A pseudo-spin model for poly(vinylidene fluoride–trifluoroethylene) copolymers

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We propose a simple four-particle interaction model to describe the phase transition in the poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)] system. The mean field treatment of this model displays the main qualitative behaviour of the copolymer by predicting a tricritical point for an equimolar VDF–TrFE sample and the thermal evolution of the order parameter for the different sample compositions.

(Keywords: vinylidene fluoride–trifluoroethylene copolymers; ferroelectric phase transition)

Poly(vinylidene fluoride–trifluoroethylene) copolymers [P(VDF–TrFE)] show ferroelectricity at room temperature for a large range of compositions[1]. Moreover, for TrFE molar contents ranging from 18 to 48%, these materials undergo a first-order phase transition (PT) to a high temperature paraelectric phase[2–9]. In the low temperature phase the chains assume a planar zig-zag conformation and are packed in a parallel manner forming a polar crystal phase, which belongs to the orthorhombic *mm*2 group. At higher temperatures, the chains assume a disordered conformation with hexagonal structure (6/*mmm*). The PT is of an order–disorder type which originates with the appearance of *gauche* sequences in the all-*trans* chains[10]. The experimental phase diagram of P(VDF–TrFE) indicates that the system has as tricritical point separating regions of first- and second-order PT[5,8,11]. It also has a diffuse character with large thermal hysteresis[12].

In spite of a large amount of experimental work (for recent reviews, see refs 11 and 13–15), very few theoretical studies have been done to understand the behaviour of such systems. A six-site model[16] and a non-equivalent four-site model[17] have been proposed which successfully predicted the first-order transition, but they had limited validity in terms of quantitative predictions.

In this work we propose a simple model to describe the P(VDF–TrFE) system. The basic idea is that the copolymers may be seen as dipoles of TrFE diluted in a matrix of VDF dipoles. In order to write the model Hamiltonian for our system we make the following considerations. First, due to the stronger polarity of the VDF monomers compared to the TrFE ones, we will only consider the bilinear interactions between VDF–VDF and VDF–TrFE dipoles. We will associate with each dipole an Ising pseudo-spin variable. Second, we will also consider a four-particle interaction among VDF dipoles in order to describe the first-order transition. This last step was inspired by a proposition of Blinc and Zeks[18], which suggested that the addition of a non-linear four-spin interaction term to the Hamiltonian which describes the ferroelectric PT of KDP[19,20], could cause the transition to change from second- to first-order. With these assumptions, the Hamiltonian for the P(VDF–TrFE) system can be written as:

$$H=-\sum_{\langle ij\rangle}[J_0\xi_i\xi_j\sigma_i\sigma_j+J_1\xi_i(1-\xi_j)\sigma_i\sigma_j]-\sum_{\langle ijkl\rangle}[J_2\xi_i\xi_j\xi_k\xi_l\sigma_i\sigma_j\sigma_k\sigma_l] \qquad (1)$$

where J terms are the interaction energies, σ is a pseudo-spin operator and ξ is an occupation operator to the VDF dipole which assumes the values 0 or 1. For simplicity we assume that σ has an Ising character ($\sigma=\pm1$). In the mean field approximation the internal energy of this model is:

$$U=\frac{1}{2}[(j_1-1)x^2-j_1x]p^2-\frac{1}{4}j_2x^4p^4 \qquad (2)$$

and the entropy is:

$$s=-\frac{x}{2}[(1+p)\ln(1+p)+(1-p)\ln(1-p)] \qquad (3)$$

where $j_i=J_i/J_0$, x is the configurational average $\langle\xi\rangle_c$, and p is the polarization. We have neglected all correlations among pseudo-spins or occupation operators.

The mean field treatment above does not allow us to decide whether the interaction terms in equation (1) come from intramolecular or intermolecular interactions. In fact short range interactions of both kinds can occur simultaneously, as has been proposed by other authors in terms of statistical calculations[17,21]. Concerning their origins, we believe that the two-particle terms represent the overall interaction between pairs of dipoles (irrespective of their host chains), while the four-particle term is associated with the possibility of interactions of a dipole pair being influenced by the fluctuations of a second pair in its neighbourhood.

