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THE PREPARATION AND ANALYSIS OF HIGH PURITY ORGANO-LITHIUM INITIATORS

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SUMMARY

The preparation and analysis of organolithium initiators with a high degree of purity, which is highly desirable for the synthesis of polymers, is described. The efficiency and accuracy of various analytical methods currently in use are compared and discussed.

The importance of alkyllithium initiators in the synthesis of highly stereospecific polydienes has long been recognised[1]. Combined with the non-terminating character of anionic polymerization first recognised and exploited by Szwarc[2], these discoveries have provided the experimentalist with powerful tools for the synthesis of polymers containing a high percentage of *cis*-1,4-polydiene. Recently, much work has been directed towards the synthesis of triblock polymers, particularly those which constitute the commercially important thermoplastic elastomers. In these polymers the central block is a polydiene and the two terminal sequences are polystyrene or a similar glassy polymer. Organolithiums of a high degree of purity are necessary to produce both the elastomeric character of the material and the overall structural perfection required to achieve their maximum potential.

Organolithiums are highly reactive towards atmospheric contaminants, in particular water and oxygen. Failure to achieve "clean" systems results in the production of non-initiating basic products according to the reactions:

$$\text{R–Li} + O_2 \rightarrow \text{ROOLi}$$

$$\text{ROOLi} + \text{R–Li} \rightarrow 2\,\text{ROLi}$$

$$\text{R–Li} + H_2O \rightarrow \text{RH} + \text{LiOH}$$

Basic impurities may be expected to be present to some degree in all samples of these initiators unless specific precautions are taken to exclude contaminants during preparation and subsequent handling. The presence of contaminants in the initiator is undesirable on two counts since lithium hydroxide affects polystyrene tacticity and both alkoxides and hydroxide reduce the *cis*-1,4-diene content. Furthermore, these

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impurities create problems in the analysis of the initiator since it is necessary for accurate predictability of molecular weight to know the amount of impurity present and to avoid further destruction of the initiator in subsequent steps. The importance of this is readily seen when one realises the dilution, *viz.* 10^{-5}–10^{-2} *M*, which is required for polymerization to high molecular weight and which is governed by the ratio of monomer and initiator charges. In this study of organolithiums it has been found possible to prepare lithium based initiators with a high degree of purity and to analyse them, without further contamination, by the use of long established vacuum line techniques.

High purity n-butyllithium and sec-butyllithium were prepared for this study by addition of the appropriate alkyl chloride to metallic lithium:

$$R\text{–}Cl + 2\,Li \rightarrow R\text{–}Li + LiCl$$

The absence of lithium chloride in the system, below detectable limits, has been established in this work. The alternative route involving the use of dialkylmercury was not considered a viable method because of the long duration of the reaction time required (*i.e.* several weeks)[3]. This would most certainly result in some decomposition of the alkyllithium. In this study we also describe the preparation of the dianionic initiator, 1,4-dilithio-1,1,4,4-tetraphenylbutane. A method for the removal of benzophenone from 1,1-diphenylethylene, which is essential to the preparation, is also described. Benzophenone is nearly always present in 1,1-diphenylethylene since it is an oxidation product of the reagent. The method of elimination described in this work offers an alternative to that proposed by Spach *et al.*[4] and is, we believe, faster and more efficient. Finally, a comparison has been made of the various methods of analysis suggested for alkyllithium compounds which are still in current use.

EXPERIMENTAL

Proton magnetic resonance (PMR) measurements were conducted on a Varian DA 60 1L NMR spectrometer. All optical densities were determined on a Gilford model 2000 and a Shimadzu QH-50 UV spectrophotometer. Optical densities over the range of wave lengths 250–310 nm were checked, using mercury lines, according to the method proposed by Haupt[5].

Benzene

A.R. grade benzene was refluxed over calcium hydride for 12 h, distilled through a 3 ft. fractionating column and the fraction boiling between 80–81° collected. Gas chromatograms were obtained on all samples and the results obtained indicated a pure product. Degassing of the solvent on the vacuum line was followed by flash distillation into a 1 l reservoir attached to the line. The distillation of the solvent was followed by the polymerization of styrene in the reservoir by n-butyllithium; the bright red colour served as an indicator, demonstrating the complete absence of contaminants. Further samples of benzene were added to this vessel from time to time until the colour eventually faded. All charges of benzene were taken from this reservoir.

Purging solutions

The preparation of purging solutions for the purging of all reaction vessels has been adequately described in an earlier publication[6]. The same procedures were adopted for this study.

