Secondary Relaxation Behavior in Ion-Containing Polymers

A. Eisenberg,* M. King,[1a] and M. Navratil[1b]

Department of Chemistry, McGill University, Montreal, Canada.

Received November 13, 1972

ABSTRACT: Polymer systems in which time–temperature superposition of viscoelastic data does not apply have been termed thermorheologically complex. Recent experimental findings indicate that the viscoelastic response displayed by a wide variety of ion-containing polymers is of this nature. A method for the analysis of viscoelastic data obtained from thermorheologically complex ion-containing polymers, which is based on previously developed techniques, is presented. Examples from two different ion-containing polymer systems are used to illustrate the method. In each case, the viscoelastic response is characterized by two relaxation mechanisms; the contributions from each mechanism are separated and two master curves for each polymer are obtained, from which the viscoelastic response at any time and temperature within the range studied can be described. The activation energies corresponding to each mechanism are obtained from an analysis of their respective shift factors.

The inapplicability of the time–temperature superposition principle in the treatment of viscoelastic data has been reported for a wide variety of noncrystalline polymers. In the absence of irreversible changes in polymer structure, the lack of superposability can be attributed to a secondary relaxation mechanism; for instance, side-chain motion in the poly(alkyl methacrylates),[2a,b] spontaneous bond interchange in polymeric sulfur,[3] or lanthanum-catalyzed bond interchange in the polyphosphates.[4]

Polymers which do not exhibit a simple viscoelastic response, such as those mentioned above, have been termed thermorheologically complex. There is growing evidence that a wide variety of ion-containing polymers also fall into this category, as has been reported in viscoelastic studies on ethylene ionomers above their melting point,[5] on styrene ionomers containing more than 6 mol % sodium methacrylate,[6] and on plasticized sodium acrylate polymers.[7] For systems in which two independent relaxation mechanisms are operative, a procedure has been developed whereby the contributions of the two mechanisms can be separated.[2a,b] In this paper, we report on an application of this procedure to the analysis of viscoelastic data from ion-containing polymers which exhibit a thermorheologically complex response. We believe that this procedure is generally applicable to this type of material, and its applicability will be illustrated by examples taken from the two last-mentioned ion-containing polymer systems—the styrene ionomers and the plasticized salts of poly(acrylic acid). It will be shown that the viscoelastic response in each of these systems, in certain concentration regions, indicates the existence of two relaxation mechanisms. The method of analysis allows for the determination of the temperature dependence of each mechanism and its contribution to the overall compliance. Finally, a discussion of the nature of the relaxation processes in these polymers will be presented.

Experimental Section

Two polymer systems were used in this study: styrene–sodium methacrylate copolymers (PS–NaMA) and plasticized poly(sodium acrylate) (PNaA). The preparation of the PS–NaMA samples and the stress relaxation experiments performed on them are described elsewhere.[6] In the PNaA study, four different plasticizers were used: water, formamide, glycerine, and ethylene glycol. Only the water-plasticized system will be described here; experimental details for the whole study are presented in another publication.[7] However, since that is available only in preprint form, a brief summary is given here.

Solutions of PNaA were prepared by neutralization of poly(acrylic acid) (free radical synthesis, $M_v \simeq 4 \times 10^5$) with aqueous NaOH. Films of the polymer were then obtained by evaporation of the aqueous solutions until the desired water content (*ca.* 30–50% by weight) was reached. Stress relaxation measurements on the PNaA films were made at various temperatures for periods of time up to 2×10^4 sec. The temperature variation during any one run was held below ±0.1°. Since a volatile plasticizer was used, the variation in sample weight was monitored, and measurements were discontinued after a weight loss of 1% was observed.

Results and Discussion

Stress relaxation data for one of the materials studied, PNaA–H_2O (50% by volume), are presented in Figure 1. Also shown in this figure is an attempt to construct a master curve by maximizing the overlap of successive curves in their short-time regions. It is apparent that the individual curves of modulus *vs.* time cannot be superimposed to form a true master curve. The curve obtained by the above procedure can be termed a "pseudo-master curve." It is worth noting that the same pattern is obtained whether measurements are made in order of increasing temperature or not. Also, the lack of superposition cannot be attributed to the loss of plasticizer because this would result in deviations in the opposite direction.

