

Solution and Bulk Properties of Branched Polyvinyl Acetates Part II—Synthesis of Some Branched Polyvinyl Acetates

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A series of comb-shaped branched polyvinyl acetates has been prepared by a graft polymerization technique. Branches of a specified average chain length have been grafted to a linear backbone polymer with a narrow molecular weight distribution. The branched polymers have a molecular weight distribution whose breadth is very close to the linear fraction used for the backbone chain. The number average molecular weight of the branches has been varied from 18 000 to 106 000. The molecular weight of the linear backbone polymers is of the order of one million.

THE bulk and solution properties of branched macromolecules have been of considerable practical and theoretical interest for a number of years. The study of branched polymers is complicated by the increased complexity of the theoretical developments and the difficulty of obtaining a branched polymer with some *a priori* knowledge of its structure. The aim of this investigation has been to prepare a series of branched polyvinyl acetates with known structures, and to examine some of their solution and bulk properties. This paper will be concerned with the preparation of such a series of branched polymers. The solution and bulk properties of the polymer obtained will be presented elsewhere.

A previous study of some branched polyvinyl acetates by Long¹, utilized samples of a polymer prepared at a high conversion. Even though these samples were fractionated according to their solubility characteristics, there remained some ambiguity in the assignment of a structure to each sample. In an attempt to avoid this difficulty, a graft polymerization has been used here to prepare branched polymers having a narrow molecular weight distribution, and a given number of branches of a certain average chain length. Vinyl acetate has been polymerized in the presence of narrow molecular weight fractions of a linear polyvinyl acetate (PVOAc), a chain transfer solvent, and an initiator. The average molecular weight of the new polymer formed in the graft polymer was kept considerably less than that of the linear backbone polymer by adjusting the molar ratio of the monomer to solvent to facilitate the later removal of the new unbound polymer. This condition placed an upper limit on the ratio of the branch to backbone chain length. The branches bound to the backbone have the same average length as the new unbound polymer formed concurrently in the polymerization²⁻⁴. Thus, the use of the chain transfer solvent allows the average length of the branches to be controlled, and one has an easy means of

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determining the length of the branches by examination of the unbound material. The number of branches per molecule resulting from the graft polymerization is dependent on the degree of conversion, allowing a series of branched polymers to be prepared with a relatively wide range of known structures.

There are several advantages to this method of preparation. The necessity of fractionating a branched polymer with a broad molecular weight distribution, as well as a wide distribution of molecular structures, is avoided^{5,6}. Since no special active sites are required to either attach the branches to the backbone chemically^{7,8}, or to initiate their growth from the backbone⁹⁻¹², the problem of residual foreign groups in the branched polymer does not arise. The use of a chain transfer solvent provides better control over the chain length of the branches than is usually obtained in a graft polymerization^{2,13-18}, and suppresses termination reactions which can lead to network formation. The choice of vinyl acetate as the monomer gives a system with the necessary high polymer chain transfer constant. Some ten to fifty branches have been placed on the backbone, approximately eighty to ninety per cent of these directly on the backbone with the remainder on other branches. This latter complication is undesirable since it broadens the chain length distribution of the branches, but it in no way limits the usefulness of the polymers. Some of the difficulties encountered will be discussed later in greater detail.