Concentrated initiator solutions

(*a*). n-Butyl chloride and sec-butyl chloride were gently refluxed over calcium hydride for several hours and finally fractionated. The fractions boiling at 78–79° (n-butyl chloride) and 68–69° (sec-butyl chloride) were collected over fresh calcium hydride. Again, gas chromatograms indicated the complete absence of impurity.

Some of the solutions of alkyllithium compounds, previously used by Cramond and Urwin[6], were observed to become cloudy after a short period of storage. These were always discarded but because of this it was considered necessary to modify the procedure. A vessel fitted with a tap and stoppered side arm and sampling ampoule, Fig. 1(a), or for large volumes, with several sampling ampoules attached, Fig. 1(b), was flamed out under high vacuum. With the tap closed, the vessel was removed from the line and dry argon allowed slowly to fill it. With argon still flushing, lithium chips, cut under benzene, were added through the side arm. The surface remained bright throughout showing that the oxidation of the surface was minimal. This precaution was found necessary for starting the reaction; often it was found that reaction with the alkyl halide was inhibited by the absence of bright surfaces. The vessel was restoppered, evacuated, and a charge of benzene admitted from the reservoir (100–120 ml). This was followed by 30 ml of dry alkyl halide, after which the mixture was frozen down. After pumping to high vacuum, the vessel was removed from the line, thawed and left in an ice bath for 12 h. It was allowed to stand for three days at ambient

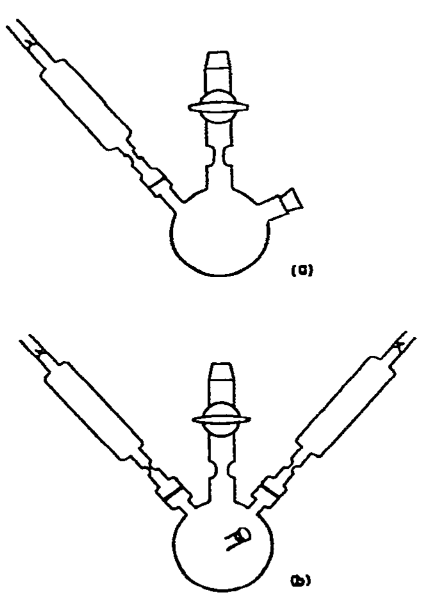

Fig. 1. Reaction vessel for the preparation of concentrated initiator solutions.

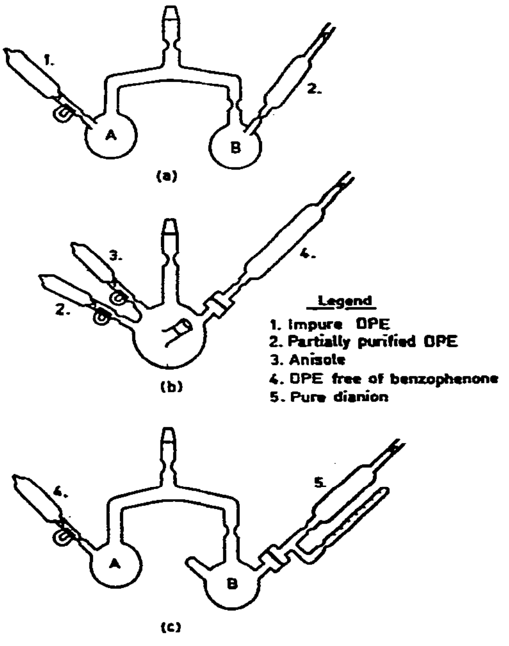

Fig. 2. Apparatus used in the preparation of the dianion.

temperature to complete the consumption of the alkyl halide. To ensure that no unreacted alkyl chloride remained, all distillable materials were removed on the line and finally a fresh charge of benzene added. After freezing and pumping to high vacuum, the vessel was sealed off at the constriction, the mixture filtered through a No. 4 porosity filter and sampled. Storage at −10° minimized decomposition of the product. The concentration at this stage was about 2.5 *M*. Two grades of lithium were employed, (*i*), B.D.H. Lab. grade 98% purity and (*ii*), Koch Light 2N8 99.8% purity.

