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ABSTRACT

The processes of $ZnCl_2$ selective sorption by macromolecules of polymethyl methacrylate and polybutyl methacrylate in binary mixtures with $ZnCl_2$ have been studied using light scattering and equilibrium dialysis methods. It has been shown that to a certain concentration of $ZnCl_2$, its average concentration in the volume of macromolecular coils is equal to that of the complexing agent in the solution, i.e., the parameter of the selective sorption $\beta = 0$. However, for the system PBMA-BMA-$ZnCl_2$ with increasing $[ZnCl_2]$, a negative value of β is observed. After the "threshold" concentration of $[ZnCl_2]$:methyl methacrylate = 0.08, butyl methacrylate = 0.15, an increase in the selective sorption of $ZnCl_2$ concentrations is found. The interaction of $ZnCl_2$ with macromolecules of polymethyl methacrylate and polybutyl methacrylate is accompanied by a change in the steric parameter and in the thermodynamic quality of the solvent. A probable mechanism of $ZnCl_2$ interaction with polymer coils is discussed.

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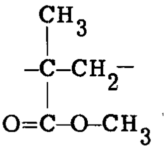
Many reactions involving the participation of macromolecules occur in multicomponent solutions, and the distribution of solvent components, within and outside of a polymer coil, can considerably affect the process features. Hence, the behavior of macromolecule in binary solvents is important in the study of the physical chemistry of polymer solutions. Radical polymerization in the presence of complexing agents (CA), where the latter considerably influence the kinetic features of the reaction [1, 2], is an example of a process in which these effects should be manifested. In particular, in methyl methacrylate (MMA) polymerization an increase in CA ($ZnCl_2$) concentration results in an increase in the chain propagation constant, influences the composition of copolymers, and can cause a sharp drop in the bimolecular termination constant. It has been assumed that the latter is connected with the specific interaction of CA molecules with the propagating macroradicals [3, 4].

This paper reports on studies of the behavior of methacrylic polymers in the binary solvent monomer-$ZnCl_2$. These studies permitted us to simulate the polymerizing system and to learn the effects of complexation on the equilibrium flexibility of a macromolecule. These data are also of independent interest because they permitted us to elucidate the specific characteristics of complexing with the participation of macromolecular ligands.

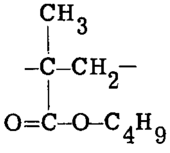
EXPERIMENTAL

Samples of polymethyl methacrylate (PMMA) and polybutyl methacrylate (PBMA) were prepared by radical polymerization. They were fractionated using the generally accepted methods. The characteristics of the fractions used are listed in Tables 1 and 2. MMA and BMA, after preliminary drying over $CaCl_2$ and $LiAlH_4$, were distilled in vacuo. $ZnCl_2$ was purified by sublimation in vacuo at 500°C. The preparation of solutions of $ZnCl_2$ in the monomers was carried out in a dry box.



$$\begin{array}{c} CH_3 \\ | \\ -C-CH_2- \\ | \\ O{=}C-O-CH_3 \end{array}$$

Polymethyl methacrylate



$$\begin{array}{c} CH_3 \\ | \\ -C-CH_2- \\ | \\ O{=}C-O-C_4H_9 \end{array}$$

Polybutyl methacrylate

A photoelectric nephelometer CPG-21 (Shimadzu, Japan) was used to study light scattering by PMMA and PBMA in binary solvents. The apparatus was calibrated by benzene by using $R_{90} = 48.5 \times 10^{-6}$. Be-

TABLE 1. Results of Studies of Light Scattering by PMMA Solutions ($\overline{M}_w$ = 16.0 × 10^4) in MMA-$ZnCl_2$ Mixtures

$[ZnCl_2]$/[MMA] in solution	$\overline{M}_{w(app)} \times 10^{-4}$	$\partial n/\partial c$	β (mL/g)	ΔN	$A_{2r} \times 10^3$ $cm^3/g{\cdot}mol$
0	16.1	0.0754	-	-	0.285
0.012	15.6	0.0450	-	-	0.268
0.060	17.8	0.0725	0.0120	3	0.289
0.080	18.5	0.0710	0.0168	4	0.318
0.106	17.5	0.0690	0.0100	-	0.317
0.115	26.3	0.0670	0.0583	11	0.682
0.141	35.0	0.0660	0.0976	21	1.116
0.165	37.7	0.0650	0.1074	23	1.110
0.200	60.0	0.0635	0.1836	39	2.213
0.250	100.0	0.0610	0.2826	60	4.000
0.325	166.0	0.0566	0.3882	83	7.003

TABLE 2. Results of Studies of Light Scattering and Equilibrium Dialysis in PBMA Solutions ($\overline{M}_w = 30.3 \times 10^4$) in BMA-$ZnCl_2$ Mixture[a]

$[ZnCl_2]$ / [BMA] in solution	$\partial n/\partial c$ before dialysis	$\overline{M}_{w(app)} \times 10^{-4}$	$\partial n/\partial c$ after dialysis	$\overline{M}_r \times 10^{-4}$[b]	β (mL/g) Light scattering	β (mL/g) Equilibrium dialysis	ΔN	$\bar{\bar{v}}_{12}$	$A_{2r} \times 10^3$ $cm^3/g \cdot mol$
0	0.0520	30.3	-	30.2	0	-	0	-	0.280
0.031	0.0509	30.3	0.0509	30.3	0	0	0	-	0.238
0.048	0.0469	30.3	0.0469	30.3	0	0	0	-	0.238
0.069	0.0442	31.3	0.0442	31.3	0	0	0	-	0.200
0.093	0.0428	21.7	0.0362	30.3	-0.0625	-0.0631	-	0.027	0.120
0.116	0.0442	21.7	0.0375	30.1	-0.0645	-0.0640	-	0.0326	0.170
0.148	0.0389	35.7	-	-	0.025	-	8	0.042	0.300
0.193	0.0335	47.6	0.0415	31.0	0.075	0.0765	23	-	0.365
0.242	0.0309	55.6	0.0415	30.8	0.1016	0.1013	30	-	0.387

[a] $\partial n/\partial u_1 = 0.1046\ cm^{-1}$.

