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Anionic polymerization of styrene and butadiene initiated by n-butyllithium in ethylbenzene: determination of the propagation rate constants using Raman spectroscopy and gel permeation chromatography

S. Auguste*, H. G. M. Edwards, A. F. Johnson†, Z. G. Meszena‡ and P. Nicol§
Interdisciplinary Research Centre in Polymer Science and Technology, Chemistry and Chemical Technology, University of Bradford, Bradford, West Yorkshire, BD7 1DP, UK
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The rate of monomer loss during the n-butyllithium-initiated anionic polymerization of styrene in ethylbenzene has been measured using Raman spectroscopy. Gel permeation chromatography measurements on the reaction products have been used as an indirect method of obtaining the concentrations of the propagating species involved in the reaction. The rate of propagation for styrene polymerization has been determined in the temperature range 25 to 70°C, and for live-end concentrations between 9.1×10^{-5} and $6.7 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$. The order of the propagation reaction with respect to live-end concentration was found to be 0.53. The measured apparent rate constant for the propagation reaction was $(1.8 \pm 0.4) \times 10^{-1}\,\mathrm{mol^{-0.5}\,l^{0.5}\,s^{-1}}$ at 70°C, and the apparent activation energy was $75 \pm 8\,\mathrm{kJ\,mol^{-1}}$. The rate of propagation for 1,3-butadiene has also been determined in the temperature range 39 to 72.3°C, and for live-end concentrations between 5.6×10^{-4} and $1.9 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$. The apparent rate constant for the propagation reaction was $(7 \pm 2) \times 10^{-2}\,\mathrm{mol^{-0.5}\,l^{0.5}\,s^{-1}}$ at 70°C and the activation energy was $72 \pm 14\,\mathrm{kJ\,mol^{-1}}$, assuming 0.5 order with respect to live-end concentration. The activation energy found, assuming an order of reaction of 0.25, was $70 \pm 17\,\mathrm{kJ\,mol^{-1}}$. The kinetic data for the butadiene system are less reliable than for styrene as can be seen from the limits of error quoted. The reaction has been confirmed to be internally first order with respect to monomer concentration to high conversions for both monomers examined. Crown copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: anionic polymerization; styrene; butadiene)

INTRODUCTION

Kinetic studies of the living anionic polymerization of styrene initiated by n-butyllithium in a number of different solvents have been reported[1–5]. The general experimental methods, notably the high vacuum techniques, used for the handling of this air-sensitive system have been reviewed[6]. Most kinetic measurements have been carried out using ultraviolet(u.v.)/visible spectroscopy to monitor the concentrations of polymeric anions and in many instances, to follow the loss of monomer also[1,2]. A major limitation of u.v./visible spectrophotometry is that the reactions can only be followed in solvents which do not have strong absorption bands in the appropriate regions of the u.v./visible spectrum where the monomer or polyanions have characteristic absorptions. Furthermore, with a monomer such as styrene, which has very strong absorption bands in the 220–300 nm region of the u.v./visible spectrum, measurements are limited to relatively low monomer concentrations. In general, these experimental limitations have not prevented meaningful kinetic studies[7] of the mechanism of the butyllithium-initiated polymerization of styrene in spectroscopically clear solvents such as cyclohexane, tetrahydrofuran, dioxane and others, at monomer concentrations up to approximately 1 M. However, relatively little is known about the kinetics of the anionic polymerization of styrene with organometal initiators in technically important solvents such as ethylbenzene, probably because of the masking effect that this has in the relevant regions of the u.v./visible spectral range for styrene and butadiene and their polymeric anions.

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* Present address: Groupe Fournier, Plasto SA, BP 160-21304, Chenove Cedex, France

† To whom correspondence should be addressed. Present address: IRC, School of Chemistry, University of Leeds, Leeds LS2 9JT, UK.

‡ Present address: Department of Mathematics, Technical University of Budapest, H-1521 Budapest, Muegyetem rkp. 3, Hungary

§ Present address: Groupment de Recherche de Lacq, BP 34, Lacq, 64170 Artix, France

Anionic polymerization chemistry permits the synthesis of polybutadienes of different microstructures by varying solvent polarity, temperature or by the addition of catalytic amounts of complexing agents to the polymerization reactions. It is, for example, possible to synthesize polybutadienes containing either less than 10% or up to 97% vinyl unsaturation in this way[8]. Raman spectroscopy has been used as a means of following various polymerization processes in our laboratories[8,9]. It is a particularly useful technique for monitoring bulk polymerizations when there are characteristic scattering bands available for the monomer which are distinctive in a wide range of solvents, or for following solution polymerizations when the vibrational bands are distinctive from those of the solvent. An attractive feature of the technique is that it can provide an accurate and non-invasive method to follow the concentration of monomer during polymerization when reaction is carried out under high vacuum conditions in glass apparatus. Also, the vibrational band intensities are directly proportional to the number of scattering centres in a solution, i.e. intensity is directly proportional to the concentration of scattering species. Raman spectroscopy has proved to be a relatively simple and accurate method to determine the microstructure of polydienes and requires virtually no sample preparation.