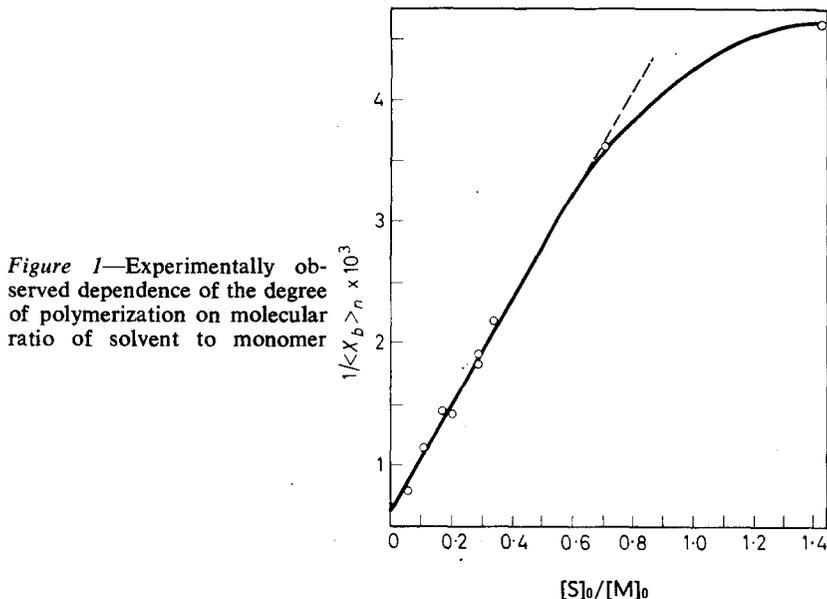
EXPERIMENTAL

Polymerization procedure and materials

The linear fractions of PVOAc used as the backbone polymer have been described fully by Long¹. These linear polymers were prepared by the photo-sensitized polymerization of vinyl acetate at low temperatures to approximately ten per cent conversion. The linearity of narrow molecular weight fractions of the resultant polymer has been demonstrated by Long. Vinyl acetate (Niacet vinyl acetate, DPA, Carbide and Carbon Chemicals Co.) was the monomer, toluene the chain transfer solvent, and azo-bis-isobutyronitrile (Eastman Organic Chemicals) the catalyst. Monomer and chain transfer solvent were purified by distillation at about 300 mm of mercury under an atmosphere of dry oxygen-free nitrogen in a column packed with glass helices. A predetermined amount of polymer was evacuated at 10^{-5} mm of mercury for 60 h after which middle fractions (boiling range of 0.1°C) of monomer and toluene and initiator were added to give an initial polymer concentration of 5 to 10 g/dl of liquid and initiator was added to give a concentration of about 10^{-4} Molar. The total amount of liquid was adjusted so that the initial polymer concentration was about 5 to 10 g/100 ml of liquid.

The contents of the tube were then cooled to about -90°C , and degassed at 10^{-4} to 10^{-5} mm of mercury to remove residual oxygen. None of the contents of the reaction vessel were lost in this degassing operation. After a degassing period of one hour, the reaction tubes were sealed and the contents agitated to cause solution of the polymer at room temperature. The tubes were then held at 88°C , the mixture being agitated with the

magnetic stirring bar. The polymerization was allowed to proceed to about 20 per cent conversion of the monomer.



The value of $[S]_0/[M]_0$, the initial solvent to monomer mole ratio, such that the new polymer formed would have the desired number-average molecular weight, $\langle M_b \rangle_n$, was determined from the correlation given in Figure 1 observed between these variables for the reaction conditions used. ($\langle M_b \rangle_v$, the viscosity average molecular weight is taken on twice $\langle M_b \rangle_n$).

Isolation of the branched polymer

The contents of the tube were added dropwise to a large volume of petroleum ether after the polymerization. The isolated polymer was washed with petroleum ether and dissolved in 50 ml of methanol per gramme of polymer. A fractional precipitation was then performed to isolate as much of the graft polymer from the unbound polymer-graft polymer mixture as possible. The fractionation was carried out at 35°C in a litre screw-top bottle with the contents being agitated by a magnetic stirrer. Distilled water was added dropwise until the mixture became turbid, at which point a large excess of water was added. Some of the low molecular weight unbound polymer was inevitably carried down with the graft polymer in the process, but this was of no concern at this stage. The contents of the vessel were then heated to a temperature sufficient to dissolve the precipitate, and then allowed to cool slowly with stirring to reprecipitate the desired polymer. After a settling period of 12 hours, the precipitate was recovered by syphoning off the solution. The unbound polymer in the solution could be recovered by evaporation to dryness. In several instances, the solution was further treated with a large excess of water before further turbidity developed. There was never very much polymer in this second precipitate,

and it had an intrinsic viscosity very near that of the unbound polymer. Thus, the fractionation appeared to be removing almost all of the graft polymer from the graft polymerization mixture.

