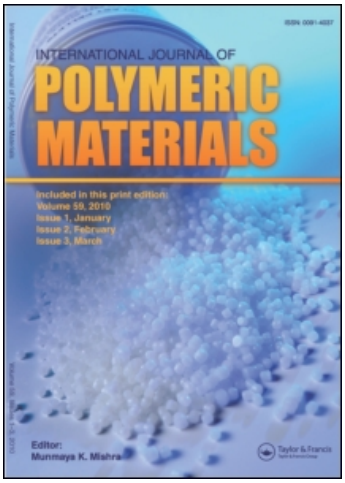

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Association of Synthetic Polymers†

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The methods available for a quantitative evaluation of solutions of associating macromolecules are reviewed. Association is defined as a rapid equilibrium between unimers (non-associated molecules) and multimers (associated molecules) in homogeneous solutions. It can be subdivided into open and closed associations. Open associations are consecutive processes. Closed associations represent all-or-none processes. Both types of associations can be of either the end-to-end type (number of associogenic sites independent of molecular weight) or the segment-to-segment type (number of associogenic sites increasing with molecular weight in a polymerhomologue series). Relations between the polymolecularity of the unimers and the polydispersity of the multimers are given. Viscometry is shown to be no reliable method for the investigation of association if used alone without the knowledge of thermodynamic data. The equilibrium constants of macromolecules seem to be higher than those of low molecular weight materials of similar constitution under comparable conditions. The association of polypropylenes increases with increasing syndiotacticity. A possible influence of the order of the solvent and of the desolvation processes on the equilibrium constants of association is discussed. Poly(γ-benzyl-L-glutamates) form cyclic multimers in dilute solutions of certain solvents and solvent mixtures.

1 INTRODUCTION

About fifty years ago, a big battle was fought between those who regarded organic colloids as associates of low molecular weight materials and those who considered them true macromolecules.[1] The battle ended—as we all know—with the victory of the macromolecules. The associates were defeated so thoroughly that the idea of associating organic macromolecules seemed to be very unattractive. Furthermore, the theory of macromolecular solutions as advanced by Huggins[2] and Flory[3] was very successful in explaining solution properties without the assumption of association. As a result, scattered indications[4–6] on associating systems seemed to point out only that the association of organic macromolecules is restricted to very peculiar polymer/solvent/

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temperature combinations. Until recently, no systematic investigations on associating synthetic macromolecules were carried out. The first reviews on associating synthetic macromolecules appeared only recently.[7,8]

The purpose of this paper is to review the methods available for a *quantitative* evaluation of solutions of associating macromolecules and their application to the investigation of the effects of constitution, configuration and conformation of the dissolved macromolecules and the influence of the solvent on the formation and the structure of the associates. A quantitative evaluation is needed because qualitative judging may lead to gross misinterpretations as will be shown below.

The phenomenon we will discuss comes in literature under different names: aggregation, association, self-association, multimerization, polymerization, complex formation, sociation, supersociation, agglomerization, etc. All processes leading to the formation of particles of higher particle weight from molecules of lower molecular weight via physical bonds will be called sociation processes.[9] They may occur between like molecules or unlike molecules. The sociation process between like molecules will be called multimerization.[10,11] Solvation is the sociation between solute and solvent.

A non-multimerized molecule will be called unimer. Like unimers of molecular weight M_I can multimerize to multimers with particle weight M_N. The multimerization number N describes the number of unimer molecules in a multimer particle. Homologue series of macromolecules with like constitution will be considered as like macromolecules. Molecular weight and configuration may vary, however.

The word "multimerization" will be used to describe the phenomena, *i.e.* the processes leading from unimers to particles of higher particle weight. Multimerization can either lead to an equilibrium state or a metastable state. The equilibrium state will be called an association equilibrium. Aggregation is the multimerization leading to metastable systems. Aggregation in polymer solutions is often caused by a crystallization process.[12] It is then accompanied by a first order transition. An aggregation thus appears as an "irreversible" process[7,11] if the temperature of measurement is far below the liquidus curve. This review will deal exclusively with association processes.

Two groups of methods can be used to detect and determine multimers: group specific and molecule specific methods. Group specific methods look at the structure of a group and its interaction with other groups. Typical examples for group specific methods are spectroscopic methods like infrared, nuclear magnetic resonance, ultraviolet, optical rotatory dispersion and circular dichroism techniques. Molecule specific methods look at the molecule as a whole, *e.g.*, their molecular weight and/or their volume, etc. Typical examples are membrane and vapor phase osmometry, light scattering, ultracentrifugation, viscometry and gel permeation chromatography.

A multimerizing macromolecule may have only few associogenic groups. Because these are only a small fraction of the total groups present, they may escape detection by group specific methods which typically become insensitive at levels of about 15% "impurities". The particle weight of the multimers may, however, increase drastically. One associogenic group in a polymer of degree of polymerization of one thousand represents only 0.1% of the total groups but the particle weight increases 100% if the dimerization is complete.

Obviously, molecule specific methods are the prime choice for the detection and determination of multimerizations. It should be remembered, however, that they are influenced by *inter*molecular multimerizations only. Information on intramolecular associations is hard, if any, to get from molecule specific methods. Furthermore, information on the structure of multimers by molecule specific methods is, at best, only indirect. Hence, for a complete elucidation of multimerization, both molecule and group specific methods have to be employed.

2 ABSOLUTE MOLECULAR WEIGHT DETERMINATIONS

2.1 Non-ideal solutions

Multimerization as an intermolecular process is accompanied by a change of particle mass. The multimerization may thus be studied via the concentration dependence of apparent molecular weights. An apparent molecular weight is the molecular weight calculated from experimental data at finite concentrations using an equation valid for infinite dilution only. The apparent number average molecular weight from membrane osmometry is thus given by

$$(M_n)_{app} = RTc/\Pi \tag{1}$$

and the apparent weight average molecular weight from light scattering experiments by

$$(M_w)_{app} = R_0/(K_{LS}c) \tag{2}$$

where R = gas constant, T = thermodynamic temperature, c = mass concentration (in mass of solute/volume of solution), Π = osmotic pressure, R_0 = reduced scattering intensity (Rayleigh ratio), and K_{LS} = optical constant. Apparent molecular weights of other averages may be defined by analogy. Apparent average molecular weights average over all components of solute (unimer included) and all existing interactions. The following discussion will be restricted to non-electrolytes.

The concentration dependence of apparent molecular weights of solutions of non-associating non-electrolytes can be expressed according to statistical thermodynamics[13]

$$(M_r)_{app}^{-1} = (M_r)^{-1} + a_2A_2c + a_3A_3c^2 + \ldots \quad (3)$$

where M_r = r-average of molecular weight (*e.g.*, $r = n$, $r = w$, etc.), A_2, $A_3 \ldots$ = 2nd, 3rd ... virial coefficients, and a_2 and a_3 = constants for the particular method, *e.g.*, $a_2 = 1$ for number average methods and $a_2 = 2$ for light scattering experiments. The influence of the third virial coefficient can be neglected in sufficiently dilute solutions of non-associating non-electrolytes. A system for which $A_2 = 0$ is called a theta system.[14]

The second virial coefficient of non-associating non-electrolyte solutions is directly related to the excluded volume u of the solute molecules[14,15]

$$A_2 = N_L u/(2M^2) \quad (4)$$

where N_L = Avogadro number. The second virial coefficient thus has three meanings: in the most general sense it is a curve fitting parameter, it is directly related to the chemical potential (or activity) of the solvent, and it is directly proportional to the excluded volume.

Consider now a situation like the one in Figure 1, where reciprocal apparent weight averages, $(M_w)_{app}$, of a poly(γ-benzyl-L-glutamate) in different solvents and at different temperatures are plotted against the concentration c. A curve fit with positive initial slope is obviously possible for the measurements in dichloroacetic acid at 25°C and for dimethylformamide at 70°C. An influence of the quadratic concentration term has to be considered for the measurements in dichloroacetic acid.

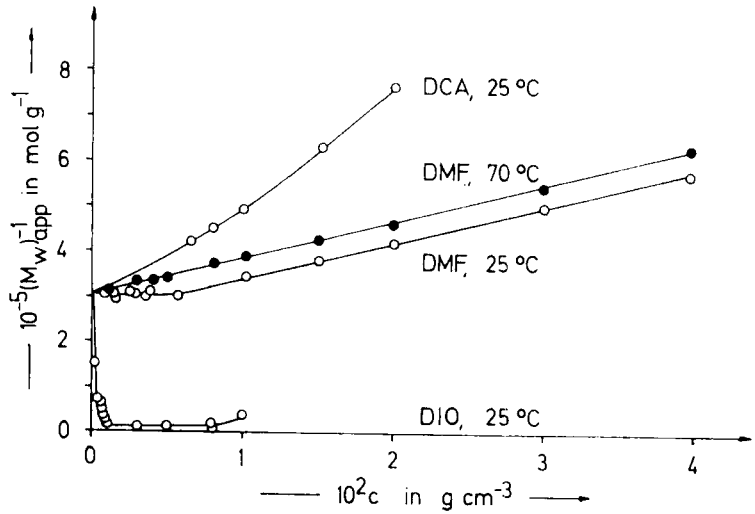


FIGURE 1 Concentration dependence of apparent weight average molecular weights of poly(γ-benzyl-L-glutamate) in dichloroacetic acid (DCA), dimethyl formamide (DMF), and dioxane (DIO) at 25 and 70°C (data from Ref. 16).

