

Poly(ethenyl-1,3,4-oxadiazole-2,5-diyl-1,4-phenylene). Electrical Properties and Phase Transition Studies

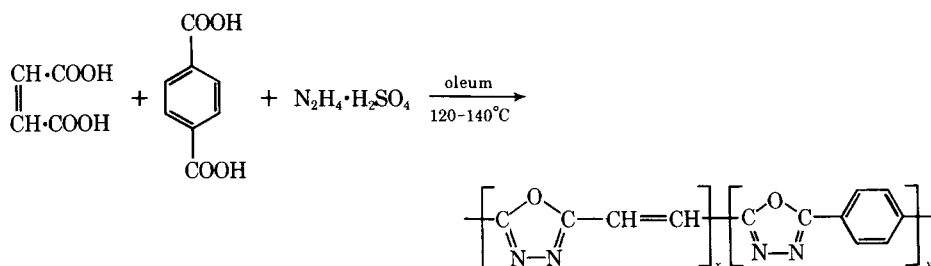
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Synopsis

The phase diagrams of the ternary system poly(ethenyl-1,3,4-oxadiazole-2,5-diyl-1,4 phenylene), sulfuric acid, and water indicated that the increase of the ethenyl residue in the copolymers increased the solubility in the acid. The critical point of separation in sulfuric acid was determined, and it decreased from 74% to 60.5% as the ethenyl ratio of copolymers was increased. The electrical properties in the temperature range of 0–90°C at a fixed frequency of 1592 Hz were also investigated. The $\tan \delta$ values increased with increase in temperature and passed through a maximum. The temperature of this maximum varied with the nature of the copolymer. The observed increase in the dielectric constant with temperature may be due to increased segmental motion in the amorphous region of the polymers.

INTRODUCTION

The preparation and characterisation of 1,3,4-oxadiazole copolymers prepared by condensing hydrazine sulfate (HS) with different molar ratios of terephthalic acid (T) and fumaric acid (F) in fuming sulfuric acid have been reported earlier.¹ The following type of structures may be introduced in the polymer backbone as a result of cyclodehydration reaction:



The values of x and y will depend upon the initial monomer ratios.

The dielectric properties of a polymer depend upon the nature and number of polar groups, substituent size, steric effect, stereoregularity, and, in a copolymer, on the constitution of the monomeric units and their ratios. It has been reported that copolymer composition may be evaluated by the measurements of dielectric constant and tangent of the dielectric loss angle $\tan \delta$.³⁻⁷ The electrical properties of these oxadiazole copolymers were, therefore, investigated to find a correlation between dielectric constants and copolymer

composition. The dielectric properties were measured at a fixed frequency of 1592 Hz and at a series of temperatures between 0°C and 90°C.

The solubility behavior of these copolymers is important because their processing into fibers is done by solution techniques. These polymers have limited solubility in organic solvents and are spun from a concentrated H_2SO_4 solution.^{8,9} Only little information is available regarding the preparation of heat-resistant fibers from such a solution.^{10,11} The composition of the coagulating bath may affect the fiber properties⁸ because one can control the crystallization and orientation to some extent at this stage. This precipitation of polymer from concentrated H_2SO_4 solution may be regarded as a phase transition in polymer, solvent, and precipitant system.¹² The phase diagrams of the ternary system, containing the oxadiazole copolymer, concentrated H_2SO_4 , and water were, therefore, investigated at 35°C.

EXPERIMENTAL

The 1,3,4-oxadiazole copolymers of terephthalic acid (T) and fumaric acid (F) were prepared by solution condensation method^{1,8} using fuming H_2SO_4 . The initial molar ratio of F and T is indicated by a subscript in naming the copolymer (FT). Thus, an F:T molar ratio of 1:1 and 1:2 is indicated as F_1T_1 and F_1T_2 , respectively.

The intrinsic viscosity of the copolymers was determined at 30°C in 98% H_2SO_4 by using Ubbelohde suspension level viscometer. The polymer concentration was varied between 0.4 g/dl and 0.1 g/dl.

