1-Methyl-2,5-di(n-butylaminomethyl)pyrrolidine (IV. R = CH_3, R′ = n-C_4H_9, R″ = NHC_4H_9-n) *trihydrochloride.* A suspension consisting of 10.5 g. of 1-methyl-2,5-bischloromethylpyrrolidine,[2,3] 25 g. of butylamine, 10 g. of anhydrous potassium carbonate, and 100 ml. of absolute ethanol was stirred and refluxed for 3 days. The solvent and the excess low boiling reagents were removed under reduced pressure and the residue was suspended in 200 ml. of water. The aqueous suspension was made strongly basic with 20% potassium hydroxide and the oil was extracted with ether. The extract was dried and distilled. B.p. 88–89°/0.05 mm., yield, 6 g. (41%). The trihydrochloride melted at 300–303° dec. (from ethanol–ethyl acetate).

Anal. Calcd. for $C_{15}H_{36}Cl_3N_3$: C, 49.38; H, 9.95; N, 11.52. Found: C, 49.41; H, 10.11; N, 11.43.

1-Benzyl-2,5-di[(2-diethylaminoethylamino)methyl]pyrrolidine (IV. R = C_7H_7, R′ = $CH_2CH_2N(C_2H_5)_2$, R″ = $NHCH_2CH_2N(C_2H_5)_2$). The above reaction was applied to 10 g. of 1-benzyl-2,5-bischloromethylpyrrolidine.[2,3] B.p. 135–140°/0.05 mm., yield, 6 g. (45%).

Anal. Calcd. for $C_{19}H_{43}N_5$: C, 71.89; H, 11.34; N, 16.77. Found: C, 71.66; H, 11.13; N, 16.49.

RESEARCH DIVISION
ETHICON, INC.
SOMERVILLE, N. J.

γ-Irradiation of Polystyrene-d_1 and Styrene-d_1-Copolymers[1]

W. BURLANT AND J. NEERMAN

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The γ-ray induced degradation of polymethyl methacrylate is indicated by main chain fracture and gas evolution. Recently,[2] it was reported that (1) protection against both degradative processes can be effected by incorporating phenyl groups (as styrene units) in the polymer chain and (2) this protective effect, the precise mechanism of which is obscure at present, is not transmitted over more than one styrene unit.

Present studies with polystyrene-d_1 (labeled in the α-, β- and p-positions) and copolymers containing monodeuterated styrene groups indicate that free radicals derived from γ-irradiation of the more sensitive methyl methacrylate moiety of the polymer abstract H atoms from neighboring styrene units. As a result of these "secondary" radical abstraction reactions, it appears that the protecting agent itself is susceptible to decomposition. The sensitivity toward radical attack of the various carbon-hydrogen bonds in the styrene molecule has been estimated by measuring the deuterium distribution in the evolved gases.

EXPERIMENTAL

Starting materials. α-d_1-Styrene. In a dry nitrogen atmosphere, a solution of 97.8 g. (0.53 mole) of α-bromostyrene (prepared from phenylacetylene and hydrogen bromide[3]) in 200 ml. of dry tetrahydrofuran was added dropwise to a stirred mixture of 28.45 g. (1.17 moles) of magnesium turnings and tetrahydrofuran. Mild refluxing was maintained during addition. Hydrolysis of the Grignard salt then was effected by the dropwise addition of 50 ml. of deuterium oxide after which 200 ml. of water, 100 ml. of diethyl ether and a few grams of sodium chloride were added. The organic layer was separated from the water; the latter was extracted with ether-benzene solutions and the combined organic material washed with saturated sodium chloride solution. After removal of the solvents *in vacuo*, a few crystals of hydroquinone were added to the residue to minimize polymerization of the styrene during subsequent handling. After two distillations, there was obtained 15.0 g. (27%) α-d_1 styrene. This product had a b.p. at 15 mm. of 43–45°, and n_D^{20}, 1.5441. Mass spectra indicated an isotopic purity of 93%; the contaminant was ordinary styrene.

Anal. Calcd. for C_8H_7D: C, 91.38; H + D, 8.62. Found: C, 91.21; H + D, 8.44.

β-d_1-Styrene. According to a procedure similar to that described for the preparation of the α-isomer (the Grignard of β-bromostyrene was prepared in diethyl ether), there was obtained 36.8 g. (35%) of β-d_1-styrene; b.p. (10 mm.), 34–35°; n_D^{20}, 1.5432. The isotopic purity was estimated to be 97%.

