

Permeability of Solutes through Cellophanes Grafted with Vinyl Monomers. II. Diffusion of Potassium Chloride through Cellophanes Grafted with Acrylic Acid

SHOJI TAKIGAMI, YASUKATSU MAEDA, and YOSHIO NAKAMURA,
Faculty of Technology, Gunma University, Kiryu, Gunma 376, Japan

Synopsis

The permeability behavior of potassium chloride through cellophane grafted with acrylic acid by a γ -irradiation method was studied by the theoretical equation derived from the phenomenological equation and compared with the results of Donnan membrane equilibrium. It was shown that the permeation of potassium chloride through the grafted cellophanes exhibited behavior typical of a polyionic membrane for grafts of more than 55% but depended on the permeability of both cellophane and graft regions for lower percents of grafting. It was found that the dominant factor affecting the permeation of potassium chloride was an effective concentration of fixed charge in the membrane.

INTRODUCTION

The permeable behavior of electrolyte through polyionic membrane has been studied hydrodynamically¹⁻⁵ and thermodynamically. However, there has been little study of the permeation of solute through a grafted membrane. In the previous paper,⁶ the diffusive permeability of urea, uric acid, and potassium chloride through cellophanes grafted with various monomers was studied. It was found that the permeation of the solutes through ionic and nonionic grafted cellophanes was explained by the free-volume concept of homogeneously water-swollen membranes,⁷⁻¹⁰ except for the permeability of potassium chloride through the membrane grafted with acrylic acid which exhibited characteristics of polyionic membranes. In this paper, the diffusive permeability of potassium chloride through cellophane grafted with acrylic acid by the γ -irradiation method was studied, and the results are discussed using the theoretical equation derived from the phenomenological equation. A comparison with results of the Donnan membrane equilibrium method is also made so as to clarify features of the permeation and the dominant factor affecting the permeation of potassium chloride through acrylic acid-grafted cellophane. Furthermore, permeation of potassium chloride was contrasted with that of urea to evaluate the permselectivity of the grafted membrane.

EXPERIMENTAL

Materials

Cellophane (3×10^{-3} cm thick) produced by Tokyo Cellophane Co., Ltd. was used. The degree of crystallinity of the cellophane determined by the x-ray method was 32%. The cellophane was used after extraction with boiling water for 48 hr to remove plasticizers (urea and diethyleneglycol). Acrylic acid (AA) was distilled under reduced pressure before use. Potassium chloride, urea, and other chemicals were reagent grade and were used without further purification.

Irradiation

The purified cellophane was irradiated under nitrogen atmosphere for 1 hr by ^{60}Co γ -rays with an exposure rate of 1.0×10^6 R/hr after drying for 20 hr at 50°C.

Graft Copolymerization

Graft copolymerization of AA onto the irradiated cellophane was carried out in a reaction system of AA-water under nitrogen atmosphere at 30°C. The liquor-to-material ratio was maintained at 200:1. After graft copolymerization, the cellophane grafted with AA was washed with distilled water, extracted with boiling water to remove homopolymer, and then dried under vacuum. The extent of grafting was expressed as weight percent increase based on the original weight of sample.

Diffusive Permeability

The diffusive permeability of potassium chloride was measured by use of a dialysis cell consisting of two compartments at $30 \pm 0.1^\circ\text{C}$ as shown in the previous paper.⁶ The ratio (r) of higher concentration (C'') in the lower compartment to lower concentration (C') in the upper cell was kept at 3, 6, 10, and 16, and C' was changed from 0.001 to 0.1 mol/liter.

The permeability coefficient (P , in cm^2/min) was calculated according to the equation

$$\ln[(C'' - C')/(C'' - C' - 2C_t)] = 2PA t / \delta V \quad (1)$$

where C'' and C' are the initial concentration of the solution in the lower and upper compartment, respectively, and C_t is the concentration of the solute transported from the lower compartment to upper one at time t (min). A is the membrane area (20 cm^2), δ is the membrane thickness (cm), and V is the volume of each compartment of the cell (100 cm^3).

