

Radiochemical “degelation” of polymethyl methacrylate networks



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ABSTRACT

Methyl methacrylate-ethylene glycol dimethacrylate networks were synthesized 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 1Expressions 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 $2 \cdot 10^{-7}$ 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 crosslinkers. We consider two possibilities:

- The radiolytic reactions occurring in crosslinkers 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.
- The reactions in crosslinkers 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: EGDMA 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”:

$$L = \frac{m_M/M_M}{2 \cdot m_E/M_E} = \frac{0.99}{r} \quad (1)$$

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

$$s = G(s)D \quad (2)$$

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

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

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]

$$y_d = 1 - \frac{1}{3^{1/L}} \quad (4)$$

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:

$$y_d = \frac{2}{L+2} \quad (5)$$

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

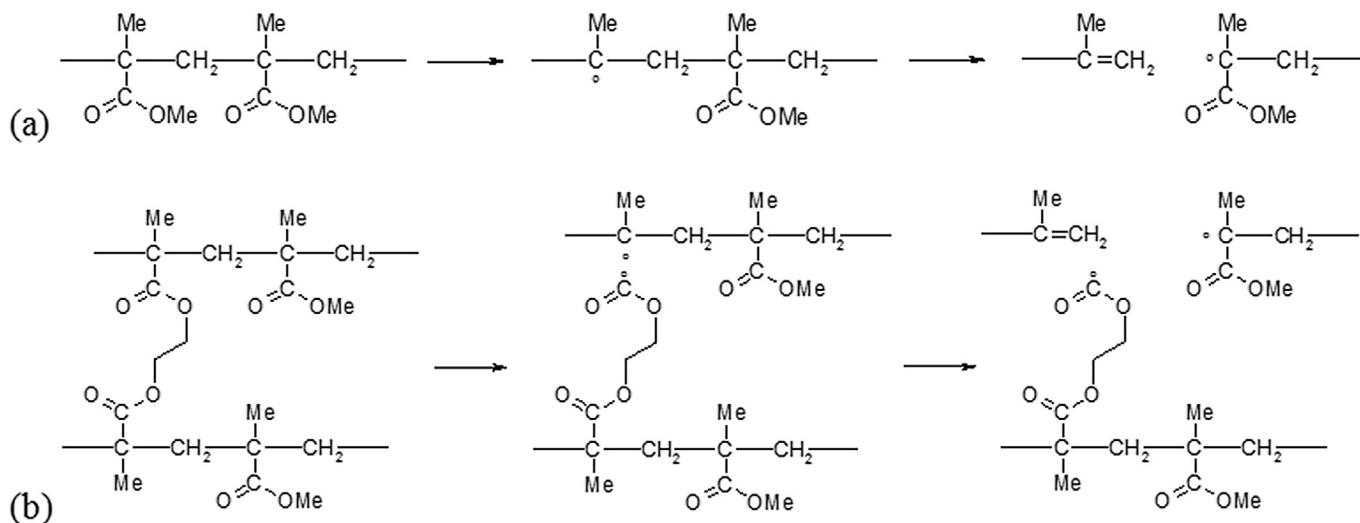


Fig. 1. The mechanisms of chain scission (a) in PMMA and (b) in EGDMA crosslinked with PMMA.

$$y = \frac{m_M G(s)D + 2m_E G(s)D}{m_M/M_M + 2m_E/M_E} \approx \frac{1+2r}{1+r} M_M G(s)D \quad (6)$$

since M_E/M_M is very close to 2. The probabilities for a site on a “short chain” to have reacted is

$$y_S = \frac{m_E G(s)D}{2 m_E/M_E} = \frac{1+r}{1+2r} y \quad (7)$$

since there are two breakable bonds per EGDMA, whereas for a site on a “long chain”

$$y_L = \frac{m_M G(s)D + m_E G(s)D}{m_M/M_M} = \frac{(1+r)^2}{1+2r} y \quad (8)$$

because of the scissions induced by “short chain” scissions, as detailed above. Therefore, the probability u_S for a “short chain” to be unbroken, i.e., for both sites of an EGDMA unit to remain unreacted, is:

