

Phase Separation of Polyelectrolyte Solutions

I. MICHAELI,* *Polymer Department, Weizmann Institute of Science, Rehovot*
 J. TH. G. OVERBEEK and M. J. VOORN, *van't Hoff Laboratory,*
University of Utrecht, Netherlands

Solutions of biocolloids and of synthetic polyelectrolytes, like those of uncharged macromolecules, may separate into two liquid phases. This phase separation, called *complex coacervation* by Bungenberg de Jong and Kruyt,¹ will be explained in the present paper by considering the entropy of dilution and the electrostatic attraction among the charged particles. We shall present general outlines for a quantitative approach, and discuss some of the implications. Detailed treatments of specific cases will be presented separately.^{2,3}

The condition for a solution to separate into two phases in equilibrium, at constant temperature, T , and pressure, P , may be derived theoretically⁴ from an expression for the free enthalpy (Gibbs free energy), G , as a function of composition. For such an equilibrium to exist it is required that the chemical potentials μ_i of each component i , be equal in both phases:

$$\mu_i^{\text{I}} = \mu_i^{\text{II}} \quad (1)$$

where I and II designate the dilute and concentrated phases, respectively. It is convenient to introduce a function \bar{G} , defined as the free enthalpy per unit volume:

$$\bar{G} = G/V \quad (2)$$

The function \bar{G} is an intensive property of the system; for constant T and P , it is dependent on composition only. With the aid of \bar{G} , the condition given by equation (1) may be transformed, in the case of constant molal volumes, into:

$$\left(\frac{\partial \bar{G}}{\partial \varphi_i} \right)_{\substack{\varphi_j \\ j \neq i \\ j \neq 1}}^{\text{I}} = \left(\frac{\partial \bar{G}}{\partial \varphi_i} \right)_{\substack{\varphi_j \\ j \neq i \\ j \neq 1}}^{\text{II}} \quad (3)$$

where φ_i is the volume fraction of component i . If the number of molecules of the i th component is designated by n_i , and the molecular volume by \bar{v}_i , then φ_i is given by:

$$\varphi_i = n_i \bar{v}_i / V \quad (4)$$

* On visit at the van't Hoff Laboratory, University of Utrecht.

Clearly:

$$\sum_i \varphi_i = 1 \quad (5)$$

Equation (3) may be derived as follows: For changes at constant T and P , G may be represented by the expression:

$$G = \sum_i n_i \mu_i \quad (6)$$

or, introducing (2) and (4):

$$\bar{G} = \sum_i (\varphi_i \mu_i / \bar{v}_i) \quad (7)$$

From (7) it follows that:

$$d\bar{G} = \sum_i \frac{\varphi_i}{\bar{v}_i} d\mu_i + \sum_i \frac{\mu_i}{\bar{v}_i} d\varphi_i \quad (8)$$

Since, according to Gibbs-Duhem:

$$\sum_i \frac{\varphi_i}{\bar{v}_i} d\mu_i = \frac{1}{V} \sum_i n_i d\mu_i = 0$$

equation (8) simplifies to:

$$d\bar{G} = \sum_i (\mu_i / \bar{v}_i) d\varphi_i \quad (9)$$

It follows from equation (5) that, for changes at constant φ_j , when $j \neq i$, and $j \neq 1$:

$$d\varphi_i = -d\varphi_1 \quad (10)$$

Therefore, for such changes we find from equations (9) and (10):

$$(\partial \bar{G} / \partial \varphi_i)_{\substack{j \neq i \\ j \neq 1}} \varphi_j = (\mu_i / \bar{v}_i) - (\mu_1 / \bar{v}_1) \quad (11)$$

Consequently equation (3) is obtained from (1) and (11).

In order to obtain a theoretical expression for the free enthalpy, G , as a function of the composition of the system, a suitable model must be chosen. For polyelectrolyte solutions the most simple cases are those in which the free enthalpy may be considered as the sum of an entropy of mixing term, G_s , and an electrical free energy, G_e , the interactions due to van der Waals forces (van Laar heat term) being neglected to a first approximation. While the latter may readily be introduced, we shall show that the electrical interaction only may suffice to bring about phase separation.

