

- FISCHETTI, M. V. AND S. E. LAUX. 1991. "Monte Carlo Simulation of Transport in Technologically Significant Semiconductors of the Diamond and Zinc-Blend Structures—Part II: Submicrometer MOSFETs", *IEEE Transactions on Electron Devices*, 38(3):650–659.
- HEIBLUM, M. 1981. "Tunneling Hot Electron Transfer Amplifiers (THETA): Amplifiers Operating up to the Infrared", *Solid State Electronics*, 24:343–366.
- IMAMURA, K., M. TAKATSU, T. MORI, T. ADACHIYARA, H. ONISHI, S. MUTO AND N. YOKOYAMA. 1991. "Arithmetic Logic Circuits Using Resonant-Tunneling Hot Electron Transistors (RHETs)", *Extended Abstracts of International Conference on Solid State Devices and Materials, Yokohama, Japan*, pp. 80–82.
- ISHIBASHI, T. AND H. NAKAJIMA. 1989. "Limiting Factors in High-Speed Operations of III-V HBTs and FETs", *Extended Abstracts of International Conference on Solid State Devices and Materials, Tokyo, Japan*, pp. 525–528.
- LIKHAREV, K. K. AND T. CLAESON. 1992. "Single Electronics", *Scientific American*, 266(6):80–85.
- LURYI, S. AND F. CAPASSO. 1985. "Resonant Tunneling of Two-Dimensional Electrons through a Quantum Wire", *Applied Physics Letters*, 47(12):1347–1349.
- SUZUKI, M., S. NOTOMI, M. ONO, N. KOBAYASHI, E. MITANI, K. ODANI, T. MIMURA AND M. ABE. 1991. "A 1.2 ns HEMT 64 kb SRAM", *Digest of IEEE International Solid-State Circuits Conference, San Francisco, CA*, pp. 48–49.
- TAKAHASHI, K. 1990. "Intelligent Materials for Future Electronics", *Journal of Intelligent Material Systems and Structures*, 1(2):248–258.

Preparation of Piezoelectric Paints and Application as Vibration Modal Sensors

SHIGENORI EGUSA*

*Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute
Takasaki-shi, Gunma 370-12, Japan*

NAOZUMI IWASAWA

*New Business Division
Kansai Paint Co., Ltd.
Hiratsuka-shi, Kanagawa 254, Japan*

ABSTRACT: Piezoelectric paints were prepared using lead zirconate titanate (PZT) ceramic powder as a pigment, and epoxy resin as a binder. The obtained paints were coated on aluminum beams and were dried at room temperature, thus forming films with thicknesses of 35 to 81 μm and PZT volume fractions of 30 to 53%. The films were then poled under electric fields of up to 350 kV/cm at room temperature, and the resulting piezoelectric activity was evaluated from vibration measurements on the aluminum beams. The piezoelectric activity obtained under a given poling field increases with increasing film thickness and with increasing volume fraction of PZT. The piezoelectric activity of the PZT/epoxy paint film has proved to be high enough to determine the natural frequencies and mode shapes of a structural material,

thus demonstrating the potential of the paint film as a built-in vibration modal sensor.

INTRODUCTION

PIEZOELECTRIC materials have recently attracted significant attention for their potential application as actuators and sensors for intelligent material systems and structures (Hagood et al., 1989; Hanagud et al., 1989; Crawley and Anderson, 1990; Ikegami et al., 1990; Garcia and Inman, 1990; Poh and Baz, 1990; Fuller et al., 1990). In this application, piezoelectric materials such as lead zirconate titanate (PZT) ceramics and polyvinylidene fluoride (PVDF) films are embedded within a structural material or bonded to the material surface, thus imparting the vibration sensing and/or control capabilities to the conventional structural material. Piezoelectric paints, if prepared successfully, will also be used as a sensor for this purpose. The advantages of such a paint sensor over the PZT and PVDF sensors will be the capability of covering a large surface area and conforming to a curved surface of a structural material. The absence of a bonding layer of adhesives between the sensor material and the structural material may be an additional advantage of the paint sensor from a viewpoint of sensors integrated into structural materials.

