

LIGHT SCATTERING FROM ASSOCIATING POLYMERS IN SOLUTIONWalther BURCHARD^a, Robert DOLEGA^a and Walter H. STOCKMAYER^{b,*}^a *Institut für makromolekulare Chemie,
Freiburg i.Br., D-79104, Germany*^b *Department of Chemistry,
Dartmouth College, Hanover, NH 03755, U.S.A.*

Received April 18, 1995

Accepted May 28, 1995

This paper is dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday, in gratitude for his friendship and with admiration of his contributions to light-scattering knowledge.

The effects of polymolecularity on the second and third light-scattering virial coefficients are calculated for some sample distributions and compared to the values obtained from an approximate treatment by Burchard and coworkers. It is concluded that the Burchard scheme, designed to facilitate the evaluation of light scattering data for associating systems, is generally reliable.

A few years ago, one of us¹ proposed a scheme for interpreting light-scattering data (LS) on associating polymers in solution. This scheme, which has been quite successful in applications to experimental results, is based on several assumptions which, while physically plausible, are only approximate. The purpose of the present paper is to explore, by means of some specific examples, the reliability of these underlying approximations.

THEORETICAL*The Scheme*

At sufficient low concentrations, below the onset of extensive overlap, the forward Rayleigh scattering can be described by a virial expansion:

$$M_{\text{app}}^{-1} \equiv Kc/R_0 = M_w^{-1} + 2A_2^{\text{LS}}c + 3A_3^{\text{LS}}c^2 + \dots, \quad (1)$$

* The author to whom correspondence should be addressed.

where R_0 is the Rayleigh ratio extrapolated to zero scattering angle, c is the polymer concentration, M_w is the weight-average molar mass, and K is the usual optical constant. If the polymer contains only a single species, the virial coefficients A_2^{LS} and A_3^{LS} are identical to those in the osmotic pressure expansion

$$\pi^*/cRT = M_n^{-1} + A_2c + A_3c^2 + \dots, \quad (2)$$

where π^* is the osmotic pressure and M_n is the number-average molar mass. However, for a polymolecular solute the light-scattering and osmotic virial coefficients are not the same. For A_2^{LS} the relations are relatively simple and well known², but the complete expression³ for A_3^{LS} is less commonly available.

The approximate scheme to be investigated makes the assumptions that the virial coefficients depend only on M_w , and in particular that they follow the relations

$$A_2^{LS} = K_A M_w^{a-1} \quad (3)$$

and

$$A_3^{LS} = g_A M_w (A_2^{LS})^2. \quad (4)$$

In these expressions K_A , a and g_A are constants independent of molar mass but dependent on solvent quality and polymer structure. For example, the values a 0.8, g 0.29 are used for flexible coils in good solvents, the set a 0.5, g 1.3 is employed for highly swollen aggregates or randomly branched clusters, and a 0, g 5/8 describes hard spheres. Equations (3) and (4) have been tested for several non-associating systems in good solvents, and fit the data quite well. It may be recalled that Eq. (4) for a single polymer species was suggested long ago⁴ on the basis of an approximate theory. It is unlikely to be reliable in poor solvents near theta conditions, where new terms specifically due to ternary segment interactions will affect the virial coefficients⁵.

For associating systems at equilibrium, Eqs (3) and (4) are retained, but with the recognition that the weight-average molar mass is now a function of concentration. In such cases, Eq. (1) reads

$$[M_{app}(c)]^{-1} = [M_w(c)]^{-1} + 2cK_n[M_w(c)]^{a-1} + 3g_A c^2 K_A^2 [M_w(c)]^{2a-1} + \dots \quad (5)$$

In particular, if higher terms in the expansion are negligible, the use of $g_A = 1/3$ leads to simple analytical and graphical results. It has been applied to solutions of β -galactosidase⁶ and of cellulose-2.5-acetate⁷ with self-consistent results. In essence, the above-described scheme purports to establish a reliable basis for the behavior of normal, non-associating polymers in dilute solution – a sort of corresponding-states reference – and then to attribute all deviations from this basis to association, simply by allowing the weight-average molar mass to become a concentration-dependent quantity $M_w(c)$. In what follows, we study the reliability of the basis, as expressed in Eqs (3) and (4), for some particular polymolecular systems.

