

## Some Effects of Emulsion Polymerization Conditions on Molecular Polydispersity and Rheological Properties of Poly(methyl Methacrylate)

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### Synopsis

Emulsion polymerization conditions of free-radical-polymerized poly(methyl methacrylate) have been examined in relation to the molecular weight and molecular polydispersity of the resulting polymers. In turn, molecular weight and molecular polydispersity have been related to the apparent viscosity and the appearance of the extrudate produced by an Instron capillary rheometer. The length of time for monomer addition to the polymerization medium was found to be a variable of primary concern in the emulsion polymerization. Continuous monomer addition (from 1 to 2 hr) resulted in a poly(methyl methacrylate) with a narrow distribution ( $\sim 2.0$ ) and medium molecular weight ( $\sim 132 \times 10^3$ ). Both molecular weight and polydispersity were found to significantly affect apparent viscosity and extrudate appearance. Differences in the rheological parameters were most marked at the lowest shear rate run in this study. The poly(methyl methacrylate) samples with medium molecular weight and more narrow molecular polydispersity exhibited the best combination of low apparent viscosity and smooth glossy appearance.

### INTRODUCTION

The purpose of this research was to determine the effect of several emulsion polymerization conditions on the molecular weight and molecular polydispersity of poly(methyl methacrylate) (PMMA). In turn, the effect of molecular weight and molecular polydispersity on the melt viscosity and extrudate appearance was determined.

There are several ways to control the molecular weight of a polymer formed by a free-radical emulsion polymerization, but many of these variations will also affect the polydispersity index (PDI) of the product. As demonstrated here, keeping all polymerization variables constant but changing the mode of monomer addition, poly(methyl methacrylates) with a relatively narrow PDI can be obtained with varying degrees of polymerization.

It was observed previously that die swell and melt fracture affected extrudate appearance<sup>1</sup> and became much less pronounced with narrow MWD polymers than broad MWD polymers.<sup>2</sup> But these characteristics, die swell and melt fracture, along with the apparent viscosity ( $\eta_a$ ) of a

polymer melt, also depended on the molecular weight above some critical molecular weight for chain entanglement ( $M_e$ ). All of the PMMA polymers used in this study were considered to be well above this critical molecular weight for entanglement. (For PMMA  $M_e = 3700$ .)<sup>3</sup> Also, it was demonstrated that polystyrene with a narrow MWD had tensile strength which was consistently higher than that of a polydisperse material.<sup>4</sup> It is well known that polymers with molecular weight above  $M_e$  have more entanglements and higher physical strength, but also higher  $\eta_a$ . Considering these facts, it should be possible to produce a PMMA with reasonably good strength, appearance, and low apparent viscosity by maximizing the molecular weight while maintaining a relatively narrow PDI.

### EXPERIMENTAL

Poly(methyl methacrylate) samples V-044, V-811 for this study were obtained from Rohm and Haas Company, and G304, G36, G38, G39, G42, G324 were prepared at Goodyear Tire & Rubber Company laboratories by simple free-radical emulsion polymerization techniques. Molecular weight parameters were determined experimentally by osmometry ( $\bar{M}_n$ ) and solution viscosity ( $\bar{M}_v$ ). It is well known that viscosity-average molecular weight ( $\bar{M}_v$ ) is not a true weight average. However, for comparative purposes, all on the same type polymers (PMMA), the viscosity-average molecular weight is used as an indication of molecular size and PDI. This approximation is further justified since the intrinsic viscosity-molecular weight relationship used originated from light-scattering measurements.<sup>5</sup> The empirical relationship used was as follows:

$$[\eta]_{30^\circ\text{C}} \text{ CHCl}_3 = 4.3 \times 10^{-5} \bar{M}_v^{0.8}.$$

The following qualitative expression is frequently used in similar rheological studies to indicate the molecular homogeneity or polydispersity:

$$\frac{\bar{M}_v}{\bar{M}_n} = \text{PDI}.$$

Samples from Rohm and Haas were used as obtained (pelletized). The PMMA samples prepared in this laboratory were milled and coarsely ground to simulate the previous processing of V-044 and V-811. All resin samples were effectively dried in a circulating air oven before rheometry was run to remove all traces of moisture.

An Instron capillary rheometer was used to obtain melt viscosity data at temperatures of 375°, 400°, and 450°F at shear rates from 21.4 to 1068 sec<sup>-1</sup>. The capillary had a 90° included entry angle, a length of 2.00 in., and a diameter of 0.056 in. It was assumed that this length-to-diameter ratio ( $L/D = 35.71$ ) was sufficient to minimize capillary end effects, and no corrections were made in the data.

