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Radiochemical ageing of an amine cured epoxy network. Part II: kinetic modelling

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Abstract

The radiochemical ageing (doses up to 70 MGy at a temperature of 120 °C in air) of an aromatic rich epoxide-amine stoichiometric network was studied by DMA (determination of the glass transition temperature), NMR (consumption of aliphatic CH groups) and ESR (radical decay). The number of chain scissions on elastically active chains is derived from T_g decreasing using the Di Marzio's theory. Then, a two steps mechanistic scheme is proposed, in which chain scissions occur in the initiation step but radicals partly recombine in the termination step. A kinetic model is derived from this scheme and its elementary rate constants are determined from NMR (initiation) and ESR (termination) measurements. It appears that the termination is diffusion controlled, which leaded us to introduce a time dependent termination rate constant using the Waite's theory. The model predictions are in acceptable agreement with experimental data in the range 0–70 MGy.

Keywords: Epoxy network; Radiochemical degradation; Glass transition

1. Introduction

The first part of this paper was devoted to the study of the effects of radiochemical ageing of an epoxide-amine network on its physical properties, especially fracture properties and glass transition temperature (T_g). It has been shown with a small number of simplifying assumptions that it is possible to establish a relationship between T_g and the number s of chain scissions. This relationship can be written:

$$s = \frac{T_{gl}}{2KF}\left(\frac{1}{T_g(t)} - \frac{1}{T_g(0)}\right) \qquad (1)$$

where T_{gl} is the glass transition temperature of a hypothetical linear copolymer containing all the structural units of the network except crosslinks, K is an universal constant, F is the average molar mass per rotatable bond of network chains, $T_g(0)$ and $T_g(t)$ are the T_g values, respectively, before and after an irradiation of duration t. This relationship is derived from the Di Marzio's theory of configurational entropy [1]. K is derived from the study of a large series of amine cured epoxies [2], F and T_{gl} have been calculated from the network structure, according to Bellenger et al. [3] Here, $K=2.91$, $F=30$ g/mol and $T_{gl}=348$ K. Eq. (1) allows in principle to predict T_g changes from a kinetic model, provided that the chain scission event has been taken into account in the model. The aim of this second part of our article is to build this kinetic model and to identify its parameters in order to predict T_g changes upon irradiation at 120 °C. The following observations and

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hypotheses will serve as points of departure for this investigation:

(i) A radical chain is postulated.
(ii) As shown in the first part, the thickness of the oxidised layer is lower than 60 μm whereas the sample thickness is 3 mm. In other words, T_g variations reflect the anaerobic degradation of the core zone of the samples.
(iii) We supposed that, in a first approach, chain scissions predominate largely. Simultaneous crosslinking, if it occurs, is negligible.

2. Experimental

The material has been described in Section 1. It is composed of a mixture of tri and diepoxide (50/50 M) cured by diamino-diphenyl sulphone in stoichiometric ratio. The network structure could be schematised by Fig. 1.

The cure conditions and specimen geometry have been described in Section 1. The samples of 3 mm thickness can be considered completely cured. The glass transition temperature was assimilated to the alpha mechanical transition determined by DMA at 1 Hz frequency using a dynamic torsiometer Rheometrics RDA III with a temperature ramp of 5 K/min. The transition temperature was determined at the inflection point of the curve storage modulus (G') vs temperature. NMR measurements of crushed samples were carried out at room temperature on an AVANCE BRUKER 400 MHz Wide Bore spectrometer with a standard X-H CP/MAS probe for 4 mm external diameter rotors. High resolution ^{13}C solid state NMR spectra were acquired in the presence of magic angle spinning (rotation frequency $\nu_r = 15$ kHz) using a cross polarization period of 2 ms, and high power proton decoupling during acquisition. A linear ramp (40–100%) on proton channel was introduced during the cross polarization period in order to avoid Hartman Hahn mismatch during polarization transfer. 20,000 scans with 3 s recycle time were recorded for each spectrum. Experimental free induction decays were multiplied by exponential function (line broadening LB = 300 Hz), Fourier transformed and a baseline correction was applied to the entire spectrum. Using present experimental settings almost quantitative spectra could be obtained as shown by the good agreement between experimental and theoretical aliphatic/aromatic ratio. Integration values are given within an error of 2%. Line assignment was made with the help of theoretical spectra calculated with ACD predictor commercial program. ESR spectra were acquired on a E9 Varian X-Band spectrometer interfaced with a PC using a computer program written in LabVIEW for data acquisition and treatment. The following parameters were used for acquisition: attenuation 30 dB, receiver gain 500, amplitude modulation 1.25 G, five scans. For quantitative measurements, spectra were recorded with a double cavity system. Four millimeter tube samples were prepared carefully in such a way that the cavity was always filled with almost the same polymer mass per linear units. Absolute spin concentrations were measured by comparison with a calibrated Strong Pitch sample from Varian used as a reference. Spectrum areas were obtained after baseline correction and double line integration. Concentrations are given within an error of 20%.

