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Dyeing in the Presence of Free Radical Initiators. Part 5—The Effects of Radical Initiators on Nylon 6.6

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ABSTRACT

The modification of nylon 6.6 imparted by four radical initiators (ammonium persulphate, potassium periodate, thiourea dioxide and glucose) is discussed in terms of their effects on the amino end-group content and tensile strength of the fibre. Fourier transform IR (FTIR) attenuated total reflectance (ATR) spectroscopy was employed to examine the extent of modification of the fibre imparted by ammonium persulphate; second-order derivative spectroscopy was used to secure higher resolution of the ATR spectra. Evidence obtained from dyeings carried out using a commercial anthraquinone disperse dye in the presence of ammonium persulphate suggests that the dye may be covalently attached to the fibre.

INTRODUCTION

In the first part of this paper,[1] dyeing in the presence of radical initiators was reviewed and the oxidative degradation of PET that occurred during dyeing with CI Disperse Yellow 54 in the presence of ammonium persulphate was discussed in terms of Fourier Transform IR (FTIR) attenuated total reflectance (ATR) spectroscopy. In subsequent parts of the paper, the effects of various oxidising and reducing agents on the dyeing of nylon 6[2] and nylon 6.6[3,4] with several classes of disperse dyes were discussed. This part of the paper describes the use of FTIR ATR

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spectroscopy, amino end-group (AEG) content determinations and tensile strength measurements to investigate the effects of various radical initiators on nylon 6.6 and to determine the mechanism involved in the dyeing of nylon 6.6 in the presence of radical initiators.

EXPERIMENTAL

Materials

Fibres
Scoured, knitted nylon 6.6 fabric was used in ATR and scanning electron microscopy (SEM) analyses as well as AEG determinations, and nylon 6.6 filament stockinette was employed in the tensile strength determinations; each type of fibre was of 3·9 dTexpf (78F20) and was generously supplied by ICI Fibres (Harrogate, UK).

Dyes and auxiliaries
Commercial samples of CI Disperse Violet 1 and CI Disperse Yellow 1, kindly supplied by Yorkshire Chemicals (YCL) plc, were employed. Dyapol PT (YCL) was used as dispersing agent and Sandozin NIE (S) as wetting agent.

Chemicals
All chemicals used in the work were laboratory grade reagents obtained from either Aldrich or BDH; ammonium persulphate (APS), potassium periodate (KIO_4), thiourea dioxide (TDO) and glucose were used as radical initiators.

Procedures

Treatment for ATR analysis
All treatments of knitted nylon 6.6 fabric were carried out in sealed, stainless steel pots of 300-cm^3 capacity housed in a John Jefferies laboratory-scale Rota Dyer. Treatment was carried out either in distilled water or in a dyebath containing 2% CI Disperse Violet 1 in both the absence and presence of 10 mM ammonium persulphate, the pH being adjusted to 5·5 using 0·02M acetic acid–0·17M sodium acetate buffer.[1] Treatment was commenced at 40°C, and the temperature was then raised to 98°C at a rate of 2°C min^{-1} and maintained at this temperature for a further 60 min. For the treatment carried out in the absence of CI Disperse Violet 1, the treated samples were rinsed thoroughly in cold tap-water and allowed to dry in the open air; in the case of the samples obtained using CI Disperse Violet 1, the rinsed (cold tap-water) dyed samples were scoured in a

solution containing 2% owf Sandozin NIE at 98°C for 5 min and the rinsed (cold tap-water) dyed samples then allowed to dry in the open air.

Treatment for amino end-group (AEG) content analysis

To investigate the effect of free radical initiators on the AEG content of nylon 6.6, samples of nylon 6.6 fabric were treated with distilled water in both the absence and presence of various concentrations (between 0 and 30 mM) of several radical initiators (APS, KIO_4, TDO or glucose) using a liquor ratio of 30 : 1, the pH of the treatment bath being adjusted to pH 5·5 using 0·02M acetic acid–0·17M sodium acetate buffer.[1] Treatment was carried out in sealed, stainless steel pots of 300-cm^3 capacity housed in a John Jefferies laboratory-scale rota dyer; the treatment bath was heated from 40°C to 98°C at a rate of 2°C min^{-1} and maintained at this temperature for 60 min, after which time the rinsed (cold tap-water) sample was allowed to dry in the open air. Determination of the AEG content of the dry, treated nylon 6.6 fabric was carried out by ICI Fibres.[5]

Treatment for tensile strength determination

To determine the effects of radical initiators on the tensile properties of the fibre, stockinettes composed of nylon 6.6 filament were treated with radical initiators using the same equipment and conditions as described above for the determination of the effects of radical initiators on AEG content. The tensile strength of the dry, treated nylon 6.6. stocking samples was determined by ICI Fibres.[5]

