Notes

Characterization and Analysis of Reactive Organometallic Polymers

DAVID E. BERGBREITER* and JAMES M. KILLOUGH

Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received May 31, 1979*

Polymer supported reagents and catalysts have become an increasingly interesting class of compounds in recent years.[1] Organometallic polymers and in particular alkali metal organometallic polymers are often used as reactive intermediates in the preparation of many of these functionalized polymers and can also be used as precursors of graft copolymers. However, in spite of the utility of alkali metal organometallic polymers, general analytical procedures for the analysis and characterization of these polymeric organometallics are not readily available; an excess of polymeric organometallic reagents is often used when using these reactive polymers. In addition, there is only a limited amount of information from synthetic studies available about the structure of these reactive alkali metal organometallic polymers.[2-4] In this paper we wish to describe a simple gas chromatographic procedure which can be used to analyze poly(styryllithium) and which can distinguish between adsorbed and polymer bound organolithium reagents. The advantages and some limitations of this analytical procedure are described. The results of experiments described in this paper also suggest that some intrapolymer site–site interactions may be occurring in organometallic functionalized cross-linked polystyrene systems.

Results and Discussion

Poly(styryllithium) is a commonly used organometallic polymer and can be prepared in a number of ways (eq 1–3).[2-4] Following these procedures, we have prepared

$$\mathrm{PSH} \xrightarrow[\mathrm{TMEDA}]{\mathrm{BuLi}} \mathrm{PSLi} \tag{1}$$

$$\mathrm{PSBr} \xrightarrow[\mathrm{THF}]{\mathrm{BuLi}} \mathrm{PSLi} \tag{2}$$

$$\mathrm{PSHgCl} \xrightarrow[\mathrm{THF}]{\mathrm{BuLi}} \mathrm{PSLi} \tag{3}$$

poly(styryllithium) from various types of insoluble divinylbenzene cross-linked polystyrene precursors. The analytical procedure we have developed for the organolithium polymers prepared in these reactions is based on the well-known reaction of soluble organolithium reagents with 1,2-dibromoethane to give ethylene and an alkyl bromide (eq 4).[5] In analogy to this reaction, we reasoned

$$\mathrm{RLi} \xrightarrow{\mathrm{BrCH_2CH_2Br}} \mathrm{CH_2{=}CH_2} + \mathrm{RBr} + \mathrm{LiBr} \tag{4}$$

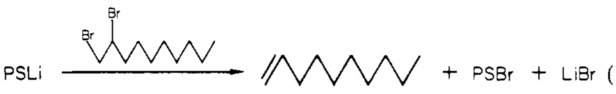
that insoluble cross-linked poly(styryllithium) should react with 1,2-dibromodecane to give brominated polystyrene and 1-decene. Since 1-decene only results from reaction of an organolithium reagent with 1,2-dibromodecane, this analytical procedure distinguishes between organolithium species and lithium alkoxides. Moreover, an adsorbed organolithium reagent like *n*-butyllithium could also be detected and quantitatively determined since it would yield equal amounts of 1-bromobutane and 1-decene. If an adsorbed alkyllithium reagent was present in addition to polymeric organolithium, the amount of each organolithium reagent can be determined since the amount of 1-decene formed from both lithium reagents can be corrected for the amount of decene from the alkyllithium reagent (as determined from the amount of alkyl bromide formed). In our procedure, gas chromatographic analysis of the 1-decene and alkyl bromide products from the reaction of excess 1,2-dibromodecane and poly(styryllithium) using internal standard techniques[6] was successfully used to analyze this organometallic polymer. The results of these analyses are listed in Table I and discussed in more detail below.

