

# SYNTHESIS AND REACTIONS OF POLYMERS WITH PHOTOACTIVE TERMINAL GROUPS—4. THE USE OF OXOCARBENIUM POLYMERIZATION FOR THE SYNTHESIS OF POLY( $\alpha$ -METHYLSTYRENE) WITH *N*-ACYL DIBENZ[b,f]AZEPINE TERMINAL UNITS\*

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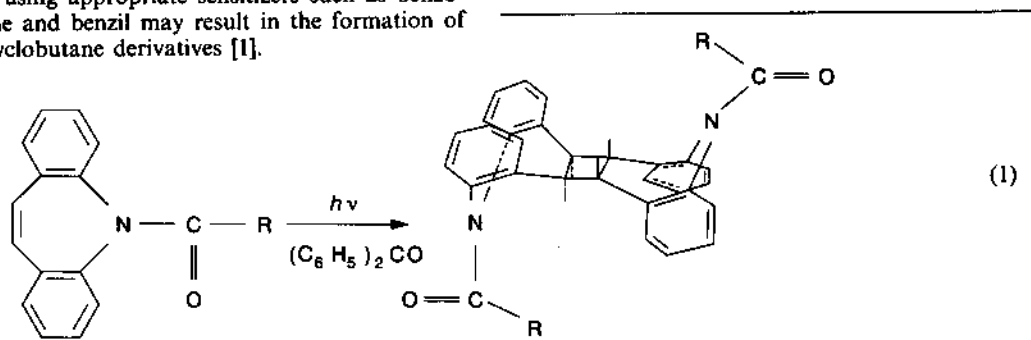
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**Abstract**—*N*-chlorocarbonyl dibenz[b,f]azepine in conjunction with  $\text{AgSbF}_6$  initiated the cationic polymerization of  $\alpha$ -methylstyrene in methylene chloride. Polymer samples obtained this way contained terminal dibenzazepine units. Chain extension occurred upon irradiating these polymers with u.v. in benzene solution containing benzophenone or benzil, via cyclobutane formation.

## INTRODUCTION

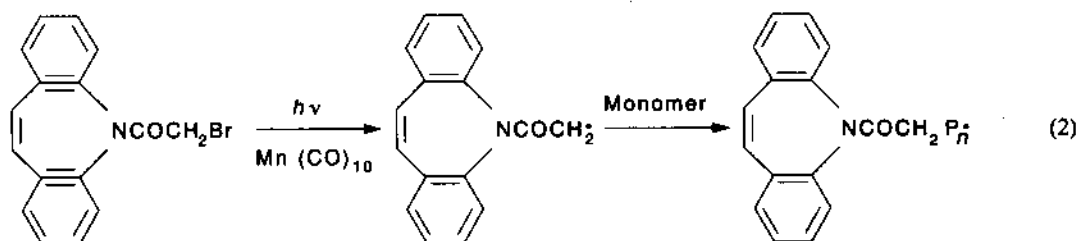
It has been shown that triplet sensitization of *N*-acyl derivatives of the dibenz[b,f]azepine ring system using appropriate sensitizers such as benzophenone and benzil may result in the formation of their cyclobutane derivatives [1].

An additional method of obtaining terminally functionalized polymers is based on the use of the azo initiator, *N*-[4,4'-azo-bis-(4-cyanopentanoyl)]-bis-dibenz[b,f] (ADBA) [3]. The azo compound is a