The type of nonsuperposability of stress relaxation data observed in the PNaA system is similar to that observed in the styrene ionomers which contain at least 6 mol % NaMA. Stress relaxation data for a typical polymer of this type—one containing 7.7 mol % NaMA—have been presented in another publication.[6] In both of these systems, the deviations at long times for any given constant temperature relaxation are toward lower values of modulus; this fact suggests the existence of two concurrent relaxation mechanisms with different activation energies, as has been observed for a variety of reasons in the nonionic polymers mentioned earlier. In such systems, if these mechanisms are completely independent, then the contributions of the two mechanisms to the total compliance should be additive.[2a] If, on the other hand, the two mechanisms are not independent, as might be possible in some phase-separated systems, then their contributions to the compliance would be more complex. However, in this case, independent evidence indicates that these materials exist in an ion-clustered structure—a discontinuous phase

---

(1) (a) Polymer Department, The Weizmann Institute of Science, Rehovot, Israel. (b) Canadian Technical Tape Co., Montreal, Canada.

(2) (a) J. D. Ferry, W. C. Child, Jr., R. Zend, D. M. Stern, M. L. Williams, and R. F. Landel, *J. Colloid Sci.*, **12**, 53 (1957). (b) W. C. Child, Jr., and J. D. Ferry, *J. Colloid Sci.*, **12**, 327, 389 (1957).

(3) A. Eisenberg and L. A. Teter, *J. Phys. Chem.*, **71**, 2332 (1967).

(4) A. Eisenberg and S. Saito, *J. Macromol. Sci., Chem.*, **2**, 799 (1968).

(5) K. Sakamoto, W. J. MacKnight, and R. S. Porter, *J. Polym. Sci., Part A-2*, **8**, 277 (1970).

(6) M. Navratil and A. Eisenberg, *J. Polym. Sci., Part B*, **10**, 537 (1972).

(7) A. Eisenberg, M. King, and T. Yokoyama, *Amer. Chem. Soc., Div. Org. Coatings Plast. Chem. Pap.*, **32**, 327 (1972).

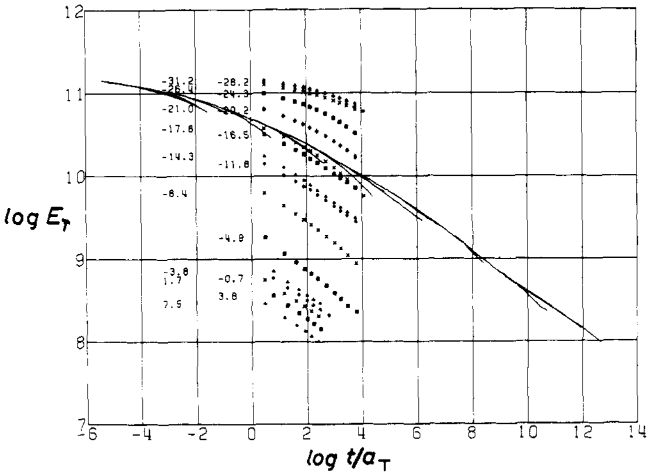

Figure 1. Stress relaxation curves for PNaA–H_2O (50%). Symbols: modulus *vs.* time as a function of temperature (°C). Solid lines: pseudo-master curve, reduced with respect to T_g.

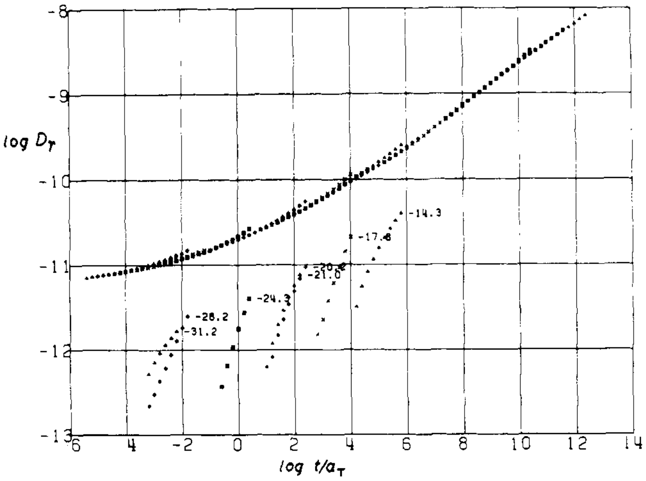

Figure 2. Computed pseudo-master curve of compliance *vs.* time for PNaA–H_2O (50%). Subtracted compliance values and corresponding temperatures (°C) are shown.

