noalkyl radicals have been studied by esr.[25] Other examples of formation of the α-aminoalkyl radical include the cyclization of ethylenic amines[26] and the functioning of triethylamine as a chain transfer agent when used as a solvent for a free radical polymerization.[27]

We propose as a possible mechanism for the thermal polymerization of DMAEM the formation of stable diradical and the stabilization of that diradical by an abstraction of the hydrogen on the carbon α to the nitrogen by the terminal carbon of the double bond. The resulting stabilized diradical could then extend by the usual mechanisms of free radical propagation (Scheme I) at both free radical positions.

The formation of the diradical is favorable because each radical is stabilized by its neighboring group. The radical on the carbon α to the carbonyl group is an allylic radical, and is further stabilized by the inductive effect of the two methyl groups. The radical on the carbon α to the nitrogen is stabilized through delocalization of its spin density by the adjacent nitrogen.

We have no evidence as to whether or not the diradical could cyclize to form a γ lactone. If cyclization did take place, even if it were favored, it would be expected to produce a relatively low yield of lactone when compared to the amount of DMAEM used by polymerization reactions. If the initial diradical intermediate were in the triplet state this cyclization would not be expected to occur.

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Polymeric Reagents. Preparation of Resins Containing Polyvinylperbenzoic Acid Units[1]

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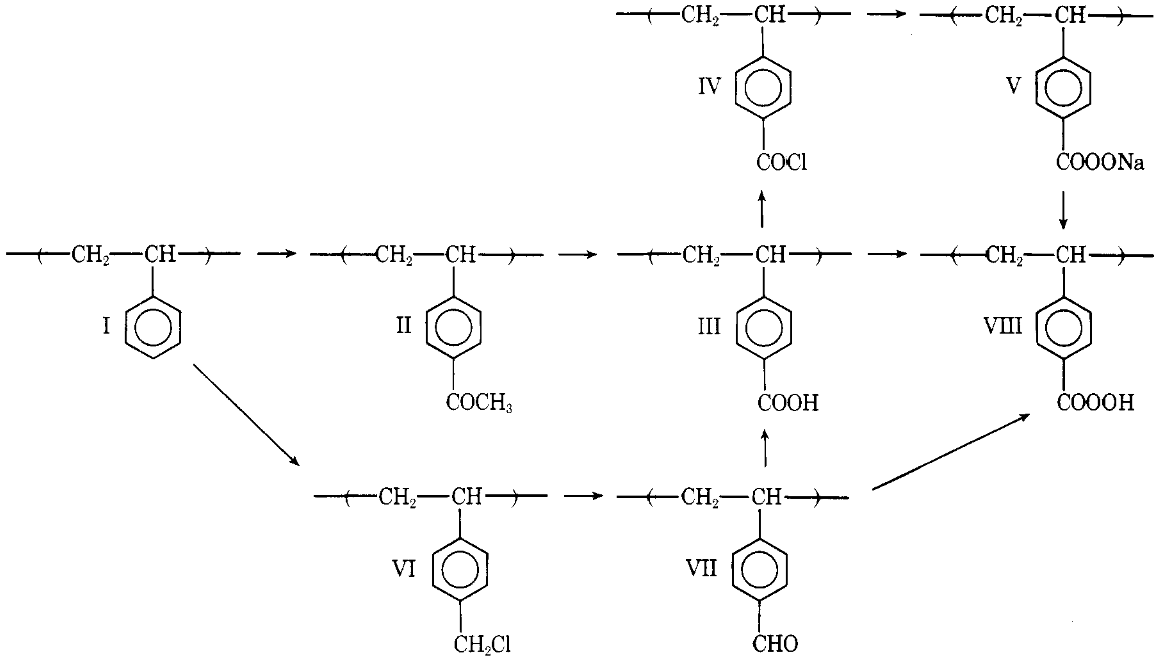
ABSTRACT: Several synthetic routes to bead polymers containing peracid functional groups have been explored. Thus, swellable or macroreticular styrene-divinylbenzene copolymers containing approximately 1 mequiv of perbenzoic acid functional group per gram were prepared from resins containing vinylbenzoic acid, vinylbenzoyl chloride, or vinylbenzaldehyde units. The polymeric peracids were stable and could be used and regenerated several times without degradation. The use of the polymers in a simple epoxidation reaction is described.

