water, and dried. Removal of the ether by distillation yielded the crude benzil, and an infrared spectrum was obtained. In no case were any organic impurities detectable. The benzils could be recrystallized from ethanol. The table summarizes the results obtained.

In runs with sodium acetate one equivalent of sodium acetate was added. The results were the same, and no by-product could be detected.

Conductometric Titrations.—A 0.1 *M* solution of the acid to be titrated in a titration cell was maintained at 90 ± 1° using an oil-bath with acetic acid–water (7:3) as solvent. To this solution was added measured amounts of 1.06 *M* sodium acetate in the same solvent and the conductivity was measured at increments of *ca.* 0.25 ml. using a conductivity bridge. The conductivities measured initially for solvent alone and the selenious acid, oxalic acid, trifluoroacetic acid and sulfuric acid solutions in mhos $\times 10^3$ were 0.9, 1.5, 3.3, 6.3 and 40, respectively. After the addition of *ca.* two equivalents of the acetate solution the conductivity observed in each case was about 20 mhos $\times 10^3$, and in each case a simple smooth curve connecting the initial and final values was obtained.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

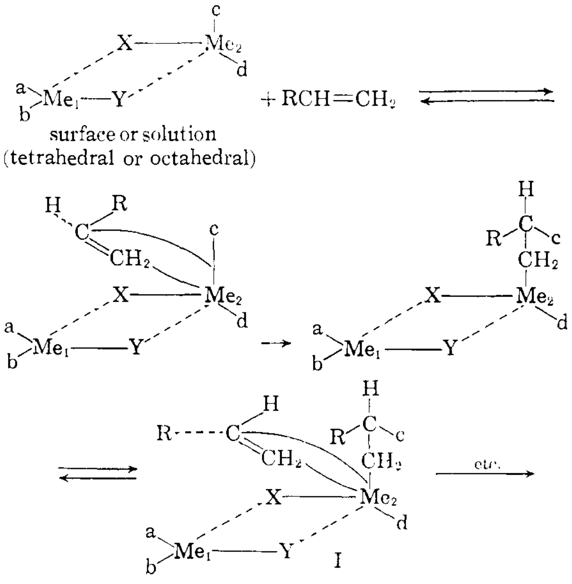
Copolymerization of Styrene and *p*-Alkylstyrenes with an Aluminum Alkyl–Titanium Trichloride Catalyst[1]

BY C. G. OVERBERGER AND F. ANG[2]

RECEIVED APRIL 7, 1959

The copolymerization of styrene and *p*-methylstyrene with the "Ziegler–Natta" catalyst system resulted in an amorphous product. From a study of their molecular weight and copolymer composition distribution, evidence was obtained to demonstrate that the products were copolymers. Additional evidence for a copolymer was obtained by comparing the properties of these products with those of a known mixture of the two homopolymers. Determination of the relative reactivity of styrene and *p*-methylstyrene show them to have about equal reactivity in this catalyst system ($r_1 = 1 \pm 0.12$, $r_2 = 1 \pm 0.12$). Analysis of the copolymer composition distribution indicated the presence of more than one type of copolymer suggesting a polyactivity of the catalyst system. The results are best explained by the assumption that at least two different types of copolymers are being formed. The copolymerization of styrene and *p*-*t*-butylstyrene failed to give appreciable copolymer; instead, from the observed crystallinity of the polystyrene and composition distribution, it was apparent that the product largely contained a mixture of the two homopolymers. The same results were obtained from the copolymerization of styrene and *p*-*n*-butylstyrene. It is tentatively concluded that the reactivity of the monomer is influenced strongly by its tendency to be coördinated on the catalyst sites and that the steric and polar factors responsible for this equilibrium will be different from these same factors which are responsible for the reactivity of monomers in solution in free radical and ionic-catalyzed polymerization.

