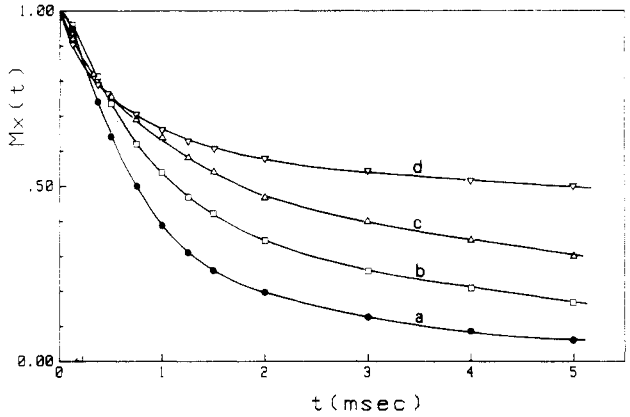

Figure 5. Transverse magnetic relaxation functions observed from a PE network at intermediate swelling ratio Q at T = 418 K illustrate a two-step swelling behavior: (a, ●) dry PE network; (b, □) Q = 2.5; (c, △) Q = 5.6; (d, ▽) equilibrium degree Q_m = 9.5.

V. Partly Swollen Gels: NMR Observation

Evidence for a Residual Energy. It is worth characterizing the relaxation functions by the pseudosolid spin–echo technique described in section II. It has been shown in a previous paper that in the case of a pure dipolar interaction when no fluctuations of the dipolar residual energy are perceived, the slope of the echo envelope at time $\tau = \tau_+$ is exactly the opposite of the slope of the relaxation function at time τ.[7] As it is shown in Figure 4, the spin–echoes are well defined and obey the symmetry property for the equilibrium swollen extracted network even along the tail of the relaxation function.

Evidence for Two-Step Swelling Behavior. For a highly cross-linked sample of given cross-link density, we performed NMR measurements at intermediate swelling degrees by progressively adding controlled amounts of deuteriated solvent to a dry extracted network up to the equilibrium swelling. The behavior of the residual energy Δ_r shows a two-step swelling behavior of the elementary chain segments defining magnetic submolecules: (i) In a first stage ranging from Q = 1 to about Q = 3.5, there is a decrease of the residual energy Δ_r as is shown by relaxation functions a and b in Figure 5. (ii) In a second step, there is an increase of the residual energy. Simultaneously, the form of the relaxation function changes and has a slowly decaying tail for high swelling degrees. This swelling range is represented by functions c and d in Figure 5.

Assay Function. For spin systems as complex as polymers, the magnetic relaxation function cannot be calculated directly. We tried to fit the measured relaxation

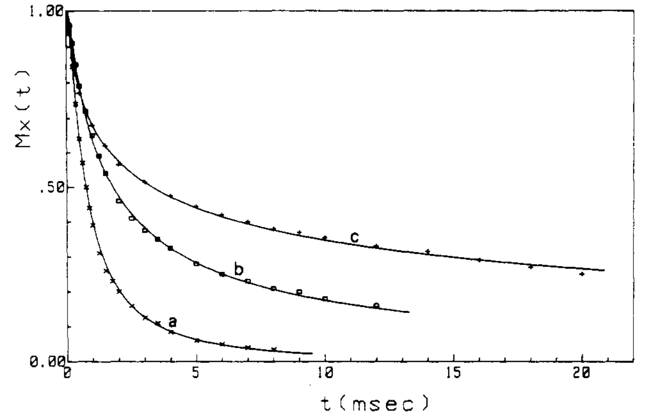

Figure 6. Experimental relaxation functions observed in partly swollen PE networks at 418 K (discrete points) are compared to the parametrized assay function $G_{\delta,\alpha}(t)$ (full lines) given by formula 16 in the text: (a, ×) $Q = 1$; fit, $\delta = 1.9$, $\alpha = 4.3$; (b, □) $Q = 3.2$; fit, $\delta = 1.5$, $\alpha = 5.3$; (c, +) $Q = 7.2$; fit, $\delta = 3$, $\alpha = 17$.

function by using a parametrized test function which obeys mathematical requirements imposed by the nuclear relaxation theory. We may thus assign a direct physical meaning to the parameters. The relaxation function can be expressed as a series expansion

$$M_x(t) = 1 - (M_2/2)t^2 + (M_4/4!)t^4 + \dots \quad (4)$$

or equivalently

$$\log \{M_x(t)\} = (-M_2/2)t^2 + [(M_4 - 3M_2^2)/4!]t^4 + \dots \quad (5)$$

where M_2 and M_4 are known to be the second and the fourth moment of the corresponding resonance line.[9]

The second moment M_2 is not affected by molecular motions and is related directly to the residual dipolar energy Δ_r. For pure dipolar interactions we have the relationship $M_2 \propto \Delta_r^2$.

Single-parameter behavior corresponds to $M_4 - 3M_2^2 = 0$ that is, Gaussian behavior. As our functions are not Gaussian, we choose to characterize relaxation functions by two parameters, directly related to the second and fourth moments.