We shall, therefore, consider the above case where:

$$G = G_s + G_e \quad (12)$$

or:

$$\bar{G} = \bar{G}_s + \bar{G}_e \quad (13)$$

Introducing (13) into (3), the requirement of equilibrium becomes:

$$(\partial \bar{G}_s / \partial \varphi_i)^{\text{II}} - (\partial \bar{G}_s / \partial \varphi_i)^{\text{I}} = (\partial \bar{G}_e / \partial \varphi_i)^{\text{I}} - (\partial \bar{G}_e / \partial \varphi_i)^{\text{II}} \quad (14)$$

$$\text{or:} \quad (\partial \Delta \bar{G}_s / \partial \varphi_i) = -(\partial \Delta \bar{G}_e / \partial \varphi_i) \quad (15)$$

where $\Delta \bar{G} = \bar{G}_{\text{II}} - \bar{G}_{\text{I}}$.

Using second derivatives, the equilibrium conditions (15) may be put in the following form:

$$\int_{\text{I}}^{\text{II}} \frac{\partial^2 \bar{G}_s}{\partial \varphi_i^2} d\varphi_i = - \int_{\text{I}}^{\text{II}} \frac{\partial^2 \bar{G}_e}{\partial \varphi_i^2} d\varphi_i \quad (16)$$

The entropy term in equation (16) usually satisfies the inequality $\partial^2 \bar{G}_s / \partial \varphi_i^2 > 0$; this means that the entropy of mixing counteracts phase separation.⁴ It will be shown below, however, that the electrical free energy term, given by the integrand on the right-hand side of equation (16), has the opposite sign, $\partial^2 \bar{G}_e / \partial \varphi_i^2 < 0$. The electrical free energy will thus be seen to favor phase separation. Consequently coacervation occurs if the electrical term is large enough or the entropy term small enough (eq. 16).

We shall examine the electrical effect for two special cases. In one case the electrical free energy will be represented by the simple Debye-Hückel expression; in the other case it will be represented by the expression of Lifson and Katchalsky⁵ that was derived for a solution of charged parallel rods with their counterions.

Considering now the Debye-Hückel approximation for univalent electrolytes, the electrical free energy per unit volume is given by:

$$\bar{G}_e = G_e / V = \kappa^3 k T / 12\pi = -B (\sum_j \alpha_j \varphi_j)^{3/2} \epsilon^{-3/2} T^{-1/2} \quad (17)$$

where κ is the inverse radius of the ionic atmosphere, k is the Boltzmann constant, T is the absolute temperature, ϵ is the dielectric constant, α_j is the number of univalent charges carried by unit volume of species j , and B is a proportionality constant given by $B = 2/3\pi^{1/2} k^{-1/2} e^3$, e being the charge of an electron.

It follows from equation (17) that:

$$\frac{\partial^2 \bar{G}_e}{\partial \varphi_i^2} = - \frac{3}{4} \frac{B \alpha_i^2}{\epsilon^{3/2} T^{1/2}} (\sum_j \alpha_j \varphi_j)^{-1/2} < 0 \quad (18)$$

Equation (18) shows that the electrical free energy according to the Debye-Hückel expression favors phase separation. However, in the case of solutions containing small ions only, we find that at reasonable concentrations phase separation will not take place, since the electrical interactions cannot counterbalance the high entropy of mixing of the small ions.

In polyelectrolyte solutions, however, the electrical interactions may be larger, and the entropy effect will be smaller, so that coacervation may take place.

Such is the case for a two-component system that consists of a parallel arrangement of electrically charged cylindrical rods in solution with an equivalent amount of counterions, but without additional electrolytes. Ac-

cording to Lifson and Katchalsky⁵ the electrical free energy of this system is given by:

$$G_e = n_m F_e \quad (19)$$

where n_m is the number of monomer units in the system, and F_e is the electrical free energy per monomer. Introducing (4) into (19), we obtain:

$$\bar{G}_e = \frac{\varphi_m}{\bar{v}_m} F_e = \frac{\varphi_{\text{polymer}}}{\bar{v}_m} F_e \quad (20)$$

where m represents the monomer.

