

Dielectric Properties of Polymers Containing Dispersed TCNQ Salts

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Synopsis

Tetracyanoquinodimethane salts have been incorporated into insulating polymers to raise their dielectric constants. Cast films prepared from mixtures of insulating polymers and tetracyanoquinodimethane salts in a solvent show a high dielectric constant (> 20). The dielectric constant of the films varies with the tetracyanoquinodimethane salts. High values were attained with the films containing high-conducting tetracyanoquinodimethane salts. These values remain constant over a range of frequencies (10^2 – 10^4 Hz). Dissipation factors and electric strength values of the films are also reported.

INTRODUCTION

With the growth of electrical and electronic industries, smaller and more efficient capacitors have been required. Dielectrics have been developed that have better characteristics, with special emphasis on both high dielectric constant and low dielectric loss. No single material, however, satisfies all these requirements. Different kinds of ceramics have been used as dielectrics of a capacitor. There are some serious disadvantages of ceramics, for example, the lack of ductility and difficulty in controlling the purity of material, degree of crystallization, uniformity of density, and size and shape during firing.

Polymeric materials, therefore, would be in great demand in the capacitor industry. Polypropylene films have been used increasingly because of low dielectric loss and high breakdown voltages.¹ It is necessary to raise the dielectric constant together with the low dielectric loss for the purpose of reducing the size of a capacitor.

Several attempts have been made so far to meet this need. One is the use of polar polymers^{2–10} with side groups with large dipole moments, as exemplified by cyanoethylated cellulose³ and poly(vinylidene fluoride).⁷ Another is the approach of dispersing fillers with high dielectric constants, such as TiO_2 and BaTiO_3 , into polymeric materials.^{11–15} Among such fillers is tetracyanoquinodimethane (TCNQ) which is known to have a large value of the dielectric constant.^{16–17}

In our previous report,¹⁸ we presented a preliminary study of dielectric properties of polymeric materials with the side groups with large dipole moments and/or containing fillers. The particularly interesting feature was that the dielectric constant was enhanced up to 20-fold when a small amount of a TCNQ salt was added to polystyrene. In the present paper, we have

investigated dielectric properties of polymer films containing various kinds of TCNQ salts. We have considered the effect of the resistivity of the TCNQ salts on the dielectric constant of the films. We have also investigated the morphology of the dielectric films and their electric strength.

Experimental

Salts of TCNQ were prepared according to procedures described in the literature.¹⁹⁻²³ Characterization was made by elemental analysis and infrared and visible spectra. The resistivity was measured on the compaction samples by the two-probe method described in the literature.²¹ Table I shows the TCNQ salts prepared and their resistivities.

Polystyrene (Mitsubishi-Monsanto Co.), acrylonitrile-styrene copolymer (Mitsubishi-Monsanto Co.), polyacrylonitrile (Aldrich Chemical Co.), polysulfone (Union Carbide Corp.), Polyvinyl chloride (Sekisui Chemical Co.), polyvinyl butyral (Sekisui Chemical Co.), polyvinyl carbazole (Wako Chemical Industries Ltd.), and polycarbonate (Aldrich Chemical Co.) were used as received.

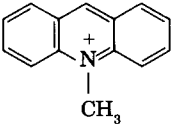
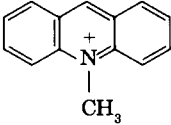
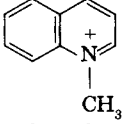
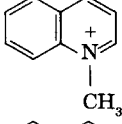
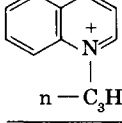
Polymer films containing microcrystalline precipitations of the TCNQ salts were prepared as follows: Polymer (1.0g) was dissolved in 10 cm³ dimethylformamide and then a weighed amount of the TCNQ salt was added to the solution. The dark green solution was stirred for several minutes at room temperature. Films were cast from the solutions on glass plates under reduced pressure, about 10 mm Hg. Further drying of cast films was continued for 24 h at 100°C under vacuum in order to eliminate the remaining solvent thoroughly. The thicknesses of the films for the electrical measurements were in the range of 0.5–1 × 10⁻² cm.