Membrane Thickness

The sample was immersed in the solution with the same concentration as the solution charged in the upper compartment of the dialysis cell. After equilibrium the membrane thickness was measured by microscope.

Density

The density of the grafted sample was measured by use of a density-gradient column consisting of carbon tetrachloride and *n*-hexane at $25 \pm 0.1^\circ\text{C}$.

Hydration

The weighed sample was immersed in an aqueous potassium chloride solution. After equilibrium the sample was placed between sheets of filter paper and rolled to remove the solution on the membrane surface prior to weighing. This procedure was repeated several times so as to plot the weight of the swollen membrane against the repeated times by roller. By extrapolation of the linear part of the curve to zero time, the weight of the swollen sample at zero time was determined, which was subsequently converted into the volume of the swollen sample by using the density of the grafted membrane. Hydration of the sample (H) was calculated according to the following equation:

$$H = \frac{\text{Volume of the solution in swollen membrane}}{\text{Volume of the swollen membrane}} \quad (2)$$

Concentration of Chlorine Ion in the Membrane

The weighed cellophane grafted with AA was immersed in 0.01*N* potassium chloride aqueous solution for 24 hr at 30°C , and after picking up the sample, the extra solution on the surface of the membrane was removed by filter paper. The sample was kept in a known amount of distilled water with stirring for 5 hr at room temperature; subsequently, mercury (II) thiocyanate and iron alum reagent were added¹¹ to the extracted solution, and the chlorine ion was analyzed colorimetrically (460 nm). The concentration of chlorine ion in the swollen membrane (\bar{C}_-) was expressed as the value converted from moles per gram of the grafted membrane to moles per liter of water in the swollen membrane² by use of the hydration and density of the grafted membrane.

Concentration of the Fixed Charge in the Membrane

The cellophane grafted with AA was immersed in 1*N* hydrochloric acid solution for 3 hr in order to convert completely the polyelectrolyte into the acidic form; the membrane was then washed with distilled water to remove the hydrochloric acid absorbed until the water was free of chlorine ion and dried under vacuum prior to weighing. The grafted membrane in acidic form was immersed in a known amount of 0.01*N* sodium hydroxide solution for 3 hr at room temperature, and the amount of carboxyl group of the grafted membrane was determined by back titration with 0.01*N* hydrochloric acid solution. The concentration of the fixed charge in the grafted membrane (X) was converted into the amount of water (in mol/liter) in the swollen membrane^{1,2} by use of the same method as mentioned above.

RESULTS AND DISCUSSION

The permeability coefficient (P_s) per unit membrane thickness of potassium chloride through the cellophane grafted with AA was determined by eq. (1) when the ratio of electrolyte ($r = C''/C'$) was 3, 6, 10, and 16. The relation between P_s and C' at $r = 16$ on the various grafted cellophanes is shown in Figure 1. The permeability coefficient of potassium chloride through the grafted membranes increased with increasing C' and decreased as the extent of grafting increased. However, the permeability coefficients of the control cellophane were almost the same value at various concentrations of the solution and did not depend on C' .

The relation between P_s and C' at various values of r on the grafted cellophane with $\sim 55\%$ grafting is shown in Figure 2. The permeability coefficient increased with increasing C' and r , but their values approached almost same value at higher concentration regardless of C' and r . A similar result was obtained with the membrane with about 20% grafting, but the permeability coefficient through the $\sim 5\%$ grafted membrane did not converge at higher concentrations. This characteristic of cellophanes grafted with more than 20% AA is similar to the permeation of electrolyte through typical ionic membrane reported previously.¹

In dilute solution, the permeability coefficient P_s of a 1:1 electrolyte through charged membrane is given by eq. (3),¹ when the Donnan membrane equilibrium is set up between the solution and membrane phase, and moreover, the mean

