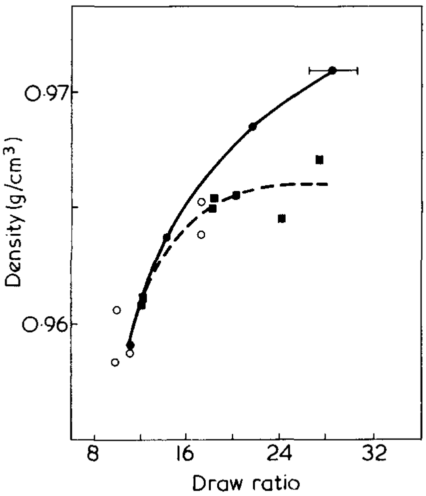

*Figure 2* Density (at 23°C) vs λ for samples of Rigidex type 140–60 (●); 50 (■); 25 (○)

high concentration of longitudinal discontinuities in the form of ruptures.

The third feature worth noting is the presence of longitudinal voids of up to 0.5 μm in width which appear to be present at both low and high λ.

The latter observation has particular relevance in the assessment of density measurements obtained by any flotation method. As shown in *Figure 2* different density/λ relationship is found for samples of different molecular weight (samples 2–4 in ref 1); this is either related to the actual molecular characteristics of the drawn samples or is just a consequence of differences in void size and distribution. The results in this case would merely reflect variations in the diffusion pattern of the solvents used into the loosely packed structure.

A reliable determination of the density is necessary whenever this parameter is used for estimates of sample crystallinity for instance and the present results underline the need for further investigations before a conclusive assessment of the general validity of the density determinations as a means of structural evaluation.

In conclusion we can say that a clear indication has been found for the presence of a fibrillar texture even in ultra-highly drawn samples of LPE. The observed differences in size and homogeneity of the fibrils are consistent with the established views of the plastic deformation of semicrystalline polymers[5] and hence no difference in kind has to be invoked between these samples and conventional highly drawn LPE (λ = 9–10).

The limitations of the SEM technique are obvious and do not allow us to state conclusively to what extent the observed features are part of the surface topography or representative of the bulk morphology. In either case however we believe that they must be taken into account for the important consequences that they can have on other physical measurements.

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## Fluorescence and photooxidation of commercial polypropylene

Recently, using luminescence techniques we established the presence of α,β-unsaturated aldehydic and ketonic carbonyl impurity groups in commercial unstabilized polypropylene[1–4]. These groups absorb light in the wavelength region above 290 nm which is the region relevant to the mechanism of the sunlight-induced oxidation of the polymer[5], (see *Figure 1*). In *Figure 2* we show a direct correlation between the concentration of these groups and the resultant light stability of the polymer.

In contrast Chakraborty and Scott[6] reported no correlation between polymer photooxidation rate and the initial concentration of α,β-unsaturated carbonyl groups as determined by infrared spectroscopy. Clearly therefore, there is some disagreement as to the exact nature of the α,β-unsaturated carbonyl impurities in the polymer and the role that they play in polymer photooxidation.

From their data Chakraborty and Scott[6] maintain that the main photoinitiating species in polypropylene are α,β-unsaturated hydroperoxide groups and these in turn are photolysed to α,β-unsaturated carbonyl groups. If this mechanism is valid, therefore, it might be expected that in the early stages of photooxidation, or indeed thermal (anaerobic) degradation there should be an increase in the concentration of α,β-unsaturated carbonyl groups. However, *Figure 3* shows that when these processes are monitored by fluorescence spectroscopy a decrease in the concentration of α,β-unsaturated carbonyl impurity groups is observed. At present we suggest that the failure by Chakraborty and Scott[6] to observe

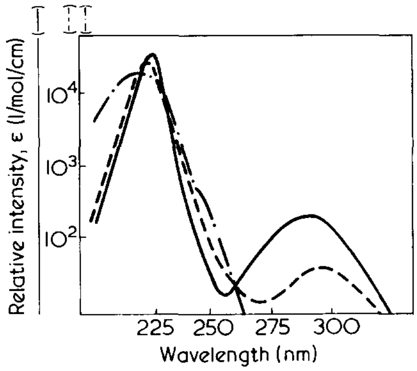

*Figure 1* Comparison of the fluorescence excitation spectrum of unstabilized polypropylene film (200 μm thickness) (———) with the absorption spectra[8] of pent-3-ene-2-one (– – –) and 2-butenoic acid (— · — ·) in n-hexane. Fluorescence spectrum was obtained using a double beam Hitachi Perkin–Elmer MPF-4 spectrofluorimeter

