TABLE VI

POLY-(*R*)-3,7-DIMETHYL-1-OCTENE OBTAINED BY COPOLYMERIZATION OF RACEMIC 3,7-DIMETHYL-1-OCTENE WITH (*S*)-3-METHYL-1-PENTENE

			—Homopolymer of 3,7-dimethyl-1-octene[b]—		
Run	R_m[a]	Catalyst	$[\alpha]^{25}D$[c]	Wt %[d] (W_h)	Prevalence (P_r) of *R* units,[e] %
C_1	3.41	$TiCl_4$–$Zn(i\text{-}C_4H_9)_2$	−51.6	3.4	27
C_2	26.0		−25.2	8.3	12
C_3	3.36	$TiCl_4$–$Al(i\text{-}C_4H_9)_3$	−19.6	30.2	10

[a] (Moles of racemic 3,7-dimethyl-1-octene)/(moles of (*S*)-3-methyl-1-pentene). [b] On the basis of the last fraction obtained by solvents extraction of the polymeric products (see Table III). [c] In cyclohexane. [d] Calculated[11] as [weight per cent of the fraction (Table III)][(weight of 3,7-dimethyl-1-octene + weight of (*S*)-3-methyl-1-pentene)/(weight of 3,7-dimethyl-1-octene)]. [e] Calculated using the rotatory power of the fraction and the curves polymer rotatory power *vs.* polymerized monomer optical purity.[13,20]

growing chain end. In fact the number of growing chain ends having an asymmetric carbon atom of a single absolute configuration in the side chain increases with increasing the amount of optically active comonomer.

This observation is, however, in contrast with the fact that the same stereoelectivity has been obtained using $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ and $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalyst (Table II) with R_m = 26 and 3.4, respectively. The contribution of the catalytic complex to the stereoelective character of the process seems therefore still actual.[19]

More complicated appears the quantitative evaluation of the dependence of stereoselectivity on the type of catalyst and on comonomers molar ratio.

The method of separation of copolymers from homopolymers, based on solvents extraction, is very simple, but also rather rough and its efficiency is certainly not very high. Furthermore the polymeric products obtained in the different experiments are different with respect to molecular weight, tacticity, and probably comonomers distribution and these factors affect remarkably the results of solvents extraction.

In the case of the copolymerization of racemic 3,7-dimethyl-1-octene with (*S*)-3-methyl-1-pentene a rough evaluation of the stereoselectivity obtained in the different experiments can be performed on the basis of the amount of poly-(*R*)-3,7-dimethyl-1-octene obtained. Considering, in substantial agreement with the infrared spectra, the fractions with negative optical activity as poly-3,7-dimethyl-1-octene, the prevalence (P_r) of *R* units in these fractions can be calculated using the curves polymer rotatory power *vs.* polymerized monomer optical purity.[13,20]

The data are reported in Table VI together with per cent weight (W_h) of homopolymer of 3,7-dimethyl-1-octene with respect to the polymerized amount of the same monomer[11]; they indicate that P_r and W_h are affected by both comonomers ratio and catalytic system. The differences between the $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ and $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ system, R_m being the same, appear to be too large to be attributed only to differences in efficiency of the separation of the homopolymer from the copolymer. It seems, therefore, that the catalytic complex plays an appreciable role in determining the stereoselective character of the polymerization process as proposed in previous papers.[1,19]

Further experiments as well as a more accurate quantitative analysis of the polymeric products are necessary for a better understanding of the parameters responsible of the particular steric requirements of the copolymerization of asymmetric α-olefins. This knowledge could allow an improvement of the stereoselectivity and eventually of the efficiency of the separation which are very useful in order to prepare optically active homopolymers by copolymerization of a racemic monomer with a small amount of suitable optically active comonomer.

Acknowledgment. The authors wish to express their appreciation to Professor P. Pino for many helpful and stimulating discussions and to Dr. E. Benedetti for recording and discussing infrared spectra. They wish to thank also Professor L. Porri for reading the manuscript before publication.

(19) P. Pino, *Advan. Polym. Sci.*, **4**, 393 (1965).
(20) F. Ciardelli, G. Montagnoli, O. Pieroni, D. Pini, and P. Pino, to be published.

Notes

On the Definition of a Permeability Function

John A. Howell

Chemical Engineering Department, State University of New York at Buffalo, Buffalo, New York 14214.

