INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

MACROMOLECULAR DIVISION
COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES
WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

STRUCTURE AND DIELECTRIC PROPERTIES OF VINYLIDENE FLUORIDE COPOLYMERS

Prepared for publication by

Y. KUBOUCHI[1], Y. KUMETANI[1], T. YAGI[1], T. MASUDA[2]
and A. NAKAJIMA[3]

[1]Daikin Industries Inc., Osaka 566, Japan
[2]Research Center for Medical Polymers and Biomaterials, Kyoto University, Kyoto 606, Japan
[3]Osaka Institute of Technology, 5-16-1 Ohmiya, Asahi-ku, Osaka 535, Japan

for the East Asia Sub-Group

Chairman: A. Nakajima; *Secretary*: T. Masuda; *Members*: C. R. Choe; A. Furumiya; T. Hayashi; M. Isshi; B. Jiang; J. C. Jung; C. Y. Kim; S. C. Kim; H. Kiuchi; Y. Kometani; H. Kondo; Y. Kubouchi; J. Li; N. Nagata; K. Nakayama; T. Ohmae; R. Qian; S. Shimotsuma; S. Suzuki; S. Tsuchiya; L. Wu; A. Yoshioka

Structure and dielectric properties of vinylidene fluoride copolymers

ABSTRACT: Molecular chain structures of vinylidene fluoride (VDF)/trifluoroethylene (TrFE) copolymers were investigated by high resolution ^{19}F NMR. It was found that the arrangement of comonomers in the VDF/TrFE copolymer chain is statistically random, and the head-to-tail connection of monomer units is predominant. The experimental results on DSC, MNR and X-ray diffraction indicated that copolymer chains are in isomorphically crystalline state in the whole range of copolymer compositions. In particular, 50-80 mol% VDF copolymers shows a ferroelectric character associated with a strong remanent polarization at room temperature. In addition, these copolymers exhibit a crystal phase transition associated with appearance of an anomalous specific heat peak, abnormal peak of dielectric constant, and disappearance of remanent polarization. These results are consistent with the fact that VDF/TrFE copolymers are ferroelectric. The dielectric constant ε' of 55 mol% VDF copolymer is 18 at 1 KHz and 24°C. The d_{31} piezoelectric constant of a roller-elongated 55 mol% VDF copolymer is 51 pC/N at 11 Hz and 24°C. The electromechanical coupling factor k_t of 75 mol% VDF copolymer in the thickness direction is 0.3. The pyroelectric constant of 55 mol% VDF copolymer is 50 x10^{-5} C/M^2 K. Accordingly, VDF/TrFE copolymers can have wide range applications as transducers.

INTRODUCTION

The principal general value of studying fluoropolymers is their great variability in properties that can be achieved. The discovery of poly (tetrafluoroethylene) (PTFE), which is still the most chemical inert and thermally stable polymer known, led to wide-spread research for other fluoropolymers possessing similar outstanding chemical and physical properties (ref. 1,2). Since then, many fluoropolymers have been prepared, and many of these materials have reseived attention widely in both chemical and physical aspects because of their superior or unique properties. For example, poly (chlorotrifluoroethylene) (PCTFE), poly (vinylidene fluoride) (PVDF), tetrafluoroethylene(TFE) / hexafluoropropylene copolymer (FEP), TFE/ethylene copolymer(ETFE) and TFE/perfluorovinylether copolymer(PFA) were commercialized as thermally stable and chemically inert polymers. On the other hand, some fluoropolymers have shown special properties as functionalized polymers. In particular, PVDF has drawn attention as a new transducer material due to its interesting piezoelectric and pyroelectric properties when the polymer film has been drawn and poled (ref. 3,4). In 1970's, PVDF was only a potential material to be practically applicable as a piezoelectric and pyroelectric polymer (ref.5). PVDF is characterized by such properties as flexibility, toughness, light weight, easy proccessability to large area thin films, and low acoustic impedance. Most of these properties, which are typical for polymeric materials, sharply contrast with ceramic material properties.

This paper concerns the molecular structure, electrical properties and applications of VDF/trifluoroethylene (TrFE) copolymers.

