

Crystallization in electric fields of a semiflexible copolymer: *p*-hydroxybenzoate/ethylene terephthalate

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This work has studied crystallization in electric fields of a semiflexible polymer containing poly(ethylene terephthalate) (PET) segments. Electric (E) stimuli were found to either suppress or enhance PET crystallization depending on E-field strength. Over a relatively narrow field range the effect changes from suppression to enhancement of crystallinity. It is suggested that either inter-chain cooperative phenomena or electromechanical effects in the context of nucleation and/or growth may be affecting crystallization. For example, electrical alignment of rigid (mesogenic) segments in the copolymer structure leading to distension of the crystallizable and more flexible PET segments.

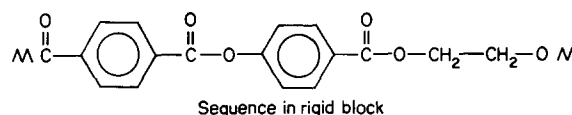
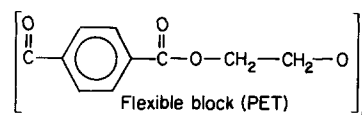
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INTRODUCTION

Since most organic macromolecules contain dipolar bonds, electrical forces can affect their conformations, molecular orientation, the nature of inter-chain bonding, and even crystallographic structure. Most previous studies of polymers under the influence of electric fields have involved exposure of materials in the solid state¹⁻⁶. Such studies are often carried out in the context of electrical phenomena, for example, the poling of polymeric solids to produce piezoelectric or pyroelectric materials. However, the role of the electric field in modifying structure during the transition from the liquid to the solid state is largely unknown.

The magnitude of dipole moments is obviously a crucial variable in possible field effects on structure. Another important factor is the nature of thermal motions since these should reduce susceptibility to field-induced molecular rearrangements. Thus, solidifying liquids of highly flexible chains may not undergo any major structural change under the influence of electrical forces. For this reason, many common dipolar polymers are not likely to reveal any effects, and susceptibility may require certain levels of backbone rigidity. We have selected for our studies a polyester of limited flexibility, containing both rigid and flexible blocks in its backbone structure. The chemical synthesis and characterization of this group of materials has been reported⁷. The specific polymer used in this investigation is synthesized by condensation of 72 mole per cent poly(ethylene terephthalate) (PET) and 28 mole per cent *p*-acetoxybenzoic acid (pab). The structure resulting from the transesterification can be described as an *n*-block polymer of flexible PET segments and a whole range of more rigid segments with random structure which contain both *p*-oxybenzoyl and ethylene terephthalate structural units. The presence of PET homopolymer in the 28/72 composition cannot be ruled

out. Segments with high content of oxybenzoyl units are known to be mesogenic, as indicated by the fact that liquid crystalline materials are formed when more than 60 mole per cent pab is used during synthesis. The experimental semiflexible polymer used here does not have a high enough content of mesogenic blocks to produce optical evidence of liquid crystallinity. The structures below show the flexible block and one possible chemical sequence in random rigid blocks (insertion of an oxybenzoyl unit in a PET segment):



EXPERIMENTAL

The copolymer investigated was supplied to us as a powder by Tennessee Eastman in Kingsport, Tennessee. Thin films of the copolymer were heat pressed between 0.05 mm thick Teflon sheets placed within an insulated aluminium housing. The platens of the press were preheated to 235°C (temperature of the surface) prior to installment of the mould. The mould was allowed to equilibrate at 235°C at which time a pressure of 165 psi was applied and the heaters were turned off immediately. The mould was then allowed to cool slowly by natural convection/radiation to room temperature. Cooling from 235°C to room temperature took ~7 h, and the material

was kept under the applied pressure during this period of time. Exposure of copolymer melts to electric fields was carried out in a thermally controlled cell where the material was placed in contact with oppositely charged electrodes. The upper electrode was shaped as a flat plate, whereas the lower one was shaped as a cup in order to contain the polymeric melt. Both electrodes were gold-plated and covered with aluminium foil which facilitates removal of samples after the thermoelectric treatment. The cell was connected to an Oyo Denshi type UZ-2140 thermal-controller device, and also to a Yokogawa type 2141 high voltage supply. Prior to any thermo-electric treatments, the cell was purged with nitrogen in order to suppress as much as possible chemical degradation in the samples. A positive pressure nitrogen atmosphere was maintained during the entire thermo-electric treatment. All melts were exposed to electric fields at $235^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ for a time period of 15 min. After the exposure period, the melts were allowed to solidify under the influence of the field. Cooling rates were reproducible for all samples as verified by comparison of the strip chart recordings of heating/cooling curves. At room temperature, the electric field was removed and all samples were subjected to calorimetric and X-ray diffraction analysis 24 h later.