Anal. Calcd. for C_8H_7D: C, 91.38; H + D, 8.62. Found: C, 91.11; H + D, 8.45.

p-d_1-Styrene. This monomer was prepared in 30% yield from p-d_1-bromobenzene (synthesized by deuterium oxide hydrolysis of the mono Grignard of p-dibromobenzene) according to the sequence of reactions employed by Overberger and Marvel[4] for structurally similar monomers; b.p. (20 mm.) 46–50°; n_D^{20} 1.5445; isotopic purity, 98%.

Anal. Calcd. for C_8H_7D: C, 91.38; H + D, 8.62. Found: C, 91.28; H + D, 8.35.

Methyl methacrylate and methyl acrylate. The commercially available monomers were redistilled under nitrogen several times before use.

Polymerization and irradiation. Appropriate mixtures of degassed monomers were polymerized thermally to less than 5% conversion. The products were reprecipitated repeatedly from benzene solution with methyl alcohol, dried *in vacuo* for 4 hr. at 100°, then analyzed for the elements to determine the composition. Each copolymer contained about 0.5 mole fraction styrene. Intrinsic viscosities, $[\eta]$, were determined in solvent benzene at 25°; all the styrene–methyl methacrylate copolymers had $[\eta] \cong 1.3$.

About 0.1-g. samples of the polymer were degassed at 80° for 1 hr. at a pressure of about 10^{-5} mm. before sealing. Mass analysis prior to irradiation failed to reveal the presence of solvent or oxygen molecules. A dose rate of 2.0 × 10^5 Rad per hour at the single total dose of 1.0 × 10^7 Rad (Co^{60} source; ferrous sulfate dosimetry) was employed for all experiments. It was assumed that 1 g. of polymer absorbed 62 × 10^{18} e.v. when given a dose of 1.0 Mrad.

Mass spectrometric gas analyses. The response of a mass spectrometer is proportional to the pressure of the gas in the ion source of the analyzer tube; micro quantities can be analyzed by reducing the volume of the reservoir into which the sample is expanded.[5]

For the present study, a novel micro sampling system (Fig. 1) was designed which was of small volume, contained an expansion chamber for "slightly oversize" samples and

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[1] Presented at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960.

[2] W. Burlant, D. Green, and C. Taylor, *J. Appl. Polymer Sci.*, **1**, 296 (1959).

[3] C. Dufraise and C. Moureu, *Compt. rend.*, **171**, 960 (1920).

[4] C. Overberger and C. Marvel, *J. Am. Chem. Soc.*, **67**, 2250 (1945).

[5] J. Neerman and F. Bryan, *Anal. Chem.*, **31**, 532 (1959).

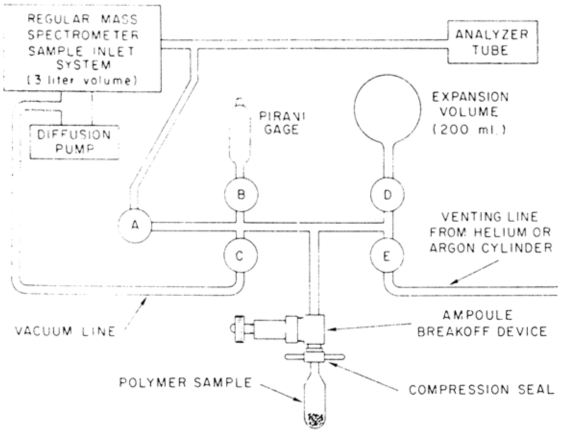


Fig. 1. Sampling manifold for small gas samples, constructed of stainless steel tubing; metal-glass connections are Kovar-Pyrex seals (Cat. No. 96.1009, Carborundum Co., Latrobe, Pa.); valves A-E are monel metal with phosphor bronze bellows and Kel-F seats (Cat. No. M484, Hoke, Inc., Cresskill, N. J.); the ampoule sampling device is explained in Fig. 2. The total volume of the manifold, including the Pirani tube and a 17-ml. ampoule is 66 ml.; under these conditions and for an ionizing current of 50 μa and a grid resistance of 4.3×10^9 ohms, 1.0×10^{-9} g.-moles of hydrogen produces 2.4 scale divisions at M/e = 2

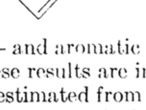
permitted venting with dry inert gas to speed evacuation between samples; the ampoules were sealed into this system by means of a Teflon gasketed compression seal (Fig. 2) fitted with a plunger to break the tip of the previously scratched ampoule. In this manner, rapid analyses of about 10^{-9} g.-moles of gas could be effected without the use of grease or wax. Absolute quantities are believed to be within 10% of the true values; relative concentrations within a few per cent. Usually more than 90% of the gases in each tube were accounted for.