EXPERIMENTAL

Materials

PVDF, VDF/TrFE copolymers and poly (trifluoroethylene) (PTrFE) were prepared by the free radical polymerization at 22°C using 3,5,6-trichloroperfluorohexanoyl peroxide as initiator. Polymerization was stopped at low conversion, under 20% so as to estimate the polymer composition. The polymer composition was determined by carbon element analysis. Three kinds of polymer films were prepared as follow:
(1) Melt-cast film. Extruded or hot-pressed at 250-260°C.
(2) Solvent-cast film. Cast from methylethylketone (MEK), and N,N,-dimethyformamide (DMA).
(3) Roller-elongated films. First the polymer powder was rolled at 200°C to prepare a
    pre-rolled film. Then, this film was rolled at 120°C.
For electrical properties measurements, aluminum electrodes were obtained on both surfaces of the film, by vaporization in vacuum.

Measurements

Carbon analysis was undertaken with a Yanako C,H,N-Coder, Type2. Thermal analysis was performed with a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of 10°C/min. Aluminum pans were used as sample containers and each specimen weight was 10 mg. High resolution ^{19}F NMR spectra were measured with a Hitachi R-42 Spectrometer at 35°C in DMA for PVDF and in acetone for VDF/TrFE copolymers and PTrFE, using α, α, α,-trifluorotoluene (BTF) as the internal reference. Wideangle X-ray diffraction profiles were obtained with a Rigaku-Denki RAD-rA diffractometer. Infrared spectra were measured by a Japan-Spectroscopic IR-G Spectrometer.

Dielectric measurements were performed with a LCR meter (type 4274A, Hewlett Pakard). Piezoelectric constant d_{31} and elastic constant C_{11} were measured by a Toyo Baldwin Reovibron DDV-III-EA. Pyroelectric constant was obtained by measuring a change in total charges on the electrodes due to an increasing or decreasing temperature. Polarization switching properties were measued by the Sawyer-Tower method using triangular electric field (ref.6). Frequency and electric field strength used were 3-6 mHz and 60-100 MV/m, respectively.

RESULTS AND DISCUSSION

Molecular chain structure

The molecular chain structure was studied from the monomer reactivity ratios and high resolution ^{19}F NMR measurements.

The monomer reactivity ratios for VDF/TrFE copolymerization obtained are r_1(VDF)=0.7 and r_2 (TrFE)=0.5. If $r_1 > 1$,a growing polymer radical p_1 prefers to add monomer M_1, whereas if $r_1 < 1$,p_1 prefers to add monomer M_2. The condition $r_1 r_2 = 1$ is defined as an "ideal copolymerization" and gives a random copolymer (ref. 7). The condition $r_1 = r_2 = 0$ implies that each of the radical $p_1\cdot$ and $P_2\cdot$ can react only with the oppsite monomer and leads to an alternating copolymer. The case in which r_1 and r_2 are both greater than 1 implies that the monomer tends to homopolymerize simultaneously, and leads to a block copolymer. Thus the results obtained indicate that the arrangement of comonomers in VDF/TrFE copolymer chain is of random structure.

The 84.5 MHz high resolution ^{19}F NMR spectra in $-CF_2-$ region are shown in Figure 1. THe main resonance peaks in VDF/TrFE copolymer and PTrFE are assigned by applying the same method as Wilson and Santee used in PVDF ^{19}F NMR analysis (ref.8).

It was found that VDF/TrFE copolymer had a statistically random configuration. The NMR results also imply that head-to-tail sequence in the copolymer chain is predominant:i.e., 90% VDF/VDF dyad, 75% VDF-TrFE of TrFE-VDF dyad and 50% TrFE-TrFE dyad. The percentages of head-to-tail and of head-to-head structures are of particular importance in PVDF and VDF/TrFE copolymers, because those affect the crystallization and properties of the polymer.

