SOLUTION PROPERTIES OF BRANCHED POLYMERS. I.
SYNTHESIS, FRACTIONATION AND CHARACTERIZATION OF POLYMERS

L.Mrkvičková-Vaculová and P.Kratochvíl

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6

Branched methyl methacrylate–ethylene dimethacrylate (0·25—1·00 mol.%) copolymers were prepared. The course of copolymerization shows that the accepted view that in this reaction all functional groups have the same reactivity does not allow an explanation of all experimental facts. The polymers obtained and their fractions were investigated by the light scattering and viscometry. Various procedures used for the characterization of branched polydisperse polymers and their fractions were compared.

The majority of experimental studies devoted to the physicochemical investigations of branched polydisperse polymers have as yet been dealing with the products of polymerization reactions, where the branching may be regarded as a side effect[1-4]. The branching (or crosslinking) of the polymer in the copolymerizations of bi- and tetrafunctional monomers is due directly to the functionality of the comonomer. The polymers of this type were studied experimentally on the example of the styrene–divinylbenzene copolymers by Thurmond and Zimm[5].

We investigated the methyl methacrylate–ethylene dimethacrylate copolymers with a low content of the divinyl units. Some authors believe[6-8], on the basis of the structural similarity of the two monomers, that all the double bonds in this system have the same reactivity. Then the location of the double bonds may be considered to be random, and relations derived from Flory's theory[9] may be used in characterizing the copolymerization products. In Stockmayer's generalization[10], it holds for the weight average degree of polymerization of a branched system, P_w,

$$P_w = \frac{P_{w,0}(1 + \varrho)}{1 - \varrho(P_{w,0} - 1)} \cong \frac{P_{w,0}}{1 - \gamma} ; \qquad (1)$$

here, $P_{w,0}$ is the weight average degree of polymerization of the primary chain[7] and ϱ is the branching density or the twofold molar fraction of the totally reacted tetrafunctional units in the copolymer, participating in the formation of the network; the tetrafunctional units closing intramolecular rings do not contribute to the value of ϱ. This equation can be applied only to the so-called pregelation stage, when for the degree of branching $\gamma = \varrho P_{w,0}$ it holds $0 < \gamma < 1$. γ may then be regarded as a fraction of the critical crosslinking of the polydisperse product (critical crosslinking occurs at the point of gelation, where $\gamma = 1$).

For the characterization of slightly branched and still molecularly soluble polymers, the physicochemical properties of their dilute solutions are best suited. The basic criterion for an estimation of the extent of branching in macromolecules is the ratio of mean squares of the radii of gyration of a branched and a linear macromolecule of the same degree of polymerization[11] ($g =$

$= \overline{S_b^2}/\overline{S_l^2}$. The parameter g, raised to the exponent b, characterizes a similar ratio of the intrinsic viscosities[12]:

$$[\eta]_b/[\eta]_l = g^b . \tag{2}$$

The value of the exponent b varies as a rule from 0·5 to 1·0 and depends on the geometrical structure of the branched macromolecule[13]. Both the above ratios may be considered to be a measure of the change in size due to branching for monodisperse polymers only. If we want to characterize the branching in the polydisperse polymers, we must either investigate a set of the individual fractions of these polymers[5], or exclude the effect of polydispersity on the physicochemical characteristics of these polydisperse systems by using adequate corrections[14,15]. According to some authors, branched macromolecules in good solvents are more expanded than the linear ones; that is, the differences in size decrease by increasing the thermodynamic quality of the solvent[16,17]. However, the influence of the volume effect has not as yet been given a sufficient quantitative treatment and the parameter g cannot therefore be properly corrected for expansion. An investigation of the solutions under ideal, *i.e.* Θ-conditions, seems to be desirable[7]. With respect to the negligible content of the tetrafunctional comonomer, the polydisperse copolymer under investigation may be regarded as a homopolymer, and its physicochemical properties may be compared directly with the properties of the linear polydisperse poly(methyl methacrylate). The distribution of the degree of polymerization (molecular weight) of poly(methyl methacrylate) prepared by radical polymerization is in most cases close to the most probable distribution[18]. Then it holds, for the z-average of the mean square radius of gyration of the molecules of a linear polymer in the solution[19], that

$$\overline{S_z^2} = A M_w^{(1+\varepsilon)} [\Gamma(4+\varepsilon)]/2^{(2+\varepsilon)} \tag{3}$$

and the dependence of the intrinsic viscosity is given by the relationship[20]

$$[\eta] = K M_w [\Gamma(2+a)]/2^{(1+a)} , \tag{4}$$

where A, K, a, and ε are constants for the system monodisperse polymer – the respective solvent.

