Photocrosslinkable polymers containing backbone triple bonds

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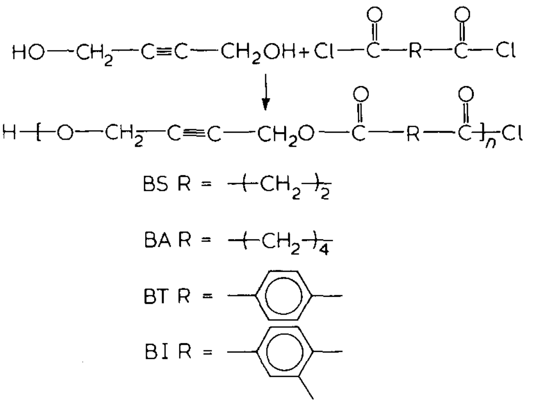
Recently Kato and Yoneshige[1] reported the preparation and the ability of homopolymers and copolymers of propargyl 4-vinylethers containing pendant triple bonds to undergo photocrosslinking. Photosensitivity studies on polymers with polydiacetylene backbones have been reported on polyethers[2,3], polyurethanes[4] and polyesters[4]. The polydiacetylene polymers were found to readily undergo crosslinking on exposure to ultraviolet light and the crosslinking reactions could also be sensitized by some additives.

In this communication we report the synthesis of a series of polyesters BS, BA, BT and BI containing backbone triple bonds (and the ability of these molecules to undergo photocrosslinking in the presence and absence of sensitizers). These polyesters were synthesized by interfacial condensation in almost quantitative yields from 2-butyne-1,4-diol and succinoyl, adipoyl, terephthaloyl and isophthaloyl acid chlorides.



The acid chlorides were prepared from corresponding diacids and thionyl chloride and further purified by vacuum distillation. The 2-butyne-1,4-diol (Fluka AG grade) was further purified by recrystallization from ethyl acetate.

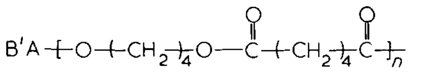
Polymer preparation[5] *and characterization*

The freshly recrystallized 2-butyne-1,4-diol (0.01 mol) was dissolved in 60 ml of 0.33 molar NaOH in 500 ml beaker and vigorously stirred at 0° to 5°C. The freshly distilled diacid chloride (0.01 mol) was dissolved in 30 ml of dry, distilled toluene and was added quickly to the butynediol solution. Stirring was continued for 5 to 10 min. The polyester thus formed was filtered through a sintered crucible, washed several times with distilled water and dried in vacuum. The elemental analysis and intrinsic viscosities of the polyesters are reported in *Table 1*.

The polyesters typically show characteristic infra-red absorption bands around 1730 cm^{-1} ($>C=0$ stretch in ester) 1145 cm^{-1} and 1260 cm^{-1} (C–O–C stretch) and a broad band at 3400 cm^{-1} (–OH stretch). The 1730 cm^{-1} band in aliphatic ester was broadened probably due to the hydrogen bonding of the carbonyl absorption for the terminal carboxylic groups. A distinct broad band was observed at 1640 cm^{-1} in the case of aromatic polyesters. Ultra-violet solution spectra and ultra-violet spectra of the polymers in the form of thin films cast from tetrahydrofuran solution on quartz plate were similar. Spectra of polyesters BS and BA were typical of the butynediol while the spectra of aromatic polyesters (BT and BI) were essentially a combination of the spectra of butynediol and aromatic chromophore. The X-ray diffraction powder patterns for polyesters exhibit sharp bands suggesting a fairly high degree of crystallinity.

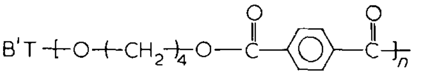
Study of photocrosslinking ability

The polyesters prepared were dissolved in tetrahydrofuran solution to obtain a 5% polymer solution. The solution was spread on quartz plate and the solvent evaporated. The film thus formed was exposed to a 200 W medium pressure mercury lamp at a distance of 28 cm for selected intervals of time and film was developed in tetrahydrofuran for 2 min. The insolubilization of the polymer film was determined by its adhesion to the quartz plate. A similar procedure was adopted for studying the effect of sensitizers. These polyesters become insoluble in the developing solvent tetrahydrofuran on exposure to ultra-violet light. The exposure times required for complete insolubilization of the film are recorded in *Table 2*. Since the exposure times for complete insolubilization were large, photocrosslinking of polymers



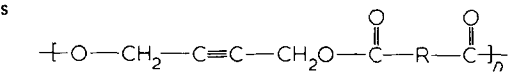
$$B'A-[O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}]_n-$$

and

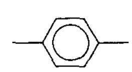
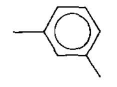


containing no triple bonds were studied. These polymers underwent only small amounts of crosslinking under comparable experimental conditions. The polyester BT is found to be somewhat more photosensitive than the other

Table 1 The intrinsic viscosities and elemental analysis of the polymers



$$-[O-CH_2-C\equiv C-CH_2O-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}]_n-$$

Polymer	R	$[\eta]^a$ dl/g	Elemental analysis C	H
BS	$-(CH_2)_2-$	0.131	$(57.14)^b$ 56.50	$(4.76)^b$ 5.48
BA	$-(CH_2)_4-$	0.134	(61.20) 60.24	(6.12) 6.59
BT		0.125	(66.66) 65.95	(3.70) 4.17
BI		0.144	(66.66) 65.92	(3.70) 3.90

[a] Intrinsic viscosities measured in phenol–tetrachloroethane (40:60) at 30° ± 0.05°C
[b] Calculated value

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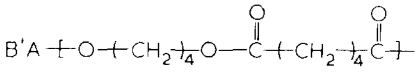
Table 2 Photocrosslinking of polyesters BS, BA, BT and BI in presence and absence of sensitizers

	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

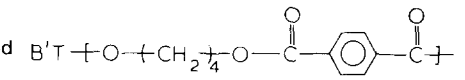
[b] Exposure time in minutes beyond which u.v. absorption spectra did not show any further change

[c] Irradiation of control



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

and



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

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.

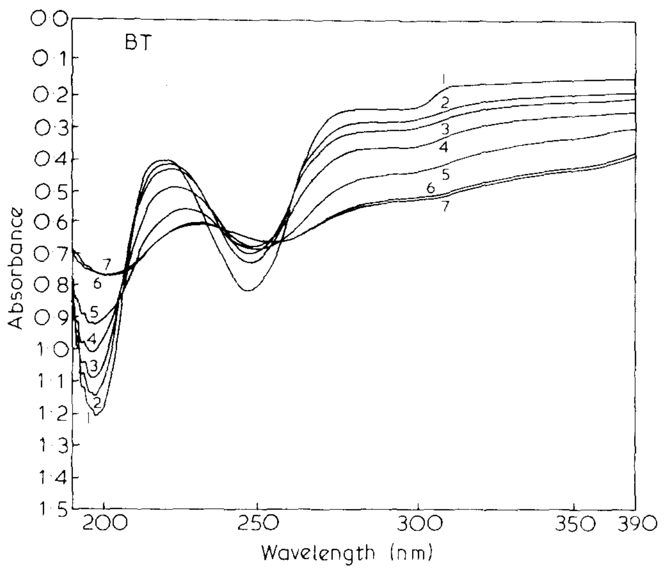


Figure 1 Variation in absorption spectrum of film of polymer BT with irradiation time: (1), 0 min; (2) 1 min; (3), 2 min; (4), 4 min; (5), 10 min; (6), 15 min; (7), 30 min

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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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