

# SOLUTION PROPERTIES AND BRANCHING OF POLY[2-(TRIPHENYLMETHOXY) ETHYL METHACRYLATE]

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Dependences of the intrinsic viscosity, of the sedimentation coefficient and of the second virial coefficient on molecular weight found for poly[2-(triphenylmethoxy) ethyl methacrylate] were interpreted as a consequence of the branching of polymer molecules. The degree of branching (c. one branched monomer unit per  $1 \cdot 10^3 - 2 \cdot 10^3$  unbranched units) was estimated from the sedimentation coefficients determined under the  $\theta$ -conditions. The value determined for the exponent  $\nu$  in the relationship  $g_\theta = g_\theta^\circ$  was approximately 3/2. An analysis of viscometric data (for solutions in toluene and mesitylene as the  $\theta$ -solvent) leads to a conclusion that the dependence of the expansion factor  $\alpha_\eta^3$  on the parameter of the excluded volume  $z$  is approximately the same for the polymer under investigation and for linear polymers.

Earlier papers on poly[2-(triphenylmethoxy) ethyl methacrylate] dealing with its preparation, acidolytic splitting<sup>1,2</sup> and determination of the flexibility characteristics<sup>3</sup> showed in accord with each other that polymer molecules were branched. In this paper some further arguments in favour of branching have been put forward, the degree of branching has been estimated, and solution properties of the polymer have been analyzed from the viewpoint of their dependence on branching.

We start with the known relationships for expansion factors<sup>4</sup>

$$\alpha_\eta^3 = [\eta]^i / [\eta]_\theta^i = 1 + C_1^i z + \dots, \quad (1)$$

$$\alpha_s^2 = (\overline{S^2}) / (\overline{S_0^2}) = 1 + a_1^i z + \dots, \quad (2)$$

in which the symbols  $[\eta]_\theta^i$  and  $\overline{S_0^2}$  stand for intrinsic viscosity and mean square radius of gyration at the  $\theta$ -temperature, respectively, the symbols without subscripts denote the same quantities at  $T \neq \theta$ , where  $C_1^i$  and  $a_1^i$  are numerical coefficients, and  $z$  is the parameter of the excluded volume.  $l$  or  $b$  is substituted for the superscript  $i$  in order to distinguish linear and branched polymers. Intrinsic viscosity  $[\eta]$  and the sedimentation coefficient  $s$  (at zero concentration and unit pressure) are defined by<sup>4</sup>

$$[\eta]_\theta^l = K_{0,\eta}^l M^{1/2}, \quad (3)$$

$$s_\theta^l = K_{0,s}^l M^{1/2}, \quad (4)$$

$$K_{0,\eta}^1 = 6^{3/2} \Phi_0 [(\overline{S_0^2})^1/M]^{3/2}, \quad (5)$$

$$1/K_{0,s}^1 = [\eta_0 N_A / (1 - \bar{v} \varrho_0)] \cdot 6^{1/2} P_0 [(\overline{S_0^2})^1/M]^{1/2}, \quad (6)$$

in which  $\Phi_0$  and  $P_0$  are universal constants,  $M$  is molecular weight of the polymer,  $\bar{v}$  is its partial specific volume,  $\eta_0$  and  $\varrho_0$  respectively are the viscosity and density of the solvent, and  $N_A$  is the Avogadro number. The parameter  $z$  is expressed by means of the ratio  $(\overline{S_0^2})^1/M$ , of the excluded volume of the segment  $\beta$  and of its molecular weight  $m_0$  using the relationship

$$z = (4\pi)^{-3/2} [(\overline{S_0^2})^1/M]^{-3/2} (\beta/m_0^2) M^{1/2}, \quad (7)$$

where

$$\beta/m_0^2 = (\beta_0/m_0^2) (1 - \Theta/T). \quad (8)$$

The branching is characterized by using the following symbols:  $j$  gives the number of branched monomer units and  $h_\theta, g'_\theta, g_\theta$  denote the ratios of the quantities  $s_\theta, [\eta]_\theta, (\overline{S_0^2})_\theta$  of branched and linear polymer at the same molecular weight ( $M_w$ ):

$$h_\theta^{-1} = s_\theta^b/s_\theta^l, \quad g'_\theta = [\eta]_\theta^b/[\eta]_\theta^l, \quad g_\theta = (\overline{S_0^2})_\theta^b/(\overline{S_0^2})_\theta^l. \quad (9, 10, 11)$$

These quantities are a function of the topology of the branched chain, *i.e.* the functionality, type and density of branching.

