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The properties and applications of fluorine-containing polymer films with piezo- and pyro-activity

V V Kochervinskii

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Abstract. Polymer films based on poly(vinylidene fluoride) and its copolymers, which exhibit piezo- and pyro-electric properties after appropriate treatment, are described. The principal advantages of materials of this class include high values of the piezomoduli, which permit their practical use. Another valuable property, which is difficult to achieve in inorganic materials, is the wide range of frequencies over which the given active element can operate. The possibility of achieving large areas and fairly simple methods of preparation of thin films also leads to the assignment of the above polymers to the category of promising materials for the creation of new classes of recording devices. The trends in the development of new instruments based on these materials, where use is made of the phenomenon of photopyroelectric activity, are demonstrated. The advantages of using these materials for medical techniques are noted. The flexibility of the film and its acoustic impedance, which is close to that of a biological tissue, as well as the properties noted above place it beyond competition with other materials. Furthermore, the ferroelectric nature of the above polymers makes them promising for use in nonlinear optics. The bibliography includes 89 references.

I. Introduction

In the search for new materials to be used in energy converters, Kawai[1] observed in 1969 intense piezoelectricity in poly(vinylidene fluoride) (PVDF). Vigorous investigation of this phenomenon began afterwards. There have been numerous individual communications and fairly detailed reviews (see, for example, Refs. 2–5), where certain current established ideas concerning the mechanisms of piezo- and pyro-activity of the given class of polymers are described. The principal results reduce to the fact that the nature of the piezo-effect is not unique. It has come to be assumed that three phenomena contribute to the magnitude of the piezoelectric response: (1) the piezo-effect in the classical sense, which requires the presence of noncentrosymmetric crystals, (2) electrostriction (which has been very little investigated in polymers), and (3) the dimensional effect, which takes into account the change in volume on deformation resulting in a change in polarisation. The contributions of these effects to the macroscopic response may vary according to the results of different workers. Poly(vinylidene fluoride) and its copolymers belong to the class of flexible chain crystallisable polymers characterised by a low glass point (−40 °C). In the initial (isotropic) state, the material has the texture of a polycrystalline substance in which the crystallites (with a volume fraction of 0.4–0.5) have a random orientation. After averaging over a fairly large volume, this is equivalent to the presence of an effective centre of symmetry in this system, and the material does not exhibit piezo- and pyro-activity. Such activities are induced by treating the film with a high-frequency field.

It has been established[6] that the above polymers are ferroelectric and that the principal coefficients of piezo- and pyro-activity are linear functions of the residual polarisation P_r. The relation between the ferroelectric characteristics of the crystallisable polymers and their structure has been poorly elucidated and much that is obscure still remains to be solved. In particular, the role of the amorphous or mesomorphic phases in ferroelectric phenomena is not understood. Such phases are frequently represented by an inert matrix in which the crystals of the polar (β) and nonpolar (α) phases are immersed. There is no doubt that the contributions of these liquid-like phases (their fraction may reach 0.7) is by no means trivial. The influence of the characteristics of the nonordered region both on the quantity[7] P_r and on other piezoelectric constants[8] may serve as evidence for this. Data[9,10] concerning the influence of small irradiation doses (whereupon the changes refer mainly to the nonordered phase) and the ferroelectric properties of PVDF also confirm the above idea. Films of PVDF and its copolymers, obtained for practical purposes, are usually uniaxially extended. The role of the extension cannot be reduced solely to the method for the conversion of the polymorphic α-form into the β-form, although a decrease in coercive fields and an increase of P_r on polarisation have in fact been noted under these conditions.[11]

Experiments involving stretching the films crystallising immediately in the piezoactive β-phase[8–12] indicate that the piezoresponse and the ferroelectric characteristics in textured films are more pronounced and that the ultimate procedure for the latter is the creation of the 'ideal single crystal' texture. The above series of studies[8–12] indicate that the piezo- and pyro-effects in these compounds are dipolar in nature, although there is no doubt that here one should take into account the contribution of the space charge generated by the injected carriers in high polarisation fields. Under the usual conditions (at room temperature, normal pressure), the nonordered phase in the above polymers is in the highly elastic state and its pliability is an order of

V V Kochervinskii Division of Pulse Energetics, Troitsk Institute for Innovations and Thermonuclear Research, 142 092 Troitsk, Moscow Region, Fax (7-095) 334 57 76

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magnitude higher than that of the crystal. Thus, when such polymers are acted upon by a mechanical (acoustic) perturbation, the phase exhibits a local response (while the specimen as a whole exhibits a macroscopic response). The high mobility of the chains in the amorphous phase ensures their response to the thermal perturbation in the observation of the pyroeffect.