Differential scanning calorimetry (d.s.c.) measurements were carried out with a DuPont thermal analyser. The interactive d.s.c. V2.0 data analysis program was used to analyse the calorimetric data. Heat flow was measured in all samples within the range 40° to 290°C , at a heating rate of 10°C per min. The weight of samples for d.s.c. analysis ranged from 5.0 to 9.0 mg. During the d.s.c. experiment, the cell was kept under a constant flow of nitrogen of $40\text{ cm}^3\text{ min}^{-1}$. X-ray scans were obtained with a Phillips Norelco Vertical Scanning Diffractometer, equipped with a graphite monochromator. The voltage and current in the instruments were 40 kV and 10 ma respectively, and the radiation was $\text{CuK}\alpha$. Scanning covered the 2θ range from 10° to 35° , at a scanning rate of $1^{\circ} 2\theta$ per min.

RESULTS AND DISCUSSION

Figures 1 and 2 show X-ray diffractometer scans of a heat pressed film of 28/72 copolymer and pure PET respectively. The similarity of both scans implies that either crystallizable PET segments exist in the *n*-block structure or PET homopolymer is present in the material. The method used to measure relative crystallinity from X-ray scans involved delineating the amorphous curve with tangent lines to shoulders of crystalline peaks. A second

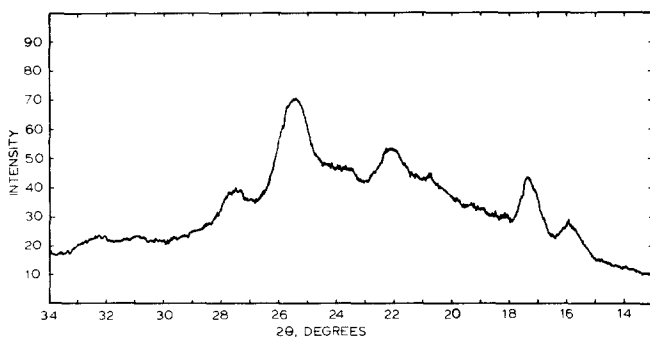


Figure 1 X-ray diffractometer scan of the copolymer synthesized with 28 mole% PET and 72 mole% *p*-acetoxybenzoic acid

method was attempted using the scan of a seemingly amorphous sample which was quenched from the melt into liquid nitrogen. Using this scan, amorphous X-ray scattering curves were traced using the method suggested by Challa *et al.*⁸. However, it was not possible to scale through the scan of the quenched sample scattering curves which did not intersect crystalline peaks. This problem introduced errors and variations which were sensitive to the intensity scales in diffractometer scans. Therefore, the alternative method of tracing the amorphous curve was judged to be more consistent and reliable in order to assess changes in degree of crystallinity. The ratio of areas under the amorphous scattering curve to the total area under the curve in semi-crystalline samples was used to calculate relative values of crystallinity. Figure 3 shows a plot of % crystallinity as a function of the electric (E) field

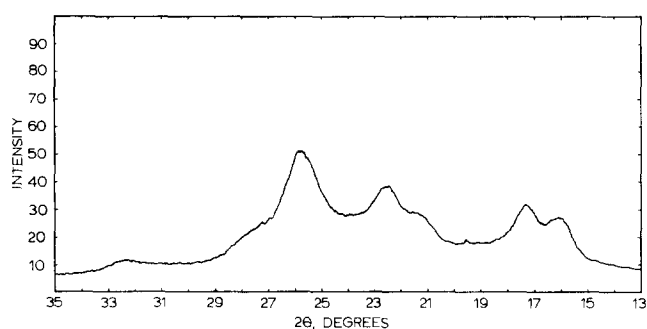


Figure 2 X-ray diffractometer scan of the PET used in the synthesis of the copolymer studied

