Macromolecules **1986**, *19*, 3001–3003

by The BFGoodrich Co. Helpful discussions with K. D. Cook (University of Tennessee) and C. L. Wilkins (Univeristy of California, Riverside) are appreciated. R. J. Bertsch and C. K. Shaw (The BFGoodrich Co.) supplied the CTB and poly-TMDQ samples, respectively.

Registry No. PEG, 25322-68-3; PPG, 25322-69-4; PEI, 9002-98-6; flectol DS, 26780-96-1.

References and Notes

(1) Schulten, H.-R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231.
(2) Lattimer, R. P.; Harris, R. E.; Schulten, H.-R. *Rubber Chem. Technol.* **1985**, *58*, 577.
(3) Matsuo, T.; Matsuda, H.; Katakuse, I. *Anal. Chem.* **1979**, *51*, 1329.
(4) Neumann, G. M.; Cullis, P. G.; Derrick, P. J. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1980**, *35A*, 1090.
(5) Saito, J.; Toda, S.; Tanaka, S. *Shitsuryo Bunseki* **1980**, *28*, 175.
(6) Lattimer, R. P.; Hansen, G. E. *Macromolecules* **1981**, *14*, 776.
(7) Lai, S.-T. F.; Chan, K. W. S.; Cook, K. D. *Macromolecules* **1980**, *13*, 953.
(8) Chan, K. W. S.; Cook, K. D. *Org. Mass Spectrom.* **1983**, *18*, 423.
(9) Chan, K. W. S.; Cook, K. D. *Macromolecules* **1983**, *16*, 1736.
(10) Mattern, D. E.; Hercules, D. M. *Anal. Chem.* **1985**, *57*, 2041.
(11) Wilkins, C. L.; Weil, D. A.; Yang, C. L. C.; Ijames, C. F. *Anal. Chem.* **1985**, *57*, 520.
(12) Brown, R. S.; Weil, D. A.; Wilkins, C. L. *Macromolecules* **1986**, *19*, 1255.
(13) Chait, B. T.; Shpungin, J.; Field, F. H. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 121.
(14) Lattimer, R. P. *Int. J. Mass Spectrom. Ion Processes* **1983/1984**, *55*, 221.
(15) Goodley, P. C., private communication.
(16) Callahan, J. J.; Cook, K. D. 32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, May 27–June 1, 1984, p 552.
(17) Lattimer, R. P.; Schulten, H.-R. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 227.
(18) Robbins, R. C.; Alai, M.; Demirev, P.; Cotter, R. J. 33rd Annual Conference on Mass Spectrometry and Allied Topics, San Diego, May 26–31, 1985, p 403.
(19) van Breemen, R. B.; Snow, M.; Cotter, R. J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 35.
(20) Tabet, J.-C.; Cotter, R. J. *Anal. Chem.* **1984**, *56*, 1662.
(21) Lattimer, R. P.; Harmon, D. J.; Welch, K. R. *Anal. Chem.* **1979**, *51*, 1293.
(22) Lattimer, R. P.; Hooser, E. R.; Zakriski, P. M. *Rubber Chem. Technol.* **1980**, *53*, 346.
(23) Diem, H. E.; Harmon, D. J.; Komoroski, R. A.; Pausch, J. B.; Bertsch, R. J. *Adv. Chem. Ser.* **1984**, *No. 208*, 65.

Notes

Characterization of the Soluble Phase beyond the Gel Point

DIMITRIS S. ARGYROPOULOS* and HENRY I. BOLKER

Pulp and Paper Research Institute of Canada,
Pointe Claire, P.Q., Canada H9R 3J9, and Department of
Chemistry, McGill University, Montreal, P.Q.,
Canada H3A 2A7. *Received July 2, 1986*

The physicochemical properties of branched macromolecules have been a subject of much interest in polymer science. Because of its complexity, the process of gelation and the chemistry of the sol fraction that the product contains well beyond the gel point have been the objects of relatively little experimental research. One line of work, arising from Gordon's team, has been devoted to correlating molecular parameters of the critically branched state of matter with those calculated from the Cascade theory.[1–6] The experimental materials were the stabilized macromolecules that appear just before and just after the gel point in the polycondensation of 1,3,5-benzenetriacetic acid with 1,10-decamethylene glycol (BTA/DMG). This combination of monomers has been a particularly good choice because it has given minimum deviations from the assumptions of the classical gelation theory.[5–7]

Beyond these experiments on the critically branched state of matter, there is no record of attempts to exploit the near ideality of BTA/DMG polymerization in order to investigate other features of gelation. The molecular properties of the soluble phase and the way they change as gelation advances well beyond the gel point have not been experimentally examined with an ideal system.