The difficulty of creating a rigorous molecular model of the above noted phenomena in such polymers is partly associated with the absence of ideas, worked out in all their details, concerning the structure of textured crystallising polymers. One may, for example, take the view that simplified ideas concerning the two-phase nature of the crystallising polymers do not help to elucidate the true mechanisms of the piezo- and pyro-response in PVDF and its copolymers. The lack of true (in the thermodynamic sense) interfaces between the ordered and amorphous phase can create a qualitatively new situation in the description of the mechanisms of the piezo- and pyro-responses in such polymers. In particular, attention has been drawn recently to the fact that the strained chains, passing through the amorphous phase and connecting neighbouring crystallites, play a special role in the response of textured crystallising polymers to the electric field.[7] In the vicinity of the interface between the above phases, which exists in a partially ordered (mesomorphic) state, the chains also behave in an unusual manner on exposure to an acoustic or thermal perturbation. This hypothesis is supported indirectly by data demonstrating an increase in the acoustic modulus and in the double refraction on deformation of textured films of the copolymer of vinylidene fluoride and tetrafluoroethylene.[8] Direct evidence for this was obtained by the X-ray diffraction method.[13] A change in the form of the azimuthal distribution of the 110 and 200 reflections after the immersion of the film was noted and was treated from the standpoint of reversible paraelectric $\rightleftarrows$ ferroelectric transitions when these phases coexist. The VDF homopolymer, a characteristic feature of which is reversible changes in crystallinity during the observation of the pyroeffect, behaves similarly.[14]

As stated in the Introduction, the mechanisms of the piezo- and pyro-effects in the compounds of the class considered are insufficiently clear. The very extensive experimental data available on this question need to be surveyed separately. Despite this, compounds of the given class have been most thoroughly investigated as regards their practical application. The aim of the present review is therefore to draw the readers' attention to branches of engineering where the given polymers are already used as the active element in the finished primary energy converters. The discovery of specific properties of the polymeric materials which make it possible to devise instruments with novel characteristics is emphasised.

Piezo- and pyro-coefficients which enable the above compounds to compete seriously with traditional piezoceramic materials have been reported in the latest communications. Thus PVDF films with the piezocoefficient $d_{31} = 60$ pC N^{-1} and the pyrocoefficient $p = 6$ nC cm^{-1} K^{-1} have been obtained by a modification of the polarisation method.[15] Table 1 presents a comparison of a series of characteristics of films of PVDF and of its copolymer with trifluoroethylene (TrFE) with the analogous characteristics of quartz and the PZT-4A ceramic.[16, 17]

The choice in favour of the above materials may be dictated by a series of their specific properties and advantages. These include the following: (1) the existence of an effective technology (here one can use the equipment already available for the manufacture of polymeric film materials); (2) the possibility of achieving high areas of the active elements, which permits the construction of second generation sensors;[18] (3) a wide transmittance band (a realistic specification is 0–500 MHz), which is required in diagnostic systems;[19,20] (4) the closeness of the acoustic impedance of PVDF to that in human tissue and water, which is used in the construction of sensors for medical diagnostics; (5) the high impact strength of polymer films (this quality of PVDF is used in shock wave sensors); (6) the high corrosion stability of PVDF (this property becomes essential for work involving reactive media); (7) the low relative permittivities of the materials ($\varepsilon' = 10-14$) and the correspondingly higher values (almost by an order of magnitude and above) of the piezoconstant g and the pyrosignal (p/ε') sensitivity; (8) the lower thermal conductivity of PVDF compared with the piezoceramic and the possibility of obtaining thin films (one micrometer and less), which ensures a higher transverse resolution in the analysis of the spatial separation of the incoming electromagnetic radiation; (9) the possibility of imparting to the material an arbitrary form (cone, self-supporting dome, etc.), which makes it possible to produce elements with unusual forms of directional emission.