Following the success of the Merrifield approach to the synthesis of polypeptides,[2] insoluble polymeric supports have been used successfully in the synthesis of polynucleotides[3] and polysaccharides.[4] More recently much attention has been devoted to the use of polymers as chemical reagents; thus, polymeric anhydrides,[5] oxygen-transfer resins,[6,7] Wittig resins,[8] polymeric carbodiimides,[9] N-halogenated polymers,[10] and several other interesting reagents have been prepared. Other applications of polymers in organic synthesis include the use of polymers as temporary blocking groups for the selective synthesis of symmetrical bifunctional molecules,[11] as supports in the Dieckmann condensation of mixed esters,[12] as sensitizers in photochemical reactions,[13] and as catalysts.[14]

The main advantage of polymeric reagents over their monomeric counterparts is the ease of separation of the excess reagent and by-product from the desired product of the reaction. Other advantages and properties of polymeric reagents have been reviewed recently.[15]

Polymeric peroxides were prepared as early as 1964 by Helfferich and Luten;[6] their product was a copolymer containing sulfonic as well as carboxylic acid residues and could be used to prepare α-glycols from alkenes. However, the polymers were fragile and could only be used for a few oxidation–reduction cycles. Furthermore, their use was limited to reactions in aqueous solvents. In a more recent

Scheme I



report,[7] the preparation of a peracid on the methacrylic acid matrix of an ion exchange resin, Amberlite XE-89, is described.

In our approach, insoluble polymers containing vinylperbenzoic acid units were prepared by chemical modification of two types of styrene–divinylbenzene copolymers. One was a hydrophobic swellable copolymer containing 1 or 2% divinylbenzene[16] and the other was a rigid macroreticular resin. The peracid-containing copolymers prepared on the 1 or 2% cross-linked supports could be used at peak efficiency only after swelling of the polymer beads in solvents such as carbon tetrachloride, chloroform, dioxane, and tetrahydrofuran. The macroreticular peracids, on the other hand, could be used in almost any solvent. In all cases the peracids were found to be quite stable; they could be dried and stored in a refrigerator for long periods of time without appreciable loss of activity, and regenerated several times without degradation of the polymer matrix.

Results and Discussion

As can be seen in the reaction scheme below, three types of functionalized styrene–divinylbenzene copolymers were used as precursors of the peracid-containing copolymers. In the following discussion, Ⓟ-COOH (III) refers to a styrene-divinylbenzene copolymer (swellable or macroreticular) in which some vinylbenzoic acid units are present. Similarly, Ⓟ-COCl (IV) refers to a copolymer containing vinylbenzoyl chloride units, Ⓟ-CHO (VII) to a polymer containing vinylbenzaldehyde units, and Ⓟ-COOOH (VIII) to a polymer containing vinylperbenzoic acid units.

Varying results were obtained in the peroxidation reactions depending on the type of substrate, swellable or macroreticular, and on the functional group of the precursor. In general, reactions with the macroreticular resins were more sluggish than those carried out on swellable resins and more drastic reaction conditions[17] were required to achieve the same degree of conversion. This was probably due to the more difficult penetration and diffusion of solvents and reagents into the pores of the macroreticular resins. Higher reaction rates could be obtained when air was removed from the pores of the macroreticular resins by refluxing in the reaction solvent prior to the addition of the reagents.[18]

The procedure of Letsinger and Jerina[19] was used, with minor modifications, for the preparation of Ⓟ-COOH from the styrene–divinylbenzene copolymers. The resins obtained by this method contained from 0.9 to 1.6 mequiv of acid per gram.

Resins containing acid chloride functional groups Ⓟ-COCl (IV) were prepared in good yields from Ⓟ-COOH by reaction with thionyl chloride in dimethylformamide and benzene.

