

## Reversible Melt Flow Rate Increase of Branched Acetal Polymers

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### Synopsis

Continued shearing of molten long-chain branched acetal polymers raises their melt flow rates manyfold. The increase is not due to molecular degradation, as evidenced by constancy of inherent viscosity, and by the ability to reverse the increase by dissolving and reprecipitating the polymer. Shearing was found to have only a relatively small effect upon the melt viscosity but a very large effect upon the entrance correction for capillary flow. It is suggested that crystallization of branched polymers from solution creates an exceptionally strong entanglement network, and that the observed rheological changes reflect the disruption by shear of this network.

### Introduction

It has been observed by Howells and Benbow<sup>1</sup> that the apparent viscosity of low-density polyethylene could be decreased by a factor of two by shearing the molten polymer, and that this decrease accompanied a decrease in the elasticity of the melt. These changes were not caused by gross changes in molecular weight, and furthermore were reversible; reversal was achieved most readily by dissolving the polymer and reprecipitating it. Merely holding the sheared melt at 190°C was reported to have required many hours in order to produce the reversal of elasticity and apparent viscosity decrease. Both the magnitude of the effect and the time scale appear to be larger than those associated with other time of shear effects reported for molten polymers,<sup>2</sup> although Howells and Benbow do not give any experimental details to make a quantitative comparison possible.

We have observed a similar effect with a number of acetal polymers, initially also by melt flow rate measurements. Subsequently one polymer was investigated in more detail. The effect has been found only with polymers containing long-chain branches and not with linear polymers. The low-density polyethylene studied by Howells and Benbow was also long-chain branched,<sup>2</sup> and here again, no large effect has been observed with the linear polymer; on the contrary, it has been reported in at least one case that shearing decreases the melt index of linear polyethylene powder.<sup>3</sup> It also appears that this effect has not been observed to occur with amorphous polymers, which suggests that the influence of the presence of long-chain branching upon the crystallization process is involved.

## Experimental

The polymers studied were acetals, produced by the cationic copolymerization of trioxane, the major constituent, with 2 wt-% ethylene oxide in the case of linear polymers, and additionally with small amounts of tetrafunctional termonomers such as vinylcyclohexene diepoxide (VCHD) or resorcinol diglycidyl ether in the case of long-chain branched polymers. Unstable ends were removed by alkaline hydrolysis in solution, and the polymers were obtained in the form of powder by precipitating into excess water. An antioxidant and an acid acceptor to protect the polymer against degradation by exposure to heat were added by dry blending. Molecular characterization of the copolymers by dilute solution viscosity, light-scattering, and osmometry have been described.<sup>4</sup> Only a few measurements of absolute molecular weights of the terpolymers were made, and these indicate that, as expected, these have broader molecular weight distributions than do the linear copolymers, and that, at a given inherent viscosity, the weight-average molecular weight of a branched polymer is higher than that of a linear polymer.<sup>5</sup> Otherwise, only inherent viscosity, calculated as  $\ln \eta_{rel}/c$  at  $c = 0.1$  g/dl in 98/2 *p*-chlorophenol/ $\alpha$ -pinene at 60°C, was used to monitor constancy of molecular weight during the various processing steps.

The x-ray diffraction patterns of these polymers are similar to those of acetal homopolymers.<sup>6</sup> Densities are about 1.41 g/cc at 25°C, from which degrees of crystallinity of about 67% are estimated.<sup>6</sup>

Most of the flow rate measurements were single determination made with the extrusion plastometer described in ASTM Procedure D 1238, at a temperature of 190°C and at two applied loads. Measurements at an applied load of 2160 g were made according to Procedure D 1238-57T, modified to maintain a constant height of melt in the reservoir at the beginning of each measurement. The reproducibility of this measurement in our laboratory has been found to be  $\pm 3\%$  with polyacetals whose flow rates are about 10 dg/min.

