

Transient Response in Nonlinear Region of Molten Polymers Subjected to a Sudden Imposition of Constant Shear Stress or Constant Electric Field

F. P. LA MANTIA and D. ACIERNO, *Istituto di Ingegneria Chimica, University of Palermo, Italy*

Synopsis

Experimental transient results in the nonlinear region are reported for a commercial polyisobutylene subjected to sudden imposition of either a constant shear stress or a constant electric field. Some steady-state results, eventually obtained in different types of experiments, are also considered. In both cases, a model analysis is presented that accounts for the nonlinear effects through changes in the free volume depending upon the applied stress. The good comparison between theoretical predictions and experimental results seems to indicate that the phenomenological approach advanced here is very promising.

INTRODUCTION

In a previous work,¹ the analogy in the nonlinear mechanical and electric behavior of polymeric materials has been pointed out, and the change of the resistivity with temperature and applied electric stress has been interpreted through free-volume changes in a manner similar to that already adopted to explain viscosity changes.² Taking into account the above concepts, in ref. 2 a model was also proposed to interpret transient mechanical results relative to molten polymers. Similarly in ref. 1, a simple model has been advanced to qualitatively explain transient DC results for polymers showing steady-state conductivity. Experimental indications of this behavior have been reported for both amorphous polymers near the glass transition temperature³⁻⁶ and semicrystalline polymers near the melting point.⁷⁻⁹

However, none of the data quoted above are relative to truly molten polymers. Furthermore, results on electric and mechanical properties relative to the same material have been taken only in the linear region, i.e., in the limit of small applied stress.¹⁰

The aim of this work is to present electric and mechanical data on a molten polymer and to compare them with theoretical predictions. In particular, the transient response of the material (a commercial polyisobutylene) when it is subjected to a sudden imposition of either a mechanical stress or an electric field (which are thereafter taken constant) is reported. Some steady-state results, eventually obtained in different types of experiments, are also reported. The models employed for the comparison are those already mentioned,^{1,2} in one case¹ slightly improved to take into account a spectrum of relaxation times.

EXPERIMENTAL

The polymer used in the experiments was a polyisobutylene manufactured by BASF, commercially known as Oppanol B50, the viscosity average molecular weight of which is $\sim 380,000$. All the experiments have been performed at temperatures well above the glass transition temperature ($\sim -70^\circ\text{C}$); the polymer can thus be considered a melt.

Mechanical Tests

All transient data presented here were taken by using a Universal Instron Testing Machine at room temperature ($T \sim 20^\circ\text{C}$). The technique was suggested by Middleman¹¹ and further adopted with some modifications by other authors.¹²⁻¹⁵ Two square samples (2×3 cm) were cut from a 0.4-cm-thick sheet of the polymeric material obtained by compression molding at 200°C . The two square samples, separated by a metal plate, were mounted in the stationary grips of the Instron machine, and the metal plate, attached to the movable grips of the instrument, was then moved, thus generating the shearing. With the aid of the load cycling accessories, the movement of the crosshead was such as to maintain a constant load, and thus a constant shear stress on the sample. It was different from the works mentioned above¹¹⁻¹⁵ where a constant velocity (and thus a constant shear rate) was imposed. The movement was followed by means of a displacement transducer of the impedance type (HBM model W 200) connected to an amplifier (HBM model KWS/6T-S) and recorded through a Kipp & Zonen Micrograph BD5. The experiments were stopped only after attainment of steady-state conditions, i.e., when a constant value of the deformation rate was obtained.

The results in the form of deformation γ vs time t are reported in Figure 1 for different values of the imposed stress. The steady-state values, obtained from the above data, in the form of deformation rate $\dot{\gamma}$ vs τ are reported in Figure 2.¹¹ In the same figure, results obtained from different experiments are also reported; they are from both transient experiments at constant $\dot{\gamma}$ and capillary viscometer measurements.¹⁴

Electric Tests

Transient current measurements, after a step voltage application, have been performed in a circuit as schematically shown in Figure 3. The equipment used for the measurements included a Keithly high voltage supply (model 244) and a Keithly electrometer (model 610 C). A disk specimen of the polymer, cut from a 0.4-mm-thick sheet, was placed between two copper electrodes 5 cm in diameter and slightly compressed to ensure electrical contact. The measurements were carried out in a Faraday cage mounted into an environmental chamber.