$$u_S = (1 - y_S)^2 \quad (9)$$

To be uncut, a “long chain” must satisfy two conditions: (i) none of its MMA units has reacted, and (ii) none of the two EGDMA esters at its extremities has reacted and induced a scission on the “long chain”. In the case where the chain contains exactly L reactive sites, the probability u_L for a “long chain” to remain uncut is therefore:

$$u_L = (1 - y_L)^L \left(1 - \frac{y_S}{2}\right)^2 \quad (10)$$

where the coefficient $1/2$ is due to two possible locations where the second scission takes place when a radiolysis event on a neighboring “short chain” occurs. In the case of a Flory distribution of “long chain” lengths, one would obtain, using a partial result of [6]:

$$u_L = \frac{1 - y_L}{1 + (L-1)y_L} \left(1 - \frac{y_S}{2}\right)^2 \quad (11)$$

The expressions of u_S and u_L will allow expressing the condition for degelation as follows. Let g_S denote the probability to reach the gel when starting from a network node through a “short chain”. The latter must be uncut and at least one of the “long chains” to which

its end is connected must lead to the gel. In the same way, let g_L denote the probability to reach the gel when starting from a network node through a “long chain”. Like for the definition of g_S , this “long chain” must be uncut and at least one of the two chains to which its end is connected (a short one and a long one) must lead to the gel. Therefore, these probabilities are linked by the following relationships:

$$g_S = u_S [1 - (1 - g_L)^2] = u_S g_L (2 - g_L) \quad (12)$$

and

$$g_L = u_L [1 - (1 - g_L)(1 - g_S)] \quad (13)$$

Substituting g_S in (13) by its expression (12) one obtains:

$$g_L = \frac{3}{2} - \frac{1}{2} \sqrt{1 + 4 \frac{1 - u_L}{u_S u_L}} \quad (14)$$

The degelation condition corresponds to $g_L = 0$ and, since g_S is proportional to g_L , $g_S = 0$ results: neither a “long chain” nor a “short chain” can lead to the gel after degelation. By setting Equation (14) equal to 0, the condition for degelation can thus be written as:

$$u_L (1 + 2u_S) = 1 \quad (15)$$

which can be solved numerically with respect to y_d , by using (9), (10) (or (11) for a Flory distribution), (7), and (8).

3. Experimental

3.1. Synthesis

Six networks (Table 2) were obtained from the bulk polymerization of methyl methacrylate (MMA, M55909-1L grade from Sigma Aldrich) and various amounts of ethylene glycol dimethacrylate (EGDMA, 335681-500ML from Sigma Aldrich), with $r = m_E/m_M$ ratios ranging from 0.011 to 0.250. Chemicals were purified from the polymerization inhibitor by liquid-liquid extraction by using first a concentrated solution of sodium hydroxide (30 g/l) and then pure water. Then, MMA was vacuum evaporated and EGDMA was dried using anhydrous CaCl₂. Both reagents were stored at low

Table 2

Main characteristics of the samples before irradiation, and bracketing of the irradiation doses at degelation.

Sample	$\frac{m_E}{m_M}$	L	E rubbery (MPa)	T_g (°C) exp.	Degel dose (MGy)
A	0	n.a.	n.a.	108.9	n.a.
B	0.011	89.1	2.2	112.6	0.25–0.75
C	0.027	36.4	3.6	117.0	0.75–1.25
D	0.053	18.7	4.7	124.4	1.75–2.75
E	0.095	10.4	8.0	131.6	4.25–5
F	0.125	7.9	13.0	125.8	5–7
G	0.250	4.0	27.5	153.2	>8

temperature prior to polymerization. Polymerization was performed in molds made of two glass plates separated by a 2 mm thick Teflon spacer and cautiously sealed with silicone. The reactants (ca 40 g of monomers plus 0.5 g of cumyl peroxide) were injected through the seal with a syringe. The mixture was allowed to polymerize at room temperature during 24 h, and gelification was evident. The polymerization was ended in oven at 60 °C. It was checked that monomer loss by evaporation was negligible.

