

Adsorption from Surfactant Solutions under Diffusion Control

PETER A. KRALCHEVSKY,^{*,1} YORDAN S. RADKOV,[†] AND NIKOLAI D. DENKOV^{*}

^{*}Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria; and [†]Central Institute of Chemical Industry, Sofia, Bulgaria

Received October 8, 1991; accepted July 7, 1993

A method for solving the nonlinear boundary problem describing diffusion-controlled adsorption from surfactant solutions is proposed. The problem is reduced to the solution of a simple set of three equations. These are one ordinary differential equation of first order and two algebraic equations, one of them being the adsorption isotherm. This approach is applicable for both ionic and nonionic surfactants below the critical micellization concentration. The developed theoretical method is verified by interpreting data for dynamic surface tension of sodium dodecylsulfate solutions measured by means of the maximum bubble pressure method. © 1993 Academic Press, Inc.

1. INTRODUCTION

In the case of diffusion-controlled adsorption from surfactant solutions at every moment the subsurface surfactant concentration $c_0(t)$ is related to the surfactant adsorption $\Gamma(t)$ by means of the equilibrium adsorption isotherm. For example, many nonionic surfactants are found (1–4) to satisfy the Szyszkowsky equation and the Langmuir adsorption isotherm

$$\frac{c_0(t)}{b} = \frac{\Gamma(t)}{\Gamma_\infty - \Gamma(t)}, \quad [1]$$

where b and Γ_∞ are constants. The ionic surfactants can also satisfy the Szyszkowsky equation (5) or some more complicated adsorption isotherm—see, e.g., Ref. (6). In general, the nonlinear relation between $c_0(t)$ and $\Gamma(t)$ leads to a nonlinear boundary problem for the diffusion equation. In some particular cases (small adsorption, small deviations from equilibrium etc.) the adsorption isotherm can be linearized and then standard mathematical methods can be applied to solve the diffusion problem—see, e.g., Refs. (2, 7–9). However, the general boundary problem is essentially nonlinear. One way to solve the nonlinear problem is to use perturbation series methods (10). Another approach is to use the nu-

merical solution of a set of equations, including the partial differential equation of diffusion—see Refs. (11–12). Below we propose an alternative simple approach for solving the same problem, which is similar to the approach of von Karman to the hydrodynamical boundary layer problem—see Ref. (13).

2. BASIC EQUATIONS

The surfactant mass balance at the solution surface reads

$$\frac{d\Gamma}{dt} + \dot{\alpha}(t)\Gamma(t) = D \left. \frac{\partial c}{\partial x} \right|_{x=0}. \quad [2]$$

Here D is the surfactant diffusivity, $c(x, t)$ is the surfactant concentration, the plane $x = 0$ corresponds to the solution surface, and the x -axis is directed inward to the solution. $\dot{\alpha}(t)$ is the local rate of interfacial dilation. If δA is an infinitesimal parcel of the interface, then

$$\dot{\alpha} = \frac{1}{\delta A} \frac{d(\delta A)}{dt} \quad [3]$$

—for the general definition of $\dot{\alpha}$ see Ref. (14).

Obviously, the right-hand side of Eq. [2] represents the diffusion flux at the interface, which is connected to the exchange of surfactant between the bulk and the adsorption layer. Since, in general, the interfacial dilation is coupled with some convective flow in the bulk of the solution, the bulk surfactant concentration $c(x, t)$ obeys the equation of the convective diffusion,

$$\frac{\partial c}{\partial t} + V_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2}, \quad [4]$$

with V_x being the x -component of the mean mass velocity. The boundary conditions are

$$\begin{aligned} c(0, t) = c_0(t), \quad \lim_{x \rightarrow \infty} c(x, t) = c_\infty = \text{const.} \\ \lim_{x \rightarrow \infty} \frac{\partial c}{\partial x} = 0. \end{aligned} \quad [5]$$

¹ To whom correspondence should be addressed.

It should be noted that Eq. [4] is applicable when there are no micelles in the solution. (The equations describing diffusion in the micellar solution can be found in Ref. (15).)

