

Interferometric Method for Determining the Distribution of Graft Concentration in Radiation-Induced Graft Copolymer

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INTRODUCTION

During the past few years considerable work has been done on the formation of high energy radiation-induced graft copolymers. Yet there remain many questions to be answered before any mechanism for graft copolymerization can be postulated. Formation of graft copolymers usually involves the diffusion of monomer across a phase boundary between a monomer source and a polymeric material. The kinetics of monomer diffusion and its simultaneous reaction with active sites created throughout the polymer in a radiation field, and the Trommsdorff effect will be understood by analyzing the effects of dose rate, film thickness, monomer concentration, and temperature on the graft composition across the phase boundary. Furthermore, properties of the graft copolymer, such as dielectric loss, tensile strength, adhesion, permeability, and dyeability, will depend not only upon the overall graft concentration but also upon the transversal distribution of graft concentration.

It appears, therefore, of great interest and of practical value to determine the composition of graft copolymer across the section to see if the grafting effect is uniform throughout the entire volume, merely a surface effect, or whether there is produced a gradient from surface to the center of the specimen. Ballantine et al.¹ had observed the inhomogeneity of graft copolymer qualitatively from polarized and phase contrast photomicrographs.

The study presented here was undertaken with the objective to estimate the distribution of graft concentration in radiation-induced polypropylene-styrene graft copolymer. Microinterferometry was developed as a quantitative method. The observed results are discussed.

EXPERIMENTAL PROCEDURE

Materials

Polypropylene-styrene graft copolymer films were prepared by simultaneous γ -irradiation technique: polypropylene films (0.1-0.5 mm. thick)

immersed in styrene-methanol solution (20:80) were irradiated *in vacuo* at 50°C. by 4,000 curies from a Co^{60} source. Graft copolymer films prepared at dose rate of 7.4×10^4 r./hr. for 5 hr. were designated as film I, 1.7×10^4 r./hr. for 8 hr. were film II, and 7.4×10^3 r./hr. for 8 hr. were film III. Immediately after completion of the irradiation the ampule containing the irradiated polymer film was broken, and the contents were poured into the cold methanol saturated with hydroquinone to avoid post-irradiation effect. To remove occluded styrene homopolymer within the film, it was subjected to Soxhlet extraction with hot benzene, for approximately 20 hr. to constant weight. The overall graft concentration in the film was usually obtained from the equation

$$G \% = [(W_f - W_i)/W_f] \times 100 \quad (1)$$

where W_i and W_f are the initial and final weights of the film, respectively. A strip of the graft film, which was embedded in a block of low melting paraffin wax, was cut in a direction transverse to the surface of the film with a microtome. A cross section 10–20 μ in thickness was used as a sample.

Microinterferometer

The schematic diagram of the microinterferometer is shown in Figure 1. A parallel beam of monochromatic light from the sodium lamp L incident upon two silvered glass plates M_1 , M_2 between which a sliced polymer section S is held, is directed by a collimator and received by a microscope in which the localized interference fringes are observed. An immersion liquid was used in order to eliminate the scattering of light at the polymer surface and to obtain a clear microphotograph. Even if the immersion

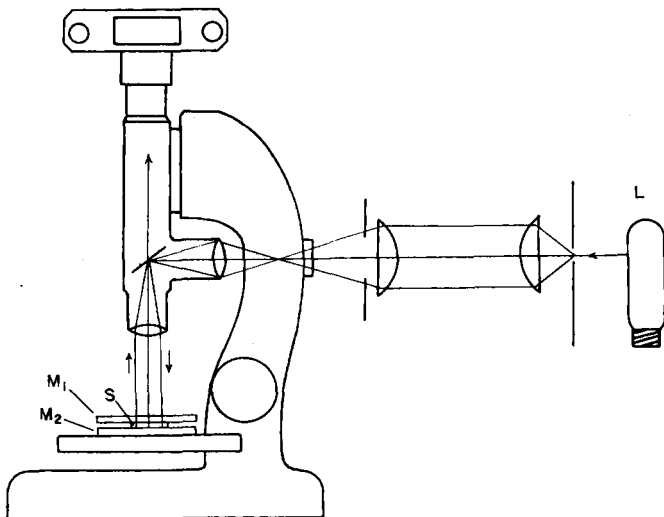


Fig. 1. Schematic diagram of microinterferometer.

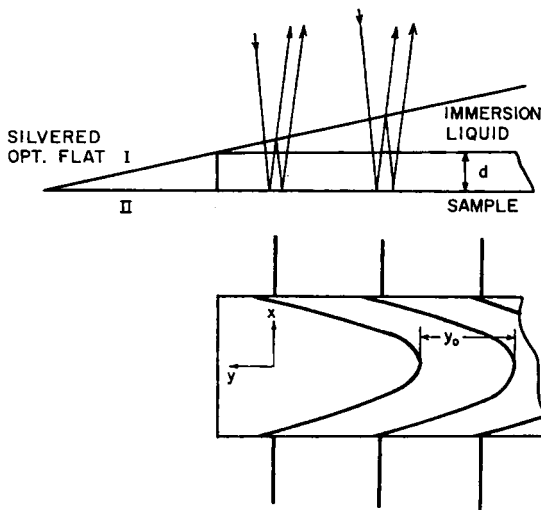


Fig. 2. Interference fringe of reflected rays.

liquid is not used, the same features of the fringe are obtainable except that the striations on the surface will disturb the appearance of the fringe.

