Molecular Characterization and Effect of Shear on the Distribution of Long Branching in Poly(vinyl Acetate)

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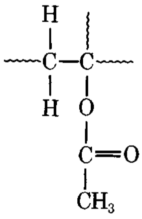
Synopsis

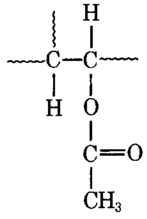
Poly(vinyl acetate) (PVAc) of $\overline{M}_w$ 750,000 $\overline{M}_w/\overline{M}_n$ 3.85 and $\overline{B}_n$ (the number of long branches per molecule) 2.2 was subjected to chain scission by mechanical (high-speed stirring) as well as chemical (saponification and reacetylation) methods to investigate the effect of shear on the branching distribution. The extent of long branching was measured by gel permeation chromatography on-line with low-angle laser light scattering photometry. It was concluded that (i) the branches through the acetate group are long and are ruptured preferentially on shearing, (ii) the branches through the α- and β-carbons are not broken on shearing, (iii) the extent of long branching through the acetate group is about 67% of total branching, and (iv) the poly(vinyl alcohol) derived from branched PVAc contains a smaller but nevertheless significant amount of branching.

INTRODUCTION

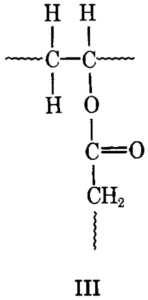
During the polymerization of vinyl acetate extensive branching occurs by chain transfer to polymer and terminal double bond reactions.[1–8] Branching frequency increases rapidly with conversion and causes a concomitant broadening of the molecular weight distribution.[4,9–14] The branch points have been previously shown to exist in three chemically distinct structures, through the α-carbon (structure I), the β-carbon (structure II), and through the acetate group (structure III)[15]:



I



II



III

Branches may be "short" or "long." Since long branches mainly affect the hydrodynamic properties of the polymer, and are thereby measureable by intrinsic viscosity measurements, we will be concerned exclusively with the measurement of long branches. The amount of branching through the acetate group was estimated to be about 70% of the total by Graessley and his co-workers.[15]

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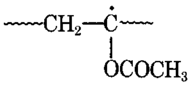
However, this percentage will obviously depend on the conditions of polymerization.

On shearing of branched poly(vinyl acetate) (PVAc) to rupture, it is not certain which main chains or branch units will be ruptured. The strength of a —C—O— bond is higher than that of a —C—C— bond.[16,17] As a result, —C—C— bonds would be expected to be ruptured preferentially. It has been shown, using electron spin resonance, that



$$\sim CH_2-\overset{\bullet}{\underset{\displaystyle OCOCH_3}{\underset{|}{C}}}\sim$$

is the principal radical observed on shearing.[18,19] However, Goto and Fujiwara[20] have determined, using chemical methods, that stirring a solution of PVAc in cyclohexanone did not result in chain scission at the —C—C— linkage, but rather at the pendant ester linkage.

The purpose of our study is to investigate which bonds are ruptured on shearing; that is, whether scission occurs at the main chains or at the branch points shown in structures I, II, and III or at a combination of them. To accomplish this, we have carried out chain scission by mechanical as well as by chemical methods. Branching through the acetate group (structure III) can be detected from changes in molecular weights when a sample is saponified to poly(vinyl alcohol) (PVA) and acetylated back to PVAc. The PVAc so obtained has a lower molecular weight than the original PVAc prior to saponification because branches through the acetate group are broken on saponification and are not re-formed on acetylation.[21] The branches through the α-carbon (structure I) and the β-carbon (structure II) are not affected by saponification since they are nonhydrolyzable. Hence, PVA obtained by saponification of branched PVAc remains partially branched.[15] To investigate which branches, if any, are ruptured on shear and to what extent, four samples were prepared as described in Table I.

Previously, branching in PVAc has been determined kinetically,[1,3,6,7,15] by gel permeation chromatography (GPC) combined with viscometry,[22–24] GPC combined with ultracentrifugation,[24] and GPC on-line with low-angle laser light scattering (LALLS) photometry.[25,26] We used GPC on-line with LALLS to analyze branching in PVAc before and after chain scission. Although highly resolving in terms of molecular weight, the method inevitably involves the analysis at each point in the chromatogram of a distribution of linear and branched chains having equivalent hydrodynamic volume.

