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ORIGINAL CONTRIBUTION

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Hyperbranched modification of unsaturated side chains of polyethylene introduced by γ-ray irradiation under a 1,3-butadiene atmosphere

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Abstract Amino and other functional groups were introduced to a polyethylene substrate starting from the unsaturated pendant and bridge groups (collectively called side chains) of polyethylene, which had been prepared by γ-ray irradiation under an atmosphere of 1,3-butadiene of the polyethylene substrate (the drawn film of ultra-high-molecular-weight polyethylene, $\overline{M}$v: 5×10^6). 2-Aminoethylamino groups were introduced to the side chains through treatment either with bromine or with peracetic acid vapor followed by immersion in ethylenediamine. Introduction of amino groups were confirmed by Fourier transform IR spectrometry, ninhydrin test, and acid–base titration. Starting from 2-aminoethylaminated polyethylene, modification cycles to grow a dendrimer on the film were applied; these consisted of 2-methoxycarbonylethylation and 2-aminoethylamidation. This technique resulted in hyperbranched modification of the polymer. The product is a kind of dendrimer grown on the surface of polyethylene film with amplified amino ends and has anion-exchange capacity and absorbs acid dye. Its application in practical uses is discussed.

Key words Polyethylene · γ-ray irradiation · 1,3-Butadiene · Dendrimer · Hyperbranched modification

Introduction

Amino or carboxy functions on side chains of high-molecular-weight polymer materials are good targets for covalent modification of polymer materials to add various kinds of molecules, such as enzymes, antibodies, nucleotides, sugars, antibiotics, etc., without making detrimental effects on the polymer properties attributed to the chemical nature of the main chain [1]. It is difficult, however, to covalently introduce the amino or carboxy functions to polyethylene (PE) by conventional organic reactions. In our previous work, unsaturated pendant or bridge groups (collectively called side chains) were successfully introduced to PE by γ-ray irradiation of PE under an atmosphere of 1,3-butadiene [2]. This work reports that the double bonds introduced to the PE substrate were converted to amino functions and that the technique to grow a dendrimer [3] applied to the amino functions resulted in hyperbranched modification of the polymer with amplified amino ends. The amplified amino groups may be used directly or converted to carboxy functions for further chemical modifications.

The dendrimer was a star-burst polymer originally synthesized by Tomalia et al. [3]. It consisted of a core of ethylenediamine or ammonia, from which amino-bearing branches are covalently and repetitively added to produce a highly branched starburst polymer. Dendrimers are characterized by their spherical symmetry and high density of terminal functionality [3, 4, 5, 6], to which functions such as photosensitivity, pH sensitivity, adsorptivity of gaseous organic matter, etc., could be added [7–9]. Several attempts have been made to prepare a multilayer film of dendritic molecules [10] or to graft a dendritic layer or layers adsorbed on gold [7, 11, 12], and the successful introduction of hyperbranched carboxy functions to PE powder was reported [13]. In this

communication, we present a new technique to combine dendrimer chemistry with the γ-irradiation technique of PE. This technique has the potential to prepare versatile polymer materials with high surface density of functionality by covalent modification.

Materials and methods

Chemicals

A gel film of ultra-high-molecular-weight PE ($\overline{M}$v: 5×10^6, a product of Himont) was drawn to 100 times its length to prepare films of 5-μm thickness [2]. Methyl acrylate, acetic anhydride, and aqueous 30% H_2O_2 solution were reagent grade products and were used without purification. Poly(ethylene glycol) acrylate with an ethylene glycol moiety of molecular weight 375 was a product of Aldrich. Ethylenediamine was distilled before use. Diacid alizarine light blue 4GL [disodium 1-amino-3-(4-acetamidophenylamino)anthraquinone-2,5(or 2,8)-disulfonate] was a product of Mitsubishi Chemical Industries.

γ-ray irradiation

The detailed procedure for the γ-ray irradiation under butadiene is given in Ref. [2], but the outline is repeated. The γ source was ^{60}Co and the dose ratio was 30 Gyh^{-1}. A weighed sample (around 3 mg) of PE film was placed in a Pyrex glass tube connected to a vacuum system equipped with a gas reservoir. The tube was evacuated to 0.13 Pa for 72 h, then a calculated amount of butadiene to give an indicated pressure (152, 304, or 456 kPa) was introduced into the glass tube. The tube was sealed, left to stand for 6 days, and exposed to the γ-ray source at room temperature. The γ-ray dose was about 5 or 10 kGy. After postirradiation annealing for 24 h at room temperature, the tube was evacuated for 48 h to remove adsorbed butadiene and weighed. The number of side chains covalently bound per PE main-chain carbon atom was calculated from the weight gain, assuming that each side chain was formed by the addition of a C_4H_6 unit, but a larger side chain containing several C_4H_6 units could not be distinguished from several side chains of a single C_4H_6 unit [2].

Plasma etching of the film

The surface of the film was etched with a Yanaco Mini Asher radio frequency plasma reactor, operated at 50 mA at 270 Pa. The duration of the etching was 10 or 20 min and the temperature during the etching was lower than 328 K.