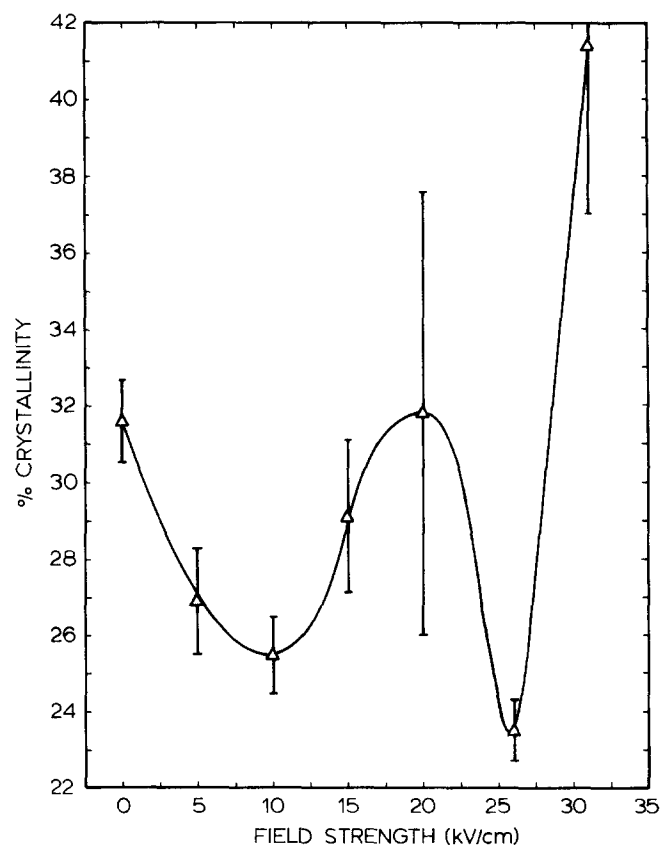


Figure 3 Variation of % crystallinity as a function of the electric field strength to which copolymer melts were exposed during solidification. The plot includes the value of crystallinity in films which served as thermal controls (error bars represent \pm one standard deviation)

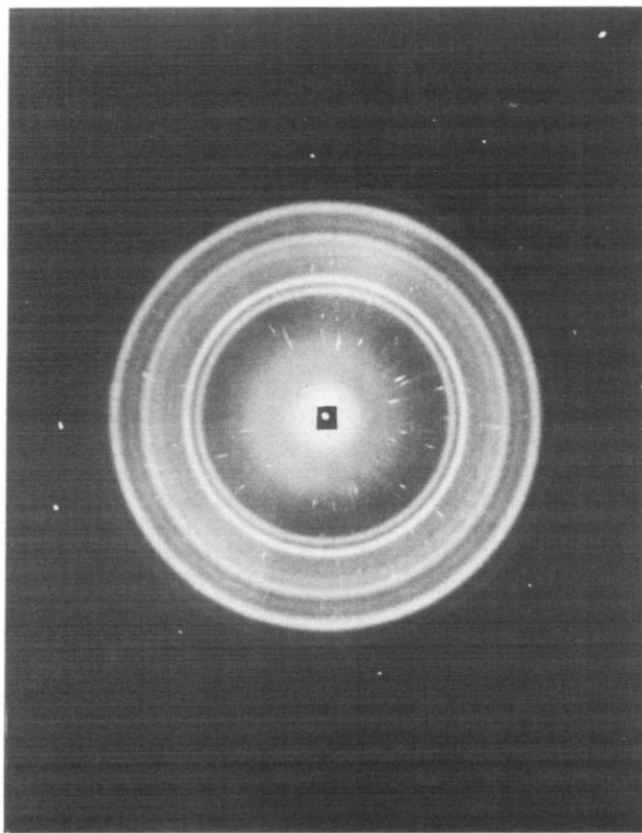


Figure 4 X-ray Laue photograph of a copolymer film E-field-crystallized at 26 kV cm^{-1} . The X-ray beam was perpendicular to the plane of the experimental film sample

strength applied during solidification of the melt. The value reported for samples exposed to zero E-field strength corresponds to crystallinity in thermal controls for electrically exposed materials. The variation observed in measured values of % crystallinity among several samples solidified under identical conditions is quantified in *Figure 3* by an error bar equal to \pm one standard deviation. This standard deviation was calculated from data consisting of five independent measurements. In spite of this variation, it is clear that E-fields affect crystallization of the polymeric liquid. In order to assess from X-ray data the effect of the field on % crystallinity, it is necessary to determine if any significant field-induced orientation of crystallites occurred.