As VDF/TrFE copolymers were prepared by the radical polymerization method, the tactic defect may be unavoidable. However, quantitative analysis of the tactic defect is not available from the NMR data.
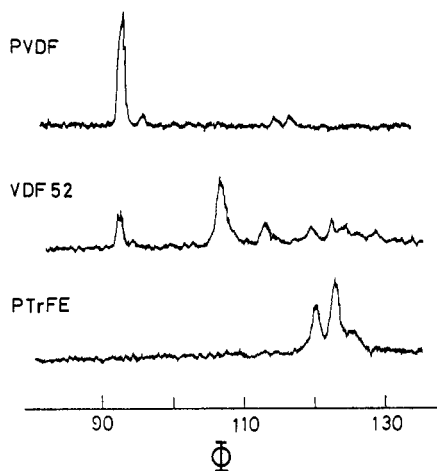

Figure 1. 84.5 MHz high resolution ^{19}F NMR spectra of VDF/TrFE copolymers in $-CF_2$-region, measured at 35°C in N,Ndimethylformamide for PVDF and in acetone for VDF/TrFE copolymers and PTrFE. Benzotrifluororide is used as internal reference. Chemical shift is expressed by adding 63.7 ppm to each original value.
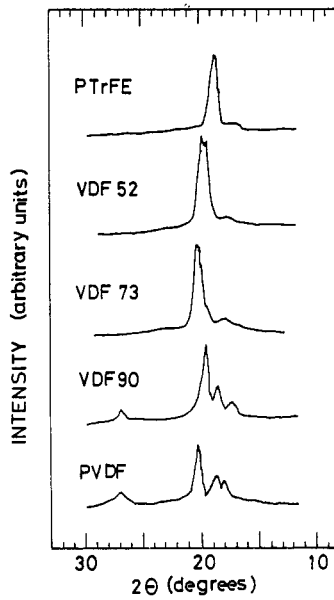
Figure 2. X-ray diffraction profiles
of VDF/TrFE copolymers.

Isomorphism

Figure 2 shows the X-ray diffraction profiles of VDF/TfFE copolymers. All the samples were
prepared by the melt cast method. The diffraction peaks arising from the crystal phase are
observed clearly in the whole range of polymer compositions. Figure 3 shows the DSC curves
of VDF/TrFE copolymers. Figure 4 shows the change of melting temperature with polymer
compositions. (Part of the data is reproduced from Figure 3.) All the data were taken from
the second run measurement. As is seen in the figure, the endothermic peak of primary
melting was observed clearly in the whole range of polymer compositions. These X-ray and
DSC results indicate that VDF/TrFE copolymers are in the crystalline state in the whole
range of polymer compositions. As the comonomer arrangement in VDF/TrFE copolymer chain is
random, this copolymer crystallizes isomorphically. The isomorphism is very special, because
mostly the introduction of the second component causes a sudden reduction of the
crystallinity in copolymerization (ref.9). The X-ray diffraction fiber patterns of the
copolymer (not shown here) were also measured, which indicated that the copolymer crystal
is very disordered.

In addition to the main melting peaks in the DSC measurement, other peaks are observed in
50-80 mol% VDF copolymer. These phase transition peaks will be discussed in the following
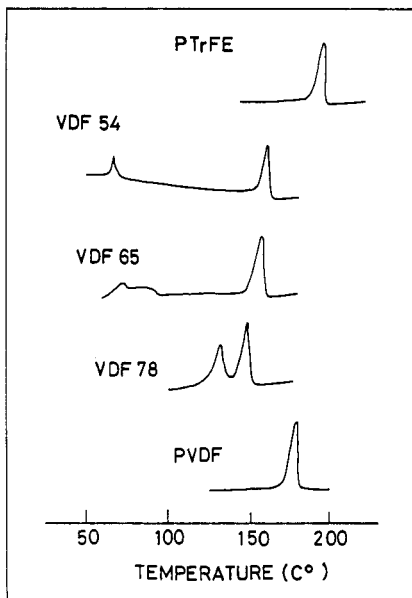section.
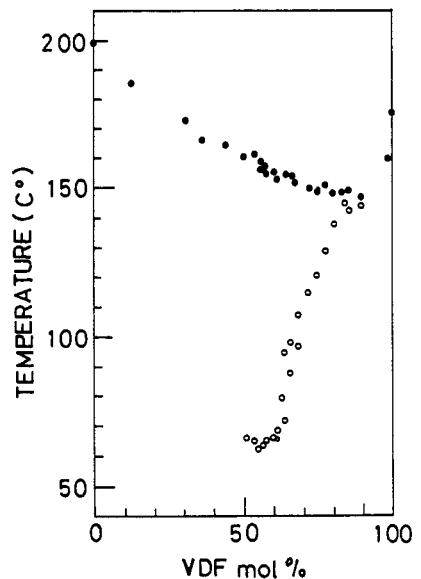

Figure 3. DSC thermogrames of VDF/TrFE
copolymers.