Treatment for SEM analysis

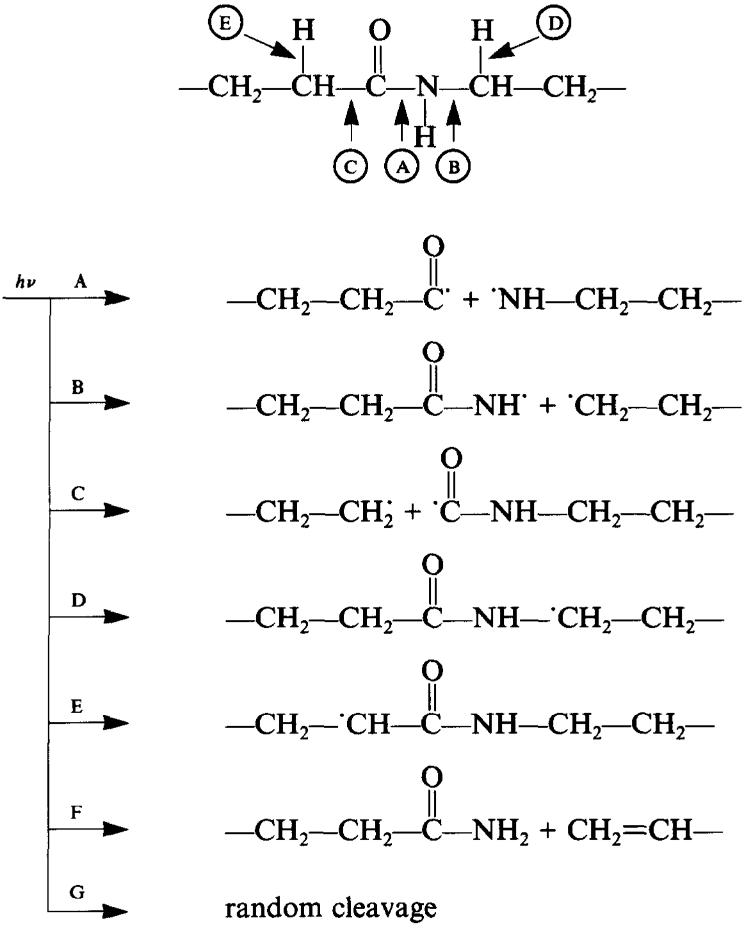
This was carried out either in distilled water or in a dyebath containing 2% CI Disperse Yellow 1 in both the absence and presence of several radical initiators, the pH being adjusted to 5·5 using 0·02M acetic acid–0·17M sodium acetate buffer. The equipment used and the conditions employed were identical to those described above for ATR analysis.

RESULTS AND DISCUSSION

Theoretical considerations regarding the modification of polyamide

The photo- and thermal degradation of nylon has been studied by many workers[6–14]; various positions for bond scission of nylon by UV light have been proposed (Scheme 1).[9]

From ESR studies,[10–12] the $—CH_2—CO—NH—C^{\cdot}H—CH_2—$ radical

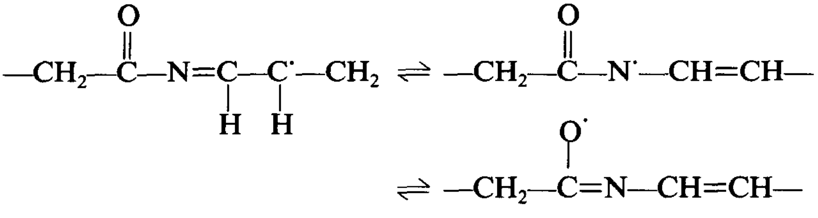


Scheme 1

has been identified as the predominant radical species produced as a result of irradiating polyamide. In an ESR study of the photodegradation of nylon 6, Heuvel and Lind[13] proposed that both $—CH_2—C^{\cdot}H—CH_2—$ and $—CH_2—C^{\cdot}{=}O$ radicals were produced. Igarashi[7] identified both $—CH_2—C^{\cdot}H—CH_2—$ and $—CH_2—CO—NH—C^{\cdot}H—CH_2—$ radicals as well as a singlet of nylon 6 using various irradiation conditions; a singlet[10,14] has been assumed to correspond to a conjugated system with an unpaired electron (Scheme 2).

ATR analysis of nylon 6.6

The ATR spectra of nylon 6.6 fabric which had been treated in distilled water at pH 5·5 for 60 min at 98°C both in the presence and absence of



Scheme 2

10 mM APS are shown in Figs 1 and 2, respectively. Subtraction of Fig. 1 from Fig. 2 yields the difference spectrum (Fig. 3), which reveals the effect of APS on nylon 6.6. The negative absorption at 3293 cm^{-1} (Fig. 3)[15] indicates the loss of N—H vibration, and the negative absorption in the regions 2928 cm^{-1}[16] and 2858 cm^{-1}[17] reflects the loss of CH$_2$ stretching. The spectral changes occurring for the bands at 1631 cm^{-1}[18] and 1271 cm^{-1}[19] may be attributed to the loss of amide I and amide III structures, respectively, and the negative absorption appearing at 1530 cm^{-1} may result from either the loss of the amide II structure[17,18] or N—H deformation.[17] The absorption at 1685 cm^{-1} may be attributed to the formation of a carboxyl group,[20,21] —CO—NH$_2$[20] and/or C=C double bonds[21] owing to cleavage of the amide groups.

