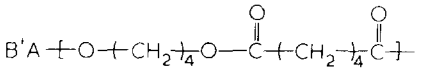
Table 2 Photocrosslinking of polyesters BS, BA, BT and BI in presence and absence of sensitizers

	Photocrosslinking time in minutes			
Sensitizer[a]	BS	BA	BT	BI
None	17(50)[b]	21[c](>30)[b]	6[c](15)[b]	18(>35)[b]
Benzophenone	7	10	4	6
Biphenyl	5	10	4	5
Benzoic acid	5	10	6	5

[a] 10 Wt % of polymer

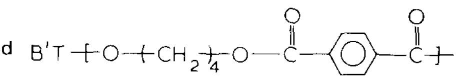
[b] Exposure time in minutes beyond which u.v. absorption spectra did not show any further change

[c] Irradiation of control



$$B'A\!-\!\!\left[O\!-\!(CH_2)_4\!-\!O\!-\!\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_4\!-\!\overset{O}{\overset{\|}{C}}\right]\!-$$

and



polymers showed less than 10% and 15% crosslinking under similar experimental conditions respectively

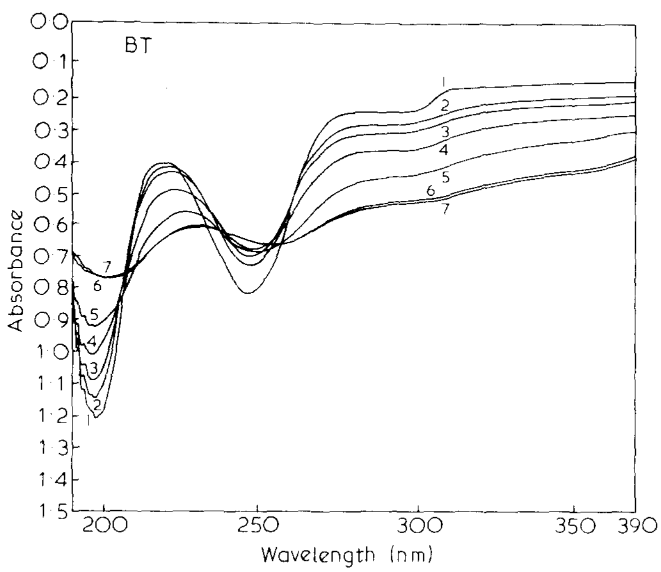


Figure 1 Variation in absorption spectrum of film of polymer BT with irradiation time: (1), 0 min; (2) 1 min; (3), 2 min; (4), 4 min; (5), 10 min; (6), 15 min; (7), 30 min

three polyesters studied. All three sensitizers benzophenone ($E_T = 69.2$ kcal), biphenyl ($E_T = 65.8$ kcal) and benzoic acid ($E_T = 78.1$ kcal) used reduced the insolubilization time by about the same extent for all the polymers. Although the nature of the crosslinking reaction in such systems has not been established, the fact that all sensitizers exhibit similar effects on both the aliphatic and aromatic polyesters is evidence against a triplet sensitization mechanism.

The change in absorption spectrum of the film as function of exposure time was obtained by exposing the polyester film on a quartz plate for various intervals of time and a typical variation is shown in *Figure 1*. In all cases the high intensity band around 205 nm due to the triple bond chromophore decreased in intensity with increased exposure time.

The exposure times beyond which the u.v. spectra of polymers showed no further change (*Table 2*) were found to be much larger than the time required for insolubilization respectively. This suggests that formation of only a few crosslinks is probably sufficient to insolubilize the polymer.

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Fluorescence emission from poly[2-(9-ethyl)carbazolylmethylmethacrylate]

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Fluorescence emission spectra of carbazole-containing polymers have been of considerable interest since it was first demonstrated that the fluorescence of solutions (and films) of poly[9-vinylcarbazole] (PVCz) arose entirely from other than isolated monomeric carbazole species[1]. The precise origins of the multi-luminescence of PVCz remain a matter for discussion but there is complete agreement as to the requirement for at least two types of trap thought to arise via excimer formation[2]. A recent review article by Holden and Guillet[3] gives an up-to-date survey of excimer trap formation and energy migration in a wide range of polymers derived from polymerizable derivatives of aromatic molecules.

Contributing to particular interest in the photophysics of carbazole-containing systems is the well known photoconducting character of PVCz and of dispersions of carbazole derivatives in inert polymeric binders[4]. In earlier studies we have reported on emission spectra of a variety of ring-vinylated carbazole homopolymers[5], copolymers of 9-vinylcarbazole[6], and homopolymers of a number of methylmethacrylates in which the carbazole substituent is linked to the polymer backbone either via a methylene unit attached to the various ring positions, or by substituents differing in chain length and attached to the carbazole nitrogen atom (9-position)[7].