Equation (2) is valid from the geometry of optical path (Fig. 2).

$$n(x) = n_0 + f(x)/d \quad (2)$$

where

$$f(x) = (\lambda/2)y(x)/y_0$$

and where $n(x)$ is the refractive index of the sample at distance x through the sample measured from the midpoint, n_0 is the refractive index of the immersion liquid, $y(x)$ is the curve of the fringe, where the coordinate $y = 0$ is set at the same fringe in background, y_0 is the distance between the neighboring fringes, d is the thickness of the sliced sample, and λ the wavelength of the used monochromatic light.

The thickness of the sliced sample can be measured accurately by the interferometric method by using two different immersion liquids whose refractive indices are known. According to eq. (2),

$$d = [f_1(L/2) - f_2(L/2)]/(n_{02} - n_{01})$$

where n_{01} , n_{02} are the refractive indices of the two immersion liquids, and $f_1(L/2)$, $f_2(L/2)$ are observed optical drifts of fringe at the phase boundary of sample in each measurement.

A correlation between the local graft concentration and refractive index was obtained by a plot of overall graft concentration [from eq. (1)] against refractive index (measured by the Becke line method), where a series of thin films (0.03 mm. thick) was used, the grafting being assumed to extend uniformly throughout the film. A linear relationship is shown within the

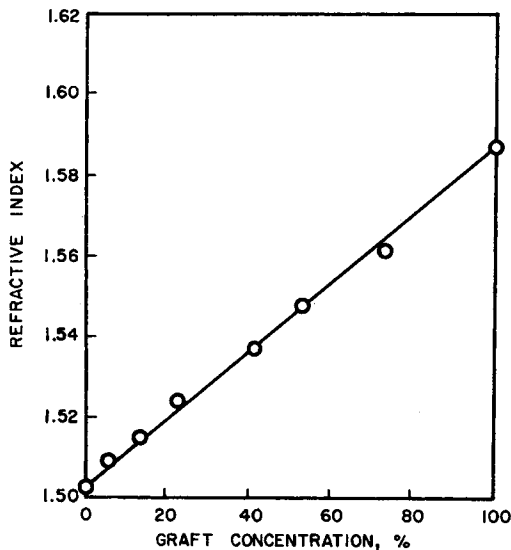


Fig. 3. Correlation between refractive index and graft concentration.

experimental uncertainty of the measurements (Fig. 3). The composition of polypropylene-styrene graft copolymer is, therefore, expressed by

$$\begin{aligned}
 c(x) &= (n(x) - n_p)/(n_s - n_p) \\
 &= [(n_0 - n_p) + f(x)/d]/(n_s - n_p)
 \end{aligned}
 \quad (3)$$

where n_s and n_p are the refractive indices of polystyrene and polypropylene, respectively.

EXPERIMENTAL RESULTS

Since polystyrene has a higher refractive index than polypropylene, the refractive index as a function of depth from the surface will give an indication for the graft composition of polypropylene-styrene graft copolymer. Figure 4 taken under polarized light, shows inhomogeneity of the graft copolymer qualitatively. As a preliminary experiment, the section was cut at one end diagonally and the refractive indices were measured along the phase boundary by the Becke line method. This was a rather tedious task, because repetitious measurements with a series of immersion liquids are necessary to obtain a distribution curve.

In order to visualize directly the transversal distribution curve of graft concentration, microinterferometry was applied. Figure 5 is a microinterferometric picture of a sample of unirradiated polypropylene for the purpose of comparison. As the feature of the fringe in the sample is the same with that in the background, uniformity of the refractive index throughout the sample is indicated. Figure 6 shows sections of graft copolymers formed by the simultaneous irradiation technique. Obvious

gradients of the refractive index from surface to the center of the specimens are observed from the localized fringes. Distributions of the graft concentration across the sections are calculated by the application of eq. (3). They are shown in Figure 7. The result is in good agreement with that obtained by the Becke line method.

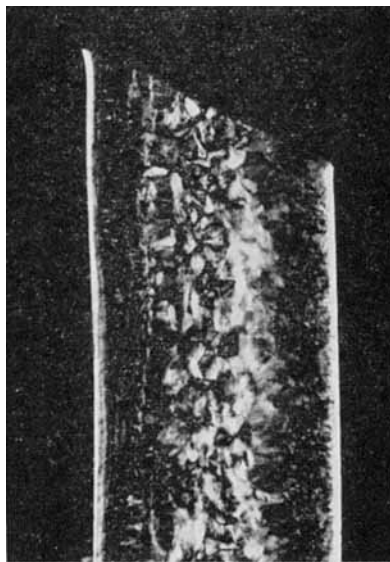


Fig. 4. Film III (polarized). Grafted at 7.4×10^3 r./hr. for 8 hr. at 50°C . in styrene-methanol solution (20:80); $L = 0.34$ mm., $G = 37\%$.

