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ORIGINAL CONTRIBUTION

S. Nakada
C. Sawatari
W. Tomoda
T. Yagi

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

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S. Nakada · C. Sawatari (✉) · T. Yagi
Division of Polymer Science
Graduate School of Education
Shizuoka University
Shizuoka 422-8529, Japan

W. Tomoda
Center for Joint Research
Shizuoka University, Shin-Miyakoda
Hamamatsu 431-2103, Japan

Abstract Ultra-high-molecular-weight polyethylene ($\bar{M}_v$: 5×10^6, 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 CO_2 [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 ($\bar{M}_v$: 5×10^6, 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 ^{60}Co 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 tube was sealed, left to stand for 6 days, and exposed to the γ-ray source at room temperature. The dose of γ-ray irradiation was less than 20 kGy. The irradiated glass tube was left to stand for 24 h before opening to extinguish radicals (postirradiation annealing in butadiene). The polyethylene sample thus processed is termed γ(BD)PE. 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 1.1×10^{18} 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 C_4H_6 unit, but the possibility remains that some pendant groups received additional C_4H_6 units and formed larger pendants of $(C_4H_6)_n$ ($n \geq 2$) composition.

Gas analyses

After γ-ray irradiation the gas sample contained in the sealed glass tube was analyzed for H_2 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 N_2, 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 CCl_4 solutions.

Solid-state NMR

Solid-state ^{13}C 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.

Quantitation of double bonds by the Br_2-absorption test

The number of double bonds was quantitated by measuring the weight increase of the polyethylene sample after exposure to Br_2 vapor. Weighed amounts of γ(BD)PE films prepared under various butadiene pressures, as well as γ(vac)PE and unirradiated films, were placed in a vial and exposed to Br_2 vapor under reduced pressure at room temperature. After 40 min Br_2 was removed and the adsorbed Br_2 in the samples was evaporated off by evacuation for 1 week at room temperature, and the samples were weighed. The complete disappearance of the double bonds was checked by FTIR spectroscopy. Evacuation and weighing was repeated until a constant weight was attained (usually it took 2–3 weeks). From the weight gained by bromination of the polyethylene sample, the number of Br_2 molecules added, i.e., the number of double bonds introduced, was estimated. As the duration of exposure of the polyethylene sample to Br_2 vapor was only 40 min in contrast to several hours employed in the classical Br_2-absorption method [20], the weight increase due to slow substitution of hydrogen by bromine was neglected.

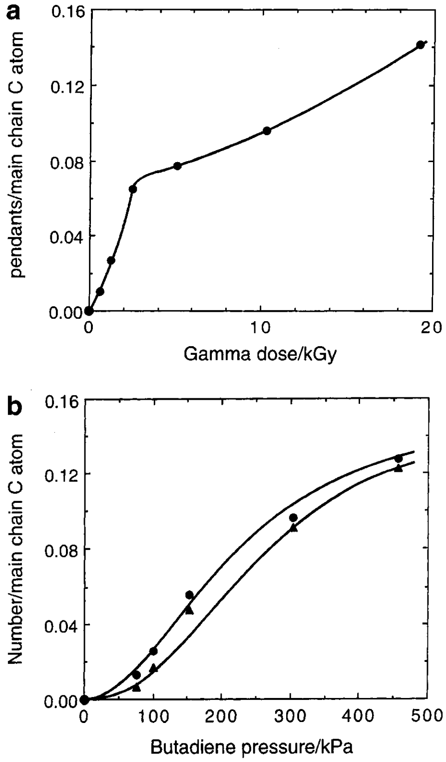

Fig. 1a, b The number of pendant or bridge groups introduced in relation to the γ-ray dose and butadiene pressure. **a** The γ-ray dose was changed with the butadiene pressure fixed at 304 kPa. As the vapor pressure of butadiene is 275 kPa at 298 K, the excess gas must have been liquified but not visually recognized. **b** The butadiene pressure was changed with the γ-ray dose fixed at 10 kGy. Number of pendant groups (●) and number of double bond (▲) per carbon atom of the polyethylene main chain