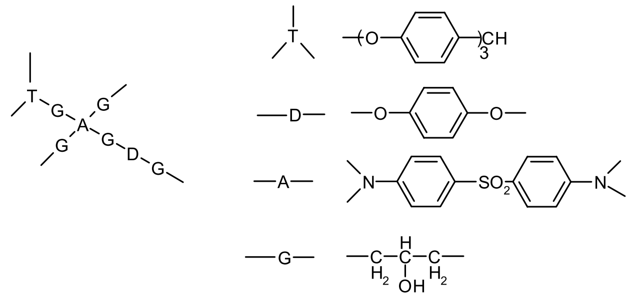
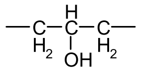


Fig. 1. Scheme of the epoxy-amine network.

3. Results and discussion

3.1. Mechanistic scheme and kinetic model

According to the well known structure–property relationships in the field of polymer radiochemistry [4], it can be assumed that the weak part of the network is the aliphatic isopropanol segment:



$$-\underset{H_2}{C}-\overset{H}{\underset{OH}{C}}-\underset{H_2}{C}-$$

The hydrogen evolution observed by certain authors [5] indicates that radiolysis of CH bonds is probably the main primary event:

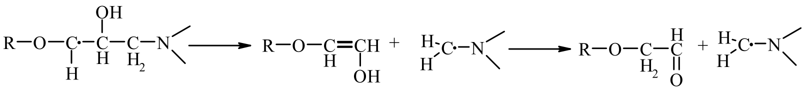
$$PH + h\nu \rightarrow P^{\cdot} + H^{\cdot} \qquad (I)$$

$$H^{\cdot} + PH \rightarrow P^{\cdot} + H_2 \qquad (II)$$

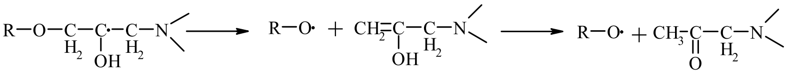
The alkyl radical can abstract hydrogen:

$$P^{\cdot} + PH \rightarrow PH + P^{\cdot} \qquad (III)$$

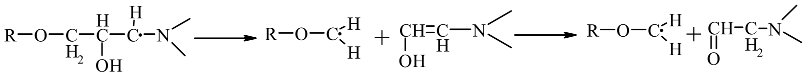
This reaction, which is neutral from a kinetic point of view, may explain the existence of a certain radical mobility in glassy matrices where the segmental motion is severely restricted. Alkyl radicals can also undergo rearrangements, among which β scissions, for instance:



(IV)



(V)



(VI)

In all the cases, a rapid rearrangement of the enol into a ketone or an aldehyde could occur. All the above processes can be summarised by the following balance equation:

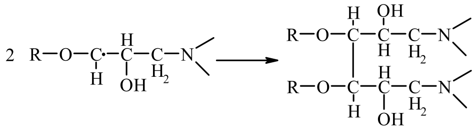
$2\text{PH} + h\nu \rightarrow 2\text{P}^{\cdot} + \text{H}_2 + \alpha s \ (k_i)$ (VII)

where s is a chain scission, and α the yield of chain scissions (i.e. the fraction of macroradicals $\text{P}^{\cdot}$ undergoing a rearrangement).

Termination is expected to result from bimolecular radical combinations:

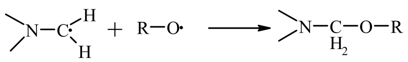
$\text{P}^{\cdot} + \text{P}^{\cdot} \rightarrow \text{inactive products}–\beta s \ (k_t)$ (VIII)

The term βs expresses the fact that certain radical combinations lead to chain extension. In fact, it would be necessary to distinguish between crosslinking and chain extension, for instance:



(crosslinking)

(IX)



(chain extension)

(X)

In a first approach, it will be assumed that crosslinking is negligible compared to chain extension for two possible reasons:

(i) Primary macroradicals are very instable and rearrange quickly to give chain end radicals ($\text{RO}^{\cdot}$, P-$\text{CH}_2^{\cdot}$). The combination of this kind of radicals gives chain extension.
(ii) Crosslinking is disfavoured by steric hindrance.

