A Few Physical Properties of Grafted Polyethylene and Nylon Films

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Synopsis

Methyl methacrylate, vinyl acetate, or N-vinylpyrrolidone was graft-copolymerized onto low-density polyethylene or nylon 6 film by simultaneous irradiation method. Higher extent of grafting was attained by liquid-phase grafting than by vapor-phase grafting. The relative change in the degree of crystallinity of backbone polymer caused by grafting was measured with differential scanning calorimetry. In polyethylene-g-vinylpyrrolidone, the degree of crystallinity decreased markedly with the extent of grafting. However, in other grafted films, especially in grafted nylon, the crystallinity decrease was limited, or substantially no decrease was observed in a few systems. Water vapor permeability of the grafted films changed uniformly with increasing extent of grafting, and particularly polyethylene- and nylon-g-vinylpyrrolidone films showed excellent permeability, and some were able to be used as dialyzer. The difference in grafting method, liquid-phase grafting or vapor-phase grafting, produced no difference in those properties. The grafting was found to bring about a change in the molecular orientation of the original film.

INTRODUCTION

It has been generally recognized that radiation grafting on semicrystalline polymer occurs mainly in its amorphous region, and the crystalline part remains unchanged unless very extensive grafting is performed. It should be emphasized that the above recognition has been deduced so far mostly from x-ray diffraction experiments.

Recently, we have examined the DSC thermograms of poly(methyl methacrylate)-grafted polypropylene fibers and observed that the degree of crystallinity of polypropylene decreases considerably by the grafting, and moreover, the thermal properties are affected by the grafting method adopted.[1]

In this paper, the change in crystallinity of backbone polymer was investigated with DSC on polyethylene and nylon 6 films, and the change in water vapor permeability, which seems to have a direct relationship with crystallinity, was studied. A few other measurements have also been carried out. Methyl methacrylate, vinyl acetate and vinylpyrrolidone were chosen as monomers in view of the wide differences in hydrophilic properties of their polymers. As for the grafting method, the gamma-ray

simultaneous irradiation method in liquid- and vapor-phase was adopted in most cases, because the method was found to affect the crystallinity of polymer more profoundly than the preirradiation method.

EXPERIMENTAL

Materials

Low-density polyethylene film (Sumikathene F222, 0.026 mm thick, prepared by inflation, abbreviated PE) and polycaprolactam film (Nylon 6, Platilon CFT 0.040 mm thick, biaxially stretched, abbreviated NY) were soaked with methanol and acetone for 8 hr each by using a Soxhlet apparatus, dried in air, and kept in a desiccator over silica gel. Methyl methacrylate (MMA), vinyl acetate (VAC), and vinylpyrrolidone (VPY) were purified by standard procedures.

Liquid-Phase Grafting

In liquid-phase graft copolymerization, about 1 g of the film was dipped into 40 ml of monomer or monomer solution. The sample mixture was thoroughly degassed by repeated freezing and thawing, sealed off at 10^{-4} mm Hg, and irradiated with gamma-rays from cobalt 60 at 25°C, 2.5×10^4 R/hr. The undiluted monomer was utilized for grafting onto PE. But the mixture of monomer with water (MMA–ethanol–water or VAC–ethanol–water, 1:3:2 by volume, and VPY–water, 1:4 by volume) was used for grafting on NY, because it was very inefficient or sometimes impossible to graft-copolymerize such monomers on NY without water in the monomers. Following the irradiation, the grafted films were soaked in the solvents of homopolymers, acetone or ethanol, and dried under vacuum at a room temperature. The results were expressed by the weight increase $(P - P_0)$ divided by the original weight P_0 of polymer film.

In a few cases, the preirradiation grafting was carried out on NY in order to achieve a high degree of grafting. The NY film in the glass tube was irradiated with gamma rays at a dose rate of 2.5×10^4 R/hr for 93 to 185 hr at −78°C in air; and after that, the monomer solution was added to the film while it was cool and sealed after degassing in freeze-thaw cycles. The grafting reaction was performed in a water bath at 40°C during 24 to 140 hr.