3.2. Irradiation

The samples were gamma irradiated by a ^{60}Co source at moderate temperature (ca 40 °C) at 5 Gy/s under air up to irradiation doses ranging from 0.25 to 8 MGy. The irradiations were performed in the SCK CEN laboratory (Mol, Belgium). Several specimens of each network were irradiated simultaneously, and subsets were withdrawn at predefined times, which produced discontinuous results in terms of irradiation dose. Therefore, the degelation dose is bracketed within a finite interval. Equations (3) and (4) were used to evaluate roughly at what irradiation doses the samples should be withdrawn.

3.3. Characterization

3.3.1. Dynamic mechanical analysis

The samples were characterized before irradiation by dynamic mechanical analysis using a DMA Q800 apparatus (TA Instruments) driven by Q Series Explorer. The specimens were submitted to

temperature sweep tests using a 2 °C/min heating ramp at 1 Hz frequency in tension mode, with a 0.1% strain amplitude and a 0.5 N preload force.

3.3.2. Differential scanning calorimetry

Ca 5 mg samples sealed in standard aluminum pans were characterized by DSC under 50 ml/min nitrogen flow at a 10 °C/min rate using a DSC Q10 apparatus (TA Instruments) driven by QSeries Explorer. The glass transition temperature was determined using TA Analysis software. The DSC apparatus was calibrated with an indium standard prior to measurements.

3.3.3. Sol-gel analysis

Two methods were used, which differed by the solvent used, either chloroform at ambient temperature or by refluxing in an acetone-chloroform (50/50) mixture. Immersion of the samples (initial mass m_0) was more than 100 h long (this duration was checked to be sufficient for reaching equilibrium). After immersion, the samples were dried at 90 °C in oven till equilibrium was reached (mass m_{Dry}). The data were used to estimate the insoluble fraction as m_{Dry}/m_0 .

4. Results

4.1. Characterization of initial samples

The DMA tests have shown that all networks have almost the same glassy modulus (ca 3 GPa at ambient temperature) and that their plateau rubbery moduli obtained at 200 °C (Table 2) are almost proportional to the EGDMA concentration (Fig. 2), with

$$E \approx 21.2[\text{EGDMA}] \quad (16)$$

obtained from a least-square fit. According to the statistical theory of rubber elasticity, the rubbery Young's modulus is expected to be given by

$$E = 3 n R T = 11.8 n \quad \text{at } 200^\circ\text{C} \quad (17)$$

where E is in MPa, which (combined with Equation (16)) leads to a ratio of approximately 1.8 between the concentration n of

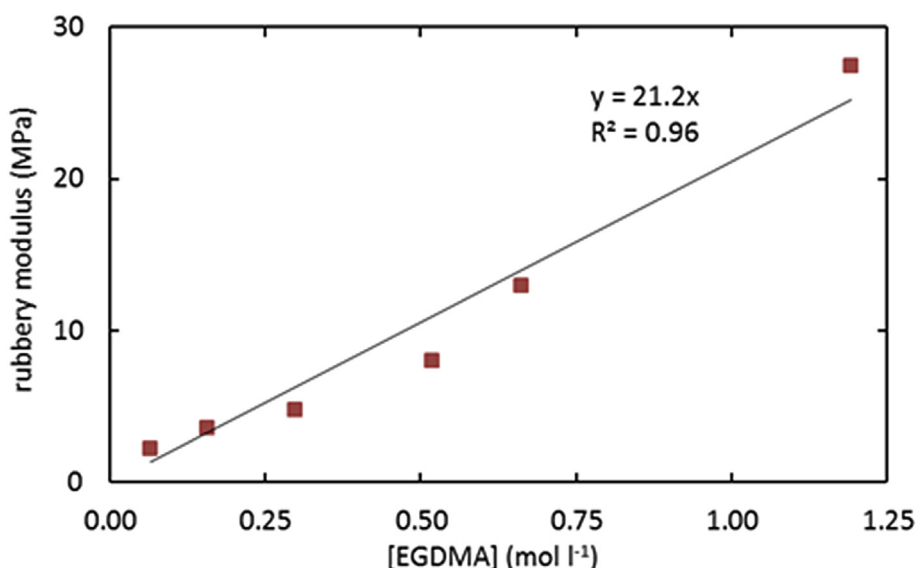


Fig. 2. Rubbery Young's modulus of the networks before irradiation versus EGDMA concentration.