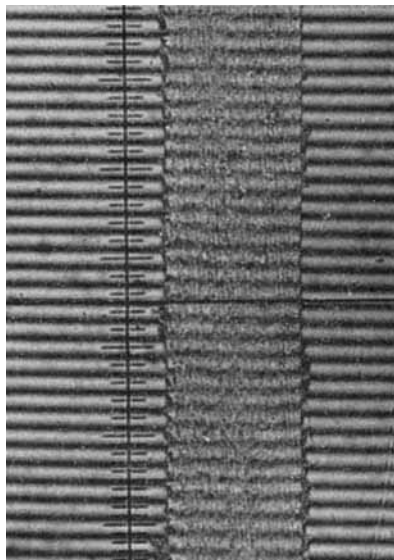
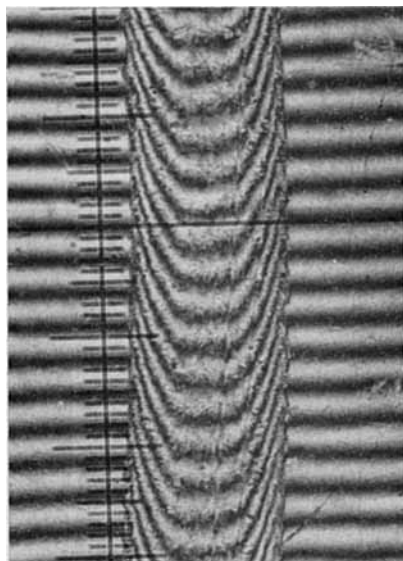
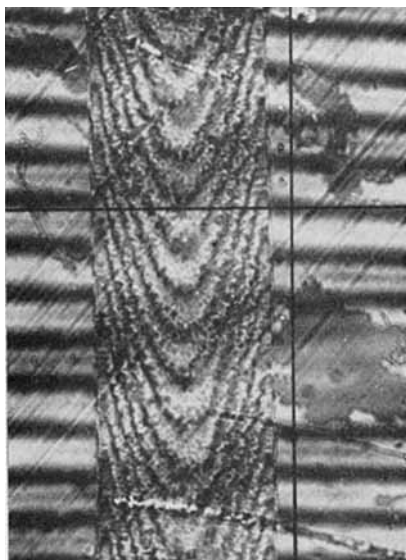


Fig. 5. Unirradiated polypropylene film.



(a)



(b)

Fig. 6. (a) Film I, grafted at 7.4×10^4 r./hr. for 5 hr. at 50°C . in styrene-methanol solution (20:80); $L = 0.35$ mm., $G = 34\%$. (b) Film II, grafted at 1.7×10^4 r./hr. for 8 hr. at 50°C . in styrene-methanol solution (20:80); $L = 0.35$ mm., $G = 43\%$.

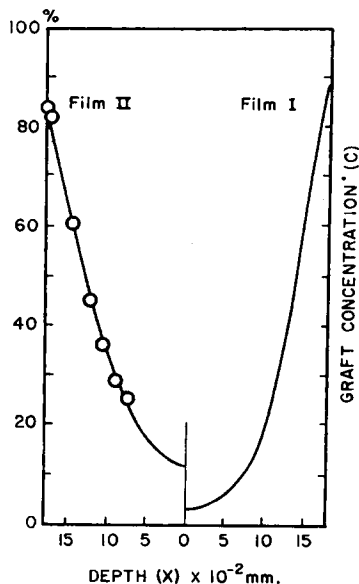


Fig. 7. Distribution curves of graft concentration in films I and II: (O) measured by the Becke line method; (—): calculated from eq. (3).

DISCUSSION

Effect of Dose Rate on the Graft Composition

In the case of grafting by the simultaneous irradiation technique, a process of monomer diffusion accompanied by an immobilizing reaction with active sites created by γ -irradiation in the parent polymer can be considered. The kinetic equation of the process is described by²⁻⁴

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x}(D \frac{\partial m}{\partial x}) - kI^{1/2}m \quad (4)$$

where m is the concentration of diffusing monomer at distance x through the specimen measured from the midpoint, and at time t . D is the diffusion coefficient, and I the radiation intensity. The grafting rate constant is $k = k_p/(2k_t)^{1/2}$, and k_p , k_t are the propagation and bimolecular termination rate constants, respectively.

The calculations are based on the assumptions that (1) the diffusion coefficient is constant, although nature of the diffusion coefficient for styrene in the irradiated polymer may be considerably more complicated, e.g., concentration-dependent;⁵ (2) a steady state of monomer distribution exists in the film; and (3) the grafting rate constant is invariable throughout the film (this is not a valid assumption, and it will be discussed later).

Monomer concentration in the film is expressed by

$$m(x) = m_s \cosh(x/L^*) / \cosh(L/2L^*) \quad (5)$$

Graft composition is obtained by the use of the equation,

$$dc(x)/dt = kI^{1/2}m(x)$$

It follows

$$c(x) = c_s \cosh (x/L^*) / \cosh (L/2L^*) \quad (6)$$

where

$$c_s = kI^{1/2}m_s t$$

and m_s is the monomer concentration at the surface of film. L is the thickness of the graft film, and $L^* = (D/k)^{1/2}I^{-1/4}$; the thickness of the effective grafting layer is inversely proportional to the $1/4$ -th power of dose rate. In Figure 7, graft compositions of two samples (films I and II) were shown. It is seen that distribution curves are catenary, and the grafting effect extends to the interior of film with the decrease in dose rate.

Effect of Film Thickness on the Overall Graft Concentration

The overall graft concentration is readily calculated from eq. (6):

$$\begin{aligned} G(L) &= 1/L \int_{-L/2}^{L/2} c(x) dx \\ &= c_s(2L^*/L) \tanh (L/2L^*) \end{aligned} \quad (7)$$

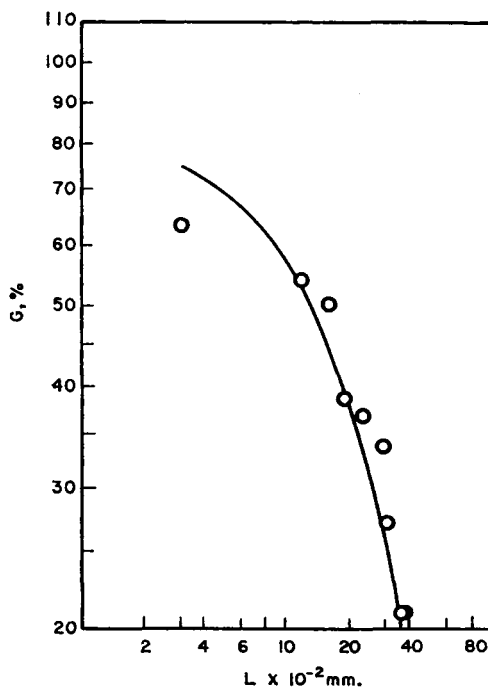


Fig. 8. Logarithmic plot of overall graft concentration against film thickness for film I: (O) measured by eq. (1); (—) calculated from eq. (7), where $km_s = 12 \times 10^{-2}\%$ (r./hr.) $^{-1/2}$ hr. $^{-1}$; $2L^* = 0.09$ mm.