Then, one disposes of a mechanistic scheme composed of only two steps (VII) and (VIII). From this scheme, it is possible to derive the following system of differential equations:

$$\frac{d[\text{P}^\bullet]}{dt} = 2k_i[\text{PH}] - 2k_t[\text{P}^\bullet]^2 \quad (2)$$

$$\frac{d[\text{PH}]}{dt} = -k_i[\text{PH}] \quad (3)$$

$$\frac{ds}{dt} = \alpha k_i[\text{PH}] - \beta k_t[\text{P}^\bullet]^2 \quad (4)$$

The resolution of this system should lead to the function $s=f(t)$ from which T_g changes can be calculated. This resolution needs, however, the determination of rate constants k_i and k_t.

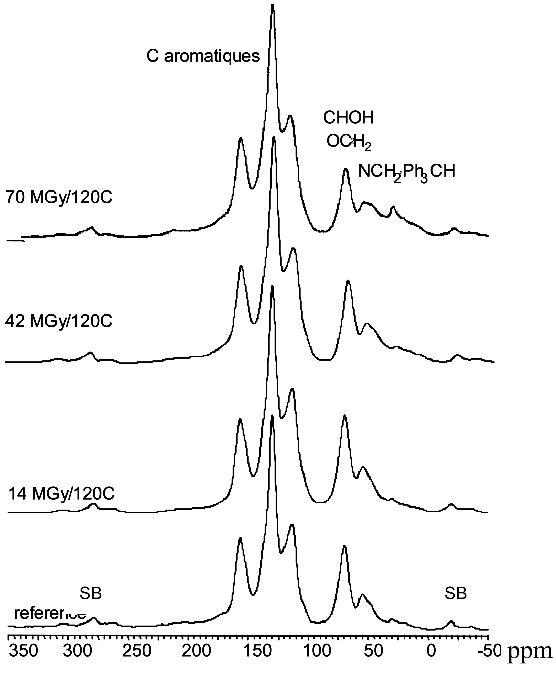


Fig. 2. NMR spectra of samples irradiated with various doses. SB stands for Side Bands due to sample rotation.

3.2. Determination of k_i

The determination of the initiation rate constant k_i is based on the hypothesis that each initiation event leads to the disappearance of one CH bond. Integrating the Eq. (3), one obtains:

$$\ln[\mathrm{PH}] = \ln[\mathrm{PH}]_0 - k_i t \tag{5}$$

Such event can be monitored by NMR if one assumes that it produces (directly or indirectly) the disappearance of a carbon signal in one region of the carbon spectrum. Actually a complete disappearance can occur as a result of gas phase product formation or due to strong line broadening in the case of stable carbon radical formation. Alternatively, the carbon signal may be shifted away from the specific chemical shift region of integration and appear in an other region depending on the product formation. NMR spectra of the samples irradiated with various doses are shown in Fig. 2.

Two lines assigned to aliphatic carbons can be observed: the most intense one at 70 ppm corresponds to carbons linked to oxygen, whereas the other peak, at c.a. 55 ppm, results from the overlapping of α amino carbons and CH connected to the three aromatic groups of the triepoxide. Aliphatic carbon intensities were measured by integrating different specific regions assuming the line area of all aromatic carbons between 350 and 95 ppm unaffected during irradiation. It appears that ageing affects essentially carbons linked to oxygen: methylene linked to phenyl ether and methine linked to alcohol. This relative selectivity could be a peculiarity of the diamino diphenyl sulphone, linked to its strong electron withdrawing effect on nitrogen [6]. The decrease of the electron density on nitrogen atoms tends to increase the resistance of the α methylene to H abstractions [7]. A first order plot of PH concentration determined by NMR is shown in Fig. 3.

ln[PH] decreases linearly, as expected, with the exposure time. The slope gives the initiation rate constant: $k_i = 4.10^{-8}\,\mathrm{s}^{-1}$.

3.3. Determination of k_t:

As previously shown [8], irradiated epoxy samples contain long lived radicals, detected by ESR. An example of ESR spectrum of our samples after irradiation is shown in Fig. 4.

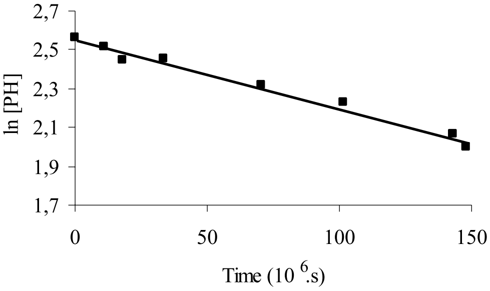


Fig. 3. ln[PH] for irradiated samples.

