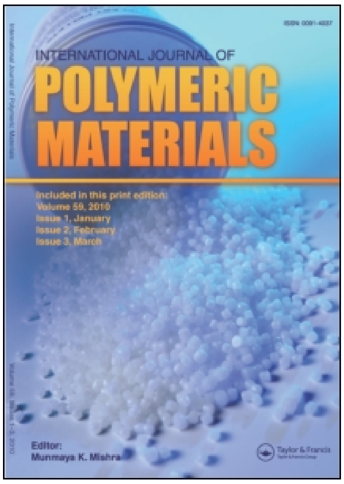

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Piezoelectricity and crystallinity studies in thermopoled Acrylonitrile-Methylacrylate copolymer films

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PIEZOELECTRICITY AND CRYSTALLINITY STUDIES IN THERMOPOLED ACRYLONITRILE–METHYLACRYLATE COPOLYMER FILMS

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Molecular ordering in Acrylonitrile–Methylacrylate copolymer, P(AN–MA), films has been achieved by hot stretching. The structure, morphology of the stretched and nonstretched films, as well as the thermally stimulated depolarization current (TSDC) measurements are discussed.

The piezoelectricity and charge storage in unstretched and stretched thermal poling P(AN–MA), films have been investigated at different poling fields. Quantitative analysis of the thermally stimulated depolarization current (TSDC) revealed that uniaxial stretching and subsequent poling at elevated temperatures give rise to high values of polarization and piezoelectricity in the films. The piezoelectric coefficient, d_{31} was measured and the maximum value $d_{31} = 8.6\,\mathrm{PCN}^{-1}$ has been obtained at $E_p = 10\,\mathrm{MVm}^{-1}$, $T_p = 373\,\mathrm{K}$ and stretching ratio $\lambda = 6$. It has been concluded that the increase in crystallinity and the polarization effects enhance the piezoelectric activity in P(AN–MA) thermoelectrets.

Keywords: piezoelectricity, Poling, Thermopoling, Acrylonitrile–Methylacrylate copolymer

INTRODUCTION

The importance of polymer electrets is receiving increasing attention due to their expanding range of suggested and realized applications such as ultrasonic transducers, electret filters, electrophotography [1], electroacoustic and electromechanical transducers [2], commercial headphone [3] and hydrophone [4]. Since the discovery of piezoelectricity in polarized poly (vinylidene fluoride), PVDF, films [5], most of the effort by various workers has been spent investigating PVDF [6–8]. In addition, many investigations have been made for other classes of polymers [9–15]. Cyanopolymers are

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relatively new materials to join the family of piezoelectric polymers. The C – CN group, an essential constituent of all cyanopolymers has a large dipole moment (3.5D). It is the high value of dipole moment that has tempted many researchers to explore their piezo-, pyro-, and ferroelectric properties. The present paper describes the results from studies of the piezoelectricity and the thermally stimulated depolarization currents carried out for unstretched and for stretched and thermally poled (acrylonitrile – methylacrylate copolymer), P (AN – MA), films; aiming to explore the influence of the sample structural modifications on the piezoelectric activity and to introduce a new type of material, suitable for future technological applications. The results revealed that the increase in the crystallinity improves the piezoelectricity.

MATERIALS AND EXPERIMENTAL PROCEDURES

Acrylonitrile – Methylacrylate copolymer (96% acrylonitrile and 4% methylacrylate) used in this study was provided by Polyscience, USA. Films were casted from the concentrated solutions of P(AN – MA) in DMF under normal atmosphere at 82°C. One set of the films were annealed at 100°C for 24 h. The other set of the films were annealed and subsequently drawn at temperatures between 90 and 130°C, the draw ratios ranged from 1 : 3 to 1 : 6. The films were highly oriented and free of microvoids. Gold paste was used as electrodes. The samples were poled by applying dc electric fields, at high temperature in the same assembly used for TSDC experiments as reported elsewhere [16]. The sample was heated to a temperature $T_p = 110°\mathrm{C} > T_g = 98°\mathrm{C}$. A voltage gradient ranging from $1 \times 10^5\,\mathrm{Vm}^{-1}$ to $4 \times 10^7\,\mathrm{Vm}^{-1}$ was applied across the sample for 1/4 h. After poling the electrodes were shorted and kept at 30°C for 10 min. before measurements to eliminate any spurious space charge. TSDC spectra were taken in the temperature range 25 – 125°C at a constant heating rate of $4°\mathrm{C\ min}^{-1}$.

