Russian Chemical Reviews, **45** (1), 1976

Translated from *Uspekhi Khimii*, **45**, 160-175 (1976)

U.D.C. 547.913; 547.914.5

Properties of Low Polymers and Their Solutions

V.P.Shaboldin, V.G.Chervin, A.I.Krasheninnikov, and V.N.Demishev

Published information is surveyed on the behaviour of low polymers of diverse chemical structure and on their dilute and concentrated solutions. Consideration is given to the important role of terminal groups, to the influence of the hydrodynamic permeability of a coil on polymer-solvent interaction, to the enhanced mobility of short chains, their flexibility, etc. A list of 108 references is included.

CONTENTS

I. Introduction 75
II. Behavioural features of low polymers and their solutions 75
III. Properties of dilute solutions 76
IV. Rheological properties 81

I. INTRODUCTION

Interest in the properties of polymers with low degrees of polymerisation has recently grown considerably, owing to the importance of their practical applications. These compounds are widely used in the manufacture of polymeric paints, coatings, varnishes, special adhesives, plastic foams, reinforced plastics, thickening additives for lubricating oils, plasticisers, cements and various compositions containing a solid filler, and diverse intermediates[1-4]. Such polymers are also employed in the synthesis of several high polymers. The ability of low polymers to undergo deformation at low shear stresses is exploited to simplify the technology of the production of several polymeric materials.

Thus it is not fortuitous that research papers on them have appeared during recent years. However, the structure and the properties of low polymers and their solutions, in contrast to macromolecular compounds, have been insufficiently studied to date, and published information is fragmentary as to the component composition of the specimens investigated and contradictory as to results. For this reason polymers with low degrees of polymerisation have not yet been fully utilised. Nor has the technology of the production of macromolecular compounds from them been adequately developed.

II. BEHAVIOURAL FEATURES OF LOW POLYMERS AND THEIR SOLUTIONS

The term "oligomers" is applied to compounds of molecular weight below 10 000, whether homogeneous or inhomogeneous in composition. Low polymers occupy a special position, in a transition region between compounds of low and of high molecular weight. The study of short-chain polymers may therefore indicate the molecular weight at which a molecule acquires the properties of a polymer and when a substance can be said to be macromolecular. Low polymer systems and their solutions, while having relatively low molecular masses, possess characteristic rubberlike elasticity[5,6]. Nevertheless, they do not obey many of the rules that have been discovered for high polymers. The past study of the structure of solutions of polymers[7,8] of low molecular weight has been relatively slight, whether theoretical or experimental. Molecular-weight determinations on such polymers and investigation of the properties of their dilute solutions have been accomplished by the modified methods used for high polymers (low-angle X-ray scattering[9], viscosimetry[10], osmometry[11-13]), as well as by methods developed solely for short-chain polymers (cryoscopy and ebullioscopy[14-16], end-group analysis[17], isothermal distillation[18]).

Light scattering provides a most sensitive and accurate method for obtaining reliable information on the structure of macromolecules in dilute solutions[19]. It is interesting in the relative simplicity of the measurements combined with the fairly rapid provision of very accurate data on the conformational properties of macromolecules, size, molecular weight, degree of chain branching, structure-forming processes, etc. However, light scattering can be used to examine polymers only of sufficiently high molecular weight, when the particle size exceeds significantly the wavelength. This method has therefore been regarded as inapplicable to oligomers.

During recent years, in connection with progress in computer techniques, it has become common to investigate model systems of oligomers with computer experiments[20-22], by particular Monte Carlo methods[20-28]. The results obtained for model systems not only provide an idea of the structure of the macromolecule and its behaviour in solution but also permit analysis of earlier theoretical views.

Published information on the properties of low polymers and their solutions shows that, unlike compounds with high degrees of polymerisation, these systems possess several characteristics that cannot be interpreted by the usual theory of polymer solutions: (i) terminal groups of short-chain macromolecules have a significant role, and such macromolecules are able to interact not only among themselves but also with solvent molecules, which may reasonably be expected to influence the shape, size, and permeability of the coil; (ii) these compounds have a transition region of conformations between coil and rod, from compounds of low molecular weight to polymers; (iii) the hydrodynamic permeability of the coil affects polymer-solvent interaction, and the permeability varies with decrease in the length of the macromolecular chain in the transition region; (iv) the effect of long-range interaction diminishes; (v) short chains show

enhanced mobility and are capable of orientation and interaction in the field of longitudinal and transverse velocity gradients at low shear stresses; and (vi) oligomers show almost the same capacity for elastic deformation, which is due to the presence of short, flexible chains, relatively unstable intermolecular bonds, and a mobile, fluctuating network. Many investigations have shown that these factors have a significant influence on the hydrodynamic, conformational, thermodynamic, and rheological properties of oligomers.

III. PROPERTIES OF DILUTE SOLUTIONS

The interaction between macromolecules in dilute solutions is divided into short-range and long-range interactions[29], between repeating units respectively comparatively near together and far apart in the polymer chain. Such interactions of units in the same chain are one of the factors responsible for the excluded-volume effect.

One of the main characteristics of a macromolecule in solution is its thermodynamic (equilibrium) flexibility $(\bar{h}_0^2/\bar{h}_{fr}^2)^{1/2}$, where the $(\bar{h}_0^2)^{1/2}$ are the unperturbed dimensions of the coils, when the effect of long-range interactions is balanced by interaction with the solvent (second virial coefficient $A_2 = 0$), and $(\bar{h}_{fr}^2)^{1/2}$ are the corresponding dimensions with free rotation of the units in the chain. The dimensions of a macromolecular coil depend on the character of the intra- and inter-molecular interactions, and can be estimated as

$$\alpha_0 = (\bar{h}^2/\bar{h}_0^2)^{1/2},$$

in which α_0 is Flory's coil-swelling coefficient[30] and the $(\bar{h}^2)^{1/2}$ are the dimensions of the coil in an actual solvent.