The ATR spectra of nylon 6.6 fabric which had been dyed with CI Disperse Violet 1 at pH 5·5 for 60 min at 98°C in both the absence and presence of 10 mM APS are shown in Figs 4 and 5, respectively. Subtraction of Fig. 4 from Fig. 5 yields the difference spectrum (Fig. 6), which indicates the effect of APS on nylon 6.6 dyeing. As described above, Fig. 3 shows the effect of APS on nylon 6.6, being the difference

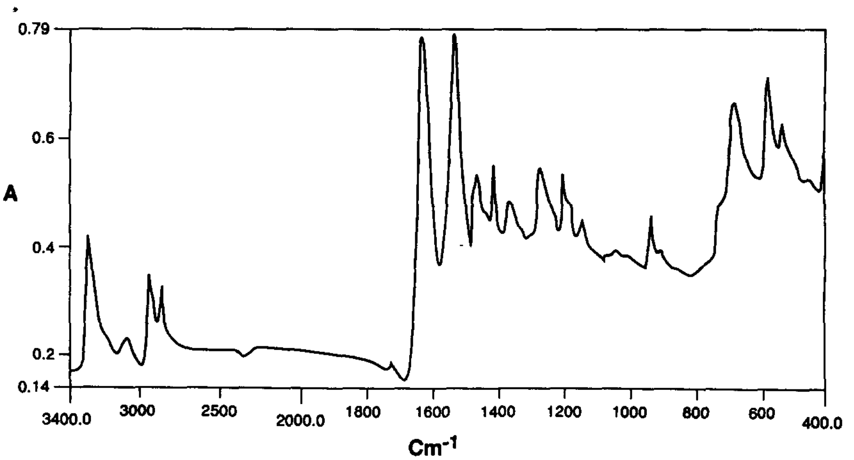


Fig. 1. ATR spectrum of nylon 6.6 treated in distilled water at 98°C for 60 min.

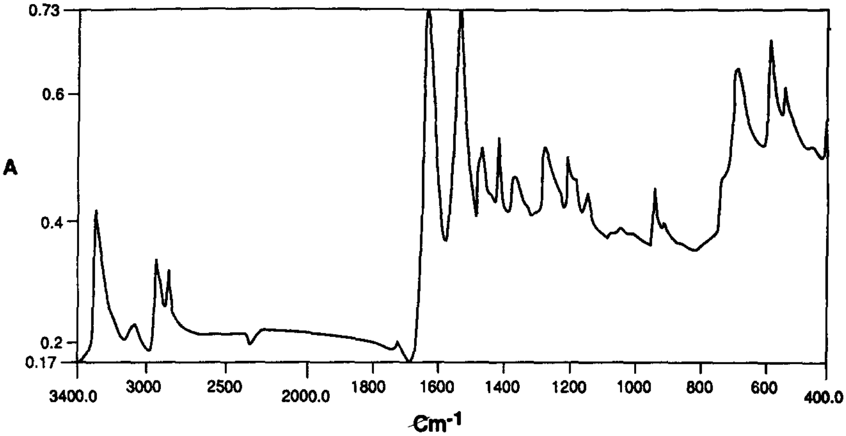


Fig. 2. ATR spectrum of nylon 6.6 treated in distilled water with 10 mM APS at 98°C for 60 min.

spectrum obtained from Figs 1 and 2; Fig. 7 (Fig. 3 overlapped onto Fig. 6) displays the differences between these two spectra. The negative absorptions of the bands at 1474 cm^{-1}, 1437 cm^{-1}, 1416 cm^{-1} and 1196 cm^{-1} in Fig. 6 were stronger than those in Fig. 3. The bands appearing at 1416 cm^{-1} [18,22] and 1196 cm^{-1} [22] indicate the loss of the CO-vicinal CH_2 groups and the band at 1474 cm^{-1} [18,22] reflects the loss of the N-vicinal CH_2 groups. The spectral change in the band at 1437 cm^{-1} [18,22] reveals the loss of both CO-vicinal and N-vicinal CH_2 groups.

Ereshchenko *et al.*,[23] in an IR study of nylon treated with hydrogen peroxide–potassium persulphate in the absence or presence of Rhodamine S, determined the optical density ratio of D_{1175}/D_{1200}, the 1175 cm^{-1} band relating to the N-vicinal CH_2 group and the 1200 cm^{-1} band relat-

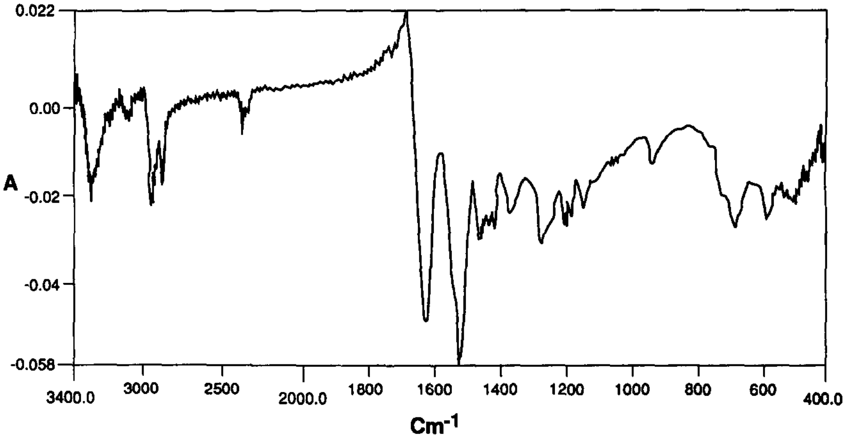


Fig. 3. Difference spectrum (Fig. 1 subtracted from Fig. 2).

