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# Divinylbenzophenone and Poly(divinylbenzophenone): On the Synthesis of Rigid Polymeric Photosensitizers

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ABSTRACT: Polymers from the monomer *p*-divinylbenzophenone have been synthesized as highly rigid macromolecular sensitizers for triplet energy transfer. Poly(divinylbenzophenone) and copolymers with methyl methacrylate, acrylonitrile, and styrene–divinylbenzene as energy-transfer donors were compared with free benzophenone under similar reaction conditions. As photosensitizers all poly(divinylbenzophenone) polymers have advantages over free benzophenone—among these are the ease by which they are separated from reaction mixtures in which they are used and the protection received by the aromatic carbonyl group from the rigid matrix.

During the past 10 years our research group has been developing polymer-based reagents for use as sensitizers in photochemical reactions.[1] A sensitizer is a special kind of catalyst, its role being to absorb radiation and to transfer the energy which it derives from that process to another molecule which then undergoes a chemical change.

Usually this process is carried out in solution; however, there are obvious advantages in carrying out sensitized reactions heterogeneously, those advantages being similar to those of heterogeneous catalysis.

Our group was the first to develop a convenient and useful polymer-based[2] photosensitizer—polymer-based rose bengal, a sensitizer for the formation of singlet oxygen—reported some 7 years ago.[3]

Recent work in our laboratories[1] has concentrated on the synthesis and development of triplet-state energy-transfer donors, or sensitizers.[4] These are photosensitizers which specifically produce excited triplet states of the compounds which accept the energy from the sensitizer. Some of the many applications of these sensitizers include their use in dimerization reactions, in isomerizations and, in certain instances, in polymerization reactions.

The most general of triplet sensitizers are those containing aromatic carbonyl groups, particularly the aryl ketones, benzophenone, and acetophenone. Though a major early problem—at least with polystyrene-based aromatic carbonyl functionalities—was production of free radicals from the sensitizer either by hydrogen-atom abstraction from the backbone or by decarboxylation, thus cross-linking and degrading the polymer,[4] this has been nicely circumvented by the synthesis and development of aryl ketone–fluorocarbon polymers such as poly[(trifluorovinyl)benzophenone].[5]

In this paper we report on the synthesis, use, and development of a new monomer—*p*-divinylbenzophenone—and on the construction of highly rigid polymer structures as in poly(*p*-divinylbenzophenone) and certain of its copolymers, which tend to render hydrogen abstraction from the polymer backbone less likely.[6–9] The benzophenone functionality of these rigid polymers is more inert toward photochemical degradation than in either poly(vinylbenzophenone),[10] prepared previously as a photosensitizer, or the polystyrene-based benzophenones.[4]

## Results

*p*-Divinylbenzophenone was prepared by the sequence of reactions described in Scheme I. The synthesis was not routine in that mono- and polybromination occurred to produce contaminating products in the *N*-bromosuccinimide reaction, though purification procedures have been developed to alleviate this difficulty. The preparation of the bisphosphonium salt was facilitated by carrying out its formation in benzene, where the phosphonium salts formed an oil rather than a precipitate at higher temperatures.

Care must be taken with the synthesis since—at each step—a highly photoreactive species is likely. In particular, we carried out all manipulations with both the impure and pure monomer in the dark, for photopolymerization is an obvious problem and occurs rapidly even with room light.

Poly(divinylbenzophenone) (DVBP) and copolymers with methyl methacrylate, acrylonitrile, and styrene–divinylbenzene were synthesized by radical polymerization, using benzoyl peroxide as the initiator. A stryene copolymer was prepared by suspension polymerization. All the polymers, except DVBP and the copolymer with acrylonitrile, swelled in benzene. The composition of the polymers studied is given in Table I.

Except for poly(divinylbenzophenone) none of the copolymers with divinylbenzophenone shows any residual vinyl groups in the infrared spectra. This is conceivable considering the higher reactivity of the vinyl groups in divinylbenzophenone compared to that in styrene. Because the mole percent of DVBP in the copolymer is 3–4 times that in the monomer feed, it may be assumed that the benzophenone content of the copolymers is a direct measure of cross-link density. In the case of homopolymer poly(divinylbenzophenone) about 6% of the unreacted vinyl groups remained (IR absorption at 990 $cm^{-1}$).