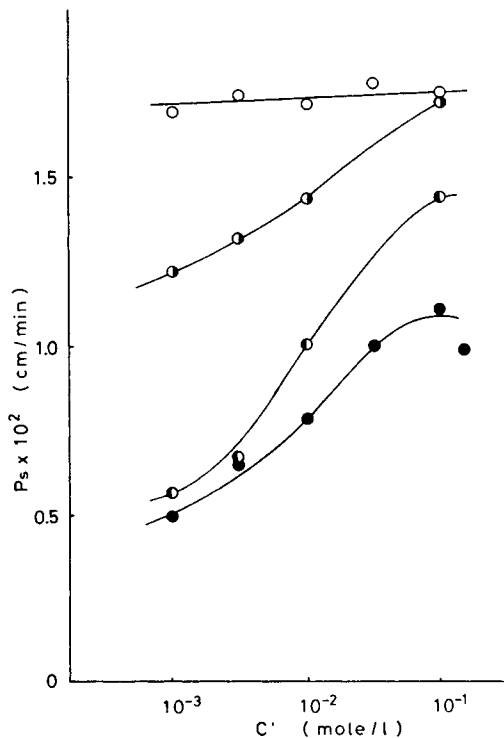


Fig. 1. Permeability coefficients of potassium chloride for AA-grafted cellophanes at $r = 16$. (—○—) control cellophane, (—○—) with 4–8% grafting, (—●—) with 15–25% grafting, and (—●—) with 50–60% grafting.

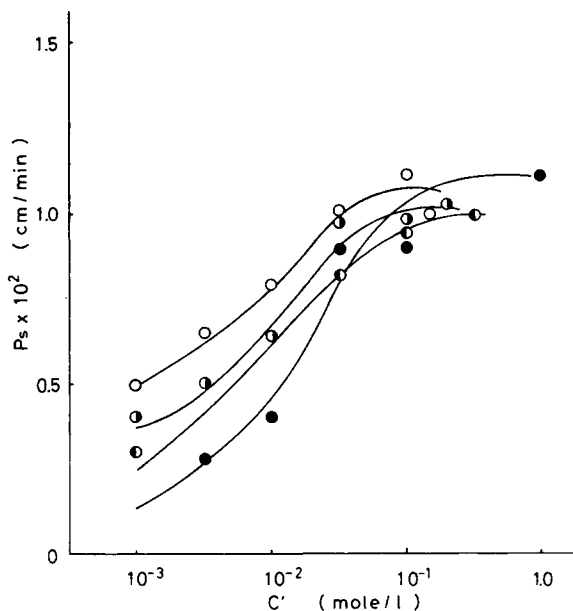


Fig. 2. Permeability coefficients of potassium chloride for AA-grafted cellophane with 50%–60% grafting. (—○—) $r = 16$, (—◐—) $r = 10$, (—●—) $r = 6$, (—●—) $r = 3$.

activity coefficient (\bar{y}_{\pm}) of electrolyte in the membrane without the fixed ion and that (y_{\pm}) in the solution can be assumed unity.

$$P_s = [RTl_-(r + 1)/\delta\phi X]C' \quad (3)$$

where δ is the membrane thickness, l_- is the mobility of coion in the membrane; ϕ is a parameter expressing the nonideality of the solution, which is denoted as \bar{y}_p/\bar{y}_{\pm} ; and \bar{y}_p is the activity coefficient of the fixed counterion in charged membrane.

In order to examine the conformity of eq. (3) in the case of AA-grafted cellophane, P_s was plotted against r for concentrations which were selected in the range of lower concentrations from $C' = 1.0 \times 10^{-3}$ to 1.0×10^{-2} mol/liter. The results for the permeation of potassium chloride through about 55% grafted cellophane are shown in Figure 3. P_s linearly increased with increasing r for each concentration. Similar results were obtained for the ~5% and 20% grafted membranes.