The polymer now could be subjected to either or both of two different operations. If the entire amount of the graft polymer was to be recycled in another grafting polymerization, the polymer was placed in a reaction vessel and dissolved in benzene. After freezing this solution along the sides of the tube, the benzene was sublimed off at 0°C, leaving the polymer in a porous form. The polymer was degassed at about 10⁻⁵ mm of mercury in preparation for a new graft polymerization, repeating the cycle given above.

If the entire amount of a graft polymer was to be used as a fraction of the branched polymer with no further graft polymerization cycles, then the precipitate was dissolved in methanol to give a concentration of 1 g of polymer in 100 ml of methanol. The fractional precipitation described above was then repeated, but an effort was made to precipitate only about 1 to 2 g fractions of the graft polymer. Successive precipitations were performed until no polymer came down with further addition of water. The unbound polymer remaining in solution was then recovered by evaporation to dryness and added to that previously recovered. Usually, most of the graft polymer came down in the first fraction. The fractions of graft polymer were dissolved in acetone and then cast in a film for solvent removal. The film was freed from residual solvent by evacuation at 10⁻⁶ mm of mercury for two to three days.

In some cases half of the graft polymer underwent further graft polymerization, the remainder being retained as a branched polymer for further study. In these instances, the polymer as recovered wet from the first precipitation fractionation was divided into equal parts by weight, and the two parts subjected to the two different operations as described above.

Some attention was given to the possibility of degradation of the backbone polymer under the graft polymerization conditions. A toluene solution of a linear polymer was held at 90°C for 12 h in the presence of the catalyst, which exceeded the usual reaction time of from one to six hours. No significant change was noted in the intrinsic viscosity of the polymer, indicating the absence of any serious degradation.

Polymer characterization

Light scattering and intrinsic viscosity measurements were made on the first fractions. In some cases where the first fraction was less than one gram in weight, measurements were also made on a mixture comprised of the first two fractions (mixtures designated by *M* in *Table 2*). The intrinsic viscosity of the unbound polymer was measured and the molecular weight of the unbound polymer, and thus of the branches on the graft polymer, was calculated from the relationship¹

$$\log \langle M \rangle_v = 5.426 + 1.48 \log [\eta] \quad (1)$$

All intrinsic viscosity measurements were performed in benzene at 35°C using a modified Ubbelohde viscometer. The data from these polymerizations are given in *Table 1*.

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Table 1. Graft polymerization data

Polymer	Conversion X	Unbound polymer $[\eta]$	Unbound polymer $\langle M_b \rangle_v$	Backbone polymer $\langle M_i \rangle_w$	$\langle M_i \rangle_w \Sigma X$	$\langle M_b \rangle_v^*$
6-20	0.365	0.520	$\times 10^3$ 113.0	$\times 10^6$ 2.27	$\times 10^4$ 132	$\times 10^3$ 118
	0.218	0.563	127.0			
6-30	0.272	0.459	99.0			
	0.289	0.373	75.0			
	0.365	0.399	69.0	1.29	119	79.2
6-40	0.163	0.213	39.6			
	0.145	0.219	39.6			
	0.106	0.185	33.0			
	0.127	0.189	34.0	1.50	81	37.0
6-41	0.159	0.207	37.5			
	0.116	0.174	31.2			
	0.171	0.193	34.6	1.50	148	36.0
6-50	0.153	0.219	40.0			
	0.233	0.267	50.0			
	0.157	0.270	52.0			
	0.209	0.253	47.0	2.02	152	47.4
6-51	0.198	0.267	50.0			
	0.185	0.261	49.0			
	0.148	0.285	54.0	2.02	260	48.8
6-60	0.348	0.821	212	3.76	131	212
6-70	0.323	0.667	158			
	0.167	0.582	133	2.16	106	149.5
6-71	0.316	0.468	99			
	0.274	0.605	139	2.16	230	134
6-80	0.257	0.544	122			
	0.228	0.554	123	2.27	110	122
6-81	0.281	0.501	108			
	0.176	0.703	170	2.27	214	127
6-90	0.226	0.418	86			
	0.226	0.479	102	2.54	115	94.0
6-91	0.268	0.381	76.5			
	0.163	0.522	112	2.54	236	87.4

*The average molecular weight of the branches after a series of graft polymerizations is calculated as $\langle M_b \rangle_v = \Sigma X \langle M_b \rangle_v / \Sigma X$ where the sums are overall polymerizations in a grafting cycle.

