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(16) Mixing of the copolymer and DPPC was accomplished in the following manner: 0.9 mL of a 1 mg/mL copolymer solution in the required phosphate buffer (note 4) was mixed at room temperature with 0.1 mL of a 10 mg/mL suspension of DPPC in the same buffer. The mixture was then heated to 50 °C for 10 min with repeated vortex agitation.
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(20) Department of Polymer Science and Engineering.
(21) Department of Physics and Astronomy.

Keith A. Borden,[20] Ki Min Eum,[21] Kenneth H. Langley,[21] and David A. Tirrell*[20]

Department of Polymer Science and Engineering and Department of Physics and Astronomy University of Massachusetts Amherst, Massachusetts 01003

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Identification of a Curie Transition in Vinylidene Fluoride/Tetrafluoroethylene Random Copolymers by Spectroscopic Methods

While copolymers of vinylidene fluoride (VF_2) and trifluoroethylene (TrFE) have been studied extensively,[1-6] only recently[7-9] has a Curie transition been observed in random copolymers of VF_2 and tetrafluoroethylene (TFE). Initial studies on a commercially available 81/19 (mol %) copolymer had mixed results[7,8,10-12] in detecting an observable Curie transition due to its proximity to the crystalline melting point. However, a systematic study[13,14] of VF_2/TFE copolymers over a wide compositional range by X-ray and thermal analysis unequivocally demonstrated the existence of a Curie transition.

Since the random addition of TFE comonomer to a VF_2 backbone does not introduce a new chemical species (as in the case of copolymerization with TrFE) but merely increases the head-to-head defect content, evidence of a Curie transition in VF_2/TFE copolymers further reinforces the notion that poly(vinylidene fluoride) (PVF_2) must also undergo a Curie transition.[7] The fact that it may coincide with the crystalline melting point remains a plausible argument for the lack of any experimental verification of this Curie point in PVF_2. In the commercially available (Kynar 7201) VF_2/TFE (81/19) copolymer, a similar observation can be made, as shown in Figure 1. On the first

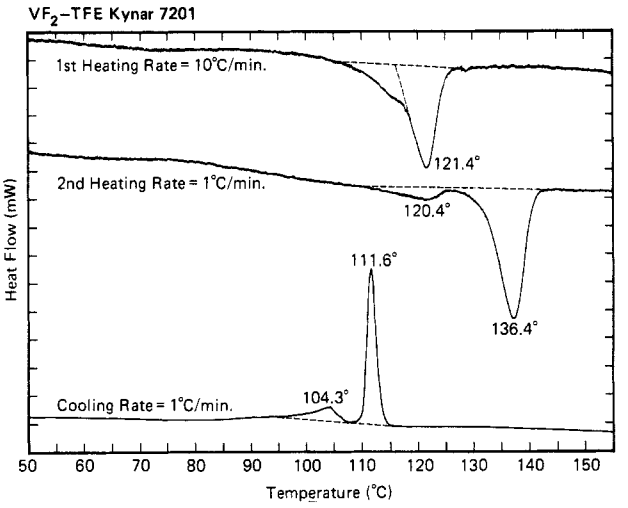

Figure 1. DSC trace of VF_2/TFE copolymer with a 81/19 (mol %) ratio. Top trace, first heating; lower trace, cooling at 1 °C/min; middle trace, sample cooled from the melt at 0.2 °C/min and then heated.

heating the DSC trace shows an asymmetric melting point curve indicating the presence of a premelting transition at 116 °C. When the sample is cooled (bottom trace), it becomes quite evident that in addition to the crystallization exotherm, there is a second, weaker feature, which might be associated with a paraelectric to ferroelectric phase transition.

As earlier work[6] indicated, Raman spectroscopy is a nondestructive technique for probing local changes in conformational order which accompany a Curie transition. In fact, bands in the 800–850-cm^{-1} region have been used[6] to investigate the loss of the planar PVF_2 structure in VF_2/TrFE copolymers as the temperature was raised to the Curie point. The intense 841-cm^{-1} asymmetric CF_2 stretching band which is characteristic of the planar form was observed to lose intensity as the 805-cm^{-1} band characteristic of TG and/or TG′ conformations became dominant at the Curie point. It was thus anticipated that similar high-temperature studies could be carried out on the VF_2/TFE copolymers and could be used to establish the absence or existence of a Curie transition.

In order to investigate the transition shown in Figure 1 by Raman spectroscopy, a sample of the Kynar 7201 copolymer was slow cooled from the melt at 0.2 °C/min. This allowed more perfect crystals to form, thereby raising the melting point by 15 °C as shown in the second heating trace of Figure 1. Moreover, of equal importance was the appearance of a well-defined transition at 120.4 °C, easily delineated from the melting point at 136.4 °C. A second portion of this same sample was used for the Raman studies shown in Figure 2. At 83 °C the spectrum is very similar to that observed[6] for the VF_2/TrFE copolymers below the Curie point. As the temperature approaches that of the observed DSC transition (120.4 °C) a dramatic change in the intensity of the bands at 805 and 841 cm^{-1} is observed, with the 805-cm^{-1} band increasing in intensity at the expense of the 841-cm^{-1} band. Lowering the temperature to 108 °C returns the relative intensity of the bands to their original value. The cyclic reversibility and the band intensity variations with temperature suggest that the 120.4 °C transition involves a reversible change in conformation from a planar structure to one of lesser order which includes short TGTG′ sequences. This order–disorder transition is thus identical with that observed[6] in VF_2/TrFE copolymers and can be characterized as a Curie transition.

