

## Melt Flow and Strength of Branched Styrene Copolymers

R. TOGGENBURGER,\* S. NEWMAN, and Q. A. TREMENTOZZI,  
*Research Department, Hydrocarbon and Polymers Division,  
 Monsanto Company, Springfield, Massachusetts 01101*

### Synopsis

In order to assess the dependence of strength properties of glassy polymers upon the extent of branching, copolymers of poly(styrene-acrylonitrile) were prepared. By using principally three methods: (a) hydroperoxide intermediates, (b) hydroxyl radical initiation, and (c) incorporation of transfer monomers, branched polymers with high levels of branching with comb and dendritic type structures were generated. The tensile strength was found to be strongly correlatable with melt flow, and, in general, the branched copolymers were found to have the same tensile strength as linear polymers of the same melt index.

### INTRODUCTION

From melt studies on high- and low-density polyethylene, it has been known for some time that the melt viscosity  $\eta$  of branched polymers is less than that for linear polymers of equivalent molecular weight.<sup>1</sup> The observed reduction in melt viscosity of branched polymers was placed on a quantitative basis by F. Bueche who theorized that for entangled chains<sup>2</sup> the ratio of the viscosity of branched polymer,  $\eta_b$ , to that of linear polymer,  $\eta_l$ , of equivalent molecular weight is equal to  $g^{7/2}$ , where  $g$  is the ratio of the squares of the radius of branched and linear polymer. Studies<sup>3</sup> with narrow distribution polystyrenes have confirmed that branched polymers exhibit much lower values of  $\eta$  at low shear rates than linear molecules of the same total molecular weight.

However, the dependence of strength properties of glassy polymers upon the extent of branching was not known at the time this investigation was undertaken. Recently, however, Wyman et al.<sup>3</sup> have reported that the tensile strengths of branched polymers (tetrachain star types) were found to level off in value at higher molecular weights than for the corresponding linear polymers.

The present investigation was undertaken in order to establish a relationship between strength properties and melt flow for branched poly(styrene-acrylonitrile) (S/AN) copolymers. This work differs principally in two respects from that of Wyman et al., i.e., this study was carried out

\* Deceased October 1965; manuscript prepared posthumously.

with highly branched dendritic and comb-type structures rather than moderately branched tetrachain star structures; and, molecular weight distributions were considerably broader in this investigation.

## EXPERIMENTAL

### Branched Polymers

#### *General Considerations*

The theoretical equation of Orofino<sup>4</sup> for idealized systems was used to estimate the branching requirements necessary to reduce the branching index  $g$  and the associated viscosity ratio to desired levels. According to Orofino,  $g$  is a function of the number of branches  $p$  and the weight fractions of branches  $N_y$  in the polymer molecule:

$$g = \overline{(S^2)_b} / \overline{(S^2)_l} \quad (1)$$

$$g = 1 - N_y + (N_y/p^2) - (3N_y^2/p^2) + (3N_y^2/p) \quad (2)$$

where  $\overline{S^2}$  refers to the mean-square radius of gyration and the subscripts  $b$  and  $l$  to branched and linear polymer, respectively. A plot of the dependence of  $g$  on these parameters is shown in Figure 1. The following

