for the nitrosamine had disappeared and that all those in the product, except for weak lines at 9.4, 9.7 and 13.8 μ, could be attributed to either the amine or the nitramine.

A larger scale preparation using 13 g. of nitrosamine was attempted in hopes of actually isolating pure nitramine but gave much poorer results, possibly because of a lower concentration of CF_3COOH (1.8 g. of H_2O_2 in 130 g. of $(CF_3CO)_2O$) and a longer reaction time. The amine was removed by washing with dilute alkali, but the final product, although giving all infrared peaks for $(CF_3)_2NNO_2$, had a mol. wt. range of 185–209, amounted to only 3 g., and was obviously impure.

Acknowledgment.—The authors are indebted to Dr. Wallace S. Brey for the n.m.r. spectra.

GAINESVILLE, FLA.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM & HAAS CO.]

Anionic Copolymerization: The Inability of the Poly-(Methyl Methacrylate) Anion to Initiate the Polymerization of Styrene[1]

BY ROGER K. GRAHAM, DAVID L. DUNKELBERGER AND WILLIAM E. GOODE

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Previous studies of the anionic copolymerization of styrene and methyl methacrylate have been conducted under reaction conditions which permit no distinction between the propagation and initiation reactions. When 9-fluorenyllithium is used as the initiator, it reacts only with the methyl methacrylate, and since it is shown that the poly-(methyl methacrylate) anion is not basic enough to initiate the polymerization of styrene, *no* styrene is detected in the polymer, regardless of the temperature, solvent or monomer ratios. The implications of this work as applied to previous anionic copolymerizations and block copolymerizations are discussed.

Landler[2] has reported reactivity ratios for the anionic copolymerization of styrene and methyl methacrylate which indicate a small but significant tendency for the poly-(methyl methacrylate) anion to react with styrene. These values, however, were derived by strict application of the classical free-radical copolymerization equation to compositional data obtained from copolymerizations initiated by sodium in liquid ammonia. It is the purpose of the present paper to emphasize the limitations of such a method in anionic copolymerizations and to demonstrate conclusively the inability of the poly-(methyl methacrylate) anion to react with styrene.

Experimental

Materials.—Methyl methacrylate (Rohm & Haas Co.) was obtained as a freshly-distilled, uninhibited sample which was stored under nitrogen at −20° in brown bottles and used within five days. Styrene (Dow, polymerization grade) was freshly distilled before use. Toluene was refluxed and the water azeotrope removed; it was then stored under nitrogen and over calcium hydride. Tetrahydrofuran (du Pont) was treated with lithium aluminum hydride until bubbling had ceased and then distilled under nitrogen. In later experiments, it was flash-distilled on a vacuum line from lithium aluminum hydride onto freshly cut sodium and naphthalene and stored under nitrogen; when needed, samples were flash-distilled from this stock directly into the reaction vessel. Fluorene (Eastman, practical grade) was extracted several times with methanol and then recrystallized thrice from hexane.

***n*-Butyllithium.**—Butyllithium was prepared from *n*-butyl bromide (Eastman) and a slight excess of lithium shot (Lithium Corp. of America) in petroleum ether (b.p. 30–78°) as solvent.[3] The material was centrifuged and the supernatant liquid withdrawn with a syringe and stored in serum-capped bottles under nitrogen at −20°. Several preparations were used; the molarity ranged from *ca.* 1.5 to *ca.* 3 *M*.

9-Fluorenyllithium.—For the polymerizations in toluene and in liquid ammonia in which only a small amount of tetrahydrofuran was used, a stock solution of fluorenyllithium prepared in tetrahydrofuran from fluorene and lithium[4] was used. Polymerizations in tetrahydrofuran and in toluene utilized fluorenyllithium prepared *in situ* from butyllithium and fluorene (10% excess). The reaction in tetrahydrofuran was rapid and required only stirring at room temperature for 30 minutes. The preparations in toluene required reflux for at least one hour. The initiator is only slightly soluble in toluene at room temperature, but is solubilized on addition of monomer. Polymerizations of methyl methacrylate initiated by fluorenyllithium in tetrahydrofuran indicate that the excess fluorene has no effect on the molecular weight.

