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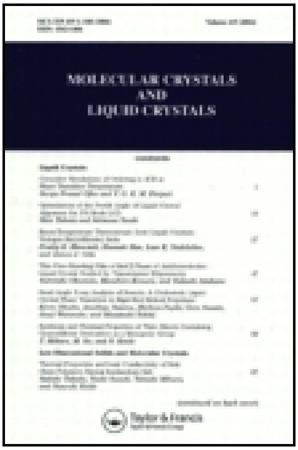

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Grafting of Trifluoroacetic Acid Allyl Ester onto Linear Low Density Polyethylene by γ-Ray Irradiation

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Grafting of linear low density polyethylene (LLDPE) is an important method used in the modification of functional group. The method of γ-ray irradiation grafting of trifluoroacetic acid allyl ester onto LLDPE was studied. The γ-ray irradiation causes molecular bond scission and produces free radical sites on the LLDPE. This process was carried out at 500 kGy γ-ray irradiation doses from a ^{60}Co source and the optimum concentration (30 wt%) of trifluoroacetic acid allyl ester. The microstructure of modified polymer film has been characterized by fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR). Thermal properties of the grafted products were also studied by thermogravimetric analysis (TGA).

Keywords: γ-ray irradiation; grafting; polyethylene; trifluoroacetic acid allyl ester

INTRODUCTION

One of the most powerful tools for modifying polymeric materials is radiation-induced grafting. A search of the literature reveals a number

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of papers deal with irradiation-induced graft polymerization techniques, including simultaneous and prior irradiation methods for various monomer-polymer combinations. And ^{60}Co was used in almost all of these studies [1–3]. Graft polymerization provides a convenient method for the synthesis of semipermeable membranes since commercially available polymer film can be used as a substrate. ^{60}Co-γ-ray-induced grafting of trifluoroacetic acid allyl ester onto polyethylene is one of the more promising methods [4–7].

It was reported that the exposure of this grafting to doses of ^{60}Co-γ-ray irradiation improves its mechanical properties [8]. Method of grafting is a well-established technique used to modify properties of synthetic polymers [9–11]. The γ-ray irradiation has the advantages of being a clean and continuous process with a very good control and is an important method in commercial use. The effects of the γ-ray irradiation on polyethylene induced crosslinking, chain scission and double bond formation, which change the molecular structure and properties [12–18].

In this paper, we investigated the grafting of trifluoroacetic acid allyl ester onto polyethynene using γ-ray irradiation. The polyethylene grafted with trifluoroacetic acid allyl ester was characterized with FT-IR, NMR, and TGA. This study will attempt to obtain a broader understanding on the antifogging film structures at the surface of a base polyethylene. More specifically, the focus will be on investigating the previously reported the blending on the nature of polyethylene phase structure as well as the effect of the trifluoroacetic acid allyl ester on polyethylene-bonding interactions. This will be achieved by combining information from the following experimental methods: contact angle analysis, differential scanning calorimetry, and scanning electron.

EXPERIMENTAL

Materials

Low density polyethylene [$(-CH_2-CH_2-)_n$, d = 0.992, PE, Aldrich] was used as base polymers. Trifluoroacetic acid allyl ester ($CF_3COOCH_2CH{=}CH_2$, 95%, TCI) was used. Solvent was used *m*-xylene (C_8H_{10}, 99%, Aldrich) and NMR solvent was used 1,2-tetrachloroethane-d$_2$ ($Cl_2CDCDCl_2$, Aldrich).

Preparation of PE Grafted with Trifluoroacetic Acid Allyl Ester by γ-Ray Irradiation

PE (5 g) was dissolved in *m*-xylene (30 mL) in a flask at 120°C. Then, 30 wt% trifluoroacetic acid allyl ester was added into the PE solution.

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The dispersion liquid was violently stirred at 120°C for 1 hr. Then the dispersion liquid was poured into a glass bottle for γ-ray irradiation. And the samples for irradiation were sealed into the 5 mL glass bottle containing PE mixed with trifluoroacetic acid allyl ester. The irradiation was performed in the liquid nitrogen using ^{60}Co-γ-ray irradiation source facility of Korea Atomic Energy Reserch Institute (KAERI). When ^{60}Co-γ-ray irradiation was performed in the nitrogen, the air in the bottle was completely replaced by nitrogen gas. After ^{60}Co-γ-ray irradiation, the product was immediately extracted with a soxhlet apparatus for 48 hrs with m-xylene to remove the ungrafted polyethylene.

