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Synthesis and reactions of polymers with photoactive terminal groups: 2. New azo-initiator for the synthesis of polymers with N-acyldibenz[b,f] azepine terminal units

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INTRODUCTION

Photochemically-induced cyclodimeri-zation[1] of ethylenically unsaturated molecules is a well known process which finds application in photoresist techno-logy[2]. The reaction may be represented generally as in equation (1) and commer-cially important examples utilize poly-mers having pendent or main-chain unsaturation of the cinnamate (ArCH═CHCOOR) or chalcone (ArCH═CHCOR) types.
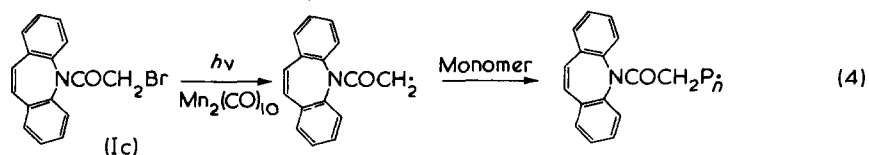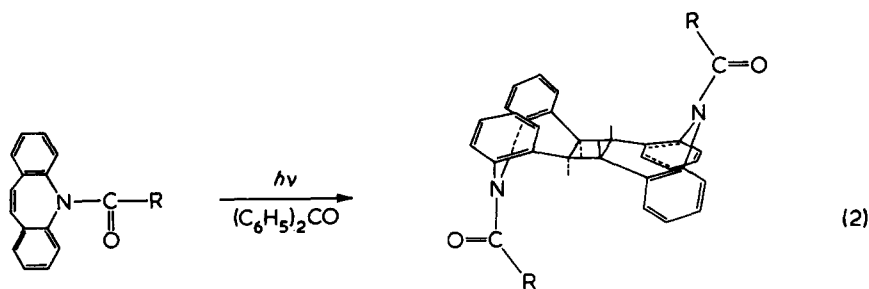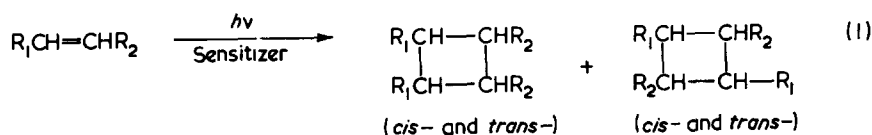
Recently it was shown[3] that N-acyl derivatives of the dibenz[b,f]azepine (iminostilbene) ring system (I) may be photochemically cyclodimerized [equa-tion (2)] with the aid of a variety of sensitizers having triplet state energies ranging from benzophenone (69.5 kcal/mol) to benzil (53.7 kcal/mol). A range of derivatives (e.g. Ib) have been synthesized and shown to be capable of homopolymerization or copolymeri-zation to products which are then photocrosslinkable via the dibenzaze-pine substituents[4].

Attachement of structurally related dibenzazepine derivatives to polymer chains as terminal units would afford a convenient procedure for chain exten-sion or block polymer formation by similar photoinduced cyclodimeriza-tions. Such incorporation of specific groups at the ends of polymer chains may be readily accomplished by utiliz-ing appropriately substituted initiator molecules, especially in the case of free radical polymerizations in which trans-

fer processes may be minimized. Photo-sensitization by metal carbonyls, of which there are numerous examples, provides a convenient initiation process for such purposes. Many initiating sys-tems of this type include a reactive organic halide (RX) which undergoes a redox reaction with species resulting from photoexcitation of the metal carbonyl to yield a radical (R·) and a halide anion which becomes associated with the oxidized form of the metal as a ligand (equation 3)[5].

Recently we have shown[6] that man-ganese carbonyl in conjunction with N-bromoacetyldibenz[b,f]azepine (Ic) affords a highly convenient photo-chemical initiating system, complying with the well established kinetic pat-tern[5], and yielding chain-ended func-tionalized polymers as indicated in equation (4).

