

# Shear Degradation of Poly(vinyl Acetate) in Toluene Solutions by High-Speed Stirring

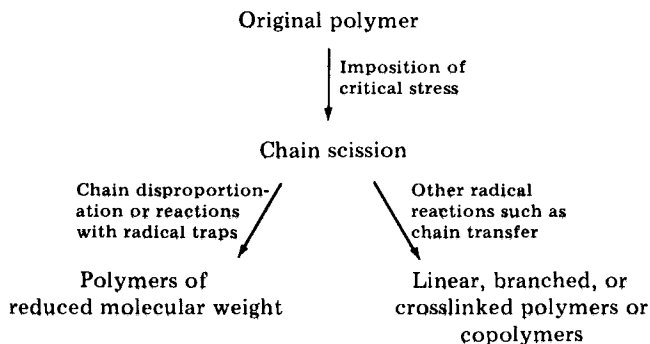
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## Synopsis

A poly(vinyl acetate) (PVAc) of  $\bar{M}_w$  750,000 and  $\bar{M}_w/\bar{M}_n$  5.10 in toluene solution was sheared in a Virtis-60 homogenizer. The polymer concentration was 3.0 to 12.0 g/100 ml, and test temperature was  $10 \pm 0.5^\circ\text{C}$ . The extent of degradation was measured by gel permeation chromatography (GPC). It was concluded that on shearing (i) the molecular weight decreases rapidly at the beginning of shearing and thereafter decreases ever more slowly toward a limiting value, (ii) the molecular weight distribution is narrowed, (iii) no degradation occurs up to 5000 rpm and thereafter increases with stirring speed, (iv) degradation is more at lower concentrations but concentration is not a sensitive variable, and (v) the chain scission occurs randomly. The Mark-Houwink relationship for PVAc in THF at  $25^\circ\text{C}$  was derived as  $[\eta] = 2.47 \times 10^{-4} \times \bar{M}_v^{0.644}$ .

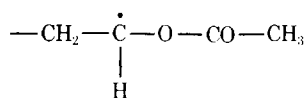
## INTRODUCTION

When polymer solutions are sheared, agitated, or extruded, shearing force is created between polymer and solvent and, where present, between polymer chains through entanglements. This force acts on the polymer to cause chain deformation and extension. The degree of deformation depends on the force applied. If the force is sufficient, polymer chains may be broken, leading to formation of macroradicals. Macroradicals may then either recombine or more likely otherwise react to form short or modified polymer molecules.<sup>1</sup> The pattern of reaction may be described as follows<sup>2</sup>:



Goto and Fujiwara, using a Homomixer, investigated the rupture of poly(vinyl acetate) (PVAc) in cyclohexanone dilute solutions.<sup>3</sup> They concluded that chain scission does not occur at the C-C linkage but at the ester linkage of the pendent group, if long branches are present and a decrease in solution concentration or solvent power or an increase in Homomixer rotational speed causes an increase

in degradation. In other studies



was detected as the principal radical by electron spin resonance spectra.<sup>4-7</sup> The degradation kinetics of PVAc on cold milling have been investigated by Baramboim.<sup>8,9</sup> It was found that decrease in molecular weight follows the equation

$$M_t = ae^{-Kt} + M_{\text{lim}}$$

where  $M_t$  is the molecular weight at any time  $t$ ,  $M_{\text{lim}}$  is the limiting molecular weight after which no more degradation occurs under the test conditions,  $K$  is the degradation rate constant, and  $a = M_{\text{in}} - M_{\text{lim}}$ , with  $M_{\text{in}}$  being the initial polymer molecular weight. The observation of  $M_{\text{lim}}$  on degradation of PVAc