It was suspected that field-induced orientation of crystallites was not significant given the appearance of Laue X-ray photographs from all experimental samples. *Figure 4* shows a typical photograph obtained with the X-ray beam perpendicular to the plane of an experimental film. A similar pattern is obtained with the X-ray beam parallel to the plane of the film. In order to assess further the possible existence of orientation, we calculated for all samples the parameter f given by the following relation:⁹

$$f = \frac{P - P_0}{1 - P_0} \quad (1)$$

where

$$P = \frac{\sum I_{(h00)}}{\sum I_{(hkl)}} \quad (2)$$

In equation (2), $\sum I_{(h00)}$ is the diffracted intensity from $(h00)$ planes (the most strongly diffracting planes in the experimental scans) and $\sum I_{(hkl)}$ is the sum of diffracted intensities from all planes. P_0 in equation (1) is the same ratio of intensities given by P but for an unoriented sample. Thus, f values are expected to be zero for unoriented samples and would approach +1 or have negative values in f oriented specimens. Our value of P_0 was obtained from an X-ray scan of the as-polymerized powder. *Figure 5* shows a plot of f values for all experimental samples (thermal control and field crystallized). Since all f values cluster about zero, we have assumed that field induced orientation of crystallites, if any, does not invalidate % crystallinity measurements.

Several observations can be made from analysis of data summarized in *Figure 3* (a total of 34 measurements of % crystallinity). A decrease in crystallinity in the range of low to intermediate field strengths relative to the thermal control is statistically significant. The observed increase in crystallinity for materials solidified under the highest field strength is statistically significant as well. Statistical significance was judged by a one-way analysis of variance using F statistics with a 99% confidence interval¹⁰ and Duncan's multiple range test¹¹. Thus, the data suggest a threshold-like phenomenon whereby the E-field's effect switches from suppression to enhancement of crystallinity at some critical value. Experimental uncertainty in crystallinity measurements and E-field values make it difficult to identify the narrow E strength window over which the reversal occurs. Furthermore, one cannot rule out the possibility that more than one minimum exists in the field strength dependence of crystallinity. The reason for the large standard deviations in data for two of the field strengths is not known at the present time. The five independent measurements of crystallinity for each field strength were carried out on different locations of one experimental sample. Thus, a possible origin of the wide variation at two specific field strengths may be sample inhomogeneity. This inhomogeneity could be caused by field-induced electrohydrodynamic flow occurring at the time of crystallization. This phenomenon is well known and it is dependent on variables such as voltage and material's constants¹².

Figure 6 shows d.s.c. scans characteristic of, the original powder, heat pressed films, thermal control films, and one field-exposed sample. Both thermal control and field-

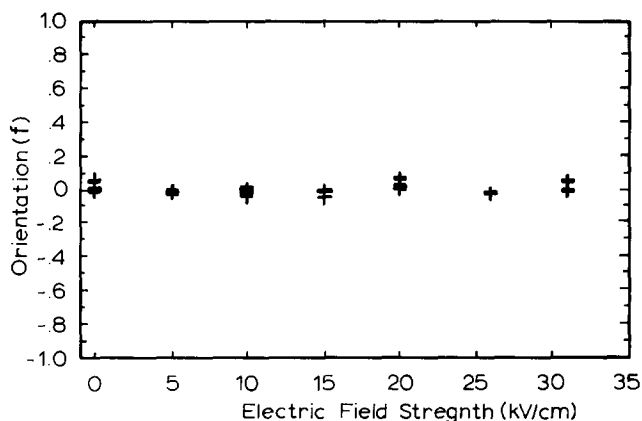


Figure 5 Crystalline orientation parameter, f (see text for definition) plotted as a function of E-field strength used during crystallization

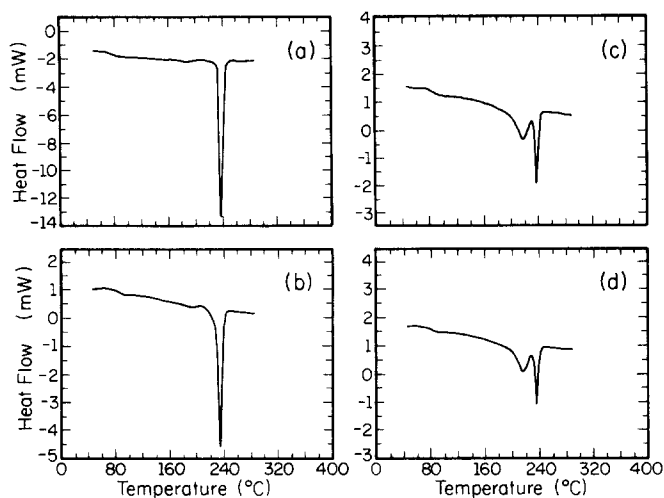


Figure 6 Differential scanning calorimetry scans corresponding to, (a) asynthesized copolymer, (b) a heat pressed film of the copolymer, (c) a copolymer film exposed to the thermal program used during experiments of crystallization under electric fields, (d) a copolymer film crystallized under electric field