The piezoelectric constant d_{31} was determined using the static method [17, 18] 3 days after poling. The charge induced on the electrodes at room temperature (RT) by a weight attached to the film was measured with a Keithley 610 C electrometer. d_{31} was calculated from:

$$d_{31} = (Q/A)(dW/F) \qquad (1)$$

where Q is the induced charge, A is the electrode area, d is the film thickness, W is the width of the sample, and F is the applied force.

The morphology of the samples was examined with the help of an optical polarizing microscope (Zeiss Model laboval 4). X-ray profiles were obtained using Shematzo diffractometer that gives CuKα radiation. The crystallinity index of P(AN – MA), I_c, was estimated using Buschle-Diller et al. method [19].

RESULTS AND DISCUSSION

X-Ray Measurements

Wide angle X-rays diagrams of P(AN – MA) films are shown in Figure 1. Cast film seems to be amorphous (curve A). On the other hand, a broad reflection at $2\theta = 17.2°$ is to be seen in the case of annealed film, at $T = 100°C$ for 24 h (curve B). Broadening of the peak could be caused by the defects between crystallinities and/or imperfections in the ordered phase [20]. This peak becomes sharp and intense on stretching the film to 3 times its original length at $T = 403$ K. Furthermore, a new broad reflection peak at $2\theta = 30.1°$ is to be seen (curve C). These two reflections in the case of the stretched films are an evidence for the presumed two-phase structure.

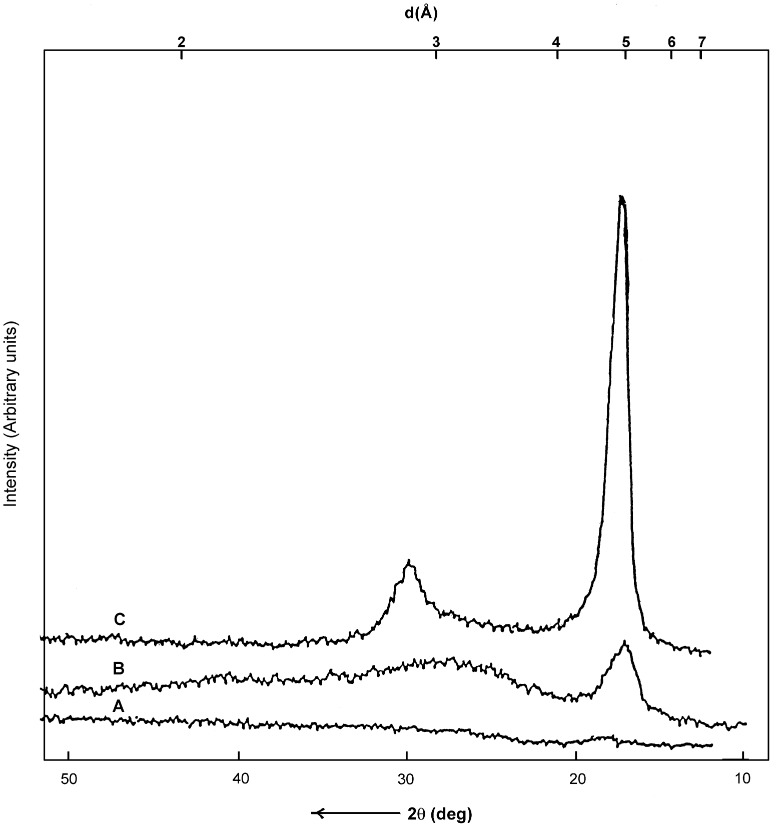

FIGURE 1 Wide angle X-ray diffractograms of P(AN – MA) films: (A) Annealed at 373 K for 24 h, and (B) stretched at 403 K to 3 times its original length ($\lambda = 3$).