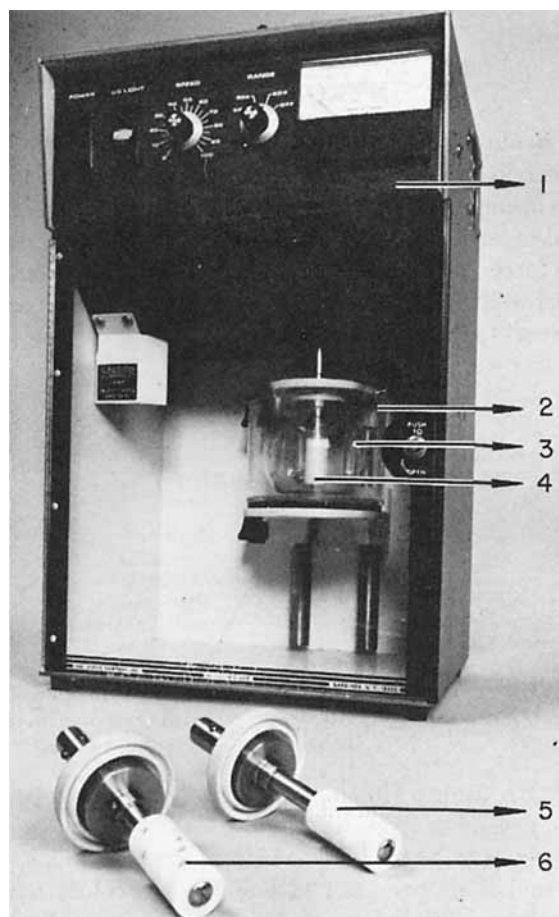


Fig. 1. High-speed stirring apparatus: (1) Virtis-60 homogenizer, (2) cooling cup, (3) 250-ml round glass flask with five flutes, (4) Teflon cylinder, (5) Teflon cylinder mounted on a stainless steel shaft, and (6) five blades and six discs mounted on a stainless steel shaft.

has also been demonstrated by many other investigators.<sup>3,10-12</sup> The degradation of PVAc has also been studied during capillary flow.<sup>13</sup> Ceresa has reported the molecular weight changes on degradation of PVAc plasticized with benzene.<sup>11</sup>

In a series of studies, PVAc solutions were irradiated by ultrasonic waves.<sup>12,14-19</sup> Degradation decreases on increasing polymer concentration<sup>17</sup> and on using a poor solvent.<sup>15</sup> Kosino and Miyagawa concluded that PVAc degradation in an acetone solution on ultrasonic irradiation occurred mainly by cavitation.<sup>18</sup> Ovenall et al. followed the consumption of the radical acceptor 1,1'-diphenyl-2-picrylhydrazyl on ultrasonic irradiation of PVAc in benzene solutions.<sup>12</sup> Nakano et al. prepared a block copolymer of PVAc and methacrylic acid by sonic irradiation at 200 kHz.<sup>19</sup> Ceresa synthesized styrene-vinyl acetate block copolymer by cold mastication of PVAc swollen with styrene.<sup>20</sup> In one study, Goto and Fjuiwara agitated PVAc plus vinyl acetate in a Homomixer at 30,000 rpm in a nitrogen atmosphere at 65°C.<sup>21</sup> They found that the macroradicals generated by mechanical scission of PVAc initiated the polymerization of vinyl acetate monomer. In addition to the formation of block and graft copolymers, there are other positive opportunities for the use of polymer mechanochemistry. These include induction of favorable changes in molecular weight, molecular weight distribution, branching, and crosslinking.

Degradation of PVAc by mechanical methods has been widely described, but

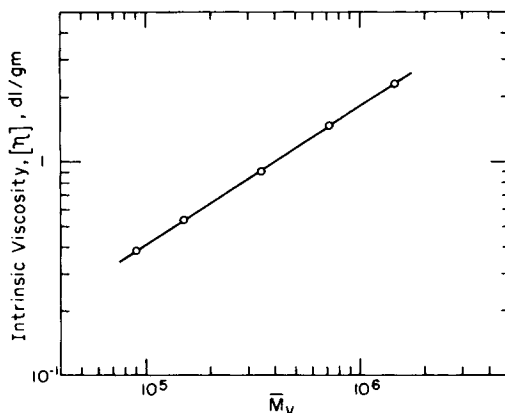


Fig. 2. Intrinsic viscosity  $[\eta]$  vs.  $\bar{M}_v$  for PVAc in THF at 25°C.

TABLE I  
Comparison of Molecular Weights of Poly(vinyl Acetate) Used for Calibration by Viscometric and GPC Measurements

Sample no.	Source	$\bar{M}_v \times 10^{-3}$	$\bar{M}_v \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
		from $[\eta]$ measurements in acetone $[\eta] = 1.76 \times 10^{-4} \times \bar{M}_v^{-0.68}$	from $[\eta]$ measurements in THF $[\eta] = 2.47 \times 10^{-4} \times \bar{M}_v^{-0.644}$		
1	Polyscience	149	149	154	4.81
2	Polyscience	346	340	350	4.20
3	Polyscience	720	722	750	5.10
4	High-end GPC cut, sample 3	1448	1450	1500	2.74
5	Low-end GPC cut, sample 1	90	91	88	2.84

the extent of reaction has been generally measured by either viscosity changes or by free-radical production. Neither of these approaches reveal changes in molecular weight distribution or location of chain scission. In this study, solutions of PVAc were agitated in a Virtis-60 homogenizer to study the effect of shearing time, stirring speed, and solution concentration on shear degradation of PVAc in toluene. To obtain the more meaningful and complete results, gel permeation chromatography was used to determine the molecular weight distributions of the starting and shear-reacted samples. The measures of number-average molecular weight  $\bar{M}_n$  were particularly important. This is because the difference between  $1/\bar{M}_n$  for before and after reaction is proportional to the minimum number of bonds ruptured. The relative changes in weight-average molecular weight  $\bar{M}_w$  and the number-average molecular weight  $\bar{M}_n$  have been used to evaluate the location of bond rupture and distributional changes.