Measurements of dielectric constant, dissipation factor, and resistivity were made on 1689 Precision RLC Digibridge manufactured by General Radio Co. Gold was evaporated onto the films to form a three-terminal electrode. The dc breakdown test of the film was carried out in an insulating oil. The film was placed on a brass electrode designed in conformity with the Japanese Industrial Standards,²⁴ and a dc voltage at 200 V/s was applied.

TABLE I
Structures of the TCNQ Salts Prepared and Their Specific Resistivities

| TCNQ salt | Specific resistivity (Ω-cm) |
|---|-----------------------------|
| Li ⁺ TCNQ ⁻ (1) | 2 × 10 ⁵ |
| Na ⁺ TCNQ ⁻ (2) | 3 × 10 ⁴ |
| K ⁺ TCNQ ⁻ (3) | 8 × 10 ³ |
| Cs ⁺ TCNQ ⁻ (4) | 3 × 10 ⁴ |
| Cs ₂ ⁺ TCNQ ₃ ⁻ (5) | 9 × 10 ⁴ |
| Ag ⁺ TCNQ ⁻ (6) | 8 × 10 ⁵ |
| Cu ⁺ TCNQ ⁻ (7) | 1 × 10 ³ |
| Cu ²⁺ TCNQ ₂ ⁻ (8) | 2 × 10 |
| (C ₂ H ₅) ₃ NH ⁺ TCNQ ₂ ⁻ (9) | 1 × 10 |
| NH ₂ (CH ₂) ₆ NH ₃ ⁺ TCNQ ₂ ⁻ (10) | 1 × 10 |
| (CH ₃) ₃ (C ₆ H ₅ CH ₂)N ⁺ TCNQ ⁻ (11) | 1 × 10 ¹² |
| (n - C ₄ H ₉) ₄ N ⁺ TCNQ ⁻ (12) | 5 × 10 ¹¹ |

TABLE I (Continued from previous page)

| TCNQ salt | Specific resistivity ($\Omega\text{-cm}$) |
|---|---|
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}(\text{CH}_3)_2 \text{TCNQ}^-$ (13) | 9×10^5 |
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}^+(\text{n} - \text{C}_6\text{H}_{13})_2 \text{TCNQ}^-$ (14) | 2×10^7 |
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}^+(\text{n} - \text{C}_8\text{H}_{17})_2 \text{TCNQ}^-$ (15) | 2×10^9 |
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}^+(\text{CH}_3)_2 \text{TCNQ}_2^-$ (16) | 3 |
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}^+(\text{C}_2\text{H}_5)_2 \text{TCNQ}_2^-$ (17) | 2 |
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}^+(\text{n} - \text{C}_4\text{H}_9)_2 \text{TCNQ}_2^-$ (18) | 9×10 |
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}^+(\text{CH}_2)_2 \text{N}^+(\text{CH}_3) = \text{C} \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} (\text{CH}_2)_2 \text{TCNQ}_3^{2-}$ (19) | 5 |
| $(\text{CH}_2)_2 \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} \text{C} = \text{N}^+(\text{CH}_2)_6 \text{N}^+(\text{CH}_3) = \text{C} \begin{array}{c} \diagup \text{S} \\ \diagdown \text{S} \end{array} (\text{CH}_2)_2 \text{TCNQ}_4^{2-}$ (20) | 2×10 |
|  TCNQ $^-$ (21) | 1×10^7 |
|  TCNQ $_2^-$ (22) | 1 |
|  TCNQ $^-$ (23) | 1×10^7 |
|  TCNQ $_2^-$ (24) | 8×10^7 |
|  TCNQ $_2^-$ (25) | 6 |