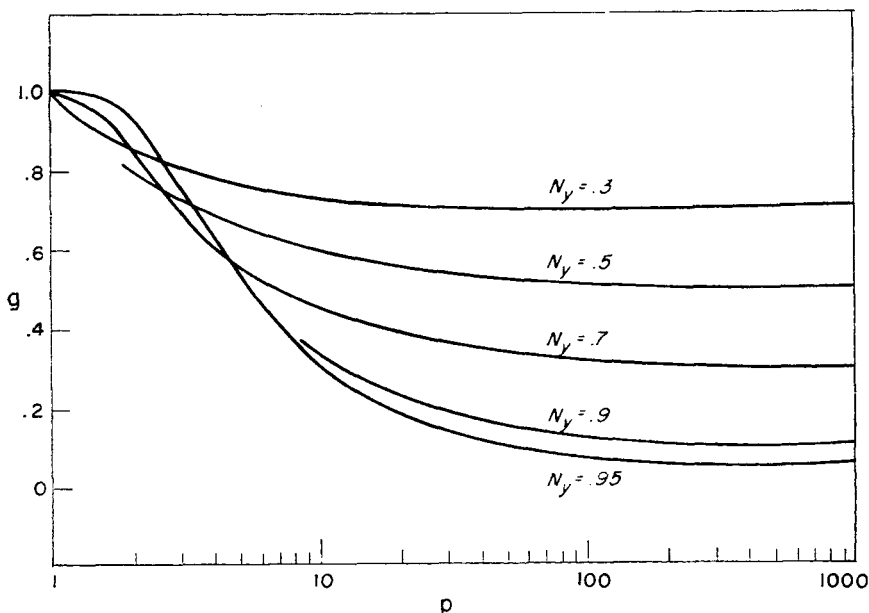


Fig. 1. Branching parameter  $g$  vs. branching frequency  $p$  for branched molecules according to eq. (2).

conclusion is evident: the ratio  $g$  decreases with increasing frequency of branching and increasing weight fraction of branches.

From these plots, it also appears advantageous to strive for a high weight fraction of branching and a low frequency of branching ( $p \leq 10$ ) in order to achieve significant reductions in the dimensions of the branched polymers. Synthetic efforts described later were guided by these general considerations.

#### *Determination of the Existence of Branching*

The ratio of the intrinsic viscosity  $[\eta]$  of branched to linear polymer has been theoretically described to be dependent on  $g$  to a smaller power than the ratio of the corresponding melt viscosities.<sup>2,5-9</sup> Based on this difference of  $[\eta]$  and melt viscosity on  $g$ , a comparison of the melt index (inversely proportional to the melt viscosity) of a suspected branched polymer to that of a linear polymer of the same intrinsic viscosity was used to determine the existence of branching. The melt index versus  $[\eta]$  data for linear S/AN and some branched S/AN samples are shown in Figure 2.

The melt index (MI) of the matrices and of the polyblend were measured on a Tinius-Olsen apparatus at a stock temperature of  $205 \pm 2^\circ\text{C}$ . with a die diameter of 0.070 in., die length of 0.315 in., and a  $180^\circ$  entrance angle. A standard weight of 5000 g. was used unless otherwise indicated. The MI was generally taken as the weight (grams) of polymer extruded in 10 min.

Intrinsic viscosity measurements were carried out according to standard procedures in dimethylformamide (DMF) at  $25^\circ\text{C}$ .

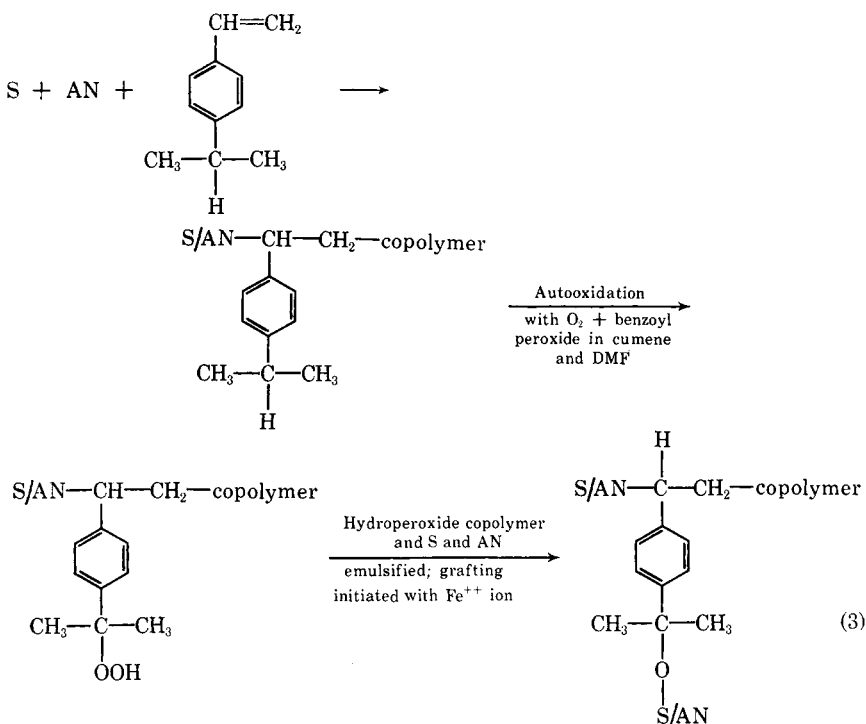
Samples for tensile testing were generally prepared by injection molding dumbbell-shaped specimens with a 1-oz. molding machine. Tensile strengths were measured with an Instron tester at low cross-head speeds of about 2% elongation/min.