In the present communication, the physicochemical behaviour of dilute solutions of branched polydisperse polymers is compared with the behaviour of the common polydisperse linear polymers. We have tried to verify whether it is possible, using the molecular parameters of fractions, to characterize sufficiently the initial branched polydisperse polymer. This would also inform us about the efficiency of the current fractionation methods.

EXPERIMENTAL

Preparation of Samples

Monomers and solvents. Methyl methacrylate (monomer *I*) and ethylene dimethacrylate (monomer *II*) were freed from the inhibitor, dried and distilled *in vacuo* on a column. The solvents (toluene, benzene, butyl acetate, acetone) and precipitating agents (methanol, light petroleum–b.p. 40—60°C) were rectified. The quality of the compounds was checked chromatographically (content of impurities <1%).

Copolymerization. Samples were prepared by radical copolymerization in a toluene solution (30% by vol. of the solvent), initiated with azo-2,2′-bis(isobutyronitrile)[21] at 45°C. At a concentration of monomer *I* in the initial reaction mixture 6·35 mol l^{-1}, the concentration of monomer *II* was 0·016, 0·030, 0·048 and 0·064 mol l^{-1} for the individual polymerization runs. The concentration of the initiator for the copolymerization was chosen so that the molecular weight of the primary chain[7], $M_{w,0}$, lay within the range 2 . 10^5 to 3 . 10^5, which was checked experimentally by means of a parallel homopolymerization of a reaction mixture not containing monomer *II*. The course of reaction was followed dilatometrically, and at a chosen conversion (and thus also a degree of branching) the polymer was precipitated from the polymerization mixture with an excess of petroleum ether. On drying *in vacuo*, the conversion was determined gravimetrically.

Fractionation. We fractionated two copolymers prepared by the polymerization of a reaction mixture having the molar ratio of monomers *I* and *II* 100 : 0·5 to various conversions, using the common method of successive precipitation[22] at 25°C, on the one hand, and the continuous elution method on a modified Baker–Williams column[23], on the other. From the initial 1% solution of the copolymer in acetone, 12 fractions were gradually precipitated with methanol. Elution yielded about 20 fractions; the initial extraction mixture contained 70% by vol. of methanol, the final mixture contained acetone only. In both cases the separation was uniform as to the weight.

Measurements

Interferometry. The refractive index increment was determined with a Zeiss interferometer at 25°C in cells adjusted for volatile and hygroscopic solvents[24]. The value found for copolymers in butyl acetate, $dn/dc = 0·097$ (λ 5461Å) coincides with the literature value for poly(methyl methacrylate)[25].

Light scattering. All scattering measurements were carried out on the Photo-Gonio-Diffusomètre Sofica in an unpolarized light, wavelength 5461 Å, angular range 30 to 150°. Benzene was used as standard; $R_{90} = 16·3 . 10^{-6}$ cm^{-1} was taken as its absolute scattering value at an angle of 90°. The experimental data were treated by the Zimm method, *i.e.* a twofold extrapolation of the Kc/R_θ values to zero angle and zero concentration. The optically pure copolymer solutions were prepared by centrifugation on a preparative ultracentrifuge Spinco L-90 at 15 000 r.p.m. for one hour (average centrifugal force 3 . 10^4 g). Purification was performed according to the principle suggested by Dandliker and Kraut[26]. The measuring cells with the solution were put directly into the buckets of the swinging bucket rotor SW-25·1, which contained a minimum amount of glycerol necessary to prevent the cell bottom from touching the bottom of the bucket. In contrast with the authors cited above, fully satisfactory results were obtained when common unsealed cylindrical cells, 22 mm in diameter, were used.

Viscometry. The measurements were carried out at 25°C in an Ubbelohde flow viscometer adapted for successive dilution. The dimensions of the capillary were so chosen as to make the flow time of the solvent 120 s at least (negligible kinetic energy corrections). Also, the corrections (if any) for the non-Newtonian flow were neglected; it was found during measurements carried out with poly(methyl methacrylates) under conditions even more favourable for the non-Newtonian flow[27] ($M_w \sim 3 . 10^6$, a better thermodynamic quality of the solvent), that the difference between the intrinsic viscosity obtained from measurements as a final shearing stress and the value of [η] determined by extrapolation to zero shearing stress did not exceed the experimental error. The intrinsic viscosity was obtained by extrapolation of η_{sp}/c, ln η_r/c and $1/2(c/\eta_{sp} + c/\ln \eta_r)$ to zero concentration[28].

Osmometry. Osmotic pressures of the benzene solutions of polymers were measured in a Hellfritz static osmometer[29] at 25°C.