The swelling characteristics of the polymers were measured in toluene in terms of the solvent retention capacity of the polymer.[11] As might be expected, the homopolymer is so highly cross-linked that there is little swelling capacity. PAN–DVBP does not swell because poly(acrylonitrile) is not soluble in nonpolar solvents.

**Photochemical Experiments.** Benzophenone undergoes one major photodegradative process with hydrocarbon polymers,[12] viz., photochemical hydrogen abstraction. The triplet-state reaction is of high quantum efficiency in model systems and is of similarly high efficiency with benzophenone residues found in polymeric matrices. Hydrogen abstraction by benzophenone triplets leads to free-radical coupling products. Pinacols are produced this way in the model systems if the hydrogen donor is an alcohol. If the hydrogen donor system is a hydrocarbon, some cross-coupling products are also observed.[13] As the reaction leads first to free radicals, which eventually lead to coupled products, this is the route to polymer cross-linking when benzophenone is used as a cross-linking agent.

It was reasoned that by immobilizing the benzophenone moiety in a rigid polymeric matrix it would have fewer degrees of freedom and the movement of the benzophenone triplet would be decreased. The only photochemical hydrogen abstractions which could take place by this triplet would be those which were intermolecular or intramolecular reactions in which the hydrogens of the

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### Scheme I

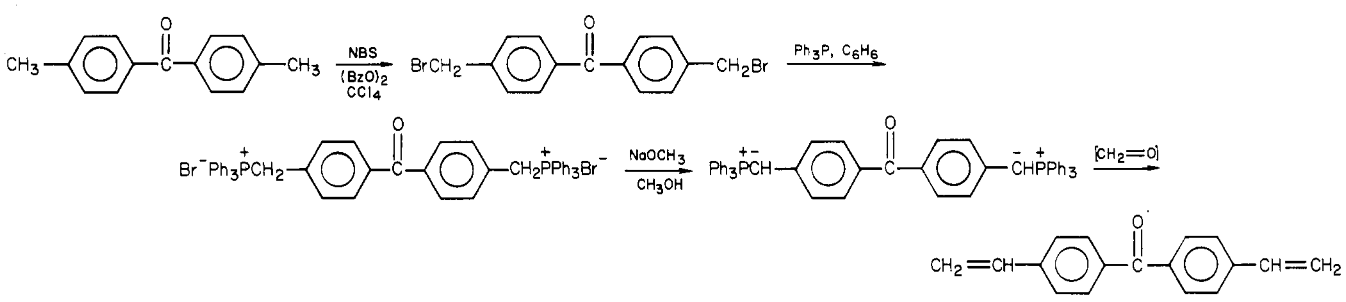


Table I
Characteristics of the Divinylbenzophenone Polymers

| monomers | symbol used for polymer | benzophenone content, % | toluene content of the swelled gel, mL/g | percentage unsaturation, % |
|---|---|---|---|---|
| divinylbenzophenone | PDVB | 100 | 1.12 | 6 |
| divinylbenzophenone, methyl methacrylate | PMMA-DVBP | 41.86 | 8.21 | |
| divinylbenzophenone, styrene | PS-DVBP | 31.03 | 3.03 | |
| divinylbenzophenone, styrene, divinylbenzene | PS-DVB-DVBP | 28.60 | 5.04 | |
| divinylbenzophenone, acrylonitrile | PAN-DVBP | 43.90 | 1.82 | |
| divinylbenzene, styrene | PS-DVB | | 14.06 | 4.5 |
| divinylbenzene, methyl methacrylate | PMMA-DVB | | 14.28 | |

polymer backbone were advantageously placed in direct proximity to the excited state.

The photostability of the benzophenone moiety in the rigid polymer matrices of divinylbenzophenone and its copolymers was compared to that of free benzophenone in model reactions by two different procedures. In one set of experiments specific divinylbenzophenone copolymers (swelled in benzene) were irradiated side by side with cross-linked copolymers, with divinylbenzene as the cross-linking agent (containing no polymer-bound benzophenone) but containing an equivalent amount of free benzophenone added to the swelled polymer in benzene.