Therefore, as an extension of our efforts[8] to characterize the soluble phase, fractions at various extents of polymerization of BTA/DMG beyond the gel point were isolated, and their viscosities and weight-average molecular weights were measured.

The relative changes of the densities and diameters of these macromolecules at various stages of the reaction beyond the gel point were calculated, thus providing more information for this rather important region of the process.

Table I
Molecular Weights, Viscosities, and Structural Parameters of the BTA/DMG Sol Fractions as a Function of Conversion beyond the Gel Point

convn (p)	W_S[c]	$\bar{M}_w \times 10^{-5}$	$[\eta]$, dL g^{-1}	equiv dens (ρ_{equ}), g mL^{-3}	equiv diam (d_{equ}), Å
0.7205[a]		8.19	0.206[a]	0.121	277
0.7206[a]		4.39	0.200[a]	0.125	222
0.7226[a]		1.75	0.130[a]	0.192	142
0.7260	0.752	1.45	0.166[b]	0.150	144
0.7670	0.347	0.18	0.199[b]	0.210	66
0.8090	0.130	0.16	0.149[b]	0.167	68

[a] Reported by Peniche-Covas et al.[5] [b] Measured at 25 °C in methyl ethyl ketone. [c] Soluble fraction, i.e., (wt sol)/(wt (sol + gel)).

Results and Discussion

Intrinsic viscosities of three sol fractions of the BTA/DMG polycondensation in the region just beyond the gel point have been reported by Peniche-Covas et al.[5] In order to obtain additional points, the viscosity numbers (Table I) of sols isolated at conversions well beyond the gel point were measured at 25 °C at four different concentrations in methyl ethyl ketone.

It is immediately apparent that these intrinsic viscosities are unusually low. The low intrinsic viscosities reported here indicate that the molecules are likely to have a highly branched structure.

Further evidence of extensive branching is seen in the small dependence of intrinsic viscosity on molecular weight (Figure 1). The exponent α and constant K of the Mark–Houwink equation were thus found to be 0.15 and 11.2, respectively ($K = 0.112$ if $[\eta]$ is expressed in deciliters per gram). The unusually low value of α indicates that the highly branched structure of these polymers confers con-

0024-9297/86/2219-3001$01.50/0

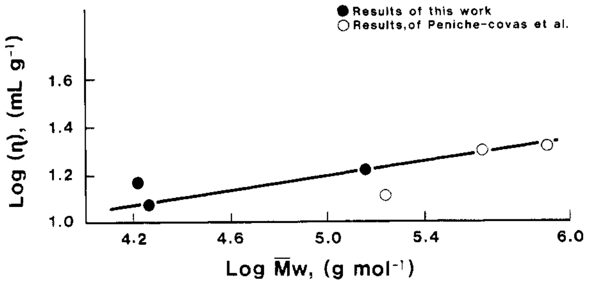

Figure 1. log $[\eta]$ vs. log $\bar{M}_w$ of the BTA/DMG soluble fractions. Mark–Houwink exponent $\alpha = 0.15$.

siderable rigidity on the individual molecules, so that, in solution, they approximate Einstein spheres rather than random coils.[9,10]

To this point, the discussion has not taken into account the sensitivity of $[\eta]$ vs. $\bar{M}$ plots to differences in molecular weight distribution among the samples. The intrinsic viscosities reported in Table I were determined on unfractionated samples of sometimes extremely high polydispersity ratios. Such considerations might account for the large deviations from linearity of two points in the log–log plot of Figure 1. These points represent samples that differ in $\bar{M}_w/\bar{M}_n$ by a factor of at least 10.[8c]

The work of Koningsveld and Tuijnman[11] has shown both theoretically and experimentally (for polyethylene) that the value of the Mark–Houwink exponent α was independent of the polydispersity ratio (the range of $\bar{M}_w/\bar{M}_n$ they studied was from 1 to 30). The value of K, however, was strongly dependent on $\bar{M}_w/\bar{M}_n$, and the dependency became greater if the molecular weight in the Mark–Houwink expression was the number average. The credibility of our conclusions with respect to BTA/DMG polymers (based on the value of α) is thus strengthened, while the derived value of K seems to need further attention.