About 1 day after irradiation, the ampoules were sealed into such a modified Consolidated Model No. 21-103 mass spectrometer.

The sensitivity of this analytical technique is reflected in the approximate calculation that for these polymers, only 1 monomer unit in 10^5 undergoes some bond breakage.

RESULTS

Poly-d_1-styrene. The radiation susceptibility of the specific sites in monodeuterated polystyrenes is indicated by the G(D) values for the α-, β- and p-bonds, summarized in Table I. It appears that the α-CD bond in the main chain is most sensitive to radiation-induced cleavage, presumably because of the resonance stability of the free radical resulting from such cleavage:



If the total number of β- and aromatic —CH bonds in the polymer is considered, these results are in accord with those of Wall and Brown,[6] who estimated from similar irradiations of deuterated polymers, that no particular site exclusively is involved in the mechanism for hydrogen formation.

A notable difference between the two studies, however, is that no D_2 was observed in irradiations in this Laboratory. The absence of D_2 suggests that the concentration of initially formed H atoms is so low that only radical abstraction at a nearby site occurs, rather than radical-radical recombination in the gas phase.

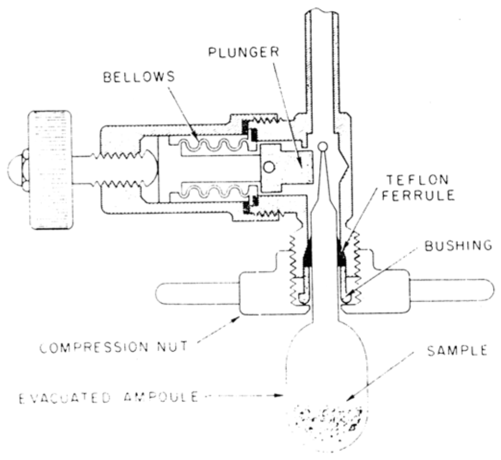


Fig. 2. Ampoule sampling device. The tip of the ampoule is scratched and inserted through the compression seal until it is opposite the plunger; the compression nut then is tightened so that a vacuum tight seal is obtained. A given Teflon ferrule will accept ampoules varying in diameter by ±0.15 mm.

TABLE I

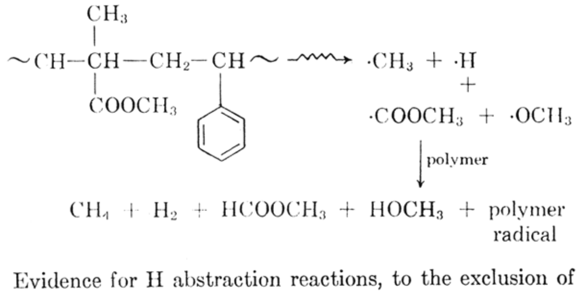
G(D)-Values from the γ-Irradiation of Monodeuterated Polystyrenes; Dose, 1.0×10^7 Rad

Bond	G(D)	Isotope Effect
α-d_1-	0.0037	4.3
β-d_1-	0.0013	4.0
p-d_1-	0.0017	5.9

Deuterated copolymers. At low doses (about 10^6 Rad), the predominant gases from the γ-irradiation of the d_0-copolymer are carbon monoxide, carbon dioxide, hydrogen, methane, methanol and methyl formate. No benzene or monomer units were found.

In addition to the nondeuterated gases formed upon irradiation of a styrene-d_1-methyl methacrylate copolymer, HD, CH_3D, $DCOOCH_3$, and CH_3OD are produced (the assumed structure of the latter two monodeuterated molecules was based on data by Todd[7]). Table II lists G-values for the ratio (d_0-gas/d_1-gas) for these gases from the α-d_1-, β-d_1-, and p-d_1-copolymers.

The carbon oxides probably are produced molecularly, but the hydrogen-containing gases ultimately detected can be explained in terms of simple displacement reactions between initially formed radicals (most of which arise from preferential decomposition of the ester side chain[7]) and polymer:



Evidence for H abstraction reactions, to the exclusion of radical recombination processes, is the observation that G(D) total for the copolymers is greater than G(D) for poly-

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(6) L. Wall and D. Brown, *J. Phys. Chem.*, **61**, 129 (1957).

(7) A. Todd, *J. Polymer Sci.*, **42**, 223 (1960).