Methods

The chemical structure of PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation was studied with FT-IR. FT-IR spectra were recorded on a Perkin Elmer Spectrum 2000 Model spectrometer from 4000 to 400 cm^{-1}. The thermal behaviors of ungrafted products and PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation were examined by TGA. The heating rate was 10°C/min and temperature range studied was from the room temperature to 700°C. TGA was run under air atmosphere using a PERKIN-ELMER (U.S.A), TGA 7 Model thermal analyzer.

NMR is a physical phenomenon involving the interaction of atomic nuclei placed in an external magnetic field with an applied electromagnetic field oscillating at a particular frequency. The ^{13}C-NMR and ^{19}F-NMR spectra were recorded using 400 MHz spectrometers (Varian) 85°C. A sample (175 mg) was dissolved in 0.7 mL of 1,1,2,2,-tetrachloroethane-d$_2$ in a 5 mm diameter NMR tube.

RESULTS AND DISCUSSION

The structure of trifluoroacetic acid allylester grafted PE and its mechanism are shown in Figure 1. The grafting of trifluoroacetic acid allyl ester onto PE chain necessarily changes its chemical structure. Hence, the study of the functionalization reactions requires the use of techniques capable of identifying the structural modifications. These results have been confirmed prior to work [19].

Figure 2 shows the FT-IR spectra of the PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation. FT-IR analysis confirmed the grafting of trifluoroacetic acid allyl ester units onto the polyethylene. In Figure 2(e), the band at 1780 cm^{-1}, corresponding to carbonyl stretching (C=O), and some bands in the 1400–1000 cm^{-1} range, corresponding to C$-$F stretching. Such bands are absent in the spectra

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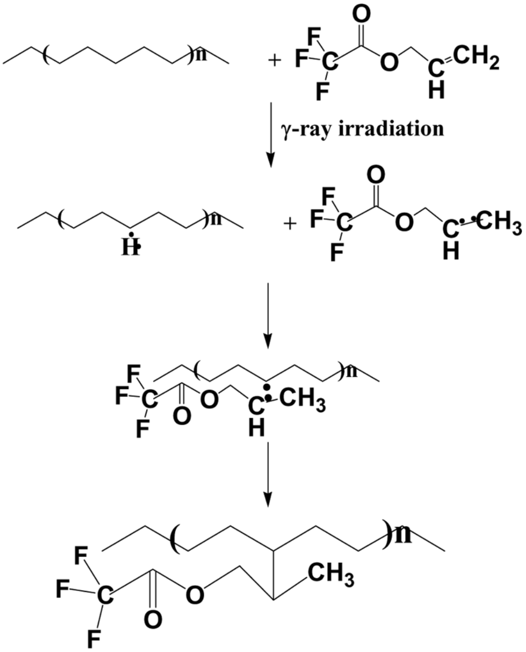

FIGURE 1 The mechanism for the irradiation grafting of trifluoroacetic acid allyl ester onto PE.

of the non-grafted irradiated PE. This is in agreement with the proposed mechanism for the grafting of trifluoroacetic acid allyl ester onto the polyethylene chains (Fig. 1).

TGA is used primarily for determining thermal stability of polymer and the structure of grafted PE. TGA data is recorded as a thermogram of weigh change versus temperature. TGA curve for the thermal degradation of PE grafted with 30 wt% trifluoroacetic acid allyl ester by γ-ray irradiation is shown in Figure 3. The initial weight losses observed in the cases of PE grafted with 30 wt% trifluoroacetic acid allyl ester by γ-ray irradiation was due to the losses of grafted functional group. The weight loss of the PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation was started at 169.71°C and 415.11°C. The weight loss at 169.71°C was due to ester functional group and the weight loss at 415.11°C was due to PE with trifluoroacetic acid allyl ester.