Instrumental analyses

Fourier transform (FT) IR spectra from 4000 to 400 cm^{-1} were recorded using a Perkin-Elmer Spectrum 1000 IR spectrometer, after 16 or 32 scans at a resolution of 4 cm^{-1}, as in Ref. [2]. Microscopic FTIR attenuated total reflection (ATR) spectra were recorded using a Perkin-Elmer FTIR 2000 IR spectrometer, after 16 scans at a resolution of 4 cm^{-1}. A germanium crystal was used as an ATR attachment, the incident angle being 45°.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Shimadzu ESCA K1 spectrometer. The X-ray source was Mg Kα, the acceleration voltage was 10 kV, and the emission current was 20 mA. The peak areas for C_{1s} (scan from 294 to 280 eV centered at 286 eV), N_{1s} (scan from 410 to 392 eV centered at 401 eV), and O_{1s} (scan from 542 to 526 eV centered at 533 eV) corrected for linear backgrounds were compared using a correction factor which depend on the sensitivity for each element. A wide-range scan from 800 to 0 eV was done to detect other elements. Angular XPS spectra at a takeoff angle of $\sin^{-1}0.4$ (23.6°) and 90° were recorded on the same spectrometer with the sample film mounted on an attached stage.

Scanning electron microscopy (SEM) micrographs were recorded using a JEOL JSM-6300 machine, with an acceleration voltage of 3.0 kV. The surface of the PE sample was coated with carbon by vacuum evaporation 15 times (auto coat mode) using a San-Yu Electronic SC-701C quick carbon coater. The thickness of the carbon coating was about 15 nm. The working distance was 8.0 mm throughout. The magnification was 5000.

Chemical analyses

Double bonds were quantitated by the Br_2-absorption method [14] as modified in our work [2]. The ion-exchange capacity (the H^+ equivalence of the conjugate base form of the polymer) was estimated by acid–base titration. Two flasks each containing 5 ml 0.025 M HCl were prepared. The weighed film sample was immersed in one of the solutions for 24 h and then taken out. Two solutions were titrated with 0.025 M NaOH, the pH being monitored with a glass-electrode pH meter. From the difference in volumes of NaOH required to neutralize the solutions, the H^+-exchange capacity was calculated.

The staining test of the sample was carried out as follows: an aqueous 40 mgl^{-1} (0.07 mmol l^{-1}) solution of diacid alizarine light blue 4GL was prepared, in which the sample film was immersed to observe the color change of the film surface and the solution.

Chemical modifications

Epoxidation

To a stoppered bottle containing acetic anhydride (5 ml) and concentrated H_2SO_4 (1 ml), aqueous 30% H_2O_2 solution (1 ml) was added gently not to decompose H_2O_2 and a little vial containing γ-ray irradiated PE film (5 kGy, 304 kPa butadiene) was placed in the bottle. Under these conditions the bottle was filled with peracetic acid vapor, to which the PE substrate in the vial was exposed.

Amination of epoxide function

A PE film bearing epoxide functions was immersed in ethylenediamine for 24 h at 313 K, washed with deionized water and ethanol several times, and dried under reduced pressure.

Hyperbranched modification of PE film

A technique to grow dendrimers [3] was applied to the PE film bearing amino functions. The film was immersed in 30% methyl acrylate solution in methanol for 24 h at 313 K to add two 2-methoxycarbonylethyl groups to each amino end of the PE side chains, then the methoxy groups of the product were replaced by 2-aminoethylamido groups by immersing the product in ethylenediamine for 48 h at 313 K. The change was traced by the weight increase, by the increase in the acid-titratable amino groups, by FTIR spectroscopy, etc.

Results

Efficiency of amino group introduction to γ-ray irradiated PE

The γ-ray irradiation conditions to give higher incorporation of functional groups to the polymer was sought,

at first. PE samples irradiated with different doses of γ-rays under different butadiene pressures were exposed to Br_2 vapor for 40 min under reduced pressure to add bromine atoms to the double bonds on the side chains followed by thorough evacuation to remove adsorbed Br_2 [2]. Figure 1 shows that the IR bands ascribable to the double bonds (top: 1640, 994, 966, and 911 cm^{-1}) introduced to the PE were superseded completely by IR bands attributed to the bromoalkyl side chains (middle: 1232, 1142, and 552 cm^{-1}). The brominated samples were weighed and immersed in ethylenediamine for 24 h at 313 K, washed with deionized water and ethanol, and dried in vacuo. This procedure brought about substitution of bromine atoms on PE by 2-aminoethylamino (AEA) functions as shown in reaction (1), where the HBr produced was trapped by the excess amine.

$$\mathrm{Br-PE + H_2NCH_2CH_2NH_2} \rightarrow \mathrm{H_2NCH_2CH_2NH-PE + HBr} \quad (1)$$

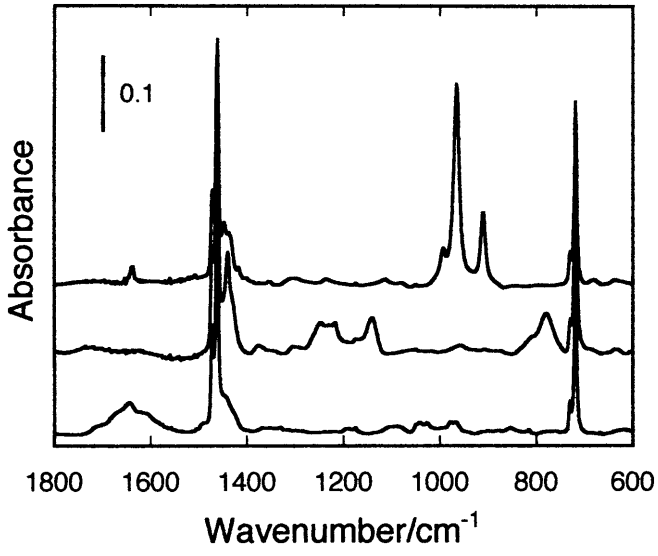
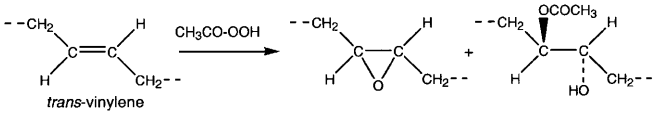


