

Excimer-laser-induced polymerization of diazido compounds

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Abstract

Excimer laser photolysis of concentrated solutions of diazidobiphenyls (4,4'-diazido-3,3'-dimethoxybiphenyl (**1a**) and disodium 4,4'-diazidobiphenyl-2,2'-disulphonate (**1b**)) gave polymers containing azo bonds in the main chain. Although the polymers formed contained a certain amount of insoluble component, the highest degrees of polymerization detected by gel permeation chromatography were 5-mer (photoproduct from **1a**) and 32-mer (photoproduct from **1b**). The intermolecular reaction of concentrated intermediates containing two reactive sites, which were generated efficiently on irradiation with pulsed excimer lasers, led to a polymer with a higher molecular weight in good yield. The degree of polymerization of the polymers obtained was dependent on the light intensity and concentration of precursors. From a comparison of the degree of polymerization of the polymers obtained by excimer laser photolysis and conventional light photolysis, it is concluded that excimer laser photolysis provides a novel method of polymerization.

Keywords: High-intensity photolysis; Excimer laser; Aromatic azide; Aromatic nitrene; Polymerization

1. Introduction

High-intensity laser photochemistry of organic molecules has been a subject of considerable interest over the last two decades since the development of excimer lasers [1]. One of the most distinguishing characteristics of excimer lasers is the high fluence, which extends from roughly 10^{23} to 10^{28} photons $\text{cm}^{-2} \text{s}^{-1}$, compared with conventional lamps (around 10^{17} photons $\text{cm}^{-2} \text{s}^{-1}$). In this high-intensity photon domain, multiple-photon excitation of molecules and high-density excitation of reactants are experimentally accessible [2]. When molecules containing two photosensitive chromophores are irradiated in a concentrated solution with an excimer laser, we can expect the generation of a high instantaneous concentration of intermediates having two reactive sites.

In a preceding paper [3], we reported the excimer-laser-induced polymerization resulting from intermolecular coupling between the reactive intermediates generated by photolysis of 1,4-diazidobenzene. Although the polymer was identified as polykis-azobenzene by UV-visible, IR, ¹H and ¹³C nuclear magnetic resonance (NMR) and Raman spectroscopies, the degree of po-

lymerization was not determined clearly because of its remarkably low solubility in the usual solvents except concentrated sulfuric acid.

In this paper, we report the excimer-laser-induced polymerization of two aromatic diazido compounds: 4,4'-diazido-3,3'-dimethoxybiphenyl (**1a**) and disodium 4,4'-diazidobiphenyl-2,2'-disulphonate (**1b**). For the photolysis of **1b**, the polymer formed was considerably soluble in water and was followed by gel permeation chromatography (GPC). The polymerization processes were investigated by GPC analysis by comparing KrF excimer laser photolysis with that using a mercury lamp.

2. Experimental details

2.1. Preparation of the diazides

The diazides **1a** and **1b** were prepared from the corresponding diamines by reaction of the diazonium salts with sodium azide by conventional procedures, and were purified by recrystallization from hexane-ether and aqueous solution respectively.

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2.2. Photolysis of the diazides

The diazides **1a** and **1b** were dissolved in hexane and water ($(2.0\text{--}5.0)\times 10^{-5}$ M for the spectroscopic studies and $1.5\times 10^{-3}\text{--}1.4\times 10^{-2}$ M for the preparative studies) respectively; these solutions were bubbled with nitrogen and irradiated in a quartz cell (optical path length, 1 cm) at room temperature with a KrF excimer laser (248 nm) (Lambda Physik EMG 201MCS; 80–100 mJ cm⁻² per pulse; full width at half-maximum (FWHM), 34 ns), an XeCl excimer laser (308 nm) (Lambda Physik EMG 102MCS; 30 mJ cm⁻² per pulse; FWHM, 17 ns) and a low-pressure mercury lamp (Riko UVL-30LA, 1.6 mJ cm⁻² s⁻¹). The photolyses of the diazides were followed by UV–visible spectroscopy (Shimadzu UV-265). The characterization of the photoproducts obtained, which were separated from the irradiated solution by evaporation of the solvent, was carried out by Fourier transform IR (FT-IR) (Shimadzu FTIR-4000) and FT-Raman (JEOL JRS-FT5500W) spectroscopy. The analysis of the degree of polymerization was carried out by GPC on the basis of polystyrene (TOSOH TSK-GEL G3000HXL and TSK guard column HXL-L; tetrahydrofuran (THF) as eluent) and polyethylene glycol (Asahipak GS-310H, GS-510H and GS-10G; 0.01 M phosphate buffer (pH 2.5) as eluent) calibration for the soluble component of the photoproducts from **1a** and **1b** respectively.