There is considerable agreement on the over-all mechanism of the aluminum alkyl–titanium halide catalyst type.[3–10] A reduced valence state compound of titanium, vanadium or zirconium either formed *in situ* by reduction or added directly, forms an interstitial type of complex with a Lewis acid. In a heterogeneous catalyst, this interstitial binding occurs occasionally on the transition metal surface and these represent catalyst sites. In homogeneous solution a certain fraction of the reduced metal compound forms a soluble interstitial complex. On these catalyst sites or complexes are adsorbed or coördinated a π-electron system followed by a transfer of a pair of electrons from a metal–alkyl bond. There is a possibility that the pair of electrons originates from the olefin and is transferred to the metal; there is no evidence on this question. A typical representation is indicated. There is an equal possibility that the alkyl group with its electrons is derived from the transition metal. In some cases, it may function as a very labile Lewis acid in the formation of an interstitial compound with a reduced form of a transition metal (Ti, V, Zr). It is also possible that this active site or interstitial compound may have considerable ionic character.[10d]



Me_1, Me_2 = Ti, Al a,b,y alkyl, X = halogen
c,d alkyl, X = halogen

---

[1] This is the 13th in a series of papers concerned with ionic polymerization; for the previous paper on this series, see C. G. Overberger, E. Pearce and N. Mayes, *J. Polymer Sci.*, **34**, 109 (1959).

[2] This paper comprises a portion of a dissertation submitted by F. Ang in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the graduate school of the Polytechnic Institute of Brooklyn.

[3] F. J. Welch, B. R. Thompson, F. E. Bailey and S. Gates, Abstracts of Papers, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956, p. 135.

[4] C. D. Nenitzescu, C. Huch and A. Huch, *Angew. Chem.*, **68**, 438 (1956).

[5] G. Natta, *Sci. American*, September, 98 (1957).

[6] G. Natta, P. Pong, E. Mantica, F. Danusso, G. Mazzanti and M. Peraldo, *Chem. e ind.*, **39**, 19 (1957).

[7] F. Eirich and H. Mark, *J. Colloid Sci.*, **11**, 748 (1956).

[8] D. B. Ludlum, A. W. Anderson and C. E. Ashby, THIS JOURNAL, **80**, 1380 (1958).

[9] H. Uelzmann, *J. Polymer Sci.*, **32**, 457 (1958).

[10] (a) G. Natta, *Angew. Chem.*, **69**, 686 (1957); (b) W. Carrick, THIS JOURNAL, **80**, 6455 (1958); (c) D. Breslow and N. Newburg, *ibid.*, **81**, 81 (1959); (d) H. Uelzmann, *J. Polymer Sci.*, **32**, 457 (1958).

All successive R groups will be complexed in the same manner as in I with R on the opposite side to the growing polymer chain and will lead to isotactic material. If this general mechanism is used as a working hypothesis or theory, then it is clear that the absorption or coördination of the monomer with the interstitial complex will be subject to very selective steric and polar factors—one would suspect both to be involved but primarily steric in the cases discussed here. The general mechanism is similar to the reaction of any polar group with an organometallic–metal complex formation which may be of a highly stereoselective type followed by rearrangement of the complex to form a new bond.[10a,b] Furthermore, steric and polar factors which govern the reactivity of monomers in a free radical or ionic polymerization in solution will operate in a situation of the above type, but probably will not provide the same conclusion. It can be seen from the proposed mechanism that large penultimate effects could be expected from the polymer chain when complexing of the monomer occurs, that is, from the group R from the second monomer unit in the chain attached to the metallic site. These very specific steric requirements may actively result in some fluctuation of the monomer reactivity ratios during the course of a copolymerization. It was the purpose of the problem to attempt to provide evidence for this latter assumption. With few exceptions, only α-olefins have been polymerized with the type of catalyst and since α-olefins have not given linear high polymers in conventional free radical or ionic catalyst systems, their reactivity cannot easily be compared. Fortunately, styrene has been polymerized in solution with conventional cationic and anionic catalyst and we then decided to use C^{14}-styrene in this original work and to copolymerize this C^{14}-styrene with *p*-methyl-, *p*-*t*-butyl- and *p*-*n*-butylstyrene. Although reactivity ratio data is not available for these copolymers in conventional radical or ionic systems they can easily be estimated from existing data. It would be very unlikely that copolymers from the monomer pairs listed above would not be obtained with catalysts in solution such as 2,2-azobisisobutyronitrile, stannic chloride in nitrobenzene and sodium amide in liquid ammonia, although these data are being obtained at present.