From the results (Figure 1) it can be seen that benzophenone loss is much less when it is affixed in a polymer matrix compared to unbound benzophenone. Of particular interest is the fact that PS–DVB–DVBP and PMMA–DVBP appear to be photostable relative to PS–DVBP + PS–DVB + BP or PMMA–DVB + BP. The latter control experiments likely eliminate from consideration absorption and reflection effects of the macromolecules and suggest the benzophenone residues are protected by their molecular environment. It also appears from the nature of the curves that some fraction of BP attached to the polymer was more vulnerable than were other benzophenone residues to photochemical reaction. This suggests the benzophenone moieties in the polymer are not equivalent and that some are held in a more rigid environment than others because of the random nature of the copolymerization and cross-linking. The PMMA–DVBP matrix showed the most protection possibly because of the fewer benzylic hydrogens in the polymer chains.

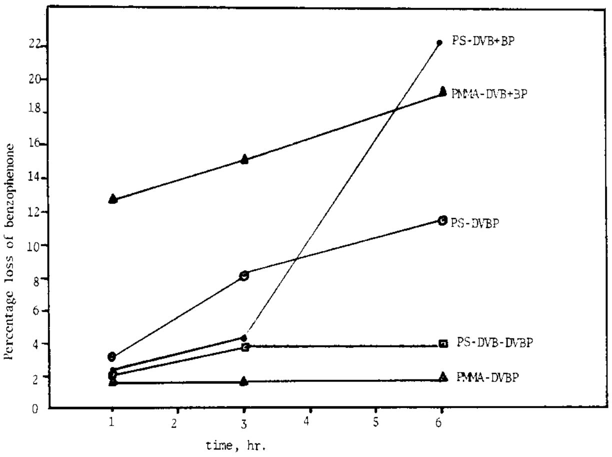


**Figure 1.** Hydrogen-abstraction studies. Plot of benzophenone loss with period of irradiation for different DVBP copolymers and mixtures of free benzophenone and poly(styrene-*co*-divinylbenzene) (PS–DVB) and poly(methyl methacrylate-*co*-divinylbenzene) (PMMA–DVB) copolymers (swelling solvent, benzene).

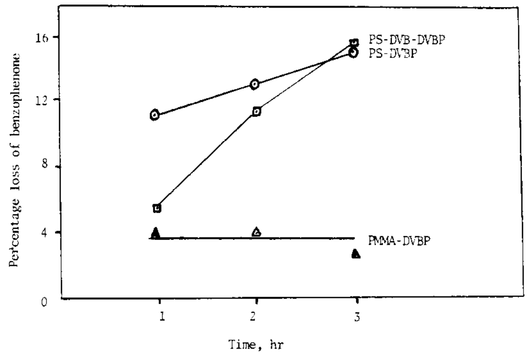


**Figure 2.** Loss of benzophenone vs. time during the reaction of DVBP copolymer with *sec*-butyl alcohol (swelling solvent, 10% by volume of *sec*-butyl alcohol in benzene).

In a second set of experiments the polymeric benzophenones and free benzophenone were irradiated in the presence of *sec*-butyl alcohol. Photoreduction of an excited triplet state by an alcohol is a reaction of near unit quantum yield in photo-pinacol formation in the case of free benzophenone[14] in an excess of the alcohol, and the comparison experiment gives the relative efficiency of hydrogen abstraction for the highly rigid polymer. While in the case of free benzophenone all the benzophenone was lost in 1 h of irradiation in *sec*-butyl alcohol, the polymer-bound benzophenone loss was much slower (Figure 2). Again in the case of PMMA copolymer the loss was very slow and almost reached a constant value. These benzophenones irradiated in *sec*-butyl alcohol remained photoreactive and still could be used to sensitize photochemical reactions, as will be shown later.

Table II
Photosensitized Reactions Using Divinylbenzophenone Copolymers

| | cycloaddition of benzo[*b*]thiophene and dichloroethylene[a] | | decomp of benzoyl peroxide[b] | |
|---|---|---|---|---|
| copolymer | rel yield, % | benzophenone lost, % | rel yield, % | benzophenone lost, % |
| PMMA-DVBP | 11.8 | 7.67 | 60.9 | 0.86 |
| PS-DVBP | 11.4 | 18.24 | 86.4 | 1.51 |
| PS-DVB-DVBP | 27.2 | 3.03 | 45.6 | 0 |
| benzophenone | 100 (80)[c] | 16.00 | 100 (21)[c,d] | 12.20 |
| no sensitizer | no products formed | | no reaction | |

[a] 350 nm, 19 h, solvent benzene. [b] 366 nm, 3 h, [$Bz_2O_2$] = 0.1 M. [c] Actual percent conversion. [d] Quantum yield = 0.27.