Polymolecularity and Virial Coefficients

We now embark on a comparison of Eqs (3) and (4) with more detailed considerations of the second and third light-scattering virial coefficients. As given by Kurata³, the general expressions for a polymolecular solute are

$$A_2^{LS} = (2M_w^2)^{-1} \sum \sum w_i M_i w_j M_j B_{ij} \quad (6)$$

and

$$A_3^{LS} = (3M_w^{-2})^{-1} \sum \sum \sum w_i w_j w_k M_i M_j B_{ijk} - (3M_w^3)^{-1} \sum \sum \sum \sum w_i w_j w_k w_l M_i M_j M_k M_l (B_{ik} B_{jk} - B_{ik} B_{jl}), \quad (7)$$

where w_i is the weight fraction of species i in the polymer sample and of course $M_w = \sum w_i M_i$. In these expressions, the coefficients B_{ij} and B_{ijk} are simply related to the more conventional virial coefficients; for example, for a single monodisperse polymer solute $B_{ii} = 2A_2$. It may be remarked that the second term on the r.h.s. of Eq. (7) has sometimes been ignored, probably because it vanishes identically in the monodisperse case.

Now combining rules for the cross-coefficients (e.g., B_{ij} for $i \neq j$) are needed. There are no exact general rules independent of molecular details. However, studies of soft repulsive potentials of interaction among small spherical molecules in the gas phase show⁸ that simple geometric-mean rules are very reliable, and are superior to assuming the additivity of effective radii. Accordingly we take

$$B_{ij} = (B_{ii} B_{jj})^{1/2} \quad (8)$$

and

$$B_{ijk} = (B_{ii}B_{jj}B_{kk})^{1/3} . \quad (9)$$

For flexible chains in good solvents, the sphericalized potentials of mean force are indeed softly repulsive, so that Eqs (8) and (9) are physically reasonable. A more detailed discussion of the combining-rule problem for the second coefficient is given by Casassa⁹. For hard spheres, Eqs (8) and (9) are not correct, and the radii are additive, but we do not investigate this more complicated case⁸ here.

It now remains only to adapt Eqs (3) and (4) to the general case. This amounts to taking

$$B_{ii} = 2K_A M_i^{a-1} \quad (3')$$

and

$$B_{iii} = 3g_A K_A^2 M_i^{2a-1} . \quad (4')$$

The algebra of using these relations in Eqs (6)–(9) is straightforward, and leads to the following results,

$$A_2^{LS}/K_A M_w^{a-1} = [\mu \left(\frac{a+1}{2} \right)]^2 / [\mu(1)]^{a+1} , \quad (10)$$

$$\begin{aligned} A_3^{LS}/g_A M_w (A_2^{LS})^2 = & \mu(1) \mu \left(\frac{2a-1}{3} \right) \left[\mu \left(\frac{2a+2}{3} \right) \right]^2 \left[\mu \left(\frac{a+1}{2} \right) \right]^4 - \\ & - (4/3g_A) \left\{ \mu(a) \mu(1) \left[\mu \left(\frac{a+1}{2} \right) \right]^{-2} - 1 \right\} , \end{aligned} \quad (11)$$

where the moments of the molar mass distribution are defined as

$$\mu(v) \equiv \int_0^\infty M^v w(M) dM \quad (12)$$

with respect to the normalized weight-distribution function $w(M)$. Thus, as usual,

$$\mu(0) = 1; \quad \mu(1) = M_w; \quad \mu(-1) = M_n^{-1} . \quad (13)$$

It is seen that the r.g.s. of Eqs (10) and (11) each reduce to unity for a monodisperse solute.

