ELSEVIER

Thermochimica Acta 322 (1998) 129–135

thermochimica acta

Thermogravimetric investigation of volatility of dioctyl phthalate from plasticized poly(vinyl chloride)

Željko Mrklić[a], Tonka Kovačić[b,*]

[a] *Faculty of Natural Sciences and Mathematics, Department of Chemistry, Nikole Tesle 12, 21000 Split, Croatia*
[b] *Faculty of Chemical Technology, Department of Organic Technology, Nikole Tesle 10, 21000 Split, Croatia*

Received 10 May 1998; accepted 29 June 1998

Abstract

The process of volatilization of dioctyl phthalate (DOP) plasticizer from plasticized poly(vinyl chloride) (PVC) folies was studied by the method of isothermal thermogravimetry in the temperature range of 120–150°C. The investigated samples contained 10.15 to 37.11 wt% of DOP. The rate constants of the process of plasticizer volatilization were calculated and the dependence of rate constant on the initial concentration of plasticizer in plasticized PVC and on temperature were mathematically defined. The concentration dependence is expressed by parameters k_0 and q. The activation energy of the process was calculated from the exponential dependence of the rate constant of volatilization on temperature. © 1998 Elsevier Science B.V.

1. Introduction

The loss of additives, particularly of plasticizers, from plasticized polymers is interesting from the point of view of processibility of polymer materials and optimization of the process as well as for the evaluation of lifetime of plasticized polymer products in use. The physical process proceeds in two simultaneous processes: the interfacial mass transport between the polymer and the surrounding medium and the transport in the bulk of a polymer to the surface. The first process in the system of solid phase–gas phase represents volatilization, and it is defined by the rate of the volatility of the additive from the polymer surface. The other process, diffusion, is described by Fick's law of diffusion. The processes of diffusion of various additives as well as of other simple or more complex organic compounds into polymers [1–5] and also the loss of additives by migration, extraction (into solid or liquid phase) or volatilization from polymers in surrounding medium [6–13] have been a matter of interest of many investigators for a long time. In case of plasticizers, the extraction in surrounding liquid medium (petroleum derivates, cooking oil, water, organic solvents) has been widely studied, while there are few data on the process of volatilization of plasticizers.

To investigate the process of additive loss from polymers, thermal methods of analysis are used among other methods. The authors [12–14] studied the loss of antioxidants and light stabilizers and arrived at the conclusion that the volatility of low molecular weight additives proceeds according to the first-order kinetics. This process is concentration dependent.

In this paper, isothermal thermogravimetry was applied to investigate kinetic parameters of the process

---

*Corresponding author. Tel.: +385-21-341633; Fax: +385-356-275.

PII: S0040-6031(98)00479-1

of volatilization of dioctyl phthalate (DOP) plasticizer from plasticized poly(vinyl chloride) folies.

2. Experimental

2.1. Materials

The materials used for this study were commercially available mass-polymerized PVC (K-value 67.9) (Adriachem, Zadar, Croatia) and dioctyl phthalate plasticizer (BASF, Ludwigshaufen, Germany). PVC-folies with the amount of 10.15, 20.26, 30.06 and 37.11 wt% of the plasticizer with the addition of 1 wt% of thermal stabilizer, modified buthyl-stannic mercaptide (BTF-80), were prepared using a Plastograph Brabender at the following terms of processing:

- temperature 170±5°C
- time of drawing 5 min
- thickness of the foil 0.1+0.03 mm

The samples were cut-off in the form of 5-mm diameter discs each weighing 3±0.5 mg.

2.2. Thermogravimetric measurements

The volatilization of plasticizer from plasticized PVC-folies was studied by the method of isothermal thermogravimetry (Perkin–Elmer TGS-2 with TADS Microprocessor) at 120°, 130°, 140°, 150°C, 120 min, under nitrogen flow of 30 cm^3/min. From the starting temperature (50°C) to the isothermal testing temperature the samples were heated at the rate of 80°C/min. After establishing the isothermal conditions, 10 min after the beginning of heating, the weight loss of each sample was taken as the starting value. The deviation of real temperature value from the programmed temperature value amounted to <±1°C. Thermogravimetric analysis, recording, saving and thermogram analysing were made by Perkin–Elmer TADS-TG Standard Kinetic Programme designed for dynamic measurements. Therefore, the Programme is adapted to isothermal measurement in order to obtain thermograms *mass* vs. *time*.