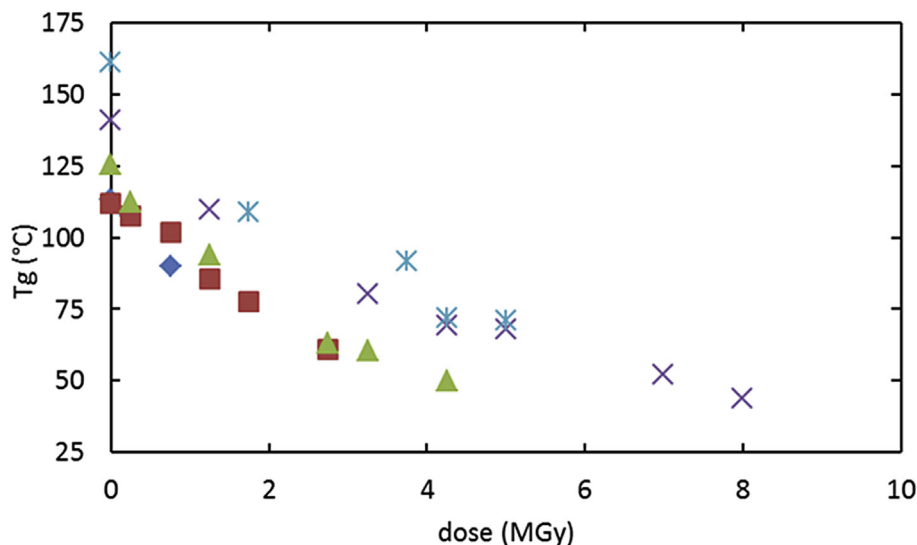


Fig. 3. Glass transition temperature of irradiated networks B(◆), C(■), D(▲), F(×) and G(*).

elastically active chains and the concentration of EGDMA. This ratio is close to the value of 2 that would apply to ideal tetrafunctional networks, whereas a coefficient of 3 would apply to trifunctional networks (since each EGDMA would join two nodes). Therefore, as regards their rubbery elasticity, the samples can be depicted as tetrafunctional and almost-ideal networks where about 10% of the EGDMA molecules are not connected to 4 elastically active chains. For the sake of simplicity, ideal networks will be considered in the computations below. It may be noted that the above rationale assumes that [EGDMA] denotes the concentration in the network as well as in the polymerization mixture, where it was measured actually. This is consistent with a complete polymerization suggested by the lack of a sol fraction after the samples were prepared.

The samples were also characterized by DSC, and they all displayed a well visible glass transition. The second scan T_g increases continuously with crosslink density, as shown in Table 2. A similar trend was observed by Loshak [24], but with a smaller T_g increase with the EGDMA concentration, which suggests that the networks studied here are closer to ideality than in Ref. [24].

4.2. Characterization of networks after irradiation

The glass transition temperature of the irradiated networks decreases continuously (Fig. 3), which confirms that they degrade mainly by chain scission. The residual insoluble fractions of the irradiated samples are shown in Fig. 4, where they are plotted versus the irradiation dose. The dose at which a sample becomes totally soluble (D_d) was estimated by considering the last dose D_{ins} at which an insoluble fraction was detected and the first dose D_{sol} at which the sample was found totally soluble. The values of D_{ins} and D_{sol} are given in Table 2 and, of course, $D_{ins} < D_d < D_{sol}$. It appears clearly that the degelation dose increases with the EGDMA concentration, i.e., it decreases with the number L of methacrylate units between two consecutive EGDMA units in a chain.