To specify the problem we restrict our considerations to the case when the surface dilation is isotropic. As proven by van Voorst Vader *et al.* (16), in this case

$$V_x = -x\dot{\alpha}(t). \quad [6]$$

Let us define

$$l(t) = \int_0^{\infty} U(x, t) dx, \quad U(x, t) = 1 - \frac{c(x, t)}{c_{\infty}}. \quad [7]$$

In general, we suppose that the diffusion is due to some disturbances of the surfactant adsorption layer. Then $l(t)$ defined by Eq. [7] characterizes the thickness of the liquid layer adjacent to the interface, in which the surfactant concentration is deviated from the equilibrium one.

Since $U(x, t)$, as defined by Eq. [7], also satisfies the equation of convective diffusion (Eq. [4]), one easily derives from Eqs. [4]–[7]

$$\frac{dl}{dt} = \frac{D}{c_{\infty}} \left. \frac{\partial c}{\partial x} \right|_{x=0} - \dot{\alpha}(t)l(t). \quad [8]$$

3. MODEL OF THE CONCENTRATION PROFILE

As far as we are interested in the time dependence of the interfacial properties (adsorption, surface tension, etc.) a model of the bulk surfactant concentration profile, $c(x, t)$, can enable us to obtain a full set of equations. Equation [8] shows that the diffusion flux in Eq. [2], which is proportional to $(\partial c/\partial x)_{x=0}$, in fact depends on an *integral*, $l(t)$, of the bulk surfactant concentration profile, $c(x, t)$ —cf. Eq. [7]. In other words, for our purpose we need an integral of $c(x)$ rather than the detailed information about the value of c at every point x . This fact enables one to use a model profile for $c(x)$ possessing appropriate integral properties, instead of the exact solution of the diffusion equation. Let us consider the following model concentration profile (see Fig. 1):

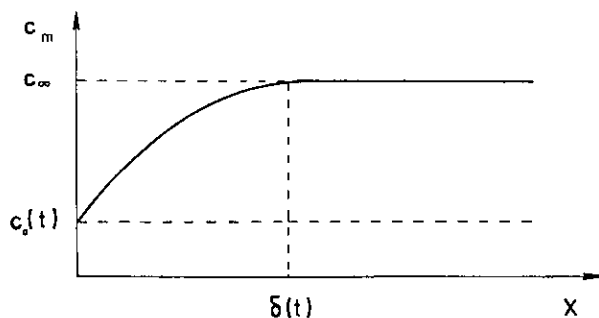


FIG. 1. The model concentration profile c_m vs x at a given moment t .

$$c_m(x, t) = c_0(t) + [c_{\infty} - c_0(t)] \sin \left[\frac{\pi}{2} \frac{x}{\delta} \right] \quad \text{for } x \leq \delta$$

$$c_m(x, t) = c_{\infty} \quad \text{for } x \geq \delta. \quad [9]$$

Equation [9] defines the model concentration c_m as a monotonic function of the distance x —cf. Fig. 1; $\delta = \delta(t)$ is an unknown function. The latter can be determined from the following integral condition for equivalence between the real and model concentration profiles:

$$\int_0^{\infty} [c_{\infty} - c(x, t)] dx = \int_0^{\infty} [c_{\infty} - c_m(x, t)] dx. \quad [10]$$

By substituting Eqs. [7] and [9] into Eq. [10] one derives

$$c_{\infty}l(t) = \left(1 - \frac{2}{\pi}\right) [c_{\infty} - c_0(t)] \delta(t). \quad [11]$$

On the other hand, by using Eq. [9] one obtains

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} \approx \left. \frac{\partial c_m}{\partial x} \right|_{x=0} = \frac{\pi}{2\delta(t)} [c_{\infty} - c_0(t)]. \quad [12]$$

The elimination of $\delta(t)$ between Eqs. [11] and [12] yields

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} = \left(\frac{\pi}{2} - 1 \right) \left[1 - \frac{c_0(t)}{c_{\infty}} \right]^2 \frac{c_{\infty}}{l(t)}. \quad [13]$$

From Eqs. [8] and [13] one finally obtains

$$\frac{dl}{dt} + \dot{\alpha}(t)l(t) = \left(\frac{\pi}{2} - 1 \right) \left[1 - \frac{c_0(t)}{c_{\infty}} \right]^2 \frac{D}{l(t)}. \quad [14]$$