## EXPERIMENTAL

### Materials

The PVAc used throughout was obtained from Polyscience. It had a  $\bar{M}_w$  of 750,000 as measured at the University of Massachusetts by GPC. The heterogeneity index  $\bar{M}_w/\bar{M}_n$  was 5.10. Toluene (spectrophotometric grade) was supplied by Allied Chemical Company, whereas tetrahydrofuran (THF) and acetone were obtained from Fisher Scientific Company.

### High-Speed Stirring

Known amounts of PVAc were placed in volumetric flasks. The required volume of toluene was then added and allowed to dissolve at room temperature (25°C) for one or more days depending on the solution concentration. High-

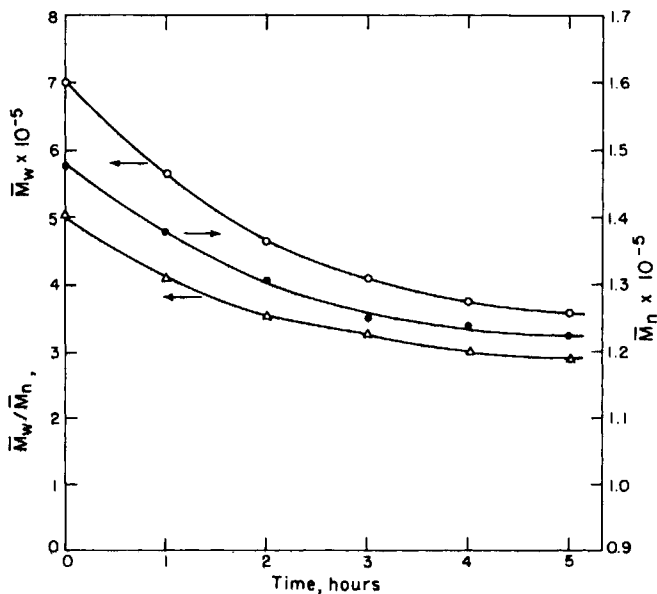


Fig. 3. Shear degradation of PVAc in toluene (3.0 g/dl), stirring at 30,000 rpm. (○)  $\bar{M}_w$ ; (●)  $\bar{M}_n$ ; (Δ)  $\bar{M}_w/\bar{M}_n$ .

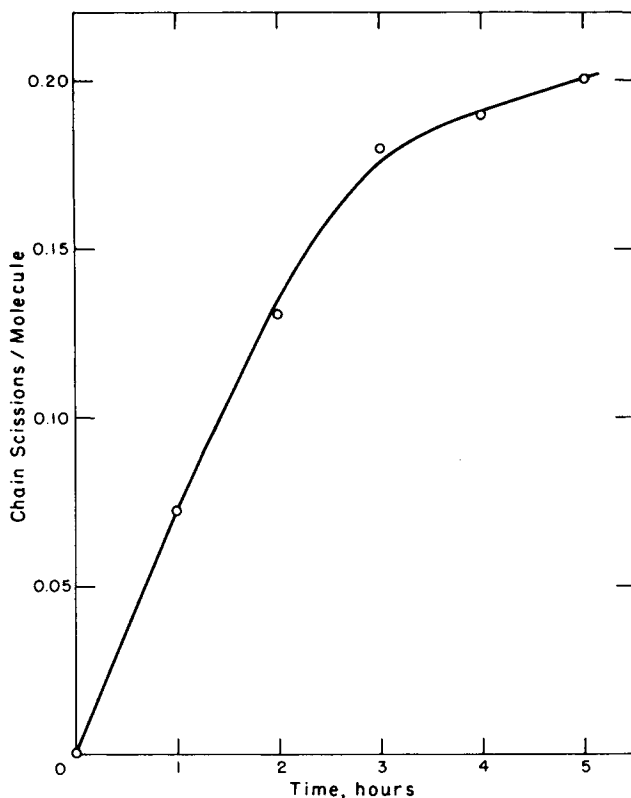


Fig. 4. Chain scissions per molecule as function of time for PVAc in toluene (3.0 g/dl), stirring at 30,000 rpm.

speed stirring was achieved by use of the Virtis-60 homogenizer (variable speed  $\leq 60,000$  rpm) (Fig. 1). This homogenizer was fitted with a Teflon cylinder (diam. 1.9 cm) connected to a stainless steel shaft. A 250-ml round glass flask with five flutes was used as a degradation vessel for all runs. The degradation vessel was set in a cooling cup and temperature was maintained at  $10 \pm 0.5^\circ\text{C}$  by packing the cooling cup with crushed ice.

