Polymer Bulletin 26, 205-208 (1991)

Polymer Bulletin

Radiation crosslinking of propylene-vinylsilane copolymer

T. Asanuma[1] and T. Matsuyama[2]

[1]Mitsui Toatsu Chemicals, INC. Osaka Research Laboratory, Takaishi, Osaka, Japan
[2]Research Reactor Institute of Kyoto University, Kumatori, Osaka, Japan

Summary

It has been found that a propylene-vinylsilane copolymer(a few mole % of vinlysilane) is crosslinked by radiation (γ-ray or electron beam) effectively. The mixture of the copolymer and a propylene homopolymer has been also crosslinked by radiation. It is proposed that the crosslinking reaction is due to the coupling of silyl-radical of vinylsilane unit with carbon-radical of propylene unit.

Introduction

Alkenylsilane is polymerized with or without olefin by a conventional Ziegler catalyst(1). The copolymers thus obtained are not crystalline. Recently improved Ziegler catalysts have been proposed, some of which are composed of titanium tetrachloride supported on magnesium dichloride, alkylaluminum and electron donative compounds (2). These catalysts are very active and can produce crystalline alkenylsilane-olefin random copolymers(3). These crystalline copolymers are interesting in applications such as nucleating, adhesive and surface coating agents(3).

In our recent work on highly crystalline propylene-vinylsilane random copolymer (hereafter abbreviated as Si-copolymer), it has been found that Si-copolymers are easily crosslinked with ionizing radiations. It has also been observed that the crosslinking reaction is very fast and proceeds under the condition of rather small amount of vinylsilane in comparison with the case of hydrolysis producing Si-O-Si linkage(4). In the present work we have attempted to elucidate the reaction mechanism of the radiation crosslinking in crystalline Si-copolymers.

Experimental

Propylene of HL-grade from Osaka Petrochemical Industries(Japan) was used without further purification. Vinylsilane was produced from trichlorovinylsilane by reduction with $LiAlH_4$. After co-pulverizing magnesium dichloride, dibutylphthalate and titaniumtetrachloride, the transition metal catalyst was prepared by treating the co-pulverized product with hot 1,2-dichloroethane. Propylene homopolymer was prepared using this transition metal catalyst, triethylaluminum and diphenyldimethoxysilane at 343K in the presence of liquid propylene. Si-copolymer was obtained in the same way as the case of the propylene homopolymer.

^{1}H-NMR spectra were obtained with JEOL GX90 in 1,2,4-trichlorobenznene solution. γ-Ray irradiation was carried out with ^{60}Co source of Research Reactor Institute of Kyoto University under the condition of 7 ~58KGY/hr at room temperature or at 77K in air or in vacuo. Electron beam irradiation was performed using scanning electron beam irradiation instrument(EPS-750) of Nissin High Voltage Co. The limiting viscosity was measured as a tetrahydronaphthalene solution at 405K. The gel fraction was obtained by extracting polymers with boiling m-xylene for 12 hours. ESR specta were measured with Varian E4(X-band) at 77K.

Results and Discussion

The ^{1}H-NMR spectrum of the Si-copolymer containing 1.6mol% vinylsilane is shown in Fig. 1. The doublet peak at about 3.6 ppm indicates the presence of vinylsilane unit. Fig. 2 shows the effect of γ-ray irradiation on the press sheet of the mixtures of Si-copolymers and 2,6-di-t-butyl-p-cresol (0.1wt%). Fig. 3 depicts the effect of electron beam irradiation on the press sheet of the mixtures similar to those on Fig. 2. In Figs. 2 and 3, it is clearly seen that even 1 Mrad irradiation is sufficient for crosslinking reaction. Moreover, it is proved in Figs. 2 and 3 that the crosslinking reaction occurs not only in air but also in nitrogen atmosphere or in vacuo. These facts imply that the oxidation or hydrolysis of Si-H into Si-O-Si is not a major process for the crosslinking reaction in this study. When the content of vinylsilane in the Si-copolymer is low, the crosslinking reaction is not efficient in air as shown in Figs. 2 and 3. It was confirmed that in the absence of vinylsilane, the gel fraction is almost zero even after 10 Mrad irradiation in air or in vacuo.

