Radiochemical "degelation" of polymethyl methacrylate networks

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ABSTRACT

Methyl methacrylate-ethylene glycol dimethacrylate networks were synthetized and submitted to radiochemical degradation, with ageing monitored by means of sol-gel analysis. The networks were shown to undergo chain scission predominantly, which leads to their degelation, i.e., the recovery of a thermoplastic-like behavior with loss of all elastically active chains. The degelation dose was shown to increase with crosslink density and the corresponding critical conversion ratio was discussed regarding a recent and general statistical theory that covers radiochemical as well as chemical chain scissions.

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1. Introduction

The degradation of polymeric networks by chain scission is a process that receives an increasing attention in the scientific literature [1—3] because it offers the opportunities to recycle materials without downgrading and to regenerate new chemical feedstock. When this process is considered from the point of view of chemical kinetics, the pertinent parameter to characterize the extent of degradation is the conversion ratio y defined by $y = N/N_0$, where N and N_0 are the number of broken bonds and the initial number of breakable bonds, respectively. There are however strong experimental obstacles in general to the determination of low values of y, owing to the analytical problems due to the structure complexity and the insolubility of polymeric networks. This is the reason why degradation is monitored generally by indirect methods aimed at determining the crosslink density x, such as the measurement of the elastic properties in the rubbery state [4—6], the solvent swelling ratio of the gel fraction [7], the sol/gel fractions [7—9], the molar mass distribution in the sol fraction [10—12]. To establish the relationship between the crosslink density and the conversion ratio, it has been assumed that degradation behaves exactly as the reverse of step by step polymerization and then the Flory-Stockmayer theory of network formation could be used [13—15], provided that degradation is a "pure" random chain scission (no simultaneous crosslinking). This is generally the case of polyester hydrolysis, which explains why this process has been used to check the theory [6,12].

In the past, attention was focused mainly on the effect of degradation on soluble/insoluble fractions and on the sol composition, but emphasis was put recently on the change of elastic properties, first at low conversions only [5], then in the whole range of conversions during which a gel fraction subsists [6]. In the latter work, analytical expressions were proposed for the crosslink density-conversion ratio relationship, which were illustrated on networks having trifunctional or tetrafunctional crosslinks and for special cases of primary chain length distributions. Experimental checking was performed on trifunctional isocyanate cured polyesters. For a given conversion ratio of the degradation process, it was found that the crosslink density depends on the crosslink functionality f, on the number L of breakable bonds per primary chain and, to a lesser extent, on the shape of the primary chain length distribution. Special attention was paid to the "degelation" point [12], i.e., the state where the gel fraction vanishes ($x = 0$) and the sample becomes totally soluble. Relatively simple functions of L were obtained [5,6] for the conversion ratio y_d at degelation, and some are recalled in Table 1. When a series of networks differing only by their chain length is available, the determination of their degelation point offers a simple way for checking the theory.

The radiolysis of polymers containing quaternary carbons in the main chain, polyalkylmethacrylates or polyisobutylene for instance, can be an alternative to polyester hydrolysis in network degradation studies. This is appropriate because it has been established half a century ago that these polymers undergo almost "pure" random chain scission, owing to the very low value of the monomer-monomer bond energy value [16,17]. Radiolysis is free of autocatalysis that can complicate the kinetic analysis of hydrolysis [5] and does not depend sharply on irradiation conditions (in the absence of oxidation). It seemed thus interesting to try to check the

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Table 1
Expressions of the conversion ratio at degelation as a function of the average number L of breakable bonds per primary chain [6].

	Trifunctional crosslinks	Tetrafunctional crosslinks
Homodisperse distribution	$1 - \frac{1}{2^{1/L}}$	$1 - \frac{1}{3^{1/L}}$
Flory distribution	$\frac{1}{L+1}$	$\frac{2}{L+2}$

theory with radical polymerized methyl methacrylate (MMA)-ethylene glycol dimethacrylate (EGDMA) copolymers differing by the molar fraction of comonomers and irradiated by gamma rays.

