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Measurement of living polybutadienyllithium anion concentrations in the presence of complexing agents by u.v.-visible spectroscopy

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The quantitative evaluation of the concentration of the propagating species in the polymerization of butadiene initiated by butyllithium in cyclohexane in the presence of complexing agents such as 1,2-dipiperidinoethane (DIPIP) and diglyme is described. The method, which may be applied to polymerizations other than the one reported here, is based on the precise knowledge of the molar extinction coefficients of the polyanion in the absence of complexing agent and the measurement of the absorbance at two different wavelengths when complexing agent is present. These measurements are made in the region 250-400 nm. The method has the advantage that it is not necessary to have any independent measure of the amounts of initiator and complexing agents used at the start of reaction. From the u.v.-visible spectroscopic studies, a slow post-polymerization reaction between polybutadienylithium and DIPIP is noted. Molecular weight and i.r. measurements on the polymers produced in the presence of DIPIP support this suggestion and a mechanism is proposed for this reaction. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: u.v.-visible spectroscopy; living polyanions; polybutadiene)

INTRODUCTION

Bywater *et al.*[1] observed a shift in the ultraviolet (u.v)-visible absorption maximum of polybutadienyllithium from 275 nm to 328 nm when complexed with DIPIP. The absorption spectrum was found to be sensitive to the ratio (r) of DIPIP to initiator used (r = [DIPIP]/[Li]), the extinction coefficient varying with r over the wavelength range 250 nm to 400 nm, making it impossible to obtain information on the concentration of the living chain-ends using any single wavelength as in the case of the uncomplexed polybutadienyllithium.

A method has been reported in an earlier publication[2] for the determination of r and the concentration of polybutadienyllithium in the presence of DIPIP using u.v.-visible spectroscopy which involved the measurement of absorption at two separate wavelengths, namely 275 nm and 325 nm. Here, the method is extended and generalized so as to be able to make use of absorption measurements at any appropriate pair of wavelengths within the spectral envelope of the complexed polyanion. The application of the method to other complexing agents, diglyme in particular, is also considered here.

EXPERIMENTAL

The experimental methods used to obtain data used here have been described in detail elsewhere[2] but are briefly reviewed for convenience here.

The u.v.-visible absorption spectrum of DIPIP-complexed polybutadienyllithium in cyclohexane was measured as follows. Low molecular weight polybutadienyllithium (approximate $\bar{M}_n = 2000$) was prepared under high-vacuum conditions in a glass apparatus fitted with a u.v.-visible absorption cell. The spectrum of the uncomplexed species was recorded after the initiation reaction had gone to completion and all the monomer consumed by subsequent polymerization at room temperature using an automatic recording spectrometer (Pye Unicam SP800). The absorption maximum was found to be at 275 nm, a value similar to that previously reported[1]. The spectrum was recorded over the range 250 nm to 400 nm. A known quantity of DIPIP was added under vacuum to the polybutadienyllithium and the spectrum of the DIPIP-complexed species recorded. Successive additions of DIPIP were made and a spectrum recorded for each different concentration of DIPIP. The value of r was determined from the known molar quantities of DIPIP used in the experiment and the initial concentration of uncomplexed polybutadienyllithium species [Li] as calculated from the known molar extinction coefficient for this species. Here, r = [DIPIP]/[Li]. The values for r were in the range 0 to 4.77.

A similar procedure to that described above was carried out to obtain values of r with well-dried diglyme as the complexing agent all other conditions being the same; here, also, r = [diglyme]/[Li].

U.v.-visible absorption spectra were recorded for a number of polymerization reactions carried out with

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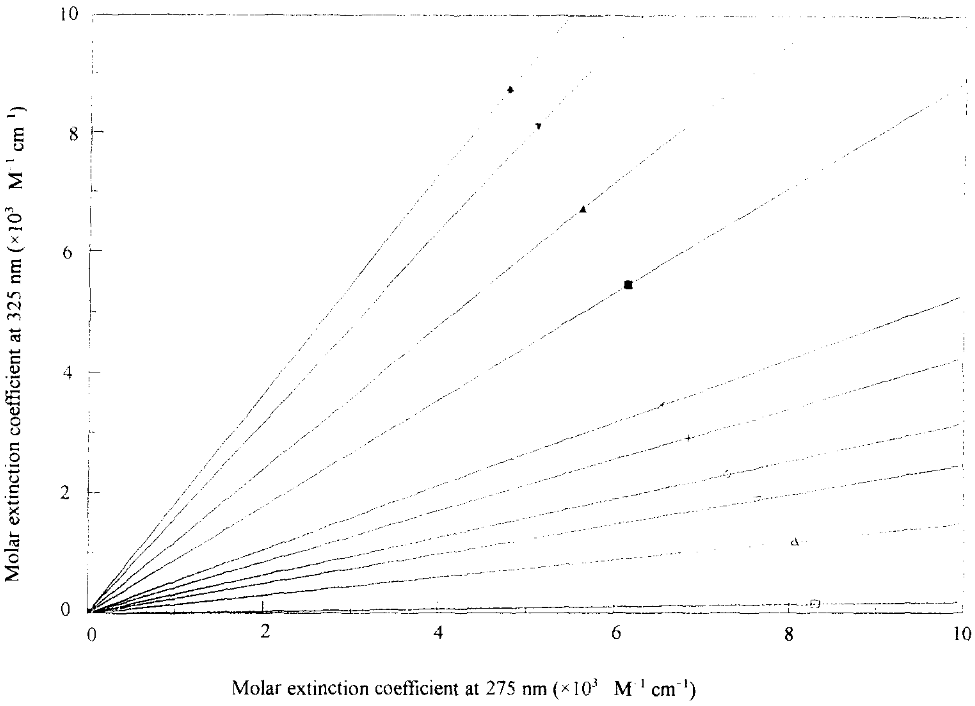

Figure 1 Plot of ϵ_{325} against ϵ_{275}; from bottom to top r = 0, 0.155, 0.180, 0.393, 0.487, 1.157, 2.241, 3.432, 4.498, and 5.610