3. Results and discussion

3.1. Photoproducts of diazides

The changes in the UV–visible spectrum of **1a** in hexane solution (5.0×10^{-5} M) on irradiation with an XeCl excimer laser are shown in Fig. 1. With an increase

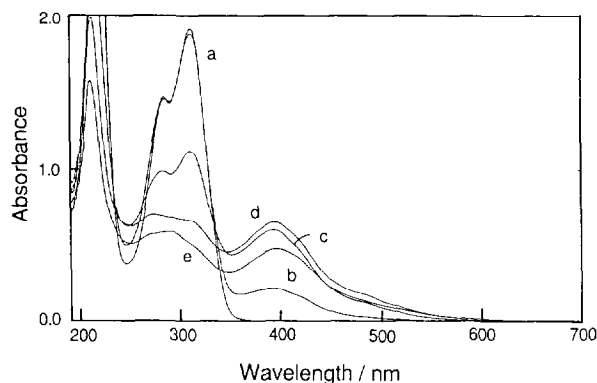


Fig. 1. UV–visible spectral changes during the photolysis of **1a** in hexane solution (5.0×10^{-5} M) by XeCl excimer laser irradiation (30 mJ cm⁻² per pulse): curve a, before irradiation; curve b, after irradiation of 10 shots; curve c, after irradiation of 30 shots; curve d, after irradiation of 100 shots; curve e, after irradiation of 300 shots.

in the number of shots, the absorption peak at 310 nm decreases while a new broad absorption band appears in the longer wavelength region at around 400 nm. The decrease in the 310 nm band does not simply correspond to the increase in the 400 nm band with an increase in the number of irradiation shots due to the formation of precipitates. The changes in the UV–visible spectrum of **1b** in aqueous solution (2.0×10^{-5} M) on irradiation with a KrF excimer laser are similar to those observed for **1a**, i.e. the absorption peak at 265 nm decreases while a new broad absorption band appears in the longer wavelength region at around 320 nm. The decrease in the absorption peaks at 310 and 265 nm suggests the decomposition of the azido group. On the other hand, the appearance of the absorption bands in the longer wavelength region is presumed to be due to the formation of azo bonds by reaction of azido-biphenylnitrene and/or biphenyldinitrene, generated by the photolysis of diazidobiphenyls, on the basis of previous investigations [3,4]. Waddell and Go [5] reported that azobenzene could be formed via the dimerization of two phenylnitrenes or via the reaction of a phenylazide with a phenylnitrene to form 1,2-diphenyltetraazadiene, which is assumed to decompose readily into azobenzene and molecular nitrogen. In the case of diazido compounds, polymerization through azo bond formation has been reported by Bössler and Schulz [6] and in our preceding paper [3].

The difference between the absorption spectra of the polymers obtained from **1a** and **1b** can be explained by the steric hindrance between the two sulphonic acid groups at the 2,2'-positions in **1b**. The conjugated π -electron system in the photoproducts of **1b** is perturbed by the twisted biphenyls containing the two sulphonic acid groups. Bössler and Schulz [6] have shown that the absorption band of the photoproduct of 4,4'-diazidobiphenyl appears at 600 nm in dichloroacetic acid. Although the absorption band is in a region of longer wavelength compared with the results of our experiments, this is because the azo bond is protonated when dichloroacetic acid is used as solvent.