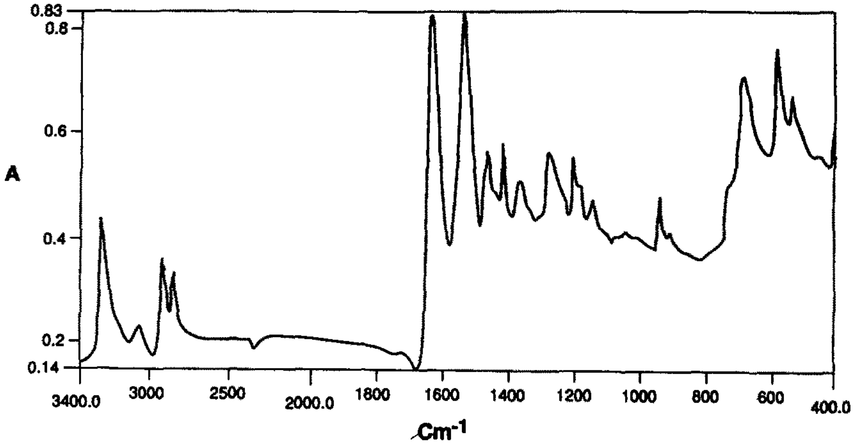


Fig. 4. ATR spectrum of nylon 6.6 dyed with CI Disperse Violet 1 in water at 98°C for 60 min.

ing to the CO-vicinal CH_2 group. In all cases, the 1175 cm^{-1} band was reduced to a greater transmittance extent than the 1200 cm^{-1} band, from which it was assumed that reaction occurred primarily at the N-vicinal CH_2 group; in the presence of Rhodamine S, a decrease in the absorbance of methylene groups (2865 cm^{-1} and 2930 cm^{-1}) was observed, from which evidence the following covalent fixation mechanism for the dye was proposed (Scheme 3).

Figures 3 and 6 reveal that a decrease in absorption at 2858 cm^{-1} and 2928 cm^{-1} (methylene groups) was observed; this finding concurs with that of Ereshchenko *et al.*[23] and, therefore, as those workers proposed,

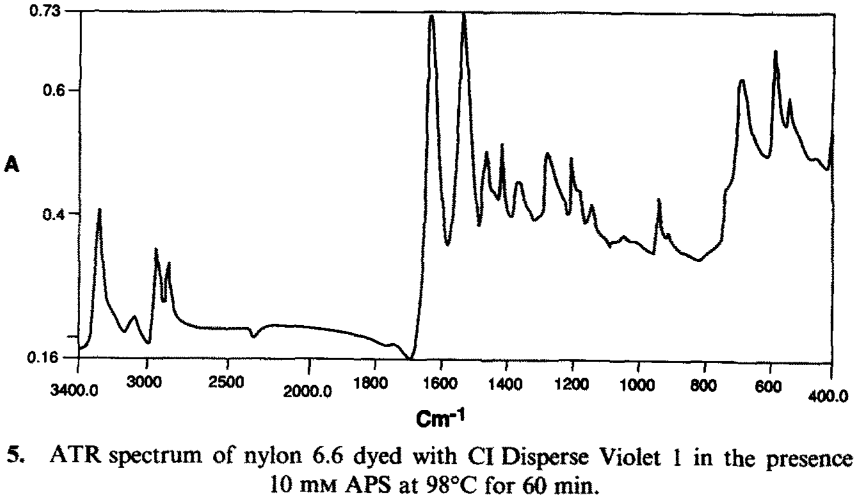


Fig. 5. ATR spectrum of nylon 6.6 dyed with CI Disperse Violet 1 in the presence of 10 mM APS at 98°C for 60 min.

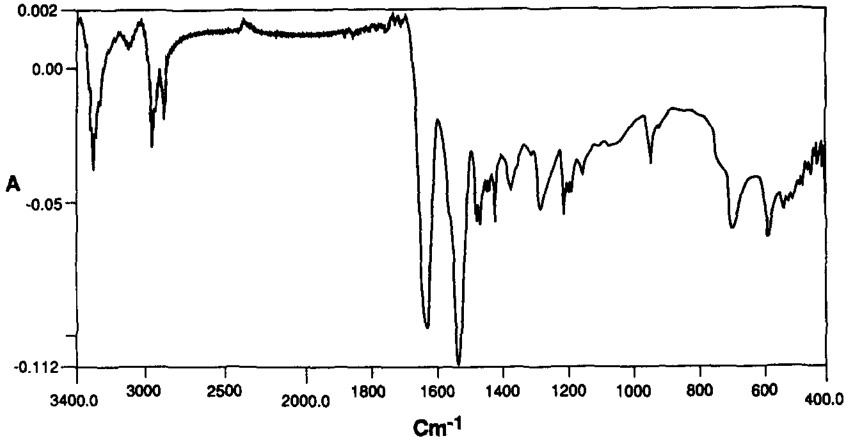
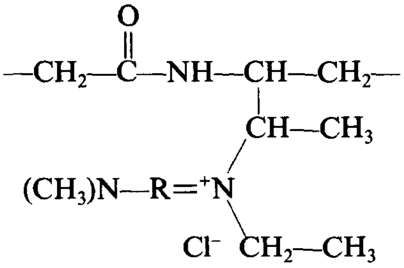


Fig. 6. Difference spectrum (Fig. 4 subtracted from Fig. 5).