It is highly likely (and customary) that the initial slopes of these two curves can be equated with the true second virial coefficient which is a measure for the excluded volume. A direct proof is possible for the system poly(γ-benzyl-L-glutamate)/DMF/70°C. According to optical rotatory dispersion measurements, the polymer assumes a helical conformation under these conditions. Rigid helices have, however, the shape of a rod. The second virial coefficient of a rod can now be calculated from[15,17,18]

$$A_2 = v_2^2/(2\pi R_2^3 N_L) \tag{5}$$

where v_2 = specific volume of the solute and R_2 = radius of the rod. For this particular polymer, the specific volume was found[19] to be $v_2 = 0.785$ cm^3 g^{-1} and the radius of the helix[20] $R_2 = 0.75$ nm. The calculated second virial coefficient of $A_2 = 3.86 \times 10^{-4}$ mol cm^3 g^{-2} agrees with the experimental average (light scattering and osmotic pressure) of 3.55×10^{-4} mol cm^3 g^{-2} (Table I).

TABLE I

Second virial coefficients A_2^{OP} (from membrane or vapor phase osmometry) and A_2^{LS} (from light scattering) of poly(γ-benzyl-L-glutamates) of different molecular weights in various helicogenic solvents (data from Gerber and Elias[16])

Polymer No.	M_w g mol^{-1}	M_n g mol^{-1}	Solvent	Tb °C	$10^4 A_2^{OP}$ mol cm^3 g^{-2}	$10^4 A_2^{LS}$ mol cm^3 g^{-2}	$10^4 A_2$ mol cm^3 g^{-2}
1535	222,000	202,000	DMF	70	3.4	3.2[c]	3.6
			DMF	25	4.0	3.5[d]	
			DIO	25	2.4	—	
			CHL	25	4.8	—	
1533	154,000	132,000	DMF	70	3.9	2.3[c]	3.6
			DMF	25	3.7	3.6[e]	
			DIO	25	4.2	—	
			CHL	25	3.8	—	
1528	33,400	31,500	DMF	70	3.4	3.9	3.5
			DMF	25	3.9	3.6	
			DIO	25	2.7	—	
			CHL	25	3.4	—	
					3.6[f]	3.4[f]	
1536	9600	—	DMF	70	7.1	—	6.6
			DMF	25	6.4	—	
			CHL	37	—	6.3	

[a] DMF—dimethylformamide, DIO—1,4-dioxane, CHL—chloroform
[b] Unless stated otherwise
[c] 60°C
[d] 29°C
[e] 27°C
[f] Average for samples 1535, 1533 and 1528 in different solvents at various temperatures

Figure 1 shows that a strong association of this polymer occurs in dioxane at 25°C and a weak one in dimethylformamide at the same temperature. Because the macromolecule is in the same helical conformation at both 70 and 25°C, the second virial coefficient should be practically identical (the temperature dependence of the specific volume can be neglected). Inspection of the curves of Figure 1 shows the slopes of the DMF measurements to be identical at higher concentrations, whereas the initial slopes are different. The initial slope of the $M_{app}^{-1} = f(c)$ curve thus can not be equated with the second virial coefficient in associating systems. This conclusion is supported by the second virial coefficients of three poly(γ-benzyl-L-glutamates) with molecular weights between 33,400 and 222,000 g mol^{-1} in the helicogenic solvents dimethylformamide, dioxane, and chloroform at temperatures between 25 and 70°C. The second virial coefficient of rigid rods should be independent of solvent, temperature and molecular weight of the solute. This is indeed found experimentally, and the average value of 3.56×10^{-4} agrees well with the one of 3.86×10^{-4} mol cm^3 g^{-2} calculated via Eq. (5). The A_2 of the low molecular weight sample 1536 is higher because of the non-negligible contribution of the chemical structure of the endgroups and because the last three units of each side of the chain are not in the conformation of the helix.[21]

This experimental argument that the initial slope of $(M_r)_{app}^{-1} = f(c)$ curves cannot be equated with the second virial coefficient in associating systems[11, 22,23] is supported by another line of reasoning.[7] Equation (3) shows A_2 to be the proportionality factor for the linear concentration term. In solutions of non-associating non-electrolytes, the mole concentration of kinetically independent particles increases directly proportional to the increase of the mass concentration. In associating systems, the increase is less than proportional. The second virial coefficient thus looses its meaning as a proportionality constant in associating systems.

Using this reasoning, it seems convenient to split the concentration dependence of reciprocal apparent molecular weights into an association term $(M_r)_{app,\theta}$ and a virial term $A_2{}^*c$ (see[7,11,23]):

$$(M_r)_{app}^{-1} = (M_r)_{app,\theta}^{-1} + a_2 A_2{}^* c + \ldots \qquad (6)$$

where $(M_r)_{app}$ is defined by Eqs. (1), (2) or similar expressions. The association term will, in general, depend on concentration, its exact functionality depending on the type of association. It describes the variation of the number of kinetically independent particles as a function of concentration in the absence of all other interactions. The term $A_2{}^*$ is then a measure of these other interactions.

The so defined second virial coefficient $A_2{}^*$ is fundamentally different from the second virial coefficient A_2 which was used exclusively in the past. It is different because it does not contain intermolecular negative excluded volumes.

Intermolecular and intramolecular positive excluded volumes, intramolecular negative excluded volume effects and polymer/solvent interactions are included in A_2^* because they cannot be caused by associations. The question is of course whether attraction forces between parts of different macromolecules will always lead to associations and whether only associations in turn always lead to negative excluded volumes.

It seems reasonable to assume that an association is always accompanied by a negative excluded volume. Neither will association lead to positive excluded volumes, nor will an attraction not leading to association do so. It may be asked, however, whether an attraction which does not lead to an association still can produce negative excluded volumes (so called sticky collisions). This possibility seems, however, very unlikely because both association and negative excluded volume are detected and measured by the same method meaning that both life-time and energy are sufficiently high to be recognizable under the conditions of measurement. Negative excluded volumes thus seem not very probable in the absence of association.

The feeling that negative excluded volumes may exist without association may be possibly traced back to the effect of dispersion forces. Dispersion forces are too weak to create "stable" associates in low molecular weight materials, because group and molecule are practically identical. In macromolecules, cooperative effects of forces exerted by neighboring groups may favorably influence the interaction energy per *molecule* although the interaction energy per group is, of course, of the same magnitude as in low molecular weight materials. In other words, association of macromolecules may not only be caused by "specific" interactions but in addition by non-specific interactions, too.

Detailed studies exist on the association term (see below). Little is known, however, about the virial term in multimerizing systems, an exception being the very recent study on associating systems with hard body interactions.[24] The term A_2^* is, in general, varying with the concentration because the size and the shape of multimers or their interactions may vary with concentration, too. An exception is the case of longitudinal association of rods.

In general, the association term is dominating in the low concentration range and the virial term at higher concentrations, as can be shown by model calculations using reasonable assumptions on the magnitude of equilibrium constants and virial coefficients. The question then is whether an association is possible in a "good" solvent.

Good solvents are commonly defined as those which give positive second virial coefficients for a particular solute/temperature combination. Consider now a solution of α,ω-dihydroxy-hectamethylene $HO(CH_2)_{100}OH$ in hydrocarbons.[7] There will be obviously an association via hydrogen bonds, giving about 2×17 kJ mol^{-1} (if related to the macromolecule). The dispersion

forces between the methylene groups of solute and solvent are in the order of 100×4.2 kJ mol^{-1}. Because the latter is higher than the former, hydrocarbons are good solvents for this solute although one can expect an association. In other words, association may occur in good solvents and it is dangerous to conclude that the tendency towards association increases with decreasing solvent power in the general case as has been done.[4] Indeed, a combination of virial terms and positive second virial coefficients can very well explain the minima in the $(M_r)_{app}^{-1} = f(c)$ functions which were found, *e.g.*, for poly(vinyl alcohol-*co*-vinyl acetates) in water,[6] polyureas in different solvents,[25] or poly(ethylene glycols) in benzene.[27] An explanation[6] based on negative second and positive third virial coefficients is purely formal.

2.2 Basic types of association

Two basic types of association may be distinguished: open and closed association. Open association[7,26] (also called random polymerization[28] or indefinite self association[29]) is a consecutive association in which all types of multimers appear:

$$\begin{aligned} M_I + M_I &\rightleftarrows M_{II} \\ M_{II} + M_I &\rightleftarrows M_{III} \\ M_{III} + M_I &\rightleftarrows M_{IV} \\ &\cdots\cdots\cdots \\ M_{N-1} + M_I &\rightleftarrows M_N, \text{ etc.} \end{aligned} \tag{7}$$

Closed associations exhibit an all-or-none process in which only unimers and N-mers are present:

$$NM_I \rightleftarrows M_N \tag{8}$$

Combinations of these types of equilibria are of course possible (*e.g.*, monomer-dimer-tetramer-octamer equilibria). They will not be treated here because they seem to be of little importance for association of synthetic macromolecules. They play a certain role in the association equilibria of biopolymers.[29–31] It may, furthermore, be remembered that a curve fitting process using equilibrium constants for dimerization, trimerization, tetramerization, etc. can very often be replaced by a process using the model of open association with only one equilibrium constant, as has been shown.[7]

Association may be further subdivided according to the variation of the number of associogenic sites per molecule with the degree of polymerization in polymerhomologeous series. The number of groups capable of association may be constant for each molecule, regardless of its length. A simple example is a linear unipolymer chain with associating endgroups. This type of association can thus be tentatively called an end-to-end association. This term should not imply that this type of association occurs exclusively via endgroups. It

should merely indicate that the number of associogenic groups per macromolecule is independent of its length.

On the other hand, the number of associogenic groups may increase proportionally to the chain length. Associogenic groups may be special groups (in a constitutional copolymer of varying degree of polymerization) or sequences of constitutional or configurational groups, diads, triads, etc. This type of association can thus be tentatively called a segment-to-segment association.

In the end-to-end association, the unit of choice is the mole concentration, whereas in the segment-to-segment association the equilibrium constants have to be based on the mass concentrations.