Typical transient results obtained at room temperature ($\sim 15^\circ\text{C}$) are reported in Figure 4 for different values of the imposed electric field, E , while steady-state results obtained at both room temperature and 85°C are reported in Figure 5, in the form of current density I vs the electric field E .

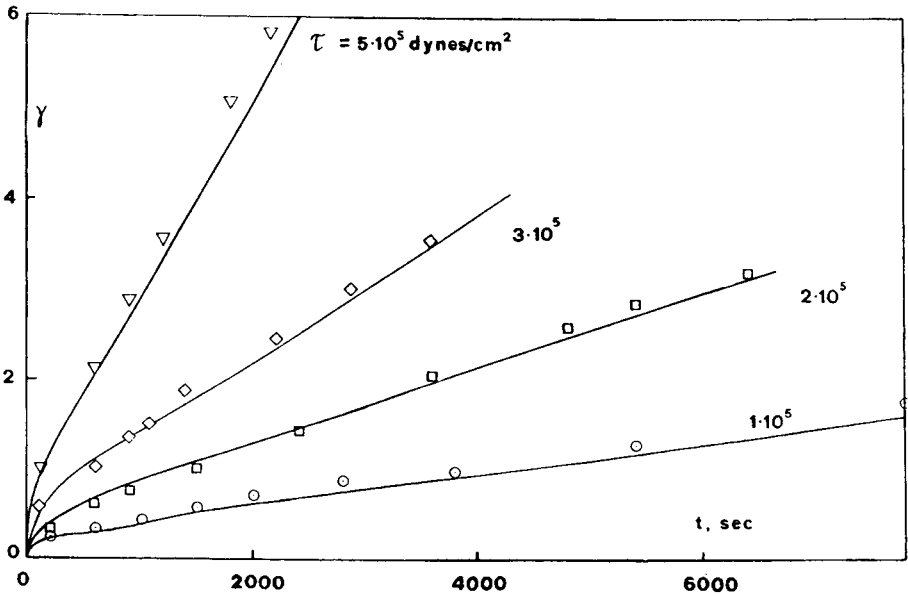


Fig. 1. Deformation γ vs time t for different values of applied stress τ . Points are experimental data, curves are theoretical predictions.

THEORETICAL PREDICTIONS

As already mentioned in the introduction, in a previous work¹ some similarities in the electric and mechanical behavior of molten polymers have been recalled and a possible interpretation has been advanced. We shall review briefly some of the most important observations and the basic hypothesis.

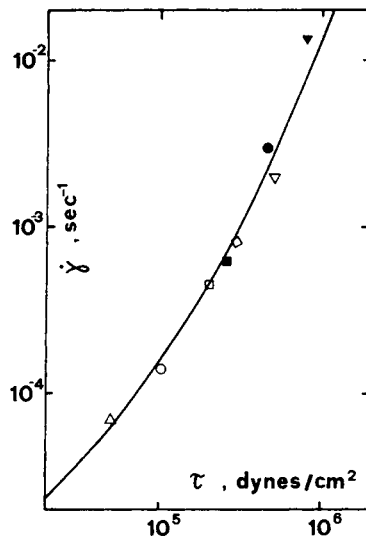


Fig. 2. Steady-state values of the deformation rate $\dot{\gamma}$ as a function of the stress τ . Open points are from creep experiments, closed points from capillary viscometer measurements, and the curve is from theory.

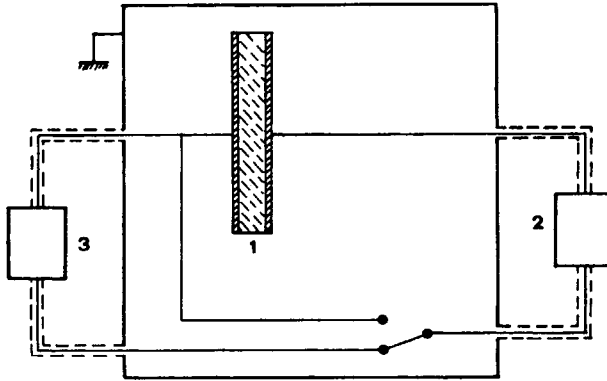


Fig. 3. A schematic drawing of the measuring circuit. 1—sample; 2—electrometer; 3—power supply.