Raman spectroscopy has already been applied to the determination of monomer concentration in polymers[10]. Sears *et al.*[11] and Chu and Lee[12] monitored the intensity variations of Raman scattering in the case of the thermal polymerization of styrene. Other studies were reported on the copolymerization of styrene with methyl methacrylate[13,14]. In principle, it is possible to use Fourier transform (*FT*)-Raman to study the initiation reaction, but this step in the reaction mechanism has not been considered in this work. There are no previous reports of anionic polymerization reactions being monitored by Raman spectroscopy. Here, the high conversion, anionically initiated polymerization of styrene and 1,3-butadiene are explored in ethyl benzene under conditions relevant to large-scale polymerization processes. Because it is not possible to obtain a direct measure of the living polyanion concentrations by spectrophotometric means under the conditions employed, gel permeation chromatography has been used to measure the number average molecular weights of the products, which are in turn related to the actual concentration of the living polyanions in the reactor. This method has proved to be successful when employed elsewhere[9].

EXPERIMENTAL

Apparatus and materials

Reactions were carried out in purpose-built glass vessels (*Figure 1*). After the reaction vessel has been evacuated, 4 to 5 ml of a 2.0 molar solution of n-butyllithium in cyclohexane (Aldrich) was introduced into a side flask through the septum and the cyclohexane removed by cold distillation. Ethylbenzene (100 ml, Aldrich) previously purified and dried over calcium hydride, was added to the reaction vessel by injection and the resultant butyllithium solution used to wash the walls of the vessel to remove traces of moisture and other reactive impurities. The ethylbenzene was then distilled repeatedly from the side flask into the main reaction flask and the distillate used to wash all residual n-butyllithium from the walls, the washings being returned to the side vessel each time. Finally, in order to obtain pure dry solvent for the reaction, the ethylbenzene was cold-distilled from the n-butyllithium, and the latter was then removed from the vicinity of the reaction vessel by closing valve A.

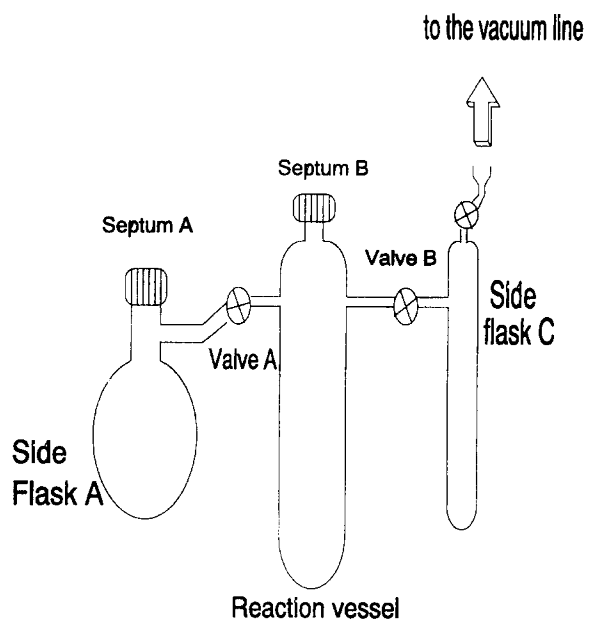

Figure 1 High-vacuum glass reaction vessel

The t-butylcatechol in the styrene (Janssen) was removed by passing the monomer through a column containing basic activated aluminium oxide (Aldrich) and the monomer then dried over calcium hydride. After being distilled from calcium hydride under nitrogen, the monomer was finally vacuum-distilled into the reaction vessel. The vessel was then pressurized with high-purity dry nitrogen and the n-butyllithium initiator introduced to the reaction vessel by injection.

The 1,3-butadiene (Union Carbide, high purity) was passed over molecular sieves and condensed at −78°C into a flask containing about 2 ml of n-butyllithium (the initiator is capable of initiating polymerization at low temperatures, but the propagation reaction is very slow at this temperature). The mixture was thoroughly shaken for approximately 30 min and the monomer then vacuum-distilled into the reaction vessel, which was finally pressurized with pure dry nitrogen.

