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Pierre GILORMINI, Jacques VERDU, Emmanuel RICHAUD - A statistical theory of polymer network degradation - Polymer - Vol. 55, p.3811-3817 - 2014

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A STATISTICAL THEORY OF POLYMER NETWORK DEGRADATION

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ABSTRACT. A statistical theory was proposed for the degradation (random scission of chains) of a network having *f*-functional nodes in the case where all chains contain equireactive groups and a chain scission event does not create new groups or suppress more than one group. Closed-form relations were established between the conversion ratio of the degradation process and the crosslink density. Emphasis was put on the value of the conversion ratio for which the gel disappears. Some limited cases already considered in the literature were recovered, but a general solution was proposed for networks having any number of reactive groups per chain, be it uniform or not, and for conversion ratios up to the degelation point. The results were applied successfully to recent experiments regarding the hydrolysis of a polyester.

KEYWORDS. Polymer network; Chain scission; Degelation

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1. Introduction

Network degradation is among the oldest problems in macromolecular science. It appeared in the middle of the nineteenth century, as soon as industrial applications of vulcanized rubber were developed. As a matter of fact, polyisoprene is a highly reactive substrate undergoing oxidative random chain scission in air, even at room temperature. The huge efforts of the rubber community to elucidate the degradation mechanisms remained unsuccessful until the 1940's where it was recognized that (i) vulcanized rubbers are macromolecular networks, especially thanks to Staudinger (1953 Nobel prize) and Flory (1974 Nobel prize), and that (ii) degradation results from radical chain oxidation, especially thanks to Semenov (1956 Nobel prize). At the same time, a theory of gelation was elaborated by Flory [1] and Stockmayer [2] to describe the structural changes of the network during synthesis. Shortly after, the classical experimental approach based on mechanical measurements performed on samples undergoing degradation was refined by Tobolsky and Andrews [3], who applied the statistical theory of rubber elasticity, and it became popular rapidly.

It is assumed generally in network degradation by random chain scission that all units are equireactive. In the absence of competitive crosslinking, degradation leads to a gradual decrease of crosslink density, with a concomitant decay of the elastic modulus, until the polymer becomes fully soluble, and this gel-sol transition may be called "degelation" [4]. The gradual degradation process can be studied by at least two experimental techniques. The first one, valid only before the degelation point, is based on the concentration of elastically active chains deduced from modulus or solvent swelling [5] measurements. The second approach focuses on such characteristics of the sol as its mass fraction [6-8] or its molar weight distribution, with its weight average molar mass being expected to be maximum at the degelation point [9].

In such investigations, the simplest approach consists in considering that degradation is the reverse of polymerization or polycondensation, i.e., that the network structure and composition of soluble fraction are the same for a degradation at conversion ratio x, defined as the ongoing number of reacted units divided by the initial number of reactive units, as for a polymerization or polycondensation at conversion ratio $1 - x$, provided that the groups that are broken during degradation are the same as the ones formed during synthesis. Horikx [7] seems to have been first to propose this approach. Like Horikx, early investigators of network degradation studied rubber oxidation, which cumulates several complications, among which the high complexity of radical oxidation mechanisms, the possibly simultaneous occurrence of a crosslinking process, and the occurrence of non-random scissions of sulphur bridges in certain cases of sulphur vulcanization [10]. Later studies considered lignin degradation in the framework of wood pulp processing, or simply to elucidate the lignin structure. Recent lignin analyses are mainly based on nuclear magnetic resonance or infrared spectrochemical analyses, performed sometimes on small molecules resulting from the total degradation of lignin (see Brunow and Lundquist [11], for instance). In the 1960-1980's, however, considerable research efforts adapted the Flory-Stockmayer theory to deduce the macromolecular structure of lignin from the analysis of the soluble products of its controlled degradation [4, 12-14]. Lignin combines several difficulties, among which a complex structure, where trifunctional and tetrafunctional crosslinks coexist, the presence of dangling chains (about 25% of the monomeric units according to Brunow and Lundquist [11]), and a variable structure depending on the type of tree and on the location of the analyzed sample in the tree (compressive vs. tensile parts, for instance).