The other load used was 21.6 kg. At this load the flow rates were measured by determining the time required to extrude 4.12 ml of molten polymer. The time was recorded by an electric timer which was turned on and off by a microswitch activated by a follower shaft of fixed length riding on top of the load weight. In principle this procedure is similar to that of Procedure B of ASTM D 1238-65T. From the measured time melt flow rates were calculated, using a density of 1.17 g/ml for the polyacetal at 190°C. The reproducibility of this method is estimated as  $\pm 5\%$ .

Swelling of plastometer extrudates was estimated by micrometer measurement of the diameter of the cooled extrudate near the bottom end; no correction was applied for contraction caused by crystallization, nor were extrudates annealed to allow relaxation of frozen-in strains.

Melt viscosity measurements were made with a rheometer similar to the one described by Bagley,<sup>7</sup> eight dies ranging from 1.7 to 15.2 in length-to-

diameter ratio being used. The Mooney-Rabinowitsch and entrance corrections were applied to the data.<sup>8</sup>

### Results

It was found that application of shear to the terpolymer melts consistently raised the melt flow rate and decreased the extrudate swelling of the terpolymers, while the inherent viscosity remained unchanged. The flow properties attained steady values after sufficient shearing. The results of a typical set of experiments are shown in Table I. In these experiments the polymers were passed through a 1 in. extruder, fitted with a  $\frac{1}{8}$  in. diameter by  $\frac{1}{2}$  in. length filament die at temperatures ranging from 200 to 220°C. It was estimated that the average residence time per extrusion was approximately 1 min. After each extrusion, samples were collected for the measurements and the polymers were then re-extruded. Similar results were obtained with other terpolymers and with other types of shearing, such as a Brabender Plastograph milling chamber. Heating the molten terpolymer powders for 15 min at 220°C without shear also caused increases in melt flow rate, but only on the order of 50% compared to the 3-fold to 15-fold increases caused by a single pass through the extruder. More prolonged heating was not done because of possible interference by thermal degradation.

TABLE I  
Effect of Repeated Extrusion

Polymer designation	Polymer type	No. of extrusions	Inherent viscosity, dl/g	Melt flow rate, dg/min		Extrudate swelling (2.16 kg load), %
				2.16 kg load	21.6 kg load	
SV-373	Linear copolymer	0	1.61	1.9	42	12
		1	1.60	2.2	47	8
		2	a	2.2	48	7
		3	1.58	2.2	49	6
SV-284	0.4% VCHD terpolymer	0	1.67	0.05	10	b
		1	1.71	0.78	53	33
		2	a	1.1	68	21
SV-283	0.4% VCHD terpolymer	3	1.68	1.2	71	16
		0	1.41	0.40	30	87
		1	1.46	1.7	85	31
		2	a	2.0	96	21
SV-285	0.6% VCHD terpolymer	3	1.46	2.0	99	19
		0	1.24	1.5	83	112
		1	1.22	4.9	217	39
		2	a	5.4	245	29
		3	1.25	5.7	254	27

<sup>a</sup> Not measured.

<sup>b</sup> Extrudate too short to measure.

The constancy of the inherent viscosity and the fact that each polymer appeared to approach a set of constant flow properties after repeated extrusion suggested that molecular weight degradation by heat, by oxidation, or by shear was not the factor responsible for the large changes of the flow properties. Indirect confirmation of this was obtained in a series of Plastograph experiments which showed that neither stabilizer concentration nor atmosphere (air or nitrogen) had any effect on the rise of melt flow rate. We were led therefore to consider the possibility that the flow rate changes were caused by shear-induced changes in the state of entanglement or aggregation of the polymer chains. As a test of this hypothesis it was attempted to reverse the melt flow rise by dissolving the sheared polymer and reprecipitating it, hopefully thereby re-establishing the original state of aggregation of the unsheared polymer. The results of one such experiment are shown in Table II. There was substantial, although not complete, recovery of both melt flow rate and of melt elasticity as measured by extrudate swelling. Similar results have been obtained with other branched terpolymers. Neither the melt flow rate rise after shearing nor a melt flow rate drop after dissolving the reprecipitating has been observed with linear copolymers having a range of melt flow rates comparable to those of the terpolymers studied.