9-Fluorenylsodium.—Amylsodium was prepared by the method of Morton[5] utilizing Ultracene (a petroleum fraction boiling at 170–250°, supplied by Atlantic Refining Co.) as solvent. To a slurry of 0.2 mole of amylsodium in 500 ml. of Ultracene under nitrogen was added 36 g. (0.217 mole) of fluorene. The mixture was refluxed for 2 hours, stirred overnight, and refluxed further for four hours. The final color was a milky reddish-brown; the initiator was a suspension, which was transferred to the reaction flask with a syringe and wide-bore (no. 14) needle.

Polymerizations under Nitrogen.—In a 200-ml. Mini-Lab reaction flask equipped with nitrogen inlet, serum cap, reflux condenser and mechanical stirrer was prepared a solution of 0.332 g. (0.002 mole) of fluorene in 89.3 ml. of toluene (Table I, line 8). The solution was freed of oxygen by bubbling through it a stream of Airco pre-purified nitrogen for 10 minutes, and 0.62 ml. of a 2.9 *M* solution of *n*-butyllithium in hexane (0.0018 mole) was added through the serum cap from a syringe. The slightly yellow solution was heated at reflux for one hour then cooled to −50° to produce a suspension of fluorenyllithium. The flask was swept thoroughly with nitrogen while the reflux condenser was replaced with a pressure-equalizing dropping funnel containing a mixture of methyl methacrylate (10.0 g., 0.10 mole) and styrene (10.4 g., 0.10 mole), which mixture had been thoroughly flushed with nitrogen before addition to the initiator. With stirring, the monomers were added over a period of two minutes; the initiator appeared to dissolve; the solution became viscous and within 30 minutes had become a tight gel so that it could be stirred only with difficulty. After 1.5 hours the reaction mixture was terminated by addition of 2 ml. of methanol, diluted with chloroform, and the polymer precipitated into an excess of petroleum ether.

Essentially the same procedure was used for experiments with fluorenyl-sodium and fluorenyllithium-tetrahydrofuranate in toluene, except that the initiator was added directly through the serum cap with a syringe. In several cases where high concentrations of styrene were used, only enough

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[1] Presented before the Division of Polymer Chemistry at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[2] Y. Landler, *Compt. rend.*, **230**, 539 (1950). In liquid ammonia at −50° with sodium metal, r_1 (styrene) = 0.12 ± 0.05, r_2 (methyl methacrylate) = 6.4 ± 0.5.

[3] H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

[4] H. Gilman and R. D. Gorsich, *J. Org. Chem.*, **23**, 550 (1958).

[5] A. A. Morton, *et al.*, THIS JOURNAL, **72**, 3788 (1950).

toluene was used to prepare the initiator. The styrene was was then added and stirred with initiator for 10 minutes; finally the methyl methacrylate was added. Control experiments in which only styrene was added were similar, except that methanol was used as precipitant. No polymer was found from these reactions.

Polymerization in Liquid Ammonia.—The reaction was carried out in a 2-l. resin flask equipped with nitrogen and ammonia inlets, high-speed stirrer, serum cap, dropping funnel and gas outlet. Anhydrous ammonia (Pennsalt Chemicals, 1 l.) was condensed into the flask which had previously been thoroughly dried and flushed with nitrogen. The solution of fluorenyllithium in tetrahydrofuran (0.0016 mole in 10 ml.) was added from a syringe through the serum cap and the temperature raised to −35°. To the light yellow solution was added a mixture of 0.514 mole of styrene and 0.326 mole of methyl methacrylate over a period of 30 seconds. Polymer formed immediately, and the color changed to a milky orange. After stirring for 1 hr. at −35°, ammonium chloride was added to terminate the reaction, whereupon the color was discharged. The polymer was filtered, washed with water, water–methanol, methanol and finally with petroleum ether in a Waring blendor. After air-drying, it was dissolved in chloroform, filtered, and precipitated by pouring into stirred boiling hexane. The procedure was repeated to remove all residual fluorene and styrene monomer (Table I, line 6).[6]

Polymerizations in Vacuo.—Preparations were done in a 500-ml., 3-necked flask (containing a glass-enclosed magnetic stirrer) attached directly to the high-vacuum line. Stopcocks were provided through which initiator solution could be added from a syringe under a nitrogen atmosphere and the solution again degassed, and also for the addition of degassed monomer from ampoules. In a typical experiment (Table I, line 11) 2.7 ml. of a 0.72 *M* suspension of fluorenylsodium in Ultracene (0.019 mole) was added under nitrogen to the reaction flask. The flask was then cooled in liquid nitrogen, the contents degassed, and 90 ml. (0.78 mole) of styrene was distilled into the reaction vessel from a graduated flask containing a magnetic stirring bar to prevent bumping. The styrene had previously been allowed to stand over calcium hydride for three hours. Methyl methacrylate (0.10 mole) was distilled in a similar manner from calcium hydride into an ampoule equipped with a vacuum stopcock. The apparatus was warmed to 0° and the methyl methacrylate then added. After 2 hr., 2 ml. of methanol was added and the polymer precipitated.

