

Fig. 3. Plots of $1 - ([\eta]_{\dot{\gamma}}/[\eta]_{\dot{\gamma} \rightarrow 0})$ vs. $(M[\eta]_{\dot{\gamma} \rightarrow 0}\dot{\gamma}/RT)^2$: (○) sample 66-3, polymerized at 60°C., $M_w = 42.7 \times 10^4$; (●) sample 66-1, polymerized at 60°C., $M_w = 29.8 \times 10^4$; (◐) sample 4, polymerized at 60°C., $M_w = 26.6 \times 10^4$; (◑) sample 5, polymerized at 60°C., $M_w = 24.8 \times 10^4$; (●) sample 66-2, polymerized at 60°C., $M_w = 17.5 \times 10^4$; (□) sample 68, polymerized at 30°C., $M_w = 38.5 \times 10^4$; (△) sample 36, polymerized at -10°C., $M_w = 12.0 \times 10^4$; (×) sample 31, polymerized at -30°C., $M_w = 19.8 \times 10^4$. Numbers on curves refer to polymerization temperature.

According to the relationship⁵

$$[\eta]_{\dot{\gamma}} = [\eta]_{\dot{\gamma} \rightarrow 0} \{1 - A(M[\eta]_{\dot{\gamma} \rightarrow 0}\dot{\gamma}/RT)^2 + \dots\} \quad (1)$$

the quantity $1 - ([\eta]_{\dot{\gamma}}/[\eta]_{\dot{\gamma} \rightarrow 0})$ should be proportional to $(M[\eta]_{\dot{\gamma} \rightarrow 0}\dot{\gamma}/RT)^2$. The application of eq. (1) to the results shown in Figure 2 is illustrated in Figure 3. The aforementioned proportionality is seen to hold very well, regardless of molecular weight, as indicated by the plots for the samples polymerized at 60°C. The proportionality constant A appears to depend remarkably on polymerization temperature.

Since it might be assumed that the stiffer the molecular chain, the more pronounced the non-Newtonian viscosity behavior, the proportionality constant A might be considered a measure of the stiffness of the chain. Therefore, it might be concluded that the lower the polymerization temperature of the original poly(vinyl acetate), the more stiff or extended the molecular chain of the poly(vinyl acetal) in the solution. This agrees well with data obtained from light-scattering studies.

References

1. Matsumoto, M., and Y. Ohyanagi, *J. Polymer Sci.*, **37**, 558 (1959).
2. Yang, J. T., *J. Am. Chem. Soc.*, **80**, 1783 (1958).
3. Motoyama, T., and S. Okamura, *Kobunshi Kagaku*, **8**, 321 (1951).
4. Wada, E., *J. Polymer Sci.*, **16**, 305 (1954); *J. Sci. Research Inst. Tokyo*, **47**, 149, 159 (1953).
5. Kuhn, W., and H. Kuhn, *Helv. Chim. Acta*, **28**, 1533 (1945); A. Peterlin and M. Cöpič, *J. Appl. Phys.*, **27**, 434 (1956); Y. Ikeda, *J. Phys. Soc. Japan*, **12**, 378 (1957).

MASAKAZU MATSUMOTO
YASUZI OHYANAGI

Research Laboratory
Kurashiki Rayon Company Ltd.
Sakazu, Kurashiki, Okayama, Japan

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Grafting of Acrylonitrile onto Polypropylene Films by a Preirradiation Method

It was reported by Chapiro¹ that polymer peroxides are formed in polypropylene during high energy irradiation in the air, and these peroxides, when heated in the presence of a monomer, decompose and initiate the polymerization of the monomer, forming a graft copolymer. In our paper, more detailed results of grafting of acrylonitrile on polypropylene films will be shown. Isotactic polypropylene (Moplen) powder was used as sample. The films (thickness, 0.12 mm.) were prepared by extruding the molten polypropylene in nitrogen. The degree of crystallinity was 75%. The films were irradiated in the air by γ -rays from a 1000-curie Co^{60} source at different intensities. The films (weight = p_0), preirradiated in the air, were heated in the presence of acrylonitrile monomer in glass ampoules at 80–135°C. After grafting, the films were immersed in a large volume of dimethylformamide at 110°C. after extraction

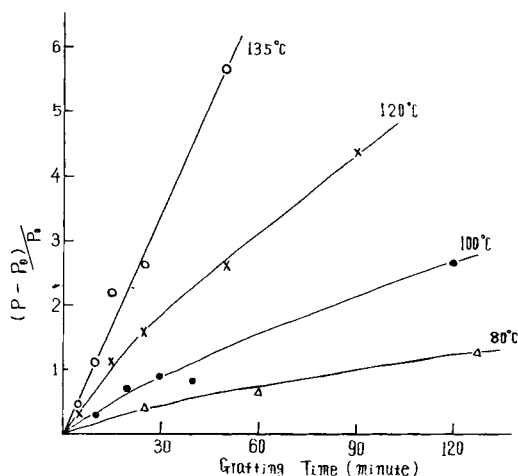


Fig. 1. Variation of $(P - P_0)/P_0$ as a function of time for various grafting temperatures at constant dose rate (3.0×10^5 r/hr.) and constant dose (1.4×10^6 r).

