Solution and Bulk Properties of Branched Polyvinyl Acetates IV—Melt Viscosity

V. C. LONG*, G. C. BERRY† and L. M. HOBBS‡

The melt viscosities of some randomly branched and some comb shaped branched polyvinyl acetate fractions were compared to the viscosities of linear polymer over a range of molecular weights. The melt viscosity of the branched polymer was usually higher than that of linear polymer of the same weight average molecular weight. The extent of this increase was related to the molecular weight of the branches but no correlation could be found which included the number of branches per molecule. This unusual behaviour is believed to be due to the fact that the length of the branches in the polymers of this study was above the critical chain length for polyvinyl acetate which made it possible for the branches to be engaged in intermolecular chain entanglements.

THE flow behaviour of molten polymers is a subject of considerable interest, both from theoretical and practical viewpoints. Fair success has been achieved in correlating the rheology and molecular parameters for linear polymers. However, the treatment of the branching parameter has not been as successful, and it was the intention of this study to extend the present knowledge in this area.

The melt viscosities of two series of branched polyvinyl acetate fractions have been compared to the viscosity of linear material over a molecular weight range of 4×10^5 to 5×10^6. The branched structures investigated were of two types, random (series 4) and comb shaped (series 6). Fractions of linear material (series 5) were studied to provide a basis of comparison for the branched polymers. The polymers used have been fully characterized in earlier publications[1-3] and the reader is referred to these articles for descriptions of the samples.

EXPERIMENTAL

(1) Melt viscosity measurement

The polymers used in the melt viscosity measurements were isolated from filtered benzene solutions by the freeze-drying technique. Care was taken to remove all traces of residual solvent. Cylindrical test specimens, 0·57 in. in diameter, were then moulded at 155°C in a plunger type mould.

The melt viscosities were measured with a Williams parallel plate plastometer[4] which had an upper plate weighing 5·0 kg. Aluminium foil was used as a parting agent. Viscosities in the range 10^6 to 10^9 poise may be measured with an error of about five per cent in the middle of the span, the error increasing toward either limit.

*Present address: E. I. du Pont de Nemours & Co., Wilmington, Delaware.
†Present address: Mellon Institute, Pittsburgh, Pennsylvania.
‡Present address: Bennettsville, South Carolina.

The measurements were made at two temperatures. The viscosities of selected fractions of series 4 and 5 (randomly branched and linear) were measured at $155° \pm 0·5°$C in a circulating air oven[5]. The viscosity of grafted branched fractions of series 6 and the linear fractions of series 5 were measured at $183°$C because of the high viscosities of the grafted polymers[6]. These measurements were carried out in a nitrogen atmosphere as a precaution against degradation. In addition, the samples were placed under nitrogen after evacuation prior to use to eliminate absorption of oxygen. Thermal stability was no problem at $155°$C as evidenced by no reduction in either melt viscosity repeated on the same sample or intrinsic viscosity as measured before and after the melt viscosity measurements. At $183°$C the linear fractions were stable within experimental error but the branched material exhibited some signs of degradation as may be seen in *Table 2*. This degradation, however, should not affect the qualitative nature of the results.

(2) *Treatment of data*

The melt viscosity in poises was calculated[4] by

$$\eta = 8·21 \times 10^6 W/mV^2 \tag{1}$$

where W is the load on the sample in kg and V is the sample volume in cm^3. In this equation, m is the slope in cm^{-4} sec^{-1} of the linear portion of the curve obtained when the reciprocal of the plate separation to the fourth power is plotted versus time. Equation (1) has been obtained under the assumptions that the flow is essentially Newtonian for the low shear rates encountered, that there is zero radial flow at the plates, that the axial flow is negligible compared to the radial flow, that steady-state flow conditions are realized, and that the diameter to height ratio exceeds about ten. The average shear rate $\bar{s}$ may be estimated[7] from