Polyester hydrolysis appears as an especially interesting case owing to the relative simplicity of the chemical mechanism (compared to oxidation, for instance) and to the high

technical interest of some polyesters (styrene cured unsaturated polyesters) used as the matrix of composites in boat hulls, swimming pools, pipes and tanks for water transport and storage. Unfortunately, these networks have a complex structure with half the elastically active chains (polystyrene) being non-reactive, with high concentrations of dangling chains [15], with many kinds of ester groups (maleates and phthalates), etc. Furthermore, they undergo osmotic cracking [16], which makes the kinetic analysis even more complex.

The theory proposed below improves and extends a model published recently [17], which combined chemical kinetics and a statistical approach of network degradation that is valid only at low conversions, much before degelation. Conversion ratios up to degelation are covered here, the number of scission sites per chain may be large, and a dispersion of this number is allowed. The initial state is a gel in the present study, which therefore differs from previous and more complex works where degradation and crosslinking occur simultaneously (Demjanenko and Dušek [18, 19], for instance, or Samoria and Vallés [20]), with an initial state defined by a set of linear chains or monomers. We study degelation, not delayed gelation.

2. Results

Let us consider an infinite perfect network (no dangling chains) with f-functional crosslinks. The chains contain a possibly non-uniform number of reactive groups (or scission sites, or breakable bonds, equivalently) with a distribution $s(i)$. This means that there is a fraction $s(i)$ of chains bearing i reactive groups each and that $\sum_i s(i) = 1$, where the sum applies over all i values found in the network. It is assumed that all groups are equireactive, and that chain scission events do not create new groups or modify the reactivities of neighboring groups. The present analysis focuses on the variations of such network characteristics as crosslink density or soluble fraction

with the conversion ratio x, defined as the fraction of reacted groups, and it analyzes the most probable structure of the degraded network. The function of time $x(t)$ is assumed known from a kinetics theory of scission. In the case of polyester hydrolysis, for instance, auto-catalysis may complicate the kinetics, and a model has been proposed recently to take this into account [17].

Since the probability for a reactive group to be unreacted is $1 - x$, the probability for a chain containing i reactive groups to be unbroken is $u_i(x) = (1 - x)^i$. Considering now the distribution of the number of reactive groups per chain, the probability for any chain to be uncut is given by

$$u(x) = \sum_i s(i)(1 - x)^i \tag{1}$$

The probability $g(x)$ that a chain starts at a node and is linked to the gel through its other end is given by

$$g(x) = u(x)\,[1 - (1 - g(x))^{f-1}] \tag{2}$$

since it must be unbroken (probability $u(x)$) and it must end at a node where at least one of the $f - 1$ other chains are connected to the gel. The probability for the latter to be true is 1 minus the probability that none of these $f - 1$ chains is connected to the gel, which is $(1 - g(x))^{f-1}$, and (2) ensues. This is a variant of the simple derivation given by Miller and Macosko [21] for post-gel properties of network polymers, which is more direct than using probability generating functions [22] alternatively. Because of this relationship, several equations obtained below are formally similar to well-known results on post-gel condensation, but they apply to network degradation instead, and function $u(x)$ has no general equivalent in network synthesis because it includes any distribution of scission sites in a given network.

The $g(x) = 0$ solution to (2) can be discarded, since it would imply there is no gel whatever the degradation level, and therefore (2) leads to

$$\sum_{k=1}^{f-2}(1-g(x))^k = \frac{1}{u(x)} - 1 \tag{3}$$

with two special cases of particular interest:

$$g(x) = 2 - \frac{1}{u(x)} \qquad \text{and} \qquad g(x) = \frac{1}{2}\left[3 - \sqrt{\frac{4}{u(x)} - 3}\right] \tag{4}$$

if $f = 3$ and $f = 4$, respectively. Degelation occurs when no chain can have infinite continuation, which corresponds to $g(x) = 0$ in (3), and therefore the conversion ratio at degelation x_d is obtained by solving

$$\sum_i s(i)(1-x_\mathrm{d})^i = \frac{1}{f-1} \tag{5}$$

for an initially perfect network (i.e. a network where all chains are elastically active) with functionality f and distribution $s(i)$ of chains bearing i breakable bonds.

