Novel Phototransformation of *o*-Nitrobenzylic Polymers to Azopolymers[1]

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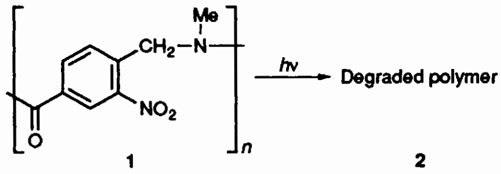
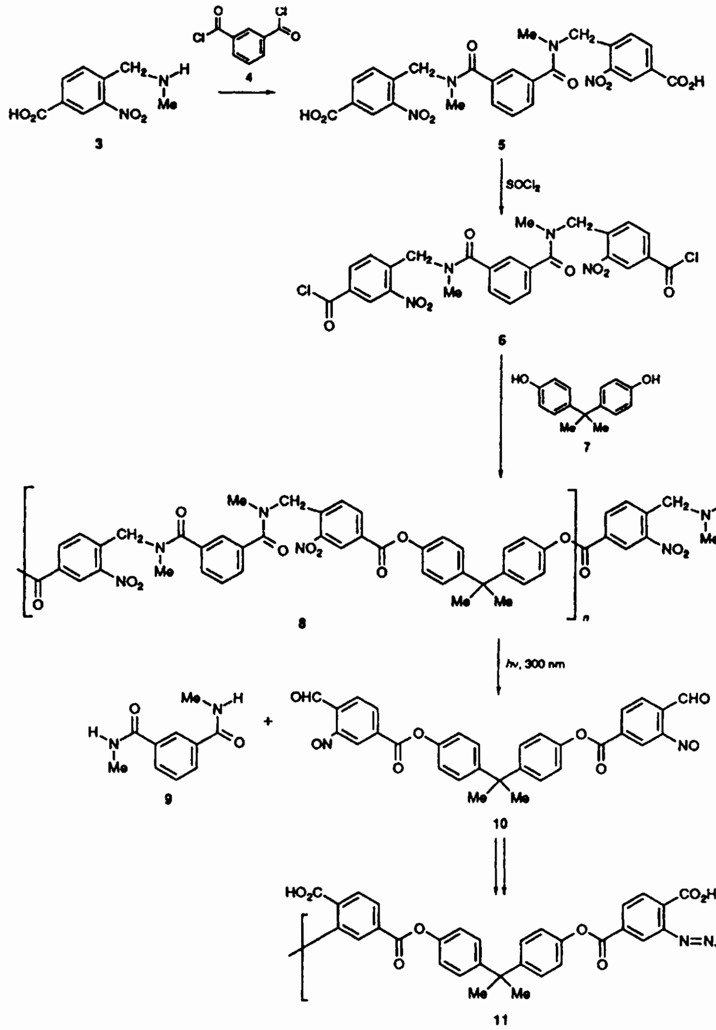
Synthesis and phototransformations of a polymer bearing two *o*-nitrobenzylic chromophores at symmetrical positions per repeating unit to a polar photochromic azopolymer are described.

Photochemistry of *o*-nitrobenzylic and related chromophores has various applications.[2-9] We have exploited this photochemistry to help design and synthesise positive type photoresist polymers, such as the new photodegradable polyamide **1** (Scheme 1).[10] We have now synthesized a new dicarboxylic acid **5**, containing two *o*-nitrobenzylic groups at symmetrical positions, which contain potential degradation sites in every repeating unit and could be easily polymerised. However, such polymers derived from **5**, instead of undergoing photofragmentation are converted to new azochromophoric polymers, such as **8**.



Scheme 1

Isopthalimido bis(α-methylamino-2-nitro-4-toluic) acid **5** was prepared by the reaction of the *o*-nitrobenzylamine derivative **3** with isopthaloyl chloride **4** in a 95% yield (Scheme 2). The dicarboxylic acid, **5**, was characterized on the basis of spectral data and high-resolution mass spectrometry. It was converted to the corresponding acid chloride **6**, by treatment with thionyl chloride and the reaction of **6** with diols gave the corresponding polyamide esters. A typical example is the interfacial condensation of **6** with 4,4-isopropylidenediphenol **7**, resulting in the formation of the polyamide ester **8** in an 80% yield. This polymer was characterized on the basis of analytical results and spectral information. The ^{13}C NMR spectrum of **8** showed peaks at δ 163.7 (–C(=O)–O), 162.7 (–C(=O)–N′–), 155.0, 148.3, 148.2, 148.1, 148.0, 147.9, 140.0, 134.7, 130.5, 129.9, 129.7, 129.3, 129.0, 127.6, 127.5, 127.3,