TABLE I

Results of the Light Scattering and Viscosity Measurements of Branched Polydisperse Samples in Butyl Acetate and Parameters Characterizing the Conditions of their Synthesis

τ Conversion, M_w weight average molecular weight, $M_{w,0}$ weight average molecular weight of a primary chain, $(\overline{S_b^2})_z$ z-average mean square radius of gyration, $[\eta]$ intrinsic viscosity.

τ %	$M_w \cdot 10^{-5}$	$M_{w,0} \cdot 10^{-5}$	$(\overline{S_b^2})_z \cdot 10^{-4}$ Å^2	$[\eta]_b$ dl g^{-1}
		$[II]_0 = 0{\cdot}25$ mol %		
3·80	3·0	2·4	—	0·320
6·40	3·4	2·4	—	0·320
8·80	4·5	2·4	—	0·331
11·90	5·9	2·4	—	0·331
13·22	7·0	2·4	16·1	0·363
		$[II]_0 = 0{\cdot}50$ mol %		
1·35	2·3	2·1	—	0·272
2·00	2·9	2·4	4·6	0·300
1·71	2·7	2·1	4·7	0·293
3·62	4·0	2·8	7·1	0·345
6·50	4·2^a	2·4	8·6	0·328
5·23	5·2	2·8	9·1	0·354
6·10	5·1	2·7	8·9	0·364
7·00	6·9	2·7	28·2	0·382
8·40	8·5	2·4	19·6	0·405
8·70	11·2^b	2·9	24·2	0·440
8·00	11·6	2·7	27·1	0·439
11·40	15·0	2·4	34·6	0·400
11·00	20·0	2·9	50·2	0·500
11·00	27·0	2·8	69·4	0·476
		$[II]_0 = 0{\cdot}75$ mol %		
1·30	2·5	2·1	—	0·284
2·00	2·7	2·1	—	0·292
3·10	5·2	2·7	—	0·379
4·30	6·5	2·7	15·0	0·390
5·60	10·5	2·7	24·5	0·436
3·60	16·0	3·9	37·8	0·570
6·70	15·8	2·7	35·5	0·463
7·70	28·0	2·7	71·1	0·520

TABLE I

(Continued)

τ %	$M_w \cdot 10^{-5}$	$M_{w,0} \cdot 10^{-5}$	$(\overline{S_b^2})_z \cdot 10^{-4}$ Å²	$[\eta]_b$ dl g⁻¹
		$[II]_0 = 1\cdot00$ mol %		
1·70	3·2	2·4	—	0·324
2·10	3·5	2·4	—	0·326
2·50	4·2	2·4	—	0·350
3·00	5·3	2·4	—	0·366
3·20	5·3	2·3	—	0·356
4·00	5·7	2·3	—	0·364
2·80	14·7	4·2	41·2	0·580
4·90	9·2	2·3	23·1	0·380
4·60	10·1	2·5	22·4	0·405
5·70	10·5	2·3	21·1	0·405
6·30	13·5	2·3	26·0	0·435
4·30	22·0	3·7	54·0	0·583
4·90	29·4	3·7	75·5	0·625
7·10	66·6	2·8	159·5	0·600

Polymers subjected after characterization to fractionation by [a] elution method, [b] successive precipitation (Table II, III).

RESULTS AND DISCUSSION

Notes on the Course of Copolymerization

When a branched polymer is formed, the average degree of polymerization increases with conversion. Under the conditions employed, the weight average degree of polymerization, P_w, is increased by more than an order of magnitude. To preclude possible autoacceleration[30], we used the method of solution polymerization. Isolated polymers were characterized by the light scattering method and viscometrically (Table I).

To correlate our experimental data (P_w as a function of conversion), it is advisable to combine Eq. (1) and the dependence of ϱ on conversion

$$\varrho = \varrho_0\, f(\tau), \tag{5}$$

where ϱ_0 is the double molar fraction of the divinyl units in the initial polymerization mixture. Then, since $[(1/P_{w,0} - (1/P_w)] \ll 1$,

$$f(\tau) = \frac{1}{\varrho_0}\left(\frac{1}{P_{w,0}} - \frac{1}{P_w}\right). \tag{6}$$