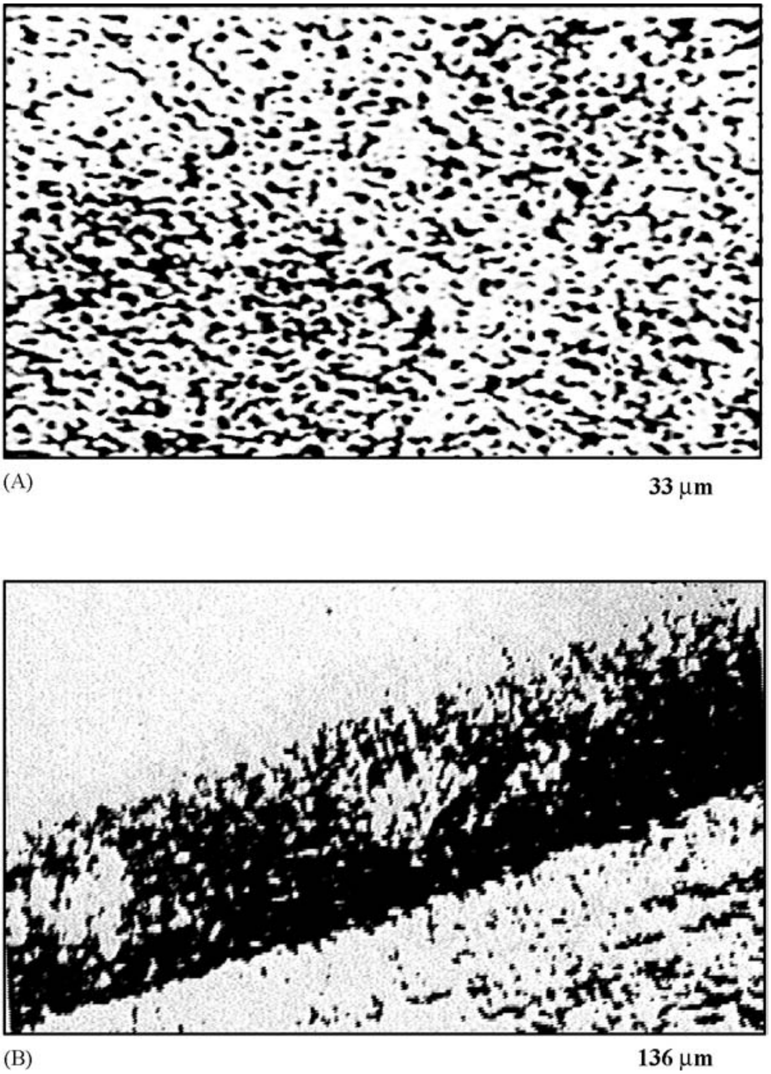

FIGURE 2 Morphology of P(AN – MA) films. (a) Annealed film, the picture shows an almost homogeneous structure, and (b) Stretched film, where a rod-like structure is to be seen and the orientation is obvious.

Additional optical microscopically observations (Fig. 2) support the two structures model. These results indicate that stretched P(AN – MA), is similar to stretched poly (acrylonitrile), PAN, [21] which has been described as a single-phase paracrystalline solid: the chain molecules are packed as small rods which can be described by two phase structure consisting of more and less ordered regions. The crystallinity index, I_c, was calculated from the formula [19]:

$$I_c = 1 - (I_{\min}/I_{\max}) \tag{2}$$

Where $I_{\min}$ is the intensity minimum between $2\theta = 16°$ and $16.5°$, and $I_{\max}$ is the intensity of the maximum between $2\theta = 17.2°$ and $18°$. The average crytallinty index of the unstretched and the stretched sample were found to be 0.48 and 0.77 respectively.

TSDC Measurements

Specific informations about the response of individual morphological phases to the DC poling field can be gained from TSDC investigations. Figure 3 (A and B) shows the TSDC spectra of the unstretched and the stretched P(AN – MA) films. The unstretched film shows a relaxation peak, associated with the glass-transition temperature, T_p, located at about 397 K. On the other hand, stretched film gives a relaxation peak whose maximum is at about 380 K. These varied peak positions reveal that the stretching and subsequently poling at elevated temperature modify the local dipole environment in P(AN – MA) films. The position of both peaks does not change