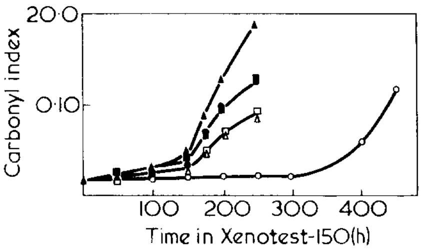

*Figure 2* Variation of carbonyl index *versus* time of irradiation in a Xenotest-150 weatherometer (50% r.h. 45°C) for different batches of commercial unstablized polypropylene film. Before irradiation the samples had relative fluorescence intensities at 340 nm: ▲, −1.0; ■, ● −0.73; □, △ −0.44, ○, −0.25 ($Ex\lambda_{max}$ = 230 and 285 nm). All polymer samples were vacuum pressed at 190°C and had M.F.I. and Ti values of 20 and 25 ppm respectively

a correlation between initial α,β-unsaturated carbonyl group concentration and rate of polymer photooxidation is due to the fact that their infra-red method was based on monitoring the broad band centred at 1685 $cm^{-1}$. This abosrption band can include a variety of unsaturated carbonylic groups such as carboxylic acids[7] that do not absorb light above 290 nm (see *Figure 1*)[8]. Consequently, these groups would not be expected to participate in the sun-light-induced oxidation of the polymer.

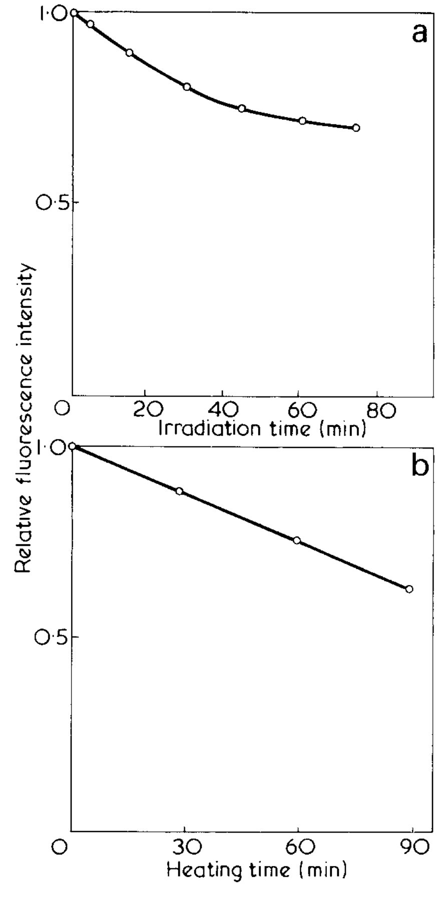

*Figure 3* (a) Effect of irradiation in a Xenotest-150 weatherometer on the intensity of the fluorescence emission ($\lambda_{max}$ = 340 nm) from commercial unstabilized polypropylene film (200 μm thickness). (b) Effect of thermal treatment at 120°C under nitrogen on the intensity of the fluorescence emission from commercial unstablized polypropylene film. $Ex\lambda$ = 285 nm

### *Experimental*

The polypropylene films were irradiated in a Xenotest-150 weatherometer (Original Hanau, Quartzlamp-en, Gmbh) set up for natural sun-light-simulated exposure conditions (45°C; 50% relative humidity). A 1500 W xenon lamp is employed as the light source. The rate of photooxidation of the polymer films was measured by monitoring the build-up in the non-volatile carbonylic oxidation products absorbing at 1710 $cm^{-1}$ using a Perkin–Elmer 157G infra-red spectrophotometer. Carbonyl index = $[(\log_{10} I_0/It)/d \times 100$; where $I_0$ = initial light intensity; $I_t$ = transmitted light intensity; $d$ = film thickness (μm).

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## Electric birefringence of sodium poly(L-glutamate) in water/organic solvent mixtures

Poly(L-glutamic acid) $(Glu)_n$, is a synthetic polypeptide with ionizable side chains. The acid form adopts uncharged helical conformations in some organic solents such as dimethylformamide and exhibits large electric birefringence[1,2]. In this case, the permanent dipole moment along the helix axis dominates in the mechanism of orientation in an electric field. When $(Glu)_n$ is ionized by adding alkali in aqueous solution, the situation is entirely different. At neutral or alkaline pH, $(Glu)_n$ assumes the 'charged coil' form. By lowering pH, a transition from coil to helix is induced[3]. Recently, Kobayasi and Ikegami[4] studied the changes of the specific Kerr constant and the birefringence relaxation time accompanied by the pH-induced helix–coil transition. The coil-to-helix transition is also induced by adding organic solvents such as dioxane[5] and methanol[6] to aqueous solutions of sodium poly(L-glutamate). In the present work we have studied the electric birefringence of sodium poly(L-glutamate) in water/organic solvent mixtures as a function of the solvent composition and the field strength.

Two samples of $(Glu)_n$ were used. Their degrees of polymerization (*DP*) were estimated from the limiting viscosity number ([η]) measured at 25°C, pH 7.3 in a 0.2 M NaCl solution, using the calibration of Wada[7]:

| Sample | [η] ($cm^3$/g) | *DP* |
|---|---|---|
| I | 135 | 380 |
| II | 182 | 670 |

$(Glu)_n$ was dissolved in sodium hydroxide solution and dialysed against distilled water. The mixtures were made up by adding organic solvent (methanol or ethylene glycol) to this original solution. The solvent composition was expressed as the volume percentage of organic solvent.

The apparatus and procedures for electric birefringence measurements have been described previously[8,9]. The