The dependence of the second virial coefficient  $A_2$  on molecular weight is analyzed in terms of the two-parameter theory, according to which  $A_2$  is expressed as a product of the term  $A$  independent of molecular weight and of the function  $h(\bar{z})$ , decreasing with increasing molecular weight<sup>4</sup>:

$$A_2 = A \cdot h(\bar{z}), \quad A = (N_A/2) (\beta/m_0^2), \quad \bar{z} = z/\alpha_s^3 \quad (12, 13, 14)$$

## EXPERIMENTAL

Experimental data (*i.e.* intrinsic viscosities, sedimentation coefficients and second virial coefficients) used throughout this work were taken from Tables I–III of ref.<sup>3</sup>. The  $[\eta]_0^b$  values for fractions of polymer 2 were determined by interpolation for  $M_w$  values<sup>3</sup> in the logarithmic plot  $[\eta]_0^b - M_w$  constructed for fractions of polymer 4. Since the logarithmic plot  $[\eta]_0^b - M_w$  of toluene solutions (*cf.* Fig. 2 in ref. 2) was common for both series of fractions, such step seems to be justified.

## RESULTS AND DISCUSSION

### Branching of Polymer

In earlier papers the branching of poly[2-(triphenylmethoxy) ethyl methacrylate] molecules was deduced from a quantitative analysis of acidolytic splitting<sup>2</sup>, from the course of the dependences  $[\eta]_\theta/M^{1/2}$  vs  $M^{1/2}$  and  $M^{1/2}/s_\theta$  vs  $M^{1/2}$  (which pos-

sessed unambiguously negative slopes), and finally from an analysis of the unusual course of the plots  $[\eta]/M^{1/2}$  vs  $M^{1/2}$  and  $M^{1/2}/s$  vs  $M^{1/2}$  for solutions in good solvents<sup>3</sup> (toluene, 1,4-dioxan, cyclohexanone). Further arguments can be obtained by combining viscometric and sedimentation data and by analyzing the dependence of the second virial coefficient on molecular weight.

Moore and coworkers have derived from the theory of hydrodynamic quantities<sup>5</sup> that for the ratio  $[\eta]_{\theta}^b/s_{\theta}^b$  it holds

$$[\eta]_{\theta}^b/s_{\theta}^b = (K_{0,\eta}^1/K_{0,s}^1) g'_{\theta} h_{\theta} . \quad (15)$$

In the case of linear polymers (where  $g'_{\theta} = h_{\theta} = 1$ ) this ratio should be independent of molecular weight, while in the case of branched polymers it should be the lower the higher the degree of branching. If the degree of branching goes on increasing regularly with increasing molecular weight, the ratio should decrease with increasing  $M$ . Accordingly, the logarithmic plot  $[\eta]_{\theta}$  vs  $s_{\theta}$  should be linear (with a unity slope) for linear polymers and curved for the branched ones (plot according to Blachford and Robertson)<sup>6</sup>. Table I and Fig. 1 compiled from data on polymer-mesitylene ( $\theta = 47^{\circ}\text{C}$ ) show that the ratio  $[\eta]_{\theta}/s_{\theta}$  is not constant, that the logarithmic dependence  $[\eta]_{\theta}$  vs  $s_{\theta}$  has not a unity slope and that it is curved. This indicates that the polymer chains are not linear.

The dependence  $A_2$ - $M$  (Fig. 2) for toluene solutions is characterized by a high quotient  $d \ln A_2/d \ln M$  (c.  $-0.4$ ). According to theory, the dependence  $A_2$ - $M$  follows from the function  $h(\bar{z})$  in Eq. (12). The perturbation theory gives this function in the form of a slowly converging power series<sup>4</sup>

$$h(\bar{z}) = 1 - B_1^1 \bar{z} + \dots , \quad (16)$$

TABLE I

Characteristics of Branching of Poly[2-(Triphenylmethoxy) ethyl Methacrylate]

Definition of symbols cf. text.  $[\eta]_{\theta}^b$  values determined by interpolation in the logarithmic plot  $[\eta]_{\theta}^b$ - $M_w$  (mesitylene,  $47^{\circ}\text{C}$ ;  $M_w$  values are given in ref.<sup>3</sup>).