[b] $\overline{M}_r$ is calculated using $\partial n/\partial c$ after equilibrium dialysis.

fore making measurements, dust was removed from the solutions by filtration through fine pore glass filters with an average pore diameter of not larger than 12 μm.

The increment of refraction index was determined with a differential refractometer DR-48 (Shimadzu, Japan) in a thermostated cuvette.

The "apparent" molecular mass was determined according to Ref. 5. The "real" molecular mass of the polymers was determined by light scattering in different single-component solvents. The values of molecular masses in various solvents differed by not more than 6%.

The selective sorption in the PMMA-MMA-$ZnCl_2$ and PBMA-BMA-$ZnCl_2$ solutions was characterized by a coefficient

$$\beta = -\partial \bar{\bar{v}}_1/\partial c$$

where $\bar{\bar{v}}_1$ = volume fraction of $ZnCl_2$ in mixed solvents

c = polymer concentration

β = coefficient of selective sorption, showing the change of the volume fraction of a good solvent in a polymer coil with increasing polymer concentration

β was determined by light scattering according to Ref. 5 by the equation

$$\beta = \left(\frac{M_{app}^{0.5}}{M_r^{0.5}} - 1 \right) \frac{\partial n/\partial c}{\partial n/\partial v_1}$$

where M_{app} = "apparent" molecular mass measured by light scattering in a mixed solvent

M_r = real molecular mass determined by light scattering in a single component solvent

$\partial n/\partial c$ = increment of refractive index

Second virial coefficients were calculated by the equation [6]

$$A_{2r} = \frac{A_{app}}{M_r} \cdot A_{2app}$$

where A_{2app} is the second virial coefficient, defined as a tangent of the slope of the dependence of K_c/R_θ on c in a binary mixture.

The equilibrium dialysis for the PBMA-BMA-$ZnCl_2$ system was carried out in a dialyzer consisting of two glass cylinders separated by a semipermeable membrane, "Sartorius Membranfilter," with a pore diameter of 50 Å. Equilibrium was achieved after 2 days in all cases. In this case the selective sorption coefficient was calculated by the formula

$$\beta = \frac{(\partial n/\partial c)_{\mu} - (\partial n/\partial c)_{u_1}}{\partial n/\partial u_1}$$

where $(\partial n/\partial c)_{u_1}$ = increment of the solution refractive index at constant concentrations of the components in a mixture of solvents

$(\partial n/\partial c)_{\mu}$ = increment of the solution refractive index at constant chemical potentials of the mixture of solvents, i.e., at a dialysis equilibrium between the polymer solution and the mixture of solvents of the corresponding composition

$(\partial n/\partial u_1)$ = increment of the refractive index of the mixture of solvents

The average number of the solvent molecules ΔN, selectively sorbed by a hundred units of a polymer chain, is calculated for both systems in accord with Ref. 7 by

$$\Delta N = \beta M_0/\underline{\underline{V}}_1$$

where M_0 = molecular mass of the chain monomer unit

$\underline{\underline{V}}_1$ = molecular volume of the solvent

Viscometric studies for both systems were carried out with an Ubbelohde viscometer. The steric factor, σ, of PMMA and PBMA macromolecules was calculated by the method of Stockmayer and Fixman [8]:

$$[\eta]/M^{1/2} = K_\theta + 0.51B\Phi_0 M^{1/2}$$

where $B = \gamma/M_c{}^2$, γ is the excluded segment volume

M_c = molecular mass of the macromolecule segment

M = polymer molecular mass

Φ_0 = Flory constant, equals 2.87×10^{21} mol^{-1}

K = coefficient of Mark-Kuhn-Houwink $[\eta] = KM^{\alpha}$ for the θ-solvent

$[\eta]$ = polymer intrinsic viscosity in a binary solvent

σ was calculated by the equation

$$\sigma = \frac{M_0^{1/2}}{3.08 \times 10^{-8}} \frac{K_\theta^{1/3}}{\Phi^{1/3}}$$

The value of the specific partial volume ($\bar{v}_2$) of PBMA in BMA-$ZnCl_2$ solutions of different concentrations was determined pycnometrically in a bicapillary dilatometer (the capillary diameter ~ 0.7 mm) with a volume of 7.30 mL. The calculations were performed using the equation

$$\bar{v}_2 = \frac{1}{\rho} \left(1 - \frac{1 - c}{m} \frac{\Delta m}{c}\right)$$

where ρ = solution density
m = solution weight
Δm = difference between the weight of solution and solvent

The change of solvent composition within the polymer coils of PBMA, $\Delta\bar{\bar{v}}_1 = (\bar{\bar{v}}_{12} - \bar{\bar{v}}_{11})$ ($\bar{\bar{v}}_{11}$ and $\bar{\bar{v}}_{12}$ are the volume fractions of $ZnCl_2$ outside and within the polymer coil, respectively, caused by the selective sorption $\Delta\bar{\bar{v}}_1 = \beta([\eta]\, 2.5 - \bar{v}_2)^{-1}$, is calculated by taking into consideration data on the intrinsic viscosity and specific partial volumes of the polymer in the mixed solvent [9].