Eddies were observed on shearing PVAc solutions in toluene. The transparent solutions became milky after agitation due to formation of microbubbles. This suggests that turbulent flow was generated and was the most probable cause for bond rupture. All reactions were carried out in the presence of air. Approximately 80 ml of solution was used for each run for speeds up to 30,000 rpm, and about 60 ml solution was used for higher speeds. This limit avoided the splashing of the solution during agitation. All solutions were filtered before agitation. Samples were withdrawn at various intervals for GPC analysis.

### Gel Permeation Chromatography

A Waters Associates GPC model 200 equipped with an automatic injection system was used. The conditions were as follows: solvent, THF; temperature,  $25^\circ\text{C}$ ; columns,  $10^7$ ,  $3 \times 10^5$ ,  $3 \times 10^4$ , and  $3 \times 10^3$  Å normal pore size; sample concentration, 0.5 mg/ml; flow rate, 1 ml/min. Polystyrene (PS) standards in

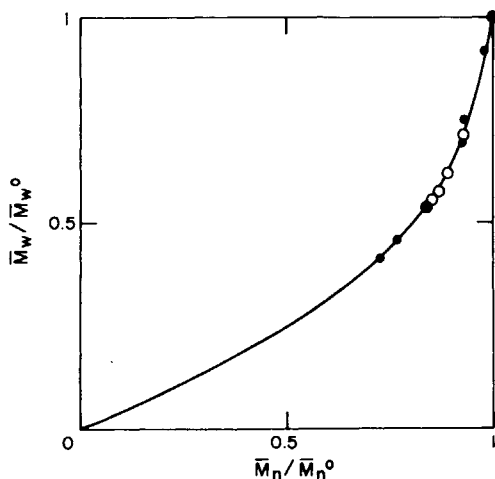


Fig. 5. Relative changes in  $\bar{M}_w$ ,  $\bar{M}_w/\bar{M}_w^0$ , vs. the relative changes in  $\bar{M}_n$ ,  $\bar{M}_n/\bar{M}_n^0$ , for shear degradation of PVAc in toluene (3.0 g/dl) compared with the theory for random scission with  $\bar{M}_w^0/\bar{M}_n^0 = 5$ , from ref. 30. (O) stirring speed 30,000 rpm, shearing time 0-5 hr; (●) stirring speed 0-50,000 rpm, shearing time 5 hr at each speed.

the molecular weight range of  $10^4$  to  $2 \times 10^6$  with narrow distributions ( $\bar{M}_w/\bar{M}_n < 1.2$ ) were obtained from the Pressure Chemical Company, Pittsburgh, PA. Intrinsic viscosities  $[\eta]$  of these standards were measured with an Ubbelohde

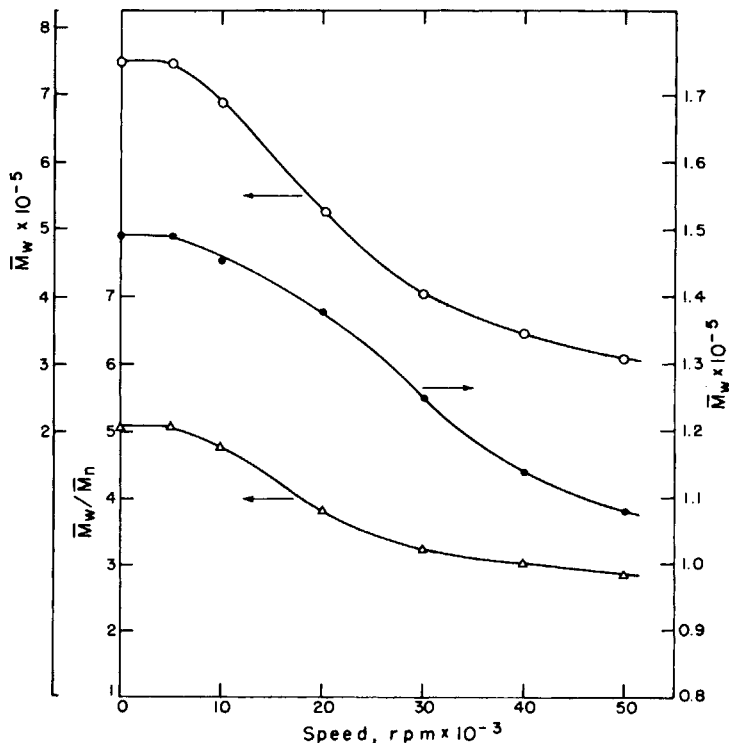


Fig. 6. Shear degradation of PVAc in toluene (3.0 g/dl) for 5 hr at each speed indicated: (O)  $\bar{M}_w$ ; (●)  $\bar{M}_n$ ; (Δ)  $\bar{M}_w/\bar{M}_n$ .