The density of the polymers was determined by the suspension method using aqueous solution of zinc chloride.

The softening temperature of the polymers was evaluated by differential thermal analysis in nitrogen atmosphere. A Stanton-Redcroft thermal analyzer having a Chromel-Alumel thermocouple was used, and a heating rate of 6°C/min was maintained. The reference cell contained alumina, and 5 mg of the polymer sample was used in each measurement. The DTA thermograms

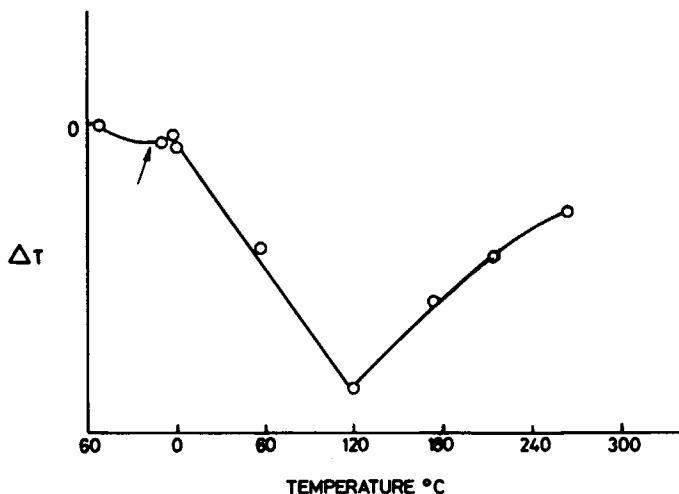


Fig. 1. DTA curve for sample $(\text{F}_1\text{T}_2)_F$.

TABLE I
Properties of the Investigated Copolymers

Sample no.	Polymer no.	Molar ratio of F:T	$[\eta]$, dl/g	Density, g/cm ³	Inflection point °C	Melting temp., °C
1	F ₀	1:0	0.315	1.515	27.0	132.0
2	F ₄ T ₁	4:1	0.355	1.472	32.0	62.5
3	F ₂ T ₁	2:1	0.195	1.450	7.0	124.0
4	(F ₁ T ₁) _a	1:1	0.060	—	—	—
5	(F ₁ T ₁) _b	1:1	0.347	1.445	20.0	124.0
6	(F ₁ T ₁) _c	1:1	0.515	1.445	—	—
7	(F ₁ T ₂) _e	1:2	0.235	1.43	—	114.0
8	(F ₁ T ₂) _f	1:2	0.435	1.43	37.0	115.0
9	T ₀	0:1	0.18	1.41	37.0	—

were recorded in the temperature range of -80°C to 400°C . An inflection point is observed before the melting temperature which may be some transition point of the polymer. These transition points, followed by a sharp endothermic peak, were observed between 7°C and 132°C (Fig. 1). Transition points in the temperature range of 39 – 45°C have been reported for aliphatic oxadiazole polymers by Unishi et al.¹³ Some characteristics of these oxadiazole copolymers are given in Table I.

Phase diagrams for the system poly-1,3,4-oxadiazole–sulfuric acid–water were obtained by determination of the turbidity points during titration with a mixture of the solvent and precipitant at 35°C . When a high polymer concentration is taken, the distribution of precipitant becomes difficult, and so only the initial branches of binodal curves were determined experimentally.

The dielectric constants of polymer pellets of known thickness and diameter coated with Aquadec were determined with the help of a Wayne Kerr (B-221A) Universal Bridge at a fixed frequency of 1592 Hz. Circular copper electrodes in direct contact with the pellet were used for measuring the capacitance. From the area and thickness of the polymer pellet, the capacitance in the absence of the pellet was calculated (C'), and the capacitance in the presence of pellet was experimentally determined (C''). From the capacitance of the pellet (C) thus obtained ($C'' - C'$), the dielectric constant was determined by the help of the following equation:

$$C = \frac{KA}{4\pi d}$$

where A = area of pellets (cm^2), d = thickness (cm), and K = dielectric constant.