Vapor-Phase Grafting

In vapor-phase graft copolymerization, about 1 g of the film was placed in the middle of the irradiation tube, and 10 ml of monomer or monomer solution was injected into the tube without touching the film. The entire tube was degassed and sealed at 10^{-4} mm Hg. The irradiation was carried out at 25°C.

Thermal Measurements

The melting point and the heats of fusion and crystallization were determined for each grafted film using a Perkin-Elmer DSC-1B differential

scanning calorimeter. The temperature was raised at a rate[2] of 5°C/ min to about 30° to 40°C higher temperatures than their melting range, and then lowered at the same rate. The temperature at the maximum of the thermogram was taken as the melting point, and the heats of fusion and those of crystallization were calculated from the areas under the thermo-gram, each point in the figures being an average of at least two or more determinations.

Water Vapor Permeability Measurement

The water vapor permeability was measured using a conventional cup method[3] at 40°C and RH 90 ~ 0%, and the results were expressed by $g/m^2 \cdot$ 24 hr without correcting the thickness increase caused by grafting.

Molecular Orientation Measurement

The angular distribution of the polarized components of the fluorescence intensity was measured on grafted films by a Polarizing Fluorometer FOM-1 (Japan Spectrometric Co. Ltd.), and the angular distribution of the degree of polarization of fluorescence was calculated in order to know the change in molecular orientation of the film which accompanied the graft-ing.[4]

RESULTS AND DISCUSSION

Grafting in Liquid Phase and Vapor Phase

Figure 1 shows the increase in extent of grafting with irradiation time on the PE–MMA system. The liquid-phase grafting was very efficient, and high extent of grafting was attained in a short time, accompanying
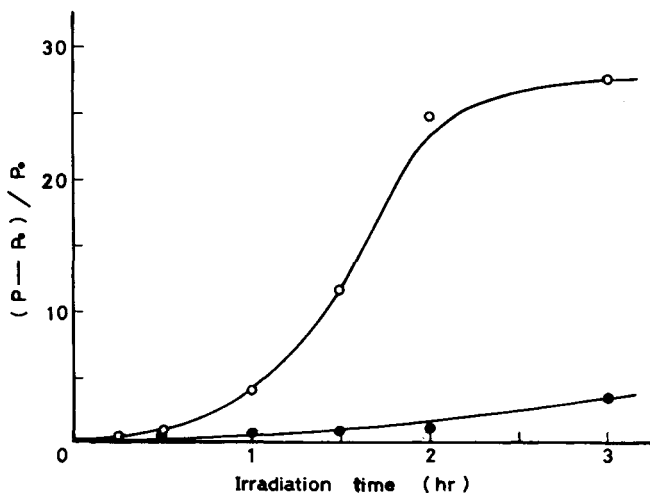

Fig. 1. Grafting of MMA on PE film; 2.5×10^4 R/hr at 25°C: (O) liquid-phase grafting; (●) vapor-phase grafting.
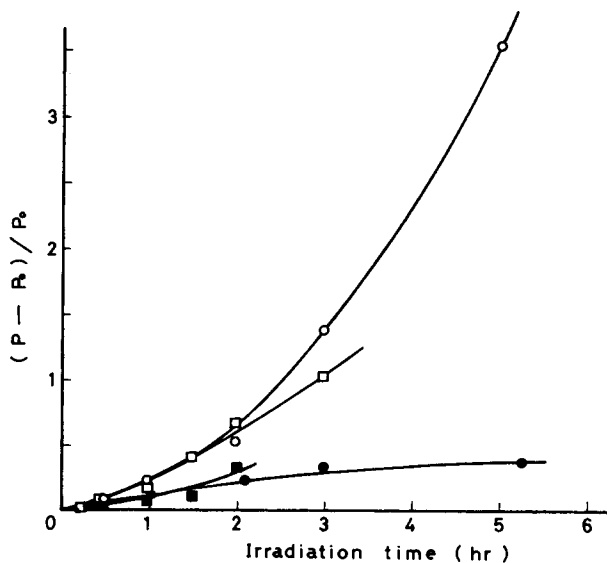
Fig. 2. Grafting of VAC and VPY on PE film; 2.5×10^4 R/hr at 25°C: (O) VPY by liquid-phase grafting; (□) VAC by liquid-phase grafting; (●) VPY by vapor-phase grafting; (■) VAC by vapor-phase grafting.