viscometer in THF at 25°C. The Mark-Houwink constants  $K$  and  $a$  were calculated from a linear plot of  $\log [\eta]$  versus  $\log M$  and were found to be  $1.90 \times 10^{-4}$  and 0.68, respectively. These values are consistent with those obtained by Cane and Capaccioli who reported  $K$  as  $1.8 \times 10^{-4}$  to  $2.8 \times 10^{-4}$  and  $a$  as 0.66 to 0.69 for PS ( $\bar{M}_n = 24,000$  to  $806,000$  and  $\bar{M}_w/\bar{M}_n = 1.2$  to  $6.4$ ) in THF at 25°C.<sup>22</sup> The GPC universal calibration curve for PS was obtained using these samples.<sup>23</sup>

To find the Mark-Houwink constants for PVAc in THF at 25°C, three samples of PVAc obtained from Polyscience were used. Their  $[\eta]$  were measured in acetone, and the viscosity-average molecular weights  $\bar{M}_v$  were found to be 149,000, 346,000, and 720,000 using the following Mark-Houwink relationship<sup>24</sup>:

$$[\eta] = 1.76 \times 10^{-4} \times \bar{M}^{0.68}$$

Two fractions of PVAc were obtained as GPC elution cuts from the highest and lowest molecular weights. The lower-end GPC cut of PVAc of  $\bar{M}_v$  149,000 and the higher end GPC cut of PVAc of  $\bar{M}_v$  720,000 were collected in a beaker during GPC fractionation and were dried at room temperature under vacuum for two days. The  $[\eta]$  values of these two fractionated samples were measured in acetone using the technique of subsequent dilutions, and  $\bar{M}_v$  values found were 90,000 and 1,448,000, respectively, using the above Mark-Houwink relationship. The acetone solutions were dried under vacuum for two days to recover the fractionated samples. The  $[\eta]$  values of the three unfractionated and two fractionated samples of PVAc were then measured in THF at 25°C. Figure 2 shows

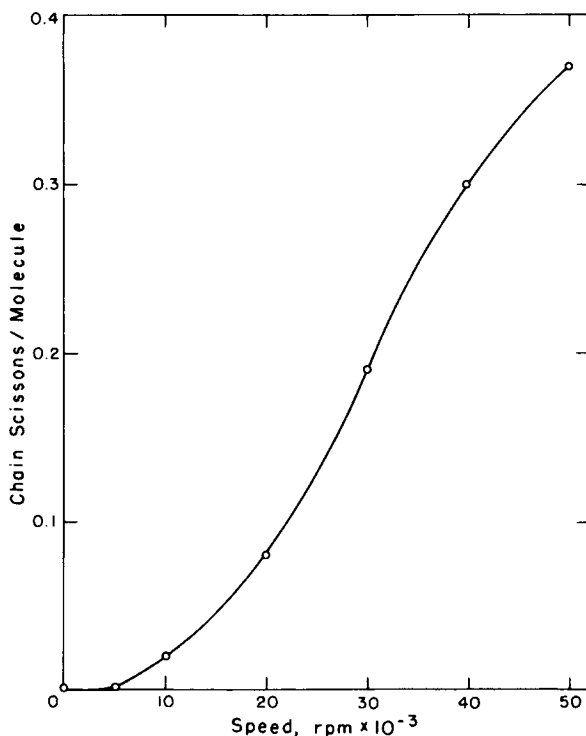


Fig. 7. Chain scissions per molecule as function of stirring speed for PVAc in toluene (3.0 g/dl).