(*b*). 1,4-Dilithio-1,1,4,4-tetraphenylbutane (TPB)Li_2, the dianionic initiator, was prepared by reacting 1,1-diphenylethylene with lithium metal. The radical ion formed first but then rapidly dimerized to yield the dianion. The preparation of a pure product is difficult owing to the presence of the oxidation product of diphenylethylene, benzophenone. Szwarc and coworkers[4] used a method involving a series of distillations of diphenylethylene onto previously prepared samples of the sodium salt of the dianion. The blue adduct between benzophenone and the dianion became progressively paler with successive distillations until all benzophenone was removed. We propose a method for removing benzophenone *in situ* as follows. The reaction vessel, Fig. 2(b), had attached an ampoule of anisole (30 ml) which is used to solubilise the dianion. Anisole was used because this ether least affected the *cis*-1,4 content of the polyisoprene. After an initial flash distillation of the 1,1-diphenylethylene, Fig. 2(a), into sealed ampoules, one of the ampoules was attached to the reaction vessel, lithium chips were added under argon gas, and the vessel was evacuated. Finally, a charge of benzene (200 ml) was admitted from the reservoir. After sealing off from the line, the impure diphenylethylene was broken in, with anisole, on to the lithium chips. In about 18 h a dark blue colour developed, which ultimately became masked by the deep red colour of the dilithio anion. The contents of the flask were filtered through a No. 4 porosity filter to separate the unreacted diphenylethylene, the benzophenone products and a small amount of the dianion from the lithium. In this way, most of the original diphenylethylene was retained. The ampoule from this step was then attached to bulb A, Fig. 2(c), lithium chips were admitted to bulb B under argon, as previously, the side arm was sealed off and the vessel evacuated. After sealing from the vacuum line, the ampoule on A was broken in. Benzene, anisole and diphenylethylene was distilled into B, leaving behind the non-distillable products of benzophenone and the previously formed dianion. Finally, bulb B was sealed off and the reaction allowed to proceed for three days. The red colour appeared within several hours but with no sign of the blue colour characteristic of the adduct. This was taken to imply that the benzophenone had been completely removed. After filtration, an ampoule of the dilithio initiator containing a concentration of about 10^{-2} *M* was obtained. Analysis was effected by acid titration, employing the calibrated side tube.

Dilution and sampling procedures

In Fig. 3 the apparatus for dilution and sampling of the initiators n-butyl- and sec-butyllithium is shown. Two ampoules, containing 100–120 ml of polystyryllithium in benzene, were attached to bulb A, whilst to bulb B was sealed a ½ to 1 ml sample of the concentrated (2.5 *M*) initiator solution. Two silica cells of 0.5 cm optical path were attached to the bulb, together with several pre-calibrated sampling tubes constructed from obsolete Pyrex burettes and pipettes. Cell corrections for each cell with respect to its matched partner had previously been calculated at 285 nm with

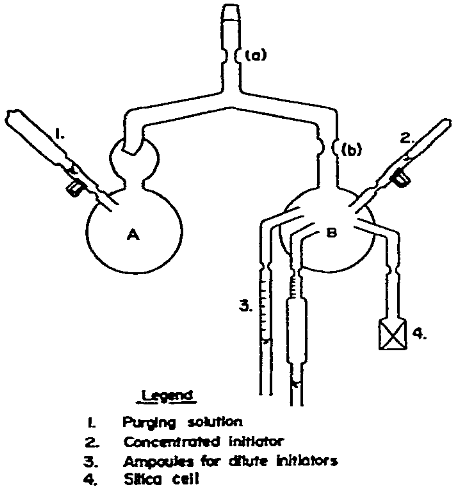

Fig. 3. Apparatus for dilution and sampling of initiators.

benzene as solvent. (BuLi was found to obey Beer's Law at 285 nm)[7].

The vessel was flamed out and sealed off, under vacuum, at the constriction. The living polymer solution was broken into A and the complete apparatus purged. The purge solution was returned to A and the vessel rinsed with solvent distilled from this bulb. After several washings, with particular attention paid to the silica cells to remove small amounts of terminated polymer, the solvent was distilled from the polystyryllithium into bulb B. The concentrated initiator solution was broken into B and mixed with the solvent to give an approximately $10^{-2}\,M$ solution. A small quantity of this solution was tipped into one of the silica cells which was then sealed from B. The concentration was determined accurately by UV analysis and, if necessary, the concentration adjusted by distillation of solvent back into A. The analysis was then repeated, using the second cell attached to B. Bulb B was then sealed off at the constriction. The volumes of initiator required to polymerize a monomer charge of 13–16 g, for various molecular weights, were calculated and this volume tipped into pre-calibrated ampoules. The ampoules were sealed from bulb B and stored in the refrigerator.