an acceleration in the rate. The yield of homopolymeric by-product was low; moreover, the homopolymer microdispersed or occluded in the grafted film was less than 2% as far as determined by the Soxhlet extraction method with acetone. The vapor-phase grafting proceeded at a much lower rate although the concentration of penetrant in the surface layer of the film should be equal in the liquid and in its equilibrium vapor since the activities of monomer are identical.[5] The above difference in rate should be brought about by too short an irradiation time to establish the equilibrium concentration of monomer inside the film in the case of the vapor-phase grafting. The penetration of monomer was reported to be much slower in the saturated vapor than in the liquid.[6]

The scope of the extent of grafting varied with the kind of monomer profoundly. Figure 2 shows the results on the grafting of VAC and VPY onto PE by both methods. The extent of grafting did not reach much higher values owing to the homopolymerization of monomer. Again, the liquid-phase grafting has brought about a higher extent of grafting, and the occluded homopolymer was shown to occupy less than 20% of the weight increase by the grafting, at most.

It was almost impossible to perform graft copolymerization on NY film in the absence of water, and it seemed to be requisite that water coexisted with monomers to achieve efficient grafting. Besides water, ethanol was added in the grafting of MMA and VAC to make the monomer mixture homogeneous. Even so, the extent of grafting is very low compared with
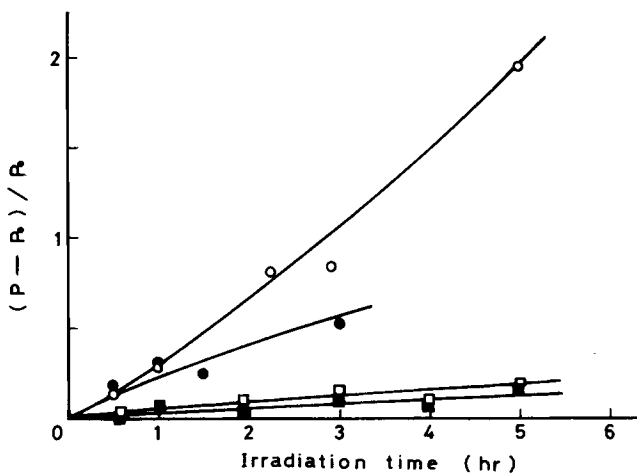
Fig. 3. Grafting of MMA and VPY on NY film; 2.5×10^4 R/hr at 25°C: (O) MMA (MMA:ethanol:water = 1:3:2 by vol) by liquid-phase grafting; (□) VPY (VPY:water = 1:4 by vol) by liquid-phase grafting; (●) MMA (MMA:ethanol:water = 1:3:2 by vol) by vapor-phase grafting; (■) VPY (VPY:water = 1:4 by vol) by vapor-phase grafting.

PE grafting, as seen in Figure 3, and especially VAC was hardly graft copolymerized on NY.

Changes in Crystallinity with Grafting

Figure 4 shows the DSC thermograms of ungrafted PE and NY. Melting and crystallization curves of both polymers are seen to be single and show no fine structures, and the gamma-irradiated but ungrafted polymer shows no detectable change in melting point or in the shape of the thermogram. This indicates that the range of the irradiation dose is too low (from 6×10^3 to 10^6 R) to produce radiation damages upon the thermograms. The grafting reaction itself also did not bring about any considerable change in the shape of the curves, except a slight melting point depression.
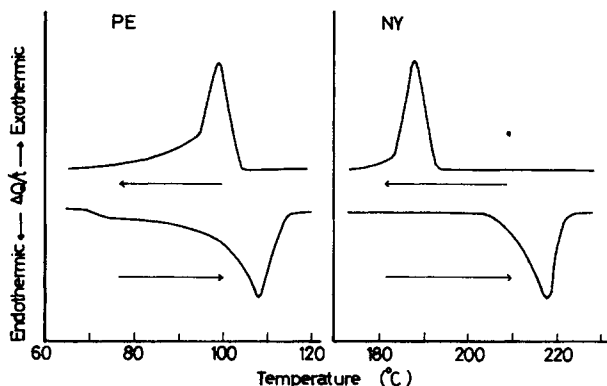