$$\bar{s} = 1·158 \times 10^6 (L^{5/2}W)(V^{3/2}\eta)^{-1} \tag{2}$$

where L cm is the plate separation. The low shear rates calculated from equation (2) ($\bar{s}$ less than $0·01$ sec^{-1}, the maximum $\bar{s}$ occurring for samples of lowest η), together with the absence of any dependence of η on the height to diameter ratio and experimental realization of a linear portion in the plot of $(1/L)^4$ versus time provide support for the use of equation (1) to compute η. In addition, data obtained here for the linear fractions at $155°$C fit very well with η/Mw data obtained by Fox and Nakayasu[8] at the same temperature on lower molecular weight fractions using capillary viscometers.

There still remains the possibility, however, that steady-flow conditions were not realized for some samples and that the value of m measured was in fact too high. This would be most likely to occur for the higher viscosity samples. In this case, the value of η reported would be too low, and would not change the character of the results, namely, increased η due to branching. We do not believe this latter source of error to be very important for this study.

A more serious source of error could be the presence of an impurity, hydroxyl groups for example, in the branched polymer which can cause

anomalous behaviour in some systems (see for example ref. 7). We have examined the possible presence of hydroxyl groups, the most likely contaminant, and have concluded that they can only be present in very small amounts, if at all[3].

Thus, we assert that equation (1) is the correct relation for analysis of our data, and that effects to be noted are due to the structural character of the polymer chains, i.e. the type of branching present.

The melt viscosity of the linear fractions may be represented by the relation $\eta_l = K_T \langle M \rangle_w^a$ where $a = 3\cdot65$ and $\log K_T$ is $14\cdot47_5$ at 155°C and $14\cdot99_1$ at 183°C. The ratios η_{br}/η_l at constant molecular weight were determined graphically. The subscripts br and l refer to branched and linear chains respectively.

RESULTS AND DISCUSSION

A complete description of the molecular flow process that results in the macroscopic property of the melt viscosity of a polymeric system does not exist although progress has been made for linear polymers. It has been generally assumed that a branched polymer should exhibit a lower melt viscosity η than a linear chain if comparisons are made at the same molecular weight and temperature[9, 10, 11, 15]. The results of this study show that this is not necessarily correct, and that the ratio η_{br}/η_l can exceed unity for some types of branched structure. All ratios of η_{br}/η_l considered here are at constant temperature and molecular weight. It should be noted that Tung[12] has observed differences in the activation energies for the melt flow of branched and linear polyethylene that would indicate $\eta_{br}/\eta_l > 1$ for these chains at high temperatures, as he has pointed out. This may not be a general situation, however, and Tung's results may be intimately connected with the presence of many very short chain (2 to 4C atoms) branches in polyethylene. Ratios of $\eta_{br}/\eta_l > 1$ have also been reported for
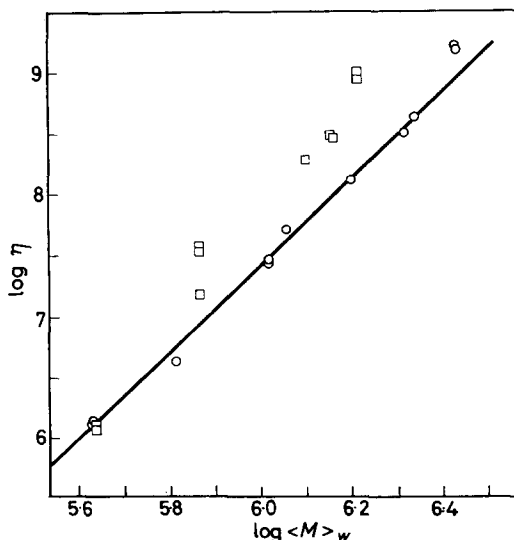

Figure 1—Melt viscosity at 155°C versus molecular weight: ▣ randomly branched polymers, series 4; ○ linear polymer, series 5

some polymers branched by irradiation, but these data are difficult to analyse since many parameters are being varied simultaneously[18].