Table 1 Heating rate dependence of endotherm intensity

Heating rate ($^{\circ}\text{C min}^{-1}$)	$A_{215^{\circ}\text{C}}$	100*
	$A_{235^{\circ}\text{C}} + A_{215^{\circ}\text{C}}$	
10	75.4	
100	74.8	

*Ratio of areas under the low and high temperature endotherms

exposed samples reveal two melting endotherms with maxima at $\sim 215^{\circ}$ and $\sim 235^{\circ}\text{C}$. The presence of two apparent endotherms is definitely the result of thermal history and not a consequence of crystallization under E-fields. However, as shown in *Figure 5*, the field strength affects the per cent of total area under the endotherms which is associated with the 215°C peak. The presence of two endotherms in d.s.c. scans of PET homopolymer has been reported by several authors¹³⁻²³. Thus, before discussing the implications of the data to field-induced phenomena we point out what have been the interpretations of the double endotherm. One of the first interpretations was the presence of two different types of PET crystals¹³. A different interpretation is that of Roberts¹⁶ who suggested that the higher temperature endotherm is associated with melting of material which recrystallizes after the first endotherm. The general idea of recrystallization during the d.s.c. scan was subsequently favoured by others^{17,18,23}. It is partly based on the experimental observation that increasingly higher heating rates used for PET samples in a d.s.c. apparatus lead to high temperature endotherms of decreasing intensity. Thus, a controversial aspect of the double endotherm problem was whether or not two types of crystals co-exist in the PET morphology. We did not obtain significant differences in the relative intensity of the two endotherms depending on heating rates (see *Table 1*). These results suggest that recrystallization may not occur as readily in the copolymer studied. The observation is important as it implies that the presence of rigid molecular segments in the system, either as components of a blend or blocks of random structure in a copolymer, hinders the normal crystallization or recrystallization behaviour of PET.

Intuitively, the observation of little or no recrystallization favours the existence of a copolymer structure in the system. The high temperature endotherm in our copolymer samples could be associated with crystallites in the original heat-pressed film which do not melt during the thermo-electric program.

Figure 7 shows the field strength dependence of % of the total area under the endotherms which is associated with the low temperature peak (peak at 215°C). From a statistical point of view, the most reasonable interpretation of this curve is that a decrease in intensity of the low temperature endotherm occurs in materials solidified under intermediate field strengths relative to thermal controls. The solid line in the plot of *Figure 7* indicates the average per cent of total area associated with the low temperature peak in thermal controls. The E-field range with less per cent area relative to the crystals for the 215°C peak corresponds roughly to the range in which X-ray diffraction data indicate suppression of crystallinity. Following the previously discussed interpretation of the double endotherm in our samples, a lower per cent area at 215°C could imply two different effects. One is that field application stabilizes thermally the high temperature crystallites formed during synthesis of the copolymer. The other implication is that a reduced volume of crystalline material grew from the melt during field application. This last interpretation is essentially consistent with X-ray

