

Polymerization of Phosphor-Containing Oligomer Induced by Electron-Beam Irradiation

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SYNOPSIS

Studies have been carried out on the polymerization of vinyl phosphonate oligomer in a form of thin liquid layer induced by electron-beam irradiation under various reaction conditions. It was found that the dose-rate exponent on the rate of polymerization was 0.92, that the presence of remaining diluent below 10% did not disturb the polymerization, but that the presence of oxygen retarded the reaction when the film thickness was as thin as 20 μm . Intermittent irradiation was effective to increase the conversion to the polymer.

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INTRODUCTION

In our research¹ and development to prepare non-flammable polyethylene foam of an open-cell type by radiation grafting of phosphor-containing oligomers onto the surface of the cells, difficulties were encountered in determining the reaction behavior due to the structure of the foam, which did not allow quick equilibrium between microscopic concentrations of reagents or oxygen on the cell walls inside the foam and macroscopic ones surrounding the foam; for example, the polymerization of the oligomer may be affected by the possible remaining diluent of the oligomer, or the oxygen effect on the polymerization could not be determined accurately because the oxygen concentration in the cell was not the same as that in the environment. It is important to know the effects of the remaining diluents and other reaction conditions in order to determine optimum reaction conditions of the grafting of the oligomer onto the surface of the foam cell, but it was difficult to obtain information on these parameters for the oligomer impregnated in the foam. Ex-

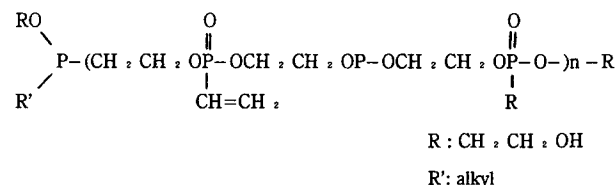
traction of unreacted oligomer from the irradiated foam to determine the conversion to polymer may not be quantitative due to its porous structure.

In the present research, studies were carried out on the effects of the dose rate, the remaining diluent or oxygen present in the irradiation atmosphere on the rate, and the conversion of polymerization of the oligomer in a form of thin liquid film, which gives more quantitative data on these parameters than in the cell of the foam.

EXPERIMENTAL

Materials

Vinyl phosphonate oligomer (VPO; Fyrol 76R, molecular weight, 500–1000, content of phosphor, 22.5% by weight) was obtained from Akzo Chemicals Co. and used as received. The chemical formula as given by the supplier is



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Methanol was obtained from Nakarai Chemicals and was of reagent grade. Distilled water used as

the diluent of the oligomer was obtained from a distilling apparatus (conductivity: $0.5 \mu\Omega$).

Preparation of the Specimens for Irradiation

Four different types of films were prepared—(i) Film of 1 mm thickness: The oligomer was cast in an aluminum foil well ($10 \times 30 \times 1$ mm) that was made by fitting the aluminum foil into an aluminum frame. The liquid was covered with PET film of $100 \mu\text{m}$ thickness to avoid oxygen dissolving into the liquid. (ii) The film prepared by the same method as (i) but without the PET film-covering liquid. (iii) Film of $20 \mu\text{m}$ thickness: A known amount of the oligomer liquid was delivered on a glass plate to spread the liquid as a thin film, the thickness of which was estimated by measuring the diameter of the film. (iv) For infrared spectrometry, the oligomer was spread on a KBr plate as in (iii).

Irradiation of the Films

The irradiation was carried out by using two accelerators: (i) a Van de Graaff electron accelerator at acceleration voltage of 1.5 MV and beam current of $50 \mu\text{A}$ of scanning width of 30 cm and (ii) an electron accelerator of a rectifying transformer type (Nissin High Voltage Co.) at an 800 kV electron acceleration voltage and a 0.2–15 mA beam current of scanning width of 30 cm. The dose rate was adjusted by selecting the proper beam current under these conditions, and the desired dose was either accumulated by repeating irradiation at a constant conveyer speed or was given by one pass irradiation, the dose being adjusted by selecting the proper conveyer speed.

A typical dose as measured by a CTA film dosimeter was 5 kGy/pass ($50 \mu\text{A}$) at a conveyer speed of 0.48 m/min for the Van de Graaff accelerator operated under the conditions mentioned above and 45 kGy/pass/mA at a conveyer speed of 0.9 m/s for the electron accelerator of the transformer type. Examples of the irradiation conditions employed in the present study are summarized in Table I. In two series of intermittent irradiation experiments, (1) the same dose (100 kGy) was given to the samples by one, two, and four passes at a conveyer speed of 1.8, 3.6 and 7.2 m/s, respectively, and (2) a dose twice as much as in experiment (1) (200 kGy) was given similarly at a conveyer speed of 0.9, 1.8, and 3.6 m/s, respectively.