Received February 6, 1969

Permeation through membranes is normally described by a permeability coefficient, which is calculated by measuring the flux across the membrane and dividing this by the mean pressure gradient. Although this coefficient is the most useful representation of permeation where solubility behavior follows Henry's law and the diffusion coefficient is concentration independent, it has some drawbacks in more complex situations. A permeability coefficient is a lumped-parameter description of the permeation process, since it ignores the different local processes which contribute to the over-all phenomenon. In contrast the diffusion coefficient and the solubility coefficient form a distributed-parameter description, since they describe the local physical processes involved in permeation. If the diffusion coefficient is a continuous function of concentration, the steady state flux is given by Fick's law

$$J = -D(c)\frac{\mathrm{d}c}{\mathrm{d}x} \tag{1}$$

where J is the flux, with respect to the local mass average velocity, $D(c)$ is the local diffusion coefficient, c is the local concentration of permeant, and x is the distance across the membrane. If there are no reactions within the membrane and if the concentration of permeant within the membrane is low, as is usually the case, bulk flow is negligible and J is then also the flux with respect to stationary coordinates. The permeability coefficient is now defined by eq 2, and is seen to be a function of both upstream and downstream pressures

$$P = \frac{Jt}{\Delta p} = \frac{1}{(p_1 - p_2)}\int_{c_2}^{c_1} D\,\mathrm{d}c \tag{2}$$

where P is the permeability coefficient and p_1, p_2 are the upstream and downstream pressures on the membrane, respectively. Normally P is measured at several upstream pressures with a constant, often zero, downstream pressure p^*, and then P can be calculated for any pair of upstream and downstream pressures greater than p^* by the use of eq 3. The permeability coefficient

$$P(p_1, p_2) = \frac{P(p_1, p^*)[p_1 - p^*] - P(p_2, p^*)[p_2 - p^*]}{p_1 - p_2} \tag{3}$$

is thus easy to measure and expresses flux in the most natural physical variable, pressure. Equation 3, however, arises from the fact that the flux is continuously dependent on concentration within the membrane rather than from the definition of the permeability coefficient. Furthermore the natural physical variable within the membrane is concentration, and its local variation, together with the local diffusion coefficient, best describe the local flux. The permeability coefficient, being an over-all coefficient, cannot be used to describe local behavior, nor can it be used in unsteady-state situations. It would be convenient under certain situations to substitute for the permeability coefficient a function of the local concentration, as locally relevant as the diffusion coefficient, yet as convenient as the permeability coefficient.

Suppose the solubility is expressed as a function of pressure by eq 4 where S is continuous and single valued. Transforming eq 1 into the new variable p by

$$C = pS(p) \tag{4}$$

formal use of eq 4, we obtain an alternative formulation of Fick's law (eq 5). The function of pressure defined

$$J = -D(p)\frac{\partial}{\partial p}(pS(p))\frac{\mathrm{d}p}{\mathrm{d}x} \tag{5}$$

by eq 6 is similar to the diffusion coefficient but is

$$\mathrm{F}(p) \equiv D(p)\frac{\partial}{\partial p}(pS(p)) \tag{6}$$

expressed in a variable which is numerically equal to the upstream and downstream pressures at the edges of the membrane, while within the membrane it may be conveniently regarded as a transformed concentration rather than pressure. A local description of the flux, which applies whenever Fick's law is valid, may then be written as

$$J = -\mathrm{F}(p)\frac{\mathrm{d}p}{\mathrm{d}x} \tag{7}$$

For steady-state permeation between p_1 and p_2 the flux can be obtained from F by simply integrating eq 7 across the membrane.

$$-J(p_1, p_2) = \frac{1}{t}\int_{p_1}^{p_2} \mathrm{F}(p)\,\mathrm{d}p \tag{8}$$

Obviously this function is an alternative to the permeability coefficient and has the conceptual advantage of being a local rather than an over-all quantity. It can be calculated from measurements of steady-state flux with varying upstream pressure and constant downstream pressure, such as are made to calculate the permeability coefficient.

$$t\left(\frac{\partial J(p_1, p_2)}{\partial p_1}\right)_{p2} = \mathrm{F}(p)\big|_{p=p_1} = D(p)\frac{\partial}{\partial p}(S(p)p)\big|_{p=p_1} \tag{9}$$

The function F is thus tabulated as a function of p_1 while the value of p_2 is unimportant as long as it is constant. If it is found that p_2 influences the calculated value of F, either Fick's law is invalid under the experimental conditions used, or else the flux varies throughout the membrane. The latter situation can arise under steady-state conditions if there are reactions taking place within the membrane. Under no other conditions would the value of p_2 influence F. The permeability function F is thus a clear representation of local transport conditions within the membrane. The efforts of some authors to express the permeability coefficient as an empirical function of a single pressure or pressure difference indicate a need for a more truly local function such as F.[1,2] The permeability function and permeability coefficient are identical when there is ideal behavior.

(1) N. N. Li and E. J. Henley, *A.I.Ch.E. J.*, **10,** 666 (1964).

(2) S. A. Stern, J. T. Mullhaupt, and P. J. Gareis, *ibid.*, **15,** 64 (1968).

Anomalous Light Scattering by Poly(4-vinylpyridine) in Nitromethane

G. R. Seely

Contribution No. 342 from the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio.

Received January 29, 1969

In the course of work with aggregates of chlorophyll derivatives with poly(4-vinylpyridine),[1] we attempted to measure the molecular weight and the radius of gyration of polymer samples in nitromethane by the light-scattering method. The attempt was frustrated by the existence of an anomaly in the dissymmetry of the scattered light which made impossible the determination of either property. The anomaly was that a greater amount of light was scattered in a backward direction than at

(1) G. R. Seely, *J. Phys. Chem.*, **71,** 2091 (1967).