Figure 4.Change of melting temperature
and phase transition temperature with
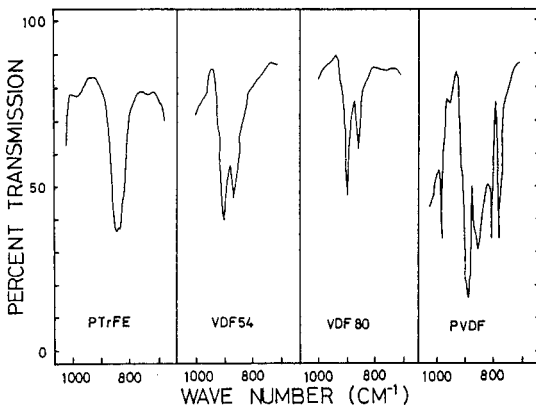polymer composition.

Figure 5. Infrared spectra of VDF/TrFE copolymers.

Crystal structure

Figure 5 shows the infrared spectra of VDF/TrFE copolymers in the 650-1050 cm^{-1} region. The sample specimens were melt cast similar to those for X-ray measurements. Both infrared and Xray results indicate that PVDF and the copolymers including more than 85 mol% VDF take a trans-gauche-trans-gauche' (TGTG') conformation in the indivisual chain arranged to yield a centrosymmentric unit cell (α-form crystal in PVDF classification) (ref. 10,11). Accordingly, this crystal is nonpolar. The 50-80 mol% VDF copolymers take all trans conformation (planar zigzag) in crystal. All the chains are oriented essentially parallel to the b axis of the unit cell with dipole pointing in the same direction, resulting in a noncentrosymmetric crystal (β-form crystal in PVDF classification) (ref. 10,11). Thus, the crystal is polar. The β-form crystal is currently most important in PVDF and VDF/TrFE copolymers, being used extensively in piezoelectric and pyroelectric application(ref.5). In order to obtain the β-form crystal from PVDF and VDF-rich copolymers from melt cast or extruded films, these must be drawn at low temperature (ref.12). PTrFE and the copolymers including less than 45 mol% take helical conformation in crystals.

Dielectric properties

Figure 6 shows the change of the dielectric constant ε' with polymer composition of VDF/TrFE copolymers, measured at 1 KHz and 24°C. As seen from the figure, ε' takes a maximum at 55 mol% VDF content. The numerical value is 18 and approximately two times higher than that of PVDF. The high value of the dielectric constant of the copolymer, especially of composition around 55 mol% VDF, is considered to arise from (1) large magnitude of dipole moment of repeating units of both VDF and TrFE monomers (VDF units is 1.96 Debye and TrFE unit is 1.63 Debye (ref. 13)), (2) predominant head-to-tail connection of units as NMR results indicated, (3) freedom of the dipole rotation in the electric field because the glass transition temperature is observed at around -20°C (ref.14), and (4) nature of ferroelectricity. In a ferroelectric polymer, crystal phase will be also related closely to the large dielectric constant. Experimentally the dielectric constant of 50-80 mol% VDF copolymer increases with increasing annealing time at high temperature of 100-140°C. Figure 7 shows the change of the dielectric constant of 54 mol% VDF copolymer with temperature, measured at 1 KHz. It shows an abnormal peak at 70°C. This kind of abnormal peak also was observed for 50-80 mol% VDF copolymers. These peaks are exactly corresponding to the DSC peak of the phase transition.
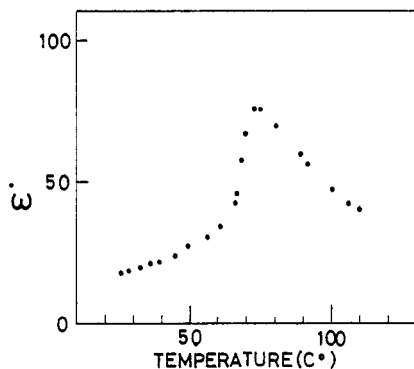

