

A contribution to the study of the thermodynamics of poly(vinyl chloride) solutions

J. POLAVKA and L. LAPČÍK

Department of Physical Chemistry, Slovak Technical University,
CS-812 37 Bratislava

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Dedicated to RNDr. M. Bohdanecký, DrSc., in honour of his 60th birthday

The solutions of two fractions of poly(vinyl chloride) (PVC) in *N,N*-dimethylformamide (DMFA), cyclohexanone (CYH), and dioxan were thermodynamically characterized. The second virial coefficients and the values of interaction parameters χ were determined osmotically for each solvent at three temperatures. Moreover, the rate of free diffusion in solutions of PVC in the above-mentioned solvents was studied as a function of composition and temperature. The thermodynamic and hydrodynamic factors of the diffusion coefficient were determined. The dependence of both factors on composition and temperature is described.

Проведена термодинамическая характеристика растворов двух фракций полихлорвинила (ПХВ) в *N,N*-диметилформамиде (ДМФ), циклогексаноне (ЦИГ) и диоксане. Осмометрически были определены вторые вириальные коэффициенты и величины параметров взаимодействия χ при трех значениях температуры для каждого растворителя. Далее, изучена скорость свободной диффузии в растворах ПХВ в перечисленных растворителях в зависимости от состава и температуры. Был определен термодинамический и гидродинамический вклад коэффициента диффузии и описаны зависимости обоих вкладов от состава и температуры раствора.

The thermodynamic characterization of polymer solutions is frequently based on the knowledge of the Flory—Huggins interaction parameter χ and diffusion coefficient D [1—3]. If we know the dependence of these quantities on composition and temperature, then we are able on the basis of the theoretical approach put forward by Rehage and coworkers [3—8] to determine some important physicochemical parameters such as thermodynamic factor $\rho_2(\partial\mu_2/\partial\rho_2)$ and mobility of polymer u_2 .

If we use the modification of the semiempirical Flory—Huggins equation (eqns (1—3)), we can osmometrically determine the values of the second virial coefficient B , B_0 and parameter χ which are a quantitative measure of the thermodynamic quality of solvent according to the Flory—Huggins theory [1—3].

$$-\frac{V_{01}p}{RT} = \ln x_1^* + \left(1 - \frac{1}{r}\right)x_2^* + \chi x_2^{*2} \quad (1)$$

$$\frac{pV_{01}}{x^*RT} = \frac{1}{r} + Bx_2^*; \quad B = 0.5 - \chi \quad (2)$$

$$\frac{p}{\rho RT} = \frac{1}{M_2} + B_0\rho; \quad B_0 = \frac{V_{01}}{M_{02}^2}(0.5 - \chi) \quad (3)$$

The symbols V_{01} , p , (x_1^* and x_2^*), ρ , M_{02} , M_2 , $r = M_2/M_{02}$, (B , B_0), and χ stand for molar volume of solvent, osmotic pressure, mole fractions of solvent and polymer ($x_1^* \equiv n_1(n_1 + rn_2)^{-1}$, $x_2^* \equiv rn_2(n_1 + rn_2)^{-1}$), mass concentration of polymer, molecular mass of basic unit of polymer, average numerical molecular mass of polymer, polymerization degree, the second virial coefficient, and the Flory—Huggins interaction parameter, respectively.

If we appreciate the thermodynamic quality of solvent on the basis of the diffusion coefficient D , we may start with the *Rehage* relationship for D and the piece of knowledge obtained in our laboratory according to which the order of the values of D correlates with the order of molar volumes of solvent in a certain temperature interval and, to a certain extent, with viscosity [5, 9, 10]. The value of D is determined not only by pure diffusivity, but it also involves a certain thermodynamic factor of interaction as shown by *Rehage* and coworkers [3, 4, 7, 8].

Then it holds for a binary system (if $D_1 = D_2$) [2] (index 1 denotes solvent and index 2 polymer)

$$D = u_1 \left(\rho_1 \frac{\partial \mu_1}{\partial \rho_1} \right) = u_2 \left(\rho_2 \frac{\partial \mu_2}{\partial \rho_2} \right) \quad (4)$$

The diffusion coefficient is a product of mobility (hydrodynamic factor) u_1 or u_2 and thermodynamic factor $\rho_1(\partial \mu_1/\partial \rho_1)$ or $\rho_2(\partial \mu_2/\partial \rho_2)$. For equal molar volume, different values of D may thus be regarded as a consequence of different degree of the polymer—solvent interaction, i.e. different values of the activity coefficients which immediately determine the value of thermodynamic factor.