Fig. 1 Fourier transform (*FT*) IR spectra of polyethylene (*PE*) after 5-kGy γ-ray irradiation in 304 kPa butadiene (*top*), after Br_2 treatment (*middle*), and after immersion in ethylenediamine (*bottom*)

Introduction of amino functions was confirmed by the appearance of bands ascribable to the stretching vibration of N–H at 3374 cm^{-1} and the bending vibration of N–H at 1645 cm^{-1} (bottom: 3374 cm^{-1} band, not shown). Table 1 illustrates the number of unsaturated side chains per carbon atom of the PE main chain, the bromine atoms added, and the H^+ equivalence of PE substituted with AEA groups. The amount of bromine atoms absorbed was the highest for the sample prepared under 456 kPa butadiene at a 10 kGy dose. However introduction of AEA group was the highest for the sample prepared under 304 kPa butadiene at a 5 kGy dose. Since the 10 kGy sample had much more cross-linking networks in the polymer chain than the 5 kGy sample [2], ethylenediamine molecule might have been more easily accessible to bromine atoms in the 5 kGy sample. As the AEA group is the starting functional group for chemical modification of PE, γ-ray irradiation conditions in the following experiments were fixed at a 5 kGy dose under 304 kPa butadiene.

2-Aminoethylamination of γ-ray irradiated PE via epoxidation

The γ-ray irradiated PE film (5 kGy, 304 kPa butadiene) was placed in a bottle filled with peracetic acid vapor at 277 K. Peracetic acid attacks double bonds and converts them partly to epoxide and partly to *vic*-acetoxy/hydroxy derivative as shown in reaction (2) [15].



(2)

The FTIR spectra shown in Fig. 2 revealed that the bands ascribable to epoxy (890 cm^{-1}), acetoxy (1240 cm^{-1}), and hydroxy (3458 and 1066 cm^{-1}) groups were growing in compensation with most of *trans*-vinylene functions (966 cm^{-1}), but some vinyl functions (994 and 911 cm^{-1}) remained (the 3458 cm^{-1} band is not shown in this figure). An expected band for the epoxy function,

Table 1 Amination efficiency of various polyethylene (*PE*) samples γ-ray irradiated under different conditions

Irradiation conditions					
Butadiene pressure/kPa	456	304	304	152	152
γ-ray dose/kGy	10.3	10.3	4.9	10.3	4.9
Irradiated products					
C_4H_6/main-chain C atom	0.127	0.096	0.086	0.056	0.059
Br_2/main-chain C atom	0.123	0.091	0.072	0.048	0.036
Br/main-chain C atom (*a*)	0.246	0.182	0.144	0.096	0.072
2-Aminoethylamino-PEs[a]					
H^+ capacity/(mmolg^{-1})	0.74	1.83	4.41	1.31	0.82
2-Aminoethylamino/main-chain C atom (*b*)	0.015	0.030	0.064	0.016	0.009
Amination efficiency (*b*/*a*)	0.061	0.166	0.444	0.167	0.130

[a] All the products contained bromine detectable by the Beilstein test

near 1260 cm^{-1}, was buried in the strong acetoxy band at 1240 cm^{-1}, and an expected band near 910 cm^{-1} overlapped the decreasing band at 911 cm^{-1} of the vinyl function. Another band at 1736 cm^{-1} for the acetoxy function buried in the strong band at 1712 cm^{-1} of acetic acid in this figure appeared upon drying the film in vacuo as shown in Fig. 3. As the product after peracetic acid treatment contained epoxy, acetoxy, and hydroxy functions on the side chains of PE, it is called epoxy/acetoxy/hydroxy-PE. Mainly acetoxy and hydroxy functions were introduced to PE to produce acetoxy/hydroxy-PE upon exposure of the irradiated PE to peracetic acid vapor for 96 h at 313 K.

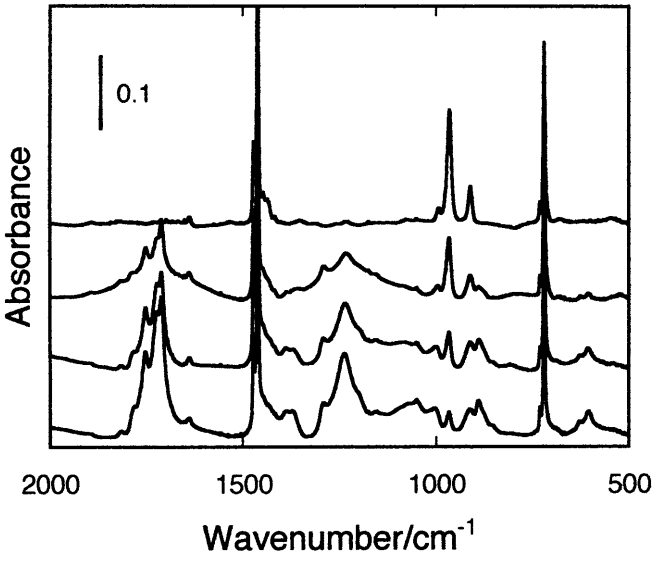


Fig. 2 Change in the FTIR spectra of PE (*top*) γ-ray irradiated with a 5 kGy dose in 304 kPa butadiene, exposed to peracetic acid vapor for definite time intervals (4, 10, and 20 h from *2nd to bottom*) at room temperature

