

Characterizing the solid-state thermal oxidation of poly(ethylene oxide) powder

John Scheirs*, Stephen W. Bigger† and Oskar Delatycki

Department of Industrial Science, The University of Melbourne, Parkville 3052, Australia

(Received 23 February 1990; revised 29 June 1990; accepted 3 July 1990)

The oxidative degradation of powdered poly(ethylene oxide) (PEO) resin was studied by polarized optical microscopy, scanning electron microscopy (SEM), differential scanning calorimetry (d.s.c.), solution viscometry and Fourier-transform infra-red spectroscopy (FTi.r.). Powdered PEO readily oxidizes under mild ageing conditions (60°C) owing to its large surface area, its strained crystalline lattice and the weak carbon–oxygen bonds in its backbone. As a result, its physical properties deteriorate after an induction period of about 23 days and, in the extreme case, the free-flowing powder is transformed into a soft wax. With increasing oxidation, there is also a pronounced change in the morphology of PEO from a spherulitic to an axialitic structure. This transition is due to oxidatively induced changes in molecular weight and dispersity that affect the crystallization conditions. Examination of the PEO powder by SEM shows that it has an intricate, fibrillar, surface structure, which produces a large surface area available for oxidation. The emergence of multiple d.s.c. melting peaks after oxidation indicates that a number of low-melting, low-molecular-weight fractions are formed as a result of chain scission processes.

(Keywords: poly(ethylene oxide); thermal oxidation; spherulites; axialites; Fourier-transform infra-red spectroscopy; scanning electron microscopy; differential scanning calorimetry)

INTRODUCTION

Poly(ethylene oxide) (PEO) has a unique combination of properties. It is a tough, ductile, highly crystalline thermoplastic and is readily soluble in water, where it displays interesting hydrodynamic, flocculating¹ and drag-reducing properties². High-molecular-weight PEO ($M_w > 1.0 \times 10^5$) is used for water-soluble packaging film³. Films of PEO are flexible, strong, 'breathable', heat-sealable and relatively resistant to atmospheric moisture because of their high degree of crystallinity³. Water-soluble PEO films are used for 'disposable' laundry bags⁴ as well as packaging for agricultural seeding⁵, hazardous dyes and detergents⁴. Low-molecular-weight PEO is used widely as a chromatographic stationary phase⁶ (Carbowax®) and as the major component in wet-tack adhesives⁷.

The spherulitic structure of melt-crystallized PEO has been reported widely^{8,9}. Extensive studies have revealed anomalous crystallization kinetics¹⁰ as well as a lack of correlation between the glass transition temperature and spherulitic growth rate¹¹. The cause of these inconsistencies has been attributed to degradation resulting from the excessive exposure to high temperatures used in the experiments¹⁰. The crystallization characteristics of the sample are thereby obscured because they are strongly dependent on the molecular weight and weight distribution. Furthermore, the extensive degradation of PEO during size exclusion chromatography demonstrates its sensitivity to shear¹².

A number of researchers have found that PEO undergoes marked thermo-oxidative¹³ and mechanical^{2,14} degradation. The sensitivity of PEO to free-radical oxidative attack during storage and the reduction of

molecular weight under shear are factors that make difficult the characterization of the polymer². Freshly polymerized, unstabilized PEO degrades rapidly in 18 days at ambient temperature¹⁵. Significant oxidation of PEO occurs when it is stored in bulk at ambient temperature for 2–4 years¹³ and measurable degradation occurs in the absence of oxygen and light¹⁵.

The oxidation of PEO has been studied, using viscometry, in aqueous and organic solutions¹⁶ as well as in the melt^{6,17,18}. However, little information concerning the solid-state thermal oxidation of PEO appears in the literature to date. Aqueous solutions of PEO are sensitive to aerobic oxidation at temperatures as low as 40°C and it has been reported¹⁹ that the viscosity of a 0.1% (w/v) aqueous solution of unstabilized PEO is reduced by about 95% after 5 h heating at 100°C. Furthermore, solution viscometry experiments have shown that polymers containing oxygen in the main chain tend to degrade more readily than those containing only carbon atoms in their backbone²⁰. This is because the carbon–oxygen bond energy is lower than that of the carbon–carbon bond in these cases²¹.

Poly(ethylene oxide) is particularly suitable for morphological studies using polarized optical microscopy since it shows large, well-defined spherulites and its nucleation and growth rates can be varied and recorded easily^{8,22}. The kinetics of melt crystallization are affected by molecular weight and polydispersity as well as the length and concentration of chain branches. In the case of PEO the changes in these properties caused by thermal oxidation can be observed in terms of the dramatic changes that are imposed on the morphology of the spherulites. Thus, polarized optical microscopy can be conveniently used to assess the effect of thermal oxidation.

Typical commercial applications of PEO require that it has adequate thermo-oxidative stability during bulk

* To whom correspondence should be addressed

† Present address: Faculty of Applied Science, Western Institute, McKechnie Street, St Albans 3021, Australia

0032-3861/91/112014-06

© 1991 Butterworth-Heinemann Ltd.

storage, melt processing and use. Furthermore, in view of the fact that PEO oxidizes rapidly in the solid state under mild thermal conditions, causing a dramatic loss of its physical properties, the effect of thermal oxidation on the spherulitic morphology and molecular parameters was investigated.

EXPERIMENTAL

Materials and sample preparation

A standard PEO homopolymer powder with \bar{M}_w of $1 \times 10^5 \text{ g mol}^{-1}$ was obtained from Aldrich Chemical Company. The polymer contained no additives and was used as received. The powder was oxidized in glass dishes in a thermostatted air-circulating oven at $60 \pm 0.5^\circ\text{C}$. The polymer was aged for a total of 33 days and samples were taken daily.