**Sensitized Photochemical Reactions.** Having demonstrated that the more rigid matrix demanded by *p,p′*-divinylbenzophenone polymers decreases the photodestruction of certain polymers synthesized from it, we next sought to establish what kind of photosensitizer resulted from polymers in which this monomer was contained. The sensitized photocycloaddition of benzo[*b*]thiophene and dichloroethylene[15] and the sensitized decomposition of benzoyl peroxide[16] ($Bz_2O_2$) were chosen to test the effectiveness of the polymers as photosensitizers. These reactions were chosen as models because they were easy to follow experimentally and because, in both cases, a polymeric photosensitizer would be of practical advantage. In the case of benzo[*b*]thiophene/dichloroethylene the photoproducts are difficult to separate from benzophenone. In the latter case, the sensitized reaction provides a source of radicals from benzoyl peroxide (1) at room temperature and (2) with long-wavelength radiation, both of which are impossible with benzoyl peroxide alone. In the former reaction the production of the 1:1 adducts could be determined by GC while in the latter case the loss of peroxide could be measured by IR analysis. The relative yield was determined as percentage conversion relative to the reaction with free benzophenone (assuming the conversion with free benzophenone as 100%). The amount of polymeric benzophenone used in each case was equivalent to the free benzophenone used for comparison. The polymeric sensitizers which could not be swollen well showed a lower efficiency as photosensitizers, so those results are not included in Table II.

It can be seen from Table II that the relative yields of $Bz_2O_2$ decomposition with the polymeric sensitizers are much higher than are those in the cycloaddition reactions. Differences in the extent of swelling in two different solvent media may also be responsible, to some extent, for this difference in efficiency.

In the cycloaddition reaction benzophenone loss from the polymeric sensitizer is much lower in the cases of PMMA–DVBP and PS–DVBP whereas with PS–DVBP, it is similar to that of the free benzophenone. On the other hand, in the case of $Bz_2O_2$ decomposition the loss of benzophenone in polymeric sensitizers is very much lowered compared to the loss of benzophenone when used as free benzophenone. This decreased loss of benzophenone, even less than in the hydrogen-abstraction study, is possibly due to competitive hydrogen-abstraction reaction with radicals from $Bz_2O_2$ decomposition. The resulting benzoic acid formation from benzoyl peroxide has been observed to be 2–4 times greater in cases of reactions sensitized by polymeric sensitizers than that observed in the free benzophenone sensitized decomposition. This possibly also indicates that all the hydrogens in the polymeric chain are not equivalent in their reaction with benzophenone excited states.

Table III
Photosensitized Decomposition of Benzoyl Peroxide by Polymeric Benzophenone Previously Irradiated in *sec*-Butyl Alcohol[a]

| polym type | rel yield, % | polym type | rel yield, % |
|---|---|---|---|
| PMMA-DVBP | 60.7 | PS-DVB-DVBP | 80.3 |
| PS-DVBP | 60.7 | benzophenone[b] | 100.0 |

[a] Irradiation time 3 h, solvent benzene. [b] An equivalent quantity of pure benzophenone was used for comparison.

Studies with PDVBP and PAN–DVBP showed that their efficiency as sensitizers is much lower than free benzophenone. These polymers were not swelled significantly in the solvent system used, and the energy-transfer process between the polymer-bound benzophenone and the reactant is likely, therefore, much less efficient, though there may be some differences which result from differential light scattering. This situation may be advantageous when there is a competition of the reaction to form product with an unwanted side reaction with benzophenone triplets. For example, in the case of the photochemical isomerization reaction of norbornadiene to quadricyclene, oxetane formation is much more prominent with free benzophenone than with PDVBP. Thus, though the yield of quadricyclene with PDVBP was about 60% of that obtained with equivalent free benzophenone, free benzophenone was completely inactive after 15 h of irradiation whereas PDVBP remained active even after 50 h.

Similar observations were made with polymers irradiated in alcohols. After 1 h of irradiation free benzophenone is completely destroyed in *sec*-butyl alcohol whereas the polymeric benzophenone, when separated after 3 h of irradiation with similar concentration of alcohols as in the case of free benzophenone, could be reused as a photosensitizer without much loss in reactivity (Table III). The high yield in the case of PS–DVB–DVBP in Table III is somewhat unexpected. Differences in the ability of the different polymer sensitizers to react with *sec*-butyl alcohol may reflect differing partition rates of the alcohol, which prefers the bulk solvent, into the polymer matrix.

