# Graft Polymerization by Pre-heating Method Applied to Polyethylene Containing Benzoyl Peroxide

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It has been found by G. Oster that some solid polymers containing photo-sensitizer such as benzophenone could initiate graft polymerization with irradiation by ultra-violet as well as by ionizing rays[1-3]. In those cases, the primary action will be not on the polymer but on the photo-sensitizer, and the decomposed sensitizer fragment may abstract hydrogen atoms from the polymer molecules. The polymer radicals thus formed can initiate graft polymerization or cross-linking reaction.

The ultraviolet pre-irradiation method for graft polymerization or cross-linking reaction cannot be generally applied to thick films or a bundle of fibers because the penetrating power of the rays may be fairly low.

It is found here that some solid polymers containing initiator of radical polymerization of vinyl monomers such as benzoyl peroxide or azobisisobutyronitrile can initiate graft polymerization. This grafting method may be easily applied to thick films or to a bundle of fibres.

## Experimental

A commercial low density polyethylene film of 0.0017 g.·cm$^{-2}$ thickness is soaked for 60 min. in the benzene solution of benzoyl peroxide (20 g. l$^{-1}$) at 50°C, the surface is washed with benzene, and dried. The sample thus obtained contains benzoyl peroxide about 0.2 wt. %. The sample is then heated in air. The sample is sealed with purified methyl methacrylate monomer in a glass tube, and

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1) G. Oster and O. Shibata, *J. Polymer Sci.*, 26, 233 (1957).

2) G. Oster, G. K. Oster and H. Moroson, *J. Polymer Sci.*, 34, 671 (1959).

3) S. Okamura and T. Manabe, *Isotopes and Radiation*, in press.

then heated in vacuum. After the treatment for graft polymerization, the sample is washed with benzene for about 20 hr. at room temperature in order to extract the homopolymer already formed. The complete extraction, however, will be very hard in such a condition, but some comparison between the graft polymerization conditions may be possible. The sample is then dried and weighed. The amount of graft polymerization will be defined here by

$$\text{graft polymerization }\% = \left( \frac{\text{weight of sample after graft polymerization}}{\text{weight of sample before graft polymerization}} - 1 \right) \times 100$$

The values of grafting thus obtained are rather scattered according to the inhomogeneity of the benzoyl peroxide content and of the sample thickness. Therefore kinetical discussion is omitted here.

## Results

**Time of Pre-heating.**—The effect of time of pre-heating on the graft polymerization is shown in Fig. 1, where the temperature of pre-heating is maintained at 110°C, and the polymerization temperature is 60°C.

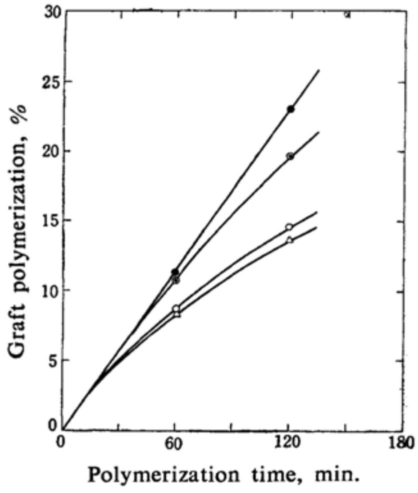

Fig. 1. Effect of time of pre-heating on graft polymerization.
Pre-heating temperature: 110°C
Polymerization temperature: 60°C
Time of pre-heating: -△- 15 min., -○- 30 min., -⊙- 45 min., -●- 60 min.

From the results shown in Fig. 1, it is recognized that the rate of graft polymerization increases with an increase of the time of pre-heating.

**Temperature of Pre-heating.**—The effect of temperature of pre-heating on the graft polymerization is shown in Fig. 2, where the time of pre-heating is maintained at 30 min., and the polymerization temperature is 60°C.

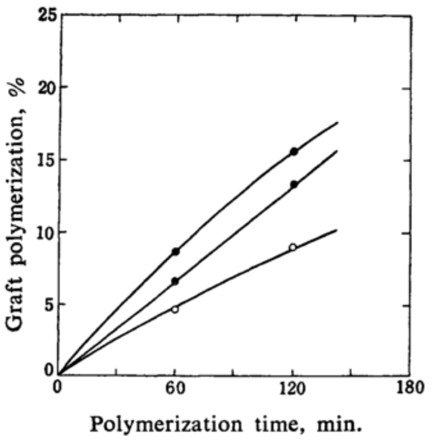

Fig. 2. Effect of temperature of pre-heating on graft polymerization.
Pre-heating time: 30 min.
Polymerization temperature: 60°C
Temperature of pre-heating: -○- 90°C, -⊙- 110°C, -●- 120°C.

From the results shown in Fig. 2, it is found that the rate of graft polymerization increases with the rise of temperature of pre-heating.

**Polymerization Temperature.**—The influence of polymerization temperature on the graft polymerization is represented in Fig. 3, where the pre-heating temperature is maintained at 110°C, and the pre-heating time is 30 min.