Subsequently, the values of P_s at $r = 1$ of the various grafted membranes were replotted against C' ; these results are summarized in Figure 4. P_s increased linearly with increasing C' for all of the grafted membranes. The straight lines of the ~20% and 55% grafted cellophanes pass through the origin of the coordinate axes but deviate from the origin at $C' = 0$ in the case of ~5% grafting. From the above results, it is found that the membranes with grafting of greater than 20% should be regarded as polyionic membranes, but it is difficult to assume that the membrane with ~5% acts as a typical charged membrane. It may be considered that the permeation of potassium chloride through the ~5% grafted cellophane is considerably affected by the contribution of the permeation through a part of cellophane as nonionic polymer. However, the influence of this part of the cellophane in the membranes with ~20 and 55% grafting on the permeation of potassium chloride may be less than for the ~5% grafted membrane.

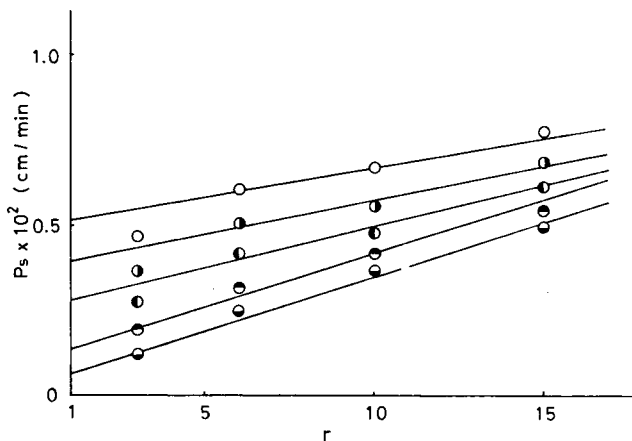


Fig. 3. Relation between the permeability coefficient and concentration ratio r for AA-grafted cellophanes with 50–60% grafting. (—O—) $C' = 1.0 \times 10^{-2}$ mol/liter, (—●—) $C' = 7.5 \times 10^{-3}$ mol/liter, (—◐—) $C' = 5.0 \times 10^{-3}$ mol/liter, (—◑—) $C' = 2.5 \times 10^{-3}$ mol/liter, and (—◒—) $C' = 1.0 \times 10^{-3}$ mol/liter.

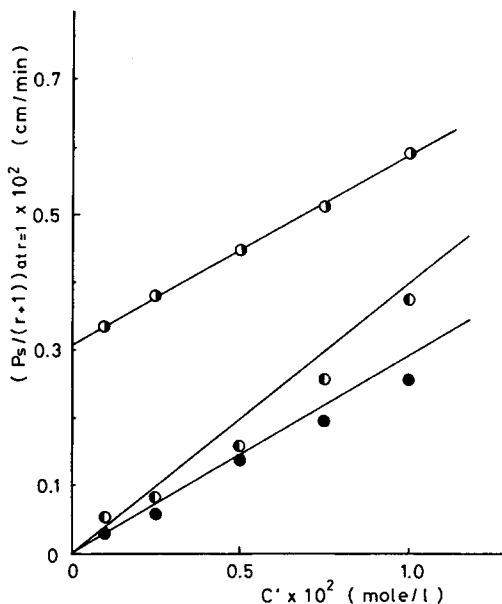


Fig. 4. Dependence of $P_s/(r+1)$ at $r=1$ on the concentration of potassium chloride for AA-grafted cellophanes. (—O—) 4%–8% grafting, (—◐—) 15%–25% grafting, (—●—) 50%–60% grafting.

Accordingly, it may be deduced that the permeability behavior of membranes with greater than 20% grafting apparently shows a polyionic character. Subsequently, the slope ($RTl_-/\delta\phi X$) was estimated from Figure 4 on AA-grafted membranes with more than 20% grafting, which were considered as polyelectrolyte membranes; these values are shown in Table I.