Despite the meaningful and apparently[11] correct value of α obtained for the sol fractions of Table I, an alternative method was sought for calculating the Mark–Houwink constant, K, by taking into account the effects of polydispersity on its magnitude. For this purpose a "single sample" method, as it is usually referred to in the literature, was employed. Voek's treatment[12] was found to be the most suitable for the present purposes.

A knowledge of $\bar{M}_w$ and $[\eta]$ allowed the calculation of α, which in turn may yield K if entered into the Mark–Houwink expression.

As predicted by Moore,[13] the values of K thus calculated were considerably lower than the one derived from the Mark–Houwink expression ($K = 0.112$). The effects of polydispersity on K and α, when taken into account, gave averages of 4.4×10^{-4} and 0.516, respectively, for all the samples of Table I.

It is worth noting that the individually calculated values of α lie very close to the value of 0.5 expected at the Θ-conditions. However, Θ-conditions are hard to establish for highly branched polymers, and it is very likely that methyl ethyl ketone at 25 °C corresponds to a good solvent for the BTA/DMG polymers.[3,5] Simha[14,15] has pointed out that the value of the constant, K, should be increased with branching. The trend, however, of the K values calculated was completely the reverse. It remains therefore to state that the Mark–Houwink expression for the postgel sol fractions for BTA/DMG gelation takes the form

$$[\eta] = 0.112\bar{M}_w^{0.15} \qquad (1)$$

and that the effects of polydispersity on the value of K remain unknown.

An Einstein sphere should possess a constant density, and its intrinsic viscosity should be independent of size.[10] By accepting that the postgel soluble fractions in solution obey the spherical non-free-draining model (or impermeable coil model), their intrinsic viscosity can be expressed as a function of their density by the relationship $[\eta] = 2.5/\bar{\rho}_{equ}$, where $\bar{\rho}_{equ}$ is the density of the empty molecule without included solvent and $[\eta]$ is expressed in milliliters per gram.

The nature of the BTA/DMG polymers, together with their low Mark–Houwink exponent, strongly supports the validity of the $\bar{\rho}_{equ}$ values calculated in this way. These molecules in solution are expected to be more spherical than coiled.

Table I shows the calculated $\bar{\rho}_{equ}$ values. The densities of these polymers are very high compared to those of common linear polymers. The large densities of the BTA/DMG fractions are likely the result of high branching coefficients or even intraparticle cross-linking.

Assuming a spherical shape for the BTA/DMG polymers in solution, $\bar{\rho}_{equ}$ may be reexpressed as $\bar{\rho}_{equ} = 6\bar{M}/N_A\pi d_{equ}^3$, where $\bar{M}$ is the molecular weight, N_A is Avogadro's number, and d_{equ}^3 is the diameter of equivalent sphere. Solving for d_{equ}, one obtains relation 2, which in principle yields the diameter of spherical macromolecules (in angstroms if $[\eta]$ is expressed in milliliters per gram), which in solution have intrinsic viscosity $[\eta]$.

$$d_{equ} = \left\{\frac{6\bar{M}\,[\eta]}{2.5\pi N_A}\right\}^{1/3} \text{[cm]} = 1.08(\bar{M}[\eta])^{1/3}\ [\text{Å}] \qquad (2)$$

The d_{equ} values for the BTA/DMG sol fractions, calculated by means of eq 2, are also shown in Table I. The calculated diameters are relatively small, indicating the compact nature of the BTA/DMG postgel sol fractions, in agreement with the high calculated densities.

It is thus shown that the hydrodynamic characteristics of soluble species throughout the postgel region obey the description of a spherically branched, compact, non-free-draining particle.