The control measurements have shown that in the temperature range and measurement times the measurable weight change of stabilized PVC does not take place.

3. Results and discussion

The thermograms of PVC, plasticized with 10.15, 20.26, 30.06 and 37.11 wt % of DOP are shown, as an example, at testing temperatures of 130° and 140°C in Figs. 1 and 2. The results show that with greater initial

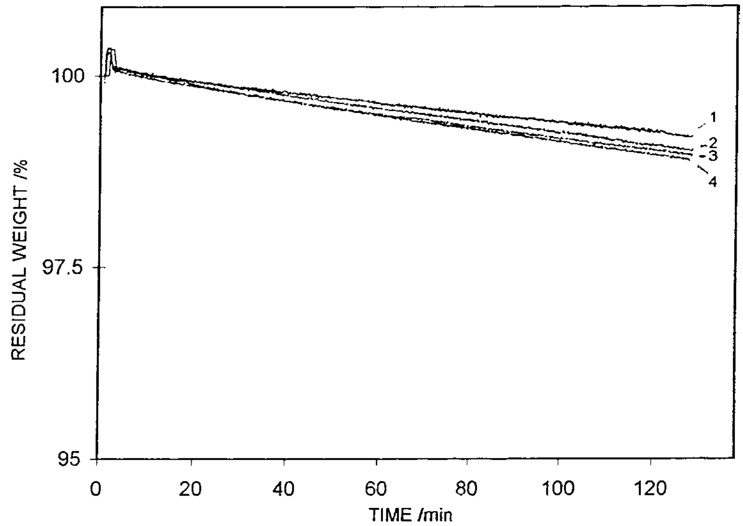

Fig. 1. Thermogram of volatilization of DOP from plasticized PVC at 130°C: (1) 10.15% DOP; (2) 20.26% DOP; (3) 30.06% DOP; (4) 37.11% DOP.

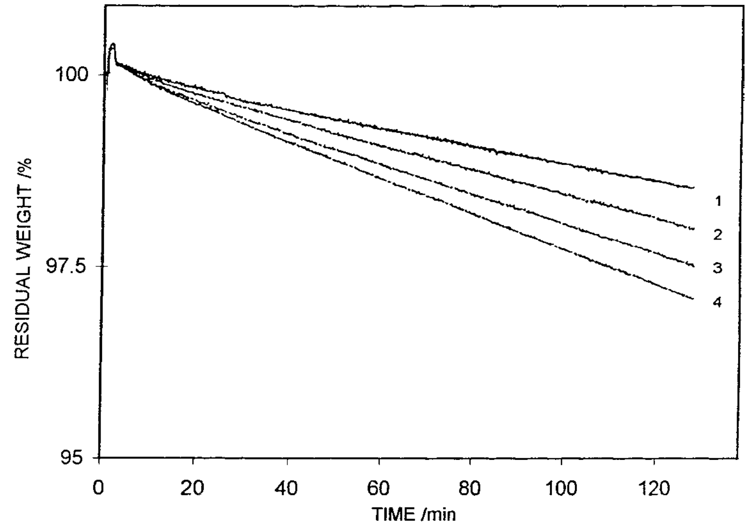

Fig. 2. Thermogram of volatilization of DOP from plasticized PVC at 140°C: (1) 10.15% DOP; (2) 20.26% DOP; (3) 30.06% DOP; (4) 37.11% DOP.

concentration of plasticizer and higher testing temperature, the residual weight of samples is smaller.

The weight losses in time were read and the values of residual concentration of plasticizer in plasticized PVC, (c_0–c), were determined, where c_0 is the initial amount of plasticizer in polymer and c the amount of plasticizer evaporated from plasticized PVC in time t.

The results are shown in Table 1.

In order to define the mathematical dependence of residual concentration of plasticizer in plasticized PVC on time:

$$c_0 - c = f(t) \tag{1}$$

the results were presented graphically as the plot (c_0–c) vs. t, shown in Fig. 3 as an example of PVC plasticized with 20.26 wt% of DOP.

The shape of the plots makes it possible to conclude the exponential dependence of the investigated variables:

$$c_0 - c = c_0 \exp^{-kt}, \quad \frac{c_0 - c}{c_0} = \exp^{-kt} \tag{2}$$

where k is the rate constant of volatilization of plasticizer.