We conclude from this work that poly(*p,p′*-divinylbenzophenone) and certain of its copolymers do contain benzophenone residues from photochemical degradation and reaction. As photosensitizers these polymers have many advantages over free benzophenone in solution—among these are the ease by which they are separated from reaction mixtures in which they are used and the protection received by the aromatic carbonyl group because it is held in the rigid polymer matrix. The efficiency of energy transfer is somewhat lower for the polymeric sensitizers than for free benzophenone because the quenching of the triplet-state benzophenone in the polymer matrix is less than the normal diffusion-controlled rate which is approximately $5 \times 10^9$ s$^{-1}$ for benzophenone in fluid solution.

## Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer 337 infrared spectrophotometer.

NMR spectra were recorded on a Varian CFT-20 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal reference. UV spectra were determined with a Beckman Acta MIV spectrophotometer. *p,p'*-Dimethylbenzophenone was used as obtained from Aldrich Chemical Co.

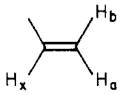
***p,p'*-Bis(bromomethyl)benzophenone.** A mixture of 19.5 g (92.8 mmol) of *p,p'*-dimethylbenzophenone, 36 g (202 mmol) of *N*-bromosuccinimide, and 0.6 g of benzoyl peroxide in 250 mL of carbon tetrachloride was heated under reflux for 3 h, after which the yellow color of the NBS had disappeared. The mixture was cooled in ice water and filtered with suction, the filtrate was washed thoroughly with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was crystallized from carbon tetrachloride, yielding 11.8 g of a product (mp 113–125 °C). The solid from the first filtration was washed thoroughly with water, taken up in benzene, and dried over $MgSO_4$. Evaporation of the solvent gave 8.79 g (mp 117–124 °C). NMR spectra of both mixtures showed that they had nearly the same composition consisting of approximately 80% of the desired bis(bromomethyl) compound, $\delta(CH_2Br)$ 4.52.

It appeared that the contaminants were *p*-(bromomethyl)-*p'*-methylbenzophenone and *p*-(dibromomethyl)-*p'*-(bromomethyl)benzophenone (instead of trying to purify the compound in this stage, which most likely results in large losses, purification was carried out on the final product).

***p,p'*-Bis(bromomethyl)benzophenone Bis(triphenylphosphonium) Salt.** The combined products of the above reaction (20.6 g, 56 mmol of pure bis(bromomethyl) equivalents) were boiled under reflux in 400 mL of dry benzene with 31.0 g (118 mmol) of triphenylphosphine for 4 h with vigorous stirring. Soon a thick oil separated. After standing overnight, the oil turned into a solid. Filtration gave 42.4 g of a slightly yellow phosphonium salt (85% yield). This material could be used for the subsequent reaction. An apparently more pure product was obtained by refluxing this phosphonium salt in acetone with an amount of triphenylphosphine. Thus 8.92 g of crude bisphosphonium salt, when heated under reflux and vigorous stirring with 5.0 g of triphenylphosphine for 4 h, gave 8.60 g of a slightly yellow material after filtration and drying.

***p,p'*-Divinylbenzophenone. A. With NaOMe and Gaseous Formaldehyde.** To a cooled solution (−10 °C) of 8.92 g (10 mmol) of the bisphosphonium salt in 40 mL of MeOH was added a solution of NaOMe in 20 mL of MeOH (460 mg of Na, 20 mmol) over a period of 10 min, giving a red solution of the bis ylide. Paraformaldehyde heated to 180–190 °C in an oil bath gave formaldehyde which was led into the ylide solution with a stream of nitrogen until the color of the solution had changed to light yellow. Upon evaporation of the solvent a large residue remained. This was taken up in ether and washed with water. Drying over $MgSO_4$ and evaporation gave an oily residue weighing 7.2 g.

