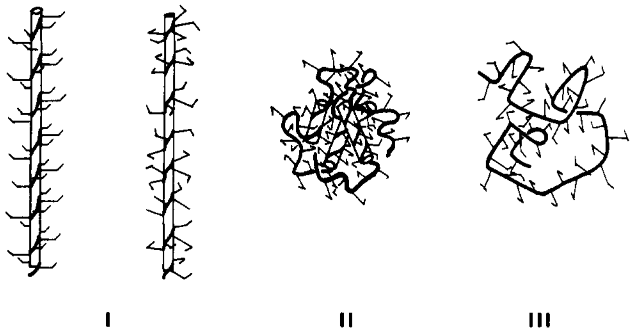

Figure 2. Schematic representation of polypeptide denaturation: region I, disruption of a secondary side-chain structure; region II, intermediate polypeptide conformation; region III, random coil.

high degree of side-chain mobility. Correspondingly, correlating these observations with specific calculated side-chain conformations does not seem relevant. Throughout the helix-coil transition (region II) an intermediate polypeptide conformation is postulated. In Figure 2 (II) this conformation is depicted as a broken helix resembling in some ways a native protein conformation. The structural details of the proposed intermediate conformation are not certain. However, the suggestion of a protein-like configuration may not be unreasonable. Somewhat analogous to hydrophobic interactions in proteins, polypeptide molecules having partial helix content might in the mixed-solvent system tend toward configurations in which the helical segments aggregate on the interior of the configuration because of preferential solvation of the random-coil residues by F_3CCOOH. In region III a posttransitional increase in the phenyl T_1 implies that the ideal, unrestricted, random-coil configuration is not attained until well after the helix-coil transition. This apparent increase in side-chain mobility occurring at high F_3CCOOH concentrations further supports the idea of a constricted intermediate conformation in the preceding helix-coil transition region.

Although the experimental data do not enable us to distinguish between the effects of polydispersity and a model utilizing a side-chain secondary structure, these preliminary findings do suggest that nmr relaxation studies may, in addition to elucidating the role side chains play in stabilizing the α helix, provide a more thorough understanding of the mechanism of the helix-coil transtion.

Acknowledgments. We are grateful to E. M. Bradbury for providing us with the $(BzlGlu)_n$ sample. The contributions of Dr. Ben Shoulders and Howard Johnson toward experimental techniques are gratefully acknowledged. We thank Dr. R. Ullman for stimulating comments on the F_3CCOOH relaxation data and on the effects of polydispersity.

Rayleigh Scattering from Solutions of Critically Branched Polycondensates

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ABSTRACT: The polycondensation system decamethylene glycol–benzene-1,3,5-triacetic acid has been shown previously to adhere very closely to the postulates of the classical random f-functional model, and to be capable of permanent stabilization in the critically branched state (*i.e.*, near the gel point). Such samples are here used for light-scattering studies. Combinatorial theories for interpreting such measurements are presented as generalizations of those deduced earlier using similar graph-theoretical methods (especially the formalism of cascades). It is shown that the situation is unusually favorable for critically and randomly branched materials: the Zimm plots are essentially rectilinear and the two parameters (the conversion α and the basic molecular length parameter b) of the model are obtained from the intercept and slope of a Zimm plot, respectively. Here $\alpha/\alpha_{\text{crit}}$ is shown to be measurable to about 0.0001, and b is constant over a nearly 15-fold range of $(MW)_w$. The value of b reveals high chain extension. Systematic departures of the Zimm plots from rectilinearity, serious only at low $(MW)_w$, are ascribed to association by H bonding.

Recent analysis of the effects, on radiation scattering, due to stiffness and finite cross-section,[2a] and of the branching[2b] of molecular chains, have increased the usefulness of scattering techniques. Such methods hold great promise for polymer science. New model calculations have helped to shed light on the structure of natural glycogen, by applying them to the scattering behavior observable after the glycogen molecules have been chemically transformed to star-shaped assemblies bearing grafts of linear amylose chains.[2b] Statistical theories often take simple forms for completely random structures. Thus, it was shown[3] that random f-functional polycondensates in solution should exhibit rectilinear scattering envelopes in conventional experimental Zimm plots. Besides glycogen in the animal kingdom, branched covalent polymer systems occur in plants, *e.g.*, dextran and amylopectin. These polymers are made under the very specific action of two enzymes. Although the reactions imply some restrictions to the randomness, the statistical problem is still easy to handle by the mentioned theories.[4,5] The natural branched materials are of high weight-average molecular

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weight, *i.e.,* they provide examples of the "critically branched state of matter"[6] which is important for life processes generally.

For synthetic systems, the covalent critically branched state has been observable only as a fleeting condition as they pass through their gel points.[7-15] Recently it has proved possible to stabilize a well-characterized system of this kind permanently by a deliberate chemical transformation. Using the esterification of decamethylene glycol-benzene-1,3,5-triacetic acid (DMG-BTA), Gordon and Kálal[16] were able to deactivate quantitatively all the free carboxyl groups by means of diphenyldiazomethane (DDM), which converts them to benzhydryl ester groups. The present work is directed to the study of critically branched DMG-BTA-DDM by means of light scattering in solution. The extension of the scattering theory from homopolycondensates, given earlier,[3] to copolymers, which is necessary for the interpretation of such measurements, is given later.