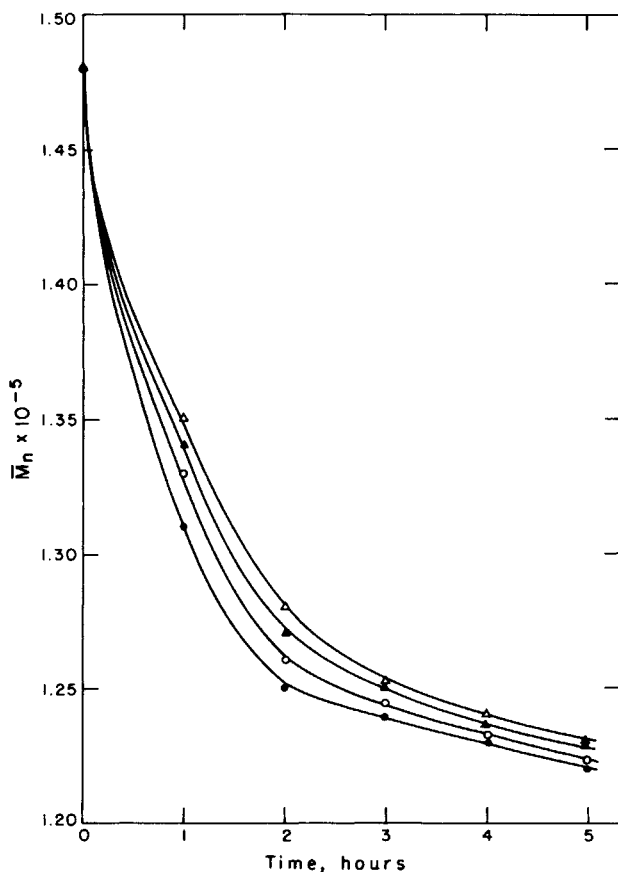


Fig. 8. Number-average molecular weight  $\bar{M}_n$  vs. time for shear degradation of PVAc in toluene, stirring at 30,000 rpm. PVAc Concentration (g/dl): (●) 3.0; (○) 6.0; (▲) 9.0; (△) 12.0.

a log-log plot of  $[\eta]$  versus  $\bar{M}_v$  for PVAc in THF at 25°C. All five points lie on the straight line obtained by the least-squares method. The Mark-Houwink constants  $K$  and  $a$  for PVAc in THF at 25°C were calculated as  $2.47 \times 10^{-4}$  and 0.644, respectively. These values are in good agreement with those obtained by prior investigators. Nichols found the Mark-Houwink exponent  $a$  for PVAc in THF at 25°C to be 0.64.<sup>25</sup> Goedhart and Opschoor derived the following Mark-Houwink relationship for PVAc in THF at 25°C:

$$[\eta] = 3.5 \times 10^{-4} \times \bar{M}_w^{0.63}$$

using a viscometric detector.<sup>26</sup>

The universal PS calibration curve was then transformed to PVAc calibration curve using the following equation:

$$M_{\text{PVAc}} = \left[ \frac{[\eta]_{\text{PS}} M_{\text{PS}}}{2.47 \times 10^{-4}} \right]^{1/1.644}$$

A computer program was used to calculate  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $\bar{M}_w/\bar{M}_n$  from GPC chromatograms. In Table I molecular weights of three unfractionated and two fractionated samples of PVAc obtained by viscometric measurements and by



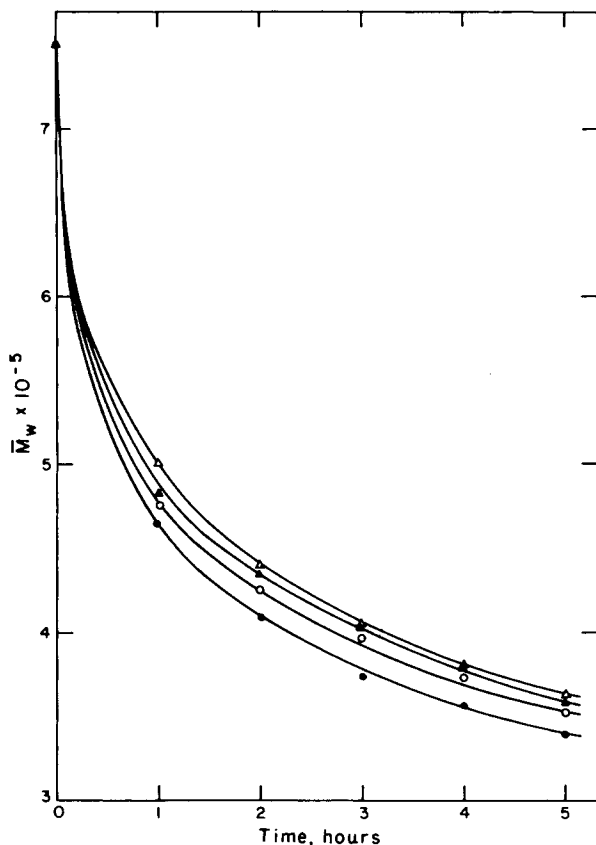


Fig. 9. Weight-average molecular weight  $\bar{M}_w$  vs. time for shear degradation of PVAc in toluene, stirring at 30,000 rpm. PVAc Concentration (g/dl): (●) 3.0; (○) 6.0; (▲) 9.0; (△) 12.0.