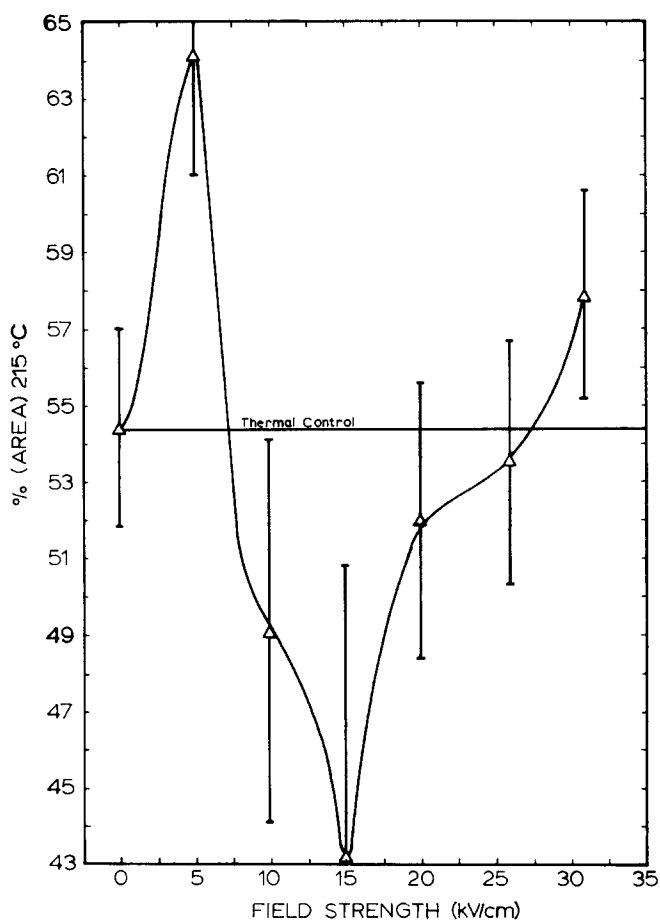


Figure 7 Percent of the total area under both endotherms which corresponds to the low temperature peak at 215°C as a function of the electric field strength used during solidification of copolymer melts. Measurements of area under the endotherms is obtained from d.s.c. data (the error bars correspond to \pm one standard deviation)

Table 2 Mean 2θ values \pm one standard deviation of maxima in X-ray diffractometer scans

Sample	Peak 1	Peak 2	Peak 3	Peak 4*	Peak 5
Thermal control	15.87 \pm 0.097	17.28 \pm 0.091	22.08 \pm 0.110	25.49 \pm 0.124	27.58 \pm 0.076
E = 5 $\times 10^3$ V cm ⁻¹	15.97 \pm 0.157	17.35 \pm 0.094	22.18 \pm 0.120	25.56 \pm 0.065	27.69 \pm 0.091
E = 1 $\times 10^4$ V cm ⁻¹	15.97 \pm 0.067	17.41 \pm 0.074	22.25 \pm 0.112	25.6 \pm 0.100	27.73 \pm 0.084
E = 1.5 $\times 10^4$ V cm ⁻¹	16.05 \pm 0.071	17.46 \pm 0.079	22.26 \pm 0.096	25.71 \pm 0.022	27.77 \pm 0.104
E = 2 $\times 10^4$ V cm ⁻¹	16.17 \pm 0.342	17.64 \pm 0.338	22.43 \pm 0.342	25.85 \pm 0.232	27.97 \pm 0.327
E = 2.6 $\times 10^4$ V cm ⁻¹	15.99 \pm 0.022	17.39 \pm 0.089	22.21 \pm 0.138	25.63 \pm 0.096	27.72 \pm 0.057
E = 3.1 $\times 10^4$ V cm ⁻¹	15.82 \pm 0.231	17.34 \pm 0.204	22.12 \pm 0.239	25.52 \pm 0.179	27.7 \pm 0.257

*A higher value of 2θ for this peak in samples crystallized under E-fields is statistically significant

results in four out of the six groups of samples crystallized under the field. X-ray results point out that average crystallinities are lower relative to the control in samples crystallized at 5, 10, 15 and 26 kV cm⁻¹. For three out of these four groups of samples (10, 15 and 26 kV cm⁻¹), the average per cent of 215°C endotherm is also lower, consistent with less crystalline material growing from the melt. For the highest field strength, 31 kV cm⁻¹, X-ray results indicate a higher average crystallinity and also the average per cent area of the 215°C endotherm in this case is higher than that of the thermal control. One must point out that the additional thermal history necessary to obtain d.s.c. scans could have eliminated or reduced correlations to X-ray data. For example, further crystallization could have occurred during the d.s.c. scan in samples with low initial values of crystallinity after field exposure. Another factor which may be affecting parameters measured by d.s.c. is the release of molecular stresses prior to or during melting of the low temperature crystallites. In our case such stresses may be induced by electrical polarization or electrohydrodynamic flows at the time of solidification. In spite of the possible inaccuracies and scatter in the data it is possibly significant that the lowest average values of % Area_{215°C} do occur in the range of E-field suppression of crystallinity. Observations on E-field suppression of crystallinity suggest the idea of inhibiting physical ageing of polymers through exposure to electrical stimuli during their previous thermal history.