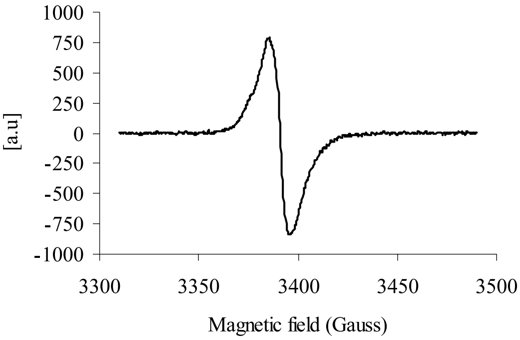


Fig. 4. ESR spectrum of a sample irradiated at 14 MGy, 120 °C.

Their recombination rate is extremely low at ambient temperature, but they disappear in a few hours at 120 °C allowing, thus, a kinetic study of the recombination reaction. To study this process, samples were placed under vacuum in sealed tubes and the decay of spin concentration was monitored at 120 °C by ESR measurements. To model this process, it was assumed the existence of a unique radical structure and that termination is a second order process: $\mathrm{P}^{\cdot} + \mathrm{P}^{\cdot} \rightarrow$ inactive products (k_t)

So that:

$$\frac{1}{[\mathrm{P}^\bullet]} - \frac{1}{[\mathrm{P}^\bullet]_0} = 2k_t t \tag{6}$$

The second order plot of $[\mathrm{P}^{\cdot}]$ is presented in Fig. 5.

A clearly non linear graph is obtained: the apparent termination rate constant decreases rapidly during exposure to tend towards zero after about 5 h. A similar behavior was observed in an epoxy resin by Seo et al. [8]. It is obviously due to the kinetic control of the reaction by the diffusion of radicals into the polymer matrix: the longer the average distance between two radicals, the lower the apparent bimolecular rate constant. This situation was analysed by Waite in the 1960s [9–12]. The model proposed by this author can be written, in our case:

$$\frac{\mathrm{d}[\mathrm{P}^\bullet]}{\mathrm{d}t} = -k\left(1 + \frac{k}{\sqrt{\pi D t}}\right)[\mathrm{P}^\bullet]^2 \tag{7}$$

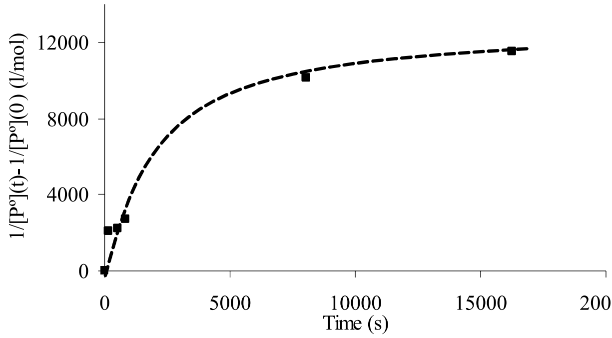


Fig. 5. Decay of the reciprocal spin concentration versus time.

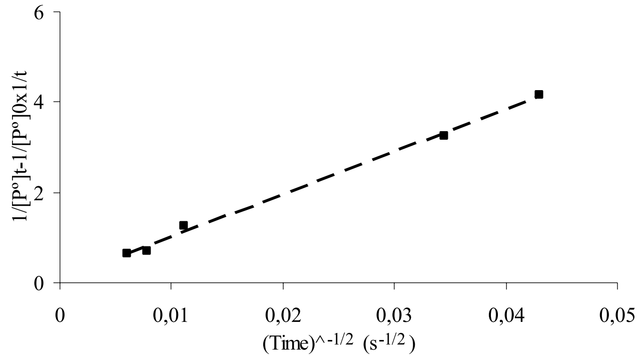


Fig. 6. Kinetics of the radical decay in the frame of Waite's model.

with $k = 4\pi r_0 D$, where r_0 is the capture radius and D the diffusion coefficient of radicals. The integration of Eq. (7) leads to:

$$\left(\frac{1}{[\mathrm{P}^\bullet]_t} - \frac{1}{[\mathrm{P}^\bullet]_0}\right)\frac{1}{t} = k + \frac{k r_0}{\sqrt{\pi D}}\frac{1}{\sqrt{t}} \tag{8}$$

Plotting the first term versus the reciprocal of the square root of time, one obtains the graph presented in Fig. 6.

From this graph, one obtains the parameter values: $r_0 = 4.4 \times 10^{-8}$ m, $D = 1.8 \times 10^{-18}$ m^2/s.

The value of D is in the range found by Emanuel and Buchachenko [13] on several polymers whereas r_0 value is about 10 times higher, but it appears difficult to appreciate the physical validity of these results. Despite that, present values were used in the kinetic model of chain scissions described below.