Table I
Reaction Products from the Reaction of 1,2-Dibromodecane with Insoluble Polymeric Lithium Reagents in Ethereal Solution at −78 °C

polymer[a]	metalation procedure (h)[b]	1-decene, mmol/g of polymer	1-BrC_4H_9, mmol/g of polymer	PSLi, mmol/g of polymer
PSH	A (1)	2.30	2.14	0.16
PSH	A (8)	1.98	1.00	0.98
PSH	A (20)	1.46	0.16	1.30
PSH	A (36)[c]	0.69	0.00	0.69
PSBr	B (4)	1.65	0.24[d]	1.41
PSBr	B (20)	1.33	1.00[d]	⩾0.33[e]
PSBr	B (12)[c]	0.70	0.00	0.70
PSHgCl	C (1.5)[c]	0.23	0.00	0.23
PSHgCl	C (2.5)[c,f]	0.96	0.00	0.96
PSHgCl	C (10.5)[c]	0.52	0.00	0.52

[a] Macroporous polystyrene was used in all examples shown and either contained no functional groups other than hydrogen (PSH), bromine at a level of 4.3 mmol/g of PSBr, or mercuric chloride, at a level of 2.8 mmol/g of PSHgCl. [b] Metalation procedures are described in ref 2 (A, eq 1 above), 3 (B, ep 2 above), and 4 (C, eq 3 above). All metalations employed *n*-butyllithium as the alkyllithium reagent. Variations in the reaction time led to different amounts of lithiated polymer (see text and Table II). [c] The lithiated polymer was first washed with solvent to remove soluble and/or adsorbed base. [d] Octane formed from reaction of *n*-butyllithium and 1-bromobutane was a byproduct in this reaction and is included in this value. [e] Since no correction was made in this datum for 1-bromobutane (and octane) formed during the metalation of the polymer, this value for lithiated polymer is a minimum value. [f] In this example, 46 equiv of *n*-butyllithium were used per equiv of mercury rather than the normal amount of 6–10 equiv of *n*-butyllithium per equiv of mercury.

As can be seen from the data in Table I, the analytical procedure described by eq 5 is applicable to poly(styryllithium) prepared by various routes. Even rather small amounts of lithiation can be determined because of the sensitivity of gas chromatography. As expected, this procedure does discriminate between polymeric and adsorbed organolithium reagents. Thus, this gas chromatographic analytical procedure has advantages over previously used methods for the analysis of polymeric organolithium reagents. Unlike a simple acid base titration, this procedure distinguishes between organolithium reagents and other basic species like lithium alkoxides. This pro-



(5)

cedure has advantages over carboxylation followed by titrimetric analysis of the resulting polymeric carboxylic acid[7] both in terms of sensitivity and in terms of convenience. A disadvantage of this procedure is that it is a batch process and either requires that a portion of insoluble lithiated polymer or an entire run be quenched. This procedure also gives only a lower limit for the amount of metalated sites since unforeseen side reactions cannot be completely excluded. A further problem in some cases was the formation of *n*-octane, presumably from the reaction of 1-bromobutane and *n*-butyllithium. Typically <10% *n*-octane formed. When present, *n*-octane was quantitatively analyzed by gas chromatography and was included in calculations of organolithium concentrations as if it were formed from *n*-butyllithium and butyl bromide. Octane formation thus does not affect the accuracy of this analysis method. Similar coupling reactions between poly(styryllithium) and bromobutane which would affect the accuracy of this method were unlikely sources of error, since under analogous conditions soluble phenyllithium and bromobutane did not give butylbenzene. The analysis in Table I deviated by <5% when carried out in triplicate on the same sample. Duplicate runs for data in Table I differed by ±15%, a variation which we ascribe to the inherent difficulty associated with attempts to reproduce heterogeneous reactions.

According to the stoichiometry of eq 5, the reaction of poly(styryllithium) with 1,2-dibromodecane should generate 1-decene and a brominated polystyrene. We have verified this bromine incorporation into the polymer by ESCA spectroscopy, although the extent of bromine incorporation has not been quantitatively determined.

