THE ANALYSIS OF BUTYLLITHIUM AT CONCENTRATIONS USED IN THE INITIATION OF POLYMERIZATION

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SUMMARY

An NMR method devised for analysis of n-butyllithium solutions is acceptably accurate down to concentrations of 0.1 M. An ultraviolet method, involving calibration with solutions analyzed by the NMR technique, is accurate to within $\pm 5\%$ down to concentrations of 10^{-3} M.

Lithium alkyls and in particular butyllithium are currently used in many studies of the reaction mechanism in anionic polymerization[1,2]. Much interest centres around the kinetics of the initiation step, particularly at low concentrations of initiator. The accuracy of these experiments depends to a marked degree upon an accurate determination of the initiator concentration. Statistical analyses on results at these low concentrations show that the reliability of data leaves much to be desired[3] and emphasizes the need for better methods of analysis.

A number of methods for the determination of n-butyllithium (BuLi) solutions are currently in use, almost all of which involve analysis by titration. Perhaps the best known of these techniques is that due to Gilman and co-workers[5,6] which employs a double titration to determine the concentration of n-butyllithium in the presence of lithium butoxide and lithium hydroxide. Recent work[7-10] however, has demonstrated certain unsatisfactory features in the technique concerning the interference by lithium butoxide.

In the single titration technique devised by Eppley and Dixon[10], it was established that butoxide does not interfere with the procedure. The presence of hydroxide however, seems to have been ignored in this technique.

Several other techniques have been proposed[7,11,12] each of which, it is claimed, is comparable to or better than the double titration method. Perhaps the most suitable standard previously devised is the thermometric titration[12] in which butyllithium is titrated against a standard n-butanol solution. However, rather elaborate equipment is required which is not generally available.

It is clear that all of these methods have certain shortcomings, not the least of which is their inability to accurately measure the low concentrations required for high polymer synthesis (*viz.* 10^{-2}–10^{-4} M)[4]. The determination of the metal alkyl at high concentrations by one of the methods described, followed by dilution, even with

the greatest care, does not overcome the problem since a proportion of the initiator is always destroyed in the process of dilution and sampling. It was with this in mind that we set out to improve on the generally accepted methods of analysis of lithium alkyls.

EXPERIMENTAL

The NMR spectrum of n-butyllithium in benzene (Fig. 1) showed a triplet 48 cps upfield from tetramethylsilane (TMS) due to the methylene protons adjacent to the lithium. This triplet can be integrated and compared with the integrated spectrum of a suitable reference liquid. All that is required is to mix a carefully measured volume of
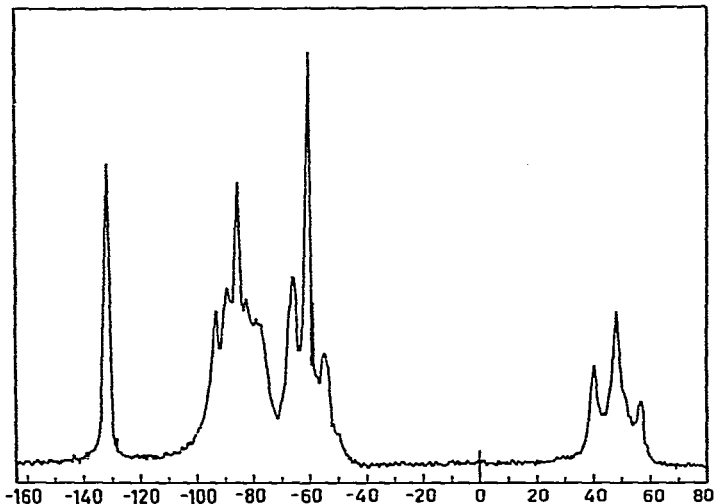

Fig. 1. Nuclear magnetic resonance spectrum at 20° of butyllithium in benzene with mesitylene as reference. Chemical shifts (in cps) are referred to the resonance position of tetramethylsilane.

the reference liquid with a given volume of the lithium alkyl solution. In this way NMR gives a direct measure of the carbon-bound lithium content. The reference substance should have a large and preferably single peak which does not overlap with the spectrum of butyllithium. A low vapour pressure is preferable since the integrated peak is a measure of the reference in the liquid phase. In this study, mesitylene was chosen as the reference since its NMR spectrum consists of a nine proton singlet 132 cps downfield from TMS (Fig. 1) giving therefore a large separation of reference and n-butyllithium peaks. Furthermore its vapour pressure at 20° (the temperature at which all experimental measurements were recorded) is negligible.