On the other hand, P_s at higher concentrations is given¹ by eq. (4) if the mobility of the anion (l_-) is almost the same value as that of cation (l_+) in the swollen membrane, since the mobility of the anion (l_-^0) is equal to that of the cation (l_+^0) in aqueous potassium chloride solutions:

TABLE I
Interference Factor (α), Fixed Charge Concentration (X), ϕ Value, and Effective Charge Concentration (ϕX) for AA-Grafted Cellophanes

Sample, % grafted	$RTl_-/\delta\phi X$ (at $r = 1$) cm liter/mol min	α , 10^{-2}	δ at 10^{-2} mol/liter, 10^{-3} cm	X , mol/liter	ϕ , 10^{-2}	ϕX , 10^{-2} mol/liter
15%-25	0.40	7.3	4.2	2.7	1.9	5.1
50%-60	0.30	6.4	6.0	5.2	0.8	4.2

$$P_s = RTl_-/\delta \quad (4)$$

The validity of eq. (4) on AA-grafted membrane with more than 20% grafting is supported by the fact that P_s approached almost the same value at higher concentrations regardless of C' and r , as mentioned above. Therefore, the mobility of coion (l_-) in the swollen membrane at $C' = 1.0$ mol/liter and $r = 3$ was determined from eq. (4).

The mobility of the coion in the swollen membrane (l_-) may be expressed by the equation

$$l_- = \alpha l_-^0 \quad (5)$$

where α is an interference factor on the anion, which diffuses in water-filled amorphous part of the charged membrane. The factor α is dependent on (1) hydration of the swollen membrane, (2) the actual distance for movement of diffusing coion from one side of the membrane to the other, and (3) the contribution of the electric interaction between coion and counterion in the membrane. The α value at $C' = 1.0$ mol/liter was estimated from eq. (5) by using $l_-^0 = 3.70 \times 10^{-14}$ cm² mol/erg min at the same concentration of potassium chloride¹² without the membrane (Table I). In the highly hydrated membrane used in this study, the influence of the actual distance for movement of coion on α may be included in the hydration contribution. The hydration of each membrane grafted with AA and measured in water and 0.01 and 1.6 mol/liter potassium chloride aqueous solutions showed almost the same value. Consequently, for grafted membranes with same degree of grafting, the value of α may be constant regardless of the concentration of potassium chloride. Subsequently, ϕ at $C' = 1.0 \times 10^{-2}$ mol/liter was calculated from the slope ($RTl_-/\delta\phi X$) by using the α value of $l_-^0 = 4.64 \times 10^{-14}$ cm² mol/erg min at 1.0×10^{-2} mol/liter aqueous potassium chloride solution,¹² membrane thickness (δ) at $C' = 1.0 \times 10^{-2}$ mol/liter, and concentration of fixed charge in the membrane (X); these values were shown in Table I. The α value of the membrane with $\sim 55\%$ grafting was a little smaller than that of the membrane with $\sim 20\%$ grafting. Remarkably, δ and X increased with increasing degree of grafting. The ϕ value of the membrane with $\sim 20\%$ grafting was considerably larger than that of $\sim 55\%$ grafting, and the effective concentration of the fixed charge (ϕX) of the grafted membrane with $\sim 20\%$ grafting was slightly larger than that of the membrane with $\sim 55\%$ grafting, although the X of at $\sim 20\%$ grafting was less than that at $\sim 55\%$ grafting. Details of ϕ and ϕX will be discussed later.

In order to examine the values of ϕ and ϕX obtained by the permeation of potassium chloride in more detail, these values for 8%, 25%, and 60% grafted cellophanes were determined from the Donnan membrane equilibrium in

aqueous potassium chloride solutions. In general, when the solution inside membrane is not thermodynamically ideal, the Donnan membrane equilibrium is approximated by the equation