Results

Copolymerization of Styrene and *p*-Methylstyrene.—The determination of the relative reactivities of the copolymerization of styrene and *p*-methylstyrene gave results summarized in Table I. Yields obtained at the different feed compositions were kept low to assure constancy of monomer concentrations during the copolymerization. A plot of the monomer composition *vs.* copolymer composition is shown in Fig. 1. This plot corresponded to a straight line at a 45° angle indicating about equal monomer reactivity in the copolymerization; $r_1 = 1 \pm 0.12$, $r_2 = 1 \pm 0.12$.

Table II shows the results obtained on fractionation of a 20% styrene–80% *p*-methylstyrene copolymer. A plot of accumulative weight *vs.* intrinsic viscosity gave the molecular weight distribution shown in Fig. 2. This distribution resembled a normal type of molecular weight distribution. A plot of intrinsic viscosity *vs.* percentage styrene gave the copolymer composition distribution shown in Fig. 3.

TABLE I

COPOLYMERIZATION[a] OF STYRENE[14] (M_1) AND *p*-METHYLSTYRENE (M_2)

M_1 in monomer mixt., mole %	Conversion, %	Product[b] activity, counts per min.	m_1[c] in copolymer
1.7298 (77)	0.87	396	0.74
0.9435 (66)	0.47	388	.73
0.8354 (49)	1.17	251	.47
1.0090 (34)	0.93	166	.31
0.9846 (29)	5.24	170	.32
3.4235 (24)	6.25	106	.20
0.6670 (23)	14.89	98	.19

[a] Copolymerization was carried out in heptane at 70–80° for 20 hr. using a 3:1 molar ratio of triisobutylaluminum–titanium trichloride catalyst. [b] Activity determined by proportional counting at 2,000 volts and P.H.S. of 0.2 volt. [c] Mole fraction of styrene in copolymer as calculated from monomer activity of 535 c.p.m.

TABLE II

COMPOSITION AND VISCOSITY DISTRIBUTION OF STYRENE–*p*-METHYLSTYRENE COPOLYMER[a]

Fraction	Weight, g.	Intrinsic viscosity	Activity[b] (net), c.p.m.	Styrene,[c] %
0	0.0720	3.3	83	20
1	.0150	7.7	123	30
2	.1508	7.1	116	28
3	.2081	4.3	104	25
4	.0307	3.0	93	22
5	.0734	1.7	70	17
6	.0599	1.3	65	16
7	.0679	0.7	63	15
8	.2906	. .	Oily residue	. .

[a] Copolymer obtained from the copolymerization of 3.4235 g. (0.03287 mole) of stryene[14] with 12.2425 g. of *p*-methylstyrene using 2.9845 g. of $TiCl_3$ and 10 ml. of $(i\text{-butyl})_3Al$ as catalyst in heptane at 70°. [b] Activity determined by proportional counting at 2000 volts and P.H.S. of 0.2 v. [c] Calculated from styrene activity of 415 c.p.m./10 mg.

A similar fractionating was then repeated on a 42% styrene copolymer. Table III summarizes

TABLE III

COMPOSITION AND VISCOSITY DISTRIBUTION OF STYRENE–*p*-METHYLSTYRENE COPOLYMER[a]

Fraction	Weight, g.	Intrinsic viscosity	Activity, c.p.m.	Styrene,[b] %
0	0.1222	5.8	113	42
1	.0350	10.5	146	54
2	.0355	8.6	139	52
3	.0338	7.4	132	49
4	.0340	6.3	111	41
5	.1527	5.2	56	21
6	.0643	1.5	30	12
7	.0337	0.4	25	10
8	.0927	. .	Oily residue	. .

[a] Copolymer obtained from the copolymerization of 10.1740 g. (0.09770 mole) of styrene[14] with 10.0860 g. (0.08537 mole) of *p*-methylstyrene using 1.2088 g. of $TiCl_3$ and a 3:1 molar ratio of triisobutylaluminum as catalyst in heptane at 70°. [b] Calculated from styrene activity of 268 c.p.m./10 mg.

