A new method for the quantitative analysis of the ultra-violet/visible spectrum of poly(butadienyl-lithium) anions when complexed with 1,2-dipiperidinoethane

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The ultra-violet/visible absorption spectrum of poly(butadienyl-lithium) anions in living anionic polymerization reactions changes significantly in the presence of the complexing agent 1,2-dipiperidinoethane (DIPIP). In the absence of complexing agent the poly(butadienyl-lithium) anion has an absorption maximum at 275 nm in cyclohexane, but on adding DIPIP two broad unresolved absorption maxima are observed in the range 250 to 400 nm, and the extinction coefficients for these peaks vary with the molar ratio of DIPIP to the living chain ends. A method has been developed for the determination of the concentration of the complexed living polyanions in cyclohexane by monitoring the absorbances at two different wavelengths (275 and 325 nm), which provides a useful means of obtaining a quantitative understanding of the living polymerization process in the presence of the complexing agent that was not possible before. The living-end concentrations obtained using the method proposed here have been found to be in good agreement with values obtained by measurement of the number-average molecular weights of the final products. Using this method, it has also been demonstrated that, in addition to forming a complex, DIPIP reacts slowly with the poly(butadienyl-lithium) anions.

(Keywords: anionic polymerization; 1,2-dipiperidinoethane; ultra-violet spectroscopy; high-vinyl polybutadienes)

INTRODUCTION

Since Halasa *et al.* reported[1,2] that 1,2-dipiperidinoethane (DIPIP) complexes with living poly(butadienyl-lithium) anions in hydrocarbon solvents and that chain growth from the complexed propagating centre gives polybutadienes with a high vinyl content, the effects of DIPIP on the organometal-initiated polymerization of butadiene have been extensively studied[3-5]. The opportunity that complexation reactions afford for the control of the microstructure of polybutadiene is of considerable technical significance. Bywater *et al.*[4] observed a shift in the u.v. absorption maximum from 275 nm to 328 nm when living poly(butadienyl-lithium) chain ends were complexed with DIPIP. At low ratios (r) of DIPIP to lithium salt ($r = [\mathrm{DIPIP}]/[\mathrm{Li}]$) there is a broadening of the u.v. absorption peak at 275 nm followed by the appearance of the peak at 328 nm as r approaches unity. When r has values greater than 3 the peak at 328 nm is the more intense and eventually as r increases the absorption maximum at 275 nm becomes insignificant.

The change in the character of the ultra-violet/visible (u.v./vis.) absorption spectrum of poly(butadienyl-lithium) anions when complexed with DIPIP is not simple. The extinction coefficient varies with the magnitude of r over the wavelength range 250 to 400 nm, which makes it impossible to measure quantitatively the living-end concentrations in polymerizations using u.v./vis. spectroscopy as is the case in the absence of complexing agent.

We report here a method for measuring r and the living-end concentration in the polymerization of butadiene initiated by n-butyl-lithium complexed with DIPIP in a hydrocarbon solvent. Use is made of spectroscopic data reported by Bywater *et al.*[4]. The validity of the procedures is established by comparing the values of the polyanion concentrations obtained from calculations based on the u.v./vis. spectroscopic data with those obtained from experiments where the polymers produced in the spectroscopic studies have been isolated and their number-average molecular weights ($\bar{M}_n$) measured to give the 'true' concentration of active species present in the reaction.

EXPERIMENTAL

High-vinyl polybutadienes were prepared by techniques described previously[6] using n-butyl-lithium as initiator, cyclohexane as solvent and DIPIP as the modifier to obtain the 1,2-mode of addition. U.v./vis. absorption spectra of the living polymer solutions were obtained using a Pye Unicam SP800 spectrometer. The polymers produced in the spectroscopic studies were isolated by precipitation in methanol and their molecular weights determined[6] by gel permeation chromatography (g.p.c.) (Waters Associates Inc., fitted with a refractometer detector) in series with a viscosity detector (Viscotek, model 110) and two 10 μm mixed beds, with a molecular weight range of 100 to $4 \times 10^6\,\mathrm{g\,mol^{-1}}$ (PL Gel, Polymer Laboratories Ltd). The viscosity detector is particularly useful since calibration makes use of the universal calibration curve; thus, the results reported are independent of the microstructure of the polymers. Calibration was

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carried out using known molecular-weight polybutadiene standards (Polymer Laboratories Ltd).