Results

Number of pendant groups introduced

γ-ray irradiation of the polyethylene film with a 10 kGy dose resulted in a weight gain of 37.2% of its original weight under a 304 kPa butadiene atmosphere. This corresponds to the introduction of 0.096 pendant groups per carbon atom of the polyethylene main chain, if the pendant groups are produced by the addition of single butadiene (C_4H_6) units to the polyethylene main chain. It should be kept in mind, however, that gravimetry could not distinguish between the addition of C_4H_6 units to the main chain and preformed pendant groups to produce larger pendant groups of $(C_4H_6)_n$ ($n \geq 2$) composition, nor could it detect the formation of crosslinks among pendants and main chains to produce bridges. The number of pendants, or more accurately, the number of butadiene units bound, per carbon atom in the main chain was dependent on the γ-ray dose (Fig. 1a) and the butadiene pressure (Fig. 1b; the plots with triangles illustrate the number of double bonds introduced as described later). Neither pendant groups nor double bonds were introduced when polyethylene was irradiated with γ-rays in vacuo (zero butadiene pressure). Washing of the irradiated sample with acetone did not result in weight loss.

Similar unsaturated pendants or bridges were introduced to polyethylene by UV irradiation. The number of butadiene units bound was 0.0016 per main chain carbon atom when irradiated for a week with a dosage of 1.1×10^{18} quanta s^{-1} under a 304 kPa butadiene atmosphere.

Gas analyses

The amount of H_2 produced from polyethylene during the 10 kGy γ-ray irradiation was between 1.1 and 1.8 nmol (1.6 nmol on average) per milligram of polyethylene either under the atmosphere of butadiene or in vacuo. In other words, 1.6 mol H_2 was produced from 7×10^4 mol CH_2 in polyethylene on average. Since an average chain of ultra-high-molecular-weight polyethylene contains 3.6×10^5 CH_2 units, eight molecules of H_2 must have been produced from every chain of the polyethylene sample.

EPR measurements

Immediately after γ-ray irradiation the polyethylene sample (5.1 mg of undrawn gel film) under a 1,3-butadiene atmosphere or in vacuo was EPR-silent when measured at room temperature; however, a very weak signal centered at $g = 2.003$ was detected at 4 K. The signal shape was not well defined after a single scan, but could be distinguished from the noise after four scans. As the detection limit of spins is about 10^{10}, the residual spins at the end of the γ-ray irradiation may be between 10^{10} and 10^{12}. This weak signal was hardly distinguishable from the noise after allowing the sample to stand for 120 min at room temperature.

FTIR spectra

The spectra of the polyethylene film before irradiation and the γ(vac)PE films were nearly identical (only the latter is shown in Fig. 2). The spectrum of the γ(BD)PE film (top in Fig. 2) had new bands at 1640 (w), 994 (w), 966 (s), and 911 cm^{-1} (m), which were different from those of butadiene at 1592 (w), 1010 (m), and 904 cm^{-1} (s). The spectrum did not change after repeated washings of the γ(BD)PE film in kerocene, tetrahydrofuran, or toluene.

Regardless of the extent of weight gain caused by γ-ray irradiation under different butadiene pressures, the new bands were always similar in shape to those of combined bands due to *trans*-vinylene (966 cm^{-1}) and vinyl functions (1640, 994, and 911 cm^{-1}) [21] in a ratio of 3:1. A band expected for the terminal methyl function (1379 cm^{-1}) [21] could not be detected.

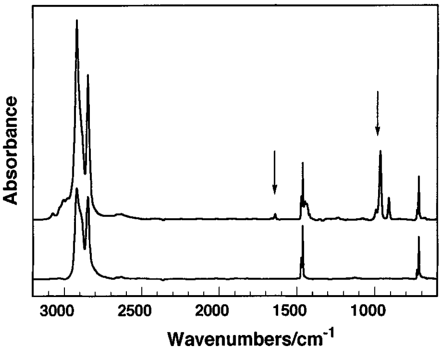

Fig. 2 Fourier transform (FT) IR spectra of a γ-ray irradiated polyethylene film (10 kGy dose) in vacuo (*bottom*), and under a 304 kPa butadiene atmosphere (*top*). *Arrows* point to the bands (1640, 994, 966, and 911 cm^{-1}) found only in the polyethylene subject to γ-ray irradiation in butadiene

Both surfaces of the γ(BD)PE film (irradiated with a 5 kGy dose) were peeled off to a thickness of 1 μm, and the FTIR spectrum of the thin film was compared with that before thinning. The bands attributed to the double bonds (966 and 911 cm^{-1}) relative to that attributed to CH_2 (720 cm^{-1}) did not change on thinning the film.

