

RELAXATION STUDIES OF ENVIRONMENTAL EFFECTS IN SOLID POLYMERS

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ABSTRACT

The scope of relaxation studies in elucidating the effect of environment on molecular behaviour is discussed. Illustrations are selected from stress relaxation and dielectric relaxation which show the effect of phase separation on the behaviour of thermoplastic elastomers, from ultrasonic relaxation which show the effect of position of a group within a polymer molecule, from dielectric relaxation showing the effect of applied pressure and external humidity, and from electronic energy relaxation showing the effect of matrix rigidity on the migration of excitation down polymer chains.

1. INTRODUCTION AND EXPLANATION OF TERMS

The word 'environment' covers such a multitude of different phenomena that it is necessary to explain what will be covered by 'Environmental Effects' within the context of this paper. Basically we are concerned with molecular behaviour, and so emphasis will be placed upon the situation in which a particular polymer molecule (or section of a molecule) may find itself. We can thus visualize three rather different aspects of this.

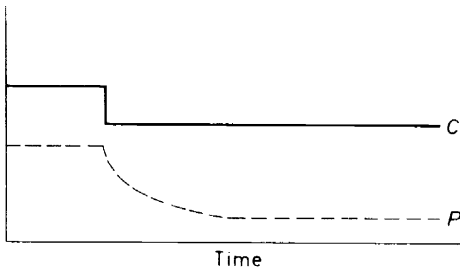
(1) True molecular environment encompassing phenomena as phase separation and dependence on morphology, presence of diluent or 'foreign' molecules, and the position of a particular segment on the polymer chain.

(2) External environmental effects, such as humidity, which act by introducing other molecules to the system of interest.

(3) Applied constraints such as pressure.

It is also necessary to consider what is meant by 'relaxation'. In general terms this is the time-dependent return to equilibrium of a system which has undergone a change in an applied constraint. The change in the constraint may be discontinuous or periodic (*Figure 1*) and the experimental observation is of some property which changes with time. The constraints may be the familiar thermodynamic variables such as temperature, pressure, chemical composition, or may involve other perturbations such as electric or magnetic fields or applied stress. In an ideal relaxation the rate of return to the equilibrium value of the property, P , is dependent on the distance from equilibrium. In these circumstances the phenomenon is described by a linear first-order differential equation with the solution

$$P - P_{eq} = (P_0 - P_{eq}) \exp(-t/\tau)$$

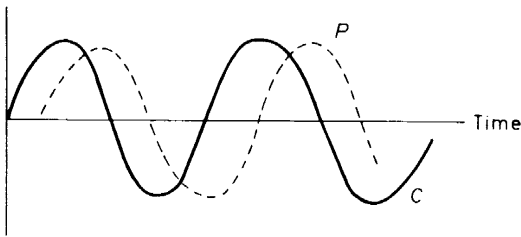


1. Relaxation in time domain:

C = Constraint in system

P = Property observed

$$\text{Ideal: } P(t) = P \exp(-t/\tau)$$



2. Relaxation to alternating perturbation

$$P(\omega) = \mathcal{L} \left(-\frac{dP(t)}{dt} \right)$$

Figure 1. Time-dependent relaxation.

Of course many molecular relaxation processes are non-ideal, and often useful information can be gained from the way systems depart from this simple behaviour.

When the variation in the applied constraint is periodic, the frequency-dependent response of the system is complex and is related to the decay function, $\phi(t)$, of the response to a step change through the Laplace transformation

$$P^*(\omega) = \mathcal{L} - d\phi(t)/dt$$

The real and imaginary parts of this response vary with frequency and temperature as illustrated in Figure 2.

In this paper we shall be concerned with stress relaxation where the applied constraint is one of position and the property measured is stress, with dielectric polarization where the constraint is electric field and the property electric polarization due to movement of charged species, acoustic relaxation where a sound wave functions as a periodic temperature change and the property observed is the dynamic specific heat, and fluorescence energy transfer where the variation occurs in the population of excited state molecules. Some relaxation phenomena are listed in Table 1 in terms of the applied constraint and response observed.