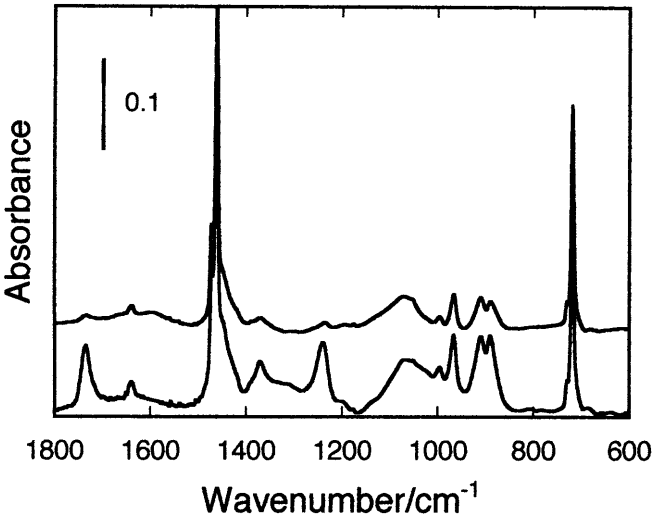
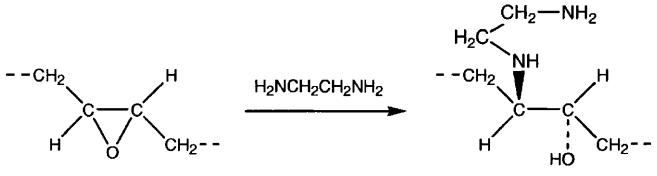
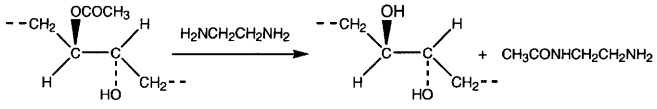


Fig. 3 Introduction of an amino function to a PE substrate through epoxidation, as revealed by the change in the FTIR spectrum: Epoxy/acetoxy/hydroxy-PE dried in vacuo (*bottom*) and PE-G0 (*top*)

The epoxy/acetoxy/hydroxy-PE (Fig. 3) was immersed in ethylenediamine for 24 h at 313 K, washed with deionized water several times and ethanol, and dried in vacuo. The FTIR spectrum of ethylenediamine-treated epoxy/acetoxy/hydroxy-PE (Fig. 3, top) shows the bending vibration of N–H at 1640 cm^{-1}, but the C=O vibration band of the acetoxy function at 1736 cm^{-1} became hardly detectable. This suggests that the amino function was introduced to the polymer from the epoxy function (reaction 3) and that the acetoxy function was removed from the polymer by treatment with the amine (reaction 4). This product was used as the starting material to grow a hyperbranched chain by the technique to grow dendrimers, and is called PE-G0, i.e. generation 0 of the dendritic growth cycle [3].



(3)



(4)

A 5.37-mg sample of PE-G0 prepared from 3.59 mg PE (256 μmol CH_2) by γ-ray irradiation under butadiene (18.43 μmol unsaturated side chains introduced) followed by epoxy/acetoxy/hydroxylation, had a H^+ equivalence of 4.94 μmol. This corresponds to 2.47 μmol AEA groups, assuming that primary and secondary amino groups behaved equally as proton acceptors. This indicates that out of 18.43 μmol unsaturated side chains, 2.47 μmol were converted to the AEA/OH form and the others (15.96 μmol) to the *vic*-diol form.

Acetoxy/hydroxy-PE prepared by prolonged exposure of the irradiated PE sample to peracetic acid vapor at 313 K failed to incorporate amino functions upon immersion in ethylenediamine, and complete conversion of the double bond to *vic*-diol was suggested to have occurred as shown in reaction 4.

Hyperbranched modification of PE-G0

A 5.37-mg film of PE-G0 containing 2.47 μmol covalently attached ethylenediamine units (obtained from the PE containing 256 μmol CH_2, vide supra) was immersed in 30% methyl acrylate solution in methanol for 24 h at

313 K to add two 2-methoxycarbonylethyl groups to each amino end of the PE side chains (reaction 5) [3]. The change was confirmed by the FTIR spectrum (Fig. 4A, bottom), which revealed a C=O stretching vibration band of saturated ester at 1736 cm^{-1}. This sample is called PE-G0.5, i.e., generation 0.5 of the dendritic growth cycle [3] applied on PE.