Differentiating equation (20), we obtain for the electrostatic term:

$$\frac{\partial^2 \bar{G}_e}{\partial \varphi_{\text{polymer}}^2} = \frac{1}{\bar{v}_m \varphi_{\text{polymer}}} \left[\frac{\partial F_e}{\partial \ln \varphi_{\text{polymer}}} + \frac{\partial^2 F_e}{(\partial \ln \varphi_{\text{polymer}})^2} \right] \quad (21)$$

For the free enthalpy of mixing, G_s , we may assume that, for this system, it is given by the accepted expression, when the latter contains only terms for the solvent and for the small counterions:

$$\bar{G}_s = \frac{G_s}{V} = \frac{\varphi_1}{\bar{v}_1} kT \ln \varphi_1 + \frac{\varphi_2}{\bar{v}_2} kT \ln \varphi_2 \quad (22)$$

Here φ_1 is the volume fraction of the solvent, and φ_2 , that of the counterions.

Differentiating equation (22) with respect to φ_{polymer} , when φ_{polymer} is the volume fraction of the electroneutral polymer component ($\varphi_{\text{polymer}} = \varphi_2 + \varphi_{\text{rods}}$), we obtain:

$$\frac{\partial^2 G_s}{\partial \varphi_{\text{polymer}}^2} = \frac{kT}{\bar{v}_1 \varphi_1} + \frac{kT}{\bar{v}_{\text{polymer}} \varphi_{\text{polymer}}} \quad (23)$$

Combining equations (21) and (23) we now find that:

$$(\partial^2 \bar{G}_e / \partial \varphi_{\text{polymer}}^2) + (\partial^2 \bar{G}_s / \partial \varphi_{\text{polymer}}^2) < 0$$

if F_e is estimated according to Lifson and Katchalsky for the case of divalent counterions and reasonable charge densities (see L. & K., Fig. 4, and their equations (27) and (7), for $\nu = 2$). In this case, therefore, coacervation will take place.

For univalent counterions, however, and for low fixed charge densities, the electrical effect is still too low to counterbalance the effect of the entropy of mixing.

It might be noted here that experimental data on polymethacrylate solutions⁶ are in accord with the above conclusions. Numerous other cases of so-called *autocomplex coacervation*, described by Bungenberg de Jong⁷ also show that polyions are coacervated by counterions of high valency, but not by those of low valency.

In a similar approach, Langmuir⁸ explained coacervation of charged-colloid solutions. He assumed that the electrical free energy in his model

was given by the Debye-Hückel approximation. Unfortunately such an approximation is not valid for the systems he chose.⁹ The expression of Lifson and Katchalsky we have used above contains no inherent similar approximation.

However, polyelectrolyte systems could be envisaged where the electrical free energy may be approximated by the Debye-Hückel expression. Such for example is the case of solutions containing two types of macroions of opposite charge together with small inorganic ions; the macroions are supposed to be intermixed flexible coils with a number of univalent charges distributed along the coil and with a charge density sufficiently low for the charges to be arranged in the solution independently of the arrangement of the coils. In that case the electrical free energy, G_e , may be estimated using the Debye-Hückel theory, while the entropy term, G_s , may be given by the single Flory-Huggins expression.¹⁰ The former is represented by the equation (17), which has already been written in a form that takes into account the presence of more than one univalent charge per coil. The latter is given by:

$$\bar{G}_s = \frac{G_s}{V} = \frac{kT}{\bar{v}_1} \left(\varphi_1 \ln \varphi_1 + \sum_j \frac{\varphi_j}{r_j} \ln \varphi_j \right) \quad (24)$$

where the solvent is indicated by 1, and the ionic species by j ; r_j is the ratio of the molecular volume of component j to that of the solvent. Differentiating equation (24) we obtain:

$$\left(\frac{\partial^2 \bar{G}_s}{\partial \varphi_i^2} \right)_{\substack{j \neq i \\ j \neq 1}} \varphi_j = \frac{kT}{\bar{v}_1} \left(\frac{1}{\varphi_1} + \frac{1}{r_i \varphi_i} \right) \quad (25)$$

It follows directly from the chosen model with the quasiindependent charges that the electrical interaction is independent of the molecular weight of the polyions. This can be seen from equation (18) in which the parameter r does not occur. The entropy contribution, however, is particularly small as far as the polyion terms are concerned, on account of the factor $1/r$. In these systems, therefore, phase separation may take place. When this occurs, the polyions will strongly accumulate in one phase, the coacervate, but in the same system the microions will be more evenly distributed.

The above implies that small ions affect phase separation mainly through their effect on $\partial^2 \bar{G}_e / \partial \varphi_{\text{polymer}}^2$; if increase of salt concentration makes the latter less negative, as is the case in the above model (see eq. 18), addition of salt will decrease the tendency for phase separation.

