Journal of Organometallic Chemistry, 122 (1976) 151—157

THE PREPARATION OF POLYMERIC ORGANOPHOSPHORUS LIGANDS FOR CATALYST ATTACHMENT

Robert H. Grubbs and Shiu-Chin H. Su

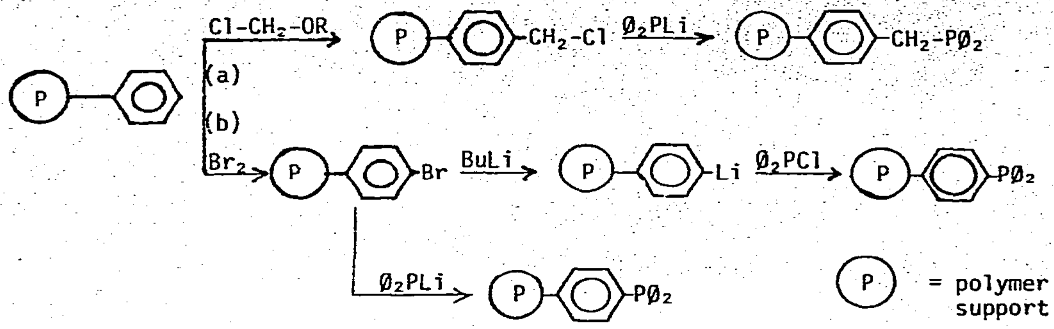
Department of Chemistry
Michigan State University
East Lansing, MI 48824

(Received June 14th, 1976)

Summary

Polystyrene crosslinked with divinylbenzene (2 or 20%) was converted to polystyrene-lithium by treatment with a 1:1 complex of butyl-lithium-tetramethylethylenediamine in cyclohexane. The lithiated polymer was allowed to react with chlorodiphenylphosphine to produce polystyryldiphenylphosphine. The radial distribution and percent substitution of phosphine could be controlled over a wide range by controlling the reaction time and temperature. Rhodium (I) hydrogenation catalysts could be prepared from these polymeric ligands.

The chemistry of homogeneous catalysts attached to polymer supports has received considerable attention in the last few years.[1] Polystyrene has served as the support in most of these studies. Two approaches to attaching the linking ligand, in most cases a phosphine, have been used. They are (a) chloromethylation[2] followed by a reaction of the chloromethylation product with a nucleophilic reagent, and (b) ring bromination followed by treatment with an alkyllithium.[3,4]



The first of these procedures suffers from a number of disadvantages. Chloromethyl ethers are suspected carcinogens and the chloromethyl groups may undergo quaternization reactions with the added phosphine. Furthermore, the phosphine, a benzyldiphenylphosphine equivalent, resulting from approach (a) gives different catalysts than does triphenylphosphine, the major ligand used for homogeneous catalysts.

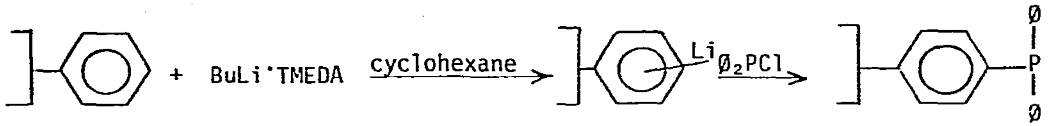
The bromination reaction required for the second procedure has proven difficult to control to give reproducible results, and the catalysts can only be removed by a long work-up procedure. Also, when used with highly cross-linked polymers, the vinyl groups remaining after polymerization take up bromine.

In order to overcome these problems, we have developed an easily-controlled, convenient route to functionalized polystyrene polymers.

There have been many reports of the direct lithiation of aromatic rings by mixtures of alkyllithium and amines.[5] Broadus reported high yields of ring substitution in the reaction of i-propylbenzene with butyllithium-tetramethylethylenediamine (BuLi·TMEDA).[6] Evans carried out a study of the kinetics and position of lithiation of polystyrene with n-BuLi·TMEDA.[7a] His work indicates a high degree of ring lithiation with a ratio of meta to para isomers of 2:1. Recently, Leznoff reported the lithiation of cross-linked polystyrenes as a means of attaching organic reagents to polymers.[7b] These results suggested that this reaction should be useful for the easy direct preparation of the polymers required for the support of transition metal catalysts. Therefore, we have carried out a series of reactions designed to explore the factors which control the percentage substitution and the distribution of reaction products in the reaction of BuLi·TMEDA with 2 and 20% divinylbenzene-styrene copolymers.

Results and Discussion

Samples of polystyrene copolymer were treated with butyllithium-tetramethylethylenediamine in cyclohexane. At the end of the reaction period, the polymer was separated, washed with more solvent, and then allowed to react with diphenylchlorophosphine.



