Introduction of unsaturated pendant groups to polyethylene by γ-ray irradiation under a 1,3-butadiene atmosphere

Abstract Ultra-high-molecular-weight polyethylene ($M_v: 5 \times 10^6$, 100-times elongated film) was irradiated with γ-rays under a 1,3-butadiene atmosphere at room temperature. Electron paramagnetic resonance (EPR) measurements indicated that the radicals formed on the polyethylene substrate during the irradiation were short-lived. EPR, Fourier transform IR spectroscopy, solid-state NMR, and differential scanning calorimetry of the as-irradiated materials indicated that butadiene molecules were covalently bound to the polyethylene chains as pendant groups bearing trans-vinylene and vinyl functions in a ratio of 3:1. Some crosslinks among the pendants, or between pendants and the main chains were produced. The number of unsaturated pendants introduced (including bridges) per carbon atom of the polyethylene main chain was dependent on the irradiation dose and the butadiene pressure, and was 0.096 butadiene units for 10 kGy irradiation under a 304 kPa butadiene atmosphere. The unsaturated pendants or bridges on the polyethylene chain thus introduced may be good targets to functionalize polyethylene by covalent modification.

Key words Polyethylene · Pendant group · γ-ray irradiation 1,3-Butadiene · Double bond

Introduction

High-energy atomic and molecular species are apt to undergo chemical reactions that involve the formation and breakage of covalent bonds in organic molecules [1]. Radicals on polyethylene molecules produced by high-energy ionizing radiation are likewise energetically excited and are prone to bring about chemical reactions. Irradiation of polyethylene with γ-rays or electron beams either in vacuo [2–4], under nitrogen [5, 6], or under acetylene [7–16] brings about crosslinking among main chains to improve its mechanical properties. In these studies, the authors’ interests were mainly focused on the changes in mechanical properties such as tensile strength, modulus, ductility, stress–strain relationship, creep behavior, etc., in relation to the degree of crosslinking and the extent of main chain scissions, and not on other chemical changes to the polymer molecules.

A carboxy function can be introduced into polyethylene by irradiation under supercritical CO₂ [17]. 1,3-Butadiene is another candidate expected to undergo chemical reactions with polyethylene upon γ-ray irradiation. γ-ray irradiation of polyethylene in the presence of butadiene and tetrafluoroethylene or chlorotrifluoroethylene [18, 19] resulted in extensive gelation due to crosslinking among polyethylene chains, and the chemical events during the irradiation have been discussed, but detailed descriptions on the chemical nature of the irradiated products have not been given.

During the studies to elucidate the effects of γ-ray irradiation on polyethylene, we noticed that the weight of polyethylene increased significantly if the γ-ray irradiation was carried out in a butadiene atmosphere.
without any halohydrocarbons. This suggested that the γ-ray irradiation facilitated covalent bond formation between butadiene molecules and polyethylene chains to produce pendant groups or bridges. This paper describes the physicochemical characterization of the pendants or bridges thus introduced into the polyethylene chains, and the effects of the γ-ray dose and the butadiene pressure on the degree of introduction of pendants and bridges. The chemical events leading to the covalent modification of polyethylene are to be discussed. This technique will open the way to modify polyethylene and other high polymers for the introduction of functional groups, because double bonds are good targets for a variety of chemical modifications.

Materials and methods

Chemicals

The sample was a linear ultra-high-molecular-weight polyethylene (Mw: 5 × 106, a product of HIMONT), from which ethanol-soluble substances had been extracted for 72 h with a Soxlet extractor. A solution containing 7.5 g polyethylene in 1.5 l decahydronaphthalene was prepared by heating the polymer at 408 K for 40 min, and was poured into a cooled aluminum tray to form a gel. The solvent was allowed to evaporate from the gel under ambient conditions. The dried gel film was maintained at 408 K for 15 min in an oven and elongated to 100-times its length. The stretcher with the sample after stretching was annealed for 10 min, and cooled slowly to room temperature. The thickness of the elongated gel film was 5–6 μm.

1,3-Butadiene, 1-octene, trans-4-octene, and bromine were reagent grade products and were used without purification.