When experiments were carried out with low polyanion concentrations, the change in monomer concentration with time could be followed directly by Raman spectroscopy using an appropriate cell attached to the high vacuum equipment; the temperature controlled to ±0.1°C (Julabo F140 HC) at selected temperatures in the range 0–100°C.

At high initiator concentrations, the colour of the reaction mixture resulted in an excessive absorption of the excitation radiation, and the scattering intensity changes of the monomer as its concentration decreased could not be followed accurately. This problem was circumvented by equipping the reaction vessel with a number of Raman cells. After injection of the initiator, the reaction mixture was rapidly distributed between these cells (a few millilitres of reaction mixture per cell), then each was sealed quickly, removed from the reaction vessel and immersed in a water bath at the desired temperature for a selected length of time. At the appropriate time the reaction was quenched by the addition of methanol.

The Raman spectroscopic apparatus employed for these studies comprised a Spectra-Physics model 2020/5 argon-ion laser with a nominal output power of 1.5 W at 488.0 nm, and a Spex Industries 1401 double monochromator with a reciprocal linear dispersion of $20.0\,\text{cm}^{-1}$ at 488.0 nm in the first order. The scan speed was 100 wave numbers per minute using a slit width of 200 μm. A PET/Thorn EMI computer was used to control the spectrometer and also for data output capture. Several scans were accumulated in order to generate the spectrum of the reaction mixture prior to initiation. During polymerization, a single scan was used to monitor monomer depletion and the reaction time was taken to be that which corresponded to the maximum of the ν(C=C) band ($1631\,\text{cm}^{-1}$), a procedure necessary to take into account the scan speed. The area of each peak was determined using a curve-fitting package (LAB-CALC, Galactic Industries Corp.).

Band intensity calculation

The ν(C=C) stretching vibration at $1631\,\text{cm}^{-1}$ has been used to monitor styrene concentration (see *Figure 2*). This band is very strong and its intensity decreases during polymerization as carbon double bonds break and monomer molecules are added to the polymer chains. Two bands at 1610 and $1595\,\text{cm}^{-1}$, which have been assigned to aromatic ring vibrations[15], have been used to normalize the intensity changes occurring during the polymerization, in order to compensate for the geometrical and optical changes of the sample arising from positional or focusing optimization of the laser beam.

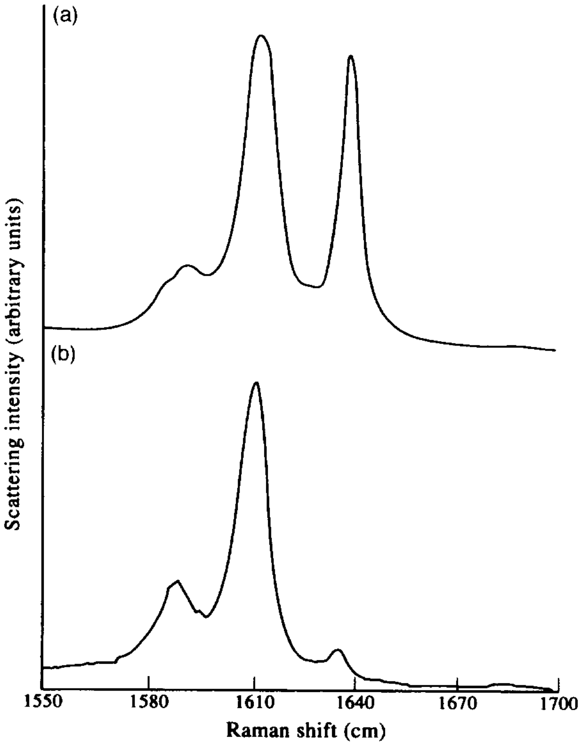

Figure 2 Raman spectrum of polymerizing styrene in ethylbenzene in the C=C stretching region. (a) Conversion 3%; (b) conversion 94%