From this point of view, we prepared piezoelectric paints using PZT ceramic powder as a pigment and epoxy resin as a binder. The obtained paints were coated on aluminum beams and were dried at room temperature. The final films of the paints were then poled at room temperature. The present paper describes the effects of the film thickness and the PZT volume fraction on the poling behavior of the PZT/epoxy paint film. This paper also describes the application of the paint film as a built-in vibration sensor of structural materials.

EXPERIMENTAL DETAILS

The epoxy resin used here was Epikoto 1001 (diglycidyl ether of bisphenol A with an average molecular weight of ca. 1000) of Yuka Shell Epoxy K. K., and the PZT ceramic powder was PE-60A of Fuji Titanium Industry Co., Ltd. Versamid 140 of Henkel Hokusui Corporation was used as epoxy hardener. A prescribed amount of the PZT powder was added to a 30 wt% epoxy solution in a mixed solvent of xylene and isobutyl alcohol (80/20 by weight), and was stirred for 30 min in a Red Devil paint shaker. To this PZT/epoxy mixture, a 30 wt% epoxy solution containing a prescribed amount of the epoxy hardener was added with stirring until the PZT/epoxy composition became 53/47, 35/65, or 30/70 by volume. The amount of the epoxy hardener was prescribed in such a way that the ratio of the active hydrogen of the hardener to the epoxide group of the epoxy resin was 1:1 by mol in the final PZT/epoxy paint.

*Author to whom correspondence should be addressed.

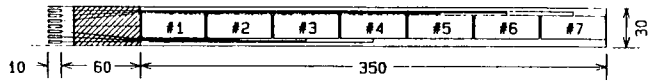


Figure 1. Configuration of silver ink electrodes and leads printed on the PZT/epoxy paint film formed on one side of an aluminum beam of 3 mm thickness, 30 mm width, and 500 mm length. The length and width of each electrode are 49 and 18 mm, respectively, and the width of the leads is 0.5 mm.

The paint thus obtained was spread with a paint brush on one side of an aluminum beam of 3 mm thickness, 30 mm width, and 500 mm length, and was dried in air at room temperature for at least 3 days. Electrodes and leads were printed on top of the dried film using a screen mask with the pattern shown in Figure 1. The film was then poled using the printed electrode as the first electrode and the aluminum beam as the second electrode. The poling was carried out in air at room temperature.

The piezoelectric activity of the poled film was evaluated from vibration measurements on the aluminum beam with a strain gauge bonded to the opposite side of the beam. The strain gauge signal and the film signal were connected to the input channels A and B of a Hewlett-Packard 3582A dual-channel FFT analyzer, respectively. Then, the transfer function from the strain gauge signal to the film signal was computed so as to refer to the ratio of the charge per unit film area to the strain developed along the beam direction. The ratio thus determined was taken as the piezoelectric activity of the film. Further details are described elsewhere (Egusa and Iwasawa, 1993a).

RESULTS AND DISCUSSION

Determination Procedure of Poling Behavior

A typical example of the vibration measurement is shown in Figure 2 for a 75 μm thick film having a PZT volume

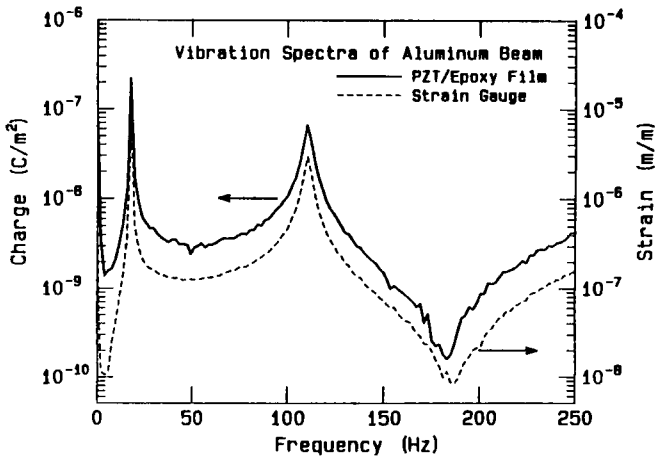


Figure 2. Frequency spectra of vibration signals from a PZT/epoxy paint film formed on one side of an aluminum beam and from a strain gauge bonded to the opposite side of the beam.

