acetate, ethyl and isobutyl alcohol) in Dowex-50 have been reported[9] in which apparent diffusion coefficients approximately an order of magnitude smaller than those for water given in Table I were found. Further, apparent activation energies generally lying between 6 and 10 kcal. mole^{-1} were observed. The lower diffusion rates then are not surprising in view of the increased E_{act}. However, in contrast with the results for H_2O^{18}, diffusion in these cases appeared to be accompanied by large, positive activation entropies.

OAK RIDGE, TENN.

[9] H. P. Gregor, F. C. Collins and M. Pope, *J. Colloid Sci.*, **6**, 304 (1951). In these experiments a "free diffusion" of the neutral molecule from the exchanger into an effectively infinite bath was allowed to occur. The possible dependence of the diffusion coefficient on the concentration of the neutral molecule in the exchanger was ignored. Further, the activation energies reported are for the over-all process, including desorption from the exchanger.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Self-diffusion of Cations in Hetero-ionic Cation Exchangers

BY B. A. SOLDANO AND G. E. BOYD

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Diffusion coefficients, D, and activation energies, E_{act}, for the diffusion of sodium, zinc and lanthanum ions were measured experimentally and compared with corresponding values for the same ions in their pure (*i.e.*, homo-ionic) exchanger salt forms. In general, the diffusion rate of the more mobile cation was lowered, and that of the less mobile ion was increased. An interpretation of the observed diffusion coefficients was based on the equation from absolute reaction rate theory, $D = ed^2(kT/h) \exp(\Delta S^{\ddagger}/R) \exp(-E_{act}/RT)$, according to which changes in D are governed by changes in E_{act} and $\Delta S^{\ddagger}$, the entropy of activation. An explanation of the magnitudes of the observed activation energies and derived entropies is proposed based on the hydration of the cations in the exchanger, on the extent of their association with the bound anionic exchange groups, and on the degree of hydration of the activated complex for diffusion.

This study has been concerned with the effects of ionic environment on the self-diffusion of cations in a cation exchanger of the sulfonated polystyrene type. Previous researches in this series have investigated the roles played by cationic size and charge, by ion-exchange polymer cross-linking[1] and by ion-exchange capacity[2] in determining the magnitudes of cation self-diffusion coefficients and the activation energies for self-diffusion in the pure (*i.e.*, homo-ionic) salt forms of ion exchangers. Here cation exchangers containing varying amounts of *two* different cations bearing either the same or different charges were employed, and self-diffusion rate and activation energy measurements were made for each ion using radioactive tracers. It is to be emphasized that the rate processes measured in these experiments were those which occur after a complete ion exchange equilibrium has been reached (*i.e.*, rates at dynamic equilibrium). No changes in composition either of the exchanger or of the external mixed aqueous electrolyte solution were involved, as has been the case in other reports[3-5] where a "free diffusion" of ions along concentration gradients *in the exchanger* occurred. The apparent diffusion coefficients given below, therefore, are believed to truly reflect environmental influences on ionic mobility, unmodified by thermodynamic activity coefficient gradients.

Preliminary results[6] for the diffusion of trace amounts of Na$^+$, UO_2^{++} and Ce^{+++} ions in an otherwise pure hydrogen form cation exchanger of another type have already indicated that diffusion rates may depend strongly on ionic charge in hetero- as well as in homo-ionic exchangers.[1]

Experimental

The well-known, commercially available sulfonated polystyrene exchangers, cross-linked with divinylbenzene (DVB) were employed in the rate measurements. Two differently linked preparations (*i.e.*, nominal 8.6% and 16% DVB) were used.[7] The general experimental procedure was closely the same as that reported in earlier studies with homo-ionic cation exchangers.[1] The desired hetero-ionic exchanger salt was prepared by repeatedly equilibrating 3.4 meq. of the hydrogen form with 200 ml. of the appropriate 0.23 *N* mixed electrolyte solution until a constant composition was achieved. The exchanger was then washed and charged with radioactively-labeled ions using an active solution of the same composition as was employed to prepare the inactive mixed salt form. The "tagged" hetero-ionic exchanger was then suspended in a well-stirred volume of pure water, and the self-exchange reaction was initiated by rapidly adding sufficient *mixed* electrolyte to give a 0.23 *N* solution containing the same relative amounts of ions as in the solution used to prepare the hetero-ionic salt form. It was, of course, necessary to employ differing diffusion theory curves in deriving self-diffusion coefficients from the rate date for each ion, owing to the ionic selectivity properties of the exchangers.