Theoretical Formalism

The solution of combinatorial problems in physical science in terms of graph theory has a history going back to Cayley in the last century. He reduced three-dimensional molecules to one-dimensional molecular graphs, in which atoms are replaced by points and chemical bonds by lines. The fundamental paper published by Pólya[17] in 1937 introduced group-theoretical notions into this subject which are necessary if the *ad hoc* treatment of combinatorial problems is to be replaced by formal procedures of statistical mechanics.[18] Physical parameters of polymer systems are frequently calculated as averages of graph-theoretical parameters over the trees of a molecular forest, *i.e.,* the molecular graphs which represent a distribution of tree-like molecules. The most helpful mathematical technique for extracting such averages is based on the theory of cascades or branching process, founded by Galton and Watson in the 19th century. The applications to polymer science have been repeatedly reviewed,[19,20] and recently a simple introduction was published[21] designed to bring together mathematical and physical scientists for fuller exploitation of these power tools. We therefore do not propose to develop the known theory here in any detail, but merely to present the requisite generalizations. For those unfamiliar with the subject, we recall that visualization of the physical meaning underlying the formal manipulation in cascade theory of probability generating functions (pgf's), which describe molecular distributions produced by stochastic bond-forming and -breaking processes, has been rendered easy[3] by the device of mapping the algebraic structure of such functions directly into that of the molecular graphs. (It emerged that each factor of a product represents a point and the operation of multiplication represents a line in a graph.[3])

We recall that a path (or "trail") of length n signifies a linear unbranched progression of n links in a graph. The attachment of certain numerical weights to the paths of a graph is occasionally considered in the theory of graphs.[22,23] So-called trail-weighting functions $\phi(n)$ were introduced[3] in connection with scattering theory and with substitution effects;[21] we now prefer the term path-weighting function for the same notion. When such functions are substituted in the pgf's, so-called path-weighting generating functions (pwgf's) result. The power of such pwgf's was more fully exploited after generalizing them from univariate to bivariate status.[24] Another familiar generalization leads from scalar pgf's for homopolymers to vectorial pgf's for copolymers,[25] in which case the different kinds of comonomers give rise to different components of the vectorial quantities which occur. This generalization can also be practiced quite widely for pwgf's, as will be shown elsewhere.[26] Here we merely present the generalization immediately required, that of the scalar pwgf $u_0(\theta)$ employed for random homopolycondensates, to the vectorial

$$\mathbf{u}_0(\theta) \equiv (u_{01}(\theta), u_{02}(\theta)) \quad \theta \equiv (\theta_1, \theta_2) \tag{1}$$

appropriate for a binary random polycondensate. A scalar version is obtained by forming the scalar product with $\mathbf{m}$ $(\equiv (m_1, m_2))$, where m_i is the weight fraction of the ith comonomer unit in the system as a whole, thus

$$U(\theta) \equiv \mathbf{u}_0(\theta)\cdot\mathbf{m} = \sum_{\mathbf{x},k} w_{\mathbf{x},k} |\mathbf{x}|^{-1} \sum_{l=1}^{|\mathbf{x}|} \theta^{\sum_{n=0}^{|\mathbf{x}|-1} \mathbf{N}_{lnxk} \wedge \phi(n)} \tag{2}$$

This equation, to be explained in detail presently, reduces to the scalar version, derived and fully explained as eq A7 in a previous paper[3]

$$U_0(\theta) = \sum_{x,k} w_{x,k} x^{-1} \sum_{l=1}^{x} \theta^{\sum_{n=0}^{x-1} N_{lnxk}\phi(n)} \tag{3}$$

for the case of a single type of repeat unit, *i.e.*, a homopolymeric condensate. In eq 2, $\wedge$ denotes the direct product of two vectors, *i.e.*

$$\mathbf{a} \wedge \mathbf{b} \equiv (a_1 b_1, a_2 b_2) \tag{4}$$

The components of the vector $\mathbf{x} \equiv (x_1, x_2)$ denote the numbers x_1 of units of type 1 and x_2 of units of type two in a molecule, which is itself called an $\mathbf{x}$-mer. Next, $w_{\mathbf{x},k}$ is the weight fraction of the kth isomer of the $\mathbf{x}$-mers and $|\mathbf{x}| \equiv x_1 + x_2$ for a binary copolymer, or the sum Σx_i of all repeat units in the general case. The ith component of the vector $\mathbf{N}_{lnxk}$ denotes the number of distinct paths of n links in the kth isomer of the $\mathbf{x}$-mers which start at the lth repeat unit and finish on a repeat unit of type i. This scaler pwgf (eq 2) is the key to the statistical parameters of a branched copolymer system; for example, the first vector derivative[25] $(\mathrm{d}U_0/\mathrm{d}\boldsymbol{\theta})_{\boldsymbol{\theta}=1}$ gives the weight-average molecular weight $(MW)_\mathrm{w}$, when we put $\phi(n) = \mathbf{M}$ (for de-

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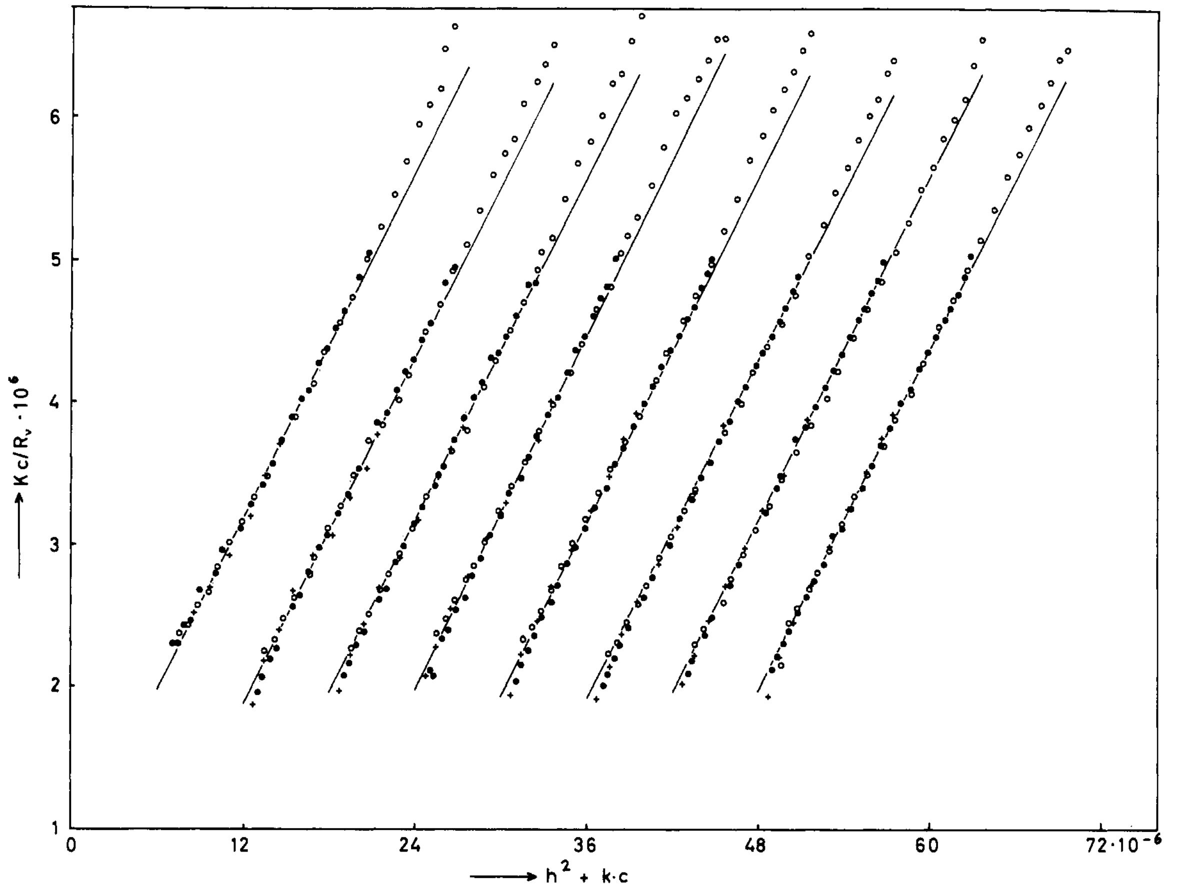