The dielectric loss was calculated by using the equation

$$\tan\delta = \frac{G}{\omega C}$$

where G = conductance, $\omega = 10^4$ for a fixed frequency of 1592 Hz, and C = capacitance.

The temperature of the pellet was varied between 0° and 90°C . This was achieved by placing the pellet and electrode assembly in a tube which was im-

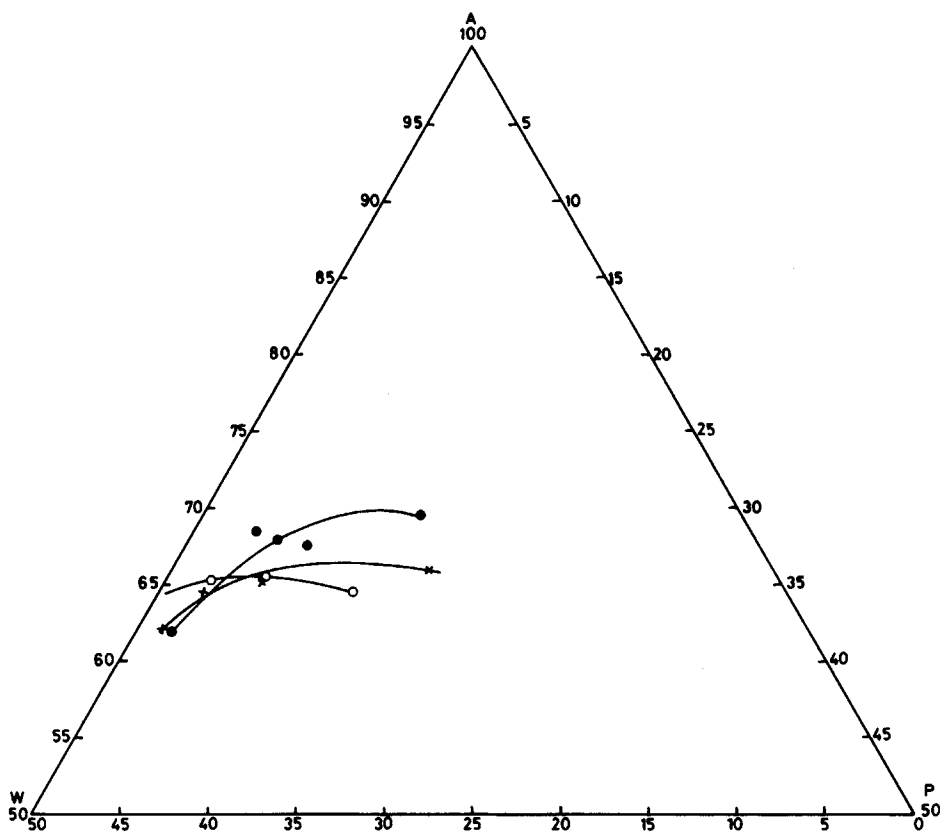


Fig. 2. Phase diagrams of the ternary systems polymer (P), sulfuric acid (A), and water (W) for $(F_1T_1)_a$ (O), $(F_1T_1)_b$ (X), and $(F_1T_1)_c$ (●) at 35°C.

mersed in a bath. The temperature of the bath was gradually increased. However, the rate of heating was not controlled. The pellet was maintained at the desired temperature for 5 min before measuring the capacitance. The temperature of the pellet was recorded by means of a Chromel-Alumel thermocouple placed in contact with the electrodes.

RESULTS AND DISCUSSION

In Figures 2 and 3, the phase diagrams of the ternary system 98% sulfuric acid (A), water (W), and polymer (P) for samples F_1T_1 (of different intrinsic viscosities), T_0 , F_1T_2 , F_2T_1 , and F_0 are given. The vertices A, P, and W correspond to 100% acid, 50% polymer, and 50% water. When aqueous solution of sulfuric acid are added to the solution of polymers, the separation of system into two phases takes place at the critical point. One of these phases is the pure mixture of acid and water, while the other phase is the precipitated polymer which separates out as a gel-like mass. This behavior is similar to the one reported for poly(*p*-phenyleneterephthalamide)¹¹ and has great importance in the formation of fibers. The gel-like precipitate is soon converted to a paste-like system, which may be due to crystallization. By varying