Fig. 2 shows the IR spectra of **1a** and the photoproduct (**2a**) obtained by XeCl excimer laser photolysis of **1a**, and Fig. 3 shows the Raman spectrum of **2a**. Although the IR spectrum of **2a** is composed of broad bands, as often observed for polymeric compounds measured by the KBr disc method, it is confirmed that the absorption band of the azido group (2120 cm^{-1}) disappears while the bands of the methoxy group (2830 and 2950 cm^{-1}) are conserved. Moreover, the Raman shifts of **2a** are observed at 1603 (intensity (a.u.), 34.95), 1439 (33.85), 1410 (23.35), 1308 (19.84), 1269 (29.84), 1200 (20.08), 1173 (14.14) and 1109 (58.59) cm⁻¹. The peak at 1439 cm^{-1} should be assigned to trans -N=N- stretching by reference to the literature [7]. Similarly, the IR and Raman spectra of the product (**2b**) obtained

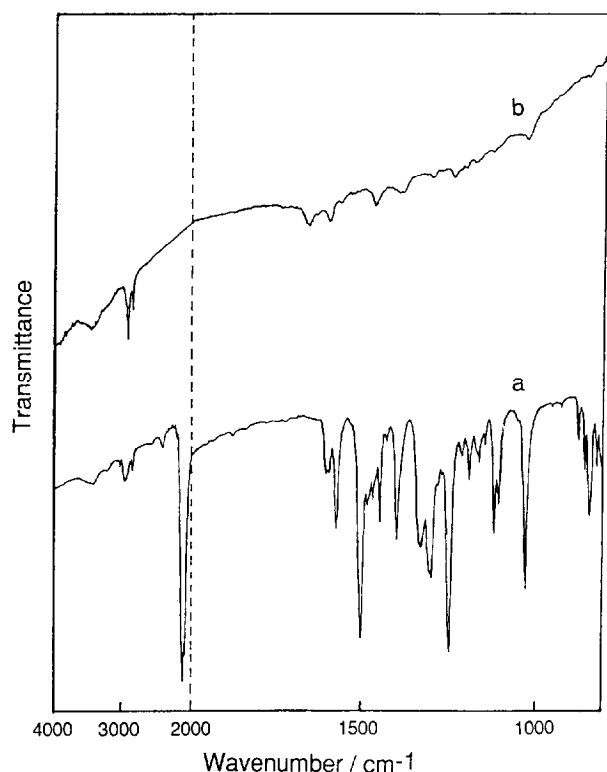


Fig. 2. IR spectra of **1a** (a) and the photoproduct of **1a** (b) obtained on XeCl excimer laser irradiation.

by KrF excimer laser photolysis of **1b** suggest the formation of an azo bond and the existence of a sulphonic acid group.

From the above-mentioned spectral data, the photoproducts from the diazidobiphenyl compounds were characterized as the expected polymers having an azo bond in the main chain as shown in Scheme 1.

Although we have not yet identified the intermediates in the photolysis of **1a** and **1b** in fluid solution at room temperature, we have reported previously that two dinitrenes (a twisted structure and a quinonoid structure of biphenyldinitrene) were found to be intermediates in the photolysis of 4,4'-diazidobiphenyl in low-temperature rigid matrices [8]. In addition, dinitrene has been identified as an intermediate in the photolysis of 4,4'-diazidobiphenyl by laser photolysis techniques [9]. It is well recognized that phenylnitrene interconverts to various intermediates (singlet nitrene, triplet nitrene, benzazirine and didehydroazepine) [10]. However, azirine and didehydroazepine were not observed as intermediates in the photolysis of diazidobiphenyl. Therefore, in the case of **1a** and **1b**, the formation of polymers containing the azepine structure, which was reported by Meijer et al. [11], can be excluded.

3.2. The degree of polymerization

In a concentrated solution of **1a** (approximately 10^{-3} M), a large amount of precipitate is formed on irradiation. However, in the case of the photolysis of **1b**, the amount of precipitate is negligibly small even in more concentrated aqueous solution (approximately 10^{-2} M).

The precipitate formed from **1a** was remarkably insoluble in the usual solvents, including concentrated sulfuric acid. Only that part which was dissolved in THF was subjected to GPC analysis. The largest degree of polymerization was 5-mer from the photolysis of 1.6×10^{-3} M **1a** in hexane. The insoluble components probably exhibit a much higher degree of polymerization.