In addition, by eliminating $D(\partial c/\partial x)$ from Eqs. [2] and [8] one derives

$$\Gamma(t) = c_{\infty}l(t) + [\Gamma(0) - c_{\infty}l(0)] \exp[-\alpha(t)], \quad [15]$$

where

$$\alpha(t) = \int_0^t \dot{\alpha}(t) dt. \quad [16]$$

Since the surface rate of dilation $\dot{\alpha}(t)$ is supposed to be known, Eqs. [1], [14], and [15] represent a set of three equations for determining the three unknown functions $\Gamma(t)$, $c_0(t)$, and $l(t)$. This set can be easily solved numerically. The initial conditions at the moment $t = 0$ depend on the specified dynamic problem. Equation [1] can be replaced with another adsorption isotherm, if necessary. One can also calculate the time dependence of the surface tension σ , when an equilibrium relation between σ and Γ is available.

4. COMPARISON WITH AN EXACT SOLUTION

The method based on Eqs. [1], [14], and [15], although consuming only a short time, yields an approximate solution because of the usage of a model concentration profile, Eq. [9]. The precision of this method can be checked against the exact analytical solution in the case of the linear adsorption isotherm. With that end in view let us consider the process of relaxation of the adsorption Γ with time for small initial deviation from equilibrium:

$$\Delta\Gamma(0) = \Gamma_{eq} - \Gamma(0) \ll \Gamma_{eq} \quad [17]$$

$$\dot{\alpha}(t) = 0 \quad \text{for } t > 0. \quad [18]$$

Here Γ_{eq} is the equilibrium adsorption. By differentiating the adsorption isotherm, say Eq. [1], one obtains

$$\Delta\Gamma(t) = \Gamma_{eq} - \Gamma(t) \approx \left. \frac{\partial\Gamma}{\partial c} \right|_{c=c_\infty} [c_\infty - c_0(t)]. \quad [19]$$

Then from Eqs. [2], [4], [6], [18], and [19] one derives a linear boundary condition

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} = a \left(\frac{\partial\Gamma}{\partial c} \right)_{c=c_\infty} \left. \frac{\partial c}{\partial x} \right|_{x=0}; \quad a = \frac{D}{(\partial\Gamma/\partial c)_{c=c_\infty}^2} \quad [20]$$

for the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \quad [21]$$

The initial condition is

$$c(x, 0) = \begin{cases} c_\infty & \text{for } x \neq 0 \\ c_0(0) & \text{for } x = 0. \end{cases} \quad [22]$$

Equations [17]–[22] yield (see, e.g., Ref. (17)):

$$G(t) = e^T \operatorname{erfc}(\sqrt{T}), \quad [23]$$

where

$$G = \frac{\Delta\Gamma(t)}{\Delta\Gamma(0)} \quad \text{and} \quad T = at \quad [24]$$

are dimensionless variables and $\operatorname{erfc}(x)$ is the complementary error function.

Now let us derive the dependence of G vs T which follows from Eqs. [14]–[15] for the same boundary and initial conditions. From Eqs. [7] and [22] it follows that $l(0) = 0$.

Then having in mind Eqs. [17]–[20] one can transform Eqs. [14] and [15] to read

$$\frac{dl^2}{dt} = (\pi - 2)a \left[l(t) - \frac{\Delta\Gamma(0)}{c_\infty} \right]^2 \quad [25]$$

$$\Delta\Gamma(t) = \Delta\Gamma(0) - c_\infty l(t). \quad [26]$$

Equation [25] can be easily integrated. In view of Eqs. [24] and [26] the result can be presented in the form

$$\left(\frac{\pi}{2} - 1 \right) T = \frac{1}{G} - 1 + \ln G \quad [27]$$

Equation [27], following from the model concentration profile, Eq. [9], is to be compared with the exact solution, Eq. [23]. For small T Eq. [23] reduces to

$$G(T) = 1 - 2 \sqrt{\frac{T}{\pi}} + O(T) \approx 1 - 1.13\sqrt{T} + O(T), \quad T \ll 1. \quad [28]$$

On the other hand, from Eq. [27] one obtains

$$G(T) = 1 - \sqrt{(\pi - 2)T} + O(T) \approx 1 - 1.07\sqrt{T} + O(T), \quad T \ll 1. \quad [29]$$