In order to check the long-term stability of the polyanions in the presence of DIPIP, low-molecular-weight ($\approx 5000\ \mathrm{g\,mol^{-1}}$) poly(butadienyl-lithium) salts were prepared in cyclohexane. DIPIP was added to the polyanions and the u.v./vis. spectra recorded with time at a controlled temperature of 30°C. The concentrations of living chain ends and DIPIP were calculated using equations (1), (2) and (3), below.

RESULTS AND DISCUSSION

Determination of r *and polyanion concentration*

The u.v. spectroscopic data and the extinction coefficients (ε) of the complexed chain ends at 275 and 325 nm can be utilized to determine the ratio r and the polyanion concentration in the system. (Any well separated wavelengths can be selected; the two taken here are for illustration only[7].) A plot of ε_{275} *versus* ε_{325} is linear with slopes that are a function of r. From these data, calculated values for $\tan^{-1}(\varepsilon_{325}/\varepsilon_{275})$ are plotted for different values of r in *Figure 1*. In order to make use of this information it is necessary to obtain a mathematical function that describes the plot in *Figure 1*. Several functions were tried and a third-order polynomial expression (equation (1)), fitted by means of a regressional analysis, was found to describe the plot best:

$$r = 1.91A^3 + 2.33A^2 + 0.41A - 0.01 \qquad (1)$$

where $A = \tan^{-1}(\varepsilon_{325}/\varepsilon_{275})$. The variation of ε_{325} with $\log(r)$ was plotted, as shown in *Figure 2*, and the best regression fit to the polynomial function gave:

$$\varepsilon_{325} = 189B^3 + 580B^2 + 1568B + 3557 \qquad (2)$$

where $B = \log_e(r)$ and the units of ε_{325} are $\mathrm{l\,mol^{-1}\,cm^{-1}}$.

It is interesting to observe that the points in *Figure 2* might well have been fitted with two linear functions, one for negative values of $\log_e([\mathrm{DIPIP}]/[\mathrm{Li}])$ and one for positive values, which intersect close to the value of $[\mathrm{DIPIP}]/[\mathrm{Li}] = 1.0$. This observation will be discussed elsewhere[7].

The value of r can be readily calculated from equation (1) and ε_{325} from equation (2) for all experimentally measured absorbances at 325 and 275 nm (A_{325} and A_{275} respectively). The concentration of living polyanions complexed with DIPIP may then be calculated from Beer's law, namely:

$$A_{325} = \varepsilon_{325} lc \qquad (3)$$

where l is the optical path length in centimetres and c the molar concentration of living polyanions.

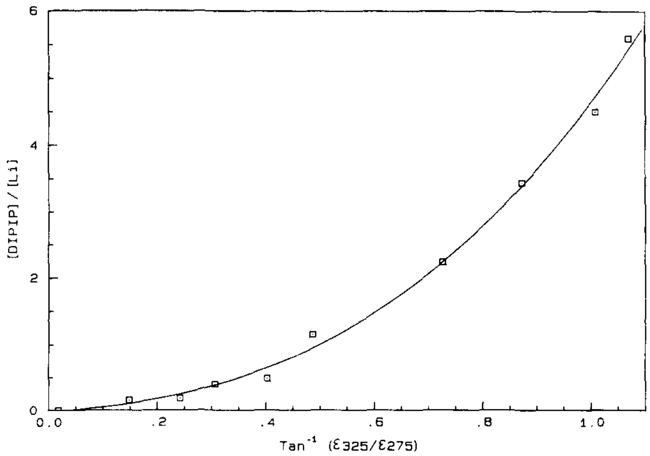

Figure 1 Relationship between $\tan^{-1}(\varepsilon_{325}/\varepsilon_{275})$ and r ratio of DIPIP-complexed poly(butadienyl-lithium) chain ends