The NMR method is clearly suitable for analysis down to concentrations where the integrated signal can be estimated with reasonable accuracy, that is in the range above 10^{-1} M, and is free from the objections raised against the titration techniques. The extension of any of these methods to the range of initiator concentrations used in high polymer synthesis demands that a dilution procedure be adopted. As previously stated, the disadvantage of sampling followed by dilution lies in the loss of initiator by adventitious termination, particularly when more than one dilution is necessary. An alternative is the measurement of optical densities in the ultraviolet at the final concentration to be used. However, to achieve this, the extinction coefficient must be

accurately known and one of the titration methods or the NMR technique must be used to calibrate. Again, the dilution procedure is required in any case. We have therefore adopted the procedure whereby the extinction coefficient is determined from optical density measurements on diluted solutions calibrated by NMR which directly measures the carbon-bound lithium content. The problem was then to design suitable glass apparatus which would connect the two physical methods and such that adventitious termination could be eliminated by prepurging with polystyryllithium within a closed system.

Butyllithium solutions were prepared under vacuum as previously described[4]. An ampoule containing the butyllithium in benzene was attached to a U-shaped vessel with a bulb on each arm so constructed that the BuLi/benzene solution could be broken in through a break seal into the bulb on one side. Several NMR tubes and sampling ampoules were attached to the second bulb. The purpose of this apparatus was to ensure that the sample of BuLi to be used for the actual analyses was sufficiently concentrated to give a large integrated α-methylene peak. Preliminary determinations of the NMR peak were the only way to achieve this. The vessel was flamed out, evacuated to 10^{-5} mm and sealed off from the line. The BuLi solution was broken into the apparatus and solvent was distilled from the main bulk until an NMR determination showed the integration peak to be large. Samples were then sealed off in break seal ampoules. This method provided about ten 10 ml samples, which were stored in a refrigerator.

The mesitylene to be used as reference was thoroughly dried by refluxing over calcium hydride for several hours and then fractionally distilled. The purity was checked by means of vapour phase chromatography (VPC). Samples of the mesitylene were prepared in break seal ampoules which had previously been accurately calibrated. The ampoules were attached to a vessel similar to the one just described. An ampoule of polystyryllithium in benzene was also attached to the vessel. This was broken in and the benzene was distilled off. A small quantity of mesitylene was distilled on to the remaining living ends. The apparatus was sealed from the vacuum line and purged with the polystyryllithium mesitylene solution.

The vessel was rinsed with the pure solvent distilled from over the living ends (which had been returned to the first bulb), to ensure complete removal of the purging material from the main vessel. The mesitylene was then carefully distilled into the ampoules and sealed off ready for use. A further check by VPC showed the absence of
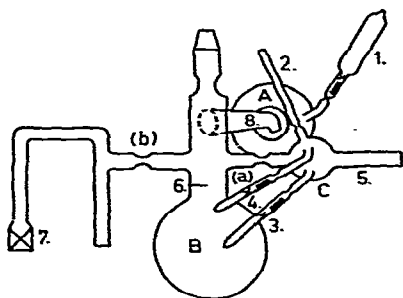

Fig. 2. Apparatus used. 1, Purging solution; 2, NMR tube; 3, BuLi/benzene; 4, mesitylene; 5, 10 ml calibrated tube; 6, 150 ml graduation mark; 7, optical cell; 8, splash head.

impurity in the mesitylene. It was estimated that the volume of mesitylene was known to within 1 %.