It is well known that viscosity and resistivity depend upon temperature in a similar way, and more particularly, that such dependencies are often written as Arrhenius-type equations:

$$\eta = A \exp(E_a/RT) \quad (1a)$$

$$\rho = B \exp(E_a/RT) \quad (1b)$$

where η and ρ are viscosity and resistivity, respectively, A and B , frequency factors, and E_a , activation energy.

Activation energy has been assumed the same in eqs. (1a) and (1b) following the Walden's rule,¹⁶ and experimental indications which certainly show close values, although sometimes discrepant by as much as a factor of two, have been found.¹⁷

Following a different approach, the dependency of viscosity upon temperature has also often been written as¹⁸

$$\eta = \eta_0 \exp\left(\frac{1}{f} - \frac{1}{f_0}\right) \quad (2)$$

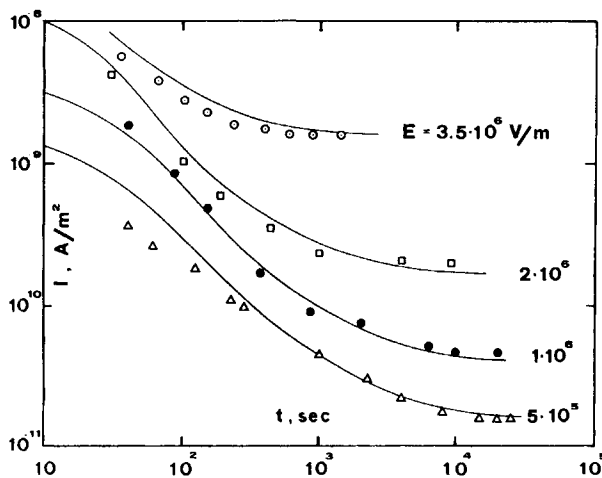


Fig. 4. Current density I , vs time, t , for different values of the imposed field E . Points are experimental data, curves are theoretical predictions.

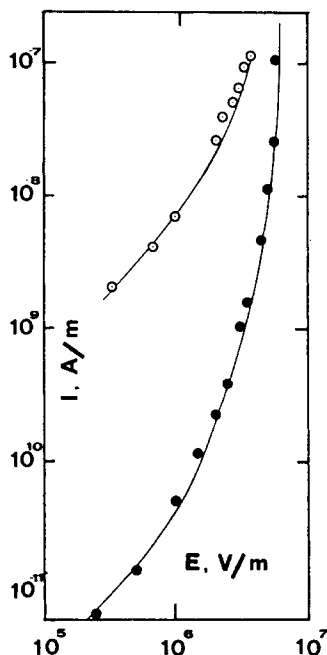


Fig. 5. Steady-state values of the current density I as a function of the electric field E . Points are experimental data (\circ , $T = 85^\circ\text{C}$; \bullet , $T = 15^\circ\text{C}$), curves are theoretical predictions.

with the free-volume fraction, f , varying linearly with temperature at least in the range $t_g - (t_g + 100^\circ\text{C})$. In eq. (2) η_0 is obviously the viscosity corresponding to the free-volume fraction f_0 , i.e., to a reference temperature t_0 . Equation (2) is perhaps more useful than eq. (1a) because it can account for the dependency of viscosity upon other parameters, such as pressure, polymer concentration (for solutions), diluent concentration, etc. The use of an equation similar to eq. (2) for the resistivity dependence has also been proposed¹:

$$\rho = \rho_0 \exp\left(\frac{1}{f} - \frac{1}{f_0}\right) \quad (3)$$

It should be appreciated that assuming eqs. (2) and (3) hold simultaneously implies that activation energies in eqs. (1a) and (1b) are equal.

Equation (2) has been recently further generalized² following the idea that the application of a stress on a polymeric material corresponds to a temperature increase. In particular, an assumption has been made that the free volume at constant temperature changes as a consequence of the applied stress through the stored elastic energy

$$f = f_0 + a E_\tau / G \quad (4)$$

In eq. (4) f_0 is the free-volume fraction at the given temperature for the stress-free sample, G is an elastic modulus which will be recalled later, E_τ the stored elastic energy, and a a material constant. Through eq. (4) and one formally equivalent to eq. (2), well-known nonlinear effects such as the non-Newtonian behavior of polymeric liquids can be explained easily.