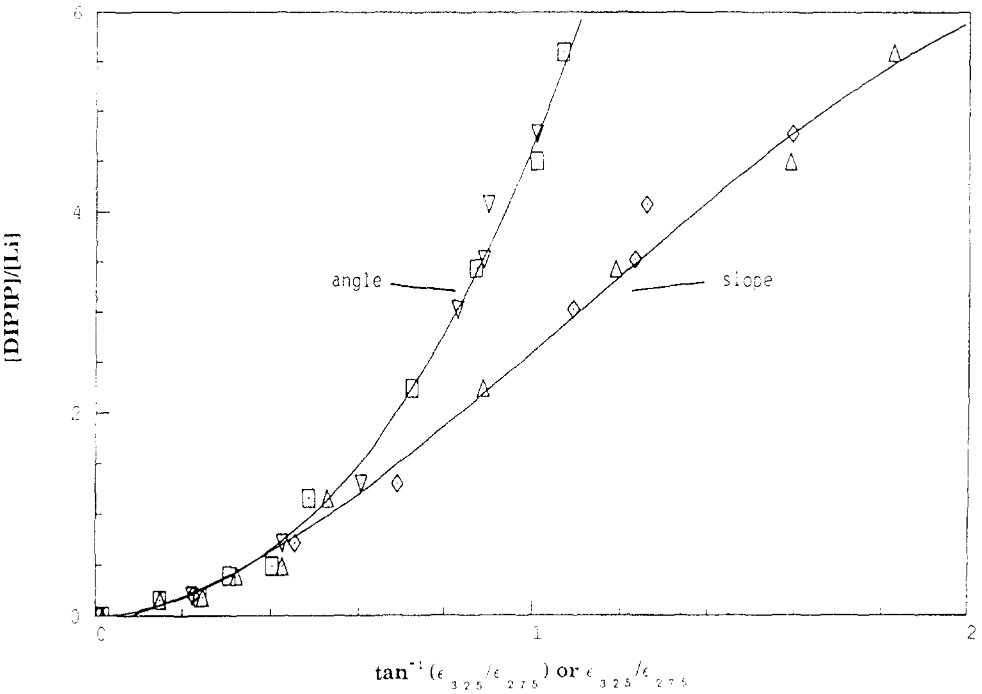

Figure 2 Relationship between $\tan^{-1}$ ($\epsilon_{325}/\epsilon_{275}$) or ($\epsilon_{325}/\epsilon_{275}$) and r ratio of DIPIP-complexed polybutadienyllithium chain ends. □, △ obtained from ref. 1; ▽, ◇ data from *Figure 4*

added complexing agent so as to produce products with a high vinyl content. All spectra were recorded as soon as possible after the initiator was added to the monomer solution containing complexing agents. At ambient temperature the characteristic absorption spectrum of the complexed polyanions develops almost instantaneously. After polymerization had gone to completion, the polymers produced were isolated by precipitation in ethanol and their number-average molecular weights determined by gel permeation chromatography (g.p.c., Waters Associates Inc.) fitted with two PL gel 10 μm mixed bed columns (Polymer Laboratories Ltd.) and a refractometer detector (Waters, Model R100) in series with a viscosity detector (Viscotek, Model 110) as described earlier[2].

The molecular weight range of the instrument is 100 to 4×10^6 g mol^{-1}. The viscosity detector is particularly useful since calibration utilizes the universal calibration curve and the results reported are independent of the polymer microstructure. Calibration was effected using polybutadiene standards of known molecular weight (Polymer Laboratories Ltd.).

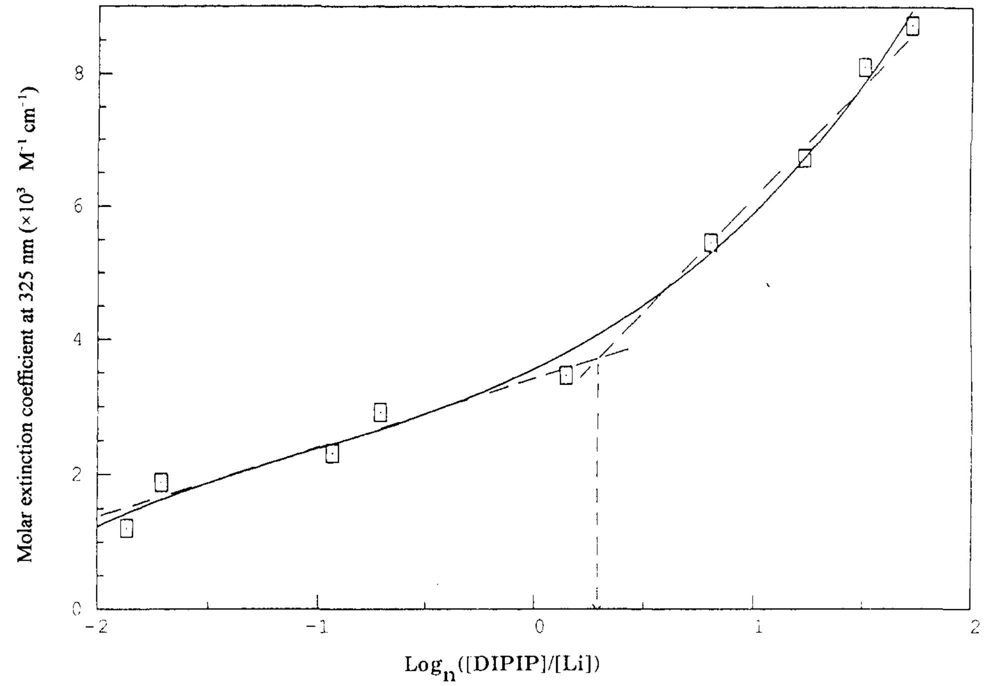

Figure 3 Relationship between $\mathrm{Log}_n\ r$ and ϵ_{325} of DIPIP-complexed polybutadienyllithium chain ends