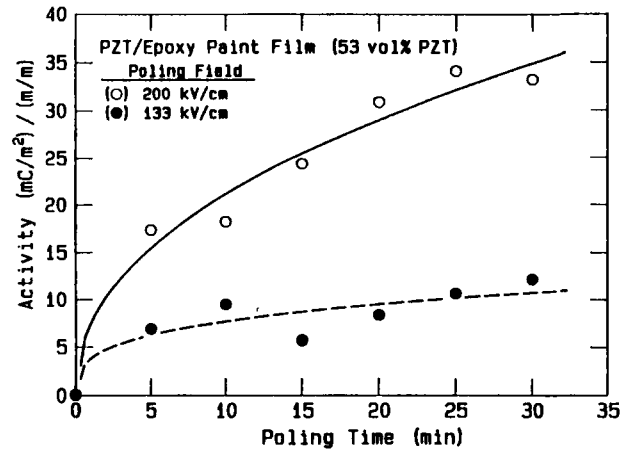


Figure 3. Plots of the piezoelectric activity after poling at 133 and 200 kV/cm versus the poling time for the 75 μm thick film having a PZT volume fraction of 53%.

fraction of 53%. This film was poled at 200 kV/cm for 30 min using the printed electrode #3 (Figure 1). It is evident that the frequency spectra of the charge signal and the strain signal include the first two natural frequencies at 18 and 112 Hz in the frequency range of 0–250 Hz. It is also noted that the spectrum shapes for the charge and strain signals are similar to each other. In the present work, the piezoelectric activity of the film was determined from the magnitude of the transfer function at the first natural frequency.

The piezoelectric activity thus determined is plotted in Figure 3 as a function of poling time for the 75 μm thick film poled at electric fields of 133 and 200 kV/cm using the printed electrode #3 (Figure 1). The piezoelectric activity is seen to increase steadily with increasing poling time for both electric fields. It is also noted that the piezoelectric activity obtained at 200 kV/cm increases much more rapidly with increasing poling time than that obtained at 133 kV/cm, thus leading to an expectation that an even higher poling field leads to a further increase in the piezoelectric activity. Increasing the poling field, however, was ultimately limited by a dielectric breakdown of the film.

In order to minimize the possibility of such a dielectric breakdown, and, furthermore, to obtain the piezoelectric activity as a function of poling voltage or field, a procedure similar to that described by Hanner et al. (1989) was adopted in the present work. We applied the poling voltage stepwise with an increment of 0.1 kV, and allowed the film to remain at each voltage for 5 min. Then the vibration measurement for the piezoelectric activity determination was carried out, followed by the 0.1 kV increase in the poling voltage. This procedure was repeated until a dielectric breakdown of the film took place.

Effect of Film Thickness on Poling Behavior

The effect of the film thickness on the poling behavior was studied for the 81, 49, and 35 μm thick films having a PZT

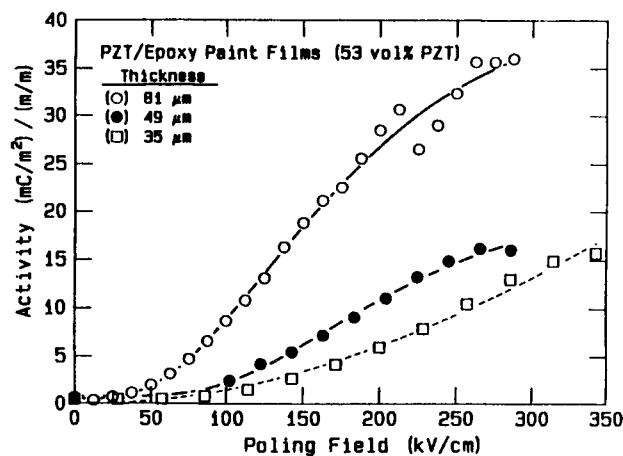


Figure 4. Plots of the piezoelectric activity versus the poling field for the 81, 49, and 35 μm thick films having a PZT volume fraction of 53%.

volume fraction of 53%. The piezoelectric activity is plotted in Figure 4 as a function of poling field. It is noted that the piezoelectric activity increases steadily with increasing poling field for all the films. It is also noted that a dielectric breakdown always occurs before the piezoelectric activity reaches a saturation value. Comparison of the 81, 49, and 35 μm thick films, on the other hand, shows that the piezoelectric activity at each poling field increases with an increase in the film thickness.