Alcohol, acetone, or similar substances of low dielectric constant affect phase separation through the influence of ϵ on $\partial^2 \bar{G}_e / \partial \varphi_{\text{polymer}}^2$. In equation (18), as is generally the case in electrostatic energy terms, the dielectric constant appears in the denominator. Decrease in ϵ therefore makes $\partial^2 \bar{G}_e / \partial \varphi_{\text{polymer}}^2$ more negative, thus increasing the tendency toward coacervation.

So, quite a number of experimental features of coacervation (influence of molecular weight (r), charge density (α), added salts, organic substances, solvent content of coacervate) are qualitatively explained by this theory when only very general properties of G_s and G_e are used. The quantitative results calculated from equations (17) and (24) are also quite reasonable.²

The effect of 1-1 electrolyte on complex coacervation is shown in Figure 1. This phase diagram shows the salt-effect calculated for a *symmetrical* case. In this most simple case the salt solution contains *equivalent* amounts of polycations P^+ and polyanions Q^- ; the macroions are supposed to be *identical* except for the sign of their charge, and the same is assumed for the microions K^+ and A^- . It follows from symmetry considerations that the above system may be treated as a three-component system, the components being H_2O , K^+A^- , and the polymer P^+Q^- . The diagram has been calculated for $r_{K^+} = r_{A^-} = 1$; $r_{P^+} = r_{Q^-} = 1000$, $\bar{v}_1 = 18/6 \times 10^{23}$ cc. per molecule, $\alpha = 5 \times 10^{21}$ electron charges per cc., and $T = 298^\circ K$.

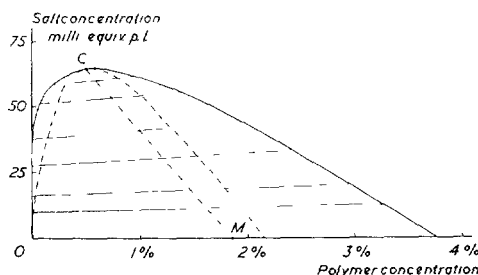


Fig. 1. Phase diagram for complex coacervation (symmetrical case).

For this system it is seen from Figure 1 that addition of salt makes the compositions of the two phases approach each other, while addition of sufficient salt will bring about complete mixing. The salt content, as given by the node lines, is seen to be higher in the coacervate. This slight accumulation of salt in the coacervate phase predicted by theory was hitherto unknown, and has been verified by additional experiments.² (The broken curve in Figure 1 represents the so-called spinodal and CM is the rectilinear diameter; see reference 2).

The treatment of phase separation as outlined above may evidently be extended to unsymmetrical multicomponent systems. For such cases it may be convenient to treat each ionic species as an independent component. For such treatment the chemical potentials should be substituted by electrochemical potentials, and equation (1) should be replaced by:

$$\mu_i^I = \mu_i^{II} + e_i\psi \quad (26)$$

where ψ represents the difference in electrical potential between the two phases and e_i is the charge of the species i .

We have now an additional variable, ψ , but also the additional equation

of electroneutrality. Such an approach has indeed been applied² to the unsymmetrical case of a solution containing polyacid and polybase in an arbitrary ratio, and it was possible to calculate many characteristic properties of such systems, known from experiment.

Grateful acknowledgment is made to the Philips Co. (Eindhoven) for a grant which made it possible for one of us (I. M.) to participate in this work.

References

1. H. G. Bungenberg de Jong and H. R. Kruyt, *Proc. Acad. Sci. Amsterdam*, **32**, 849 (1929). See also L. W. J. Holleman, H. G. Bungenberg de Jong and R. S. Tjaden Modderman, *Kolloid Beih.*, **39**, 334 (1934).
2. M. J. Voorn, *Thesis*, Utrecht, 1956, *Rec. trav. chim.*, **75**, 317, 405, 427, 925, 1021 (1956).
3. I. Michaeli, in preparation.
4. H. A. Stuart, *Die Physik der Hochpolymeren*, Vol. II, *Das Makromolekül in Lösung*, Springer, Berlin, 1953.
5. S. Lifson and A. Katchalsky, *J. Polymer Sci.*, **13**, 43 (1954).
6. I. Michaeli, unpublished data.
7. H. G. Bungenberg de Jong in H. R. Kruyt, *Colloid Science*, Vol. II, Elsevier, Amsterdam, 1949, Ch. X.
8. I. Langmuir, *J. Chem. Phys.*, **6**, 893 (1938).
9. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948, p. 195 ff.
10. P. J. Flory, *J. Chem. Phys.*, **12**, 425 (1944).