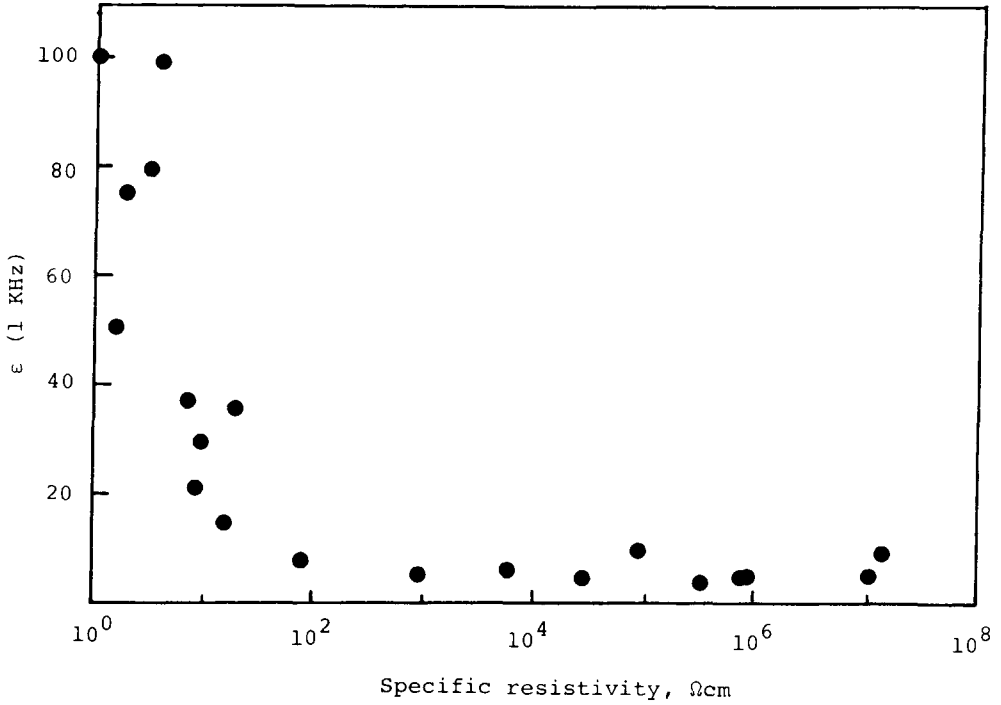


Fig. 1. Plots of dielectric constants at 1 KHz of the polystyrene films containing 2 wt% of the TCNQ salts vs. specific resistivities of the TCNQ salts.

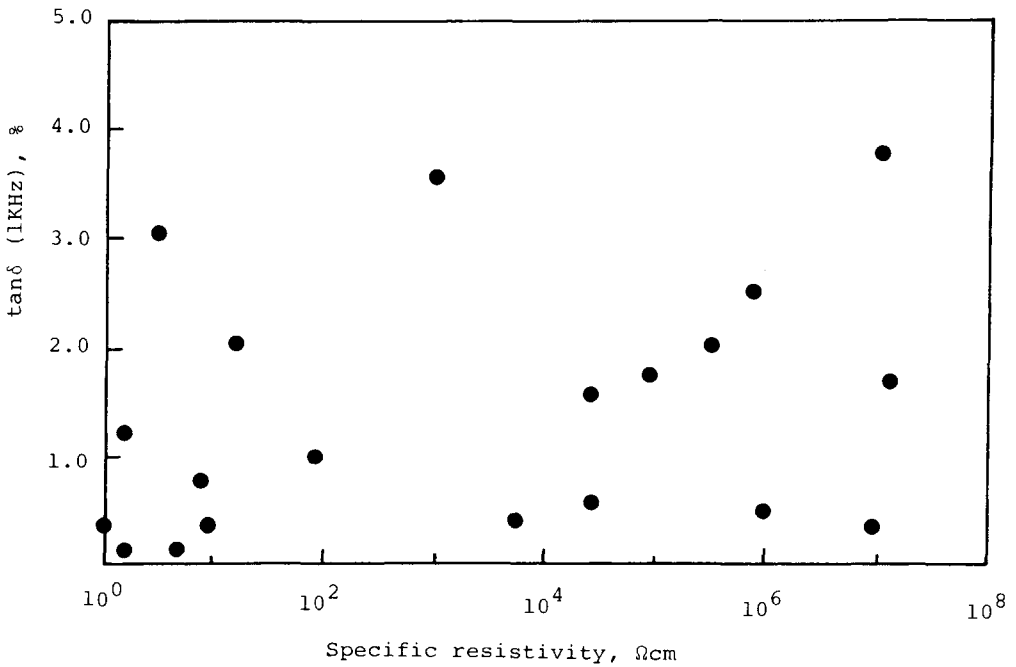


Fig. 2. Plots of dissipation factors at 1 KHz of the polystyrene films containing 2 wt% of the TCNQ salts vs. specific resistivities of the TCNQ salts.