RESULTS AND DISCUSSION

The interaction of PMMA and PBMA macromolecules with $ZnCl_2$ in binary solutions of MMA-$ZnCl_2$ and BMA-$ZnCl_2$ has been studied. The main feature of these systems is that CA can interact both with the ester groups of the monomer substituents and with the polymer chain units.

Experimental data on light scattering by solutions of PMMA and PBMA in binary solvents (MMA-$ZnCl_2$ and BMA-$ZnCl_2$, respectively) of different composition are shown in Figs. 1 and 2. It is seen that the dependences are linear over the whole range of polymer concentrations. This fact suggests that at a change of concentration of polymer solution, no processes of aggregation or dissociation of the macromolecules are observed. Studies of PMMA-MMA-$ZnCl_2$ mixtures by the speed sedimentation method have shown one sedimentation peak. This indicates the absence of processes connected with the nonuniform distribution of $ZnCl_2$ molecules between the polymer chains as observed in Ref. 10.

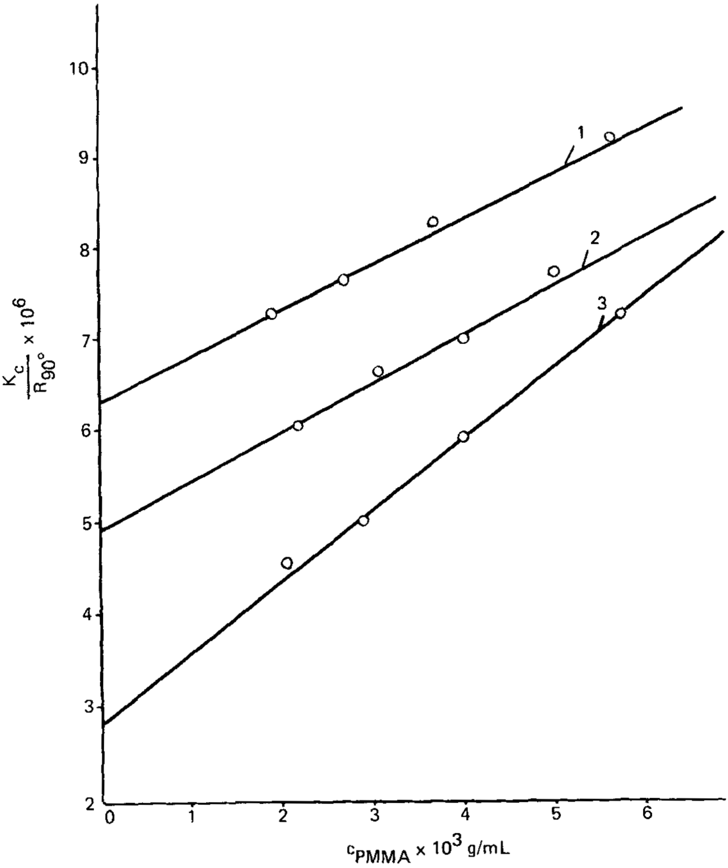


FIG. 1. Dependences of $K_c/R_{90°}$ on PMMA concentration in MMA-$ZnCl_2$ mixtures at $ZnCl_2$ concentration in the binary solvent MMA-$ZnCl_2$ equal to 0.012 (1), 0.106 (2), and 0.115 (3).

The "apparent" average molecular weights of polymers have been calculated from the concentration dependences of light scattering. The data are listed in Tables 1 and 2. It is seen that the values of $\overline{M}_w$ depend on the mixture composition. The parameters of the selective sorption β are calculated from the values of the "apparent" average molecular masses of the polymers. Note that when the values of $\partial n/\partial c$ are used, measured after achievement of the dialysis equilibrium of the polymer solution in binary solvent, $\overline{M}_w$ of the polymer sample

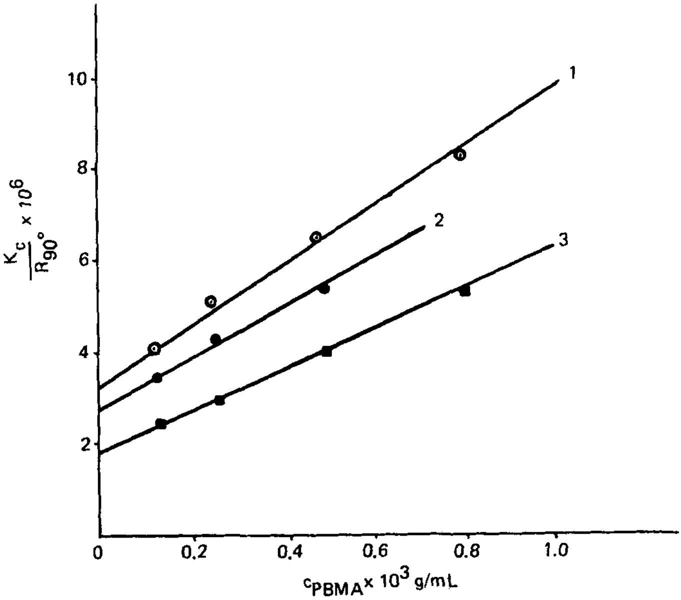


FIG. 2. Dependences of K_c/R_{90° on concentration in BMA-$ZnCl_2$ mixtures at $ZnCl_2$ concentration in the binary solvent BMA-$ZnCl_2$ equal to 0 (1), 0.148 (2), and 0.242 (3).

ceases to depend on the solvent composition and coincides with the "real" molecular mass as measured in a single-component solvent.

In a number of cases the values of β were determined by a second independent method, equilibrium dialysis, since for the solutions with a high $ZnCl_2$ concentration the values of the increments of refractive indices $(\partial n/\partial c)_{app}$ are small (see Table 2) and that can cause considerable error in the determination of the "apparent" molecular masses and therefore of the values of β.