However, since the intensities of the bands at 1577 and $1602\,\text{cm}^{-1}$ contain contributions from styrene, polystyrene and ethylbenzene, the relative contributions of each species to the integrated intensities had to be resolved. Before the polymerization, the scattering at these wave numbers is due only to styrene and ethylbenzene. As polymerization proceeds, the mass of the monomer decreases and the mass of the polymer increases proportionately, the amount of solvent remaining unchanged. The intensity of a band, measured by its area, is equal to

$$I = \alpha(f_{\text{st}}\{\text{st}\} + f_{\text{ps}}\{\text{ps}\} + f_{\text{eb}}\{\text{eb}\}) \qquad (1)$$

where $f_{\text{st}}, f_{\text{ps}}$ and f_{eb} are the scattering factors for styrene, polystyrene and ethylbenzene, respectively; {st}, {ps} and {eb} are, respectively, the proportions by weight of styrene, polystyrene and ethylbenzene in the solution, and α is a geometric factor that can vary during the experiment due to changes in the position of the sample in the laser beam, but which is assumed to remain constant during any single scan. A simple normalization of the band at $1631\,\text{cm}^{-1}$ with respect to the sum of the intensities of the bands at 1577 and $1602\,\text{cm}^{-1}$ would only be correct if the three scattering factors f_{st}, f_{ps} and f_{eb} happen to be identical.

At every instant in time, the intensities are equal to:

$$I_1 = \alpha(f_{1\text{st}}\{\text{st}\} + f_{1\text{ps}}\{\text{ps}\} + f_{1\text{eb}}\{\text{eb}\}) \qquad (2\text{a})$$

$$I_2 = \alpha(f_{2\text{st}}\{\text{st}\} + f_{2\text{ps}}\{\text{ps}\} + f_{2\text{eb}}\{\text{eb}\}) \qquad (2\text{b})$$

$$I_3 = \alpha(f_{3\text{st}}\{\text{st}\}) \qquad (2\text{c})$$

where f_{1xx}, f_{2xx} and f_{3xx} are the scattering factors for the constituents, where xx refers to the bands at 1577, 1602 and $1631\,\text{cm}^{-1}$, respectively, for each of the species st, ps and eb.

It can be shown that the proportion of styrene is then given by equation (3):

$$\{\text{st}\} = \frac{R((f_{1\text{ps}} + f_{2\text{ps}})\{\text{st}\}_0 + (f_{1\text{eb}} + f_{2\text{eb}})\{\text{eb}\})}{f_{3\text{st}} - R(f_{1\text{st}} + f_{2\text{st}} - f_{1\text{ps}} - f_{2\text{ps}})} \qquad (3)$$

The initial proportions of styrene $\{\text{st}\}_0$ and ethylbenzene {eb} were determined for each experiment by simply weighing the reaction vessel before and after each distillation or injection.

The determination of the scattering factors of styrene, polystyrene and ethylbenzene for the band at $1602\,\text{cm}^{-1}$ was achieved using solutions of each of these three products in cyclohexane at various concentrations. A strong band in the Raman spectrum of cyclohexane at $1265\,\text{cm}^{-1}$ was used as a reference standard.

In the case of 1,3-butadiene polymerization, the ν(C=C) stretching vibration at $1634\,\text{cm}^{-1}$ was used to monitor the monomer concentration, and the bands at 1577 and $1602\,\text{cm}^{-1}$ due to scattering by ethylbenzene were used as reference for the calibration.

The living anion concentration during polymerization has been obtained from the number average molecular weight (M_n) of the polymers isolated from the polymerization systems used for the kinetic data studies. Gel permeation chromatography (g.p.c.) was used to obtain M_n as described previously[9].

The gel permeation chromatograph was fitted with two 30 cm PLgel 10 μm mixed bed columns (Polymer Laboratories) using filtered and degassed tetrahydrofuran as eluant and solvent for the polymers. Toluene was used as an internal standard and the nominal flow rate was 1 ml min^{-1}. The system was calibrated using polystyrene and polybutadiene standards (Polymer Laboratories). Data reduction was made using in-house software which is now commercially available[16].

Kinetics of living anionic chemistry

It seems likely that n-butyllithium and the living polystyryllithium or polybutadienyllithium anions are aggregated in ethylbenzene containing high concentrations of styrene and butadiene of the type used in this work, i.e. the polymerization mechanism is similar to that for polymerizations carried out at lower monomer concentrations in other hydrocarbon solvents:

$$(\mathrm{BuLi})_m \overset{K_\mathrm{d}}{\Leftrightarrow} m(\mathrm{BuLi}) \qquad (4)$$

$$\mathrm{BuLi} + \mathrm{M} \xrightarrow{k_\mathrm{i}} \mathrm{Bu-M^-Li^+} \qquad (5)$$

where M = styrene or 1,3-butadiene and BuLi = *n*-butyllithium.