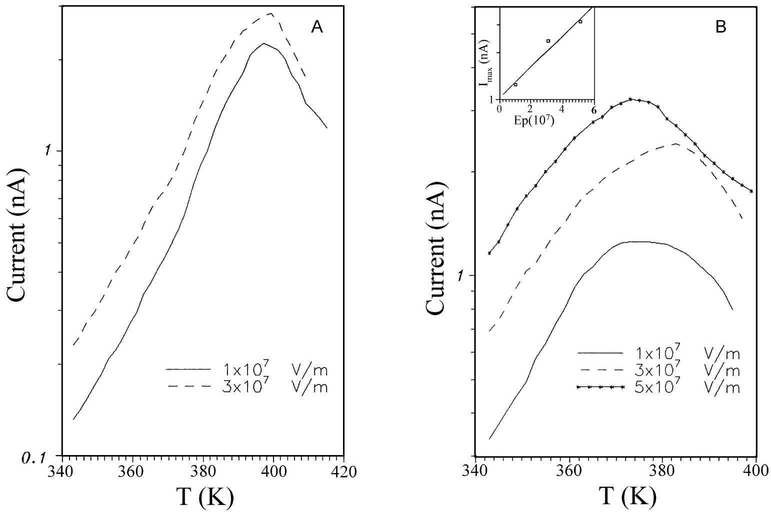

FIGURE 3 Family of short-circuited TSDC thermograms for (A) unstretched film of thickness 25 μm polarized at 373 K for 15 min for various initial polarizing fields, heating rate $\beta = 4\,\mathrm{K\,min}^{-1}$. (B) stretched film of thickness 14 μm polarized at 373 K for 15 min, $\lambda = 3$, heating rate $\beta = 4\,\mathrm{K\,min}^{-1}$.

on changing the electric field intensity. Furthermore the linearity between $I_{\max}$ and E_p (see the inset of Fig. 3B), indicated dipolar relaxation [22]. The activation energy, E_a, of the relaxation was evaluated using the initial rise method [23]:

$$I = I_0 \exp(-E_a/kT) \tag{3}$$

An Arrhenius plot of TSDC versus T^{-1} for film poled at optimum condition yields average values of 0.57 eV and 0.67 eV for stretched and unstretched films respectively. The asymmetry of the TSDC curves may be attributed to the distribution function of relaxation times because of the various processes involved [16]. The stretched film may be considered in equilibrium state in which the probability of the creation and ordering of a crystalline phase is more than the case of the unstretched one, and therefore, the activation energy of the dipole relaxation in the stretched film is less than the corresponding one in the unstretched sample. Hence, the relaxation peak of the unstrerched film (129°C) is attributed to a molecular motion in the amorphous region, and the peak of the stretched film (100°C) might be attributed to molecular motion related to the crystalline region [16]. These results are comparable with those reported by Lestriez et al. [24] that in crystalline and semi-crystalline polymer blends, a new process due to the motion in the crystalline phases may also appear in addition to the other relaxation mechanisms of the amorphous phase.

Piezoelectric Measurements

It is of interest to investigate the piezoelectric activity achieved for fixed poling temperature, T_p, and time, t_p, but at various polarizing electric field, E_p, and to this we present the results in Figure 4, which relates to unstretched (Fig. 4A) and stretched (Fig. 4B) P(AN – MA) films. As it is clear from the figure, the value d_{31} increases linearly as E_p increases in case of stretched film. Figure 5 shows the variation of d_{31} with the stretching ratio λ. The piezoelectric coefficient d_{31} is improved from 0.6 PCN^{-1} for the unstretched film to 8.6 PCN^{-1} for the six times stretched and thermally poled film. The increase in crystallinity and greater dipolar polarization are believed to be the chief contributors to the higher d_{31} in the stretched film [15].

The increase in d_{31} with poling field could be due to an increase in the dipolar orientation in the direction of the field. That is to say, when a high dc electric field is applied to polar polymers such as P(AN-MA) at high temperatures, the dipoles of the polymer are oriented in the direction of the field. By cooling the material to room temperature while maintaining the field, we get frozen dipole orientation in the material. Piezoelectricity is