The thermodynamic factor of polymer $\rho_2(\partial \mu_2/\partial \rho_2)$ may be calculated from the concentration dependence of the chemical potential in basic mole fractions of polymer [3]

$$\rho_2 \frac{\partial \mu_2}{\partial \rho_2} = (x_1^* V_1 + x_2^* V_2) x_2^* \frac{\partial \mu_2}{\partial x_2^*} \frac{1}{V_1} \quad (5)$$

where V_1 and V_2 are partial molar volume of solvent and of basic building unit of polymer, respectively.

The knowledge of intermolecular interactions in polymer solutions is of fundamental importance for investigating the structure and properties of the polymer phase in solid state as well as in solution. In this line, a great role is played by temperature and concentration — the influence of which on the mentioned parameters has the character of a very intricate relationship. For this reason, the polymer—solvent interaction must always be carefully estimated and attentively investigated [8—12].

Starting from the technological and theoretical problem involving the polymer molecules transition in a solution as well as the properties of these solutions, the aim of this study was to call attention to some possibilities of application resulting from the study of molecular-kinetic properties of a macromolecular substance (*i.e.* PVC) in solution. Moreover, on the basis of determination of physicochemical parameters of the investigated systems (PVC/dioxan, *N,N*-dimethylformamide, cyclohexanone), we wanted to point out the possibility of their further theoretical processing and use for thermodynamic valuation and characterization of PVC fractions in relation with individual solvents.

Experimental

Osmotic pressure was measured with an automatic membrane osmometer (Hewlett—Packard, model 501). The accuracy of osmotic pressure measurement was $\pm(10^{-4} m) \rho_s$ (ρ_s is solvent density).

The osmotic measurements were carried out in the temperature interval of the useability of instrument, *i.e.* 25 °C—65 °C while three temperatures were always chosen for a certain system according to the boiling point of solvent.

The diffusion coefficients were measured with a Jamin interferometer modified by Antweiler [13] by means of which we could measure variations of concentration and refractive index (observe or photograph) as a function of the coordinate z .

The Jamin interferometer modified by Antweiler can be used only if the index of refraction of dissolved substance is different from the index of refraction of solvent. As a matter of fact, only in this case two solutions of different concentration have different indices of refraction. Provided the concentration interval is not too broad, the change in the index of refraction is proportional to the change in concentration. The rightfulness of this assumption for a chosen region of composition expressed in mass fractions is illustrated in Fig. 1. If we know both initial compositions, then we immediately obtain from an interferogram the relationship between the coefficient of diffusion D and composition for a certain time moment t .

The interferograms were taken on black-and-white film (27 DIN) and 6—8 shots of interference field were taken for each measurement. Before each experiment, the measuring channel of the cell (width 1 mm) was photographed. This procedure served for determining

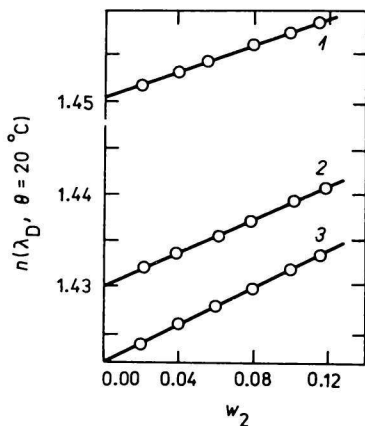


Fig. 1. Variation of the index of refraction n (λ_D , $\theta = 20^\circ\text{C}$) with composition for the system PVC 2—solvent.

1. CYH; 2. DMFA; 3. dioxan.
 w_2 — mass fraction of polymer.

enlargement of the concentration curves which were translated on parchment paper by means of a projector and subsequently evaluated on the basis of the method of common points by the use of constructed stencils.

A laminated cell made of SiO_2 glass which consisted of two main parts *B* and *C* and two plates *A* and *D* (Fig. 2) was used as measuring cell. Fig. 2a represents the cell in measuring arrangement and Fig. 2b in filling arrangement. Both main parts contain four channels (I—IV). Channel I is the measuring cell where the proper diffusion takes place. Channel II is the comparing channel which is filled with a solution of lower concentration. Channel III serves for placement of a thermometer. Channel IV is filled with a solution of higher concentration. The relative precision of the determination of D is loaded with an error ± 2 —4% and the values of activation parameters are loaded with an error ± 4 —8%.