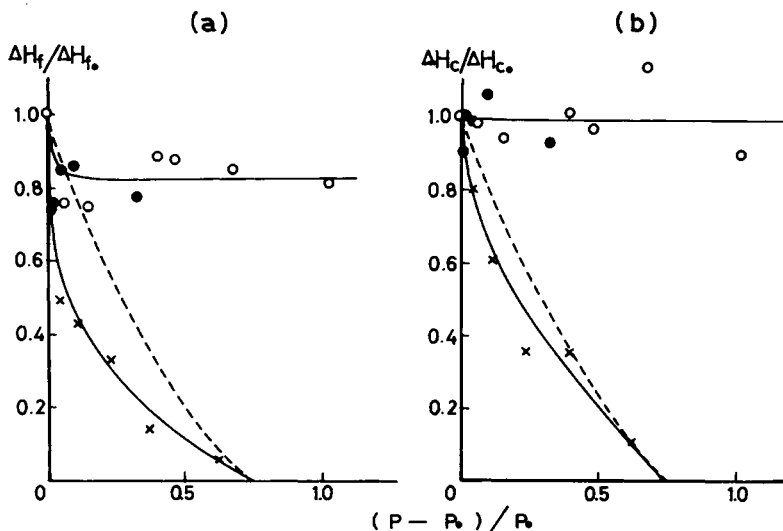Fig. 4. DSC thermograms of PE and NY; scanning speed, 5°C/min.

Fig. 5. Relative heat of fusion (a) and that of crystallization (b) of polyethylene-g-vinyl acetate and poly(ethylene-co-vinyl acetate): (O) PE-g-VAC prepared by liquid-phase grafting; (●) PE-g-VAC prepared by vapor-phase grafting; (X) EVA; (- - - -) calculated value for EVA.

The relative heat of fusion or crystallization, which can be calculated from the thermogram area, is directly proportional to the degree of crystallinity. Because the grafted branches are amorphous, the calibrated area divided by $(1 + G)$, where G pertains to the extent of grafting, represents the heat of fusion or crystallization per an amount of the backbone polymer in the grafted polymer. Therefore, $\Delta H_f / \Delta H_f^0$ or $\Delta H_c / \Delta H_c^0$ represents the relative change in the degree of crystallinity by the grafting, where ΔH_f and ΔH_c are the heat of fusion and that of crystallization, respectively, corrected for the extent of grafting as above; and ΔH_f^0 and ΔH_c^0 pertain to those of the ungrafted backbone polymer, respectively.

Usually, the heat of fusion does not coincide with that of crystallization for the identical sample, and instead tends to have a lower value than that of crystallization in PE-g-VAC (Fig. 5). It indicates that the grafted chains substantially influenced the crystallinity of the backbone polymer, but that the effect was eliminated when the crystals were melted and recrystallized.[7] The separation of the occluded homopolymer did not bring about any significant change in the heat of fusion or crystallization.