The microstructure of trifluoroacetic acid allyl ester grafted PE was measured with ^{19}F-NMR and ^{13}C-NMR spectroscopy. Figure 4 shows ^{19}F-NMR spectrum of PE grafted with trifluoroacetic acid allyl ester

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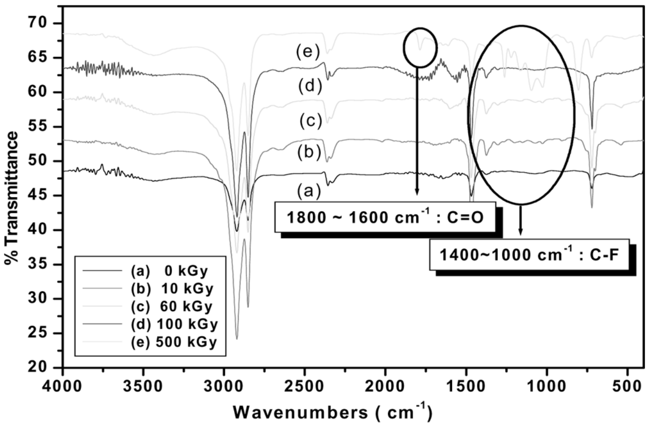

FIGURE 2 FT-IR spectra of PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation at various irradiation dose; (a) 0 kGy, (b) 10 kGy, (c) 60 kGy, (d) 100 kGy, (e) 500 kGy.

by γ-ray irradiation. The ^{19}F-NMR shows singlet peak corresponding to CF_3 group at -75.0873 ppm.

Figure 5 shows the aliphatic part of ^{13}C-NMR spectrum of PE grafted with trifluoroacetic acid allyl ester and PE of none grafted with trifluoroacetic acid allyl ester in the melt at 85°C. By comparison of these spectra to that of PE and trifluoroacetic acid allyl ester under

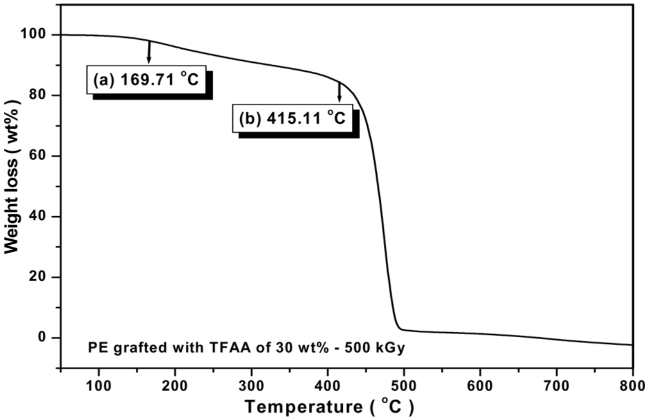

FIGURE 3 TGA curve of PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation.

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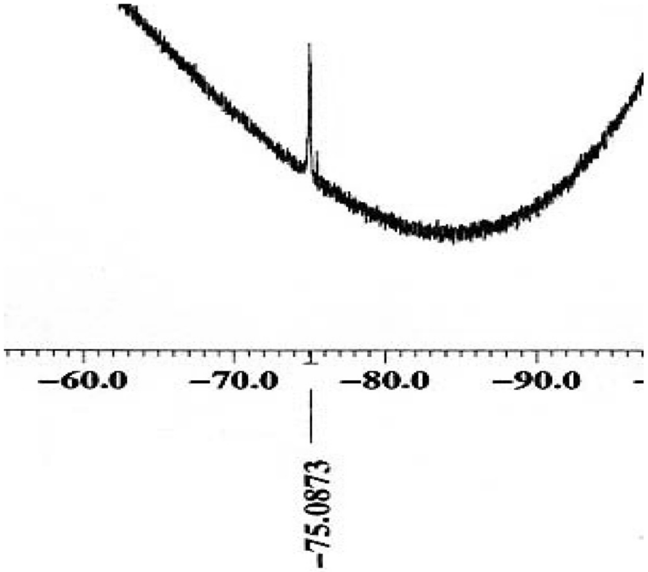
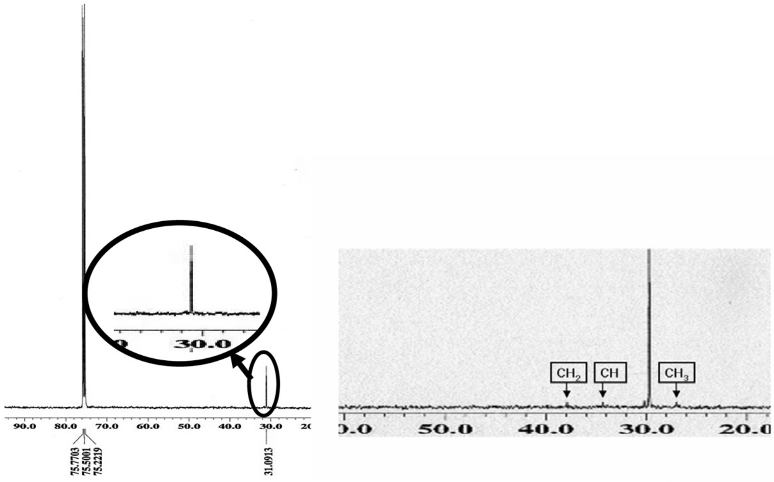