Scheme 3

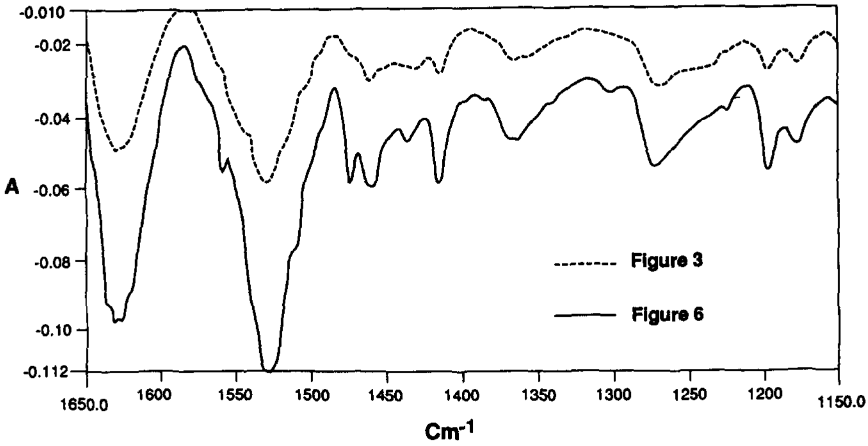


Fig. 7. Overlapped spectra of Figs 3 and 6.

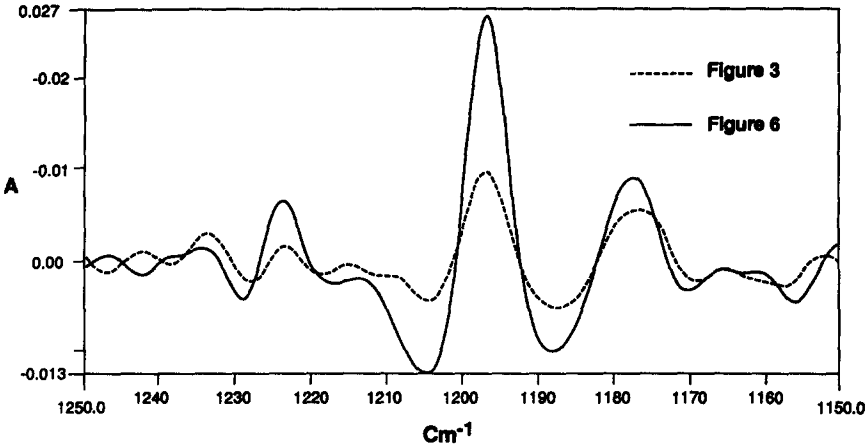


Fig. 8. Second-order derivative spectra of Figs 3 and 6 (1150 cm^{-1}–1250 cm^{-1}).

can be considered to indicate that the dye (CI Disperse Violet 1) has become covalently attached to the substrate.

It was considered that, to obtain further information, second-order derivative spectroscopy[24,25] should be used to examine the difference between Figs 3 and 6; Fig. 8 (1150–1250 cm^{-1}) and Fig. 9 (1400–1500 cm^{-1}) are the second-order derivative spectra of Figs 3 and 6. According to Figs 8 and 9, the bands occurring at 1196 cm^{-1} and 1416 cm^{-1} in Fig. 6, which relate to the CO-vicinal CH_2 groups, were of lower absorbance than those of Fig. 3; of the 1178 cm^{-1} and 1474 cm^{-1} bands, which relate to the N-vicinal CH_2 groups, the former were of lower absorbance in Fig. 6. Thus, in contrast to the proposal of Ereshchenko *et al.*,[23] the findings obtained in this work suggest that covalent attachment of the

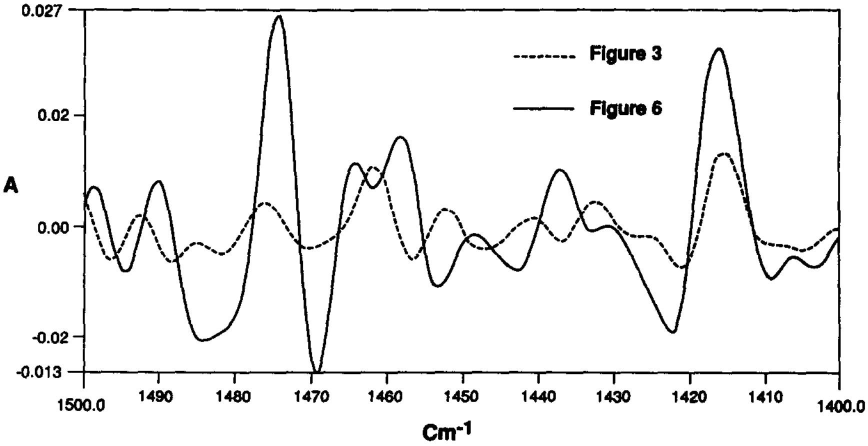


Fig. 9. Second-order derivative spectra of Figs 3 and 6 (1400 cm^{-1}–1500 cm^{-1}).