Whether or not the product polymer possesses one or two photochemically active end-groups depends mainly on the ratios of disproportionation to com-bination for the particular polymeriza-tion; in either case photosensitized chain extension may be accomplished essentially as indicated in equation (2) with R representing a preformed poly-

$$R_1CH═CHR_2 \xrightarrow[\text{Sensitizer}]{hv} \begin{matrix} R_1CH—CHR_2 \\ | \quad\quad | \\ R_1CH—CHR_2 \end{matrix} + \begin{matrix} R_1CH—CHR_2 \\ | \quad\quad | \\ R_2CH—CH—R_1 \end{matrix} \quad (1)$$

(cis- and trans-) (cis- and trans-)

(2)

(I) (a) R═CH₃; (b) R═CH═CH₂; (c) R═CH₂Br;

$$RX + metal° \xrightarrow{hv} R· + metal^I X \quad (3)$$

(4)

(Ic)

mer chain.

In continuation of these studies we now report the synthesis of N-[4,4'-azo-bis-(4-cyanopentanoyl)] -bis-dibenz[b,f,] azepine (IV) a new initiator having the appropriate functionality for subsequent photochemically induced chain extension (equation 5).

The azo-compound IV henceforth referred to as ADBA, is a useful initiator for thermal and photochemically induced free radical polymerizations, yielding polymeric products having one or two dibenzazepine end-groups per chain in accord with normal kinetic behaviour for the particular monomers involved.

EXPERIMENTAL

All monomers and solvents were purified as described.

Polymerization procedures

Bulk monomers, or approximately 1:1 monomer/benzene mixtures, containing ADBA at a concentration of 50mg/5ml were outgassed in the usual manner and placed in a hot water bath at $70°-80°C$ for between 15 and 30 min. At the end of this time the reaction mixtures were poured into a ten-fold excess of methanol and the precipitated polymers filtered. All polymers were then reprecipitated from benzene into methanol at least three times before use in the chain extension experiments. Polymerization times and temperatures were chosen so as to produce polymer in approximately 10% conversion.

Photochemically initiated polymerizations were performed on very similar reaction mixtures contained in quartz tubes with the temperature maintained at $25°C$ and unfiltered irradiation from a 250 watt medium pressure mercury lamp. Photolysis times were approximately 3 h.

Photosensitized chain extension experiments

Appropriate solutions of purified polymers and sensitizers contained in 9 mm internal diameter pyrex glass tubes were degassed in the usual manner before irradiation in a Rayonet Merry-go-Round Photoreactor. The Rayonet 350 mm irradiation source was used throughout. After irradiation the glass reaction tubes were opened and the polymers recovered by precipitation into methanol.