(9a) R. T. Morrison and M. Wishman, THIS JOURNAL, **76**, 1059 (1954).

(10b) C. G. Swain and H. B. Boyles, *ibid.*, **73**, 870 (1951).

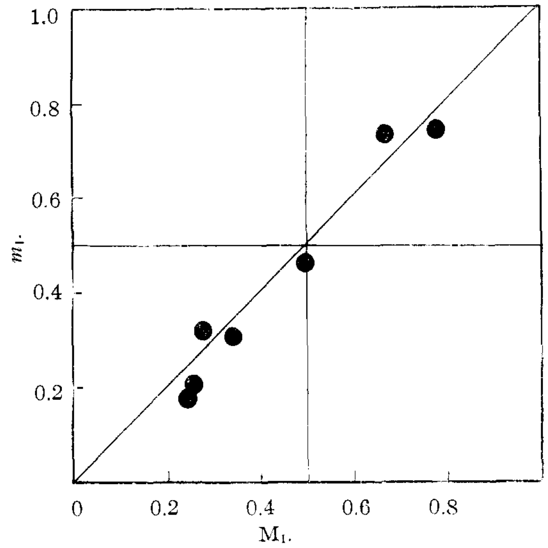


Fig. 1.—Copolymerization of sytrene[14] (M_1) and *p*-methylstyrene (M_2).

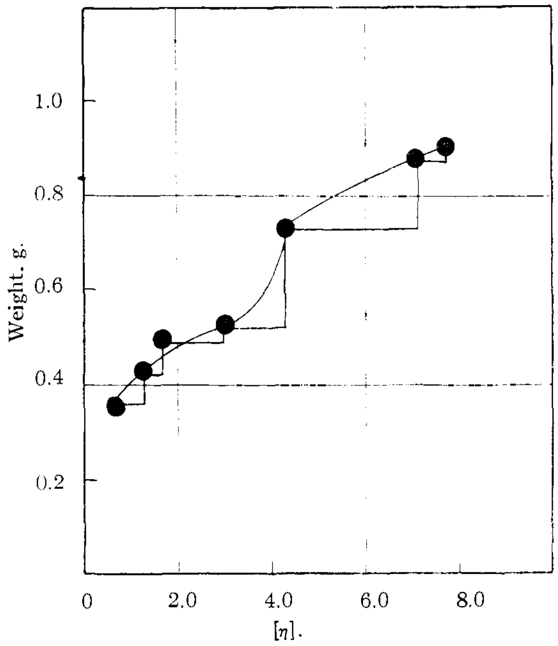


Fig. 2.—Molecular weight distribution of styrene–*p*-methylstyrene copolymer (0.03 mole–0.10 mole).

the data. An analogous molecular weight distribution to the 20% styrene copolymer was obtained. The copolymer composition distribution was also similar and confirmed the results obtained with the previous copolymer.

A Polystyrene and Poly-*p*-methylstyrene Mixture.—For comparative purposes a molecular weight distribution and chemical composition of a mixture of the two homopolymers were determined. The results are shown in Table IV. The polystyrene sample used was an atactic, heptane-soluble fraction of polystyrene. To this was added a small quantity of crystalline polystyrene. This was added in order to test its facile separation from such a mixture because of its great difference in solubility. Amorphous poly-*p*-methylstyrene was also prepared with the use of the same catalyst system. The average intrinsic viscosities of these homopolymers corresponded to 4.6 for the atactic