A third type of functionalized polymer containing vinylbenzaldehyde units, Ⓟ-CHO (VII), was prepared by dimethyl sulfoxide oxidation of chloromethylated styrene–divinylbenzene copolymers (VI) as described earlier.[4,20] Since a relatively high degree of functionalization could be obtained in the chloromethylation and subsequent oxidation steps, this procedure was used to prepare Ⓟ-COOH polymers containing up to 3.4 mequiv of acid per gram. Although these polymers may have some interest in other types of reactions they were not used extensively in this research as they seemed to contain a number of functional groups located in less accessible sites which could not be peroxidized satisfactorily.

Peroxidation of the Ⓟ-COOH resins (Scheme I) was accomplished by reaction with 70% hydrogen peroxide in the presence of a sulfonic acid such as methanesulfonic or *p*-toluenesulfonic acid. As can be seen in Table I, swelling of the polymer matrix was an important factor in the reaction of the 1% cross-linked resin. Thus, the extent of the peroxidation reaction was increased by more than 50% when the reaction medium was changed from methanesulfonic acid–hydrogen peroxide to *p*-toluenesulfonic acid–tetrahydrofuran–hydrogen peroxide. Accessibility of the reactive sites was not a problem with the macroreticular resins and almost quantitative yields were obtained in the peroxidation reactions.

The peroxidation of Ⓟ-COCl (IV) resins was studied only in the case of the swellable 1% cross-linked styrene–divinylbenzene polymers since the direct peroxidation reaction from acid to peracid produced excellent yields with the macroreticular resins.

Table I
Preparation of Copolymers Containing Polyperbenzoic Acid Units

Substrate[a]	Capacity, mequiv/g	Reaction conditions[b]	Ⓟ-COOOH, mequiv/g	Yield
III S	0.92	PTSA[c]	0.53	58
III S	0.92	PTSA–THF[c]	0.61	66
III S	0.92	MSA[c]	0.37	40
III S	0.92	MSA–THF[c]	0.39	42
III S	1.55	MSA[c]	1.04	67
III M	0.94	MSA[c]	0.91	97
III M	1.0	MSA[c]	0.96	96
IV S	1.36	Na_2O_2–H_2O–THF	0.92	68
IV S	1.18	Na_2O_2–H_2O–THF	0.73	62
IV S	1.18	Na_2O_2–H_2O_2–THF	1.03	87
VII S	1.02	CCl_4–EtOAc[d,e]	0.83	81
VII S	1.02	EtOAc[d,e]	0.57	56
VII S	1.02	CCl_4[d,e]	0.60	59
VII M	1.09	EtOAc[d,e]	0.52	48
VII M	1.09	CCl_4–EtOAc[d,f]	0.71	65

[a] S, swellable resin; M, macroreticular resin. [b] PTSA, *p*-toluenesulfonic acid; MSA, methanesulfonic acid; EtOAc, ethyl acetate. [c] 70% H_2O_2 added. [d] Reaction with O_2O_3 mixture. [e] Reaction time 4 hr. [f] Reaction time 6 hr.

As can be seen in Table I, best results were obtained when a slurry of Ⓟ-COCl swollen in tetrahydrofuran was added to a mixture of sodium peroxide and 70% hydrogen peroxide. No reaction occurred in the absence of the swelling agent, and other swelling agents nonmiscible with water were unsatisfactory. Here again, accessibility is a major factor in the reaction.

The third method of preparation of Ⓟ-COOOH shown in Scheme I makes use of a resin containing vinylbenzaldehyde units, Ⓟ-CHO (VII). Although this third approach is not useful for repetitive oxidation–reduction cycles since no simple regeneration of the aldehyde resin, after peroxidation and use of the resin, can be envisioned, it is nevertheless interesting due to its extreme simplicity and the fact that it requires little washing of the peracid prior to its use or its drying for storage.

Reaction of the vinylbenzaldehyde polymer VII with oxygen in the presence of ozone was carried out at room temperature on both the swellable and macroreticular resins (Table I). Best results with the swellable resins were obtained when the polymer was suspended in a 1:1 mixture of carbon tetrachloride and ethyl acetate, and lower yields were obtained when either of these solvents was used alone. Thus the reaction seemed to require at the same time the presence of a relatively polar solvent such as ethyl acetate which is inert toward ozone[21] and of a good swelling agent such as carbon tetrachloride. The reaction with the macroreticular resin was more sluggish and seemed to be diffusion controlled. The increase in yield shown in the last two lines of Table I is due to an increase in the reaction time.

