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Radiation aging and chemi-crystallization processes in polyoxymethylene

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ABSTRACT

The radiochemical degradation of a polyoxymethylene homopolymer (POM) was used to study the effects of molar mass changes in the crystalline structure. The dose rate was 20 kGy h^{-1} with doses of up to 30 kGy used. Both WAXS and SAXS were used to analyse the structures. Results showed that, under irradiation, the polymer undergoes random chain scission. The radiochemical yield was found to be $G = 1.6$ chain scission events per 100 eV. It was found that no crosslinking occurs and that only one chain scission mechanism, leading to the formation of formate groups, operates. Proof for the existence of chemi-crystallization is evidenced by (i) an increase in the crystallinity ratio as well as (ii) a decrease in the amorphous layer thickness. Simple models, derived from Rault's theory, are used to predict both (i) and (ii) from molar mass values.

1. Introduction

Although a semi-crystalline material always exists outside of a thermodynamic equilibrium, it reaches a quasi equilibrium when it is kept at a constant temperature (T) above its glass transition temperature (T_g) and below its melting point (T_m). As a result of the existence of this quasi equilibrium, it was possible to establish suitable relationships between the molar mass distribution and characteristics such as the crystallinity ratio (x_C) or the amorphous layer thickness (l_a) [1,2].

If a quasi equilibrated sample, which is kept at a particular temperature (T), undergoes a random chain scission in its amorphous phase, it will undergo a secondary crystallization. This is often known as chemi-crystallization because it is induced by a chemical process. It can be assumed that, if the chain scission is slow enough, compared to crystallization, the morphology of the polymer can reach at any time the quasi equilibrium state characteristic of its new molar mass distribution.

From a practical point of view, chemi-crystallization can be important because it leads to serious embrittlement [3]. There are industrial application reasons, therefore, why it is not only interesting but also pertinent to establish the relevant relationships between the chemical variables (number of chain scissions, molar mass) and the morphological ones (x_C, l_a, etc.).

Experimental data regarding chemi-crystallization are relatively abundant in the literature. Already in the early 1980's, it was observed in the case of polyolefine oxidations [4–8] and poly(ethylene terephthalate) hydrolysis [9–11]. More recently there have been reports on polypropylene radiolysis [12,13] photooxidation [14]. In our early study involving the thermal oxidation of POM, chemi-crystallization was in fact observed [15]. However, although the occurrence of a depolymerization process did lead to the destruction of the amorphous phase and subsequently contributed to an increase in the crystallinity ratio, due to its complicated nature and the involvement of annealing effects, an accurate analyses of the chemi-crystallization kinetics proved too difficult. A more extensive study, using gamma ray irradiation at ambient temperature, specifically aimed at overcoming or at least minimizing these depolymerization and annealing effects is presented here.

It has been long established, that polymers which undergo thermal depolymerization i.e. polymers in which the monomer–monomer link is particularly weak, can undergo random chain scission when they are irradiated by ionizing radiations. Since POM belongs to this family of

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the polymers, which undergo facile (almost complete) thermal depolymerization, it is expected that on irradiation POM will undergo "pure" (no crosslinking) random chain scission. It is therefore a model polymer and a good candidate for investigating both chemi-crystallization mechanisms and kinetics.

2. Experimental

The POM used for this study was a homopolymer (Delrin 100) supplied by Dupont. Average molar masses were $M_n = 70\ kg\ mol^{-1}$, $M_W = 140\ kg\ mol^{-1}$ and polydispersity index (PI) = 2. Glass transition temperature (T_g) of the amorphous phase was −50 °C and melting point (T_m) was 177 °C.

Samples of 4 mm thickness were injection moulded. Specific attention was paid to processing conditions in order to obtain quasi isotropic samples. The presence of a low degree of orientation was checked by SAXS (see below). The samples were annealed under vacuum 24 h at 130 °C in order to reach quasi equilibrium before irradiation.

Gamma irradiation (60Co source) was performed in the SCK-CEN (Belgium) facility. The dose rate was 20 kGy h^{-1}. Samples were exposed in air at 25 °C to doses of up to 30 kGy.