The excess initiator was collected in a large calibrated ampoule, removed from B, broken open under water and the benzene evaporated off. The resulting hydroxide solution was analysed by acid titration using standard hydrochloric acid with phenolphthalein or bromothymol blue as indicator. This method of analysis was considered satisfactory, particularly when coupled with the special preparative procedures adopted above, and the fact that no initiator losses were observed during dilution and sampling operations in prepurged vessels.

The same apparatus was used for dispensing samples of sec-butyllithium. Concentrations were therefore all determined by simple acid titration after demonstrating the efficacy of the procedures adopted. Accurate volumes of the sec-butyllithium were dispensed and also stored under refrigeration.

Similar apparatus was also used to convert the dianion 1,4-dilithio-1,1,4,4-tetraphenylbutane to polyisoprenyldilithium "seed". The object in using the seeding technique was to avoid precipitation due to the limited solubility of 1,4-dilithio-1,1,4,4-tetraphenylbutane. The "seeding" technique was achieved by mixing the sample of purged isoprene in bulb A, sufficient to convert all the dianion, attached to bulb B, to the low molecular weight "seed" ($\overline{M}_n \approx 2000$).

Lithium butoxide

The NMR spectrum of lithium n-butoxide was determined to provide a routine check for the presence of this impurity in initiator samples. The butoxide was prepared by reacting n-butanol with n-butyllithium

$$\text{BuOH} + \text{BuLi} \rightarrow \text{BuOLi} + \text{BuH}$$

A reaction vessel was evacuated and sufficient n-butanol to consume $\frac{1}{4}$ of the n-

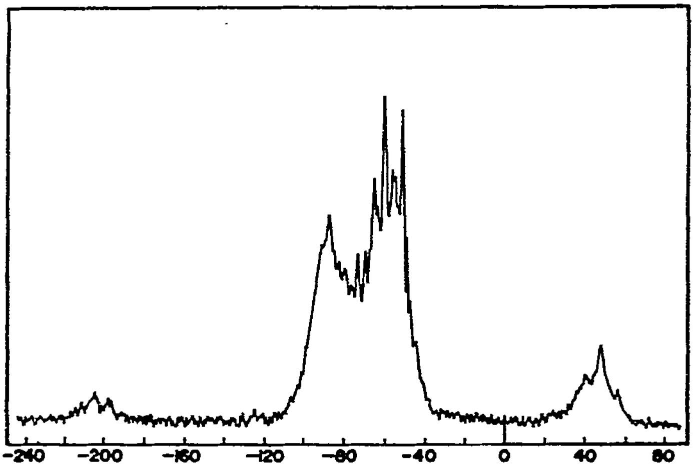

Fig. 4. PMR spectrum of n-butyllithium in benzene containing butoxide (in Hz referred to TMS).

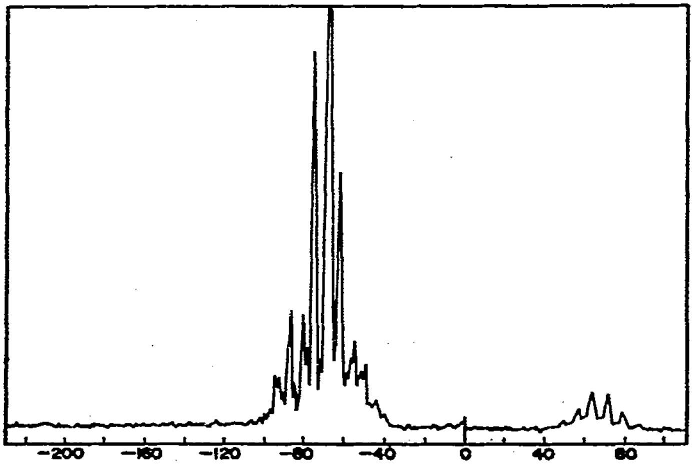

Fig. 5. PMR spectrum of sec-butyllithium in benzene (in Hz referred to TMS).

butyllithium to be added was distilled in. The vessel was sealed from the line, n-butyllithium broken in and a vigorous reaction ensued. After reaction, samples were tipped into NMR tubes sealed to the reaction flask and sealed off from the vessel. The NMR spectrum (Fig. 4) showed a triplet, centre peak 206 Hz downfield from TMS. The n-butyllithium triplet was 48 Hz upfield from TMS. The areas of the two triplets showed the ratio 3/1 as expected, indicating complete consumption of the butanol. The wide separation of these peaks allowed rapid checks to be made on all initiator samples. No resonances were observed in the 200 Hz region in any sample, thereby indicating the absence of butoxide within the limit of detection of the spectrometer (*i.e.* 1 %).