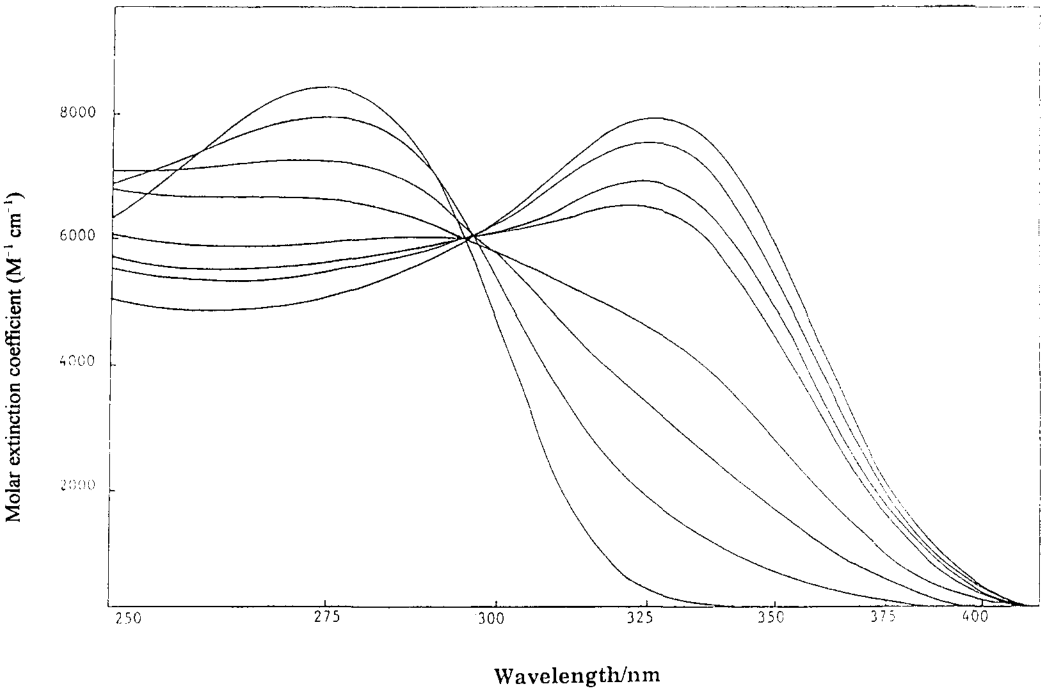

Figure 4 U.v.–visible absorption spectra of DIPIP-complexed polybutadienyllithium chain-ends in cyclohexane; from bottom to top at 325 nm $r = 0$, 0.20, 0.71, 1.33, 3.02, 3.52, 4.07, and 4.77

The long-term stability of the living chain-ends in the presence of DIPIP was checked by letting some of the solution used to establish values for r stand in the dark for 3 weeks, the spectrum being recorded with time. Eventually, the residual species were 'killed' with a small quantity of ethanol. The molecular weight of the polymer was obtained by g.p.c. as above. The infra-red (i.r.) absorption spectra of the isolated polymers were obtained (Perkin Elmer *FT*i.r., Model 1720X) in order to help establish the mechanism of the reaction between DIPIP and polybutadienyllithium proposed in the previous report[2].

RESULTS AND DISCUSSION

Method for the determination of r *and polybutadienyllithium concentration*

The u.v.–visible spectroscopic data and the molar extinction coefficients (ϵ) of the DIPIP-complexed polybutadienyllithium chain-ends obtained by Bywater *et al.*[1] can be utilized to determine r and the living chain-end concentration in the system.

It can be seen in *Figure 2* that when the molar extinction coefficients at 325 nm and 275 nm as measured by Bywater are plotted against one another for different

Table 1 Living end concentrations calculated from u.v. spectra and from $\bar{M}_n$ of DIPIP-complexed polymerizations

Experiment number	r	Calculated values [Li] × 10^3 M		
		$\tan^{-1}(\epsilon_{325}/\epsilon_{275})$	$(\epsilon_{325}/\epsilon_{275})$	$\bar{M}_n$
1	0.46	1.27	1.23	1.45
2	0.86	1.67	1.65	1.73
3	2.32	1.44	1.46	1.59
4	2.92	1.32	1.35	1.18
5	3.71	1.42	1.43	1.29

values of r, a series of points is obtained which, when linked to the origin, produces a distinctive pattern of lines. The angles subtended by the lines with the x axis increase with r. *Figure 3* displays the plots of $\epsilon_{325}/\epsilon_{275}$ (slope) and $\tan^{-1}\epsilon_{325}/\epsilon_{275}$ (angle) of the data in *Figure 2* against r. In order to make quantitative use of this information it is necessary to obtain mathematical functions which describe the plots in *Figure 3*. Several functions were tried, and a third order polynomial expression, fitted by means of a regressional analysis, describes each of the plots well, the explicit functions being given by

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

$$r = -0.74B^3 + 2.55B^2 + 0.87B - 0.08 \quad (2)$$

where $A = \tan^{-1}(\epsilon_{325}/\epsilon_{275})$
$B = \epsilon_{325}/\epsilon_{275}$

The variation of ϵ_{325} with $\log_n r$ was also plotted, as shown in *Figure 4*, and the best fit to a third order polynomial function gives

$$\epsilon_{325} = 189C^3 + 580C^2 + 1568C + 3557 \quad (3)$$

where $C = \log_n r$ and the units of ϵ_{325} are M cm^{-1}.

The value of r can be readily calculated from equation (1) or equation (2) for experimentally measured absorbances at 325 and 275 nm (A_{325} and A_{275}, respectively) since the ratio of A_{325}/A_{275} is equal to $\epsilon_{325}/\epsilon_{275}$. The concentration of living chain-ends complexed with DIPIP may then be calculated from Beer's law, namely:

$$A_{325} = \epsilon_{325}.l.c \quad (4)$$

where l is the optical pathlength in centimetres and c is the molar concentration of living polybutadienyllithium chain-ends.

In order to check the validity of the proposed method, the concentrations of DIPIP-complexed polybutadienyllithium, as determined by measurement of the $\bar{M}_n$ of polymers produced in reactions for which the absorption spectra has been measured, are shown in *Table 1*. Also included are the calculated concentrations obtained by using the spectra obtained soon after the addition of complexing agent and equations (1)–(4). The difference between the concentrations determined by both methods is never greater than 15%, which is acceptable considering the likely experimental errors in handling low concentrations of such reactive species.

U.v.–visible absorption spectra of DIPIP-complexed polybutadienyllithium in cyclohexane are displayed in *Figure 1*. The absorption profiles at different r values are very similar to those of Bywater *et al.*[1]. The data obtained from *Figure 1* are plotted alongside those obtained from Bywater *et al.*[1] in *Figure 3*. The plot of r against $\epsilon_{325}/\epsilon_{275}$ is also shown in *Figure 3*. Regressional analysis was also applied to these data, giving two equations similar in form to the equation reported earlier[2] namely;

$$r = 1.57A^3 + 3.50A^2 - 0.32A \quad (5)$$

$$r = -1.76B^3 + 5.13B^2 - 0.72B + 0.06 \quad (6)$$

where $A = \tan^{-1}(\epsilon_{325}/\epsilon_{275})$
$B = \epsilon_{325}/\epsilon_{275}$

It can be seen, in *Figure 4* that, although the data were fitted with a third order polynomial expression, two linear functions (dotted lines) might also have been used