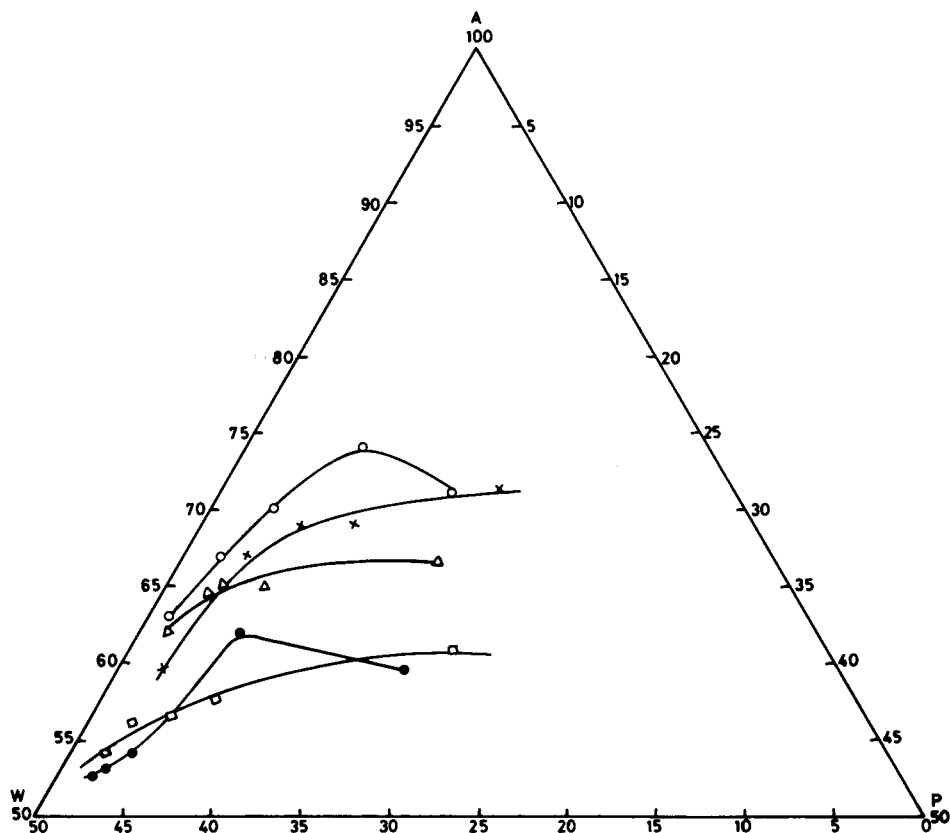


Fig. 3. Phase diagrams of the ternary systems polymer (P), sulfuric acid (A), and water (W) for T_0 (O), F_1T_2 (x) (F_1T_1)_b (Δ), F_2T_1 (\bullet), and F_0 (\square) at 35°C.

the composition of the precipitating bath, one may control the crystallization process, and improved fibers may be obtained from these polymers. In ternary systems, the size of the region of the complete miscibility depends on the nature of the components.¹⁴ In this system, the composition of copolymers and the molecular weights of the samples vary. In Figure 2, the effect of intrinsic viscosity (molecular weight) on the phase diagram is indicated. The sample having higher intrinsic viscosity precipitated out by the addition of a smaller amount of the precipitant. The higher solubility of low molecular weight samples is a known phenomenon in polymer systems. The critical point of separation in H_2SO_4 is around 70.5, 67, and 65.5 for samples (F_1T_1)_a, (F_1T_1)_b, and (F_1T_1)_c, respectively. As the fumaric acid content of the copolymers was increased, the solubility in H_2SO_4 increased, and more precipitant was required to precipitate the polymer. The critical point of separation is in the region of sulfuric acid concentration of 74, 72, 67, 62, and 60.5 for samples T_0 , F_1T_2 , (F_1T_1)_b, F_2T_1 , and F_0 , respectively.