Dependences of the parameter of selective sorption of $ZnCl_2$ on concentration for the systems PMMA-MMA-$ZnCl_2$ and PBMA-BMA-$ZnCl_2$ as determined by light scattering and equilibrium dialysis are given in Figs. 3 and 4. It is seen that bonding of $ZnCl_2$ by the macromolecules is of an anomalous character. At low contents of $ZnCl_2$ ($[ZnCl_2]/[M] < 0.08$), the $ZnCl_2$ concentration within the polymer coils is equal to the average concentration of $ZnCl_2$ in the solution in

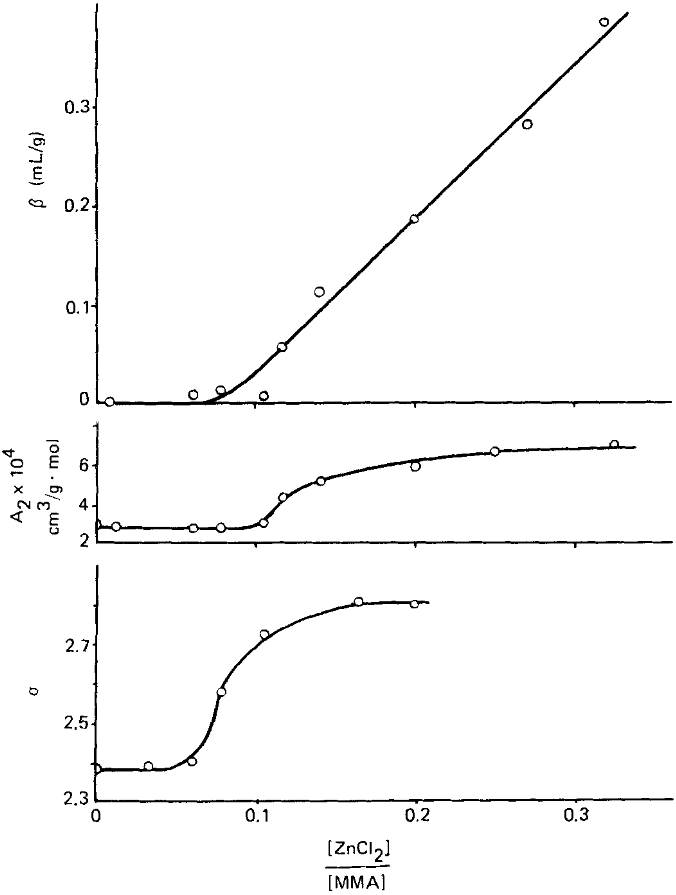


FIG. 3. Dependences of the selective sorption coefficient β, second virial coefficient A_2, and steric factor σ on the $ZnCl_2$ content in the PMMA-MMA-$ZnCl_2$ system.

both systems, i.e., specific bonding of CA by the macromolecules is not observed ($\beta = 0$). In the PMMA-MMA-$ZnCl_2$ system, starting from some "threshold" concentration of $ZnCl_2$ in solution ($[ZnCl_2]/[M] > 0.08$), the selective sorption of $ZnCl_2$ by PMMA macromolecules is observed. For the PBMA-BMA-$ZnCl_2$ system, at first $\beta = 0$, then it becomes smaller than zero, and then, having passed a pronounced minimum, it starts to increase.

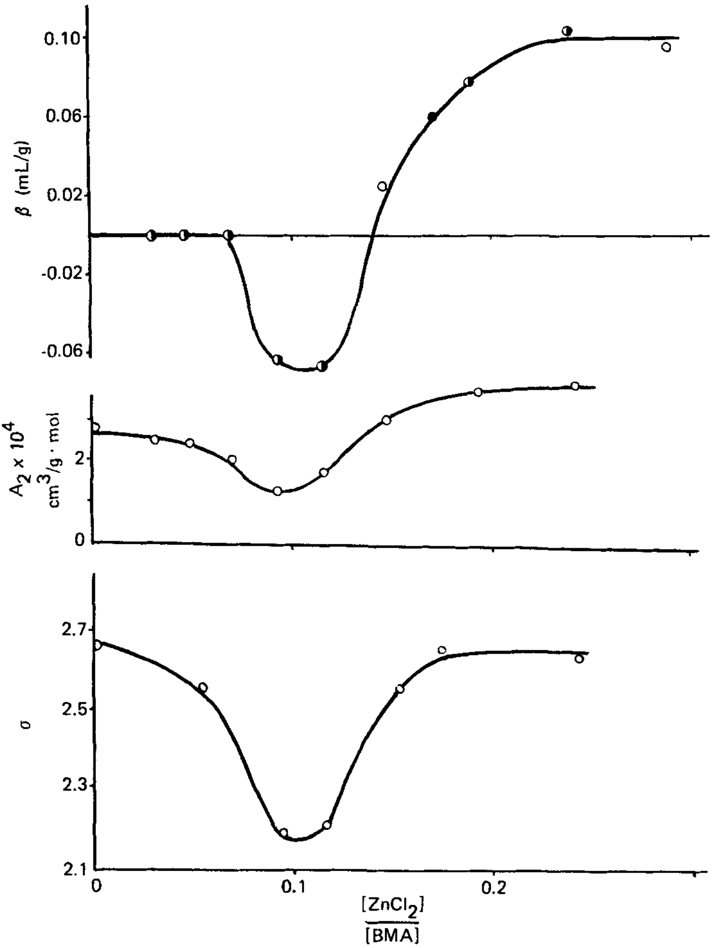


FIG. 4. Dependences of the selective sorption coefficient β, second virial coefficient A_2, and steric factor σ on the $ZnCl_2$ content in the PBMA-BMA-$ZnCl_2$ system.