Analogously, in ref. 1, a similar dependence of free volume upon the electric field has been considered as

$$f = f_0 + aE_E \quad (5)$$

with E_E , the energy stored in the dielectric, given by

$$E_E = \frac{1}{2} \epsilon' \epsilon_0 E^2 \quad (6)$$

E is the electric field, ϵ' is the dielectric constant of the polymer, ϵ_0 is the dielectric constant of vacuum, and a a material constant. With these assumptions [eqs. (5) and (6)] through eq. (3), the resistivity is considered to decrease with the applied field, and it is thus possible to interpret the non-ohmic behavior of polymers, i.e., the nonlinear voltage current curves.

In order to interpret transient results for both mechanical and electric behavior, a more detailed modeling is needed, and we prefer to treat the two cases separately.

Mechanical Behavior

A generalized Maxwell model, written with the contravariant derivative of the stress tensor, has been chosen to interpret the mechanical behavior. The nonlinearity is included in it through the relaxation times which are allowed to change with the stress, in the same form as the viscosity in the previous section [see eqs. (2) and (4)]. This implies that the relaxation moduli are assumed not to be affected by the flow.

While we refer to the original work² for the basic formulation of the model, in the following discussion we shall specialize the model equations for the two cases which we have experimentally studied here: shear creep and steady shear.

For transient shear, the equations for the nonzero stress components read:

$$\tau^{12} = \sum \tau_i^{12}, \quad \tau^{11} = \sum \tau_i^{11} \quad (7)$$

$$\tau_i^{12} + \lambda_i \frac{d}{dt} \tau_i^{12} = G_i \lambda_i \dot{\gamma} \quad (8)$$

$$\tau_i^{11} + \lambda_i \frac{d}{dt} \tau_i^{11} = 2 \lambda_i \tau_i^{12} \dot{\gamma}$$

$$\lambda_i = \lambda_{0i} \exp \left(\frac{1}{f_i} - \frac{1}{f_{0i}} \right) \quad (9)$$

$$f_i = f_{0i} + \frac{1}{2} a \tau_i^{11} \quad (10)$$

Equations (7) give the stress components as the sum of the contributions, one for each relaxation time. The spectrum is made discrete and the "intensity" by which each relaxation time is represented is the modulus G_i . $\sum G_i$ is the previously introduced elastic modulus [eq. (4)] and is derivable from the spectrum as

$$\int_{-\infty}^{\infty} H d \ln \lambda$$

Equations (8) are the Maxwell model equations for the tangential and the normal stresses, $\dot{\gamma}$ being the shear rate. Equation (9) describes how the relaxation times

λ_i are modified in the nonlinear range starting from the equilibrium values λ_{0i} of linear viscoelasticity. In eq. (10), which relates the free volume to the existing stress, a is the single parameter of the model.

Considering as known the values of λ_{0i} and G_i from the linear viscoelasticity, quantitative predictions of the model in the nonlinear range can be easily made, for assumed values of the parameter a when the deformation history is assigned. In our case (shear creep), however, the overall tangential stress is assigned and the various modes cannot be separated: the whole set of equations thus must be simultaneously integrated. A possible solution is the following: sum over the modes equations like the first set of eqs. (8) and isolate $\dot{\gamma}$ to obtain

$$\dot{\gamma} = \frac{1}{\sum G_i} \dot{\tau} + \sum \left(\frac{\tau_i}{\lambda_i} \right) \quad (11)$$

where $\dot{\tau}$ is the time derivative of the known function $\tau(t)$ which, in particular, is zero at all times but for a short initial interval in which, on the contrary, $\dot{\gamma}$ is assigned. Thus starting from equilibrium conditions at $t = 0$ ($\tau_i^{12} = \tau_i^{11} = 0$; $f_i = f_{0i}$) the set of eqs. (7)–(10) can be easily integrated until τ reaches the assigned value, while thereafter eqs. (8) can still be numerically integrated in time, each independently from the others, and at each instant the value of $\dot{\gamma}$ is given by the algebraic equation (11), which provides the link among the modes. Of course, $\gamma(t)$ can be calculated from the $\dot{\gamma}(t)$ function also and compared with the experimental results.