The determinated relationship is in accordance with Luston's investigations of the loss of light stabilizers from polypropylene [12,13], and also with Matsumota's [14] investigations, who found the same relationships for the evaporation of phenolic antioxidants from polypropylene, previously pointed out by Angert et al. [15]. The physical process of volatilization of DOP from plasticized PVC was correlated according to first-order kinetics, while the constant k may be regarded as the characteristic of the physical process of volatilization of DOP from polymer.

3.1. Determining the rate constant of volatilization of plasticizer from plasticized PVC

The Eq. (2) was linearized by taking the logarithm in the form of

$$-\ln\frac{c_0 - c}{c_0} = kt \tag{3}$$

and then from the diagram ($-\ln c_0$–c/c_0) vs. t (Fig. 4) the values of rate constant of volatilization of plasticizer were calculated as the slopes of the linear dependences by the method of linear regression analysis (Table 2).

From the data in the table the influence of two variables, temperature t and initial concentration c_0, on the value of constant k can be observed.

The values of the rate constant of the process of volatilization of DOP increase, as temperature increases, approximately two times for every 10°C, which is in accordance with the well-known kinetic

Table 1
Residual amount of plasticizer in time *t*

Time/min	Residual amount of DOP, c_0-c											
	10	20	30	40	50	60	70	80	90	100	110	120
Initial amount of DOP												
c_0=0.1015												
120°C	0.1015	0.1015	0.1014	0.1014	0.1013	0.1013	0.1013	0.1012	0.1012	0.1012	0.1011	0.1011
130°C	0.1015	0.1014	0.1014	0.1013	0.1012	0.1011	0.1011	0.1010	0.1009	0.1008	0.1008	0.1007
140°C	0.1014	0.1012	0.1011	0.1010	0.1008	0.1007	0.1005	0.1003	0.1002	0.1001	0.0999	0.0998
150°C	0.1014	0.1011	0.1009	0.1006	0.1003	0.1001	0.0999	0.0997	0.0995	0.0993	0.0991	0.0989
c_0=0.2026												
120°C	0.2024	0.2023	0.2022	0.2021	0.2020	0.2019	0.2018	0.2017	0.2016	0.2015	0.2014	0.2013
130°C	0.2024	0.2022	0.2020	0.2018	0.2017	0.2015	0.2013	0.2011	0.2010	0.2008	0.2007	0.2005
140°C	0.2022	0.2018	0.2014	0.2011	0.2008	0.2004	0.2001	0.1998	0.2015	0.1992	0.1988	0.1987
150°C	0.2018	0.2011	0.2003	0.1996	0.1990	0.1984	0.1978	0.7973	0.1967	0.1961	0.1956	0.1953
c_0=0.3006												
120°C	0.3004	0.3002	0.3000	0.2999	0.2998	0.2996	0.2994	0.2993	0.2992	0.2990	0.2989	0.2987
130°C	0.3002	0.2999	0.2996	0.2993	0.2991	0.2989	0.2986	0.2983	0.2981	0.2978	0.2977	0.2975
140°C	0.2997	0.2990	0.2983	0.2977	0.2971	0.2965	0.2959	0.2953	0.2947	0.2942	0.2935	0.2931
150°C	0.2993	0.2983	0.2973	0.2964	0.2954	0.2945	0.2935	0.2926	0.2907	0.2907	0.2899	0.2897
c_0=0.3711												
120°C	0.3710	0.3710	0.3709	0.3708	0.3705	0.3703	0.3701	0.3700	0.3699	0.3697	0.3695	0.3695
130°C	0.3705	0.3710	0.3697	0.3694	0.3689	0.3686	0.3683	0.3680	0.3676	0.3673	0.3670	0.3665
140°C	0.3699	0.3690	0.3680	0.3671	0.3662	0.3653	0.3644	0.3636	0.3627	0.3619	0.3610	0.3600
150°C	0.3696	0.3684	0.3670	0.3658	0.3646	0.3635	0.3623	0.3612	0.3601	0.3590	0.3577	0.3458