The melt viscosity data obtained here are given as a function of molecular weight in *Figures 1* and *2* and *Tables 1* and *2*. It is immediately evident that many of the branched polymers have viscosities greater than those of linear chains of the same molecular weight, and further that the effect is quite large (η_{br}/η_l *ca.* 10) in some cases. We will show below that existing theories
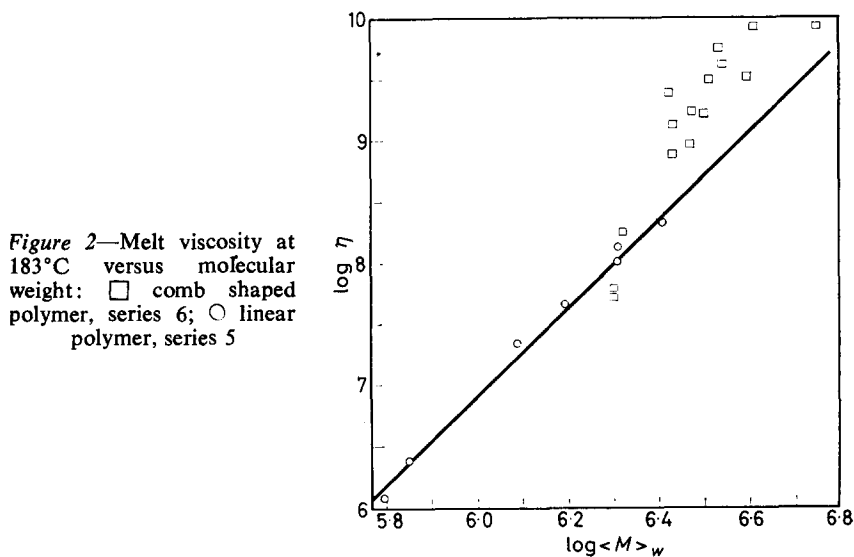

Figure 2—Melt viscosity at 183°C versus molecular weight: □ comb shaped polymer, series 6; ○ linear polymer, series 5

Table 1. Data for the linear polymer (series 5)

Fraction	T (°C)	$\langle M \rangle_w \times 10^{-6}$	$\eta \times 10^{-8}$ (poise)
5–3–2	155	2·66	15·5
5–3–2	155	2·66	(15·7)‡
5–2–3	183	2·53	20·5
5–3–3	155	2·17	4·41
5–3–3	183	2·17	1·37
5–3–3	183	2·17	(1·03)
Mixture*	155	2·07	3·33
5–5–3	155	1·57	1·30
5–T†	183	1·57	0·651
5–T	183	1·57	(0·610)
5–6–2	155	1·14	0·542
5–6–2	183	1·14	0·223
5–6–3	155	1·05	0·313
5–6–3	155	1·05	(0·315)
5–7–1	183	0·71	0·0249
5–7–2	155	0·65	0·0442
5–7–2	183	0·65	0·0120
5–7–4	155	0·43	0·0129
5–7–4	155	0·43	(0·0138)

*Fractions 5–3–2 and 5–6–3 combined.
†Unfractionated polymer 5.
‡( ) denotes second measurement on a single sample.

Table 2. Data for the randomly branched polymer (series 4) and the comb shaped polymer (series 6)