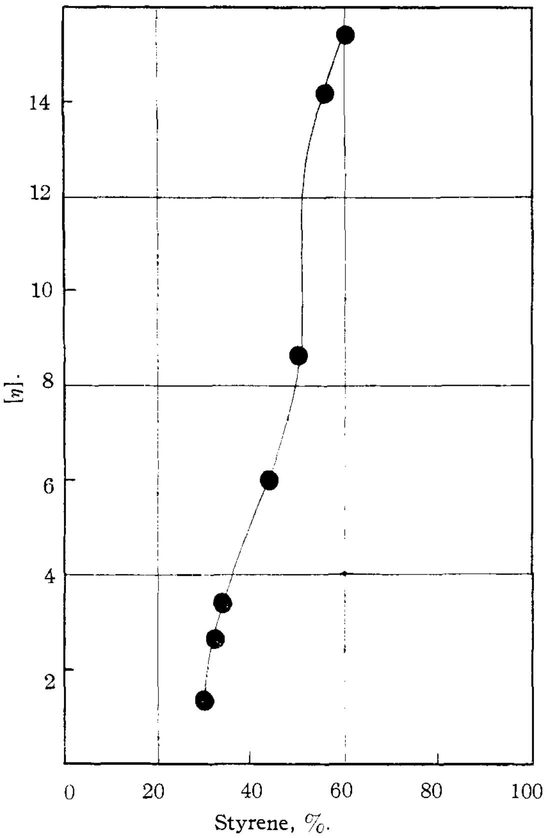


Fig. 3.—Plot of intrinsic viscosity *vs.* percentage styrene for fractions of a copolymer of styrene (M_1, 0.03 mole) and *p*-methylstyrene (M_2, 0.10 mole).

TABLE IV

COMPOSITION AND VISCOSITY DISTRIBUTION OF A POLYSTYRENE AND POLY-*p*-METHYLSTYRENE MIXTURE[a]

Fractions	Weight, g.	Intrinsic viscosity	Activity,[b] c.p.m.	Styrene,[c] %
	0.2243	4.6	360	100[d]
	.0448	..	360	100[e]
	.2243	5.4	0	0[f]
Insol.	.0146	..	360	100
1	.0212	..	358	100[g]
2	.0186	8.1	295	82
3	.0202	6.9	287	80
4	.0670	5.6	345	96
5	.0497	5.3	357	99
6	.0695	5.1	146	41
7	.1319	4.8	65	18
8	.0832	0.7	154	43
9	.0075	0.4	140	39
10	.0100	..	Oily residue	

[a] Polystyrene obtained from the polymerization of 3.9051 g. of styrene[1] using 0.8850 g. of $TiCl_3$ and a 3:1 molar ratio of Al/Ti as catalyst in heptane at 70°. Poly-*p*-methylstyrene obtained from the polymerization of 5.6045 g. of *p*-methylstyrene using 1.0400 g. of $TiCl_3$ and a 3:1 molar ratio of Al/Ti as catalyst in heptane at 70°. [b] Activity determined by means of proportional counting at 2000 volts and P.H.S. of 0.2 v. [c] Calculated from styrene activity. [d] Polystyrene extracted with heptane; soluble fraction. [e] Original polystyrene. [f] Poly-*p*-methylstyrene. [g] Difficultly soluble.

polystyrene and 5.4 for poly-*p*-methylstyrene. The molecular weight distribution of this mixture was normal but it differed from that of the copolymer (Fig. 2) in that there was present another slope at the lower end of the molecular weight range. The copolymer composition distribution shown is completely different from that of the copolymer (Fig. 3) and there appears to be a random distribution.

Copolymerization of Styrene with *p*-*t*-Butylstyrene and *p*-*n*-Butylstyrene.—Unlike the amorphous product obtained from the copolymerization of styrene and *p*-methylstyrene, the product resulting from the copolymerization of styrene and *p*-*t*-butylstyrene showed crystallinity. The results of its fractionation and analysis are summarized in Table V. The molecular weight distribution is indicative of product of quite random distribution and appreciable deviation from the normal S-type of distribution was observed. The copolymer composition distribution was random and clearly showed the presence of primarily homopolymers. The copolymerization of styrene and *p*-*n*-butylstyrene also resulted primarily in a mixture of homopolymers although some copolymerization may have taken place.