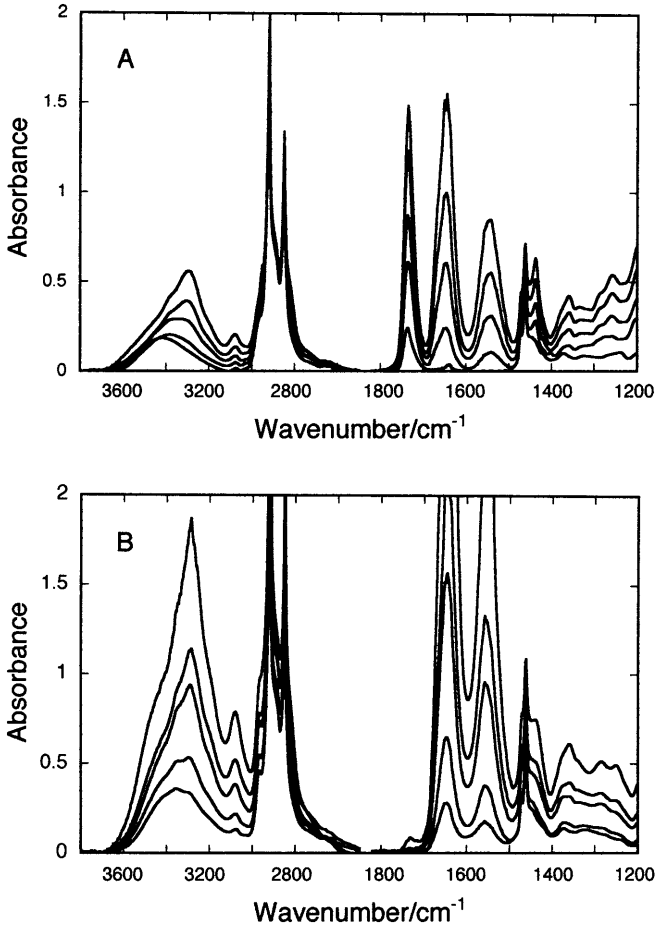
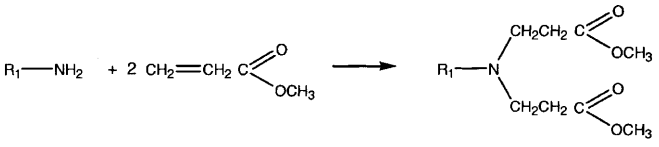
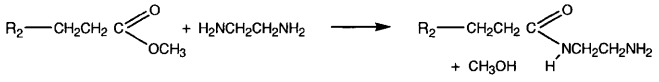


Fig. 4A, B Growth of dendrimer on a PE substrate, as revealed by FTIR spectroscopy. **A** PE-G0.5, G1.5, G2.5, G3.5, and G4.5 (*bottom* to *top*). **B** PE-G1, G2, G3, G4, and G5 (*bottom* to *top*)



(5)

PE-G0.5 was immersed in ethylenediamine for 48 h at 313 K to produce PE-G1 (generation 1 of the dendritic growth cycle on PE), in which the methyl ester ends of the polymer side chains were expected to be converted to 2-aminoethylamido ends (reaction 6) [3]. The weight increase of 0.59 mg from PE-G0 to PE-G1 corresponded to addition of 5.17 μmol of branch groups to the film, assuming that each branch was composed of a $-CH_2CH_2CO-NHCH_2CH_2NH_2$ groups (Table 2). The H^+ equivalence of the amino group per film increased from 4.94 to 6.9 μmol. The FTIR spectrum (Fig. 4B, bottom) revealed the appearance of a broad band ascribable to the N–H stretching vibration in the amide function around 3355–3290 cm^{-1} and the C=O stretching vibration bands of secondary amide at 1648 and 1556 cm^{-1} in compensation with the esteric C=O stretching vibration at 1736 cm^{-1} in PE-G0.5 (Fig. 4A, bottom).



(6)

Treatment of PE-G1 with methyl acrylate produced PE-G1.5, which produced PE-G2 on treatment with ethylenediamine. This dendritic growth cycle was repeated until PE-G5 was obtained. Table 2, together with

Table 2 Growing number of branches during the dendritic growth cycle applied to the amino-bearing PE film

Sample[a]	Film weight (mg)	Weight increment (mg)	Added branch (μmol)		H^+ equivalent (μmol)	
			Observed	Expected[b]	Observed	Calculated[c]
PE-G0	5.37				4.94[d]	
PE-G1	5.96	0.59	5.17	4.94	6.9	10.1
PE-G2	6.70	0.74	6.5	10.3	10.9	16.6
PE-G3	8.07	1.37	12.0	13.0	21.8	28.6
PE-G4	10.31	2.24	19.6	24.0	40.6	48.2
PE-G5	13.63	3.32	29.1	39.2	64.1	77.3

[a] The starting material of PE film before the γ-ray irradiation under butadiene was 3.59 mg, i.e., contained 256 μmol CH_2 in the main chain
[b] The number of branches expected for doubling of branches by the dendritic growth cycle applied to the immediate predecessor. Each primary amino end of 2-aminoethylamino-PE was expected to receive two branches of $-CH_2CH_2CONHCH_2CH_2NH_2$
[c] The calculated H^+ equivalent is the number of amino-nitrogen atoms including the primary (amino ends), secondary (located at the bottom of the branches), and tertiary (located at the branching points) amino groups present in the sample film.
[d] This corresponds to 0.019 H^+ equivalent/main-chain C atom