Figure 1. Composite Zimm plot. The results of light-scattering measurements made at three different wavelengths on the polycondensate KP-1 in butanone are superposed.

tails, see ref 26).

It is known that some intramolecular esterification reaction occurs in the system DMG–BTA studied below, but that the extent of this side reaction is almost negligible.[19b] The pwgf will, therefore, be written for a ring-free system, consisting of an alternating copolymer of a bifunctional unit (DMG) and an f-functional one ($f = 3$ for BTA).

In the recursive formulation employed previously, the pwgf then takes the form

$$u_{01}(\theta) = \theta_1^{\phi_1(0)}\{1 - \alpha_a + \alpha_a u_{12}(\theta)\}^2 \qquad (5)$$

$$u_{02}(\theta) = \theta_2^{\phi_2(0)}\{1 - \alpha_b + \alpha_b u_{11}(\theta)\}^f \qquad (6)$$

$$\mathbf{u}_n(\boldsymbol{\theta}) \equiv [u_{n1}(\boldsymbol{\theta}), u_{n2}(\boldsymbol{\theta})] \quad n \geq 1 \qquad (7)$$

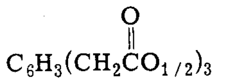
$$u_{n1}(\boldsymbol{\theta}) = \theta_1^{\phi_1(n)}\{1 - \alpha_a + \alpha_a u_{n+1,2}(\boldsymbol{\theta})\} \qquad (8)$$

$$u_{n2}(\boldsymbol{\theta}) = \theta_2^{\phi_2(n)}\{1 - \alpha_b + \alpha_b u_{n+1,1}(\boldsymbol{\theta})\}^{f-1} \qquad (9)$$

We apply this to DMG–BTA ($f = 3$) and neglect the loss of weight due to the escape of water; only two types of unit are required, and labeled as

$-O_{1/2}(CH_2)_{10}O_{1/2}-$

unit 1



$C_6H_3(CH_2\overset{\overset{\displaystyle O}{\|}}{C}O_{1/2})_3$

unit 2

The components of the molecular weight vector of units are $M_1 = 156$ and $M_2 = 225$. α_a is defined as the fractional conversion of hydroxyl groups and α_b as that of carboxyl groups. Two fractional conversions are related stoichiometrically, thus

$$2\alpha_a = \frac{fm_2M_1}{m_1M_2}\alpha_b \qquad (10)$$

For the special case of a stoichiometric polycondensate used here, $\alpha_a = \alpha_b$. From eq 2 and 3 we obtain the relationship

$$[\partial U(\boldsymbol{\theta})/\partial\boldsymbol{\theta}]_{\theta=1} \equiv [\partial u_0(\boldsymbol{\theta})/\partial\boldsymbol{\theta}]_{\theta=1}\cdot\mathbf{m} = \sum_{\mathbf{x},\mathbf{k}} w_{\mathbf{x},\mathbf{k}}|\mathbf{x}|^{-1}\sum_{l=1}^{|\mathbf{x}|}\sum_{n=0}^{|\mathbf{x}|-1}\mathbf{N}_{ln\mathbf{x}k}\phi(n) \qquad (11)$$

where $[\partial U(\boldsymbol{\theta})/\partial\boldsymbol{\theta}]$ is calculated as

$$[\partial U(\boldsymbol{\theta})/\partial\boldsymbol{\theta}]_{\theta=1} = m_1\phi_1(0) + \alpha_b\sum_{n=0}^{\infty}[(f-1)\alpha_a\alpha_b]^n[2m_1(f-1)\alpha_a\phi_1(2n+2) + fm_2\phi_1(2n+1)] + m_2\phi_2(0) + \alpha_a\sum_{n=0}^{\infty}[(f-1)\alpha_a\alpha_b]^n[2m_1\phi_2(2n+1) + fm_2\alpha_b\phi_2(2n+2)] \qquad (12)$$