CALCULATIONS AND DISCUSSION

We now apply Eqs (10)–(12) to several well-known distribution functions¹⁰.

a) The Schulz–Zimm (SZ) or “gamma” distribution is

$$w(M) dM = [\Gamma(z + 1)]^{-1} q^{z+1} M^z \exp(-qM) dM \quad (14)$$

and has the familiar properties $M_w \equiv \mu(1) = (z + 1)/q$ and $M_n^{-1} = q/z$, so that the usual polymolecularity index is

$$M_w/M_n = 1 + z^{-1} . \quad (15)$$

The general equation for the moments is

$$\mu(v) = q^{-v} \Gamma(1 + z + v) / \Gamma(1 + z) = M_w^v \Gamma(1 + z + v) / (1 + z)^v \Gamma(1 + z) . \quad (16)$$

TABLE I
Values of $A_2^{LS}/K_A M_w^{a-1}$

z	a = 0.8, g _A = 0.29		a = 0.5, g _A = 0.33		a = 0.0, g _A = 0.625	
	SZ	LN	SZ	LN	SZ	LN
0.1	0.9307	0.8057	0.8564	0.6379	0.8019	0.5491
0.2	0.9356	0.8511	0.8664	0.7146	0.8161	0.6389
0.5	0.9469	0.9059	0.8897	0.8138	0.8488	0.7598
1	0.9589	0.9395	0.9146	0.8781	0.8836	0.8409
2	0.9718	0.9642	0.9412	0.9268	0.9204	0.9036
5	0.9854	0.9837	0.9697	0.9664	0.9592	0.9554
10	0.9919	0.9915	0.9832	0.9823	0.9775	0.9765
20	0.9958	0.9956	0.9911	0.9909	0.9882	0.9879
50	0.9982	0.9982	0.9963	0.9963	0.9951	0.9951
100	0.9991	0.9991	0.9981	0.9981	0.9975	0.9975

The results for this distribution are given in Tables I and II and shown as the unfilled symbols in Figs 1 and 2 for the dimensionless quantities defined in Eqs (10) and (11). They would of course be identically unity for all values of z if the scheme was exact. One sees that even for rather broad distributions (e.g., $M_w/M_n \approx 10$) the treatment is quite successful.

b) The logarithmic normal (LN) distribution function is

$$w(M) = (M\sigma)^{-1}(2\pi)^{-1/2} \exp [-(\ln M - \ln M_0)^2/2\sigma^2] , \quad (17)$$

where

$$\ln M_0 = \int_0^{\infty} (\ln M)w(M) dM = \ln M_w - (\sigma^2/2) \quad (18)$$

and

$$M_w/M_n = \exp(\sigma^2) . \quad (19)$$

The moments are given by

$$\ln \mu(v) = v \ln M_0 + (v^2\sigma^2/2) . \quad (20)$$

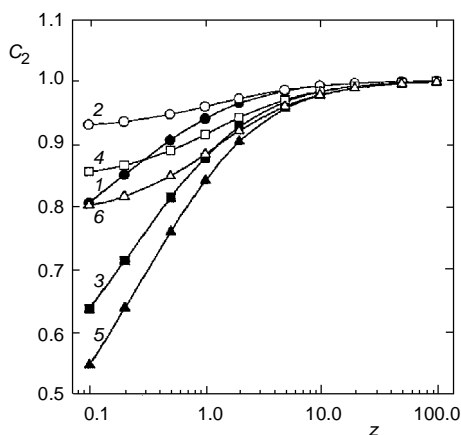


FIG. 1

Values of reduced light-scattering second virial coefficient, $A_2^{LS}/K_A M_w^{a-1}$ (C_2), as functions of polymolecularity index z , for several distributions and polymer structures: 1 $a = 0.8$, $g_A = 0.29$ (LN), 2 $a = 0.8$, $g_A = 0.29$ (SZ), 3 $a = 0.5$, $g_A = 0.33$ (LN), 4 $a = 0.5$, $g_A = 0.33$ (SZ), 5 $a = 0$, $g_A = 0.625$ (LN), 6 $a = 0$, $g_A = 0.625$ (SZ)

We relate the parameter σ of the LN distribution to the parameter z of the SZ distribution by means of Eqs (15) and (19), i.e.