At the end of the reaction, the polymer was purified by washing and analyzed for phosphorus. The distribution of phosphorus in a sample from each reaction was determined by electron-microprobe analysis of a cross section of random polymer beads.[8] By sweeping the electron beam across the cross sectional surface of the bead with the x-ray detector of the apparatus tuned for phosphorus, a radial distrubution of phosphorus in the polymer bead can be determined from the intensity of the emission from each point in the cross sectional surface.

The variation of the radial distribution of phosphorus and the percent phosphorus substitution has been examined as a function of a number of variables. The results of a study in which time and the relative ratios of reactants were varied are presented in Table I. In this work, a factor Ic is used to indicate the ratio of the intensity of radiation at the center of the bead divided by the maximum intensity. Since the reactions of the polymeric group progress from the surface into the center, this factor varies between 0 and 1.0. An Ic value of 0 indicates that all the phosphorus was near the outer edge of the bead and a value of 1 was obtained for beads which contained the phosphorus evenly distributed throughout the polymer. The beads used were 425-500 microns in diameter. Beads with a low Ic contained the majority of the phosphorus in the first 100-150 microns from the surface.

As can be seen from Table I, this reaction provided a route to polymers

Table I

% Crosslinkage	% n-BuLi	Time (hr)	Temp (°C)	Swelling[a]	% Substitution[b]	meq/ g beads[c]	Ic[d]
1.8	100	4	81	None	13.29	1.030	--
1.8	100	1	60	None	9.87	0.8039	0.10
1.8	100	1	60	24 hrs.	11.20	0.8943	0.15
1.8	100	8	60	None	15.02	1.1398	0.30
1.8	100	12	60	None	11.97	0.9493	--
1.8	100	24	60	None	15.62	1.1753	0.13
1.8	10	1	60	None	3.82	0.3422	0.18
1.8	10	12	60	None	11.78	0.9330	0.40
1.8	10	19	60	None	0.51	0.049	--
1.8	10	24	60	None	1.21	0.113	--
1.8	10	43	60	None	5.24	0.459	1.00
1.8	10	48	60	15 min	5.57	0.4876	0.21
1.8	40	3	60	18 hr (60°)	11.73	0.9298	0.37
1.8	50	22	3 hr (60°)	24 hr (60°)	8.02	0.6715	0.28
1.8	20	18	5 hr (60°)	24 hr (60°)	8.41	0.7006	0.36
1.8	100	48	R.T.	15 min			0.723
20	100	4	81	None	9.557	0.7819	--
20	100	40	60	24 hr	8.50	0.7070	1.0
20	100	38	81	None	12.54	0.9334	--
20	100	48	R.T.	15 min	--	--	1.0

---

[a] Time and temperature of treatment of dry beads with cyclohexane before the addition of the reagents

[b] Calculated from equation % sub. = $(M \times 10^{-1})/[1 - M \times 288.3)]\ 1/104.7] + M \times 10^{-3}$, M = meq/g.beads

[c] meq P/gm bead = $\frac{\%P}{30.974} \times 10$, %P from elemental analysis

[d] Ic defined in text

of a wide variety of substitution percentages, from 0.5 to 15.6, and a wide variety of distribution, Ic = 1 to 0.1. Cyclohexane is a poor solvent for polystyrene and requires a long period for maximum swelling to be reached. It was observed that heating the beads in cyclohexane for an extended period before the reagents were added increased the rate of the reaction.

The data in the tables indicate that the percent substitution increases to a maximum at around 20 to 24 hours, and then falls off. This is apparently due to the slow decomposition of TMEDA by the alkyllithium reagents. The extended heating does result in a more even distribution of the reagents throughout the polymer.

The reaction of 20% macroreticular divinylbenzene-styrene copolymer under similar conditions always gave an Ic of near 1 and gave high substitutions.

Selected samples of the phosphinated polymer were equilibrated with tris (triphenyl phosphine)chlororhodium, and the attached catalysts were then used to reduce various olefins. One batch prepared from polymer with an Ic of .368 and a P/Rh ratio of 4.29 gave a rate of reduction of cyclohexene of 7.65 ml/min/mmol of Rh. This rate is better than that observed with a similar batch of material prepared by the bromination route. For example, one sample prepared by the bromination route with a P/Rh ratio of 4.2 reduced cyclohexene at a rate of 2.8 ml/min/mmol Rh.[9]