TABLE 1

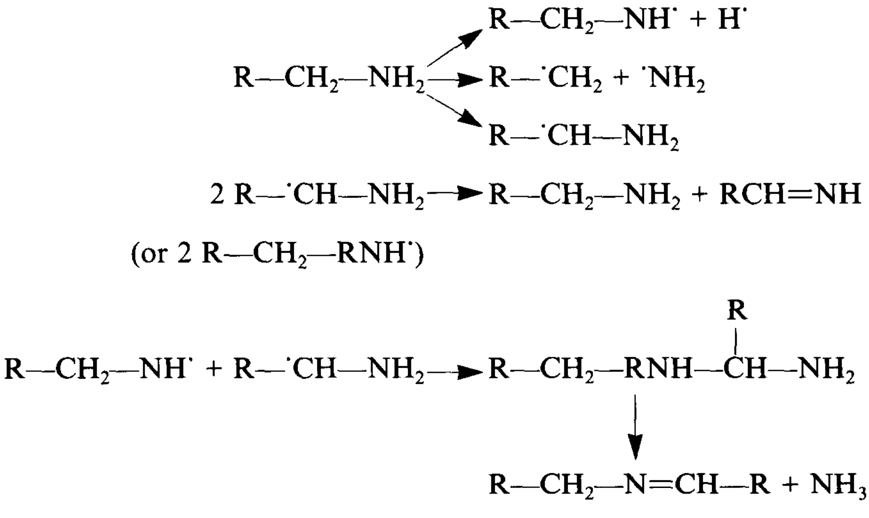
AEG Content of Nylon 6.6 (g equiv 10^{-6} g); AEG content of Untreated Fibre was 41·7

Concentration (mM)	*APS*	*KIO$_4$*	*TDO*	*Glucose*
6·25	34·5	33·3	34·6	40·2
10	33·6	30·3	32·6	39·9
20	34·0	30·6	24·8	40·0
30	34·2	30·4	23·7	40·7

dye did not occur primarily at the N-vicinal CH_2 groups of the fibre, and indicate that in the presence of ammonium persulphate the dye could have become attached covalently to both the N-vicinal and CO-vicinal CH_2 groups of the substrate.

AEG Analysis of nylon 6.6

AEG analysis was carried out on nylon 6.6 fabric that had been treated with various concentrations of several radical initiators in distilled water at pH 5·5 for 60 min at 98°C. The results (Table 1) reveal that the AEG content of nylon 6.6 decreased with increasing concentration of APS, KIO_4 or TDO used; the finding that glucose had little effect on AEG content can be attributed to its weak reducing power.[4]



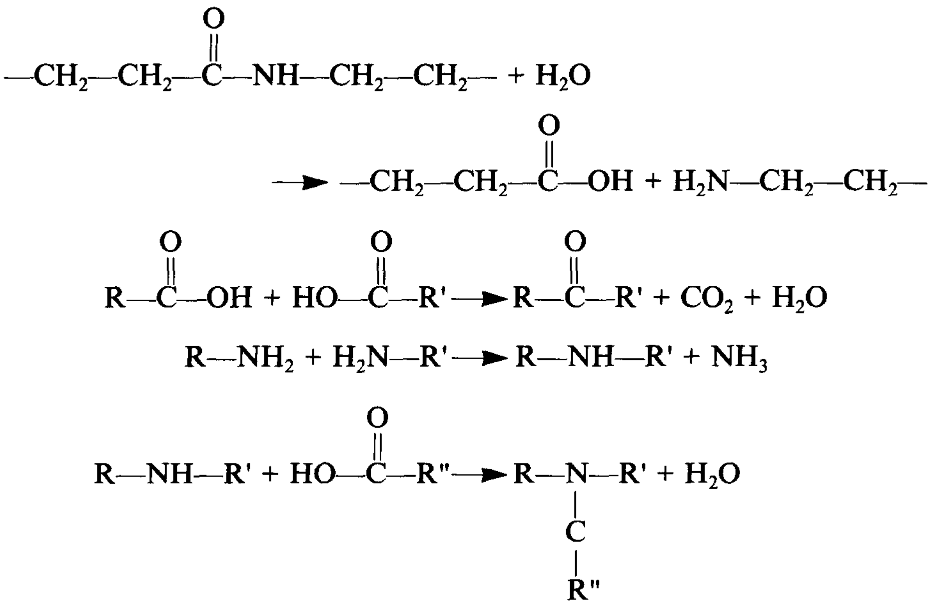
$$R{-}CH_2{-}NH_2 \rightarrow \begin{cases} R{-}CH_2{-}NH^{\cdot} + H^{\cdot} \\ R{-}{}^{\cdot}CH_2 + {}^{\cdot}NH_2 \\ R{-}{}^{\cdot}CH{-}NH_2 \end{cases}$$

$$2\,R{-}{}^{\cdot}CH{-}NH_2 \rightarrow R{-}CH_2{-}NH_2 + RCH{=}NH$$

$$(\text{or } 2\,R{-}CH_2{-}RNH^{\cdot})$$

$$R{-}CH_2{-}NH^{\cdot} + R{-}{}^{\cdot}CH{-}NH_2 \rightarrow R{-}CH_2{-}RNH{-}\overset{R}{\overset{|}{C}}H{-}NH_2 \rightarrow R{-}CH_2{-}N{=}CH{-}R + NH_3$$

Scheme 4



$$-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2- + H_2O \longrightarrow -CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH + H_2N-CH_2-CH_2-$$

$$R-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-R' + CO_2 + H_2O$$

$$R-NH_2 + H_2N-R' \longrightarrow R-NH-R' + NH_3$$

$$R-NH-R' + HO-\overset{\overset{O}{\|}}{C}-R'' \longrightarrow R-\underset{\underset{R''}{|}}{\underset{C}{\underset{|}{N}}}-R' + H_2O$$