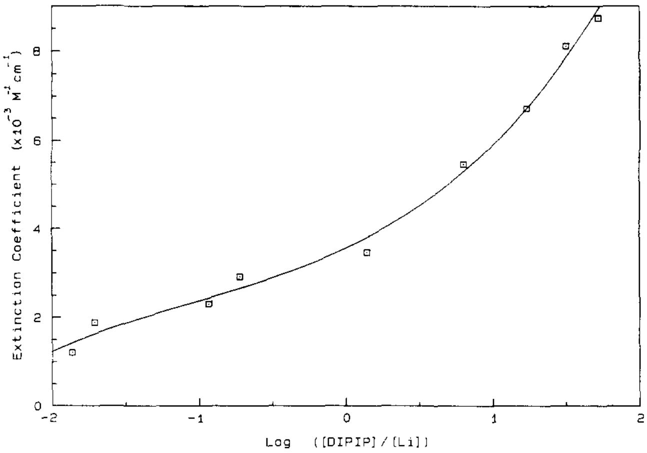

Figure 2 Relationship between $\log_e r$ and ε_{325} of DIPIP-complexed poly(butadienyl-lithium) chain ends

Table 1 Living-end concentrations calculated from u.v. spectra and values obtained from $\bar{M}_n$

Experiment no.	r	$[\mathrm{Li}] \times 10^3\ (\mathrm{mol\,l^{-1}})$ Calculated values	Obtained from $\bar{M}_n$
1	0.46	1.27	1.45
2	0.86	1.67	1.73
3	2.32	1.44	1.59
4	2.92	1.32	1.18
5	3.71	1.42	1.29

The two wavelengths chosen to test the procedure were selected because absorption maxima were observed close to these values that were characteristic of the species in solution, they were convenient for experimental measurements and they were well separated by 50 nm.

The concentrations of the poly(butadienyl-lithium)–DIPIP complexed anions were determined by measurement of the $\bar{M}_n$ of polymers produced in reactions for which the absorption spectra had been measured, are shown in *Table 1*. Also shown in *Table 1* are the calculated concentrations from the spectra taken immediately after the reaction started, using equations (1)–(3). The difference between these concentration values is less than 15% in all cases, which is acceptable considering the likely experimental errors in handling low concentrations of such reactive species. The concentrations of reagents used in this work were selected to be similar to those employed by Bywater *et al.*[4]; the implication is that our findings strongly support the results presented in ref. 4.

The method is very useful for the determination of living-end concentration as it can be carried out rather easily without disturbing the system. In particular, the concentration of the living species can be monitored in-line and it is thus possible to adjust the amount of initiator to compensate for the killing effect on the initiator of impurities present in the reaction. Hence, the molecular weight of the final product can be predicted and controlled.

Equations (1) and (2) are valid within the range $r = 0$ to 5.60. When $r > 5.6$, the equations might have to be modified to account for the effect of DIPIP on the u.v. absorption of the complexed chain. However, polybutadienes with the highest possible vinyl content can readily be produced experimentally (e.g. 97%) at r values well below the maximum r limit studied in our work. Bywater *et al.*[5] have also shown that the profile of the u.v. spectrum is unchanged when the concentration of the living ends is varied in the range between 10^{-2} and $10^{-4}\,\mathrm{mol\,l^{-1}}$ at a fixed ratio of DIPIP to Li. Therefore, the method described here can be applied over a wide range of living-end concentrations, which is useful for the preparation of high-molecular-weight polymers.