Molecular weight measurements

Number-average molecular weights were estimated from measurements of
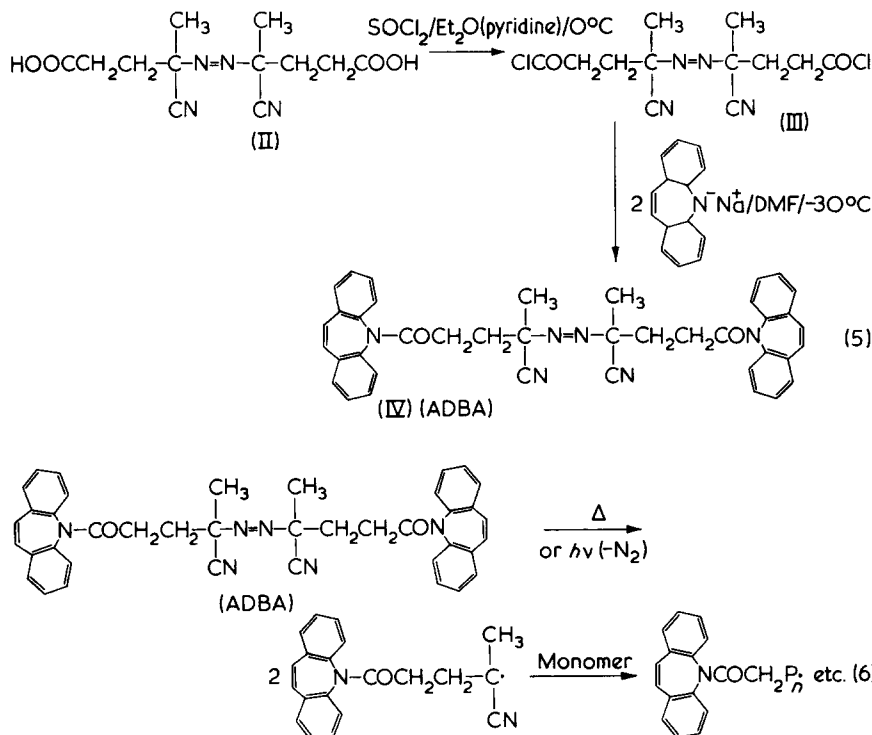
solution viscosity in benzene at $30°C$ with the aid of the relationships:

$$[\eta] = 0.97 \times 10^{-4}\bar{M}_n{}^{0.74}$$
(polystyrene)[7]

$$[\eta] = 0.869 \times 10^{-4}\bar{M}_n{}^{0.76}$$
[poly(methyl methacrylate)][8]

$$[\eta] = 4.59 \times 10^{-5}\bar{M}_n{}^{0.795}$$
[poly(methyl acrylate)][9]

Synthesis of N-[4,4'-azo-bis-(4-cyanopentanoyl)] -bis-dibenz[b,f] azepine (ADBA)

10 ml of thionyl chloride were added over a period of 2 h to a stirred solution of 2.8 g 4,4'-azo-bis-(4-cyanopentanoic acid) (II) (Fluka) in 20 ml dry ether containing 2 drops of pyridine. The reaction mixture was maintained at ice temperature and eventually became slightly yellow in colour. Solvent was removed without heating to yield a pale yellow oil which was redissolved in benzene and re-evaporated in order to remove traces of thionyl chloride. The final oily produce (III) was dried in a vacuum oven without heating. The acid chloride (III) was easily distinguished from the starting acid (II) by the characteristic strong infra-red band at 1800 cm^{-1} (COCl group).

The sodium derivative of iminostilbene was prepared by heating a mixture of 1.93 g of iminostilbene [commercial product (Aldrich) was purified by chromatography on alumina] with

0.96 g sodium hydride (50/50 wt % dispersion in oil) in 20 ml dry dimethylformamide until evolution of hydrogen had ceased. The final solution which had a deep red colour was then cooled (dry ice/methanol) to about $-30°C$ and maintained at this temperature and stirred during the dropwise addition of the acid chloride (III) dissolved in dimethylformamide (10 ml). Addition of the acid chloride solution took about 10 min, after which the product was allowed to stand overnight at approximately $0°C$ before pouring into a large excess of water. The mixture was then extracted with benzene, washed successively with aqueous $NaHCO_3$ solution and water, and dried over calcium chloride. The benzene solution was partly evaporated at room temperature and the product induced to crystallize by addition of a small amount of petroleum ether and standing in a refrigerator overnight. White crystals of (IV) were eventually obtained [m.p. $98°-100°C$ (d), 50% yield based on (II)]. This product had strong i.r. bands (KBr) at 1670 (C=O), 1600, 1490, 1385, 800 and 765 cm^{-1}. ^1H n.m.r. (CDCl₃, ext. TMS) τ 2.1 (16H, ArH, s), 2.45 (4H, olefinic-H, s), 6.8–7.5 (4H, $2CH_2$, m), 7.5–8.5 (10H, $2CH_2$ + $2CH_3$, m).

