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Predictive Analysis of Thermally Degrading Polymers by Fluorescence Reflectometry. C.H. Stapfer, Metrastat PSD, Duesseldorf, Germany, and R.C. Poller, Dept. of Chemistry, King's College, London, England.

Interest in the study of fluorescence in synthetic polymers is increasing and the technique is beginning to be used to monitor degradation [1]. In particular, thermally degraded PVC has been shown to fluoresce in the visible region when irradiated with UV light. Since however only PVC which contains a heat stabilizer becomes fluorescent upon thermal degradation, an interaction between some defective part of the polymer molecule and the stabilizer is likely to be involved in this phenomenon.

In an attempt to elucidate the cause of the fluorescence we have examined a typical organotin stabilizer dibutyltin bis(iso-octyl thioglycolate) and its degradation product dibutyltin dichloride in solution together with various model compounds representative of the candidate structures for PVC most cited in the literature. None of the solutions showed significant fluorescence when the model compounds were combined with tin compounds. Methyl vinyl ketone was considered to be the most likely compound to form a complex with the tin stabilizer but, as with all other model compounds, there was no change in the fluorescence of its hexane solution when equimolar quantity of DBTIOTG or DBTCI was added [2]. Furthermore, had complexation between the two species occurred, there would have been a shift in the maximum of the ultraviolet absorption spectrum for the combined solution. Also a shift in the carbonyl stretching frequency would have been observed in the infrared spectrum. However, both types of spectra were unchanged by the addition of the tin compounds.

We then looked at the fluorescence of solid PVC samples from a single batch of polymer after oven exposure at 200°C for varying lengths of time, either unstabilized or stabilized with various commercial products based on tin, barium or zinc compounds. Fluorescence spectra obtained from a fluorescence spectrophotometer (Perkin Elmer 203) revealed that marked fluorescence occurs only in stabilized PVC, develops during thermal degradation, attaining a maximum value where discoloration is first observed or even before and then declines. A maximum broad peak emission at ~490nm occurs with exciting radiation of 365nm. This peak is absent in undegraded PVC and in stabilizer free degraded polymer.

A more continuous representation of this time dependent, heat stability related fluorescence was obtained by loading a series of long polymer strips in an automatic testing oven maintained at a constant temperature, then removing them progressively from the oven as to generate a degradation gradient over the length of the samples and finally scanning each sample on a Fluorescence Reflectometer (Metrastat) where it passed, at a fixed speed, under a 365nm light source. The resulting fluorescent radiation was then collected using a photocell adjusted to receive the band centered at 490nm. Here, as in the previous discontinuous experiment, we observed the same increase and then decrease of fluorescence intensity as thermal degradation progresses, but this time as a continuous fluorescence curve representative of the relative efficacy of the stabilizers at retarding the degradation. Fluorescence spectra from all sections of a test strip show that most of the fluorescence is emitted in a band centered at ~490nm and while its intensity varies with the time of exposure, its position is not changed.

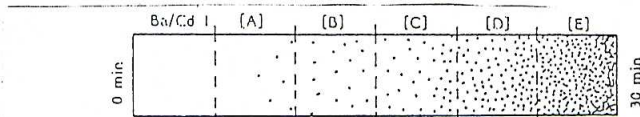


Fig. 1

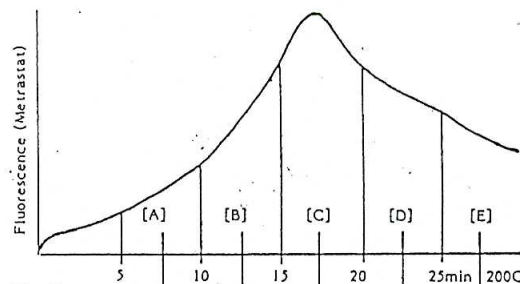
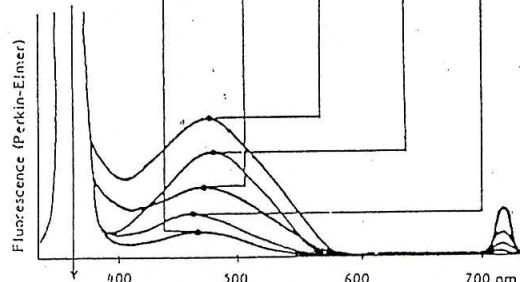


Fig. 2



Since neither the extraction of any of the samples by heating under reflux with hexane nor the removal of the sample's surface seem to affect the 490nm band, it is likely to be a polymer-bound species induced by the stabilizers. A reasonable speculation is that the rise of the dominant fluorescence band at 490nm originates in short chain polyene sequences which are known to give rise to fluorescence [3]. These polyene sequences would only be expected to accumulate in the polymer if the presence of a stabilizer prevents them from growing into long chain non fluorescent chromophores.

It has been shown that for unsubstituted polyenes fluorescence is absent in trienes, at a maximum in tetraenes and then falls off rapidly in compounds with five and six conjugated double bonds. It is therefore implicit that substitution on the triene would cause fluorescence and we thus decided to synthesize a model compound containing the 1-chloro-2,4,6-trienyl group. After considerable difficulties due to the unstable nature of the intermediates, a mixture of the pure 1-chloro-2,4,6-octatriene and its allylically rearranged 2-chloro-3,5,7-octatriene was isolated. Irrespective of how this material was stored, it discolored rapidly and tlc indicated polymerization.

It is clear from the literature that structure units in PVC containing a chlorine atom in the allylic position to two or more double bonds would be extremely unstable, much more than has been realized hitherto. Thus the short sequences of double bonds which are postulated could only exist if the chlorine atoms had been replaced by stabilizer residues and it is likely that the observed fluorescence in the polymer is caused by products of reaction between short polyenes and the stabilizer. To confirm this experimentally, a sample of freshly prepared chloro-octatrienes was immediately mixed with a dibutyltin stabilizer and the fluorescence spectrum recorded. The spectrum obtained is identical with those obtained from heated stabilized PVC and is very strong evidence that the fluorescence in the polymer is due to the accumulation of units of $-XCH(CH=)_n-$ where $n=3$ or 4 and X is a stabilizer derived grouping (e.g. $RCOO-$ or $ROCOCH_2S-$). As stabilization breaks down, these give way to longer sequences which do not fluoresce but absorb in the visible region and cause discoloration.