Figure 6. Change of dielectric constant ε' with polymer composition in VDF/TrFE copolymers at 1KH an 24°C.
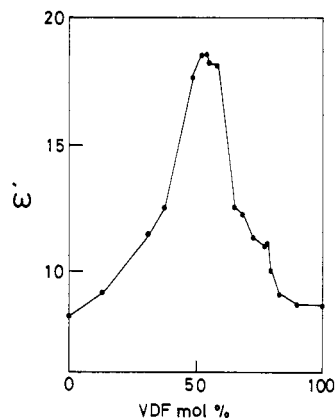

Figure 7. Change of dielectric constant ε' of 54 mol% VDF copolymer with temperature at 1KHz.
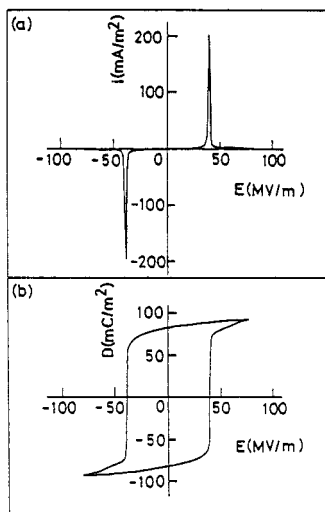
Figure 8. Polarization reversal current (a) and electrical displacement-electric field hysteresis loop (b) for 75 mol% VDF copolymer at 24°C. The loop is obtained by integrating reversal current.

Ferroelectricity

Figure 8 illustrates the polarization current (a), and the dielectric displacement (b), as functions of the electric field measured by the Sowyer-Tower method (ref. 6) under a triangular electric field of 80 MV/m at 5mHz and 24°C. The clear polarization reverse current and ferroelectric hysteresis loop indicate that the copolymer is a ferroelectric material. The intersections of the hysteresis loop with X and Y axis give the coersive field Ec and the remanent polarization Pr' respectively. Figure 9 shows the change of the remanent polarization of 75 mol% VDF copolymer with temperature. The remanent polarization disappears at 120°C, which is exactly the same transition temperature observed in both DSC and dielectricity measurements. It indicates clearly that this is a ferroelectric transition.

Figure 10 shows the temperature dependence of $1/\varepsilon'$ for 54 mol% VDF copolymer, measured at 1 KHz. Data was reproduced from Figure 7. This plot is the so-called "Curie plot". For a ferroelectric material, the experimental data can be fitted to the following equation.

$$1/\varepsilon' = (1/C)(T-Tc) + \alpha_0 \qquad (1)$$

where Tc and C are phase transition temperature and the Curie constant, respectively, and α_0 is a constant. As seen from the figure, there is a linear relation between $1/\varepsilon'$ and temperature below and above Tc. This result confirms that the phase transition is associated with a ferroelectric transition.
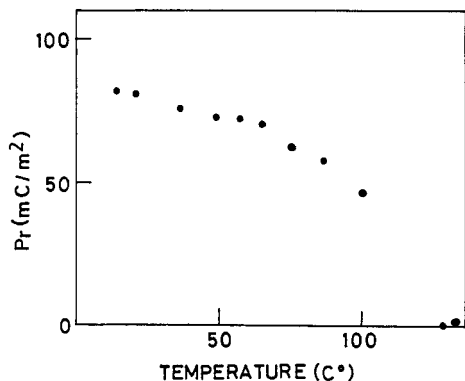

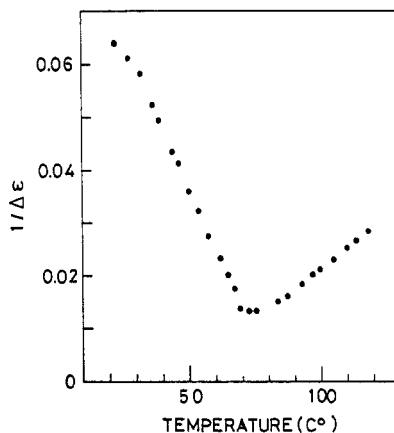Figure 9. Change of remanent polariation of 75 mol% VDF copolymer with temperature.