On the other hand, the higher degree of polymerization for **1b** could be determined due to its good

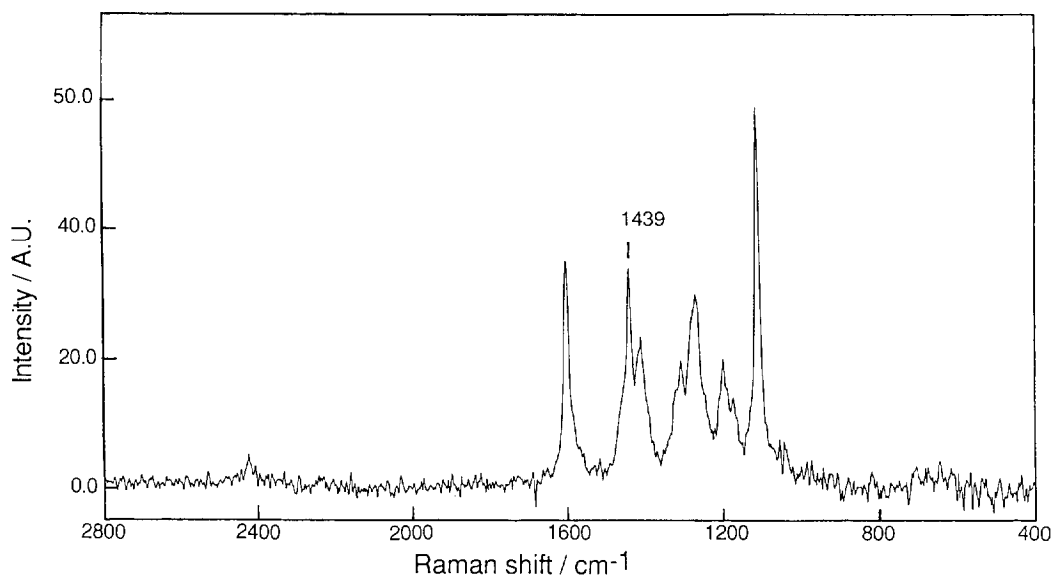
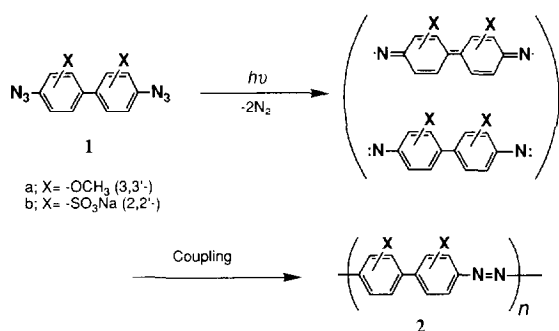


Fig. 3. Raman spectrum of the photoproduct of **1a** obtained on XeCl excimer laser irradiation (measured in the precipitate using the 1064 nm line of a neodymium-doped yttrium aluminium garnet (Nd:YAG) laser as excitation source).



Scheme 1.

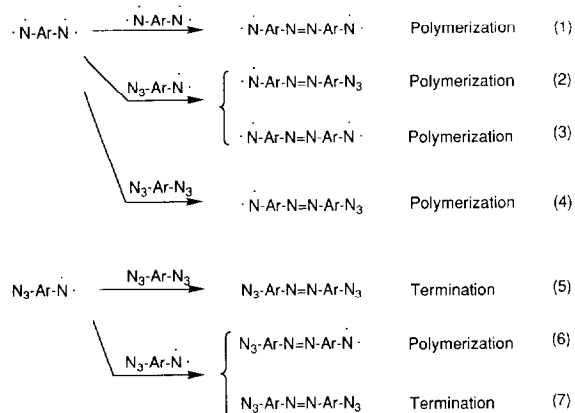
solubility in aqueous solution. The molecular weight distribution of **2b** was shifted to higher values with increasing concentration of **1b**. The largest degree of polymerization (32-mer) was obtained by photolysis of an aqueous solution of 1.32×10^{-2} M of **1b**.

3.3. Processes of polymerization

The difference in the polymerization of **1b** between KrF excimer laser photolysis and photolysis with a low-pressure mercury lamp was investigated by GPC analysis; it could not be performed in the case of **1a** because of the low solubility of the photoproducts obtained from **1a**. Fig. 4 shows the ratio of the photoproducts as a function of the number of photons, and Fig. 5 shows the GPC profiles of the photoproducts. Remarkable differences are observed between laser and lamp photolyses during the initial irradiation step: photoproducts of more than 20-mer are formed rapidly in the case of KrF excimer laser irradiation.