in which the ionic material is concentrated, dispersed in a continuous, largely nonionic matrix.[6,7] The mechanical response of such a system will depend on the relative compliances of the two phases. If the discontinuous phase yields at a slower rate than the continuous phase, then the coupling will be that of two series of Maxwell elements connected in parallel, and two distributions of relaxation times will be seen. If the discontinuous phase yields at a faster rate than the continuous phase, then the coupling will be in series and only one distribution of relaxation times will be seen. In the present case, the former hypothesis seems to be intuitively reasonable and will be borne out in the subsequent analyses. The method used in separating the contributions of the two mechanisms in the ion-containing polymers, which is based on the procedure of Ferry *et al.*[2a,b] was the following.

The upper envelope of modulus *vs.* reduced time and the moduli of the original stress relaxation curves were converted to compliance values by the method of Hopkins and Hamming,[8] with the aid of a computer program written for this purpose.[9] It was found that, in regions of rapid stress relaxation, the values generated by this method differed significantly from those generated by the more approximate relationship[10]

$$D(t) = \sin m\pi/m\pi E(t) \tag{1}$$

Shift factors for the individual curves of compliance *vs.* time were recalculated by maximizing the overlap between their short-time regions. No significant differences were noted in the shift factors calculated from the original moduli. The conversion of stress relaxation data to compliances results in a pseudo-master curve of compliance *vs.* reduced time. Examples of this for the two polymer systems discussed in this paper are presented in Figures 2 and 3 for PNaA–H_2O (50%) and PS–NaMA (7.7%), respectively. The data in Figure 2 correspond to those in Figure 1; on the scale shown here, the two curves are nearly mirror images.

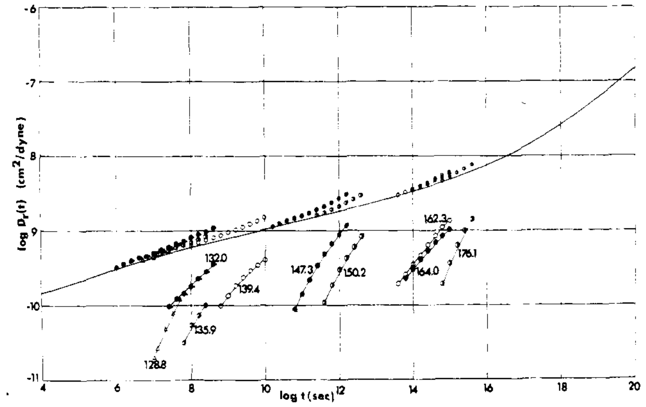

Figure 3. Computed pseudo-master curve of compliance *vs.* time for PS–NaMA (7.7%). Subtracted compliance values and corresponding temperatures (°C) are shown.

It is assumed that, at any given temperature, the short-time compliance is mainly due to the primary relaxation mechanism; the upward deviations from the lower envelope of compliance *vs.* reduced time are therefore due to the second mechanism, whose contribution is computed by means of point-by-point subtraction of compliance values from the lower envelope and the individual deviations in compliance corresponding to long-time relaxations at any given temperature. These subtracted curves of compliance versus reduced time are shown in Figures 2 and 3 for the two respective polymer systems they represent.

The subtracted curves of compliance versus reduced time were converted back to real time by subtraction of the original shift factors, a_t. These curves were then reshifted into a secondary master curve of subtracted compliance *vs.* reduced time by shifting horizontally with respect to one of the curves chosen as a reference. As a result, a new set of shift factors, b_t, is obtained. The subtracted compliance curves and the secondary master curves for PNaA–H_2O (50%) and PS–NaMA (7.7%) are shown in Figures 4 and 5, respectively. The implications of the dashed lines in Figures 4 and 5, which represent a theoretical slope of unity, will be discussed later. The significance of the two master curves should be pointed out; just as one master curve allows the complete description of the viscoelastic response in a system with a single relaxation mechanism, then two master curves allow the complete description of the viscoelastic response in a system with two relaxation mechanisms, as seems to be the case here.