Cyclohexanone (CYH), *N,N*-dimethylformamide (DMFA), and dioxan which were used as solvents were anal. grade chemicals. They were distilled before use. The fractionated PVC was prepared by fractionation of the industrial product (CHZWP, Nováky) (it was amorphous PVC of the emulsion type the syndiotactic portion of which amounted to 60%) and used as basic polymer. The individual fractions were obtained by precipitating the 1% solution of polymer in tetrahydrofuran with water. In order to obtain the possibly narrowest distribution function of individual fractions, we subjected these fractions to two fractional precipitations. The polydispersity of the investigated fractions may be characterized by the ratio of average mass to average number molecular mass (M_w/M_n), i.e. by the value of the

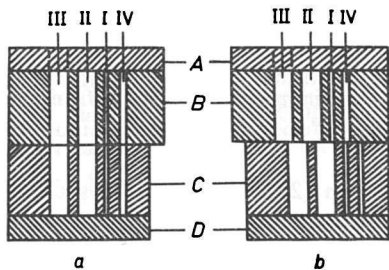


Fig. 2. Diffusion cells: a) working arrangement; b) filling arrangement.

coefficient of polydispersity. The value of this coefficient is 2.54 ($M_w = 126 \text{ kg mol}^{-1}$) for fraction PVC 1 and 2.88 ($M_w = 83.0 \text{ kg mol}^{-1}$) for fraction PVC 2 [5].

Because of the ability of PVC to aggregate in solution [14], all measured solutions were steadily heated for 60 min at 150 °C and subsequently allowed to stand for two days in dark at laboratory temperature [8].

Results and discussion

The graphical interpretation of the osmometric data is presented in the form of the plot of reduced osmotic pressure (multiplied by $1/RT$) against mass concentration (Fig. 3). The slope of the straight line directly determines the value of the second virial coefficient and the intercept on the ordinate gives the numerical value of $1/M_2$. The values of the obtained physicochemical data relating to the investigated systems are listed in Table 1. On the basis of the measured values of

Table 1

Physicochemical quantities of the investigated systems

M_2 — relative average number molecular mass, r — degree of polymerization, χ — Flory—Huggins interaction parameter, B, B_0 — second virial coefficient

System	θ °C	M_2 kg mol ⁻¹	r	χ (eqns (1—3))	$B_0 \cdot 10^3$ m ³ mol kg ⁻²	$B \cdot 10^2$
PVC 1—CYH	25	49.5	792	0.453	1.236	4.89
	45	50.1	802	0.453	1.019	3.99
	65	50.0	800	0.471	0.802	2.98
PVC 2—CYH	25	28.3	453	0.450	1.298	5.25
	45	28.7	459	0.454	1.224	4.81
	65	29.5	471	0.457	1.159	4.54
PVC 1—DMFA	25	46.8	748	0.449	1.009	5.32
	45	48.2	771	0.462	0.748	3.89
	60	47.7	763	0.474	0.509	2.66
PVC 2—DMFA	25	25.9	414	0.444	1.127	6.05
	45	27.4	439	0.453	0.972	5.14
	60	27.6	441	0.462	0.789	4.16
PVC 1—dioxan	25	52.3	837	0.506	-0.136	-0.513
	35	52.2	836	0.502	-0.0546	-0.095
	45	52.1	833	0.499	0.0138	0.182
PVC 2—dioxan	25	30.6	489	0.505	-0.127	-0.393
	35	30.3	485	0.501	-0.0504	-0.023
	45	30.3	484	0.498	0.0367	0.381

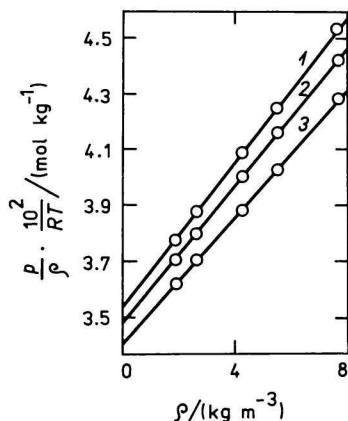


Fig. 3. Variation of the osmotic pressure factor $p/\rho RT$ with composition for the system PVC 2—CYH.

1. 25 °C; 2. 45 °C; 3. 65 °C.

p — osmotic pressure, ρ — mass concentration of polymer.