The film prepared by method (i) was irradiated on a conveyer that traveled 10 cm below the irradiation window of the accelerators. The films pre-

Table I Irradiation Conditions

	VdG	Transformer Type	
Electron accelerating voltage	1.5 MeV	0.8 MeV	
Beam current (mA)	0.05	4.0	15.0
Scanning width (cm)	30	30	30
Dose rate (kG/s)	0.92	23.0	90.0
Traveling velocity (m/min)	0.48	0.9	3.0
Dose (kGy/pass)	5.0	180	200

pared by methods (ii), (iii), and (iv) were arranged in a container covered with PET film on its top to keep the atmosphere in the container at the desired oxygen concentration that was adjusted by nitrogen stream. The oxygen concentration was monitored by an electrolytic oxygen meter (Touken Model ECOAZ-CG). The bottom of the container was fixed on the conveyer so that the film to be irradiated may come to 10 cm below the irradiation window.

Determination of Conversion

The conversion to polymer was determined by the following two methods: (i) Irradiated VPO was immersed in acetone at 25°C for 12 h and the undissolved fraction was separated from the solution by filtration and the precipitate was dried in a vacuum oven to a constant weight at 50°C and then weighed to determine the conversion. (ii) VPO film irradiated on a KBr cell plate was subjected to infrared spectrometry on a Hitachi 215 spectrophotometer to determine remaining vinyl groups in the film. The conversion to polymer was followed by the disappearance of the bands at 1410 cm^{-1} using the bands at 1450 cm^{-1} as the internal standard.

RESULTS AND DISCUSSION

Dose and No. Cycles of Irradiation

Figure 1 shows a part of the infrared spectra of VPO and the change of the spectra during irradiation using the Van de Graaff accelerator at dose rate of 0.92 kGy/s at a constant conveyer speed. The dose was

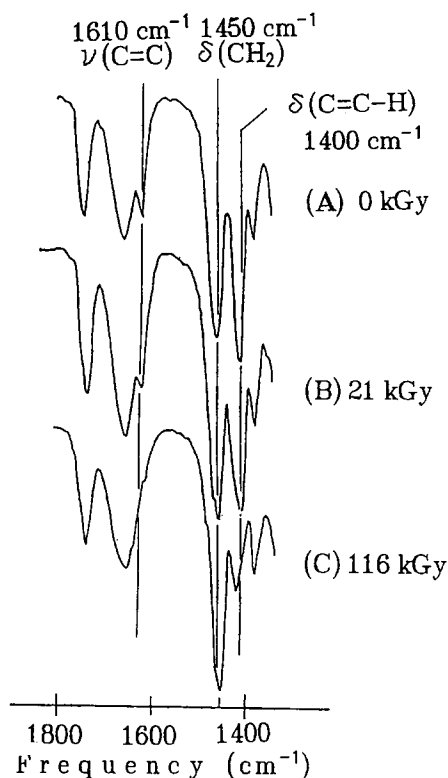


Figure 1 Change of IR spectrum of VPO by electron beam irradiation. Dose: (A) unirradiated; (B) 21 kGy; (C) 116 kGy.

increased by increasing the number of passes. Peaks that appeared at 1610 and 1400 cm^{-1} are assigned to the stretching vibration of the double bond and the out-of-plane deformation vibration of the vinyl group, respectively, and the peak that appeared at 1450 cm^{-1} is assigned to the deformation vibration of the methylene group. As shown from the figure, the intensities of the former two decreased with increasing dose, whereas the intensity of the latter did not change during the irradiation. Relative concentration of the double bonds was calculated using following formulas:

$$[\text{Double bonds}] (\%) = (D_2 - D_{2\infty})/D_R$$

$$[\text{Double bonds}] (\%) = D_1/D_R$$

where D_1 , D_2 , and D_R are intensities at 1610, 1400, and 1450 cm^{-1} , respectively, and $D_{2\infty}$ is the residual intensity at 1400 cm^{-1} . In Figure 2, the concentration of the double bonds obtained on the basis of the two bands are plotted as a function of dose that was increased by a repeating cycle of irradiation. The results obtained from the two bands agree quite well.