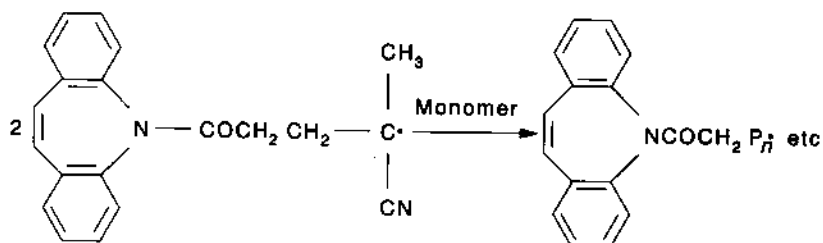
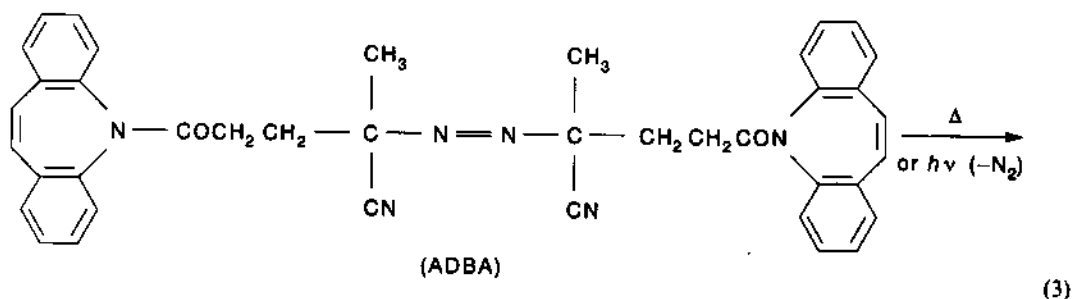


This type of reaction may be used for controlled chain extension or block copolymer formation when structurally related dibenzazepine derivatives are attached to polymer chains as terminal units. Such incorporation of specific groups at the end of polymer chains may be realized in several ways. The photolysis of manganese carbonyl in conjunction with *N*-bromo-acetyldibenz[b,f]azepine affords a highly convenient photochemical initiating system for free radical polymerizations yielding chain-ended functionalized polymers as shown below [2].

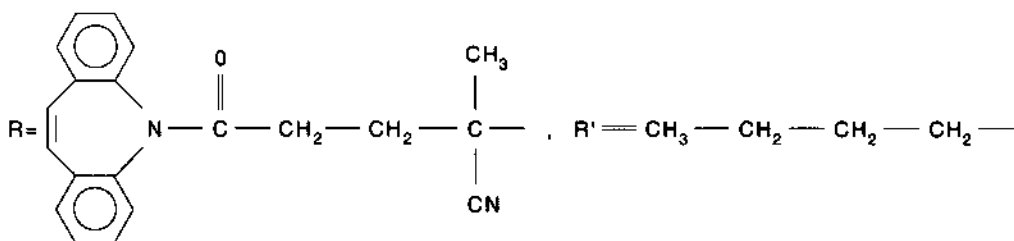
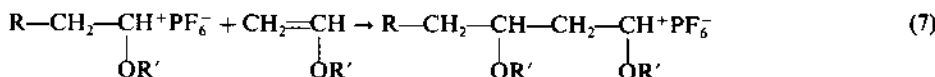
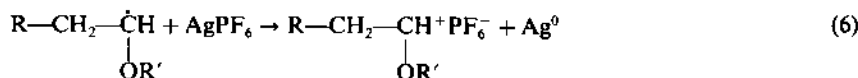
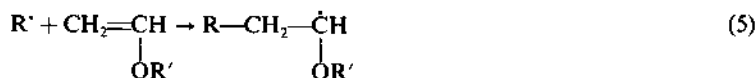
useful initiator for thermally and photochemically induced free radical polymerizations, yielding polymeric products having dibenzazepine end-groups. Whether or not the product polymer possesses one or two photochemically active end-groups depends on the ratio of disproportionation and combination in the polymerization of the particular monomer. In both cases, photosensitized chain extension may be accomplished according to reaction (1) with R representing a preformed polymer chain.



\*For Part 3 of this series, see *Eur. Polym. J.* 23, 737 (1987).

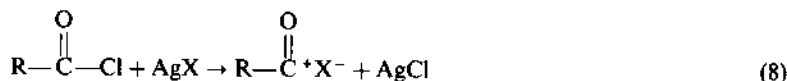


In other work [4], ADBA was used as a free radical source in conjunction with an iodonium salt or a silver salt in the promoted cationic polymerization of *n*-butyl vinyl ether. Since the azo initiator possesses dibenzazepine groups, this procedure made it possible to synthesize poly(*n*-butyl vinyl ether) having the appropriate functionality for subsequent photochemically induced chain extension.