The nature of the two relaxation mechanisms is not perfectly clear; however, an examination of their activa-

---

(8) I. L. Hopkins and R. W. Hamming, *J. Appl. Phys.*, 28, 906 (1957).
(9) M. King, Ph.D. Thesis, McGill University, 1972.
(10) J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970, Chapter XI.

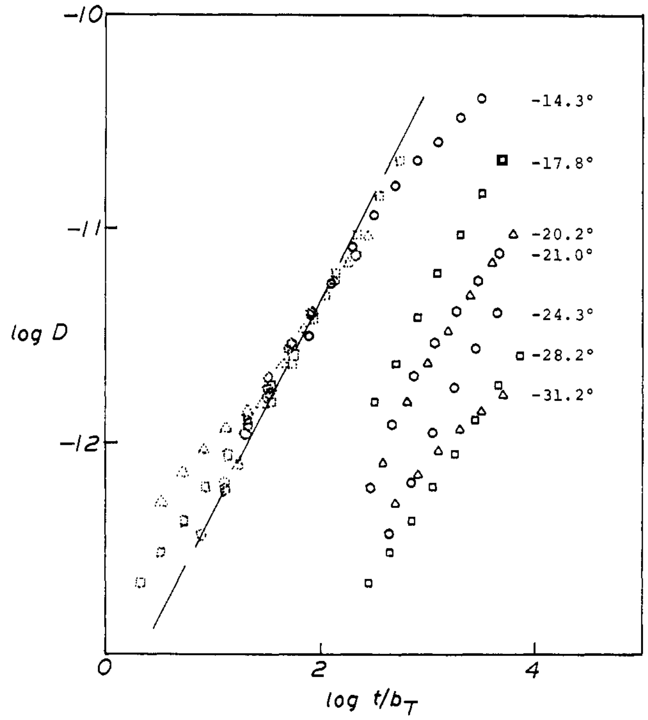

Figure 4. Master curve of subtracted compliance *vs.* time for PNaA-H_2O (50%). Individual curves and corresponding temperatures (°C) are shown. Dashed line: theoretical slope of 1.

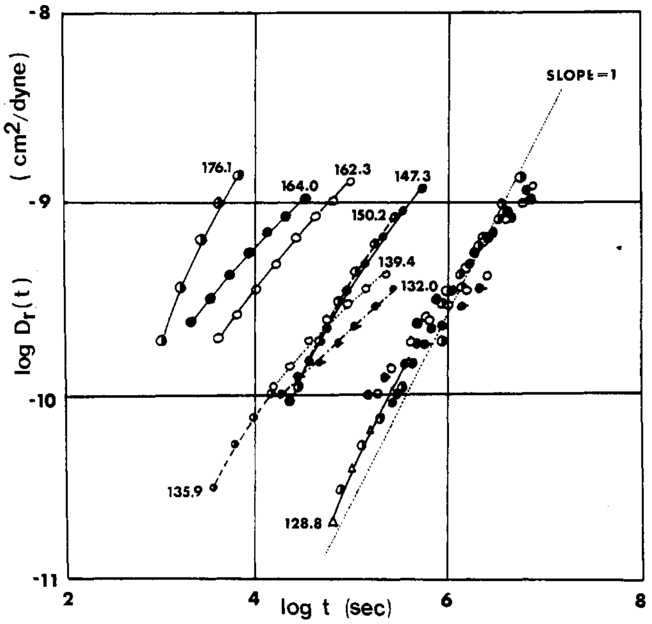

Figure 5. Master curve of subtracted compliance *vs.* time for PS-NaMA (7.7%).

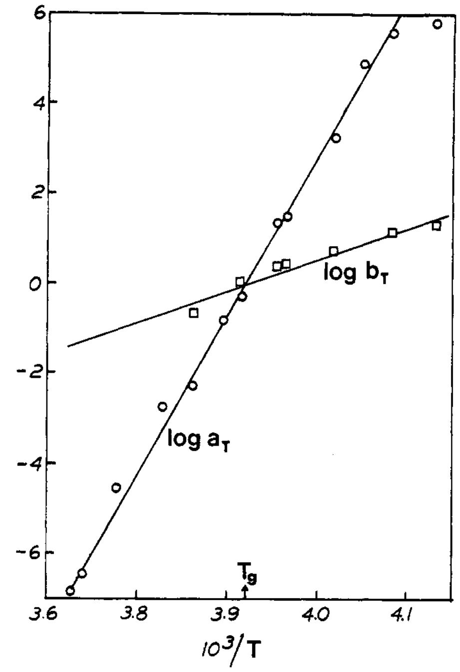

Figure 6. Log a_T and log b_T *vs.* $1/T$ for PNaA-H_2O (50%).