TABLE I
Description of Poly(vinyl Acetate) Samples

Sample no.	Sample description
1	Original branched PVAc
2	From sample no. 1 by saponification and reacetylation for removal only of branches through acetate group
3	After high-speed stirring of toluene solution of sample no. 1 (0.03 g/mL)
4	From sample no. 3 by saponification and reacetylation

EXPERIMENTAL

Materials: The PVAc used was obtained from Polysciences, Pa. It had a $\overline{M}_w$ 750,000 $\overline{M}_w/\overline{M}_n$ 3.85, and $\overline{B}_n$ (the number of long branches per molecule) 2.2.

Saponification: A 5% methanolic potassium hydroxide solution was added with stirring to 10 times its volume of a 2% methanol solution of PVAc at room temperature. The agitation was continued overnight to insure complete alcoholysis.[21] The PVA obtained was then filtered and repeatedly washed with methyl acetate.

Reacetylation: The drained, but not dry, PVA was then dispersed in an acetylating solution in approximate proportions of 40 mL of solution for each gram of PVA. The acetylating solution consisted of one volume of pyridine, five volumes of acetic acid, and 15 volumes of acetic anhydride. The dispersion was agitated slowly at room temperature for 24 h longer than the time required for the PVA to dissolve.[1] The reconstituted PVAc was recovered by precipitation with a large excess of water at room temperature. The PVAc was washed extensively with water, purified by reprecipitation into water from an acetone solution, and dried overnight under vacuum at 40°C. The purified PVAc was then dissolved in benzene and freeze-dried to remove the last traces of the acetylating solution.[7,15]

High-speed stirring: High-speed stirring was achieved by use of a Virtis-60 homogenizer (see Fig. 1). The homogenizer was fitted with a teflon cylinder mounted to a stainless steel shaft. A 250-mL round glass flask with five flutes was used as a degradation vessel. The degradation vessel was set in a cooling cup and temperature was maintained at 10 ± 0.5°C by packing the cooling cup with crushed ice. The toluene solution of PVAc (0.03 g/mL) was agitated at 50,000 rpm for 5 h to achieve extreme agitation and shear. A turbulent flow was generated during shearing and was believed to be the most probable cause for bond rupture.[27]

Refractive index increment measurements: The refractive index increments ($\Delta N/\Delta C$) of all samples were measured in tetrahydrofuran (THF), Fisher certified-grade, at 25°C using a Chromatix KMX-16 differential refractometer. This unit incorporates a He—Ne laser source which operates at the same wavelength as the LALLS (633 nm). The concentration range was varied from 2 to 5 g/L. The variation in $\Delta N/\Delta C$ values obtained for the four samples was less than 2%. The average value of $\Delta N/\Delta C$ used here was 0.054 mL/g.

Gel permeation chromatography on-line with low-angle laser light scattering photometry: The GPC used was a Water Associates Model 201 equipped with four μ-styragel columns of nominal pore size 10^3, 10^4, 10^5, and 10^6 Å. The LALLS used was a Chromatix KMX-6, Chromatix Inc., Calif. The inlet of the LALLS was fitted with a 0.5-μ fluoropore filter (Millipore Corp., Mass.). This filter provided a good signal relatively free from dust particles, without removal of the high molecular weight fraction of the sample.

The GPC was calibrated using a series of narrow molecular weight distribution polystyrene samples, obtained from Pressure Chemical Co., Pittsburgh, Pa. Viscosity measurements were performed on each of the polystyrene standards using a conventional Ubbeholde viscometer at 25°C. A universal calibration curve was obtained from the product of intrinsic viscosity and molecular weight plotted vs. retention volume.