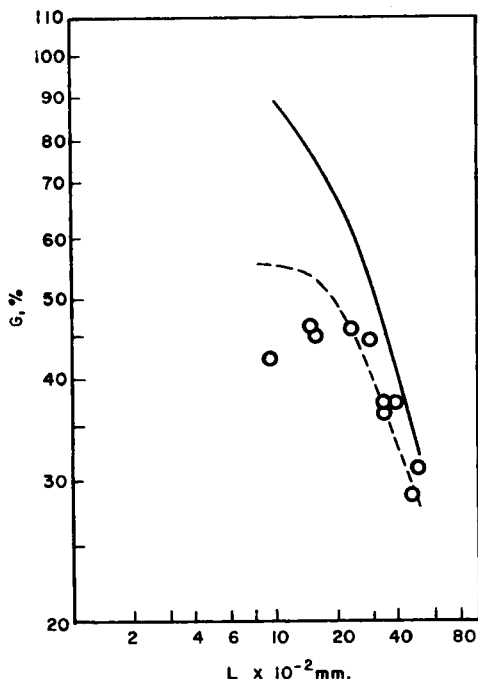


Fig. 9. Logarithmic plot of overall graft concentration against film thickness for film III: (O) measured by eq. (1); (—) calculated from eq. (7), where $km_s = 14 \times 10^{-3}\%$ (r./hr.) $^{-1/2}$ hr. $^{-1}$; $2L^* = 0.16$ mm. (---) calculated from eq. (11).

A logarithmic plot of the overall graft concentration against film thickness is presented in Figure 8. Experimental results of samples of film I are in fair agreement with eq. (7). Figure 9 is the same plot for a series of samples of film III. In this case, however, with the decrease in film thickness, deviation from eq. (7) becomes more pronounced, and eventually a decrease in the overall graft concentration appears. In other words, the higher rate of overall grafting is obtained with the thicker film in this range of film thickness, as Chen et al.⁶ had observed in the case of polyethylene-styrene graft copolymer. There appears to be a possibility that the previously mentioned assumptions are not always valid and unexpected distribution of the graft concentration appears in some cases.

Retardative Effect Near the Surface

Distribution of the graft concentration in a sample of film III was examined by the interferometric method. Results are shown in Figure 10. An apparent retardative effect on grafting is observed in the vicinity of the surface. The effect appears in every sample of film III over a wide range of film thickness as shown in Figure 11. On the other hand, in the case of film II, the effect appears with the decrease in film thickness as shown in Figure 12. For simultaneous γ -irradiation technique under the same con-

dition previously described, the effect becomes apparent when the grafting is performed at lower dose rate or with thinner film. The effect is not due to oxidation, because the effect is not eliminated even if the grafting

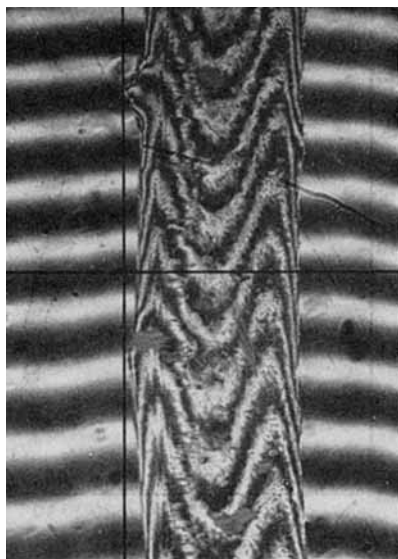


Fig. 10. Film III, grafted at 7.4×10^3 r./hr. for 8 hr. at 50°C . in styrene-methanol solution (20:80), $L = 0.34$ mm., $G = 37\%$.

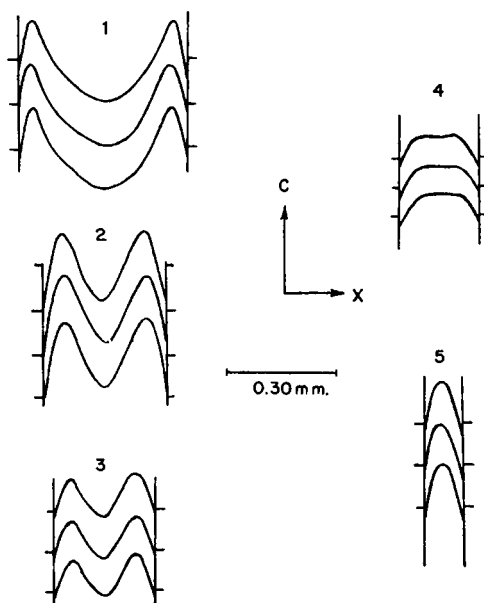
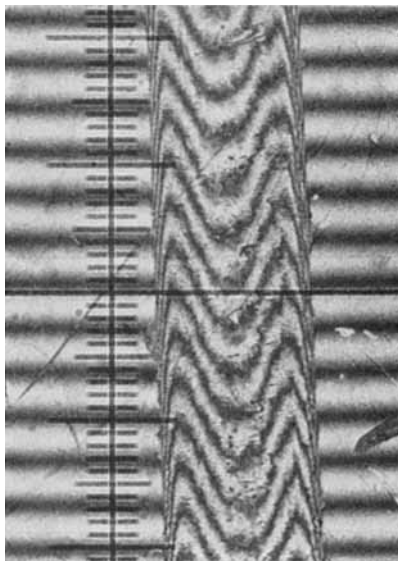