On prolonged exposure of the γ(BD)PE film to air at room temperature, the bands ascribable to double bonds were superseded by bands ascribable to keto (C=O stretching vibration at 1715 cm^{-1}) and hydroxy functions (O-H stretching vibration at 3410 cm^{-1} and C-O stretching vibration at 1060 cm^{-1}).

^{13}C NMR

Solid-state ^{13}C NMR spectra of γ(BD)PE and γ(vac)PE are shown in Fig. 3. In CP-MAS mode (Fig. 3A), in which the ^{13}C nuclei in rigid segments are mainly observed, the spectrum of γ(BD)PE had a small signal from the *trans*-vinylene carbon atom at 130.4 ppm in addition to a signal at 32.6 ppm from a secondary carbon atom in the main chain with a small side signal at 110.6 ppm (only this signal moved upon changing the spinning speed of the rotor). In PST-MAS mode (Fig. 3B), in which the ^{13}C nuclei in flexible segments are focused, the spectrum of γ(BD)PE had a signal from the *trans*-vinylene carbon at 130.3 ppm, a pair of

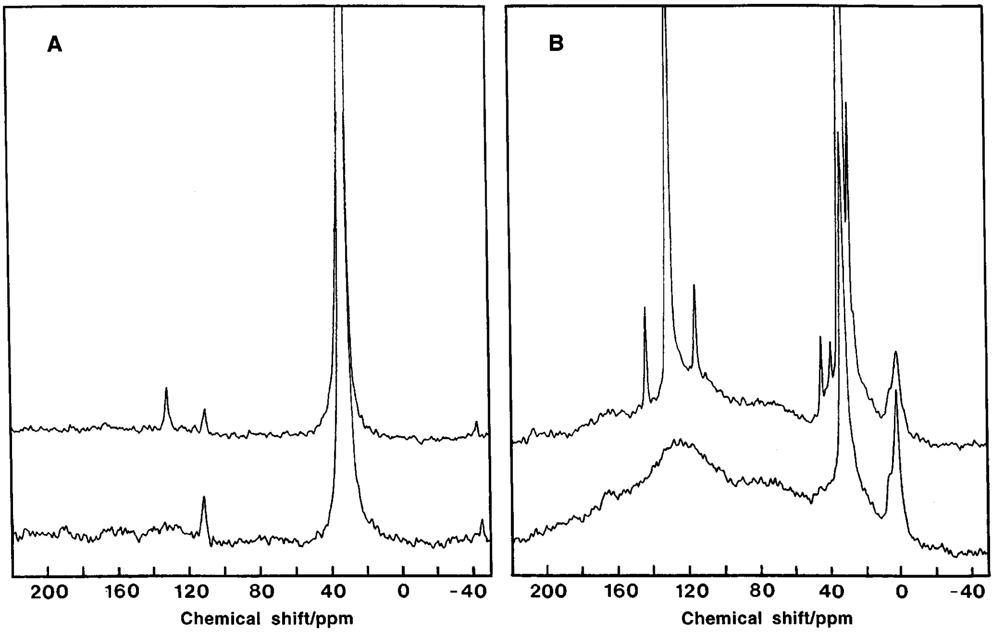

Fig. 3 Solid-state ^{13}C NMR spectra of a polyethylene drawn film in **A** CP-MAS mode and **B** PST-MAS mode subject to γ-ray irradiation (10 kGy-dose) in vacuo (*bottom*), and under a 304 kPa butadiene atmosphere (*top*). The spectra of the polyethylene before irradiation were identical with those of the γ-ray irradiated sample in vacuo, and not shown. The signal at about 1 ppm and a broad signal around 124 ppm in **B** are background signals and should be disregarded

