ACS Symposium on:

LIFETIME, DEGRADATION AND STABILIZATION OF MACROMOLECULAR MATERIALS

Chicago, Aug. 22-25, 1993

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 DBTCl 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.

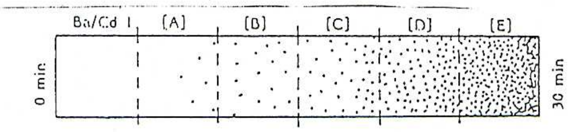

Fig. 1

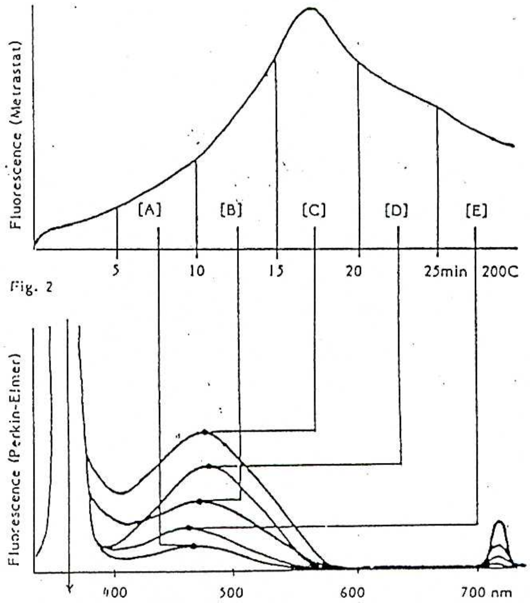

Fig. 2

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.

The build-up of units of this nature in the polymer is further supported by the UV absorption spectra of tin- or zinc stabilized PVC samples heated in air or under nitrogen. The Woodward's Rules to estimate the position of the main absorption band for the system - $CH2-CH=CH-CH=CH-CH=CH-CHX-CH2-$ would give a value close to the 224-236nm observed for all the PVC samples examined.

In light of the above, the fluorescence appears to be closely related to the amount of stabilizer consumed by the polymer during the early stage of its thermal decomposition. Since the phenomenon does not seem to be limited to PVC but was also observed in a number of non halogenated polymers, it became of interest to us to see if the technique of fluorescence reflectometry could be applied to polyolefins.

Fluorescence measurements on solid PP and PE samples on a Lumospectrophotometer (Perkin Elmer 255) revealed that, prior to their exposure to heat, undegraded polyolefins with or without stabilizers show a strong initial fluorescence with emission centered at 350nm for excitation at 260nm. During thermal degradation at 190°C the initial fluorescence spectrum of the unstabilized polymer disappears after heating for 10min to be replaced by a strong single band EX390nm/EM460nm. Altering the time of heating in an attempt to obtain specimens with an intermediate fluorescence was unsuccessful and it seems that the transformation of initial spectrum to post-oxidation spectrum occurred over a very short time interval. The experiment was repeated with a PP sample containing a commercial radical scavenger and peroxide decomposer combination. The initial fluorescence was identical to that observed previously and the fluorescence behavior of the stabilized PP was the same as that of the virgin polymer except that the post-oxidation spectrum did not appear until the sample had been heated at 190°C for 120min. -

To compare the fluorescence of two pieces of the same polymer which had been degraded for different periods, we generated specimens by placing polymer powder in the 260mmx26mm trays of our automatic testing oven which were then fed at a constant speed out of the oven (set at 190°C) producing polymer strips which were progressively degraded along the length of the specimen. The specimen was then scanned in the fluorescence reflectometer where it passed under either a 254nm or 365nm light source. The photocell could be adjusted to receive either a band centered at 340nm (for monitoring the initial EX260nm/EM340nm band) or at 490nm (suitable for the EX390nm/EM460nm post-oxidation band). The advantage of the method is that the variation in intensity of an initial or a post-oxidation fluorescent band can be monitored for a sample which has been progressively degraded.

Unstabilized PP which had only been heated at 190°C long enough to solidify and then immediately ejected from the oven had yellowed, showed no initial fluorescence using the 254nm lamp but a strong signal with increasing intensity along the strip excited with the 365nm source. Maximum intensity was achieved when the specimen had been heated for 100min in air but 133min under nitrogen. In stabilized PP, the onset of yellowing was delayed and coincided with the appearance of the post-oxidation fluorescence signal. The Reflectometer trace now showed a weak initial fluorescence using the 254nm source which reached a maximum at 30min and decayed to zero after 100min. Repeating the scan using the 365nm source showed that this sample did not produce the post-oxidation signal until it had been heated for ca. 130min thus showing the effect of the antioxidant stabilizer in retarding the phenomenon.

Samples of unstabilized and stabilized PE showed a similar trend. In general the initial fluorescence decayed rapidly and this was followed by a build-up of post-oxidation fluorescence. The point where yellowing occurred was roughly coincident with the point where post-oxidation fluorescence began.

Whatever the species responsible for the initial fluorescence in polyolefins, it is either an impurity introduced during polymerization or a product of reaction, presumably oxidation, of the polymer. Since popan-2-ol fully extracted the fluorescence from PP but only partially from PE one could assume that some fluorescing structure emitting at 340nm occurrs in the atactic fraction of PP and in the low molecular weight fraction of PE. When the polymer is heated, the structure is destroyed and replaced with another which emits at 460nm. We have examined a number of model compounds as candidates for the structure causing fluorescence and found that while polynuclear aromatics and catalyst fragments such as transition metal compounds do not affect the fluorescence of polyolefins, α,β -unsaturated carbonyl compounds do so considerably. When added at 1% to stabilized PE or PP, 4-cholesten-3-one and 3,5-dimethylocta-3,7-dien-2-one showed the intense band at EX260nm/EM340nm characteristic of the initial fluorescence in the virgin polymer. These also accelerate the oxidative degradation by decreasing the time to the onset of yellowing as the concentration in the polymer increases. Interestingly, these model unsaturated carbonyl compounds showed no fluorescence in solutiuon. A reasonable conclusion is that the α,β -unsaturated carbonyl structures are not only implicated in the fluorescence of polyolefins but they also accelerate thermal degradation in a stoichiometric manner.

As for the post-oxidation fluorescence we considered the possibility of short chain polyenes as being again the most likely responsible structures. We therefore included short chain polyenes as candidates bearing in mind that both intensity and position of fluorescence are sensitive to the presence of substituents. Our choice were octa-2,4,6-triene and the pentaene with a conjugated carbonyl group, trans, trans-retinal. Both were incorporated by milling into polymer strips which after exposure in the automatit oven revealed strong post-oxidation fluorescence signals (EX390nm/EM460nm), more intense when the compounds were in PE than when in PP.

These results indicate that the rate at which stabilizers, or decomposition products, become chemically involved during the process of thermal degradation of PE, PP and PVC can easily be monitored. Since the fluorescence is remanent, it can be measured long after completion of the thermal exposure and if such measurements are carried out in the laboratory on a polymer compound submitted to progressive exposure to heat, it should be possible to predict the behavior this same compound will show when exposed later on in various processing equipments.

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[3] K.L. D'Amico, R.L. Christensen, J ACS 102, 1777 (1980)