### **Synthesis Methods**

Several methods were explored to obtain branched structures suitable for evaluating melt flow and strength properties. Structures obtained were of two types: (a) comb structures, which were formed when grafting occurred only on a preformed prepolymer backbone and (b) dendritic structures, which resulted when grafting took place by radical transfer to an existing chain irrespective of whether the transfer site was on a backbone or on a branch.

#### *Comb-Type Structures*

**Hydroperoxide Intermediate.** The method of Metz and Mesrobian<sup>10</sup> was used as the basis for numerous experiments. The method consisted of using a hydroperoxide of a polymer to initiate grafting of monomers on the prepolymer. An example of this synthesis route is shown in eq. (3).



Graft systems produced by this general scheme were normally either cross-linked or excessively high in molecular weight. Numerous studies were made of the effects of several synthesis parameters on the various component reactions and final graft systems in order to minimize these difficulties.

The more pertinent findings of these studies may be summarized as follows: (a) the hydroperoxide activity of the prepolymer could be controlled by varying the *p*-isopropylstyrene (PIPS) content of the prepolymer; (b) under optimized autooxidation conditions (3–8 hr. at 70°C. in a 50–50 mixture of DMF and cumene) the hydroperoxide was found to be linearly dependent on the mole fraction of PIPS. (The hydroperoxide content of hydroperoxide prepolymers was determined by a modified procedure of Kolthoff et al.<sup>11</sup>); (c) the hydroperoxide prepolymers formed grafted systems in the presence of AN and S monomers as evidenced by the fact that carefully purified prepolymer hydroperoxides initiated polymerization of monomers at room temperature in the presence of Fe<sup>2+</sup> ion. However, in the absence of retarders or transfer agents, crosslinked polymers generally resulted despite variation of the prepolymer OOH/monomer ratio, the hydroperoxide activity, the prepolymer molecular weight, or the degree of conversion. Only a few soluble “grafts” were obtained, and most of these were of high molecular weight with  $[\eta]$  normally being greater than 3 (Table I).