On the assumption of an identical reactivity of methyl methacrylate and the first double bond of ethylene dimethacrylate, a theoretical dependence[31] may be derived

$$f(\tau) = \frac{1}{\tau(2r-1)} \left[(1-\tau)^2 - 2r(1-\tau)^{1/r} + 2r - 1) \right] ; \qquad (7)$$

here, r represents the effective copolymerization parameter of monomer I with respect to the pendant double bond of the built-in monomer II; the difference between the effective and actual copolymerization parameter may be caused by the steric effects upon the reactivity of the double bond. The experimental points do not fit the theoretical dependence (7) for $r = 1$ (Fig. 1), as it would correspond to the frequently assumed identical reactivity of all double bonds.* The function $f(\tau)$, and thus also the weight average degree of polymerization, P_w, increase with conversion slower than at $r = 1$. The cause of this phenomenon can be twofold: a) The pendant double bond is in this case less reactive by its nature, or the pendant vinyl
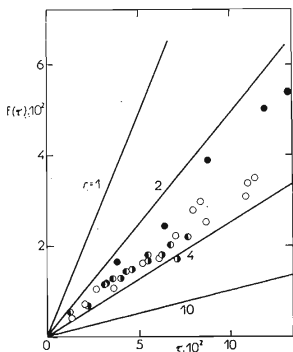

FIG. 1

Dependence of the Degree of Polymerization on Conversion According to Eq. (6)

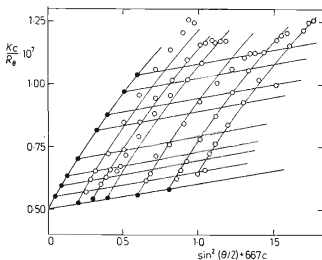$[II]_0$ (mol%): ● 0·25, ○ 0·50, ◑ 0·75, ◐ 1·00; the course of the curves was calculated according to Eq. (7) for r.

FIG. 2

A Typical Zimm Plot of a Polydisperse Branched Polymer

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* In our communication[32], analogous theoretical dependences were incorrectly parametrized; the identical reactivities of the double bonds were there represented by a straight line marked $r = 2$ instead of $r = 1$, and all the other parameters should be divided by two.

groups are sterically hindered by the branched structure of the macromolecules[33]. b) A portion of the pendant vinyl groups is consumed in the process of formation of the intramolecular rings; these reactions do not contribute to the increase in the degree of polymerization, and their occurrence may lead to conclusions about a decreased reactivity of the pendant vinyl groups. The choice between these two possible interpretations may be made only on the basis of a quantitative determination of small amounts of the branching agent built-in in the polymer. An investigation of branched copolymers with a model branching agent accessible to an analytical determination is under way.

Polydisperse Branched Polymers

All common Θ-solvents were tried while choosing solvent for the investigation of branched copolymers[19]; in none of them, however, did the copolymers having a degree of branching $\gamma > 0.5$ dissolve molecularly. Reproducible measurements of light scattering were not obtained until a thermodynamically good solvent, butyl acetate, was used. The angular dependences of reciprocal reduced intensity of the scattered light were slightly curved for almost all copolymers (Fig. 2); the Zimm plot of a polydisperse branched system did not virtually differ from the graph
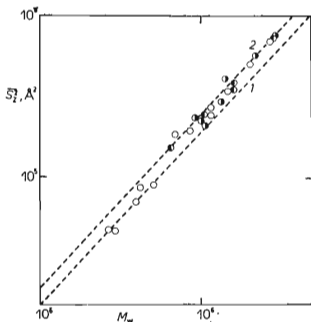
FIG. 3

Dependence of the z-Average Mean Square Radius of Gyration $\overline{S_z^2}$ on the Weight Average Molecular Weight M_w of Polydisperse Branched Copolymers

·········· Dependences described by Eq. (3) for $\varepsilon = 0.067$ and the limit literature values[25,38] of A; 1 $A = 4.95 \cdot 10^{-2}$, 2 6.00 . . 10^{-2}; $[II]_0$ (mol%): ● 0.25, ○ 0.50, ◑ 0.75, ◔ 1.00.
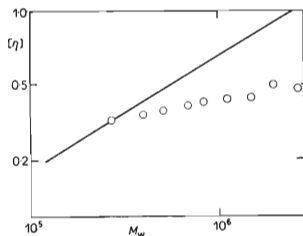
FIG. 4

Dependence of the Intrinsic Viscosity, $[\eta]$, in dlg^{-1} of Branched Polydisperse Copolymers on the Weight Average Molecular Weight, M_w

The monomer II content in the initial polymerization mixture 0.5 mol%; $M_{w,0} \sim$ $\sim 2.7 \cdot 10^5$; —— dependence for a linear polydisperse polymer.

for a polydisperse linear polymer. The calculations according to Henrici-Olivé[34], based on the kinetic data[35,36] and applied to our conditions of preparation, show that the distribution of the molecular weights of the primary linear polymer used by us might be considered normal. Its behaviour in a dilute solution can therefore be described by Eqs (3) and (4). The numerical values of constants in both equations were calculated from the literature data[37-39] and the results of our own measurements.