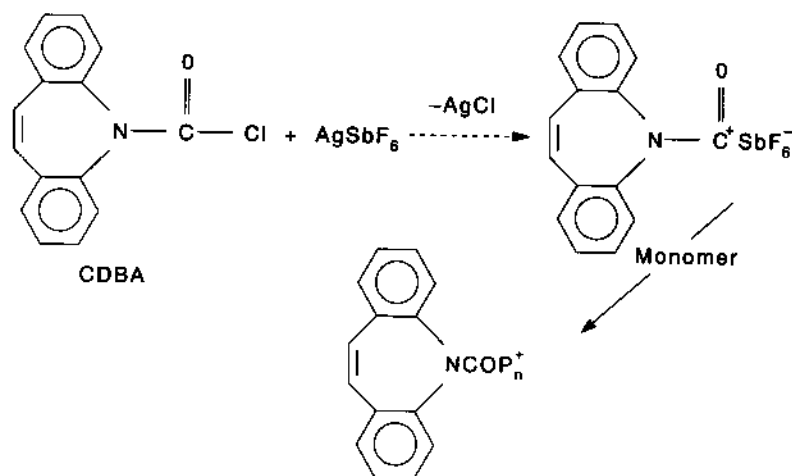


Alternatively, terminally monofunctionalized and terminally mono- and bifunctionalized polymers may be synthesized by chain transfer or via anionically prepared model prepolymers, respectively [2, 5].

It has been shown [6, 7] that oxocarbenium ions with low nucleophilic counterions can easily be prepared by reacting an acid chloride with a stoichiometric amount of a corresponding silver salt. Initiation will then ensue provided that cationically polymerizable monomers are present.



*N*-Chlorocarbonyl dibenz[*b,f*]azepine, referred to as CDDBA, is an organic acid halide which reacts with silver salts in the same manner to yield initiating cations; the resulting polymeric product carries the photochemically active *N*-acyldibenzazepine moiety attached to the ends of polymer chains.



The present paper presents results which support the initiation mechanism proposed and demonstrate the feasibility and scope of chain extension via terminal dibenzazepine units.

## EXPERIMENTAL PROCEDURES

### Materials

Iminostilbene (dibenzazepine) (Fluka) was purified by column chromatography on neutral alumina with an eluting mixture of methylene chloride-cyclohexane (1:1). Benzophenone and benzil were recrystallized from methanol. All solvents were purified by conventional drying and distillation procedures.  $\alpha$ -Methylstyrene ( $\alpha$ -MeSt) was purified by washing with 10% (w/v) aqueous NaOH and water to remove stabilizer, and then drying over  $\text{CaCl}_2$ . It was then fractionally distilled over calcium hydride. Phosgene (Fluka) was used as received.

CDBA was obtained by the reaction of iminostilbene with phosgene. Iminostilbene (19.3 g) was dissolved in hot toluene (100 ml). The solution was cooled to room temperature and a solution of phosgene in toluene (12.5%, w/w) (160 g) was added. The mixture was maintained at reflux for 5 hr and, after addition of a few drops of methanol, evaporated to dryness at reduced pressure. Recrystallization of the residual solid from benzene with addition of petroleum ether yielded colourless crystals m.p. 155°.

### Polymerization procedures

Polymerizations were carried out under dry  $\text{N}_2$ . Appropriate stock solutions of  $\text{AgSbF}_6$  and CDBA in  $\text{CH}_2\text{Cl}_2$  were prepared. The polymerizations were initiated by mixing the two solutions and a given amount of monomer, by means of a syringe, in a reaction vessel sealed under  $\text{N}_2$ . Upon mixing at the defined reaction temperature, the precipitation of  $\text{AgCl}$  was quickly completed. After a given time of reaction, the polymerization was terminated by addition of methanol. The polymer was filtered through Sartorius membrane filter to remove  $\text{AgCl}$ , and precipitated in methanol. All polymers were then reprecipitated from  $\text{CH}_2\text{Cl}_2$  into methanol several times before use in the chain extension experiments.

### Photosensitized chain extension experiments

Appropriate solutions of purified polymers and sensitizers in benzene contained in 10 mm i.d. pyrex glass tubes were degassed in the usual manner before irradiation in a 450 W Annular Photoreactor (Applied Photophysics) emitting nominally at 350 nm. After irradiation, the tubes were opened and polymers recovered by precipitation into methanol.