Table 1. Comparative characteristics of piezo- and pyro-electric materials.[16–19]

Characteristic	Material			
	PVDF	PVDF/TrFE	Quartz	PZT-4A
Density, ρ/g cm^{-3}	1.78	1.88	2.65	7.5
Velocity of sound, v/km s^{-1}	2.25	2.40	5.7	4.63
Acoustic impedance, $Z = \rho v/10^6$ kg m^{-2} s^{-1}	4.02	4.51	15.1	34.8
Modulus of elasticity, C_{33}/GPa	9.1	11.3	86	159
Electromechanical coupling coefficient, k_t	0.2	0.3	0.1	0.51
Piezoconstants:				
d_{31}/pC N^{-1}	60	25	–	–
g_{31}/V m N^{-1}	0.18	0.16	–	–
e_{33}/C m^{-2}	0.16	0.23	0.17	15.1
g_{33}/V m N^{-1}	0.32	0.38	0.05	0.017
Relative permittivity, ε'	12	20	4.6	625
Pyroelectric coefficient, p/nC cm^{-2} K^{-1}	6	–	–	38
Pyroelectric Q factor (p/ε')/nC cm^{-2} K^{-1}	0.5	–	–	0.061

II. Technical applications of poly(vinylidene fluoride) and its copolymers

A number of devices are described below in which the above qualities of the materials under considerations are actually employed. One of the most important properties is the presence in films of PVDF and its copolymers of longitudinal and transverse piezoeffects, which is used in the construction of headphones and high-frequency speakers. The possibility of using such films in piezoelectric piano-key switches and in the receptor sensors of electric pianos has been demonstrated.[17]

Piezoelectric polymer films are most widely used as bimorphic elements consisting of two combined films. By virtue of the elasticity of the polymeric materials, high vibration amplitudes are achieved in the bimorphic elements. As early as 1981, the Kodak company reported the development on the basis of PVDF of bimorphic elements operating under the conditions of the reverse piezoeffect and generating high-amplitude low-frequency vibrations.[21] Bearing in mind the low density and high pliability of the PVDF piezofilm, it was possible to achieve on the latter, under the conditions of the same fixing geometry, parameters of the excited bending vibrations approximately twice as high as on traditional materials such as $BaTiO_3$ and PZT.[21] An attempt has been made recently to use this property in displays, small pumps, light switching devices, etc.[22]

Because of the flexibility of the polymer films, completely new aspects of their application arise under these conditions. For example, it has become possible for the first time to focus sound waves. Thus standing concentric ultrasonic waves have been

achieved in water (with a frequency of 10 MHz) with the aid of PVDF [23] and have been recorded from the diffraction of light. Piezoelectric speakers, the operation of which is based on the transverse piezoeffect, have already become commercially available. Sound waves arise in them as a result of the bending movements of the polymer membrane.[24] A spherical emitter with a unique directional diaphragm has been constructed from PVDF.[25] PVDF is a suitable material for use in pressure measuring devices, for example, in presses operating in the quasi-static region, and also as a pressure switch in various switching devices.[24]

Bearing in mind that polymeric piezoelectric elements have a low Q factor, it is possible to generate short pulses with a low reverberation. This property ensures the wide-band characteristics of these materials, noted above, which has been used to construct an ultrasonic spectrometer for the simultaneous measurement of the absorption and velocity of ultrasound over a wide frequency range. For example, it has been possible to obtain with its aid information about the mechanisms of the phase transition in liquid crystals from the nematic state to the isotropic phase.[26,27] The changes in strongly frequency-dependent properties can be inferred from the analysis of the form of a single pulse. The principle of this measurement was proposed a long time ago, but its practical realisation became possible only after the appearance of polymeric piezoelectric converters with wide-band characteristics. Yet another advantage of materials based on PVDF is the possibility of creating very small sensors, which are used, for example, in the study of the elastic characteristics of certain superconductors and their anomalies in the region of transitions.

Taking into account the wide-band property of the converters considered, it has been suggested [28] that they be used to estimate all the components of the elasticity tensor in an anisotropic body. The possibilities of the methods were tested on quartz crystals. A satisfactory agreement was found between the elastic constants obtained by this method and those measured by other procedures.