The fourth moment may be expressed as

$$M_4 = M_4^{\circ} + M_2\tau_f^{-2} \quad (6)$$

where τ_f is a fictitious time and is artifically introduced to model the higher moment behavior of the relaxation function.

Testing of several functions, we have chosen the following best-fitting a priori function $G_{\delta\alpha(t)}$:

$$G_{\delta\alpha(t)} = \exp(-\delta^2/\alpha^2[\log \{1 + \alpha t + 1 + \alpha^2 t^2\}]^2) \quad (7)$$

which corresponds to the following expansion near the origin ($\alpha t < 1$)

$$G_{\delta\alpha(t)} = 1 - (2\delta^2)t^2/2 + (12\delta^4 + 8\delta^2\alpha^2)t^4/4! + \dots \quad (8)$$

Fits proved to be very good as is shown in Figure 6 and we could thus simulate the second and fourth moment behavior during swelling, M_2 and M_4 being evaluated by the following relations

$$M_2 = 2\delta^2 \qquad M_4 = 12\delta^4 + 8\delta^2\alpha^2$$

The parameter δ thus reflects the dipolar energy Δ_r and α^{-1} is a fictitious time related to the asymmetry of monomeric diffusive motions. The ratio M_4/M_2^2 indicates the departure from Gaussian behavior.

We drew the determined values of δ, α^{-1}, and M_4/M_2^2 as a function of Q in Figure 7. The evolution of δ clearly shows the two-step swelling behavior discussed qualitatively above. The change between both regimes occurs at $Q = 3.5$. No specific scaling behavior could, however, be attributed to the residual energy as a function of swelling degree Q. The parameter $\alpha - 1$ decreases continuously with increasing swelling degree and linearly for $Q > 3.5$. This indicates that for high swelling degrees, the distribution function of the dipolar energy changes and the asymmetry of diffusional motions diminishes. The form of the relaxation function drastically changes above $Q = 5$ as it is shown by the ratio M_4/M_2^2, which corresponds to the appearance of a slowly decaying tail at high swelling degrees.

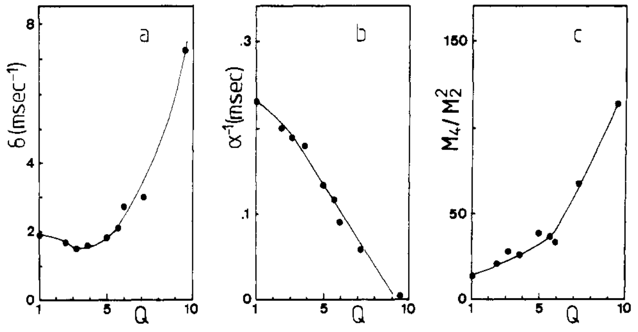

Figure 7. Parameters obtained from fitting the experimental relaxation functions measured in a PE network at intermediate swelling ratios Q at 418 K: (a, b) parameters δ and α^{-1} drawn as a function of Q; (c) ratio of the fourth moment to the square of the second moment M_4/M_2^2 drawn as a function of Q.

Discussion. When swollen by a low molecular weight solvent, the network structure necessarily unfolds and elementary chains become separated.[10]

(i) We suggest that in the first stage of the swelling behavior, which corresponds to a gradual decrease of the residual energy until $Q \cong 3.5$, elementary chains remain gaussian and are not stretched. At $Q = 3.5$, we get a loose structure unfolded to a maximum degree compatible with topological hindrances.

In the dry network, the magnetic submolecule is determined by two consecutive entanglements or cross-links. Upon dilution, these statistical domains grow because of vanishing entanglements. The upper length of the submolecule is considered to be fixed by two consecutive cross-links or trapped entanglements. Hence the dipolar energy, which varies as the inverse of the number N of monomers constituting magnetic submolecules, decreases as becomes obvious from formula 1.

(ii) In a second step, elementary chains building up the network structure get more and more stretched to reach excluded-volume configurations at equilbrium swelling. This isotropic deformation of elementary chain segments induces an increase of the residual energy because the number N_e of skeletal bonds is a constant. To explain the tail behavior of the relaxation function at high swelling degrees, the observed symmetry of spin–echoes is of capital importance.

Comparing the spin–echoes of an equilbrium swollen sample to the spin–echoes of the PE melt, which are nonsymmetric and completely vanish for long relaxation times, clearly demonstrates that in spite of a similar behavior at long times for both relaxation functions, the physical reasons for slowly decaying tail amplitudes are very different in the melt and in the equilibrium swollen network. In the melt the nonsymmetrical pseudosolid echoes are due to fluctuations of chain segments defined by temporary entanglements within the dipolar relaxation time Δ_r^{-1}. At long times, dipolar relaxation processes have completely cancelled and relaxation is due to isomeric rotational processes. In the dry gel, these fluctuations are blocked by the presence of covalent bridges. When