Comparison of the relative amounts of 1-decene and 1-bromobutane for entries in Table I for which both poly(styryllithium) and *n*-butyllithium are present demonstrate that polymeric and nonpolymeric organolithium reagents can be distinguished. Experiments in which these metalated polymers were exhaustively washed with pentane and tetrahydrofuran until no soluble base could be detected in the wash solution also show that a polymeric lithium reagent can be prepared such that it is completely free of any adsorbed lithium reagent. The resulting poly(styryllithium) in such cases presumably exists as a monomeric or more likely as an intrapolymerically aggregated lithium reagent.[8] While we cannot unambiguously distinguish between these alternatives, experiments in which addition of *n*-butyllithium to a thoroughly washed poly(styryllithium) led to adsorption of lithium reagent by the polymer suggest that aggregation of polymeric lithium reagents can occur. In this experiment, poly(styryllithium) prepared from metalation of polystyrene with *n*-butyllithium–tetramethylethylenediamine was thoroughly washed with pentane until no soluble base could be detected in the wash solutions. Although it is difficult to completely exclude adventitious hydrolysis during such repetitive washings, *n*-butyllithium free poly(styryllithium) can eventually be obtained in this way. Addition of 0.65 mmol of *n*-butyllithium to such a lithiated polymer led to adsorption of an amount of lithium reagent approximately equal to the amount of poly(styryllithium) present as determined by first quenching an aliquot of the solution with 1,2-dibromodecane and then quenching the entire reaction mixture with 1,2-dibromodecane and comparing the amounts of 1-bromobutane (from *n*-butyllithium) and 1-decene (from *n*-butyllithium or poly(styryllithium)) from each quench. In this particular case, 0.12 mmol of poly(styryllithium) (0.24 mmol of Li/g of polymer) adsorbed ca. 0.10 mmol of *n*-butyllithium. We presume that this adsorption of *n*-butyllithium reagent represents aggregation of the soluble lithium reagent with the polymeric lithium reagent rather than a nonspecific adsorption since control experiments in which *n*-butyllithium was added to polystyrene failed to show any adsorption of *n*-butyllithium under similar conditions.

Table II
Polystyrene Metalation with
n-Butyllithium-Tetramethylethylenediamine
as Determined by 1,2-Dibromodecane Quenching
of Reaction Mixtures

time,[a] h	1-decene, mmol/g of polymer	1-BrC$_4$H$_9$,[b] mmol/g of polymer	PSLi, mmol/g of polymer
0	0.60	0.59	0.01
0.5	0.88	0.86	0.02
1.0	1.15	1.07	0.08
3.0	1.06	0.84	0.22
8.0	1.01	0.49	0.52
8.0	0.99	0.49	0.50
8.0	0.94	0.50	0.44
24.0	0.73	0.08	0.65

[a] Metalation reactions were carried out individually following procedures described in the Experimental Section. The amounts of starting polymer and/or added *n*-butyllithium were not necessarily the same except for the three 8-h reactions. [b] Small amounts of *n*-octane were detected in some runs. In such cases the calculated amount of 1-bromobutane includes the 1-bromobutane detected and one-half the amount of octane.

This procedure also permits us to readily determine conditions for maximizing the amount of lithiated polymer formation. Table II illustrates this for *n*-butyllithium–tetramethylethylenediamine metalation. In this particular example, 12–24 h was the best reaction time. Similar studies carried out for metalation of brominated polystyrene with *n*-butyllithium show slightly shorter reaction times (i.e., 8 h) to be better.

Experimental Section

General Methods. All reactions of air- and water-sensitive materials were carried out under argon and nitrogen atmospheres, using standard techniques.[9] Nitrogen was purified by passage through a drying tower of calcium chloride, and argon was used without further purification. Tetrahydrofuran and other ethereal and hydrocarbon solvents were distilled from a purple suspension or solution of disodium benzophenone dianion prior to use. Perkin-Elmer Model 3920 and Hewlett-Packed 5830A gas chromatographs were used for GLC analyses. Analyses were carried out on a 6 ft × $^1/_8$ in. OV-17 column. All organic chemicals were purchased from the Aldrich Chemical Co. or other commercial sources and used as supplied. Lithium reagents were purchased from the Aldrich Chemical Co. and analyzed prior to use by the method of Watson and Eastham.[10] Macroporous polystyrene and brominated macroporous polystyrene beads containing 4.36 or 4.1 mmol of Br/g of polymer were purchased from the Aldrich Chemical Co., extracted with THF for 24 h in a Soxhlet extractor, and dried prior to use. All reactions were performed in 40-mL centrifuge tubes unless otherwise specified. Shaking refers to agitation on a Burrell Model 75 wrist action shaker. 1,2-Dibromodecane was prepared by bromination of 1-decene and purified by distillation followed by passage through an alumina column.