Generally in the spinning of the polyoxadiazole fibers, 40–50% H_2SO_4 is used in the coagulating bath. Our results indicate that the critical sulfuric acid concentration ranges between 74% and 60%. The presence of large quantities of precipitant may not be beneficial for crystallization and orienta-

TABLE II
Electrical Properties of Poly(ethenyl-1,3,4-oxadiazole-2,5-diyl-1,4-phenylene)

Sample no.	T_{\max} , °C	Dielectric constant	Activation energy, kcal/mole
F_0	23.5	13.12	9.1
F_4T_1	32	11.86	7.4
F_2T_1	22	9.3	4.6
$(F_1T_1)_b$	26.2	11.21	7.0
$(F_1T_1)_c$	19.5	11.54	8.7
$(F_1T_2)_e$	24	9.63	3.1
$(F_1T_2)_f$	23	12	10.1
T_0	29.5	12.46	1.8

tion which is needed in fibers. It has been reported by Imai⁸ that in the spinning of fibers, if water is taken as the precipitant, the resulting fibers are opaque and have low tensile properties. With the help of these phase diagrams, one can select the optimum conditions for the spinning of the fibers.

Figures 4 and 5 show the variation of $\tan \delta$ as a function of temperature at a fixed frequency of 1592 Hz for the various FT copolymers. In the temperature range of 0–90°C, the loss factor passes through a maximum in the region of 20–36°C. The temperatures at which $\tan \delta$ passes through a maximum are given in Table II. Since this maxima lies above the transition point for most of the polymers, it may be attributed to the dipole segmental losses which depend on chemical composition of polymers. The intra- and intermolecular

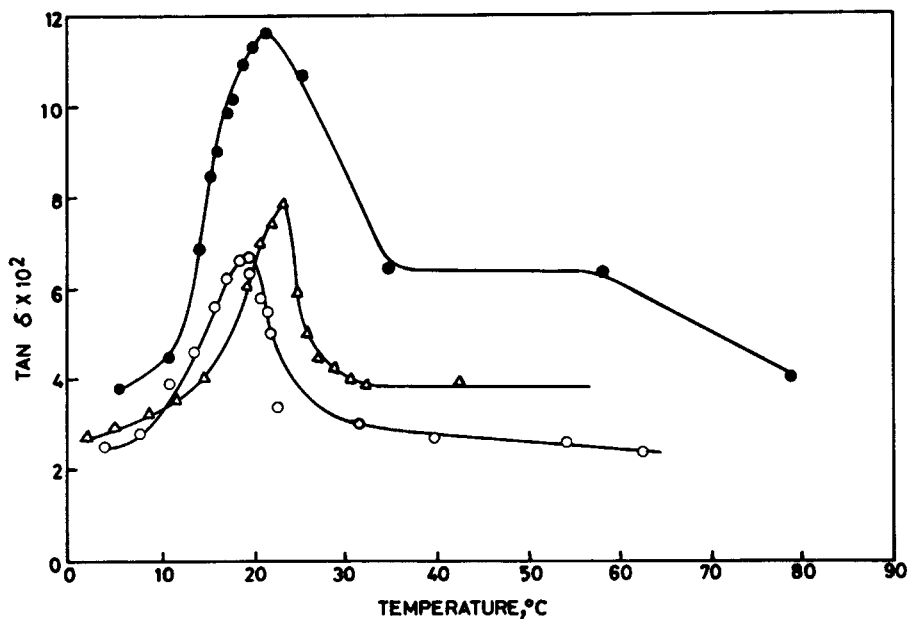


Fig. 4. Temperature dependence of $\tan \delta$ at a frequency of 1592 Hz for poly(ethenyl-1,3,4-oxadiazole-2,5-diyl-1,4-phenylene): samples F_0 (Δ), $(F_1T_1)_e$ (\circ), and F_2T_1 (\bullet).