For oligomers little experimental study has been made of the effects of the nature of the solvent and of the degree of polymerisation on the dimensions of the coil and its properties. Coil size and shape have been determined by optical and viscosity measurements in studies of the properties of dilute solutions of low polymers[9,10,31-35]. Tsvetkov, Frisman, et al.[33-35] examined the dependence of the intrinsic dynamic birefringence on the molecular weight of polyoxypropylene glycols and polystyrene of low molecular weights. From the results the persistent lengths of macromolecules of the oligomers and the molecular-weight dependence of the intrinsic viscosity could be determined. In an investigation of the properties of dilute solutions of polyurethanes and of butadiene–acrylonitrile rubbers of low molecular weight in various types of solvents use of the Stockmayer–Fixman theory enabled the dimensions and the swelling coefficients of real coils to be determined and the flexibility of the macromolecular chain to be estimated by light scattering[10,31,36]. The depolarisation factor, characterising the form of a macromolecular coil of polypropylene glycol, was investigated[32] as a function of the molecular weight and the concentration of the polymer by the use of light scattering. The low-angle scattering of light and of X-rays was used[9] not only to determine the molecular weight and the shape of macromolecules of cellulose nitrate with low molecular weight but also to establish the presence in dilute solution of association complexes, which break down with time.

In contrast to these fragmentary results, a considerably larger number of theoretical studies have been made on the conformational properties of oligomer macromolecules, e.g. on the effect of terminal groups[37,38] (to which a significant role was assigned, in contrast to high polymers). However, conclusions reached from different theories are often mutually contradictory. Experimental results cannot be used for an objective assessment of theoretical predictions, since an exact analytical relation between the measured parameters and the conformations of the macromolecules is lacking. In this situation the application of modern computer experiments and numerical methods has permitted a close approach to solving important problems in connection with the properties of the macromolecules of oligomers.

The majority of results obtained by the Monte Carol method in computer experiments have led to a dependence of the mean distance between end-groups h_N and the mean radius of inertia R_N on the number of segments N of the form

$$\langle h_N^2 \rangle = AN^{Y_n}; \quad (1)$$

$$\langle R_N^2 \rangle = BN^{Y_R}, \quad (2)$$

where A, B, Y_n, and Y_R are empirical constants. The results in most papers lead to the condition $Y_n = Y_R = Y = 1.2$ for all lattices. Simulation by a continuum[28] gives $Y_n \neq Y_R$, which shows that representation of $\langle h_N^2 \rangle^{1/2}$ as a multiple of $\langle R_N^2 \rangle^{1/2}$ is not always correct: these parameters increase at different rates with increase in the degree of polymerisation. Equations (1) and (2) were deduced from the condition that the interaction potential of the segments is represented by a rigid sphere:

$$\Phi(r) = \begin{cases} 0, & r > d; \\ \infty, & r < d, \end{cases} \quad (3)$$

where r is the distance between the centres of the segments and d is the sum of their van der Waals radii. The functional dependence (1) and (2) is preserved for interaction between segments of a different type, but Y_n and Y_R vary with $\Phi(r)$. With increase in the energy of attraction the index Y_n decreases, to reach unity at some $\Phi(r)$ (the θ point). Equations (1) and (2) are inapplicable in worse solvents than the θ solvent. The interesting result was also obtained that the θ conditions do not correspond to a single point but occupy a region in which most of the conformational parameters, e.g. $\langle h_N^2 \rangle$ and $\langle R_N^2 \rangle$, assume their own θ values. Computer methods yielded

$$\alpha_N^2 = \langle h_N^2 \rangle / N; \quad (4)$$

$$\alpha_{j,N}^2 = \langle h_{j,N}^2 \rangle / j, \quad (5)$$

where α_N^2 and $\alpha_{j,N}^2$ are the increases in the distances respectively between the terminal segments and between segments separated by j other segments in a macromolecule comprising N segments. The method of dimerisation was used[39] to construct chains containing up to 4096 segments. Values of $\alpha_{j,N}^2$ were calculated for $j = 16, 32, \ldots, \frac{1}{2}N$. The results showed that

$$\alpha_N^2 \propto N^{1/2}, \quad (6)$$

as suggested by Flory[30], and that the relation

$$\alpha_N^2 - 1 \propto N^{1/2}, \quad (7)$$

which follows from Fixman's theory[40], is incorrect.

Knowledge of the coordinates of each segment for the whole time of a computer experiment permits not only calculation of the quantities of Eqns. (4) and (5) but also determination of the number of various types of contacts

$$E = E_{ll} + E_{lm} + E_{mm} \quad (8)$$

between segments of the same and different macromolecules in solution, where E_{mm}, E_{lm}, and E_{ll} are the numbers of intramolecular contacts between respectively internal, terminal and internal, and terminal segments. An analogous expression can be written for the number of intermolecular contacts k between macromolecules. Fig. 1 illustrates the dependence of the number of the various types of contacts on the degree of polymerisation P found in a computer experiment. For a model of a macromolecule based on a simple cubic lattice the variation in the total number of intramolecular contacts was given[41] as

$$E = 0.292 \cdot P - 1.15. \quad (9)$$

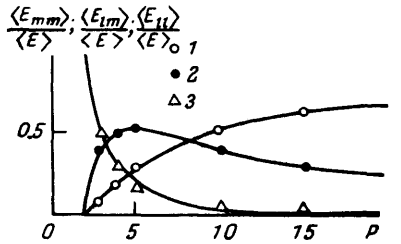


Figure 1. Dependence of number of polymer–polymer contacts on the degree of polymerisation P for a model based on a simple cubic lattice: 1) $\langle E_{mm}\rangle / \langle E\rangle$; 2) $\langle E_{lm}\rangle / \langle E\rangle$; 3) $\langle E_{ll}\rangle / \langle E\rangle$.

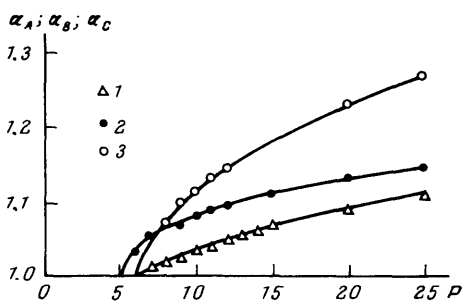


Figure 2. Dependence of coefficients of expansion on degree of polymerisation for a model based on the graphite lattice: 1) α_A (poor solvent); 2) α_B (good solvent for terminal groups); 3) α_C (good solvent for internal groups).

(*a*) Effects of Terminal Groups and of Coil Permeability on Hydrodynamic Properties

Fig. 2 illustrates the dependence of the coefficient of expansion of the macromolecule on the degree of polymerisation and the quality of the solvent, obtained by the Monte Carlo method. This experiment clearly reveals the effect of terminal groups and their relationship to the solvent. The coefficient of expansion always increases with the degree of polymerisation, but most rapidly in a good solvent for terminal and internal segments.