$$\sigma^2 = \ln(1 + z^{-1}) . \quad (21)$$

TABLE II
Values of $A_3^{\text{LS}}/g_A M_w (A_2^{\text{LS}})^2$

z	$a = 0.8, g_A = 0.29$		$a = 0.5, g_A = 0.33$		$a = 0.0, g_A = 0.625$	
	SZ	LN	SZ	LN	SZ	LN
0.1	1.2487	2.1482	1.1789	1.8044	1.1567	1.5648
0.2	1.2297	1.7558	1.1597	1.4792	1.1223	1.2440
0.5	1.1868	1.4021	1.1197	1.2226	1.0648	1.0578
1	1.1422	1.2338	1.0833	1.1180	1.0277	1.0106
2	1.0961	1.1291	1.0509	1.0605	1.0068	0.9972
5	1.0486	1.0556	1.0230	1.0245	0.9985	0.9960
10	1.0266	1.0286	1.0119	1.0122	0.9981	0.9974
20	1.0140	1.0145	1.0060	1.0061	0.9987	0.9985
50	1.0058	1.0058	1.0024	1.0024	0.9994	0.9994
100	1.0029	1.0029	1.0012	1.0012	0.9997	0.9997

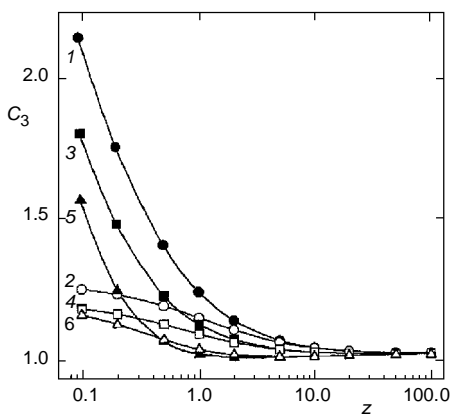


FIG. 2
Values of reduced light-scattering third virial coefficient, $A_3^{\text{LS}}/g_A M_w (A_2^{\text{LS}})^2$ (C_3), as functions of polymolecularity index z , for several distributions and polymer structures. Numbering as in Fig. 1

Results for this distribution are also given in Tables I and II and shown as the filled symbols in Figs 1 and 2. Here z has been related to σ by means of Eqs (15) and (19). The scheme is observed to be rather less successful than for the SZ distribution at low z values, though still not hopelessly bad. We may take some comfort from the rather severe criticism of the LN distribution offered by Kotliar¹¹, and of course the hard-sphere results (triangles) are not reliable because Eqs (8) and (9) do not apply to this case.

It is interesting to note the relative contribution of the last term on the r.h.s. of Eq. (11). For the broadest distributions ($z = 0.1$), this amounts to only 1.6% for the SZ distribution and 5% for the LN distribution in the case of flexible coils in good solvents; to 13.5% and 27%, respectively, for randomly branched clusters, and to 31% and 53% for hard spheres (the least likely case), respectively.

c) It might be suggested that randomly branched aggregates should follow a distribution based on percolation theory¹². Unfortunately such distributions, though similar at high M to SZ distributions with negative z , are not simple or accurately known for low M , and so at present we do not pursue this line further.

Our general conclusion, based on Figs 1 and 2, is that the Burchard scheme is indeed useful.

REFERENCES

1. Burchard W.: *Makromol. Chem., Macromol. Symp.* 29, 179 (1990).
2. Yamakawa H.: *Modern Theory of Polymer Solutions*, p. 220. Harper and Row, New York 1971.
3. Kurata M.: *Thermodynamics of Polymer Solutions*, p. 206. Harwood Academic Publishers, Chur 1982.
4. Stockmayer W. H., Casassa E. F.: *J. Chem. Phys.* 20, 1560 (1952).
5. Norisuye T., Nakamura Y., Akasaka K.: *Macromolecules* 26, 3791 (1993).
6. Auersch A., Littke W., Lang P., Burchard W.: *J. Cryst. Growth* 110, 202 (1992).
7. Schulz L., Burchard W.: *Das Papier* 43, 665 (1989); Burchard W., Schulz L., Auersch A., Little W.: *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 31 (2), 131 (1990); Burchard W., Lang P., Schulz L., Coviello T.: *Makromol. Chem., Macromol. Symp.* 58, 21 (1992).
8. Mason E. A., Spurling T. H.: *The Virial Equation of State*, p. 260. Pergamon Press, Oxford 1969.
9. Casassa E. F.: *Polymer* 3, 625 (1962).
10. Peebles L. H.: *Molecular Weight Distributions in Polymers*, p. 11. Interscience, New York 1971.
11. Kotliar A. M.: *J. Polym. Sci., A* 2, 4303, 4327 (1964).
12. Stauffer D.: *Introduction to Percolation Theory*, p. 36. Taylor and Francis, London 1985.