The weight-average molecular weight, and the z-average mean-square radius of gyration, are calculated in a routine manner. Thus

$$(MW)_w = [M_1\{m_1(1 + (f-1)\alpha_a\alpha_b) + fm_2\alpha_b\} + M_2^*\{2m_1\alpha_a + m_2(1 + \alpha_a\alpha_b)\}]/[1 - (f-1)\alpha_a\alpha_b] \quad (13)$$

$$(DP)_w = [1 + \alpha_a\alpha_b\{(f-1)m_1 + m_2\} + (2\alpha_a m_1 + f\alpha_b m_2)]/[1 - (f-1)\alpha_a\alpha_b] \quad (14)$$

by putting $\phi_1(n) = M_1$ and $\phi_2(n) = M_2^*$ ($n = 1, 2, \ldots$) for the weight-average molecular weight, or $\phi_1(n) = \phi_2(n) = 1$ for the weight-average degree of polymerization. (The exact equation for $(MW)_w$, allowing for the loss of water, has also been published[26]). Again we find

$$\langle S^2\rangle_z = \frac{b^2}{2(DP)_w}\{2(2(f-1)m_1 + fm_2)\alpha_a\alpha_b + (2m_1\alpha_a + fm_2\alpha_b)(1 + (f-1)\alpha_a\alpha_b)\}/[1 - (f-1)\alpha_a\alpha_b]^2 \quad (15)$$

by putting $\phi_1(n) = \phi_2(n) = nb^2$ in eq 12, where b is the effective end-to-end distance of units 1 and 2 which we take as the average

$$b = [(b_1^2 + b_2^2)/2]^{1/2} \quad (16)$$

of the individual effective end-to-end distances of units 1 and 2. All these quantities are calculated more generally and exactly for a formal three-component system[26] and the result reduce to eq 13-15 under the present approximation. M_2^* denotes the modified molecular weight of unit 2 due to the large (benzhydryl ester) substituents attached to the carboxyl ends, introduced to stabilize the polymer, so that

$$M_2^* = \alpha_b^3M_2 + \alpha_b^2(1 - \alpha_b)(2M_2 + M_3) + \alpha_b(1 - \alpha_b)^2(M_2 + 2M_3) + (1 - \alpha_b)^3M \quad (17)$$

where M_3 denotes the molecular weight of the benzhydryl substituent (= $-O_{1/2}CH(C_6H_5)_2$).

The normalized angular intensity distribution scattered from polydispersed branched system is given by

$$P_z(\nu) = (DP_w)^{-1}\sum_{\mathbf{x},k} w_{\mathbf{x},k}|\mathbf{x}|^{-1} \times \sum_{\substack{\text{all paths in}\\ k\text{th }\mathbf{x}\text{-mer}}} \left\langle\frac{\sin(hr_n)}{hr_n}\right\rangle \quad (18)$$

$$h = 4\pi \sin(\nu/2)/\lambda \quad (19)$$

where ⟨⟩ denote the configurational average, ν is the scattering angle, λ the wavelength of the incident light and the suffix z denotes the z average, which is measurable by the usual light-scattering experiments. r_n is defined as the distance between two ends of a path of length n in a molecule. The average featured in eq 18 is written for random-flight models[27] as

$$\left\langle\frac{\sin(hr_n)}{hr_n}\right\rangle = \left[\frac{\sin(hb)}{hb}\right]^n \quad (20a)$$

and for Gaussian subchains[28] as

$$\left\langle\frac{\sin(hr_n)}{hr_n}\right\rangle = \exp(-h^2\langle r_n^2\rangle/6) \quad (20b)$$

$$\langle r_n^2\rangle = b^2n \quad (21)$$

Table I
Molecular Weight, α/α_c, Mean-Square Radius of Gyration and Structure Parameter b of the Four Samples

Sample	10^{-3} $(MW)_w$	α/α_c	$10^{-4}\langle S\rangle_z^2$ (Å^2)	b (Å)
KP 1	512	0.99928	30.9	21.1
KP 2	370	0.99905	23.8	21.7
KP 3	172	0.99764	10.0	21.3
KP 4	37	0.99003	2.2	20.9
			Average	21.2

The z average of the normalized angular intensity distribution for poly(DMG-BTA) is readily calculated as ($\phi(n) = \langle(\sin(hr_n)/hr_n)\rangle$)

$$P_z(X)(DP)_w = \frac{1 + \alpha_a\alpha_b\{(f-1)m_1 + m_2\}(\sin X/X)^2 + (2\alpha_a m_1 + f\alpha_b m_2)(\sin X/X)}{1 - (f-1)\alpha_a\alpha_b(\sin X/X)^2} \quad (22a)$$

for a random-flight model, and

$$P_z(X)(DP)_w = \frac{1 - \alpha_a\alpha_b\{(f-1)m_1 + m_2\}\exp(-X^2/3) + (2\alpha_a m_1 + f\alpha_b m_2)\exp(-X^2/6)}{1 - (f-1)\alpha_a\alpha_b\exp(-X^2/3)} \quad (22b)$$

for a Gaussian subchain model. The reduced scattering angle X is given by

$$X \equiv hb \quad (23)$$

Expansion of $(P_z(X)(DP)_w)^{-1}$ shows (*cf.* ref 3) that over the range of X and α values covered, the Zimm plot is indistinguishable from a straight line.

Results

Four samples (Table I) of equimolar polycondensates of DMG-BTA were produced by polycondensation in the melt to different conversions all close to the gel point, and then stabilized by benzhydrylation of the carboxyls using DDM. The preparative methods were exactly those described by Devoy, Gordon, and Kálal.[29]

Composite Zimm Plots. The light-scattering measurements were performed with the three different Hg lines at wavelengths λ_0 = 546 nm (green), 436 nm (blue), and 361 nm (near-uv range) to widen the range of angular dependence and the accuracy. In the basic equation

$$\frac{Kc}{R_\theta} = \frac{1}{(MW)_wP_z(\nu)} + 2A_2c \quad (24)$$

the molecular weight $(MW)_w$ and the particle scattering factor are considered independently. To superpose the results into a single Zimm plot, the appropriate abscissa is $h^2 + kc$, with k a constant and $h^2 = [(4\pi/\lambda)\sin \nu/2]^2$, not merely $\sin^2(\nu/2)$. As regards the ordinates, the intensities for the three wavelengths could in principle be fitted together, in a single curve, if the refractive index increments were measured sufficiently accurately. The values obtained from the $(\partial n/\partial c)$ measurements were 0.166 at λ_0 = 546 nm and 0.172 at λ_0 = 436 nm. However, the absolute accuracy attained in the green and blue regions was about 3%; in the uv range, no measurements were possible. We have therefore adjusted the scattering intensities of green and uv lights at *one* fixed h^2 value. This procedure implies that the molecular weight is determined by the