Careful chromatography (in the dark!) of this mixture over silica gel with 3:2 dichloromethane–carbon tetrachloride as eluent gave 2.40 g of crude *p,p'*-divinylbenzophenone. Recrystallization from ether–pentane gave 1.59 g of product: mp 109–113 °C (68%); IR (KBr) $\nu(C{=}O)$ 1650, $\nu(C{=}C)$ 1640 $cm^{-1}$, characteristic $CH{=}CH_2$ absorption at 920 and 994 $cm^{-1}$; $UV_{max}$ (EtOH) 293 nm, $\log \epsilon = 4.46$ (tail to 400 nm); the NMR ($CDCl_3$) spectrum consisted of an ABX pattern strongly resembling that of styrene for the vinyl protons and an AB quartet for the four aromatic protons ($\delta$ 7.64).



| | | |
|---|---|---|
| $H_x$ | $\delta$ 6.81 as a quartet | $J_{ax} = 10$ Hz |
| $H_b$ | $\delta$ 5.82 as a quartet | $J_{bx} = 20$ Hz |
| $H_a$ | $\delta$ 5.39 as a quartet | $J_{ab} = 0.9$ Hz |

**B. With NaOH and Aqueous Formaldehyde Solution.** To a cooled solution of 8.60 g (9.64 mmol) of bisphosphonium salt in 75 mL of methanol was added 20 mL of 37% formaldehyde solution in water. NaOH solution (4 N) was added dropwise to the stirred solution, and, as each drop was added, a red color developed which quickly disappeared. The addition of NaOH was continued until no more red color could be observed on subsequent addition. During this process a solid precipitated which was filtered off, dissolved in carbon tetrachloride, and dried over $MgSO_4$. This carbon tetrachloride solution was chromatographed over silica gel. Addition of small amounts of chloroform to carbon tetrachloride was useful as an eluent mixture, giving 2.04 g of crude divinyl compound. The progress of the elution of the divinyl compound could even be followed visually. Recrystallization (ether–pentane) gave 1.72 g of divinyl compound, mp 110–114 °C (yield 76%). Very small amounts of compounds having a $CH_2Br$ or $CHBr_2$ function may be found in the final product following these procedures.

**Polymerization and Polymer Characterization.** The homopolymer of DVBP and all the copolymers except the copolymer with styrene were prepared in benzene solution in degassed sealed tubes. Benzoyl peroxide ($1 \times 10^{-3}$ M) was used as the free-radical source and polymerization was carried out at 80 °C up to 20–30% conversion. A typical composition for copolymerization contained 0.104 g of DVBP and 0.5 mL of the other comonomer (for PS–DVB–DVBP, 0.5 mL each of styrene and divinylbenzene) in 3 mL of benzene (6 mL for PS–DVB–DVBP).

The polymers were precipitated with methanol and filtered. The filtered insoluble polymers were stirred vigorously in an excess of benzene to make a dispersion of fine particles of swelled gel and precipitated again in an excess of methanol, with stirring, filtered, washed with methanol, and dried under vacuum.

The copolymer with styrene (PS–DVBP) was made by suspension polymerization. In a three-necked flask (100 mL), fitted with a mechanical stirrer, condenser, and $N_2$ inlet tube, 20 mL of water, 60 mg of sodium lauryl sulfate, and 5 mg of gelatin powder were added and the flask was flushed with $N_2$ for 30 min. The flask was then placed in a thermostated bath maintained at 80 °C, and a solution containing 150 mg of DVBP, 1 mL of styrene, 2 mL of *n*-heptane, and 3 mg of benzoyl peroxide was added, with stirring. The polymerization was allowed to continue for 5 h, and the precipitated powdery polymer was filtered and washed with hot water followed by washings with methanol and drying under vacuum. The powdery polymer was purified as before by dispersing in an excess of benzene and precipitating with an excess of methanol.

The percentage of benzophenone in the polymer was determined by IR from the ratio of the absorption at 1670 $cm^{-1}$ due to benzophenone and a characteristic peak for the other comonomer. Calibration curves obtained from a series of known mixtures of homopolymers of DVBP and the other monomer were used to determine the composition of unknown samples.

**Irradiation and Product Analysis.** All irradiations were done in sealed degassed tubes at 366 nm (except when stated otherwise). After the irradiation the polymers were precipitated with known amounts of *n*-hexane and the reaction product was analyzed from the supernatant solution. The precipitated polymer was then separated, washed with methanol, dried under vacuum, and analyzed for benzophenone loss. A 1:1 adduct of benzothiophene and dichloroethylene was determined by GC. The percentage decomposition of benzoyl peroxide was measured by IR.