TABLE II  
Effect of Reprecipitation

	SV-284	SV-310	SV-367
Treatment	Precipitated powder	Extruded pellets made from SV-284	Powder from dissolving SV-310 and reprecipitating
Inherent viscosity, dl/g	1.64	1.57	1.56
Melt flow rate (2.16 kg load), dg/min	0.05	1.1	0.23
Extrudate swelling, %	a	22	52

<sup>a</sup> Extrudate too small to measure.

The melt flow rate measurements were useful for monitoring these experiments, particularly because only small samples are required. However, since they are one or two point measurements, it is not possible to determine from them the changes in the various rheological parameters that control the flow rate. Polymers SV-284 and SV-310 (Table II) were therefore studied in more detail by CIL rheometer.<sup>7</sup> The viscosity data obtained are shown in Figure 1 and the entrance corrections in Figure 2. For comparison data are also shown for a linear copolymer whose melt flow rate is 2.8 dg/min.

There was some concern that the data on the original powder (SV-284) might be in error because of possible shear-induced changes during the viscosity measurement itself. To check this possibility a quantity of the

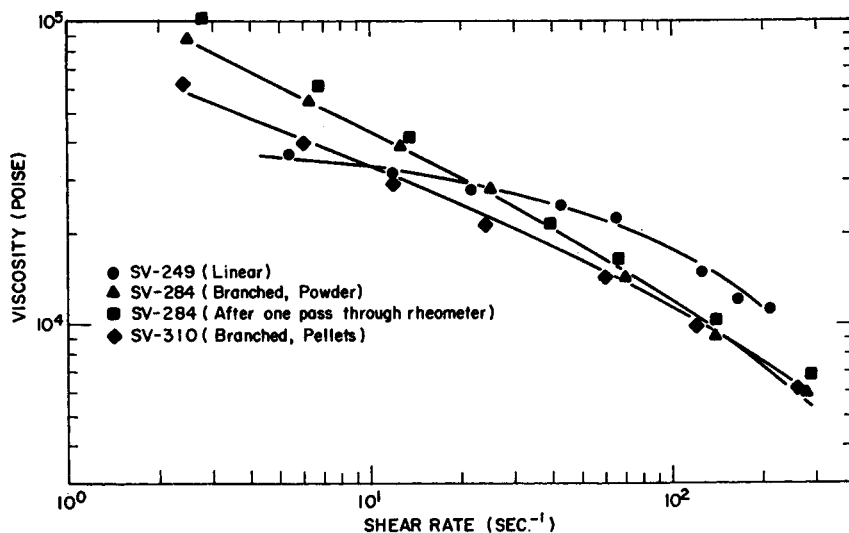


Fig. 1. Viscosity vs. shear rate for linear polymer and for branched polymer powder and pellets.

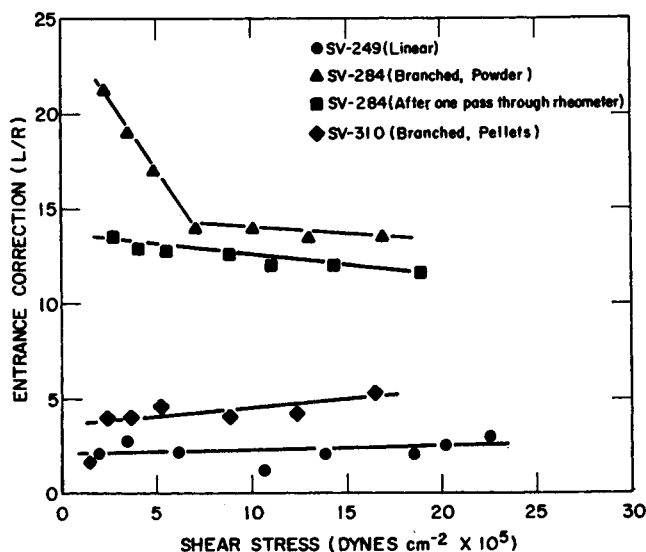


Fig. 2. Entrance correction vs. shear stress for linear and branched polymers.