From the previously reported mechanistic studies on azo bond formation during the photolysis of aromatic azides [3,6], it is assumed that two intermediates (dinitrene ($:N-Ar-N:$) and mononitrene ($:N-Ar-N_3$)) are formed during the photolysis of diazido compounds,

and the possible mechanisms of polymerization are as follows



From a consideration of the photon density of the light source and the concentration of the diazido compound, the most probable mechanism is presumed to be Eqs. (1), (2) and/or (3) for laser photolysis and Eq. (5) for lamp photolysis.

The initial photoproducts containing a nitreno group at one end can propagate to higher polymers (Eqs. (1), (2), (3), (4) and (6)). If these photoproducts couple with other photoproducts containing a nitreno group to form a polymer with azido groups at both ends, propagation stops. The photoproducts containing azido groups at both ends and the remaining unreacted diazido compounds are consumed by stepwise polymerization on prolonged irradiation. Stepwise polymerization was observed during irradiation with both the laser and the lamp. The amounts of the 3-, 5- and 6–10-mer photoproducts (curves a, b and c) decrease with an increase in the number of photons, whereas the amounts of the 11–20-mer and above 20-mer photoproducts (curves d and e) increase.

The photoproducts obtained in the largest amount in the stationary state were the above 20-mer product

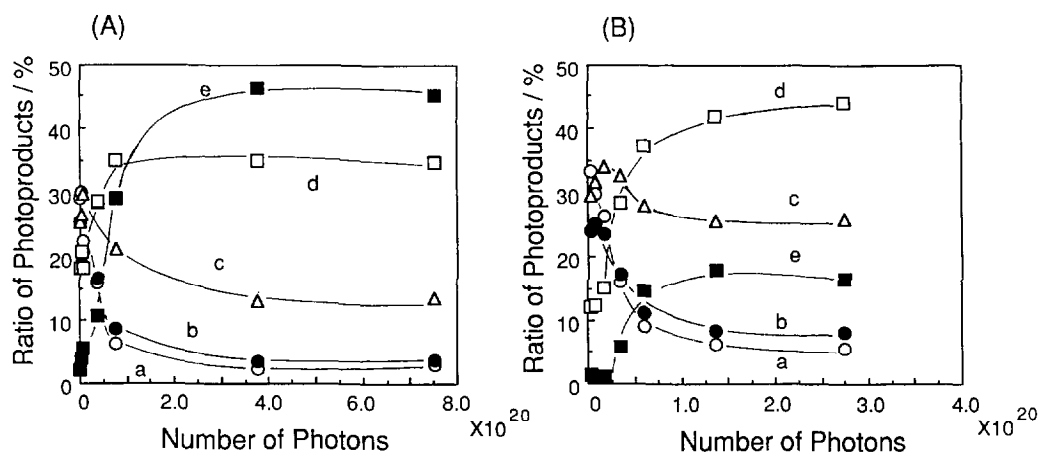


Fig. 4. Ratio of the photoproducts (yield of photoproduct/total yield of photoproducts) as a function of the number of photons: (A) KrF excimer laser photolysis of **1b**; (B) low-pressure mercury lamp photolysis of **1b**. Curve a, 3-mer; curve b, 5-mer; curve c, 6–10-mer; curve d, 11–20-mer; curve e, above 20-mer.