In this connection, we recently found that the piezoelectric activity obtained at a given electric field is correlated with the electrical conductivity tested at the same electric field (Egusa and Iwasawa, 1993b). The correlation indicates that the poling behavior of the PZT/epoxy composite film is primarily determined by the ratio of the electrical conductivity of the epoxy matrix to that of the PZT particles because the electric field acting on the PZT particles is controlled by this ratio during the poling process (Sa-Gong et al., 1986). Thus, the effect of the film thickness on the poling behavior may be explained by assuming the presence of impurities, which remain in the dried film and contribute to the electrical conductivity during the poling process. Such impurities could be xylene and isobutyl alcohol used as solvent or unreacted epoxy hardener of Versamid 140. The diffusion of these impurities will be very slow and, consequently, the probability of these impurities remaining in the dried film will increase with increasing film thickness, thus leading to the increasing electrical conductivity and piezoelectric activity with increasing film thickness. A more comprehensive explanation, however, requires further study of the identification of such impurities and their role in the poling process.

Effect of PZT Volume Fraction on Poling Behavior

The effect of the PZT volume fraction, V_{PZT} , on the poling behavior was studied for films having V_{PZT} values of 53, 35, and 30%. The thickness of these films was 35, 45, and

37 μm , respectively. The piezoelectric activity is plotted in Figure 5 as a function of poling field. It is noted that the maximum piezoelectric activity obtained is quite low for V_{PZT} values of 35 and 30% compared with a V_{PZT} of 53%, thus indicating that a film having a V_{PZT} value lower than 35% is hardly poled under the present poling conditions.

Scanning electron micrographs of films having V_{PZT} values lower than 35% showed that the PZT particles with diameters of 0.5–1.5 μm are isolated from one another by the continuous phase of epoxy resin. For a film having a V_{PZT} value of 53%, on the other hand, the micrograph showed that most of the PZT particles are in contact with each other, thus forming a continuous chain of PZT particles. According to the experimental result by Furukawa et al. (1986), such a chain of PZT particles appears to be poled much more easily compared with PZT particles isolated from one another, thus leading to a high piezoelectric activity for the film having a V_{PZT} value of 53%. It will be reasonable to conclude, therefore, that the effect of the PZT volume fraction on the poling behavior should be interpreted primarily in terms of the connectivity of the PZT phase in the final film of the PZT/epoxy paint (Newnham et al., 1980).

Application as Vibration Modal Sensor

As one application of the PZT/epoxy paint film, we tried to determine the vibration mode shapes of a cantilever beam. A 46 μm thick film having a PZT volume fraction of 53% was formed on the surface of an aluminum beam and was poled at 170 kV/cm for 30 min, resulting in a sensitivity of 9.0 $(\text{mC/m}^2) / (\text{m/m})$ as a vibration sensor. A set of transfer function measurements was carried out for the printed electrodes #1 to #7, with an identical excitation force applied at a point of the electrode #1 (see Figure 1). The measured transfer function from the force signal to the film signal was computed so as to refer to the ratio of the strain at each electrode to the excitation force. Then, the modal strain shapes

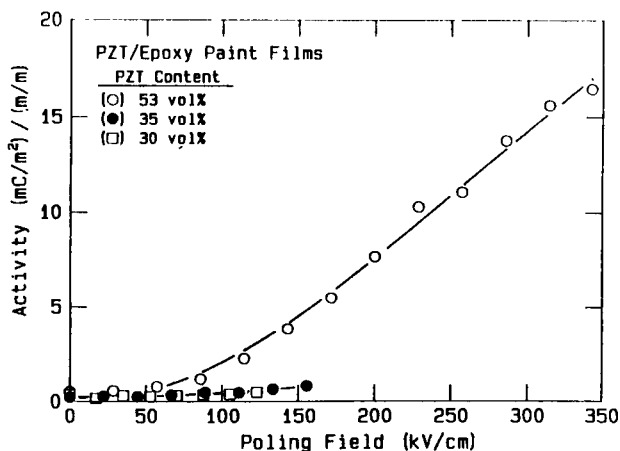


Figure 5. Plots of the piezoelectric activity versus the poling field for films having PZT volume fractions of 53, 35, and 30%. The thickness of these films is 35, 45, and 37 μm , respectively.