Polymer / fraction	$[\eta]_{\theta}^b$	$[\eta]_{\theta}^b/s_{\theta}^b$	$h_{\theta}$	$g'_{\theta}$	$j$
2/2	0.287	0.309	0.91	0.57	4
2/4	0.220	0.385	0.94	0.71	3
2/5	0.200	0.410	0.96	0.75	2
2/7	0.145	0.442	0.98	0.87	1

in which the numerical coefficient  $B_1^1$  depends on the degree and type of branching. It can be said<sup>7</sup> that

$$B_1^b \leq B_1^1 / g_\theta^{3/2}, \quad (17)$$

where  $B_1^1 = 2.865$ . The increase in the coefficient  $B_1^b$  with increasing degree of branching is the cause why the dependence  $A_2-M$  is steeper for branched polymers (if their degree of branching increases systematically with molecular weight) than for linear polymers. Eq. (16) can be employed only at very low  $\bar{z}$ . At higher  $\bar{z}$ , i.e. in good solvents, other functions must be used, based on approximate theories<sup>4</sup>. Since, however, the coefficient  $B_1^b$  appears also in these theories, the preceding conclusion holds qualitatively also for good solvents. This is why the high value of the quotient  $d \ln A_2 / d \ln M$  found for the polymer investigated in this work with toluene as solvent can be regarded as an argument in favour of branching of the polymer.

Of our results, only the sedimentation data can be used in the estimation of the degree of branching, because the theory of the translational frictional coefficients of nonlinear polymers<sup>8</sup> has been worked out in much more detail than the theory of intrinsic viscosity. Experimental values of  $s_\theta^b$  for fractions of polymer 2 and the constant  $K_{0,s}^1 = 3.1 \cdot 10^{13}$  (cf. Fig. 3 in ref.<sup>3</sup>) are used to calculate the  $h_\theta$  values by means of (9); hence, employing the theoretical function<sup>8</sup>, one obtains  $h_\theta(j)$  and

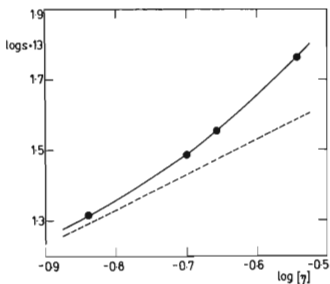


FIG. 1

Plot According to Blachford and Robertson<sup>6</sup> for the System Poly[2-(Triphenylmethoxy)-ethyl Methacrylate]-Mesitylene ( $\theta = 47^\circ\text{C}$ )

Broken line is that with unity slope.

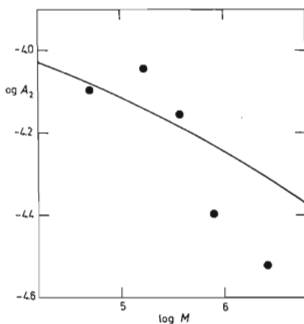


FIG. 2

Dependence of the Second Virial Coefficient on Molecular Weight

Points for the system polymer-toluene ( $25^\circ\text{C}$ ); — calculated using Eqs (12)–(14), (22) and (23) with  $\beta/m_0^2 = 4.09 \cdot 10^{-28}$ .

the degree of branching  $j$  (Table I). Since for the polymer under investigation branching is probably due to a transfer reaction<sup>2</sup>, we assume a trifunctional branching with a statistical distribution of the lengths of linear parts of the chain. The  $h_\theta$  values are situated in the interval ( $h_\theta > 0.9$ ), in which the theoretical functions are virtually identical both for the statistical and for the comblike type of branching<sup>8</sup>. The  $j$  values determined in the measurements (Table I) indicate that the degree of branching is low; there is one branched monomer unit per c.  $1 \cdot 10^3 - 2 \cdot 10^3$  unbranched units.

### Correlation of Hydrodynamic Data

A procedure similar to that employed in the determination of  $h_\theta$  values can be used in the determination of  $g'_\theta$  (Table I) by means of Eqs (10), (4) and of  $K_{0,\eta}^1 3 \cdot 10^{-4}$  (ref.<sup>3</sup>). For reasons given above we shall not use these values to estimate the degree of branching, but shall try to establish the correlations  $g'_\theta-h_\theta$  and  $g'_\theta-g_\theta$  for the polymer under investigation. Fig. 3 shows a comparison of the experimental dependence  $g'_\theta-h_\theta$  with four theoretical dependences<sup>9</sup>. Curve 1 corresponds to the function

$$g'_\theta = h_\theta^3. \quad (18)$$

Data needed for the construction of three further curves have been obtained as follows:  $g_\theta$  values were taken from Table I, ref.<sup>8</sup> (column 3) and transformed into  $g'_\theta$  according to

$$g'_\theta = g_\theta^\nu \quad (19)$$

using  $\nu = 1/2, 1, 3/2$ . The  $g'_\theta$  values thus obtained were then plotted against the  $h_\theta$