The PMR spectrum of sec-butyllithium in benzene was examined in the same way. The sextet from the sec-butyllithium occurs at 66 Hz upfield from TMS, Fig. 5. Again, no resonances attributable to butoxide could be observed in any of the samples prepared.

RESULTS AND DISCUSSION

The purity of all organolithiums prepared in this study has been shown to be high. In the case of BuLi, the high degree of purity suspected was confirmed by carrying out several common methods of analysis in conjunction with a qualitative proton magnetic resonance (PMR) spectrum. The methods of analysis used were the acid titration procedure and the Gilman extension of this, the Volhard methyl iodide procedure, the Clifford and Olsen iodine procedure and the quantitative PMR technique discussed by us in an earlier publication[7]. The results of these analyses, performed in a concentrated solution of BuLi in benzene, are shown in Table 1 below. It should be mentioned at this point that the Gilman, the Volhard and the Clifford and Olsen procedures all involve the addition of a chemical reagent to the alkylmetal compound, converting it to a non-basic, titratable product. The added reagent must therefore be scrupulously contaminant-free (*i.e.* no oxygen or water), otherwise the subsequent titration will be in error to the extent of further organolithium destruction. This aspect, while important in the analysis of concentrated alkylmetal compounds, is clearly of critical importance in the determination of the very low alkylmetal compound concentrations required for polymer synthesis (*viz.* 10^{-4}–10^{-2} *M*). The meth-

TABLE 1

ANALYSIS OF A CONCENTRATED n-BUTYLLITHIUM SOLUTION BY VARIOUS ANALYTICAL METHODS

	Method of analysis	*Concentration of BuLi found (mole·l^{-1})*
1.	Acid titration (Std. HCl)	2.63[a]
2.	Gilman double titration	2.61[a]
3.	Volhard methyl iodide	2.67[a]
4.	Iodine titration	2.40
5.	PMR method	2.59[b]

[a] Averaged value of two analyses. [b] Averaged value of four analyses.

ods of analysis involving chemical reagent addition, were therefore used only for concentrated alkylmetal determinations. Our previously reported analysis procedure involved addition of mesitylene to concentrated BuLi solutions, however, the addition was made under completely contaminant-free conditions since, as indicated, it was purged with polystyryllithium prior to analysis. Also, in regard to the PMR analysis, considerably less complex apparatus was eventually developed[12] than was previously described. Although an "absolute" method, reproducibility using the PMR technique was, in view of its complexity, less attractive than a simple titration method used in conjunction with the precautions outlined above.

The general agreement between the above methods, *cf.* 2.62±0.05 (except for the iodine titration) is very satisfactory, especially when it is considered that all BuLi samples were dispensed under vacuum, from pre-calibrated break seals. The low result for the iodine titration is consistent with one of the shortcomings reported for this method of analysis, *viz.* a coupling reaction. Ideally, the reaction of iodine with the alkylmetal compound;

$$\text{R–Li} + \text{I}_2 \rightarrow \text{R–I} + \text{LiI}$$

is quick and quantitative, however, in practice a coupling reaction between the alkyl iodide and further alkylmetal compound may occur.

$$\text{R–Li} + \text{RI} \rightarrow \text{R–R} + \text{LiI}$$

In the above analysis the low result is therefore consistent with the expected coupling between BuLi and butyl iodide. None of the methods of analysis used are without some shortcomings. The acid and the methyl iodide methods, for example, do ***not*** account for the alkoxide and hydroxide impurities; they measure the total lithium and are therefore suitable only for analysis of alkylmetal solutions with high carbon-bound-lithium content. The Gilman procedure, although it accounts for basic impurities, likewise is inaccurate if alkoxide is present, because of reaction of the alkoxide with the added alkyl halide[13]. All three methods may therefore give too high a value for the alkylmetal concentration; they are satisfactory only when the basic impurity content is negligible. The latter, of course, can not be known *a priori*, and it was primarily for this reason (and because of the non-interference by basic impurities, in particular alkoxide) that we proposed the PMR analysis, which in conjunction with UV analysis, is a suitable alternative method.