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# Copolymerization of Ethyl Glycidate with Cyclic Ethers by Organometallic Initiators

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ABSTRACT: Ethyl glycidate (EG) was copolymerized with propylene oxide (PO), 1-butene oxide (BO), and oxetane by organoaluminum initiators to produce high molecular weight polyethers with pendant ester groups. The ternary initiator system $AlEt_3/H_2O/AcAc$ (1/0.3/0.5) gave the best results with PO and BO, yielding polymers of $\eta_{inh}$ 0.6–4.3 dL/g containing up to 4 mol % of EG units. EG was relatively unreactive in these copolymerizations; the concentration of EG in the copolymer was always significantly less than that in the feed, and increased EG feed concentrations depressed both the rate of polymerization and the product molecular weight. Oxetane copolymers containing ca. 1 mol % of EG units were obtained with $\eta_{inh}$ 0.7–1.0 dL/g, along with oligomeric products, using a similar initiator system. Conversion of these polyethers into novel ionomers was demonstrated: treatment of the ester with NaOH gave the polymeric sodium salt, which was further converted to the free acid by reaction with glacial acetic acid in dioxane.

## Introduction

The incorporation of ionic groups into organic polymers can produce remarkable effects on physical and mechanical properties.[1] Particularly successful has been the preparation of polyolefin ionomers containing pendant metal carboxylate groups. Despite the technical and commerical success of these materials, though, there remain unanswered significant questions concerning the solid-state morphologies of ion-containing polymers; ionic groups could be embedded in a nonpolar hydrocarbon matrix to aggregate, or "cluster", and, in fact, evidence for cluster formation has been obtained through infrared and X-ray techniques.[2,3]

But what if the polymer backbone (polymer "matrix") can interact more favorably with ("solvate") the ionic groups? What kinds of morphologies and physical properties will then be observed? One means of providing this kind of solvation is to incorporate into the polymer backbone heteroatoms (or "donor" atoms) which interact strongly with metal cations. In particular, one might expect the incorporation of oxygen atoms into the chain to accomplish this, by analogy to the solvation of metal cations by crown ethers. Ionization may then affect polymer properties in a manner quite different from that observed in olefin polymers. In order to investigate this possibility, we have undertaken the preparation of polyethers with pendant carboxylate groups and, in particular, we have focused on the preparation of homopolymers and copolymers of ethyl glycidate (EG).[4-9] Ethyl glycidate was previously shown to polymerize with an aluminum alkyl/water initiator system to a crystalline homopolymer.[10] The initiator system which was the basis of this paper was reported in detail in a separate communication.[11] Carboxyl-modified polyethers were also made by substitution reactions on polyethers, particularly on polymers and copolymers of epichlorohydrin.[12]

In recent papers, we have described the copolymerization of EG with trioxane[4-7] and tetrahydrofuran,[8,9] using cationic initiators. The preparation of low molecular weight EG homopolymer by cationic polymerization has also been reported.[8,9] In all of these experiments, EG was found to be a rather unreactive monomer, probably as a result of the electron-withdrawing inductive effect of the carboethoxy group. The adverse effect of the electron-withdrawing group of the epoxy ring and its effect in copolymerization have been reported in the unfavorable copolymerization of epichlorohydrin with ethylene oxide.[13] EG was incorporated into poly(oxymethylenes) (POM) via bulk, solution, or gas-phase techniques, and terpolymerization with trioxane and 1,3-dioxolane was also accomplished, but in all cases, the resulting polymers contained only low percentages of carboxylate groups. In copolymerization with THF, an interesting 1:2 EG–THF copolymer was formed under conditions precluding THF homopolymerization, indicating that homopropagation of EG is very slow under cationic conditions.[9]

In the present paper, we report the copolymerization of EG with several oxiranes and with oxetane, using organometallic initiators. Conversion of the resulting copolymers to the salt and acid forms is also described briefly.

## Experimental Section

**Materials.** Ethyl glycidate (EG) was prepared from ethyl acrylate by the method of Emmons and Pagano[14] and stored in vacuum-sealed ampules at room temperature in the dark. Before use, ethyl glycidate was dried overnight over freshly activated molecular sieves.

Other monomers were twice distilled from $CaH_2$ under dry nitrogen and used immediately: propylene oxide (PO) (bp 34 °C), 1-butene oxide (BO) (bp 63 °C), epichlorohydrin (ECH) (bp 116

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