to 1.5 ml., of which about 0.35 ml. was water. There was obtained 8.00 g. of crude product, m.p. 121–123°. One recrystallization from butyl alcohol yielded 6.85 g. (83%), m.p. 124–125°; reported melting point 126–127°.[26] The melting point was not further changed by recrystallization from butyl alcohol, glacial acetic acid or benzene–heptane.

Anal. Calcd. for $C_{20}H_{14}Br$: Br, 38.64. Found: Br, 38.40.

Displaced bromine, determined as above, amounted to 2.9% of the total bromine.

9-Benzyl-2-aminofluorene.—A mixture of 6 g. (0.033 mole) of 2-aminofluorene,[27] 10 ml. of benzyl alcohol, 0.1 ml. of benzaldehyde and 0.1 g. of KOH was refluxed for 4 hours in an atmosphere of nitrogen. After cooling, it was treated with 20 ml. of water and filtered. As filtration became increasingly slow owing to the presence of some oil, the mass was taken off the filter, treated with petroleum ether, filtered, washed with petroleum ether and water and dried in a vacuum oven at 60°; yield 9.1 g., m.p. 110–120°. The crude amine was converted to the hydrochloride by heating with 55 ml. of alcohol and 5.5 ml. of concentrated hydrochloric acid on a steam-bath for 40 minutes. After cooling, the hydrochloride was filtered and washed with alcohol and benzene; yield 8.5 g., m.p. 240°. It was reconverted to the amine by refluxing with 50 ml. of alcohol and 5 ml. of a 30% sodium hydroxide solution. After cooling, the amine was filtered, washed with 80% alcohol and with water, and dried in a vacuum desiccator; yield 7.1 g. (80%), m.p. 126–127°; after one recrystallization from benzene–heptane 1:3, m.p. and mixed m.p. 126.5–127°.[28]

9-(*p*-Methylbenzyl)-fluorene.—4.15 g. (0.025 mole) of fluorene, 7 g. of *p*-tolylcarbinol,[29] 0.05 ml. of *p*-tolualdehyde[30] and 0.12 g. of KOH were heated to 186°, and then during 40 minutes to 232°. The distillate amounted to 0.5 ml. After treating with 10 ml. of water, the product was filtered and washed with water and with 15 ml. of 80% alcohol; yield 6.55 g., 97%, m.p. 136–138°; after one recrystallization from heptane, m.p. 137–138°; reported m.p. 136–137°.[31]

9-(*p*-Methoxybenzyl)-fluorene.—4.15 g. of fluorene, 8 g. of *p*-anisyl alcohol, 0.1 ml. of anisaldehyde and 0.4 g. of KOH were heated to 185°, and then, during 15 minutes, to 223°. The distillate consisted of 0.6 ml. of water. After cooling, the mixture was treated with 10 ml. of water; the crystals were filtered and washed with water and with 20 ml. of 80% alcohol; yield 6.86 g. (96%), m.p. 107–109°; after one recrystallization from heptane and a little charcoal, m.p. 109–110°; reported m.p. 112°.[15]

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.11; H, 6.29. Found: C, 88.0; H, 6.44.

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(26) A. Sieglitz, *Ber.*, **53**, 2241 (1920).

(27) W. E. Kuhn, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 448.

(28) E. D. Bergmann, B. Pullman and Y. Sprinzak, *Bull. soc. chim. biol.*, **34**, 586 (1952).

(29) Reference 27, p. 590.

(30) Reference 27, p. 583.

(31) A. Sieglitz and H. Jassoy, *Ber.*, **54**, 2133 (1921).