Experimental Results and Discussion

The first experiments were performed with mixed exchangers containing either two alkali metal cations, or one of these and hydrogen ion. The results (Table I) appeared to confirm the finding, reported some time ago for another cation exchanger,[8] that sodium ion diffused most slowly when present in pure sodium exchanger. Several new observations were also made:

1. The increase in D_{Na^+} when sodium diffuses in an exchanger containing another alkali cation or hydrogen ion is accompanied by a decrease in both its activation energy, E_{act}, and entropy, $\Delta S^{\ddagger}$.

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[1] G. E. Boyd and B. A. Soldano, THIS JOURNAL, **75**, 6091 (1953).

[2] G. E. Boyd, B. A. Soldano and O. D. Bonner, to be published

[3] D. K. Hale and D. Reichenberg, *Faraday Society Disc.*, **7**, 79 (1949).

[4] T. R. E. Kressman and J. A. Kitchener, *ibid.*, **7**, 90 (1949).

[5] D. Reichenberg, THIS JOURNAL, **75**, 589 (1953).

[6] G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., *ibid.*, **72**, 4807 (1950).

[7] These Dowex-50 type cation exchangers were obtained from the Physical Research Laboratory, Dow Chemical Co., Midland, Mich.

[8] G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., THIS JOURNAL, **69**, 2836 (1947).

Table I

Self-diffusion of Alkali Metal Cations in Hetero-ionic Cation Exchangers of the Dowex-50 Type

Exchanger composition, %	Diffusing ion	Self-diffusion coefficient (cm.² sec.⁻¹) 0.3°	25°	Activation energy, cal. mole⁻¹	$d(e^{\Delta S^{\ddagger}/R})^{1/2}$
Nominal 8.6% DVB exchanger (5.25 meq./g. dry H-form)					
Na^+ 100	Na^+	3.42×10^{-7}	9.44×10^{-7}	6500	6.0
Rb^+ 100	Rb^+	6.06×10^{-7}	1.38×10^{-6}	5140	2.2
Cs^+ 100	Cs^+	6.61×10^{-7}	1.37×10^{-6}	4610	1.4
Na^+ 31	Na^+	3.85×10^{-7}	9.36×10^{-7}	5760	3.3
H^+ 69	H^+	....	....	..	..
Na^+ 7	Na^+	3.87×10^{-7}	8.82×10^{-7}	5320	2.1
H^+ 93	H^+	....	....	..	..
Na^+ 43	Na^+	4.71×10^{-7}	1.12×10^{-6}	5760	3.5
Rb^+ 57	Rb^+	5.76×10^{-7}	1.32×10^{-6}	4810	1.6
Na^+ 0.6	Na^+	4.64×10^{-7}	9.80×10^{-7}	5140	1.9
Cs^+ 99.4	Cs^+	....	....	..	..
Nominal 16% DVB exchanger (5.10 meq./g. dry H-form)					
Na^+ 100	Na^+	6.58×10^{-8}	2.40×10^{-7}	8400	15.4
Na^+ 8.1	Na^+	1.36×10^{-7}	3.90×10^{-7}	6880	5.3
H^+ 91.9	H^+	....	....	..	..
Na^+ 3.4	Na^+	1.38×10^{-7}	3.63×10^{-7}	6280	3.1
K^+ 96.6	K^+	....	3.74×10^{-7}	..	..
Na^+ 1.8	Na^+	0.97×10^{-7}	2.62×10^{-7}	6480	3.1
Cs^+ 98.2	Cs^+	1.11×10^{-7}	3.10×10^{-7}	6680	4.0
Na^+, 90	Na^+	....	....	..	..
Cs^+ 10	Cs^+	5.42×10^{-8}	1.91×10^{-7}	8220	11.8

According to the absolute reaction rate expression[9] for D_{Na^+}

$$D_{Na^+} = ed^2(kT/h) \exp (\Delta S^{\ddagger}/R) \exp (-E_{act}/RT)$$

a decrease in E_{act} will increase D_{Na^+}, while a decrease in $\Delta S^{\ddagger}$ will decrease the self-diffusion coefficient. The effect of a second ion on the diffusion of sodium ion is thus determined by the relative contributions from each of these factors.