## DISCUSSION

With reference to the polymerization work, G304 was used as a control. Both increasing the temperature and the amount of transfer agent effectively decreased  $\bar{M}_v$  (Table I, G36 and G38). When varying the time of the monomer mixture\* addition (monomer mixture contains methyl methacrylate and a mercaptan transfer agent, *t*-dodecyl mercaptan), both  $\bar{M}_v$  and molecular polydispersity decreased (G39 and G324) compared to G304. The results of this study indicate that  $\bar{M}_v$  and the molecular polydispersity of a free-radical emulsion polymerized PMMA can be controlled simply by varying the time period of the monomer mixture addition, all other variables remaining constant. This variation becomes significant when considered in relation to the ease of processing of the high polymer.

TABLE I  
Potassium Persulfate Emulsion Polymerization Conditions and Molecular Weight Parameters of Poly(methyl Methacrylate)

Sample	Mercaptan, phr <sup>a</sup>	Time for monomer addition	Temp., °C	$\bar{M}_v \times 10^{-5b}$	$\bar{M}_n \times 10^{-4b}$	PDI
G304	1	instantaneous	60	3.5 ± 1.4	15.15	2.3
G36	1	instantaneous	70	1.6 ± 0.01	6.42 ± 1.37	2.4
G38	2.5	instantaneous	60	0.9 ± 0.3	3.89 ± 0.17	2.4
G39	1	2.5 hr	60	1.1 ± 0.1	5.42 ± 0.80	2.0
G42	1	1 hr	60	2.1 ± 0.6	9.54	2.3
G324	1	1.2 hr	60	1.3 ± 0.6	7.44 ± 1.58	1.8
V-044	—	—	—	1.7 ± 0.0	7.23	2.3
V-811	—	—	—	1.1 ± 0.4	2.78	4.0

<sup>a</sup> Based on monomer charge.

<sup>b</sup> 95% Confidence limits.

V-044 and V-811 are included in this study to demonstrate that not only the molecular polydispersity, but also  $\bar{M}_v$  have profound effects on  $\eta_a$  and on the appearance of the PMMA extrudate. V-044 has a more narrow PDI than V-811, but the former has a slightly higher  $\bar{M}_v$ . Yet, the apparent viscosity at 400°F\* of both PMMA samples is the same at low and high shear rates (Table II). The lower PDI of V-044 may effectively reduce  $\eta_a$ , but this is negated by the higher  $\bar{M}_v$ . When V-811 is compared with G38, which has a smaller  $\bar{M}_v/\bar{M}_n$  ratio but almost the same  $\bar{M}_v$ , the effect of reduced polydispersity is seen to effectively reduce the apparent viscosity at low and medium shear rates. However, at the higher shear rate, the  $\eta_a$  was not significantly reduced with reduced polymer polydis-

\* The apparent viscosity data showed the same trend for all temperatures. The data at 400°F were chosen for illustration and to eliminate the temperature variable for ease of data analysis.