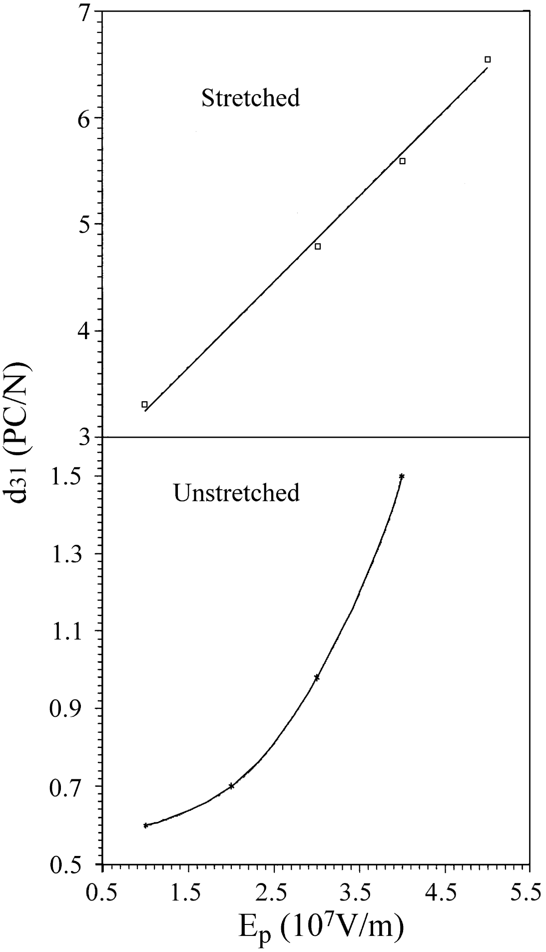

FIGURE 4 The variation of d_{31} with the poling field E_p for unstretched and stretched films. The poling parameters $T_p = 373\,\mathrm{K}$, $t_p = 15\,\mathrm{min}$, and $\lambda = 1$ (for unstretched) and 4 (for stretched) were kept constant. Two separate tests were performed at each E_p.

observed for such a system, which in this case resulted from frozen polarization. The remnant polarization is due to real space charge, which could be formed within the film during poling, and permanent dipole moments oriented during poling at temperature $T > T_g$ and immobilized by cooling below T_g. From elementary electrostatics, real space charges do not contribute to piezoelectric effect [25]. Hence, the stored or remnant polarization, P_r, is simply the polarization during the film poling minus

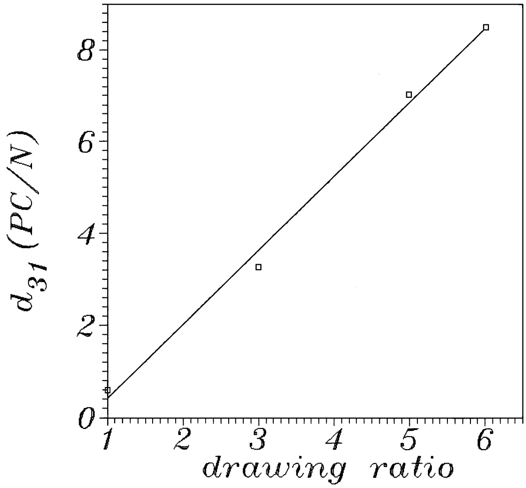

FIGURE 5 Variation of d_{31} with the stretching ratio (λ). The poling parameters were $E_p = 10\,\mathrm{MVm}^{-1}$, $T_p = 373\,\mathrm{K}$ and $t_p = 15\,\mathrm{min}$. Two separate tests were performed at each λ.

the electronic and atomic polarization that relax at room temperature when the poling field E_p is removed [26]:

$$P_r = \varepsilon_0(\varepsilon_{PT} - \varepsilon_{RT})E_p \tag{4}$$

where ε_{PT} is the dielectric constant at the poling temperature, and ε_{RT} is the dielectric constant in the glassy state. Two mechanisms are possible for the build up of polarization in polymers. They are space charge polarization and dipole orientation polarization, although persistent polarization due to stretching has been reported [25]. Using $\varepsilon_o = 8.85419 \times 10^{-12}\,\mathrm{Vs/Am}$, $\varepsilon_{PT} = 21$ and $\varepsilon_{RT} = 7$ [27], in Eq. (4), P_r value of $6.2 \times 10^{-3}\,\mathrm{cm}$ is obtained for $E_p = 50\,\mathrm{MV}^{-1}$ which is in good agreement with the value of SAN copolymer films [28]. The correlation between remnant polarization and piezoelectric coefficient, (Fig. 4B and Eq. (4)) led to the conclusion that stretched films are characterized by the existence of spontaneous remnant electric polarization that is sensitive to, or can influence stress (piezoelectric).

CONCLUSION

P(AN–MA) copolymer is a good piezoelectric material. However, the piezoelectric response in the present sample is not high compared to PVDF. The crystallinity was found to increase with stretching for P(AN–MA) films. This ordering may be useful to establish the remnant polarization by poling and therefore stretching and poling is a useful method to enhance the piezoelectric coefficient, d_{31}, in the films. TSDC investigation reveals the dipolar origin of the piezoelectricity in these films. The origin of piezoelectric polarization may be attributed to the crystallinity and the polarization of the films.

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