The Mark–Kuhn–Houwink equation[42,43]

$$[\eta] = KM^a$$

expresses the relation between the intrinsic viscosity $[\eta]$, from which the hydrodynamic volume of the coiled macromolecule in dilute solution is estimated, and its molecular weight M, where K and a are constants for a given homologous series. The parameter a, representing the form and the density of the coil, depends on the nature of the solvent and on the hydrodynamic interaction within the space of the coil, and varies mainly from 0.5 to 1. Experimental study of this dependence for several oligomers has established that, for a series of polymer–solvent systems, a decreases as the molecular weight diminishes: i.e. the dependence of $\lg[\eta]$ on $\lg M$ is nonlinear (Fig. 3).

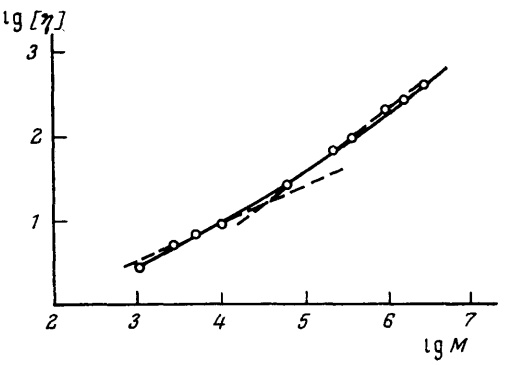


Figure 3. Dependence of $\lg[\eta]$ on $\lg M$ for poly(methyl methacrylate) in benzene at 30°C.

Thus it was shown, for the binary systems formed by benzene with poly(methyl methacrylate)[44] and by water with polyethylene glycol[45], that a is independent of the nature of the solvent for small molecular weights, and is close to 0.5 (which is characteristic of a θ solvent). A possible explanation is that the swelling coefficient α_0 approaches unity in the absence of θ conditions: i.e. long-range interactions are absent. This contradicts all existing theories of solutions, which predict that $\alpha_0 = 1$ only at the θ point with either the second virial coefficient A_2 or the molecular weight approaching zero. The results indicate also that, with decrease in chain length in macromolecules of these oligomers, a small hydrodynamic permeability appears, which is typical of macromolecules under θ conditions. This effect can be attributed to the possibility of interaction between end-groups of small macromolecules, which will change the form of the coil, by decreasing its dimensions (making it more compact), which explains the diminished viscosity.

Several other studies[16,46–49], on oligourethanes, rubbers of low molecular weight, polyethers, polyethylene glycols, etc., showed that a varies from 0.5 to 1 depending on the nature of the solvent, as with high polymers. But several other investigations[50–52] revealed a tendency for a to increase—not to decrease—as the molecular weight fell. Hydrodynamic theories of polymer solutions suggest that, for permeable Gaussian chains[53], such behaviour is probably due to an increase in the permeability of the coils

with decreased molecular weight of the polymer. As a consequence, the slope of the plot of $\lg[\eta]$ against $\lg M$ should increase with fall in molecular weight. The Debye–Bueche[54], Kirkwood–Riseman[55,56], and Zimm–Kuhn[57-60] theories predict, with increase in permeability (weakening of hydrodynamic interaction) and short chains, direct proportionality between viscosity and molecular weight ($[\eta] = KM^a$, where $a = 1$), and decrease in the shielding coefficient σ.

Long-range effects (non-ideality of solutions), like short-range effects (chain rigidity), influence the conformations of flexible chains[61,62]. High values of the exponent a obtained in a θ solvent (in the absence of the excluded-volume effect) indicate a loose structure and permeability of the coil, and hence enhanced rigidity of the chain. Nevertheless, volume effects in non-ideal solvents lead to swelling of the coil and to a corresponding increase in a. In order to determine the true flexibility of a macromolecular chain, therefore, the influence of volume effects should be excluded.

Calculation then becomes useful, since the excluded-volume effect can either be disregarded or estimated. Thus at high degrees of polymerisation 32% of terminal groups occur within a sphere described by the radius of inertia of the macromolecule[27]. Nevertheless, taking into account excluded-volume effects lowers the number of end-groups in this sphere to 18%.[23] Thus the excluded-volume effect leads to the removal of terminal groups from the sphere of the macromolecule.

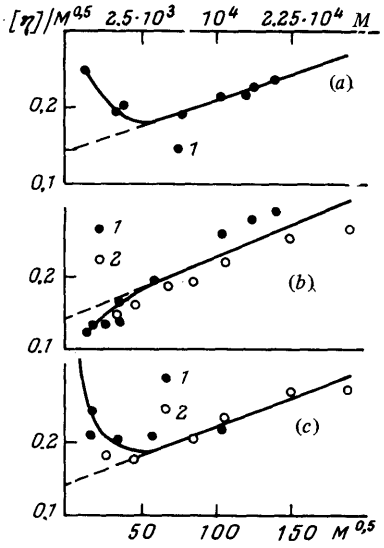


Figure 4. Dependence of $[\eta]/M^{0.5}$ on $M^{0.5}$ for polyethylene glycol in: *a*) methanol; *b*) benzene; *c*) water at: 1) 20°C; 2) 30°C.

The theories of Kuhn[58,59], Hearst[63], etc. are applied to rigid chains. With relatively flexible macromolecular chains, which are coiled quite compactly even in good solvents, the flow effect is almost absent, and the Stockmayer–Fixman equation is used[40]. With such molecules volume effects can be eliminated by extrapolating the hydrodynamic parameters to low molecular weights by means of the theory of the excluded volume[48,62]. Stockmayer and Fixman suggested the formula

$$[\eta] = KM^{0.5} + FM,$$

for the molecular-weight dependence of intrinsic viscosity, in which F and K, both independent of molecular weight, represent respectively short-range and long-range interactions. The constants are found by plotting the dependence of $[\eta]/M^{0.5}$ on $M^{0.5}$ by means of the Stockmayer–Fixman graph, and thus these interactions are determined for wider molecular-weight limits than is possible from the Mark–Kuhn–Houwink equation.