114.9 and 142.8 ppm signals from terminal and penultimate carbons of the vinyl function ($CH_2{=}CH$-), a signal at 44.0 ppm from the tertiary carbon atom at the branch point, a signal at 38.8 ppm from the methylene carbon α to the branch point, and a signal at 28.0 ppm from the methylene carbon β to the branch point, in addition to a signal at 33.1 ppm from the secondary carbon atom in the main chain. A signal from the terminal methyl function (about 18 ppm) could not be observed, in agreement with the absence of a methyl band in the FTIR spectrum. ^{13}C NMR spectra of γ(vac)PE did not have any signals other than that of the main chain carbon atom either in CP-MAS or PST-MAS mode.

Gel content and melting point

The unirradiated polyethylene sample, as well as that subject to γ-ray irradiation (10 kGy dose) in vacuo, readily dissolved in decahydronaphthalene at 413 K, and hence the gel content was 0%. The gel content of the γ-ray irradiated drawn polyethylene film (10 kGy dose) under a 304 kPa butadiene atmosphere was 26.5%. The sample irradiated with a 5 kGy dose under a 304 kPa butadiene atmosphere resisted dissolution in hot decahydronaphthalene for more than 48 h, but finally decomposed to small granules that were difficult to weigh. Some crosslinking must have occurred, but full networks did not seem to be formed in this sample.

All thermograms displayed two apparent melting endotherms: an initial melting of crystals was observed at about 424 K, then the thermograms returned to the baseline. The final melting point of the 100-times drawn polyethylene film was about 430 K before γ-ray irradiation. The final melting point was 427 K after γ-ray irradiation with a 5 kGy dose either in vacuo or under a 304 kPa butadiene atmosphere. The heat of fusion estimated from the final peak decreased for γ(BD)PE, but not for γ(vac)PE.

Quantitation of double bonds by the Br_2-absorption test

Figure 4 illustrates that all the IR bands attributed to the double bonds (1640, 994, 966, and 911 cm^{-1}) in γ(BD)PE were substituted by new, small bands at 1232, 1142, and 552 cm^{-1}. The 552 cm^{-1} band was assigned to C-Br stretching, and the 1232 cm^{-1} band to the wagging vibration of CH_2 in $-CH_2Br$. The number of double bonds estimated from the weight gain from the Br_2-absorption test is plotted in Fig. 1b (triangles). The unirradiated polyethylene, as well as γ(vac)PE, gained no weight according to the Br_2-absorption test, in agreement with the absence of FTIR bands ascribable to the double bonds.

Correlation between the FTIR spectrum and the number of double bonds

The number of double bonds introduced into polyethylene estimated from the Br_2-absorption test was correlated to the intensities of the FTIR bands attributable to double bonds (966 cm^{-1} band of *trans*-vinylene and 911 cm^{-1} band of vinyl) relative to the one attributable to the rocking vibration of CH_2 (720 cm^{-1} band), and is illustrated in Fig. 5, where the (RA) relative absorbance is defined by Eq. (1):

$$\mathrm{RA} = (A_{966} + f A_{911})/A_{720} \ , \tag{1}$$

where f is the ratio of molar absorption coefficients (ε), (ε_{966} of *trans*-vinylene)/(ε_{911} of vinyl), and was estimated to be 0.8 from measurements of model compounds of low molecular weight (*trans*-4-octene and 1-octene). This

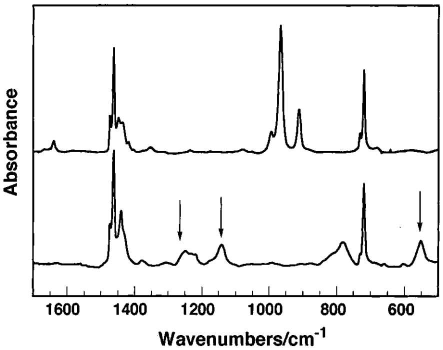

Fig. 4 Change in the FTIR spectrum of polyethylene annealed in butadiene after irradiation upon treatment with Br_2. Before (*top*) and after (*bottom*) Br_2 treatment. *Arrows* point to the bands (1232, 1142, and 552 cm^{-1}) formed by Br_2 treatment