Viscosity-average molecular weight

Solutions of PEO in benzene for viscometry measurements were prepared by gentle heating. In this solvent, PEO does not thermally degrade over extended periods¹⁶. Vigorous stirring was avoided because it has been reported that chain cleavage can result from shearing of the solution³. A concentration range of 0.25–2.0% (w/v) was used, since at lower concentrations the Huggins plot displays a severe dependence on the accuracy of the flow times, while at higher concentrations the solutions have non-Newtonian flow characteristics²³.

Viscosities were measured at $25 \pm 0.1^\circ\text{C}$ using an Ubbelohde-type capillary viscometer. The flow time of the pure solvent was 158 s. The kinetic energy and shear corrections²⁴ were negligibly small. Intrinsic viscosities were determined using a method described elsewhere²⁵. Viscosity-average molecular weights (\bar{M}_v) were calculated from the intrinsic viscosity values by the Mark–Houwink equation²⁶. The \bar{M}_v of the unoxidized PEO used in this study was measured as $1.02 \times 10^5 \text{ g mol}^{-1}$. Assuming that the PEO has a narrow molecular-weight distribution, the average molecular-weight values quoted by the manufacturer and measured in this work are comparable within experimental error.

Scanning electron microscopy (SEM)

Samples for SEM examination were mounted on aluminium stubs with double-sided adhesive tape. The samples were coated with a 30 nm layer of gold in a vacuum sputterer in order to prevent charging. Electron micrographs were taken on an Hitachi model S570 scanning electron microscope equipped with a lanthanum hexaboride (LaB_6) crystal electron source. This source has a greater electron efficiency than conventional tungsten sources and was operated at a voltage of 5 kV to reduce electron beam damage of the delicate microstructure of the polymer powder.

Infra-red analysis

Samples of PEO were cast onto NaCl plates from 1.0% (w/v) chloroform solution and examined with a Mattson FTi.r. using the transmission mode. Infra-red spectra were obtained by averaging 16 scans of each sample.

Differential scanning calorimetry (d.s.c.)

Melting endotherms and crystallinities were determined using a Perkin–Elmer DSC-7 calorimeter with a

standard heating and cooling rate of $10^\circ\text{C min}^{-1}$. Samples of approximately 10 mg were run in a nitrogen atmosphere over the temperature range 25 to 80°C . Indium ($T_m=156.6^\circ\text{C}$) and azobenzene ($T_m=68.5^\circ\text{C}$) were used for temperature calibration. The degree of crystallinity was calculated from the ratio of the experimentally determined enthalpy of melting of a sample, ΔH_m , to that of 100% crystalline PEO^{27,28}.

Polarized optical microscopy

An Olympus model OM-2 optical microscope was used to obtain the polarized optical micrographs. The polymer samples were pressed between a coverslip and slide on a Mettler FP82 hot stage. The films were first melted at 85°C for 3 min to obtain a relaxed melt and to destroy all crystal nuclei²⁹, then cooled rapidly and crystallized isothermally at 61°C . It was necessary to press the PEO into very thin films ($\sim 15 \mu\text{m}$), since in thicker films the nucleation and growth rates are functions of film thickness²².

RESULTS AND DISCUSSION

Viscosity-average molecular weight

The thermal oxidation of PEO at 60°C causes a considerable change in its physical properties. Figure 1 shows the change in \bar{M}_v of PEO with oven ageing at 60°C in air. The molecular weight decreases slowly during the initial 23 days. This is followed by a severe drop in molecular weight during the auto-accelerating stage of the free-radical degradative process.

After 30 days of thermal oxidation, PEO is transformed from a free-flowing powder to a soft, waxy solid. The susceptibility of PEO to degradation at relatively low temperatures has been reported previously¹⁵. Poly(ethylene oxide) has a much lower resistance to thermal degradation than polyethylene³⁰ and this may be attributable to dipole–dipole interactions between neighbouring methylene and oxygen groups¹⁵. These lead to exceptionally high strains in the helical crystalline

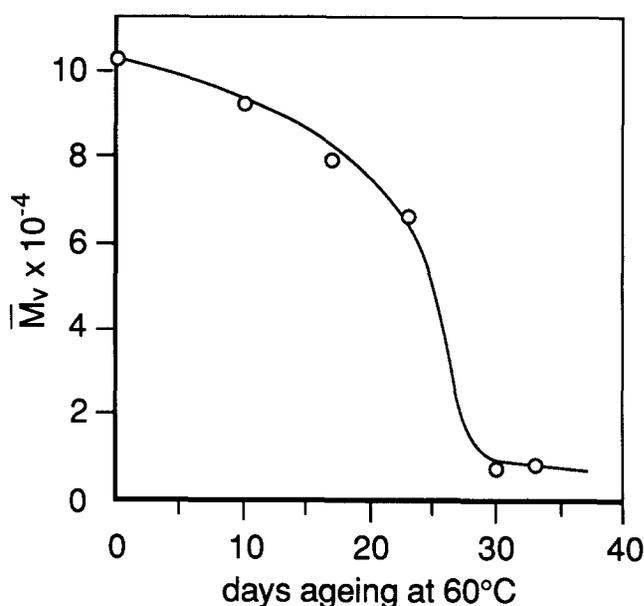


Figure 1 Viscosity-average molecular weight (\bar{M}_v) of PEO as a function of ageing time (days) at 60°C

Download English Version:

<https://daneshyari.com/en/article/5199093>

Download Persian Version:

<https://daneshyari.com/article/5199093>

[Daneshyari.com](https://daneshyari.com)