Conversion to the polymer is plotted in Figure 2. It is noted that the conversion to the polymer corresponds approximately to the decrease of double bonds, and 100% conversion was attained by 100 kGy. Dose conversion curves were also obtained using the accelerator of a transformer type at 23 kGy/s by the two different methods of irradiation, and the results are shown in Figure 3. A similar dose-conversion curve at the higher dose rate was obtained in the same way as that obtained at a lower dose rate (Fig. 2), when the dose is accumulated by repeating irradiation at a constant conveyer speed. When the dose was increased by decreasing the speed of the conveyer so that the necessary dose was given by one pass of irradiation, conversion came below that obtained by the former method above 15 kGy. The result seems to indicate that in the irradiation where the dose was accumulated by repeated irradiation on the conveyers postpolymerization may occur to increase the conversion. This effect is more clearly shown by the intermittent irradiation experiments described below.

In Table II, conversions are shown for the experiments where the same amounts of dose were given by one, two, and four passes under the irradiation zone while the dose was kept constant as possible. The conversion was higher when the number of cycles is increased, possibly due to the post-

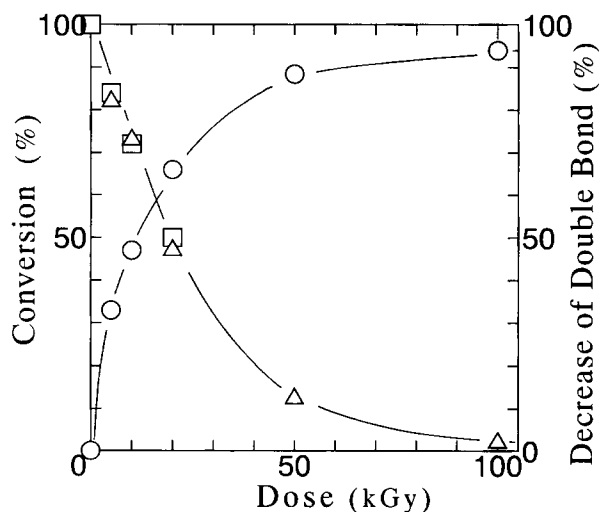


Figure 2 Conversion and relative intensities of bands as a function of dose; dose rate, 5 kGy/pass; film thickness, 20 μm ; oxygen concentration, 20 ppm; dose rate, 920 Gy/s; film thickness, 1 mm; (O) conversion; (Δ) 1400 cm^{-1} ; (\square) 1610 cm^{-1} ; conveyer speed: 0.48 m/s; dose was accumulated by increasing number of passes through the irradiation zone.

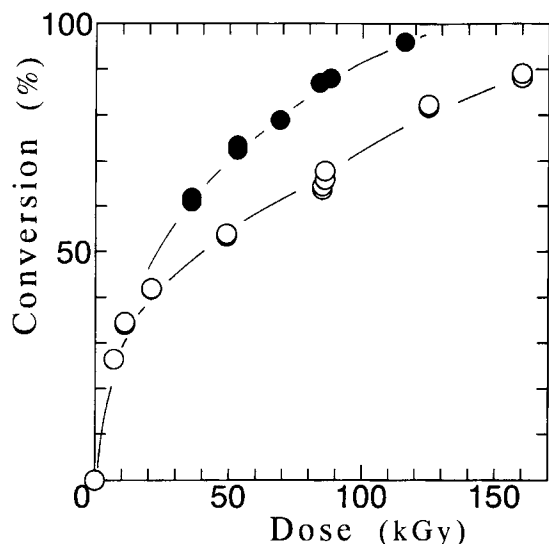
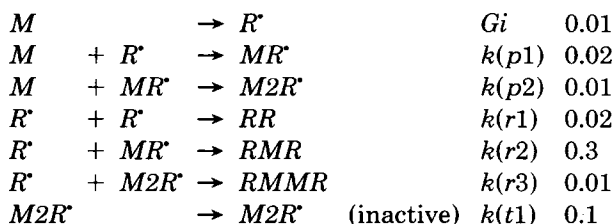


Figure 3 Conversion as a function of dose; dose rate, 23 kGy/s; film thickness, 20 μm ; oxygen concentration, 20 ppm; (●) dose was accumulated by increasing the number of irradiations while dose absorbed by one pass of irradiation was kept constant; (○) dose was given by one pass through irradiation zone and dose was adjusted by changing conveyor speed while dose rate was kept constant.