Initiation takes place by reaction of the monomer with free BuLi. Similarly, propagation takes place by reaction of monomer with the free polystyryllithium or polybutadienyllithium:

$$(\mathrm{Bu-M}_j^-\mathrm{Li}^+)_n \overset{K_\mathrm{s}}{\Leftrightarrow} n(\mathrm{Bu-M}_j^-\mathrm{Li}^+) \qquad (6)$$

$$\mathrm{Bu-M}_j^-\mathrm{Li}^+ + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{Bu-M}_{j+1}^-\mathrm{Li}^+ \qquad (7)$$

If this mechanism is correct then $k_{\mathrm{iapp}} = k_\mathrm{i}(K_\mathrm{d})^{1/m}$ and $k_{\mathrm{p,app}} = k_\mathrm{p}(K_\mathrm{S})^{1/n}$, where k_{iapp} and $k_{\mathrm{p,app}}$ are the apparent rate constants. It is accepted that in living polymerizations in which the initiation reaction takes place rapidly relative to propagation and where there is no termination, the products will have a narrow Poisson-type molecular weight distribution with a dispersity index ($D_\mathrm{n} = M_\mathrm{w}/M_\mathrm{n}$) of approximately 1.04. All the materials isolated from the polymerizations described here had values of $D_\mathrm{n} \leq 1.05$, hence, for the purposes of discussion, it can be assumed that (i) the rate of equilibration described in equations (1)–(4) is very fast, and (ii) the overall rate of the initiation process is fast relative to the overall rate of the steps involved in the propagation process.

The overall rate of loss of monomer during polymerization can therefore be simplified to:

$$\frac{\mathrm{d[M]}}{\mathrm{d}t} = -k_{\mathrm{i,app}}[\mathrm{BuLi}]^{1/m}[\mathrm{M}] - k_{\mathrm{p,app}}[\mathrm{LE}]^{1/n}[\mathrm{M}] \qquad (8)$$

If the initiation reaction is very rapid, loss of monomer can be attributed to the propagation reaction only,

Table 1 Apparent propagation rate measurements with Raman spectroscopy in the alkyllithium-initiated polymerization of styrene in ethylbenzene. EB, ST and LE refer to ethylbenzene, styrene and live ends, respectively

Temp. (°C)	EB weight (g)	ST weight (g)	$\frac{\mathrm{d}\ln\left(\frac{[\mathrm{ST}]_0}{[\mathrm{ST}]}\right)}{\mathrm{d}t}$ $\times 10^5$ (s^{-1})	[LE] $\times 10^5$ (mol l^{-1})	M$_\mathrm{n}$ $\times 10^{-3}$ (g mol^{-1})	$k_\mathrm{p} \times 10^3$ (l$^{0.5}$ mol$^{-0.5}$) s^{-1})
70.0	69.98	7.08	249.2	22.54	337	166
70.0	61.14	26.10	264.0	23.99	1.080	170
56.4	80.25	9.75	489.7	673.5	13.5	59.7
54.7	81.55	22.55	197.9	131.4	139	54.6
50.0	91.45	8.85	168.3	155.8	47.8	42.6
43.0	74.30	11.44	36.32	66.48	171	14.1
35.0	44.46	5.78	8.289	9.11	1.084	8.69
25.0	20.35	17.50	14.17	177.6	229	3.36

Table 2 Apparent propagation rate measurements in the alkyllithium-initiated polymerization of 1,3-butadiene in ethylbenzene. EB, BD and LE refer to ethylbenzene, 1,3-butadiene and live-ends, respectively

Temp. (°C)	EB weight (g)	BD weight (g)	$\frac{\mathrm{d}\ln\left(\frac{[\mathrm{BD}]_0}{[\mathrm{BD}]}\right)}{\mathrm{d}t}$ $\times 10^5$ (s^{-1})	[LE] $\times 10^5$ (mol l^{-1})	$M_n \times 10^{-3}$ (g mol^{-1})
72.3	90.34	7.72	241.9	129.9	48.0
69.0	76.42	9.00	199.0	85.92	96.5
65.0	77.76	6.38	147.4	71.44	85.0
59.0	81.22	7.88	77.79	90.00	78.7
52.7	84.64	7.98	66.20	120.1	58.0
50.0	76.20	5.52	23.59	55.61	99.3
44.0	82.80	6.62	32.30	107.3	56.65
39.0	85.84	11.56	23.59	190.6	50.5

Table 3 Apparent propagation rate measurements in the alkyllithium-initiated polymerization of 1,3-butadiene in ethylbenzene. The two sets of values assume a partial order of 1/2 and 1/4 with respect to live-end (LE) concentration