The right-hand side of (5) demonstrates a connection between the present model for degelation and the classical gelation model of Flory [1]: if there is a single breakable bond per chain (then $\sum_i s(i)(1-x_\mathrm{d})^i = 1 - x_\mathrm{d}$), the degradation level at degelation is equal to 1 minus the fraction of reacted groups at gelation in RA_f polymerization. This connection is limited to special cases where network degradation is equivalent to reversed polymerization, though, i.e. either for one breakable bond per chain, or for two (RA_f + $R'B_2$ polymerization), essentially. The present theory considers any number of equally reactive breakable bonds per chain, be it uniform or not, and thus it covers such degradation processes as the hydrolysis of polyesters, for instance. For conciseness, this presentation is limited to homofunctional networks, but extension to polyfunctional networks may be performed by using appropriate averages weighted by the amount of each functionality present. Initially imperfect networks may also be considered, where dangling chains and primary loops are present, for instance. An evaluation of the fraction of chains involved in loops may be obtained from a rate theory [23], from Monte Carlo simulations

[24-26], or from specific experimental techniques [27]. Let β denote the fraction of breakable bonds such that their scission does not modify the number of elastically active chains in the initial state: as far as crosslink density is concerned, the present theory can still be applied by replacing x by the effective degradation ratio $(1-\beta)\,x$. Of course, the distribution of the number of breakable bonds per chain used must refer to the backbone of the initial elastically active chains, which may be difficult to evaluate in an imperfect network. The effect of an increased number of scission sites per (elastically active) chain may compensate the effect of ineffective scissions occurring on dangling chains and loops. The Monte Carlo simulations of Galina and Lechowicz [28] illustrate the impact of the network structure on the degelation point.

A node is an effective crosslink if at least 3 chains starting from this node are connected to the gel. If $3 \le k \le f$ chains from this node are connected to the gel and $f-k$ are not, with $\binom{f}{k}$ possibilities, the number of effective crosslinks divided by the initial number of nodes n_0, i.e. the relative crosslink density, is given by

$$\frac{n(x)}{n_0} = \sum_{k=3}^{f} \binom{f}{k}\, g(x)^k \left(1-g(x)\right)^{f-k} \tag{6}$$

for $0 \le x \le x_d$ (and $n(x)/n_0 = 0$ for $x > x_\mathrm{d}$), with zero slope and zero curvature of the $n(x)/n_0$ curve at the degelation point, consequently, since the first and second derivatives are proportional to $g(x)$. Using (4), one obtains:

$$\frac{n(x)}{n_0} = \left(2-\frac{1}{u(x)}\right)^3 \quad \text{and} \quad \frac{n(x)}{n_0} = \frac{3}{16}\left(3-\sqrt{\frac{4}{u(x)}-3}\right)^3\left(\sqrt{\frac{4}{u(x)}-3}-\frac{1}{3}\right) \tag{7}$$

if $f=3$ and $f=4$, respectively.

The number ν of elastically active chains can be computed similarly to (6) by considering that they connect two effective crosslinks and by counting k ends of elastically active chains at effective crosslinks where k chains are connected to the gel (with $\nu_0 = \nu(0) = f n_0/2$):

$$\frac{\nu(x)}{\nu_0} = \frac{1}{f}\sum_{k=3}^{f}\binom{f}{k}\, k\, g(x)^k \left(1-g(x)\right)^{f-k} \tag{8}$$

with $\nu(x)/\nu_0 = 0$ for $x > x_\mathrm{d}$, which may be used to deduce the elastic shear modulus from the affine network theory or, combined with (6) to obtain the cycle rank, from the phantom [29] or intermediate [30] network theory. Therefore:

$$\frac{\nu(x)}{\nu_0} = \left(2-\frac{1}{u(x)}\right)^3 \qquad \text{and} \qquad \frac{\nu(x)}{\nu_0} = \frac{1}{8}\left(3-\sqrt{\frac{4}{u(x)}-3}\right)^3\sqrt{\frac{4}{u(x)}-3} \tag{9}$$

if $f = 3$ and $f = 4$, respectively. For a trifunctional network, the initial slope of the $\nu(x)/\nu_0$ curve (i.e., for x=0) is equal to minus three times the average number of reactive groups per chain $\sum_i i\, s(i)$, according to (9). This simple result is in agreement with the trivial observation that cutting one chain of such a network decreases by 3 the number of elastically active chains (and two of them double their lengths). By contrast, if the functionality, uniform or not, is larger than 3 at all nodes of a perfect network, a similar elementary geometric analysis shows that cutting one chain decreases by 1 the number of elastically active chains (and does not modify crosslink density). This is in agreement with the initial slope of $\nu(x)/\nu_0$ deduced from (8) when $f > 3$ (and with a zero derivative of $n(x)$ in (6) for x=0 if $f > 3$). These initial slopes were already obtained by Richaud et al. [17]. According to (8), both the slope and the curvature of the $\nu(x)$ curve are zero at the gelation point.