molten polymer was extruded from the rheometer at the conditions corresponding to the highest shear rate measured. The extrudate was collected and its viscosity and entrance correction measured over the same shear rate range as the original polymer. Within the uncertainty of the viscosity measurement caused by the very large entrance correction the results are in agreement, indicating that no appreciable change had occurred during the measurement of the viscosity of SV-284. The entrance correction was, however, decreased by this one pass through the rheometer.

### Discussion

The requirements for the occurrence of the phenomenon studied appear to be that first, the polymer possesses long-chain branches, second, that it be crystallizable, and third, that it have no "recent" shear history. The first conclusion cannot be inferred from this work alone, for the branched acetal terpolymers differ from the linear polymers also in that they have broadened molecular weight distributions. However, no such effect has been observed with mixtures of linear polymers. Also, linear polyethylenes, which also have very broad molecular weight distributions, fail to show a melt index rise on shearing; in fact, the opposite has been observed.<sup>3</sup> The conclusion that the presence of long branches is necessary seems a reasonable one therefore.

The second point, that the polymers be crystalline as solids, rests on the fact that the effect has been observed only with polyethylene and polyoxymethylene, and although a number of amorphous long-chain branched polymers have been investigated, including *n*-butyllithium-initiated polybutadiene,<sup>11</sup> poly(vinyl acetate),<sup>12</sup> and polystyrene,<sup>13,14</sup> no effect of such magnitude has been reported to occur with these. It may be redundant to emphasize the third point about the lack of shear history for the very nature of the effect studied is that shearing causes the melt flow to rise and that this increase can be reversed by erasing the shear history by dissolving the polymer, or possibly, by holding the melt for a very long time without shear. However, merely crystallizing the bulk polymer does not reverse the melt flow rate rise, but rather, the polymer must be dissolved and reprecipitated.

Presumably in solution the polymer coils swell and also, being more mobile than in the melt, have more opportunity to interpenetrate. Upon precipitation whatever structure is responsible for the original low melt flow is restored.

Kraus and Gruver,<sup>11</sup> who studied the rheological properties of linear and long-chain branched polybutadienes, noted that the branched polymers behaved differently from the linear polymers at low stresses, exhibiting extremely high apparent tensile viscosity and nonlinear elasticity. They hypothesize that the cause of these anomalies is that entanglements involving branch points require excess expenditure of energy to untangle at low shear stresses. However, Kraus and Gruver do not report any such effect such as found by Howells and Benbow or as in this work; in their paper on linear monodisperse polymers<sup>11</sup> it is stated explicitly that no evidence of thixotropy or degradation was observed. In many respects, however, their hypothesis provides a basis for explaining our results. In the absence of any direct evidence for the morphology of long-chain branched crystalline polymers, it can only be speculated about, but it seems reasonable to suppose upon crystallization from solution the various chains emanating from a branch point may find themselves in different crystals, thereby providing effective interpenetration of polymer coils

upon subsequent melting. The entanglements resulting from this interpenetration may then be responsible for the structure that is broken down by shear.

Branch point entanglements of the same sort can be formed by ordinary processes of Brownian motion, by the strength of the entanglement couplings and the time required to disrupt them by shear may be much greater for the entanglements formed by crystallization from solution, in which the polymer molecules are swollen and mobile, than of those formed in the melt. As Kraus and Gruver point out, their tensile creep results can be explained by the presence of an easily disrupted structure; it is concluded here that the process of dissolving and crystallizing the polymer produces a much stronger structure. The significance of this structure lies in the large magnitude and the long persistence of its effect on the flow properties, and in the possibility of mistaking its occurrence for polymer degradation.

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