Experimental Section

The polymerization of BTA/DMG is described elsewhere.[8a–c] In order to extract the soluble polymers at various extents of reaction beyond the gel point, the network within the polymerization tube was first allowed to swell to 10 mL of THF overnight. The swollen gel was then broken into small pieces. The pulverized gel was quantitatively extracted with fresh THF (usually 8 × 10 mL). The solvent was filtered through a fine porous funnel into a 150-mL predried preweighed round-bottom flask. Gels produced in the $0.720 \leq p \leq 0.795$ region were found to swell extensively. This property made them difficult to wash free of sol through a porous funnel. In these cases, the sol was recovered quantitatively by washing the gel in centrifuge tubes. After centrifugation, the supernatant liquid was carefully withdrawn and filtered through a porous funnel. After 8–10 such washings, the gel was quantitatively transferred in a filter-paper cone and thoroughly washed with solvent. The collected washings after further filtration (through a porous funnel filter) were combined with the original extract, and the solvent was evaporated under reduced pressure at 40 °C. Additional THF was removed from the sols by applying high vacuum (10^{-3} mmHg) overnight and then by drying to constant weight in a vacuum desiccator over KOH. Complete removal of THF required almost a week of standing over fresh KOH in a 10^{-3} mmHg vacuum. Each sample was then redissolved in methyl ethyl ketone and microfiltered (0.5 μm Millipore filter, Waters), so as to give a 1–2 mg/mL solution, accurately known. Its viscosity was measured in a modified Ubbelohde, viscometer, five to seven times, at 25 °C. The lower bulb of the viscometer was reduced in size so that the viscosities of even 2 mL of solution could be measured. This was necessary because some of the samples, especially those from fractions taken well beyond the gel point, were never available in greater than 2–5-mg quantities. The viscosity of each sample was thus measured at four different concentrations, by appropriate careful dilution within the viscometer, with fresh prefiltered solvent. Extreme care was exercised to keep the solutions and equipment dust-free during the measurements.

Molecular weights were measured by injecting 250–500 μL of approximately 1–2% w/v of the above solutions into a KMX-6 Chromatix GPC/LALLS photometer equipped with six μStyragel (Waters Associates) columns of porosity varying between 10^5 and 100 Å.

Registry No. (BTA)(DMG) (copolymer), 34606-50-3.

References and Notes

(1) Gordon, M.; Kajiwara, K.; Peniche-Covas, C. A. L.; Ross-Murphy, S. B. *Makromol. Chem.* **1975**, *176*, 2413.
(2) Gordon, M.; Kajiwara, K.; Charlesby, A. *Eur. Polym. J.* **1975**, *11*, 385.
(3) Burchard, W.; Kajiwara, K.; Gordon, M.; Kalal, J.; Kennedy, J. W. *Macromolecules* **1973**, *6*, 642.
(4) Gordon, M.; Roe, R. J. *J. Polym. Sci.* **1956**, *21*, 27, 75.
(5) Peniche-Covas, C. A. L.; Gordon, M.; Judd, M.; Kajiwara, K. *Discuss. Faraday Soc.* **1974**, *57*, 165.
(6) Kalal, J.; Gordon, M.; Devoy, C. *Makromol. Chem.* **1972**, *152*, 233.
(7) Ross-Murphy, S. B. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 53*, 11.
(8) Argyropoulos, D. S.; Bolker, H. I. (a) *Ind. Eng. Chem. Prod. Res. Dev.* in press. (b) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*(2), 130. (c) Argyropoulos, D. S. Ph.D. Thesis, McGill University, 1985.
(9) Rezanowich, A.; Yean, W. Q.; Goring, D. A. I. *Sven. Papperstidn.* **1963**, *66*(5), 141.
(10) Einstein, A. *Ann. Phys. (Leipzig)* **1906**, *19*, 289; **1911**, *34*, 591.
(11) Koningsveld, R.; Tuijnman, C. A. F. *Makromol. Chem.* **1960**, *38*, 39, 44.
(12) Voek, J. F. *J. Polym. Sci.* **1959**, *36*, 333.
(13) Moore, W. R. *Prog. Polym. Sci.* **1967**, *1*, 3.
(14) Simha, R. *J. Colloid Sci.* **1950**, *5*, 385.
(15) Simha, R. *J. Res. Natl. Bur. Stand.* **1949**, *42*, 409.

Equilibrium Copolymerization

RYSZARD SZYMANSKI

Polish Academy of Sciences, Center of Molecular and Macromolecular Studies, Boczna 5, 90-362 Łódź, Poland.

Received September 24, 1985

In a recent paper Szwarc and Perrin[1] discussed equilibrium copolymerization in living polymer systems. In their treatment, which correctly allows detailed calculations of all the properties of such systems, they used a matrix **M**

$$\mathbf{M} = \begin{pmatrix} K_{11}a & K_{21}a \\ K_{12}b & K_{22}b \end{pmatrix}$$

where *K*'s denote the equilibrium constants of reactions such as $A_n^* + A \rightleftharpoons A_nA_{n+1}^*$, $A_n^* + B \rightleftharpoons A_nB_{n+1}^*$, etc. The symbols *a* and *b* are the equilibrium concentrations of the respective monomers, and A_n^*, B_n^*, $A_nA_{n+1}^*$, and $A_nB_{n+1}^*$ are the equilibrium concentrations of living *n*-mers terminated by A and B and living (*n* + 1)-mers terminated by diads AA and AB, etc., respectively.