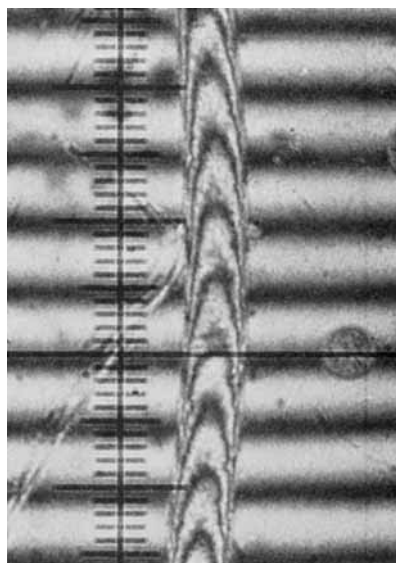
Fig. 11. Features of interference fringe of film III for various film thicknesses.

is performed in a higher vacuum. In this sense, it is the embedded grafting other than that observed by Henglein et al.⁷

The anomalous phenomenon can be interpreted by considering that if the graft reaction is diffusion-controlled the grafting rate may be lower in the vicinity of the surface where the monomer concentration is higher due



(a)



(b)

Fig. 12. Film II, grafted at 1.7×10^4 r./hr. for 8 hr. at 50°C . in styrene-methanol solution (20:80): (a) $L = 0.30$ mm., $G = 54\%$; (b) $L = 0.12$ mm., $G = 60\%$.

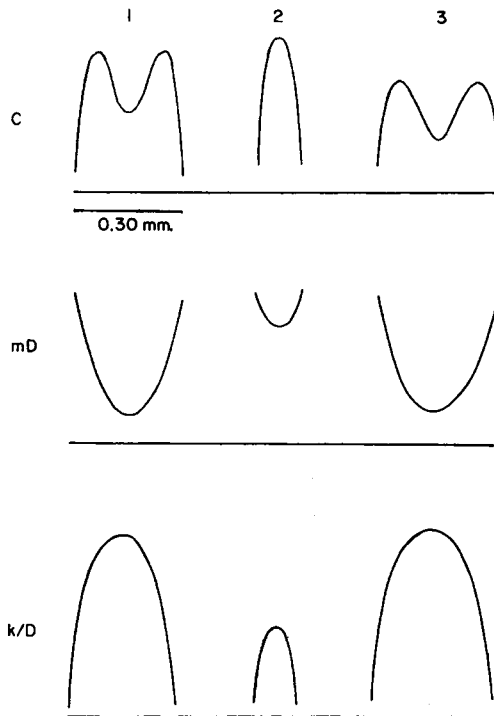


Fig. 13. Graft concentration, monomer concentration, and grafting rate constant as functions of depth: (1, 2) film II; (3) film III.

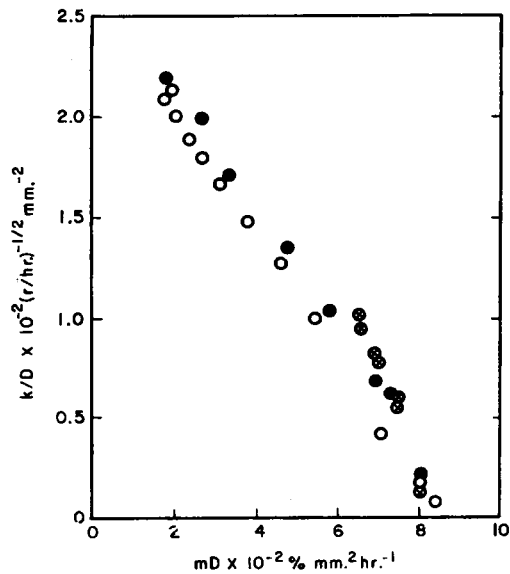


Fig. 14. Plot of grafting rate constant against monomer concentration: (O), (⊗) film II; (●) film III.

to the Trommsdorff effect as Chen⁸ had pointed out. It is of interest to examine the values of grafting rate constant for various monomer concentrations in the film. The calculation is based on the assumptions that (1) the grafting rate constant varies from surface to the center of film, (2) the diffusion coefficient of styrene is invariant throughout the film, and (3) the distribution of graft concentration is expressed by

$$c(x) = kI^{1/2}tm(x,k) \quad (8)$$

By substituting eq. (8) into eq. (4),

$$m(x,k) = (1/Dt) \int_0^x \int_0^x c(x,k) dx dx + m_0 \quad (9)$$

is obtained in a steady state, where m_0 is the value of m at $x = 0$. Therefore,

$$c/I^{1/2}t = (k/D) [(1/t) \int_0^x \int_0^x c(x,k) dx dx + m_0 D] \quad (10)$$

is valid. By plotting $c/I^{1/2}t$ against $\iint c dx dx/t$, values of $m_0 D$, and therefore mD and k/D , are found. The indicated integrations were performed numerically for a variety of the graft composition curves obtained by the interferometric method. They are illustrated in Figure 13. A plot of the grafting rate constant against monomer concentration is shown in Figure 14. Although it is still in question whether the relation is entirely due to the Trommsdorff effect, it is seen that the grafting rate constant becomes low when monomer concentration in the film increases, and consequently the retardative effect extends to the interior with the decrease in dose rate and film thickness.