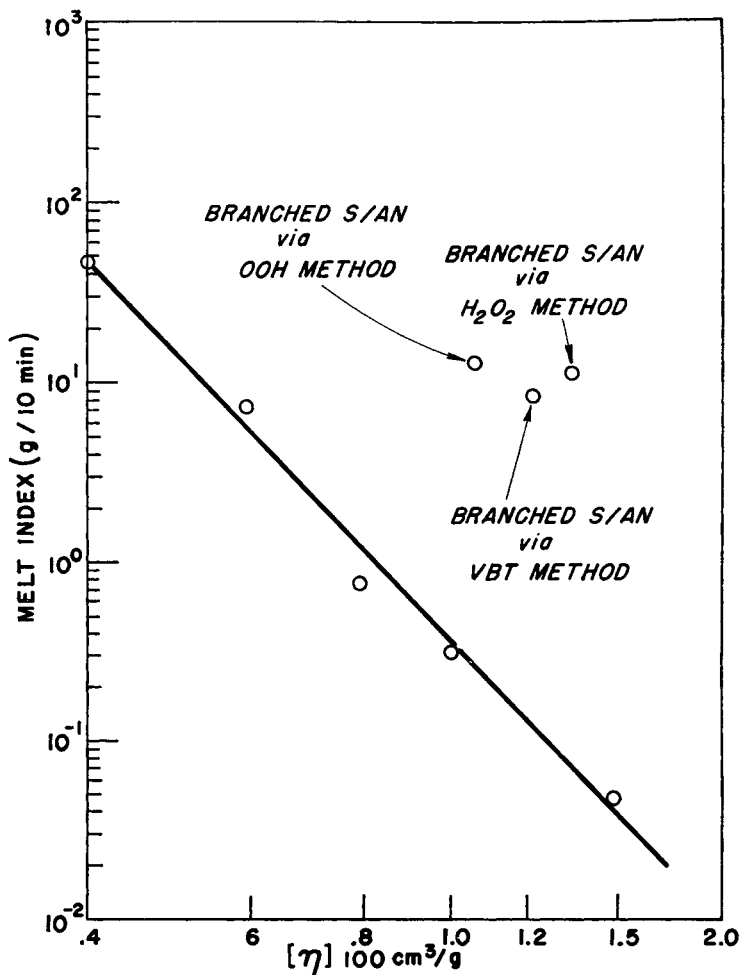


Fig. 2. Melt index vs. intrinsic viscosity for linear S/AN copolymers and a few selected branched S/AN's.

TABLE I  
Melt and Strength Properties of Some Branched S/AN's  
Initiated with Hydroperoxide

Sam- ple	$[\eta]$ of prepoly- mer	Hydro- peroxide activity, OOH/100 monomer units	Monomer/ prepolymer ratio	$[\eta]$ of whole poly- mer	Tensile strength, psi	Tensile elongation at failure, %	MI
1	0.665	1.2	4:1	1.22	4500	2.0	4.5
2	0.355	2.4	4:1	1.03	3500	1.7	12.5
3	0.355	2.4	20:1	5.4	2500	—	
3a	0.355 <sup>a</sup>	2.4	20:1	—	5600	3.2	
4	0.40	2.0	20:1	2.1	—	—	

<sup>a</sup> Methanol solubles removed.

TABLE II  
 Synthesis and Properties of Some Branched S/AN's Initiated with H<sub>2</sub>O<sub>2</sub>

Method of preparation		Properties of S/AN					
Prepolymer/ monomer	Temp., °C.	H <sub>2</sub> O <sub>2</sub> (35% solids), g./100 g. monomer	[η]	MI branched <sup>b</sup>		Tensile strength, psi	Elonga- tion, %
				MI <sup>a</sup>	MI linear		
0	15	2.46	2.10	0.18	90	8190	5.0
0	15	3.07	1.81	0.35	23	8360	5.1
0	15	3.68	1.42	0.60	12	6330	3.9
0	15	4.60	1.28	3.00	34	5810	3.8
0.05	30-40	1.86	2.14	0.32	160	6700	3.5
0.05	30-40	3.64	0.84	5.5	6	3150	—
0.05	30-40	3.64	0.70	10.8	4.7	3710	2.7
0.05	30-40	3.34	1.34	11.0	157	—	—
0	30-40	3.34	1.48	0.7	18	6900	4.5
0.05	30-40	4.0	0.89	10.0	16	5500	—

<sup>a</sup> Grams of extrudate/10 min.

<sup>b</sup> Ratio of melt indices of branched to linear S/AN of equivalent [η].

Reduction of the graft molecular weight by using small amounts of a transfer agent (*tert*-dodecyl mercaptan) or a retarder (dinitrobenzene) resulted in the formation of linear polymer and very low conversion, respectively. Attempts to carry out the grafting reaction in homogeneous solution and thereby reduce gel formation resulted in little or no grafting.