General Procedure for the Lithiation of Polystyrene with Tetramethylethylenediamine and *n*-Butyllithium. A modification of the procedure of Grubbs and Su[2] was used. The following is representative: First 0.5003 g of polystyrene was added to a centrifuge tube and flushed with nitrogen. Then 10 mL of pentane, 0.5 mL (3.31 mmol) of tetramethylethylenediamine, and 1.0 mL (1.6 mmol) of 1.6 N *n*-butyllithium were added, and the reaction mixture was shaken for the appropriate length of time.

General Procedure for the Lithiation of Poly(styryl bromide) with *n*-Butyllithium. A modification of the procedure

Macromolecules 1980, 13, 189–190

of Crosby et al.[3] was used: A 250-mL round-bottomed flask was charged with 2.06 g (8.45 mmol of Br) of macroporous brominated polystyrene (4.1 mmol of Br/g of polymer) and 100 mL of THF. Then the reaction mixture was cooled to −78 °C, 6.4 mL (10.2 mM) of 1.6 N *n*-BuLi was added, and the reaction mixture was shaken at −78 °C for the desired length of time.

General Procedure for the Lithiation of PSHgCl. A modification of the procedure of Burlitch and Winterton[4] was used. The following is representative: First 0.5024 g (1.41 mM Hg) of chloromercurated polystyrene in 10 mL of THF was cooled to −78 °C and treated with 1.0 mL (6.67 mM) of 6.67 N *n*-butyllithium. The reaction mixture was then shaken for 1 h at −78 °C and washed twice with 10 mL of THF, and the resulting poly(styryllithium) was suspended in 10 mL of THF.

General Analytical Procedure. A suspension of metalated polymer containing ca. 30% or more ethereal solvent at −78 °C was allowed to react with 1,2-dibromodecane added slowly at −78 °C, using a syringe. The resulting polymer suspension was allowed to sit at −78 °C for 30 min with occasional shaking and then warmed to room temperature with continuous agitation. Aliquots were withdrawn by syringe and quenched with 10% HCl. After separating the aqueous and ethereal phase, the organic solution was used for GLC analysis.

Acknowledgment. This work was generously supported by the Office of Naval Research.

References and Notes

(1) Y. Chauvin, D. Commereuc, and F. Dawans, *Prog. Polym. Sci.*, **5**, 95 (1977); C. E. Carraher, J. Sheats, and C. U. Pittman, "Organometallic Polymers", Academic Press, New York, 1978.

(2) R. H. Grubbs and S. H. Su, *J. Organomet. Chem.*, **122**, 151 (1976).

(3) N. M. Weinshenker, G. A. Crosby, and J. Y. Wong, *J. Org. Chem.*, **40**, 1966 (1975).

(4) J. M. Burlitch and R. C. Winterton, *J. Am. Chem. Soc.*, **98**, 5605 (1976); J. M. Burlitch and R. C. Winterton, *J. Organomet. Chem.*, **159**, 299 (1978).

(5) H. Gilman and F. K. Cartledge, *J. Organomet. Chem.*, **2**, 477 (1964).

(6) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography", Consolidated Printers, Berkeley, Calif., 1969, Chapter 7.

(7) T. M. Fyles and C. C. Leznoff, *Can. J. Chem.*, **54**, 935 (1976).

(8) For examples of site–site interactions in cross-linked polystyrenes see: S. Mazur and P. Jayalekshmy, *J. Am. Chem. Soc.*, **101**, 667 (1979); J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, **9**, 135 (1976).

(9) H. C. Brown, "Organic Syntheses Via Boranes", Wiley, New York, 1975, Chapter 9.

(10) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).

Dipole Moment of Poly(methyl vinyl ketone)

J. A. GUEST, K. MATSUO, and W. H. STOCKMAYER*

Steele Chemistry Laboratory, Dartmouth College, Hanover, New Hampshire 03755. *Received October 3, 1979*

Polymers of alkyl vinyl ketones have been known for a long time,[1] but relatively little attention has so far been paid to their chain-conformational properties. In the present note we present data on the dipole moment of atactic poly(methyl vinyl ketone), PMVK, and its temperature coefficient. Our work was undertaken as a preliminary to measurements of dielectric and nuclear magnetic relaxation, which will be reported at a later time. The keto group also permits the attachment of fluorescent or spin labels, and indeed spin-label dynamic studies of PMVK and of styrene/MVK copolymers have already been published by Bullock, Cameron, and Smith.[2]

After completion of our experiments, we learned that Suter[3] had already made extensive semiempirical calculations of the conformational potential energies of simple and polymeric ketones and had in fact derived a two-state rotational isomeric state model for PMVK based on these calculations. Applied to the dipole moment, his model accounts quantitatively for our results. Here we confine ourselves simply to a presentation of the experimental data.