Synopsis

It is shown theoretically that phase separation may arise in solutions of polyelectrolytes due to electrostatic interactions alone. Two models are considered thermodynamically. In both models the free energy is represented as the sum of an entropy of mixing term and an electrostatic free energy term, while the van der Waals attractions are neglected. In the one model, electrically charged rigid cylindrical rods are in solution with an equivalent amount of counterions but without additional electrolyte. The free electrical energy, in this case, is given by the expression of Lifson and Katchalsky. In the other model the solution contains two types of macroions of opposite charge. The macroions are flexible coils carrying a number of univalent charges, the charge density being sufficiently low. The electrical free energy in this case may be approximated by the Debye-Hückel expression. For both models, it is shown that the decrease in the electrical free energy in a phase separation can, at given temperature and pressure, more than compensate for the increase in the entropy of mixing term. The effects of polymer concentration, dielectric constant, charge density, and salt content follow directly from the thermodynamic treatment of the models.

Résumé

On montre théoriquement qu'une séparation de phase peut se produire dans les solutions de polyélectrolytes, uniquement par suite d'interactions électrostatiques. Deux modèles sont considérés thermodynamiquement. Dans les deux modèles l'énergie libre est représentée comme la somme d'une entropie de mélange et d'une énergie libre électrostatique, tandis qu'on néglige les attractions de van der Waals. Dans l'un des modèles, des bâtonnets rigides électriquement chargés sont présents en solution avec une quantité équivalente d'ions de signe contraire, toutefois sans électrolyte en excès. L'énergie libre électrique est donnée dans ce cas par l'expression de Lifson et Katchalsky. Dans l'autre modèle la solution contient deux types de macro-ions de charge contraire.

Les ions sont des pelotes flexibles portant un nombre de charges univalentes, la densité de charge étant suffisamment faible. L'énergie libre électrique peut dans ce cas être estimée par l'expression de Debye-Hückel. Pour les deux modèles on montre que la diminution d'énergie libre électrique au cours de la séparation de phase peut, à température et pression déterminées, dépasser l'augmentation du terme d'entropie de mélange. Les effets de la concentration en polymère de la constante diélectrique, de la densité de charge et de la teneur en sels résultent directement du traitement thermodynamique des modèles.

Zusammenfassung

Es wird theoretisch gezeigt, dass in Lösungen von Polyelektrolyten Phasentrennung auftreten kann, welche durch elektrostatische Interaktionen allein bedingt ist. Zwei Modelle werden thermodynamisch betrachtet. In beiden Modellen wird die freie Energie als die Summe einer Entropie von Mischungsausdrücken und einem elektrostatischen Frei-Energie-Ausdruck dargestellt, während die van der Waals'schen Anziehungen vernachlässigt werden. In dem einen Model befinden sich elektrisch geladene, steife, zylindrische Stäbchen in Lösung mit einer äquivalenten Menge von Gegenionen, aber ohne zusätzliche Elektrolyte. Die freie elektrische Energie wird in diesem Falle durch den Ausdruck von Lifson und Katchalsky gegeben. In dem anderen Model enthält die Lösung zwei Arten von Makro-Ionen von entgegengesetzter Ladung. Die Hauptionen sind biegsame Windungen, die eine Anzahl von univalenten Ladungen tragen, während die Ladungsdichte niedrig genug ist. Die elektrische freie Energie kann in diesem Falle durch den Ausdruck von Debye-Hückel angenähert werden. Für beide Modelle wird gezeigt, dass die Annahme der elektrischen freien Energie in einer Phasentrennung bei gegebener Temperatur und Druck für die Zunahme in der Entropie der Mischungsausdruckes mehr als kompensieren kann. Die Wirkungen von Polymerkonzentration, dielektrischer Konstante, Ladungsdichte, und Salzgehalt folgen direkt aus der thermodynamischen Berechnung der Modelle.