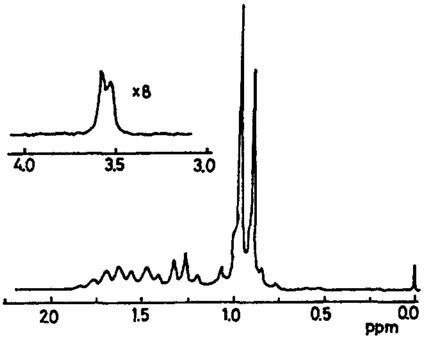

Fig. 1 ^{1}H-NMR of vinylsilane-propylene copolymer.

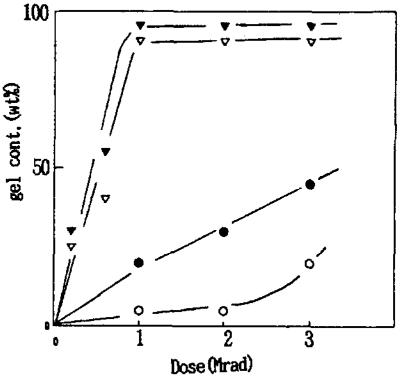

Fig. 2 Relation between gel fraction and dose of γ-ray for copolymers.
○ vinylsilane 0.4mole% irradiated in air,
● vinylsilane 0.4mole% irradiated in vacuo,
▽ vinylsilane 1.2mole% irradiated in air,
▼ vinylsilane 1.2mole% irradiated in vacuo.

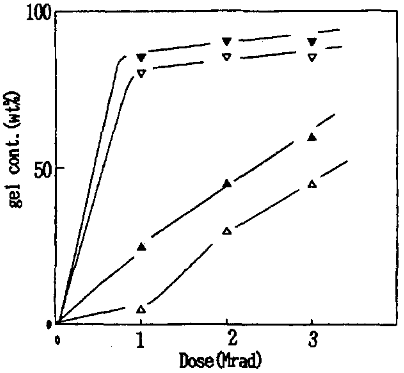

Fig. 3 Relation between gel fraction and dose of E.B. for copoymers
△ vinylsilane 0.5mole% irradiated in air ,
▲ vinylsilane 0.5mole% irradiated in N2 ,
▽ vinylsilane 1.2mole% irradiated in air ,
▼ vinylsilane 1.2mole% irradiated in N2 ,

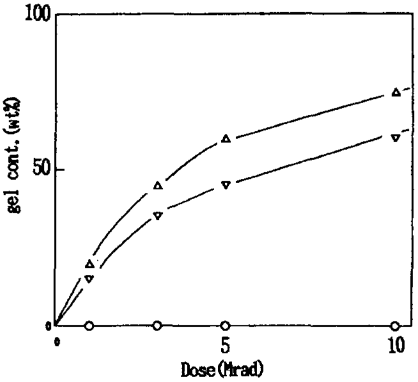

Fig. 4 Relation between gel fraction and dose of γ-ray for mixtures.
△ mixture of the Si-copolymer (20wt%) and the propylene homopolymer (80wt%),
▽ mixture of the Si-copolymer (10wt%) and the propylene homopolymer (90wt%),
○ the propylene homopolymer

Fig. 4 shows the effect of γ-irradiation on the press sheets of the mixtures of the Si-copolymer(vinylsilane 1.6 mole%), the propylene homopolymer(boiling n-heptane insoluble fraction 98.4wt%) and 2,6-di-t-butyl-p-cresol(0.1wt%). The effect of γ-irradiation on the homopolymer is also indicated in Fig. 4. It is shown that for the mixed sample which contains only 10 wt% of the Si-coplymer, the gel fraction becomes over 50 wt% at the level of 10 Mrad irradiation. This result suggests that the crosslinking reaction occurs between the Si-copolymer and the propylene homopolymer.

Fig. 5 shows the ESR spectra of the Si-copolymer(vinylsilane 1.2mole%) and the propylene homopolymer after γ-irradiation. The curve (a) shows the ESR spectrum of the Si-copolymer and the curve (b) shows that of the propylene homopolymer measured at 77K.