The design of the apparatus used for the analysis is shown in Fig. 2. Before use, the bulb C and the calibrated tube 5 were thoroughly cleaned to ensure free draining of the BuLi/benzene solution. The vessel was evacuated to 10^{-5} mm and sealed off from the vacuum line. The whole apparatus was thoroughly purged with a benzene/polystyryllithium solution 1 and the solution returned to A. Pure solvent was distilled from this solution to other parts of the vessel and after rinsing poured back into A. The splash head 8 was required to avoid bumping. The rinsing process was performed several times until it was considered that all purging solution had been removed. When it was certain that all purging solution had been returned to A the 10 ml sample of BuLi in benzene was broken into the calibrated tube. After allowing sufficient draining time the liquid level was read using a cathetometer. Approximately half the BuLi/benzene solution (5 ml) was carefully tipped into B, and the liquid level in 5 was read again with the cathetometer. The calibrated tube and its contents were then sealed off at (a), and the known volume of mesitylene broken in and thoroughly mixed with the BuLi solution. A small quantity of the mixture was poured into the NMR tube 2 which was sealed off for measurement in the Varian 60 Mcps NMR spectrometer. The integrated NMR peaks of BuLi and mesitylene were compared giving the concentration of the BuLi solution in bulb B. Benzene over the living ends in A was then distilled into B to make the solution up to an accurate 150 ml graduation mark. An error of 0.5 ml in 150 ml is estimated at this point. A known volume of the BuLi solution was run off into a dilution vessel and sealed off at (b).

The optical density of the BuLi solution was measured in the optical cell attached to the dilution vessel. This cell was constructed from rectangular quartz tubing and attached to the glass vessel through a graded seal. A series of dilutions were made by pouring a small quantity of the BuLi solution into the optical cell, noting its volume and distilling benzene from the main bulk followed by careful mixing. Both side arms of the vessel were calibrated for volume which allowed by a simple calculation the determination of the new concentration. Optical densities were determined on a Gilford model 2000 UV spectrophotometer. The path length of the quartz cell was determined by internal calipers in the region of the light path. The error in this measurement is estimated to be less than 1 %.

RESULTS AND DISCUSSION

The optical density over the range 275 mμ to 305 mμ was measured for a series of butyllithium concentrations from 6×10^{-3} to 3.1×10^{-2} moles/litre. The maximum absorption shifted from 278 mμ at the lowest concentration to 282 mμ at the highest and changed monotonically with concentration. The reasons for the shift are not clear at this stage and are at present being investigated. Nevertheless at 285 mμ Beer's Law was obeyed and an extinction coefficient of 91 l·mole^{-1}·cm^{-1} was calculated at this wavelength.

Concentrations of approximately 10^{-3} moles/litre in butyllithium have been used in this laboratory to initiate high molecular weight polymers. Further dilutions in the dilution vessel and the use of larger cell path lengths should allow concentrations of this order to be satisfactorily reached. This is being further studied as is the

estimation of a concentration limit for this particular system. However over the concentration range studied and at least to 10^{-3} M it is felt that butyl lithium can be determined to within 5% using the combined NMR-UV techniques.

No direct comparison was made between the standard titration techniques and our NMR method in estimating butyllithium, however a check on the accuracy of the NMR result was nevertheless made. A sample of butyllithium/benzene was hydrolysed with water and titrated against standard hydrochloric acid. The titre results were consistently 2–3% higher than the NMR analysis. This is expected since titration gives the total lithium content comprising butyllithium, butoxide and hydroxide. The reproducibility of NMR integrals was also checked. Spectra for each tube were integrated in triplicate and excellent reproducibility was obtained. A further check was made for the absence of polystyryllithium by examining the absorption at 334 mμ. No absorption was found indicating that no detectable amounts of living ends from the purging process remained after the washing procedure. Furthermore this precluded possible association between butyllithium and polystyryllithium, a condition which would yield an erroneous butyllithium absorption in the ultraviolet.

From the brief studies performed so far we believe that our main purpose, to establish that the ultraviolet method employing calibration by NMR is feasible, has been achieved and that accurate estimations of butyllithium at the low concentrations required for the synthesis and kinetic studies in high polymers seem possible. The practicability of such a method is clear. Knowledge of an extinction coefficient over a certain concentration range makes the determination of initiator by measurement of its optical absorption relatively simple. Further studies involving comparisons with standard techniques, simpler apparatus design and extensions to other solvents and initiators are now in progress.

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