Temp. (°C)	[LE] × 10^5 (mol l^{-1})	$k_p \times 10^2$ ($l^{0.5}$ mol$^{-0.5}$ s^{-1})	$k_p \times 10^2$ ($l^{0.25}$ mol$^{-0.25}$ s^{-1})
72.3	129.9	6.71	1.27
69.0	85.92	6.79	1.16
65.0	71.44	5.52	0.90
59.0	90.00	2.59	0.45
52.7	120.1	1.19	0.36
50.0	55.61	1.00	0.15
44.0	107.3	0.99	0.18
39.0	190.6	0.54	0.11

Table 4 The order of the propagation reaction with respect to live-end concentration in the n-Butyllithium-initiated homopolymerization in ethylbenzene

Monomer	1/*n* found by 2D regression	Lower 95%	Upper 95%	Value chosen
Styrene	0.529	0.422	0.637	0.5
1,3-Butadiene	0.623	0.069	1.18	0.25, 0.5

allowing equation (8) to be simplified to:

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = -k_{\mathrm{p,app}}[\mathrm{LE}]^{1/n}[\mathrm{M}] \qquad (9)$$

Integration of equation (9) gives:

$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = -k_{\mathrm{p,app}}[\mathrm{LE}]^{1/n}t \qquad (10)$$

where t is the reaction time.

The importance of the relative rate of the initiation reaction to that of propagation in determining the magnitude of the polydispersity index will be discussed elsewhere[17]. It is also known that transfer reactions are very slow compared with polymerization rates and can be ignored here[18 21].

RESULTS

The experimental results obtained for the polymerization of styrene and 1,3-butadiene are summarized in *Tables 1–3*.

The range of styrene concentrations examined was approximately 10-fold (0.3–3.9 M) and the initiator approximately 70-fold (0.9–67 × 10^{-4} mol l^{-1}). In the case of 1,3-butadiene polymerizations, live-end concentrations were varied between 5.6 × 10^{-4} and 1.9 × 10^{-3} mol l^{-1}. Monomer and live-end concentrations were different for each experiment. The temperatures at which the reactions were studied were in the range 25 to 70°C for styrene polymerizations and 39 to 72.3°C for 1,3-butadiene polymerizations (*Figure 5*).

The values of $-k_{\mathrm{p,app}}[\mathrm{LE}]^{1/n}$ were obtained from plots of $\ln[\mathrm{M}]/[\mathrm{M}]_0$ against time (*Figure 3*). Typically, these plots were good straight lines up to 95% conversion of monomer. The apparent propagation rate constant has been determined using the model shown in equations (11) and (12):

$$k_{\mathrm{p,app}} = A\mathrm{e}E/RT \qquad (11)$$

$$\ln\left(\frac{\mathrm{d}}{\mathrm{d}t}\ln\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]}\right)\right) = \ln(A) + \left(-\frac{E}{RT}\right)\frac{1}{T} + \frac{1}{n}\ln([\mathrm{LE}]) + \epsilon \qquad (12)$$

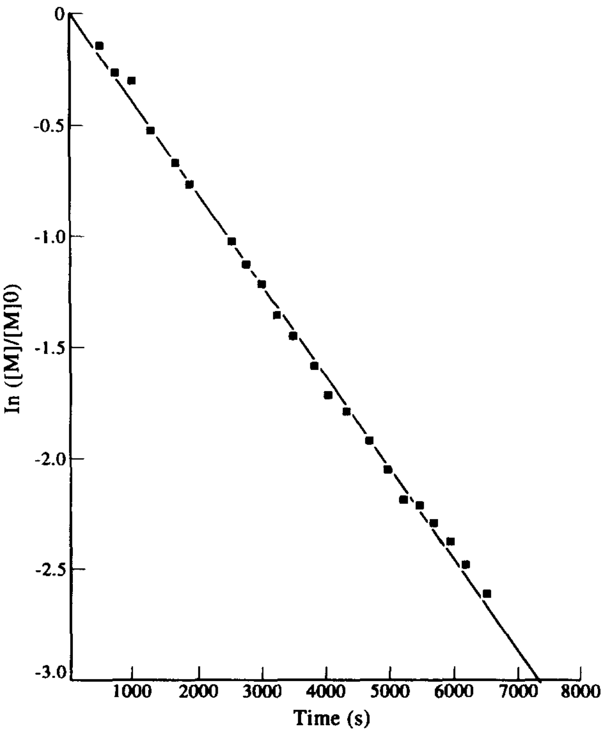

Figure 3 Logarithmic plot of styrene concentration, ln $[\mathrm{M}]/[\mathrm{M}]_0$ as a function of time in the n-buthyllithium-initiated polymerization of styrene in ethylbenzene, determined using Raman spectroscopy. ($[\mathrm{M}]_0$ = 1.0 mol l^{-1}. Temperature = 49.5°C)