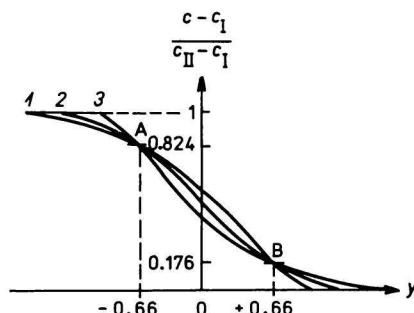


Fig. 4. Integral curves according to Stokes.

A, B are common points, $y = z/2\sqrt{Dt}$, z — coordinate, t — time, D — diffusion coefficient at molar concentration of polymer $c = (c_1 + c_{II})^2$.

1. $D_I/D_{II} = 7.11$; 2. $D_I/D_{II} = 1$; 3. $D_I/D_{II} = 0.141$.

average number molecular mass M_2 (these values are in the interval of precision of their determination $\pm 4\%$), we may state that no dependence of M_2 on temperature has been disclosed for PVC dissolved in the investigated solvents. Equal conclusion was also reported by Roskopf [8]. A great dependence of M_2 on the temperature of measurement is, however, to be observed if PVC is dissolved in poor solvents (anisole, dibenzyl ether) [8], which is evidently due to a very intense association in these systems. The values of χ parameters determined by means of eqns (1—3) are consistent with one another and in good agreement with literature data [15]. These data are independent of concentration in the investigated concentration interval and increase with temperature for CYH and DMFA whereas they slightly decrease with increasing temperature for dioxan, which is in conformity with literature data [8]. The aim of osmotic measurements was to reveal the dependence of the interaction parameter χ on temperature, molecular mass and concentration. The knowledge of these values was very necessary for further processing of the polymer because literature data in this region are not only very rare but also frequently widely different in relation with the author, molecular mass, tacticity of polymer, and temperature. For instance, the values of the Flory—Huggins interaction parameter χ for the PVC—CYH system vary within the range 0.07—0.46 [16]. Moreover, their dependence on molecular mass, temperature, and concentration is differently interpreted and is not fully elucidated.

The processing of experimental data obtained by measuring free diffusion was performed by the Stokes method of common points. This method is based on the assumption of a linear relationship between D and concentration [17]. If we substitute a new independent variable $y = z/2\sqrt{Dt}$, the concentration curves will go through two common points which are symmetrical with respect to the Matan plane [4] (Fig. 4). Fig. 4 represents the plot of $(c - c_I):(c_I - c_{II})$ against $y = z/2\sqrt{Dt}$, where c is the molar concentration and D is the diffusion coefficient for $c = (c_I + c_{II})/2$ while c_I and c_{II} are the initial molar concentrations of polymer in two investigated polymer solutions. The plots are constructed for different values of D_I/D_{II} , where D_I and D_{II} are the diffusion coefficients for concentrations c_I and c_{II} , respectively. The coordinates of the common point according to Stokes [17] are

$$y = 0.66 (c - c_I):(c_{II} - c_I) = 0.176$$

$$y = -0.66 (c - c_I):(c_{II} - c_I) = 0.824$$

The graphical representation of the concentration course of the measured diffusion coefficients (temperature is a parameter) is given in Fig. 5. As the results obtained with the described experimental equipment were not reproducible in the region of very low concentrations (in Fig. 5 sections drawn in dashed lines), the concentration dependence of the diffusion coefficient was extrapolated and drawn in dashed lines. For instance, *Tsvetkov and Klenin* [16] talk about the region of the so-called free diffusion, where a stagnation of D sets in. *Bugdahl* [18] came to

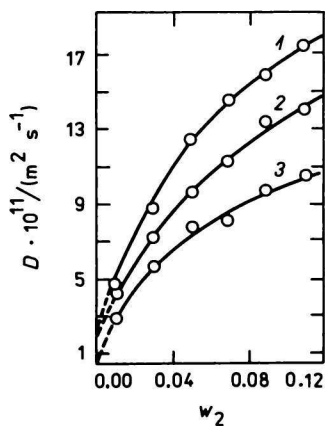


Fig. 5. Variation of the diffusion coefficient D with composition for the system PVC 2—DMFA.
1. 65 °C; 2. 50 °C; 3. 25 °C.
 w_2 — mass fraction of polymer.

