

LETTERS TO THE EDITORS

**Non-Newtonian Viscosities of Poly(vinyl Acetal) Solutions**

In a previous letter<sup>1</sup> it was shown that the molecular dimensions of poly(vinyl acetal) in methyl ethyl ketone and in methyl isobutyl ketone solutions depend on the polymerization temperature at which vinyl acetate was polymerized to the original poly(vinyl acetate); that is to say, the lower the polymerization temperature, the more extended the molecular dimensions.

Recently Yang<sup>2</sup> has indicated that the non-Newtonian behavior of the viscosity of poly- $\gamma$ -benzyl-L-glutamate solution is remarkably affected by the configuration of the polypeptide, which is rodlike  $\alpha$ -helix in *m*-cresol and a random coil in dichloroacetic acid. On this basis we might expect a similar effect with poly(vinyl acetal) solutions, i.e., a correlation between the non-Newtonian viscosity and the polymerization temperature of the original poly(vinyl acetate).

In this letter, an experimental study of the non-Newtonian viscosity of poly(vinyl acetal) in methyl ethyl ketone solution will be described.

Samples used are listed in Table I. The method of preparation of the acetal samples was that of Motoyama and Okamura.<sup>3</sup> Non-Newtonian behavior of the viscosity in methyl ethyl ketone solution was followed in an inclined Ostwald-type viscometer proposed by Wada.<sup>4</sup> Three viscometers with different capillary diameters (0.314, 0.652, and 0.998 mm.) were used in order to cover a wide range of shear rates. The measured range was actually from  $1 \times 10^2$  to  $2 \times 10^3$  sec.<sup>-1</sup>.

TABLE I  
Samples Used in the Investigation and Values of the Constant A

Expt. no.	Polymerization temperature, °C.	Poly(vinyl acetal) molecular weight (by light scattering) MW $\times 10^{-4}$	Value of A in eq. (1) $\times 10^{20}$
66-2	60	17.5	4.0
5	60	24.8	
4	60	26.6	
66-1	60	29.8	
66-3	60	42.7	7.3
67	30	52.1	
68	30	38.5	18.2
34	-10	11.4	
36	-10	12.0	25.1
23	-30	19.3	
31	-30	19.8	
40	-30	21.1	

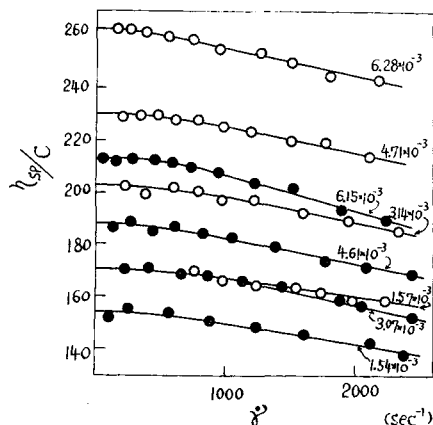


Fig. 1. Plot of  $\eta_{sp}/c$  against  $\dot{\gamma}$  for poly(vinyl acetal) in methyl ethyl ketone at 30°C.: (O) sample 4, polymerized at 60°C.,  $M_w = 26.6 \times 10^4$ ; (●) sample 40, polymerized at -30°C.,  $M_w = 21.1 \times 10^4$ . Numbers on the curves are solution concentrations in g./ml.

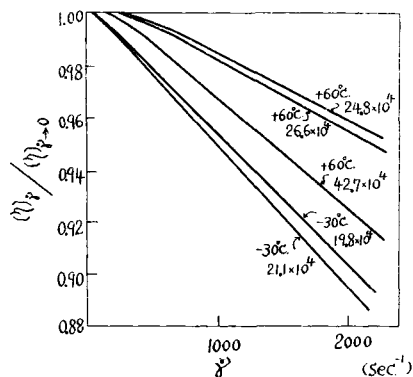


Fig. 2. Plot of  $[\eta]_{\dot{\gamma}}/[\eta]_{\dot{\gamma} \rightarrow 0}$  against  $\dot{\gamma}$ . Numbers on curves refer to polymerization temperature and molecular weight.

Some examples of the observed non-Newtonian behavior are illustrated in Figure 1. The sample polymerized at lower temperature exhibits a greater shear rate dependency of the viscosities; functions of shear rate  $(\eta_{sp}/c)\dot{\gamma}$  can be easily estimated from the interpolated curves illustrated in Figure 1.