A comparison of experimental dependences of the radii of gyration of branched copolymers in butyl acetate on M_w with the dependences for linear poly(methyl methacrylate) according to Eq. (3) shows (Fig. 3) that almost all points for branched copolymers lie within the strip of values observed by various authors for linear polymers. The cause of this effect has been explained by Kilb[14]. He showed that the decrease in the z-average radius of gyration due to branching is compensated for by the growth of polydispersity with the extent of branching. At the same time, the range of compensation in the case of the Stockmayer distribution is just such that the dependence of the z-average square radius of gyration, $\overline{S_z^2}$, on the weight average molecular weight, M_w, is identical for both the branched and the linear polymer (whose polydispersity does not vary with the molecular weight). It follows therefrom that a comparison of the sizes of polydisperse branched polymers with those of polydisperse linear polymers having the same molecular weight M_w does not yield any information on the degree of branching (in contrast with fractions in which this

TABLE II

Characterization of Fractions Obtained by Precipitation Fractionation of the Polymer Having $M_w = 11.2 \cdot 10^5$ and $[\eta]_b = 0.440$ dl g^{-1}; (w weight fraction)

Fraction	$w \cdot 10^2$	$M_w^* \cdot 10^{-5}$	$\dfrac{2M_w^*}{M_{w,0}}$	$[\eta]$ dl g^{-1}
1	3·47	0·25	0·18	0·080
2	7·82	0·80	0·56	0·163
3	7·73	1·20	0·82	0·213
4	11·41	2·00	1·38	0·265
5	6·90	2·90	2·00	0·301
6	7·99	3·65	2·52	0·344
7	8·90	4·50	3·10	0·405
8	8·87	6·85	4·72	0·444
9	6·93	10·90	7·50	0·501
10	10·39	15·50	11·68	0·615
11	11·66	30·00	20·68	0·755
12	7·89	52·60	36·23	0·980

$$\sum_i w_i M_{w,i}^* = 11.80 \cdot 10^5 \qquad \sum_i w_i [\eta]_i = 0.450$$

method of determination of the degree of branching is in principle possible). In the relationship between $[\eta]$ and M_w (Fig. 4) the differences in the behaviour of branched and linear polymers are very marked. The dependence for branched polydisperse copolymers prepared from a reaction mixture of the same composition and differing as to their conversion is obviously parametrized by the molecular weight of the primary chain, which is given by the intersection of this dependence with a straight line representing expression (4) for $K \ 1.87 \cdot 10^{-2}$ and $a \ 0.60$. The difference between the viscosities of a linear and a branched polymer, increasing with growing M_w, is a consequence not only of the increasing degree of branching, but also of the growth of polydispersity, because the weight-average molecular weight, M_w, increases faster than the viscosity average, M_v.

However, a direct comparison between the viscosities of a polydisperse linear and a polydisperse branched polymer having the same M_w gives only a semiquantitative idea of the degree of branching, since the distribution of both polymers is fairly different. The problem of viscometric determination of the degree of branching of polydisperse branched polymers is dealt with in a forthcoming communication[40].

Distribution of the Degree of Polymerization

In an attempt to investigate the character of distribution of the degree of polymerization, two common fractionation procedures were used. The ratio of the volumes of the concentrated and dilute phases during successive precipitation fractionation in the system acetone–methanol used was approximately 10^{-2}. If the dilution was higher, isolation of the individual fractions became difficult. Molecular weights of the fractions obtained were determined by light scattering (M_w^*); some were determined also osmometrically (M_n^*). The individual fractions are characterized in Tables II and III.

Assuming that in the system under investigation the degree of polymerization is the only solubility determining parameter (*i.e.*, that solubility is unaffected by bran-

TABLE III

Characterization of Some Fractions Obtained by Elution Fractionation of the Polymer Having $M_w \ 4.2 \cdot 10^5$ and $[\eta]_b = 0.328$ dl g^{-1}

Fraction	$M_w^* \cdot 10^{-5}$	$[\eta]$ dl g^{-1}	Fraction	$M_w^* \cdot 10^{-5}$	$[\eta]$ dl g^{-1}
9	2·80	0·285	14	6·10[c]	0·440
10	2·95	0·304	15	9·00	0·510
11	3·30	0·326	16	11·50	0·558
12	4·45[a]	0·380	17	14·70	0·574
13	5·00[b]	0·390			

$M_n^* \cdot 10^{-5}$: [a] 3·72; [b] 4·54; [c] 5·54.