polymerization effect. This is supported by a simulation calculation based on the following reaction scheme:



where M is VPO; R' , the initiating radical; M_iR' ($i = 1, \dots$), propagating radicals; G_i , the G -value of initiation; $k(pi)$'s, rate constants of propagation reactions, $k(ri)$'s, rate constants for termination by recombination, and $k(t1)$, the unimolecular termination reaction constant. The reaction steps are representatives for many other similar reaction steps and are to be edited so that computation results may fit those obtained under wider experimental conditions. G -values of initiating radical formation and the rate constants are adjusted so that the sum of the final polymeric products ($3[RMR] + 4[RM2R] + 3[MMR]$) agrees with the experimental results shown in Table II, column (a). An example of calculation using the above parameters is shown in Figure 4. The result given in column (b) obtained by a higher dose (slower conveyor speed) shows a smaller effect of the number of irradiation cycles, indicating that most of the VPO was consumed by the irradiation. In the experiments described below, the irradiations were carried out using the accelerator of the rectifying transformer by one pass on the conveyor and the dose was adjusted by changing the conveyor speed.

Dose Rate

In Figure 5, the logarithm of rate of polymerization was plotted as a function of dose rate in the logarithmic scale. The conversion to the polymer was determined by two methods: one by the precipitation method and the other by the infrared absorption method. In this experiment, the dose was 30 kGy and the dose rate was varied from 1 to 90 kGy/s by changing beam current from 0.2 to 15 mA. The concentration of oxygen of the irradiation atmosphere was 20 ppm. Conversion to the polymer was determined by both the extraction method and infrared

Table II Conversion and Intermittent Irradiation—Dose Rate: 23 kGy/s; Oxygen Concentration; 500 ppm; Thickness of the Film: 1 mm

No. Repeated Cycles of Irradiation	(a)			(b)		
	Dose (kGy)	Conveyor Speed (m/s)	Conversion (%)	Dose (kGy)	Conveyor Speed (m/s)	Conversion (%)
1	100	1.8	66.9	197	0.9	87.0
			67.7			88.0
2	96	3.6	68.8	193	1.8	86.8
			68.8			87.0
4	97	7.2	82.8	190	3.6	88.8
			83.2			89.1

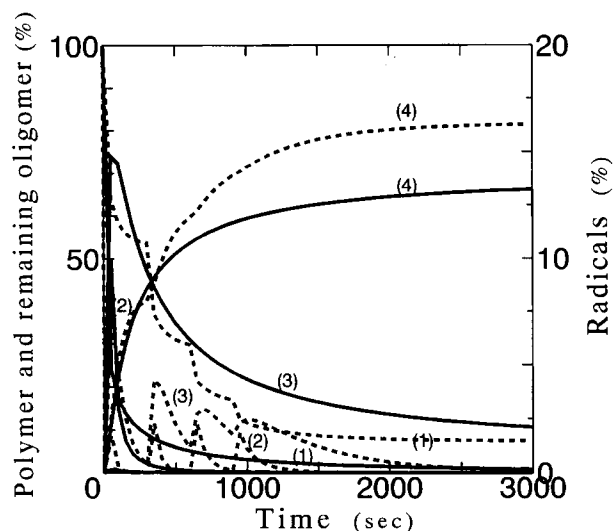


Figure 4 Relative amounts of remaining VPO, polymer, and intermediate radicals as a function of time; continuous lines: continuous irradiation; broken lines: intermittent irradiation; (1) remaining VPO[M]; (2) radical [R']; (3) radical [RM']; (4) polymer $3 \times [\text{RMM}] + 4 \times [\text{RMMR}] + 3[\text{RMR}]$; for details, see text.

spectrometry, which gave linear lines of the same slope. Dose-rate dependencies obtained from the slopes of the plots by the precipitation method and infrared method gave the same value: 0.92. The dose

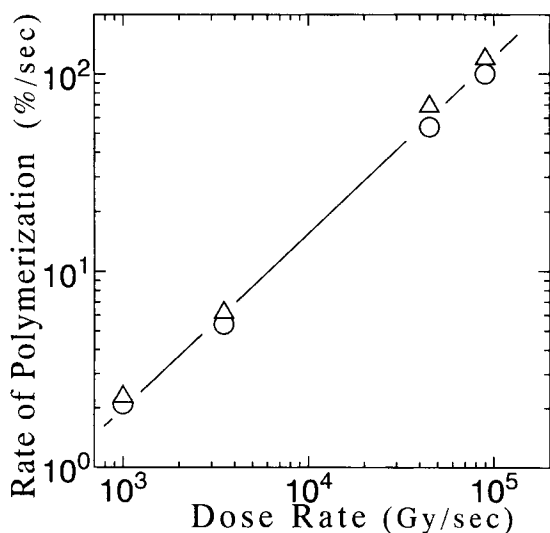


Figure 5 Dose-rate dependence of rate of polymerization; dose, 30 kGy; (O) obtained by the precipitation method using methanol; film thickness, 1 mm; film being covered with PET film; and (Δ) obtained by the infrared absorption method; film thickness, 20 μm ; oxygen concentration, 20 ppm.