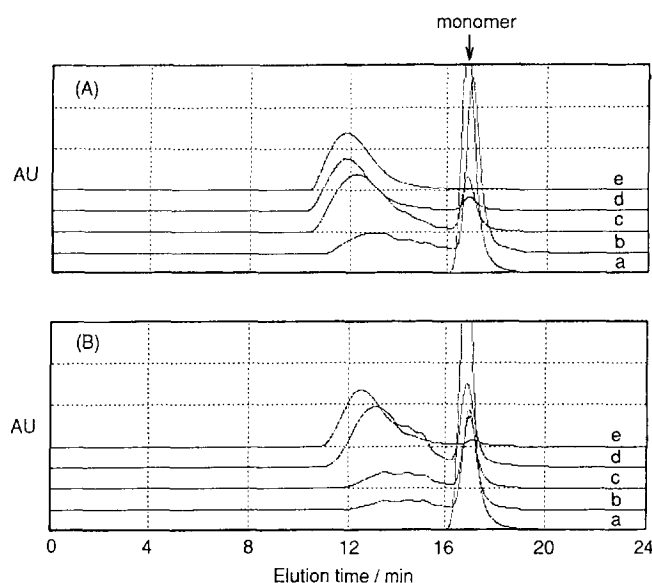


Fig. 5. GPC analysis of photoproducts from **1b** (1.49×10^{-2} M): (A) KrF excimer laser photolysis of **1b** (curve a, before irradiation; curve b, after 500 shots; curve c, after 1000 shots; curve d, after 5000 shots; curve e, after 10 000 shots); (B) low-pressure lamp photolysis (curve a, before irradiation; curve b, after 30 min; curve c, after 60 min; curve d, after 120 min; curve e, after 960 min).

for laser photolysis and the 11–20-mer products for lamp photolysis. These results indicate that the dinitrene generated by excimer laser photolysis is very effective for polymerization.

Finally, we must discuss the mechanism of termination. From the results of the IR spectra, no absorption due to the azido group was observed among the final photoproducts. Therefore the termination must be ascribed to another reaction for saturation of the nitreno group. This remains unidentified, however, because we could not assign the end group by FT-IR or NMR spectroscopy.

4. Conclusions

The highest degrees of polymerization of the polymers obtained were 5-mer and 32-mer in the excimer laser photolysis of **1a** and **1b** respectively (although it was considered that the insoluble components of the pho-

toproduct from **1a** had a higher degree of polymerization). The processes of polymerization were investigated by GPC analysis, which gave the distribution of the photoproducts as a function of the number of photons. The process using conventional light was mainly a stepwise reaction, in which the nitreno group formed on irradiation successively attached to the unreacted azido group. In contrast, in the case of laser photolysis, the main process was efficient coupling of the dinitrene and/or mononitrene generated in high yield within the high-intensity irradiation domain.

Acknowledgment

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References

- [1] R.M. Wilson and K.A. Schnapp, *Chem. Rev.*, **93** (1993) 223, and references cited therein.
- [2] G. Kaupp and O. Sauerland, *J. Photochem. Photobiol. A: Chem.*, **56** (1991) 375. G. Kaupp, O. Sauerland, T. Marquardt and M. Plagmann, *J. Photochem. Photobiol. A: Chem.*, **56** (1991) 381.
- [3] T. Ohana, A. Ouchi, H. Moriyama and A. Yabe, *J. Photochem. Photobiol. A: Chem.*, **72** (1993) 83.
- [4] A. Reiser and L.J. Leyshon, *J. Am. Chem. Soc.*, **93** (1971) 4051. W.H. Waddell and N.B. Feilchenfeld, *J. Am. Chem. Soc.*, **105** (1983) 5499.
- [5] W.H. Waddell and C.L. Go, *J. Am. Chem. Soc.*, **104** (1982) 5804.
- [6] H.H. Bössler and R.C. Schulz, *Makromol. Chem.*, **158** (1972) 113.
- [7] R. Kübler, W. Lüttke and S. Weckherlin, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.*, **64** (1960) 650.
- [8] T. Ohana, M. Kaise and A. Yabe, *Chem. Lett.*, (1992) 1397. T. Ohana, M. Kaise, S. Nimura, O. Kikuchi and A. Yabe, *Chem. Lett.*, (1993) 765.
- [9] A. Reiser, H.M. Wagner, R. Marley and G. Bowes, *Trans. Faraday Soc.*, **63** (1967) 2403. A. Miura and T. Kobayashi, *J. Photochem. Photobiol. A: Chem.*, **53** (1990) 223.
- [10] O.L. Chapman and J.P. Le Roux, *J. Am. Chem. Soc.*, **100** (1978) 282. O.L. Chapman, R.S. Sheridan and J.P. Le Roux, *J. Am. Chem. Soc.*, **100** (1978) 6245. O.L. Chapman and R.S. Sheridan, *J. Am. Chem. Soc.*, **101** (1979) 3690. I.R. Dunkin and P.C.P. Thomson, *J. Chem. Soc., Chem. Commun.*, (1980) 499. G.B. Schuter and M.S. Platz, *Adv. Photochem.*, **17** (1992) 69.
- [11] E.M. Meijer, S. Nijhuis and F.C.M. van Vroonhoven, *J. Am. Chem. Soc.*, **110** (1988) 7209.