Irradiation with γ-rays

The γ-ray source was 60Co at the Radiochemistry Research Institute, Shizuoka University, the dosage ratio being 30 Gy h⁻¹. A weighed sample of polyethylene film was placed in a Pyrex glass tube (length 120–150 mm, inside diameter 14.6 mm, wall thickness 1.2 mm) connected to a vacuum system equipped with a gas reservoir. The tube was evacuated to 0.13 Pa for 72 h to remove atmospheric oxygen dissolved in the polyethylene film, then a calculated amount of butadiene to give an indicated pressure was introduced to the glass tube at room temperature. The dose of γ-ray irradiation was less than 20 kGy. The irradiated glass tube was kept for 24 h before opening to extinguish radicals (postirradiation annealing in butadiene). The polyethylene sample thus processed is termed BDPE. The control sample subjected to γ-ray irradiation in vacuo after postirradiation annealing in vacuo is termed γ(vac)PE.

In some experiments, the polyethylene sample was sealed in a quartz tube (outer diameter 6 mm) under a 304 kPa butadiene atmosphere and exposed to UV radiation of intensity 1.1 × 10¹⁸ quanta s⁻¹.

Number of pendant groups introduced

The irradiated sample was weighed, placed in a glass tube, and the tube was evacuated at 0.13 Pa at room temperature to remove adsorbed materials and weighed. It took about 48 h of evacuation until a constant weight was attained. Weighing as well as other physicochemical examinations were performed on the sample evacuated for 48 h. As shown later, the weight gain caused by γ-ray irradiation was due to covalent binding of pendants (including bridges) to the polymer. The total number of pendants and bridges introduced per carbon atom into the polyethylene main chain was calculated from the weight gain, assuming that each pendant group was formed by the addition of a C2H4 unit, but the possibility remains that some pendant groups received additional C2H6 units and formed larger pendants of (C2H4)n (n ≥ 2) composition.

Gas analyses

After γ-ray irradiation the gas sample contained in the sealed glass tube was analyzed for H2 with a Shimadzu GC-4B gas chromatograph with molecular sieves 5A as column fillings. Chromatography was conducted at 313 K, and the carrier gas was argon.

Electron paramagnetic resonance (EPR)

After γ-ray irradiation the tubes containing the polyethylene samples were immediately (within 2 min) placed in a Dewar vessel filled with liquid N2, and kept at 77 K until the EPR measurements were made. X-band EPR spectra were recorded on a Bruker EPS 820E at room temperature, or on a Bruker EPS 400E spectrometer equipped with an Oxford Instruments continuous flow cryostat at 4 K.

Fourier transform IR (FTIR) spectra

FTIR spectra from 4000 to 400 cm⁻¹ were recorded using a Perkin-Elmer Spectrum 1000 infrared spectrometer, after 16 or 32 scans at a resolution of 4 cm⁻¹. Films were measured by direct transmission. 1-Octene and trans-4-octene were measured as CCl4 solutions.

Solid-state NMR

Solid-state 13C NMR measurements were made with a JEOL 270 instrument, in CP-MAS (cross-polarization, magic-angle spinning) mode and PST-MAS (pulse saturation, magic-angle spinning) mode. The sample was packed into a zirconia rotor with a small amount of powdered NaCl and spun at the magic angle at 5600 rpm. The one-pulse experiments consisted of a single 90° radio-frequency pulse (duration 4.0 μs) and a recycle time of 12 s with high-power proton decoupling during the data acquisition. The spectrum was recorded after 2000 scans. The observed attenuation was 105 with 2048 sampling points and resonance frequency of 67.8 MHz. The chemical shift (δ) relative to tetramethylsilane was calculated, using hexamethylbenzene (δ = 17.3 ppm) as an external standard.

Gel content and melting point of the polyethylene samples

The polyethylene sample was heated at 413 K in decahydronaphthalene until no morphological change was observed. The weight of the residue remaining undissolved relative to the original weight was assumed to be the gel content of the polyethylene. This reflects the degree of crosslinking introduced into the polyethylene.

The melting point was measured with a Perkin-Elmer DSC 7 differential scanning calorimeter. A 2-mg sample of polyethylene was heated at a rate of 10 K min⁻¹, and the apparent melting point was defined as the peak temperature at which a sharp endothermic change was observed.