The 2θ positions and half intensity widths of maxima in X-ray scans were analysed for all samples. Mean values and their respective standard deviations for 2θ values are reported in Table 2. Statistical analysis on the data yields a significantly higher value of 2θ in the maximum near $2\theta = 25^\circ$ for samples crystallized under the influence of E-fields. Even though a similar effect could be associated with the other four maxima, it was not formally significant from a statistical point of view. The fourth maximum corresponds to a Bragg spacing of 3.47 Å. We utilized a computer program to match a set of diffracting planes with this particular *d*-spacing. The program identified {100} planes as the diffracting planes assuming the following crystallographic parameters for the triclinic unit cell of PET (24): $a = 4.56$ Å, $b = 5.94$ Å, $c = 10.75$ Å, $\alpha = 98.5^\circ$, $\beta = 118^\circ$, $\gamma = 112^\circ$. Examination of PET unit cell and the direction of ester bond dipole moments suggest a possible explanation for a shorter spacing between {100} planes. Flory²⁵ pointed out that the ester bond dipole, which has a magnitude of ~ 1.8 Debye units, is inclined only 20° to 30° with respect to the C=O bond axis. Thus, head-to-tail coupling of dipole moments sharing a common direction due to the E-field could shorten the spacing

between {100} planes. Formation of such polar structures could also introduce a significant extent of crystallographic distortion. In relation to this last possibility, differences in half intensity widths for each X-ray peak were measured but not found to be statistically different.

A theoretical prediction is considered in order to understand the basis of fields affecting the development of structure as the liquid solidifies. The simplest approach would be to consider the prediction of the Langevin equation. This equation predicts the magnitude of polarization due to oriented dipoles at a given temperature and magnitude of electric field. The average angle θ between dipolar moments of magnitude μ and the external field E is given by:

$$\mu \langle \cos \theta \rangle = \frac{\int_0^\pi \mu \cos \theta \exp\{(\mu E \cos \theta)/kT\} \sin \theta d\theta}{\int_0^\pi \exp\{(\mu E \cos \theta)/kT\} \sin \theta d\theta} \quad (3)$$

Integration yields the Langevin function $L(x)$:

$$L(x) = \langle \cos \theta \rangle = \coth x - \frac{1}{x} \quad (4)$$

where $x = \mu E/kT$. Since x is usually $\ll 1$ and polarization, P , is given by:

$$P = N \mu \langle \cos \theta \rangle \quad (5)$$

Then:

$$P = \frac{N \mu^2 E}{3kT} \quad (6)$$

where N is the number of dipoles per unit volume. According to the Langevin equation, dipolar polarization in PET crystals at the highest field and lowest temperature used in our experiments is equal to 8.22×10^{-9} C cm⁻². This implies that on average 0.15% of the ester dipoles align with the field. It is difficult to envision how the material's structure (e.g., its crystallinity) can be modified with such a small degree of alignment with the E-field. One could suggest two different phenomena to reconcile experimental findings with predictions of the Langevin function. One is that strong localized coupling among molecular dipoles enhances field effects on the crystallizing melt. Rigid se-

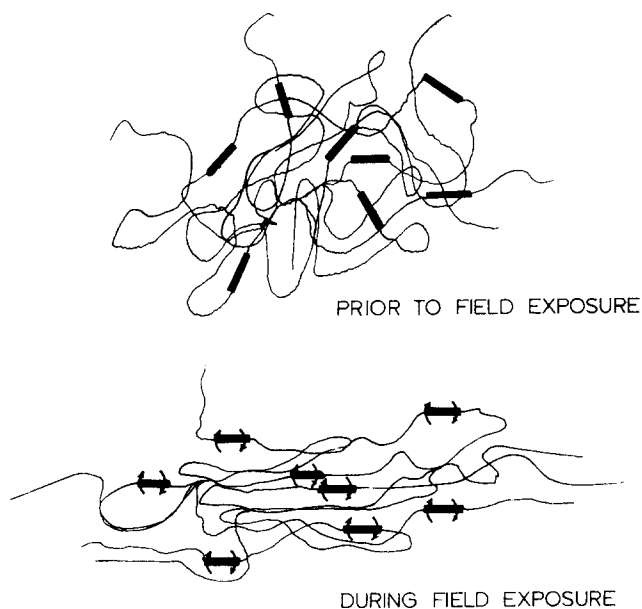


Figure 8 Schematic representation of a possible electro-mechanical effect produced during crystallization under electric fields. Mesogenic (rigid) segments of the copolymer orient nearly perpendicular to the electric field, thus distending the more flexible segments and leading to flow induced crystallization

quences in the copolymer could restrict conformational degrees of freedom sufficiently for the field to induce inter-chain coupling of dipoles. When dipolar coupling occurs, static permittivity theories such as those of Kirkwood, Frölich and Cole^{26, 28} predict an enhancement of dipolar polarization by a factor referred to as the local order parameter, g :

$$\frac{(\bar{M} \cdot \vec{\epsilon})}{V} = P = \frac{\epsilon(n^2 + 2)^2 N g \mu^2 E}{3(2\epsilon + n^2) 3kT} \quad (7)$$

where \bar{M} represents the total electric moment, $\vec{\epsilon}$ the field direction, and V is the dielectric's volume. Most importantly, $g > 1$ if neighbouring dipoles couple through parallel orientation, ϵ is the static dielectric constant, and n is the refractive index. Except for the parameter g , expression (7) is identical to that obtained by Onsager²⁹ which takes into account the magnitude of the internal field. We suggest a different phenomenon which even in the absence of dipolar coupling could produce E-field-induced structural modifications. The concept is an electromechanical effect schematically illustrated in Figure 8 and explained below.