Results and Discussion

The dependence of the dielectric constant and dissipation factor of the polystyrene films containing 2 wt% of the TCNQ salts on the specific resistivities of the salts is shown in Figures 1 and 2. The dielectric constants of the films increase with a decrease of the specific resistivity of the TCNQ salt, whereas the dissipation factor is not much affected by the resistivity. This dependence suggests that ease of migration of carrier electrons in the TCNQ salt is closely concerned with the dielectric behavior of the film. As seen in Figure 1, the dielectric constant is increased by a factor of more than 20 when high-conducting TCNQ salts are used. The results of high dielectric constants of the TCNQ salts of **9**, **10**, **16**, **17**, **19**, and **25** are consistent with those of the *N-n*-butylquinolinium,¹⁴ *N*-methylquinolinium,¹³ quinolinium,¹³ and *N*-methylacridinium¹² salts of TCNQ. Such a high value of the dielectric constant is not an ordinary occurrence in organic polymers. Most organic polymers exhibit dielectric constants of the order of 2–10.

Several authors^{4-6,11,13,14} have attempted to design models and interpret results of such high values of dielectric constants, mainly on the basis of a Maxwell-Wagner-Sillars interfacial polarization²⁵ in the heterogeneous dielectrics composed of conducting particles dispersed in an insulating matrix. According to this theory, the migration of carrier electrons occurs in the conducting particles isolated by the insulating polymer with the application of an electric field. This results in the interfacial polarization. The extent of polarization, therefore, depends on the ease of electron migration of the

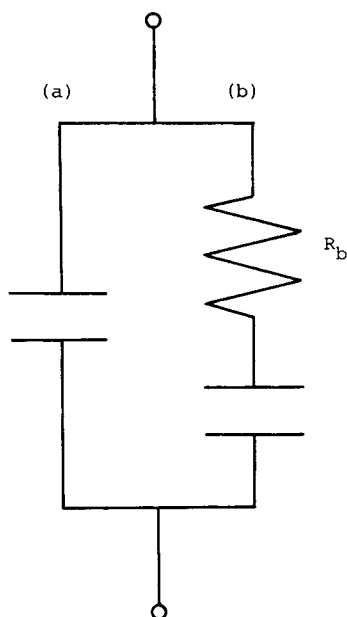


Fig. 3. Equivalent electric circuit of the polymer films containing the TCNQ salt: (a) the capacitance due to the insulating polymer; (b) the capacitance due to the polarization in the heterogeneous dielectrics.

conducting particles. The lower the resistivity of the conducting particles becomes, the higher the value of dielectric constant becomes. This agrees well with the results in Figure 1. Figure 3 shows the equivalent electric circuit of the film containing the TCNQ salt, where path a represents the capacitance due to the insulating polymer and path b represents the capacitance due to the interfacial polarization. In path b, R_b corresponds with the resistivity of conducting particles dispersed in the insulating matrix.

Table II shows dielectric constants and dissipation factors of the films containing 2 wt% of the TCNQ salt. The dielectric constant values of the films are almost unaffected by frequency over a range of 10^2 – 10^4 Hz, whereas the dissipation factor varies with the frequency. This behavior is in accord with results reported previously.^{13,14} Table II also shows the effect of matrix polymer on the dielectric properties of the films containing TCNQ salts. The dielectric constants of the films vary with the matrix polymers. High ϵ values were obtained with polystyrene, styrene-acrylonitrile copolymer, polysulfone, and polyvinyl butyral. In the present system, it can be said that a needlelike microcrystallite growth of the TCNQ salt in the polymer matrix is a necessary condition for the high ϵ value. Micrographs of a polystyrene film and a polyvinyl chloride film containing 3 wt% of the TCNQ salt **16** are shown in Figure 4a and b, respectively. Clearly, the needlelike microcrystallites are not grown in the polyvinyl chloride film. Such microcrystallization of the salt in the film is dependent on the matrix polymer, the condition of the cast-film formation, and the salt concentration. To preserve appropriate conditions for microcrystallite growth, the rate and