continued from inside front cover

ELIGIA TURSKA et MARCELI ŁACZKOWSKI: Sur la coacervation des polyamides.....	285
<i>Discussion:</i> C. Mussa, E. Turska.....	295
L. VALENTINE: Interaction of Polyamides with Solvents. I. A Preliminary Survey of the Swelling of Crosslinked Nylon 66 in Various Types of Solvents.....	297
<i>Discussion:</i> A. Charlesby, L. Valentine, M. Magat.....	313
R. M. BARRER, J. A. BARRIE, and J. SLATER: Sorption and Diffusion in Ethyl Cellulose. Part I. History-Dependence of Sorption Isotherms and Permeation Rates.....	315
R. M. BARRER and J. A. BARRIE: Sorption and Diffusion in Ethyl Cellulose. Part II. Quantitative Examination of Settled Isotherms and Permeation Rates.....	331
P. T. MORA: Solution Behavior of Chemically Synthesized Polyglucoses.....	345
<i>Discussion:</i> A. Katchalsky, P. T. Mora.....	354
PETER ALEXANDER and ARTHUR CHARLESBY: Effect of X-Rays and γ -Rays on Synthetic Polymers in Aqueous Solution.....	355
<i>Discussion:</i> M. Magat, A. Charlesby, A. Chapiro, V. Desreux.....	375
ADOLPHE CHAPIRO: Gonflement des copolymères greffés d'acrylonitrile sur le polyéthylène dans le diméthylformamide.....	377
<i>Discussion:</i> A. Banderet, A. Chapiro, G. Smets.....	386
I. ELIEZER and H. J. G. HAYMAN: Mean Square Length and Mean Square Radius of Gyration of 1,4'-Polysaccharides and of Polybutadienes.....	387
<i>Lecture given but not received for publication:</i>	
C. WATTERS, A. HORTH, and M. RINFERT: Heat of Mixing and Partial Specific Volume of Macromolecules in Dilute Solution	
SECTION II. GENERAL BEHAVIOR OF BIOPOLYMER AND POLYELECTROLYTES IN SOLUTION	
ROBERT MACFARLANE, JR., and RAYMOND M. FUOSS: Polyelectrolytes. XII. Conductance of Partially Quaternized Poly-4-vinylpyridine in Methanol-Butan-2-one Mixtures.....	403
<i>Discussion:</i> H. Morawetz, R. M. Fuoss, J. J. Hermans, A. Dobry-Duclaux.....	419
FUMIO OOSAWA: A Simple Theory of Thermodynamic Properties of Polyelectrolyte Solutions.....	421
SHNEIOR LIFSON: On the Additivity of the Configurational and Electrostatic Properties of Polyelectrolytes in Solution.....	431
I. MICHAELI, J. TH. G. OVERBEEK, and M. J. VOORN: Phase Separation of Polyelectrolyte Solutions.....	443
HARRY P. GREGOR and MICHAEL FREDERICK: Potentiometric Titration of Polyacrylic and Polymethacrylic Acids with Alkali Metal and Quaternary Ammonium Bases.....	451
HARRY P. GREGOR, DANIEL H. GOLD, and MICHAEL FREDERICK: Viscometric and Conductometric Titrations of Polymethacrylic Acid with Alkali Metal and Quaternary Ammonium Bases.....	467
IKUMI KAGAWA and HARRY P. GREGOR: Theory of the Effect of Counterion Size upon Titration Behavior of Polycarboxylic Acids.....	477
<i>Discussion:</i> M. Breuer, J. R. Bourdais.....	483
J. BOURDAIS et A. DOBRY-DUCLAUX: Sur l'activité des ions dans les solutions colloïdales. III. Variation du coefficient d'activité des ions compensateurs en fonction de la concentration.....	485
<i>Discussion:</i> H. Morawetz, A. Dobry-Duclaux.....	496
A. DOBRY-DUCLAUX: Sur la notion de l'activité dans les solutions colloïdales.....	499

POLYMER NEWS

The International Union of Pure and Applied Chemistry will hold an International Symposium on Macromolecular Chemistry in Prague, Czechoslovakia, September 9-15, 1957.

The work of the Symposium will be divided into two main divisions:

- (a) physics and physical chemistry of macromolecular products
- (b) polyreactions

Papers may be presented in any language. All papers and discussions will be translated into English and Russian, and possibly into other languages.

For further information, correspondence should be addressed to:

Comité D'Organisation du Symposium IUPAC
5, Technická,
Prague 6
Czechoslovakia

HIGH POLYMERS

A Series of Monographs on the Chemistry, Physics, and Technology of High Polymeric Substances.

Editorial Board: H. MARK, C. S. MARVEL, H. W. MELVILLE, G. S. WHITBY.