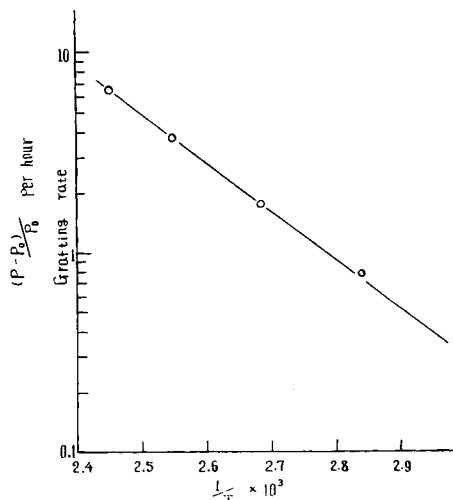


Fig. 2. A logarithm of the grafting rate for acrylonitrile as a function of $1/T$.

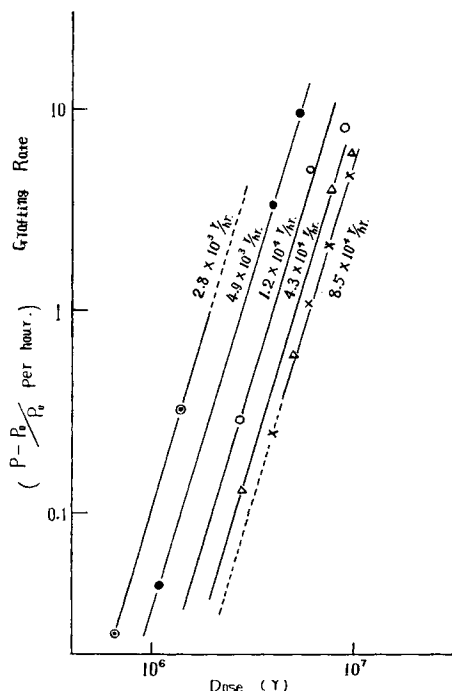


Fig. 3. The rate of grafting as a function of dose for different dose rates (log-log scale).

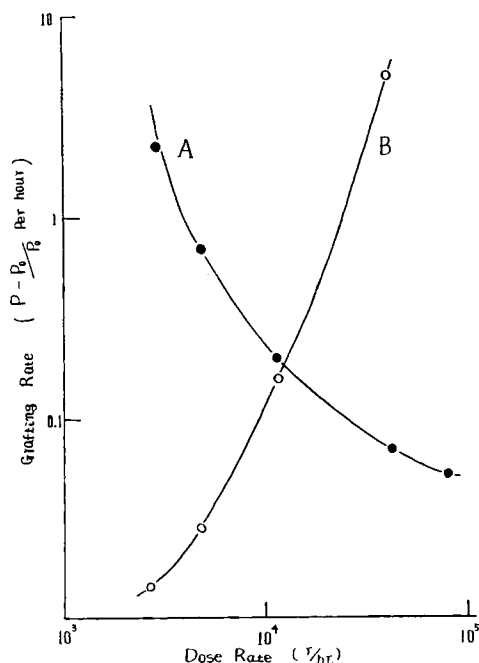


Fig. 4. Variation of grafting rate as a function of dose rate: (A) preirradiation dose of 2-5 Mr; (B) preirradiation of 200 hr.

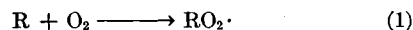
of a large amount of polyacrylonitrile homopolymer, then dried and weighed (weight = P). The grafting ratio $(P - P_0)/P_0$ was determined by measuring the change in weight due to grafting ($P - P_0$). In Figure 1, the grafting ratio is plotted as a function of reaction time at different temperatures for fixed preirradiation conditions.

The dose rate was 3.5×10^5 roentgen/hr., and the dose was 1.4×10^7 roentgen. It appears that the grafting ratio increases linearly with grafting time, at least up to 60 min. No indication of saturation was observed.

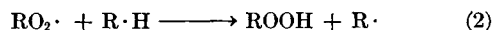
Figure 2 shows the logarithm of the hourly grafting rate $(P - P_0)/P_0$ as function of grafting temperature $1/T$ ($K.^{\circ}$) according to the results of Figure 1. The apparent activation energy of overall reaction was calculated to be 11.5 kcal. in this range of 80-135°C. Figure 3 shows the relation of initial grafting rate to preirradiated dosage at various dose rates. The grafting temperature was 135°C. It appears that at a fixed dose, the smaller the dose rate, the higher the grafting rate.

The facts indicate that in the following irradiation oxidation mechanism, the recombination reaction (4) occurred more at higher dose rate and that the diffusion of oxygen into the polymer film was the rate-determining factor.

Peroxidation



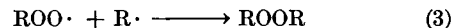
Transfer reaction



Chain peroxidation



Stabilization



Recombination



At any dose rate, the grafting rate V is proportional to the 3.4 power of the preirradiation dose R , that is, $V = KR^{3.4}$, indicating that considerable chain peroxidation (1') occurs during preirradiation.

This is shown very clearly in Figure 4, where grafting rate is plotted as function of dose rate for a constant preirradiation time of 200 hr. and for constant dose 2.5 Mr. The grafting temperature was 135°C. The rate of grafting is related to preirradiation intensity I according to $V = KI^{1.2-1.6}$, but the relation is not so strictly linear as that of polyethylene.²

References

1. Chapiro, A., *J. Polymer Sci.*, **29**, 321 (1958).
2. Chapiro, A., *J. Polymer Sci.*, **34**, 439 (1958).

HIROSHI SOBUE
YOSHIO TAZIMA
YOICHI SHIMOKAWA

Department of Applied Chemistry
Faculty of Engineering
University of Tokyo
Tokyo, Japan

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