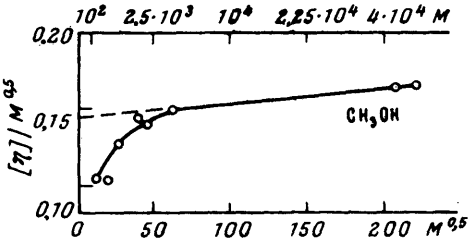


Figure 5. Dependence of $[\eta]/M^{0.5}$ on $M^{0.5}$ for the monophenyl ether of polyethylene glycol in methanol at 25°C.

Experimental viscosity results obtained for solutions of polyethylene glycol in methanol, benzene, and water and for its monophenyl ether in methanol[46,64], together with other results[47,48], have revealed more clearly the applicability of the Stockmayer–Fixman equation. Positive and negative departures from the equation are usually observed at a molecular weight of 3000, independent of the nature of the solvent and the end-groups (Figs. 4 and 5). This is apparently due to the effects both of the polymer chain and of the terminal groups. The value of K is independent of the solvent, which indicates that short-range interaction is independent of solvent and end-groups. Positive departures from the equation in methanolic and aqueous solutions of polyethylene glycol are caused by increase in size of the oligomer macromolecules resulting from interaction between terminal hydroxyls and the solvent. Negative deviations, which are observed both in benzene solutions of polyethylene glycol and in methanolic solutions of its monophenyl ether, are apparently caused by coiling of the macromolecule under the influence of repulsive forces between end-groups and solvent molecules. This range of molecular weights is regarded as the region of oligomers, possessing the properties of compounds of low molecular weight.

The general Stockmayer–Fixman equation shows that the intrinsic viscosity of oligomers is proportional to the square root of their molecular weight, which is confirmed by several investigations. Nevertheless, this principle does not hold for certain oligomers: here there is an approximately linear variation with the molecular weight[65]. The Huggins constant K' in the equation

$$\eta_{sp}/c = [\eta] + K'[\eta]^2 c$$

is a measure of the affinity between polymer and solvent. On the basis of data for high polymers K' is now regarded

as independent of molecular weight[66]. In θ solvents it is usually approximately 0.5 (or greater), and in good solvents $K' = 0.2-0.3$.

However, experiments on oligomers indicate that in most cases the Huggins constant assumes anomalous values. Several studies showed that the constant increases with decrease in the molecular weight of the oligomers[67-69], and may even exceed those for high polymers[70,71]. In certain cases a considerable increase occurs (to several units) with decrease in the chain length[72]. This is governed by the structure of the macromolecules and the nature of the solvent. The variation of K' with molecular weight is usually less marked in poor than in good solvents. Another study showed[73] that the experimental values correspond to the Huggins equation only within a narrow range of molecular weights. The formula

$$K' = eM^{d_0} + b_0,$$

was proposed, in which d_0 and b_0 were independent of molecular weight.

A complicated dependence of K' on molecular weight has been found in several studies[72]. Values of K' are largest at very low molecular weights. Increase in M to 2000–3000 is accompanied by a rapid fall in K', and further increase by a smooth decrease, which then slows down (Fig. 6). The increase in K' with decrease in molecular weight is attributed by some authors to an increase in the density of the coiled macromolecule. Molecules of greater chain length are regarded as more prolate and less spherical than those with short chains. This is apparently because short molecules are densely packed, weakly solvated coils, relatively impermeable to the solvent. This is consistent with diffusion results.

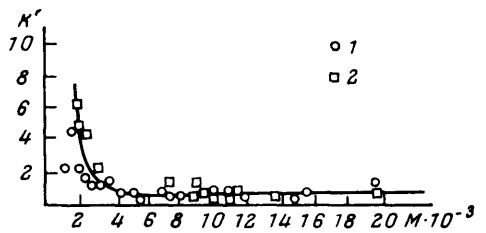


Figure 6. Dependence of the Huggins constant K' on the molecular weight of poly(methyl acrylate) in: 1) acetone; 2) θ solvent.

Dimensions of macromolecular coils approaching the unperturbed values were determined[72-76] from the measured diffusion coefficients of polystyrene in solutions, which enables the Flory coefficient[30] to be calculated. The chain rigidity thus found for the oligomer macromolecule approached that of high polymers, which was attributed to an increased effect of thickness on the chain dimensions[77]. Other workers[78,79] also obtained for certain oligomers (polyoxypropylene and polyoxyethylene glycols) values of q in the equation $D = K_\alpha M^{-q}$ closely similar to the corresponding values for long chains. This indicates that the hydrodynamic characteristics of oligomer molecules in solution can be described quite accurately by hydrodynamic theories based on the model of an impermeable Gaussian coil exhibiting slight thermodynamic interaction with the solvent.

(*b*) Conformational Transitions in Macromolecules of Oligomers

The second virial coefficient A_2 represents the interaction between polymer and solvent:

$$\pi/c = RT\,(1/M + A_2c + \ldots),$$

where R is the universal gas constant, T the absolute temperature, c the concentration, M the molecular weight, and π the osmotic pressure. According to Flory's theory[80,81] A_2 is independent of the molecular weight of the polymer. In practice, however, agreement with theory is found only at the θ point or with slight departures from ideality. The greater the deviation from θ conditions, the more marked is the dependence of the second virial coefficient on the molecular weight.

An equation for this dependence based on many experimental results was[82]

$$A_2 = a_1/M^{0.5} + b_1,$$

where a_1 and b_1 were theoretical constants independent of the molecular weight. Research showed that the equation was valid for exothermic and endothermic systems, as well as for θ conditions over a wide range of molecular weights. In the study of solutions of polystyrene in benzene, toluene, and naphthalene (exothermic systems), for example, a linear dependence was observed for molecular weights from 500 to 5×10^6 (Fig. 7).[14] The corresponding range for an endothermic system (poly(methyl methacrylate) in acetone) was from 200 to 7.8×10^6.[83]

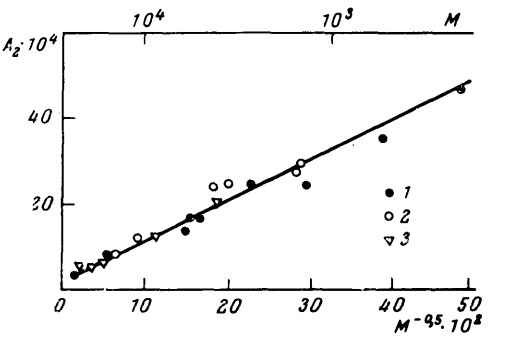


Figure 7. Dependence of second virial coefficient A_2 on molecular weight M for the exothermic systems comprising polystyrene in: 1) naphthalene; 2) benzene; 3) toluene.