The negative values of β imply that the average concentration of CA in the macromolecule volume is lower than that in the solution, although the volume fraction of $ZnCl_2$ molecules within the polymer coil continues to increase with increasing $ZnCl_2$ in the solution (Table 2).

The existence of the "threshold" concentration for the occurrence of specific sorption of low molecular substances on macromolecules is by no means trivial. A few theoretical papers on selective sorption in ternary systems (polymer-mixed solvent) predict the extremal dependence of the parameter β on solvent composition. Similar dependences were found for most experimentally studied systems. However, in these systems no coordination bonds with the units of macromolecules could be formed by any component of the mixed solvent.

The interaction of PMMA and PBMA macromolecules with $ZnCl_2$ results in a change of thermodynamic quality of the solvent, reflected by the dependence of the second virial coefficient, A_2, on $ZnCl_2$ concentra-

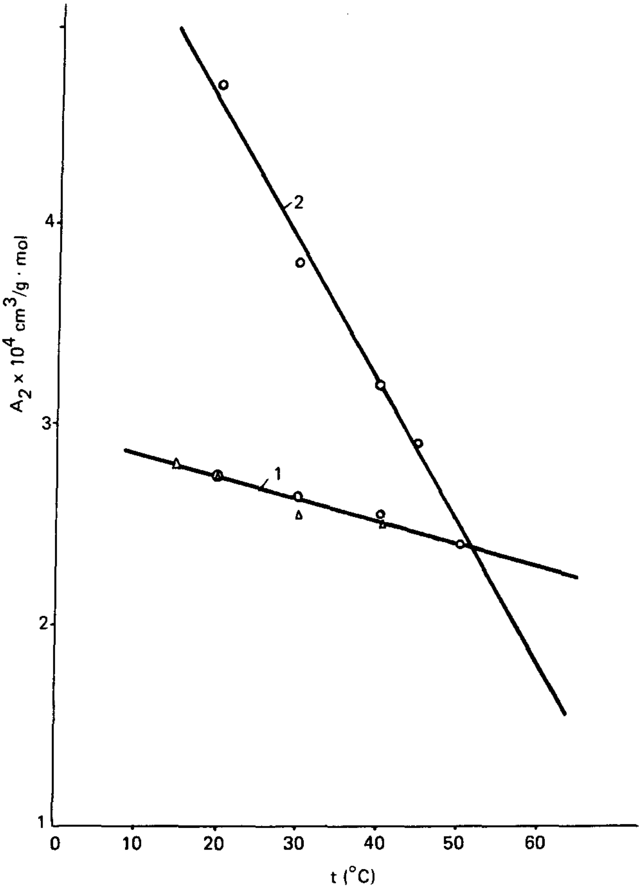


FIG. 5. Temperature dependences of second virial coefficients for the PMMA-MMA-$ZnCl_2$ system: 1, C_{ZnCl_2} = 0.012 (○) and 0.08 (△) g/mL; 2, C_{ZnCl_2} = 0.165 g/mL.

tion in the solution. The dependences of A_2 on $ZnCl_2$ concentration (for both systems) are represented in Figs. 3 and 4. At a small $ZnCl_2$ content ($[ZnCl_2]/[MMA] < 0.08$; $[ZnCl_2]/[BMA] < 0.09$), A_2 decreases, i.e., $ZnCl_2$, in small amounts, acts as a precipitant with respect to PMMA and PBMA.

An increase in $ZnCl_2$ content in the solution causes an increase in the second virial coefficient in that concentration range where an increase in the selective sorption parameter is observed.

The dependence of A_2 on temperature for the PMMA-MMA-$ZnCl_2$ system is given in Fig. 5. It is seen that PMMA solutions in MMA-$ZnCl_2$ mixtures are characterized by negative temperature coefficients, indicating that these solutions are characterized by a lower critical temperature of mixing (see Table 3). In the range $\beta \leq 0.016$, the change

TABLE 3. Results of Studies of the Temperature Dependence of $ZnCl_2$ Selective Sorption in the PMMA-MMA-$ZnCl_2$ System

Composition of the solvent of MMA-$ZnCl_2$: C_{ZnCl_2} (g/mL)	T (°C)	$M_{app} \times 10^{-4}$	β (mL/g)	$A_{2app} \times 10^4$ cm^3/g·mol
0	25	16.0	-	2.85
0.0123	20	15.3	0	2.75
0.0123	30	15.7	0	2.65
0.0123	40	16.0	0	2.56
0.0123	50	17.0	0.007	2.40
0.080	15	17.7	0.011	2.80
0.080	20	18.5	0.016	2.75
0.080	30	20.2	0.027	2.55
0.080	40	22.0	0.038	2.50
0.165	20	37.7	0.107	4.7
0.165	30	35.7	0.100	3.8
0.165	40	35.0	0.096	3.2
0.165	45	37.7	0.106	2.9

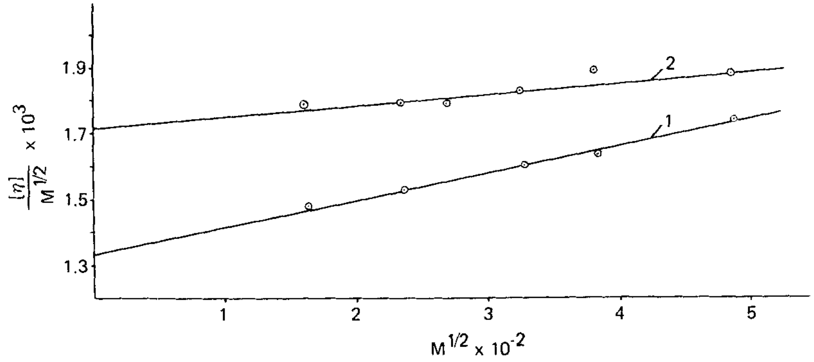


FIG. 6. Stockmayer-Fixman extrapolation for the PMMA-MMA-$ZnCl_2$ system at the concentrations of complexing agent 0.073 (1) and 0.201 (2).

of second virial coefficients with temperature is negligible (Curve 1). Abrupt changes of A_2 with temperature are observed in the range of $ZnCl_2$ concentrations (~0.165 g/mL) where an increase in the selective sorption parameter occurs. Thus, the thermodynamic quality of the solvent strongly depends on the $ZnCl_2$ content and the solution temperature.