Post-polymerization reactions

Figures 3 and *4* show the changes in the concentration of the polyanion and DIPIP after the reaction mixtures had been allowed to stand at room temperature in the dark for 2 days. The concentrations of both the complexed and uncomplexed species decrease significantly. The decrease in the intensity of the u.v. absorptions at 275 and 325 nm is ascribed to a reaction taking place between the living chain ends and DIPIP. The killing of the living polyanions by other impurities is not considered to be important since this should result in an increase in the value of r with time and the concentration of DIPIP calculated using the method proposed here should remain constant throughout the experiment. *Figure 5* reveals that r decreases slowly at the beginning of the experiment and more quickly after 20 h. The most likely reactions between the poly(butadienyl-lithium) and DIPIP are shown in *Figure 6*.

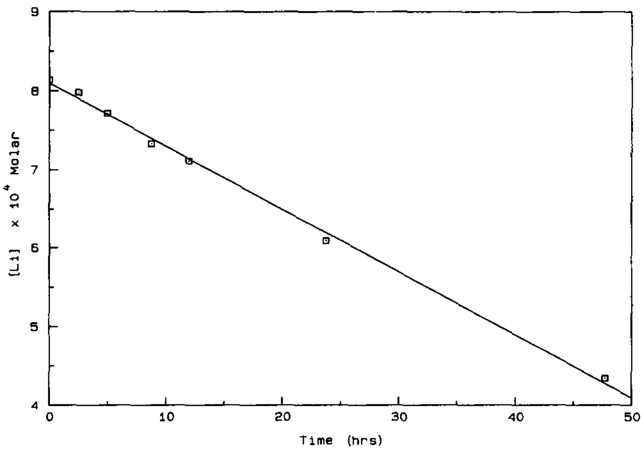

Figure 3 Plot of poly(butadienyl-lithium) concentration *versus* time after leaving the reaction mixture to stand in the dark at 30°C for 48 h

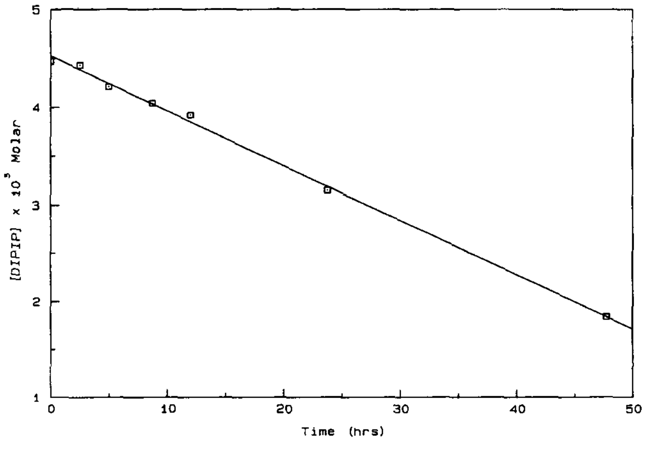

Figure 4 Plot of DIPIP concentration *versus* time after the reaction mixture was allowed to stand in the dark at 30°C for 48 h

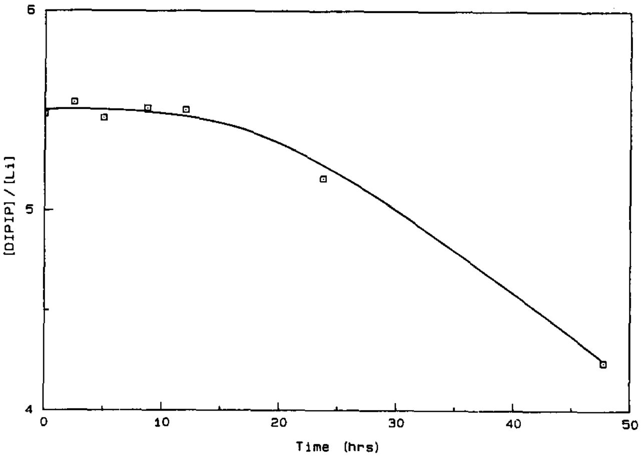

Figure 5 The change in the value of r with time for poly(butadienyl-lithium) anions complexed with DIPIP