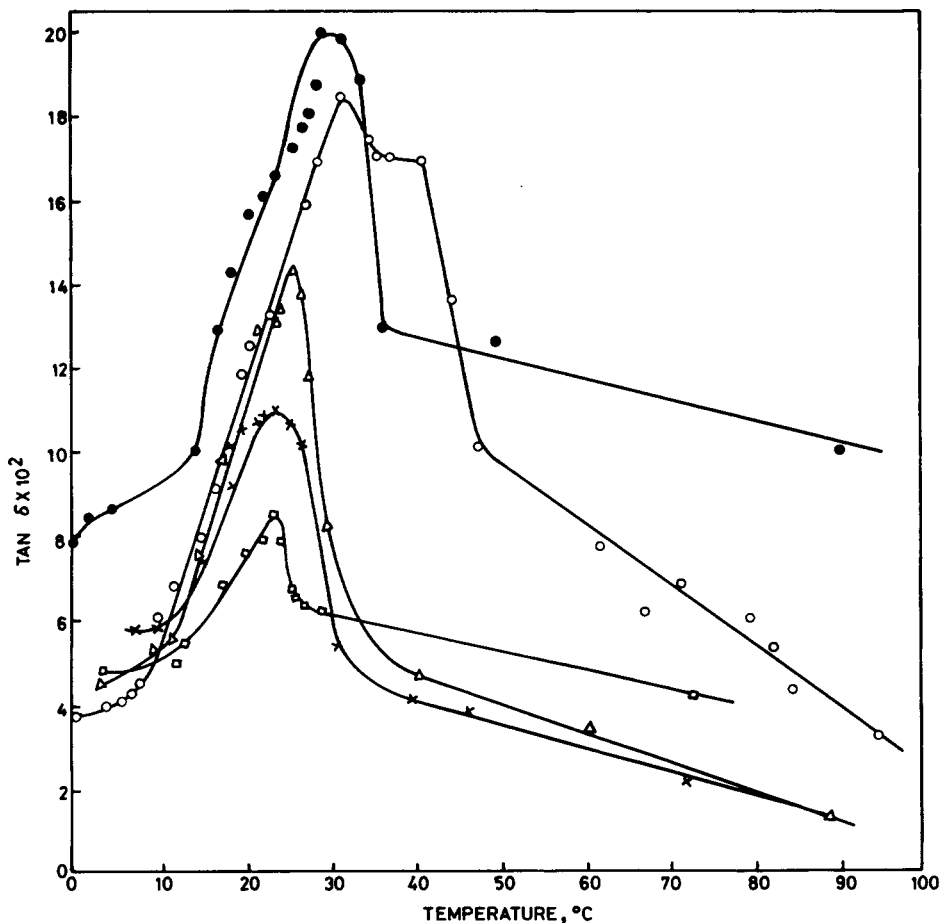


Fig. 5. Temperature dependence of $\tan \delta$ at a frequency of 1592 Hz for poly(ethenyl-1,3,4-oxadiazole-2,5-diyl-1,4-phenylene): samples F_4T_1 (O), T_0 (●), $(F_1T_1)_e$ (Δ), $(F_1T_2)_e$ (\square), and $(F_1T_2)_f$ (x).

interaction and unit mobility and relaxation times are dependent on the chemical composition. The polarity of substituent and the steric hindrances of the substituent are the two main factors which determine the dielectric loss behavior of polymers. The T_{\max} value of F_0 is lower than that of T_0 , which may be due to more rigidity of aromatic ring. However, the T_{\max} value of copolymers has no obvious dependence on the composition. An increase in fumaric acid concentration in the copolymer should impart more flexibility, thus lowering the T_{\max} value. However, the polarity of the polymers will increase due to an increase in the oxadiazole ring concentration in fumaric acid copolymers. This will enhance the dipole-dipole interactions. These two opposing effects may be responsible for the observed values of T_{\max} .