The average crosslink functionality of the degraded network can be deduced similarly to (6) as

$$\bar{f}(x) = \frac{\sum_{k=3}^{f}\binom{f}{k} k\, g(x)^k \left(1-g(x)\right)^{f-k}}{\sum_{k=3}^{f}\binom{f}{k} g(x)^k \left(1-g(x)\right)^{f-k}} = \frac{\sum_{k=3}^{f}\binom{f}{k} k\, g(x)^{k-3} \left(1-g(x)\right)^{f-k}}{\sum_{k=3}^{f}\binom{f}{k} g(x)^{k-3} \left(1-g(x)\right)^{f-k}} \tag{10}$$

which gives $\bar{f}(x_\mathrm{d}) = 3$ (since $g(x_\mathrm{d}) = 0$): the degraded network is trifunctional when degelation occurs, whatever its initial functionality. It may be recalled that Miller and Macosko [21] have shown that RA_4 polymerization leads to a trifunctional network at the gel point.

A node belongs to the sol when none of the f chains attached to it initially is left connected to the gel, and therefore

$$f_\mathrm{s}(x) = (1 - g(x))^f \tag{11}$$

gives the soluble fraction of the total number of nodes (and $f_\mathrm{s}(x) = 1$ for $x > x_\mathrm{d}$). Using (4), this leads to

$$f_\mathrm{s}(x) = \left(\frac{1}{u(x)} - 1\right)^3 \quad \text{and} \quad f_\mathrm{s}(x) = \frac{1}{16}\left(\sqrt{\frac{4}{u(x)} - 3} - 1\right)^4 \tag{12}$$

if $f = 3$ and $f = 4$, respectively. The various species in the soluble fraction can also be obtained like in gelation theory, but will not be given here for conciseness.

3. Discussion

3.1 Uniform number of reactive groups per chain

The case of a uniform number L of reactive groups over all chains of the initial network is interesting in several respects, although it may seem unrealistic for practical applications. First, it will allow a connection with previous studies, which are limited to a small and uniform number of breakable bonds per chain. Second, it will give a first evaluation of the effect of a large number of bonds per chain. Finally, this simple case will provide a reference before adding complexity with a distributed number of bonds, in order to appreciate its impact.

Here, the only value of i for which $s(i) \neq 0$ is $i = L$, and $s(L) = 1$ leads to

$$u(x) = (1 - x)^L \tag{13}$$

Figure 1 illustrates the effect of the L value on the variations of the crosslink density and soluble fraction for a trifunctional network, as given by (7) and (12). A given degradation ratio tends to alter the network increasingly when L increases (the relative crosslink density $n(x)/n_0$ decreases and the soluble fraction f_s increases). As a result, the conversion ratio at the degelation point decreases when L increases, and (5) leads to a very simple expression:

$$x_{\mathrm{d}} = 1 - \frac{1}{(f-1)^{1/L}} \tag{14}$$

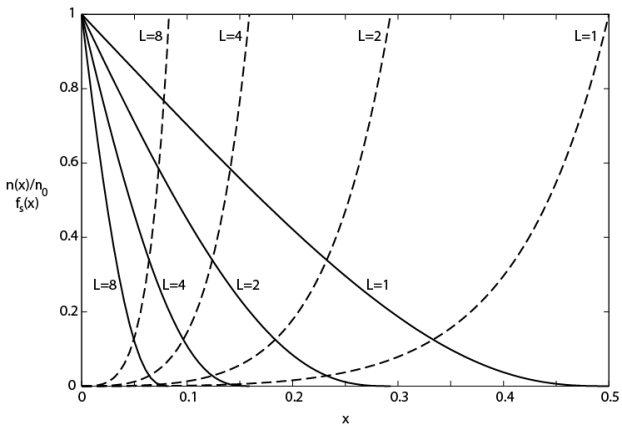

Figure 1. Variations of crosslink density (solid lines) and soluble fraction (dashed lines) during degradation of trifunctional networks with various uniform numbers L of breakable bonds per chain.