ching[41,42]), we constructed integral and differential curves, using a procedure suggested by Schulz (Fig. 5). (A more accurate construction method could not be used, since in the case of high fractions M_n^* cannot be determined.) If we compare the distribution curves obtained here with the theoretical distributions calculated by Kilb[14] from relations derived by Stockmayer[10], we find, for the experimental curves, a somewhat higher representation of the polymer having a high degree of polymerization at the expense of the weight representation of the low-molecular-weight polymer. This effect was more pronounced in the case of the elution fractionation. In comparison with the distributions of linear polymers, distributions of branched polymers are characterized by an extended shape in the region of higher molecular weights. Even in the case of an ideally sharp fractionation according to molecular weights, the fractions having high molecular weights would have — at the weight
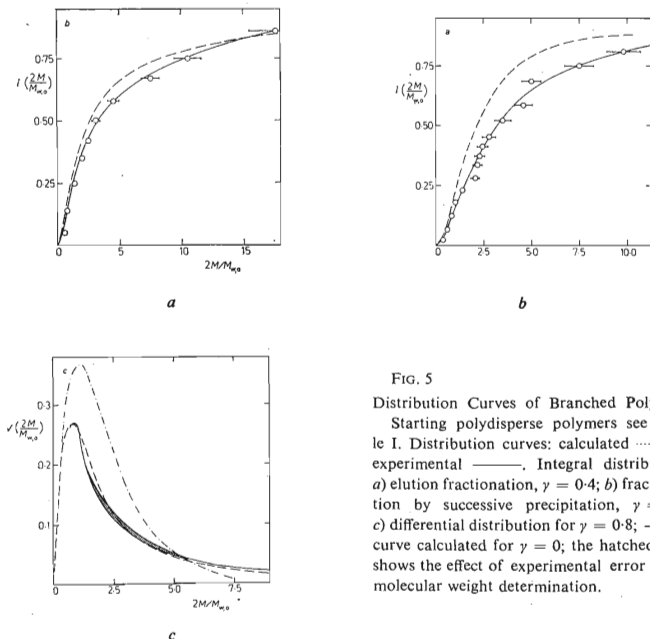

a

b

c

Fig. 5

Distribution Curves of Branched Polymers

Starting polydisperse polymers see Table I. Distribution curves: calculated ···········, experimental ————. Integral distribution: *a*) elution fractionation, $\gamma = 0.4$; *b*) fractionation by successive precipitation, $\gamma = 0.8$; *c*) differential distribution for $\gamma = 0.8$; –·–·–·– curve calculated for $\gamma = 0$; the hatched area shows the effect of experimental error in the molecular weight determination.

fraction ~ 0.1 — a high polydispersity; in the case of a real fractionation this polydispersity is of course considerably higher[43,44]. We therefore believe that the differences between the theoretical and experimental distribution curves may be explained by a limited resolving power of the fractionation processes, determined by their physicochemical nature, and that in our case the Stockmayer distribution satisfactorily describes the molecular weight distribution of the polymers under investigation. (A similar conclusion was also proposed by Thurmond and Zimm[5] on the basis of results which are comparable with ours as to agreement between the theoretical and experimental dependences.)

Characterization of Fractions

The dependence of the intrinsic viscosity of fractions on M_w (Fig. 6) has the usual course[5]. Fractions having low molecular weight are virtually linear. With increasing molecular weight the difference between the intrinsic viscosities of fractions of the linear and the branched polymer also increases, because the average number of the branch units in the macromolecule increases with molecular weight. It is important to know the average number of branches present in the individual fractions. For the case of a random tetrafunctional branching, Zimm and Stockmayer[11] have derived the dependence of the ratio of mean square radii of gyration of branched and linear macromolecules, monodisperse in both cases and having the same molecular weight, on the average number of the branch units, $\bar{n}$:

$$g = [(1 + \bar{n}/\sigma)^{1/2} + 4\bar{n}/3\pi]^{-1/2} . \qquad (8)$$

We have made no attempt, however, to determine $\bar{n}$ from the radii of gyration. Although the light scattering method yielded molecular weights of fractions of
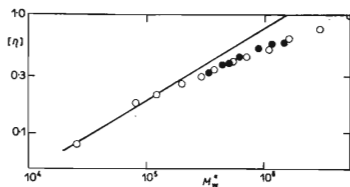

FIG. 6

Dependence of the Intrinsic Viscosity of Fractions of Branched Copolymers, $[\eta]$, in dlg^{-1}, on Molecular Weight M_w^*

   Fractions obtained by successive precipitation (Table II) (○) and by elution fractionation (Table III) (●); ——— dependence for a monodisperse linear polymer.

polymers with the usual accuracy, the angular dependences, especially those obtained with the middle fractions, were strongly curved downwards (Fig. 7), which made it impossible to determine the radii of gyration with sufficient accuracy. Similarly to our earlier paper[24], the curvature of the angular dependences might be explained by the presence of large particles in the solution; in the system under investigation, however, we have as yet no information on their magnitude and origin.