GPC are compared. PVAc of  $\bar{M}_w$  750,000 and  $\bar{M}_w/\bar{M}_n$  5.1 was used throughout for degradation studies. Band-spreading corrections for GPC were not employed.

## RESULTS AND DISCUSSION

A common feature of mechanochemical processes is an exponential decrease in molecular weight with time. The toluene solution of PVAc (3.0 g/dl) was sheared at a constant speed of 30,000 rpm. The molecular weight decreases rapidly at the beginning of shear, and thereafter, decreases ever more slowly towards a limit. It can be seen from Figure 3 that a limiting molecular weight is nearly reached in 5 hr. The change in molecular weight is superimposed by an alteration of molecular weight distribution (MWD). The changes in MWD are important because they influence polymer performance. The PVAc used in this study had a broad initial MWD ( $\bar{M}_w/\bar{M}_n = 5.10$ ). The MWD is narrowed on shearing. The heterogeneity index decreases rapidly at first, followed by an ever more gradual decrease (Fig. 3). The  $\bar{M}_n$  obtained by GPC is used to cal-

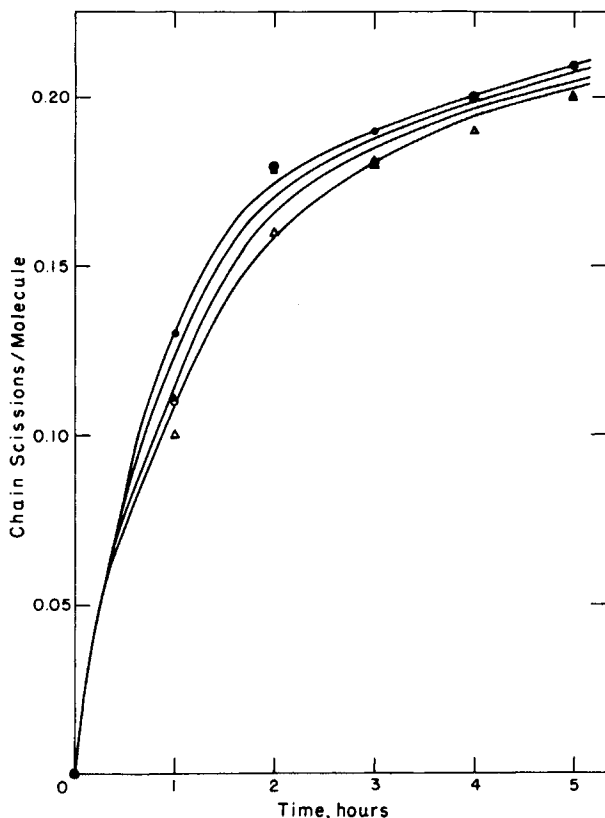


Fig. 10. Chain scission per molecule as function of time for PVAc in toluene, stirring at 30,000 rpm. PVAc Concentration (g/dl): (●) 3.0; (○) 6.0; (▲) 9.0; (△) 12.0.

culate chain scission which equals  $(\bar{M}_n^\circ - \bar{M}_n)/\bar{M}_n$ . Figure 4 shows how the total number of chain scission per molecule increases with shearing time.

The PVAc chain may break at a C-C bond in the main chain<sup>4-7</sup> or at a C-O bond in the ester linkage if long branches are present.<sup>3</sup> The macroradicals formed may terminate by disproportionation or chain transfer reactions. Recombination is unlikely because oxygen present acts as a radical acceptor. Oxygen reacts readily with macroradicals to form peroxy radicals which deactivate by hydrogen abstraction.<sup>27-29</sup> The abstracted hydrogen atom may be on the acetate group, or it may be on the main-chain vinyl links. Various criteria have been used to assess the location of bond rupture. The relative changes in  $\bar{M}_w$  and  $\bar{M}_n$  provides a somewhat preferred criterion for random scission because it utilizes the maximum information available and essentially includes the other criteria commonly used. The relative changes in  $\bar{M}_w$  and  $\bar{M}_n$  are fairly sensitive to variations in  $\bar{M}_w/\bar{M}_n$  but less so to details of MWD.<sup>30</sup> The curve in Figure 5 represents the theoretical behavior of random chain scission with an initial  $\bar{M}_w/\bar{M}_n^\circ$  of 5. The relative changes in  $\bar{M}_w$  and  $\bar{M}_n$  for shear degradation of PVAc ( $\bar{M}_w/\bar{M}_n^\circ = 5.1$ ) in toluene solution at 30,000 rpm are shown by open circles which lie on the theoretical curve, indicating that chain rupture occurs randomly under the experimental condition of turbulent flow.