TABLE II
Dielectric Properties of Films Containing 2 wt% of TCNQ Salts

| Matrix polymer | TCNQ Salt ^a | Film Morphology ^b | Dielectric constant (ϵ) | | | Dissipation factor ($\tan\delta$), (%) | | |
|---------------------------------|------------------------|------------------------------|------------------------------------|-----------|-----------|--|-----------|-----------|
| | | | 10^2 Hz | 10^3 Hz | 10^4 Hz | 10^2 Hz | 10^3 Hz | 10^4 Hz |
| Polystyrene | 16 | N | 75.3 | 75.0 | 75.1 | 0.51 | 0.18 | 0.18 |
| | 15 | T | 6.50 | 5.56 | 4.91 | 9.88 | 10.2 | 7.20 |
| | — | T | 2.21 | 2.74 | 2.45 | 0.01 | 0.01 | 0.01 |
| Polycarbonate | 16 | T | 6.17 | 6.24 | 6.09 | 0.89 | 0.85 | 1.11 |
| | — | T | 3.38 | 3.35 | 3.32 | 0.70 | 0.62 | 0.79 |
| Styrene-acrylonitrile copolymer | 16 | N | 20.7 | 20.6 | 20.5 | 0.99 | 0.22 | 1.10 |
| | — | T | 3.40 | 3.36 | 3.32 | 0.01 | 0.01 | 0.02 |
| Polyvinyl chloride | 16 | T | 7.44 | 7.26 | 7.06 | 1.80 | 2.07 | 2.30 |
| | — | T | 3.70 | 3.65 | 3.55 | 1.60 | 1.60 | 1.71 |
| Polysulfone | 16 | N | 21.0 | 19.2 | 12.1 | 1.02 | 0.74 | 0.10 |
| | — | T | 4.13 | 4.09 | 4.05 | 0.79 | 0.67 | 0.52 |
| Polyvinyl carbazole | 16 | T | 4.87 | 4.79 | 4.72 | 1.23 | 1.02 | 0.82 |
| | — | T | 4.89 | 4.83 | 4.77 | 0.65 | 0.84 | 0.81 |
| Polyacrylonitrile | 16 | T | 5.63 | 5.15 | 4.80 | 6.69 | 5.49 | 4.41 |
| | — | T | 6.17 | 5.69 | 5.32 | 5.85 | 5.06 | 4.36 |
| Polyvinyl butyral | 16 | N | 79.2 | 76.3 | 70.2 | 2.62 | 4.59 | 14.4 |
| | 14 | T | 9.46 | 8.73 | 8.18 | 7.20 | 4.98 | 4.35 |
| | 19 | N | 30.3 | 29.4 | 28.6 | 2.11 | 2.07 | 3.16 |
| | — | T | 6.24 | 6.08 | 5.93 | 1.74 | 1.77 | 1.99 |

^a See Table I.

^b N = needlelike microcrystallite, as shown in Figure 4a, and T = transparent or homogeneous as is shown in Figure 4b.

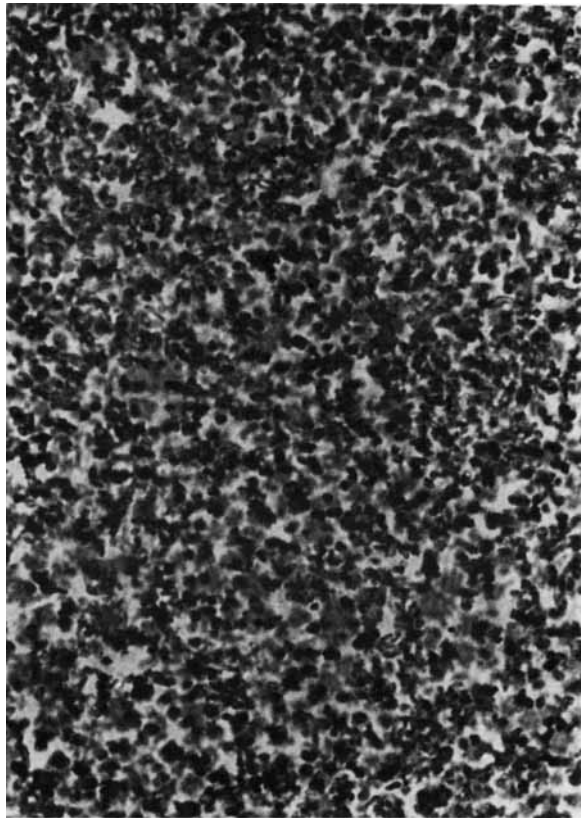


Fig. 4. Micrographs of polystyrene (a) and polyvinylchloride (b) films containing 3 wt% of the TCNQ salt 16.

temperature of solvent evaporation must be controlled. The films obtained either by casting at the slow removal rate or by heating do not show the high ϵ value. At the slow removal rate, the crystallite size tends to increase so that the film becomes conductive; by heating, the film becomes transparent. Mechanical mixing of polymers with the TCNQ salts followed by melt compounding is also much less effective.