### Molecular weight measurements

GPC chromatograms were obtained using a Knauer M64 instrument with tetrahydrofuran as eluent and a flow rate of  $1 \text{ ml min}^{-1}$ . Molecular weights were calculated by reference to polystyrene standards.

## RESULTS AND DISCUSSION

Typical data for the polymerization of  $\alpha$ -MeSt initiated by dibenzazepine oxocarbenium initiator are given in Table 1, which shows that the cationic polymerization of  $\alpha$ -MeSt can be initiated readily by the interaction of CDBA with  $\text{AgSbF}_6$ .

Samples of poly( $\alpha$ -methylstyrene) (PMeSt) obtained by initiation with dibenzazepine oxocarbenium ions were subjected to benzophenone or benzil photosensitized chain extension as described previously for related polymers, and gave evidence for the ability of dibenzazepine chain-ends to participate in cycloaddition [equation (1),  $\text{R} = \text{PMeSt}$ ]. Typical results are given in Table 2; it is clear that the average molecular weights were increased depending on the experimental conditions. The chain extension was also indicated by GPC measurements, as can be seen from Fig. 1. The chromatogram obtained with the polymer irradiated by u.v. is shifted to the higher molecular weight range with respect to the chromatogram of the unirradiated polymer.

It should be noted that chain extension was accomplished in a similar way in the case of polymers produced by free radical mechanism [2, 3]. In these cases, the observed increase in average molecular

Table 1. Polymerization<sup>a</sup> of  $\alpha$ -MeSt by the dibenzazepine oxocarbenium initiator in  $\text{CH}_2\text{Cl}_2$

Temperature (°C)	Time (min)	Conversion (%)	$\bar{M}_n^b$ (g/mol)	$\bar{M}_w/\bar{M}_n^b$
-10	30	3.4	—	—
0	30	34.0	—	—
+10	15	25.2	1300	1.6
+10	30	46.2	1460	1.5
+10	45	48.2	1450	1.5
+10	90	60	1600	1.5

<sup>a</sup>[CDBA] =  $5 \times 10^{-3}$  mol/l, [AgSbF<sub>6</sub>] =  $5 \times 10^{-3}$  mol/l, [ $\alpha$ -MeSt] = 4.1 mol/l.

<sup>b</sup>Determined by GPC.

Table 2. Photosensitized chain extension of PMeSt with dibenzazepine terminal groups. Solvent: benzene, [Sensitizer] = 0.1 mol/l

[PMeSt] (g/l)	Sensitizer	Photolysis time (min)	$\bar{M}_n$ (g/mol)		Increase in $\bar{M}_n$ (%)
			Before photolysis	After	
100	Benzophenone	120	1100	1500	36
100	Benzophenone	120	1600	2050	28
100	Benzophenone	240	1600	2200	37.5
100	Benzophenone	480	1600	2500	56
150	Benzil	480	1600	2100	31
150	Benzophenone	120	1600	2200	37.5

\*Determined by GPC.

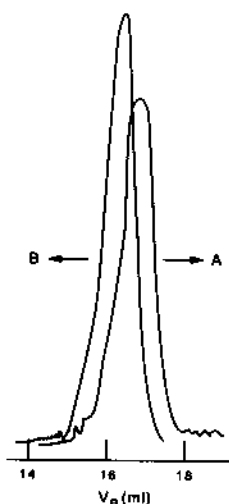


Fig. 1. GPC traces (solvent THF) of PMeSt synthesized by initiation with the dibenzazepine oxocarbenium ion. (A) Before, (B) after photolysis.

weight was much more pronounced, however, because each macromolecule contained one or two dibenzazepine groups depending on the termination mode of the particular monomer involved.

PMeSt chains synthesized by means of dibenzazepine oxocarbenium initiation can possess only one photoactive terminal group, provided initiation is exclusively by the addition mechanism. Macromolecules generated by hydride transfer initiation and after chain transfer are expected to possess no dibenzazepine groups. That the fraction of macromolecules having the desired end-groups was quite high, however, became evident from the chain extension experiments.

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