The corresponding limiting viscosity number  $[\eta]_{\dot{\gamma} \rightarrow 0} = (\eta_{sp}/c)_{\dot{\gamma} \rightarrow 0}$  can be determined from plots of  $(\eta_{sp}/c)\dot{\gamma}$  vs.  $c$ . In this manner relationships between  $[\eta]_{\dot{\gamma}}$  and shear rate  $\dot{\gamma}$  were obtained for the samples investigated. The relationships were found to be dependent upon the molecular weight, the limiting viscosity number, and the polymerization temperature.

The plot of relative ratios of limiting viscosity numbers  $[\eta]_{\dot{\gamma}}/[\eta]_{\dot{\gamma} \rightarrow 0}$  against shear rate on several samples (Fig. 2) shows that the relationship depends on the molecular weight and the polymerization temperature.

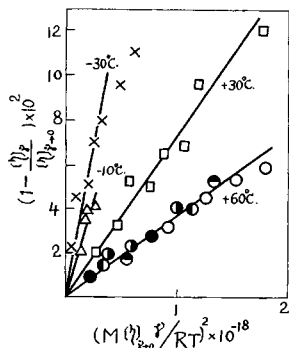


Fig. 3. Plots of  $1 - ([\eta]_{\dot{\gamma}}/[\eta]_{\dot{\gamma} \rightarrow 0})$  vs.  $(M[\eta]_{\dot{\gamma} \rightarrow 0}\dot{\gamma}/RT)^2$ : (O) sample 66-3, polymerized at 60°C.,  $M_w = 42.7 \times 10^4$ ; (●) sample 66-1, polymerized at 60°C.,  $M_w = 29.8 \times 10^4$ ; (○) sample 4, polymerized 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.,  $M_w = 38.5 \times 10^4$ ; (Δ) 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 relationship<sup>5</sup>

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

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

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## Grafting of Acrylonitrile onto Polypropylene Films by a Preirradiation Method

It was reported by Chapiro<sup>1</sup> 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  $\gamma$ -rays from a 1000-curie  $\text{Co}^{60}$  source at different intensities. The films (weight =  $p_0$ ), preirradiated in the air, were heated in the presence of acrylonitrile monomer in glass ampules at 80–135°C. After grafting, the films were immersed in a large volume of dimethylformamide at 110°C. after extraction

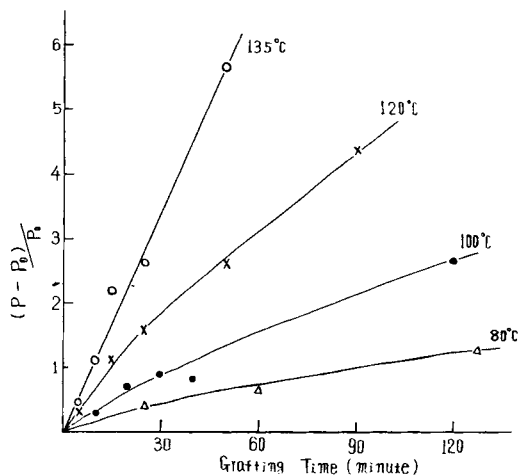


Fig. 1. Variation of  $(P - P_0)/P_0$  as a function of time for various grafting temperatures at constant dose rate ( $3.0 \times 10^5$  r/hr.) and constant dose ( $1.4 \times 10^6$  r).

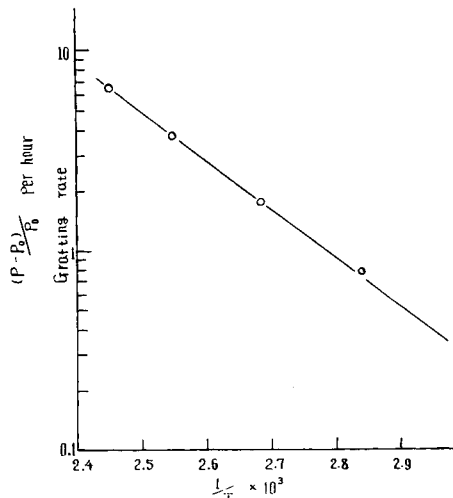


Fig. 2. A logarithm of the grafting rate for acrylonitrile as a function of  $1/T$ .