Two general conclusions may be drawn from these and related studies[8] of other groups; (i) the existence of more than one emitting excimer state is restricted to PVCz, (ii) normal (i.e. rotationally controlled) excimer emission is restricted mainly to sequences of carbazole-containing monomer units in which the carbazole substituent is attached directly to the polymer backbone (as in ring-

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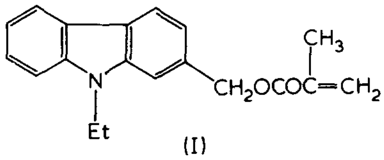
vinylated carbazoles). It should be noted, however, that absence of excimer emission does not necessarily imply the absence of energy migration and may result from a low quantum efficiency for excimer emission rather than a low probability for formation of excimer-like pairs of chromophores.

An apparent and notable exception to the second generalization made above is the homopolymer of [2-(9-ethyl)-carbazolyl]methylmethacrylate (I).



(I)

Fluorescence of solutions and certain cast films of poly(I) were shown to exhibit two components: a typical structured isolated carbazole emission centred around 350 nm, and a broad structureless emission centred around 450 nm. The excitation spectra of both these emitting states correspond closely to the absorption spectrum of the substituted carbazole chromophore. In the original paper[7], and in a more recent report[9], the long wavelength emission has, for convenience, been described as excimer emission although its occurrence contrasts with the behaviour of all other homopolymers of carbazole-containing monomers in which the carbazole is not attached directly to the polymer backbone.

Whilst the existence of this long wavelength emission is not in doubt, for the samples investigated, its origins have always given cause for concern since, even in the original paper, it was noted[7] that the emission maximum occurred at longer wavelengths with increasing solvent polarity. Whilst such solvent dependence is typical of exciplex emissions, excimers are considered to be essentially free from polar contributions. The effect of temperature on the ratio of relative intensities of long wavelength-to-isolated carbazole emissions which, in methyltetrahydrofuran solvent exhibited a pronounced maximum[9], is now shown in solvent CH_2Cl_2 to be represented by a simple linear plot with a slope of only 1.4 kJ mole^{-1}. Furthermore the apparent excimer binding energy calculated[9] from the temperature effect in methyltetrahydrofuran solvent (40 kJ mol^{-1}) is greatly in excess of the usual range of excimer binding energies (typically 10–20 kJ mole^{-1}).

In order to clarify this anomaly the rather tedious synthesis of (I)[10] has been repeated and the properties of newly prepared samples of poly(I) characterized. Freshly prepared samples of poly(I) have absorption spectra identical to that of the material used in the earlier investigations but differ in that solutions of poly(I) do not exhibit the long wavelength emission centred around 450 nm — so typical of the earlier material. Rather the emission consists only of the structured carbazole fluorescence centred at 350 nm and shown in the earlier papers. However, solutions of poly(I) left to stand in the light slowly develop the previously recorded long wavelength emission band. Clearly this new emission is the result of a photochemical degradation process in poly(I) which is apparently accelerated by atmospheric oxygen. The degradation is sufficiently rapid that attempts to cast films of poly(I) from solvents nearly always resulted in materials exhibiting the dual luminescence, probably arising from degradation during solvent evaporation and film handling. Rapid (chain scission) degradation of poly(I) and its structural isomers had already been noted during viscosity and osmotic pressure measurements in the early work[7] but was not correlated with the emission properties. It is interesting that whereas the light-induced degradation was readily observed in dichloromethane, tetrahydrofuran, and toluene solvents, degradation apparently does not occur in methyltetrahydrofuran solvent. Reprecipitation of polymer from any of these degraded solutions does not remove the species responsible for the long wavelength emission and solid samples of poly(I) exhibit similar degradation but over longer periods of time. The original samples of poly(I), characterized for luminescence in Toronto and in Strathclyde[7], had been made in Liverpool many months prior to the measurements of fluorescence emission properties as part of a NATO collaborative programme, and were clearly already in the degraded state. Since fluorescence spectroscopy is such a highly sensitive technique only extremely low concentrations of fluorophore would be necessary to explain the present observations, and other spectroscopic methods would not detect such low degrees of degradation.

At the present time it is not realistic to speculate as to the identity of the species responsible for the long wavelength emission in degraded samples of poly(I) but the polymer exhibits ratios of long wavelength emission/carbazole emission which depend on its concentrations, when dispersed in such different polymer hosts as polyvinylacetate, polystyrene and polymethylmethacrylate.

It is concluded that, in contrast to many other polymers having condensed aromatic substituents, carbazole-containing polymers do not exhibit excimer emission except when the carbazole unit is directly bound to the polymer backbone. This conclusion is entirely consistent with the fact that simple alkyl carbazoles do not exhibit excimer emission in solutions or when dispersed in a host polymer matrix.

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