with, consequently, $x_{\mathrm{d}} \sim (\ln(f-1))/L$ when L takes large values. The value $x_{\mathrm{d}} = 1 - 1/\sqrt{2} = 0.293$ for $L = 2$ when $f = 3$ has already been obtained by Argyropoulos and Bolker [31] in their effort [31-33] to test gel degradation theories. This is in agreement with their experiments, where a model network resulting from the condensation of 1-3-5 benzene triacetic acid with 1-16 hexadecane diol was hydrolyzed and the soluble fraction was measured, leading to $x_{\mathrm{d}} = 0.288$. When $f = 3$, the $L = 1$ case was considered in the Monte Carlo simulations of Galina and

Lechowicz [34], where a degelation point at $x_d \approx 0.45$ was obtained. The difference with the analytical prediction (x_d =1/2) given by equation (14) may be due to cyclization. It should be noted in Figure 1 that the shape of a curve of soluble fraction versus conversion ratio allows a more precise assessment of the degelation point than the corresponding variation of crosslink density, because of its nonzero slope at this point.

Tetrafunctional networks are considered in Figure 2, where it can be observed that network alteration for a given degradation ratio is less than for trifunctional networks. As a consequence, the degelation point is shifted to larger values. Here, each scission event reduces the number of elastically active chains by one, against three for trifunctional networks. Furthermore, each scission event transforms two tetrafunctional effective crosslinks into trifunctional ones, keeping the total number of effective crosslinks unchanged, while two effective crosslinks are lost per scission event in the case of trifunctional networks.

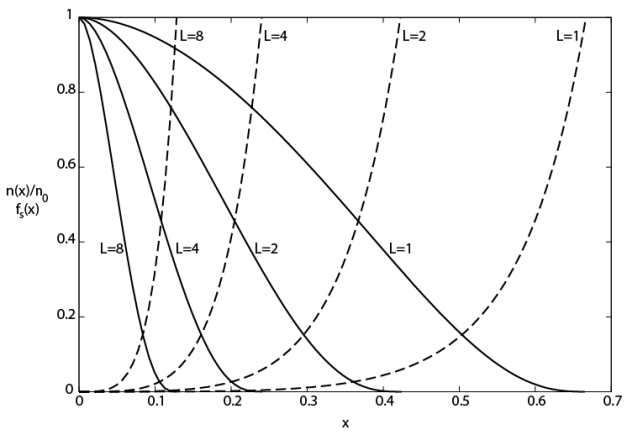

Figure 2. Variations of crosslink density (solid lines) and soluble fraction (dashed lines) during degradation of tetrafunctional networks with various uniform numbers *L* of reactive groups per chain.

3.2 Non-uniform number of reactive groups per chain

Let now the number of reactive groups per chain be non-uniform, with an average value $L = \sum_i i\, s(i)$. A general consequence is a delayed degelation point with respect to the case where all chains bear L reactive groups. In other words, the conversion ratio at degelation is increased by dispersion of the number of reactive groups per chain. This can be proved by introducing $\phi(X) = (1-x)^X$, where $0 < x < 1$ is fixed, which is a strictly convex continuous function of X since its second derivative $\phi''(X) = (\ln(1-x))^2(1-x)^X$ is positive. Consequently, Jensen's inequality [35] can be applied as

$$\sum_i s(i)\, \phi(i) > \phi(\sum_i i\, s(i)) \tag{15}$$

since $\sum_i s(i) = 1$, and therefore

$$\sum_i s(i)\, (1-x)^i > (1-x)^L \tag{16}$$

for $0 < x < 1$, which means that the $\sum_i s(i)\, (1-x)^i$ curve is above the $(1-x)^L$ curve in this interval, where these two functions decrease from 1 to 0. Therefore, the $1/(f-1)$ value is reached by $\sum_i s(i)\, (1-x)^i$ for a larger x value than by $(1-x)^L$, and (5) implies that degelation occurs for a larger conversion ratio when dispersion is present.