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

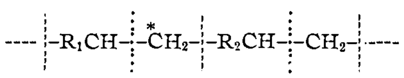
Pyrolysis of Labeled Copolymers in Relation to Structure[1]

BY F. W. MORTHLAND AND WELDON G. BROWN

RECEIVED SEPTEMBER 12, 1955

Copolymers of styrene-β-C^{14} with *m*-methylstyrene and with *p*-methylstyrene, when degraded thermally, give rise to monomer mixtures in which the distribution of the radioactive tracer between the two monomers closely approximates the theoretical (3:1) ratio for randomly constructed copolymers. This proves that the degradation process is not one of spallation from the original chain ends, that the initial chain breaks produce odd and even fragments with equal probability, and that no reversal (re-polymerization of monomers) occurs during degradation. The potential utility of the carbon isotope exchange as a means of studying alternation tendencies in copolymerization is indicated.

If the thermal depolymerization of vinyl-type polymers is initiated by the random fission of C–C bonds, the net result of a polymerization–depolymerization sequence must be an exchange of carbon atoms between monomers. This will be observable in the case of a copolymer derived from two monomers, $R_1CH{=}\overset{*}{C}H_2$ (isotopically labeled) and $R_2CH{=}CH_2$, the structure of which will contain segments such as



$$\text{----}\,\vdots\text{–}R_1CH\text{–}\vdots\text{–}\overset{*}{C}H_2\text{–}\vdots\text{–}R_2CH\text{–}\vdots\text{–}CH_2\text{–}\vdots\,\text{----}$$

Of the two equally probable modes of cleavage, one, indicated by the vertical dashed lines, re-forms monomers of the original isotopic constitution. The other, indicated by the dotted lines, is accompanied by a transposition of the terminal carbon atoms of the resulting monomer molecules. There will thus have been effected a carbon exchange between monomers, the extent of which will depend upon the number of points in the polymer chain at which two unlike monomer units are contiguous. It will be greatest for copolymers showing regular alternation in structure and least where there is no true cross-polymerization. The predicted distribution ratios for a number of special cases are given in Table I.

TABLE I

PREDICTED DISTRIBUTION OF ISOTOPE IN MONOMERS GENERATED FROM EQUIMOLAR COPOLYMERS OF $R_1CH{=}\overset{*}{C}H_2$ AND $R_2CH{=}CH_2$

	Copolymer type	$R_1CH{=}\overset{*}{C}H_2$/ $R_2CH{=}\overset{*}{C}H_2$
I	Regular alternation of monomer units	1:1
II	Random sequence of monomer units	3:1
III	Predominantly sequences of like units	>3:1
IV	No cross-polymerization	No exch.

The occurrence of carbon exchange will exclude from further consideration any mechanism of depolymerization involving the shedding of monomer units from the chain ends (reversal of the chain-growth process) but it will not be inconsistent with a mechanism of irregular primary fragmentation followed by spallation of monomer from the newly formed ends. According to Jellinek[2] the experimental observations relating to thermal degrada-

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(1) Paper presented at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 8–12, 1951.

(2) H. H. G. Jellinek, *J. Polymer. Sci.*, **4**, 13 (1949).

tion are best explained by the assumption of preexistent weak links which upon rupture give rise to fragments capable of rapid spallation. For any particular fragment undergoing spallation the isotopic composition of the resulting monomers will be determined by whether the active chain end was an odd or an even carbon atom in the original chain. It is conceivable that weak links could exist which would direct the primary fragmentation toward the production of even-numbered fragments, *e.g.*, peroxide links formed by copolymerization with oxygen. But if, as Jellinek suggests, they consist of hydroperoxidized tertiary carbon atoms no distinction could be made as to which of the two adjacent methylene groups is to become an active chain end and carbon atom exchange must occur.

The value of the isotope exchange technique in the elucidation of adjacency relationships in copolymers hinges upon one further requirement, namely, that the depolymerization must be essentially irreversible. Otherwise, by a repetition of polymerization and depolymerization the distribution ratio would approach unity for any finite degree of monomer alternation.