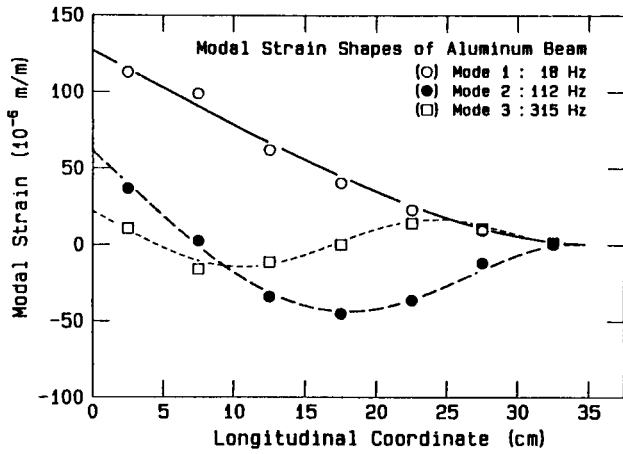


Figure 6. Modal strain shapes of a cantilever beam for the first (○), second (●) and third modes (□) determined by a PZT/epoxy paint film formed on the beam surface. The solid, broken, and dotted curves are the results of fitting Equation (3) to the data points of symbols ○, ●, and □, respectively (see text).

of the cantilever beam were obtained by plotting the imaginary part of the strain-to-force ratio against the distance from the clamped end of the beam to the center of each electrode. The modal strain shapes thus obtained are shown in Figure 6 for the first three modes at 18, 112, and 315 Hz.

The transverse displacement of a uniform cantilever beam, ϕ , can be calculated by double integration of the following equation with respect to the longitudinal coordinate of the beam, x :

$$d^2\phi/dx^2 = -\epsilon/\eta \tag{1}$$

where ϵ is the longitudinal strain in the beam surface and η is the half-thickness of the beam. The numerical integration of the strain data shown in Figure 6, however, was found not to yield reliable results for the modal displacement shapes, especially for higher frequency modes.

For this reason, in the present work we assume the following equation as the modal displacement shape function, $\phi(x)$:

$$\begin{aligned} \phi(x) = & A_1 \cos(\lambda x/L) + A_2 \cosh(\lambda x/L) \\ & + A_3 \sin(\lambda x/L) + A_4 \sinh(\lambda x/L) \end{aligned} \tag{2}$$

where A_1, A_2, A_3, A_4 and λ are constants for each mode, and L is the length of the beam. Double differentiation of this equation by x and substitution of the result into Equation (1) give the following equation as the modal strain shape function, $\epsilon(x)$:

$$\begin{aligned} \epsilon(x) = & \eta(\lambda/L)^2 [A_1 \cos(\lambda x/L) - A_2 \cosh(\lambda x/L) \\ & + A_3 \sin(\lambda x/L) - A_4 \sinh(\lambda x/L)] \end{aligned} \tag{3}$$

This equation is fitted to the strain data in Figure 6 by using the non-linear least squares method referred to as the Marquardt Method, thus giving the numerical values of A_1, A_2, A_3, A_4 , and λ for each mode. These numerical values are then used to calculate the modal displacement shapes from Equation (2).

The modal displacement shapes thus determined are shown in Figure 7 by the solid, broken, and dotted curves for the first, second, and third modes of the cantilever beam, respectively. In this figure, the corresponding modal displacements determined by a Graphtec AT3100 laser Doppler vibrometer are also shown by the data points of symbols ○, ●, □. It is noted that the modal displacements determined by the PZT/epoxy paint film and the laser Doppler vibrometer agree closely with each other for each mode, thus demonstrating that the piezoelectric paints prepared here have the potential for use as built-in vibration modal sensors.