TABLE V

COMPOSITION AND VISCOSITY DISTRIBUTION OF STYRENE–*p*-*t*-BUTYLSTYRENE COPOLYMERIZATION PRODUCT[a]

Fraction	Weight, g.	Intrinsic viscosity	Activity[b] (net), c.p.m.	Styrene,[c] %
Original	0.0104		242	85
Insol.	.0197		287	100
1	.0177	9.5	267	94
2	.0298	8.6	267	94
3	.0222	7.4	284	100
4	.0146	5.6	287	100
5	.1614	4.8	246	86
6	.0718	2.3	194	68
7	.0272	0.7	238	84
8	.0607	..	Oily residue	

[a] Product obtained from the copolymerization of 8.5373 g. (0.08198 mole) of styrene[14] with 8.2974 g. (0.05178 mole) of *p*-*t*-butylstyrene using 1.5435 g. of $TiCl_3$ and a 3:1 molar ratio of triisobutylaluminum as catalyst in heptane at 80°. [b] Activity determined by means of proportional counting at 2000 volts and P.H.S. at 0.2 mv. [c] Calculated from styrene activity of 286 c.p.m./10 mg.

Discussion

From the data presented, it is clear that copolymerization of styrene and *p*-methylstyrene has probably occurred with the titanium trichloride–aluminum triisobutyl catalyst system. It remains therefore to interpret the data in a logical way. Poly-*p*-methylstyrene prepared with this catalyst system only gave amorphous polymer. On the other hand, styrene prepared with this catalyst system gave over 30% yield of crystalline isotactic polystyrene.[11] None of the copolymers which were prepared showed any evidence of crystallinity even after attempted orientation. Furthermore, no evidence of isotactic polystyrene could be detected and this led us initially to suspect that homopolymerization of the two monomers was probably not occurring. It is quite probable that the copolymers prepared might have stereoregular sequences, but because of the heterogeneity of the copolymers they cannot crystallize. Fractionation of two copolymers, one containing 20% styrene, and one 40% styrene, strengthened the point of view that the products were copolymers rather than mixtures of two homopolymers. As noted, in the Results section, the normal composition distribution for a copolymer was not obtained but rather the data demonstrated a regular gradual transition in styrene content with molecular weight. In order to obtain further evidence that the product from these copolymerizations were not mixtures of homopolymers, a known mixture of homopolymers was prepared which included a small amount of isotactic polystyrene as a third component and the mixture fractionated. The composition distribution curve was quite different from the fractionated copolymers mentioned above—there being a random change in styrene content with molecular weight. Again, this result confirms that copolymers are obtained rather than mixtures of homopolymers.

It has been shown in the polymerization of α-olefins that a solid phase is necessary for a high degree of stereospecificity.[12–14] In the titanium–aluminum alkyl catalysts systems it has been reported that coarsely crystalline solids give higher percentages of isotactic polymers than do finely dispersed ones, and with polypropylene it has been found that the isotactic fraction is of higher molecular weight than the amorphous material. On the basis of these facts, one can speculate that there exists sites of different catalytic activity in these heterogeneous systems. Stated in a more precise way: there are catalyst sites which give less stereospecific control than others. The results obtained here may be explained by the presence of two or more copolymers of different compositions—a stereoregular copolymer with a higher content of styrene of higher molecular weight and a non-stereospecific copolymer of lower styrene content and lower molecular weight.

No copolymer could be detected in the copolymerization of styrene and *p*-*t*-butylstyrene, and it is concluded that *p*-*t*-butylstyrene is much less reactive in this system than one would predict on the basis of free radical or conventional ionic mechanisms. As noted also, there did not seem to be any copolymerization with *p*-*n*-butylstyrene and styrene. The data, however, are not sufficiently accurate in either case to say that no copolymer was formed; rather they indicate that most of the product was isotactic and amorphous polystyrene. It can be concluded that steric and polar requirements for the coördination of the monomer with the catalyst site is specific and in the presence of an excess of both monomers relatively small change in structure exclude one monomer from the catalyst site in the presence of another. It is suggested that relative activities of

---

(11) C. G. Overberger, F. Ang and H. Mark, *J. Polymer Sci.*, **35**, 381 (1959).

(12) G. Natta, P. Pino, G. Mazzanti, U. Gianni, G. Mantica and M. Peraldo, *Chim. e ind.*, **39**, 19 (1957).