The copolymers selected for an experimental study of the carbon exchange were combinations of styrene-β-C^{14} with nuclear-methylated styrenes. Because of their chemical similarity these would be expected to form copolymers of random structure (type II of Table I). These combinations also fulfilled the requirement that the monomer mixtures must be separable for purposes of isotopic analysis, this being readily accomplished by hydrogenation of the double bonds and fractional distillation of the resultant materials.

Evidence as to the degree of departure from the completely random arrangement was sought by evaluation of the monomer reactivity ratios by the methods of Mayo and Walling.[3] Hitherto these methods have been restricted to cases in which copolymer compositions could be determined by ordinary analytical procedures. In our case, ordinary analytical procedures being inadequate because of the small differences in chemical composition, the estimation of copolymer composition was based upon radioactivity measurements. This was done for the copolymerization of styrene-β-C^{14} with *o*-, *m*-, *p*- and α-methylstyrene with the results shown in Table II.

TABLE II

MONOMER REACTIVITY RATIOS FOR THE COPOLYMERIZATION OF STYRENE-C^{14} (M_1) WITH METHYL-SUBSTITUTED STYRENES

Monomer, M_2	r_1	r_2	Product, r_1r_2
o-Methylstyrene	0.90	0.89	0.80
m-Methylstyrene	0.83	0.93	0.77
p-Methylstyrene	1.02	1.21	1.23
α-Methylstyrene	0.71	0.14	0.10

The departure from random structure, as indicated by the products, r_1r_2, is greatest for the copolymerization with α-methylstyrene for which a strong tendency toward alternation is thus demonstrated. The values for the three nuclear-methylated styrenes should be interpreted as showing a slight tendency toward alternation (in excess of statistical) for the *ortho* and *meta* isomers and a slight tendency toward segregation for the *para* isomers. However the significance of these results is doubtful since in the subsequent depolymerization experiments the copolymers containing *m*-methylstyrene and *p*-methylstyrene showed no corresponding difference.

The depolymerization experiments were conducted by heating, in high vacuum, a glass vessel containing the copolymer as a thin film on the inner surface, collecting the volatile products in a cold trap, and analyzing the monomer fraction by the procedures to be described later. The temperature and the period of heating were varied and the results, given in Table III, show that the distribution of radioactivity between monomers is not entirely independent of the experimental conditions during depolymerization.

The copolymers submitted to thermal decomposition differed slightly in composition from the equimolar mixtures for which the theoretical isotope distribution ratios have been given (Table I). The theoretical values corresponding to the compositions taken are listed in Table III and were derived from the relationship, applicable to copolymers of random sequence, $\alpha_1/\alpha_2 = 2 + (m_2/m_1)$, where the α's refer to the molar activities of the regenerated monomers and the m's represent the mole fractions.

There is general agreement between the experimental and the calculated values and hence no doubt as to the occurrence of carbon exchange to approximately the predicted extent. Since, however, the deviation between the observed and calculated values is in the nature of a systematic and unaccountable trend toward higher values (less exchange) at higher temperatures further work will be required to establish the method on a quantitative basis.

One weakness in our analytical procedure is the assumption, unsupported by actual analysis, that the monomers are present in the regenerated mixture in the same ratio as in the copolymer. In any future work this source of error could be eliminated through the device of double labeling, a second label being introduced in a non-exchangeable position purely for analytical purposes.

Experimental

Styrene-β-C^{14}.—Carboxyl-labeled phenylacetic acid was prepared in 80% radiochemical yield by the reaction of radioactive carbon dioxide (0.04 mole containing 0.8 mc. of C^{14}) with benzylmagnesium chloride in a procedure generally similar to that described by Calvin and co-workers.[4] The reduction of 4.39 g. of the acid by lithium aluminum hydride provided 3.85 g. of β-phenylethanol-α-C^{14}, b.p. 219–221°, n^{20}_D 1.5292 (lit.[5] b.p. 218.5–219°, n^{20}_D 1.53594). This material was heated with 3.5 g. of crushed potassium hydroxide and a little hydroquinone to effect dehydration according to the method of Sabetay.[6] The distillate consisted of 3.25 g. (72%) of nearly pure styrene, n^{20}_D 1.5468 (lit.[7] n^{20}_D 1.5471). Without further purification the radio-

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[3] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[4] M. Calvin, *et al.*, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 172, 180.