To examine the applicability of the above way of measuring the crystallinity change, the relative heats of fusion and crystallization of the poly-(ethylene–co–vinyl acetate) (Evatate, Sumitomo Chemical Industries, Ltd., abbreviated EVA) were plotted against the ethylene–vinyl acetate ratio in Figure 5. On EVA, which is said to be the random copolymer, the relationship between the degree of crystallinity measured with x-ray diffraction and the composition was already reported by Kamath and Wake-
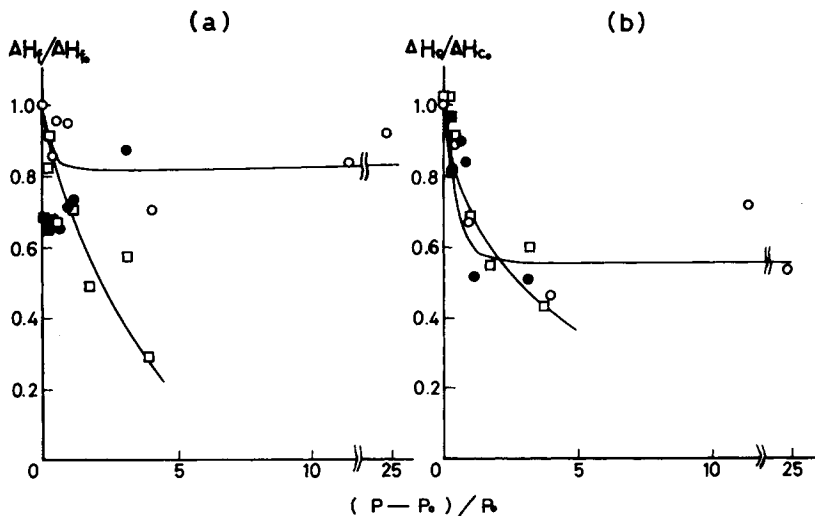
Fig. 6. Relative heat of fusion (a) and that of crystallization (b) of PE–g–MMA and PE–g–VPY: (O) PE–g–MMA and (□) PE–g–VPY prepared by liquid-phase grafting; (●) PE–g–MMA, and (■) PE–g–VPY prepared by vapor-phase grafting.

field.[8]   Their calculated values were plotted in Figure 5.   It is seen that the coincidence of the observed value with the calculated one is better in $\Delta H_c/\Delta H_c^0$, and the depression of the heat of fusion appears to be more than expected from the degree of crystallinity, that is, the heat of fusion is affected more profoundly by the grafting.

Similar phenomena were observed on PE–g–VAC.   When Figure 5a is compared with Figure 5b, $\Delta H_f/\Delta H_f^0$ is lowered at the initial stage and then stays almost unchanged with increasing extent of grafting, whereas $\Delta H_c/\Delta H_c^0$ stays constant inspite of the increase in the extent of grafting.   The above results would show that the random copolymerization of VAC decreases the relative crystallinity, whereas the grafting of VAC does not influence the crystallinity substantially.   The melting point also is lowered profoundly in random copolymer with composition, but it does not vary in graft copolymer.

The decrease in the heat of fusion observed on the grafted film at a low degree of grafting seems to be difficult to explain.   Perhaps there exist some regions very feasible to be destroyed by grafting, or it would be more plausible that the change of crystalline morphology is induced by the swelling owing to the sorption of monomer.

The results on PE–g–MMA were somewhat different, as is shown in Figure 6, although the extents of grafting were much higher than those of PE–g–VAC.   The relative heat of crystallization was smaller than that of fusion.   The grafting lowered the relative heat of fusion and crystallization at low extent of grafting, but the further increase in grafting did not induce a big change in crystallinity.
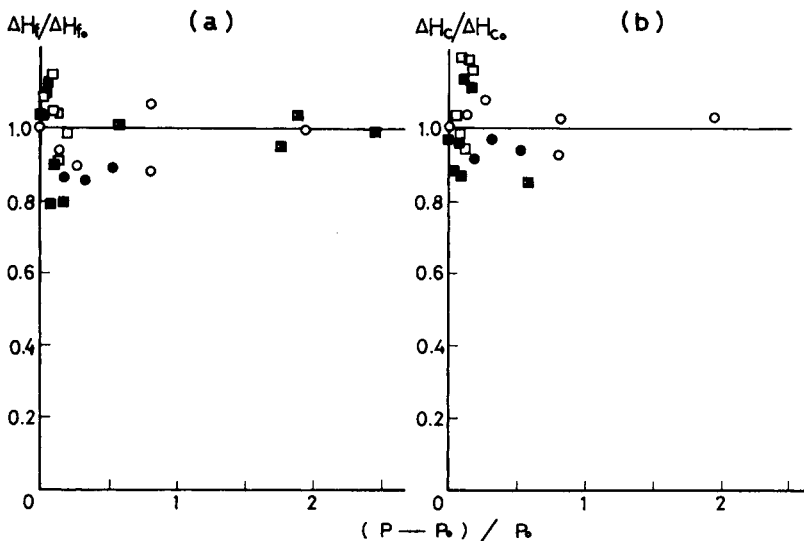
Fig. 7. Relative heat of fusion (a) and that of crystallization (b) of NY–g–MMA and NY–g–VPY: (O) NY–g–MMA and (□) NY–g–VPY prepared by liquid-phase grafting; (●) NY–g–MMA and (■) NY–g–VPY prepared by vapor-phase grafting; (⊠) NY–g–VPY prepared by preirradiation grafting.