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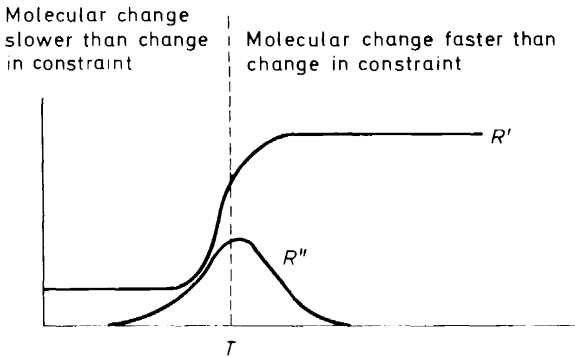
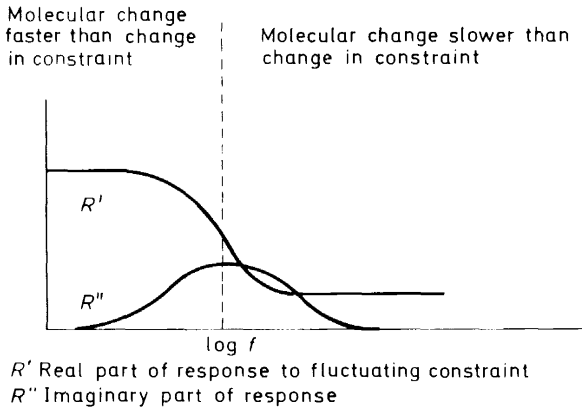


Figure 2. Frequency and temperature dependence of real, R' , and imaginary, R'' responses to a periodic change in constraint.

Table 1. Molecular relaxation phenomenon to be discussed

Phenomenon	Constraint	Observed property	Molecular property
Dielectric relaxation	Electric field	Electric polarization, loss	Orientation of dipole vector, migration of charge
Ultrasonic relaxation	Pressure, temperature	Sound absorption, velocity	ΔG of molecular change
Mechanical relaxation	Stress, strain	Compliance, modulus	Molecular movement
Luminescence depolarization	Polarized electromagnetic field (irradiation)	Fluorescence, phosphorescence polarization	Rotation of transition vector
Electronic energy relaxation	Irradiation	Fluorescence quenching	Migration and transfer of energy

The content of this paper has been selected so as to give a number of examples of different relaxation studies and environmental effects. Consequently it is not a comprehensive review, but rather a series of illustrations of what can be done in this field.

2. TWO-PHASE SYSTEMS

It is interesting to start with a consideration of some two phase systems where the molecular behaviour of the system depends on the nature of the separate phases.

2.1 Stress relaxation in thermoplastic elastomers

Some of the first relaxation studies of molecular environmental effects were the stress relaxation and modulus measurements of Cooper and Tobolsky¹. In these studies the modulus of polystyrene-polydiene-polystyrene block copolymers was measured as a function of temperature, and the observations yielded a profile illustrating the onset of segmental motion (glass transition) of the polydiene segments in essentially a polydiene environment and of the polystyrene segments in the phase-separated polystyrene domains (Figure 3).

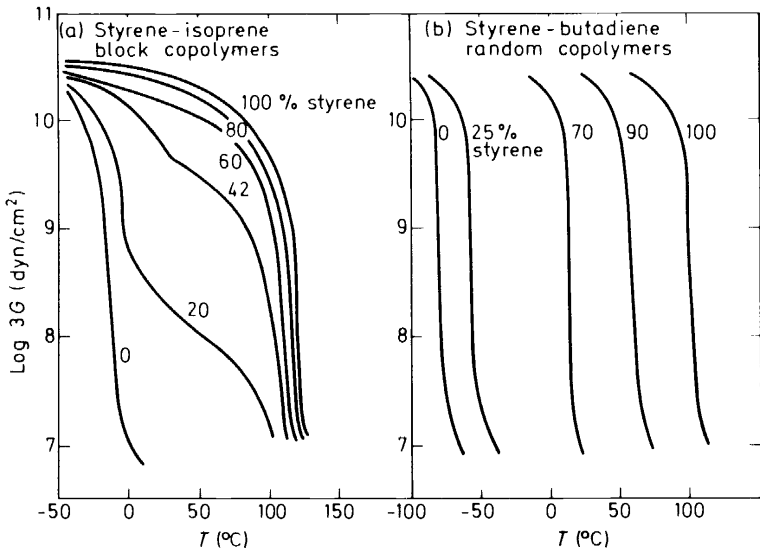


Figure 3. Modulus-temperature behaviour of 3-block elastomers, after Cooper and Tobolsky¹.