Figure 10. Temperature dependence of $1/\varepsilon'$ for 54 mol% VDF copolmer, measured at 1KHz. Data is a reproduction from Figure 7.
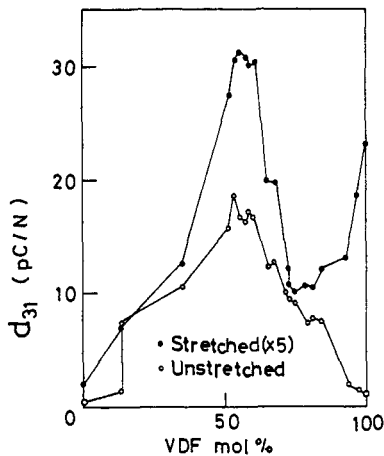
Figure 11. Change of d_{31} piezoelectric constant with polymer composition of VDF/TrFE copolymer at 11Hz and 24°C.
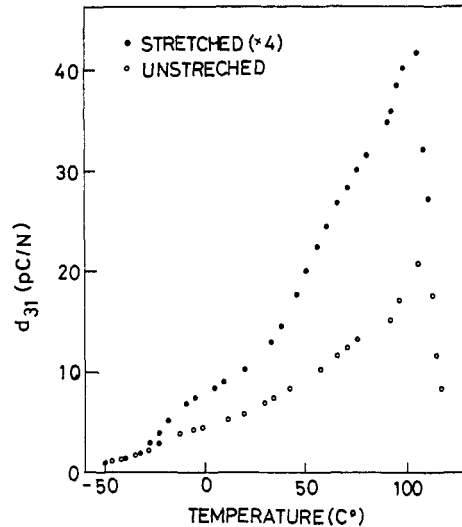

Figure 12. Change of d_{31} piezoelectric electric constant of 75 mol% VDF copolymer with temperature at 11 Hz.
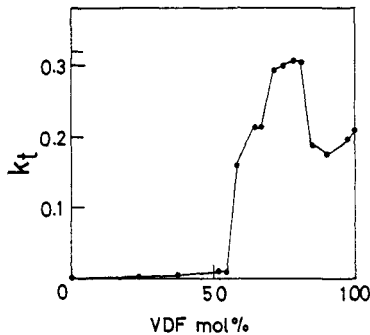

Figure 13. Change of electromechanical coupling factor k_t in thichness direction with polymer composition of VDF/TrFE copolymer at 24°C.

Piezoelectric and pyroelectric properties

Figure 11 shows the change of the d_{31} piezoelectric constant with the polymer composition, measured at 11 Hz and 24°C. Samples were prepared from MEK or DMA solution by the cast method. The stretched films were obtained by elongation the solvent cast films by five times of the original length. The poling conditions are 80-120°C, 30-80 MV/m and 1 hour. As seen in Figure 11, the stretching proccess enlarges the piezoelectric constant by about 1.7 times the value of the unstretched sample, for 55 mol% VDF copolymer. Both stretched and unstretched samples of 55 mol% VDF copolymer exhibit maximum d_{31} piezoelectric constants. The numerical values of d_{31} constant are 19 pC/N for unstretched sample and 32 pC/N for stretched sample, which appear to be larger than those of PVDF. It should be noticed that in the case of VDF/TrFE copolymers large piezoelectric constants can be obtained even for

unstretchen films and so the polarized films having an isotropic piezoelectricity of $d_{31} = d_{32}$ could be obtained. This is a big difference compared to the case of PVDF. In particular, the d_{31} constant of the roller-elongated film of 55 mol% VDF copolymer, poled at 120°C, 40 MV/m and 30 min, reaches a value of 51 pC/N (11Hz). To our knowledge, this is the largest value ever attained for a polymeric material.

A 75 mol% VDF copolymer takes a minimun value of d_{31} constant in stretched samples. As d_{31} constant is given by

$$d_{31} = e_{31} / G_{11} \qquad (2)$$

where e_{31} is the piezoelectric stress constant and G_{11} is the tensile modulus, the small value of d_{31} constant in stretched VDF 75 mol% copolymer is due to the large G_{11} compared with those of PVDF and 55 mol% VDF copolymer, while e_{31} constant is almost unchanged in those samples.