On the other hand, the grafting of VPY has lowered the crystallinity of PE considerably. Both the relative heat of fusion and that of crystallization decreased with the increase in the extent of grafting. Therefore, the effect of grafting on the backbone polymer differs according to the kind of monomer.

Such difference in the effect of grafting is not manifested in the case of grafting on NY in Figure 7. Some of the NY–g–VPY were prepared by the preirradiation technique, because it was difficult to attain high extent of grafting by the simultaneous irradiation techniques. It seems that NY–g–MMA and NY–g–VPY retained the original degree of crystallinity, as far as the melting behavior was concerned, in spite of high extent of grafting.

As for the grafting method (vapor-phase grafting or liquid-phase grafting), no significant difference in the effect of crystallinity were observed.

The x-ray diffraction angle of the grafted film was almost the same with that of the original one, and the change on the relative intensity was insignificant. It seemed to be inadequate to discuss the effect of grafting on the crystallinity from these values.

Change in Water Vapor Permeability with Grafting

Figure 8 shows the results of water vapor permeability measurement on PE–g–MMA, PE–g–VAC, and NY–g–MMA. Since the films of higher grafting extent were stiff, the measurements were confined to the films of low grafting extent. The grafting naturally causes thickening of the film,
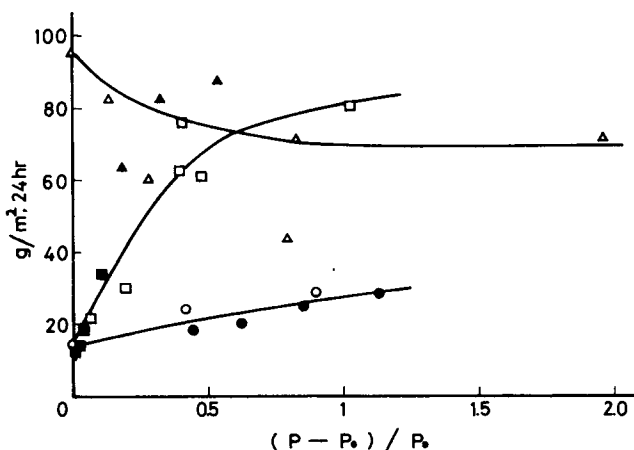
Fig. 8. Water vapor permeability of PE–g–MMA, PE–g–VAC, and NY–g–MMA films; 40°C, R.H. 90%: (O) PE–g–MMA, (□) PE–g–VAC, and (△) NY–g–MMA prepared by liquid-phase grafting; (●) PE–g–MMA, (■) PE–g–VAC, and (▲) NY–g–MMA prepared by vapor-phase grafting.
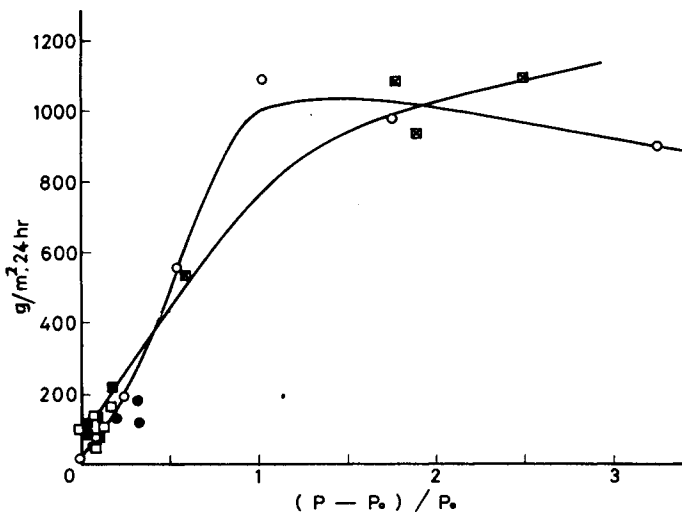