The variation of dielectric constant of the copolymers with temperature shows a maximum value (Figs. 5 and 6). The dielectric constant (ϵ') at these maximum values for different copolymers is given in Table II. The ϵ' values for F_0 is highest, followed by T_0 (Fig. 7). This can be explained on the basis of greater 1,3,4-oxadiazole ring concentration in F_0 than in T_0 , which in-

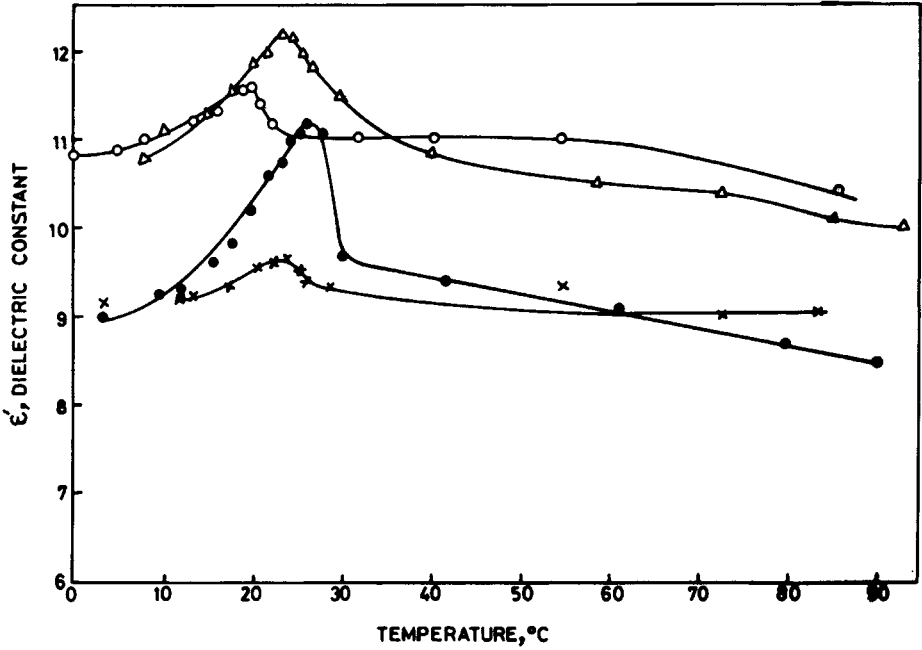


Fig. 6. Temperature dependence of dielectric constants at a frequency of 1592 Hz: samples (F₁T₂)_f (O), (F₁T₁)_c (Δ), (F₁T₂)_e (x), and (F₁T₁)_b (●).

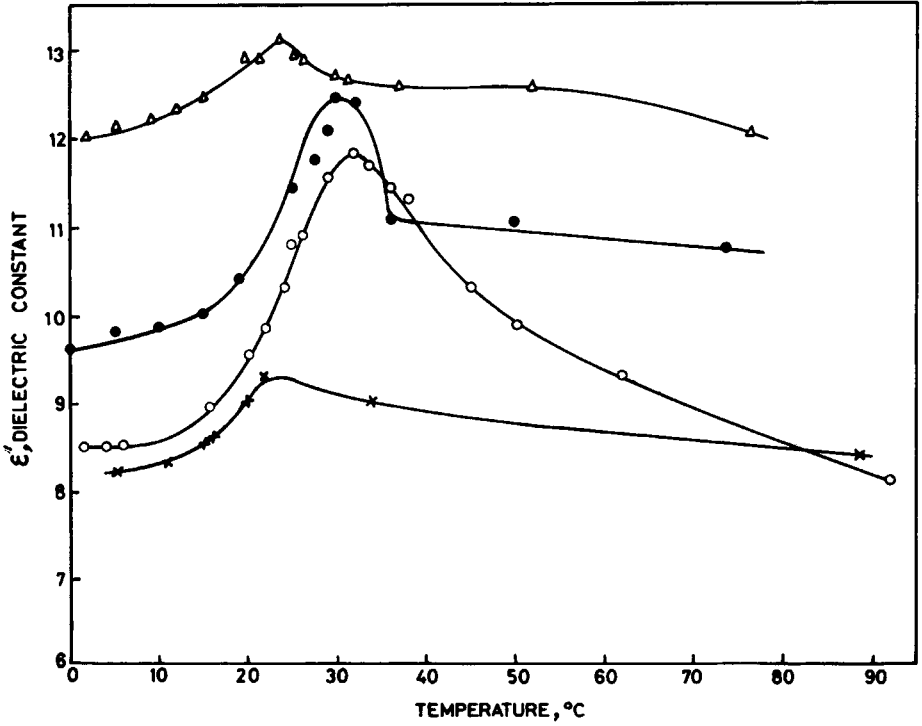


Fig. 7. Temperature dependence of dielectric constants at a frequency of 1592 Hz: sample F₀ (Δ), T₀ (●), F₄T₁ (O), and F₂T₁ (x).