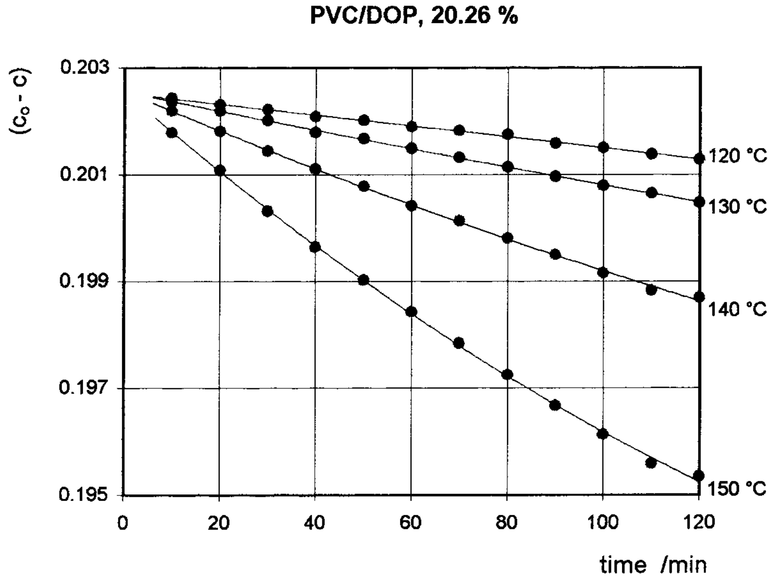

Fig. 3. Graphical presentation of dependence of residual concentration of plasticizer on time.

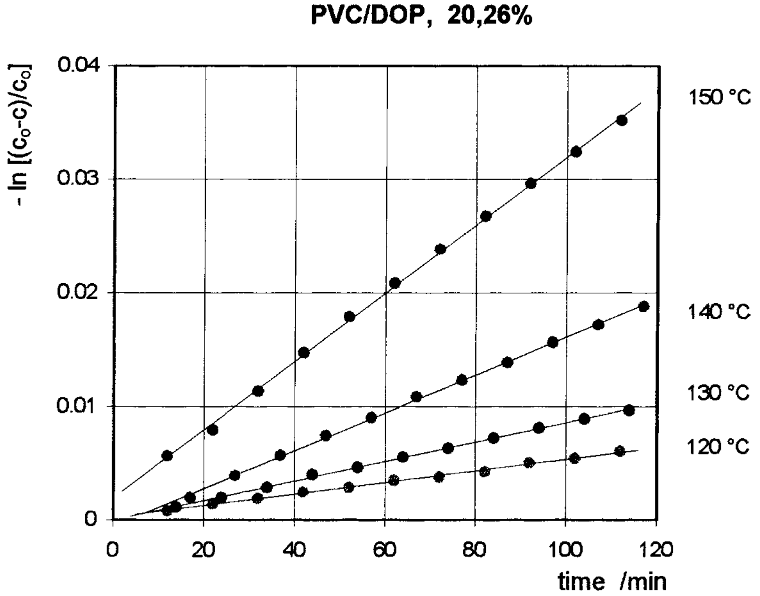

Fig. 4. Graphical determining of the rate constant of volatilization process of plasticizer.

Table 2
The rate constant of volatilization of DOP, k

Amount of DOP, c_0/wt%	$k\times10^4$/min^{-1} Temperature/°C			
	120	130	140	150
10.15	0.418	0.684	1.28	2.13
20.26	0.507	0.857	1.66	3.09
30.06	0.511	0.869	2.05	3.22
37.11	0.463	0.947	2.43	3.25

principles. In addition, the rate constant of volatility at the same temperature rises with the initial concentration of plasticizer in plasticized PVC, except with c_0=37.11 at 120°C, which is attributed to experimental error. The influence of temperature is much more significant than the influence of initial concentration. Thus, the rate constants of volatility of the samples with equal concentration of plasticizer increase in the temperature range of 120–150°C up to 7.1 times (6.12 times on average), while the increase of the amount of DOP from 10.15 to 37.11 wt% influences the increase of the value of the rate constant to a maximum of 3.5 times (2.2 times on average).

The dependence of the constant of the process of volatilization on temperature and on the initial concentration of plasticizer DOP was also investigated and mathematically determined in this study.