2. The changes in D_{Rb^+} and D_{Cs^+} caused by the presence of sodium ion appear to be smaller than the experimental uncertainties in their values. The same may be true for the activation energies, although E_{act} for Rb^+ ion in the presence of 43% sodium may be significantly lower than for pure rubidium exchanger. When the equivalental fraction of sodium ion becomes quite small (*i.e.*, <5%), D_{Na^+} may approach the value for the self-diffusion coefficient for the major ion in the exchanger. Thus, in a predominantly potassium exchanger (96.7% K^+, 16% DVB) $D_{Na^+} = 3.63 \times 10^{-7}$ at 25° which is nearly the same as the value, 3.74×10^{-7}, for D_{K^+}. The activation energies appeared to show a similar behavior, for in a 98.2% cesium exchanger E_{act} for sodium ion was 6480 cal. mole⁻¹ compared with 6680 cal. mole⁻¹ for cesium ion. Conversely, when small amounts of Cs^+ ion diffuse in sodium exchanger (*i.e.*, 90% Na^+, 16% DVB) its activation energy was 8220 cal. mole⁻¹, a value not greatly less than 8400 cal. mole⁻¹ for the E_{act} for the self-diffusion of Na^+ ion in pure sodium exchanger.

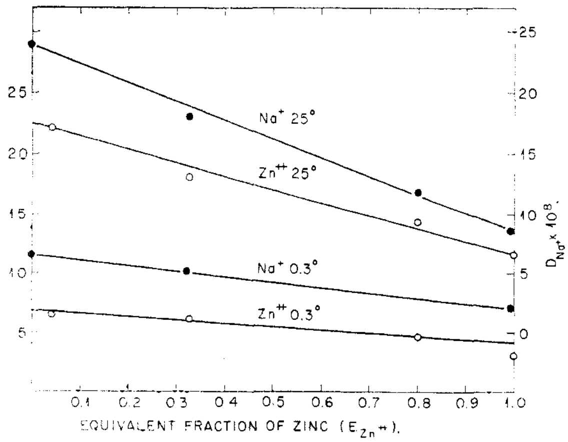

Fig. 1.—Dependence of diffusion coefficients for sodium and zinc ions on cation exchanger composition (scale for D_{Na^+} on right).

3. The effect of increased cross-linking in lowering the self-diffusion coefficients for hetero-ionic salt forms may also be seen. Thus, sodium ion diffuses more slowly, and with a larger E_{act} and $\Delta S^{\ddagger}$ in both the mixed $Na^+ + H^+$ and $Na^+ + Cs^+$ salt forms of the 16% than of the 8.6% DVB exchanger.

A second series of measurements was carried out using exchangers containing varying amounts of sodium and zinc ions (Table II). The mutual effects of these cations on the diffusion of one another were expected to be appreciable, for in their homo-ionic exchanger salts at 25° they self-diffuse with an approximately twenty-fold difference in rates. The measurements do in fact show that E_{act} for the diffusion of zinc ion was significantly lower than for pure zinc exchanger. However, the activation *entropy* was also decreased, so that at most only an approximately twofold increase in $D_{Zn^{++}}$ was observed. The activation energy for the diffusion of sodium ion appeared to remain constant within experimental errors (or to increase when present in low relative amounts), while $\Delta S^{\ddagger}$ decreased so that D_{Na^+} decreased by approximately twofold.