$$(y_{\pm}C)^2 = \bar{y}_{\pm}^2 \bar{C}_- (\bar{C}_- + \phi X) \quad (6)$$

where y_{\pm} is mean activity coefficient of electrolyte in solution, \bar{y}_{\pm} is that in the membrane, C is concentration of electrolyte in the solution, and \bar{C}_- is that in the membrane, respectively. In this study, \bar{C}_- was experimentally determined at $C = 1.0 \times 10^{-2}$ mol/liter, and values of y_{\pm} and \bar{y}_{\pm} were assumed to be unity because of the dilute solution, as described previously. The ϕ and ϕX calculated from eq. (6) are shown in Table II. The ϕ of 60% grafted cellophane is almost the same value as that obtained from the permeation of potassium chloride shown in Table I. In the case of cellophane with 25% grafting, ϕ determined by the Donnan membrane equilibrium was clearly less than that by transport phenomena. It has been found that ϕ represents the fraction of free counterion which is not bound in the vicinity of the polyions, and the ϕ values determined thermodynamically and hydrodynamically agrees with each other over a wide range of polyelectrolyte concentration.^{3,5} Therefore, the difference in the ϕ values obtained by permeation and membrane equilibrium for 25% grafting is considered to be due to the fact that the parts of cellophane in the grafted membrane also make some contribution to the permeation of potassium chloride because of comparatively less grafting in addition to the permeable behavior of the electrolyte through the polyionic parts. Accordingly, it is inferred that the permeation of potassium chloride through the cellophane with $\sim 20\%$ grafting might be obtained by the permeation theory of electrolyte through ionic polymer membrane,¹ even if the behavior of the permeation is apparently similar to that in polyionic membranes. On the other hand, it is found that cellophane with $\sim 55\%$ grafting can be regarded as a typical polyionic membrane, because the ϕ value derived from hydrodynamics is almost the same as that by the membrane equilibrium. As seen in Table II, the effective concentration of the fixed charge (ϕX) for 60% grafted membrane was similar to that for 25% grafting but more than for 8% grafted membrane. When the values of ϕX derived by membrane equilibrium (Table II) were compared with the results from permeation (Table I), we find that the ϕX of 25% grafted membrane derived by hydrodynamics is larger than that derived by membrane equilibrium. This may be attributed to the different values of ϕ , as mentioned above. For 60% grafted membrane, ϕX determined thermodynamically was almost the same as the value estimated hydrodynamically, because the value of ϕ determined by permeation coincided with that from membrane equilibrium, as previously described. The values of ϕX in all of the cellophanes grafted with AA used in this study are considerably

TABLE II
 ϕ Value and Effective Fixed Charge Concentration (ϕX) Obtained by Donnan Membrane
Equilibrium Measurement for AA-Grafted Cellophanes

Sample, % grafted	\bar{C}_- , 10^{-2} mol/liter	X , mol/liter	ϕ , 10^{-2}	ϕX , 10^{-2} mol/liter
8	0.47	1.2	1.4	1.7
25	0.31	2.7	1.1	2.9
60	0.30	5.2	0.6	3.0

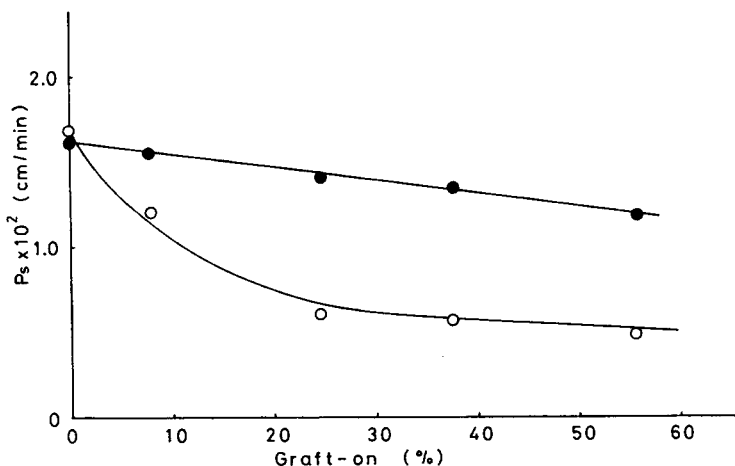


Fig. 5. Effect of the degree of grafting on the permeability coefficients of potassium chloride and urea for AA-grafted cellophane at $C' = 1.0 \times 10^{-3}$ mol/liter and $r = 16$. (—○—) potassium chloride and (—●—) urea.

larger than that of an interpolymer membrane of collodion and sulfonated polystyrene reported by Tasaka et al.¹ It is a feature of the grafted membrane that the ϕX of the membrane can be easily varied over a wide range while keeping the membrane shape and strength.