In order to illustrate more detailed results on simple cases, let a Flory distribution [9] be considered first:

$$s(i) = \frac{(L-1)^{i-1}}{L^i} \tag{17}$$

with, therefore,

$$\sum_{i=1}^{\infty} s(i) = 1 \qquad \text{and} \qquad \sum_{i=1}^{\infty} i\, s(i) = L \tag{18}$$

as expected. The degelation point is thus given by a very simple expression:

$$x_{\mathrm{d}} = \frac{f-2}{L+f-2} \tag{19}$$

since (17) leads to

$$u(x) = \frac{1-x}{1+(L-1)x} \tag{20}$$

Equation (7) gives

$$\frac{n(x)}{n_0} = \left[\frac{1-(L+1)x}{1-x}\right]^3 \quad \text{and} \quad \frac{n(x)}{n_0} = \frac{3}{16}\left(3 - \sqrt{\frac{1+(4L-1)x}{1-x}}\right)^3 \left(\sqrt{\frac{1+(4L-1)x}{1-x}} - \frac{1}{3}\right) \tag{21}$$

if $f = 3$ and $f = 4$, respectively, and (12) leads to

$$f_{\mathrm{s}}(x) = \left(\frac{L\,x}{1-x}\right)^3 \quad \text{and} \quad f_{\mathrm{s}}(x) = \frac{1}{16}\left(\sqrt{\frac{1+(4L-1)x}{1-x}} - 1\right)^4 \tag{22}$$

if $f = 3$ and $f = 4$, respectively. Consider now a Poisson distribution:

$$s(i) = \frac{(L-1)^{i-1}}{(i-1)!} \exp\,(1-L) \tag{23}$$

where, again, L denotes the average number of reactive groups per chain. The resulting probability for a chain to be unbroken has a simple expression

$$u(x) = (1-x)\exp\,[(1-L)x] \tag{24}$$

as well as the crosslink density and soluble fraction of nodes

$$\frac{n(x)}{n_0} = \left(2 - \frac{\exp[(L-1)x]}{1-x}\right)^3 \quad \text{and} \quad f_{\mathrm{s}}(x) = \left(\frac{\exp[(L-1)x]}{1-x} - 1\right)^3 \tag{25}$$

if, for instance, $f = 3$. The degelation point must be obtained numerically by solving

$$(1-x_{\mathrm{d}})\exp[(1-L)x_{\mathrm{d}}] = \frac{1}{f-1} \tag{26}$$

and one has $x_{\mathrm{d}} \sim (\ln(f-1))/L$ when L takes large values, like in the uniform case of the preceding paragraph. In the $L = 1$ case, the two types of distribution considered coincide with a uniform number of reactive groups per chain, and therefore Figure 3 illustrates the results for $L \geq 2$. For a given average number of reactive groups per chain, degradation does appear to be slowed down by a dispersion of this number. This effect is more evident for soluble fraction than for crosslink density, and the Flory distribution keeps separate from a uniform distribution,

whereas the Poisson distribution gets increasingly closer at moderate and large L values. This is due to the decreasing breadth of the Poisson distribution when L increases. As a consequence, a uniform distribution can be used with reasonable precision for random scission instead of the more complex Poisson distribution, for trifunctional networks with, say, at least 20 scission sites per chain on average, and for tetrafunctional networks with at least 30 scission sites per chain on average.

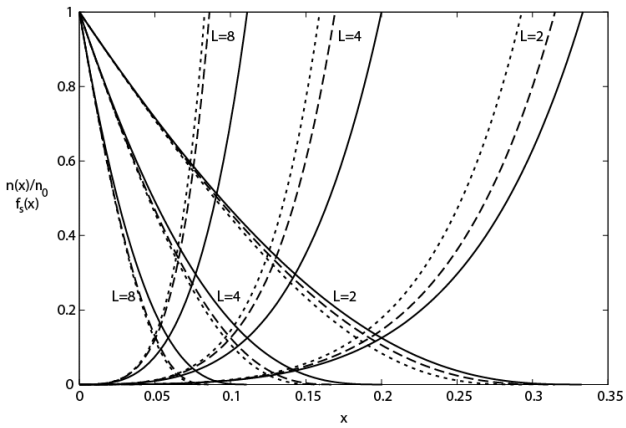

Figure 3. Variations of crosslink density and soluble fraction during the degradation of trifunctional networks with average numbers L of reactive groups per chain. Solid lines: Flory distribution, dashed lines: Poisson distribution, dotted lines: no dispersion.