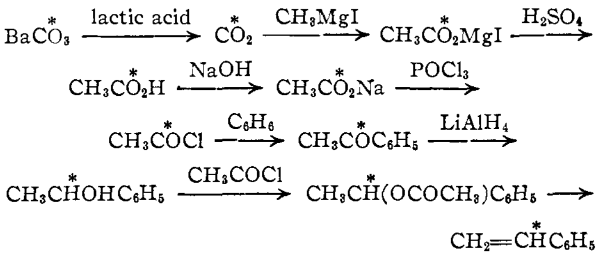
(13) G. Natta, P. Pino, G. Mazzanti and U. Gianni, THIS JOURNAL, **79**, 2975 (1957).

(14) D. S. Breslow and N. R. Newberg, *ibid.*, **79**, 5072 (1957).

some monomers may need to be revised somewhat for this type of system in accordance with the principle proposed.

Experimental

Monomer Synthesis.—In order to have a more accurate way than spectral or elemental analysis to determine copolymer compositions of styrene and *p*-alkylstyrene copolymerization products, the use of the isotope technique was utilized. Consequently, radioactive styrene was synthesized from radioactive barium carbonate according to the reactions[15-18]



$$\mathrm{Ba\overset{*}{C}O_3} \xrightarrow{\text{lactic acid}} \mathrm{\overset{*}{C}O_2} \xrightarrow{\mathrm{CH_3MgI}} \mathrm{CH_3\overset{*}{C}O_2MgI} \xrightarrow{\mathrm{H_2SO_4}}$$

$$\mathrm{CH_3\overset{*}{C}O_2H} \xrightarrow{\mathrm{NaOH}} \mathrm{CH_3\overset{*}{C}O_2Na} \xrightarrow{\mathrm{POCl_3}}$$

$$\mathrm{CH_3\overset{*}{C}OCl} \xrightarrow{\mathrm{C_6H_6}} \mathrm{CH_3\overset{*}{C}OC_6H_5} \xrightarrow{\mathrm{LiAlH_4}}$$

$$\mathrm{CH_3\overset{*}{C}HOHC_6H_5} \xrightarrow{\mathrm{CH_3COCl}} \mathrm{CH_3\overset{*}{C}H(OCOCH_3)C_6H_5} \longrightarrow \mathrm{CH_2{=}\overset{*}{C}HC_6H_5}$$

Using 0.02336 g. of barium carbonate which corresponded to an activity of 0.8 millicurie and incrementally diluting each reaction step with inactive reactants, a yield of 150 ml. of the acetate was obtained. Pyrolysis of the acetate gave radioactive styrene which was further diluted to give a monomer having an activity of approximately 350 c.p.m./10 mg. (2000 volts, *p*H 5, 0.2 v.). Appropriate amounts of the acetate were pyrolyzed and purified when needed.

p-Methylstyrene was prepared from *p*-bromotoluene according to the procedure of Mowry.[19]

Samples of *p*-*t*-butylstyrene and *p*-*n*-butylstyrene were prepared from the isomeric butylbenzenes by a method previously described.[18-21]

Copolymerization.—The apparatus consisted of a 100-ml. three-necked flask equipped with a Trubore Teflon stirrer, a Claisen adapter with a nitrogen inlet tube and a dropping funnel. In the third neck a condenser was inserted, fitted with a drying tube. The reaction flask was thoroughly flushed and flamed under a heavy flux of dry prepurified nitrogen flow.

Into a polyethylene bag was inserted an opened weighing vial, the titanium trichloride container and a nitrogen inlet tube. The bag was then securely tied with a string around the nitrogen inlet tube. Nitrogen was then introduced to replace the air in the bag. This was effectively accomplished by inflating and deflating the bag several times. While maintaining a steady positive nitrogen flow the titanium trichloride container was opened. An appropriate amount of the titanium trichloride was then poured into the weighing bottle. After securely closing the containers the weighing bottle was removed and weighed.

To the polyethylene bag was now placed a small bottle of triisobutylaluminum and a nitrogen inlet tube. After similar replacement of the air with nitrogen the bottle was opened. A syringe of appropriate size equipped with a stainless steel stopcock and a long stainless steel needle was first thoroughly flushed with nitrogen. The sample of triisobutylaluminum was withdrawn by introducing the needle in the bottle through the plastic bag, after initial reflushing of the syringe at the outlet of the nitrogen tube. After withdrawal of the appropriate amount of triisobutylaluminum, the needle was cleared of the liquid by drawing in some nitrogen. The stopcock was then closed and the needle quickly withdrawn and submerged in a small beaker of heptane.