In the actual calculations, not having sufficient information on how to perform the spectral decomposition of the free-volume fraction, we have simply assumed $f_{0i} = f_0^\infty$ with f_0^∞ the free volume associated with an infinite molecular weight. Such an assumption, however, has been previously shown² to be of no consequence.

In steady shear the situation is certainly much simpler; eqs. (8) and (10) become:

$$\tau_i^{12} = \dot{\gamma} \lambda_i G_i \quad (8')$$

$$\tau_i^{11} = 2 \dot{\gamma}^2 \lambda_i^2 G_i$$

$$f_i = f_{0i} + a \dot{\gamma}^2 \lambda_i^2 \quad (10')$$

For any $\dot{\gamma}$, eqs. (9) and (10') must be solved simultaneously to determine λ_i . Then one can easily calculate the viscosity as a function of $\dot{\gamma}$:

$$\eta = \frac{\sum \tau_i^{12}}{\dot{\gamma}} = \sum \lambda_i G_i \quad (12)$$

Electric Behavior

A simple model was presented in ref. 1 which was able to give a good qualitative comparison with experimental indications. It consisted of a capacitor C and a resistor R' added in parallel to a resistor R , the latter being essential for the steady state. The ratio R/R' was supposedly very large, R being the ohmic resistance of the material (and thus very large in general) and R' the loss resistance of the real dielectric (and thus much smaller than R). Both resistors were considered to depend upon the applied voltage through equations similar to eq. (3), thus allowing prediction of correct nonlinear effects.

Now we shall consider an extension of such a model, as depicted in Figure 6. Following experimental indications,^{16,20} we have taken a whole set of real dielectrics in parallel with the ohmic resistance R , i.e., a set of R' - C circuits. The equations of the model, in the case of a constant applied electric field, are

$$I = \frac{E}{\rho} + E \sum \frac{1}{\rho_i} \exp(-t/\lambda_i) \quad (13)$$

$$\lambda_i = \lambda_{0i} \exp\left(\frac{1}{f_i} - \frac{1}{f_{0i}}\right) \quad (14)$$

$$f_i = f_{0i} + a E_{Ei} \quad (5')$$

$$E_{Ei} = \frac{1}{2} \epsilon_0 \epsilon'_i E^2 \quad (6')$$

λ_i in eq. (15) is the time constant of the i th R' - C element given by $\lambda_i = \rho_i \epsilon'_i \epsilon_0$. As in the previous section, the equilibrium value of the free-volume fraction of each element has been equal to f_0^∞ . For a given material, the ϵ'_i values are to be intended as assigned and in fact they can, in principle, be obtained from experiments in the linear region [$\epsilon'(\omega)$, $\epsilon''(\omega)$ measurements] by inversion techniques similar to those widely employed in the mechanical case.²¹

Actual values were not available, however, for the same polymer nor for a similar sample in a sufficiently large ω region, which is required to obtain the spectrum observed in ref. 22. We have thus assumed a box type of relaxation spectrum which is compatible with the Cole-Cole plots²³ in the region of time, as suggested by the linear response of the material, and with an ordinate value to fit the linear data. In the nonlinear region then, it is very easy to derive $I(t)$ from previous equations for any assigned E and an assumed value of the parameter a . In fact, for a given spectrum and assigned value of the electric field from eq. (6'), we get the energy contribution and, in turn, f_i [from eq. (5')] and thus λ_i [from eq. (14)]. Finally, for each time, we can directly calculate I from eq. (13).

Steady-state values can be calculated in one even easier way from the relationship

$$I = E/\rho \quad (13')$$

and eqs. (14), (5'), and (6').

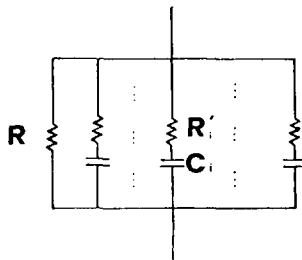


Fig. 6. The electric model.

RESULTS AND DISCUSSION

As already observed in the previous sections, the relaxation time spectra for both the mechanical and the electrical case can be considered as characteristic of the material and are obtainable from measurements in the linear region. For the polymers employed in this work, the mechanical spectrum was in fact available in ref. 14, while for the electric case, some simplifying assumptions have been made and a box type of spectrum has been considered in the range $10\text{--}10^4$ sec, with a value of about 7×10^{-14} F/m.