Experimental

Materials

The divinylbenzene-styrene copolymers were a gift of the Dow Chemical Company. A sample of 25-60 mesh 2% divinylbenzene-styrene copolymer (= 1.8% crosslinked) was separated by the use of sieves. The 35-32 mesh (425-500μ) fraction was used for the experiments. The selected polymer was refluxed with a large excess of benzene for 24 hours, filtered, and then washed with 1:0, 3:1, 1:1, 1:3, and 0:1 benzene-methylene chloride mixtures. The purified polymer was dried for 24 hours at 80° and 10 mm before use. N,N,N',N'-tetramethylethylenediamine (TMEDA) and n-butyllithium (1.6 M in hexane) were purchased from Aldrich Chemical Company. The TMEDA was dried over molecular sieves (4A) and refluxed with sodium for 2 hours before distilling under nitrogen. The diphenylchlorophosphine was purchased from Pressure Chemical Company and distilled before use. Tris(triphenylphosphine)chlorohodium (I) was prepared by the procedure of O'Conner and Wilkinson,[10] from trichlororhodium (III) trihydrate and recrystallized triphenylphosphine. All reactions were carried out under a nitrogen atmosphere.

Lithiation of Polystyrene

A 3 g sample of the purified polymer was suspended in 20 ml. of freshly distilled cyclohexane. The mixture was heated to 60° for the required swelling period and then the required amount of TMEDA and butyllithium (1.6M in hexane) was added by means of a syringe. This reaction mixture was heated for the required time period. After cooling, the polymer was washed three times with cyclohexane and dry, oxygen-free tetrahydrofuran (THF). The solvent was removed after each wash by the use of a gas dispersion tube.

Phosphination

The lithiated polymer from above was suspended in 50 ml. of THF and 6 ml. of diphenylchlorophosphine was added with a syringe. After stirring for two days, the solution was removed with a gas dispersion tube and the polymer was washed with 30 ml portions of:

(a) degassed THF (3 times), (b) 10% NH_4Cl (1:1 THF:H_2O) (3 times), (c) 1:1 THF:H_2O (3 times), (d) THF, (e) 3:1, 1:1, and 1:3 THF:benzene, and (f) benzene.

Analysis

The percent phosphorus was determined by elemental analysis by Gailbraith

Laboratory. Microprobe spectra were determined on an American Research Laboratories EMX-SM Microprobe. X-ray intensities were measured from PKα line emission. Random beads were sliced under a microscope and mounted in the apparatus on graphite disks using the adhesive from freezer tape. The plates were covered with a thin film of graphite before being scanned.

Metalation

A 9.6 g. sample of phosphinated 2% polystyrene containing 0.957 meq of P/g. and with an Ic of 0.37 was equilibrated with 2.76 gm. of tris(triphenylphosphine)chlororhodium (I) in 100 ml of benzene for 16 days. The polymer was washed with benzene until no coloration of the rinses was noted. The polymer contained 0.167 meq Rh/g. Cyclohexene [1M] was reduced in benzene solution at atmospheric pressure by procedures published earlier.[11]

References

1. J.C. Bailar, Jr., Cat. Rev. Sci. Eng., 10(1), (1974), 17.
   Z.M. Michalska and D.E. Webster, Platinum Metals Review, 18, (1974), 65.

2. (a) S.V. McKinley and J.W. Rakshys, Jr., U.S. Patent 3,708,462, (1973) C.A. 78, 8 5410; (b) R.H. Grubbs and L.C. Kroll, J. Amer. Chem. Soc., 93, 3062 (1971); (c) W. Haag and D. Whitehurst, Catalysis, Vol. 1, J.W. Hightower Ed, North Holland, New York, 1973.

3. J.P. Collman, L.S. Hegedus, M.P. Cooke, J.R. Norton, G. Dolcetti, and D.N. Marquardt, J. Amer. Chem. Soc., 94, (1972), 1789.

4. C.U. Pittman and L.R. Smith, J. Amer. Chem. Soc., 97, (1975), 341.

5. A.J. Chalk, Polymer Lett., 6, (1968), 649.

6. C.D. Broadus, J. Org. Chem., 35, (1970), 10.

7. (a) D.C. Evans, L. Phillips, J.A. Barrie, and M.H. George, J. Poly. Sci., Poly. Lett. Ed., 12 (1974), 199; (b) T.M. Fylesand, and C.C. Leznoff, Can. J. Chem., 54, (1976), 935.

8. R.H. Grubbs and E.M. Sweet, Macromol., 8, (1975), 241.

9. R.H. Grubbs and E.M. Sweet, unpublished results.

10. C. O'Conner and G. Wilkinson, J. Chem. Soc. A, (1968), 2665.

11. R.H. Grubbs, L.C. Kroll, and E.M. Sweet, J. Macromol. Sci. Chem. A7, (1973), 1047.