Among the new applications of piezoelectric polymers, mention should be made of their use in the stereospecific vision sensors in robots,[27] in field sensors where the optical fibres are coated by the piezoelectric polymer,[29] and also in sonic pressure sensors of a hybrid type consisting of layers of the piezopolymer and semiconductor in direct contact.[30] Digital signals can be converted directly into sound signals in digital speakers based on piezoelectric polymers.[31]

The possibility of creating sensors (in the form of an elastic body), one of the elements of which is a piezoelectric PVDF film, has been discussed.[32] The mechanical stresses developing as the sensor moves along the object generate a charge on PVDF. The available mathematical procedure makes it then possible to estimate the rate of sliding of the sensor along the object and its coefficient of friction respectively from the real and imaginary components of the signal arising on PVDF. PVDF piezofilms can be used to create a gas sensor, the resonance parameters of which in the torsional and bending modes depend on the composition of the binary gas (SF_6 + air) and on its pressure. It has been found that, although such a sensor is less sensitive than the sensor based on silicon resonators, it can compete with other sensors. The possible region of application is in the monitoring of binary gas mixtures with known components.[33]

PVDF-based piezofilms are also used to combat deposits arising from microorganisms on the bottoms of ships. The film operates under the conditions of the reverse piezoeffect where the supplied electrical energy is transformed into the vibrational energy of the surface. The film adheres to the surface in contact with the aqueous medium. Here it has been noted that the control panel (without the piezofilm) becomes fully covered by microorganisms after only 2 months, whereas the panel with PVDF, on which vibrations developed (at a frequency of 5 kHz for a 0.05 g level), remained completely clean even after 5.5 months.[34]

Because of the ability of PVDF to be moulded into any shape, one can use it to construct ultrasonic converters and hydrophones with a spherical or needle-shaped receiving surface.[35] The high flexibility of the PVDF films makes it possible to construct sensors that can be used to estimate the nature of the air stream in aerodynamics. It has been shown that such sensors are fairly simple to construct and make it possible to record the transition from the laminar flow of air to a turbulent flow around the relevant body.[36] The piezoactive PVDF is used in sensors for the recording of shock waves, where the maximum pressure reaches 100 MPa. It is emphasised that sensors of this kind can find an application in underwater studies and in medicine, where one has to deal with focussed waves.[37]

The possibility of achieving high working areas and the high flexibility of the PVDF films provide a basis for the conversion of the energy of sea waves into electrical energy. According to the data of Hausler and Stein,[38] this idea may be not only ecologically attractive but also economically promising.

III. The use of piezopolymer films in medicine

Studies concerning the use of such materials in medicine need a separate consideration. Their advantages are associated with their low acoustic impedance Z and its closeness to the value for water and biological objects ($Z = 1.4 \times 10^6$ kg m^{-2} s^{-1}). Since the amplitude coefficient of the transmittance T_{12} for an ultrasonic element having an acoustic impedance Z_1 into a medium having an impedance Z_2 is given by the relation

$$T_{12} = \frac{2Z_1}{Z_1 + Z_2},$$

it follows that an important factor is that the impedances should be matched. This makes it possible to transmit 50% of the energy generated in the film into water, whereas in the case where a piezoceramic is used this amount is an order of magnitude smaller.[19] The above quality of the PVDF films permits their employment for the recording of electrocardiograms or for the monitoring of respiration.[19] By virtue of the large area of the sensor, the signal arising under these conditions is fairly high, so that it is possible to record it immediately on the pen recorder without preliminary amplification. The possibility of observing the difference between the incoming blood flow pulses at two different points on the human body may be of interest for physicians.[19] The copolymer of VDF and TrFE, for which the electromechanical coupling coefficients k is higher than for PVDF (see Table 1), is used widely in ultrasonic probes for medical diagnostics where bulky resonators are normally employed (see Yagi [17] and contained references). Owing to the similarity of the acoustic impedances of the probe and the living tissue, in this case the presence of an adjusting layer is no longer required. By virtue of the ability of the polymer film to assume the shape of the given body, there is also no need to employ an acoustic lens. All these factors lead to a better focussing of the ultrasonic waves and make it possible to record defects with a satisfactory resolution even for deep regions. Therefore, such probes are employed for the diagnostic investigation of internal organs — mammary glands, vocal chords, and the liver (see Yagi [17] and contained references).