Fraction	T $(°C)$	$\langle M_{br}\rangle_w$ $\times 10^{-6}$	$\langle M_s\rangle_w$ $\times 10^{-3}$	g	$\eta \times 10^{-8}$ (poise)	η_{br}/η_l
4–4–2	155	1·64	78	0·58	8·92	5·65
4–4–2	155	1·64	78	0·58	(10·3)†	(6·53)
4–5–1	155	1·43	62	0·55	3·10	3·00
4–5–1	155	1·43	62	0·55	(3·13)	(3·03)
Mixture*	155	1·25	—	—	1·97	—
4–5–2	155	0·730	56	0·66	0·383	4·49
4–5–2	155	0·730	56	0·66	(0·353)	(4·14)
4–4–3	155	0·731	42	0·62	0·152	1·85
4–5–3	155	0·432	46	0·69	0·0127	1·06
4–5–3	155	0·432	46	0·69	(0·0117)	(0·98)
6–20–M	152	2·80	118	0·821	66·8	5·2
6–20–M	183	2·80	118	0·821	(9·51)	(2·9)
6–40–1	183	2·00	37·0	0·750	0·506	0·53
6–40–1	183	2·24	37·0	0·751	(0·624)	(0·66)
6–41–M	183	2·09	36·0	0·718	1·88	1·63
6–50–1	180	2·71	47·4	0·744	7·87	2·53
6–50–1	183	2·71	47·4	0·744	(7·08)	(2·35)
6–51–M	183	3·21	48·8	0·641	16·4	2·26
6–70–1	183	2·65	149·6	0·777	24·7	10·8
6–71–1	183	3·43	134	0·630	55·9	7·70
6–80–1	183	3·29	122	0·693	31·4	5·29
6–81–1	183	4·11	127	0·553	84·4	6·32
6–90–1	183	3·45	94	0·736	40·7	5·76
6–91–1	183	3·96	87·4	0·641	40·2	3·47

*Fractions 4–4–2 and 4–4–3 combined.
†( ) denotes second measurement on a single sample.

for the melt viscosity of linear chains may not be extended in a straightforward way to explain this behaviour, as has been previously supposed[14, 15], and will suggest some reasons for the deficiency.

The effect of branching on the isothermal melt viscosity for systems where interchain entanglements may be ignored has been treated theoretically by Ham[16] in a normal coordinate calculation of the relaxation times for melt flow. This calculation yields

$$\eta'_{br}/\eta' = g \tag{3}$$

where the primes denote viscosities under conditions of no interchain entanglements and g is the ratio of the mean square radii of branched and linear chains under theta-conditions. The parameter g is always less than or equal to unity. The same result may be extracted from the work of Bueche[17] or of Zimm and Kilb[18]. The effects of chain entanglement may be formally introduced by defining a function ϕ such that

$$\eta = \eta'\phi \tag{4}$$

In general, ϕ may be a complicated function of chain length, structure, etc., but $\phi \geqslant 1$. Thus, the ratio η_{br}/η_l becomes

$$\eta_{br}/\eta_l = g\phi_{br}/\phi_l \tag{5}$$

Equation (5) anticipates that chain entanglements may be accounted for

by determining the proper dependence of the chain mobility factor on molecular weight and chain structure, as has been suggested by others[16, 19, 20].

As a first approximation, one might try to carry over Bueche's method of calculating ϕ_l to obtain an expression for ϕ_{br} since there is nothing in that calculation explicity requiring linearity in the chain. In so doing, one must ignore all details of the chain geometry and consider instead only conformation averaged segment density functions. Necessarily then, the only remaining parameter related to branching will be some function of averaged dimensions, such as g. In fact, Bueche[15] has given the result $\eta_{br} = g^{3\cdot5}\eta_l$, or $\phi_{br} = g^{2\cdot5}\phi_l$ without providing details of the calculation. This result is in good accord with empirical results obtained by Fox and Allen[14] on star shaped polymers although other details do not agree. It is clear that this expression cannot fit our data, however, since $g \leqslant 1$ and we find $\eta_{br} > \eta_l$ in some cases. Moreover, examination of the data in *Table 2* reveals that samples with the same value for g may have different values for η_{br}/η_l. This indicates that any model that ignores the details of the chain geometry (e.g. number and length of branches, etc.), using instead smoothed segment density functions, cannot provide an adequate general prescription for ϕ_{br}/ϕ_l.