An important factor which must be considered when a new polymeric reagent is prepared is the ease of regeneration of the spent reagent after reaction. Of the three preparative methods described above, only one (III → VIII) allows for a one-step regeneration, while another (IV → VIII) requires two steps since Ⓟ-COCl must be generated from Ⓟ-COOH. This additional step is a definite drawback even though a higher overall yield of swellable Ⓟ-COOOH (77 to 66%) is obtained *via* the acid chloride derivative, thus Ⓟ-COOH is probably the most useful precursor of the peracid Ⓟ-COOOH. The third preparative method (VII → VIII) does not allow for regeneration through Ⓟ-CHO. The spent reagent can, however, be regenerated by the direct peroxidation route (III → VIII) as shown in Scheme I.

A study of the effect of repeated use of the polymers in oxidation reduction cycles (III → VIII → III) was undertaken to determine whether repeated use would affect the oxidation capacity or the physical form of the resin.

Both the swellable and the macroreticular resins were submitted to several oxidation–reduction cycles. The oxidation capacity and the particle size of the resins were monitored during the tests. While the swellable resin did not show any apparent change in physical form after 12 such cycles, the macroreticular resin was found to be much more fragile and the proportion of fine particles increased with each oxidation–reduction cycle. The repeated handling of the resin was responsible for the break up of the large resin beads. This problem was alleviated by packing a small column with the macroreticular resin and passing the reagents through the resin bed, applying gentle suction whenever necessary. The oxidation capacity of the macroreticular resin was monitored after each oxidation step by withdrawing some resin through the top of the column. The 1% cross-linked styrene–divinylbenzene could not be used efficiently when packed in a column due to mechanical problems caused by the very large changes in volume which occur as a result of swelling and unswelling in the various steps.

Although the swellable resin was easier to prepare and to handle than the macroreticular resin, the latter was found to give more consistent results in repetitive oxidation–reduction cycles. Thus, while the oxidation capacity of the macroreticular resin showed variations of less than 10% in ten successive cycles, the oxidation capacity of the swellable resin varied by as much as 25% in some of the ten cycles. These variations did not, however, show a trend toward a permanent lowering of the resin capacities with repeated use as the original oxidation capacities could be equaled or even bettered after several oxidation–reduction cycles.

Finally, the use of the polymeric reagent in simple epoxidation reactions was studied. As can be seen in Table II, good yields of epoxide were obtained with the 1% cross-linked resins when the solvent chosen for the reaction was a good swelling agent. A drastic lowering of the yield of the reaction was observed when a poorer swelling agent such as acetone was used. In general the molar ratio of peracid to alkene was of 1.5 to 1 and although the consumption of peracid was higher than theoretical, the resin usually still contained a small percentage of peracid after the reaction mixture was filtered to separate the epoxide from the spent reagent. The reactions with the macroreticular resins could be carried out in various types of solvents and were probably diffusion controlled as an increase in yield was observed when the contact time between the resin and the alkene solution was increased. The epoxidation reaction was monitored by gas chromatography and was accompanied by little or no soluble side-product formation.

The main advantage of immobilized peracids over their soluble counterparts is the ease of separation of the oxidized product from excess reagent and acid by-product. Other advantages include the possible selectivity of the bulky reagent in reactions with substrates containing several reactive sites, and the quantitative recovery and easy regeneration of the spent reagent.

Experimental Section

General. The styrene–divinylbenzene copolymers used were Bio-beads SX1, SX2, and SM2 purchased from Bio-Rad Laboratories, Richmond, Calif. Samples of 70% hydrogen peroxide were

Table II
Epoxidation of Cyclohexene with ⓟ-COOOH[a]

Type of resin	Capacity, mequiv/g	Solvent	Time, hr	Yield, % epoxide
Swellable	1.04	CH_2Cl_2	4	86
Swellable	1.0	Dioxane	4	84
Swellable	1.0	Acetone	4	27
Macroreticular	0.96	Dioxane	4	54
Macroreticular	0.96	Dioxane	6	68
Macroreticular	0.91	Acetone	6	65

[a] Reaction of 1.5 equiv of ⓟ-COOOH with 1 equiv of cyclohexene at 40°.

gifts of Du Pont of Canada and Canadian Industries Limited. Solvents were dried over calcium hydride and distilled when required. Acetyl chloride and cyclohexene were purified by distillation. Infrared spectra were measured on a Beckman IR 20 infrared spectrophotometer on potassium bromide pellets. Elemental analyses were carried out by Galbraith Laboratories. Some chlorine analyses were performed in this laboratory using the modified Volhard procedure.