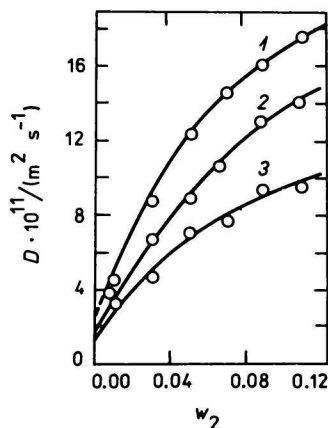


Fig. 6. Variation of the diffusion coefficient D with composition for the system PVC 2—solvent at 65 °C.
1. DMFA; 2. CYH; 3. dioxan.
 w_2 — mass fraction of polymer.

similar conclusion. He determined the boundary region of free diffusion for the styrene—toluene system to be 0.1—0.2 g/100 ml whereas *Tsvetkov* and *Klenin* quote 0.04 g/100 ml for the polystyrene—carbon tetrachloride system.

Fig. 6 shows the qualitative influence of the interaction effect of solvent on the value of the diffusion coefficient D in the investigated system. DMFA, which is less used as a solvent for PVC, appears to be still better solvent than CYH.

The diffusion curve ought to pass through a maximum [7] in the region of higher values of the mass fractions of polymer (about 0.1). It results from the measured concentration curves of the diffusion coefficient that this maximum has not been reached. This maximum may be shifted in the region of higher concentrations.

If we consider that diffusion is disordered motion involving place exchange of the moving molecules, we may describe the temperature dependence of D by an equation of the Arrhenius type

$$D = D_0 \exp(-E_D/RT) \quad (6)$$

where E_D is the activation energy of diffusion and D_0 is the diffusion coefficient at the hypothetical infinitely high temperature.

The values of the concentration dependence of the activation energy of diffusion E_D (Fig. 7) obtained by processing the experimental data by means of the logarithmic form of eqn (6) varied in the range 8—25 kJ mol⁻¹, which was in good agreement with the values obtained earlier for equal fractions of PVC, measured in CYH and tetrahydropyran [19, 20].

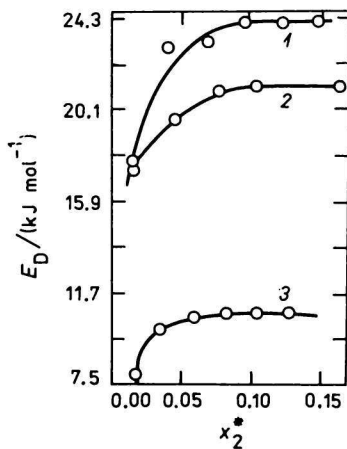


Fig. 7. Activation energy of diffusion E_D as a function of composition for the system PVC 2—solvent, temperature range 25 °C—65 °C.

1. Dioxan; 2. CYH; 3. DMFA.

x_2^* — basic mole fraction of polymer.

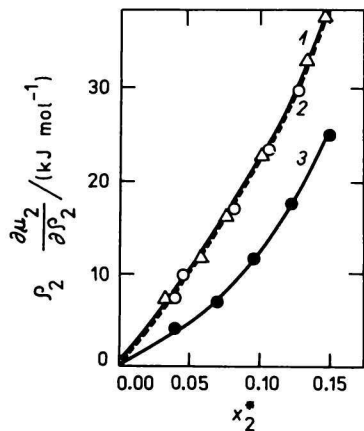


Fig. 8. Thermodynamic factor of polymer $\varrho_2(\partial\mu_2/\partial P_2)$ as a function of composition for the system PVC 2—solvent at 25 °C.

1. CYH; 2. DMFA; 3. dioxan.

x_2^* — basic mole fraction of polymer.

Furthermore, eqns (4) and (5) were used for determining the thermodynamic factor and mobility. The values of molar volumes of pure components necessary for calculation were determined on the basis of literature data [5, 8]. The calculation of molar values, basic mole and volume fractions as well as further calculations necessary for thermodynamic processing of the measured data referring to diffusion and osmosis was performed with a computer TR-4 in the language Algol 60. Then the values of parameters obtained by osmotic pressure measurements served as further input data for calculating the thermodynamic factor and mobility of the investigated polymer in harmony with the procedure put forward by Rehage and coworkers which was especially elaborated by Ernst [3].

The values of the change in chemical potential of polymer $\Delta\mu_2$ were determined on the basis of the following equation

$$x_2^* \frac{\partial \mu_2}{\partial x_2^*} = RT[1 + (r-1)x_2^* - 2\chi r x_2^* x_2^*] \quad (7)$$

which was derived from the Flory—Huggins semiempirical equation and Gibbs—Duhem equation by Ernst [3]. A practical application according to Rehage was successfully put into practice for polystyrene [3] and poly(vinyl chloride) [8].