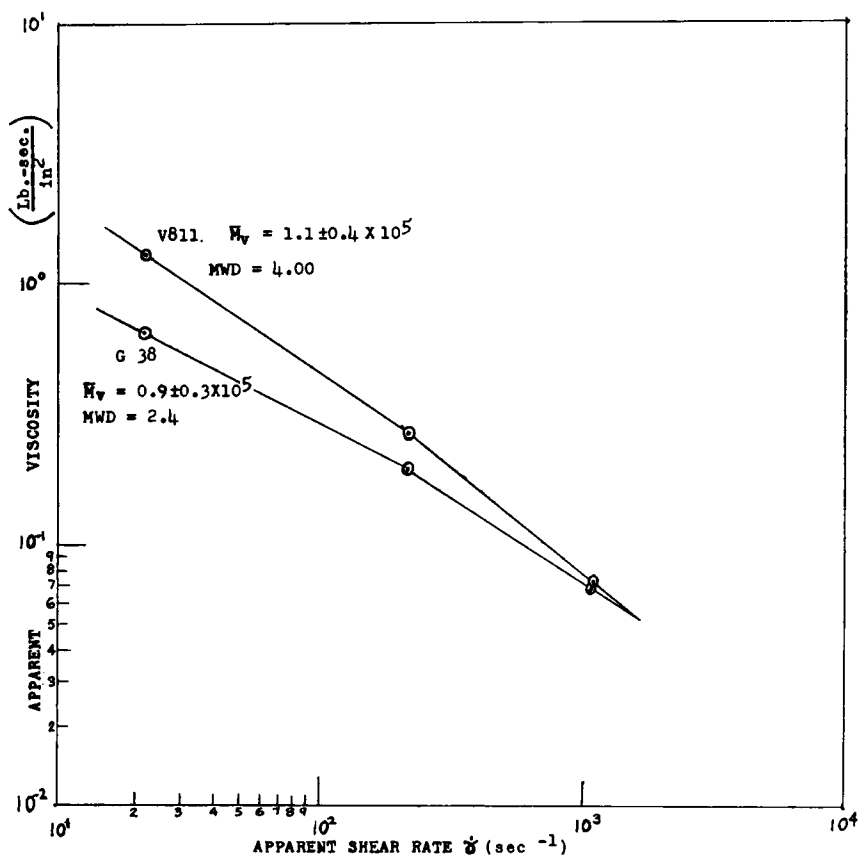


Fig. 1. Plot of apparent viscosity vs. apparent shear rate at 400°F for poly(methyl methacrylates) with about the same  $\bar{M}_v$ , but different polydispersities.

persity (Fig. 1). G304 is compared with V-044 to demonstrate that V-044 with lower  $\bar{M}_v$ , and about the same polydispersity has lower  $\eta_a$  at all shear rates run in this study, but the difference is more pronounced at the lowest shear rate (Fig. 2).

Confirming data have been obtained to demonstrate that both  $\bar{M}_v$  and molecular dispersity affect the apparent viscosity of a PMMA melt, and this effect is most marked at low shear rates. But the apparent viscosity of the poly(methyl methacrylate) is not the only factor to be considered when preliminary decisions are being made about the processability of the polymer. The appearance of the extrudate is also of vital importance. Melt fracture and irregularities in the flow of the polymer will cause the extrudate to appear anywhere from knobby with gross surface roughness to slightly shark-skinned or orange-peeled.<sup>1</sup> Obviously, the most desirable extrudate is one with a smooth glossy surface. The appearance of the extrudate, like apparent viscosity, is influenced by  $\bar{M}_v$  and molecular poly-

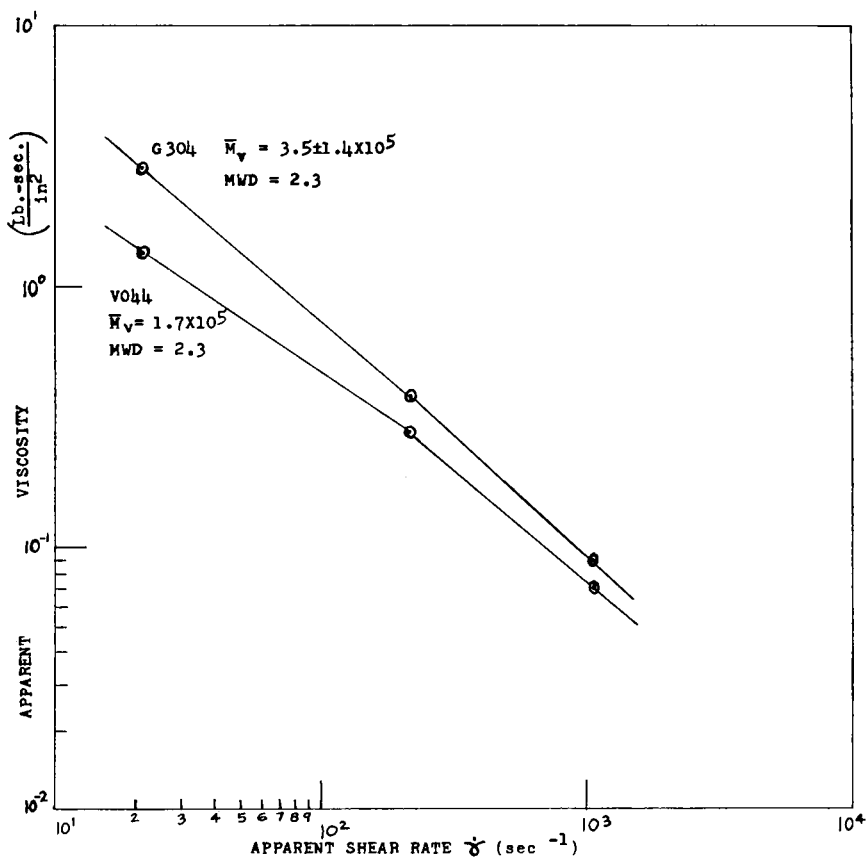


Fig. 2. Plot of apparent viscosity vs. shear rate at 400°F for poly(methyl methacrylates) with the same polydispersity but different  $\bar{M}_v$ .