The external E-field could produce an electro-mechanical effect on the crystallizing melt given the covalent attachment of mesogenic (rigid) segments to flexible ones. The short rigid sequences which may partly segregate are likely to experience an orienting torque under the influence of the field. This alignment would be analogous to the orientation of low molecular weight liquid crystals by E- or magnetic fields^{30, 31}. The various modes of electric or magnetic alignment by external fields are known collectively as the Frederiks transitions. These transitions occur rather rapidly (fractions of a second) in low molecular weight liquid crystals. On the other hand, mesogenic rods within a high molecular weight polymer are expected to exhibit a much more sluggish response. Mesogens tend to align perpendicular or parallel to the

field depending on the relative magnitudes of dielectric constants parallel or perpendicular to the director's axis, \vec{n} ,

$$\begin{aligned} \epsilon_{\parallel} > \epsilon_{\perp} &, \quad \vec{n} \parallel \vec{E} \\ \epsilon_{\perp} > \epsilon_{\parallel} &, \quad \vec{n} \perp \vec{E} \end{aligned}$$

In a rod/coil copolymer such as the one we have investigated, the electrical force leading to rod alignment could mechanically strain or distend covalently bonded flexible blocks. It is in this indirect way that an electric field could affect the crystallization of flexible chain segments. Thus, we postulate the possibility of an electro-mechanical effect in which a phenomenon similar to flow induced crystallization occurs through the electrical alignment of mesogenic segments with the applied field.

We have considered several explanations for the transition from suppression to enhancement of crystallinity under the influence of the E-field. Initial suppression of crystallinity could be viewed as the result of conformational distortion induced by the field. Another possible explanation for suppression of crystallinity is a high surface energy of 'poled' nuclei. Unless the poled nucleus is energetically favoured (as may be the case in materials like poly(vinylidene fluoride)), this effect could lead to a lower nucleation rate. At low field strengths, long range dipolar coupling should not be a strong effect and thus distortion and high surface energy nuclei may lead to lower crystallinities. However, greater degrees of dipolar coupling at higher fields could gradually counteract this effect, producing at such fields higher rates of nucleation and/or growth. The combined action of these two phenomena could explain the partial recovery of crystallinity at intermediate fields. However, it is difficult to draw conclusions on this specific point given the observed variations in crystallinity at some fields (e.g., 20 kV cm⁻¹). As mentioned earlier, these variations may reflect inhomogeneities due to electrohydrodynamic flow. The significant suppression at 2.6×10^4 V cm⁻¹, just prior to the transition to enhanced crystallinity, could be related to the onset of field-induced orientation of mesogenic segments. In the context of flexible segment crystallization, this alignment would produce at first significant distortion before leading to the electro-mechanical effect described above. The threshold-like change to crystallinity enhancement could be produced by the synergistic effect of strong dipolar coupling and chain distention as the field aligns most of the rigid segments in a common direction or plane. In monodisperse and low molecular weight liquid crystals, alignment occurs at threshold values of applied voltage. In the experimental rod/coil copolymer, on the other hand, alignment is probably more gradual since the mesogenic segments are polydisperse and involved in various levels of segregation.

CONCLUSIONS

Exposure of solidifying melts of a semi-flexible copolymer to electric fields was found to either suppress or enhance the material's crystallinity depending on the field's magnitude. The transition from suppression to enhancement of crystallinity is observed over a relatively narrow window of field strength. Possible factors in crystallinity suppression are conformational distortion of segments and

formation of unstable nuclei due to electrical alignment. However, enhancement of crystallinity at high field strengths could result partly from large electric moments produced by local coupling of dipolar bonds sharing common orientations. A contribution to enhanced crystallinity under a field in copolymers of rod/coil structure could involve an electro-mechanical effect whereby flexible segments are subjected to a 'flow induced crystallization' effect by electrical alignment of the rigid segments.

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