The addition of plasticizer molecules is interesting, because it is possible to observe how the preferential absorption of the additive changes the molecular environment in one or other of the phases, depending upon the solvent power of the plasticizer (Figure 4).

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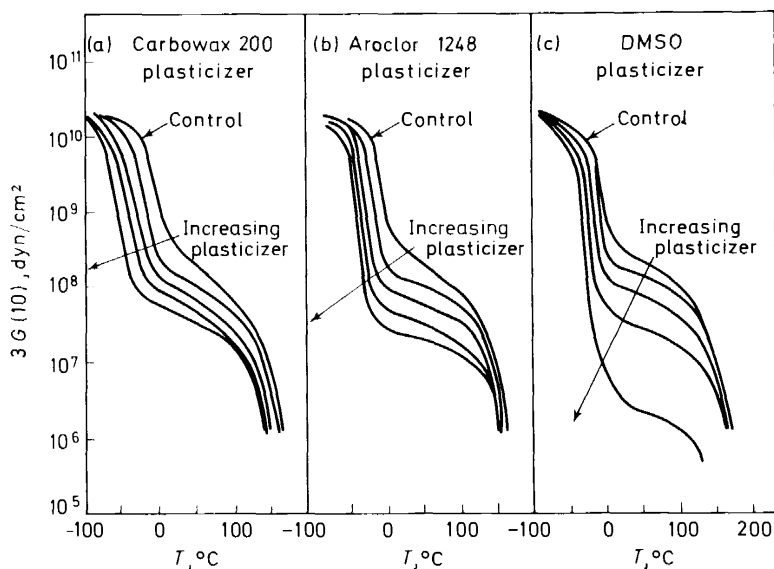


Figure 4. Modulus temperature behaviour of plasticized 3-block elastomers, after Cooper and Tobolsky¹.

2.2 Dielectric relaxation in polyurethane elastomers

Further information on the molecular environment in this kind of system can be obtained from dielectric studies of polar elastomers. An interesting example of this can be seen in studies of the submicroscopic phase separation in segmented polyether-polyurethanes².

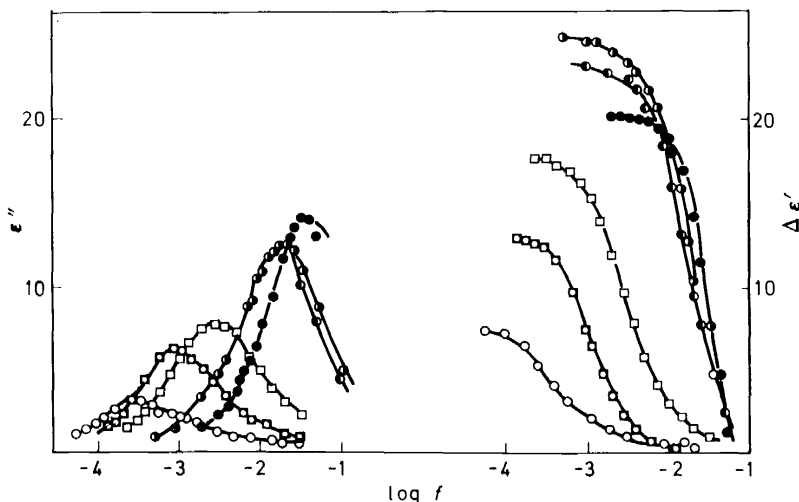


Figure 5. Interfacial polarization in poly(propylene oxide)-polyurethane with 400 molecular weight polyether segments. ● 63 °C, ● 58 °C (measured by charging transient), ● 58 °C (measured by discharging transient), □ 49 °C, ■ 45 °C, ○ 40 °C, after North and Reid².