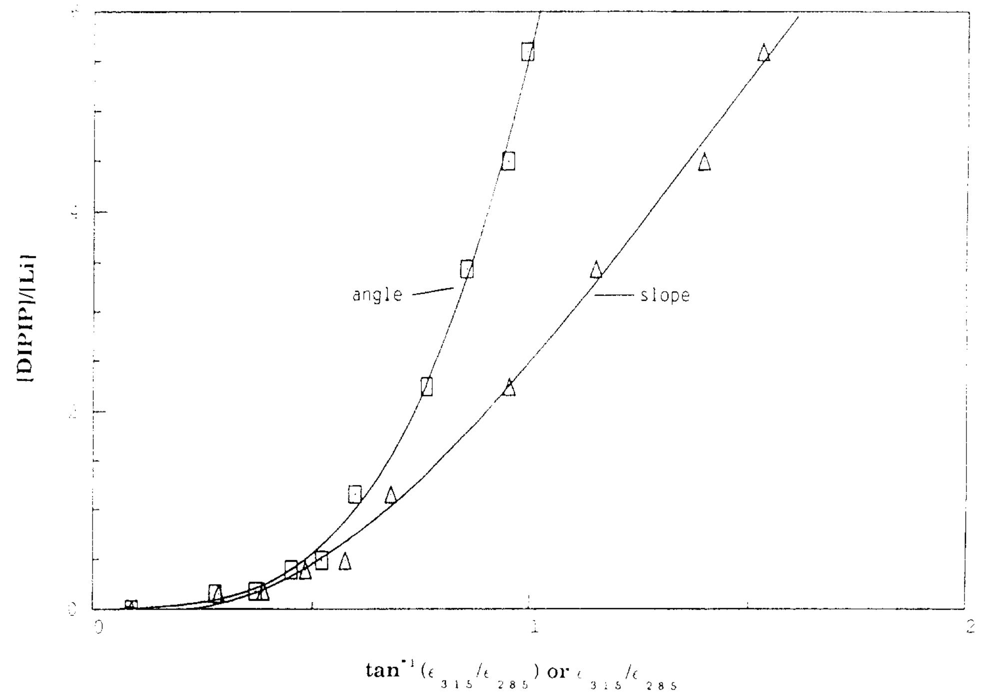

Figure 5 Relationship between $\tan^{-1}(\epsilon_{315}/\epsilon_{285})$ or $(\epsilon_{315}/\epsilon_{285})$ and r ratio of DIPIP-complexed polybutadienyllithium chain ends

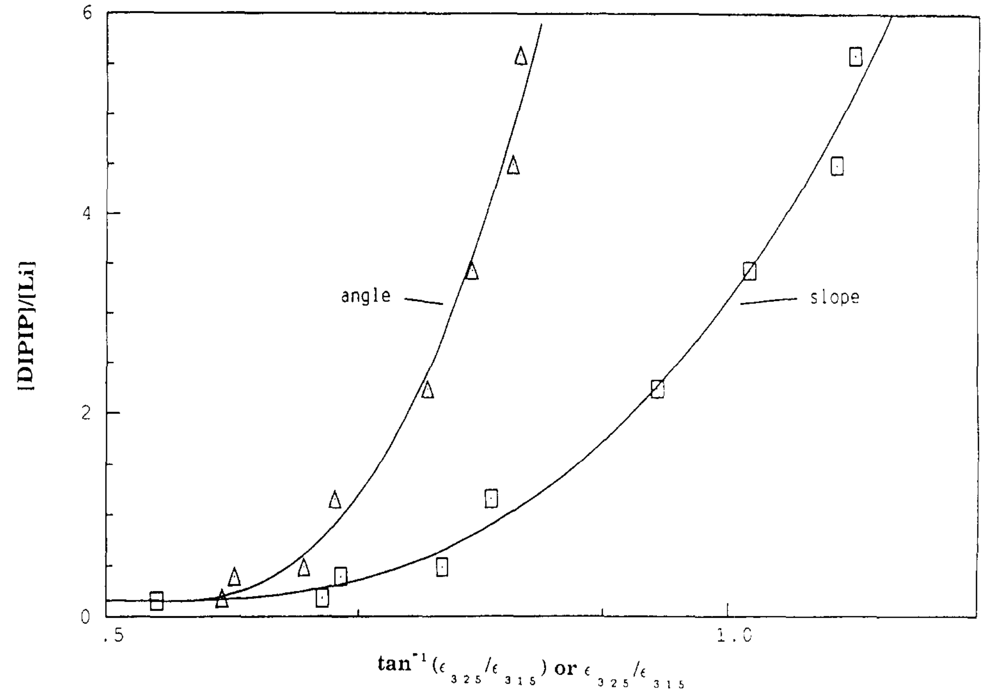

Figure 6 Relationship between tan^{-1} ($\epsilon_{325}/\epsilon_{315}$) or ($\epsilon_{325}/\epsilon_{315}$) and r ratio of DIPIP-complexed polybutadienyllithium chain ends

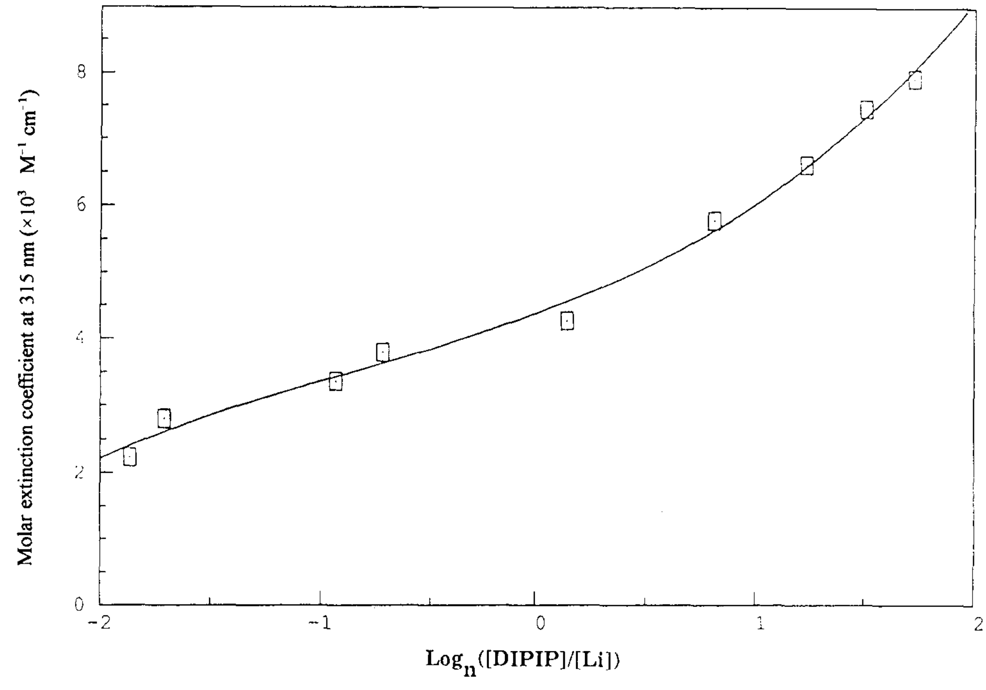

Figure 7 Relationship between log$_n$ r and ϵ_{315} of DIPIP-complexed polybutadienyllithium chain ends

which intersect close to a value for r of 1.0 (log$_n$ $r = 0$). This observation might relate to the fact that the polybutadienyllithium anions, when complexed with DIPIP, are more than 90% *trans* in conformation in hydrocarbon solvent when $r > 1.0^3$. The absorption spectrum for $r > 1.0$ might be considered as the absorption spectrum of the *trans* active species. When r becomes greater than 1, ϵ_{325} increases rapidly suggesting that there is also a rapid increase in the concentration of *trans* living chain-ends. The majority of the chain ends for polyisoprenyllithium when complexed with DIPIP are in a *cis* form[4], and no significant change in extinction coefficient of the complexed species was detected for $r > 1$, and the absorption for this complexed species appearing only as a shoulder on a major peak whose λ_{max} was close to that of the uncomplexed species.