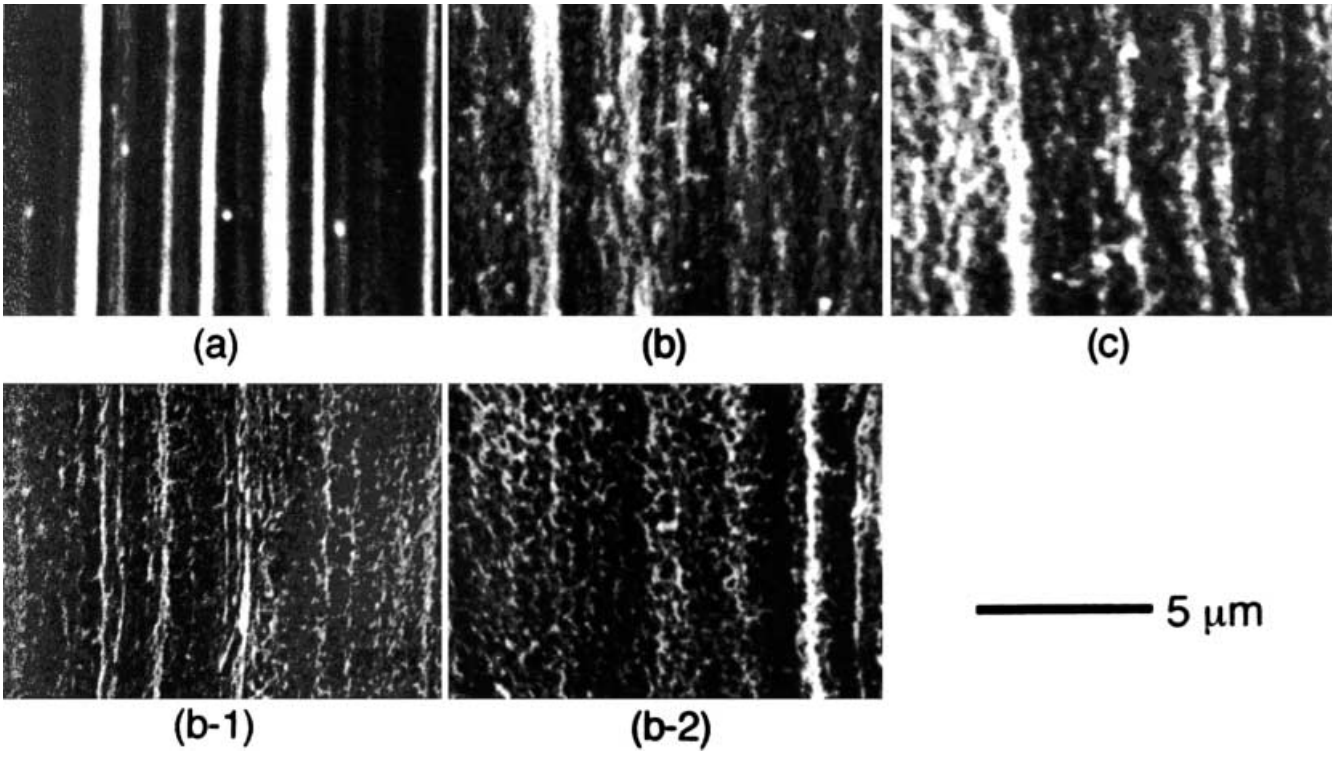


Fig. 5 Scanning electron micrographs of PE films in some stages of the dendritic growth cycle. *a* PE-G0, *b* PE-G3, *c* PE-G5, *b-1* PE-G3 plasma-etched for 10 min, and *b-2* plasma-etched for 20 min

Fig. 4A and B, shows that the number of the amino-bearing branches increased by a factor of 2 after the first cycle, 1.26 after the second cycle, 1.85 after the third cycle, etc., and the final product (PE-G5) contained about 12 times the number of amino functions as that of PE-G0.

Properties of PE-G5

The surface of untreated PE film, as well as that of the γ-ray irradiated PE film in butadiene, repelled water, and the film floated on water. On the other hand, the surface of the modified film at the stage of PE-G2 or later wetted with water, and the film sank in water. A film of PE-G5 (about 13 mg, 11×38 mm) was immersed in a 5-ml batch of the acid dye solution (0.07 μmolml^{-1} diacid alizarine light blue 4GL). The color of the solution faded rapidly and became colorless in 3 h, and the film was stained blue. The film was withdrawn and transferred to another 5-ml batch of the acid dye solution to repeat the complete decolorization of the dye solution. This corresponds to the absorption of 0.7 μmol acid dye molecules (1.4 μmol sulfonate groups). This amount is within the capacity of anion absorption of the film (64 μmol anion, Table 2). The blue color stained on the film did not fade on prolonged washing in water, but gradually faded away on immersing in aqueous 0.1 M NaOH for more than 1 week.

SEM micrographs of the surfaces of the PE films at different stages of the dendrimer growth cycles are shown in Fig. 5. The stripes of the macrofibrils on the film surface which were clearly discernible for PE-G0 became indiscernible owing to the growing bushy matter which covered the macrofibrils upon repetition of the dendritic growth cycle (Fig. 5b, c). On removing the bushy matter, some microcraters were observed in the plasma-etched film of PE-G3 (Fig. 5d, e). The thickness of the film was 7.00 μm before the etching and 6.02 and 5.99 μm after 10- and 20-min etching, respectively.

The XPS spectra (two examples are shown in Fig. 6) gave some information supplementary to the FTIR spectroscopy. Although the quality of the spectra were not sufficient to allow precise curve-fitting, the following features were observed: On repeated cycles of the dendritic growth

1. The peak position of C_{1s} shifted slightly to a higher binding-energy region.
2. The half-maximum width of the peak (ΔE) became wider and asymmetric.
3. A little shoulder at around 289 eV (amide–C = O C_{1s}) became detectable for PE-G2 and later.

The shape of the C_{1s} spectrum did not change significantly on changing the takeoff angle from 90° to 23.6°. The N_{1s} peak buried in the noise for PE-G0

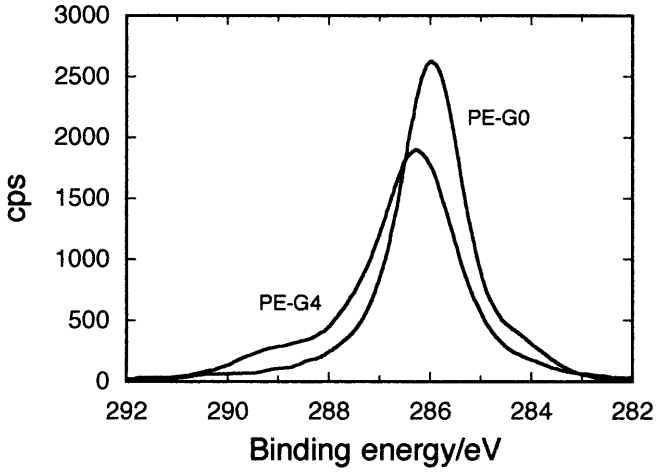


Fig. 6 Two examples of X-ray photoelectron spectroscopy spectra in the binding-energy region of C_{1s}, those of PE-G0 and of PE-G4