The effect of the TCNQ-salt concentration on the dielectric properties of the film is shown in Figures 5 and 6. The dielectric constants increase with an increase in salt concentration but the dissipation factors also undergo an increase. Furthermore, increase in the salt concentration reduces the resistivity greatly so that the film becomes conductive and it is not suitable for the dielectric material.

Figure 7 shows Weibull plots of the dc breakdown data of the films containing the TCNQ salt. We can evaluate the average dc breakdown voltage of 20 and 11 kV/mm, respectively, for polystyrene and polyvinyl butyral films containing 2 wt% of the TCNQ salt 16. These values are 30% smaller than those of the films without the TCNQ salts. This may be explained by



(b)

Fig. 4. (continued)

the difference in uniformity between the homogeneous insulating matrix and the heterogeneous films containing the salt.

Conclusions

It has been demonstrated that the dielectric constants of cast films prepared from mixtures of insulating polymers and tetracyanoquinodimethane salts depend on the specific resistivities of the salts. High values were attained with the films containing high-conducting salts. A needlelike microcrystallite growth of the salts is also a necessary condition for the high ϵ value. Such microcrystallization of the salt in the film is dependent on the matrix polymer, the condition of the cast-film formation, and the salt concentration.

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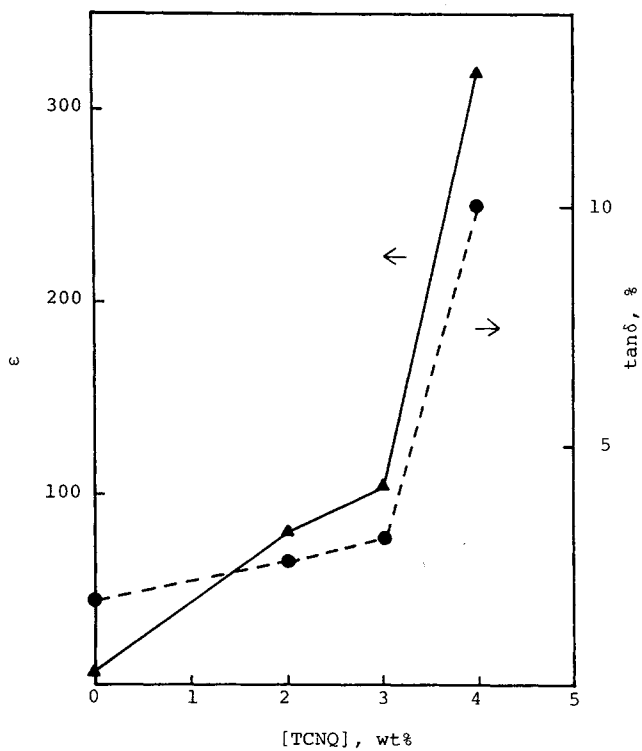


Fig. 5. Dielectric constant (ϵ) and dissipation factor ($\tan\delta$) at 1 KHz of the polyvinylbutyral film as a function of the TCNQ salt (16) concentration.

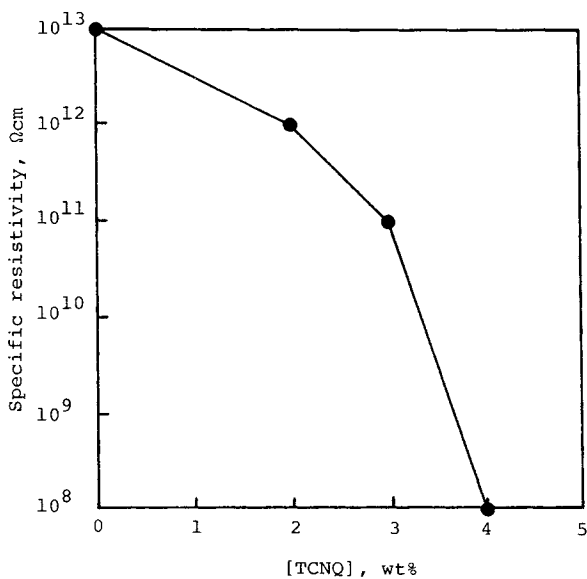


Fig. 6. Specific resistivity of the polyvinylbutyral film as a function of the TCNQ salt (16) concentration.