In the most simple case, the equilibrium constants are independent of the multimer size. The following equilibrium constants can thus be defined:

Open end-to-end association

$$ {}^{n}K_o = \frac{[M_N]}{[M_{N-1}]\,[M_1]} \qquad [dm^3\ mol^{-1}] \quad (9) $$

Open segment-to-segment association

$$ {}^{w}K_o = \frac{c_N}{c_{N-1}c_N} \qquad [cm^3\ g^{-1}] \quad (10) $$

Closed end-to-end association

$$ {}^{n}K_c = \frac{[M_N]}{[M_1]^N} \qquad [(dm^3\ mol^{-1})^{N-1}] \quad (11) $$

Closed segment-to-segment association

$$ {}^{w}K_c = \frac{C_N}{C_1{}^N} \qquad [(cm^3\ g^{-1})^{N-1}] \quad (12) $$

The equilibrium constants for open and closed associations are interrelated[8]:

$$ ({}^{n}K_c)_{I,N} = ({}^{n}K_o)^{N-1} \quad (13) $$

$$ ({}^{w}K_c)_{I,N} = ({}^{n}K_c)^{N-1} \quad (14) $$

This treatment assumes the equilibrium constants of open association to be independent of the particle size, *i.e.*, $K_{I,II} = K_{II,III} = \ldots K_N = K$.

Molar and mass equilibrium constants can be converted into each other for finite degrees of association N, giving for closed associations:

$$ ({}^{w}K_c)_{I,N} = \frac{10^{3(N-1)}\,N\,({}^{n}K_c)_{N-1,N}{}^{N-1}}{(M_I)_n{}^{N-1}} \quad (15) $$

and for open associations

$$ ({}^{w}K_o)_{N-1,N} = \frac{10^3\,N\,({}^{n}K_o)_{N-1,N}}{(N-1)\,(M_I)_n} \quad (16) $$

The latter reduces for $N \to \infty$ to

$$({}^{w}K_0)_{N-1,N} = \frac{10^3\,({}^{n}K_0)_{N-1,N}}{(M_I)_n} \tag{17}$$

2.3 Polymolecularity

Most synthetic polymers are polymolecular, *i.e.*, the unimers possess a distribution of degrees of polymerization. The problem on how the polymolecularity of the unimers influences the polydispersity of the multimers has been solved recently for end-to-end and segment-to-segment associations.[32]

In the case of end-to-end associations, the number average molecular weight of the N-mer is exactly N times the number average of the unimer.[7,32] The weight average of the N-mer is, however, given by both the weight and the number average of the unimer.[32] The situation is even more complicated for the z-average:[32]

$$(M_N)_n = (M_I)_n + (N-1)\,(M_I)_n = N\,(M_I)_n \tag{18}$$

$$(M_N)_w = (M_I)_w + (N-1)\,(M_I)_n \tag{19}$$

$$(M_N)_z = (M_I)_z + (N-1)\,(M_I)_n \left[1 + \frac{2(M_I)_w - (M_I)_n - (M_I)_z}{(M_I)_w - (N-1)\,(M_I)_n}\right] \tag{20}$$

Two conclusions may be drawn immediately. Firstly, the determination of true weight average molecular weights for end-to-end associating systems is possible only if the number average molecular weights are known. Secondly, the interrelationship between polydispersity $(M_N)_w/(M_N)_n$ and polymolecularity $(M_I)_w/(M_I)_n$ leads to a sharpening of the N-mer distribution. From Eqs. (18) and (19), we get

$$\frac{(M_N)_w}{(M_N)_n} = 1 + \frac{1}{N}\left(\frac{(M_I)_w}{(M_I)_n} - 1\right) \tag{21}$$

At sufficient high N, the influence of polymolecularity on polydispersity is negligible as a rule (Figure 2).

For the segment-to-segment associations, we get[32]

$$(M_N)_n = (M_I)_n + (N-1)\,(M_I)_w \qquad \text{(Schulz-Flory distributions only)} \tag{22}$$

$$(M_N)_w = (M_I)_w + (N-1)\,(M_I)_w = N(M_I)_w \tag{23}$$

$$(M_N)_z = (M_N)_z + (N-1)\,(M_I)_w \tag{24}$$

No closed expression could be found for the relationships between unimer

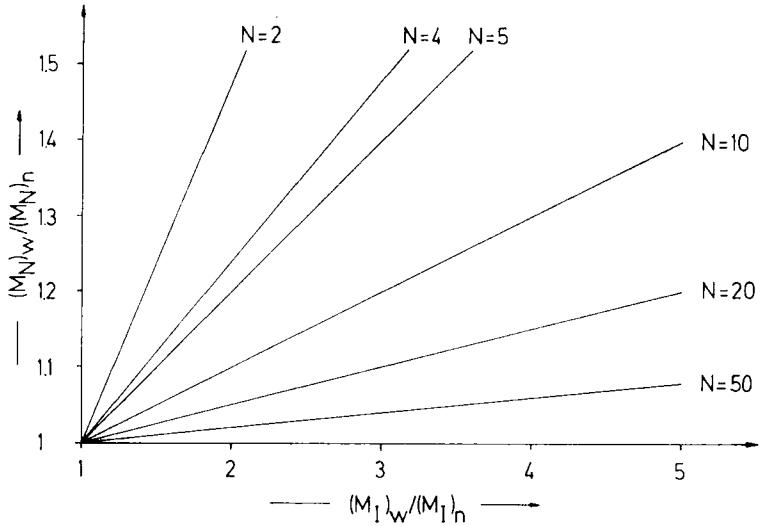


FIGURE 2 Influence of polymolecularity $(M_I)_w/(M_I)_n$ on polydispersity $(M_N)_w/(M_N)_n$ for end-to-end associations. The relationships are independent of the particular type of molecular weight distribution.

and multimer number average molecular weights other than for Schulz-Flory distributions. Again, the influence of polymolecularity on polydispersity

$$\frac{(M_N)_w}{(M_N)_n} = \frac{N(M_I)_w/(M_I)_n}{1 + [(N-1)(M_I)_w/(M_I)_n]} \quad \text{(Schulz-Flory distributions only)} \quad (25)$$

leads to a sharpening effect (Figure 3) which is bigger than in the case of end-to-end associations and leads, furthermore, to a saturation effect at high polymolecularities.

2.4 Open association

Open association will lead to a steady increase of apparent molecular weights in the theta state, *i.e.*, a steady decrease of the reciprocal apparent molecular weights. This behavior is shown by α-hydrogen-ω-hydroxy-poly(oxyethylenes), $H(OCH_2CH_2)_nOH$, in solvents like carbon tetrachloride or benzene (Figure 4). The concentration dependence of apparent average molecular weights is given for theta conditions for end-to-end associations[7,32]

$$(M_n)_{app,\theta} = (M_I)_n + {}^nK_o(M_I)_n[c/(M_n)_{app,\theta}] \quad (26)$$

$$(M_w)_{app,\theta} = (M_I)_w + 2\,{}^nK_o(M_I)_n[c/(M_n)_{app,\theta}] \quad (27)$$

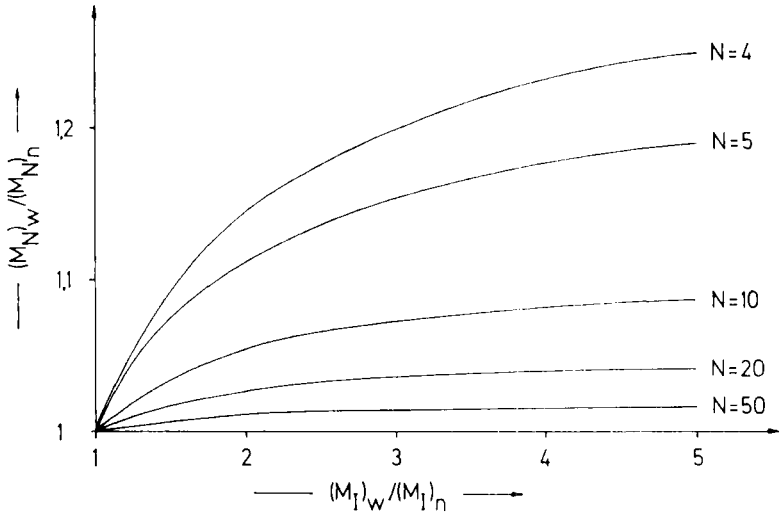


FIGURE 3 Influence of polymolecularity $(M_I)_w/(M_I)_n$ on polydispersity $(M_N)_w/(M_N)_n$ for unimers with Schulz-Flory molecular weight distributions undergoing segment-to-segment associations.

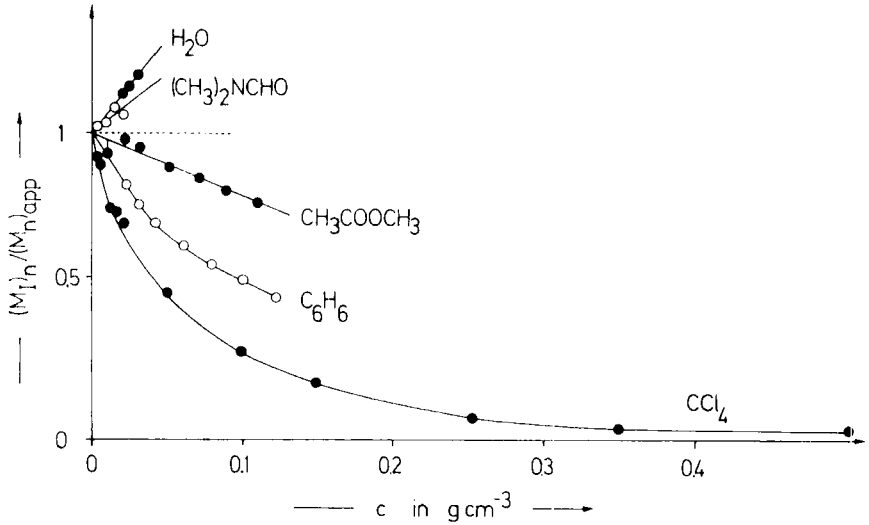


FIGURE 4 Concentration dependence of reduced reciprocal apparent number-average molecular weights of α-hydrogen-ω-hydroxy-poly(oxyethylene) AG 400-X $[(M_I)_n = 405$ g mol$^{-1}]$ in different solvents at 25°C (H.-G. Elias and H. Lys[31]).

$$(M_z)_{app,\theta} = (M_I)_z \left(\frac{(M_I)_w}{(M_w)_{app,\theta}} \right) + 3^n K_o (M_I)_n \left(1 + \frac{(M_I)_w}{(M_w)_{app,\theta}} \right) [c/(M_n)_{app,\theta}] \quad (28)$$

and for segment-to-segment associations[32]

$$(M_n)_{app,\theta} : \text{no simple function} \quad (29)$$

$$(M_w)_{app,\theta} = (M_I)_w + {}^w K_o (M_I)_w c \quad (30)$$

$$(M_z)_{app,\theta} \simeq (M_I)_z + 2\, {}^w K_o (M_I)_w c \quad (31)$$

The knowledge of $(M_n)_{app,\theta}$ is needed for all types of molecular weight averages in end-to-end associations, in contrast to segment-to-segment associations.