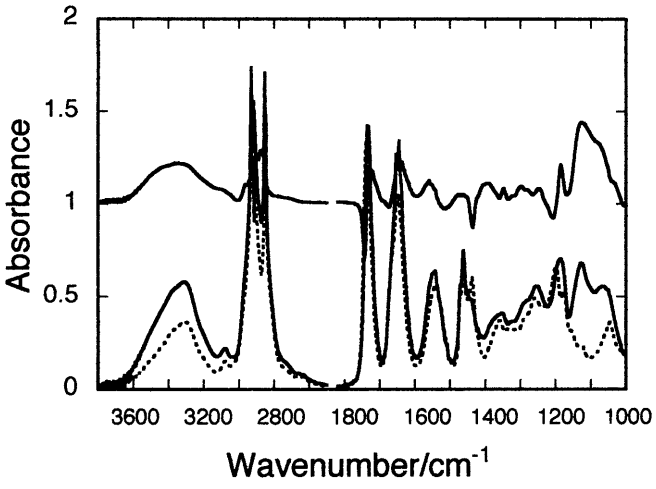


Fig. 7 The FTIR spectra of PE-PEG (*solid line* at the *bottom*) and PE-G4.5 (*broken line* at the *bottom*) and the difference spectrum thereof (*top*)

became a distinguished peak for PE-G2 and later, and the ratios of the peak areas, N_{1s}/C_{1s} and O_{1s}/C_{1s}, of the film increased (not shown). The ratio did not change significantly on etching the film for 10–20 min. On the other hand, the absorbances of the amide bands relative to that of the methylene rocking band as observed by FTIR-ATR became halved on etching the film as shown in Table 3. These features are in agreement with incorporation of electronegative oxygen and nitrogen atoms to the surface of the PE film.

Table 3 The absorbance ratios of amide bands to that of CH_2-rocking as observed by microscopic Fourier transform IR attenuated total reflection spectrometry

Absorbance ratio[a]	$A_{\text{amido I}}/A_{\text{methylene}}$	$A_{\text{amido II}}/A_{\text{methylene}}$
Before etching	3.87	3.14
10-min etched	2.09	1.71
20-min etched	1.76	1.45

[a] The peak of amide band I located at 1638 cm^{-1}, that of amide band II at 1550 cm^{-1}, and that of the methylene-rocking band at about 720 cm^{-1}

Covalent modification of PE film with poly(ethylene glycol)

A 6.97-mg portion of PE-G4 film, which has amino ends on the dendritic polymer, was immersed in 30% methyl acrylate in methanol and incubated for 48 h at 313 K to produce PE-G4.5. The product, after washing and drying, weighed 8.22 mg. Another 6.97-mg portion of PE-G4 film was immersed in 60% poly(ethylene glycol) acrylate in methanol and incubated for 48 h at 313 K. The product, which weighed 9.20 mg after washing and drying, was named PE-PEG. The FTIR spectra of PE-PEG and PE-G4.5 (both at the bottom) and the difference spectrum thereof are shown in Fig. 7. The band of the OH stretching vibration at around 3350 cm^{-1} and that of the C–O–C antisymmetric stretching vibration at 1125 cm^{-1} of the difference spectrum were characteristic of the bands of poly(ethylene glycol). The weight increment of 1.25 mg from PE-G4 to PE-G4.5 corresponds to the addition of 14.5 μmol methoxycarbonylethyl branches to the film and that of 2.23 mg from PE-G4 to PE-PEG corresponds to the addition of 5.2 μmol ω-hydroxy(polyethoxy)carbonylethyl branches to the film.

Discussion

Chemical modification of PE to give functionality, such as catalytic ability, affinity, ion-exchange ability, etc., requires covalent binding of enzymes, antibodies, nucleotides, sugars, antibiotics, etc., through amino, epoxy, hydroxy, or carboxy groups covalently bound to the polymer with as little scission or deformation of the main chain as possible [1]. Such attempts have, however, been hampered by the chemical inertness of PE. We have reported that γ-ray irradiation of PE in a 1,3-butadiene atmosphere brings about covalent binding of unsaturated side chains to the main chain and that the extent of incorporating unsaturated side chains is dependent on the γ-ray dose and butadiene pressure [2]. This technique might have the potential to chemically modify PE, because double bonds can be converted to amino, epoxy, hydroxy, or carboxy groups by conventional organic reactions.