Nevertheless, polystyrene[84] and poly(methyl methacrylate)[85] in good solvents showed departures from the suggested equation at low degrees of polymerisation (Fig. 8). In particular, the second virial coefficient was found[84] to be negative for dimers, to reach a positive maximum when $P = 4$, and then gradually to decrease with increase in molecular weight (Fig. 9). These results indicate that the equation holds up to the maximum, where the substance possesses polymeric properties. The presence of a maximum indicates a transition in the form of the macromolecule from coiled to rod-shaped, which can apparently be interpreted as a transition to compounds possessing the properties of polymers.

The above considerations are consistent with the dependence of the entropy contribution B_S on the degree of polymerisation P in the polystyrene–benzene system (Fig. 10).[14] The entropy is approximately zero for the dimer, reaches a maximum when $P = 4$, and then gradually diminishes with increase in molecular weight. It is known to have its maximum value when the molecule is elongated into a rod, and its minimum value when the molecule is coiled into a sphere. Maximum entropy was therefore interpreted as the transition point between extended and coiled states of the molecules.

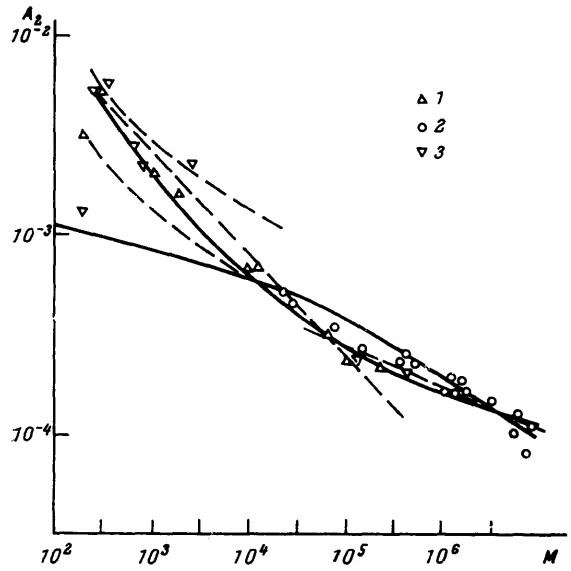


Figure 8. Dependence of second virial coefficient A_2 on molecular weight M for the endothermic system comprising poly(methyl methacrylate) in acetone, obtained by: 1) osmometry; 2) light scattering; 3) X-ray examination.

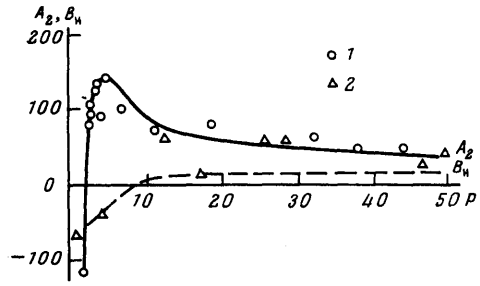


Figure 9. Dependence of second virial coefficient A_2 and of enthalpy coefficient B_H on degree of polymerisation of oligostyrene in: 1) naphthalene; 2) benzene.

Application of a calorimetric method[86] to polystyrene in benzene and cyclohexane, poly(methyl methacrylate) in acetone, and polyvinylcarbazole in benzene showed[84] that, at the initial degrees of polymerisation, the enthalpies of mixing almost always pass through maxima (as do the second virial coefficient and the entropy). Further increase in molecular weight produces hardly any change in the enthalpy (Fig. 11). This effect was explained in terms of the interaction energy of end-groups in the oligomer macromolecules.

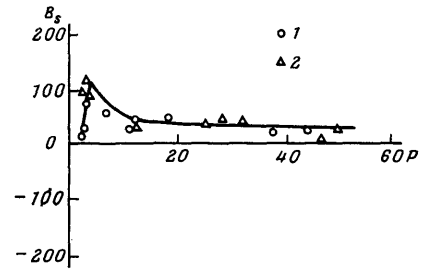


Figure 10. Dependence of entropy coefficient B_S on degree of polymerisation P for oligostyrene in: 1) naphthalene; 2) benzene.

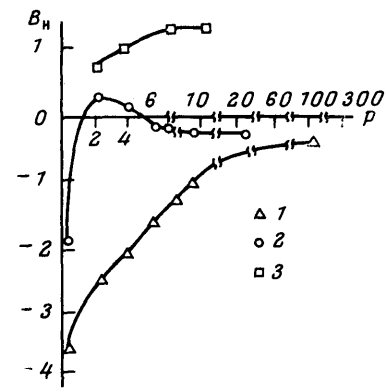


Figure 11. Dependence of enthalpy coefficient B_H on degree of polymerisation for: 1) poly(methyl methacrylate) in acetone; 2) polyvinylcarbazole in benzene; 3) a polycarbonate in dioxan.

(*c*) Structure Formation in Solution with Increase in Concentration of Low Polymers

With increase in the concentration of dilute solutions of polymers the macromolecules interact and form association complexes or aggregates. Staudinger[87] first formulated the concept of the lowest concentration—the critical concentration c_{cr}—at which the polymer molecules begin to come into mutual contact. Many studies have shown that this concentration depends on the molecular weight of the polymer and its chemical structure, the nature of the solvent, and the temperature. The critical concentration usually increases with decrease in molecular weight, deterioration in the quality of the solvent, and rise in

temperature, which is a consequence of the weakening of interaction between the macromolecules under these conditions. It can be determined from the break in the linear concentration dependence of viscosity, intensity of light scattering, optical density, and other properties of the polymer. However, some studies[77,88] of the concentration c dependence of the reduced viscosity η_{sp}/c revealed a breakdown of the linear dependence at subcritical concentrations. These anomalies were attributed to supercoiling of the macromolecules at high dilutions[77,88], and by other workers to decrease in the effective radius of the capillary resulting from adsorption of the polymer on its walls[89,90].