The association of α-hydrogen-ω-hydroxy-poly(oxyethylene) is known to proceed via hydrogen bonds between the hydroxyl endgroups and either other hydroxyl endgroups or ether groups.[34] The former will lead to an open end-to-end association if no special structures of the associates are involved. The latter will be somehow in the middle between an end-to-end and a segment-to-segment association.

The concentration dependence of reciprocal apparent number average molecular weights for a number of these polymers in benzene at 25°C is shown in Figure 5. The effects of association are especially pronounced for the low molecular weights for a number of these polymers in benzene at 25°C is shown weight polymer H 6000. The polymer AG 1518 shows both the influences of the association and the virial term. This behavior should not lead to the conclusion that the association decreases with increasing molecular weight. The association tendency is given by the equilibrium constant of association which is identical with the slope of a $(M_n)_{app,\theta}/(M_I)_n = f[c/(M_n)_{app,\theta}]$ plot [see Eq. (26)]. The initial slopes of a corresponding plot are indeed approximately parallel indicating an independence of the equilibrium constant on molecule size as demanded by an end-to-end open association (Figure 6). The upward curvature for the low molecular weight materials indicates a negative second virial coefficient.

2.5 Closed association

The model of closed association has first been used by Jones and Bury[34] to explain the existence of a "critical micelle concentration" (CMC) in soap solutions. As one can see immediately from model calculations,[7,8] the CMC very often does not exhibit a sharp break in the $1/(M_r)_{app,\theta} = f(c)$ function

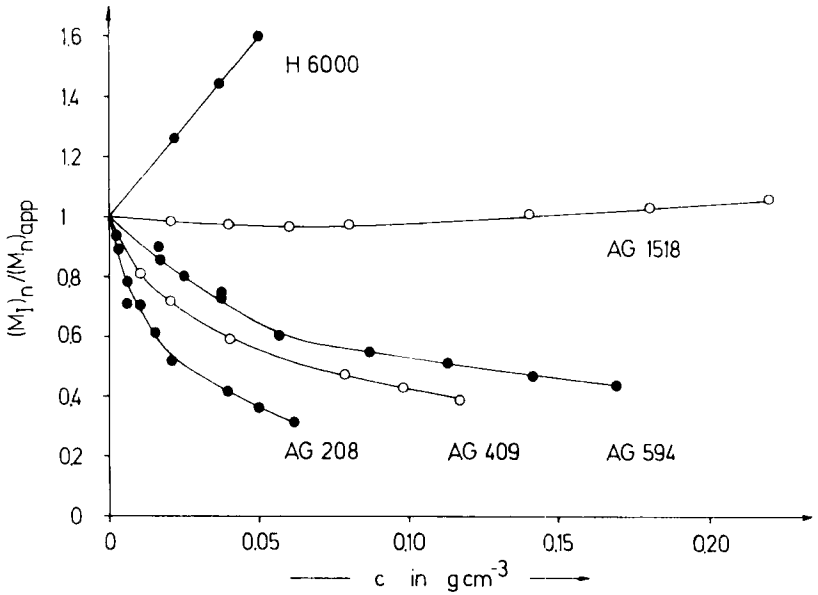


FIGURE 5 Concentration dependence of reciprocal apparent number-average molecular weights for a series of α-hydrogen-ω-hydroxy-poly(oxyethylenes) in benzene at 25°C (data from Ref. 31). The numbers indicate approximate molecular weights.

(see Figure 7). The position of the CMC, furthermore, depends on the averaging power of the method used. The CMC is *not* the point where the first micelles appear, it is only a region above which micelles can be detected with the particular method used.

The apparent particle weight is approaching its true value very slowly. Because of a possible influence of a virial term, the true particle weight $(M_N)_r$ cannot be taken directly from $(M_r)_{app} = f(c)$ or $1/(M_r)_{app} = f(c)$ plots. Gross misinterpretations may occur if these effects are neglected (see also Figure 8).

3 VISCOMETRY

Model calculations have been carried out for open[36] and closed[37] end-to-end associations of molecularly homogeneous polymers. An additivity of the specific viscosities $\eta_{sp} = (\eta - \eta_0)/\eta_0$ of the i-mers and the validity of the Huggins equation[38] were assumed for the calculations:

$$(\eta_{sp}/c)_1 = [\eta]_i + (k_\eta)_i [\eta]_i^2 c_i \qquad (32)$$

Thermodynamic and hydrodynamic crossinteractions were thus assumed to be

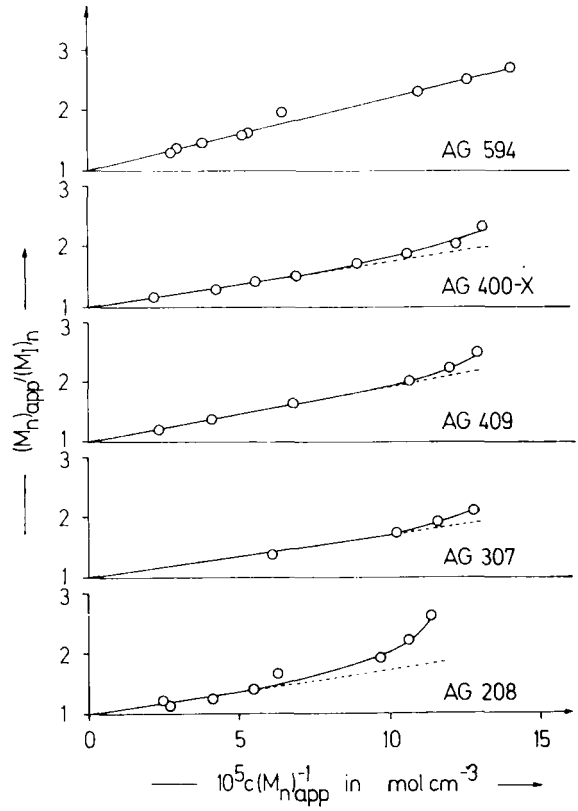


FIGURE 6 Normalized apparent number-average molecular weights as functions of $c/(M_n)_{app}$ for the same polymers as in Figure 5.

absent. The validity of this assumption is suggested by measurements of different detergent solutions.

All varieties of curve types can be found for closed end-to-end associations (Figures 9 and 10). The individual curve type depends on the particular magnitude and combination of the seven independent parameters: molecular weight M_I of the unimer, intrinsic viscosities $[\eta]_I$ of the unimer and $[\eta]_N$ of the N-mer, Huggins constants $(k_H)_I$ of the unimer and $(k_H)_N$ of the N-mer, association number N, and equilibrium constant $({}^nK_c)_{I,N}$. A maximum will appear in the plot of η_{sp}/c *vs.* c, if[37]

$$[\eta]_I + (k_H)_I[\eta]_I^2 c_{CMC} > [\eta]_N \tag{33}$$

where c_{CMC} is the mass concentration at the critical micelle concentration as given by the bend in the $c_I = f(c)$ or $c_N = f(c)$ functions. A minimum in the

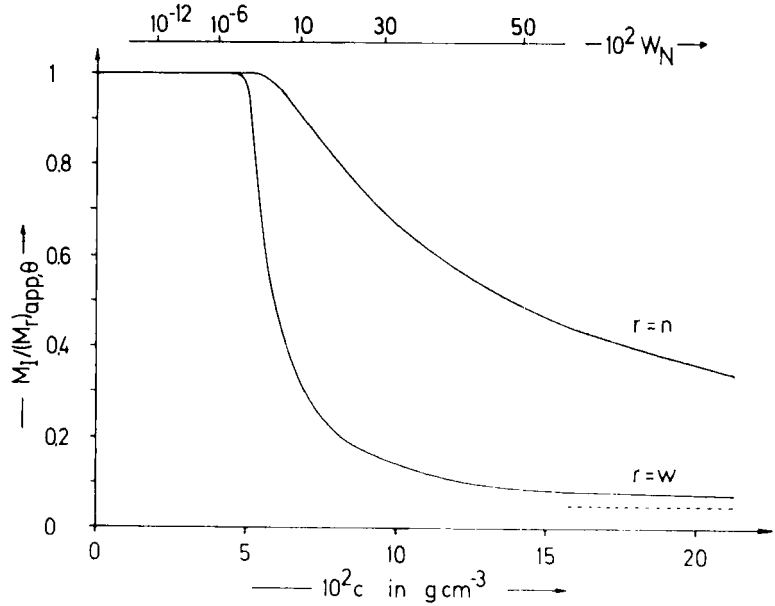


FIGURE 7 Concentration dependence of reciprocal average molecular weights for the case of a closed end-to-end association. Data were calculated with $(M_I)_n = (M_I)_w = 100$ g mol^{-1}, $N = 20$ and $({}^nK_c)_{I\,N} = 50$ (dm^3 mol^{-1})$_N{}^{-1}$.