exponent close to unity may suggest that the unimolecular termination (t_1) is superior to bimolecular ones in the viscous oligomer system, as predicted by the calculation.

Diluent Remaining in the Oligomer

In Figure 6, conversion is plotted as a function of the concentration of water or methanol added in the oligomer film as the diluent. The thickness of the oligomer was 1 mm, and the acceleration voltage and beam current were 800 kV and 4 mA, respectively, and the dose and dose rate were 180 kGy and 23 kGy/s, respectively. Both conversions decreased with increasing concentration of water in the oligomer, but only a 10% decrease was observed with a 10% water concentration. A similar plot was obtained when methanol instead of water was used, indicating that water and methanol have a retardation effect on the polymerization to a similar extent, which is not very significant when the concentration of the diluent is below 10%.

Oxygen Concentration in the Atmosphere

Dose-conversion curves obtained for oligomer films of two different thicknesses, one 1 mm and the other 20 μm , are shown in Figure 7, where the irradiation atmosphere was nitrogen-containing oxygen at 20 ppm or air. The conversion for the 1 mm (both in

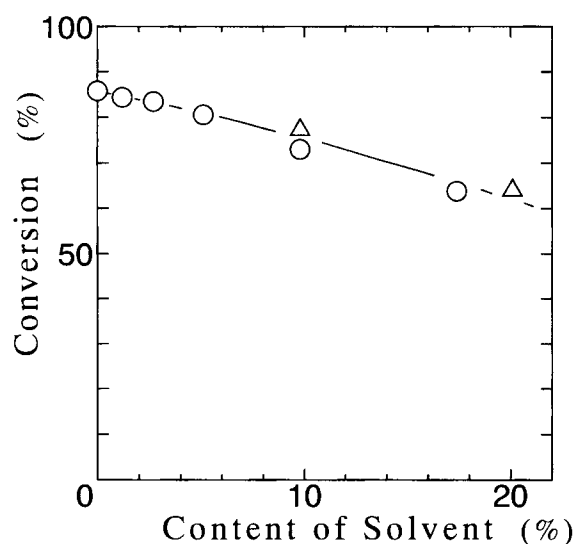


Figure 6 Conversion as a function of solvent content in the film; dose, 184 kGy; dose rate, 23 kGy/sec; film thickness, 1 mm; conversion, (O) diluent, water; conversion, (Δ) diluent, methanol conversion.

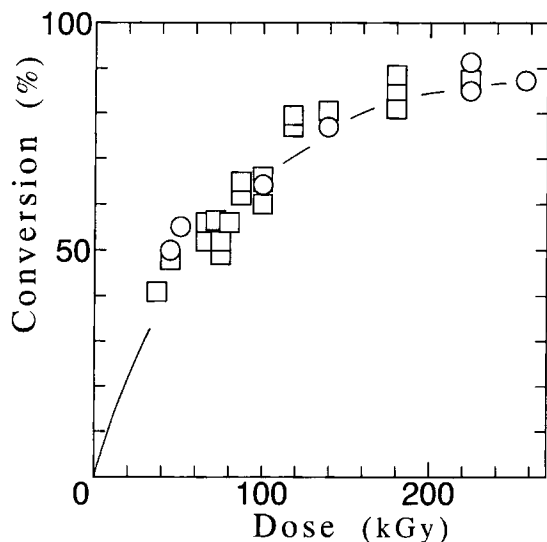


Figure 7 Conversion as a function of dose; the dose was given by one pass through the irradiation zone, the dose being varied by changing the speed of conveyer; dose rate, 23 kGy/s; (□) film thickness, 1 mm; (○) film thickness, 20 μm ; open symbols: oxygen concentration, 20 ppm; filled symbols: air (21%).