3.2. The dependence of rate constant of volatilization of plasticizer on initial concentration

The evaporation of additives from polymers depends on the concentration of the additive on the surface of polymer material and, according to literature data [12–15], that dependence should be linear according to the first order of kinetics. The graphical presentation of dependence $k=f(c_0)$ (Fig. 5) does show the linear dependence of the rate constant of volatilization of DOP on the initial concentration in plasticized PVC at the investigated temperature in the form:

$$k = k_0 c_0 + q \qquad (4)$$

The linear dependence of the constant rate of volatilization of DOP from plasticized PVC indicates that the controlling step in the physical process of plasticizer loss is the interfacial mass transport between polymer and surrounding medium.

Parameters k_0 and q were determined by the linear regressive analysis. Their values are shown in Table 3.

It is noticeable that the values of these parameters are very small, which explains the smaller influence of

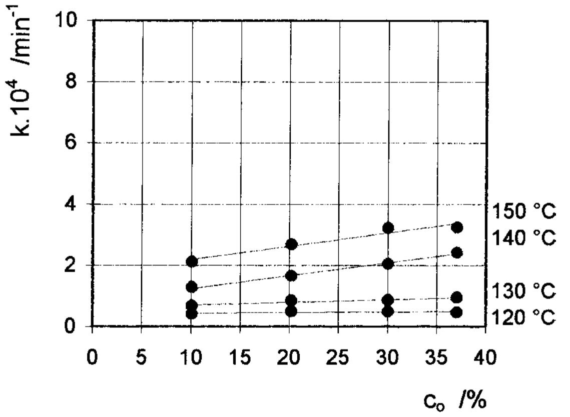

Fig. 5. Dependence of the rate constant of volatilization process of plasticizer on the initial concentration of DOP in plasticized PVC.

initial concentration in relation to a relatively great influence of temperature on the rate constants of volatilization of plasticizer.

3.3. Dependence of the rate constant of volatilization of plasticizer on temperature

The dependence of the rate constant of volatilization of DOP from plasticized PVC on temperature is shown in Fig. 6. The exponential dependence is noticeable, which indicates Arrhenius's dependence:

Table 3
The values of parametres k_0 and q

Temperature/°C	k_0/min^{-1}	q/min^{-1}
120	1.75×10^{-7}	4.32×10^{-5}
130	8.89×10^{-7}	6.22×10^{-5}
140	4.21×10^{-6}	8.28×10^{-5}
150	3.97×10^{-6}	1.95×10^{-4}

$$k = z\mathrm{e}^{-E/RT} \tag{5}$$

where z is preexponential factor, E the energy needed for the molecules of plasticizer to leave the plasticized polymer surface. In literature this energy is usually called activation energy, although this is a physical process.

The Arrhenius plots ln k vs. $1/T$ were made by linearization of the Eq. (5). By method of linear regression the most probable lines were determined and the values of activation energy E and preexponential factor z were calculated from their slopes and intercepts, respectively. Results are shown in Table 4.

According to the Moisan [8] who investigated the activation energy of the diffusion process of stabilizers and antioxidants from polyethylene, one part of activation energy is attributed to the deformation of

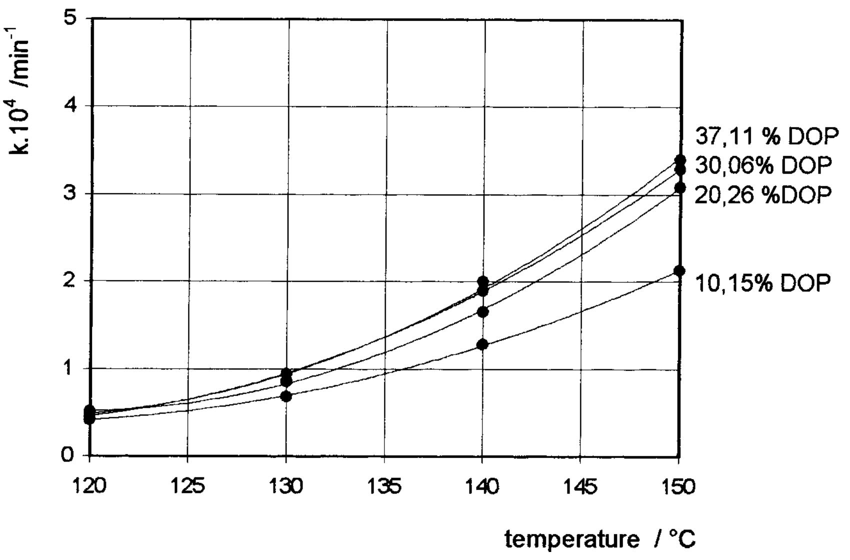

Fig. 6. Dependence of the rate constant of volatilization process of plasticizer on temperature.