The radiolysis mechanisms have been elucidated in the case of PMMA [18,19]. The primary event is the splitting of the chain-ester lateral bond, leading to a tertiary macroradical which evolves by beta scission to give a terminal double bond and the (relatively stable) polymerization radical. The latter can potentially initiate zip depolymerization at elevated temperature but this is unlikely at the temperature of 40 °C considered below. The radiochemical yield for random chain scission $G(s)$ is of the order of 2 events per 100eV (about 2 10^{-7} mol/J) [20–23]. Knowing the non-selectivity of radiolytic processes, it can be assumed that this yield takes the same value in tridimensional methyl methacrylate copolymers, except possibly at high crosslink densities where interactions can occur between any MMA monomer unit and the close crosslink mers. We consider two possibilities:

(i) The radiolytic reactions occurring in crosslink mers are negligible, which is probably true for low crosslink densities, i.e., for long PMMA chains. In such cases, the networks would behave as tetrafunctional networks from the point of view of degradation statistics.

(ii) The reactions in crosslink mers are not negligible and must be taken into account in degradation statistics. But what is the radiolysis mechanism in this case? There is no helpful published data on this aspect, to our knowledge. We found interesting to make the following assumption: EGMDA units react like MMA ones, by splitting of the chain-ester bond.

The present paper thus aims at studying the radiolytic degradation of several MMA-EGDMA networks differing by their crosslink density and at characterizing the conversion ratio y_d at their degelation point. Two approaches of degradation statistics differing by the assumed mechanisms will then be used to predict degelation, using the statistical theory presented in Ref. [6].

2. Theory

Consider a sample prepared from a mixture of a mass m_M of methyl methacrylate (MMA, molar mass $M_M = 100$ g/mol) and a mass m_E of ethylene glycol dimethacrylate (EGDMA, molar mass $M_E = 198$ g/mol). The network is composed of two kinds of chains: "long chains" of PMMA containing an average of L monomer units, i.e., L breakable bonds, and "short chains" made of two ester groups interconnected by a dimethylene unit. The question of the number of breakable bonds in "short chains" will be examined later. The average number of breakable bonds in "long chains" is obtained readily by assuming the network is ideal as a first approximation, each EGDMA being thus connected to 4 "long chains":

$$L = \frac{m_M/M_M}{2 \; m_E/M_E} = \frac{0.99}{r} \tag{1}$$

where r denotes the mass ratio m_E/m_M.

There are two ways of considering the network connectivity as regards degradation. In the first one, the probability of chain scission in the "short chains" is assumed negligible, so that an EGDMA unit plays the role of a tetrafunctional crosslink. The second approach takes scissions in the EGDMA units into account, two "long chains" and one "short chain" are connected to a quaternary carbon which plays the role of a trifunctional crosslink. For the sake of simplicity, it will be assumed in the latter case that "short chains" react like "long chains" by the radiolysis of the chain-ester bond. In other words, short chains would contain 2 breakable bonds with the same radiochemical yield as those of "long chains".

The condition for degelation is detailed now, which is characterized by the conversion ratio y_d, i.e., the number of scissions at degelation per initial breakable bond. Let us make first the assumption that only "long chains" carry breakable bonds. The number of scissions induced by an irradiation dose D per unit mass is given by

$$s = G(s)D \tag{2}$$

where $G(s)$ denotes the radiochemical yield of PMMA (in mol/J) and, consequently, the fraction y of the number of breakable sites that have reacted is

$$y = \frac{m_M G(s)D}{m_M/M_M} = M_M G(s)D \tag{3}$$

Two subcases can be distinguished: in the first one, all "long chains" bear the same number of breakable bonds and the critical value of y at degelation is given by Ref. [3]

$$y_d = 1 - \frac{1}{3^{1/L}} \tag{4}$$

Actually, L must be an integer in (4), which is not the case for all the samples under study. It seems thus more realistic to suppose that "long chain" lengths are more or less dispersed, L being the average number of breakable bonds per "long chain". We have previously shown [6] that y_d would then be larger than in the homodisperse case. For instance, in the case of a Flory distribution, one would have:

$$y_d = \frac{2}{L+2} \tag{5}$$

We make now the alternative hypothesis that scissions can occur in both "long chains" and "short chains". If, as proposed above, the primary event is the scission of the carbonyl-chain bond, this reaction leads to the same macroradical as the one resulting from PMMA radiolysis (Fig. 1a); it must thus react by beta scission. In other words, each radiolysis event in the EGDMA moiety must give two chain scissions (Fig. 1b). This, and the presence of two types of breakable chains in the system, requires the following modifications of the model developed in Ref. [6], which is quite general and can be applied to any type of chain scission, chemical or radiochemical. Making the assumption that EGDMA has the same radiochemical yield $G(s)$ as MMA, whereas the above approach assumed this yield was negligible, the fraction y of the total number of breakable sites that have reacted for an irradiation dose D is