20 ppm oxygen and in air) and 20 μm (in 20 ppm oxygen) films increased with increasing dose almost similarly to one another, whereas the conversion curve for 20 μm film (in air) increased with increasing dose, but with considerable retardation. This

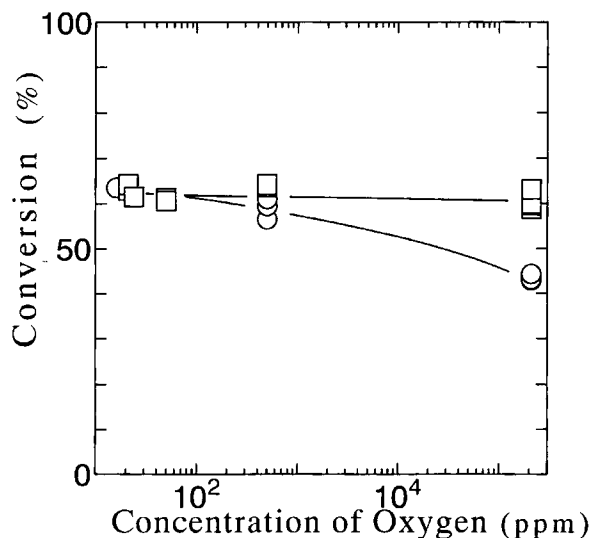


Figure 8 Conversion as a function of oxygen content in the film; dose, 100 kGy; dose rate, 23 kGy/s; (□) film thickness, 1 mm; (○) film thickness, 20 μm .

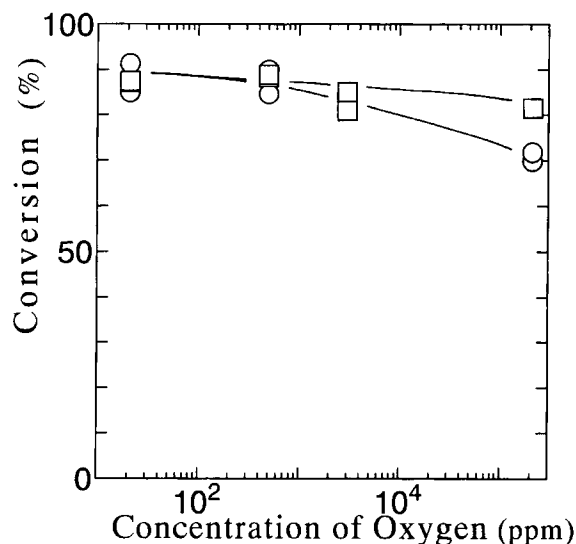


Figure 9 Conversion as a function of oxygen content in the film; dose, 200 kGy; dose rate, 23 kGy/s; (□) film thickness, 1 mm; (○) film thickness, 20 μm .

means that for thin film (20 μm) the amount of oxygen delivery to the reaction zone by diffusion is large enough to balance the consumption of oxygen by irradiation to inhibit the polymerization, but for thick film (1 mm thick), the amount of oxygen delivery is not enough to retard the polymerization.

Conversion was measured as a function of oxygen concentration in the irradiation atmosphere for oligomer films of the two different thicknesses. Conversion at 100 and at 200 kGy are shown in Figures 8 and 9, respectively. It is noted that polymerization was not retarded by oxygen when the oligomer film is as thick as 1 mm, but some retardation by oxygen was observed for 20 μm film at a 100 kGy dose, supporting the above discussion. This effect seems to become smaller at a higher dose such as 200 kGy. This may indicate that formation of a polymer network in the oligomer film at high dose prevents the diffusion of oxygen into the film.

CONCLUDING REMARKS

Several important conclusions were obtained to develop grafting of the oligomer onto the inner surface of cells of polyethylene foam: Vinyl phosphonate oligomer was found to polymerize to give a polymer insoluble to solvent and dose of 150 kGy was enough to give high conversion to the polymer. The presence of a diluent to decrease the viscosity of the oligomer

did not disturb the polymerization of the oligomer if the concentration of the diluent is below 10%. The retardation effect of oxygen became significantly large when the thickness of the oligomer film was as thin as 20 μm , and, therefore, the oxygen concentration has to be as low as possible because the radiation-grafting of the oligomer existed as thin film in the foam material. The dose-rate exponent close to unity found in the present study indicates that the grafting of the oligomer can be carried out effectively at a high dose rate without loss of radicals due to recombination reactions of the radicals.

Higher conversion is expected in multiple irradiation than in single-pass irradiation if the dose is the same, possibly owing to the postpolymerization effect.

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