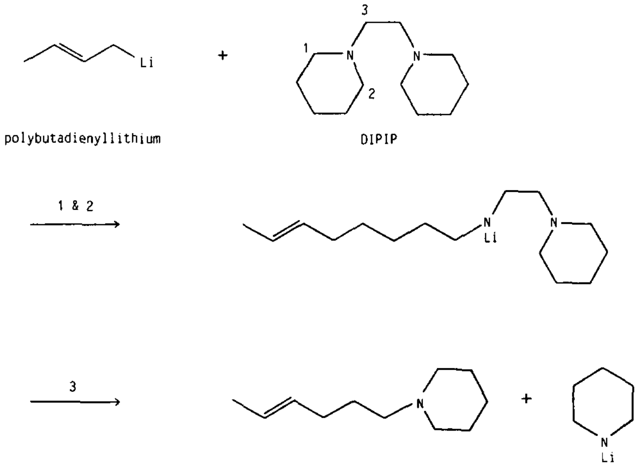

Figure 6 Some possible reactions between DIPIP and poly(butadienyl-lithium) anions

It is suggested that the living chain end can attack the DIPIP molecule at any one of three carbon atoms, which, if correct, results in the Li atom and a free electron being removed from the polyanion. The disappearance of the allylic chain ends, which facilitate the delocalization of the electron, causes a decrease in intensity in the absorption at 275 and 325 nm. The new species formed between DIPIP and the chain end has no chromophore to give rise to an absorption band in the spectral region of interest here. The ratio of the slopes of the plots of [Li] and [DIPIP] against time in *Figures 3* and *4* implies that up to seven molecules of DIPIP can react with a single lithium chain end. Whether the successive addition of DIPIP molecules to the living chain end actually takes place remains unknown. However, it is possible that once one amine group of the DIPIP molecule has interacted with a living chain end, the unreacted amine group can still complex with another living chain end, giving rise to a change in the absorption spectrum. The mechanism we propose is similar to that outlined by others[1] who

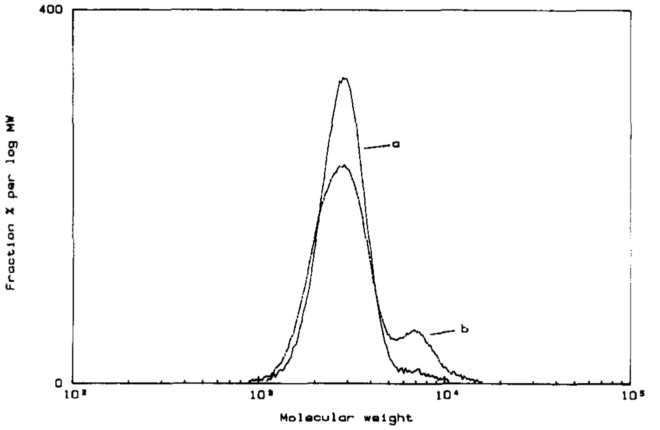

Figure 7 G.p.c. data for polymer produced (a) before the addition of DIPIP and (b) after the addition of DIPIP and being allowed to stand for a minimum of 4 days

have used different complexing agents. For the polymerization of ethylene using butyl-lithium as initiator in the presence of tetramethylethylenediamine (TMEDA) as complexing agent, it has also been proposed[7] that a β-proton abstraction occurs from the complexing agent by the butyl-lithium. Further experiments are being carried out in order to substantiate the proposed mechanism[8]. Our preliminary findings show that there is clear evidence for a coupling reaction of the type proposed when the DIPIP molecule is attacked by two living chain ends. In *Figure 7*, data obtained from g.p.c. are shown and it can be seen that a distinct peak appears at high molecular weight, which indicates a coupling reaction involving molecules of the more predominant low-molecular-weight species. The high-molecular-weight peak increases with time at the expense of the low-molecular-weight peak.

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