This extraordinary behavior of polymer molecules in the binary solvent can evidently be connected with the macromolecular nature of the ligands; in particular, with conformational changes of the macromolecules. These changes were studied viscometrically by the Stockmayer-Fixman method which permits estimation of the unperturbed chain dimensions even in good solvents, i.e., at $A_2 > 0$.

Viscometric data in the coordinates of Stockmayer-Fixman are given in Figs. 6 and 7. The dependences are linear over the entire range of the polymer molecular weights studied, indicating the applicability of this method to these systems. The coefficient K_θ of Mark-Kuhn-Houwink equation for θ-solvents was calculated from viscometric data. The steric factor σ can be easily calculated as

$$\sigma = \frac{\langle \overline{h}_\theta^{\,2} \rangle^{1/2}}{\langle h_{fr}^{\,2} \rangle^{1/2}}$$

where $\langle \overline{h}_\theta^{\,2} \rangle$ = mean square distance between the ends of the macromolecule, measured in the θ-solvent

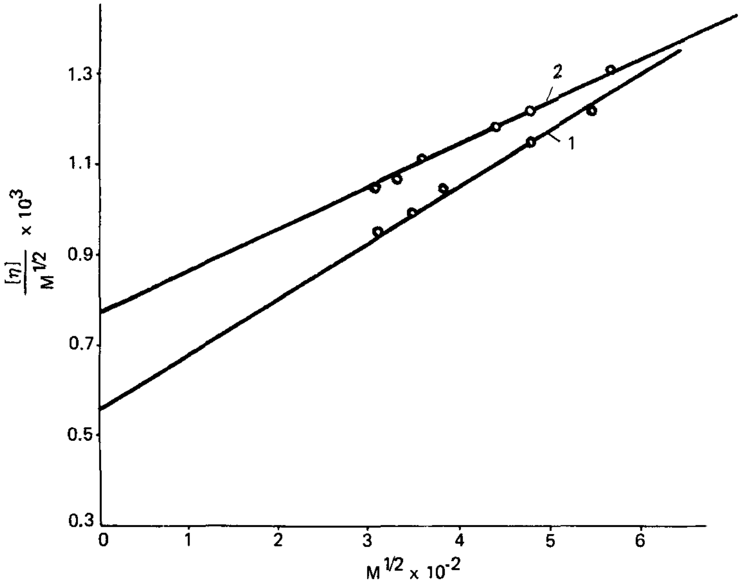


FIG. 7. Stockmayer-Fixman extrapolation for the PBMA-BMA $ZnCl_2$ system at the concentrations of complexing agent 0.117 (1) and 0.154 (2).

$\langle \overline{h}_{fr}^2 \rangle$ = mean square distance between the ends of the macromolecule calculated under the assumption of free rotation

Figures 3 and 4 show the dependence of the steric factor on $ZnCl_2$ concentration for the PMMA-MMA-$ZnCl_2$ and PBMA-BMA-$ZnCl_2$ systems in the range $0 < [ZnCl_2]/[M] < 0.06$. It is seen that macromolecules maintain their initial equilibrium flexibility over the range of β values equal to zero. In the PBMA-BMA-$ZnCl_2$ system, an increase in $ZnCl_2$ concentration results in a decrease in unperturbed dimensions of macromolecules where $\beta < 0$. At a further increase in CA concentration in the solution, growth of the unperturbed dimensions of macromolecules is observed in the region where $\beta > 0$. In other words, the dependence of σ on c_{ZnCl_2} is similar to the behavior of β.

The values of the steric factor σ for both systems in the absence of $ZnCl_2$, obtained in this paper, are somewhat higher than the values of σ

for the same polymers in θ-solvents [11, 12], evidently due to the effect of the solvent on the flexibility of the polymer chain.

Thus, complexation of PMMA and PBMA macromolecules in a mixed solvent (monomer $ZnCl_2$) is accompanied by unusual changes of the parameters β, A_2, and σ. The latter change symbatically with increasing CA concentration in the solution.

To explain these phenomena, let us consider a possible mechanism of $ZnCl_2$ interaction with PMMA and PBMA macromolecules in solutions of their monomers. It is known that a zinc ion in $ZnCl_2$ has the coordination number 4, and therefore, due to the two free vacancies, it can form strong coordination complexes with carbonyl-containing organic substances [13]. Hence, it can be assumed that in a solution of the monomers the main part of $ZnCl_2$ exists in the form of a complex with MMA and BMA molecules that can be presented schematically as

$$M - - - ZnCl_2 - - - M$$

At low $ZnCl_2$ content, where $\beta \approx 0$ (the average concentrations of $ZnCl_2$ in the solution and in the volume occupied by a macromolecule are the same), the polymer molecules can interact with $ZnCl_2$ via the formation of single complexes of the type represented in Fig. 9, Scheme A,) where one coordination valency interacts with the carbonyl group of the polymer chain and the second one interacts with the carbonyl group of the monomer.