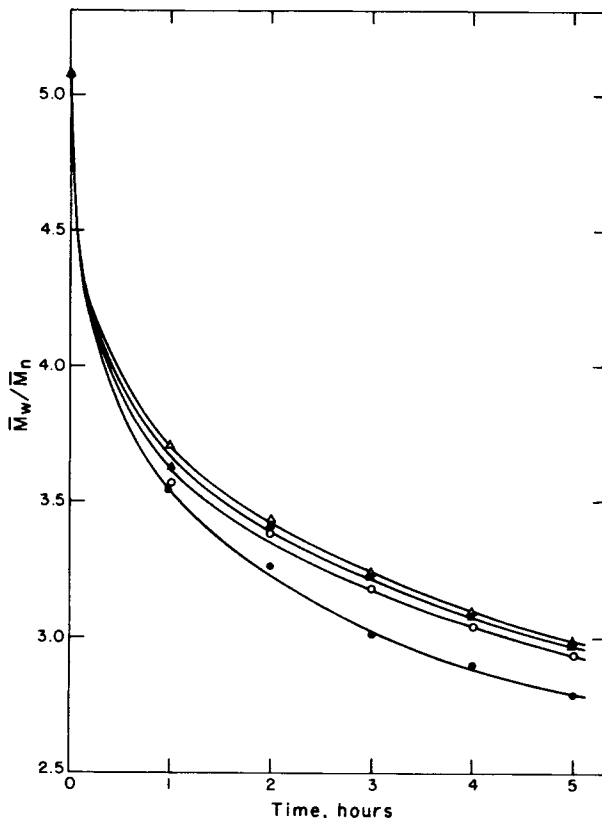


Fig. 11. Heterogeneity index  $\bar{M}_w/\bar{M}_n$  vs. time for shear degradation of PVAc in toluene, stirring at 30,000 rpm. PVAc Concentration (g/dl): (●) 3.0; (○) 6.0; (▲) 9.0; (△) 12.0.

### Effect of Stirring Speed

Variations in stirring speed is a direct demonstration of dependence of degradation on applied shear. The toluene solution of PVAc (3.0 g/dl) was agitated at different speeds from 0 to 50,000 rpm. At each speed a fresh original solution was used, and each solution was sheared for the same time (5 hr). There is no change in molecular weights and MWD, i.e., no reaction up to 5000 rpm. Above 5000 rpm the molecular weight decreases rapidly with increasing speed, consistent with a minimum critical force required to cause chain scission.<sup>31-34</sup> MWD correspondingly decreases rapidly after 5000 rpm with increasing speed, followed by an ever more gradual decrease (Fig. 6). Figure 7 presents this information in terms of chain scission per molecule. The relative changes in  $\bar{M}_w$  and  $\bar{M}_n$  at different rotational speeds are compared with the theoretical behavior for random scission for an initial  $\bar{M}_w/\bar{M}_n$  of 5 (Fig. 5). The experimental data (closed circles) fit the theoretical curve indicating that chain rupture occurs randomly.

### Effect of Concentration

Toluene solutions of PVAc in the concentration range of 3.0 to 12.0 g/dl were sheared in the homogenizer at 30,000 rpm for the same time (5 hr). An assembly of five blades and six discs was used for agitation instead of the Teflon cylinder

(Fig. 1). This shear geometry produced more degradation. Generally, the higher-concentration solution, i.e., the more viscous, is expected to exhibit more degradation because of higher stress.<sup>35-37</sup> But it can be seen from Figures 8 through 10 that concentration does not have substantial effect on degradation of PVAc in toluene solution in the range of 3.0 to 12.0 g/dl and that degradation is actually more at the lower concentration. This is consistent with turbulent flow being the most probable cause for bond rupture rather than lamellar shear. Likewise, concentration does not have much effect on MWD, with the narrowest distribution being reached at the lowest concentration (Fig. 11).

The results obtained in this study agree qualitatively with those of Goto and Fujiwara.<sup>3</sup> They studied shear degradation of PVAc in cyclohexanone in the concentration range 1.2 to 4.0 g/dl. But in their study, the extent of degradation was measured only by  $[\eta]$  and did not involve the determination of  $\bar{M}_n$  or MWD. Hence, their results could not provide information on changes in MWD and location of bond rupture as has been done in this study.

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