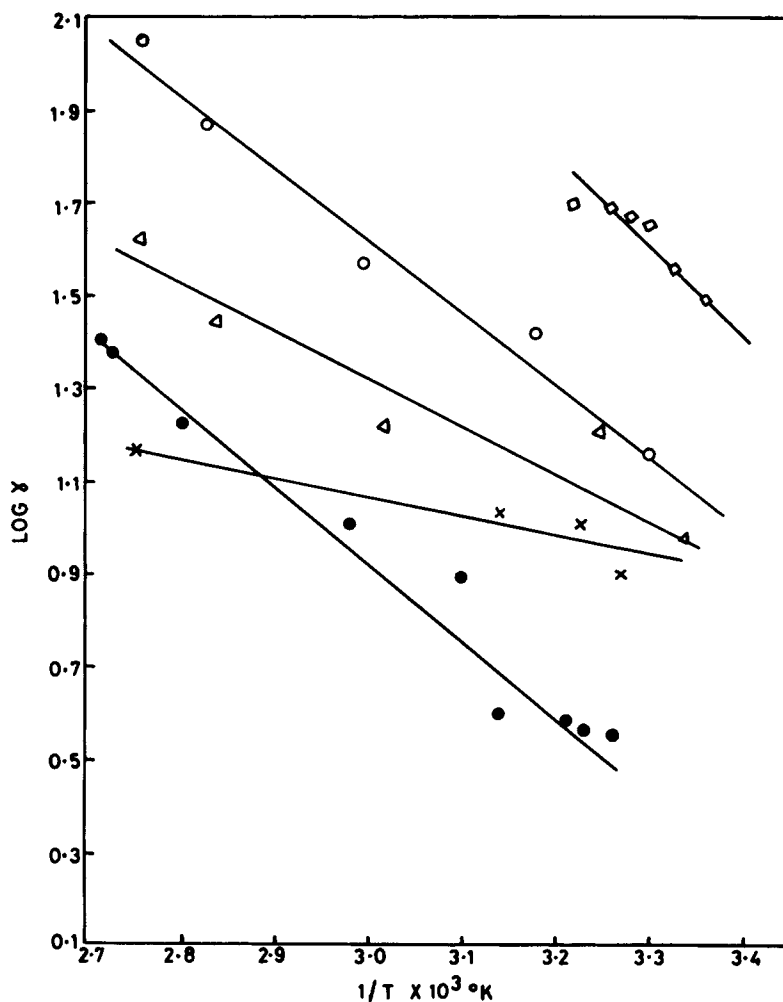


Fig. 8. Plot of $\log \gamma$ (conductivity) vs. reciprocal absolute temperature for samples F_0 (\square), $(F_1T_1)_b$ (\circ), F_2T_1 (Δ), F_4T_1 (\bullet), and T_0 (\times).

creases the polarity of the polymer. T_0 , on the other hand, has a benzene ring where more polarizable π electrons are present, and this helps in the increase in ϵ' :



The relationship of electrical conductivity to temperature may be expressed as follows (Fig. 8):

$$\gamma = \gamma_0 e^{-u/RT}$$

where γ_0 is preexponential factor and u is activation energy. Table II gives the activation energy values for these polymers. The activation energy of the copolymers decreases as the terephthalic acid content increases, with the exception of sample $(F_1T_2)_f$.

As a result of these investigations, it may be concluded that in the oxadiazole copolymers the conductivity measurements cannot be used to determine the copolymer composition.

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