This method for the determination of r and living species concentration has been explored using other combinations of molar extinction coefficients taken at quite different combinations of wavelengths. *Figure 5* shows the plots obtained using ϵ_{315} and ϵ_{285}, the solid line being the regression fitted curves obtained in a similar manner to that described above for equations (1) and (2). *Figure 6* shows a similar plot obtained using data points at ϵ_{325} and ϵ_{315}. The variation of ϵ_{315} with r is shown in *Figure 7*. The wavelengths were used to calculate the

Table 2 Living end concentrations calculated from u.v. spectra of DIPIP-complexed polymerizations

Experiment number	Calculated values [Li] × 10³ M				
	$\tan^{-1}(\epsilon_{315}/\epsilon_{285})$	$\epsilon_{315}/\epsilon_{285}$	$\tan^{-1}(\epsilon_{325}/\epsilon_{315})$	$\epsilon_{325}/\epsilon_{315}$	$\bar{M}_n$
1	1.32	1.31	1.13	1.11	1.45
2	1.68	1.67	1.63	1.60	1.73
3	1.39	1.39	1.41	1.43	1.59
4	1.35	1.35	1.30	1.32	1.18
5	1.45	1.45	1.46	1.47	1.29

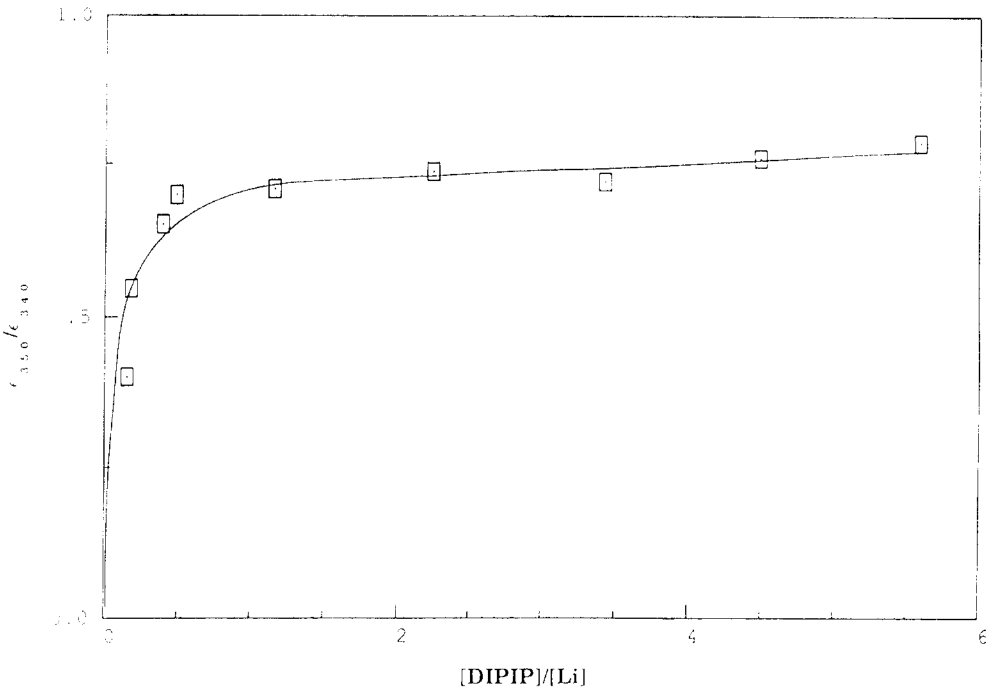

Figure 8 Plot of $\epsilon_{350}/\epsilon_{340}$ as a function of r

concentrations of the living species of the sample shown in *Table 1* using the following equations:

$$r = 7.77D^3 - 2.72D^2 + 0.58D - 0.02 \qquad (7)$$

$$r = 1.23E^3 + 5.28E^2 - 1.68E + 0.13 \qquad (8)$$

$$r = 196.66F^3 - 323.06F^2 + 178.21F - 32.78 \qquad (9)$$

$$r = 23.32G^3 - 35.66G^2 + 18.73G - 3.26 \qquad (10)$$

where $D = \tan^{-1}(\epsilon_{315}/\epsilon_{285})$
$E = \epsilon_{315}/\epsilon_{285}$
$F = \tan^{-1}(\epsilon_{325}/\epsilon_{315})$
$G = \epsilon_{325}/\epsilon_{315}$

The variation of ϵ_{315} with r can be described by the following equation:

$$\epsilon_{315} = 130.14H^3 + 320.74H^2 + 1202H + 4373 \qquad (11)$$

where $H = \log_n r$ and ϵ_{315} has the units M^{-1} cm^{-1}.

The calculated species concentrations are shown in *Table 2*. These values are close to those obtained using the ϵ_{325} and ϵ_{275} data within experimental error. This indicates that the method is not sensitive to the wavelengths selected for making measurements; so the procedures which have been described are very useful, even when data taken at wavelengths well removed from the absorption maxima are used. It was believed initially that the pair of wavelengths chosen should be on either side of the absorption maximum. However, it can be seen quite clearly in *Figure 6* that two wavelengths separated by only 10 nm on the same 'side' of the absorption maximum can also be used. The most likely explanation for this observation is that at 315 nm and 325 nm the uncomplexed species still contributes to the measured absorbance. If only two species contribute to the absorption spectra, i.e. complexed and uncomplexed species, the spectrum at the wavelengths used for the calculations must comprise contributions from each of the two species, i.e. wavelengths in the region where the two characteristic absorption peaks of the species involved overlap. However, by selecting spectral data at two wavelengths which are close to peak maxima for the species involved must give the most accurate result since the peak maxima are sensitive to changes in r.