The use of PVDF-sensors make it possible to obtain a series of characteristics of the pulse (frequency and rhythm), the pulse rate (in the two sensors version), and also a property which may be characterised by the form of the pressure wave.[39] The high flexibility of the piezofilm and its low acoustic impedance serve as a basis for transducers used to monitor the parameters of the contractions of the heart and of intrauterine contractions.[40]

The low Q factor of PVDF films makes it possible to generate short pulses with a low reverberation, while the high degree of resolution as regards position in space permits their application in elements for ultrasonic diagnostics in medicine.[41-43] Using piezoelectric bimorphic polymer films, it is possible to monitor the movement of the lips and to recognise vocal sounds and words (see Yagi [17] and contained references). Piezoelectric polymers can be used in medical diagnostics to monitor the blood flow pressure

and heart beat.[44] There have been reports of the use of PVDF films for the treatment of osteopathic affections, which is based on the influence of piezoelectricity on the human organism.[44,45]

IV. Thermal radiation sensors based on piezofilms

Films based on PVDF have found application as pyroelectric materials in local IR radiation sensors. They are used in fire detectors, in security signalling devices,[46] in contact-free instruments for the measurement of temperature, and in radar calorimeters. The employment of these materials in two-dimensional sensors, in particular in pyrovidicons, is expected in the future. An IR detector has been described[47] in which a small thickness (several micrometers) of the active element is achieved by spinning a solution of the vinylidene fluoride–trifluoroethylene copolymer immediately onto a silicon support. The use of this polymer arises from the fact that it crystallises as the polar ferroelectric β-phase, which renders the material pyroactive after polarisation. As a comparative detector, the pyrosensor based on PVDF can operate over a wide spectral range: from visible light to $\lambda = 12$ μm.[48] When an active layer of the VDF/TrFE copolymer is deposited onto an optical fibre, phase modulation is achieved.[49] Comparison of the characteristics of pyrovidicons based on triglycine sulfate crystals and PVDF films have shown that the sensitivity of the former is only 30% higher, while PVDF has a significant advantage as regards resolving power.[50]

The Siemens company has reported that PVDF is likely to be useful as a material for passive IR detectors.[51] The latter may be used to record the presence of a heat source, the directions and distances between the detector and the heat source, and also the rate of movement of the latter.[51,52] According to the ideas being developed and experiments on the recording of a moving object, it has been concluded that the response times of the above sensors are an order of magnitude shorter than those of traditional pyroelectric materials.

In discussing the question of the use of a pyroelectric PVDF-based calorimeter for the measurement of thermal diffusion, it was shown that the material has a number of undoubted advantages. In the first place, there is the possibility of making measurements under the conditions of minimal heating of the specimen and with a very low temperature gradient in the latter. This may be useful in studies on materials with a low thermal conductivity or materials extremely sensitive to temperature. On pulsed excitation, thermal diffusion may be recorded in a time interval of several milliseconds.[53] The possibility of using this type of calorimeter for the investigation of transient thermal processes with a time resolution of several nanoseconds and a sensitivity to within several nanocalories has been demonstrated.[54] A study has been devoted to technical problems associated with the improvement of the characteristics (including resolution) of such calorimeters.[55] Problems concerning the conditions in the preparation of the active element of such pyrodetectors have been touched upon.[56] PVDF-based pyrodetectors have proved successful in the estimation in a single experiment of a series of properties: specific heat, thermal diffusion, etc.[57]

The wide-band nature of photopyroelectric PVDF-based receivers has been used to estimate the distribution of the absorption coefficient in depth in specially formulated multilayer thin-film structures.[58] The form of the response curve, transformed into an optical absorption profile as a function of depth, has been analysed. The improvement of contrast in such spectra in the case of a discrete multilayer structure, combined with other procedures, makes it possible to minimise the thickness of the PVDF detector.