Preparation of ⓟ-COOH (III). The swellable polymers were prepared as described by Letsinger and Jerina.[19] In most cases, resins containing from 1 to 1.6 mequiv of acid per gram were obtained.

The preparation of III on the macroreticular resin was as follows. Resin I (5 g), dried *in vacuo* at 80°, was placed in a round-bottom flask containing 20 ml of carbon disulfide. The mixture was refluxed briefly then cooled to room temperature. After addition of 5 g of aluminium chloride the mixture was stirred for 1 hr, then 3 ml of acetyl chloride was added rapidly and with stirring. An exothermic reaction occurred and the reaction mixture became thicker and darker. After addition of 10 ml of carbon disulfide, the mixture was refluxed for 2 hr then stirred overnight at room temperature. The reaction mixture was poured into 200 ml of ice-water. The polymer was then collected and washed several times with a mixture of concentrated HCl–water–dioxane (1:7:8), then with water, dioxane, and finally methanol.

An infrared spectrum showed two absorbtion bands attributable to carbonyl groups at 5.94 and 5.96 μ.

Acetylated resin II (3 g) was suspended in 10 ml of dioxane; after refluxing for a few minutes, the suspension was cooled in an ice-water bath. A cold solution of hypobromite prepared by adding slowly 3 ml of bromine to a solution of 10 g of KOH in 15 ml of water and 65 ml of dioxane was then added dropwise to the stirred polymer suspension while its temperature was kept to below 10°. After 2 hr of reaction, the cooling bath was removed and the mixture was left overnight at room temperature. The polymer was collected, rinsed with water, and washed repeatedly with a 1:1 mixture of dioxane–3 *N* HCl, then with water, dioxane, and finally methanol. An infrared spectrum of the resin taken after drying in a vacuum oven at 70° showed carboxyl absorptions at 5.9 and 5.79 μ for the hydrogen bonded and free carboxyl group, respectively. A weighed sample of the macroreticular resin was titrated by adding excess sodium hydroxide (solution in 50% alcohol) and back titrating with standard acid; the resin was found to contain 1 mequiv of acid per gram.

Titrations of the swellable resins were effected as described previously[4] by treating a weighed sample of the resin with an excess of butyllithium in benzene and back titrating with standard acid.

In an alternate procedure, ⓟ-COOH was prepared from ⓟ-CHO as follows. A suspension of 1 g of the macroreticular ⓟ-CHO resin (1.32 mequiv/g) in 20 ml of glacial acetic acid saturated with sodium dichromate was treated with 0.3 ml of concentrated sulfuric acid and heated at 70° for 4 days. The reaction mixture was cooled and the polymer collected. After washing with hot acetic acid, hot water, acetone, and methanol, the resin was titrated and found to contain 1.15 mequiv of acid per gram (87% yield).

Preparation of ⓟ-COCl (IV). This reaction was carried out only on the swellable resin as follows. To a suspension of 60 g of ⓟ-COOH (1.32 mequiv/g) in 600 ml of a mixture of benzene and dimethyl formamide (5:1) was added slowly 25 ml of thionyl chloride. The reaction mixture was stirred and heated to 75° for 3 hr. After cooling, the resin was collected and washed repeatedly with dimethyl formamide, benzene, dry dioxane, and finally methylene chloride. After drying under vacuum the chlorine content of the resin was determined by the modified Volhard procedure and found to be of 1.18 mequiv/g indicating a yield of 89%.