3.4. Kinetic model of chain scissions

The chain scission rate is given, for the chosen mechanistic scheme, by:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \alpha k_i[\mathrm{PH}] - \beta k\left(1 + \frac{r_0}{\sqrt{\pi D t}}\right)[\mathrm{P}^\bullet]^2 = F(t) \tag{9}$$

Chain scission can occur as well on elastically active chains (EAC) as on dangling chains (DG). To predict T_g, we need to know the concentration of elastically active chains (initial value n_0) and thus the number x of chain scissions on EAC. Assuming that the rate of chain scission on EAC is proportional to the EAC concentration, one can write:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\mathrm{d}s}{\mathrm{d}t}\frac{n_0 - 2x}{n_0} = F(t)\frac{n_0 - 2x}{n_0} \tag{10}$$

So:

$$\frac{\mathrm{d}x}{n_0 - 2x} = \frac{1}{n_0}F(t)\mathrm{d}t \tag{11}$$

By integrating this equation, one obtains:

$$x(t) = \frac{n_0}{2}\left[1 - \exp\left(-\frac{2}{n_0}\int_0^t F(t)\mathrm{d}t\right)\right] \tag{12}$$

$x(t)$ was calculated numerically using the routine ODE23S of the Matlab software. The stoichiometric coefficients α and β were obtained from an optimisation procedure. The values giving the best results were: $\alpha = 1$, $\beta = 0.4$.

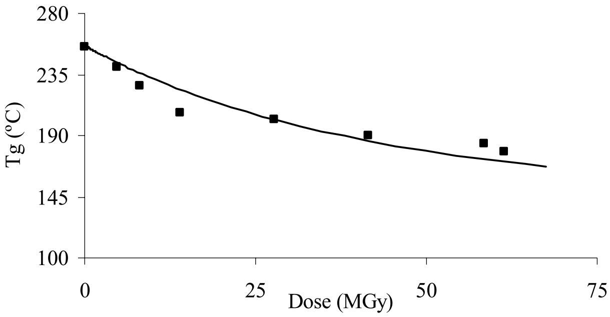


Fig. 7. Comparison between experimental (points) and calculated (curve) glass transition temperature.

3.5. Model validation

Eq. (1) in which s is replaced by x to take into account the existence of ineffective chain scissions on dangling chains was used to calculate T_g in the case of irradiation at 120 °C. The calculated and experimental values of T_g were plotted versus dose in Fig. 7.

Considering all the sources of scatter, the agreement between both series of T_g values can be considered satisfactory, the difference between experimental and calculated values being generally lower than 10 °C except for one point where it reaches about 20 °C.

4. Conclusion

A kinetic model has been established for the chain scission process induced by gamma rays in an aromatic rich epoxide-amine stoichiometric network. This model is based on a radical mechanistic scheme involving two elementary steps:

$$2\mathrm{PH} + h\nu \rightarrow 2\mathrm{P}^{\cdot} + \mathrm{H}_2 + \alpha\ (k_i) \tag{12}$$

$$\mathrm{P}^{\cdot} + \mathrm{P}^{\cdot} \rightarrow \text{inactive products}-\beta s\ \ (k_t)$$

The initiation rate constant k_i can be estimated from the rate of PH (aliphatic carbons) consumption determined by solid state NMR At 120 °C, $k_i = 4.10^{-8}\ \mathrm{s}^{-1}$. The radical decay in vacuum was monitored at 120 °C by ESR in order to determine k_t. In fact, the P˙ disappearance does not obey simple second order kinetics, but rather diffusion controlled second order kinetic with a time dependent rate constant given by Waite's theory [9–12]:

$$k_t = k\left(1 + \frac{r_0}{\sqrt{\pi D t}}\right) \text{ where } k = 4\pi r_0 D.$$

The model is in good agreement with the experimental results with $r_0 = 50$ nm and $D = 1.8 \times 10^{-18}$ m^2/s. The number of chain scissions on elastically active chains is then given by:

$$x(t) = \frac{n_0}{2}\left[1 - \exp\left(-\frac{2}{n_0}\int_0^t F(t) \times \mathrm{d}t\right)\right] \text{ where } F(t)$$

$$= \alpha k_{\mathrm{i}}[\mathrm{PH}] - \beta k\left(1 + \frac{r_0}{\sqrt{\pi D t}}\right)[\mathrm{P}^{\cdot}]^2$$

From x, it is possible to calculate T_{g} using the Di Marzio's law [1]. This model agrees reasonably well with experimental results obtained by gamma irradiation at 120 °C, using $\alpha = 1$, $\beta = 0.4$.

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