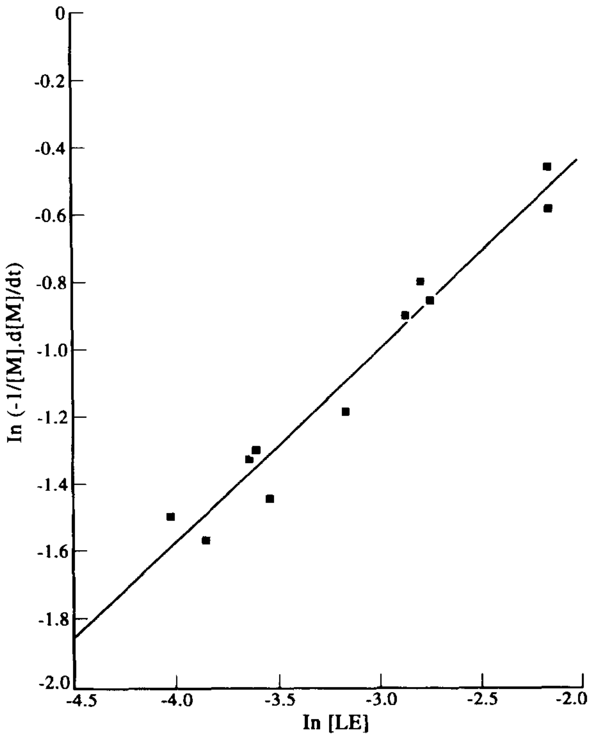

Figure 4 Dependence of the rate of propagation on the live-end concentration in the n-buthyllithium-initiated polymerization of styrene in ethylbenzene. Reaction order with respect to live-end concentration = 1/2. Rate of monomer loss is transposed to a common temperature

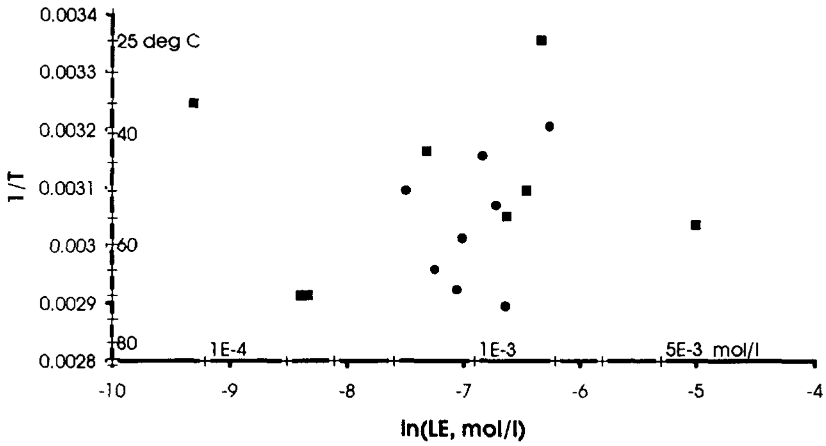

Figure 5 Summary of experimental settings in the n-buthyllithium-initiated homopolymerization of styrene and 1,3-butadiene in ethylbenzene: ■, styrene; ●, 1,3-butadiene

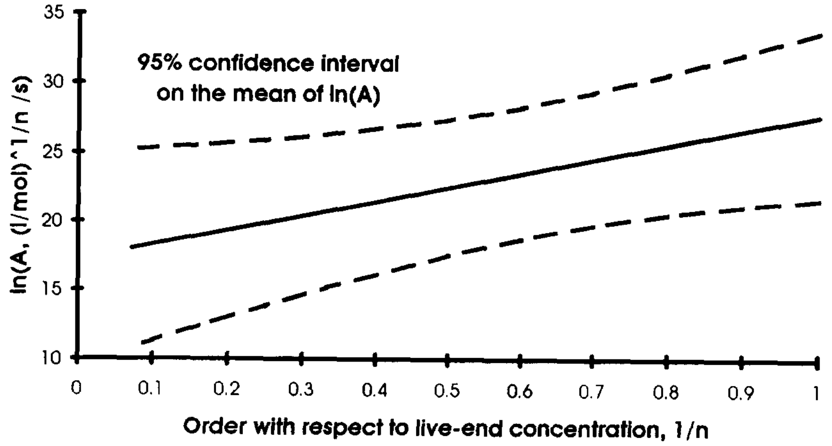

Figure 6 Pre-exponential factor of the apparent propagation rate constant as a function of the order of the propagation reaction with respect to live-end concentration, $1/n$, in the n-buthyllithium-initiated polymerization of 1,3-butadiene in ethylbenzene