The unsaturated side chain of the irradiated PE can be aminated through bromination, but substitution of bromine with an AEA group on immersion in ethylenediamine is incomplete (Table 1). As the presence of

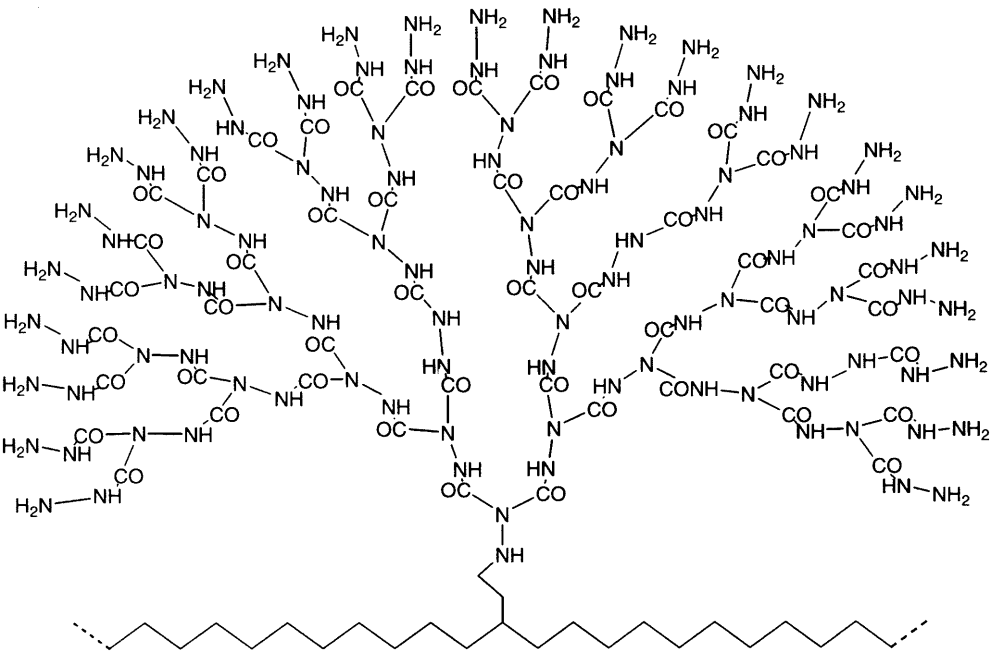


Fig. 8 A schematic illustration of the dendritic construction of the hyperbranched modified PE film

residual bromine on the polymer may be undesirable if the modified polymer is to be employed for practical uses, AEA incorporation through epoxidation was tried as an alternative route. Peracetic acid at low temperatures is known to attack double bonds in organic molecules [15], preferentially of *trans*-vinylene type, and to convert partly to epoxide and partly to *vic*-acetoxide/hydroxide (reaction 2), of which only epoxide can be converted to an AEA derivative by ring opening in the presence of amine (reaction 3). The FTIR spectra shown in Fig. 2 clearly demonstrate that double bonds on the PE side chains behaved like those in low-molecular-weight organic molecules, i.e., the IR band due to *trans*-vinylene at 966 cm^{-1} disappeared completely in 20 h, but a small portion of the vinyl function survived as evidenced by a small residual band at 911 cm^{-1}. The vinyl function can be completely extinguished by prolonged exposure of the irradiated polymer to peracetic acid vapor at 313 K, but this treatment reduces the epoxide content and is valuable only when the *vic*-diol function, instead of AEA, is required for further modification.

The number of AEA groups introduced to the PE film (2.47 mol/256mol in-chain CH_2, i.e., 0.01 mol/mol CH_2) seems to be insufficient for further chemical modification to functionalize the polymer effectively. Therefore, the technique to amplify the amino ends by means of a dendritic growth cycle [3] was applied to increase the number of amino functions of the AEA groups on the PE. One cycle of dendritic growth consists of immersion of the film (PE-G0) in methyl acrylate/methanol followed by immersion in ethylenediamine to add two branches of 2-[*N*-(2-aminoethyl)carbamoyl]ethyl groups to the amino ends of the polymer [3] to produce PE-G1. The results shown in Table 2 indicate that 5.17 μmol branches were added to 2.47 μmol amino ends of the polymer, i.e., the amino ends were doubled as was expected for the dendrimer growth cycle, but the titratable amino groups (6.9 μmol) were fewer than expected (10.1 μmol). The amplification of the branches was less than expected for an ideal dendritic growth cycle. This may be partly due to steric hindrance encountered for the reactions near the surface of the PE substrate, in contrast to the dentrimer growth in the homogeneous solution system [3]. This kind of structural defect may not be a drawback in practical application of the modified film. The product after the fifth dendritic growth cycle (PE-G5) had as many as 64.1 μmol titratable amino functions on the film. Figures 4A and B show FTIR spectra of PE samples having terminal methoxycarbonyl and amino groups, respectively, at various stages of the dendritic growth cycle. The bands due to the amide function (3355–3290, 1646, and 1558 cm^{-1}) in Fig. 4B, and those due to the ester (1736 cm^{-1}) and amide functions in Fig. 4A, increased steadily upon repeating the cycles. The results of SEM measurements (Fig. 5) also support the growth of dendrimer on the PE film.

The plasma-etching of the film produced microcraters as shown in Fig. 5. The surface density of amide groups relative to that of methylene chains as observed by FTIR-ATR spectroscopy halved upon etching. The surface densities of N and O atoms relative to that of C atoms as estimated by XPS did not change significantly on the same etching treatment. The superficial discrepancy between FTIR-ATR and XPS may be ascribable to the difference in the depths to which these

two measurements can give information. Whereas XPS gives information of sample depth of a few nanometers, FTIR-ATR gives IR information as deep as 0.4 μm at 1600 cm^{-1} and 0.9 μm at 720 cm^{-1} when measured at an incident angle of 45°. The image of the hyperbranched modified PE prepared in the present study was schematically illustrated in Fig. 8.

The reaction of poly(ethylene glycol) acrylate with PE-G4 produced a PE film whose surface was covered with poly(ethylene glycol). As macromolecules covered with poly(ethylene glycol) have a tendency to get rid of attack by cellular immune systems [16–21], it might have a potential for use in artificial organs or vessels. The assessment for practical use of hyperbranched modified PE covered with poly(ethylene glycol) will need a different series of experimental approaches and will be made in future work.

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