To compare the permeation of electrolyte with that of nonelectrolyte through the grafted cellophane with various degrees of AA grafting, the permeability coefficients of potassium chloride and urea were measured under the same conditions ($C'' = 1.0 \times 10^{-3}$ mol/liter, $r = 16$). The influence of the degree of grafting on permeability is shown in Figure 5. The P_s of potassium chloride decreased considerably with increasing degrees of grafting up to $\sim 20\%$ grafting, decreasing slightly thereafter. On the other hand, the P_s of urea decreased a little with increasing degrees of grafting, but a marked dependence of degree of grafting on P_s was not observed. Such results are probably based on the fact that the permeation of potassium chloride through AA-grafted cellophanes is mainly dependent on the effective concentration of the fixed charge (ϕX), in contrast with the case for urea.

In conclusion, the permeation of potassium chloride through the cellophane with the AA grafting at greater than 55% can be explained by the theory of the permeation of electrolyte through ionic membranes as derived from the phenomenological equation. However, it is a little difficult to apply the theory to the permeation of potassium chloride through the $\sim 20\%$ grafted membrane, even if the behavior of permeation is apparently similar to that of polyionic membrane. Membranes with grafting of less than 5% clearly show features characteristic of both uncharged and charged membranes for the permeation of potassium chloride. It was found that the cellophane grafted with AA had the characteristics of ionic membrane while the cellophane with more than 20% grafting had the permselectivity of potassium chloride in dilute solution because of the increase of the effective concentration of fixed charge (ϕX) in membranes.

References

1. M. Tasaka, N. Aoki, Y. Kondo, and M. Nagasawa, *J. Phys. Chem.*, **79**, 1307 (1975).
2. N. Kamo, Y. Toyoshima, H. Nozaki, and Y. Kobatake, *Kolloid Z. Z. Polym.*, **248**, 914 (1971).
3. T. Ueda, N. Kamo, N. Ishida, and Y. Kobatake, *J. Phys. Chem.*, **76**, 2447 (1972).
4. N. Kamo, M. Oikawa, and Y. Kobatake, *J. Phys. Chem.* **77**, 92 (1973).
5. T. Ueda and Y. Kobatake, *J. Phys. Chem.*, **77**, 2995 (1973).
6. S. Takigami, Y. Maeda, and Y. Nakamura, *J. Appl. Polym. Sci.*, **24**, 1419 (1979).
7. H. Yasuda, C. E. Lamaze, and L. D. Ikenberry, *Makromol. Chem.*, **118**, 19 (1968).
8. H. Yasuda, C. E. Lamaze, and L. D. Ikenberry, *Makromol. Chem.*, **125**, 108 (1969).
9. H. Yasuda, A. Peterlin, C. K. Colton, K. A. Smith, and E. W. Merrill, *Makromol. Chem.*, **126**, 177 (1969).
10. H. Yasuda and C. E. Lamaze, *J. Macromol. Sci., Phys.*, **5**, 111 (1971).
11. S. Utsumi, *Nippon Kagaku Kaishi*, **73**, 835 (1952).
12. H. Falkenhagen and G. Kelbg, in *Landolt-Börnstein Tabellen*, Vol. 2, Part 7, 6th ed., E. Schmutzer, Ed. Springer-Verlag, Berlin, 1960, pp. 51-55.

Received November 14, 1978

Revised March 13, 1979