Table II

Self-diffusion of Sodium and Zinc Ions in a Cation Exchanger of Varying Composition

(Nominal 16% DVB Dowex-50 type exchanger)

Exchanger composition, %	Diffusing ion	Self-diffusion coefficient, cm.² sec.⁻¹ 0.3°	25°	Activation energy, cal. mole⁻¹	$d(e^{\Delta S^{\ddagger}/R})^{1/2}$
Na^+ 100	Na^+	6.58×10^{-8}	2.40×10^{-7}	8400	15.4
Zn^{++} 100	Zn^{++}	3.12×10^{-9}	1.16×10^{-8}	8520	3.7
Na^+ 95.8	Na^+	....	....	..	..
Zn^{++} 4.2	Zn^{++}	6.42×10^{-9}	2.21×10^{-8}	8020	3.7
Na^+ 67.3	Na^+	5.16×10^{-8}	1.81×10^{-7}	8200	11.3
Zn^{++} 32.7	Zn^{++}	6.13×10^{-9}	1.81×10^{-8}	7080	1.4
Na^+ 20	Na^+	....	....	..	..
Zn^{++} 80	Zn^{++}	4.73×10^{-9}	1.43×10^{-8}	7220	1.4
Na^+ 0.7	Na^+	2.09×10^{-8}	8.56×10^{-8}	9220	18.5
Zn^{++} 99.3	Zn^{++}	....	....	..	..

An interesting feature of this hetero-ionic system was the apparently nearly linear dependence of D_{Na^+} and $D_{Zn^{++}}$ on the composition of the exchanger expressed in terms of the equivalental fraction either of zinc or sodium ($E_{Zn^{++}}$ or E_{Na^+}) in the exchanger (Fig. 1). Evidently, the diffusion rates for *both* Na^+ and Zn^{++} ions decrease as the capacity of the exchanger becomes increasingly saturated

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[9] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 524.

with the latter ion. The dominant effect of cationic *charge* in setting diffusion rates in ion exchangers is seen to persist in hetero-ionic systems. In no case did the ratio $D_{Na^+}:D_{Zn^{++}}$, which is *ca.* 20 for the homo-ionic salt forms, fall below about 8 for the mixed exchangers. Such behavior appears to be a consequence (*cf.* Table II) of the fact that the characteristic activation entropies for each ion are retained, or else change in a way such as to counterbalance the effects of a changed activation energy.

Finally, the rate of diffusion of sodium ion in a predominantly lanthanum exchanger salt form (>90% La^{+++}) was measured (Table III). As expected, D_{Na^+} was reduced from its value in homo-ionic sodium exchanger, but only by a factor of six, which is small considering that the ratio, $D_{Na^+}:D_{La^{+++}}$, of the diffusion coefficients for the pure salt forms is nearly 500. Here, as in the zinc–sodium exchange system, when relatively small amounts of Na^+ ion occur in the exchanger the activation energy for its diffusion is increased over that for pure sodium exchanger. It is again of especial significance that sodium ion retains its comparatively large activation entropy. It is this factor which is responsible for the large values for D_{Na^+} in the hetero-ionic exchangers as well as in the pure sodium salt form.

TABLE III

SELF-DIFFUSION OF SODIUM AND LANTHANUM IONS IN A CATION EXCHANGER OF VARYING COMPOSITION

(Nominal 16% DVB Dowex-50 type exchanger)

Exchanger composition, %		Diffusing ion	Self-diffusion coefficient, cm.^{2} sec.$^{-1}$ 0.3°	25°	Activation energy, cal. mole^{-1}	$d(e^{\Delta S^{\ddagger}/R})^{1/2}$
Na^+	100	Na^+	6.58×10^{-8}	2.40×10^{-7}	8400	15.4
Na^+	<10	Na^+	1.04×10^{-8}	4.07×10^{-8}	8900	9.8
La^{+++}	>90	La^{+++}	....	....	..	..
La^{+++}	100	La^{+++}	1.53×10^{-10}	5.10×10^{-10}	7870	0.4

The findings reported in Tables I, II and III may be partially summarized by the qualitative statement that in hetero-ionic cation exchangers the more mobile ion is slowed and the less mobile ion is speeded. The activation energy for the more mobile ion (*e.g.*, Na^+) appears to be almost unchanged by increasing amounts of less mobile ion in the exchanger, while its activation entropy is generally lowered. On the other hand, E_{act} for the less mobile ion is decreased by increasing amounts of more mobile ions, although its entropy of activation is also usually lowered. An exception to this apparent regularity appears when the more diffusible ion is present in low relative concentration; then, both E_{act} and $\Delta S^{\ddagger}$ are increased and may exceed the values for these quantities found with the pure salt forms.