[5] V. Grignard, *Ann. chim.*, [8] **10**, 28 (1907).

[6] S. Sabetay, *Bull. soc. chim.*, [4] **45**, 72 (1929).

[7] W. Patnode and W. J. Scheiber, THIS JOURNAL, **61**, 3449 (1939).

TABLE III

DEPOLYMERIZATION DATA FOR COPOLYMERS OF STYRENE WITH *p*- AND *m*-METHYLSTYRENE

Expt.	Polymer, g.	Styrene mole fract.	Me-Styrene mole fract.	Time, min.	Temp., °C.	Monomer recovd., g.	Styrene mol. act., c./min.	Me-Styrene, mol. act., c./min.	Styrene activity / Me-Styrene activity	
									Obsd.	Calcd.
Styrene–*p*-methylstyrene										
3a	4.0269	0.469	0.533	60	310	0.2233	3311.1	1082.5	3.059	3.141
3b	4.0269	.469	.533	75	355	1.1420	12304.4	3967.9	3.102	3.141
3c	4.0269	.469	.533	135	375	0.3520	12943.9	3287.9	3.937	3.141
Styrene–*m*-methylstyrene										
5a	2.1159	0.482	0.518	30	400	1.2640	10910.0	3327.2	3.279	3.075
5b	2.1649	.484	.516	1560	300	1.4876	6998.5	2679.0	2.612	3.066

active material was diluted with 150 ml. of inactive styrene from a commercial source (Dow Chemical Co.) to provide the stock supply of styrene-β-C^{14} used in all subsequent experiments. Chromic acid oxidation furnished inactive benzoic acid; the label is thereby shown to be exclusively in the β-position.

Inactive Methylstyrenes.—The three nuclear-methylated styrenes were synthesized by vapor phase dehydration of the appropriate methyltolylcarbinols over an alumina catalyst.[8] α-Methylstyrene was obtained from a commercial source (Dow Chemical Co.) and was purified by distillation prior to use. In each case the physical constants of the monomer were in satisfactory agreement with literature values.

Copolymerization Technique.—In duplicate experiments throughout, each monomer pair was combined in three different feed ratios, 4:1, 1:1 and 1:4. The mixtures, with 0.1% of added benzoyl peroxide, were contained in evacuated sealed tubes and were heated in an oil-bath at 60°. Those containing styrene in combination with a nuclear-methylated styrene were heated for periods of 16–18 hours at which time the extent of polymerization ranged from 20 to 40%. In this series mixtures rich in *o*-methylstyrene showed the lowest conversion and, almost independently of feed ratio, mixtures of styrene and *m*-methylstyrene showed the greatest conversion to polymer. Mixtures of styrene and α-methylstyrene which polymerized much more slowly were heated for periods ranging from 46 hours for the 4:1 mixtures (29% conversion) to 238 hours for the 1:4 mixture (6.5% conversion).

The polymeric material was separated from unreacted monomer by dissolving the mixture in methylene chloride and adding an excess of methanol. After centrifuging and decanting, the precipitated polymer was re-dissolved in methylene chloride and subjected to two additional precipitations. The final product was dried by the frozen benzene technique of Lewis and Mayo.[9] Mechanical losses were avoided by carrying out the entire sequence of operations, including the final drying, in centrifuge bottles.