Figure 12 shows the temperature dependence of d_{31} piezoelectric constant of the 73 mol% VDF copolymer for both unstretched and four times stretched films. The poling conditions were 80°C, 30MV/m and 1 hour. As is seen in the figure, the d_{31} piezoelectric constant increases with increasing temperature, and decreases rapidly above the Curie point. Curie point is also the transition temperature from piezoelectric to non-piezoelectric state.

Figure 13 shows the change of the electromechanical coupling factor k_t in the thickness direction with temperature for VDF/TrFE copolymer, measured at 24°C. The 75 mol% VDF copolymer takes a maximun value of k_t=0.3.
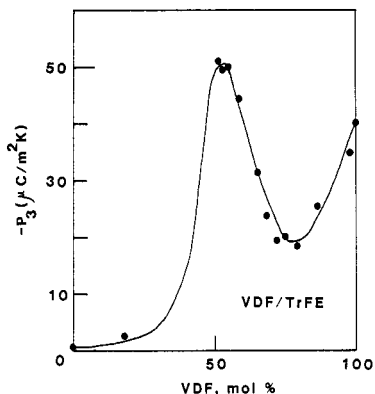
Figure 14. Change of pyroelectric constant with polymer composition at 24°C.

Figure 14 shows the temperature dependence of the pyroelectric constant of VDF/TrFE copolymer, measured at 24°C. A maximum value of $50 \times 10^{-5} C/M^2 K$ is obtained for 55 mol% VDF copolymer.

To summarize the electrical properties of VDF/TrFE copolymers, 55 mol% VDF copolymer exhibites a very large dielectric constant, a very large d_{31} piezoelectric constant, and a very large pyroelectric constant at 24°C. On the other hand , ca. 75mol% VDF copolymer provides a very strong piezoelectricity in the thickness direction at 24°C.

Table I. Applications of VDF/TrFE copolymers

Audio frequency transducer	Headphone
	Tweeter speaker
	Telephone transmitter
	Medical sensor
	Acceleometer
Ultrasonic transducer	Hydrophone
	Ultrasonic medical transducer
Electromechanical transducer	Typewriter and keyboard
	Pressure sensor
	Telephone dial
	Impact detector
Pyroelectric devices	Infrared detector
	Pyrovidicon
	Laser calorimeter

APPLICATIONS

The most important applications of VDF/TrFE copolymers are in the general catagory of transducers. The unique combination of piezoelectric (as well as pyroelectric) and mechanical properties may provide this copolymer with major advantages over ceramic transducers. The piezoelectric and pyroelectric applications of VDF/TrFE copolymers are summarized in Table I(ref.5).

REFERENCES

1. P.J.Plunkett, U.S. Patent 2,230,654 (1941).
2. L.A.Wall, "Fluoropolymer", Wiley-Linterscience, (1972).
3. H.Kawai, Japan J. Appl. Plys.,8, 975 (1969).
4. Y. Wada and R. Hayakawa, Japan J. Appl. Phys.,15, 2041 (1976).
5. G.M.Sessler, J. Acoust. Soc. Am., 70, 1596 (1981).
6. T. Furukawa, M. Date and E. Fukada, J. Appl. Phys., 51, 1135 (1980).
7. M.Fineman and S.D. Ross, J. Polym. Sci., 5, 259 (1950).
8. C.W. Wilson, III and E. R. Santee, Jr., J. Polym. Sci., PartC, 8, 97 (1965).
9. L. Manderkern, "Crystallization of Polymers", MacGraw-Hill, New York, (1964).
10. R. Hasegawa, Y. Takahashi, T. Chatani, and H. Tadokoro, Poly. J. 3, 600 (1972).
11. A.J.Lovinger, "Developments in crystlline polymers-I", ed., D.C. Bassett, Applied Science Publishers, 195 (1982).
12. J.B. Lando and W.W.Doll. J. Macromol. Sci., Phys., 2, 205 (1968).
13. T. Yagi, Polym. J., 11, 711 (1979).
14. T. Yagi, M. Tatemoto and J. Sako, Polym. J., 12, 209 (1980).