Table 4
Activation energy and preexponential factor of the process of volatilization of DOP

Amount of DOP, c_0/wt.%	E_a/kJ mol^{-1}	z/min^{-1}
10.15	76.38	5.5×10^5
20.26	84.29	7.5×10^6
30.06	88.49	2.8×10^7
37.11	94.07	1.5×10^8

polymer matrix, and the other to the deformation of the molecules of diffusant, $E_d=E_p+E_a$, where E_d is the activation energy of diffusion, E_p the energy needed for the polymer deformation, and E_a the energy needed for the deformation of the molecules of the diffusant.

The values of the activation energy from Table 4 slightly rise with the increase of plasticizer concentration in plasticized PVC. As the preexponential factors are also changed, the change of the activation energy can be the result of different influences of experimental parameters on the tested samples, which have different physical states of polymer because of different concentration of plasticizer. It is also possible that, due to greater mobility of PVC macromolecule segments in the samples with greater initial content of plasticizer, the available free volume in polymer matrix is greater. This is in accordance to the results of Storey et al. [3] who found that the activation energy for the diffusion of dialkyl phthalate into poly(vinyl chloride) is lower below the glass-transition temperature (T_g) than above T_g. The authors explained it by the cooperative motion of a great number of consecutive chain segments above T_g.

4. Conclusion

The method of isothermal thermogravimetry is convenient for the investigation of kinetic parameters of the physical process of plasticizer loss caused by the volatilization from polymer surface. The process of volatilization of DOP from plasticized PVC proceeds according to the first order of kinetics. The rate constant of the process can be regarded as the characteristic of the physical process of DOP volatilization from plasticized PVC, and it depends on temperature and on the initial concentration of plasticizer in polymer. The influence of temperature is much more expressed than the influence of plasticizer concentration. The linear dependence of the rate constant on the initial concentration shows that the rate-controlling step in the physical process of plasticizer loss is the interfacial mass transport in the surrounding medium. With the rise of DOP concentration in polymer, activation energies and preexponential factors also rise. This rise could be attributed to the influence of experimental parameters on the tested samples of different physical state of polymer or to some kind of redistribution of additive in polymer matrix due to greater mobility of macromolecule segments in plasticized polymer with greater initial concentration of plasticizer.

References

[1] O. Cicchetti, M. Dubini, P. Parrini, G.P. Vicario, E. Bua, European Polymer Journal 4 (1968) 419.
[2] T. Schwarz, G. Steiner, J. Koppelmann, Journal of Applied Polymer Science 38 (1989) 1.
[3] R.F. Storey, K.A. Mauritz, B.D. Cox, Macromolecules 22 (1989) 289.
[4] K.A. Mauritz, R.F. Storey, S.E. George, Macromolecules 23 (1990) 441.
[5] K.A. Mauritz, R.F. Storey, Macromolecules 23 (1990) 2033.
[6] E.M. Kampouris, Polymer Engineering and Science 16(1) (1976) 59.
[7] P.D. Calvert, N.C. Bilingham, Journal of Applied Polymer Science 24 (1979) 357.
[8] J.Y. Moisan, European Polymer Journal 16 (1980) 979.
[9] C.D. Papaspyrides, Journal of Applied Polymer Science 32 (1986) 6025.
[10] C.D. Papaspyrides, Journal of Applied Polymer Science 38 (1989) 1859.
[11] N.S. Allen, L.M. Moore, G.P. Marshall, C. Vasiliou, J. Kotecha, Polymer Degradation and Stability 27 (1990) 145.
[12] J. Luston, V. Pastušakova, F. Vašš, Journal of Applied Polymer Science 47 (1993) 555.
[13] J. Luston, V. Pastušakova, F. Vašš, Journal of Applied Polymer Science 48 (1993) 219.
[14] S. Matsumoto, Journal of Polymer Science, Polym. Chem. 21 (1983) 557.
[15] L.G. Angert, A.I. Zenchenko, A.S. Kuzminskii, Kolloid Zh., 2 (1960).