Light scattering measurements were carried out in 1,2,4-trichlorobenzene by a method described in Part III of this series. The measured values of $\langle M_g \rangle_w$, the weight average molecular weight of the graft polymer, are given in Table 2.

RESULTS AND DISCUSSION

The data given in *Table 2* are the primary evidence that the grafting polymerizations have provided the desired branched polymers. An increase in the molecular weight of the graft product relative to the backbone material is observed for every case. In order to better evaluate these results,

Table 2. Parameters of the branched polymer

Fraction	$\langle M_1 \rangle_w \Sigma X$	Backbone polymer $\langle M_1 \rangle_v$	Graft polymer $\langle M_g \rangle_w$	Branch polymer $\langle M_b \rangle_n$	No. branches molecule $\langle k \rangle$	Wt/frac. mat. in branches $\langle w \rangle$
	$\times 10^4$	$\times 10^6$	$\times 10^6$	$\times 10^3$		
6-20-1	—	2.27	3.81	59	26	0.38
6-20-M	132	2.27	2.80	59	9	0.18
6-30-1	—	1.29	2.33	40	26	0.44
6-30-M	119	1.29	1.68	40	10	0.24
6-30-M	119	1.29	1.61	40	8	0.20
6-40-1	81	1.50	2.00	18.5	27	0.25
6-41-1	—	1.50	2.24	18	41	0.33
6-41-M	148	1.50	2.09	18	33	0.29
6-50-1	152	2.02	2.71	23.7	29	0.26
6-51-1	—	2.02	3.67	24.4	67	0.48
6-51-M	260	2.02	3.21	24.4	45	0.36
6-60-1	131	3.76	5.60	106	17	0.33
6-60-1	131	3.76	5.43	106	16	0.31
6-70-1	106	2.16	2.65	74.8	7	0.18
6-70-1	106	2.16	2.92	74.8	10	0.26
6-71-1	230	2.16	3.43	67	19	0.37
6-80-1	110	2.27	3.29	61	17	0.31
6-80-1	110	2.27	3.55	61	21	0.36
6-81-1	214	2.27	4.11	63.5	29	0.45
6-90-1	115	2.54	3.45	47	19	0.26
6-91-1	236	2.54	3.96	43.7	33	0.36

however, some of the aspects of the kinetics of the polymerization will now be considered. Following this, a general evaluation of the structure parameters assigned to the comb-shaped branched polymers.

Kinetic analysis

A simplified steady-state analysis of the reaction kinetics for the polymerization of a monomer in the presence of its polymer and a chain transfer solvent has been given elsewhere¹⁹. It was shown that $\langle k \rangle$, the average number of branches per molecule grafted onto the backbone, is approximated at low conversion by

$$\langle k \rangle = C_p \langle x_i \rangle X \quad (2)$$

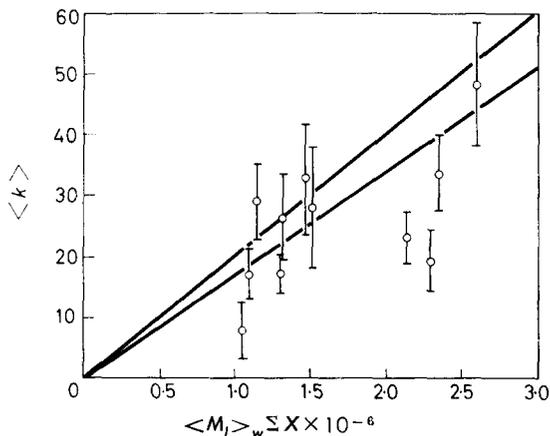
where C_p is the polymer chain transfer constant, $\langle x_i \rangle$ is the average degree of polymerization of the backbone, and X is the degree of conversion in the the graft polymerization. The fraction F of the new polymer that is bound to the backbone is approximated at low conversion by