The composition of the polymer samples was derived from radioactivity measurements on calcium carbonate resulting from the total oxidation of the samples.[10] Because of the relatively high degree of conversion to polymer it was necessary to use the integrated form of the copolymerization equation derived by Mayo and Lewis[11] and to evaluate the monomer reactivity ratios by the graphical methods described by these authors. The values thus obtained are listed in Table II.[12]

Oxidation and Counting Procedures.—The organic samples were oxidized by the Van Slyke–Folch reagent and the resulting carbon dioxide was absorbed from a stream of nitrogen gas by hot 1 *M* sodium hydroxide solution. Sufficient 4 *M* ammonium chloride solution was added to bring the *p*H to approximately 9 and precipitation of calcium carbonate was effected by the addition of 4 *M* calcium chloride solution.

The carbonate samples were mounted in aluminum dishes providing a thickness several times the "infinite thickness" and a sample area of 2.88 cm.². These were counted in a windowless GM counter similar to that described by Kelsey.[13] Individual determinations were taken to a total of at least 10,000 counts.

Thermal Degradation.—The copolymer samples were deposited, by evaporation of solvent from a methylene chloride solution, as thin films on the inner surface of tubes connected through liquid nitrogen-cooled traps to a high vacuum system. After evacuation the tubes were inserted in a pre-heated furnace and all volatile products were collected. At the end of the heating period the monomeric products were separated from high-boiling products by vacuum distillation and were then subjected to radiochemical analysis with the aid of carriers as described below.

The lowest temperature at which depolymerization could be detected was about 300°. In one series of experiments carried out with a styrene–*p*-methylstyrene copolymer the apparatus was so arranged that three successive samples, at progressively increasing temperatures, could be collected from a single sample of the copolymer. The degradation was rapid at 400° with quite noticeable production of particulate matter; no experiments were done at higher temperatures.

In all experiments practically no residue remained in the heated tube. The yield of monomeric products was low, not exceeding in any case 60%, as a consequence of conditions favoring the rapid escape not only of monomer but also of intermediate products.

Radiochemical Analysis of Monomer Fractions.—The procedure involved first the conversion of the styrenes to the corresponding ethylbenzenes by catalytic hydrogenation, secondly separation of the components by fractional distillation with the aid of added carriers, and finally determination of the activity in the separated products. The re-distilled monomer fractions were dissolved in benzene containing a little hydroquinone, known amounts of pure ethylbenzene and of the appropriate ethyltoluene were added and the mixtures were hydrogenated at 10 p.s.i. over a platinum catalyst. The liquid, amounting to about 10 ml., was transferred to the pot of a Piros–Glover spinning-band micro-column and after removing the forerun of benzene the further distillate was collected in a series of small fractions. Very sharp separations were secured as would be expected for a 26° difference in boiling points; this was best demonstrated by the constancy in the activity of samples collected over the whole length of a plateau.

In the oxidation of ethylbenzene and related hydrocarbons by the Van Slyke procedure difficulty was experienced from incomplete oxidation. This difficulty was resolved by a modification of the procedure in which the sample is vaporized in a stream of nitrogen which is bubbled through the hot reagent.

To derive relative molal activities for the monomers from the count rates observed on carbonate mounts corrections were applied for the dilution due to added carrier and for the difference in carbon content of the two monomers. Since only ratios of activities are required no attempt was made to determine absolute activities. The reliability of the individual count rate determinations, expressed as standard error, was generally better than 1.5%.

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[8] D. T. Mowry, M. Renoll and W. F. Huber, THIS JOURNAL, **68**, 1105 (1946).

[9] F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 134 (1945).

[10] Taking into consideration the difference in carbon content of styrene and methylstyrene, the mole fraction of styrene in a polymer is given by $9(\alpha/\alpha_0)/(8 + \alpha/\alpha_0)$, where α_0 is the activity of calcium carbonate formed from styrene alone and α is the activity of the carbonate formed from the copolymer.

[11] F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944).

[12] The numerical data are recorded in full by F. W. Morthland, Ph.D. Dissertation, The University of Chicago, 1950.

[13] F. E. Kelsey, *Science*, **109**, 566 (1949).