For large T Eqs. [23] and [27] yield $G(T) \propto T^{-1/2}$ and $G(T) \propto T^{-1}$, respectively. Hence, one can expect good agreement between Eqs. [23] and [27] for not too large values of T . This is confirmed by Fig. 2, where the plots of G vs T calculated from these two equations are compared. One can conclude that the approximated method based on Eqs. [14] and [15] is applicable to describing the first stage of the relaxation process, when G drops from 1 to ca. 0.3; this method is not applicable in the cases when the relaxation for larger T ($G < 0.3$) represents a special interest.

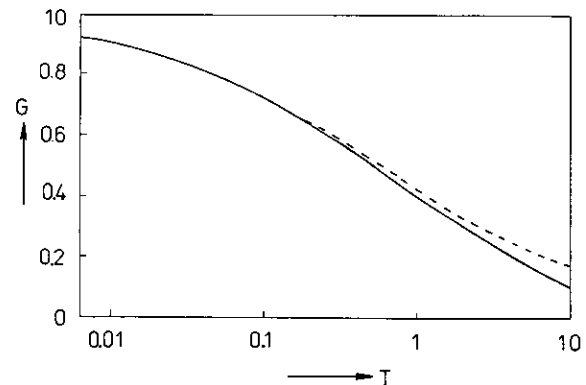


FIG. 2. The relaxation curve G vs T calculated from the approximated Eq. [27] (the solid line) and from the exact Eq. [23] (the dashed line).

5. COMPARISON WITH EXPERIMENT

The method developed above is not restricted to the case of small deviations of the surfactant adsorption from its equilibrium value. It is applicable when the convective transport of surfactant toward the interface is important for the surface mass balance also. Such experimental conditions are realized in the maximum bubble pressure (MBP) method for measuring the surface tension. Although this method is widely used, the interpretation of the measured dependence $\sigma(\nu)$ is very difficult when surfactant solutions are investigated (18); σ is the dynamic surface tension and ν is the frequency of bubble release. In a separate study (19) the role of the experimental set-up design for the interpretation of MBP data was investigated in detail. Among the other results, the dependence of $\sigma(\nu)$ for $4 \times 10^{-4} M$ sodium dodecylsulfate (SDS) solution in the presence of $0.128 M$ NaCl at $30.6^\circ C$ was measured in Ref. (19). The data were analyzed in terms of the dependence $\sigma(t_m)$, where t_m is the time for attaining a maximum pressure (corresponding to a hemispheric shape of the bubble surface) calculated as

$$t_m = \frac{1}{\nu} - t_d, \quad [30]$$

with t_d being the so-called "dead time." The latter was directly measured by using an oscilloscope connected to the pressure transducer. The frequency, ν , was varied between 0.23 and 15 Hz in these experiments.

To interpret the data one can use Eqs. [14]–[16] derived above, along with some appropriate expressions for the surface dilation rate $\dot{\alpha}(t)$ and for the SDS adsorption isotherm.

(a) The Surface Dilation

By using a video camera, the shape of a growing bubble at a given small frequency ($\nu = 0.23$ Hz) was directly registered. From the bubble shape was calculated the dependence $\alpha(t)$ and the experimental points were fitted by the empirical formula (19)

$$\alpha(t) = A_1[\tan A_2 + \tan(A_3 t/t_m - A_2) + A_4 t/t_m], \quad 0 \leq t \leq t_m, \quad [31]$$

where the adjustable coefficients $A_1 - A_4$ was determined by the least-squares method. Since the direct measurement of $\alpha(t)$ at higher frequency was impossible it can be assumed that this formula (with the same coefficients $A_1 = 0.0395$, $A_2 = 1.4539$, $A_3 = 2.7678$, $A_4 = 4.9926$) can be applied to all investigated frequencies, i.e., to all t_m .