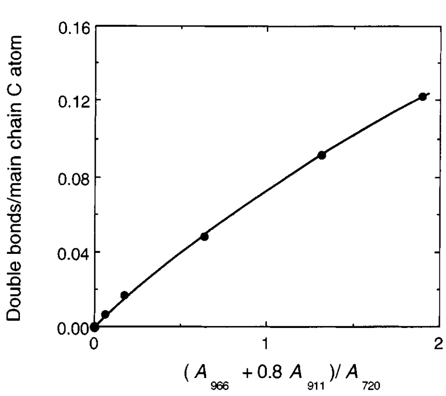

Fig. 5 Correlation between the FTIR spectra and the number of double bonds introduced per carbon atom into the polyethylene main chain. The *data points* were obtained experimentally, and the *curve* was drawn according to Eq. (3)

value was slightly larger than that (0.7) reported before [20].

Plots of the number of double bonds (Δ) introduced per carbon atom of the polyethylene chain against the RA align on a hyperbola that is expressed by Eqs. (2) or (3).

$$\mathrm{RA} = 11.7\Delta/(1 - 2.0\Delta) \qquad (2)$$

$$\Delta = \mathrm{RA}/(11.7 + 2.0\mathrm{RA}) \qquad (3)$$

This reflects the fact that each pendant or bridge group interrupts the CH_2 chain which gives a band at 720 cm^{-1}, and introduces a double bond which gives a band at 966 or 911 cm^{-1}. Equation (3) enables us to estimate the number of double bonds introduced into the polyethylene samples by mere FTIR spectroscopy without the tedious time-consuming gravimetry of the Br_2-absorption test.

Discussion

γ-ray irradiation of polyethylene under a 1,3-butadiene atmosphere introduced covalently bound pendants or bridges into the polyethylene chains as evidenced by the weight gain. At the same time new functional groups detectable by FTIR spectroscopy were introduced. The new FTIR bands that were not removed by repeated washings in kerocene, tetrahydrofuran, or toluene were assigned as combined bands of *trans*-vinylene and terminal vinyl functions in a ratio of 3:1. The pendant groups having *trans*-vinylene and vinyl functions must have been produced by the 1,4- and 1,2-addition of 1,3-butadiene, respectively. The preference of 1,4-addition over 1,2-addition is commonly observed in low-molecular-weight chemistry of butadiene [22]. Since no double bonds were detected in the FTIR spectrum of polyethylene irradiated with a 10 kGy dose of γ-rays in vacuo, the number of double bonds introduced into the polyethylene main chain must be below the detection level of FTIR spectroscopy. Assuming that the liberation of H_2 from polyethylene (1.6 nmol/mg) during γ-ray irradiation had been caused by the production of double bonds due to hydrogen extraction from adjacent methylenes, one double bond must have been introduced into every 4.5×10^4 CH_2 units of the main chain. The amount of H_2 liberation is comparable to that (2.9 nmol/mg) reported for polyethylene powder irradiated with a 10 kGy dose of γ-rays in vacuo [2], and the estimated number of double bonds produced in vacuo is comparable to the estimate (one in every 2.2×10^4 CH_2 units for a 10 kGy dose) reported for polyethylene powder irradiated with γ-rays in vacuo [2].

As is generally accepted, γ-ray irradiation of polyethylene produces $>CH\cdot$ radicals by extraction of a hydrogen atom from CH_2 [2, 10, 13, 23]; these radicals attack surrounding butadiene molecules to produce pendant groups. The EPR measurements indicated that the sample immediately after γ-ray irradiation had short-lived residual spins around $10^{11}/5$ mg. This corresponds to a $>CH\cdot$ radical in every 2×10^9 CH_2 units in polyethylene. Covalent bond formation to produce pendant groups must therefore, have occurred during γ-ray irradiation, the extent of which depends on the number of butadiene molecules surrounding the radicals. Since the total number of radicals transiently formed on the polyethylene substrate is proportional to the γ-ray dose, and γ-ray irradiation was conducted with a large excess of butadiene, the number of pendant groups introduced is expected to be proportional to the γ-ray dose. The biphasic reaction shown in Fig. 1a suggests, however, that the rate of pendant addition in the later phase of the irradiation is not limited by the rate of radical formation, but is limited by the diffusion of butadiene into the solid phase across the polymer surface. At the beginning of the γ-ray irradiation, every $>CH\cdot$ radical is able to find butadiene molecules during its short life, but only a small fraction of radicals will find butadiene molecules in the later phase of irradiation. This could mean that the diffusion rate from the gas phase slowed down, probably because of the formation of crosslinking networks, in the later phase of irradiation. As the double bonds were introduced evenly on surfaces and the inner body of the polyethylene film for a 5 kGy dose, 6 days incubation of the film in butadiene before irradiation seemed to be sufficient for homogeneous diffusion of the gas into the film. The effect of butadiene pressure on pendant addition (Fig. 1b) also suggests the importance of butadiene diffusion into the polyethylene substrate.