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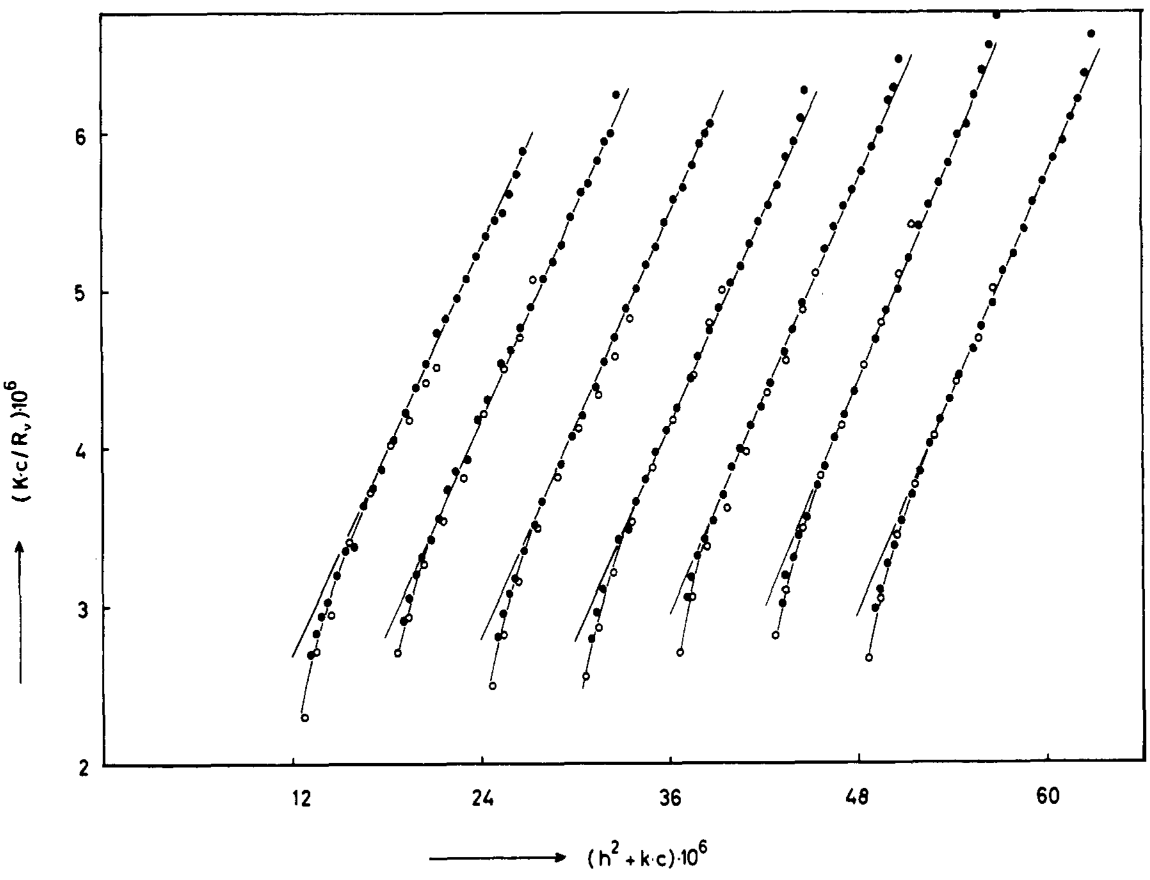

Figure 2. Composite Zimm plot for KP-2 in butanone, *cf.* Figure 1.

measurements using green light only. The overall error in molecular weight is thought to be less than 5%; but the standard deviation of the 15 points or so at three wavelengths is less than 0.5%. Figures 1-4 show the result of generalized Zimm plots for the samples KP-1, KP-2, KP-3, and KP-4. It is seen that the data for different wavelengths are consistent after the adjustment of scattering intensities.

Qualitative Interpretation of the Scattering Curves. Even though theory predicts rectilinear Zimm plots for random polycondensates,[3] the experimentals plots (Figures 1-4) show systematic deviations from linearity. For the highest molecular weights, the plots *are* nearly linear, with a small upturn at high h^2 values; and they show only a slight downturn tendency at low angles. The upturn at high angles hardly exceeds the experimental error. If it is real, it indicates some tendency opposing excessive branching. Such a tendency is expected, and is also observed as a delay in the gel point from the classical value of $2^{-1/2}$ (= 0.707) for a random system to 0.722 ± 0.006 for the real system. The effect is reliably attributed to a small amount of cyclization during the chemical polycondensation. *Intramolecular* H bonding may also contribute to the upturn.[30a] Finally, steric hindrance opposes the formation of extremely crowded structures,[21] but this effect is likely to be small.

As regards the downturn at low angles, this is attributed to *intermolecular* aggregation of the polycondensate molecules due to OH groups. The fraction of unreacted OH groups in KP-2 is about 29.5%, and in KP-4 about 31.5%. The downturn was more prominent in the KP-3 dioxane solutions and this fact supports the above speculation because H-bond formation is facilitated in nonpolar solvents.

In view of this discussion of the systematic deviations from linearity, we conclude that the chemistry of the polycondensation process is essentially as postulated in the random model. This is confirmed conclusively by analysis of the computational fit of the data in the next section.

Computational Fit of the Scattering Data. Since the downturn at low angles is considered as a superimposed effect due to aggregates, which naturally decays with increasing scattering angles, we have disregarded the extreme lower parts of the scattering curves for a comparison with theory. The analysis of randomly branched materials by scattering methods is greatly facilitated by an interplay of the intercept and the slope of the linear Zimm plot, in the determination of the two basic parameters. In the present case they are: (i) the fraction α of OH groups which have reacted (with carboxyl groups), and (ii) the structural parameter b. Thus the value of α is estimated from the intercept (molecular weight), and b from the slope (mean-square radius of gyration), see eq 13 and 15. The value of α was estimated from the value of Kc/R_ν at $\nu = 0$ for green light. The structural parameter b was estimated, as a first approximation, directly from the mean square radius of gyration, estimated from the slopes of straight lines which approximate the scattering envelopes. It was finally determined by allowing small variations of b to obtain the best fit of the scattering curves to eq 22 with $\alpha_a = \alpha_b = \alpha$ and eq 24.