(b) Adsorption Isotherm and Equation of State of the Surfactant Adsorption Layer of SDS

In the case of SDS aqueous solutions Tajima *et al.* (20, 21) showed that the measured surface tension isotherm, $\sigma(c)$,

and the surfactant adsorption, Γ , can be described by means of the Gibbs' equation

$$\Gamma = - \frac{d\sigma}{kT d \ln c} \quad [32]$$

and the two-dimensional equation of state of the adsorption layer,

$$\left(\sigma_0 - \sigma + 6.03\sqrt{c_i} + \frac{0.43}{A} kT \right) (A - A_0) = kT, \quad [33]$$

where c is the surfactant concentration, σ_0 is the surface tension of a pure water surface, kT is the thermal energy,

$$A = \frac{1}{\Gamma} \quad [34]$$

is the area per molecule in the adsorbed layer, c_i is the electrolyte concentration in the solution (expressed in mols per dm^3), and $A_0 = 25 \text{ \AA}^2$ is an adjustable parameter representing the area per molecule in a hypothetical adsorption layer of tightly packed surfactant molecules. (Another two-dimensional equation of state, similar to Eq. [33], was previously proposed by Davies—see, e.g., Ref. (6)).

For the computations it is convenient to derive a direct relationship between Γ and c , i.e., to obtain the corresponding adsorption isotherm. By integrating Eq. [32] (see also Eqs. [33], [34]) one obtains

$$c = 2.1795 \times 10^{-8} \left(\frac{\Gamma_\infty}{\Gamma} \right)^{0.43} \left(\frac{\Gamma_\infty}{\Gamma} - 1 \right)^{-1} \times \exp\left(\frac{\Gamma}{\Gamma_\infty - \Gamma} \right), \quad [35]$$

where $\Gamma_\infty = 1/A_0$ and c is expressed in mol/cm^3 . The multiplicative integration constant in Eq. [35] is determined by comparison of the theoretical expression with the experimental results of Tajima *et al.*—see Fig. 5 in Ref. (21).

The experiments of Tajima *et al.* (21) were carried out at slightly lower electrolyte concentration, $c_{\text{NaCl}} = 0.115 M$, than that in the experiments from Ref. (19) ($c_{\text{NaCl}} = 0.128 M$). We believe this small difference is not substantially important for the interpretation of the experimental results.

(c) Numerical Procedure and Discussion

Eqs. [14], [15], [33], and [35] (the latter with $c = c_0(t)$) represent a full set of equations for the calculation of the unknown functions $l(t)$, $c_0(t)$, $\Gamma(t)$, and $\sigma(t)$. $\alpha(t)$ and $\dot{\alpha}(t)$ are given by Eqs. [16] and [31]. To start the numerical integration of Eq. [14] one needs initial conditions for $c(x, t)$, $l(t)$, and $\Gamma(t)$. If one assumes that Eq. [22] describes the initial condition for $c(x, t)$, from Eq. [7] one can deduce

$$l(0) = 0.$$

It is now known in advance what the adsorption in the initial moment, $\Gamma(0)$ is. That is why $\Gamma(0)$ was considered as an adjustable parameter, which was assumed to be the same for all frequencies. Then Eq. [14] (along with Eqs. [15], [31], and [35]) was integrated numerically from $t = 0$ up to $t = t_m$ and the value $\sigma(t_m)$ was calculated and compared with the experimentally measured surface tension. The diffusion coefficient D and $\Gamma(0)$ were the two adjustable parameters which were determined by the nonlinear least-squares method applied to the experimental data for σ vs t_m (Fig. 3). The procedure yields the following values: $D = 4.3 \times 10^{-6} \text{ cm}^2/\text{s}$ and $\Gamma(0)/\Gamma_{\text{eq}} = 0.14$. The agreement between the calculated curve and the measured data is very good (see Fig. 3)—the standard deviation is 0.68 mN/m. Besides, the determined value of the diffusion coefficient of a SDS monomer is in good agreement with the experimental value $D = 5.5 \times 10^{-6} \text{ cm}^2/\text{s}$ measured in Ref. (22).