The formation of a gel by γ-ray irradiation in butadiene suggests that some bridges were produced between two pendant groups of different chains, or between a main chain and a pendant of another chain, but not between two polyethylene chains, since no gel was produced by γ-ray irradiation in vacuo for a 10 kGy γ-ray dose. Insertion of a butadiene molecule whose C1–C4 distance is 0.39 nm between a radical pair produced by γ-ray irradiation [23] must have facilitated bridging between two chains separated by 0.45–0.49 nm even in crystalline polyethylene [24]. Differential scanning calorimetry (DSC) results attributed to the partial melting and reorganization processes appeared in all samples, with the largest peak area being for γ(vac)PE and the smallest peak area being for γ(BD)PE. This might mean that the reorganization of crystals during DSC measurement was prevented by crosslinking points in γ-ray irradiated polyethylene under a butadiene atmosphere.

^{13}C NMR spectra gave information about the conformation of double bonds introduced into polyethylene: signals of olefinic carbons were hardly detectable except that of *trans*-vinylene at 130.4 ppm in CP-MAS mode which spotlights the ^{13}C nuclei in rigid segments, whereas they were clearly detected in PST-MAS mode which spotlights the ^{13}C nuclei in flexible segments. This indicates that the double bonds introduced by γ-ray irradiation of polyethylene under a butadiene atmosphere were mostly in flexible pendant or bridge groups, and little (if any) were present in polyethylene main chains. Detection of signals at 44.0 ppm (tertiary carbon at the branch point), 38.8 ppm (methylene carbon α to the branch point), and 28.0 ppm (methylene carbon β to the branch point) only in PST-MAS mode suggests that the pendant or bridge groups introduced are mainly in a noncrystalline region of the polymer. Since the crystallinity of 100-times drawn polyethylene is more than 90%, and is not affected by high-energy irradiation of up to 2 MGy [5], it seems difficult to assume that pendant groups were introduced only into a noncrystalline region of the polymer. Instead, polyethylene radicals produced in a crystalline region migrated to the lamella fold surface [14] and accepted butadiene molecules to produce pendants in a noncrystalline region. Another possibility for the 100-times drawn film that might have fewer lamella fold surfaces due to full extension of polymer chains is that local conformational deformation of the crystalline region of the main chain caused by high-energy γ-ray irradiation triggered the introduction of pendant groups. The decrease of the apparent melting temperature by 3 K (from 430 to 427 K) may indicate local conformational deformation by γ-ray irradiation.

The number of double bonds relative to that of the pendant groups introduced into the polyethylene sample was nearly unity when γ-ray irradiation was carried out under higher butadiene pressures, but was less than unity when the sample was irradiated with γ-rays under rather low butadiene pressures. Neither pendant groups nor double bonds were introduced if polyethylene was irradiated in vacuo with a 10 kGy dose of γ-rays. These lines of evidence clearly indicate that γ-ray irradiation of polyethylene under higher butadiene pressures introduces covalently bound unsaturated C_4 pendant groups bearing *trans*-vinylene and terminal vinyl functions, some of which might have bound to another main chain to produce bridges of *trans*-vinylene ($-CH_2-CH{=}CH-CH_2-$) type. The addition of butadiene to the preformed pendant groups to produce larger pendant groups ($CH_3-CH{=}CH-CH_2-CH_2-CH{=}CH-CH_2-$, and branched and bridged forms thereof, etc.) might have occurred, but these were not distinguished from the simple pendant by gravimetry. The absence of terminal methyl groups in the γ-ray irradiated samples under a butadiene atmosphere as suggested by FTIR and ^{13}C NMR spectroscopies might mean that most of the pendants are involved in crosslinking.