There is evidence that there are more than two chemically distinct species contributing to the measured absorption spectra shown in *Figure 1*. For a situation where only two absorbing species are involved in an equilibrium, e.g. complexed and uncomplexed polyanions, then the following equilibrium situation is readily described

$$\text{uncomplexed chain} \overset{K}{\rightleftharpoons} \text{complexed chain}$$

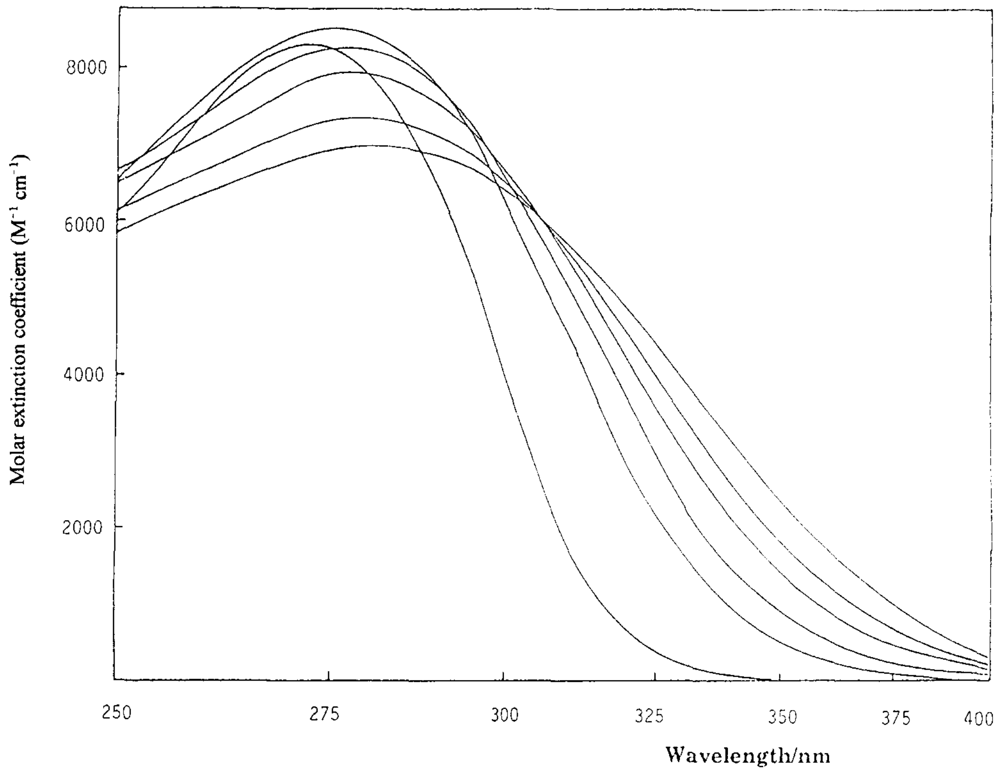

Figure 9 U.v.–visible absorption spectra of diglyme-complexed polybutadienyllithium chain-ends in cyclohexane; from bottom to top at 325 nm, $r = 0$, 0.41, 0.82, 1.6, 3.2, and 6.6

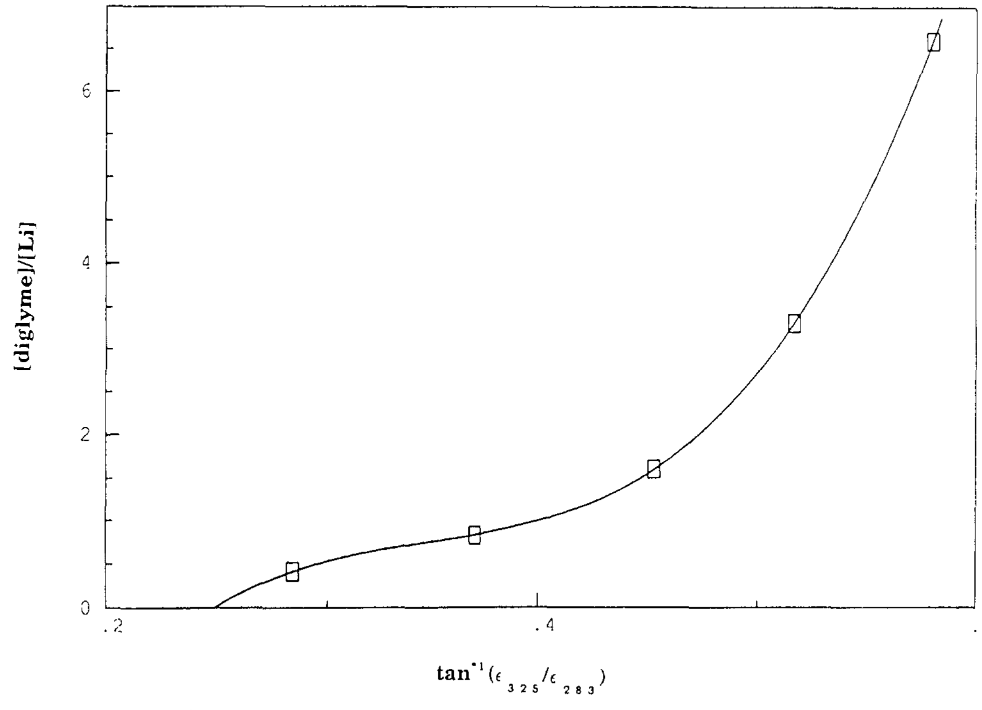

Figure 10 Relationship between tan^{-1} ($\epsilon_{325}/\epsilon_{283}$) and r ratio of diglyme-complexed polybutadienyllithium chain ends

If the ratio of the absorption is taken at two wavelengths where there is no contribution to the absorption by one of the species, is plotted as a function of r, the absorption ration should be independent of r. However, *Figure 8* shows that when $\epsilon_{350}/\epsilon_{340}$ is plotted against r a curve is obtained; $\epsilon_{350}/\epsilon_{340}$ increases rapidly when r is small, reaching a plateau at $r > 0.75$. This plot clearly indicates the value of r above which one species is predominant or where the molar ratio of the two species is constant.