6. CONCLUSION

In this study we propose a simple approximate method for solving the nonlinear boundary problem of diffusion controlled adsorption from surfactant solutions. By using an appropriate model function to describe the surfactant con-

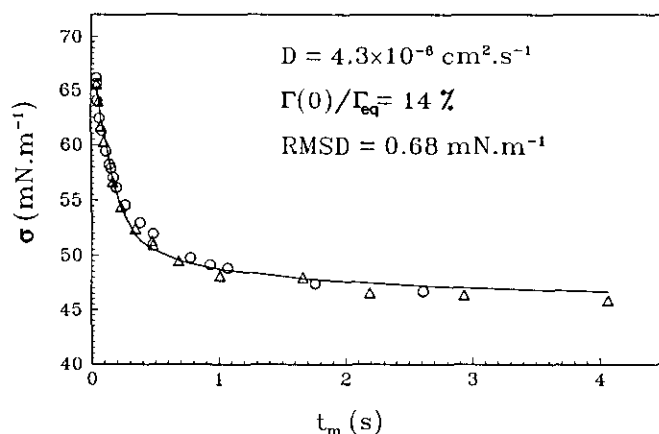


FIG. 3. Experimental data from two independent runs for σ vs t_m obtained by means of the MBP method (19) and fitted by using our theory (see the text).

centration profile in the bulk of the solution we calculated the time dependence of the adsorption $\Gamma(t)$. The dilation of the surface, as well as the convective transport of surfactant toward the interface, is taken into account in the proposed theory. This makes the method applicable to cases when large deviations of the adsorption from its equilibrium value take place under dynamic conditions. For instance, our method based on Eqs. [14] and [15] can be used to interpret the data for σ vs t_m obtained by means of the maximum bubble pressure method (Fig. 3).

ACKNOWLEDGMENTS

This study was supported by Colgate-Palmolive, Piscataway, NJ. The authors are indebted to Professor I. B. Ivanov and Dr. K. Danov for the helpful discussions.

REFERENCES

1. Lange, H., *J. Colloid Sci.* **20**, 50 (1965).
2. Joos, P., and Rillaerts, E., *J. Colloid Interface Sci.* **79**, 96 (1981).
3. Miller, R., and Lunkenheimer, K., *Colloid Polym. Sci.* **264**, 357 (1986).
4. Miller, R., and Lunkenheimer, K., *Colloid Polym. Sci.* **261**, 585 (1983).
5. Lucassen-Reynders, E. H., *J. Phys. Chem.* **70**, 1777 (1966).
6. Davies, J., and Riedal, E., "Interfacial Phenomena." Academic Press, New York, 1963.
7. Sutherland, K. L., *Austr. J. Sci. Res. A* **5**, 683 (1952).
8. Frisch, H. L., and Mysels, K. J., *J. Phys. Chem.* **87**, 3988 (1983).
9. Mysels, K. J., and Frisch, H. L., *J. Colloid Interface Sci.* **99**, 136 (1984).
10. McCoy, B. J., *Colloid Polym. Sci.* **261**, 535 (1983).
11. Miller, R., *Colloid Polym. Sci.* **259**, 375 (1981).
12. Rakita, Yu. M., Fainerman, V. B., and Zadara, V. M., *Zh. Fiz. Khim.* **60**, 376 (1986). [in Russian]
13. Batchelor, G. K., "An Introduction to Fluid Dynamics." University Press, Cambridge, 1970.
14. Kralchevsky, P. A., *J. Colloid Interface Sci.* **137**, 217 (1990).
15. Dushkin, C. D., Ivanov, I. B., and Kralchevsky, P. A., *Colloids Surf.* **60**, 235 (1991).
16. van Voorst Vader, F., Erkelens, Th. F., and van den Tempel, M., *Trans. Faraday Soc.* **60**, 1170 (1964).
17. Loglio, G., Rillaerts, E., and Joos, P., *Colloid Polym. Sci.* **259**, 1221 (1981).
18. Mysels, K. J., *Langmuir* **5**, 442 (1989); *Colloids Surf.* **43**, 241 (1990).
19. Horozov, T. S., Velez, O. D., Arnaudov, L. N., Basheva, E. S., Danov, K. D., Dushkin, C. D., and Ivanov, I. B., to be submitted for publication.
20. Tajima, K., Muramatsu, M., and Sasaki T., *Bull. Chem. Soc. Japan* **43**, 1991 (1970).
21. Tajima, K., *Bull. Chem. Soc. Japan* **43**, 3063 (1970).
22. Kamenka, N., Lindman, B., and Brun, B., *Colloid Polym. Sci.* **252**, 144 (1974).