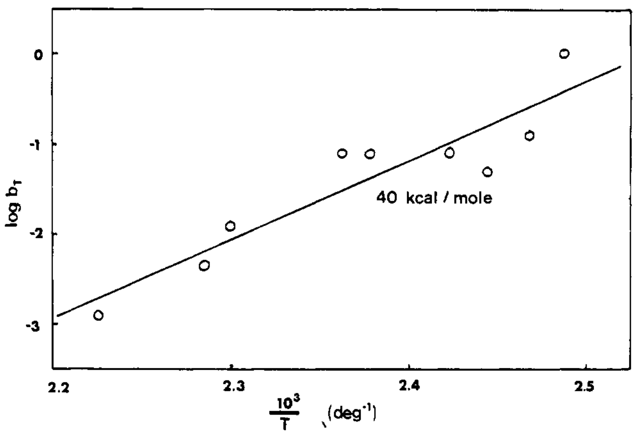

Figure 7. Log b_T *vs.* $1/T$ for PS-NaMa (7.7%).

tion energies may be helpful in relating them to physical processes. This may be accomplished by an analysis of the temperature dependence of their respective shift factors. In the styrene ionomer system, it was found that the shift factors corresponding to the short-time superposition obeyed the W.L.F. equation[10]

$$\log a_T = c_1^g(T - T_g)/[c_2^g + (T - T_g)] \quad (2)$$

although the constants differ from both pure polystyrene and the un-ionized copolymer.[6] For the ionomer PS-NaMA (7.7 mol %), the W.L.F. parameters $c_1^g = 60$ and $c_2^g = 240$, referred to $T_g = 118°$, were obtained. Measurements on the PNaA-H_2O system were not carried far enough above T_g to establish W.L.F. parameters because of plasticizer loss; however, in the system PNaA-glycerine, W.L.F.-type temperature dependence of the short-time shift factors is observed at higher temperatures.[7] In either case, in the vicinity of T_g, the short-time shift factors can also be described by an Arrhenuis-type temperature dependence since there is little difference between the two types of temperature dependence in this region. This fact enabled the determination of the activation energies when no other way was possible.

It was found that the shift factors corresponding to the secondary master curves also fit Arrhenius-type relationships. These relationships are shown in Figure 6, for PNaA, and in Figure 7, for PS-NaMA. The best-fitting linear relationships were used to calculate the activation energies corresponding to the two mechanisms in each polymer. For PNaA-H_2O (50%), activation energies of 160 and 32 kcal are obtained for the primary and secondary mechanisms, respectively. For PS-NaMA (7.7 mol %), the activation energies obtained for the two mechanisms are 170 and 40 kcal, respectively.

It is known from studies on a variety of polymers that the activation energies in the vicinity of T_g for normal chain diffusional processes are of the order of 100–200 kcal.[10] In view of this fact and the fact that, at higher temperatures, W.L.F.-type temperature dependence is obtained for the shift factors corresponding to the primary mechanism, it seems reasonable to assign the primary mechanism to the usual diffusional process associated with the glass transition of nonionic polymers; it seems likely, however, that the mechanism is modified in some way by the ions, since unusually high W.L.F. parameters are obtained.

The secondary relaxation process is likely ionic in its origin. There is theoretical[11] and experimental[6,7] evidence for ion clustering in these ion-containing systems. The activation energies for the secondary mechanism, of the order of 25 kcal, could correspond to the energy required to remove an ion pair from an ionic cluster. Whatever its form, if the secondary mechanism were due to the yielding of ionic structure, it would be expected to correspond to a pure viscosity in the same fashion as bond interchange.[3] In this case, the approximate relationship

$$D(t) \simeq t/\eta \qquad (3)$$

should hold. It can be seen in Figures 4 and 5, by comparison with the hypothetical doubly logarithmic slope of unity, that this is approximately true for each case.