Association begins sooner in oligomers than in high polymers. Incipient structure formation was observed, in solutions of butadiene–acrylonitrile rubbers having molecular weights of $(1.4–2.7) \times 10^4$, at concentrations of 0.1–0.5 g/100 ml.[31] Critical concentrations in benzene solutions of polystyrene of molecular weight $(1.5–33) \times 10^3$ varied from 0.5 to 1.5 g/100 ml.[90]

In several studies[15,91] anomalies were absent up to fairly high concentrations of low polymers in solution. This applied to poly(methyl methacrylate) and poly(ethyl acrylate) of molecular weight $(1–20) \times 10^3$ up to 0.2 g/100 ml.[15] Investigation of dilute solutions ($c < 0.1$ g/100 ml) of SKN-18 [butadiene–acrylonitrile synthetic rubber] at 20–60°C showed that the intensity of light scattering by the solutions remained unchanged with rise in temperature, which indicated that association had not occurred[31]. In solutions containing macromolecules of high polymers at corresponding concentrations, however, the apparent molecular weight decreased at 60°C; this was attributed to the breakdown of association complexes[92].

IV. RHEOLOGICAL PROPERTIES

Considerably less study has been made of the structure of low polymers and their concentrated solutions than of dilute solutions. Only comparatively recently have publications appeared on the rheological properties of certain polyethers and polyisobutylenes of low molecular weight and on those of their solutions. The structural features of polymers and their solutions (great size of macromolecules, formation of network structures, etc.) are responsible for several flow anomalies, e.g. departure from Newton's viscosity law[29]. This is apparent in the rubberlike elasticity possessed by solutions of several polymers.

Unlike high polymers, oligomers possess almost the same capacity for rubberlike elastic deformations, which are in the nature of relaxation processes involving change in the conformations of the macromolecules under the influence of shear stresses. This feature is attributed to great flexibility of the macromolecules and the presence of a mobile, fluctuating network with temporary contacts produced by intermolecular interaction. The systems are mainly thixotropic in character, with relatively unstable bonds and long relaxation times. They can be regarded as a new type of cross-linked systems, occupying a position intermediate between concentrated solutions, polymer jellies, and solutions of substances of low molecular weight capable of cross-linking[6,93,94].

Many methods have now established that several concentration ranges exist in solutions of polymers, differing in degree of order of the chains, conformational properties of the macromolecules, and their interaction. This is responsible for differences in rheological properties[95,96]. The concentration ranges can be arbitrarily divided as indicated below.

1. Very dilute solutions, in which macromolecules are present as isolated coiled coils. With increase in concencentration the chain molecules straighten out, interact, and form structures.
2. More concentrated solutions, in which, as a consequence of intermolecular contacts, the macromolecules in the form of prolate coils form the ideal three-dimensional network described by Büche[97] or are arranged in isolated association complexes or aggregates. A structural network appears at higher concentrations of oligomers than of high polymers.
3. Concentrated solutions, in which the ideal network may be consolidated by the formation of new bonds with other macromolecules ($c > c_{cr}$). The macromolecules then have small free volumes and are characterised by considerable mutual penetration of segments.
4. Highly concentrated solutions, in which ordered structures are formed, different for polymers in different physical states and of different chain lengths[98]. The mutual interlacing of segments of the macromolecules produces a continuous network of bonds, with a consequent considerable increase in viscosity[97].

All the above ranges for transformation in polymer solutions are reversible with change in concentration. Examination of the viscoelastic properties of such solutions over all concentration ranges will give an idea of the nature and the rates of redistribution of conformations of chain molecules, as well as of their mutual arrangement, i.e. of the structure of the solutions[99,100].

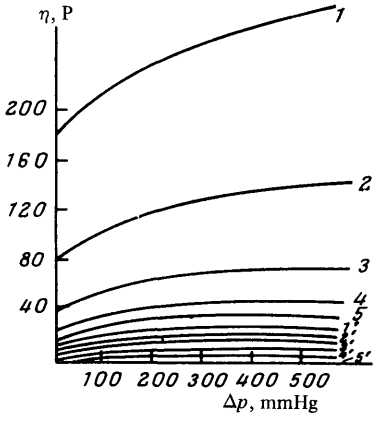


Figure 12. Flow curves for polyesters—poly(ethylene glycol adipates)—of molecular weight 2050 and 790 (unprimed and primed curves respectively) at (°C): 1) 20; 2) 30; 3) 40; 4) 50; 5) 60.

Study of the flow of certain oligomers and their concentrated solutions has shown a difference in rheological behaviour between these compounds and high polymers. For example, investigation of polyethers—polyoxolanyloxypropylene glycols—and polyesters—poly(diethylene glycol adipates)—and their concentrated solutions has shown[101] that the viscosity of the system in a longitudinal velocity

gradient (in a capillary viscometer) increases with the shear stress, in some cases reaching a maximum. These antithixotropic effects degenerate with rise in temperature and with dilution. They were attributed to intensified interaction of the macromolecular chains of the oligomers on orientation in the flow. The viscosity is then affected by the molecular weight. With several oligomers such antithixotropic effects develop only at low stresses. When the shear stress arises above a critical value, thixotropic breakdown of the previously formed structure occurs, and the usual process of flow is observed, as with high polymers[102]. Other studies[103-105], using both capillary and rotary viscometers, revealed in the oligomers investigated and their concentrated solutions, together with thixotropic breakdown, a region of antithixotropy at low shear stresses. This phenomenon is also connected with intensified interaction of oriented macromolecules under the influence of transverse and longitudinal velocity gradients. Anomalous viscosity effects are more marked with oligomers of lower molecular weight, which can be explained by the enhanced rigidity of shorter chains and their greater mobility (Fig. 12).

Büche[106] used the concept of free volume to develop theoretically the resistance to the flow of polymers, which arises from interaction between segments, mutual friction of segments during movement of the polymer chain, and the formation of a network structure by the meshing of segments and macromolecular chains. Relative movement of macromolecules is facilitated with decrease in the molecular weight of the polymer or dilution of its solution, and flow becomes more intense. This is apparent in a decrease in viscosity and in the heat of activation of viscous flow[107,108], which, after certain fairly high degrees of polymerisation have been reached, remains constant and independent of molecular weight[103]. The smaller the macromolecules the higher the concentrations at which intermolecular interaction and departure from Newtonian flow become apparent.