One of the latest reviews by Lang[59] surveys the possible applications of pyrodetectors based on ferroelectric polymers. Detectors for the monitoring of laser power in the range from 1 mW to 50 W,[60] for the determination of the energy of microwave radiation,[61,62] for the investigation of the change in temperature on nerve excitation,[63] for the recording of phase transitions in solids,[64] for the detection of defects in CdS crystals,[65] for the recording of changes in the surface of copper following the desorption of xenon from the latter by a laser pulse,[66] for the detection of thermal waves by measuring radiative emission,[67] for the investigation of adsorption phenomena,[68] for the detection of ultraheavy nuclei,[69] and for the detection of cosmic radiation[70–72] have been noted among them (in addition to those listed above). Such detectors are used in medicine,[73] in the optical fibre technology,[74,75] in photopyroelectric spectroscopy[76–78] (including the pulse response version[79]), and in photopyroelectric scanning microscopy.[80]

Reports on the potential possibility of using PVDF in vibrodiagnostics[81] and in calibration measurements of the rate of deformation[82] also merit attention.

There are definite prospects of using PVDF as a material with nonlinear optical properties. This is based on the conclusion, reached by Tsutsumi et al.,[83] according to which the internal field in the PVDF—poly(methyl methacrylate) polymer mixture can reach values of the order of 1 MV cm^{-1}. Combined with a high optical transparency of the above mixture, this makes it possible to obtain the optical nonlinearity coefficient $d_{33} = 9 \times 10^{-9}$ esu. Compared with other organic materials used in nonlinear optics, the stability of the characteristics of which is as a rule low, in the case of PVDF there is a definite possibility of increasing it by modifying the technological film preparation process. It has been shown, for example, that, on vacuum sputtering of PVDF in an electric field onto a support at a specified temperature, the stability of the resulting optical nonlinearity was increased significantly.[84] At the present time, attempts have been made to achieve these properties of PVDF films in memory elements. One of the latest reports[85] concerns advances in the use of the vinylidene fluoride–trifluoroethylene copolymer in optical memory elements. Bearing in mind that these polymers are characterised by high coercive fields and that control is usually achieved by a potential of several volts, it proved possible to obtain by a spinning method films with thicknesses less than 1 μm. It was then shown that a decrease in film thickness to ~0.2 μm is not accompanied by any significant changes in the ferroelectric characteristics. An increase in the coercive field and a decrease in the residual polarisation have been noted in films with $d < 0.2$ μm. When recording is carried out with the aid of a focussed laser beam, the minimum area employed for the recording is ~50 μm^2. Information can also be recorded and read over a period of about 1 μs and the signal-to-noise ratio has been estimated as 50 dB.[86] It appears that the presence of large internal fields in such ferroelectric materials makes them promising for use as elements in electrooptical light modulators operating in the mode involving the reflection of the light beam from a polarised polar polymer films with a dye.[87,88] On the basis of the foregoing considerations, a device has been constructed for the recording of an image in which use is made of a thin (2 μm) film of a vinylidene fluoride–trifluoroethylene copolymer. It has been shown that there are good prospects for the employment of such devices in electrophotography.[89]

References

1. H Kawai *Jpn. J. Appl. Phys.* **8** 975 (1969)
2. R G Kepler, R A Andersen *Adv. Phys.* **41** 1 (1992)
3. R P Singh *SETE Techn. Rev.* **9** 140 (1992)
4. H S Nalwa *Rev. Macromol. Chem. Phys.* **31** 341 (1991)
5. G M Sessler *IEEE Trans. Elec. Insul.* **24** 395 (1989)
6. T Furukawa *IEEE Trans. Elec. Insul.* **24** 375 (1989)
7. V V Kochervinskii, V G Sokolov *Vysokomol. Soedin., Ser. A* **33** 1625 (1991)
8. V V Kochervinskii, V F Romadin, V A Glukhov, V G Sokolov, M A Sandakhmetov *Vysokomol. Soedin. Ser. A* **31** 1382 (1989)
9. K A Verkhovskaya, V V Kochervinskii *Vysokomol. Soedin., Ser. A* **32** 1669 (1990)
10. V V Kochervinskii *Vysokomol. Soedin., Ser. A* **35** 1978 (1993)