dispersity. Using V-044 as a control, a comparison of the extrudate appearance with V-811 reveals that, even though the  $\bar{M}_v$  of V-811 is slightly lower than that of V-044, the PDI of V-044 is more narrow and the extrudate has a better appearance than V-811 (Table III). When comparing V-044 with G304, which has similar polydispersity but a smaller  $\bar{M}_v$ , it is seen that the G304 extrudate is knobby, while the V-044 extrudate is smooth and glossy. It appears that both  $\bar{M}_v$  and molecular polydispersity have a pronounced effect on polymer extrudate appearance as well as  $\eta_a$ . Further investigation revealed that the best combination of properties was obtained with PMMA sample G42:  $\bar{M}_v = (2.14 \pm 0.63) \times 10^5$ ,  $\bar{M}_v/\bar{M}_n = 2.25$ ,  $a = 1.63$  lb-sec/in.<sup>2</sup> at a low shear rate, and smooth glossy extrudate at low shear rate. The samples from the low shear rate were used for comparison of extrudate appearance because at high shear rate some samples exhibited evidence of depolymerization (bubbles).

TABLE II  
 Rheology of PMMA at 400°F

Sample	Shear stress, lb/in. <sup>2</sup>	Shear rate, sec <sup>-1</sup>	Apparent viscosity, lb-sec/in. <sup>2</sup>
V-811	27.9	21.4	1.30
	58.4	214	0.273
	78.8	1068	0.074
V-044	29.2	21.4	2.36
	59.5	214	0.278
	76.2	1068	0.071
G304	61	21.4	2.84
	81.3	214	0.38
	95.2	1068	0.089
G38	13.8	21.4	0.648
	42.5	214	0.199
	73.0	1068	0.070
G42	34.9	21.4	1.63
	66.1	214	0.308
	92.7	1068	0.087

 TABLE III  
 Comparison of Molecular Weight Parameters of PMMA with Appearance of Extrudate  
 at 400°F and Low Shear Rate (21.4 sec<sup>-1</sup>)

Sample	$\bar{M}_v \times 10^{-5}$ <sup>a</sup>	PDI	Appearance of extrudate
V-811	1.1 ± 0.4	4.0	shark skin <sup>b</sup>
V-044	1.7 ± 0.0	2.3	smooth
G304	3.5 ± 1.4	2.3	knobby <sup>c</sup>
G36	1.6 ± 0.0	2.4	smooth
G38	0.9 ± 0.3	2.4	orange peel <sup>d</sup>
G39	1.1 ± 0.1	2.0	smooth
G42	2.1 ± 0.6	2.3	smooth
G43	3.7 ± 0.2	2.1	knobby

<sup>a</sup> 95% Confidence limits.

<sup>b</sup> Shark skin indicates a rough, grainy surface.

<sup>c</sup> Knobby indicates gross irregularities in the extrudate.

<sup>d</sup> Orange peel indicates a relatively smooth but slightly blistered surface.

## RESULTS

In the present investigation it was determined that a free-radical, emulsion-polymerized poly(methyl methacrylate) could be obtained with a narrow molecular polydispersity and varying viscosity-average molecular weight by controlling the time period of the monomer mixture addition.

This result from the polymerization of methyl methacrylate is similar to the result from the polymerization of styrene reported by Krackeler and Naidus.<sup>6</sup> They proposed a monomer-starved particle to explain the lower  $\bar{M}_v$  of a polymer resulting from continuous monomer addition and a concentration gradient of monomer within the particles to explain the similar molecular weight distribution of continuous and batch monomer addition.

It was also demonstrated that  $\bar{M}_v$  and molecular polydispersity must be considered together, and are of equal importance, when determining rheological flow characteristics of poly(methyl methacrylate). G39 and G42, typical emulsion PMMA's, but prepared by continuous monomer mixture addition, had the best combination of molecular weight parameters and rheological flow characteristics of all poly(methyl methacrylate) samples included in this study.

### CONCLUSIONS

Simple correlation has been drawn between polymerization conditions and viscosity-average molecular weight and molecular weight polydispersity. In turn, these molecular parameters have been related to appearance and apparent viscosity of the extrudate produced by an Instron capillary rheometer. From the results obtained in this study and confined to the parameters investigated, it appears that for emulsion-polymerized poly(methyl methacrylate),  $\bar{M}_v$  may approach an upper limit of about  $2.0 \times 10^5$  if PDI is relatively narrow ( $\text{PDI} \leq 2.3$ ), while maintaining a good extrudate appearance and relatively low apparent viscosity. The results of this work also indicate that a poly(methyl methacrylate) having both a viscosity-average molecular weight and a molecular polydispersity of this order can be obtained by variations in the time period of the monomer mixture addition during the free-radical emulsion polymerization.

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