From equations (2) and (8) also follows a relationship between the ratio $[\eta]_b/[\eta]_l$ and the average number of the branch units in an assembly of branched monodisperse macromolecules. To compare the theoretical and experimental dependences of relative sizes of branched macromolecules on $\bar{n}$, only results of the intrinsic viscosity measurements were used. We plotted (Fig. 8) the dependences of the ratio $[\eta]_b/[\eta]_l$ on the average number of the branching centres $\bar{n}$ for three values of the exponent b covering the range of its possible values. The other system of curves in Fig. 8 consists of theoretical dependences $2M/M_{w,0}$ on $\bar{n}$ for three different values of γ (Table I, ref.[14]). The abscissa of the experimental point in Fig. 8 is equal to the abscissa of a point having coordinates $(2M/M_{w,0}, \gamma)$ for the calculation of which the necessary data are available; the ordinate of the experimental point is determined by the measured value $[\eta]_b/[\eta]_l$.
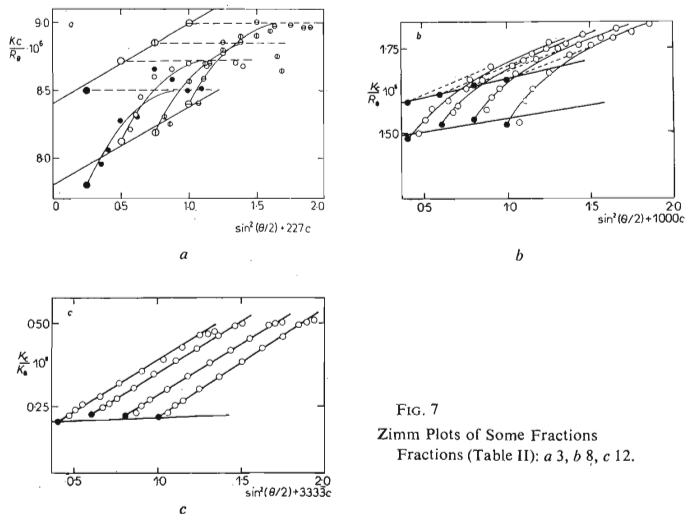

a

b

c

FIG. 7

Zimm Plots of Some Fractions
Fractions (Table II): *a* 3, *b* 8, *c* 12.

For fractions from both fractionations, dependences are observed which differ considerably from the theoretical dependence for $b = 0.5$, so far most frequently used[12,14]. (The tables given by Zimm and Kilb[12] cannot therefore be applied universally.) Fractions obtained by successive precipitation fit fairly well the theoretical dependence for $b = 0.8$ (the value $b = 0.8$ has also been verified by other methods[40]).
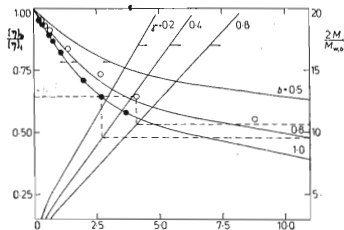

FIG. 8

Dependences of the Ratio $[\eta]_b/[\eta]_l$ on the Average Number of the Branch Units $\bar{n}$ in Fractions, Parametrized by the Exponent b (Eq. (2)), and Dependences Representing the Relationship Between the Relative Degree of Polymerization of a Fraction, $2M/M_{w,0}$, and $\bar{n}$, Parametrized by γ

Dependence parametrized by $b = 1$ is also valid for the ratio $\overline{S_b^2}/\overline{S_l^2}$. Fractions obtained by successive precipitation ($\circ$) and elution fractionation ($\bullet$).

We deduce from the agreement between the experimental and theoretical dependences that the precipitation fractionation occurred in principle according to the molecular weights, and the transition of the individual molecules into the gel phase was not too much affected by their branching. In the opposite case, the experimental points would not fit the theoretical curve and would give a different number of the branching centres than corresponds to this curve at the given ratio $[\eta]_b/[\eta]_l$. This situation probably arose during elution fractionation, when the experimental points lie below the curve for $b = 0.8$. (The fact that the points fit very well the theoretical dependence for $b = 1.0$ is probably only an incidental one.) It seems that under the given conditions the effect of branching of the macromolecules also played its part during elution fractionation, in such a way that also the low-molecular-weight, prevailingly linear fractions were stripped into the high-molecular-weight, strongly branched fractions. The low-molecular-weight fractions will reduce the M_w^* of the fraction more than its intrinsic viscosity (because of their smaller branching), thus effecting the observed deviation from the theoretical dependence.