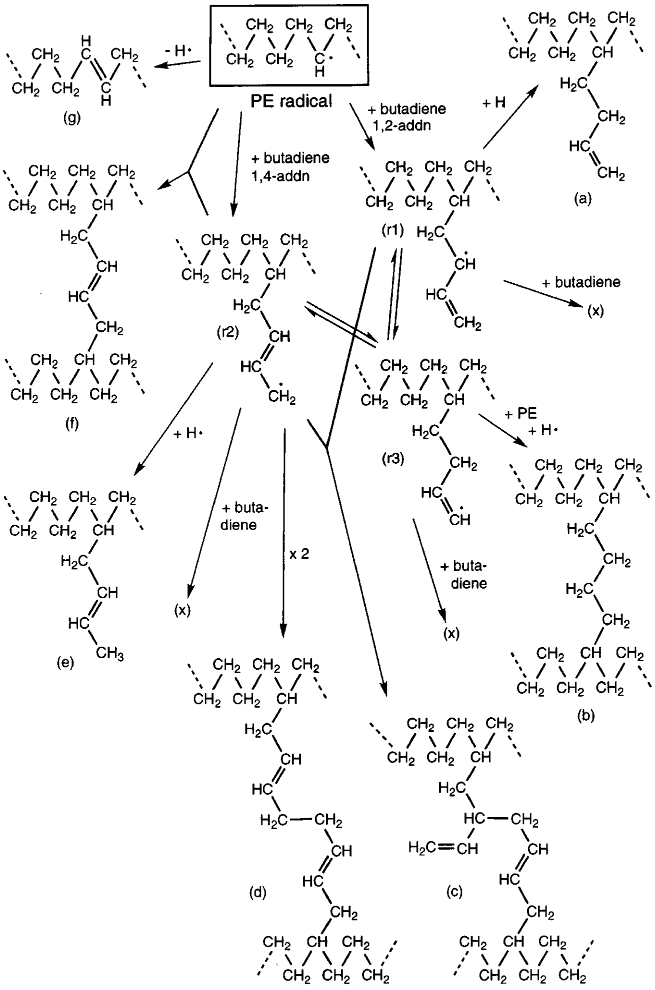

Fig. 6 Proposed chemical pathways resulting in the formation of pendant and bridge groups in polyethylene chains during γ-ray irradiation under an atmosphere of 1,3-butadiene. See text for details

The mechanism of introducing unsaturated pendant and bridge groups into polyethylene by γ-ray irradiation under a butadiene atmosphere is outlined in Fig. 6. The primary event is hydrogen extraction from the polyethylene chain to form a radical (PE radical) that adds a butadiene molecule either in 1,2-addition or 1,4-addition mode to produce radical intermediates (r1 and r2, in equilibrium with r3), but the route to produce a double bond in the main chain (g) is negligible (1 per 4.5×10^4 CH_2 units). Radicals (r1, r2, and r3) may have a variety of chemical routes including addition of more butadiene molecules in chain-reaction mode to produce pendants and bridges bearing two or more butadiene units (x), but formation of a single pendant bearing a terminal methyl group (e) might not be predominant. Introduction of unsaturated pendant groups by UV irradiation of polyethylene under a butadiene atmosphere may proceed by a similar mechanism, since the photon energy of a UV ray shorter than 260 nm (greater than 460 kJ mol^{-1}) is larger than the C-H bond energy of 413 kJ mol^{-1} [25].

Double bonds in pendant or bridge groups of high polymers are good targets for a number of chemical transformations to introduce functional groups into the polymer [26, 27]. γ-ray irradiation of polyethylene under a butadiene atmosphere that introduces unsaturated pendant or bridge groups efficiently at rather low irradiation doses (less than 10 kGy) may provide a new technique to introduce functional groups into polyethylene.

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