Purification and Analysis of the Polymers.—After termination of the polymerization, the polymers were precipitated by slow addition of the solution to a stirred tenfold excess of petroleum ether (b.p. 30–78°), filtered, and washed. (Polystyrene, if present in the polymer, would be precipitated by this treatment.) The weight of polymer formed was determined. If the mixture was very viscous or gelled, the precipitation was carried out in a stainless steel Waring Blendor equipped with an explosion-proof motor. The polymers were then washed for 3 hr. with a mixture of 50 parts methanol, 50 parts water and 10 parts concd. HCl to remove ionic impurities, followed by a final water wash. A small sample was dried, redissolved in chloroform, filtered, and the polymer reprecipitated into petroleum ether for an analytical sample.

Molecular weights were estimated from the reduced specific viscosity, determined in benzene solution at 25° at a concentration of 2 g./l. The relationship[8]

$$[\eta] = 5.2 \times 10^{-5} \bar{M}_v^{0.76}$$

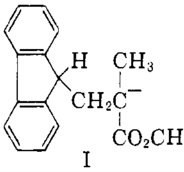
was used; since only an approximation of the molecular weight was desired, the value of the reduced specific viscosity was used as the intrinsic viscosity. The actual values of the viscosity–average molecular weight are probably 10% lower than the reported values.

The styrene content was determined by elemental analysis and by the infrared absorption at 14.35 μ, which should detect 0.1% styrene, as determined from spectra of polymer mixtures. Spectra were obtained using a Perkin–Elmer model 21 double beam infrared absorption spectrometer; polymer films were deposited from benzene solution onto AgCl plates and were baked at 135° for 1 hr. Ultraviolet analysis could not be used to determine the styrene content[9] of these polymers because of the intense absorption of the fluorenyl end group.[10] The infrared absorption was also used to determine the *J*-value, which is a measure of the chain structure of the poly-(methyl methacrylate) formed.[11] Details of the effect of solvent and initiating species on polymer structure[12] and the determination and interpretation of *J*-values[11] will appear in future publications; the variation in *J*-value and in tacticity of the polymers formed has no effect on the incorporation of styrene.

Results and Discussion

The accurate interpretation of anionic copolymer composition data requires an appreciation of the nature of the initiation reaction. It is necessary to ensure that the incorporation of each monomer occurs by means of the propagation reactions rather than through some peculiar consequence of the initiation step. This condition can be met, at least for the present system, by proper choice of the initiator.

As a part of their study of the mechanism of the anionic polymerization of styrene, Wooding and Higginson[7] observed a correlation between the base strength of an initiator and the ability of that initiator to polymerize various vinyl monomers. Thus relatively weak bases, such as methoxide ion, were shown to initiate the polymerization of acrylonitrile; styrene, a much weaker Lewis acid, requires initiators of correspondingly higher basicity. The fluorenyl anion is sufficiently basic to initiate the polymerization of methyl methacrylate but is unreactive toward styrene. If, therefore, 9-fluorenyllithium is used as an initiator for the copolymerization of styrene and methyl methacrylate, all chains must form from the anion I. It is difficult to conceive of termination or transfer processes by which styrene can enter the chain, so that any styrene found in the polymer must be incorporated by the propagation reactions.



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Since 9-fluorenyllithium does not react with styrene and since anion I cannot be a stronger base than the fluorenyl anion, then anion I also should not add to styrene. The products should contain *no* styrene, even at very high charge ratios of styrene monomer to methyl methacrylate. This prediction is verified by the experimental results shown in Table I.