The free energy ($F=U-Ts$) minimization in p gives us the mean field value of the spontaneous polarization p_0. After minimization of F we get:

$$p_0=\tanh\left\{\frac{[x+j_1(1-x)+j_2x^3p_0^2]p_0}{t}\right\} \qquad (4)$$

where t is the reduced temperature ($t=T/J_0$).

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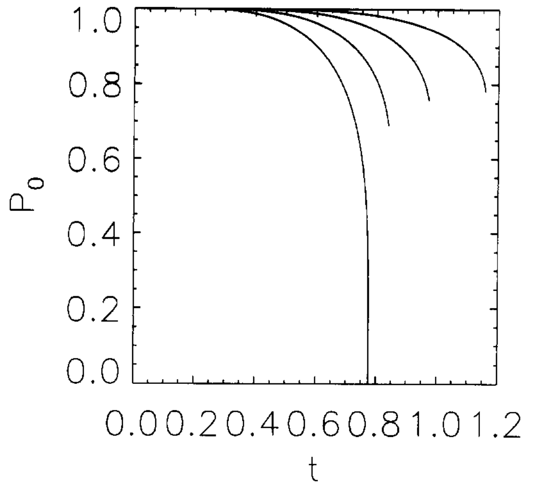

Figure 1 Spontaneous polarization (p_0) as a function of the reduced temperature ($t = T/J_0$) for various concentrations (x) of VDF: from left to right $x = 0.5, 0.6, 0.7$ and 0.8. At $x = 0.5$ there is a tricritical point

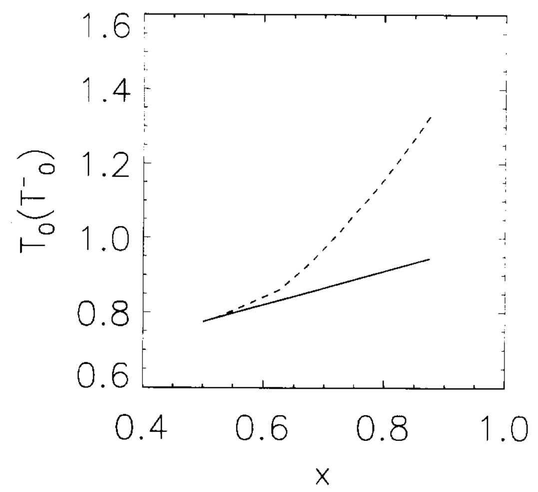

Figure 2 Diagram of the thermal hysteresis $T_0(x)$ (——) and $T_0^-(x)$ (– – –)

Figure 1 shows a plot of the calculated spontaneous polarization as a function of t, for various concentrations x. We have used the values $j_1 = 0.55$ and $j_2 = 2.06$, suggested by Moreira *et al.*[9,22]. The discontinuity in the polarization decreases monotonically with x. At $x = 0.50$ there is a tricritical point separating regions of first- and second-order PT. The obtained thermal evolution of the spontaneous polarization would be the correct behaviour of the order parameter for each microregion of the sample that undergoes normal (non-diffuse) PT[12].

Figure 2 shows a diagram of the limits of stability of ferroelectric and paraelectric regions as a function of concentration x. The curves $T_0(x)$ and $T_0^-(x)$ represent, respectively, the limits of paraelectric and ferroelectric phases. The results shown in this figure are in good qualitative agreement with the measured phase diagram of the P(VDF–TrFE) system[5,8,11].

The above results support the conclusion that the essential features of the P(VDF–TrFE) behaviour can be described by a simple four-particle interaction model. The relative success of this approach can be understood in the following way: the two-particle interaction terms act to line up the dipoles, while the non-linear term is responsible for the first-order character of the transition. The effect of the dilution of VDF dipoles by the TrFE dipoles is seen by the reduction of the transition temperatures, thermal hysteresis and the first-order character of the transition.

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