3.3 Application to the hydrolysis of a polyester network

Richaud et al. [17] proposed recently an approximate model to describe the variations of the shear modulus of a polyester network degraded by hydrolysis. The polyester studied was a polycondensate resulting from the reaction of 60% by weight adipic acid, 12% ethylene glycol and 28% diethylene glycol, which was crosslinked by a stoichiometric amount of benzene

triisocyanate. Size-exclusion chromatography lead to an average number L of esters per chains ca. 18 and to a polydispersity index of ca. 1.7.

Since each primary chain bears an even number of esters, the present model will be applied with a suitably modified Flory distribution defined as

$$s(i) = \left(\frac{2}{L}\right)^{\frac{i}{2}} \left(\frac{L}{2} - 1\right)^{\frac{i}{2}-1} \qquad (i \text{ even}) \tag{27}$$

which does satisfy (18). Since this leads to

$$u(x) = \sum_{i=2,4\ldots}^{\infty} s(i)(1-x)^i = \frac{2(1-x)^2}{L-(L-2)(1-x)^2} \tag{28}$$

one obtains

$$\frac{n(x)}{n_0} = \frac{1}{8}\left[L + 2 - \frac{L}{(1-x)^2}\right]^3 \tag{29}$$

for a trifunctional network, and the degelation point is given by

$$x_{\mathrm{d}} = 1 - \frac{1}{\sqrt{1+2/L}} \tag{30}$$

Figure 4 compares (29), using an average value $L = 18$, to a uniform number of reactive groups per chain, and the same trend of a delayed degradation is observed as in the previous paragraph, the degelation point being shifted from 0.0378 to 0.0513. Moreover, Figure 4 also shows that the approximate model of Richaud et al. [17], which is strictly valid for low conversion ratios only, does coincide with the present model at low and moderate conversions if all chains are assumed to bear the same number of scission sites, but it underestimates the variation of crosslink density for larger conversion ratios, and the degelation point is underestimated at 0.0258.

In the experiments, the specimens were exposed to humid aging under three temperature and relative humidity conditions, namely 60°C and 29% RH, 60°C and 75% RH, 70°C and 25% RH. The shear modulus was deduced from mechanical tensile tests and, since the network is trifunctional, it is assumed here proportional to crosslink density, as in the classical affine model

of rubber elasticity. As hydrolysis proceeds, the conversion ratio $x(t)$ must be evaluated as a function of time, and the following relation has been obtained by Richaud et al. [17]:

$$x(t) = \frac{1-\exp[-(1+A)k\,w\,t]}{1+A\,\exp[-(1+A)k\,w\,t]} \tag{31}$$

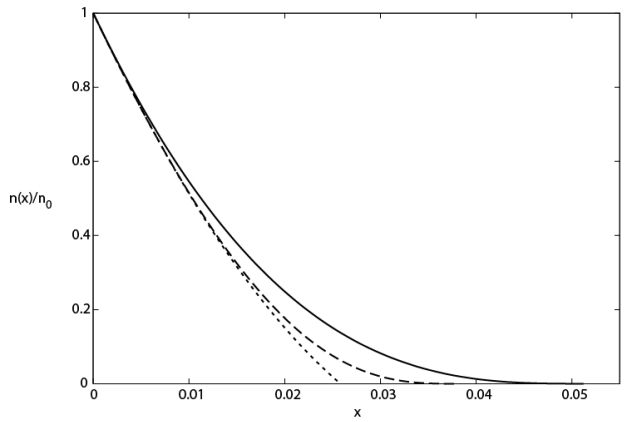

Figure 4. Variations of crosslink density during the hydrolysis of a trifunctional network with 18 esters per chain on average. Solid line: Flory distribution with even numbers of esters per chain, dashed line: no dispersion, dotted line: model of Richaud et al. [17].

Two constants define the kinetics of hydrolysis in this equation, namely the rate constant k for uncatalyzed hydrolysis, and the autocatalysis ratio A. The latter is due to esters being transformed into acid during hydrolysis. The water concentration w is assumed fixed in a given experiment, and it is deduced from sorption isotherms measured at constant temperatures. The same procedure as in Richaud et al. [17] is used here to obtain the k and A constants: a parabolic fit of the experimental results at low conversions provides k (and the same values as in Richaud et al. [17] are used, consequently), whereas A is adjusted so that the combination of (29) and (31) provides an exposure time for a shear modulus divided by 2 that is in agreement with the experiments. Values of 175, 385, and 153 were obtained for A with this procedure in the three

conditions listed in Figure 7, where a good agreement can be observed between the model and the experiments. These *A* values are larger (by 10-18%) than those obtained with the model of Richaud et al. [17], which is consistent with degradation being accelerated when *A* increases. The present theory is simpler in its formulation, it is not limited to low conversion ratios, and it is more likely to predict the degelation point, consequently.