4.3. Analysis of degelation data

The conversion ratio y_d at degelation can be obtained from the theory when the reactivity of EGDMA units is neglected or taken

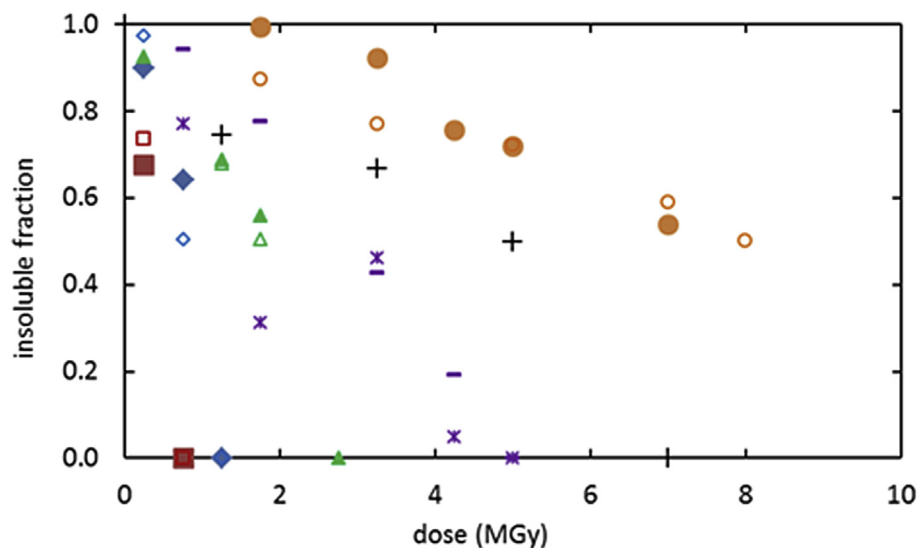


Fig. 4. Residual insoluble fraction after irradiation of networks B(■,□), C(◆,◇), D(▲,△), E(-,*) , F(+), and G(●,○). Open and closed symbols correspond to analyses in chloroform and 50/50 chloroform/acetone mixture, respectively, except for E: "-" for chloroform and "*" for chloroform/acetone.

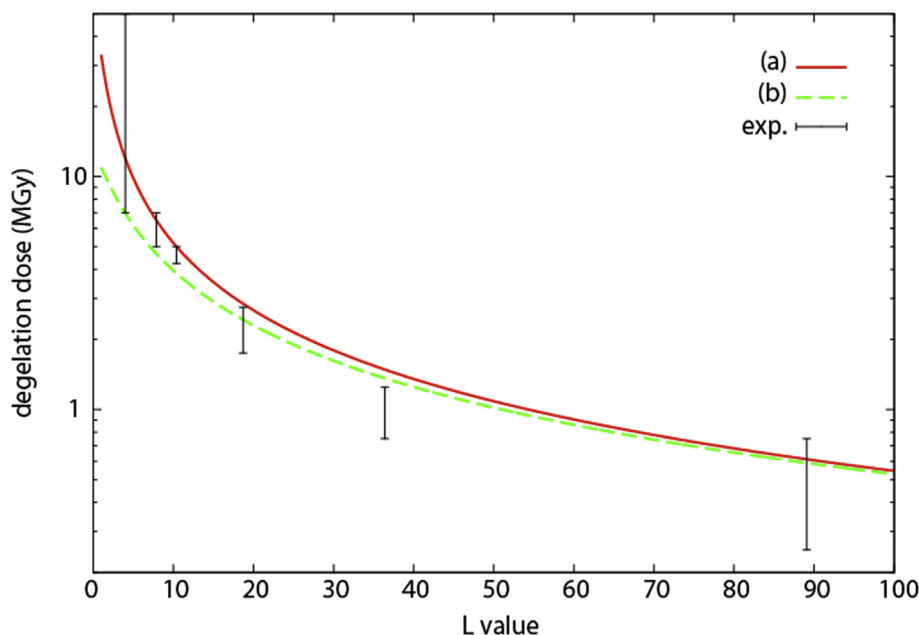


Fig. 5. Degelation dose against average L value for $G(s) = 2 \cdot 10^{-7}$ mol/J, a uniform L distribution, and either (a) non-reactive or (b) reactive EGDMA.

into account by either using Equation (4) (or (5), for a Flory distribution), or combining (15) with relations (9–10) (or (11), for a Flory distribution). The corresponding degelation dose D_d can then be obtained from either (3) or (6).