Fig. 6 shows the ESR spectra recorded after heating the sample up to 293K, where the curves (a) and (b) show the ESR spectra of the Si-copolymer and the propylene homopolymer, respectively. The curves (b)'s shown in Figs. 5 and 6 are similar to those of polypropylene(4). The curves (a)'s shown in Figs. 5 and 6 are expected to contain ESR signals attributable to both vinylsilane and propylene units.

In Figs. 5 and 6, the central parts of the curves (a)'s are remarkably different from those of curves (b)'s . After normalizing the wing components of ESR signal ascribed to the propylene homopolymer in the curves(a) and (b) for these figures, a difference spectra between the curve (a) and (b) were calculated and these are the curves (c)'s in Figs. 5 and 6. The curves (c)'s are very similar to each other with rather strong signal intensity. Since the difference between the Si-copolymer and the propylene homopolymer is the presence of vinlysilane units, the curves (c)'s in

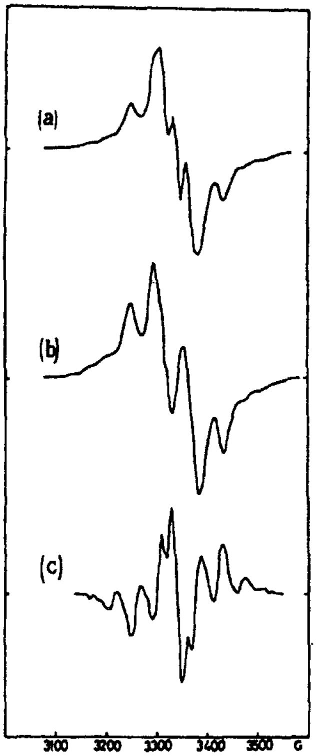

Fig. 5 ESR spectra obtained after γ-ray irradiation at 77K: (a) Si-copolymer, (b) popylene homopolymer, (c) difference spectrum between curves (a) and (b)

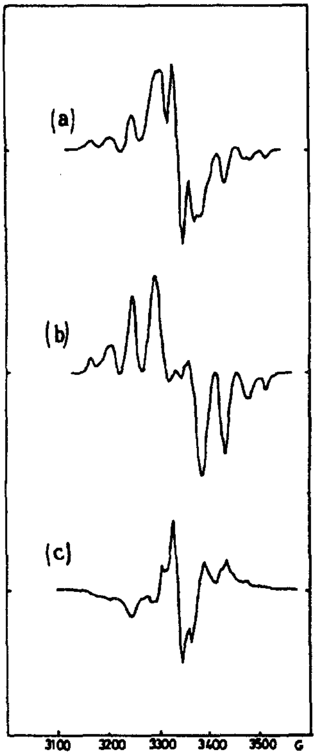

Fig. 6 ESR spectra obtained after heating up to 298K: (a) Si-copolymer, (b) propylene homopolymer, (c) difference spectrum between curves (a) and (b)

Figs. 5 and 6 are assigned to the signals of radicals of vinylsilane units, probably to the signals of silyl-radicals. The fact that the signal is observed even after heating up to 298K, means that the silyl-radical is very stable.

It has been established that irradiated propylene homopolymer is degradable through the carbon radical of propylene unit(6). Here we propose that the present crosslinking reaction with ionizing radiations is caused by coupling between carbon radicals of propylene units and silyl-radicals of vinylsilane units. This is a new way to improve the property of propylene polymers.

References
1)U. S. Patent 3223686(Dec. 14, 1965)
2)J. Boor, Jr., Ziegler-Natta Catalysts and Polymerization (1979, Academic Press)
3)T. Asanuma, K. Yamamoto, K. Kawanishi, and N. Uchikawa, The 1989 International Chemical Congress of Pacific Basin Societies, Macro. 360(1989)
4)U. S. Patent 3644306(Feb. 22, 1972)
5)M. Iwasaki, T. Ichikawa, and K. Toriya, J. Polym. Sci. Polym. Letters, 5, 423(1967)
6)D. O. Geymer, Makromol. Chem., 99, 159(1966)

Accepted February 21, 1991 S