Scheme 5

According to Scheme 1, the oxidative degradation of nylon should, in general, generate amino end groups. However, as treatment with both APS and KIO_4 resulted in a decrease in AEG content (Table 1), it is possible that in the presence of such radical initiators, the amino end groups may, as proposed by Do *et al.*,[9] undergo photolysis as shown in Scheme 4 and, as proposed by Fetts,[26] crosslinking may also occur as shown in Scheme 5,[26] both mechanisms serving to reduce the AEG content of the substrate. The observation that treatment of nylon 6.6 fibres with a concentration in excess of 10 mM TDO resulted in a lower AEG content than treatment with either APS or KIO_4 (Table 1) implies that the reductant caused considerable modification of the fibre. However, in view of the finding that treatment of nylon 6.6 fibres with TDO increased the tensile strength of the substrate, it is suggested that the reductant induced crosslinking of the fibre, possibly according to Scheme 5.[26]

Tensile strength analysis of nylon 6.6

Tensile strength determinations were carried out on nylon 6.6 filament samples which had been treated with various concentrations of four radical initiators in distilled water at pH 5·5 at 98°C for 60 min. The results (Table 2) show that although the physical properties of the fibres

TABLE 2
Tensile Strength Analysis of Nylon 6.6 Filament

Reagent	*Concentration (mM)*	*Breaking load (N)*	*Extension (%)*	*Tenacity*
APS	0	2·64	33·63	33·79
	6·25	2·28	32·16	29·21
	10	2·16	30·20	27·75
	20	2·31	31·95	29·57
	30	2·34	30·62	30·01
KIO_4	6·25	0·64	14·49	8·27
	10	0·66	14·34	8·42
	20	0·83	16·23	10·70
	30	1·30	21·26	16·67
TDO	6·25	2·91	36·65	37·31
	10	3·04	37·98	38·93
	20	3·03	40·28	38·85
	30	2·88	33·24	36·88
Glucose	6·25	2·49	28·52	31·87
	10	2·48	27·50	31·83
	20	2·49	28·79	31·94
	30	2·36	26·91	30·23

were degraded by treatment with APS, KIO_4 and glucose, the physical properties of the fibre were enhanced by treatment with TDO.

Scheme 1 shows that the oxidative degradation of nylon results in a decrease in the relative molecular mass of the polymer; indeed, it has been reported[27] that the photo- and thermal oxidation of nylon 6 results in a decrease in the tensile strength and relative molecular mass of the fibre. Consequently, the observed reduction in the tensile strength of the fibre imparted by treatment with both oxidants can be attributed to such degradation. Although it has been recommended[28] that the high-temperature dyeing of nylon in the presence of thiourea or hydroxylamine sulphate should be carried out at pH values of not less than five, to minimise fibre degradation and antioxidant destruction, the observed increased tensile strength and decreased AEG content imparted to the fibre by treatment with TDO may be attributed to crosslinking of the constituent polymer chains.

Scanning electron microscopic analysis of nylon 6.6

An investigation was carried out of the surface of nylon 6.6 fabrics which had been treated with various radical initiators in either the absence or presence of 2% owf CI Disperse Yellow 1 at pH 5·5 at 98°C for 60 min. According to Figs 10 and 11, in the absence of disperse dye, each of the four radical initiators caused serious damage to the fibre surface, whereas in the presence of disperse dye considerably less damage occurred for each of the radical initiators employed. This finding therefore implies that the dye has reduced the damaging effect of each radical initiator; two possible explanations may be proposed to explain this result. First,