A confrontation of the experimental data with the theory requires to combine three hypotheses, one relative to the radiochemical yield of chain scission $G(s)$, the second relative to the possible contribution of EGDMA esters to the radiolytic chain scission process, and the third one relative to the distribution of L values. We know from the literature on PMMA radiolysis that the radiochemical yield $G(s)$ should be close to $2 \cdot 10^{-7}$ mol/J [20–23], and Fig. 5 compares the predictions of the model obtained for $G(s) = 2 \cdot 10^{-7}$ mol/J when the reactivity of EGDMA units is neglected or taken into account, for a uniform distribution of L

values. The experimental values D_{ins} and D_{sol} are represented as the (lower and upper, respectively) extremities of a vertical segment. It appears clearly that the degelation dose is a decreasing function of the number of reactive sites per chain, as predicted in Ref. [6]. It appears also, naturally, that the degelation dose decreases when scissions may occur on EGDMA units. Indeed, a good predicted curve should intersect all the segments ideally, which would be obtained practically in Fig. 5 by accounting for EGDMA reactivity with a radiochemical yield lower than for MMA, i.e., for an intermediate between the two curves shown in the figure. Neglecting the EGDMA reactivity allows to use the very simple Equation (4), it raises the degelation doses a little but gives very acceptable results.

Fig. 6 illustrates the effect of raising $G(s)$ from 2 to $3 \cdot 10^{-7}$ mol/J in the simulations, still with homodisperse L values, which can be

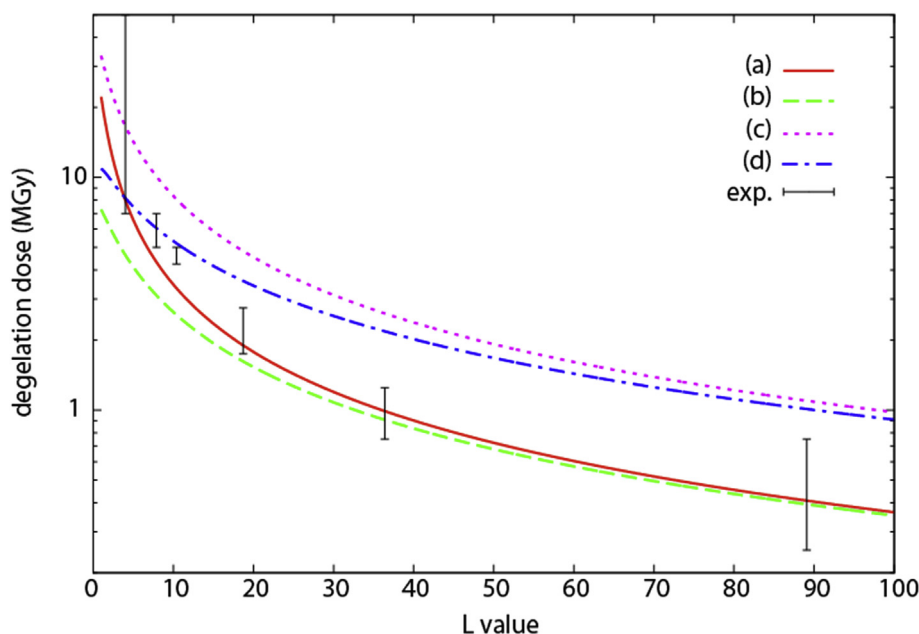


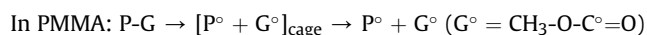
Fig. 6. Degelation dose against average L value with either $G(s) = 3 \cdot 10^{-7}$ mol/J and homodisperse L values (non reactive (a) or reactive (b) EGDMA), or $G(s) = 2 \cdot 10^{-7}$ mol/J and a Flory distribution (non reactive (c) or reactive (d) EGDMA).