Fig. 9. Water vapor permeability of PE–g–VPY and NY–g–VPY films; 40°C, R.H. 90%: (O) PE–g–VPY and (□) NY–g–VPY prepared by liquid-phase grafting; (●) PE–g–VPY and (■) NY–g–VPY prepared by vapor-phase grafting; (☒) NY–g–VPY prepared by preirradiation grafting.

but the correction regarding the thickness change was not performed because the films might be inhomogeneous along the section. Uniform increase or decrease in permeability was observed, though the change was minor. The minimum permeability was not found in these systems as was reported elsewhere.[9]

Figure 9 shows the permeability changes on PE–g–VPY and NY–g–VPY. The tremendous increase observed is due partly to the hydrophilic
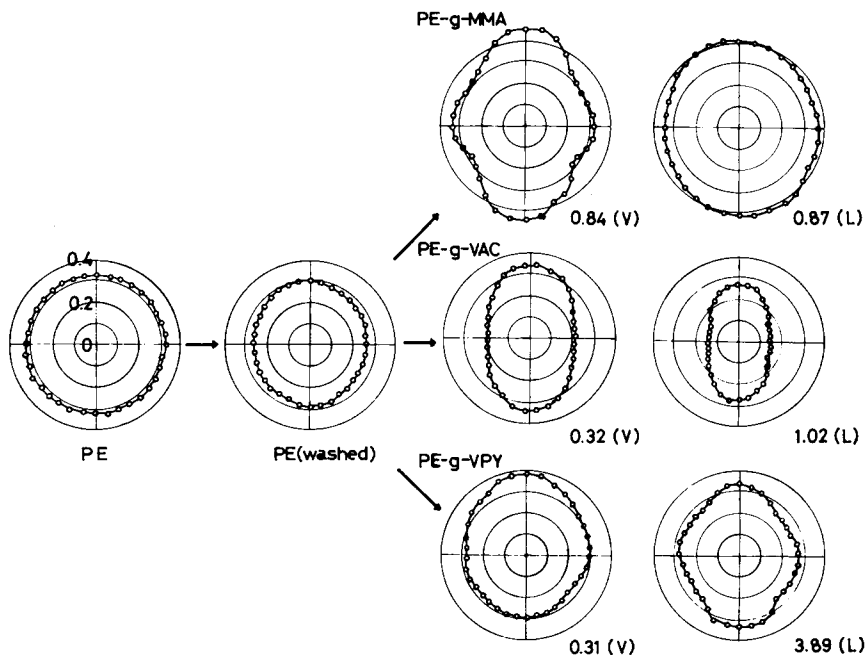
Fig. 10. Angular distribution of degree of polarization of fluorescence on grafted PE films. Extent of grafting, $(P - P_0)/P_0$, is shown under each figure together with the grafting method: (V) vapor-phase grafting; (L) liquid-phase grafting.

nature of the grafted poly-VPY, because the water sorption was found to increase proportionally to the square of the extent of grafting. But besides these, the effect of the decrease of crystallinity should be considered. As is well known, the permeability coefficient P is given by the solubility coefficient S multiplied by the diffusion coefficient D, where S is said to be proportional to the fraction of amorphous region, and D also increases correspondingly. Lasoski and Cobbs[10] reported that the water vapor permeability of semicrystalline polymer occurs through amorphous regions and increases directly as the square of the amorphous volume fraction. In the case of graft copolymer, however, the circumstances become more complicated, as the value of S or D of the grafted branch should differ from that of the backbone polymer. Nevertheless, as far as grafting is concerned, the major additional factor affecting the permeability should be the crystallinity change of the backbone polymer and the extent of advance of the grafting reaction from the surface to the inner part of the film.[11]