Fig. 8 represents the concentration dependence of the thermodynamic factor of three systems. We can see that the value of the thermodynamic factor very significantly increases with concentration. However, if we compare the solvents with each other at a certain temperature, it decreases with increasing quality of solvent.

Fig. 9 shows the concentration dependence of the mobility of poly(vinyl chloride) in the investigated solvents. It is evident that the influence of solvent on mobility is much more significant at lower concentrations. A similar conclusion was also drawn by Rehage and Ernst [7] for polystyrene. The values of mobility

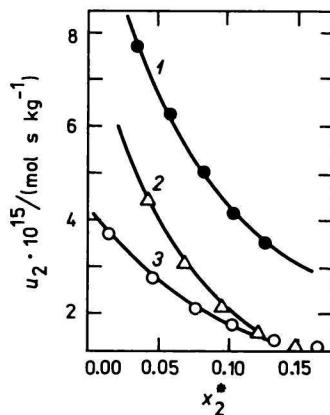


Fig. 9. Variation of mobility u_2 with composition for the system PVC 2—solvent at 25 °C.

1. DMFA; 2. dioxan; 3. CYH.

x_2^* — basic mole fraction of polymer.

measured in this case were, however, three and four times higher, which was obviously due to greater flexibility of the molecular chains of polystyrene when compared with the chains of poly(vinyl chloride). The mobility decreases with increasing concentration, *i.e.* it behaves inversely with respect to viscosity. This dependence is not caused by a relationship between the diffusion coefficient and viscosity but is in relation with the above-mentioned consideration that the diffusion coefficient goes through a maximum. We may so explain this fact that the diffusion coefficient is a product of two physicochemical quantities (thermodynamic factor and mobility) which are significantly dependent on concentration. The dependence of these two quantities has, however, opposite character, which gives rise to a relative extreme.

On the basis of the obtained data, we may state that CYH and DMFA are very good solvents for PVC. From thermodynamic view-point, dioxan appears to be a poorer solvent. Similar conclusions were also drawn by *Adelman and Klein* [21] on the basis of correlation between interaction parameters and electron donor capacity.

References

1. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, New York, 1953.
2. Haase, R., *Thermodynamik der irreversiblen Prozesse*. Steinkopf Verlag, Darmstadt, 1963.
3. Ernst, O., *Thesis*. Rheinisch-westphällische Technische Hochschule, Aachen, 1962.
4. Rehage, G., Ernst, O., and Fuhrmann, J., *Discuss. Faraday Soc.* 49, 208 (1970).
5. Polavka, J., *Thesis*. Slovak Technical University, Bratislava, 1976.
6. Roszkopf, G., Polavka, J., Rehage, G., and Borchard, W., *Ber. Bunsenges. Phys. Chem.* 83, 360 (1979).
7. Rehage, G. and Ernst, O., *Kolloid. Zh.* 197, 64 (1964).
8. Roszkopf, G., *Thesis*. Technische Universität, Clausthal, 1975.
9. Lapčík, L., *Habilitation Thesis*. Slovak Technical University, Bratislava, 1972.
10. Lapčík, L., Panák, J., Kellö, V., and Polavka, J., *J. Polym. Sci., Polym. Phys. Ed.* 14, 981 (1976).
11. Kratochvíl, P., Petrus, V., Bohdanecký, M., and Šolc, K., *J. Polym. Sci., Part C* 16, 1257 (1967).
12. Carenza, M., Palma, G., and Tavan, M., *J. Polym. Sci., Symp. No.* 42, 1031 (1973).
13. Antweiler, H. J., *Chem.-Ing.-Tech.* 24, 284 (1952).
14. Illers, K. H., *Makromol. Chem.* 127, 1 (1969).
15. Nakijama, A., *Kobunshi Kagaku* 7, 309 (1950).
16. Tsvetkov, V. N. and Klenin, S. J., *J. Polym. Sci.* 30, 187 (1958).
17. Stokes, R. H., *Trans. Faraday Soc.* 48, 887 (1952).
18. Bugdahl, V., *Kaut. Gummi Kunstst.* 22, 486 (1969).
19. Roubal, V., *Diploma Thesis*. Slovak Technical University, Bratislava, 1973.
20. Valášek, J., *Diploma Thesis*. Slovak Technical University, Bratislava, 1974.
21. Adelman, R. L. and Klein, I. M., *J. Polym. Sci.* 31, 77 (1958).

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