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(6) Wooding and Higginson[7] reported that fluorenylpotassium (from fluorene and potassium amide) in liquid ammonia would not initiate the polymerization of methyl methacrylate. In these laboratories, polymer has been formed when the fluorenyllithium is introduced as a solution in an ether solvent or when solid fluorenyllithium is dissolved directly in liquid ammonia (W. H. Snyder, private communication).

(7) N. S. Wooding and W. C. E. Higginson, *J. Chem. Soc.*, 774 (1952).

(8) T. G Fox, unpublished work from these laboratories.

(9) K. F. O'Driscoll, R. J. Boudreau and A. V. Tobolsky, *J. Polymer Sci.*, **31**, 115 (1958).

(10) D. L. Glusker, E. Stiles and B. Yoncoskie, paper presented before the Division of Polymer Chemistry at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959; Abstracts, p. 14-S.

(11) A. Spell, paper presented before the Society for Applied Spectroscopy, New York, N. Y., November, 1958.

(12) T. G Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell and J. D. Stroupe, THIS JOURNAL, **80**, 1768 (1958).

TABLE I

PREPARATION AND ANALYSIS OF POLYMERS PRODUCED FROM STYRENE–METHYL METHACRYLATE MIXTURES

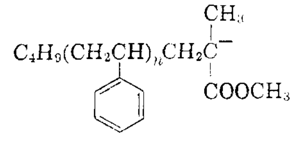
Initiator, m./l.	Solvent	St, m./l.	MMA, m./l.	Temp., °C.	Time of reacn., hours	Conv.,[a] %	$\bar{M}_v \times 10^{-5}$ [b]	Carbon,[c] %	Infrared: Styrene[d]	Infrared: J-Value[e]
FlLi, 0.02: THF, 0.4	Tol.	1.0	1.0	0	2.5	53	10.5	60.10	None	47
Same	None	6.7	2.0	0	2	64	10.9	59.75	None	52
Same	Tol.	2.0	None[f]	Range[g]	6.5	No polymer formed				
FlLi, 0.005	THF	1.0	0.5	−78	0.5	100	0.17	59.98	None	110
Same	THF	1.0	None[f]	−78	1.5	No polymer formed				
FlLi, 0.0015	NH_3	0.51	0.33	−35	1	97	0.69	59.90	None	107
FlLi, 0.02	Tol.	1.0	1.0	0	2	28	2.3	60.15	None	35
Same	Tol.	1.0	1.0	−50	1.5	68	10.4	60.06	None	34
Same	None	7.2	1.0	−50	1	76	9.6	59.78	None	..
FlLi, 0.001	None	8.1	0.25	−30	2	30	1.6	60.11	None	33
FlNa, 0.01	None	7.8	1.0	0	2	69	0.56	60.01	None	42
Same	Tol.	1.0	None[f]	0, 30	3	No polymer formed				
BuLi, 0.02[h]	None	8.2	0.5	30	5	48	0.78	60.93, 60.66	*ca.* 1%	..
BuLi, 0.02: THF, 0.02[h]	None	8.2	0.5	0	4	39	0.85	60.58, 60.26	*ca.* 1%	..

St = styrene; MMA = methyl methacrylate; FlLi = 9-fluorenyllithium; FlNa = 9-fluorenylsodium; BuLi = butyllithium; Tol. = toluene; THF = tetrahydrofuran. [a] Conversion based on MMA charged. [b] Viscosity–average molecular weight estimated from the reduced specific viscosity in benzene solution. [c] Pure poly-(methyl methacrylate) contains 59.98% carbon; pure polystyrene contains 92.26% carbon. [d] None ≦0.1%. [e] Measurement of chain structure. [f] Experiments run in the absence of methyl methacrylate to confirm[2] inability of initiator to polymerize styrene. [g] Varied from −75° to +60°; no polymer found at any temperature. [h] Performed to confirm[9,13,14] that some styrene is incorporated when an initiator capable of reaction with both monomers is used.