11. V V Kochervinskii *Vysokomol. Soedin., Ser. A* **33** 2106 (1991)
12. V V Kochervinskii, V G Sokolov, V M Zubkov *Vysokomol. Soedin., Ser. A* **33** 530 (1991)
13. V V Kochervinskii, V A Glukhov, V G Sokolov, Yu K Ovchinnikov, N A Trofimov, B V Lokshin *Vysokomol. Soedin., Ser. A* **31** 1829 (1989)
14. R G Kepler, R A Andersen, R R Lagasse *Ferroelectrics* **57** 151 (1984)
15. T Kaura, R Nath, M M Perlmann *J. Phys. D, Appl. Phys.* **24** 1848 (1991)
16. K Matsushige *Kino Dzaire* **6** 30 (1986)
17. T Yagi *Kindzoku Khemen Gidzyutsu* **37** 640 (1986)
18. Kh Aoki *Kobunshi Kagaku* **38** 14 (1988)
19. H Sussner, K Dransfeld *Colloid Polym. Sci.* **257** 591 (1979)
20. H Sussner, D Micbas, A Assfalg, S Hunklinger, K Dransfeld *Phys. Lett. A* **45** 475 (1973)
21. J K Lee, M A Marcus *Ferroelectrics* **32** 93 (1981)
22. M Toda *Ferroelectrics* **32** 127 (1981)
23. H Sussner, Doctoral Thesis, Universität Konstanz, 1976
24. N Murayama, K Nakamura, H Obara, M Segawa *Ultrasonics* **14** 15 (1976)
25. M V Schickfus, H Sussner, DDR P. 241 796
26. K Matsushige, H Okabe, S Shichijyo, T Takemura *Jpn. J. Appl. Phys. Suppl.* **24** 30 (1985)
27. K Matsushige, T Takemura *Oe Butsuri* **54** 940 (1985)
28. S D Maynard *J. Acoust. Soc. Am.* **91** 1754 (1992)
29. P D Dario, D DeRossi *Preprint of the 13th ISIR, 1983* p. 13; see Ref. 17
30. R G Swartz, J D Plummer *IEEE Trans. Elec. Dev.* **26** 1921 (1979)
31. J L Flanagan *Bell Syst. Tech. J.* **59** 1693 (1980)
32. H Shinoda, T Kinoshita, S Ando *Ann. Report Eng. Res. Institute Faculty Eng. University Tokyo* **51** 191 (1992)
33. R Block, G Fickler, G Lindner, H Muller, M Wohnas *Sensors and Actuators* **7** 596 (1992)
34. M Latour, P V Murphy *Ferroelectrics* **32** 33 (1981)
35. M Platte *Ferroelectrics* **75** 327 (1987)
36. W Nitsche, N Weiser *Ferroelectrics* **75** 339 (1987)
37. G Heine *Ferroelectrics* **75** 357 (1987)
38. E Hausler, L Stein *Ferroelectrics* **75** 363 (1987)
39. W Nitsche, R Thunker *Ferroelectrics* **75** 381 (1987)
40. K Kobayashi, T Yasuda *Ferroelectrics* **32** 181 (1981)
41. N Murayama, H Obara *Jpn. J. Appl. Phys. Suppl.* **22** 3 (1983)
42. Kh Okhigashi *Seidenki Gakkaisi* **7** 92 (1983)
43. E Sanko *Seidenki Gakkaisi* **7** 85 (1983)
44. P Dario, D DeRossi, R Bedini, F Francesconi, M G Trivella *Preprint of INPBBD, 1983,* p. 38; see Ref. 17
45. J J Ficat, P Durroux, M J Fanzan, G Escourrou, P Ficat, C Lacabanne *Polymer Preprints* **24** 30 (1983)
46. K Okhara *Dzaire Kagaku* **20** 164 (1983)
47. E Yawaka *Ferroelectrics* **57** 327 (1984)
48. G W Day, C A Hamilton, K W Pyatt *Appl. Opt.* **15** 1865 (1976)
49. A Odajima, M Imai, in *Abstracts of Reports at the 1st European Conference and International Symposium on the Application of Polar Dielectrics and Ferroelectrics, E-8, Zurich, 1986* p. 35
50. J E Jacobs, S A Remily *Infrared Phys.* **19** 1 (1979)