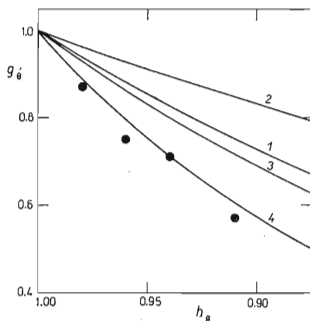


FIG. 3  
Dependence  $g'_\theta-h_\theta$   
Points for polymer-mesitylene ( $47^\circ\text{C}$ ).  
Theoretical dependences: 1  $g'_\theta-h_\theta^3$ , 2 to 4  $g'_\theta-g_\theta^\nu$  at  $\nu = 1/2, 1$  and  $3/2$ .  $g_\theta$  and  $h_\theta$  from ref.<sup>8</sup>.

values corresponding to the same type and degree of branching (*cf.* Table II, ref.<sup>8</sup>, column 5). The comparison of experimental data with theoretical dependences showed that in our case Eq. (19) and  $\nu = 3/2$  are quite adequate. However, although a detailed analysis of procedures used for obtaining the correlated data showed that the errors, if any, are not large, it cannot be ruled out that the actual  $\nu$  is somewhat lower. On the other hand, it lies undoubtedly near the upper boundary of the interval  $1/2 < \nu < 3/2$  within which the  $\nu$  values can move<sup>9</sup>. Very similar values were found for low-density polyethylene ( $\nu \approx 1.2-1.3$ , *cf.*<sup>9</sup>), where branching is also due to transfer. For poly(vinyl acetate), on the other hand, the branching of which is of similar origin,  $\nu$  was found to be  $1/2$  at a low degree of branching<sup>9</sup>.

In discussing the hydrodynamic properties of branched polymers one often meets with the question whether and to what extent the coefficient  $C_1^b$  in Eq. (1) depends on the type and degree of branching. There is no theoretical answer to this question. Judging by experimental results obtained with several samples of branched polystyrene, Berry assumes<sup>10</sup> that branching never makes the coefficient  $C_1^b$  increase as markedly as the coefficient  $a_1^b$  in Eq. (2) and that it even may lead to its decrease. We shall try to find out how poly[2-(triphenylmethoxy) ethyl methacrylate] behaves in such case.

Differentiating Eq. (1) with respect to temperature gives for  $T = \Theta$

$$(d \ln [\eta]^b/dT)_\Theta = (d \ln [\eta]_\Theta^b/dT)_\Theta + C_1^b(dz/dT)_\Theta. \quad (20)$$

For a nondraining coil the quotient  $d \ln [\eta]_\Theta^b/dT$  is determined by the temperature dependence of unperturbed dimensions, *i.e.* by the quotient  $d \ln (\bar{S}_0^2)^b/dT$ . Since the

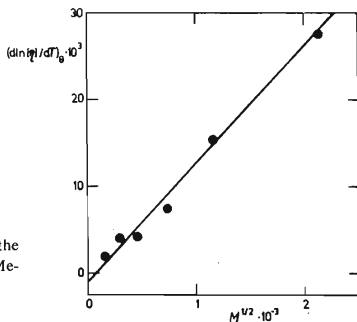


FIG. 4

Dependence  $(d \ln [\eta]^b/dT)_\Theta$  on  $M^{1/2}$  for the System Poly[2-(Triphenylmethoxy)ethyl Methacrylate]-Mesitylene ( $\Theta = 47^\circ\text{C}$ )

latter is related only to short-range interactions (barriers of free rotation), it can be regarded as equal to  $d \ln (\bar{S}_0^2)^{1/2} / dT$ , especially at a low degree of branching. Then it holds (with respect to Eqs (3), (5), (7), and (8))

$$(d \ln [\eta]^b / dT)_\theta = (d \ln K_{0,\eta}^1 / dT)_\theta + C_1^b [(3/2\pi)^{3/2} (\Phi_0 / K_{0,\eta}^1) (\beta_0 / m_0^2 \Theta)] \cdot M^{1/2} \quad (21)$$

If the coefficient  $C_1^b$  is the same for a number of branched fractions, it can be expected that the plot  $d \ln [\eta]^b / dT$  vs  $M^{1/2}$  will be linear. This is really the case with the polymer under investigation (mesitylene,  $\Theta = 47^\circ\text{C}$ ) (Fig. 4). The slope of this plot gives us  $C_1^b(\beta_0 / m_0^2)$  for the polymer-mesitylene system ( $1.45 \cdot 10^{-21}$ ); this value along with Eqs (7) and (8) allows to calculate the  $C_1^b z$  values for 55 and  $65^\circ\text{C}$ , which are then correlated with the expansion factors  $\alpha_\eta^3$ , calculated from experimental values of  $[\eta]^b$ . The dependence is linear (Fig. 5) and common for all fractions, though differing in the degree of branching.