We find *no* detectable styrene (less than 0.1%) in polymer formed from initial molar ratios of styrene:methyl methacrylate as high as 32.4:1, even at high conversion of methyl methacrylate to polymer. It should be stressed that the reactivity ratios quoted[2] for anionic copolymerization would predict the initial polymer formed from this particular system to contain 80 ± 3% styrene. It seems unlikely that the exclusion of styrene is due to a selective solvation of the growing polymeric anion by methyl methacrylate,[15] since identical results are found in toluene, tetrahydrofuran and liquid ammonia as solvents, and with fluorenyllithium and fluorenylsodium as initiators. The temperature of polymerization also does not affect the results, no styrene being incorporated either at −78° or at 0°. It should also be noted that no styrene is incorporated regardless of the stereospecificity of the polymerization of the methyl methacrylate, which is affected by the solvent. Thus, polymers prepared from styrene–methyl methacrylate mixtures in toluene with fluorenyllithium appear to be identical with isotactic[16] homopolymers of methyl methacrylate prepared under similar conditions, whereas those prepared in tetrahydrofuran at −78° from a mixture of monomers are similar to (presumably) syndiotactic homopolymers of methyl methacrylate prepared with fluorenyllithium in 1,2-dimethoxyethane at −60°.[12]

The present results disagree with those of Landler.[2] Several difficulties can be found with his experimental system. The polymers are of very low molecular weight, so that small amounts of styrene introduced through any reaction other than propagation could affect the results strongly. Secondly, it has recently been shown by O'Driscoll, Tobolsky, *et al.*,[9,13] that certain initiators which act by an electron-transfer mechanism to form radical-ions can under certain experimental conditions introduce detectable amounts of both monomers into the copolymer by a concurrent radical copolymerization process. Although such a radical propagation is unlikely in liquid ammonia,[17,18] it would be preferable to utilize an initiator which functions exclusively as an anion.[19]

Most important, sodium in liquid ammonia (and all other initiators which have been used in quantitative studies of anionic copolymerization[20]) can initiate the polymerization of either of the monomers separately. Depending on the relative rates of initiation, the initial monomer ratios, and the nature of the initiator and reaction medium, both monomers may become incorporated, but by formation of a block copolymer rich in the more reactive monomer. More specifically, the small amount of styrene found by us and by others[9] in the butyllithium-initiated copolymerization of styrene–methyl methacrylate mixtures is probably introduced as



$$C_4H_9(CH_2\underset{C_6H_5}{CH})_nCH_2\overset{CH_3}{\underset{COOCH_3}{C^-}}$$

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(13) A. V. Tobolsky, D. J. Kelley, K. F. O'Driscoll and C. E. Rogers, *J. Polymer Sci.*, **28**, 426 (1958).

(14) K. F. O'Driscoll and A. V. Tobolsky, *ibid.*, **31**, 123 (1958).

(15) Selective solvation of the polymeric anion by a single monomer has been postulated by G. V. Rakova and A. A. Korotkov (*Doklady Akad. Nauk. S.S.S.R.*, **119**(5), 982 (1958)) to explain the unusual reactivity ratios for the butyllithium-initiated copolymerization of isoprene and butadiene and of butadiene and styrene in hexane.

(16) J. D. Stroupe and R. E. Hughes, THIS JOURNAL, **80**, 2341 (1958).

(17) N. S. Wooding and W. C. E. Higginson, *J. Chem. Soc.*, 1178 (1952).

(18) C. G. Overberger, E. M. Pearce and N. Mayes, *J. Polymer Sci.*, **34**, 109 (1959).

(19) It has here been tacitly assumed that organolithium compounds are initiators of *anionic* polymerization, in accordance with their general behavior in organic reactions.

(20) G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, Inc., New York, N. Y., 1954, p. 423.

where n is small, such an anion being unable to react further with styrene monomer. The possibility that styrene is introduced into these polymers only through the initiation step does not seem to have been clearly recognized previously.[21]

The reactions which apply to the anionic copolymerization of styrene and methyl methacrylate are shown below, where M_1 is styrene, M_2 methyl methacrylate, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The present work indicates that reaction 3 does not occur, and that, therefore, $r_2 >> 1$; r_1 cannot be determined for polymerizations initiated with fluorenyllithium, as neither of the reactions which determine its value occur. Landler[2,22] had earlier concluded that there is no alternating effect in anionic copolymerization. All values of the product r_1r_2 were essentially unity, or $k_{11}/k_{12} = k_{21}/k_{22}$, which would mean that the relative reactivities of the two monomers toward different terminal ionic units are the same and that the nature of the carbanion is not important. We conclude from the present work and from the results of Higginson and Wooding[7] that for the anionic polymerization of a styrene–methyl methacrylate mixture (and probably for all systems where the monomers differ greatly in polarity), the nature of the anionic species, both initiating and propagating, is *highly* important. The polymers of Landler are probably not true copolymers, but instead block copolymers (or polymer mixtures), and his experimental results cannot be used to calculate true reactivity ratios for the propagation steps in anionic copolymerization. Interpretations of "anionic copolymerizations"[20,22,23] should be revised in view of these findings.