4. Conclusion

(i) The relation between crosslink density and conversion ratio during a random chain scission process occurring on *f*-functional networks has been studied, including a distribution of the number of reactive groups on the chains.

(ii) A very strong influence of the average number of reactive groups per chain on the conversion ratio at degelation has been demonstrated, and an important effect of the dispersion of this number has also been found for broad distributions, which delays degelation.

(iii) Accordance has been obtained with a previous experiment on a trifunctional network having two reactive groups per chain, and with recent experimental results regarding the hydrolysis of a polyester having 18 reactive groups per chain on average, by using a suitable kinetics with autocatalysis.

(iv) The proposed statistical theory can be applied to the degradation of networks provided that random chain scission only (no crosslinking) is involved and that all the elastically active chains contain reactive groups. It can be suitable for certain cases of hydrolysis and for radiolysis, for instance.

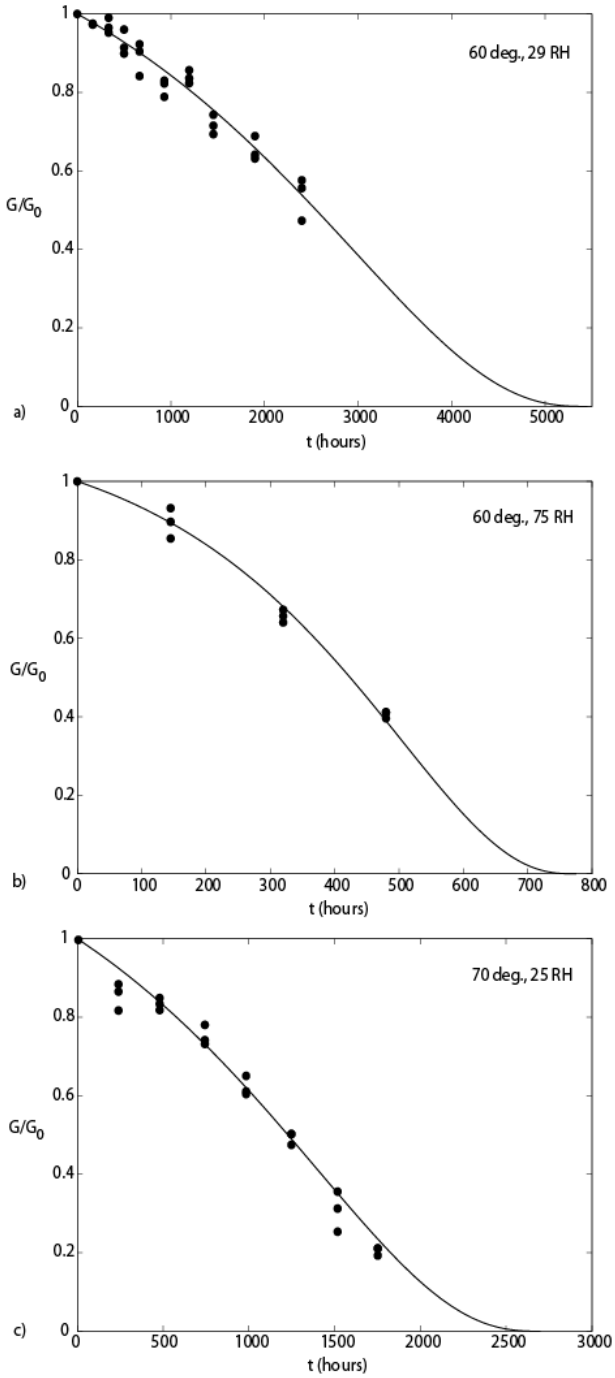

Figure 5. Analytical predictions of the variations of the shear modulus (solid lines) during the hydrolysis of a polyester, compared to the experimental results of Richaud et al. [17] (symbols), for three temperatures and/or hygrometric conditions.

Acknowledgement

The Herakles (SAFRAN group) company is acknowledged for financial support.

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