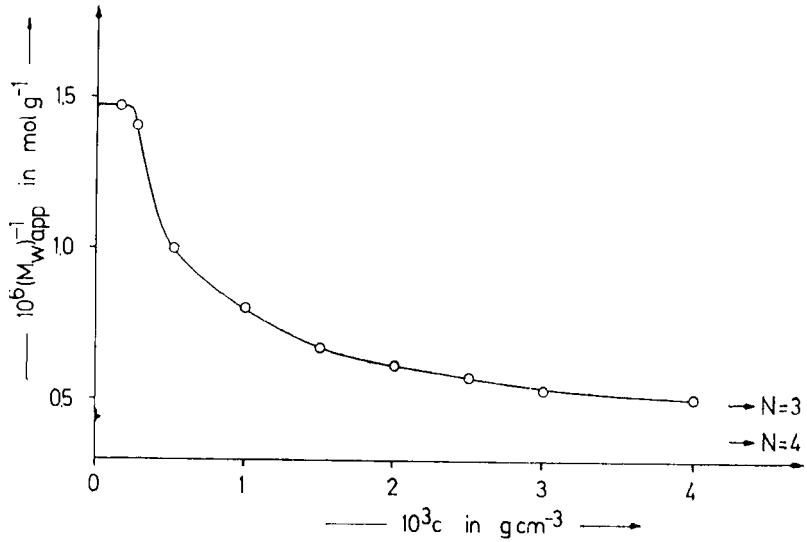


FIGURE 8 Concentration dependence of reciprocal weight-average molecular weights for L-glutamic dehydrogenase in potassium phosphate (0.2 mol dm^{-3}; pK = 7.18 ± 0.007) at 25°C (data from Ref. 35). The curve was calculated under assumption of theta state. The best fit was found for $M_I = 675\,000$ g mol^{-1}, $({}^nK_c)_{I,IV} = 10^{10{\cdot}8}$ (dm^3 mol^{-1})^3 and $N = 4$ (whereas the authors assumed $N = 3$). Arrows indicate the reciprocal weight average of N-mer particle weight for $N = 3$ and $N = 4$ respectively. (From Ref. 8.)

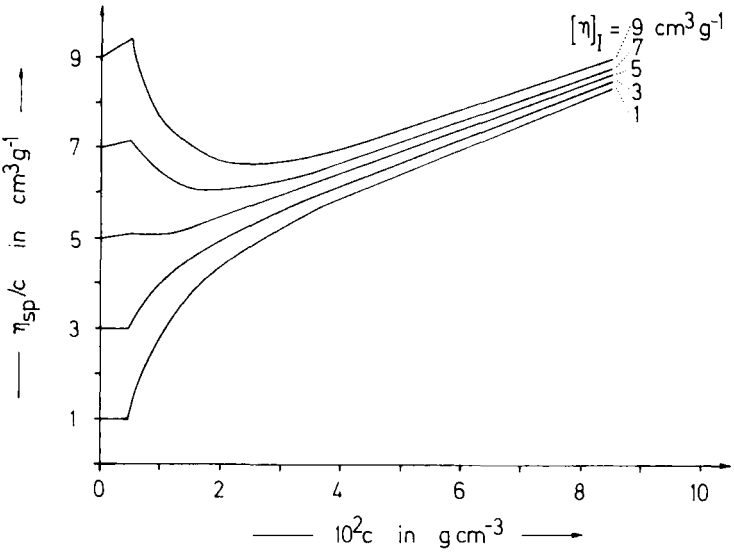


FIGURE 9 Concentration dependence of η_{sp}/c for closed end-to-end associations assuming $[\eta]_N = 5$ cm³ g^{-1}, $(k_\eta)_I = 1$, $(k_\eta)_N = 2$, $N = 60$, $({}^nK_c)_{I,N} = 10^{100}$ (dm³ mol^{-1})[59] and $(M_I)_n = (M_I)_w = 312$ g mol^{-1}. The intrinsic viscosities $[\eta]_I$ of the unimer were varied as indicated. (From Ref. 37.)

$\eta_{sp}/c = f(c)$ function can be expected if $[\eta]_I$ and $[\eta]_N$ are of the same magnitude and/or if the CMC is very high. High CMC's can be expected for low equilibrium constants and high association numbers. Under certain conditions, extremal values may be completely absent. Their absence can thus not be taken as an indication for open associations.

Open associations can also exhibit maxima in the $\eta_{sp}/c = f(c)$ plot although this seems to be a rather rare case. The plots may be either concave or convex against the c axis (Figure 11). A pronounced increase of η_{sp}/c with c is thus not necessarily a characteristic feature of open associations. There might be cases where the $\eta_{sp}/c = f(c)$ plots look perfectly straight. This comes from a compensation of different effects and the apparent Huggins constants may be found either too high or too low in conventional evaluations.[36]

In his now classical papers, Staudinger[1] used the temperature dependence of intrinsic viscosities to distinguish between macromolecules and association colloids. He assumed that a strong temperature dependence of intrinsic viscosities should be observed for association colloids because of the temperature dependence of intermolecular forces. According to Staudinger, the intrinsic viscosity of free macromolecules should show no significant variation with temperature because their particle weight is not changing with temperature. It was, however, pointed out by many authors[4,39-42] that the temperature

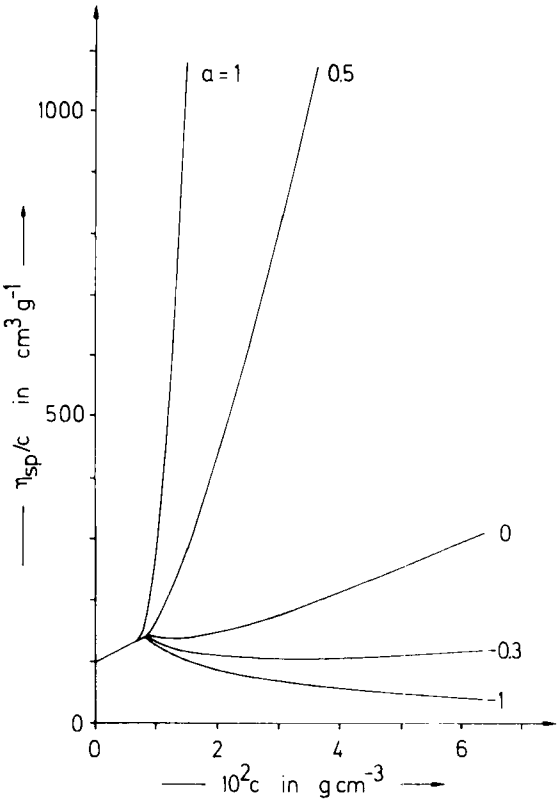


FIGURE 10 Concentration dependence of η_{sp}/c for closed end-to-end associations assuming $(M_I)_n = (M_I)_w = 30\,000$ g mol^{-1}, $N = 10$, $({}^nK_c)_{I,N} = 10^{30}$ (dm^3 mol^{-1})^9, $(k_\eta)_I = (k_\eta)_N = 0.5$ and $[\eta]_I = 100$ cm^3 g^{-1}. The intrinsic viscosities $[\eta]_N$ of the N-mers were calculated via $[\eta]_N = N^a[\eta]_I$ using the a-values given in the diagram. (From Ref. 37.)

and solvent dependence of conventionally determined intrinsic viscosities is not a good criterion for or against the presence of association. Indeed, the temperature dependence of intrinsic viscosities of associating detergents is very small, whereas non-associating polymers show a strong temperature dependence at temperatures near the theta point.

Of course, the near independency of intrinsic viscosities of detergent micelles on temperature is caused by their spherical shape. The intrinsic viscosities of spheres are, however, independent of their size according to the Einstein equation. The observed weak temperature influence is caused by a weak change of densities due to different packing of unimer molecules in the micelles.

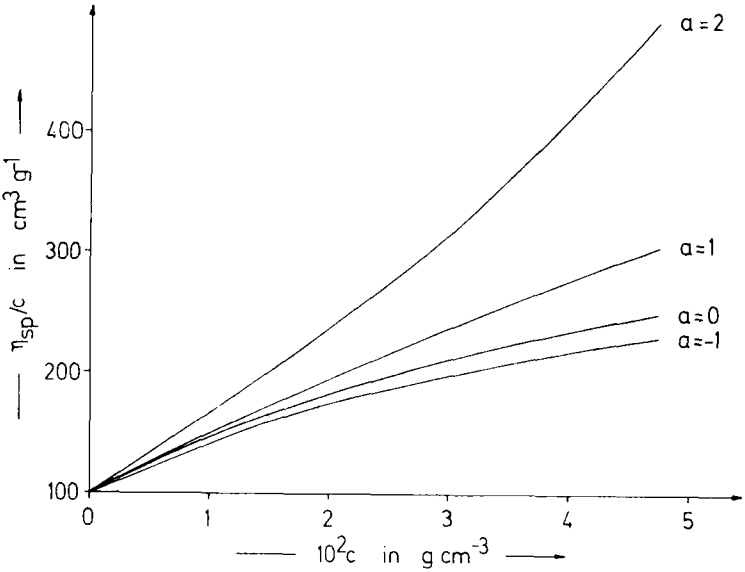


FIGURE 11 Concentration dependence of η_{sp}/c for open end-to-end associations; calculations under assumption of $[\eta]_I = 100$ cm^3 g^{-1}, a Huggins constant of $k_N = 0.5$, and $({}^nK_0) = 100$ dm^3 mol^{-1} for different exponents a of the intrinsic viscosity/molecular weight relationship $[\eta] = KM^a$ as indicated (from Ref. 36).