$$-M_1^- + M_1 \xrightarrow{k_{11}} -M_1^- \tag{1}$$

$$-M_1^- + M_2 \xrightarrow{k_{12}} -M_2^- \tag{2}$$

$$-M_2^- + M_1 \xrightarrow{k_{21}} -M_1^- \tag{3}$$

$$-M_2^- + M_2 \xrightarrow{k_{22}} -M_2^- \tag{4}$$

Szwarc[24] has reported that when methyl methacrylate is polymerized in tetrahydrofuran with sodium–naphthalene complex as initiator and styrene is then added, no polymerization of the styrene is observed. The result is cited as one of the proofs that the poly-(methyl methacrylate) anion is self-terminating in such systems. However, such a result would be expected from the present work and has no bearing on the proof of existence of the "living polymer" anion of poly-(methyl methacrylate), especially as we have shown[1] that the polymeric methyl methacrylate anions are still active even after the addition of styrene. Szwarc[24] has also cited as further proof of the self-termination of the poly-(methyl methacrylate) anion the observation that it will not initiate polymerization of more added methyl methacrylate. Evidence that these anions are indeed long-lived and capable of initiating further polymerization of methyl methacrylate has recently been obtained[1,10] and will be discussed in detail in future publications.

Acknowledgments.—We are grateful to Mr. J. E. Moore, Mr. F. Zimmerman and Dr. F. H. Owens for preparation of initiators, Mr. J. H. Rorapaugh for carrying out the polymerization in liquid ammonia, Dr. Aldenlee Spell for infrared determinations and interpretations, and Mr. C. W. Nash for elemental analyses. The advice of Dr. D. L. Glusker is gratefully acknowledged.

BRISTOL, PENNA.

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[21] O'Driscoll and Tobolsky[13] have described the n-butyllithium-initiated copolymerization of an equimolar mixture of these monomers as a "classical anionic polymerization in which the less electro-negative methyl methacrylate polymerizes preferentially to such an extent that little or no styrene (less than 1%) is discernible in the polymer, regardless of the solvent used." These authors have since shown (*J. Polymer Sci.*, **37**, 363 (1959)) that with butyllithium at high ratios of styrene to methyl methacrylate, quite appreciable amounts of styrene are incorporated into low conversion polymers. We find little styrene in similar polymerizations carried to higher conversions (Table I, lines 13–14), which is consistent with the above postulates.

[22] Y. Landler, *J. Polymer Sci.*, **8**, 63 (1952).

[23] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 227.

[24] M. Szwarc and A. Rembaum, *J. Polymer Sci.*, **22**, 189 (1956).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Preparation of Silyl- and Germylmetallic Compounds

BY M. V. GEORGE, DONALD J. PETERSON AND HENRY GILMAN

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Triphenylsilyllithium was prepared by the reaction of chlorotriphenylsilane and lithium in solvents like tetrahydrofuran, 2-methyltetrahydrofuran and tetrahydropyran. Similarly, dimethylphenylsilyllithium, triphenylsilylpotassium, triphenylsilylrubidium, triphenylsilylcesium, tri-*o*-tolylsilyllithium and tri-*o*-tolylsilylcesium were prepared by the treatment of the respective chlorosilanes with corresponding alkali metals. Hexaphenyldisilane was the product when either sodium or magnesium was treated with chlorotriphenylsilane. The reaction of bromotriphenylgermane and lithium gave a fair yield of triphenylgermyllithium. Some tentative observations concerning the probable course of the reaction are made.

The first report of the successful preparation of a triarylsilylmetallic compound was the formation of triphenylsilylpotassium by the cleavage of triphenyl-(phenylisopropyl)-silane with sodium–potassium alloy.[1] Shortly thereafter[2] an improved procedure was reported for the preparation of triphenylsilylpotassium, by the cleavage of hexaphenyldisilane with sodium–potassium alloy in diethyl

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[1] R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

[2] H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951); H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *ibid.*, **74**, 561 (1952); H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953); A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 278 (1954).