Any modification in molecular structure was monitored using FTIR spectrophotometry, which followed the formate build-up, as well as molar mass measurements. The chemical changes and the homogeneity of the degradation was established using IR micro-spectrophotometry in transmission mode (Brucker IFS 28 with 4 cm^{-1} resolution). Samples consisted of transversal microtomed slices of 35 μm thickness.

Rheometry in dynamic oscillatory mode at 190 °C under nitrogen was used to make molar mass measurements. An ARES rheometer (Rheometrics Scientific) in parallel plate configuration (diameter 25 mm, gap 0.5 mm) at atmospheric pressure in the 0.1–100 rad s^{-1} frequency range was used. The maximum strain amplitude was optimized in order to measure reliable torque values in the Newtonian domain. Weight average molar mass (M_W) was determined from Newtonian viscosity (η) using the well-known scaling law $\eta = KM_W^{3.4}$ with $K(190\ °C) = 9.56 \times 10^{-15}$ SI. The molar mass distribution was determined from the viscoelastic spectrum using Mead's model [16] in order to assess polydispersity index and M_n.

Wide-angle X-ray Scattering (WAXS) and Small-angle X-ray Scattering (SAXS) were used to study the crystalline structure of the polyoxymethylene. This was achieved by means of a 2D diffraction system (Inel, France) equipped with a copper anode. The selected tension and the intensity were 30 kV and 40 mA, respectively. The $K_{\alpha 1}$ copper radiation ($\lambda Cu_{\alpha 1} = 0.154$ nm) wavelength used was selected by means of a parabolic multilayer mirror (Osmic) and a very thin capillary. The 2D transmission patterns recorded on an image plate system were digitalized by means of a scanner with a resolution of 25 microns. The diffraction intensity was corrected using the Lambert equation $I = I_0 \exp(\mu \cdot t/\cos(2\theta))$, t being sample thickness. The diffraction angle was 2θ. In the cases studied, the absorption coefficient μ was 11.204 cm^{-1}. [17] The samples were parallel pipedic with a thickness of 0.8 mm. In the subsequent WAXS analysis, the Lorentz-corrected SAXS profiles, $I(2\theta)$, were analyzed using PeakFit software (SPSS Inc.) with a view to extracting the different components: (i) background, (ii) crystalline peaks and (iii) amorphous halo. The weight crystallinity ratio (x_C) was calculated from the relative area of the crystalline peaks. Subsequently, the long period (l_p) was obtained from the corrected diffraction curve $I(2\theta)$ after derivation using Bragg law.

3. Results and discussion

3.1. Chain scission process

From molar mass measurements, it was found that irradiation induces a decrease in both M_n and M_W, without a concomitant change in the polydispersity index (PI) (see Fig. 1a). The fact that the PI remains equal to 2.0 indicates that a "pure" random chain scission process is occurring. When M_W is plotted as a function of the dose, as shown in Fig. 1a, it clearly decreases in a hyperbolic way.

These results can be interpreted on the basis of the classical theory for random chain scission and crosslinking processes [18]. If s and x are numbers of moles of chain scissions and crosslinks per mass unit in an initially linear polymer respectively, it can be written:

$$\frac{1}{M_n} - \frac{1}{M_{n0}} = s - x \tag{1}$$

$$\frac{1}{M_W} - \frac{1}{M_{W0}} = \frac{s}{2} - 2x \tag{2}$$

Crosslinking is expected to predominate if $x > s/4$. In this case, the viscosity would continuously increase and would diverge at a gel point defined by:

$$2x_g - \frac{s_g}{2} = \frac{1}{M_{W0}} \tag{3}$$

With x_g and s_g are crosslinks and chain scission number at the get point respectively.

For $s/4 > x > 0$, gelation would not occur but crosslinking would induce branching and this in turn would be responsible for the progressive disappearance of the Newtonian plateau in the curve viscosity as a function of shear rate. Here, there is no disappearance of the Newtonian plateau. On the contrary, it widens while Newtonian viscosity decreases. This behavior is clearly indicative of a large predominance of chain scission and a negligible crosslinking.

If crosslinking is negligible, Eqs. (1) and (2) simplify then as:

$$\frac{1}{M_n} - \frac{1}{M_{n0}} = s \tag{4}$$

$$\frac{1}{M_W} - \frac{1}{M_{W0}} = \frac{s}{2} \tag{5}$$

This leads to the following expression for the polydispersity index: