

Applications of ultra-violet microscopy to studies of the oxidation and stabilization of polymers

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Abstract The ultra-violet microscope, operating in the wavelength range 230 to 400nm, can be used to visualise the distribution of absorbing or fluorescent centres in a polymer. The absorbing molecules may be added small molecules, whose distribution or migration is of interest, or reagents which can react with centres in the polymer to give bound absorbers. Applications of the microscope are illustrated by studies of the localization of oxidative degradation in polypropylene and by studies of the diffusion of low molecular weight additives and of atactic fractions in polypropylene.

INTRODUCTION

The optical microscope has become almost a symbol of science but it has made far more impact in biology and medicine than in polymer science. When a sample is introduced into a microscope, image contrast arises because different regions of the sample affect the illumination to differing extents. The image may result from many effects, including diffraction, refraction, reflection, scattering, interference, polarization, fluorescence and absorption, and microscopes have been designed to take advantage of most of these phenomena, polarized light microscopy being the most common application to polymers. The great power of the microscope in biology arises from the development of reagents ("stains") which are capable of dissolving in, or binding to, regions of interest in the sample and enhancing their absorption or fluorescence. It has been our belief that the potential for a similar approach to the study of polymers is considerable, in that absorbers or fluorescers can be selectively bound to specific chemical entities in the polymer or will preferentially interact with, or dissolve in parts of the structure. In this way these molecules can be used as stains and probes of the morphology or chemical reactions of the polymer on the scale from 0.25 μ m upwards, in a manner very similar to that in which the biologist uses his stains to develop contrast in tissue specimens. Further, in so far as the added molecules resemble other small molecules of interest, such as drugs and pesticides, they can be used to study the transport of such molecules in polymers.

In principle, absorption microscopy could be done with coloured substances using a normal visible light microscope. However, in all forms of light microscopy the depth of focus is limited, particularly as the magnification is increased. The result is that very thin samples are required for successful microscopy and only absorbing species with high extinction coefficients will yield acceptable contrast. We have found that there are great advantages in moving to shorter wavelengths and we have been involved for some years in the development of optical microscopy in which the illuminating light is in the blue/ultra-violet range, from around 230 to 400nm. In this range the main intentional sources of image contrast are uv absorption and fluorescence emission, although other mechanisms, notably diffraction, may cause problems. The main advantages of uv are the greater range of absorbing compounds with a high extinction coefficient and the number of uv absorbing substances which are of interest in their own right. A further advantage of the uv microscope is that it can be used for fluorescence, although the reverse is not true. Observation of fluorescing substances can offer greater sensitivity as the fluorescence is observed against a dark background but the range of suitable compounds is more limited.

We have applied our microscope to a wide range of problems, including studies of polymer crystallization and morphology, of polymer-polymer mixing and of the curing inhomogeneities in thermosetting resins. These and other applications have all been reviewed (refs. 1,2). In this paper we illustrate the power of the techniques by reference to two applications, the study of the location of oxidation in polyolefins and the study of the diffusion of stabilizer molecules in polymers.

EXPERIMENTAL

The uv microscope which we use has been described in detail elsewhere (ref. 1). Basically it is a conventional optical microscope, modified by fitting quartz optics, a 150W Xenon arc source, with appropriate filters and a TV camera system to allow viewing of the image. Quantitative microdensitometry is performed with a waveform monitor, though we are now developing digital methods using a computer image analyser. Samples are sectioned on a base sledge microtome with a glass knife and mounted in glycerol on quartz or glass slides. For quantitative work it is essential that the spectrum of the illuminating light lies inside the absorption envelope of the sample and preferably as close as possible to the absorption maximum, for maximum contrast. Most of the work described in this paper used wavelengths around 350nm and the light was filtered with the combination of a UG1 UV filter with a BG38 red suppression filter. At these wavelengths glass slides are adequate although shorter wavelengths require much more expensive quartz slides.

Staining of samples and specific features of sample preparation are described in the appropriate sections below.

OXIDATIVE DEGRADATION OF POLYOLEFINS

Introduction

Polyolefins, particularly those with tertiary hydrogen atoms, are very vulnerable to oxidative degradation by the familiar peroxidation chain reaction (ref. 3), accelerated by the influence of sunlight or modestly elevated temperatures, and resulting in the material becoming discoloured and embrittled.

The main technical problem with oxidative degradation in polyolefins is that mechanical breakdown occurs at very low levels of chemical reaction. Absorption of less than one oxygen molecule per 100 carbon atoms, leading to a reduction in molecular weight by a factor of about 2 can often lead to complete loss of toughness in a PP sample. Although this is undoubtedly due to the fact that PP is a semi-crystalline polymer whose oxidation is confined to the amorphous phase, the detailed reasons for embrittlement are not clear. Carlsson and Wiles (ref. 4) have suggested that photo-oxidation of PP film takes place on the surface, leading to extensive recrystallization and the production of surface cracks which can propagate through thin film and fibre samples. Oswald and Turi (ref. 5) proposed that embrittlement occurs because of preferential scission of 'tie-molecules', linking crystallites in the polymer and carrying a disproportionate amount of the applied stress.

Although it is reasonable to assume that oxidation is random in the molten liquid polymer it is by no means certain that this is still true of the amorphous part of the solid. Aggregation of polar impurity groups in the hydrocarbon polymer or their rejection by the crystallization process might be expected to lead to local concentrations of the initiating centres and thus to local variations in oxidation rate. A number of observations suggest that degradation is indeed not wholly uniform but that some species or some parts of the sample are preferentially attacked. Thus discolouration is often seen as an expanding yellow spot on a sample, suggesting that oxidation products themselves locally enhance oxidation. Fracture of embrittled PP samples often appears to follow the spherulite boundaries or spherulite radii rather than an arbitrary path (refs. 6,7); also embrittled polymers may be melted and remoulded with the regain of most of their toughness (refs. 5,8). This implies that spherulite boundaries and interfibrillar regions may be particularly vulnerable to oxidation.

A proper study of these problems requires a technique which can reveal not the overall effect of oxidation but its distribution within a sample of polymer and we have attempted to reveal the distribution of oxidation in polypropylene (PP) by using ultra-violet microscopy. In order to render the oxidised regions visible we have treated sections of PP by reaction of the oxidised polymer with reagents which will form highly uv absorbing products bound to the oxidised regions.

Oxidation of isotactic and atactic PP

The isotactic PP used for most of this work was an additive-free grade produced by a diluent process which removes most of the undesirable atactic polymer into the hydrocarbon polymerisation medium. The Ziegler catalyst is removed by an alcohol wash with typical remaining levels of Ti, Al and Cl being 30, 45 and 45ppm respectively. As we received the polymer it contained 2.5% of residual atactic material extractable in boiling n-heptane.

In Fig. 1, we show the oxygen absorption curve for the polymer and for the atactic material extracted from the bulk polymer by n-heptane reflux. The atactic fraction has about half the induction period of the whole polymer and oxidises at about 3 times the rate. The bulk polymer becomes noticeably embrittled after oxidation for times greater than one induction time.

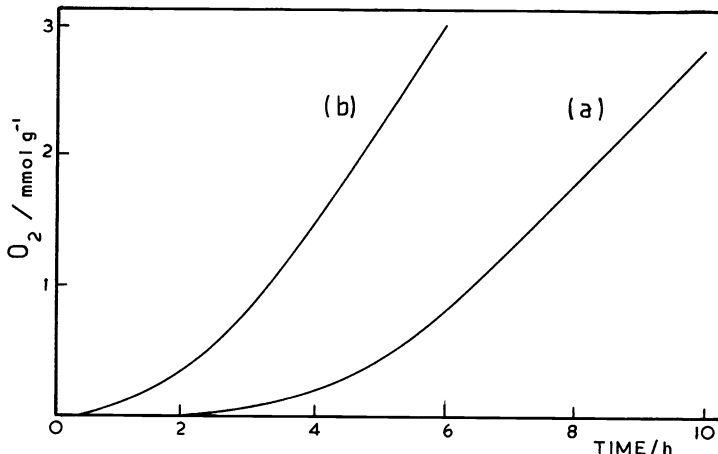


Fig.1 Oxygen uptake at 120°C of 100 μ m films of a) PP and b) its atactic fraction.

In a separate study (ref. 9) we have used reaction with 2,4-dinitrophenylhydrazine (DNPH) to monitor the carbonyl formation in the bulk polymer and in the heptane-soluble fraction as a function of oxidation time. We find that the amount of heptane-soluble material increases from 2.5% initially to 2.9% after 2h and 12.8% after 4h at 120°C; it then increases rapidly and becomes crystalline. At the beginning of the reaction the heptane-soluble fraction (2.5%) has a carbonyl content equivalent to 7.25 μ mol DNPH g⁻¹, with a corresponding value of 1.2 for the insoluble fraction. After 2h the corresponding figures are 75.5 and 13.2 and at the end of the induction time (4h) they have risen to 185 and 74 μ mol DNPH g⁻¹. Thus after 2h oxidation the concentration of carbonyl groups in the atactic fraction is 5.7 times higher than that in the isotactic polymer, even though the former represents only 2.9% of the total weight. DSC analysis shows that the heptane-soluble fraction remains essentially amorphous up to about 3h oxidation though its crystallinity rises rapidly thereafter.

From these observations we conclude that the 2-5% heptane-soluble fraction of PP oxidises 2-4 times faster than the isotactic material, both in isolation and when present in the isotactic polymer. This is in agreement with the similar conclusion of Frank et al (ref 10). Apparently this effect stems from the higher levels of unsaturation of the atactic polymer

as Osawa et al (ref. 11) found that, on hydrogenation, atactic PP becomes as stable as the isotactic polymer. In the later stages of oxidation the extractable fraction increases as more low molecular weight chains are formed. When PP crystallizes from the melt, both atactic polymer and low molecular weight impurities are expected to be excluded from the crystals of the growing spherulite and to concentrate in the liquid ahead of the growth front. This segregation will tend to give weak zones at spherulite boundaries and weak radial lines between the fibrils. With increasing oxidation, during processing and prior to crystallization, the amount of rejectable material would be expected to rise and the boundary strength would be expected to decrease. With these ideas in mind we set out to answer two questions, 1) Does atactic material reject during crystallization of PP and 2) Does this contribute to preferential oxidation at spherulite boundaries?

Atactic polypropylene is not visible by uv microscopy so that, to answer the first question, it must be rendered visible by staining. To do this we have attached fluorescent groups to the polymer. The group which we use is the dimethylaminonaphthylsulphonyl (dansyl) group, which can be covalently bound to the polymer at high temperatures via the sulphonyl azide (ref. 12). The concentration of the staining group must be kept as low as possible to minimise alterations in the properties of the polymer - we typically use 1% by weight.

The use of the sulphonyl azide provides a very convenient and efficient method of binding a range of fluorescent or absorbing groups to hydrocarbon polymers and has many potential applications in the study of mixing phenomena in polymer systems, including polymer blends. Using samples of PP containing atactic polymer which has been labelled in this way we have been able clearly to reveal the concentration of the atactic fraction during the crystallization (ref.1). This experiment can also be reversed and fluorescence microscopy of samples of fluorescently labelled isotactic PP containing unlabelled atactic polymer also clearly shows the rejection process (ref. 13). Thus, the uv microscope, in combination with appropriate stains, reveals that atactic fractions can indeed be rejected from spherulites during crystal growth. In order to use the microscope to examine whether this redistribution has any significance for oxidation we require a method of staining the oxidised polymer to reveal the distribution of oxidation.

Staining reagents for oxidation

When partly degraded, PP contains a variety of carbonyl compounds, such as carboxylic acids, ketones and aldehydes, which absorb uv below 300nm. However, the absorption is too weak to be observed directly with our Xenon source, so that staining methods are needed to enhance the visibility of oxidation in a polymer which is only slightly oxidised. Our first approach has been to use reagents which will react with carbonyl groups in a polymer. Two such reagents have been used, DNPH, which has been used previously as a reagent for carbonyl groups in oxidising polyolefins (ref.14), and dansyl hydrazine (1-dimethylaminonaphthalene-5-sulphonylhydrazine, (DNSH)) which behaves similarly but is fluorescent and so inherently more sensitive. Although DNSH seemed initially promising, more careful study shows that it has little solubility or permeability in the polymer so that only the surface is stained. DNPH is more satisfactory and oxidation can readily be seen at levels corresponding to about one quarter of the induction time in unstabilised PP.

An alternative staining procedure is to use the reaction of sulphur dioxide with hydroperoxides. The initial product of this reaction is the polymer alkyl sulphate (ref. 15) and in polyethylene these groups are fairly stable. In PP the hydroperoxides, and thus the alkyl sulphates, are formed in sequences of 2-4 groups so that on heating these groups eliminate sulphuric acid to give short sequences of double bonds. Exposure of oxidised PP to sulphur dioxide, followed by heating at 80°C under vacuum produces strong uv absorption at 280nm. This procedure has the advantage of being totally non extractive but it requires quartz slides and cover slips; we find that the absorption maximum at reasonable levels of oxidation is still too weak for adequate image contrast. For this reason all of the work described below was carried out using DNPH as the staining reagent.

For the staining process thin (10 μ m) sections of polymer were immersed in an acid solution of dinitrophenylhydrazine (DNPH) in isopropanol for 24 hours at 60°C. Since DNPH itself is highly uv absorbing, excess reagent was extracted from the films by immersion for 24 hours in isopropanol at 60°C. The stained polymer has a strong UV absorption at 350nm with an extinction coefficient 1000x that of the unstained polymer.

Infra-red spectroscopy showed that treatment of the films with pure isopropanol at 60°C reduces the carbonyl absorption of the sample by more than 30%. The extracted polymer contains a 40x higher carbonyl concentration than the remaining insoluble polymer and the fraction of the total carbonyl extracted by isopropanol increases with oxidation time. No extraction occurs when unoxidised polymer is refluxed with isopropanol. Treatment with DNPH removed 66% of the carbonyl absorption at 1715 cm⁻¹ remaining after an isopropanol extraction, and most of the hydroperoxide. A strong peak remained at 1735 cm⁻¹ which could be removed by KOH and was attributed to esters and lactones. Thus the DNPH stain is not ideal, in that it extracts much of the oxidation and does not react with all carbonyls. Nonetheless it is a very suitable qualitative marker for local oxidation levels by making visible the local concentration of those reactive carbonyl groups which are in the amorphous phase but firmly bound to the crystal structure.

Location of oxidation

As we have shown, increasing oxidation rapidly increases the amount of non-crystallizable material present in a PP sample. We might expect that rejection of these impurities during crystallization would concentrate them at the spherulite boundaries with two possible consequences, weakening of the boundary regions and enhanced oxidation of these regions in subsequent exposure. We have attempted to use the uv staining technique to look at the localisation of oxidation in PP samples which have been partly degraded and then crystallized. Figure 2 shows a section of PP which has been oxidised for 12 hours at 100°C before staining. It can be seen that much material has been extracted from the spherulite boundaries but there is no evidence of non-uniform staining of the remaining material.

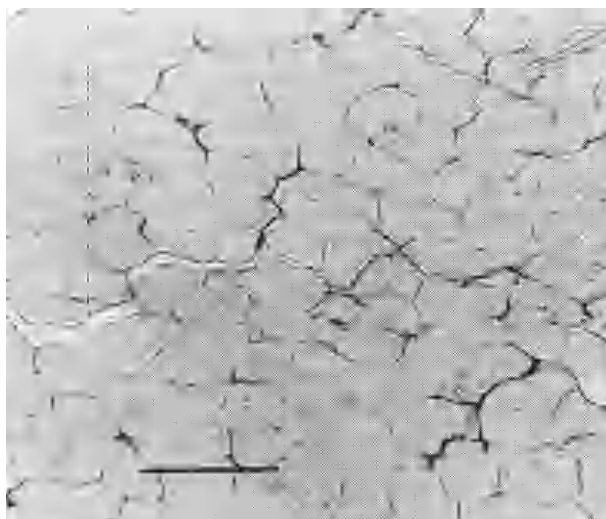


Fig. 2 Section of PP film oxidised at 100°C for 12h prior to bulk crystallization at 125°C. DNPH stained and viewed at 350nm. Note the boundary cracking and extensive extraction of the boundary regions. Bar is 200 μ m.

Samples crystallized at 135°C were similarly uniform. Thus with our staining technique we conclude that the only material which is rejected to the boundaries is that which is also extracted in the staining process. Non-uniform staining is seen in samples which are partly crystallised and quenched (Fig. 3) and in some cases we do see a wave of rejected material ahead of the growing spherulite which would be expected from our studies of rejection of other impurities (ref. 16). However, this effect may also be

partly due to differences in extraction from the slowly crystallised and from the quenched regions. A similar effect is seen after photo-oxidation of partly crystalline sections.

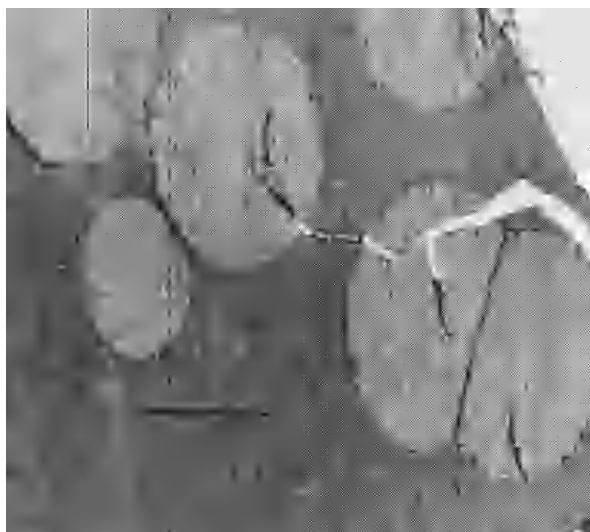


Fig. 3 DNP-stained section of PP film oxidised for 16h at 100°C prior to partial crystallization at 135°C. Viewed in uv. Bar is 200 μ m.

Given that impurity species do tend to concentrate at spherulite boundaries we might expect that oxidation would be more rapid in these regions in slowly crystallised, and thus more segregated, samples. Figure 4 shows a sample crystallised at 125°C and oxidised for 2 hours at 120°C before staining. Non-uniform oxidation is evident but there is no sign of its preferring the boundaries. We have similarly looked for evidence of local oxidation in samples photo-oxidised after crystallization. Again oxidation is invariably non-uniform but no preferential oxidation associated with the spherulite morphology was seen.

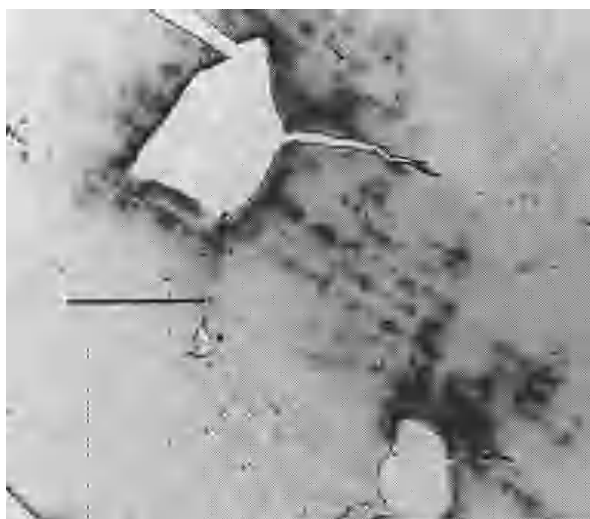


Fig. 4 Uv micrograph of a section of PP film, oxidised at 120°C in air for 2h. following crystallization at 125°C. Sample stained with DNP and viewed at 350nm. Bar is 50 μ m.

Conventional polarizing microscopy showed boundary cracking in a sample that had been oxidised for 12 hours at 100°C then crystallised at 125°C and sectioned. Less oxidation prior to crystallization gave less cracking. Slower crystallization, at 135°C, allows much more segregation to occur and the boundary weakness becomes marked at lower oxidation levels. Samples cracked at random when they had been crystallised under vacuum, sectioned and then oxidised, suggesting that there is little tendency for the oxidation reaction itself to be limited to boundaries. In samples crystallized as thin films on a microscope slide we do see preferential radial and boundary cracking on subsequent oxidation which we believe is due to shrinkage stresses which arise on cooling. Thus although oxidised material is rejected to spherulite boundaries it does not apparently enhance the subsequent oxidation of the surrounding structure. We would not expect to detect enhanced oxidation unless it were to an extent of 20% or more.

The role of catalyst residues

In the absence of morphological effects on oxidation, an alternative source must be found for the uneven oxidation seen in many samples and typified in Figure 4. Using very light compression we were able to produce films where the original polymer particles were still visible and which show that about 5% of them are oxidising much faster than the rest as shown in Fig. 5. Also visible in the sections are clusters of black dots, less than 1µm in size. These are in patches that correspond to the individual grains of the original powder and are more evident in the more oxidised grains. Like the oxidation, the dots do not extend right to the particle boundaries. The differences between the different grains persist to high levels of oxidation. Very little staining was seen in such samples when unoxidised.

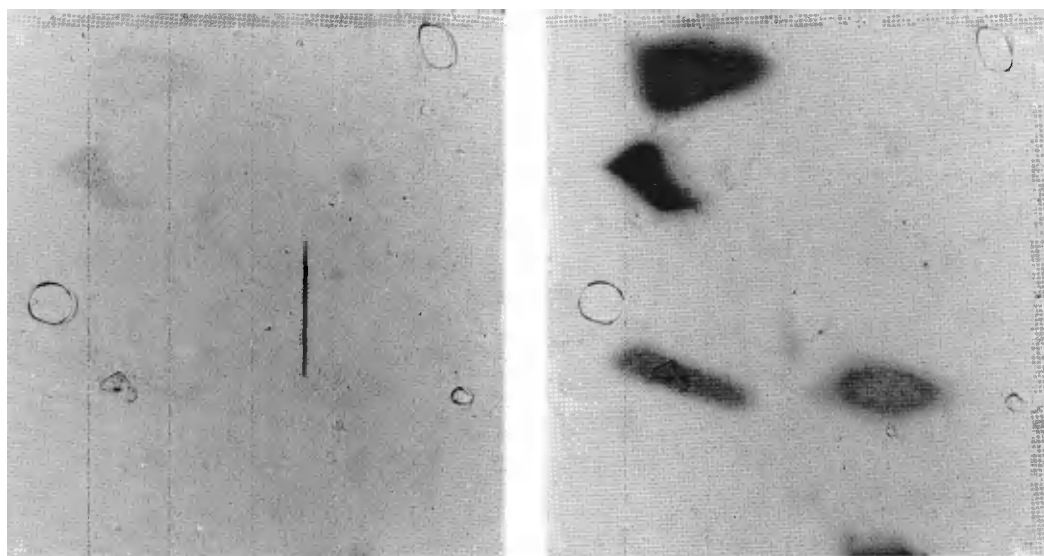


Fig. 5 Section microtomed from a PP plaque produced by gentle compression moulding from powder. Oxidised for 2h in air at 100°C and DNPH stained. Left picture viewed in visible light, right in uv. Bar is 200µm.

The dots are believed to be catalyst residues and can still be seen in a small proportion of the original powder grains when they are individually melted and examined in visible light. They show no sign of dissolving or coalescing on heating. We have not been able to obtain analyses of individual dots but energy dispersive X-ray analysis of ash from polypropylene shows Ti, Al and Cl present. The variability of individual polymer particles can also be shown by DNPH staining of oxidised powder, which produces a mixture of light and dark particles, resembling a mixture of salt and pepper. Support for the catalytic role of the residues has recently been obtained by extracting the ash from a batch of PP and introducing it into a new film; oxidation and staining show extensive local oxidation around the ash particles (ref. 17).

Conclusions

In this section we have illustrated how the uv microscope can be used with a reactive staining system to reveal the location of oxidation in a PP sample. The system has not proved sufficiently sensitive to allow us to detect significant effects of uneven distribution of the traces of carbonyl and hydroperoxide impurities in the polymer but it reveals how the oxidation is invariably very non-uniform and how this non-uniformity can be associated with catalyst residues in the polymer. More details of this aspect of the work and of studies of gas-phase polymers will be published elsewhere (ref. 18).

DIFFUSION RATE MEASUREMENTS

An understanding of the diffusion of small molecules in polymers is of great importance both for their application as packaging and barrier materials and for controlling the migration and loss of stabilizing additives. Measurement of diffusion coefficients requires the determination of the concentration profile for the diffusant as a function of time. This has conventionally been done either by the use of multi-film stacks or by diffusing the additive into a rod of material, followed by sectioning and analysis of the sections. Both methods are time-consuming since diffusion distances of the order of mm are used. Additionally analysis has usually been by use of radiolabelled additives with all of the expense and problems of synthesis which they imply. We have found that the diffusion of uv absorbing compounds in solid polymers can easily be monitored by following the progress of the additive into a sample of polymer in the uv microscope. The polymer may be in the form of a small rod immersed in a solution of the additive in a solvent which does not swell the polymer; for PP suitable solvents are water and glycerol. The rod is sectioned longitudinally when the additive has penetrated about 100 μ m and the concentration profile of the diffusant within the polymer is measured by uv microscopy of single sections. An alternative method is to use film samples, either immersed in a solution of the additive or clamped between layers of finely powdered solid additive. At the end of the required time the film is sectioned so that the concentration profile through its cross-section can be measured on a single section. If powdered additive, or a saturated solution, is used, the solubility of the additive in the polymer can also be estimated, although the difficulty of measuring section thicknesses limits the accuracy which can be achieved.

The concentration profiles are usually measured from photographs of the waveform monitor trace. Once the profile is established the diffusion coefficient of the additive may be determined by fitting the profile to the expected form (ref. 19):

$$C/C_0 = 1 - \operatorname{erf}(x/2D^{1/2}t^{1/2})$$

Where C is the measured concentration, C_0 that at the surface of the polymer, x the distance from the polymer surface, t the time and D the diffusion coefficient.

Figure 6 shows data determined in this way for a strongly uv absorbing molecule diffusing into PP at 60°C for varying times. The data are all fitted with a single diffusion coefficient of $1.03 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and agreement with experiment is good.

This method can only be used with molecules having strong uv absorption or fluorescence but this is not a severe limitation for polymer stabilizers. Its main advantage is that the concentration profile is measured over a distance of only about 100–200 μ m so that the method is much quicker and can be used over a wider range of temperatures than the more conventional macroscopic methods.

Although we have mainly used uv absorbers, the same methods can be applied to fluorescent molecules. As an example, we have used fluorescence microscopy to monitor the diffusion into PP of an atactic fraction of molecular weight about 8000, rendered visible by covalently bound fluorescent groups as described earlier. Figure 7 shows data for diffusion at 130°C for two different times, fitted by diffusion coefficients of around $2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

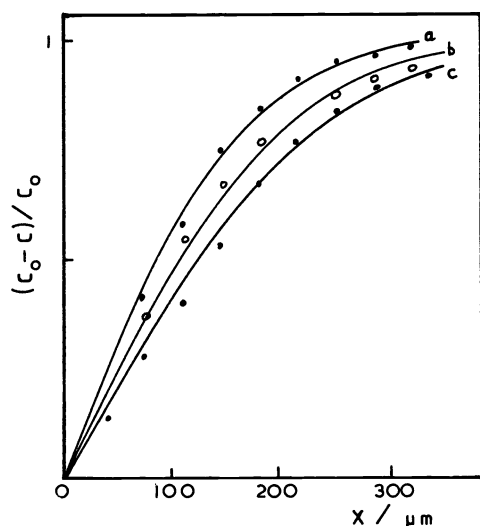


Fig. 6 Diffusion of 2-hydroxy-4-dodecyloxy benzophenone into PP at 60°C. Points are experimental for diffusion times of a) 22h. b) 30h. and c) 46h. Solid lines are calculated for $D = 1.03 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

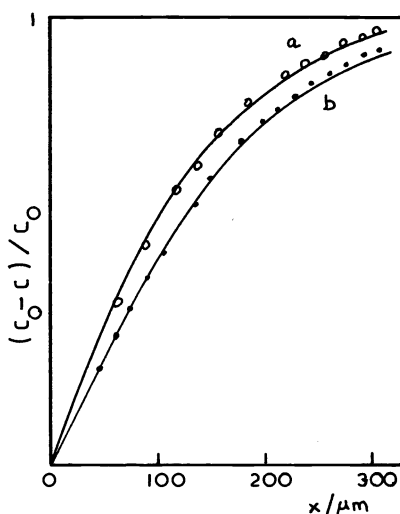


Fig. 7 Experimental points and fitted line for diffusion of atactic PP into the isotactic polymer at 130°C. Curve a: time 8h. $D = 2.98 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Curve 2: time = 18h. $D = 1.83 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

An alternative approach to measuring diffusion coefficients is to begin with a polymer film which contains the dissolved additive, uniformly distributed through it. If the film is placed in contact with a liquid which is a good solvent for the additive and non-swelling for the polymer then loss of the additive from the surface is controlled by the rate of diffusion of the solute to the surface. To a good approximation, the concentration profile in this situation is given by:

$$\frac{C}{C_0} = \frac{4}{\pi} \left[\exp(-A) \cos \frac{\pi x}{2l} - \frac{1}{3} (\exp(-9A)) \cos \frac{3\pi x}{2l} \right]$$

where $A = D\pi^2 t / 4l^2$. Computer fitting of this equation to the measured profile from one edge to the centre of the film then allows the diffusion coefficient to be evaluated. Figure 8 shows such an analysis for one of the benzophenones at 40°C.

We have studied the homologous series of 4-alkoxy-2-hydroxybenzophenones with 1,8 and 12 carbon atoms in the alkyl group, measuring diffusion coefficients by diffusion-out and diffusion-in experiments. Table 1 shows the results for the three compounds at two temperatures. For the long alkyl chains the diffusion coefficients measured by the two methods are in very good agreement. For the methyl side chain the agreement is rather less good, the diffusion coefficient for migration into the polymer being about half of that for diffusion out. It is not entirely clear why this should be so. The diffusion-out experiments were performed using methanol

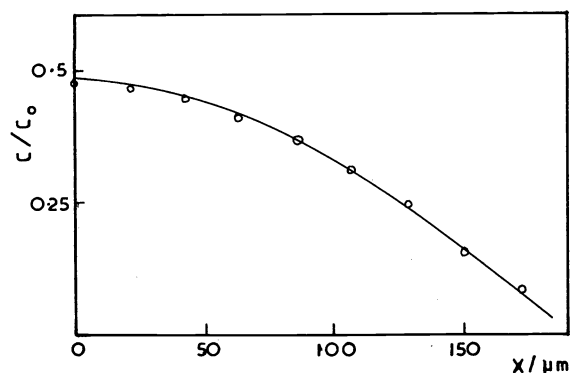


Fig. 8 Experimental points and fitted curve for diffusion of 2-hydroxy-4-methoxybenzophenone out of PP at 40°C. Time 192h. $D = 1.26 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$.

TABLE 1. Diffusion coefficients ($\times 10^{11} \text{ cm}^2 \text{ s}^{-1}$) for benzophenones in PP.

No. of C atoms	Diffusion-out		Diffusion-in	
	40 °C	50 °C	40 °C	50 °C
1	13	125	8.23	62.1
8	6.43	42.4	4.48	38.8
12	5.8	31.9	4.47	28.8

as the solvent, whereas the diffusion-in experiments were carried out using the solid additive. It is possible that the discrepancy reflects the effect of slight penetration of the polymer by methanol. This would be expected to have the greatest effect on the short-chain additive since this has the lowest solubility in the polymer and the highest in the solvent.

CONCLUSIONS

In this brief review we have attempted to illustrate the main ways in which the uv and fluorescence microscope can be applied to problems in polymer science, illustrating the applications by reference to our particular interest in degradation and stabilization of polymers. The approaches which we have used include the monitoring of migration and extraction of small molecules, the use of stains which will react with functional groups to reveal their location and the use of covalently bound labels for polymer-polymer mixing studies. None of these applications is specific to polymer degradation studies and all could equally well be applied in other areas of polymer science. We hope that this paper will help to stimulate a more general interest. Although uv microscopes are rare and expensive devices, there is a fluorescence microscope in almost every biology laboratory.

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