The same calculation procedure for obtaining the concentration of the active species has also been applied to reactions where diglyme is used as complexing agent for the polybutadienyllithium anion. The absorption spectra of diglyme-complexed living chain-ends are shown in *Figure 9*. There is not such a distinctive shift of the peak maximum on addition of complexing agent to the polybutadienyllithium anion as seen in the case of DIPIP. At low values of r the peak broadens towards longer wavelengths; the absorption maximum also moves from 275 nm when $r = 0$ to 283 nm where

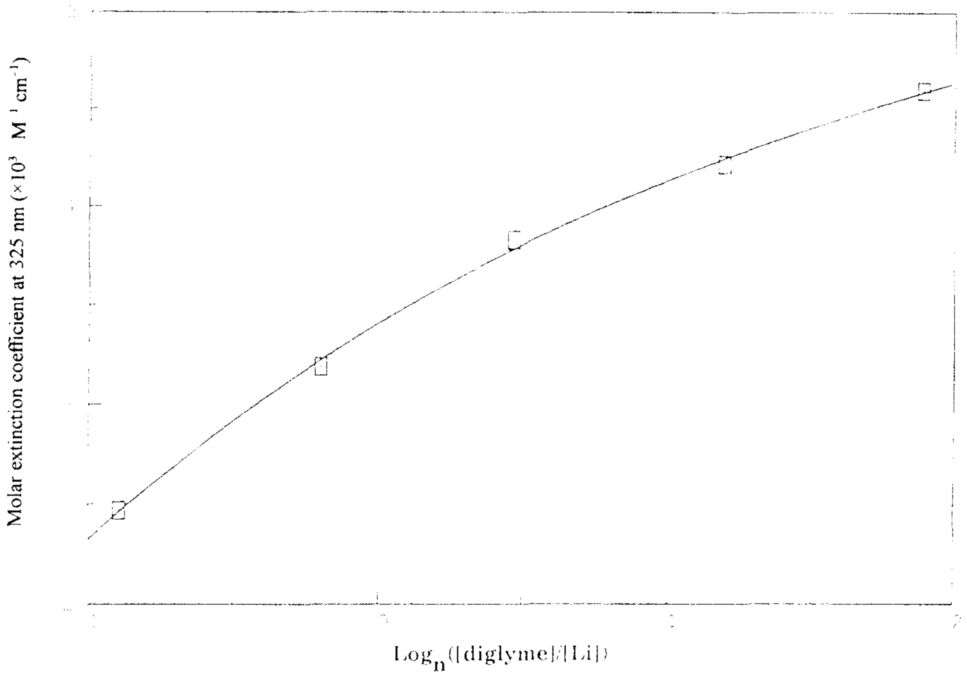

Figure 11 Relationship between $\log_n r$ and ϵ_{325} of diglyme-complexed polybutadienyllithium chain ends

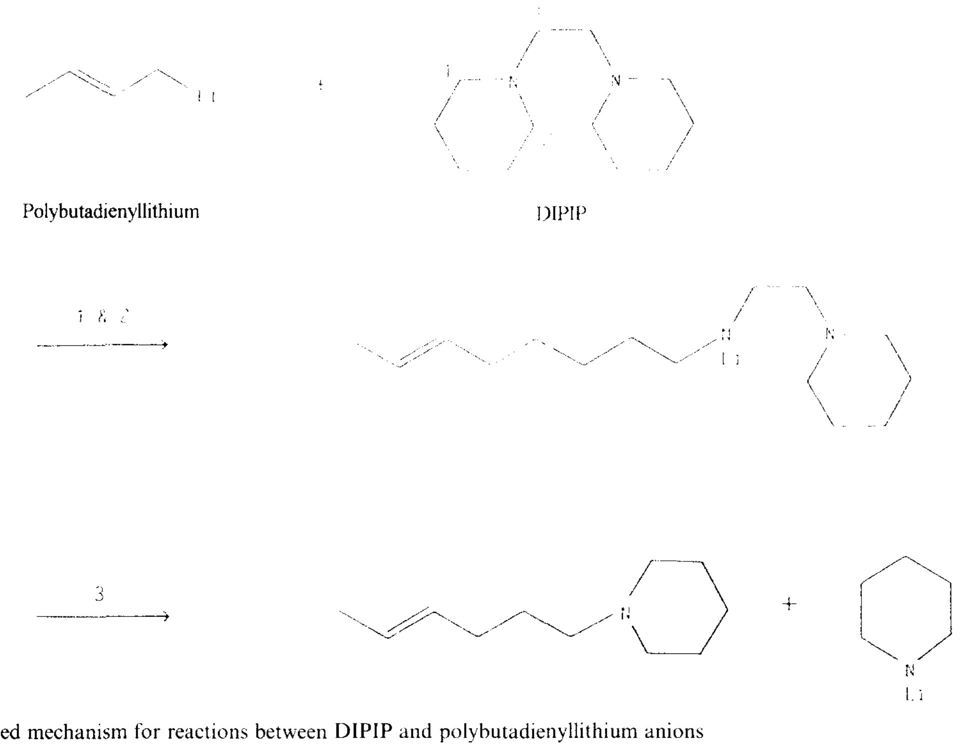

Figure 12 Proposed mechanism for reactions between DIPIP and polybutadienyllithium anions

$r = 6.6$. The two wavelengths chosen here for the determination of living chain-end concentration are 283 nm and 325 nm. The plot of r as a function of $\tan^{-1}(\epsilon_{325}/\epsilon_{283})$ is shown in *Figure 10*. A third-order polynomial equation was again used to obtain an equation which describes the experimental data

$$r = -17.13J^3 + 398.24J^2 - 415.08G + 147.86 \qquad (12)$$

where $J = \tan^{-1}(\epsilon_{325}/\epsilon_{283})$.

The dependence of ϵ_{325} on r is also shown in *Figure 11*, the fitted curve being described by

$$\epsilon_{325} = 23.34K^3 - 179.46K^2 + 882K + 3406 \qquad (13)$$

where $K = \log_n r$ and ϵ_{325} has the units M^{-1} cm^{-1}.

The calculated concentrations of polybutadienyllithium are shown in *Table 3*, along with the values

Table 3 Living end concentrations calculated from u.v. spectra and from $\bar{M}_n$ of diglyme-complexed polymerizations

Experiment number	r	Calculated values [Li] × 10^3 M	
		$\tan^{-1}(\epsilon_{325}/\epsilon_{283})$	$\bar{M}_n$
1	1.05	1.51	1.86
2	2.17	1.31	1.54
3	4.43	1.62	1.95