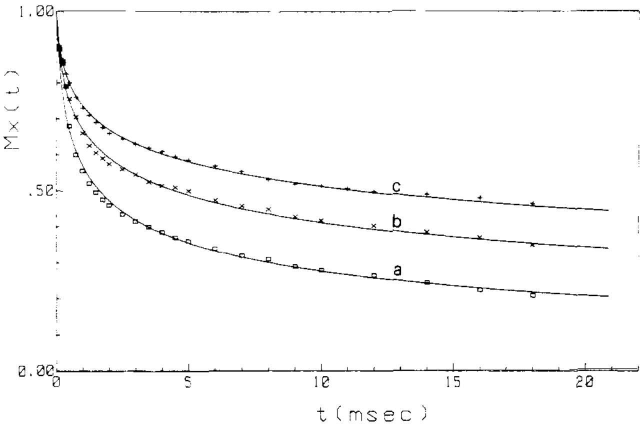

Figure 8. Experimental relaxation functions observed in PE networks swollen at equilibrium at 418 K and the corresponding assay functions $G_{\delta,\alpha}(t)$: (a, □) $Q_m = 7.2$; fit, $\delta = 7.5$, $\alpha = 45$; (b, ×) $Q_m = 9.5$; fit, $\delta = 7.5$, $\alpha = 56$; (c, +) $Q_m = 16.5$; fit, $\delta = 7.5$, $\alpha = 66$.

swelling the gel up to equilibrium, we do not significantly increase the fluctuations of chain segments defined by permanent cross-links.

We suggest that for high swelling degrees diffusive motions of the monomers building up chain segments become more and more important and the dipolar energy distribution function along elementary chains changes with a minimum value expected at the middle of each subchain.

VI. Gels at Equilibrium Swelling: NMR Observation

Observation. We measured the transverse relaxation functions on samples with different cross-link densities swollen to equilibrium in an excess of solvent. They are drawn in Figure 8 and correspond to weakly and highly cross-linked samples. Whereas the tail of the relaxation function decays more slowly for the weakly cross-linked sample, the relaxation curve is independent of cross-link density for small times ($t < 1$ ms). Applying the preceding signal analysis, the cross-link density in swollen samples only changes the higher moments of the relaxation curves, the second moment remaining unchanged. Values of parameters δ and α are indicated in Figure 8. Both features have to be explained.

Discussion. In a swollen cross-linked polymer network, the characteristic length R_f of a swollen network mesh is reduced by increasing the cross-link density. When observing the swollen network in a length scale higher than R_f it behaves like a regular network but on length scales below R_f, the network is filamented and irregular. For weak cross-link densities, the typical mesh size exceeds several times the length of a swollen primary chain. Between two nodes of the swollen incipient percolation network with mesh size R_f, we have a succession of swollen primary-chain segments. The independence of the second moment of the relaxation curve with cross-link density suggests that the screening length of the spin-spin interactions remains smaller than R_f for all cross-link densities. For swollen polymer chain segments, it is plausible that the magnetic submolecule is defined by two successive cross-links or trapped entanglements. For weak cross-link densities, the chains are not multilinked and the average number of monomers between two cross-links of a same primary chain does not change significantly with cross-link density. When increasing cross-link density, we reduce the node to node distance R_f by attaching more and more chains to the network. At the same time, network defects such as dangling chains are more and more suppressed. For a higher cross-link density, the structure is more densely built up and it becomes plausible that the asymmetry of monomer diffusive motions increases. This may explain the presence of higher moments in the relaxation functions at equilibrium swelling as related to cross-link density.

VII. NMR Picture of the Swelling Process

Description of the vulcanization process in the bulk state as the gradual invasion of a mobile phase by a stiffened phase is observed. Each cross-link bridging chains creates a microregion of clotted chains and severely restricts the junction fluctuations in this domain. The average size of the frozen region as it is perceived from NMR is related to the average distance between two consecutive entanglements in the melt. Cross-link formation in the highly intertwining precursory chains is thus perceived by NMR as a random freezing process on a three-dimensional lattice with a lattice constant directly related to the average entanglement spacing.

In the presence of a solvent, the unattached chains are washed out and the remaining covalently bound network swells due to vanishing screening effects. In a first stage, due to disappearing entanglements, the average size of the statistical lattice constant as it is perceived by NMR increases until it corresponds to the average distance between two cross-links or trapped entanglements. In a second step, these statistical subunits are swollen to exhibit excluded-volume behavior.

The macroscopic swelling ratio q is due at least to three features: disengagement of interpenetrated networks, swelling of individual chain segments, and a change of the fractal dimension of the branched percolation network. The residual energy as it is perceived by NMR is essentially sensitive to the swelling of individual chain segments.

VIII. Conclusion

Insight into the complex structure of imperfect gels has been achieved by comparing gel fraction, equilibrium swelling ratio, and NMR measurements in partly cross-linked systems. The following assumption was put forward to get a coherent interpretation of all results: primary chains are considered to be not multilinked and in the considered cross-link density range, vulcanization is merely the building up of a percolation network by attaching more and more chains to the infinite cluster. The mesh size of this network is gradually reduced and tends toward a theoretical limit given by the average distance between two cross-links of a primary chain. This elementary segment was considered to define the submolecule as perceived by NMR in the equilibrium swollen state. Beyond this range, additional cross-links would reduce the length of the submolecule and chains would get multilinked.

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