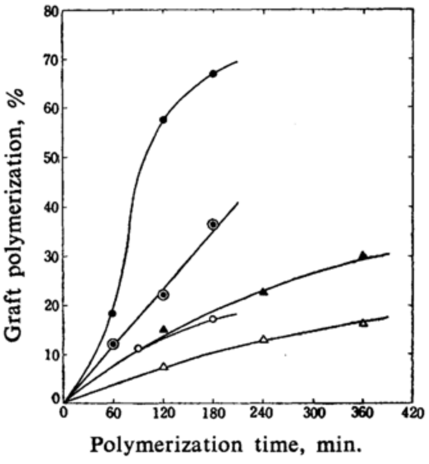

Fig. 3. Effects of polymerization temperature, pre-heating and benzoyl peroxide sensitization on graft polymerization.
Pre-heating: 110°C, 30 min.

-●-
-⊙- No pre-heating
-○- No BPO sensitization
} Polymerization temperature: 70°C

-▲-
-△- No BPO sensitization
} Polymerization temperature: 50°C

**After-effect of Pre-heating.**—The after-effect of pre-heating is shown in Fig. 4, where the pre-heating temperature is maintained at 110°C, the pre-heating time is 30 min. and the polymerization temperature is 60°C.

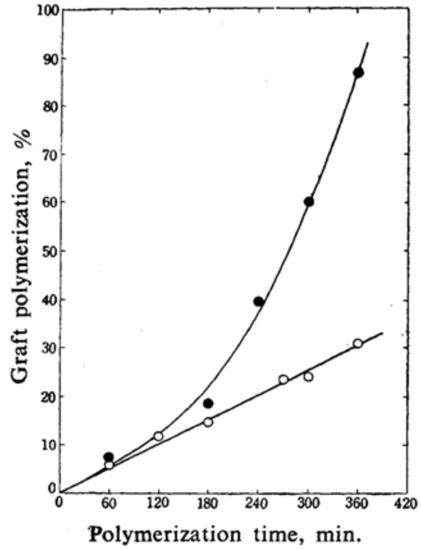

Fig. 4. After effect of pre-heating on graft polymerization.
Pre-heating: 110°C, 30 min.
Polymerization temperature: 60°C
Time interval after pre-heating until polymerization: -○- 4,300 min., -●- 300 min.

From the results represented in Fig. 4, it is shown that the rate of graft polymerization decreases with an increase of time interval after pre-heating until polymerization. And also, the difference of rates between two experiments having different intervals increases with an increase of polymerization time.

## Discussion

The mechanism of graft polymerization reported here may be as follows. I represents the initiator of radical polymerization, P the polymer, M the monomer, and $O_2$ the oxygen respectively.

**Reaction in Pre-heating.**

$I \rightarrow R\cdot$ (1) decomposition of initiator

$R\cdot + P \rightarrow P\cdot + RH$ (2) radical transfer to polymer, production of polymer radical

$P\cdot + O_2 \rightarrow POO\cdot$ (3) production of polymer peroxide radical

$P\cdot + R\cdot \rightarrow$ product (4) disappearence of polymer radical

$P\cdot + P\cdot \rightarrow PP$ (5) cross-linking reaction

$P\cdot + POO\cdot \rightarrow POOP$ (6) production of polymer diperoxide

$POO\cdot + R\cdot \rightarrow POOR$ (7) production of polymer peroxide

**Reaction in Graft Polymerization.**

$I \rightarrow R\cdot$ (8) decomposition of initiator

$POOP \rightarrow PO\cdot + PO\cdot$ (9) decomposition of polymer diperoxide

$POOR \rightarrow PO\cdot + RO\cdot$ (10) decomposition of polymer peroxide

$R\cdot + M \rightarrow RM\cdot$ (11) polymerization by initiator fragment

$PO\cdot + M \rightarrow POM\cdot$ (12) polymerization by polymer diperoxide fragment

$RO\cdot + M \rightarrow ROM\cdot$ (13) polymerization by polymer peroxide fragment

$P\cdot + M \rightarrow PM\cdot$ (14) polymerization by frozen polymer radical at the inside of polymer

$POO\cdot + M \rightarrow POOM\cdot$ (15) polymerization by frozen polymer peroxide radical

The increasing of time and the rise of temperature of pre-heating increase the initiator fragment $[R\cdot]$, and then the increase of graft polymerization may be expected (Figs. 1 and 2). The increase of time interval after pre-heating until polymerization results in the decrease of the concentration of frozen polymer radical (reactions 4 and 5), and then the decrease of graft polymerization may also be expected (Fig. 4). Reaction 14 is expected at the inside of polymer molecule, for the reaction of oxygen with radical (reaction 3) will be very fast.

## Summary

Some solid polymers containing initiator of radical polymerization of vinyl monomers can initiate graft polymerization by heating in air or in vacuo prior to polymerization. In the experiment on polyethylene film containing benzoyl peroxide (monomer: methyl methacrylate), the increase of time (from 0 to 60 min.) and the rise of temperature (from 20 to 120°C) in pre-heating procedure increase the graft polymerization rate. And also, the increase of time interval after pre-heating until polymerization results in the decrease of the graft polymerization rate.

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