In the attempt to understand these experimental facts it first may be remarked that a radioactive ion may distribute itself uniformly throughout an hetero-ionic exchanger either by (a) self-exchange with another like, isotopic ion, or, by (b) ionic exchange with an unlike ion. When the relative amounts of two different ions in an exchanger do not differ greatly, but one of them diffuses much more slowly than the other, it may be supposed that mechanism (a) will be chiefly responsible for the migration of the faster moving ion. When, however, one of the ions is present only in very low relative concentrations, its diffusion probably occurs by process (b). The conditions for local electric neutrality in the interior of the exchanger when applied together with Fick's law of diffusion lead to the conclusion that the D's must be equal when diffusion occurs only by "place change" of unlike ions. In the mixed alkali ion exchangers this condition appeared to be satisfied, but not in the sodium–zinc exchange systems. In the latter, either the concentration of one or the other ion was not sufficiently low to exclude self-exchange, or, the exchange, $2Na^+ \rightleftarrows Zn^{++}$, does not occur in the manner indicated.

In considering the self-exchange mechanism (a) in hetero-ionic exchangers it must not be assumed that the activation energies and entropies will be the same as in the homo-ionic forms. Again using the sodium–zinc system as an example, sodium ion here moves in an environment probably containing less "free water" than in its own pure salt form, while zinc ion probably moves in a medium containing more "free water." Accordingly, there should be more association of sodium ion with the anionic exchange groups, and less association of zinc ion.

The same general hypotheses already employed in the interpretation of self-diffusion coefficients and activation energies and entropies for homo-ionic exchangers[1] should apply to hetero-ionic systems: The competing factors, cationic hydration and cationic association with the structurally-bound exchange groups (accompanied by partial dehydration), act to determine the magnitudes of the observed E_{act} and $\Delta S^{\ddagger}$. Strongly hydrated, weakly associated cations have been found to diffuse with appreciable *net* positive activation entropies, while strongly associated cations diffuse either with a small net positive, or even appreciable *net* negative entropies. Positive activation entropies are assumed to originate in the more or less strong interaction of large hydrated ions with their environment during diffusion. Negative entropy contributions are supposed to arise from the electrostriction of the solvent (*i.e.*, coöperative entropy of activation) accompanying the dissociation of ion-pairs to form the activated complex for diffusion. Hydration of the activated complex also appears to be responsible for a lowering of the activation energy from that expected on the basis of cationic charge. Thus, from electrostatic considerations, E_{act} might be expected to increase considerably in going from Na^+ to Zn^{++} and to La^{+++} ions. Actually, the activation energies for these cations in the 16% DVB exchanger were 8400, 8520 and 7870 cal. mole^{-1} at 12.6°, respectively.

According to the foregoing views, then, sodium ion in an exchanger containing zinc ion shows the observed decreased $\Delta S^{\ddagger}$ because of its increased association. Since, however, the hetero-ionic sodium–zinc exchanger contains less water than pure sodium exchanger, the activation energy for Na^+ ion may be increased. The mixed exchanger, however, contains more water than the homo-ionic *zinc* form, so that Zn^{++} ion may diffuse with less disturbance, and hence with a smaller, positive entropy of activation. Further, since the activated complex for the diffusion of zinc ion may become more hydrated, the E_{act} for this ion will also be lowered.

The extension of this interpretation to the diffusion of ions present in trace quantities in otherwise homo-ionic exchanger salts does not seem feasible until the results from additional quantitative measurements are available.

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[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY]

The Molecular Structure of Polyethylene. I. Chain Branching in Polyethylene during Polymerization[1]

BY M. J. ROEDEL

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Two types of branching can occur during the free radical polymerization of ethylene. These two types depend upon different polymerization variables and affect different physical properties of the formed polymer. Long chain branching is due to intermolecular hydrogen transfer, is dependent upon polymer concentration, and mainly affects rheological properties. Short chain branching is believed to be due to intramolecular hydrogen transfer *via* transient ring formation, is dependent upon polymerization temperature, and mainly affects properties in the crystalline state.