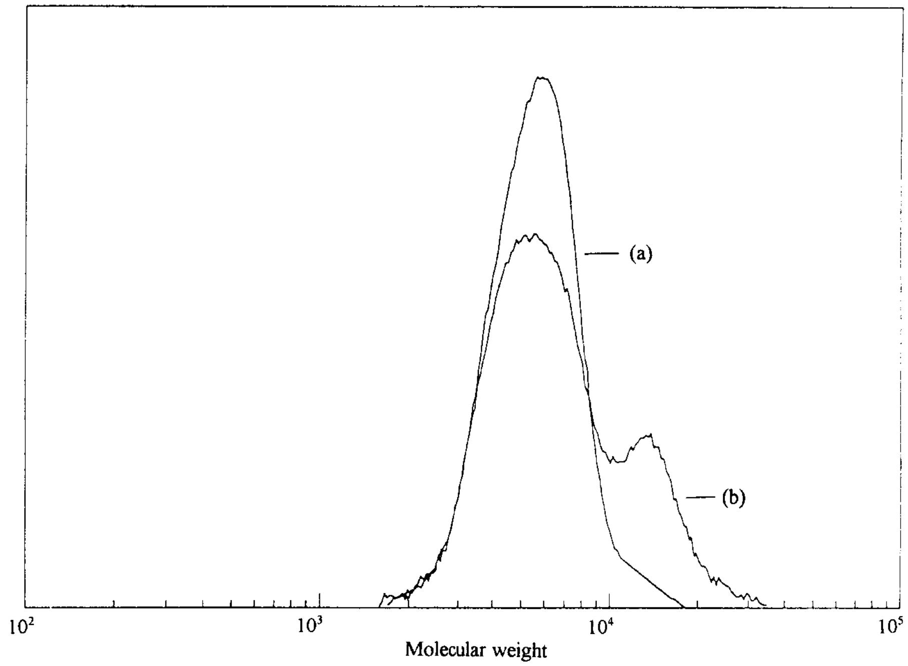

Figure 13 Molecular weight distribution of polybutadiene obtained (a) before and (b) after the reaction with DIPIP

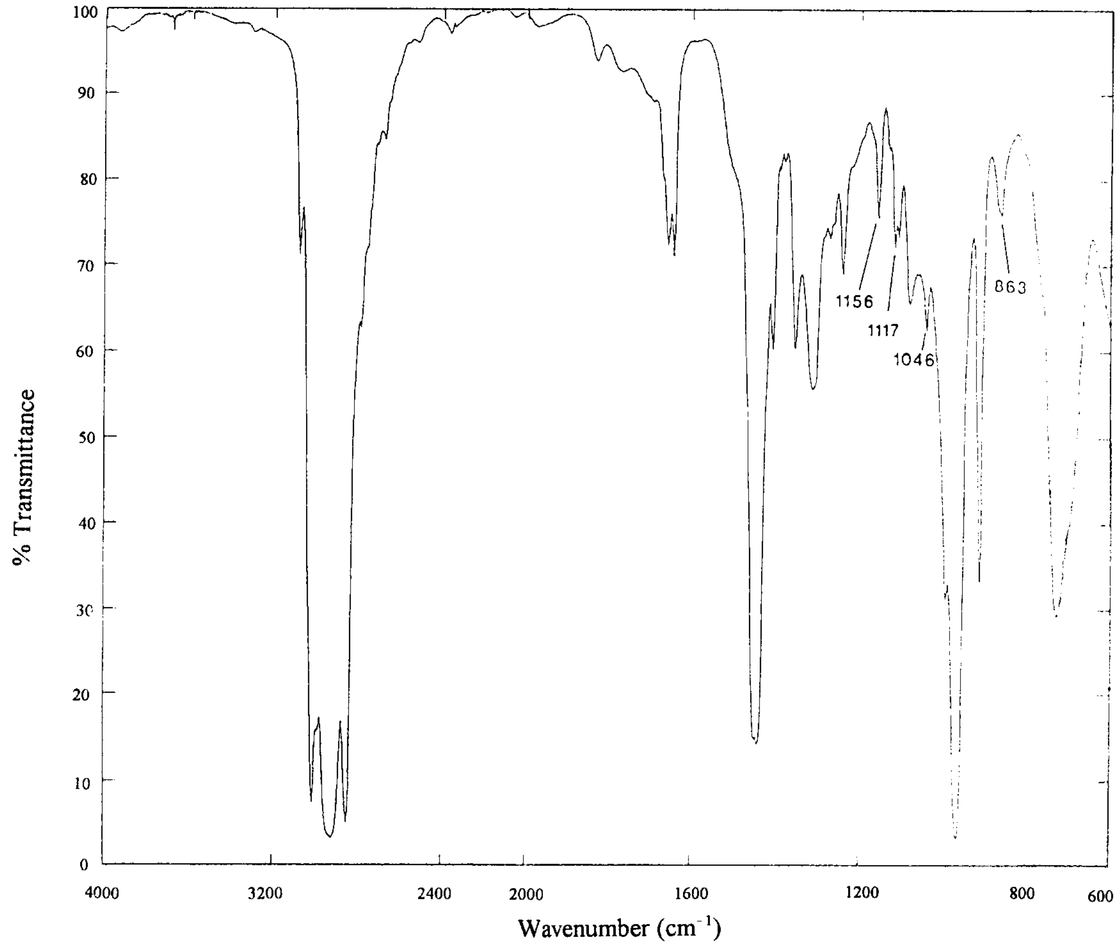

Figure 14 I.r. absorption spectrum of polybutadiene obtained after the reaction with DIPIP, showing new features at 1156, 1117, 1046, and 863 cm^{-1}

obtained from $\bar{M}_n$ measurements. The difference between the calculated and experimental concentrations is less than 20% in all cases which indicates that the proposed method may also be applied to diglyme-complexed species.

Post-polymerization reaction between DIPIP and polybutadienyllithium

It has been suggested[2] that the living chain-end can attack the DIPIP molecule at any one of the three carbon atoms adjacent to the nitrogen atom (*Figure 12*).

If one DIPIP molecule is attacked by two living chain-ends at both piperidine rings then chain coupling occurs with a consequential increase in molecular weight. Results from g.p.c. measurements on the reaction products after ample time has been allowed for the post polymerization reactions to occur are shown in *Figure 13*. The smaller high molecular weight peak in *Figure 13* appears at a molecular weight which is approximately twice that of the main peaks. Furthermore, four new weak bands can be observed in the i.r. spectra of the isolated polymers at 1156, near 1117, 1040 and 863 cm^{-1} as shown in *Figure 14*. The band at 1156 cm^{-1} is ascribed to the C–N asymmetric stretching of a secondary amine[5], whereas the doublet at 1117 and 1110 cm^{-1} is ascribed to C–N stretching band of a tertiary amine as well as the band at 1040 cm^{-1} [5]. The band at 863 cm^{-1} is also found in the spectrum of DIPIP and clearly results from the incorporation of the DIPIP into the polymer.

The g.p.c. and i.r. findings support the mechanism for the post-polymerization reaction shown in *Figure 12*. Characteristic bands of both secondary and tertiary amines are found. The secondary amine arises from the DIPIP molecule being attacked by the living chain-end at carbon atoms adjacent to the nitrogen. If reaction occurs at other carbon atoms in the DIPIP, a tertiary amine results. The intact piperidine ring of partially-attacked DIPIP may also give rise to the characteristic tertiary amine absorption bands.

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