51. H Meizner *Ferroelectrics* **75** 345 (1987)
52. R Freitag, H Meixner *IEEE Trans. Elec. Insul.* **24** 469 (1989)
53. H Coufal, P Hefferle *Appl. Phys. A* **38** 213 (1985)
54. H Coufal *IEEE Trans. Elec. Insul.* **21** 495 (1986)
55. W Mieszkowski, K F Leung, A Mandelis *Rev. Sci. Instrum.* **60** 306 (1989)
56. A H Franzan, N F Leite, L C M Miranda *Appl. Phys. A* **450** 431 (1990)
57. S Bauer, B Ploss *J. Appl. Phys.* **60** 6361 (1990)
58. J F Power *Appl. Spectrosc.* **45** 1240, 1252 (1991)
59. Y Dang Quan, S B Lang *IEEE Trans. Elec. Insul.* **23** 503 (1988)
60. M Hammer, A Olafson *J. Phys. E* **21** 80 (1988)
61. T Iwasaki, T Inoue, T Nimoto *IEEE Trans. Inst. Meas.* **28** 88 (1979)
62. T M Lee, A P Andersen, F A Bensen *Elec. Lett.* **22** 200 (1986)
63. I Tasci, K Iwaga *Biochem. Biophys. Res. Commun.* **101** 172 (1981)
64. A Mandelis, F Care, K K Chan, L C M Miranda *Appl. Phys. A* **38** 117 (1985)
65. A Mandelis, W Lo, R E Wagner *Appl. Phys. A* **44** 123 (1987)
66. I Hussla, H Coufal, F Trager, T J Chuang *Can. J. Phys.* **64** 1070 (1986)
67. H Coufal *IEEE Trans. Ultrason. Ferroelectrics Freq. Contr.* **33** 507 (1986)
68. H J Coufal, R Crygier, D E Horue, J E Fromm *J. Vac. Sci. Technol. A* **5** 2875 (1987)
69. J A Simpson, A J Tuzzolino *Phys. Rev. Lett.* **52** 601 (1984)
70. J A Simpson, A J Tuzzolino *Nucl. Instrum. Methods Phys. Res. A* **236** 187 (1985)
71. M A Perkins, J A Simpson, A J Tuzzolino *Nucl. Instrum. Methods Phys. Res. A* **236** 310 (1985)
72. J A Simpson, R Z Sagdeev, A J Tuzzolino, M A Perkins, L V Ksanfomality, D Rabinowitz, G A Lentz, V V Afonin, J Ero, E Keppler, J Kosozokov, E Petrova, L Szabó, G Umlauft *Nature (London)* **321** 278 (1986)
73. D DeRossi, P Dario *Ferroelectrics* **49** 49 (1983)
74. R Kashyap, P Pantelis *J. Phys. D* **18** 1709 (1985)
75. N Iwasaki, I Yokoshima, K Nokamura *Electron. Lett.* **18** 385 (1982)
76. A Mandelis *Chem. Phys. Lett.* **108** 388 (1984)
77. H Coufal *Appl. Phys. Lett.* **44** 59 (1984)
78. A Mandelis, M M Zver *J. Appl. Phys.* **57** 4021 (1985)
79. J F Power, A Mandelis *Rev. Sci. Inst.* **58** 2018, 2024, 2033 (1987)
80. I F Faria, C C Chizzoni, L C M Miranda *Appl. Phys. Lett.* **47** 1154 (1985)
81. J Irens, W Kennedy *Proc. Inst. Mech. Eng.* **204** 43 (1990)
82. K-C Lee, T C Sillivan *J. Acoust. Soc. Am.* **90** 945 (1991)
83. N Tsutsumi, Y Veda, T Kiyotsukuri *Polymer* **33** 3305 (1992)
84. A Kubono, T Kitoh, K Kajikawa, S Umemoto, H Takezoe, A Fukada, N Okui *Jpn. J. Appl. Phys.* **31** 1195 (1992)
85. K Tashiro, S Watanabe, T Furukawa *Polymer Preprints Jpn.* **34** 2977 (1985)
86. T Furukawa *Polymer Preprints* **33** 381 (1992)
87. G H Cross, Y Karalcus, D Bloor *IEEE Trans. Elec. Insul.* **29** 136 (1993)
88. C C Teng, H T Man *Appl. Phys. Lett.* **56** 1734 (1990)
89. Y Guo, K Hoshino, S-I Hanna, H Kokado *Jpn. J. Appl. Phys.* **31** 1432 (1992)