The range of  $\alpha_\eta^3$  values encompassed by this dependence also comprises the values for two fractions of the polymer under investigation (4/3 and 4/4) in toluene ( $\alpha_\eta^3 = 1.37$  and  $1.56$ ). This fact can be employed to determine  $C_1^b(\beta / m_0^2)$  for this system ( $4.33 \cdot 10^{-28}$ ). Now let us assume that  $C_1^b = C_1^1 = 1.06$  (cf.<sup>4</sup>); we obtain  $\beta / m_0 = 4.09 \cdot 10^{-28}$ .

By using this value we calculate the theoretical dependence  $A_2-M$  and compare

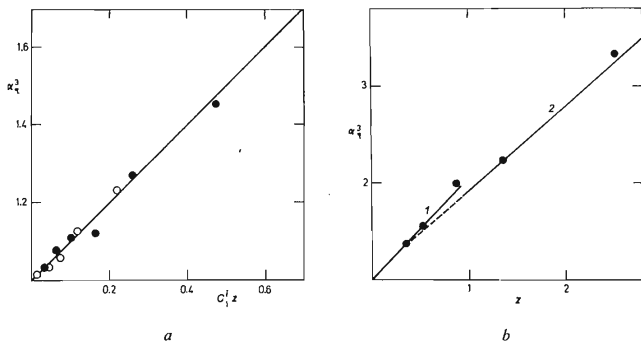


FIG. 5

Dependence of  $\alpha_\eta^3$  on  $C_1^b z$  (a) and of  $\alpha_\eta^3$  on  $z$  (b) for the System Poly[2-(Triphenylmethoxy)ethyl Methacrylate]-Solvent

a) Mesitylene;  $\circ$   $55^\circ\text{C}$ ,  $\bullet$   $65^\circ\text{C}$  b) Toluene,  $25^\circ\text{C}$ ; calculated dependences: 1 from Eq. (24), 2 from Eq. (25).

it with the experimental one. We expect that a wrongly chosen  $C_1^b$  would lead to an incorrect  $\beta/m_0^2$ , and thus to wrong  $A_2$  values. The calculations are based on equations of the Orofino-Flory theory<sup>11</sup> (with the coefficients<sup>4</sup>  $a_1^1 = 134/105$ ,  $B_1^1 = 2.865$ ):

$$h(\bar{z}) = (B_1^1 \bar{z}) \ln(1 + 2B_1^1 \bar{z}), \quad (22)$$

$$\alpha_s^5 - \alpha_s^3 = a_1^1 \bar{z}. \quad (23)$$

The above relationships are used because of their simplicity. More involved relationships could be substituted for them. However, nothing would be gained because — as it has been shown with several model systems<sup>4</sup> — all the theoretical  $h(\bar{z})$  functions give an almost identical representation of experimental data in the range of  $\alpha_s^3$ -values found in this paper.

The calculated  $A_2$ - $M$  dependence has been compared with the experimental one in Fig. 2. At  $M < 4 \cdot 10^5$ , the calculated values differ from the experimental ones by  $\pm 5\%$  in two cases, and by  $+20\%$  in one case. We therefore believe that  $C_1^b$  has been chosen rather correctly. At higher molecular weights the  $A_2$  values are lower by 25 and 100%. The difference exceeds the experimental error. It could not be removed by substituting other value of  $\beta/m_0^2$ , but only by using higher  $B_1^1$  values (c. 4–5) corresponding to branched polymers.

By using  $\beta/m_0^2$ , it is also possible to calculate the  $z$  values for toluene solutions of further fractions having a higher molecular weight. In Fig. 5b,  $\alpha_\eta^3$  values *i.e.*  $[\eta]^b/M^{1/2}g'_\theta$  have been plotted against the parameter  $z$  for all fractions of polymer 4. They have been compared with semiempirical dependences, which for linear polymers have been established by Yamakawa<sup>4</sup>

$$\alpha_\eta^3 = 1 + 1.06z \quad 1 < \alpha^3 < 1.6 \quad (24)$$

$$\alpha_\eta^3 = 1.05 + 0.87z \quad 1.6 < \alpha^3 < 2.5. \quad (25)$$

It is clear from Fig. 6 that for poly[2-(triphenylmethoxy)ethyl methacrylate] in the range of higher  $\alpha_\eta^3$  the dependence  $\alpha_\eta^3$ - $z$  can be adequately described by Eq. (25) with the coefficient valid for linear polymer.

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