Due to the close basicity of carbonyl groups in a monomer molecule and in a monomer unit of the polymer, it follows from $\beta = 0$ at small $ZnCl_2$, the substitution of the monomer molecule in the complex $M - - - ZnCl_2 - - - M$ for the polymer chain group does not result in an appreciable change of the system free energy. This is also indicated by the temperature dependence of the selective sorption parameter for the PMMA-MMA-$ZnCl_2$ system (Fig. 8). Within experimental error, the parameter β does not depend on the solution temperature. This means that the enthalpy of recomplexation is close to zero and the interaction force is of an entropic nature.

When the concentration is increased above the "threshold" value, the interaction of polymer chain units with a $ZnCl_2$ molecule cannot be limited by substitution of one molecule of the solvent for the polymer chain unit, but probably proceeds further. As a result of this, a $ZnCl_2$ molecule becomes coordinationally bonded to two units of polymer chain, and two free molecules of MMA or BMA are eliminated into the solution (Fig. 9, Scheme B). The total number of solvent-free mole-

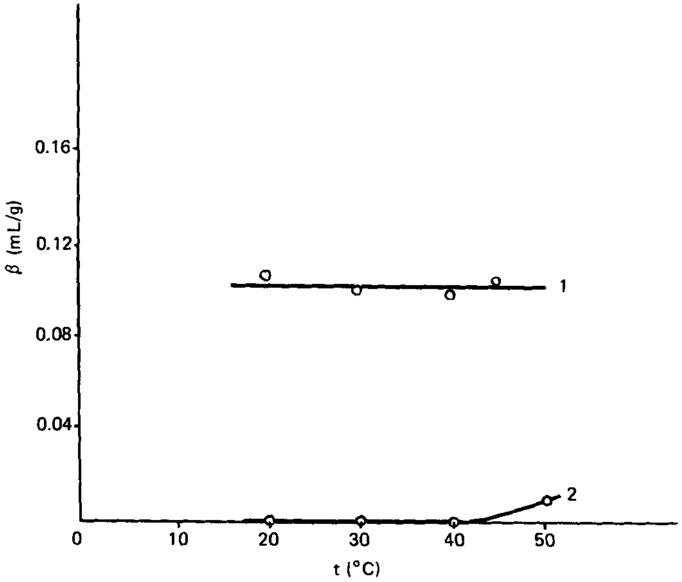


FIG. 8. Temperature dependence of the selective sorption coefficient β for the PMMA-MMA-$ZnCl_2$ system: 1, C_{ZnCl_2} = 0.012 g/mL; 2, C_{ZnCl_2} = 0.165 g/mL.

cules is increased, and that must lead to an increase in entropy of the polymer-solvent system. On the other hand, the formation of this complex between monomer units in PMMA or PBMA at large distances along the chain (reversible cross-link) is accompanied by a decrease in the conformational set of macromolecules and thus by a decrease in their entropy.

The negative value of β found in another range of $ZnCl_2$ concentrations ($0.07 < [ZnCl_2]/[BMA] < 0.15$) indicates that the formation of intramolecular reversible cross-links is the main contribution to the change of the total entropy of the system ($\Delta S_{tot} < 0$). This is shown by a decrease in the unperturbed dimensions of the BMA chain (Figs. 3 and 4; Fig. 9, Scheme B).

Finally, in the range $\beta > 0$, the main contribution to the entropy change of the PMMA-MMA-$ZnCl_2$ and PBMA-BMA-$ZnCl_2$ system is evidently made by the change of the entropy of solution mixing. Really, as shown in Ref. 14, entropy of the macromolecule is not decreased proportionally to the number of cross-links, but considerably slower, while the configurational entropy of the system as a whole is increased

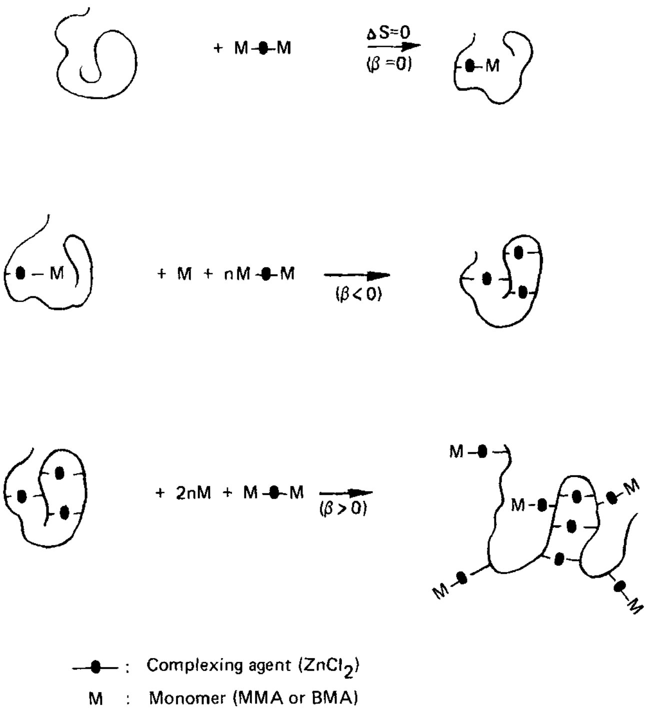


FIG. 9. Scheme of complexation for the PMMA-MMA-ZnCl$_2$ and PBMA-BMA-ZnCl$_2$ systems.

proportionally to the number of MMA and BMA molecules eliminated due to ZnCl$_2$ bonding to the polymer chain.

Hence it follows that at some "threshold" of ZnCl$_2$ concentration the total change of the system entropy is larger than zero, resulting in a predominant bonding of ZnCl$_2$ to the polymer ligand. The excess number of ZnCl$_2$ molecules bonded to the polymer in the range of positive selective sorption are listed in Tables 1 and 2. It should be noted that in this range of ZnCl$_2$ concentration the growth of the unperturbed chain dimensions is observed as well as is an improvement in the solvent thermodynamic quality for the PMMA and PBMA solutions.