Comparison of our PMR method and the acid titration results shows the latter to be higher by approximately 2% and this, we proposed in our earlier publication, is possibly due to lithium butoxide and lithium hydroxide being present. Since the basic impurity content has been demonstrated to be low, the somewhat more accurate Gilman procedure was at first preferred. Our comparison of the acid and Gilman methods now shows that the impurity levels in BuLi, using the precautions outlined here, are less than 1% of the total lithium. High purity alkyllithium compounds may therefore be prepared by the procedure given above, and under these conditions, their purity is such that analysis by acid titration is quite acceptable and because of its obvious simplicity, preferable. The close agreement between the results of the Volhard and the acid titrations is of particular interest, since it precludes the presence of lithium chloride in BuLi solutions. Lithium chloride is not accounted for by the acid titration, but is involved in the Volhard procedure by reaction with silver nitrate. The absence

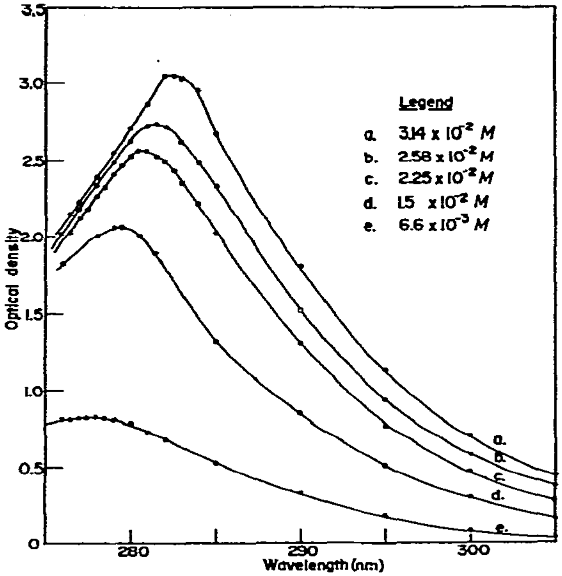

Fig. 6. UV spectra of n-butyllithium at various concentrations.

of lithium chloride removes any possibility that there can be complex formation, such as [R–Li–ClLi], which presumably can occur in certain initiating systems, and which may result in a loss of initiator efficiency.

The PMR method was used specifically in the calibration of dilute n-butyllithium solutions in benzene to allow an absolute determination of the extinction coefficient of carbon-bound-lithium. The UV absorption as a function of concentration is of some interest. The curves resulting from a series of concentrations are shown in Fig. 6. It can be seen that the maximum has shifted to higher wave lengths with increasing concentration. Nevertheless, concentrations of n-butyllithium showed an excellent linear Beer–Lambert plot over the range 2×10^{-3} to 3.1×10^{-2} *M* at 285 and 290 nm despite this shift in the peak. The extinction coefficient including maximum calculated error is 91 ± 4 ($l\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$) at 285 nm which was employed in this study. The excellent agreement between the UV and acid titration methods is most satisfactory and suggests that the maximum error may be lower than originally calculated. The results of titrations made under these conditions are shown in Table 2. The apparent agreement between these two results would indicate that the simple acid

TABLE 2

COMPARISON OF ANALYSES OF n-BUTYLLITHIUM IN THE UV WITH ACID TITRATION

Method of analysis	*Concentration* ($l\cdot mole^{-1}$) $\times 10^{-2}$
UV analysis (calibration by NMR)	1.06_2
Acid titration	1.05_6

titration is, under conditions described above, as satisfactory as the UV analysis for determining low BuLi concentrations, nevertheless, the UV method is a quick and simple procedure.

The UV spectrum of n-butyllithium in benzene is difficult to explain. The shift in maximum, on casual inspection, would appear to suggest that more than one species is present in solution, however, the application of Beer's law provides conflicting evidence; the linear plot is indicative of a single species. A conjectural explanation for this shift is that the tail of the benzene peak significantly overlaps the n-butyllithium spectrum in the region 260 nm. This would have the effect of causing the solvent blank to "over compensate" at higher concentrations of n-butyllithium.

In conclusion, "high purity" organolithium initiators may be prepared, under high vacuum conditions, provided that strict attention is paid to the details of synthesis. PMR spectra can be qualitatively employed to detect the presence, or otherwise, of likely basic impurities, particularly alkoxide. Unfortunately, this method is not applicable to the case of the dianionic initiator, 1,4-dilithio-1,1,4,4-tetraphenylbutane, because of its low solubility in the benzene/anisole solvent mixture.

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