Preparation of ⓟ-CHO (VII). The swellable 1% divinylbenzene–styrene resin was chloromethylated as described by Pepper, *et al.*[22] The chloromethylated resins contained from 1 to 4.2 mequiv of functional groups as determined by chlorine analysis. Chloromethylation of the macroreticular resin was performed as follows. A suspension of 5 g of resin in 20 ml of chloromethyl methyl ether was refluxed for 1 hr. The mixture was cooled in an ice–water bath and a solution of 1 ml of $SnCl_4$ in 9 ml of chloromethyl methyl ether was added slowly with stirring. Once the addition was complete, the ice–water bath was removed and the mixture was stirred for an additional 2 hr at room temperature. The resin was then collected and washed three times on filter with each of the following solutions allowing about 30 min of contact between the resin and the solutions before filtration: concentrated HCl–water–dioxane (1:1:8), water–dioxane (3:7); water; dioxane; methanol. The resin was then dried under reduced pressure. Chlorine analyses indicated that it contained 1.3 mequiv/g.

The same reaction carried out at reflux for 3 hr gave a product containing 1.86 mequiv of chlorine per gram.

A 3-g sample of the chloromethylated macroreticular resin (1.3 mequiv/g) was suspended in 50 ml of dimethyl sulfoxide containing 5 g of sodium bicarbonate. The reaction mixture was heated at 155° for 12 hr. After cooling, the resin was collected, washed twice with dimethyl sulfoxide, then rinsed with hot water, acetone, and finally methanol.

After drying under vacuum, the resin was found to contain 0.91 mequiv of functional group[4] per gram (70% yield).

Preparation of ⓟ-COOOH. (1) From ⓟ-COOH. One gram of swellable ⓟ-COOH containing 0.92 mequiv of acid per gram was suspended in 8 ml of tetrahydrofuran containing 3 g of *p*-toluenesulfonic acid. After stirring for 15 min at room temperature 3 ml of 70% hydrogen peroxide were added while the reaction mixture was kept at 20°. After 2 hr of reaction, the resin was collected and rinsed with cold (−20°) tetrahydrofuran and then cold (−20°) methanol. An iodometric titration of the resin showed that it contained 0.61 mequiv of peracid per gram (66% yield).

To a mixture of 1 g of macroreticular ⓟ-COOH (1 mequiv/g) in 4 ml of methanesulfonic acid was added slowly and with stirring 6 ml of 70% hydrogen peroxide while the mixture was kept at 20°. After 6 hr of reaction the mixture was washed with cold methanol (−20°) until the effluent was free from any peroxide. An iodometric titration showed that the product contained 0.96 mequiv of peracid per gram (96% yield).

(2) From ⓟ-COCl. To a stirred mixture of 2 g of sodium peroxide, 0.4 g of magnesium sulfate, 15 ml of 70% hydrogen peroxide, and 10 ml of distilled water was added slowly a slurry of 2 g of ⓟ-COCl (1.18 mequiv/g) in 25 ml of tetrahydrofuran. The mixture was stirred for 30 min at room temperature then filtered. After several washings with cold water, cold tetrahydrofuran–1 *N* HCl (4:1), water–tetrahydrofuran, and cold methanol the resin was dried under vacuum. An iodometric titration showed that it contained 1.03 mequiv of peracid per gram (87% yield).

(3) From ⓟ-CHO. The reactions were carried out in a cylindrical 50-ml all-glass reactor equipped with a fritted gas dispersion tube at the bottom, and vented at the top. A typical run was as follows. One gram of resin VII (1.02 mequiv/g) was suspended in a mixture of 10 ml of ethyl acetate and 10 ml of carbon tetrachloride. The mixture was refluxed briefly then cooled to room temperature. A stream of oxygen containing some ozone was passed through the suspension at a rate of 200–300 ml/min while portions of solvent were added as required to keep the volume constant. After 4 hr of reaction at room temperature, the resin was collected, washed with methylene chloride, and dried *in vacuo* at room temperature. An iodometric titration of the dry resin showed that it contained 0.83 mequiv of peracid per gram (81% yield). The reaction was carried out in a similar manner for the macroreticular resin although the reaction conditions were varied slightly. Thus 3 g of macroreticular ⓟ-CHO (1.09 mequiv/g) were soaked in 10 ml of refluxing ethyl acetate. After cooling, enough carbon tetrachloride (4.5 ml) was added to increase the density of the solvent and thus prevent settling of the macroreticular resin at the bottom of the reaction vessel. After 6 hr of reaction with ozone and oxygen, a resin containing 0.71 mequiv of peracid per gram (65% yield) was obtained.

