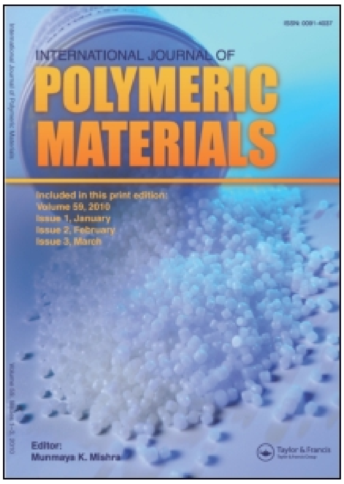

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Electrical and Optical Properties of Vinylidene Fluoride – Trifluoro Ethylene Copolymers Prepared by Solution Cast

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The dielectric and non-linear optical properties of a 60/40 copolymer of vinylidene fluoride with trifluoro ethylene prepared as thin films by a solution cast procedure are described. The relation of these properties with the microstructure of the system as derived by wide and small angle X-ray scattering experiments is also discussed. Some implications regarding to the use of these copolymers in electrooptics are pointed out.

Keywords: Vinylidene fluoride–trifluoro ethylene copolymer; non-linear optical properties; microstructure

1. INTRODUCTION

Random copolymers of vinylidene fluoride (VF_2) and trifluoro ethylene (F_3E) are semicrystalline systems which exhibit ferroelectricity when the F_3E molar content is higher than 50% [1,2]. The microstructure of these copolymers consists of stacks of ferroelectric lamellar crystals separated by amorphous non polar regions. The crystals suffer a ferroelectric to paraelectric phase transition at a Curie temperature below the melting temperature. The phase diagram for

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*Corresponding author.

these copolymers as a function of the VF_2 molar content has been determined by several techniques including: X-ray diffraction, dielectric and dynamic mechanical spectroscopy microhardness and calorimetry among others [1, 2]. Until now most of the experiments performed in these copolymers were restricted to melt processed samples. However, when dealing with optical properties relative thin transparent films are required. These can be obtained, for example, by spin coating, solution casting or Langmuir – Blodget deposition [3].

The aim of the present paper is to illustrate some of the electrical and optical properties of solution cast films of a 60/40 VF_2/F_3E copolymer and highlight some of the implications regarding to the use of these polymers in electrooptics.

2. EXPERIMENTAL

2.1. Materials

Samples of $VF_2/F_3E(60/40)$ were obtained from Atochem in the form of pellets. Free standing films (≈ 20 μm thick) were prepared by solution cast using *N-N*-dimethylformamide as solvent. Any traces of solvent were eliminated by vacuum drying at 40°C.

2.2. Techniques

Measurements of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ were performed in the $10^6 - 10^9$ Hz frequency range by using a coaxial line reflectometer operating with 4191A Hewlett-Packard Analyzer [4]. In both cases the experimental arrangement was introduced in a Novocontrol temperature controlled nitrogen gas jet and cryostat. The temperature, under this conditions can be varied between -150°C up to 100°C with an accuracy of ±0.01°C.

The nonlinear optical properties of these films were characterized by using a Maker fringe at a fundamental wavelength of 1542 nm. Films were previously poled at room temperature with a corona discharge at 7 kV being the sample to needle distance of about 2 cm. The laser beam was focused into a 1 meter Raman cell and recolimated. Both the laser intensity and polarization of the light were controlled by a polarization rotator. The Second Harmonic Generation (SHG) signal was detected with a photomultiplier.

3. RESULTS AND DISCUSSION

The existence of a ferro-to-paraelectric transition in the $VF_2/F_3E(60/40)$ solution cast films is evidenced by the measurements of ε'' and ε' as a function of frequency and temperature as illustrated in Figures 1 and 2 respectively. The ferro-to-paraelectric transition manifests itself as a sudden increase of both ε' and ε'' around 75°C where the transition has been observed by other techniques including DSC and WAXS [6–8]. The paraelectric phase is characterized by the onset of a dielectric relaxation as revealed by the maximum in ε'' shown in Figure 1 indicating an increase of molecular mobility as the phase transition occurs [9–11]. Combined studies of dielectric spectroscopy [12] and incoherent quasielastic neutron scattering [11] in the 60/40 melt crystallized copolymer have shown that in the paraelectric phase, the chain segments in the crystalline region exhibit a slow jump diffusive motion restricted by the volume defined by the neighboring chains [11].

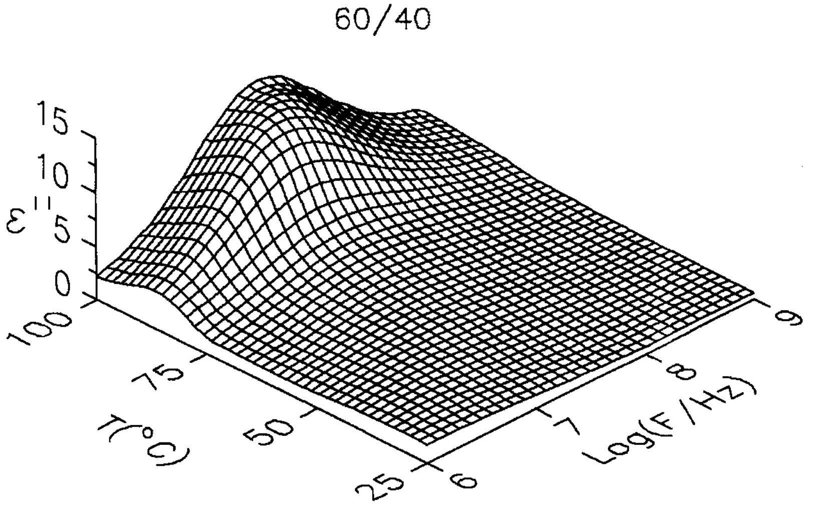

FIGURE 1 Plot of the dielectric loss, ε'', as a function of temperature and frequency for the solution cast $VF_2/F_3E(60/40)$ copolymer.