$$F = C_p (B/M)_0 \{C_m + C_s [s]_0 / [M]_0 + C_p (B/M)_0\}^{-1} \quad (3)$$

where $(B/M)_0$ is the initial ratio of polymer to monomer on a weight basis

and C_s and C_m are the solvent and monomer transfer constants, respectively. (Certain terms in the denominator, small compared to those given, are omitted.) For a typical set of reaction conditions, these expressions give $\langle k \rangle \sim .30X$ and $F \sim 0.15$.

Figure 2—Number of branches per molecule versus degree of conversion, equation (4)



Since the conversion must be kept below 25 per cent, it is evident that a single graft polymerization will only result in about six to eight branches per molecule for the conditions used here, and that the branched polymer will be contaminated by a considerable amount of new unbound polymer. This was, in fact, the observed behaviour. In order to obtain the desired number of branches and still prevent undesirable reactions such as monomer transfer leading to the formation of a crosslinked network at high conversion, it was necessary to subject the graft polymer to additional polymerization cycles. Thus, after a graft polymerization, the graft polymer was separated from most of the unbound new polymer by a fractional precipitation, redissolved in monomer and chain transfer solvent and used as the substrate in a new graft polymerization. This recycle procedure was continued as often as necessary to obtain the desired number of branches.

Equation (2) suggests a method of correlating the data obtained from these polymerizations. Calling ΣX the sum of the degrees of conversion X obtained for each of the graft polymerizations on a particular linear backbone polymer, then equation (2) becomes approximately

$$\langle k \rangle \simeq C_p \langle x_i \rangle \Sigma X \quad (4)$$

This expression ignores the change in the degree of polymerization of the graft polymer as it goes through a number of grafting cycles, but the approximation is not serious for the polymerizations considered here. The average number of branches per molecule may be computed by the expression

$$\langle k \rangle = (\langle M_g \rangle - \langle M_l \rangle) / \langle M_b \rangle_n \quad (5)$$

where $\langle M_g \rangle$, $\langle M_l \rangle$, and $\langle M_b \rangle$ are the average molecular weights of the graft, linear backbone and linear branch polymer, respectively. As previously

indicated, the molecular weight of the branch polymer is determined from measurements of the molecular weight of the unbound new polymer.

The values of $\langle k \rangle$ estimated from equation (5) are shown in *Table 2* and *Figure 2* as a function of $\langle M_i \rangle_w \Sigma X$. The two straight lines drawn in that figure correspond to values of C_p at 90°C given in the literature^{21, 22}. These data fit best with C_p equal to 15×10^{-4} . The vertical lines drawn for each point are indicative of the errors estimated for $\langle k \rangle$ by assuming a seven per cent error in both $\langle M_o \rangle_w$ and $\langle M_i \rangle_w$ in equation (5). The weight fraction, $\langle w \rangle$, of the graft polymer to be found in the branches is also included in *Table 2*. An important point to note in *Table 2* is that the recycle operation always caused an increase in $\langle k \rangle$, as would be expected, and that this increase is within experimental error of that expected from equation (4).

Molecular weight distribution

The molecular weight distribution of a graft polymer resulting from the placement of $\langle k \rangle$ branches of constant molecular weight M_b on a backbone polymer of molecular weight M_i has been calculated in the appendix. It is shown there that the ratio of $\langle M \rangle_w / \langle M \rangle_n$ changes from the value for the linear backbone to approximately

$$\langle M_o \rangle_w / \langle M_o \rangle_n = (\langle M_i \rangle_w / \langle M_i \rangle_n) \{1 + \langle k \rangle / (\langle M_i \rangle / \langle M_b \rangle + \langle k \rangle)^2\} \quad (6)$$