REFERENCES

1. Mendelson R. A., Drott E. E.: J. Polymer Sci. *B6*, 795 (1968).
2. Schneider N. S., Traskos R. T., Hoffman A. S.: J. Appl. Polymer Sci. *12*, 1567 (1968).
3. Dautzenberg H., Ruscher Ch.: Rheol. Acta *4*, 119 (1965).
4. Graessley W. W., Mittelhauser M.: J. Polymer Sci. *A-2*, 5, 431 (1967).
5. Thurmond G. D., Zimm B. H.: J. Polymer Sci. *8*, 477 (1952).
6. Walling J.: J. Am. Chem. Soc. *67*, 441 (1945).
7. Flory P. J.: *Principles of Polymer Chemistry*. Cornell University Press, Ithaca 1953.
8. Gordon M., Roe R. S.: J. Polymer Sci. *21*, 27 (1956).
9. Flory P. J.: J. Am. Chem. Soc. *63*, 3083 (1941).
10. Stockmayer W. H.: J. Chem. Phys. *11*, 45 (1943); *12*, 125 (1944).
11. Zimm B. H., Stockmayer W. H.: J. Chem. Phys. *17*, 1301 (1949).
12. Zimm B. H., Kilb R. W.: J. Polymer Sci. *37*, 19 (1959).
13. Berry G. C.: Symposium on Macromolecular Chemistry, Preprints VI, 144. Tokyo 1966.
14. Kilb R. W.: J. Polymer Sci. *38*, 403 (1959).
15. Shultz A. R.: J. Polymer Sci. *A3*, 4211 (1965).
16. Kron A. K., Pticyn O. B.: Vysokomolekularnyje Sojedinenija *5*, 397 (1963).
17. Berry G. C., Orofino T. A.: J. Chem. Phys. *40*, 1614 (1964).
18. Schulz G. V.: Z. Physik. Chem. (Leipzig) *B30*, 379 (1935); *B43*, 25 (1939).
19. Lütje H., Meyerhoff G.: Z. Physik. Chem.; Neue Folge *38*, 364 (1963).
20. Koningsveld R., Tuijnman C. A. F.: Makromol. Chem. *38*, 39 (1960).
21. Arnett L. M.: J. Am. Chem. Soc. *74*, 2027 (1952).
22. Cragg L. A., Hammerschlag H.: Chem. Rev. *39*, 79 (1946).
23. Poláček J., Kössler I., Vodehnal J.: J. Polymer Sci. *A3*, 2511 (1965).
24. Kratochvíl P.: This Journal *26*, 2767 (1964).
25. Cantow H. J., Bodmann O.: Z. Physik. Chem., Neue Folge *3*, 65 (1955).
26. Dandliker W. B., Kraut J.: J. Am. Chem. Soc. *78*, 2380 (1956).
27. Quadrat O., Bohdanecký M., Munk P.: J. Polymer Sci. *C 16*, 95, (1967).
28. Heller W.: J. Colloid Sci. *9*, 547 (1954).
29. Hellfritz H.: Makromol. Chem. *7*, 184 (1951).
30. Norish R. G. W., Smith R. R.: Nature *150*, 336 (1942).
31. Wesslau H.: Angew. Makromol. Chem. *1*, 56 (1967).
32. Vaculová L., Červenka A., Kratochvíl P.: Symposium on Macromolecular Chemistry, Preprints IV, 331, Budapest 1969.
33. Minnema L., Staverman A. J.: J. Polymer Sci. *29*, 281 (1958).
34. Henrici-Olivé G., Olivé S.: Fortschr. Hochpolymer. Forsch. *2*, 469 (1961).
35. Talat-Erben M., Bywater S.: J. Am. Chem. Soc. *77*, 3712 (1955).
36. Tobolsky A., Baysal B.: J. Polymer Sci. *11*, 471 (1953).
37. Bohdanecký M.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1963.
38. Schulz G. V., Graubner H.: Z. Elektrochem. *63*, 301 (1959).
39. Schulz G. V., Kirste R.: Z. Physik. Chem. (Frankfurt) *30*, 171 (1961).
40. Mrkvičková-Vaculová L., Kratochvíl P.: This Journal *37*, 2029 (1972).
41. Stockmayer W. H., Fixman M.: Ann. N. Y. Acad. Sci. *57*, 334 (1953).
42. Booth C., Beason L. R.: J. Polymer Sci. *42*, 81, 93 (1960).
43. Bohdanecký M.: J. Polymer Sci. *C 23*, 257 (1968).
44. Koningsveld R., Staverman A. J.: J. Polymer Sci. *A 2*, 6, 305 (1968).

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