TABLE II

G-VALUES FOR GASES FROM COPOLYMERS[a] OF STYRENE-d_1-METHYL METHACRYLATE AND STYRENE-d_1-METHYL ACRYLATE[b]; DOSE 1.0 × 10^7 RAD

	G(Gas) From Nondeuterated Copolymer[c]	G(d_0-Gas/d_1-Gas)[c] α-d_1-Copolymer	β-d_1-Copolymer	. p-d_1-Copolymer	Isotope Effect[d]
H_2	0.072	18 (19)	36 (34)	33 (35)	7.0
HD					
CH_4	0.137	23 (23)	36 (36)	69 (62)	7.0
CH_3D					
$HCOOCH_3$	0.125	17 (12)	34 (30)	52 (93)	5.0
$DCOOCH_3$					
CH_3OH	0.068	[e] (12)	[e] (36)	41 [e]	5.1
CH_3OD					

[a] Containing 0.5 mole fraction styrene. [b] Figures in parentheses. [c] Corrected for the contribution of hydrogen and HD by the styrene units in the copolymer. [d] Calculated only for the methyl methacrylate copolymer. [e] Not determined.

d_1-styrene, and deuterium or molecules such as ethane, dimethyl ether, or methyl acetate, possibly only from bimolecular radical coupling processes, were not detected.[8]

It is apparent that the bond in the styrene moiety of the copolymer most sensitive to abstraction by ·H, ·CH_3, ·OCH_3, and ·$COOCH_3$ is the α-CH; the β- and p-CH bonds are somewhat more stable to such attack.

The reactions of the initially derived free radicals occur to about the same extent and specificity in the styrene–methyl acrylate copolymer (Table II). The latter is a crosslinking system,[2] in which protection against crosslinking is afforded by the styrene groups present. While the gas yields of this copolymer depend not only on its composition, but on the degree of crosslinking (the unirradiated copolymer is more radiation sensitive than the crosslinked product) the ratio G(d_0-gas/d_1-gas) clearly indicates the significance of abstraction reactions in the radiation chemistry of the copolymer.

The implication of these conclusions is that radiation initiated damage noted in organic polymers is not a simple function of the radiation stability of a particular bond in the molecule.

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DEPARTMENTS OF CHEMISTRY AND ANALYTICAL SERVICES
SCIENTIFIC LABORATORY
FORD MOTOR CO.
DEARBORN, MICH

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[8] γ-Irradiation of a mixture of polystyrene-d_1 and polymethyl methacrylate, obtained by coprecipitation from a solution of these substances, afforded HD (from polystyrene-d_1) as the only deuterated species.

Some 4,4′-Bisdialkylaminostilbenes

F. H. C. STEWART

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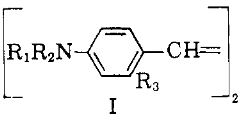
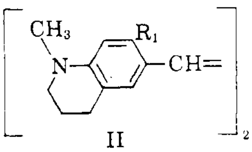
The compound obtained by the action of tin and hydrochloric acid on p-dimethylaminobenzaldehyde was described as 2,6-bisdimethylaminoanthracene by Albano,[1] but was later found to be 4,4′-bisdimethylaminostilbene.[2] This reaction had been extended to various other p-dialkylaminobenzaldehydes and the products erroneously considered to be anthracene derivatives.[3,4] Consequently, in view of the interest which attaches to certain aminostilbenes as carcinogenic agents,[5] it seemed desirable to collect these compounds, with relevant data, under their correct designation as 4,4′-bisdialkylaminostilbenes (I). The compounds are arranged in Table I, which also includes two heterocyclic dialkylaminostilbenes of structure (II). With one exception these stilbene derivatives have not been mentioned in the literature.



I



II

EXPERIMENTAL

The p-dialkylaminobenzaldehydes were prepared from the corresponding tertiary amines by the N,N-dimethylformamide–phosphorus oxychloride procedure of Campaigne and Archer,[7] and the reduction of the aldehydes by tin and hydrochloric acid effected by the standard procedure previously described.[3]

The following intermediates and derivatives have not been reported hitherto.

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(1) J. D. Albano, *Anal. Assoc. Quim. Argentina*, **34**, 18 (1946).

(2) F. H. C. Stewart, *Chem. & Ind. (London)*, 761 (1957).

(3) F. H. C. Stewart, *J. Chem. Soc.*, 1026 (1957).

(4) F. H. C. Stewart and J. W. Rasburn, *J. Chem. Soc.*, 2237 (1957).

(5) A. Haddow, R. J. C. Harris, G. A. R. Kon, and E. M. F. Roe, *Phil. Trans.*, **241A**, 147 (1948).

(6) E. Campaigne and W. M. Budde, *Proc. Indiana Acad. Sci.*, **58**, 111 (1949).

(7) E. Campaigne and W. L. Archer, *J. Am. Chem. Soc.*, **75**, 989 (1953).