The tendency toward high molecular weight or crosslinked polymer systems is believed to result from termination by coupling between two growing radicals. Such a mechanism becomes increasingly important with increasing prepolymer OOH functionality. Grafting was carried out with prepolymers having from 4 to 10 hydroperoxide groups per prepolymer chain, a value considered to be necessary to obtain desired degrees of branching. Thus, any substantial reduction in OOH activity to avoid gel formation would lead to low degrees of branching.

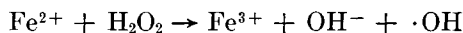
The postulated termination mechanism by radical coupling would necessarily modify the comb structures. The flow and strength properties of OOH graft polymers, therefore, are only approximations of those to be expected from an idealized branched comb structure.

**Ceric Ion Method.** The reaction of  $Ce^{4+}$  with a polymer containing hydroxyl groups in the presence of monomers was reported to result in graft polymerization.<sup>12</sup> Several attempts to prepare graft systems were based on this reaction. A copolymer of S/AN/vinyl benzyl alcohol (VBA), 80:20:10, was used as the graft backbone. Grafting procedures were carried out in emulsion with the use of a nonionic surfactant, i.e., acetylated Triton X-100 (isooctylphenyl polyethoxy ethanol) as the emulsifier. Acetylation of the surfactant was carried out to eliminate its OH function as a possible grafting site. Reactions were also carried out in homogeneous solution using dioxane as the solvent. Despite variation of reaction parameters (temperature and prepolymer to monomer ratio) yield studies show that at best, only low degrees of grafting took place. The properties of these polymers were, therefore, not examined further.

**Radical Transfer with Tertiary Amines.** Efforts were directed toward the grafting in benzene solution of styrene and acrylonitrile monomers on copolymers of styrene-dimethylaminoethyl methacrylate. Grafting is presumed to occur by transfer from a growing AN radical to the carbon atom  $\alpha$  to the amine group. Using a monomer/prepolymer ratio of 5/1 and azobisisobutyronitrile as initiator at 70°C., high conversion of monomers were obtained in 16–24 hr. but with relatively little grafting as judged by melt index-intrinsic viscosity measurements.

#### *Dendritic Type S/AN Structures*

**Branched S/AN via Hydroxyl Radical Initiation.** When hydrogen peroxide is decomposed with ferrous ion, a high-energy radical (the hydroxyl radical) is formed.



Due to the high energy of this free radical, it readily abstracts hydrogen, thereby forming new free-radical sites on a growing polymer chain or dead polymer.<sup>13</sup> If the ratio of formed polymer to monomer is sufficiently large, considerable grafting should result. The structure of the graft should tend to be dendritic because hydrogen abstraction takes place indiscriminately on either backbone or a branching chain. In addition, the molecular weight will be broad since the greater the size and exposure time to hydroxyl radicals, the greater the probability that a hydrogen is abstracted.

Two methods were used to synthesize branched polymers with hydrogen peroxide. In one, catalyst and monomers were added slowly to an emulsion of a linear prepolymer dissolved in a small amount of monomers. By keeping the monomer/prepolymer ratio low and by starving the emulsion of additional monomer, grafting was encouraged. In the second method, prepolymer was omitted. A nonionic surfactant, Triton X-100, was used to prevent precipitation of the iron.

Results of the hydroxyl radical initiated polymerization are shown in Table II. Conclusions drawn from this data are as follows.

(1) Initiation with  $H_2O_2$  results in branched S/AN. This is indicated by the fact that the melt indices of the  $H_2O_2$ -initiated polymers were up to 160 times that of linear S/AN of equivalent intrinsic viscosity.

(2) Branched S/AN was obtained in both the presence and the absence of prepolymer indicating abstraction takes place readily on any formed polymer.

(3) Control of the relative proportions of  $H_2O_2$  and monomers allowed the synthesis of materials with a wide range of  $[\eta]$  values.