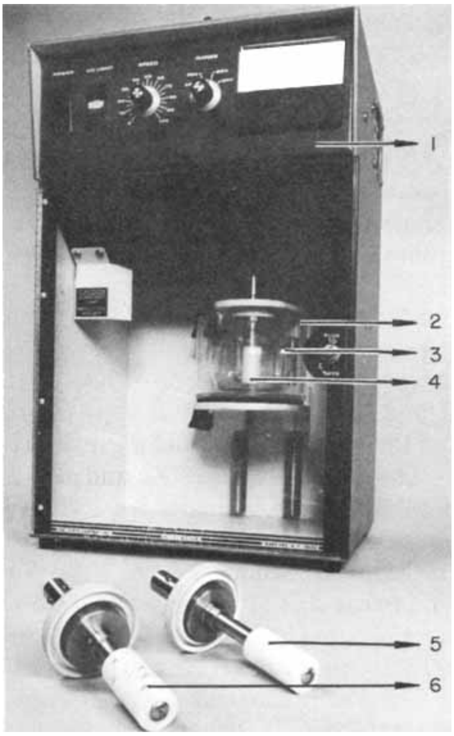


Fig. 1. High-speed stirring apparatus: (1) Virtis-60 homogenizer, (2) cooling cup, (3) 250-mL round glass flask with five flutes, (4) Teflon cylinder, (5) Teflon cylinder mounted on a stainless steel shaft, and (6) five blades and six discs mounted on a stainless steel shaft.

The flow rate used was 1 cc/min at 25°C. Injection volumes were 0.5 cc and concentrations were $1\text{–}2.5 \times 10^{-4}$ g/mL. The output from both the differential refractometer and LALLS detectors was displayed on a dual pen recorder. The scattered intensity, as measured by the LALLS, is a product of the concentration and the molecular weight, whereas the differential refractometer is sensitive only to the concentration. As a result the LALLS is extremely sensitive to the high end of the MWD and correspondingly less sensitive to the low end. This results in an offset between the output of the two detectors which increases with the MWD and makes calculation of the molecular weights of the sample at both ends of the chromatogram imprecise for broad MWD samples. Consequently, data aquisition is limited to a region where adequate response from the two detectors can be obtained. This problem may, of course, be handled electronically as described by Hamielec and Ouano.[25]

Calculation of intrinsic viscosity, $[\eta]_i$: From the GPC/LALLS system, a series of M_{w_i} is obtained; that is, the weight average molecular weight at any point across the polymer distribution. Through the use of universal calibration, which relates hydrodynamic volume, $[\eta]\ M$, to the elution volume, the corresponding value for the intrinsic viscosity, $[\eta]_i$, is generated.

A problem which needs to be considered here is which average of the molecular weight is correct for use in universal calibration. If it were M_n as recently proposed,[25] dividing $[\eta]\ M_n$ by M_w would result in an incorrect value for the intrinsic viscosity. We chose to avoid this problem by using the $1/(\alpha + 1)$ average of the hydrodynamic volume, ϕ, where $\phi = [\eta]M$ and α is the Mark–Houwink exponent. That is, it can simply be shown that

$$\overline{M}_w = \frac{\sum c_i(\phi/K)^{1/(\alpha+1)}}{\sum c_i} \tag{1}$$

where c_i is the concentration and K is the Mark–Houwink constant. Consequently, dividing the $1/(\alpha + 1)$ average of ϕ by M_w will result in a correct average for the intrinsic viscosity.[28] This procedure is carried out on incremental M_{w_i} values across the polymer distribution. That is, measurement of M_{w_i} at incremental points across the distribution is made using the LALLS and the corresponding incremental values of $\phi\langle 1/(\alpha + 1)\rangle$ obtained from the universal calibration. These values are divided by M_{w_i} to obtain the corresponding value for $[\eta]_i$.