Scheme 2

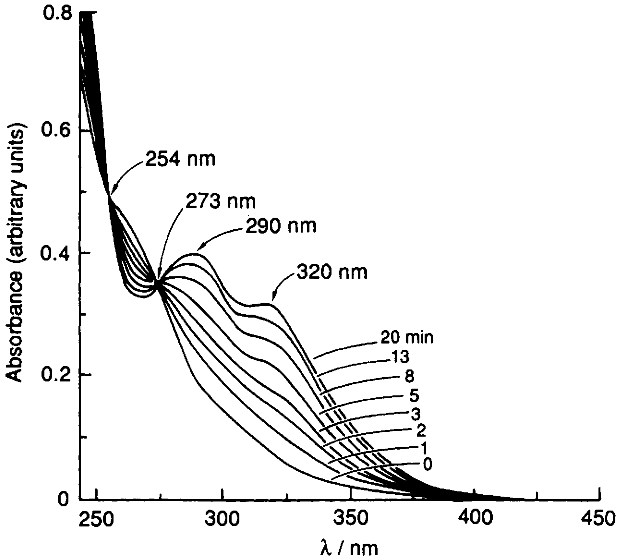


Fig. 1 UV spectra changes of **5**, on irradiation

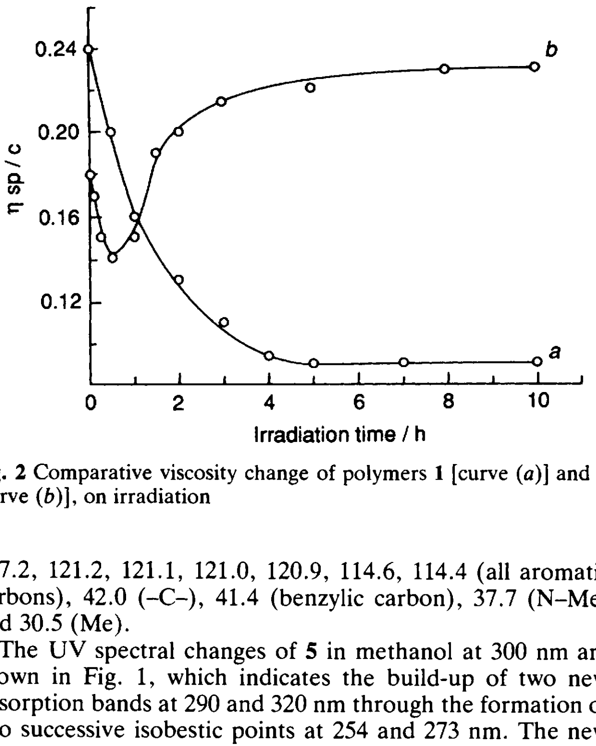


Fig. 2 Comparative viscosity change of polymers **1** [curve (*a*)] and **8** [curve (*b*)], on irradiation

127.2, 121.2, 121.1, 121.0, 120.9, 114.6, 114.4 (all aromatic carbons), 42.0 (-C-), 41.4 (benzylic carbon), 37.7 (N-Me) and 30.5 (Me).

The UV spectral changes of **5** in methanol at 300 nm are shown in Fig. 1, which indicates the build-up of two new absorption bands at 290 and 320 nm through the formation of two successive isobestic points at 254 and 273 nm. The new bands at 290 and 320 nm are attributed to the presence of an azo chromophore, formed through the intermediacy of a nitroso aldehyde.[11] The UV spectral changes of polymer **8** were found to be identical with those of **5**, indicating thereby that the pathways for the photochemical changes of **5** and **8** must be identical.

The visocity changes of the polymers **1** and **8** on irradiation at 300 nm in DMF solution are compared in Fig. 2. Curve *a* represents the changes for the polymer **1**, which contains only one *o*-nitrobenzylic group per repeating unit of the polymer. This polymer undergoes degradation, on irradiation, to smaller fragments as evidenced by its decrease in the inherent viscosity. However, in the case of polymer **8**, contrary to our expectations, we found that after an initial decrease, the inherent viscosity increases with irradiation, which is evident from curve *b* in Fig. 2.

Increase in viscosity on irradiation clearly indicates that the polymer **8** does not undergo photofragmentation to smaller molecules. In order to assess the reason for the viscosity increase on irradiation, the polymer **8** was subjected to steady state photolysis and product analysis. Photolysis of a DMF solution of **8** results in a reddish-brown solid **11**, which is soluble only in highly polar solvents such as DMF and Me_2SO. The inherent viscosity of the photoproduct was found to be 0.2 dl g^{-1} which is higher than that of the starting polymer **8**, indicating that the photoproduct is polymeric. The IR spectrum of the polymer did not show characteristic absorption peaks due to the nitro group, but contained new absorption peaks, corresponding to carboxylic acid and azo groups. The UV spectrum of the photoproduct indicated the presence of a chromophore, absorbing at 290 and 320 nm. The ^1H NMR spectrum did not show peaks at δ 5.0 and 3.15, corresponding to the *o*-nitrobenzylic protons and the N-Me protons, respectively. The ^{13}C NMR spectrum of **11** showed peaks at δ 165.4 [-C(=O)-OH], 163.7 [-C(=O)-O], 148.2, 147.9, 140.0, 134.7, 130.5, 129.9, 129.7, 129.0, 128.2, 127.6, 127.5, 121.2, 121.0, 114.6 (all aromatic carbons), 42.0 (-C-) and 30.5 (Me). Even though the spectrum of **11** shows the presence of some unchanged chromophore of **8**, a comparison of both spectra indicates clearly that the characteristic peaks owing to the amide carbon (δ 162.7), aromatic carbon bearing the nitro group (δ 148.0) and the *o*-nitrobenzylic carbon (δ 41.4) have nearly disappeared in the spectrum of **11**. A new carbonyl peak at δ 165.4 has appeared in the spectrum of **11**, due to the formation of carboxylic acid groups. The carboxylic acid content of **8** and of the photoproduct were 0.13 and 0.88 mmol g^{-1}, respectively. These observations lead to the conclusion that polymer **8** has been transformed, on irradiation, into a new polymer **11**, having azo chromophores in its main chain (Scheme 2).

The phototransformation of **8** to the azo polymer **11** can be further substantiated on the basis of the earlier reports on the photorearrangements of *o*-nitrobenzylic and related systems.[2,10,11] The presence of the azo chromophore in **11** was further confirmed through its *cis–trans* isomerization and the resultant reversible photoviscosity effects, which are characteristic properties of polymers containing azo chromophores.[12,13] In addition to this, we could obtain a positive photoresist pattern of polymer **8** with 1 μm line and space after exposure and development. The irradiated portions become highly soluble in aqueous base, compared to the unirradiated portions of polymer **8**. This indicates clearly the formation of polar carboxylic acid groups, through the suggested pathway.

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