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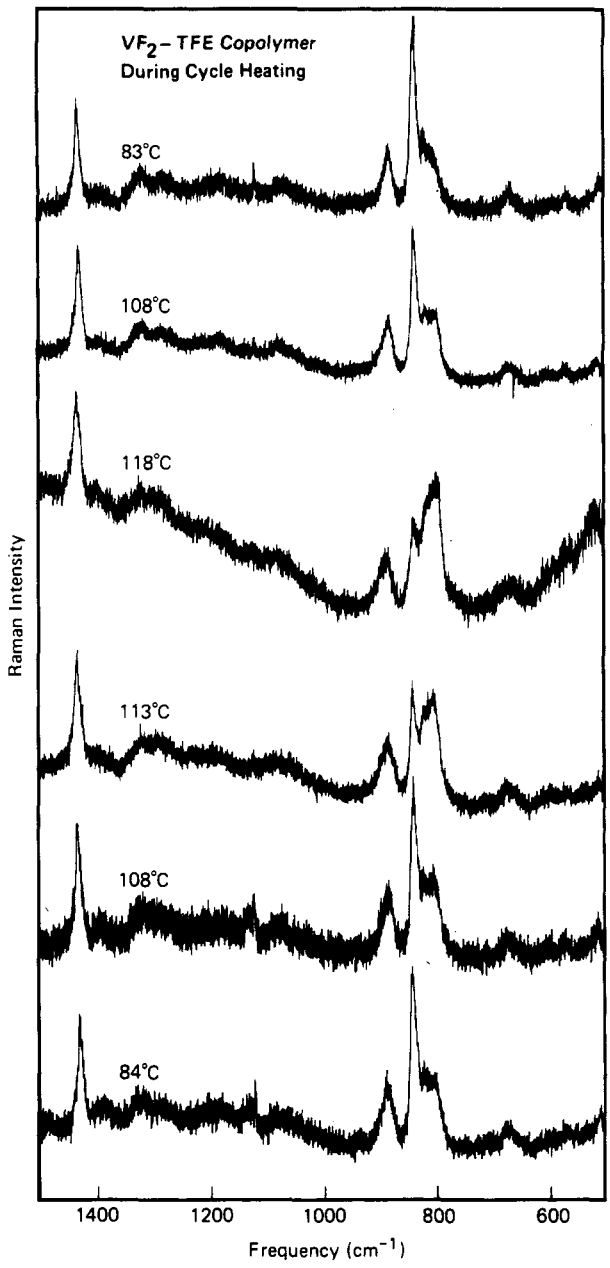

Figure 2. Raman spectra of VF_2/TFE copolymer as a function of temperature. (excitation wavelength = 488.0 nm, resolution = 4 cm^{-1}).

The feasibility of using Raman measurements to determine Curie behavior in VF_2 copolymers has been demonstrated. The characterization of these order–disorder transitions by nondestructive spectroscopic methods will be of extreme importance in studying VF_2/TFE copolymers with VF_2 compositions[15] less than 50%. In these cases the Curie point will occur below room temperature and will not be easily accessible by conventional X-ray diffraction methods.

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Jennifer Green and J. F. Rabolt*
IBM Almaden Research Center
San Jose, California 95120
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Direct Measurement of Propagating Radical Concentration in a Semicontinuous Emulsion Polymerization

Achievement of a better fundamental understanding of free radical emulsion polymerization requires knowledge of the nature and concentration of the propagating free radical species. Direct observation of propagating free radicals in an emulsion polymerization had not been reported until the recent work of Ballard et al.,[1,2] who applied modern ESR techniques to observe propagating free radicals in a batch emulsion polymerization of methyl methacrylate. We have extended ESR analysis to semicontinuous acrylic emulsion polymerization and have studied the propagating free radical species as a function of polymerization temperature and particle size.

Semicontinuous emulsion polymerization, in which monomer is continuously added over several hours, is commonly used for the commercial preparation of latex polymers. This method is preferred primarily because it allows easy control of the polymerization temperature and the preparation of uniform copolymer compositions. Under suitable conditions the rate of polymerization is governed by the monomer feed rate. If it is assumed that monomer diffusion is not a rate-limiting process and that the bulk of the polymerization occurs isotropically within the latex particles, then in a semicontinuous system that has reached steady state the polymerization kinetics can be represented by eq 1, where [M] and [R•] represent the

$$\text{rate of monomer feed} = \text{rate of polymerization} = k_p[M][R^\bullet] \quad (1)$$

steady-state monomer and radical concentrations in the latex particles and k_p is the propagation rate constant. The validity of this equation has not been previously tested by independently measuring each term. The rate of monomer feed and the steady-state monomer concentration can be measured experimentally, and k_p can be estimated from analogous homogeneous polymerizations. The ESR measurements reported here now give us the steady-state radical concentration data which show that eq 1 is valid

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