**Branched S/AN via a Transfer Monomer.** Grafting will result when polymerization of monomer takes place in the presence of polymer chains containing radical-transfer sites.<sup>14</sup> This principle was utilized to achieve high degrees of branching of S/AN based polymers by polymerizing S and AN monomers in the presence of a transfer monomer, vinyl benzyl thiol (VBT). Since grafted chains are subject to further grafting, the structure will be dendritic. In addition, the molecular weight distribution will be broader than if no transfer occurred, since the larger the kinetic chain, the greater the probability that a transfer site on that chain has become a graft site for a chain containing further transfer (grafting) capabilities.<sup>14</sup> Vinyl benzyl thiol was readily synthesized in good yields by the hydrolysis of the vinyl benzyl chloride-thiourea adduct.<sup>15</sup>

Polymerization was carried out in emulsion,  $K_2S_2O_8$  being used as the initiator. Monomer feeds were controlled so as to increase the VBT to S and AN ratio in the reaction flasks as the polymerization proceeded in an effort to narrow the molecular weight distribution of the final polymer system. The effectiveness of this monomer feed control was not assessed.

Samples produced by this method were shown to be highly branched as indicated by melt flow- $[\eta]$  data (Fig. 2). Materials with a range of intrinsic viscosities of 0.41–1.24 were made with VBT concentrations in the range of 2–5%.



## DISCUSSION

The MI- $[\eta]$  properties of S/AN samples produced by the hydroperoxide,  $H_2O_2$ , and VBT routes indicated the existence of branching. For the dendritic S/AN samples (VBT and  $H_2O_2$  routes), the MI was some 5 to 150 times that for linear S/AN. Similar comparisons for the hydroperoxide grafts were less dramatic; MI values ranged generally from 2 to 30 times that of linear S/AN of equivalent  $[\eta]$ , with lesser increases being more prevalent. Such increases in the melt index values are substantially greater than could be attributed to differences in molecular weight distribution.

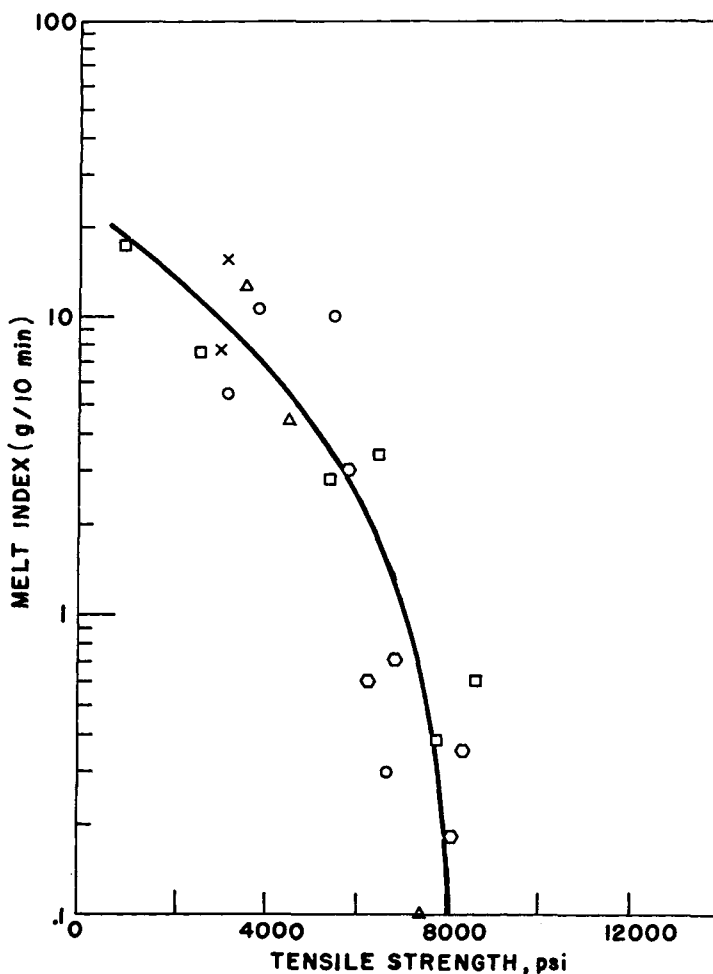


Fig. 3. Log melt index vs. tensile strength for both linear and branched S/AN: (□) linear S/AN; (○) branched S/AN via the  $H_2O_2$  route with prepolymer; (○) branched S/AN via the  $H_2O_2$  route without prepolymer; (△) branched S/AN via the OOH route; (×) branched S/AN with VBT.