Table I
Dipole Moments of PMVK and MEK in Dioxane

temp, °C	$<\mu^2>/x$[a]
15 (PMVK)	2.42 ± 0.15
25 (PMVK)	2.52 ± 0.03
35 (PMVK)	2.61 ± 0.15
45 (PMVK)	2.71 ± 0.15
55 (PMVK)	2.82 ± 0.15
25 (MEK)	7.83 ± .07

[a] All $<\mu^2>$ are in units of D^2.

Experimental Section

A sample of PMVK, prepared by benzoyl peroxide initiation in hexane solution, was purchased from Scientific Polymer Products, Inc., and is presumed to have an atactic, head-to-tail structure.[1] Insoluble colored impurities were removed by dissolving the sample in acetone, filtering, and precipitating in cyclohexane. The resulting polymer IR spectrum matched Aldrich No. P1346A for PMVK. The intrinsic viscosity of the polymer in chloroform at 25 °C was 2.23 dL/g. No viscosity–molecular weight relationship is known to us for the atactic polymer, but if we use the results of Merle-Aubry, Merle, and Selegny[4] for an isotactic polymer (a maneuver which turns out to be essentially correct[3]) we estimate the weight-average molecular weight of our sample to be about 1×10^6. In any case, knowledge of the molecular weight is unnecessary for the present purpose, since the mean square dipole moment per repeat unit is independent of chain length except for oligomers; for the same reason, no fractionation was needed or performed.

Capacitances were measured for dilute solutions of PMVK and of its repeat-unit model, methyl ethyl ketone, in freshly distilled dioxane, with a General Radio Model 1620 capacitance bridge assembly at a frequency of 5 kHz. The home-built capacitance cell requires about 10 mL of solution and has been described elsewhere.[5] From results at three concentrations of the order of 1–2%, initial dielectric increments $\mathrm{d}\epsilon/\mathrm{d}w$ were determined, where w signifies weight fraction. Refractive-index increments $\mathrm{d}n/\mathrm{d}w$ were measured with a Brice-Phoenix Model BP-1000V differential refractometer at a wavelength of 546 nm. In this instrument, rapid solvent evaporation precluded accurate determinations above 35 °C, so extrapolations based on the data at lower temperatures had to be used.

A simplified form of the equation of Guggenheim[6] and Smith[7] was used to evaluate the mean-square dipole moment per repeat unit:

$$\frac{\langle \mu^2 \rangle}{x} = \frac{27kTM_0}{4\pi N_A d_1}\left[\frac{(\mathrm{d}\epsilon/\mathrm{d}w)}{(\epsilon_1 + 2)^2} - \frac{2n_1\,(\mathrm{d}n/\mathrm{d}w)}{(n_1^2 + 2)^2}\right] \tag{1}$$

in which d_1 is the density and n_1 the refractive index of the pure solvent, N_A is Avogadro's number, M_0 is the molecular weight of the repeat unit, and kT is the thermal energy. This relation neglects the difference in vibrational ("atomic") polarization between solute and displaced solvent, but the attendant error is surely less than 1% in the present case.

Results and Discussion

Table I gives the mean-square dipole moment per repeat unit of PMVK in dioxane at five temperatures and that of MEK at 25 °C. (The latter is presumed independent of temperature.) The dipole moment ratio at 25 °C is

$$D_\infty = \langle \mu^2 \rangle / x\mu_1^2 = 0.32 \pm 0.01 \tag{2}$$

where μ_1 is the dipole moment of MEK. The temperature coefficient is positive, with a value $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T = (4 \pm 2) \times 10^{-3}\ \mathrm{K}^{-1}$.

0024-9297/80/2213-0189$01.00/0