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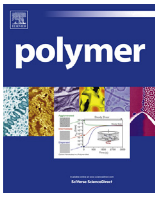

A statistical theory of polymer network degradation

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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.

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 sulfur bridges in certain cases of sulfur 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,

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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

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

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:

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

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

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

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 $\sum_i s(i)(1-x_d)^i = 1 - x_d$), 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

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