In these experiments two types of molecular movement have been used to shed light on the molecular environment. At low frequencies the migration of partially mobile charge carriers can take place up to the point where the carriers become trapped at a phase boundary. This Maxwell-Wagner-Sillars interfacial polarization (*Figure 5*) is shown in the real (storage) and imaginary (loss) parts of the complex low-frequency permittivity. The

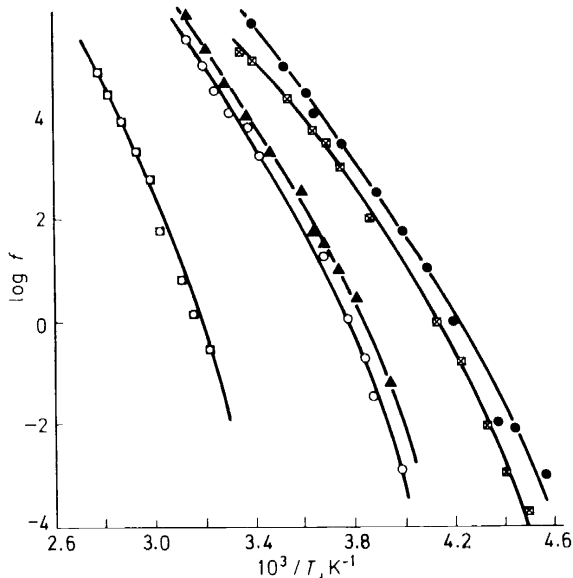


Figure 6. Log dipole orientation frequencies of poly(propylene oxide)-polyurethane with polyether segments of molecular weight: \square 400; \circ 1025; \blacktriangle 1000; \boxtimes 1670; \bullet 1670; after North and Reid².

magnitude of the effect confirms the existence of submicroscopic phase separation in which the occluded glassy domains are markedly imperfect (nonspherical) in shape.

In addition to this the orientation polarization of the ether chain units shows that the flexibility of the polyether chain units increases with increasing distance from the urethane hard segments (*Figure 6*).

2.3 Chain flexibility of α -methylstyrene-alkane copolymers

The elastomeric materials discussed above owe many of their physical properties to the different chain flexibilities of the molecular segments localized in the different phases. In pursuing the understanding of chain flexibilities the technique of ultrasonic relaxation has been used. Basically the frequency dependence of the relaxing specific heat can be used to measure the frequency of conformational change from one rotational isomer to another.

The regular copolymers of α -methylstyrene and alkane units³ (*Figure 7*) have alternating 'stiff' and 'flexible' units, and studies of the dissolved polymer show how the rotational behaviour of the aromatic moiety (frequency of

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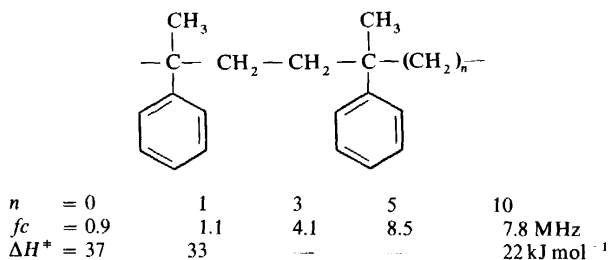


Figure 7. Ultrasonic relaxation frequencies and activation energies in α -methylstyrene-alkane copolymers.

rotational isomeric change and energy barrier opposing rotation) becomes easier the larger is the neighbouring alkane unit.

2.4 Effect of pressure on dielectric relaxation of poly(propylene oxide)

The molecular environment within a polymer is affected by applied pressure. As a result of this molecular rotational behaviour is modified, and indeed changes can be used to obtain information on the effects of pressure. As an illustration we can return to the polyether chain and quote measurements⁴ of dielectric relaxation in poly(propylene oxide) made as a function of temperature and pressure (Figure 8). Such studies are able to yield the activation volume for the segmental rotation process, and show that it is similar in magnitude to the monomer unit molar volume.