On examining the strength-melt flow relationship, it was found that the tensile strength and elongation at fail of the branched S/AN were always less than that of linear S/AN of equal  $[\eta]$ . However, the branched S/AN had the same tensile strength as linear S/AN of the same melt index at 210°C. (Fig. 3). Both the dendritic and comb-type branched S/AN's exhibited this behavior. It was concluded that no advantage in melt flow-strength properties can be achieved over linear S/AN through a branched structure.

To a first approximation, the above results suggest that the tensile strengths of both linear and branched S/AN are dependent on the melt viscosity of the polymer. It is of interest to compare this result with Berry's molecular interpretation of crack propagation in glassy materials.<sup>16</sup> Berry used the Griffith equation of brittle fracture relating the tensile strength  $T$  to the size of a flaw  $c$ , the elastic modulus  $E$ , and the specific surface energy  $\gamma$  through the equation

$$T = A (E\gamma/c)^{1/2} \quad (4)$$

where  $A$  is a constant. Berry found a general adherence to the Griffith equation for polystyrene and poly(methyl methacrylate). However, in order to explain an inordinately large value for  $\gamma$  he postulated that  $\gamma$  was composed primarily of an energy of viscous flow resulting from molecular orientation occurring ahead of a propagating crack.

While the actual numerical values obtained for  $\gamma$  are open to question due to the severe assumptions involved, note for instance, the use of a time-independent  $E$ , Berry's findings combined with optical observations on fractured surfaces do point to the existence of considerable ductility on a microscale in the zone at the crack front. Further pertinent discussions concerning cold drawing and localized yielding in glassy polymers have been given elsewhere.<sup>17</sup>

Our findings relating melt flow and tensile strength (Fig. 3), while crude, nevertheless indicate that to a first approximation, the tensile strength is strongly related to melt flow and is independent of the particular molecular structure and weight which determines that melt flow. Inspection of eq. (4) suggests, in fact, that the  $\gamma$  term could be related to both the size of the ductile zone at the crack tip and its viscous flow characteristics.

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### Résumé

En vue de déterminer la dépendance des propriétés de polymères vitreux en fonction du degré de ramifications on a préparé des copolymères de poly(styrène-acrylonitrile). En utilisant principalement trois méthodes à savoir, (a) des intermédiaires hydroperoxydés, (b) initiation par des radicaux hydroxyles, (c) incorporation de monomères par transfert, on a préparé des polymères ramifiés à taux de ramification élevé avec une structure en peigne ou en forme de dendrites. La force à la tension pouvait être très bien mise en relation avec l'écoulement à l'état fondu, en et général les copolymères ramifiés présentent la même force à la tension que les polymères linéaires de même indice de fusion.

### Zusammenfassung

Um die Abhängigkeit der Festigkeitseigenschaften von Polymeren im Glaszustand vom Verzweigungsgrad zu ermitteln, wurden Styrol-Acrylnitril Copolymere hergestellt. Unter Verwendung von im Prinzip drei Methoden: (a) Hydroperoxyd-Zwischenprodukte, (b) Hydroxylradikalstart und (c) Einbau von Übertragungsmonomeren wurden verzweigte Polymere mit hohem Verzweigungsgrad und einer Struktur vom Kamm- und Dentritttyp erzeugt. Die Zugfestigkeit stand in guter Korrelation zum Schmelzfließen. Im allgemeinen besaßen die verzweigten Copolymeren die gleiche Zugfestigkeit wie lineare Polymere mit dem gleichen Schmelzindex.

Received June 20, 1966

Revised July 12, 1966

Prod. No. 1441