CONCLUSIONS

The present work has shown that a piezoelectric film can be formed on the surface of a structural material from a paint made up of PZT ceramic powder and epoxy resin. The piezoelectric activity obtained under a given poling field increases with increasing film thickness and with increasing volume fraction of PZT. It was also shown that the piezoelectric film of the PZT/epoxy paint is quite promising as a built-in vibration sensor capable of determining the natural frequencies and mode shapes of the structural material.

ACKNOWLEDGEMENTS

This work was supported by the Special Program for Fundamental Research at the Japan Atomic Energy Research Institute. The authors are grateful to Dr. H. Nakayama and T.

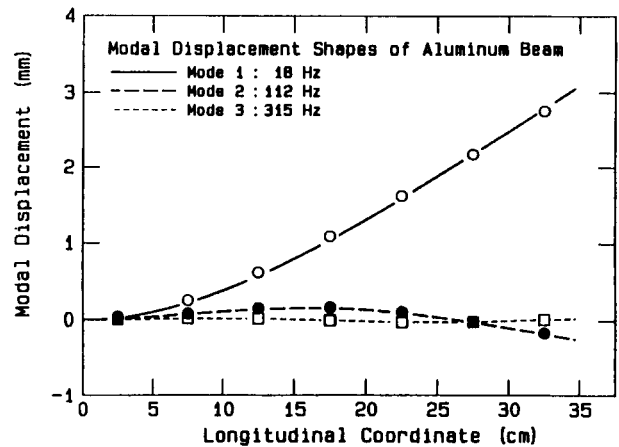


Figure 7. Modal displacement shapes of a cantilever beam for the first three modes determined by a PZT/epoxy paint film formed on the beam surface. The data points of symbols ○, ●, and □ show the modal displacements determined by a laser Doppler vibrometer.

Sato of the Kansai Paint Co., Ltd. for their valuable advice and suggestions. Special thanks are extended to Prof. T. Furukawa of the Science University of Tokyo, K. Furuta of the Ube Industries, Ltd., and E. H. Anderson of the Massachusetts Institute of Technology for their stimulating discussion on all aspects of this work.

REFERENCES

- CRAWLEY, E. F. AND E. H. ANDERSON. 1990. "Detailed Models of Piezoceramic Actuation of Beams", *J. Intell. Mater. Syst. Struct.*, 1:4-25.
- EGUSA, S. AND N. IWASAWA. 1993a. "Piezoelectric Paints: Preparation and Application as Built-in Vibration Sensors of Structural Materials", *J. Mater. Sci.*, 28:1667-1672.
- EGUSA, S. AND N. IWASAWA. 1993b. "Poling Characteristics of PZT/Epoxy Piezoelectric Paints", to appear in *Ferroelectrics*.
- FULLER, C. R., G. P. GIBBS AND R. J. SILCOX. 1990. "Simultaneous Active Control of Flexural and Extensional Waves in Beams", *J. Intell. Mater. Syst. Struct.*, 1:235-247.
- FURUKAWA, T., K. SUZUKI AND M. DATE. 1986. "Switching Process in Composite Systems of PZT Ceramics and Polymers", *Ferroelectrics*, 68:33-44.
- GARCIA, E. AND D. J. INMAN. 1990. "Advantages of Slewing an Active Structure", *J. Intell. Mater. Syst. Struct.*, 1:261-272.
- HAGOOD, N. W., E. F. CRAWLEY, J. DE LUIS AND E. H. ANDERSON. 1989. "Development of Integrated Components for Control of Intelligent Structures", *Smart Materials, Structures, and Mathematical Issues*. Lancaster, PA: Technomic Publishing Co., Inc., pp. 80-104.
- HANAGUD, S., M. W. OBAL AND A. G. CALISE. 1989. "Piezoceramic Devices and PVDF Films as Sensors and Actuators for Intelligent Structures", *Smart Materials, Structures, and Mathematical Issues*. Lancaster, PA: Technomic Publishing Co., Inc., pp. 69-79.
- HANNER, K. A., A. SAFARI, R. E. NEWNHAM AND J. RUNT. 1989. "Thin Film 0-3 Polymer/Piezoelectric Ceramic Composites: Piezoelectric Paints", *Ferroelectrics*, 100:255-260.
- IKEGAMI, R., D. G. WILSON, J. R. ANDERSON AND G. J. JULIEN. 1990. "Active Vibration Control Using NiTiNOL and Piezoelectric Ceramics", *J. Intell. Mater. Syst. Struct.*, 1:189-206.
- NEWNHAM, R. E., L. J. BOWEN, K. A. KLICKER AND L. E. CROSS. 1980. "Composite Piezoelectric Transducers", *Materials in Engineering*, 2:93-106.
- POH, S. AND A. BAZ. 1990. "Active Control of a Flexible Structure Using a Modal Positive Position Feedback Controller", *J. Intell. Mater. Syst. Struct.*, 1:273-288.
- SA-GONG, G., A. SAFARI, S. J. JANG AND R. E. NEWNHAM. 1986. "Poling Flexible Piezoelectric Composites", *Ferroelectrics Letters*, 5:131-142.