for the branched polymer. Thus, if the backbone had a weight to number average molecular weight ratio of 1.1, then the corresponding ratio for the graft polymer would be calculated from equation (6) with $\langle M_i \rangle_w / \langle M_i \rangle_n = 1.1$. The change in the molecular weight ratio indicated by equation (6) is quite small for all of the samples of interest here, the term in brackets ranging from a value of 1.00₃ to 1.03. The effect of this change in the distribution is well within the experimental accuracy of the estimate of $\langle k \rangle$, and no attempt has been made to include this effect in the reported data. Thus, weight average values are used for $\langle M_o \rangle$ and $\langle M_i \rangle$ in equations (4) and (5). The correction to a number average would be about the same for both the graft and linear polymer, and would cause about a ten per cent decrease in the absolute value of $\langle k \rangle$.

Chemical impurity

Among other factors which could lead to some ambiguity in the specification of the structure of the branched polymer, is the presence of hydroxyl groups in the graft polymer. The polymerizations were performed in the absence of oxygen and water, using purified monomer, polymer and chain transfer solvent, conditions that should have prevented the formation of hydroxyl groups. An infra-red spectrum was obtained on one of the graft polymers and on one of the linear backbone polymers since it has been shown that even low percentages of hydroxyl can be detected in this manner²³. No hydroxyl groups were indicated by the spectrum for either polymer.

Fractionation

The effect of the fractionation procedure on the measured and deduced chain lengths reported for the graft polymers is less easily determined. The fractionations of the graft polymer between recycle polymerizations were designed to recover as much of the graft polymer as possible. It must be

realized, however, that a certain amount of the high molecular weight material will remain in the soluble portion of the system in any given separation even if a large excess of non-solvent is present²¹. However, the fact that repeated additions of the non-solvent did not precipitate additional graft polymer after the first fraction was recovered is evidence that these fractionations were effective.

It was not desirable to add a large excess of non-solvent in the final fractionation since this step was designed to recover the graft polymer free from the unbound low molecular weight material. Thus, the amount of non-solvent added was adjusted to recover about three fourths of the graft polymer in the first fraction. The remainder was then recovered in the second fraction. In all cases, a considerable amount of non-solvent had to be added to recover the unbound low molecular weight polymer after the last of the graft polymer was recovered. The first and second fractions were combined in a few instances where less than three fourths of the polymer was recovered in the first fraction. The value of $\langle k \rangle$ measured for this mixture was used in testing the data by equation (4), since this relationship requires a value of $\langle k \rangle$ averaged over all of the graft polymer species. The exact value of $\langle M_i \rangle$ to be used in equation (5) to compute $\langle k \rangle$ becomes uncertain, however, when anything less than complete recovery of the graft polymer is achieved, since there may be some change in $\langle M_i \rangle$ due to the selective loss of certain species of the graft polymer. There would, of course, be no ambiguity if the backbone polymer was monodisperse with respect to molecular weight. The assumption made here is that the value of $\langle M_i \rangle$ is unchanged by the fractionation.

It is difficult to assess the validity of this assumption. It is made on the basis of the use of a backbone polymer which has a narrow molecular weight distribution. The effect of the fractionation of the graft polymer on $\langle M_i \rangle$ is not necessarily the same as the direct fractionation of the linear polymer itself, since the branched polymer will tend to be more soluble than linear polymer of the same molecular weight^{10, 24}. Thus, a trial fractionation of a mixture of a high molecular weight linear polymer, such as that used for the backbone material, and a low molecular weight polymer, such as that obtained in the graft polymerization, would not necessarily give a direct measure of the change to be expected in the average molecular weight of the backbone material in the graft polymer. It is seen from equation (5) that an error of x per cent in $\langle M_i \rangle$ will cause an error of $x \langle M_i \rangle / (\langle M_g \rangle - \langle M_i \rangle)$ per cent in $\langle k \rangle$ or $\langle w \rangle$.