Thus, we are led to conclude that the details of the structure of the chain must have a strong effect on the flow properties, no doubt through an effect on the probability for entanglement of various segments of the chain. Simple equivalence of g, that is of average chain dimensions, does not ensure equivalence of flow properties. Other variables, such as distribution and length of branches in the structure, appear to be required for a complete description of η_{br}. This suggests that ϕ_{br}/ϕ_l could depend on some
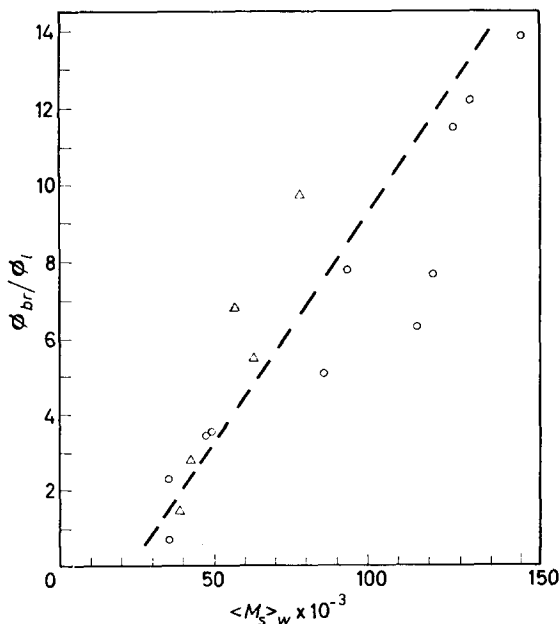

Figure 3—Ratio ϕ_{br}/ϕ_l calculated on $\eta_{br}/g\eta_l$ versus the molecular weight of branches in a branched polymer: △ randomly branched polymer, series 4; ○ comb shaped polymer, series 6

detail of the chain geometry, such as the branch length or frequency in a comb shaped polymer, if only this parameter were varied while the main features of the chain geometry were held constant. In particular, one can vary the length of the branches in a comb shaped polymer containing a relatively few branches of length short compared to the backbone. This is the approach taken here, and *Figure 3* shows the correlation between ϕ_{br}/ϕ_l, calculated as $\eta_{br}/g\eta_l$, and the molecular weight of the branches $\langle M_s \rangle_w$ in a comb shaped polymer. The values of $\langle M_s \rangle_w$ are taken from Part II[2]. In addition, data for the randomly branched series 4 have been included in *Figure 3* since the chain geometry is not very different from that of the comb shaped polymers. Here $\langle M_s \rangle_w = \langle M_{br} \rangle_w / (2k+1)$ where k is the number of branches in a chain of molecular weight[3] $\langle M_{br} \rangle_w$. It is clear that a strong dependence of ϕ_{br}/ϕ_l on $\langle M_s \rangle_w$ does exist, and that it yields $\phi_{br}/\phi_l = 1$ for $\langle M_s \rangle_w \approx 28\,000$. The fact that this value of $\langle M_s \rangle_w$ is in good agreement with the critical chain length of linear polyvinyl acetate determined by Fox and Nakayasu[8] is significant and will be commented on below. Various other correlations were attempted, e.g. ϕ_{br}/ϕ_l versus g, k, etc., but these uniformly showed considerable scatter. The absence of a clear dependence of ϕ_{br}/ϕ_l on k at a given value for $\langle M_s \rangle_w$ for the comb shaped polymers is surprising, but probably the data are not extensive enough or the span in k is not large enough to reveal such a dependence.