Scattering methods provide absolute measurements of weight-average molecular weight and z-average mean-square radius. The problem always arises of interpreting these results in terms of molecular models. For randomly branched materials the situation is unusually favorable.

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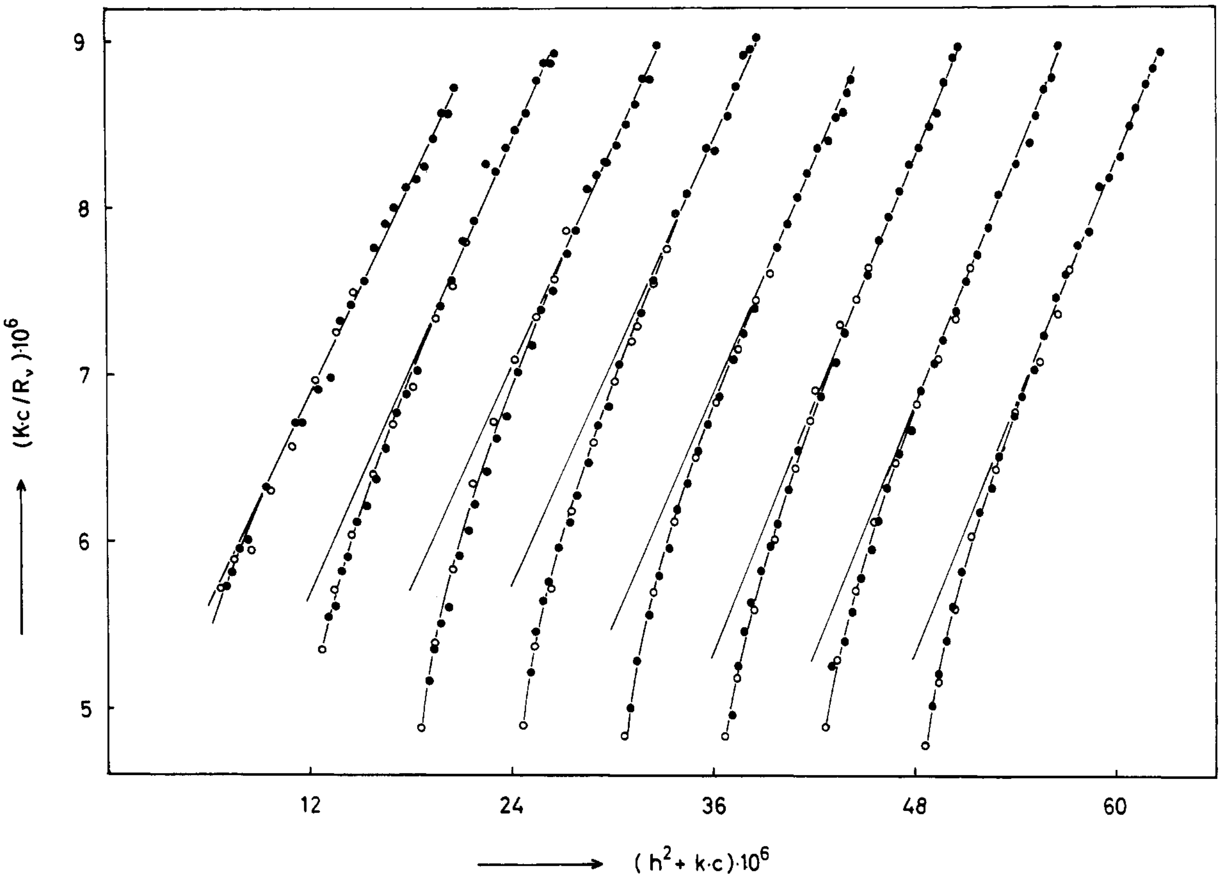

Figure 3. Composite Zimm plot for KP-3 in butanone, *cf.* Figure 2.

Not only are the Zimm plots essentially linear, but also the model assumptions are not stringent, and their effect is further reduced by testing for the constancy of b over wide ranges of $(MW)_w$.

Discussion

Invariance of b. The fit of the theory to the experimental results (Table I) is satisfactory, as regards the lack of dependence on molecular weight of the structural parameter. If $\langle S^2\rangle_z/(MW)_w$ is calculated from eq 13 to 15, it is indeed found to be practically proportional to b^2, since over the small range of conversion encompassing critical branching, the functional dependence on conversion (through $\alpha_a = \alpha_b$) is negligible. Because eq 15 was derived for the case $\phi_1(n) = \phi_2(n) = nb^2$, it is valid if the excluded volume effect can be neglected or represented in terms of uniformly expanded Gaussian subchains. Figure 5, through the proportionality of $\langle S^2\rangle_z$ to $(MW)_w$, supports this assumption.

Correlation between the Structural Parameter b and the Bond Length l. The structural parameter b is defined as a proportionality factor between the number of links and their mean-square end-to-end distance. Further analysis is required to yield information about molecular parameters, such as the chain stiffness, or rotational hindrances of the single bonds C–C and C–O. The following treatment of b is preliminary, and merely intended to give insight into the general conformational behavior of our system.

An average bond length, $l = 1.54$ Å, and an average valence angle, given by $\cos(180 - X) = \beta = 1/3$, will be assumed. Then, the end-to-end distance of a Gaussian subchain of $n/2$ units of monomer 1 and $n/2$ units of monomer 2 is

$$\langle r^2\rangle_n = l\,\frac{1+\beta}{1-\beta}\,\sigma^2(m/2)n \qquad (25)$$

where σ is the short-range expansion factor characterizing the extent of the rotational hindrance and m (= 19 here) the number of bonds contributed by any two neighboring units to a path through the structure. Comparison of eq 25 and 21 yields a correlation between l and b (*cf.* eq 16)

$$b^2 = l\left\{\frac{1+\beta}{1-\beta}\right\}\sigma^2(m/2) \qquad (26)$$

From eq 26 we find

$$\sigma = 3.17 \qquad (27)$$

where the values of b, l, and m required for the calculation are listed in Table II. Usually, synthetic linear polymers such as PMMA and polystyrene have an expansion factor, σ, approximately 2–2.5.[31] Compared to this, the expansion factor for poly(DMG-BTA) is rather high; indicating rather extended subchains for these branched polycondensates.