Interpolymer Complexes Formed by Polyelectrolyte Gels

ALEXANDER B. ZEIN,* VALENTINA B. ROGACHEVA
AND VICTOR A. KABANOV
*Department of Polymer Science
Faculty of Chemistry
M. V. Lomonosov
Moscow State University
Moscow, USSR*

*Author to whom correspondence should be addressed.

ABSTRACT: The approaches to synthesis and modification of polymers based on the assembly of chemically complementary macromolecules have been recently widely developed. Interpolyelectrolyte complexes (IPEC) are more common polymers of this type. They are the products of interaction between oppositely charged polyelectrolytes (Bixler and Michaels, 1969; Tsuchida and Abe, 1982). IPEC are of special interest as the effective adhesives for solving ecological, biomedical and agrotechnological problems due to their unique structure (Zein and Baranovskii, 1983; Zein et al., 1987). The utilization of cross-linked polyelectrolytes gives new opportunities for the construction of polycomplex substances and materials. These opportunities are based on the phenomenon of active transport of linear polyelectrolytes into oppositely charged networks (Rogacheva et al., 1988; Kabanov et al., 1988; Kabanov et al., 1989). The driving force of this transport and the mechanism of transport of linear polyions in polyelectrolyte gels are directly connected with the interpolyelectrolyte reaction (IPR) which proceeds between polyions and gel. Slightly cross-linked polyelectrolytes absorb oppositely charged linear polyions from aqueous solutions. This gradual uptake is followed by production of small counter ions of linear and cross-linked polyelectrolytes. For example, the reaction between slightly cross-linked poly(2-dimethylaminoethyl methacrylate) (PDMA) and linear poly(acrylic acid) (PAA) is presented in Scheme (I).

THE left part of Scheme (Ia) describes the process of ionization of weak linear polyacid while it is in contact with cross-linked polycation. The right part (Ib) corresponds to ionization of weak cross-linked polybase while it is in solution of linear polyanions. Both processes result in formation of IPEC which contains positively charged network segments and negatively charged linear polyelectrolyte segments in the equivalent ratio. Thus, all of the functional groups of the cross-linked polymer participate in IPR (i.e., IPR proceeds not only on the gel surface but within the whole volume as well). IPR between linear and network polyelectrolytes are cooperative by nature like the IPR between corresponding pairs of linear polyelectrolytes which was described in the previous studies (Zein et al., 1972). The considerable slope of IPR profiles as compared with curves of ionization of corresponding weak polyelectrolytes gives the evidence of IPR cooperativity. The dependencies of the degree of conversion, θ , in the reactions 1a and 1b on pH are given in Figure 1. $\theta = C_k/C_o$, C_k is the amount of interpolyelectrolyte salt bonds, and C_o is the amount of monomer units of one of the reacting polyelectrolytes.

It is important that the resulting IPEC is much less swellable in water (ca. two orders less) as compared with initial polyelectrolyte gel. Thus, the IPR is followed by a very large network contraction similar to the known gel collapse (Tanaka, 1978). The IPEC composition depends strongly on the degree of conversion, θ , in the IPR so that the products of uncompleted reactions, $\theta \ll 1$, formed in acidic or alkali media, are significantly enriched (two times or more) by the weakly ionized polyelectrolyte. The opposite is the case when we deal with the products of completed reactions $\theta \cong 1$. The monomer units of cross-linked and linear polyions are included in such IPECs in the equivalent ratio.

Obviously, the time that is necessary for the setting chem-