From the results shown in Figures 8 and 9, it is seen that the grafted branch did not play the role of "filler," and instead contributed to the transmission of water molecules inspite of the film thickening. This means that the grafting reaction proceeded into the matrix of the backbone polymer. Moreover, the abnormally high degree of increase in permeability observable on PE–g–VPY (more than 100 times at its most)

seems to be contributed by the decrease of crystallinity, because in NY–g–VPY, where almost no change in crystallinity was observed throughout the range of grafting, the increase is remarkable but not so high (about 10 times) compared with PE–g–VPY.

Using PE–g–VPY and NY–g–VPY, the qualitative dialysis tests in water were performed on several dialyzates. Ungrafted PE or NY was not able to act as a dialyzer, whereas the grafted films passed sodium chloride, urea, and sucrose very easily, and the order of ease accorded to the molecular weight of the dialyzate, but those resisted the Congo Red completely.

Change in Molecular Orientation with Grafting

Figures 10 and 11 show the angular distribution of polarization of fluorescence on the grafted PE and NY films. PE originally has a random distribution in the plane, but by the grafting came to resemble the uniaxial distribution; which means the amorphous region that interposes between the crystalline regions was stretched and forced to orient to one direction by the intervening of the grafted polymer. It was also observed that the surface of the film as well as the thickness increased with increasing extent of grafting. On NY films in Figure 11, the effect of grafting is much ob-
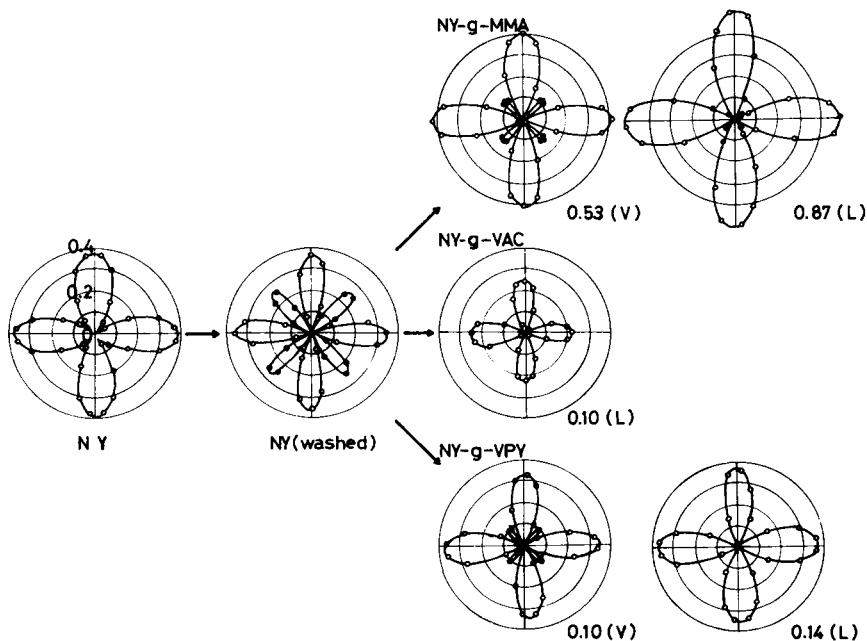

Fig. 11. Angular distribution of degree of polarization of fluorescence on grafted NY films. Extent of grafting, $(P - P_0)/P_0$, is shown under each figure together with the grafting method: (V) vapor-phase grafting; (L) liquid-phase grafting; (O) positive value; (●) negative value.

scured, but the heterogeneous increase of polarization was observed in a few cases.

No data have been obtained yet in this experiment on the relationship between the changes brought about on the orientation and permeability of the film. So far as reported, the relationship is complicated in each case, but generally the orientation seems to have almost no effect on the water vapor permeability.[10]

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