Thus, the interaction of PMMA and PBMA macromolecules with ZnCl$_2$, the latter playing the role of a physical bifunctional cross-linking agent, leads to important conformational changes of macromolecules as reflected by the appearance of both positive and negative selective sorption of the bifunctional complexing agent on a polymer chain. The features of complexation of PMMA and PBMA with $ZnCl_2$ are therefore determined by the polymeric nature of the ligand.

The results obtained permit us to understand the previously revealed CA effect on the bimolecular termination constant (k_t) at the MMA radical polymerization in the presence of CA [1]. The dependence of k_t on the $ZnCl_2$ content in the reaction mixture at the initial stages of transformation is given in Fig. 10 for comparison, the dependence of $ZnCl_2$ selective sorption on PMMA chains in a binary solution is given in the same figure. It follows that the region of the k_t sharp drop coincides with the beginning of an increase in CA selective sorption by the macromolecules. This fact confirms the hypothe-

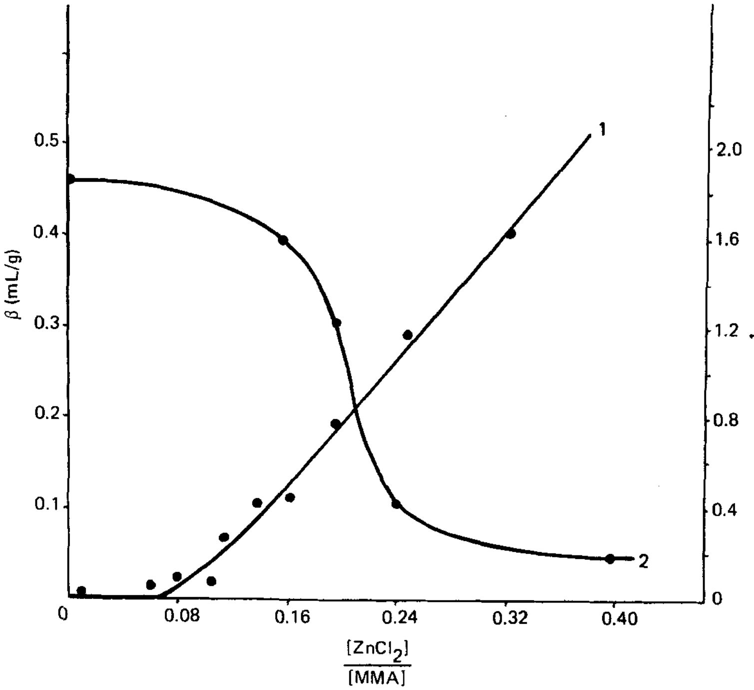


FIG. 10. Dependences of the selective sorption coefficient β (1) of PMMA solutions in MMA-$ZnCl_2$ binary solvent on the solvent composition and the dependence of the chain termination constant k_t (2) in the radical polymerization of MMA in the presence of $ZnCl_2$ on the complexing agent content in a monomer mixture.

sis, suggested previously [1], that a decrease in k_t is caused by bonding of polymer chains to CA and the corresponding increase in rigidity of the propagating macroradicals.

At low temperature postpolymerization of MMA in the presence of $ZnCl_2$, the same effects result in practically complete suppression of the reaction of bimolecular termination, permitting continuous radical polymerization according to the "living chains" mechanism [15].

SYMBOLS

β	selective sorption coefficient
c	polymer concentration
$\bar{\bar{v}}_1$	volume fraction of $ZnCl_2$ in mixed solvents
M_{app}	"apparent" molecular mass measured by light scattering in a mixed solvent
M_r	real molecular mass measured by light scattering in a single component solvent
$\partial n/\partial c$	increment of the refractive index
A_{2r}	second virial coefficient determined as a tangent of the slope of K_c/R_θ dependence on C in a single component solvent
A_{2app}	second virial coefficient determined as a tangent of the slope of K_c/R_θ dependence on C in a binary mixture
$(\partial n/\partial c)_{u_1}$	increment of the refractive index at constant concentrations of the components of a solvent mixture
$(\partial n/\partial c)_\mu$	increment of the refractive index at constant chemical potentials of the components of a solvent mixture, i.e., at the dialysis equilibrium between the polymer solution and the solvent mixture of the corresponding composition
$(\partial n/\partial u_1)$	increment of the refractive index of a mixture of solvents
ΔN	average number of solvent molecules selectively sorbed by 100 units of polymer chain
M_o	molecular mass of the chain monomer unit
$\underline{\underline{V}}_1$	molecular volume of the solvent
σ	steric factor
γ	excluded volume of the segment
M_c	molecular mass of the macromolecule segment

M	polymer molecular mass
Φ_o	Flory's constant
K	coefficient of Mark-Kuhn-Houwink for a θ-solvent
$[\eta]$	polymer intrinsic viscosity in a binary solvent
$\bar{v}_2$	specific partial volume of the polymer in a solvent
ρ	solution density
m	solution weight
Δm	difference between the weight of solution and solvent
$\Delta\bar{\bar{v}}_1$	change of the solvent composition inside of polymer macromolecule coils
$\bar{\bar{v}}_{11}, \bar{\bar{v}}_{12}$	volume fractions of $ZnCl_2$ out of and inside of a polymer coil respectively
$\langle \bar{h}_\theta^2 \rangle$	mean square distance between the ends of the macromolecule, measured in the θ-solvent
$\langle \bar{h}_{fr}^2 \rangle$	mean square distance between the ends of the macromolecule calculated under an assumption of free rotation
ΔS_{tot}	change of the system total entropy
k_o	constant of chain bimolecular termination

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