4 INFLUENCE OF CONSTITUTION

Polymers with hydrophilic groups are intuitively considered to undergo association in less polar solvents. Copolymers of methyl methacrylate units do indeed associate in solvents like dioxane, acetone and dimethylformamide.[43] The tendency towards association (as judged from the extrapolated apparent degree of polymerization) increases with increasing hydroxyl content of the polymers (Figure 12) and with decreasing relative permittivity (dielectric constant) of the solvent. It is interesting to note that the possibility to form hydrogen bonds between the solute and the solvent does not exclude intermolecular associations.

No such intermolecular associations could be observed, however, for copolymers of vinylacetate and a few vinylalcohol units in acetone, methanol and butanone.[44] This is probably due to the formation of sterically favored intramolecular hydrogen bonds:

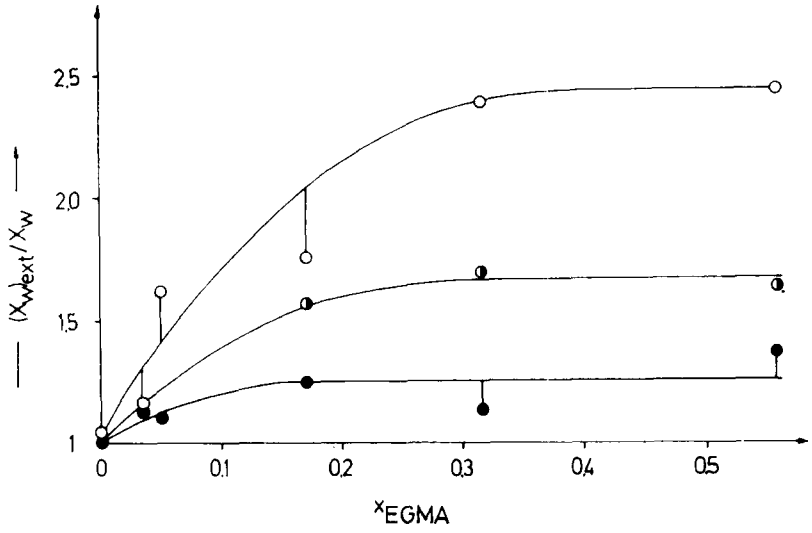
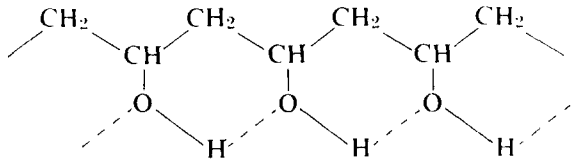


FIGURE 12 Dependence of reduced extrapolated weight average degrees of polymerizations on the ethylene glycol methacrylate content for copolymers of methyl methacrylate and ethylene glycol methacrylate in different solvents: (○) dioxane, (◑) acetone, (●) dimethylformamide. (From Ref. 43.)



The different behavior of the two different copolymers shows that even qualitative predictions on intermolecular associations are hard to make *a priori*. The quantitative separation of inter- and intramolecular associations is even more difficult.

An interesting problem is whether low and high molecular weight materials of similar constitution behave differently under associogenic conditions. The data on the α-hydrogen-ω-hydroxy-poly(oxyethylenes) should allow such a comparison.

The equilibrium constants of Table II refer to the association of the molecule. Assuming two associating sites per molecule (*e.g.* the hydroxyl endgroups), the equilibrium constants per associating site are half of the values given in Table II. Even so, an equilibrium constant ${}^{n}K_0 = 12\ dm^3\ mol^{-1}$ per hydroxyl

TABLE II

Equilibrium constants of open end-to-end associations of α-hydrogen-ω-hydroxy-poly(oxyethylenes) in various solvents at 25°C [as calculated via Eq. (28)]. The equilibrium constants refer to the whole molecule (based on data from Ref. 26)

Polymer No.	$(M_1)_n$ g mol^{-1}	${}^nK_o$ (dm^3 mol^{-1})			
		CCl_4	Benzene	Dioxane	Acetonitrile
H 2000	2630	24	—	—	—
AG 1005	980	27	—	—	—
AG 594	560	—	12	—	—
AG 400-X	405	21	11	0.7	—
AG 409	375	—	12	—	—
AG 307	327	—	—	1.1	0.6
AG 208	212	—	9	—	—
AG 200-X	216	—	—	1.4	0.8
Triglycol	152	—	—	—	—
Diglycol	105	—	—	1.1	0.8
Average		24	11	1.1	0.7

group in carbon tetrachloride is higher than it is found for low molecular weight materials. For instance, the equilibrium constant of 1-octanol in CCl_4 at 25°C is ${}^nK_o = 3.9$ dm^3 mol^{-1}, or, because a tetramer formation was found, $({}^nK_c)_{I,IV} = 50$ (dm^3 mol^{-1})^3 (see Ref. 45).

The reason for this behavior is not clear at the moment. It might well be that additional entropic effects are responsible for the enhanced equilibrium constants of association of high molecular weight materials.

5 INFLUENCE OF CONFIGURATION

Increasing stereoregularity of polymers normally leads to increased crystallization and decreased solubility. One can thus expect an influence of tacticity of polymers on the association behavior.

Measurements on a series of oligomeric polypropylenes of approximately the same molecular weight but varying tacticities showed a systematic variation of the equilibrium constant of association with the fraction of isotactic triads (Table III). The association was assumed to be of the open end-to-end type because attempts to apply the model of closed end-to-end associations led to negative degrees of association in some cases.[40] In the light of our more recent work, it is, however, open to discussion whether a closed segment-to-segment association is not the more appropriate model, but in that case, the mass equilibrium constant $({}^wK_c)_{I,N}$ of closed association will be even higher than the mole equilibrium constant $({}^nK_o)_{N-1,N}$ of open association [see Eq. (17)].

Because of the already very high open end-to-end equilibrium constants, the possibility of a closed segment-to-segment association instead of an open end-to-end one does not destroy the qualitative conclusions presented below.

TABLE III

Equilibrium constants ${}^{n}K_{o}$ for open end-to-end association of different polypropylenes in CCl_4 at 37°C (data from Refs. 40, 46)

Sample	$(M_I)_n$ g mol^{-1}	x_{ii}[a] %	${}^{n}K_{o}$ dm^3 mol^{-1}
5-Ae	2500	0	825
0-Ae-0	2160	10	800
0-Ae-8	1350	—	225
1-Ae	1600	44	190
4-Ae	2200	46	170
6-Ae	1250	73	20
6 E	1050	75[b]	0
13 E-GT	5350	78[b]	0
13 H-GT	9910	94[b]	0

[a] Fractions of isotactic triads, unless stated otherwise
[b] Fractions of isotactic diads (the corresponding triad fractions have to be smaller)

The equilibrium constants are decreasing with increasing isotacticity of the samples, *i.e.*, they increase with syndiotacticity. The same behavior has been found for measurements in benzene.[40,46]

This type of association can be interpreted most likely as a sort of hindered crystallization. It is assumed that stereoregular sequences of sufficient length can come together laterally and form a cluster or fringed micelle. Because the sequences are rather short, however, the "crystallization" cannot proceed to more extended ordered structures.

This view is supported by IR-spectroscopic determinations of the helix content of a practically 100% syndiotatic polypropylene in dilute benzene solutions.[46] The helix content decreased with increasing temperature as did the tendency towards association (Figure 13). It is very likely that in this case the tendencies to undergo intramolecular association between nearest neighbors (helix formation) and between segments of different molecules (association) go hand in hand (see also Ref. 47).

6 INFLUENCE OF SOLVENT

Hydrophilic solute groups in a hydrophobic solvent, or hydrophobic solute groups in a hydrophilic solvent are often considered necessary prerequisites for

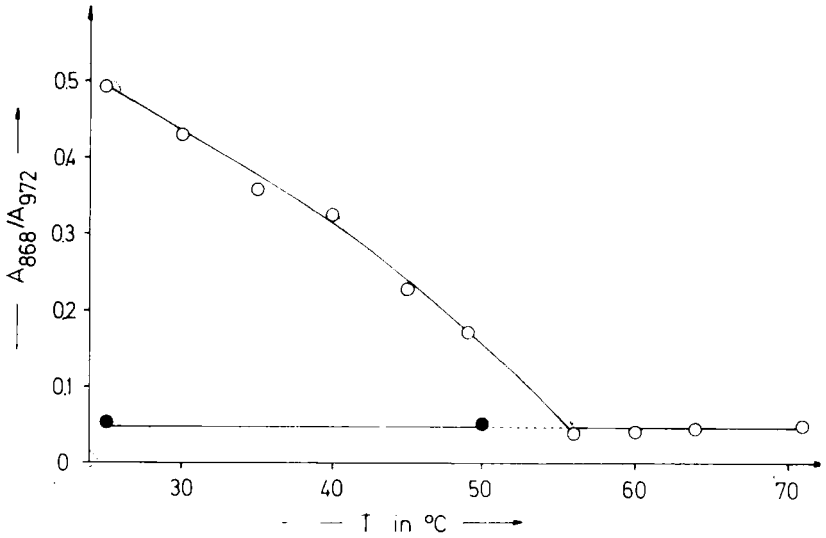


FIGURE 13 Temperature dependence of relative absorbance A_{868}/A_{972} for polypropylene 16 GT in benzene (○) and in carbontetrachloride (●) (from Ref. 46).

the association of the solute. The association of the hydrocarbon polypropylene in solvents like benzene or carbontetrachloride is ruling out immediately such view as the sole cause for association. Replacement of the hydrophilicity/hydrophobicity concept by a concept based on polarity does not help either to establish a general explanation for the solvent influence on association behavior, because benzene and carbontetrachloride exhibit about the same polarity but behave quite differently as associogenic solvents in the case of polypropylene.

Thermodynamic data provides better information on the actual role of solvents in associating systems. The association of polypropylene in bromobenzene was shown to be accompanied by an increase of entropy.[40] Two processes might be responsible for this behavior: solvophobic bonding and/or desolvation.