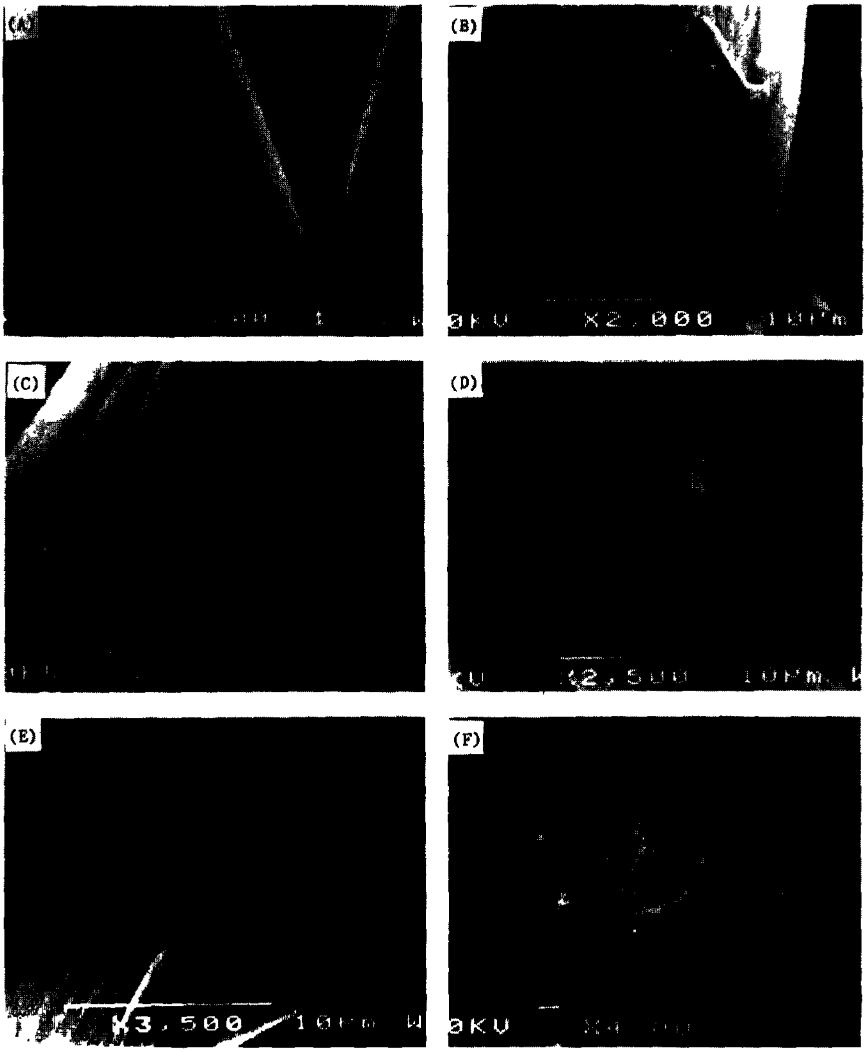


Fig. 10. Scanning electron photomicrograph of nylon 6.6 treated with (A) distilled water, (B) 10 mM APS, (C) 20 mM KIO_4, (D) 20 mM TDO, (E) 10 mM glucose, (F) 20 mM glucose.

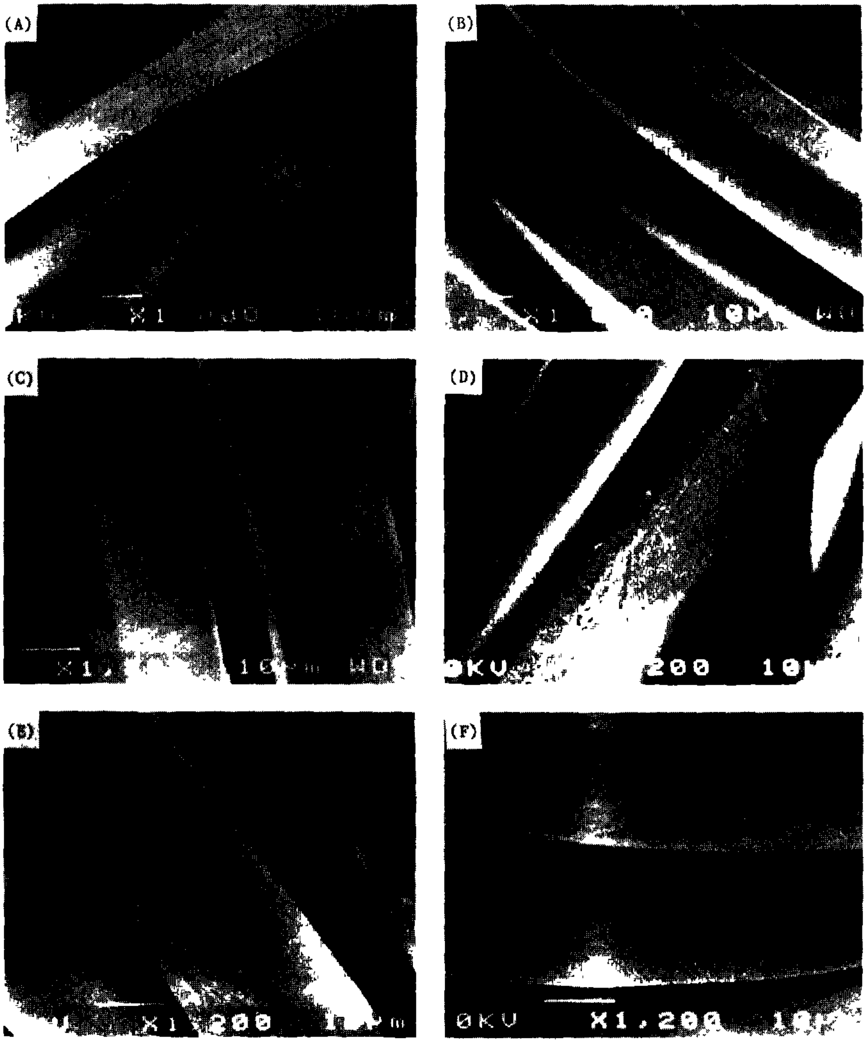


Fig. 11. Scanning electron photomicrograph of nylon 6.6 dyed with CI Disperse Yellow 1 in the presence of (A) dye alone, (B) 10 mM APS, (C) 20 mM APS, (D) 20 mM KIO_4, (E) 20 mM TDO, (F) 20 mM glucose.

the 'effective' concentration of radical initiator adsorbed by the fibre and, thus the extent of damage caused to the substrate, may have been reduced owing to the radical initiator interacting with the dye in the dyebath. Alternatively, it may be possible that dye which is adsorbed onto the fibre may have reduced the extent of the radical initiator–fibre reaction by virtue of, for example, a 'sacrificial' effect or simply by the provision of a physical barrier to adsorption of the radical initiator.

CONCLUSIONS

The results obtained from ATR analysis support the view that disperse dyes become covalently attached to nylon 6.6 during dyeing in the presence of radical initiators. The AEG content and tensile strength of the fibre were significantly influenced by the nature of radical initiators.

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