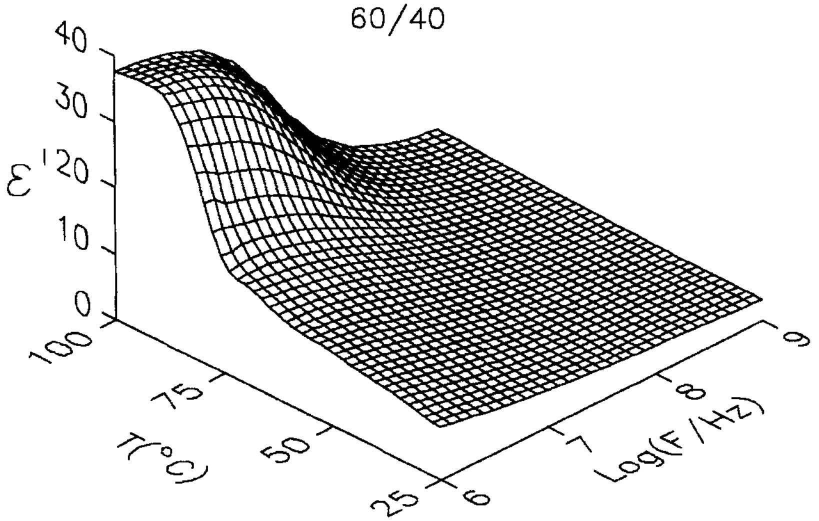

FIGURE 2 Dielectric constant, ε' as a function of frequency and temperature for the same sample as in Figure 1.

It is known that during the ferro-to-paraelectric phase transition a reversible structural change takes place within the crystalline portion of the copolymer [1, 2]. At room temperature molecules are packed in the crystals in an orthorhombic unit cell with the polymer chains in a polar trans conformation similar to the β-phase of the PVF_2 [1,2]. Above the Curie temperature, in the paraelectric phase, the diffraction pattern is characteristic of a pseudohexagonal lattice [1,2,13]. The changes in the lattice spacing during the ferro-to-paraelectric transition can be correlated with the appearance of conformational change produced by the introduction of gauche conformations g^+ and g^- leading to random sequences of tg^+ and tg^- isomers similarly to the non-polar disordered 3/1 helical conformation of PF_3E [1,2,13,14].

The ferro-to-paraelectric transition can be also characterized by recording the second harmonic generation (SHG) intensity [1] as a function of the temperature (Fig. 3). Here, the phase transition can be detected by the change in the slope with temperature of the SHG signal occuring at about 70°C. It is noteworthy that a non-linear optical behaviour is a competition between the molecular orientational polarization achieved by the poling process and the thermal

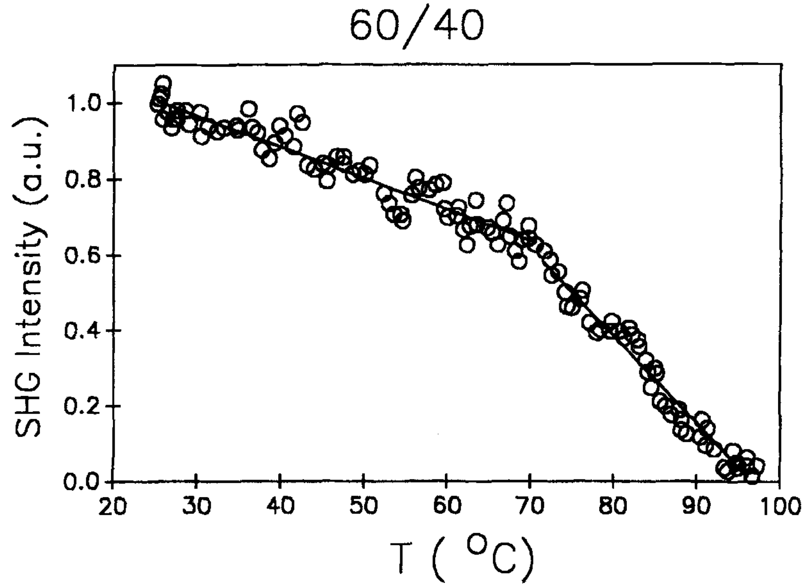

FIGURE 3 Variation of the second harmonic generation signal intensity as a function of temperature for the solution cast VF_2/F_3E(60/40) copolymer.

randomization of the dipoles. Eventhough lamellar crystals of ferroelectric VF_2-F_3E are polar they are randomly oriented giving rise to a macroscopic absence of polarization. The application of a high electric field by the poling process produces an orientation of the dipoles [15] which is stable enough to give rise to a non-linear optical behaviour. The design of non-linear optical polymeric materials typically involve the addition of non linear optical cromophores to a polymer matrix or the incorporation of the cromophore as part of the polymer chain [3, 16]. Ferroelectric VF_2-F_3E copolymers are suitable materials to obtain non-linear optical properties without especial modifications. It is interesting to mention that these copolymers additionally to SHG exhibit electrooptic effects depending on molar composition [15].

In conclusion, we have briefly reviewed some electrical and optical properties of thin films of vinylidene fluoride/trifluoroethylene copolymers prepared by solution cast derived from dielectric spectroscopy, X-ray scattering techniques and second harmonic generation.

The investigated physical properties show that these copolymers can be suitable candidates in terms of processability and physical properties to be used as active elements in electrooptics.

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