While maintaining a positive nitrogen pressure, the condenser was removed from the apparatus and the titanium trichloride poured into the flask. The condenser was then replaced in position. The triisobutylaluminum was added by inserting the needle through the stopcock of the dropping funnel. The syringe was then withdrawn and rinsed with heptane prior to opening to air. The catalyst suspension was heated to 70° in an oil-bath and gently stirred at this temperature for 15 minutes. Copious formation of fumes was observed during which time the catalyst suspension darkened. A solution of the two monomers dissolved in an equivalent volume of purified heptane was heated to 70° and added to the dropping funnel. This solution was then added to the catalyst under stirring over a period of 15 minutes. Sitrring was continued for 20 hours at 70°.

To the reaction product, cooled to room temperature, was added, dropwise initially, 50 ml. of methanol. Stirring was continued for one hour to complete separation of the catalyst from the polymer precipitate. The polymer was then filtered and further treated with a boiling 10% solution of methanolic hydrochloric acid to remove traces of catalyst decomposition product. This treatment was continued until a colorless filtrate[22] was obtained. The polymer was then washed free of acid with methanol and dried in a vacuum oven at 60° overnight.

Fractionation.—The partial precipitation method was used in all the fractionations. The solvent used was toluene and the non-solvent was methanol. Fractionation was carried out by addition of the precipitant to a 0.05% polymer solution at 30°. The precipitated gel phase, after being separated from the solution phase, was dissolved again in toluene and then poured into a large amount of cold methanol. The precipitated copolymers were then filtered, washed and dried under vacuum at 60° to constant weight. Viscosities were measured with a Ubbelholde type viscometer at 30° in xylene.

Determination of Radioactivity.—The determination of radioactive carbon was carried out by means of the proportional counting technique.[23-26] The radioactive sample was first burned to give carbon dioxide and this was treated with barium hydroxide solution and isolated as solid barium carbonate. The weight of the carbonate was determined and its activity measured as gaseous carbon dioxide, which was trapped in a Bernstein-Ballantine tube upon acidification of the barium carbonate.

Acknowledgment.—We gratefully acknowledge the support given by a grant-in-aid from the Shell Development Co.

BROOKLYN 1, N. Y.

---

(15) R. P. Linstead, J. A. Elridge and M. Whalley, "A Course in Modern Techniques of Organic Chemistry," Butterworth's Scientific Publications, London, 1955, p. 80.

(16) G. A. Rapp, V. A. Raaen and A. J. Weinberger, THIS JOURNAL, **75**, 3694 (1953).

(17) A. V. Grosse and S. Weinhouse, *Science*, **104**, 402 (1946); *C. A.*, **41**, 2009 (1947).

(18) S. Ruben, M. B. Allen and R. Nahinsky, THIS JOURNAL, **64**, 3050 (1942).

(19) D. T. Mowry, M. Renoll and W. F. Huber, *ibid.*, **68**, 1105 (1946).

(20) R. H. Boundy and R. F. Boyer, "Styrene, Its Polymers, Copolymers and Derivatives," Reinhold Publishing Corp., New York, N. Y., 1952, p. 767.

(21) C. G. Overberger, C. Frazier, Y. Mandelman and H. F. Smith, THIS JOURNAL, **75**, 3326 (1953).

(22) All the filtrates containing radioactive residues were collected in a separate bottle for appropriate disposal.

(23) D. D. Van Slyke, R. Steele and G. Plazin, *J. Biol. Chem.*, **2**, 769 (1951).

(24) M. Calvin, "Isotope Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 93.

(25) J. B. Niederl and V. Niederl, "Micro Methods of Quantitative Organic Analysis," second edition, John Wiley and Sons, Inc., New York, N. Y., 1941, Chapter V.

(26) J. Steigman, 5th Interim Report to U. S. Army Signal Corps on High Value Insulators, 1952.