Chain configuration

The above analysis has implicitly assumed that all of the branch material is bound directly to segments of the backbone polymer, although it is obvious that at least some must attach to other branches instead. This complication will not alter the figures given above, but may be important in a later discussion of the properties of the branched polymers. A simplified analysis of the branch placement shows that if the average ratio of the branch to backbone molecular weight is $\langle r \rangle_n$, then $\langle k^* \rangle$ the average number of branches attached directly to the backbone when a total of $\langle k \rangle$ branches have been placed is given by

$$\langle k^* \rangle = \sum_{j=0}^{k-1} (1 + j \langle r \rangle_n)^{-1} \quad (7)$$

For the range of k and r encountered here, this may be approximated by

$$\langle k^* \rangle \simeq (1/\langle r \rangle_n) \ln [1 + \langle k \rangle \langle r \rangle_n]$$

Inspection of the data in *Table 2* shows that for most of the samples, only *ca.* 15 per cent of the branch material will be attached to other branches, the figure being somewhat greater or smaller for some of the structures. The large percentage of the branches attached to the backbone is a consequence of the small branch to backbone length ratio, and was one reason for confining attention to such conditions. Similarly, the polymerizations were performed in the presence of a chain transfer solvent and limited to low conversions to preclude the possibility of network formation at high conversions.

CONCLUSION

A series of branched polymers has been synthesized to obtain a range of branching frequency and length of branches. Moreover, the molecular weight polydispersity of these branched polymers should not be appreciably different from good fractions of a linear polymer.

This method of synthesis offers several advantages. The average length of the branches can be controlled by the chain transfer solvent. Also, the presence of the chain transfer solvent in the quantities used precludes difficulties encountered from the termination of the branches on different substrate molecules by a coupling mechanism^{11,12}. The recycle operation allowed a high number of branches to be placed without the formation of a network structure. Approximately eighty to ninety per cent of the branches were attached directly to the backbone, the remainder attaching to other branches. The latter is undesirable, but in no way limits the use of the branched polymer for the investigation to follow. Due to the control over the average length of the branches, the information about the kinetic scheme of the reaction, the use of a fractionated linear backbone polymer, and the estimate available for the average number of branches per molecule, this scheme gives a reasonably well characterized branched polymer.

We wish to thank the Allied Chemical and Dye Corporation for financial assistance to one of us (G.C.B.) during the period when this work was being completed.

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(Received December 1962)

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APPENDIX

EFFECT OF GRAFTING ON MOLECULAR WEIGHT DISTRIBUTION

This calculation is intended to show the effect on the molecular weight distribution of placing k branches of average molecular weight M_b on a monodisperse backbone polymer with n sites for branching and of molecular weight M_l .

If p is the probability that a site on the backbone contains a branch, then the number fraction of chains with i branches, f_i , is given by

$$f_i = \binom{n}{i} p^i (1-p)^{n-i}$$

where f_i is normalized by

$$\sum_{i=0}^n f_i = 1$$

Calling the average molecular weight of the branched polymer $\langle M_g \rangle$, the number average of M_g is calculated as

$$\langle M_g \rangle_n = \sum_{i=0}^n f_i (M_l + iM_b)$$

$$\langle M_g \rangle_n = M_l + npM_b$$

But p is simply k/n for n very large so that

$$\langle M_g \rangle_n = M_l + kM_b$$

The weight average value of M_g becomes

$$\langle M_g \rangle_w = \frac{\sum_{i=0}^n M_g^2 f_i}{\sum_{i=0}^n M_g f_i}$$

$$\langle M_g \rangle_n \langle M_g \rangle_w = (M_l + kM_b)^2 + kM_b^2 (1 - k/n)$$

Thus the new value for the ratio of the weight to number average molecular weight is seen to be (for k/n much less than unity)

$$\langle M_g \rangle_w / \langle M_g \rangle_n = 1 + k / (k + M_i / M_b)^2$$

This result is not strictly applicable here, however, since the backbone polymer used here is not monodisperse, but is instead a narrow molecular weight fraction with $\langle M_i \rangle_w / \langle M_i \rangle_n$ less than about 1.1. It is assumed, however, that this expression does indicate to a good approximation the relative change to be expected in the weight to number molecular weight average. This final approximation is included in equation (6) given in the text.