Chain Expansion. If a potential symmetric about the trans position ($\phi = 0$) is assumed, σ^2 can be written as

$$\sigma^2 = \frac{1 + \overline{\cos\phi}}{1 - \overline{\cos\phi}} \qquad (28)$$

where $\overline{\cos\phi}$ is the average of the cosine of the rotational angle ϕ. Thus, for this assumption, the chain stiffness can be characterized in terms of $\overline{\cos\phi}$. Alternatively, we may estimate a persistence length a, first introduced by

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(31) See, for example, J. Brandrap and E. H. Immergut, Ed., "Polymer Handbook," Wiley-Interscience, New York, N. Y., 1966.

(32) (a) G. Porod, *Monatsh. Chem.*, **2**, 25 (1949). (b) G. Porod, *J. Polym. Sci.*, **10**, 157 (1953).

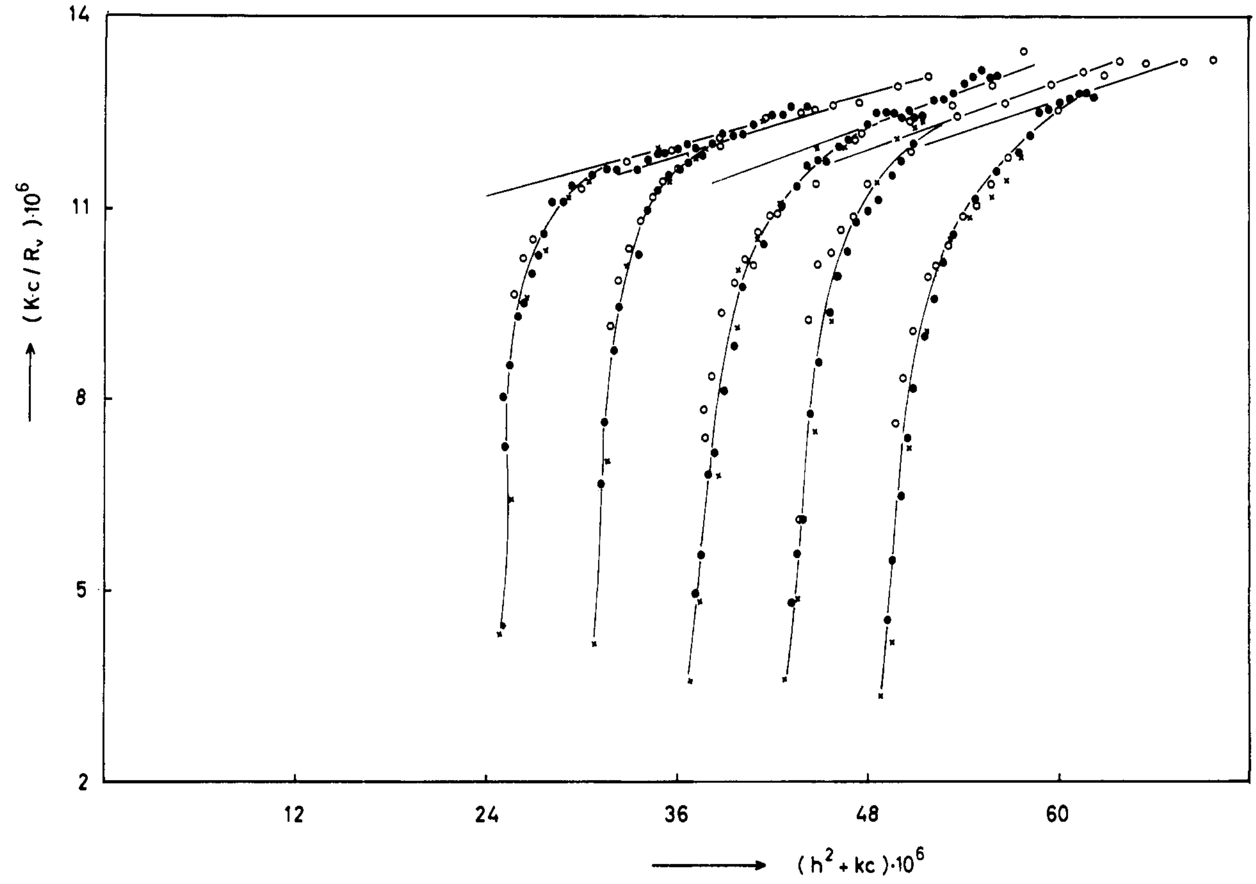

Figure 4. Composite Zimm plot for KP-4 in butanone, *cf.* Figure 3.

Porod.[32,33] As pointed out elsewhere,[34,35] the definition of a persistence length involves an abstract chain model. However, on the approximation of a symmetric rotation potential, a persistence length is expressed in terms of the rotational angle

$$a = b/(1 - \lambda) \tag{29}$$

where λ is defined by

$$\frac{1 + \lambda}{1 - \lambda} = \frac{1 + \beta}{1 - \beta}\,\frac{1 + \overline{\cos \phi}}{1 - \overline{\cos \phi}} \tag{30}$$

so that

$$a = l\left\{\frac{1 + \beta\,\overline{\cos \phi}}{(1 - \beta)(1 - \overline{\cos \phi})}\right\} \tag{31}$$

Using the σ value given by eq 27, a persistence length for poly(DMG/BTA) was calculated from eq 31 as 16.2 Å; which is about 50 ~ 60% larger than the value found for PMMA. The coil expansion factor σ, defined by eq 26, has a larger value than that of linear polystyrene ($\sigma \approx 2.4$) or PMMA ($\sigma \approx 2.0$). An extra factor of about 1.5–2 has often been reported[36-38] for polystyrene systems, giving $\sigma \sim 3$-5 depending on branch density. There are no comparable data of σ available for the *linear* poly(DMG-benzenediacetic acid) system, but a value smaller than that of polystyrene or PMMA may be expected as found in the case of poly(ethylene terephthalate),[39] which has a similar structure to the present system. (In fact, the approximate calculation of σ for the linear poly(DMG–BDT) system using the rotational isomeric state model shows an even smaller value of σ than that of poly(ethylene terephthalate). Details will be given in a future paper.[40]) Thus, the amount of chain expansion due to branching in the present system may be estimated to give a factor of 2 ~ 2.3 times. The free OH groups will form intramolecular H bonds as well as intermolecular ones (see Figures 1 ~ 4). This effect may also affect the coil expansion. When intramolecular H bonding is suppressed the averaged subchain expands and the structure parameter b is found to increase from 21 Å (*cf.* Table II) to 27 Å. The details will be found in the following paper.[40]