REFERENCES

1. A. N. Kuksin, in "Sintez i Fiziko-khimiya Polimerov" (Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1974, No. 13, p. 153.
2. P. Simaus, Rubber Plastics Age, **45**, 1347 (1964).
3. J. M. Buist, Indian Rubber Bull., **6**, 269 (1971).
4. Q. Kraus and J. T. Cruver, Rubber Chem. Technol., **42**, 800 (1969).
5. Yu. S. Lipatov, L. V. Khailenko, and L. S. Zborozhin, Dokl. Akad. Nauk SSSR, **179**, 141 (1968).
6. L. S. Zborozhin, Yu. S. Lipatov, and L. V. Khailenko, in "Modifikatsiya Polimernykh Materialov" (Modification of Polymer Materials), Izd. Rizhsk. Politekh. Inst., Riga, 1969, Vol. 2, p. 49.
7. H. Sotobayashi and J. Springer, Adv. Polymer Sci., **6**, 472 (1969).
8. E. A. Bekturov and Z. Kh. Bakauova, Trudy Inst. Khim. Nauk Akad. Nauk Kazakh. SSR, **28**, 24 (1970).
9. O. Kratky, H. Leopold, and G. Puchwein, Kolloid Z., **216**, 255 (1967).
10. A. E. Nesterov, Yu. S. Lipatov, and N. A. Pilyushina, Vysokomol. Soed., **B9**, 695 (1967).
11. G. Meyerhoff, Z. Elektrochem., **61**, 325, 1249 (1957).
12. F. B. Rolfson and H. Coll, Analyt. Chem., **36**, 888 (1964).
13. W. C. Feist, J. Polymer Sci., **B3**, 875 (1965).
14. G. V. Schulz and H. Marzolph, Z. Elektrochem., **58**, 211 (1954).
15. C. A. Glover and R. R. Stanley, Analyt. Chem., **33**, 447 (1961).
16. V. I. Valuev, P. A. Shlyakhter, E. G. Erenburg, and N. P. Nikitina, Vysokomol. Soed., **B12**, 251 (1970).
17. Ahad Elieer, J. Appl. Polymer Sci., **17**, 365 (1973).
18. H. Hayer, Angew. Chem., **73**, 465 (1965).
19. V. E. Eskin, "Svetorasseyanie Rastvorami Polimerov" (The Scattering of Light by Solutions of Polymers), Nauka, Moscow, 1973.
20. A. I. Krasheninnikov and V. G. Chervin, Zhur. Fiz. Khim., **49**, 1541 (1975) [Russ. J. Phys. Chem., No. 6 (1975)].
21. A. I. Krasheninnikov, M. A. Lagutin, and V. G. Chervin, Zhur. Fiz. Khim., **47**, 1061 (1973) [Russ. J. Phys. Chem., No. 4 (1973)].
22. A. I. Krasheninnikov, M. A. Lagutin, and V. G. Chervin, Zhur. Fiz. Khim., **47**, 490 (1973) [Russ. J. Phys. Chem., No. 2 (1973)].
23. H. Sotobayashi, Kolloid. Z., **251**, 739 (1973).
24. Z. Alexandrowicz, J. Chem. Phys., **51**, 561 (1969).
25. H. Warwari, K. Knaell, and R. Scott, J. Chem. Phys., **56**, 2903 (1972).
26. F. McCrackin, J. Mazur, and G. Guttman, Macromolecule, **6**, 859 (1973).
27. W. Bruns, Makromol. Chem., **134**, 193 (1970).
28. S. Stellman and P. Gans, Macromolecule, **5**, 516 (1972).
29. A. A. Tager, "Fiziko-khimiya Polimerov" (Physical Chemistry of Polymers), Izd. Khimiya, Moscow, 1968.
30. P. J. Flory, J. Chem. Phys., **97**, 958 (1953).
31. V. P. Shaboldin, A. G. Sukhomudrenko, and A. I. Krasheninnikov, Vysokomol. Soed., **A14**, 1462 (1972).
32. G. Meyerhoff and U. Moritz, Makromol. Chem., **109**, 143 (1967).
33. E. V. Frisman and M. A. Sibileva, Vysokomol. Soed., **7**, 674 (1965).
34. V. N. Tsvetkov, Vysokomol. Soed., **8**, 890 (1966).
35. V. N. Tsvetkov and S. I. Klenin, Ukrain. Fiz. Zhur., **12**, 324 (1967).
36. H. Beachell and J. Peterson, Amer. Chem. Soc. Polymer Preprints, **8**, 456 (1967).
37. E. Wall, J. Chem. Phys., **26**, 1742 (1957).
38. M. Fischer and B. Hiley, J. Chem. Phys., **34**, 1253 (1961).
39. Z. Alexandrowicz and Y. Accad, J. Chem. Phys., **54**, 5338 (1971).
40. W. H. Stockmayer and M. Fixman, J. Polymer Sci., **C1**, 137 (1963).
41. H. Sotobayashi, Makromol. Chem., **123**, 157 (1969).
42. W. Kuhn, Kolloid Z., **68**, 2 (1934).
43. R. Houwink, J. prakt. Chem., **157**, 15 (1940).
44. G. Cohn-Ginsberg and H. Mason, Polymer, **3**, 97 (1962).
45. F. Bailey, J. Kucera, and L. Imhof, J. Polymer Sci., **32**, 517 (1958).
46. C. Sadron and P. Rempp, J. Polymer Sci., **29**, 127 (1958).
47. H.-G. Ellas and H. Lys, Makromol. Chem., **80**, 229 (1964).
48. M. Kurata and W. Stockmayer, Fortschr. Hochpolym.-Forsch., **3**, 196 (1963).
49. V. P. Shaboldin, A. I. Krasheninnikov, and V. N. Demishev, Vysokomol. Soed., **B13**, 887 (1971).
50. R. Fordyce and H. Hibbert, J. Amer. Chem. Soc., **61**, 1912 (1939).