In the latter case, however, decrease in film thickness has little influence on monomer distribution near the surface until the film becomes so thin ($\sim 2L^*$) that diffusing monomer from the opposite side of the surface affects the distribution. From this consideration, behavior of the overall graft concentration as a function of film thickness will be expressed by

$$G(L)_{\text{corr}} = G(L) - (Q/L) \quad (11)$$

where $G(L)_{\text{corr}}$ is the overall graft concentration corrected for the retardative effect, $G(L)$ is the value obtained from eq. (6) putting k as a constant, i.e., not considering the retardative effect, and Q as a constant. The corrected values were represented in Figure 9, where the value of Q was determined from the area between the distribution curve of the graft concentration [for eq. (6)] and the experimental one obtained by using a planimeter.

Post-Irradiation Effect

After completion of the irradiation, a few of the films were allowed to continue in the state of grafting. It can be seen that an increase in the overall graft concentration is achieved by this (Fig. 15). The change in the graft distribution during standing periods subsequent to the irradiation was followed by the interferometric method (Fig. 16).

An increase in the amount of grafted styrene is observed in layers comparatively near the surface which extends progressively to the interior with the standing time. This will be understood by considering that the steady

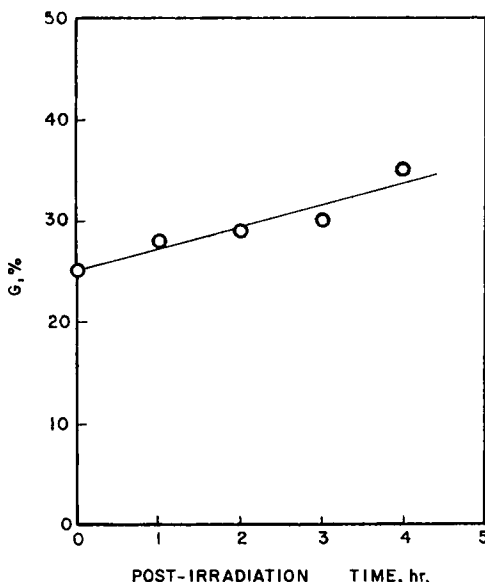


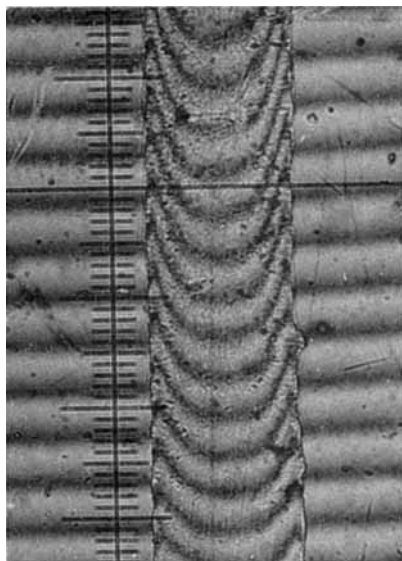
Fig. 15. Increase in overall graft concentration as a function of post-irradiation time at 50°C. Grafted at 4.2×10^4 r./hr. for 3 hr. at 50°C. in styrene-methanol solution (20:80).

state of monomer distribution is disturbed in the standing condition. As the monomer concentration in the film increases, the retardative effect appears and progresses to the interior of the film.

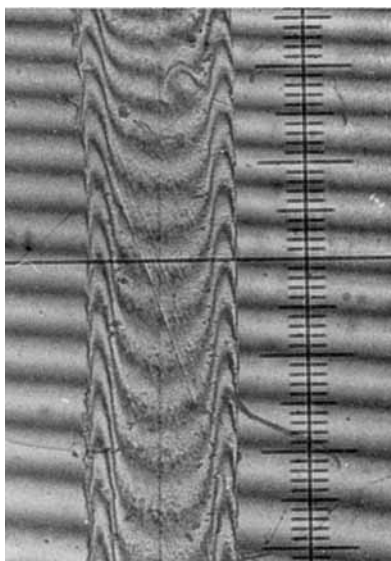
Accelerative Effect of Methanol

Odian et al.⁹ found that methanol accelerates grafting rate of styrene to polyethylene. They suspected that the grafts formed with undiluted styrene are mainly volumetric or homogeneous grafts, whereas the grafts formed with styrene-methanol solutions might consist, in large part, of surface grafts, but obtained volumetric grafts in all cases.

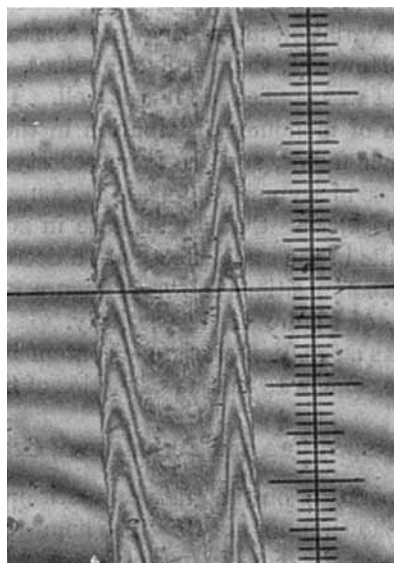
In this study, a similar accelerative effect of methanol on the overall rate of grafting is observed, as shown in Figure 17. To elucidate distribution of the graft concentration in films grafted with various styrene contents in outside styrene-methanol solution, the interferometric method has been applied. The results are shown in Figure 18. Each of the graft films shows distinctive features of the graft composition. It is seen that the grafting effect extends to the interior of the film (0.4 mm. thick), and simultaneously a retardative effect near the surface appears with an increase of styrene content in the outside solution. This can be interpreted



(a)



(b)



(c)

Fig. 16. (a) Immediately after grafting at 4.2×10^4 r./hr. for 3 hr. at 50°C . in styrene-methanol solution (20:80), $G = 25\%$; (b) after standing for 3 hr. at 50°C . $G = 30\%$; (c) after standing for 4 hr. at 50°C ., $G = 35\%$.