ADBA exhibits the well-known strong u.v. absorption of the dibenzazepine units with λ_{max} 287 nm, ϵ_{max} 2.44 $\times$ 10^4 $M^{-1}cm^{-1}$ in addition to the usual very weak absorption of azo-compounds

in the 340—400 nm region. Elemental analysis was satisfactory but with some evidence for varying, but small, residual amounts of the acid (II) as an impurity. The azo-initiator is adequately soluble in the common polymerizable monomers and in solvents such as benzene, CH_2Cl_2, tetrahydrofuran.

RESULTS AND DISCUSSION

Styrene, methyl methacrylate and methyl acrylate were used as monomers to test the efficiency of ADBA as a thermal and photochemical initiator of free radical polymerization. Qualitative results confirm that ADBA initiates polymerization in a manner very similar to other, more common, azo-compounds such as AIBN (equation 6). The strong u.v. absorption of ADBA makes it particularly useful for photoinitiation when using quartz vessels.

Samples of polystyrene (p-Sty—DBA), poly(methyl methacrylate) (p-MMA—DBA) and poly(methyl acrylate) (p-MA—DBA) obtained by initiation with ADBA were subjected to benzophenone photosensitized chain extension as described previously for related polymers[6], and
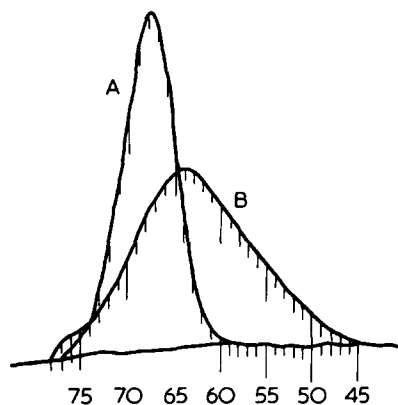

Figure 1 G.p.c. analysis of *p*-Sty-DBA in toluene. A, Initially $\bar{M}_W$ = 59 000; B, after photolysis $\bar{M}_W$ = 294 000

Table 1 Benzophenone photosensitized (λ = 350 nm) chain extension of polymers with dibenzazepine terminal groups

[Polymer] (g/l)	Photolysis time (min)	$10^{-3}\,\bar{M}_n$ Initially	$10^{-3}\,\bar{M}_n$ After photolysis	Increase in $\bar{M}_n$ (%)
p-MMA—DBA[a] (125)	180	59.6	100.4	68.5
p-MMA—DBA[a] (100)	240[c]	90.9	120.0	32.0
p-MMA—DBA[b] (100)	130	63.9	107.7	68.8
p-Sty—DBA[a] (125)	125	52.1	265.0	410
p-Sty—DBA[b] (100)	130	47.4	109.5	131
p-MA—DBA[a] (50)	120	81.7	245.9	200

[Sensitizer] = 0.1 M, solvent benzene in all cases
Values of $\bar{M}_n$ estimated from measurements of $[\eta]$ in benzene at 30°C. [a]Polymer prepared by thermal initiation with ADBA. [b]Polymer prepared by photochemical initiation with ADBA. [c]Sensitizer benzil

gave even more positive evidence for the ability of dibenzazepine chain ends to participate in cycloaddition [equation (2), R = polymer chain].

Typical results are given in *Table 1* and representative g.p.c. traces for a polystyrene sample before and after chain extension are shown in *Figure 1*.

Although these data are preliminary in nature, they serve to indicate the efficiency and convenience of using ADBA to introduce photochemically active chain ends into polymers. The results obtained are entirely consistent with the usual assumptions that propagating MMA radicals terminate by (mainly) disproportionation whilst both styrene- and methyl acrylate-derived radicals terminate by combination. However, it is interesting that poly(methyl acrylate) appears to undergo chain extension more efficiently than polystyrene, indicating the possible significance of polymer chain conformations. Further studies are in progress to clarify this point.

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