compared with Fig. 5. As expected, the degelation dose decreases when the radiochemical yield increases, but the effect is moderate and suggests that a $G(s)$ value slightly above $2 \cdot 10^{-7}$ mol/J might improve the predictions of the model. Of course, this statement must be balanced by the large uncertainties of the experimental results. Fig. 6 also shows the effect of a dispersion of the number of reactive sites on “long chains”, illustrated by a Flory distribution, still using $G(s) = 2 \cdot 10^{-7}$ mol/J. Except when $L = 1$, where coincidence with the homodisperse case applies, comparison with Fig. 5 shows that the degelation dose is increased significantly when dispersed L values are considered, which leads to unsatisfactory results.

5. Discussion

Globally, the above results confirm that the radiolysis of PMMA networks can be an interesting way to study degelation and there is no apparent contradiction between the experiments and our theory. However, some questions remain open, among which the following ones:

- 1) *About network ideality.* Our theory is based on the hypothesis that the networks under study are ideal initially, i.e., free of such defects as dangling chains or loops, for instance. A non ideal network can nevertheless be considered simply if the concentration of dangling chains is known and if equivalence with a “predegraded” network is reasonable as a first approximation. This would change only the origin of the irradiation dose (as well as the conversion) axis, and the curves in Figs. 5 and 6 would be lowered.
- 2) *About the reactivity of EGDMA units.* It may be noted first that the difference between the degelation doses in the cases of reactive and unreactive EGDMA should vanish when the length of PMMA chains increases, and this is in agreement with Figs. 5 and 6. This difference remains small for short PMMA chains, indicating that EGDMA units are presumably less reactive than PMMA ones, as already suggested in the comments of Fig. 5. A possible explanation is related to the local segmental mobility, which determines the efficiency of cage recombination of primary radicals, as illustrated by the following representation of the splitting of a chain-ester bond in PMMA and in EGDMA units:



In EGDMA: $P-P' \rightarrow [P^\bullet + P'^\bullet]_{\text{cage}} \rightarrow hP-P' + (1-h)P^\bullet + (1-h)P'^\bullet$ where P^\bullet and P'^\bullet are macroradicals and G^\bullet is a microradical; h is the yield of cage recombination. In the case of PMMA, the small radical G^\bullet escapes rapidly from the cage, recombination is negligible. In the case of EGDMA, the big radicals resulting from the chain scission are less mobile than G^\bullet , they can undergo cage recombination and thus reduce $G(s)$ for this unit.

- 3) *About the effect of a distribution of L values.* Primarily, there is no reason to have a uniform distribution of PMMA chain lengths; despite that, the corresponding hypothesis gives better

simulation results than a Flory distribution in the domain of long PMMA sequences. A conceivable explanation can be found in the copolymerization kinetics of MMA and EGDMA. As a matter of fact, it can be first recalled that the Flory distribution corresponds to polydispersity ratios close to 2 where species covering more than two orders of magnitude in molar mass coexist. In the cases under study, at least for small to moderate EGDMA/MMA molar ratios, with a reactivity ratio close to unity, PMMA length distribution cannot be so broad; this is the possible reason why the hypothesis of a homodisperse L distribution gives better results.

6. Conclusion

The degradation by gamma irradiation of PMMA-EGDMA networks differing by their EGDMA concentration, i.e., by the length L of PMMA chains, has been studied by using glass transition temperature and soluble fraction measurements. Special attention was paid to the degelation phenomenon where the polymer becomes totally soluble. This copolymer was chosen because it was expected to react by random chain scission, which has been checked to apply predominantly and which allows trying to check statistical degradation theories. In the frame of a set of reasonable hypotheses, among which the initial network ideality, a reactivity of EGDMA mers comparable to MMA ones, and a radiochemical yield independent of EGDMA content, it was found that the conversion ratio of chain scission at degelation obeys fairly well a recently established and general statistical model for network degradation.

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