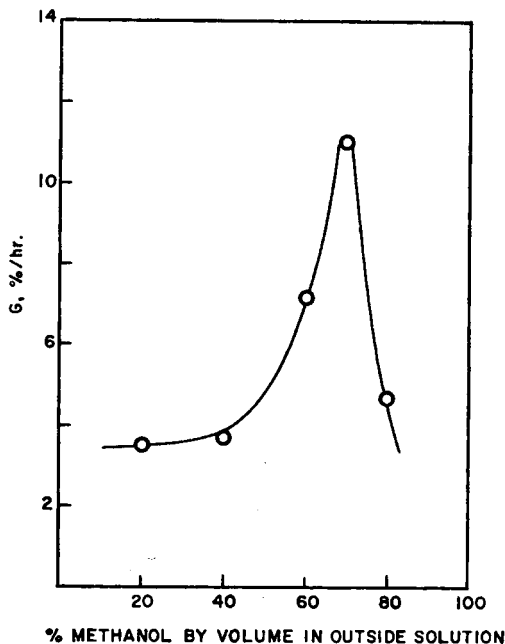


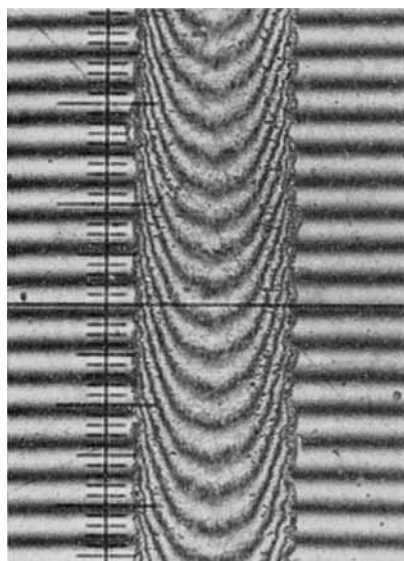
Fig. 17. Effect of methanol content in outside styrene-methanol solution on the overall rate of grafting under irradiation at 2.5×10^6 r./hr. at 50°C .

qualitatively by the variation in grafting rate constant in the film as previously described. However, the calculated values, where the same value of diffusion coefficient was applied, do not fit well. The discrepancy is due to further expansion of monomer distribution in the film than expected. It seems as if another factor, such as increased styrene solubility of the film^{5,9} with an increase of styrene content in the outside solution, plays an important role. Considering that an increase in styrene content of the outside solution results in the same effect with a decrease in film thickness, features of the graft compositions shown in Figure 18 can be compared to those in 1, 4, and 5 of Figure 11, respectively. Behavior of the overall graft concentration as a function of styrene content in the outside solution (Fig. 17) is, therefore, similar to that as a function of film thickness (Fig. 9).

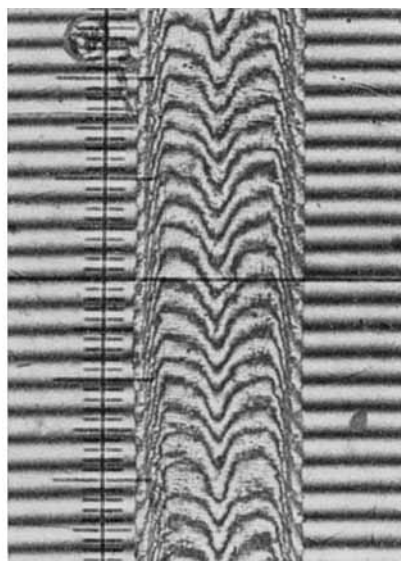
Effects of Temperature and Technique of Graft Formation

The effect of temperature on the graft composition is observed by comparing two samples shown in Figure 19. The homogeneity of graft composition increases with an increase in temperature, while the overall graft concentration decreases.

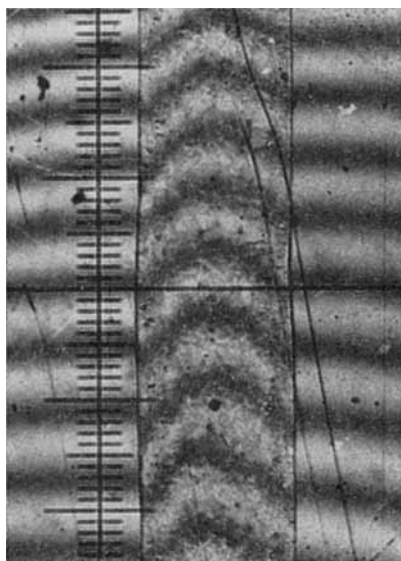
Furthermore, a difference in homogeneity occurs, depending on the technique of graft formation. Composition of the graft film formed by the technique of preirradiation in air is shown in Figure 20. The higher de-



(a)



(b)



(c)

Fig. 18. Grafted films at 4.2×10^4 r./hr. for 6 hr. at 50°C . in styrene-methanol at various volume ratios: (a) 20:80; (b) 30:70; (c) 80:20.

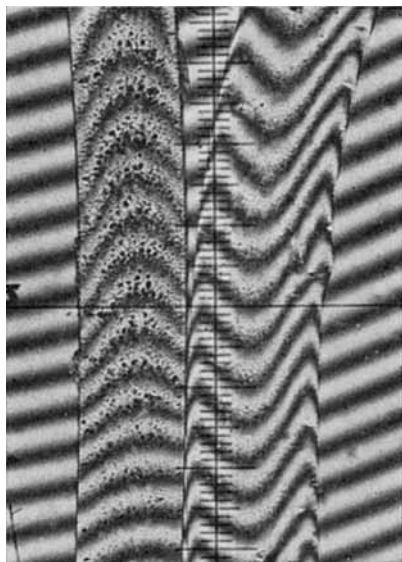


Fig. 19. Grafted films at 1.0×10^4 r./hr. for 6 hr. in styrene-methanol solution (20:80): (left) at 85°C ., $G = 21\%$; (right) at 50°C ., $G = 43\%$.