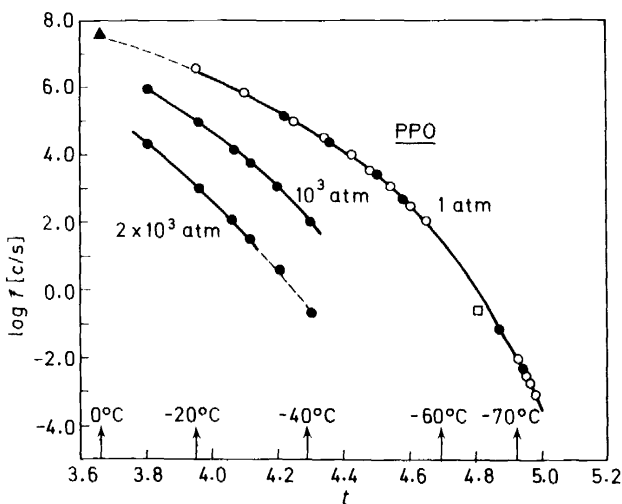


Figure 8. Effect of pressure on dipole orientation frequency in poly(propylene oxide), after Williams⁴. Frequency-temperature location of the dipole process: ○ temperature of maximum loss at given frequencies; ● frequency of maximum loss at given temperatures; ○● dielectric; □ mechanical (G).

Such studies can be interpreted in terms of free volume theories, and as such give information on the nature of the 'free volume' in the environment of the orienting chain unit. Thus the dielectric technique can be used to study polyether movement in a variety of physical (as in this example) and chemical (*Figure 6*) environments.

2.5 Effect of humidity on resin-paper laminates and polyurethane elastomers

As a rather technical example of the effect of external environment one can quote the influence of humidity on the electrical properties of phenol-formaldehyde resin-paper laminates. Such studies have been made for many years, and those illustrated (*Figure 9*) show the main features.

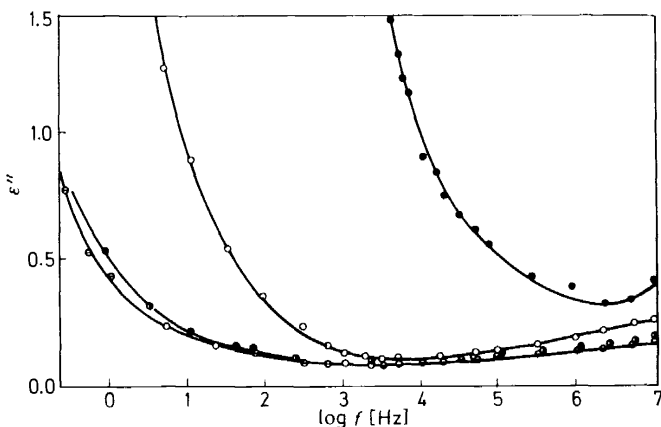


Figure 9. Effect of humidity on dielectric loss in cellulose resin laminate and on phenol-formaldehyde resin: ○, laminate, ○ resin room humidity; ● laminate, ● resin after 30 days at 100 per cent relative humidity.

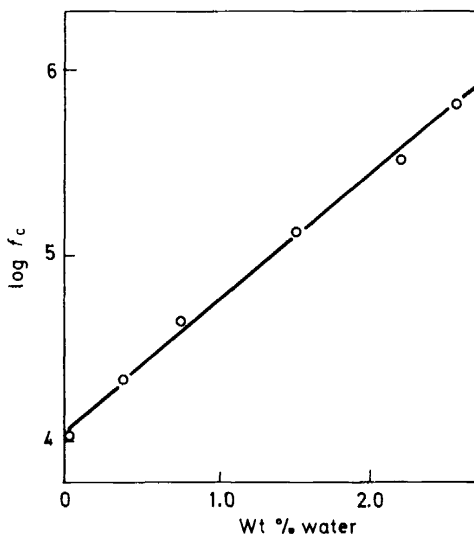


Figure 10. Effect of water on ether segmental motion in poly(ethylene oxide 200)-polyurethane.

The dielectric loss is much increased when water is absorbed by the laminate, the effect being associated with the presence of the cellulose filler since there is little effect on the resin in absence of paper. The frequency range covered shows a low-frequency loss ascribed to conduction by mobile charge carriers and also to interfacial polarization at the resin-cellulose boundary, and a high-frequency loss ascribed to orientation polarization of hydroxylic groups.

In addition the plasticizing action of absorbed water on the polyurethane elastomers discussed earlier can be seen in *Figure 10*.

3. ENERGY MIGRATION AND TRANSFER

The relaxation phenomena mentioned so far have been typical of those observed using familiar techniques (dielectric, dynamic mechanical and ultrasonic relaxation) for observation of molecular movement. However other techniques are available, and it would seem appropriate in such a paper to cover some aspects of molecular electronic energy transfer.