Since α in eq. (1) is an unknown, some means of evaluating α must be available before it is possible to calculate the correct average of ϕ. In addition, some correction for axial dispersion should be applied. To resolve both of these, we chose to use the method of Marais et al.[29] The use of this method has previously been described in detail.[28] It is sufficient to note that, although α may vary with the molecular weight for a branched polymer, the method is insensitive to the exact value of the α and consequently an average may be used. The average value of α used here was 0.644.[27]

A series of values of $[\eta]_i$, the intrinsic viscosity of a branched polymer, and M_{w_i} were generated across the distribution of the polymer using a computer program.[30] The values reported here for M_{w_i} and $[\eta]_i$ represent data obtained from the portion of the MWD where adequate response was obtained from both the DRI and the LALLS which is ~10% less than the entire distribution. All GPC points were used to calculate $\overline{M}_w$ of 750,000. The value of intrinsic viscosity, $[\eta]_{li}$, for the corresponding linear polymer, at any molecular weight, M_{w_i}, was obtained using the following Mark–Houwink relationship for linear PVAc[22]:

$$[\eta]_{li} = 1.877 \times 10^{-4} M_{w_i}^{0.686} \tag{2}$$

The viscosity ratio g at any molecular weight M_{w_i} was then obtained by dividing the intrinsic viscosity of the branched polymer by that for the corresponding linear polymer.

RESULTS AND DISCUSSION

It is well accepted that polymers in solution with long branches are more compact than are their corresponding linear analogs. As a result, the intrinsic viscosity of polymers with long chain branching is smaller than that for linear polymers of the same molecular weight. Figure 2 compares intrinsic viscosities as a function of molecular weight for the four PVAc samples under study. At any molecular weight, the intrinsic viscosity of the original polymer (sample no. 1) is much smaller than that of the linear PVAc with the difference in intrinsic viscosity increasing with molecular weight. This indicates that sample no. 1 is highly branched, and the extent of branching increases with molecular weight. On shearing, the intrinsic viscosity of the polymer for a given molecular weight is increased whereas the average molecular weight is decreased (sample no. 3). This increase in intrinsic viscosity for a given molecular weight indicates that

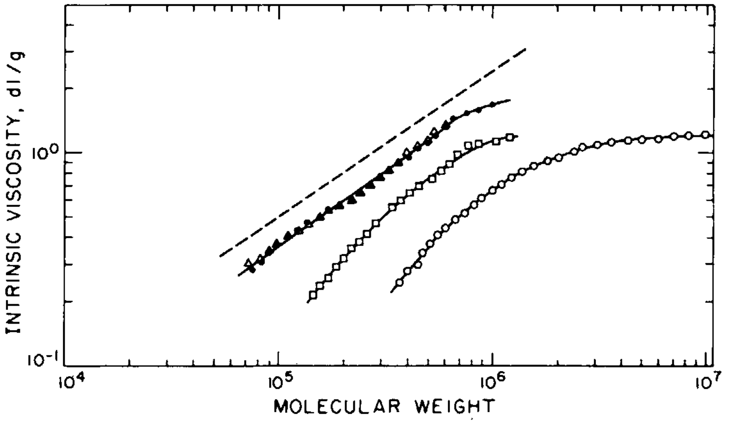


Fig. 2. Intrinsic viscosity as a function of molecular weight for four samples of poly(vinyl acetate) of different degrees of branching, in THF at 25°C. The dotted line is for linear polymer.[22] Sample no.: (○) 1; (△) 2; (□) 3; (●) 4.

branches are preferentially ruptured during shear. On saponification and reacetylation of the sheared sample (sample no. 3), a further increase in the intrinsic viscosity is observed for a given molecular weight. This is consistent with saponification of additional branches joined through the acetate group and produces a more linear polymer (sample no. 4). Similar results are obtained for sample no. 2. That is, the intrinsic viscosity at a given molecular weight is higher than that of the original branched polymer and the average molecular weight is lower. This is because on saponification the branches through the acetate group (structure III) are broken and not reformed on acetylation. However, any branches through the α- and β-carbons (structures I and II) would not be affected by saponification since these branches are nonhydrolyzable. Hence the saponified and reacetylated sample contains a smaller but significant amount of branches. This implies that any PVA derived from a branched PVAc will not be linear. It is of note that the data for samples no. 2 and no. 4 coincide within error (Fig. 2). This qualitatively indicates that, on shearing, nonhydrolyzable branches (structure I and II) are not broken and the branches through the acetate group (structure III) are preferentially ruptured. Those left are then removed on saponification and reacetylation.