The dependence of ϕ_{br}/ϕ_l on the length of a branch exhibited above is evidence that the presence of branches can alter the effect of the cooperative motion of segments necessary for flow provided the branches are long enough. It has been suggested several times that the cooperative motion of segments should be enhanced in a branched structure due to the chain geometry, thus leading to a decreased viscosity[9, 11]. This is probably correct in the absence of chain entanglements, but the very fact that the segments must experience an enhanced cooperative mode of flow can make the existence of chain entanglements more important in branched polymers. That is, the branched polymer may be more effectively trapped by its entanglements because its various arms do not allow a simple snaking motion through the entanglements. The observation that ϕ_{br}/ϕ_l decreases to unity as the branch length decreases to the critical chain length supports this view since this should represent the minimum chain length upon which effects due to interchain entanglements of the branches should appear. Opposing this effect, the probability for interchain entanglement must decrease with branching due to the more compact nature of the chain structure.

We suggest, then, that branching can cause an increase in the melt viscosity provided that:

(1) the branches are long enough to become engaged in interchain entanglements, e.g. at least longer than the critical chain length, and

(2) the chain structure is such that the chain elements have a high probability for *interchain* entanglement.

A comb polymer with very short branches is an example for which condition 1 is not fulfilled, and a star polymer with all the branches emanating from a single node provides an example for which condition 2 is not obeyed, unless the branches are very much longer than the critical chain length. It

is clear that the single parameter g will not in itself be sufficient to characterize η_{br}/η_l under these circumstances.

Obviously it would be desirable to have these ideas expressed quantitatively and to be able to give ϕ_{br}/ϕ_l in terms of the chain configuration, chain length, etc. Unfortunately, this problem does not appear near a general solution. The failure of the attempted modification of Bueche's results for a linear chain suggests that a considerable amount of detail about the chain configuration must be included in the calculation, and in particular that the use of conformation averaged segment density functions will not be sufficient. This will require a more precise statement about the nature of interchain entanglements.

Chemical Engineering Department,
University of Michigan,
Ann Arbor, Michigan.

REFERENCES

[1] HOBBS, L. M. and LONG, V. C. *Polymer, Lond.* 1963, **4**, 479
[2] BERRY, G. C. and CRAIG, R. G. *Polymer, Lond.* 1964, **5**, 19
[3] BERRY, G. C., HOBBS, L. M. and LONG, V. C. *Polymer, Lond.* 1964, **5**, 31
[4] DIENES, G. F. and KLEMM, H. F. *J. appl. Phys.* 1946, **7**, 458
[5] LONG, V. C. *Ph.D. Thesis*, University of Michigan, Ann Arbor, Michigan, 1958
[6] BERRY, G. C. *Ph.D. Thesis*, University of Michigan, Ann Arbor, Michigan, 1960
[7] LONGWORTH, R. and MORAWETZ, H. *J. Polym. Sci.* 1958, **29**, 307
[8] FOX, T. G. and NAKAYASU, H. Abstracts of Papers, 137th Meeting of the American Chemical Society, III, April 1960
[9] WEIL, L. L. *Thesis*, Columbia University, New York, N.Y., 1945
[10] FOX, T. G and LOSHACK, S. *J. appl. Phys.* 1955, **26**, 1680
[11] MOORE, L. D. *J. Polym. Sci.* 1959, **36**, 155
[12] TUNG, L. H. *J. Polym. Sci.* 1960, **46**, 409
[13] CHARLESBY, A. and THOMAS, D. *Symposium über Makromolekulen*, 1959. I–C–8
[14] FOX, T. G and ALLEN, V. R. Preprints, Division of Polymer Chemistry, American Chemical Society, V3, No. 1, 6 (1962)
[15] BUECHE, F. *J. Polym. Sci.* 1959, **42**, 551
[16] HAM, J. S. *J. chem. Phys.* 1957, **26**, 625
[17] BUECHE, F. *J. chem. Phys.* 1952, **20**, 1959; 1956, **25**, 599
[18] ZIMM, B. H. and KILB, R. W. *J. Polym. Sci.* 1959, **37**, 19
[19] FERRY, J. D. *Viscoelastic Properties of Polymers.* Wiley: New York, 1961
[20] PETICOLAS, W. L. *J. Polym. Sci.* 1962, **58**, 1405