The linear dependence of the radius of gyration on molecular weight indicates only that Gaussian statistics are fulfilled for subchains. This result does not necessarily imply the absence of solvent effects on the chain dimension. Excluded volume effects cause deviations from Gaussian statistics for linear chains, but for reasons of symmetry of randomly branching structures, these deviations might cancel here and this would justify use of the uniform-expansion model. We have tried to clarify the effect of symmetric branching on subchain configuration, by performing scattering measurements on KP-3 both in butanone and in dioxane. The tendency to H-bond formation is greater in dioxane than in butanone, and a particle weight about three times larger was found in dioxane than

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(33) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).

(34) H. E. Daniels, *Proc. Roy. Soc. Edinburgh, Sect. A*, **63**, 290 (1952).

(35) J. J. Hermans and R. Ullman, *Physica*, **18**, 951 (1952).

(36) I. Noda, T. Horikawa, T. Kato, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 795 (1970).

(37) G. C. Berry, *J. Polym. Sci., Part A-2*, **9**, 687 (1970).

(38) (a) F. Candau, Ph.D. Thesis, 1971. (b) F. Candau and E. Franka, *Makromol. Chem.*, **149**, 4 (1971). (c) F. Candau and P. Rempp, *Eur. Polym. J.*, **8**, 757 (1972).

(39) A. D. Williams and P. J. Flory, *J. Polym. Sci., Part A-2*, **5**, 417 (1967).

(40) M. Gordon, K. Kajiwara, C. Peniche, and S. Ross-Murphy, to be published.

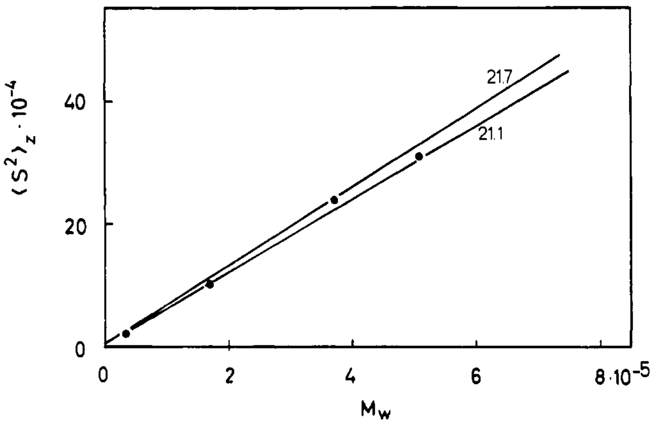

Figure 5. Plot of $\langle S^2 \rangle_z$ *vs.* $(MW)_w$. The invariance of the ratio $\langle S^2 \rangle_z/(MW)_w$ demonstrates that over the range of α/α_c covered by the four polycondensate samples the excluded volume effect can be adequately represented in terms of uniformly expanded Gaussian subchains. The resulting single structural parameter, σ, is found to lie in the range 21.1-21.7.

in butanone solutions. The downturn of the Zimm plot in dioxane is so marked that it is impossible to disentangle the effects of association.

Critically branched materials seem to have very small second virial coefficients by light scattering measurements. At least, this was observed for amylopectin carbanilate[4] as well as here. Moreover, branched samples generally have lower second virial coefficients than corresponding linear samples. For the present system, as was found experimentally and theoretically for regularly branched polymers,[30b,38,41-43] a theoretical justification was given by Kajiwara[24] within Zimm's double-contact approximation,[44] which is strictly valid only for poor-solvent systems, but the same effect might be expected for better solvents.

The model for the bulk polyesterification reaction justifiably neglects intramolecular reactions. The hydrogen bonding equilibrium is observed in dilute solution, where ring-chain competition is much more pronounced. If H bonding were merely an intermolecular bond-forming mechanism superimposed on the preformed polyester links, we should expect a linear Zimm plot of higher slope and smaller intercept. The observed downturn is taken to be due to a marked intermolecular component in H-bonding. Empirically, this often leads to bimodal distributions.

Table II
Conformational Parameters

Bond length (C-C or O-C)	$l = 1.54$ Å
Cosine of the complementary bond angle	$= \frac{1}{3}$
Average number of bonds per monomer unit	$m/2 = 9.5$
Structure parameter	$b = 21.2$
Coil expansion factor	$\sigma = 3.17$
Average cosine of the rotation angle	$\cos \phi = 0.819$
Persistence length	$a = 16.2$
Number of bonds per persistence length	$a/b = 10.5$
Number of monomer units per persistence length	$\frac{a/b}{m/2} = 1.1$

Even in covalent bond formation at high dilution, the formation of so-called "micro gel" is often observed, and is thought to reflect a similar ring-chain competition mechanism, though of an irreversible type.

Measurement of α/α_c. The quantity α/α_c can be obtained rather accurately from experimental measurements such as those presented here. In fact, few quantities in polymer science can be derived to such a higher precision. α and α_c separately are not known nearly so accurately. For the DMG-BTA system α_c has been found to be 0.722 ± 0.006 compared with the classical value of $2^{-1/2}$ (= 0.707···). The difference between these two values is quantitatively ascribed to minor cyclization effects which affect both α and α_c similarly. They are therefore only second order effects on the ratio (α/α_c), which renders it insensitive to such deviations from the classical random polycondensation model. The applicability to DMG-BTA of this model, which is a rather basic one for chemistry generally,[45] has now been demonstrated by tests ranging from higher moments of the molecular distribution (here $\langle S^2 \rangle_z$) to the "minus infiniteth moment" (*viz.*, the monomer concentration).[46]

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