The viscosity ratio g as a function of molecular weight for the four samples is shown in Figure 3. The value of g depends on the type and location of the branches as well as on the number of branch points per molecule.[31] The value of g is 1.0 for a linear polymer and decreases with increase in branching. We observe that the value of g for sample no. 1 is low and decreases with increase in molecular weight, indicating that the extent of branching increases with molecular weight. The value of g increases towards 1.0 on saponification and reacetylation (sample no. 2). This is because the branches through the acetate group are removed on saponification and reacetylation. The fraction X of long branches through the acetate link can be calculated from the value of g before (b) and after (a) sponification followed by acetylation:

$$X = \frac{g_a - g_b}{1 - g_b} \tag{3}$$

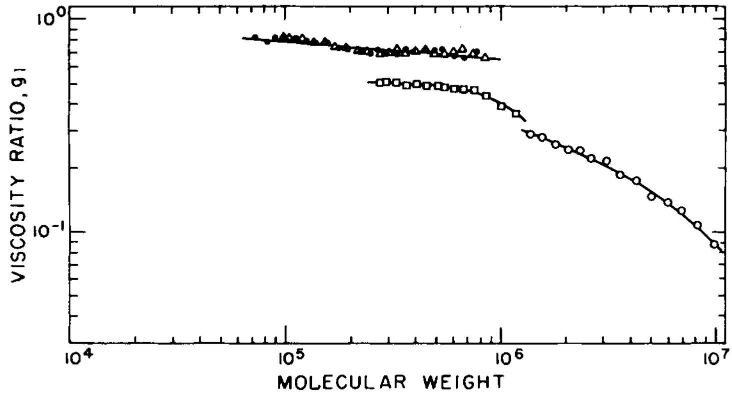


Fig. 3. Viscosity ratio g as a function of molecular weight for four samples of poly(vinyl acetate) of different degrees of branching, in THF at 25°C. Sample no.: (○) 1; (△) 2; (□) 3; (●) 4.

The average of g for sample no. 2 is 0.74, compared to 0.20 for sample no. 1. This implies that about 67% of the branching in PVAc occurs through the acetate group. This is an agreement with the results of Graessley et al.,[15] who determined that about 70% of the branches in PVAc were through the acetate group (structure III). The effect of shearing (sample no. 3) on the value of g is also shown in Figure 3. Comparison of the data for samples no. 1 and no. 3 indicates that, in addition to the decrease in molecular weight, the value of g increases, indicating the removal of some long branches as a result of shearing. In addition, Figure 3 shows the results of shearing followed by saponification and reacetylation (sample no. 4). It is apparent that saponification and reacetylation of the sheared sample no. 3 results in removal of the remaining branches through the acetate group, as indicated by the coincidence of the data for samples no. 2 and no. 4.

The number average molecular weights $\overline{M}_n$ for the four samples are compared in Table II. Each scission, whether by shear or by saponification and reacetylation, increases the number of molecules by one without altering the number of repeating units. Thus, by counting molecules before and after scission, we obtain[15]

$$\frac{\text{chain scission}}{\text{molecule}} = \frac{(\overline{M}_n)_b - (\overline{M}_n)_a}{(\overline{M}_n)_a} \tag{4}$$

where subscripts b and a signify before and after saponification–reacetylation or shear. The number of chain scissions per molecule thus calculated is shown in Table II.

Since the strength of the —C—O— bond is higher than that of —C—C—

TABLE II
Comparison of Poly(vinyl Acetate) Samples

Sample no.	$\Delta\overline{M}_n \times 10^{-5}$ from GPC	Chain scission/ molecule
1	1.95	—
2	0.789	1.47
3	1.44	0.35
4	0.766	1.54

bond, it would be expected that, on shearing, —C—C— bonds would be ruptured preferentially. However, our results, as well as those of Goto and Fujiwara,[20] indicate that the rupture occurs preferentially through the —C—O— bond of the ester group. This implies that the branches through the acetate group must be long, since long chains would be expected to rupture on shearing,[17,32] particularly as they can participate in entanglements.

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