51. P. J. Flory and P. B. Stickney, J. Amer. Chem. Soc., 62, 3032 (1940).
52. A. P. Meleshevich, A. E. Fainerman, and R. M. Verbik, Plast. Massy, 51, 9 (1966).
53. P. Rouse, J. Chem. Phys., 21, 2172 (1953).
54. P. Debye and A. Bueche, J. Chem. Phys., 16, 573 (1948).
55. J. Kirkwood and J. Riseman, J. Chem. Phys., 16, 565 (1948).
56. J. Kirkwood and J. Riseman, J. Chem. Phys., 17, 442 (1948).
57. B. Zimm, J. Chem. Phys., 24, 269 (1956).
58. H. Kuhn, J. Colloid Sci., 5, 331 (1950).
59. H. Kuhn, F. Moning, and W. Kuhn, Helv. Chim. Acta, 36, 73 (1953).
60. W. Kuhn, Kolloid Z., 68, 2 (1934).
61. V. N. Tsvetkov, Zhur. Vses. Khim. Obshch. Mendeleeva, 6, 428 (1961).
62. P. J. Flory, J. Chem. Phys., 10, 51 (1942).
63. J. Hearst and W. Stockmayer, J. Chem. Phys., 37, 1425 (1962).
64. G. Müh, Kolloid Z., 196, 140 (1964).
65. W. Kern, W. Gruber, W. Heitz, H. Wirth, and J. Ziegler, Makromol. Chem., 51, 1 (1962).
66. V. N. Tsvetkov, V. E. Eskin, and S. Ya. Frenkel', "Struktura Makromolekul v Rastvorakh" (Structure of Macromolecules in Solution), Nauka, Moscow, 1964.
67. T. Gillespie, J. Polymer Sci., C3, 31 (1963).
68. F. Eirich and J. Riseman, J. Polymer Sci., 4, 417 (1949).
69. D. K. Thomas and A. Charlesby, J. Polymer Sci., 42, 195 (1960).
70. L. H. Gragg and C. C. Bigelow, J. Polymer Sci., 16, 177 (1955).
71. A. Orsag and E. Feigin, Vysokomol. Soed., 5, 1861 (1963).
72. R. E. Legkuents, Z. G. Zemskova, M. K. Moldabaeva, Z. Kh. Bakauova, and E. A. Bekturova, Izv. Akad. Nauk Kazakh. SSR, Ser. Khimiya, 5, 73 (1968).
73. H. Sotobayashi, Makromol. Chem., 73, 235 (1964).
74. C. Rossi, U. Bianchi, and E. Bianchi, Makromol. Chem., 41, 31 (1960).
75. C. Rossi and E. Bianchi, J. Polymer Sci., 41, 189 (1959).
76. C. Rossi, E. Bianchi, and G. Conio, Chem. Ind., 45, 1498 (1963).
77. R. Boyer and R. Spencer, J. Polymer Sci., 5, 375 (1950).
78. S. I. Klenin, V. L. Migdal, S. V. Bushin, and V. N. Tsvetkov, Vysokomol. Soed., 8, 882 (1966).
79. C. Rossi and V. Magnasco, Makromol. Chem., 41, 45 (1960).
80. P. J. Flory, J. Chem. Phys., 10, 51 (1942).
81. M. Hyggins, J. Phys. Chem., 46, 151 (1942).
82. H. Sotobayashi and K. Ueberreiter, Z. Elektrochem., 67, 178 (1963).
83. R. G. Kirste and W. Wunderlich, Z. phys. Chem. (Frankfurt), 58, 133 (1968).
84. G. V. Schulz and A. Horbach, Z. phys. Chem. (Frankfurt), 22, 377 (1959).
85. J. Springer, K. Ueberreiter, and E. Möller, Z. Elektrochem., 69, 494 (1965).
86. P. J. Streeter and P. F. Spencer, J. Polymer Sci., 14, 5 (1954).
87. H. Staudinger, "Die hochmolecularen organischen Verbindungen" (Translated into Russian), Inostr. Lit., Leningrad, 1935, p. 184.
88. P. J. Streeter and P. F. Spencer, J. Polymer Sci., 14, 5 (1954). [Identical to Ref. 86].
89. H. G. Fendler, H. Rohlender, and H. A. Stuart, Makromol. Chem., 18–19, 383 (1956).
90. D. C. Pepper and P. P. Rutherford, J. Polymer Sci., 35, 299 (1959).
91. B. A. Feit, J. Wallach, and A. Zilkhs, J. Polymer Sci., A2, 4743 (1964).
92. N. V. Mikhailov and S. G. Zelikman, Kolloid. Zhur., 19, 465 (1957).
93. A. I. Krasheninnikov, V. A. Morozov, V. P. Shaboldin, and L. Ya. Galishnikova, Vysokomol. Soed., A14, 274 (1972).
94. V. P. Shaboldin, A. I. Krasheninnikov, E. V. Gruzinov, and V. N. Demishev, in "Issledovaniya Protsessov Proizvodstva v Mashinostroenii" (Research on Production Processes in Engineering), Trudy Vses. Zaoch. Mashinostroit. Inst., Moscow, 1973, Vol. 2, p. 217.
95. A. A. Tager and V. E. Dreval', Uspekhi Khim., 36, 588 (1967) [Russ. Chem. Rev., No. 4 (1967)].
96. J. Schurz, Kolloid. Z., 227, 78 (1968).
97. F. Büche, J. Appl. Phys., 26, 738 (1955).
98. V. E. Gul' and V. N. Kuleznev, "Struktura i Mekhanicheskie Svoistva Polimerov" (Structure and Mechanical Properties of Polymers), Izd. Vysshaya Shkola, Moscow, 1966.
99. J. D. Ferry, "Viscoelastic Properties of Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1963.
100. W. Kuhn, H. Kuhn, and P. Buchner, Ergebn. exakt. Naturwiss., 25, 1 (1951).
101. Yu. S. Lipatov, Yu. N. Panov, L. M. Sushko, and S. Ya. Frenkel', Vysokomol. Soed., B12, 500 (1970).
102. O. I. Nachinkin, A. I. Ageev, and I. G. Ruban, Vysokomol. Soed., B15, 520 (1973).
103. V. A. Kargin and G. L. Slonimskii, "Kratkie Ocherki po Fiziko-khimii Polimerov" (Short Essays on the Physical Chemistry of Polymers), Izd. Moskov. Gos. Univ., 1967.
104. Yu. S. Lipatov, Yu. N. Panov, L. M. Sushko, and S. Ya. Frenkel', Dokl. Akad. Nauk SSSR, 176, 1341 (1967).
105. S. Ya. Frenkel', S. A. Agranova, and V. G. Baranov, International Conference on the Chemistry of Macromolecular Compounds, Prague, 1965.
106. F. Büche, in "Fizika Polimerov" (The Physics of Polymers) (Translated into Russian), Inostr. Lit., Moscow, 1960.
107. A. A. Tager, V. E. Dreval', and F. A. Khasina, Vysokomol. Soed., 5, 432 (1963).
108. V. E. Dreval', A. A. Tager, and A. S. Fomina, Vysokomol. Soed., 5, 1404 (1963).

All-Union Engineering Correspondence Institute, Moscow