FIGURE 4 ^{19}F-NMR spectrum of PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation.



(a) (b)

FIGURE 5 ^{13}C-NMR spectra: (a) PE of the none grafted with trifluoacetic acid allyl ester; (b) PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation.

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identical conditions it is evident that the strong signal at 29.8 ppm is the natural abundance background of the PE backbone. ^{13}C-NMR shows chemical shifts of the methylene (37.8 ppm), methine (34.3 ppm) and methyl (26.8 ppm) carbons in the trifluoroacetic acid propyl ester of trifluoroacetic acid allyl ester grafted PE. No resonance of carbons on the C=C bond is observed. Therefore, the chemical bond was observed between PE and fluorinated agent in the grafted PE with NMR spectroscopy.

Figure 6 shows ^{13}C NMR-DEPT 135° spectrum corresponding to PE grafted with trifluoroacetic acid allyl ester. The application of ^{13}C NMR-DEPT technique allows the study of the variation of the signals corresponding to CH, CH_2, and CH_3 groups with the grafting. This technique facilitated the precise assignment of the signals, since in DEPT 135° experiment the bands corresponding to CH_2 groups were presented with negative phase, and those corresponding to CH and CH_3 groups with positive phase. It therefore seems likely that when a great number of branches are present in polyethylene, trifluoroacetic acid allyl ester molecules can be grafted very close to the branching points. The results presented in this section show that trifluoroacetic acid allyl ester insertion onto polyethylene chains preferentially occurs in secondary carbons of the main chain regardless of the branch type and content of the copolymer.

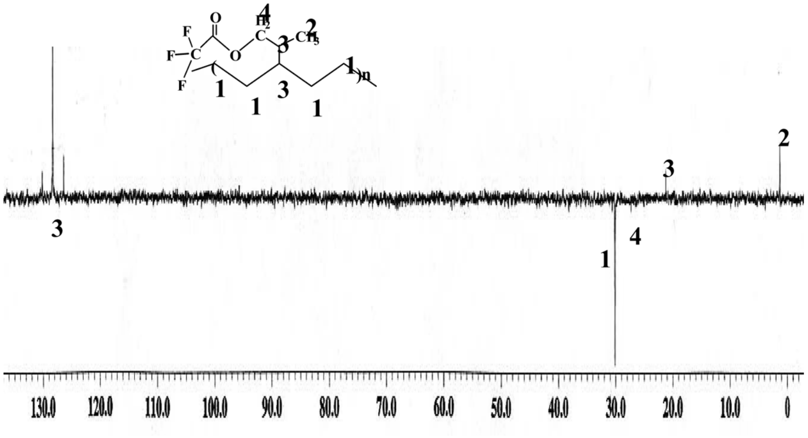

FIGURE 6 ^{13}C-NMR (DEPT 135°) spectrum PE grafted with trifluoroacetic acid allyl ester by γ-ray irradiation.

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CONCLUSIONS

The fluorinated agent (trifluoroacetic acid allyl ester) was successfully grafted onto linear low density polyethylene by γ-ray irradiation. The structure of grafted PE was elucidated by FT-IR, ^{19}F-, and ^{13}C-NMR spectroscopy. The use of γ-rays to graft fluorinated agent onto polyethylene can be useful in the functionalization of polyolefins.

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