Table IV shows the variation of equilibrium constants of association of a polypropylene with the type of the solvent. It is interesting to note that the equilibrium constant is highest in benzene which has a tendency to form stacked associates of benzene molecules. The equilibrium constant is by far lower in carbontetrachloride which has no inherent order. Cyclohexane molecules form with themselves weak complexes. The equilibrium constants seem thus to be influenced by the order of the solvent. The situation seems to be similar to the so-called hydrophobic bonding[48] or hydrophobic groups in water. The introduction of a hydrophobic group into the ordered solvent water will lead

to an iceberg formation around the hydrophobic group. The order of the water thus increases. Association of hydrophobic groups destroys a part of the iceberg: the order decreases and the entropy increases. Because the effect is based on changes of order in a solvent, it should be a general effect for all ordered solvents.

TABLE IV

Influence of solvent structure on the association of polypropylene 0-Ae-0 (see Table III) at 37°C (from Ref. 40)

Solvent	${}^{n}K_{o}$ $dm^3\ mol^{-1}$
Benzene	82 000
Toluene	10 600
Cyclohexane	4100
Methylcyclohexane	3000
Carbon tetrachloride	800
Bromobenzene	330
Trichloroethylene	230

Desolvation might be another driving force for association. If segments of two dissolved macromolecules are coming together, many solvating molecules may be released per macromolecule. This situation is different from the one in low molecular weight chemistry where only few solvent molecules are released in an association process. In the latter case, the entropy increasing effect of association can be easily outweighed by the loss of translational entropy. Direct studies of solvation and desolvation of synthetic macromolecules are missing, however.

7 STRUCTURE OF THE ASSOCIATES

The associates of detergent and protein molecules normally exhibit compact structures. On the other hand, the association via endgroups very often leads to loose structures. The concentration dependence of apparent molecular weights (and other association dependent quantities) of detergents and proteins can be described by the model of closed association, whereas the latter follows the pattern of open association. One is thus tempted to conclude that compact structures and closed association on one hand and loose structures and open association on the other go hand in hand.

This conclusion is dangerous because there is at least one exception. Poly(γ-benzyl-L-glutamates) undergo a closed association in many solvents[16] and solvent mixtures.[49] In these systems, the association proceeds via the

endgroups—and only the endgroups—because the linear relationship between the Gibbs free energy of association per mole repeat unit and the reciprocal number average molecular weight of the unimers passes through the origin (Figure 14). The poly(γ-benzyl-L-glutamate) molecules remain in the helix conformation (as shown by ORD), whereas the associates behave as if they form random coils. Closed association as an all-or-none process and an association via the endgroups seem to exclude each other at the first moment, because the latter normally leads to all types of multimers if the association of an associogenic group is not influenced by the presence of another.

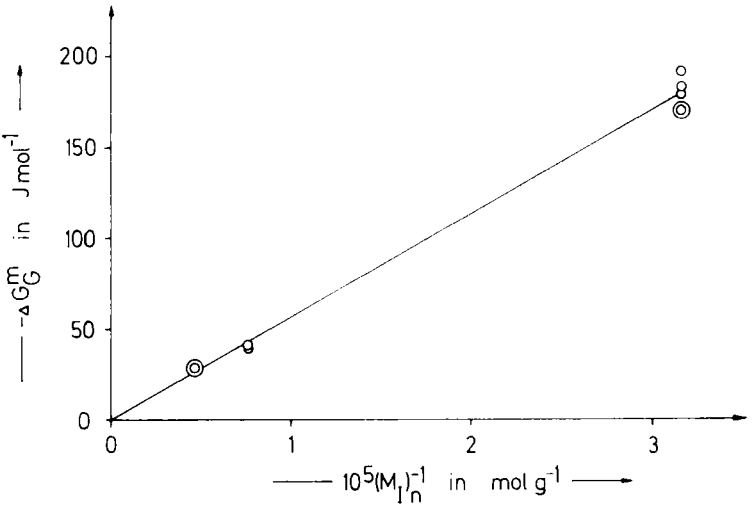


FIGURE 14 Molecular weight dependence of Gibbs energy of association per mole constitutional repeat unit of poly(γ-benzyl-L-glutamates) of different molecular weights in various solvents at 25°C (from Ref. 49).

The behavior of the poly(γ-benzyl-L-glutamates) can be explained by cyclic associates. Cyclization is very well known to dominate over chain formation in chemical reactions in very dilute solutions. The twisted rings of these associates will assume the shape of a random coil, whereas the unimer molecules themselves may well stay in their native helix conformation. Because IR and NMR measurements at oligomeric poly(γ-benzyl-L-glutamates) have shown the association to occur largely by hydrogen bond formation,[50] the ease of formation of these rings will be influenced by the bond angle of the hydrogen bonds. Rings composed of few unimer units possess unfavorable bond angles. Indeed, the Gibbs energy of association per multimer is approaching an asymptote at high degrees of association (great number of unimer molecules in the multimer) (Figure 15). At $N = 5$, a sudden break occurs. Extrapolation of

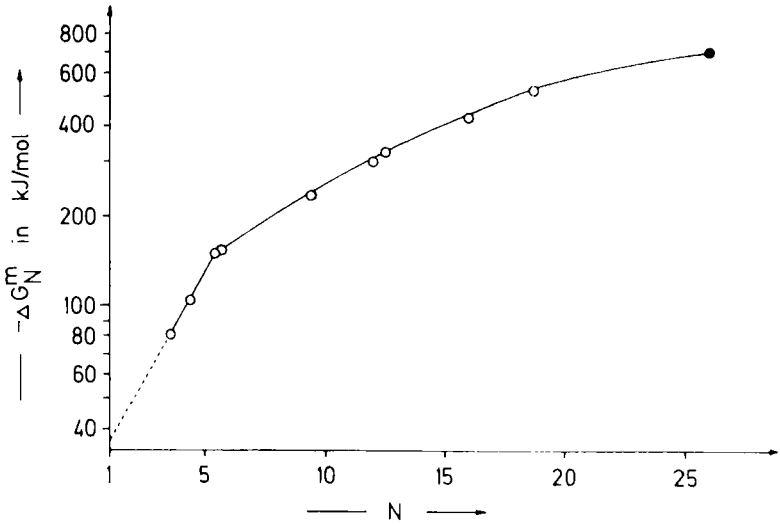


FIGURE 15 Relationship between Gibbs energy of association per mole multimer of poly(γ-benzyl-L-glutamates) of various molecular weights and the association number N in different solvents (from Ref. 49).

the Gibbs energies to $N \to 1$ leads to a $\Delta G_N = -33.4\,\text{kJ mol}^{-1}$ ($-8\,\text{kcal mol}^{-1}$). This gives a value of -16.7 kJ mol^{-1} per endgroup which coincides well with the figures normally given for the energy of hydrogen bonds. One would, furthermore, expect a competition for hydrogen bonds between certain solvents and the endgroups. An influence of the relative permittivity (dielectric constant) on the degree of association has been found indeed.[49]

8 CONCLUSIONS AND OUTLOOK

We now have the mathematical apparatus to investigate the intermolecular association behavior of polymolecular synthetic macromolecules. The basic types of multimerization are well known, too. In many cases, the sensitivity of the experiments is, however, not good enough to distinguish between the different types of multimerization.

The relative contribution of intramolecular associations is less well known. Information about intramolecular associations can be expected in principle from the study of second virial coefficients. The theory of the second virial coefficients of associating systems is, however, in its very first beginning at present. This is not astonishing if one considers the numerous attempts to establish a theory of second virial coefficients of non-associating random coils. Spectroscopic data may help in addition to distinguish between inter- and intramolecular multimerizations.

Viscometry is of little value for the quantitative evaluation of associating systems unless the thermodynamic data are known. Viscometry is even not well suited to detect multimers or distinguish between different types of multimerization.

The influence of constitution, configuration and conformation of the dissolved macromolecules on the multimerization behavior certainly deserves more studies. The difficulty here is to select a proper synthesis because predictions on structure/association behavior relationships are difficult to make at the present time. At present, the study of structural influences on multimerization resembles much more a gamble than a science.

The apparent effects of solvent structure on certain multimerizations are very interesting. They deserve a more thorough study.

References

1. H. Staudinger, *Die hochmolekularen organischen Verbindungen*, Springer, Berlin (1932).
2. M. L. Huggins, *J. Chem. Phys.* **9,** 440 (1941).
3. P. J. Flory, *J. Chem. Phys.* **9,** 660 (1941); **10,** 51 (1942).
4. P. M. Doty, H. Wagner, and S. Singer, *J. Phys. Colloid Chem.* **51,** 32 (1947).
5. P. M. Doty and E. Mishuck, *J. Amer. Chem. Soc.* **69,** 1631 (1947).
6. F. F. Nord, M. Bier, and S. N. Timasheff, *J. Amer. Chem. Soc.* **73,** 289 (1951).
7. H.-G. Elias and R. Bareiss, *Chimia (Aarau)* **21,** 53 (1967).
8. H.-G. Elias, in *Light Scattering from Polymer Solutions* (Edited by M. B. Huglin), Academic Press, London and New York (1972), Chapter 9.
9. E. A. Guggenheim, *Trans. Faraday Soc.* **56,** 1159 (1960).
10. M. Davies, in *Hydrogen Bonding* (Edited by D. Hadzi and H. W. Thompson), Pergamon Press, London (1959), p 560.
11. H.-G. Elias, *Helv. Chim. Acta* **48,** 1018 (1965).
12. W. Borchard, G. Kalawrytinos, B. Mohadjer, M. Pyrlik, and G. Rehage, *Angew. Makromol. Chem.* **29/30,** 471 (1973).
13. W. G. McMillan and J. E. Mayer, *J. Chem. Phys.* **13,** 276 (1945).
14. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y. (1953), p 523 ff.
15. B. H. Zimm, *J. Chem. Phys.* **14,** 164 (1946).
16. J. Gerber and H.-G. Elias, *Makromol. Chem.* **112,** 142 (1968).
17. G. V. Schulz, *Z. Naturforsch.* **2A,** 348 (1947).
18. L. Onsager, *Ann. N.Y. Acad. Sci.* **51,** 627 (1949).
19. J. Gerber, *Ph.D. Thesis*, ETH Zurich, Switzerland, 1968.
20. L. Pauling, R. B. Corey, and H. R. Branson, *Proc. Nat. Acad. Sci. U.S.* **37,** 205 (1951); L. Pauling and R. B. Corey, *Proc. Nat. Acad. Sci. U.S.* **37,** 235 (1951).
21. P. Rohrer and H.-G. Elias, *Makromol. Chem.* **151,** 281 (1972).
22. P. Doty, M. Gellert, and B. Rabinovitch, *J. Amer. Chem. Soc.* **74,** 2065 (1952).
23. E. T. Adams, Jr., *Biochemistry* **4,** 1646 (1965).
24. T. L. Hill and Y.-D. Chen, *Biopolymers* **12,** 1285 (1973).
25. J. Feisst and H.-G. Elias, *Makromol. Chem.* **82,** 78 (1965).
26. H.-G. Elias and H. Lys, *Makromol. Chem.* **96,** 64 (1966).
27. H.-G. Elias, *Makromoleküle*, 2nd ed., Hüthig and Wepf, Basel (1972), p 206.
28. K. E. Van Holde and G. P. Rossetti, *Biochemistry* **6,** 2189 (1967).
29. E. T. Adams, Jr., *Fractions* **3,** 1 (1967) (issued by Beckman Instruments, Spinco Div., Palo Alto, Calif.).
30. D. F. Waugh, *Advan. Protein Chem.* **9,** 325 (1954).