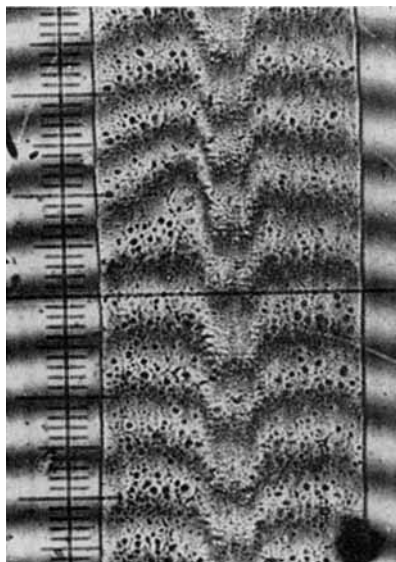


Fig. 20. Grafted film for 5 hr. at 100°C . in styrene-methanol solution (40:60), after irradiation at 1.7×10^5 r./hr. for 17 hr. in air; $L = 0.66$ mm., $G = 23\%$.

gree of homogeneity of the graft is indicated as Ballantine et al.¹ had observed.

CONCLUSION

It has been seen that the microinterferometric method is useful to clarify the distribution of graft concentration and to understand the mechanism involved. The method has also proved useful in routine examination of graft copolymer. The overall amount of grafting is determined, and a qualitative estimate of the grafts, i.e., surface, volumetric, and embedded grafts, is achieved by examining features of the fringes. The method could be applied to another appropriate combination of materials with different refractive indices, e.g., polytetrafluoroethylene-styrene or polyethylene-vinylidene chloride graft copolymers.

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Synopsis

Microinterferometry was applied as a quantitative method for determining the transversal distribution of graft concentration instead of the usual determination of an overall graft concentration of the radiation-induced polypropylene-styrene graft copolymer. Since polystyrene has a higher refractive index than polypropylene, the features of the interference fringe provide direct visualization of the distribution curve of graft concentration. The application of the method leads to clarify the effects of radiation dose rate, film thickness, monomer concentration, temperature, and grafting technique on the graft composition. A retardative effect on grafting appears in the vicinity of the surface, when the grafting is performed in lower radiation field and with thinner film. This is well explained by the variation in the grafting rate constant as a function of monomer concentration in the film. Furthermore, the post-irradiation effect and accelerative effect of methanol were followed. They act effectively to form the surface, volumetric, and embedded grafts. The method has also proved useful in routine examination for a qualitative estimate of the graft copolymer.

Résumé

On a appliqué la micro-intéférométrie comme méthode quantitative pour déterminer la distribution transversale de la concentration en greffes au lieu de la détermination habituelle d'une concentration globale en greffé au sein du copolymère greffage du polypropylène par le styrène induit par radiation. Étant donné que le polystyrène possède un indice de réfraction supérieur à celui du polypropylène, le caractère de la

frange d'interférence visualise la courbe de distribution de la concentration en greffé. L'application de la méthode permet d'éclaircir les effets de la vitesse de dose de radiation, de l'épaisseur du film, de la concentration en monomère, de la température et de la technique du greffage sur la composition du copolymère greffé. Un effet retardateur de greffage apparaît au voisinage de la surface, lorsque le greffage s'opère dans un champ de radiation plus faible et avec un film plus mince. Cet effet est bien expliqué par la variation de la constante de vitesse de greffage en fonction de la concentration en monomère dans le film. En outre on a suivi l'effet de la post-irradiation et de l'effet accélérateur du méthanol. Ils agissent effectivement pour former des copolymères greffés en surface, volumétriques et insérés. La méthode s'est également révélée utile dans des examens de routine pour obtenir une estimation qualitative du copolymère greffé.

Zusammenfassung

Zur quantitativen Bestimmung der transversalen Verteilung der Pfropfkonzentration an Stelle der üblichen Bruttopfropfkonzentrationsbestimmung am strahlungsinduzierten Polypropylen-Styrolpfropfcopolymeren wurden mikrointerferometrische Messungen herangezogen. Da Polystyrol einen höheren Brechungsindex als Polypropylen besitzt, lässt die Anordnung der Interferenzstreifen direkt die Verteilungskurve für die Pfropfkonzentration erkennen. Die Anwendung der Methode führt zu einer Klärung der Einflüsse von Strahlungsintensität, Filmdicke, Monomerkonzentration, Temperatur und Aufpfropfverfahren auf die Zusammensetzung der Pfropfpolymeren. Eine Verzögerung der Aufpfropfung tritt in der Nähe der Oberfläche auf, wenn die Aufpfropfung in einem niedrigeren Strahlungsfeld und mit dünneren Folien ausgeführt wird. Diese Erscheinung lässt sich auf Grund der funktionellen Abhängigkeit der Pfropfungsgeschwindigkeitskonstanten von der Monomerkonzentration in der Folie gut verstehen. Weiters wurden der Strahlungs-Nacheffekt und der Beschleunigungseffekt von Methanol untersucht. Ihre Wirkung besteht in der Bildung von Oberflächen-, Volums- und Einbettungspfropfungen. Die Method erwies sich auch als Routineprüfung zur qualitativen Bestimmung des Pfropfcopolymeren brauchbar.

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