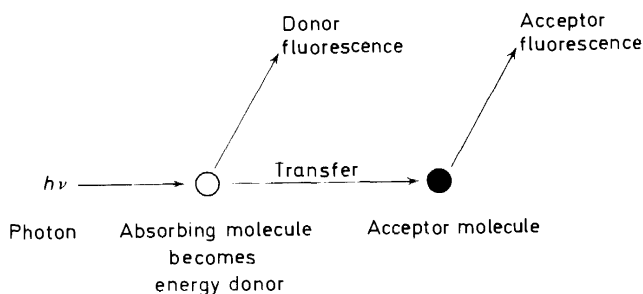


Figure 11. Energy transfer in small molecules.

Such processes are important in a number of different situations, perhaps most importantly in the photophysical phenomena that precede photo-activated polymer degradation (*Figure 11*). One of the molecular processes of

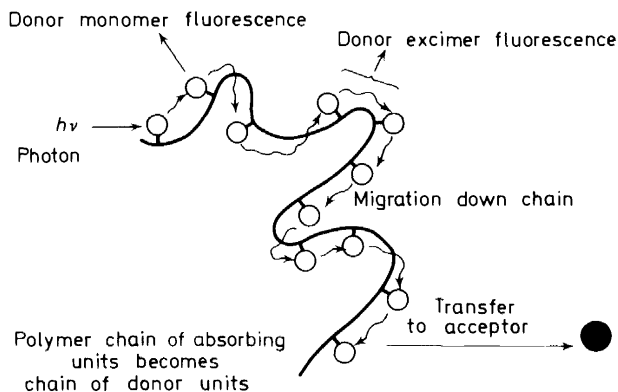


Figure 12. Energy migration and transfer in a polymer chain with photoactive side-groups.

interest is the migration of electronic energy along a polymer chain from an initial site to some point where the energy may be transferred to another molecule or cause chemical reaction (*Figure 12*).

In such studies the molecular property which relaxes is the population of an electronically excited state. After the removal of excitation this decays by a number of processes of which fluorescence and transfer to another molecule are important in the present context. The simplest fluorescence measurements are stationary-state techniques in which continuous irradiation is used so that the rate of formation of excited molecules balances the relaxation to the ground state.

Without commenting further on the theory, it suffices to say that measurements of fluorescence intensities and quenching can be used to calculate a 'diffusion or migration coefficient', Λ , for energy migration down isolated polymer chains. Some of these are illustrated in *Table 2*, which shows also that in a fluid environment comparison of the observed and calculated migration

Table 2. Some migration coefficients for movement of singlet electronic energy along a polymer chain

Polymer	Λ exp. $\text{cm}^2 \text{s}^{-1}$	Λ calc. for rigid chain $\text{cm}^2 \text{s}^{-1}$	Λ calc. for flexible chain $\text{cm}^2 \text{s}^{-1}$
Poly(1-vinylnaphthalene) in tetrahydrofuran	2.8×10^{-4}	1.0×10^{-5}	3.1×10^{-4}
Poly(<i>N</i> -vinylcarbazole) in toluene	8.9×10^{-5}	9.1×10^{-5}	2.1×10^{-4}
Poly(<i>N</i> -vinylcarbazole) in poly(methyl methacrylate)	7.3×10^{-5}	7.9×10^{-5}	1.5×10^{-4}
Poly(phenylacetylene) in tetrahydrofuran	2.4×10^{-3}		
Poly(phenylacetylene) in poly(methyl methacrylate)	6.2×10^{-5}		

coefficients can show whether the chain is flexible or effectively rigid within the excited state lifetime (usually one or two nanoseconds) and that the migration coefficient in efficient systems [poly(phenylacetylene)] is less in a rigid environment than in one permitting molecular motion.

REFERENCES

- ¹ S. L. Cooper and A. V. Tobolsky, *J. Appl. Polymer Sci.*, **10**, 1837 (1966).
- ² A. M. North and J. C. Reid, *Europ. Polymer J.*, **8**, 1129 (1972).
- ³ D. H. Richards, N. F. Scilly and F. Williams, *Polymer*, **10**, 603 (1969).
- ⁴ G. Williams, *Trans. Faraday Soc.*, **61**, 1564 (1965).