31. F. J. Reithel, *Advan. Protein Chem.* **18,** 123 (1963).
32. K. Šolc and H.-G. Elias, *J. Polymer Sci., Phys. Ed.* **11,** 137 (1973).
33. H. Langbein, *Kolloid-Z.Z. Polym.* **203,** 1 (1965).
34. E. R. Jones and C. R. Bury, *Phil. Mag.* **4,** 841 (1927).
35. H. F. Fischer, D. G. Cross, and L. L. McGregor, *Nature* **196,** 895 (1962).
36. J. G. Watterson and H.-G. Elias, *Makromol. Chem.* **157,** 237 (1972).
37. J. G. Watterson, H.-R. Lässer, and H.-G. Elias, *Kolloid-Z.Z. Polym.* **250,** 64 (1972).
38. M. L. Huggins, *J. Amer. Chem. Soc.* **64,** 2716 (1942).
39. W. Kuhn, P. Moser, and H. Majer, *Helv. Chim. Acta* **44,** 770 (1961).
40. H.-G. Elias and H. Dietschi, *Makromol. Chem.* **105,** 102 (1967).
41. Q. A. Trementozzi, R. F. Steiner, and P. Doty, *J. Amer. Chem. Soc.* **74,** 2070 (1952).
42. H.-G. Elias, *Makromol. Chem.* **103,** 214 (1967).
43. P. Vogt and H.-G. Elias, *Makromol. Chem.* **157,** 257 (1972).
44. H.-G. Elias and P. Vogt, *Makromol. Chem.* **157,** 263 (1972).
45. A. N. Fletcher, *J. Phys. Chem.* **73,** 2217 (1969).
46. B. H. Stofer and H.-G. Elias, *Makromol. Chem.* **157,** 245 (1972).
47. A. V. Tobolsky, *J. Phys. Chem.* **68,** 2267 (1964).
48. W. Kauzmann, *Advan. Protein Chem.* **14,** 1 (1959).
49. H.-G. Elias and J. Gerber, *Makromol. Chem.* **112,** 122 (1968).
50. P. Rohrer, *Ph.D. Thesis*, ETH Zurich, Switzerland, 1971.

DISCUSSION

Prof. S. Krause (*Rensselaer Polytechnic Institute, Troy, New York*): Near the beginning of your talk, you warned us about the extrapolation of osmotic pressure and light scattering data to infinite dilution, especially if the data were obtained at fairly high concentrations. Do you have any guidelines to give us concerning the concentration range in which such data should be obtained?

Prof. H.-G. Elias: Data should be taken in the lowest concentration range possible, the range varying according to polymer structure, multimerization, polymer-solvent interaction and sensitivity of the method used. It is here where you can see the differences in the solution behavior and where you can avoid the pitfalls of extrapolations. I admit that this is not a good practical advice, but it is the only one I can give because the situation might be very complicated.

Prof. H. Sund (*University of Constance, Constance*): Each nomenclature has its advantage and its disadvantage, and one can discuss the different systems. However, there should be no discussion about the expression "polymerization" in connection with the association of biopolymers. Polymerization denotes an irreversible process which links the unimers covalently together. Therefore it is completely wrong to use the term "polymerization" for reversible association phenomena discussed in this and in my paper.

Prof. H.-G. Elias: I agree wholeheartedly that the term "polymerization" should not be used for the formation of "physical molecules", *i.e.*, particles held together by physical bonds. Polymerization should be used only for the

formation of macromolecules where the units are held together by either covalent, coordinative or electron-deficient bonds. Polymerization can be reversible, however (the so-called living polymerizations).

Prof. H. Sund: According to one of your slides the closed association of poly(γ-benzyl-L-glutamate) (PBG) yields a ring structure containing nine unimers. Is the number of unimers in the multimer always exactly nine? Does the number depend on the molecular weight of PBG? And, finally, is it possible that the multimer is composed of two layers like the glutamate dehydrogenase oligomer or the TMV disk?

Prof. H.-G. Elias: The ring structure of the multimers of PBG seems to be present in certain solvents only, especially in certain solvent/nonsolvent mixtures the composition of which can be determined by cloud-point titration. The multimerization number N varies with the solvent/nonsolvent mixture, the molecular weight of the unimers and the temperature. We have found no indication for a layer structure. The multimer structure is best described by rings made up of rigid rods, the rings being twisted to give random coil-like structures, provided the multimerization number is high enough.

Prof. A. J. Hopfinger (*Case Western Reserve University, Cleveland, Ohio*): What is the "organizing" force which is necessary to overcome the entropy barrier in order that ring-formation results from the end-to-end association in poly(γ-benzyl-L-glutamate) and related polymers?

Prof. H.-G. Elias: The experiments were carried out in very dilute solutions. Under these circumstances the intra-association is more probable than the inter-association, and this is for entropy reasons.

Dr. R. F. Boyer (*Dow Chemical Company, Midland, Michigan*): The glass temperature, T_g, of most polymers decreases with decreasing molecular weight according to

$$T_g = T_g^{\infty} - K_g M^{-1}$$

where T_g^{∞} is the limiting T_g for infinite molecular weight and K_g is a constant, lying in the range of $2\text{–}50 \times 10^4$.[1] It is usually assumed that end groups contribute additional free volume and thereby cause a lowering of T_g with decreasing molecular weight. Now K_g is zero for poly(propylene oxide)[2,3] and poly(butylene oxide)[2] having hydroxyl end groups but is finite though small for poly(propylene oxide) with methylether end groups. We have suggested elsewhere[4] that hydroxyl end group association, such as you have found for low molecular weight ethylene glycols, might be sufficiently strong in bulk polymers so that these OH terminated polymers are essentially lacking in effective end groups. The normal behavior of ether-blocked end groups is

consistent with this view. Do you think that your method of treating association of end groups might be extended to bulk polymer, *i.e.*, very high concentrations, with the usual assumption that a bulk polymer is a Θ-solvent for any of its own polymer chains?

Prof. H.-G. Elias: Yes. Neutron scattering of "solutions" of normal polymers in their deuterated polymer analogs should be a good method to get information on concentration dependence of apparent molecular weights in the bulk (glassy) state. [For the method see R. G. Kirste, W. A. Kruse, and J. Schelten, *Makromol. Chem.* **162,** 299 (1972)].

Prof. G. Challa (*State University of Groningen, Groningen*): You indicated that poly(methyl methacrylate) and poly(2-hydroxyethyl methacrylate) do show intermolecular association, whereas poly(vinyl acetate) and poly(vinyl alcohol) do not because of intramolecular hydrogen bonding in poly(vinyl alcohol). I think that the α-CH_3 groups in the first pair also play an important role in the association, and the second pair does not possess such groups. Moreover, the comparison of poly(methyl methacrylate) and poly(vinyl acetate) may be less suitable since the ester side groups in both polymers produce dipoles with opposite directions.

Prof. H.-G. Elias: I did not speak about the four homopolymers you mentioned but about the copolymers of methyl methacrylate and 2-hydroxyethyl methacrylate on one hand, and copolymers of vinyl acetate and vinyl alcohol on the other hand. Furthermore, my comments were restricted to certain solvents. But you are right, the α-CH_3 group in poly(methyl methacrylate) may play a role in association. We found that the tendency towards association *decreases* with increasing hydroxyl content of the poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) in solvents like butanone [P. Vogt and H.-G. Elias, *Makromol. Chem.* **157,** 257 (1972)]. Association of poly(methyl methacrylate) has been furthermore observed in diamyl ketone [W. R. Moore and M. Murphy, cited in W. R. Moore, *Progr. Polymer Sci.* **1,** 3 (1967)]. My remarks in the lecture were restricted to solvents like acetone, dioxane and dimethylformamide.

Discussion references

[1] For a recent summary article see G. Pezzin, F. Zilio-Grandi, and P. Sanmartin, *Europ. Polym. J.* **6,** 1053 (1970).
[2] J. A. Faucher, *J. Polymer Sci. B* **3,** 143 (1965).
[3] G. Allen, C. Booth, M. N. Jones, D. J. Marks, and W. D. Taylor, *Polymer* **5,** 547 (1964).
[4] R. F. Boyer, manuscript on *Glass Temperature—Molecular Weight Considerations for Organic Polymers*, in preparation.