As for the a value, in the mechanical case it was chosen from curve fitting with some steady-state values in ref. 2 and has been already proved good enough in other comparisons^{2,25}; the value, which has been used also in this work, is 6×10^{-3} . Predictions with the above value are reported in Figures 1 and 2.

In the electrical case, a has been chosen for curve fitting with the steady-state data at room temperature reported in Figure 5 ($a = 3.5 \times 10^{-2}$ m²/N). It has then been used for the steady-state theoretical predictions at a different temperature reported in the same figure and also for the transient results reported in Figure 4.

The comparison between the theoretical predictions and the experimental results is very good in the mechanical case for both the steady-state and the transient values. In the electrical case it is, on one hand, somewhat worse for the transients, but this is due perhaps to the spectrum simplification. It is, on the other hand, also very good for the steady-state at a different temperature. We observe that the values of the free-volume fraction at any temperature have been derived from the relationship

$$f_T = f_g + \Delta\alpha (T - T_g)$$

with f_g , T_g , and $\Delta\alpha$ assumed as 0.025, 205 K, and 4.9×10^{-4} °C⁻¹, respectively.²¹

This seems to indicate to us the validity of the main assumptions, eqs. (3) or (14), both in the linear and nonlinear region.

In conclusion, the reported data seem to confirm the similarities in the mechanical and electric behavior of molten polymers. The good comparison between theoretical predictions and experimental results seems to indicate that the phenomenological approach presented here is very promising.

Thanks are due to Dr. F. Di Quarto for his help in setting up the electric apparatus, to BASF for providing free samples of the polymer, and to CNR for financial support under grant No. 77.01781.07.

References

1. F. P. La Mantia and D. Acierno, *Polymer*, **19**, 851 (1978).
2. F. P. La Mantia, *Rheol. Acta*, **16**, 302 (1977).
3. L. E. Amborski, *J. Polym. Sci.*, **62**, 331 (1962).
4. V. Adamec, *Kolloid Z. Z. Polym.*, **237**, 219 (1970).
5. V. Adamec, *Z. Angew. Phys.*, **29**, 291 (1970).
6. V. Adamec, *Kolloid Z. Z. Polym.*, **249**, 1085 (1971).
7. D. D. Eley and D. J. Spivey, *Trans. Faraday Soc.*, **57**, 2280 (1961).
8. G. Stetter, *Kolloid Z. Z. Polym.*, **215**, 112 (1967).
9. A. E. Binks and A. Sharples, *J. Polymer Sci. Part A-2*, **6**, 407 (1968).
10. J. M. Kallweit, *J. Polym. Sci. Part A-1*, **4**, 337 (1966).
11. S. Middleman, *Trans. Soc. Rheol.*, **13**, 123 (1969).

12. C. Goldstein, *Trans. Soc. Rheol.* **18**, 357 (1974).
13. F. Nazem and C. T. Hill, *Trans. Soc. Rheol.*, **18**, 87 (1974).
14. D. Acierno, F. P. La Mantia, B. De Cindio, and L. Nicodemo, *Trans. Soc. Rheol.*, **21**, 261 (1977).
15. I. Furuta, V. M. Lobe, and J. L. White, *J. Non-Newt. Fluid Mech.*, **1**, 207 (1976).
16. A. D. Jenkins, *Polymer Science*, North-Holland, London, 1972.
17. See for instance: A. Reiser, M. B. W. Lock, and J. Knight, *Trans. Faraday Soc.*, **65**, 2168 (1969); refs. 3, 8, 9; and V. P. Privalko, Y. S. Lipatov; *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1725 (1976).
18. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
19. G. C. Sarti and G. Marrucci, *Chem. Eng. Sci.*, **28**, 1053 (1973).
20. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London (1967).
21. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York (1970).
22. H. Frölich, *Theory of Dielectrics*, Oxford University Press, 1949.
23. V. V. Daniell, *Dielectric Relaxation*, Academic, London, 1967.
24. A. van Roggen, *IEEE Trans. Electrical Insul.*, **E. J. 3**, 11 (February 1968), **E. J. 5**, 47 (June 1970).
25. F. P. La Mantia and D. Acierno, *Polym. Eng. Sci.*, **19**, 800 (1979).

Received April 3, 1979

Revised May 24, 1979