Introduction

The first suggestion of branching in vinyl polymers was made by Staudinger and Schulz[2] in 1935 after observing discrepancies between osmotic and viscosity molecular weights for polystyrenes prepared over a wide temperature range. This was confirmed by Alfrey, Bartovics and Mark[3] in 1943. In 1937 Burk[4] speculated that free radical polymerization should lead to extensive branching. Flory[5] suggested branching by intermolecular hydrogen transfer, first in 1937 and again in 1947. Fox and Martin[6] in 1940 stated that the infrared analysis of polyethylene indicated a high degree of branching with the proportion of methyl groups varying between 1 CH_3 per 8 CH_2 for a low molecular weight fraction to 1 CH_3 per 100 CH_2 for a high molecular weight fraction. They also suggested that the presence of these methyl groups might confer special properties on the polyethylene. Roland and Richards[7] recently have discussed branching *via* grafting polyethylene to polyvinyl acetate.

In the early 1940's during the course of research on the high pressure polymerization of ethylene, following the original discovery by Fawcett, Gibson and Perrin,[8] it became apparent that marked differences in physical properties exist among polyethylenes polymerized under different synthesis conditions. These differences are of considerable magnitude in many basic physical properties such as density, crystalline melting point, Young's bending modulus, tensile strength and vapor permeability. Furthermore, these differences are relatively independent of the viscosity molecular weight over a considerable range. This phenomenon was attributed by some to molecular weight distribution and by others to branching by the intermolecular hydrogen transfer process suggested by Flory.[5]

Fractionation studies to determine the molecular weight distribution were complicated by the insolubility of polyethylene at ordinary temperatures. Also, we felt that if branching existed, fractionation would give a molecular weight distribution complicated by a branching distribution. Since the Flory branching mechanism would be directly dependent upon the polymer concentration during synthesis, this variable was studied with respect to its effect on the physical properties of the resulting polymers.

Results

Research was carried out in high-pressure polymerization equipment using a peroxide catalyst in a solvent medium. Synthesis conditions included constant temperature and pressure with variable polymerization time in order to vary the polymer concentration. Table I lists the data obtained from two polyethylene runs carried out at low and at high polymer concentration.

TABLE I

EFFECT OF POLYMER CONCENTRATION

Final monomer/polymer ratio[a]	Inh. visc.[b]	Tensile prop. p.s.i./% elong.	Melt flow rate[c]	Melt flow temp.,[d] °C.	Insoluble fraction
94/6	0.79	2980/625	1.29	138	Low
13/87	1.06	1590/240	0.09	>250	High

[a] See Example 1 of U. S. Patent 2,409,996 for one method of experimental operation. [b] Determined on a 0.125% solution of polyethylene in xylene at 85°. [c] The number of grams extruded in a 10-minute interval through a 1/16 inch orifice at 190° under 25 p.s.i. nitrogen. [d] Temperature at which sample flowed out under its own weight wetting the melting point block. > 250° indicates the sample was elastic up to the decomposition temperature.

The data in Table I indicate that at least one of the samples is not linear in structure because, *a priori*, for a linear polymer structure the tensile

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[1] Presented at the 123rd National Meeting of the American Chemical Society, Los Angeles, Cal., March 16, 1953.

[2] H. Staudinger and G. V. Schulz, *Ber.*, **68**, 2320 (1935).

[3] T. Alfrey, A. Bartovics and H. Mark, THIS JOURNAL, **65**, 2319 (1943).

[4] R. E. Burk, H. E. Thompson, A. J. Weith and I. Williams, "Polymerization," A. C. S. Monograph Series, Reinhold Publ. Corp., New York, N. Y., 1937, p. 140.

[5] P. J. Flory, THIS JOURNAL, **59**, 241 (1937); **69**, 2893 (1947).

[6] J. J. Fox and A. E. Martin, *Proc. Royal Soc.* (*London*), **A175**, 226 (1940).

[7] J. R. Roland and L. M. Richards, *J. Polymer Sci.*, **9**, 61 (1952).

[8] E. W. Fawcett, R. D. Gibson and M. W. Perrin, U. S. Patent 2,153,553.