Volume I:

COLLECTED PAPERS OF WALLACE HUME CAROTHERS ON HIGH POLYMERIC SUBSTANCES

Edited by H. MARK, *Institute of Polymer Research, Polytechnic Institute of Brooklyn*, and G. STAFFORD WHITBY, *University of Akron, Ohio*. With a biography by Roger Adams, *University of Illinois*.

1940. 479 pages, 38 illus., 51 tables, 2 plates. \$10.50

Volume II:

PHYSICAL CHEMISTRY OF HIGH POLYMERIC SYSTEMS

Second Edition by H. MARK, *Institute of Polymer Research, Polytechnic Institute of Brooklyn*, and A. N. TQBOBSKY, *Frick Chemical Laboratory, Princeton University*.

1950. 520 pages, 155 illus., 107 tables. \$7.50

Volume III:

MECHANISM OF POLYMER REACTIONS

By G. M. BURNETT, *Chemistry Department, The University, Edgbaston, Birmingham, England*.

1954. 509 pages, 86 illus., 110 tables. \$11.00

Volume IV:

NATURAL AND SYNTHETIC HIGH POLYMERS

Second Edition. By K. H. MEYER, *Professor of Organic Chemistry, University of Geneva, Switzerland*.

1950. 411 pages, 186 illus., 80 tables. \$15.00

Volume V:

CELLULOSE AND CELLULOSE DERIVATIVES

In Three Parts. Second completely revised and augmented edition.

Prepared under the editorship of EMIL OTT, HAROLD M. SPURLIN, and MILDRED W. GRAFFLIN, *Hercules Powder Co., Wilmington, Del.*

Part I: 527 pages, 139 illus., 11 tables. \$12.00

Part II: 555 pages, 118 illus., 54 tables. \$12.00

Part III: 556 pages, 127 illus., 41 tables.

With indexes to Parts I-III. \$12.00

Volume VI:

MECHANICAL BEHAVIOR OF HIGH POLYMERS

By TURNER ALFREY, Jr., *Associate Professor of Polymer Chemistry, Polytechnic Institute of Brooklyn*.

1946. 595 pages, 245 illus., 27 tables. \$11.00

Volume VII:

PHENOPLASTS—

Their Structure, Properties and Chemical Technology

By T. S. CARSWELL, *Manager, Research and Development Departments, Commercial Solvents Corp., Terre Haute, Ind.* With the collaboration of Donald S. Herr and Carl H. Whitlock.

1947. 279 pages, 80 illus., 74 tables. \$6.50

Volume VIII:

COPOLYMERIZATION

By TURNER ALFREY, Jr., *Physical Research Laboratory, The Dow Chemical Co., Midland, Mich.*, JOHN J. BOHRER, *International Resistance Co., Philadelphia, Pa.*, and HERMAN MARK, *Institute of Polymer Research, Polytechnic Institute of Brooklyn, N. Y.*

1952. 279 pages, 77 illus., 41 tables. \$8.00

Volume IX:

EMULSION POLYMERIZATION

By FRANK A. BOVEY, *Minnesota Mining and Manufacturing Co., St. Paul, Minn.*, I. M. KOLTHOFF, *University of Minnesota, Minneapolis, Minn.*, AVROM I. MEDALIA, *Boston University, Boston, Mass.*, and EDWARD J. MEEHAN, *University of Minnesota, Minneapolis, Minn.*

1955. 457 pages, 104 illus., 79 tables. \$12.50

Volume X:

POLYMER PROCESSES

Edited by C. E. SCHILDKNECHT, *Stevens Institute of Technology, Hoboken, New Jersey*.

1956. 932 pages, 171 illus., 139 tables. \$19.50

Volume XI:

POLYETHYLENE

By R. A. V. RAFF, *Manager, Technical Development Section, Chemical Division*, and J. B. ALLISON, *Technical Information Branch, Research Department, Koppers Company, Inc., Pittsburgh, Pa.*

1956. 564 pages, 228 illus., 123 tables. \$16.00

IN PREPARATION:

Volume XII:

CHEMICAL ANALYSIS OF PLASTICS

A Collective Volume edited by GORDON M. KLINE, *National Bureau of Standards, Washington, D. C.* In two parts.



INTERSCIENCE PUBLISHERS, INC.

250 Fifth Avenue, New York 1, N. Y.