In the special case of a singular matrix **M**, i.e., for $|\mathbf{M}| = 0$, its reciprocal does not exist, and the treatment has to be modified. The modified treatment is discussed at the end of Szwarc and Perrin's Appendix II. It reveals that for $|\mathbf{M}| = 0$, the probabilities for finding the units A or B in any *n*-mer, $n > 1$, are constant for all *n*-mers and all segments but the first and last. The probabilities are again constant, independent of $n > 1$, for the last segments, although their values differ from the previous ones, whereas the probabilities for A or B being in the first segments of *n*-mers (including $n = 1$) remain undefined. In an attempt to get the latter probabilities, Szwarc and Perrin wrote eq A20 as

$$\mathbf{M}\begin{pmatrix} {}^{\circ}A_1 \\ {}^{\circ}B_1 \end{pmatrix} = \begin{pmatrix} A_2^* \\ B_2^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} {}^{\circ}A_1 \\ {}^{\circ}B_1 \end{pmatrix}$$

whereas the correct form is

$$\mathbf{M}\begin{pmatrix} {}^{\circ}A_1 \\ {}^{\circ}B_1 \end{pmatrix} = \begin{pmatrix} A_2^* \\ B_2^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} {}^{\circ}A_2 \\ {}^{\circ}B_2 \end{pmatrix}$$

where ${}^{\circ}A_1$ and ${}^{\circ}B_1$ denote the equilibrium concentrations of the initiating 1-mers, ${}^{\circ}A_2$ and ${}^{\circ}B_2$ the equilibrium concentrations of the *dimers* starting with A and B, respectively, and A_2^* and B_2^* the equilibrium concentrations of the dimers terminated by the corresponding units. This error invalidates their last equation (eq A21), needed for solution of the problem. It is necessary, therefore, to derive the correct method yielding the probabilities for *A* and *B* in the first segments of the polymers.

The author of this note presented a simple solution[2] of equilibrium copolymerization for high degrees of polymerization ($\overline{\mathrm{DP}}_n \to \infty$). This solution may be applied also to the case when $|\mathbf{M}| = 0$, provided $\overline{\mathrm{DP}}_n$ is high. However, it gives no access to values such as concentrations of *n*-mers and their microstructure.

Therefore, one of the equations from ref 2, e.g., the relation equating the concentrations of diads AB and BA

$$(a_0 - a)(1 - K_{11}a) = (b_0 - b)(1 - K_{22}b) \qquad (1)$$

(where a_0 and b_0 are the starting concentrations of the respective comonomers) can be used (after replacing the erroneous (A20) and (A21)) to get the approximate solution of Szwarc and Perrin's equations when $|\mathbf{M}| = 0$. The solution would be only approximate because (1) is valid only for $\overline{\mathrm{DP}}_n \to \infty$ and the difference between the concentrations of heterodiads is especially important for low $\overline{\mathrm{DP}}_n$.

References and Notes

(1) Szwarc, M.; Perrin, C. L. *Macromolecules* **1985**, *18*, 528–533.
(2) Szymanski, R. IUPAC 7th International Symposium on Cationic Polymerization and Related Processes, Jena, 1985; *Makromol. Chem.* **1986**, *187*, 1109–1114.

Reply to the Preceding Note. Solution of the Equilibrium Copolymerization Equations for the Case of the Singular Matrix M

MICHAEL SZWARC

Department of Chemistry, University of California, San Diego, La Jolla, California 92093.

Received April 7, 1986

Dr. Szymanski is correct. The next to last equation (eq A20) of our paper[1] is erroneous. It reads

$$\mathbf{M}\begin{pmatrix} {}^{\circ}A_1 \\ {}^{\circ}B_1 \end{pmatrix} = \begin{pmatrix} A_2^* \\ B_2^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} {}^{\circ}A_1 \\ {}^{\circ}B_1 \end{pmatrix}$$

instead of the correct

$$\mathbf{M}\begin{pmatrix} {}^{\circ}A_1 \\ {}^{\circ}B_1 \end{pmatrix} = \begin{pmatrix} A_2^* \\ B_2^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} {}^{\circ}A_2 \\ {}^{\circ}B_2 \end{pmatrix}$$

0024-9297/86/2219-3003$01.50/0