Iodometric Titration of ⓟ-COOOH. The oxidation capacities of the peracid resins were determined by the potassium iodide method. A weighed sample of resin VIII was suspended in a 1:1

mixture of chloroform and glacial acetic acid (for the swellable resins) or pure glacial acetic acid (for the macroreticular resins) and an excess of 50% potassium iodide solution was added. After stirring under nitrogen for 10–30 min, the iodine liberated was titrated with 0.1 *N* sodium thiosulfate. Blank titrations were carried out on the corresponding Ⓟ-COOH resins and corrections were made when required.

Epoxidation of Cyclohexene. A suspension of 3 g (2.9 mmol) of macroreticular Ⓟ-COOOH in 10 ml of purified dioxane containing 0.2 ml (2 mmol) of cyclohexene was stirred at 40° for 6 hr. Analysis of the product was effected by gas chromatography on a column packed with 5% SE-30 liquid phase on Chromosorb W. The absence of α-glycol by-product was shown by titration with sodium metaperiodate. Results of the epoxidation reactions are shown in Table II.

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Studies of the Dimensions of Oligopeptides by Singlet–Singlet Energy Transfer and Theoretical Calculations. I. Influence of Glycine on the Dimensions of Tetrapeptides

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ABSTRACT: The efficiency of energy transfer between a fluorescent donor, L-tyrosine, and a fluorescent acceptor, L-tryptophan, has been determined in R′-L-Trp-L-Ala-L-Tyr-R″, R′-L-Trp-L-Ala-L-Ala-L-Tyr-R″, and R′-L-Trp-Gly-L-Ala-L-Tyr-R″ in ethanol solution. The protecting groups R′ and R″ were respectively *tert*-butyloxycarbonyl and methyl ester. A conformational theoretical analysis of molecules studied has been performed in parallel on the basis of semiempirical conformational potential energy functions. In the theoretical models all the side chains have been represented by a methyl group. From the distribution of distances between chromophores obtained theoretically, transfer efficiencies have been computed assuming a random orientation of the chromophores ($\kappa^2 = \frac{2}{3}$). The comparison of calculated efficiencies with the values determined experimentally for the same value of κ^2 has been used as a check for the theoretical model. Both experimental and theoretical studies have shown that the glycyl residue produces a reduction of dimensions when it replaces in a tetrapeptide a residue with a β-carbon atom such as the L-alanyl residue. However, only a qualitative agreement between experimental and theoretical values of the efficiencies has been obtained.

It is well established from experimental[2] and theoretical[2,3] investigations that the average dimensions of random coils of poly(L-alanine) or its analogs are markedly reduced when glycine is incorporated into the chain, thus replacing an amino acid residue with a β-carbon atom.

In oligopeptides, the glycyl residue should produce a similar reduction of dimensions but this effect has not been investigated up to now. Such an investigation is reported here, and this is the first part of a more general experimental and theoretical study of the dimensions of oligopeptides undertaken in our laboratory by means of nonradiative energy transfer[4,5] and of theoretical conformational analysis with semiempirical potential functions.[6,7]

The most complete description of the dimensions of flexible molecules is given by the normalized distribution $f(r)$ of the end-to-end distances or of any other representative distances in the molecule. However, $f(r)$ is difficult to obtain experimentally; therefore, only average dimensions of the molecules are studied, principally by measuring the mean dipole moment.[8] The efficiency of singlet–singlet energy transfer between chromophores attached to the ends of the molecule can be used to determine the donor–acceptor distance and can also be correlated to the dimensions of the molecule.[5] In oligopeptides which are flexible, the efficiency of energy transfer is equal to the average value of the ratio $R_0^6/(R_0^6 + r_c^6)$ where r_c is the distance between the chromophores, assumed not to vary during the donor lifetime, and R_0 a characteristic spectroscopic constant,