The assignment of viscoelastic mechanisms in these ion-containing polymers requires a more complete investigation. Further discussion of the viscoelastic behavior in these systems will be reserved for future publications.

Conclusions

A general method for the analysis of viscoelastic data from ion-containing polymers in which the breakdown of time–temperature superposition occurs has been presented. Examples from two different ion-containing polymer systems were used to illustrate the method. In each case, the viscoelastic response was characterized by two relaxation mechanisms; the contributions from each mechanism were separated and two master curves for each polymer were obtained, from which the viscoelastic response at any time and temperature within the range studied could be described. The activation energies corresponding to each mechanism were obtained from an analysis of their respective shift factors.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. M. K. is indebted to the N. R. C. Canada for a 1967 scholarship.

---

(11) A. Eisenberg, *Macromolecules*, **3**, 147 (1970).

Nuclear Magnetic Resonance Studies on Microstructure of Ethylene Copolymers. V. 220-MHz Proton Resonance Spectra of Ethylene–Vinyl Chloride Copolymers[1]

Ting Kai Wu

Plastics Department, Polymer Products Division, E. I. Du Pont De Nemours and Company, Experimental Station, Wilmington, Delaware 19898.

Received January 26, 1973

ABSTRACT: 220-MHz proton nmr spectroscopy has been utilized to examine the microstructure of ethylene–vinyl chloride (E–VCl) copolymers. It was found that the monomers are distributed in an ideally random fashion and that the formation of racemic dyads of vinyl chloride units is slightly favored over that of meso dyads during copolymerizations. Moreover, the polyethylene segments of E–VCl polymers, when dissolved in 1-chloronaphthalene solution, undergo intramolecular conformational transitions similar to those observed for ethylene–vinyl ester copolymers.

The high-resolution proton resonance spectra of ethylene–vinyl chloride (E–VCl) copolymers have been investigated by a number of authors. Schaefer[2] showed that 100-MHz nmr spectroscopy when used with spin decoupling provides a powerful tool for determining the chemical and stereochemical sequence distributions in these copolymers. In a systematic study of the 60-MHz copolymer spectra, Wilkes *et al.* have deduced the comonomer dyad distributions and the kinetics of bulk E–VCl polymerizations.[3] A similar nmr method was utilized by Misono and coworkers to elucidate the microstructure of E–VCl copolymers prepared by trialkylboron catalysis.[4]

In the previous papers of this series, we demonstrated that 220-MHz proton nmr spectroscopy is extremely useful for investigating the microstructure of ethylene copolymers. This high radiofrequency (magnetic field) spectroscopic technique has been successfully applied to determine: (1) monomer sequence distributions in ethylene–vinyl formate (E–VF)[5] and ethylene–vinyl acetate (E–VA)[6] polymerizations, (2) complex formation between the segments of E–VA copolymers and the solvent molecules,[7] and (3) intramolecular conformational transitions of the polyethylene sequences of E–VF and E–VA polymers in solution.[1,7] Recently we have extended our studies to include copolymers of ethylene and vinyl chloride. The results of our studies are presented in this paper.

Experimental Section

Ethylene–vinyl chloride (E–VCl) copolymers were prepared by high-pressure free-radical copolymerizations of ethylene ($CH_2{=}CH_2$) and vinyl chloride ($CH_2{=}CHCl$). The conversions

---

(1) Part IV: T. K. Wu, *Macromolecules*, **3**, 610 (1970).

(2) J. Schaefer, *J. Phys. Chem.*, **70**, 1975 (1966); eq 3, 4, 5, and 6 are only valid for the terminal model.

(3) C. E. Wilkes, J. C. Westfahl, and R.H. Backderf, *J. Polym. Sci., Part A-1*, **7**, 23 (1969).

(4) A. Misono, Y. Uchida, K. Yamada, and T. Saeki, *Bull. Chem. Soc. Jap.*, **41**, 2995 (1968).

(5) T. K. Wu, *J. Phys. Chem.*, **73**, 1801 (1969).

(6) T. K. Wu, *J. Polym. Sci., Part A-2*, **8**, 167 (1970).

(7) T. K. Wu, *Macromolecules*, **2**, 520 (1969).