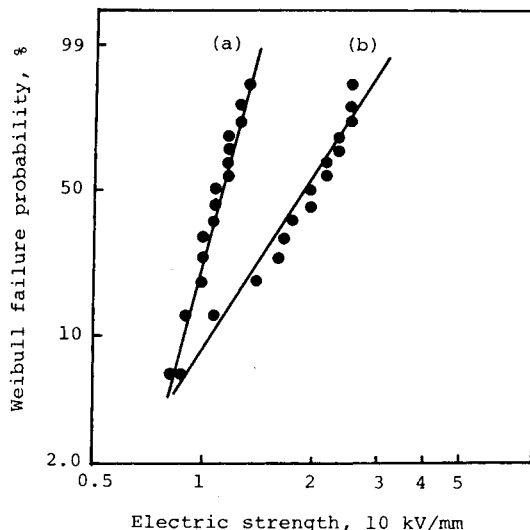


Fig. 7. Weibull plots of electric strength for the films containing 2 wt% of the TCNQ salt 16: (a) polyvinyl butyral; (b) polystyrene.

References

1. Y. Yoshida, M. Nishimatsu, S. Mukai, T. Kashiwazaki, and S. Yasufuku, CIGRE paper, 15-01 (1980).
2. G. L. Link, in *Polymer Science, Dielectric Properties of Polymers I*, A. D. Jenkins, Ed., North-Holland, Amsterdam, 1972, p. 1289.
3. C. W. Lewis and D. H. Hogle, *J. Polym. Sci.*, **21**, 411 (1956).
4. R. Rosen and H. A. Pohl, *J. Polym. Sci., A-1*, **4**, 1135 (1966).
5. R. D. Hartman and H. A. Pohl, *J. Polym. Sci., A-1*, **6**, 1135 (1968).
6. J. R. Wyhof and H. A. Pohl, *J. Polym. Sci., A-2*, **8**, 1741 (1970).
7. S. Osaki, S. Uemura, and Y. Ishida, *J. Polym. Sci., Polym. Phys. Ed.*, **9**, 585 (1971).
8. S. Ikeno, K. Matsumoto, M. Yokoyama, and H. Mikawa, *Polym. J.*, **9**, 261 (1977).
9. S. Ikeno, M. Yokoyama, and H. Mikawa, *Polym. J.*, **10**, 123 (1978).
10. M. Watanabe, N. Toneaki, Y. Takizawa, and I. Shinohara, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2669 (1982).
11. S. Dasgupta, *J. Appl. Polym. Sci.*, **22**, 2383 (1978).
12. T. Tamura, N. Ojima, and S. Kondo, *Nippon Kagaku Kaishi*, 1209 (1978).
13. S. Ikeno, M. Yokoyama, and H. Mikawa, *Polym. J.*, **10**, 231 (1978).
14. S. Ikeno, M. Yokoyama, and H. Mikawa, *Polym. J.*, **11**, 371 (1979).
15. R. E. Newnham, D. P. Skinner, K. A. Klicker, A. S. Bhalla, B. Hardiman, and T. R. Gururaja, *Ferroelectrics*, **27**, 49 (1980).
16. P. M. Lenahan and T. J. Rowland, *Solid State Commun.*, **27**, 223 (1981).
17. A. A. Gogolin, *Solid State Commun.*, **45**, 361 (1983).
18. S. Mukai, O. Yamaguchi, M. Kanba, and H. Kita, Proceedings of Annual Meeting of the Institute of Electrical Engineers of Japan, No. 369, p. 423 (1983).
19. D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).
20. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).
21. S. Araki, H. Ishida, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 407 (1978).
22. S. Araki and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 1311 (1978).
23. Y. Yumoto, R. Nishioka, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **53**, 1247 (1980).
24. Japanese Industrial Standards, JIS-C-2330.
25. R. W. Sillars, *J. Inst. Elec. Eng.*, **80**, 378 (1937).

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