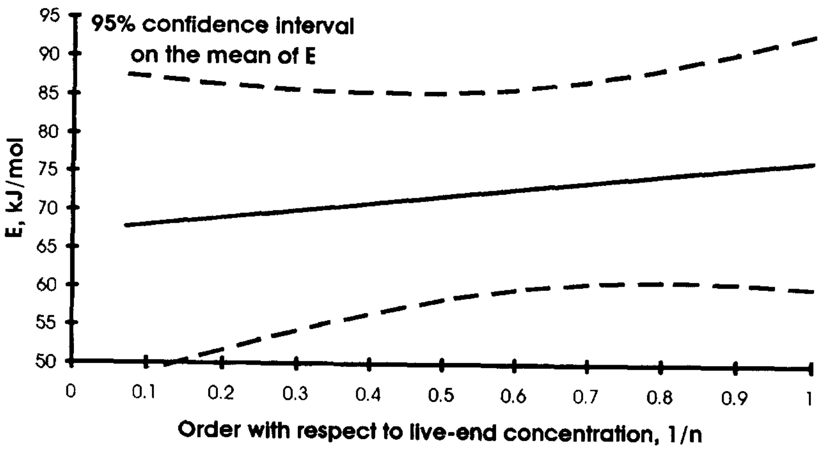

Figure 7 Activation energy of the apparent propagation rate constant as a function of the order of the propagation reaction with respect to live-end concentration, $1/n$, in the n-buthyllithium-initiated polymerization of 1,3-butadiene in ethylbenzene

where A is the frequency factor, E the activation energy, R the gas constant, T the temperature, and ϵ the measurement error. It is assumed that the error function ϵ has a normal probability distribution with zero mean and constant variance.

Nominally, the equation (12) model has two controllable variables: the temperature and the live-end concentration, but due to the unavoidable impurities the latter cannot be set precisely in practice. Consequently, while the order of the propagation reaction with respect to live-end concentration, $1/n$, is unknown, no simple (one-dimensional) linear regression is possible to obtain

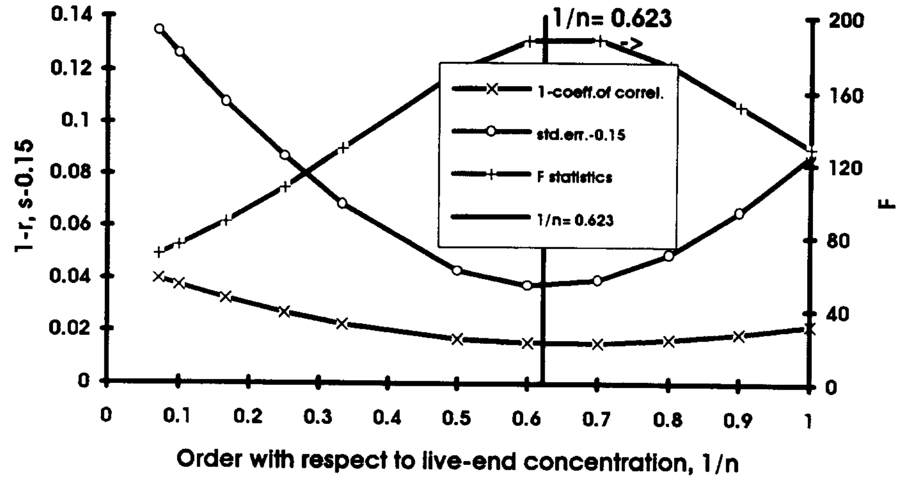

Figure 8 Goodness of fit with model: $\ln(k_{\mathrm{p,app}}) = \ln(A) - E/R \times 1/T$, in the n-buthyllithium-initiated polymerization of 1,3-butadiene in ethylbenzene

the activation energy and the pre-exponential factor. For this reason a two-dimensional linear regression analysis has been carried out on the experimental results to find the order, $1/n$. The values obtained are shown in *Table 4*. Consistent with the assumed kinetic scheme (equations (4)–(7)), within the confidence interval, integral values have been chosen for n. Having obtained the reaction order with respect to the live-end concentration, one-dimensional linear regression analysis has been carried out in order to determine the activation energy and the pre-exponential factor of the apparent propagation rate constant.

It can be seen from *Table 4* that a two-fold aggregation is confirmed for styrene, if the proposed kinetic scheme is valid. The effect of the live-end concentration on the rate of reaction is shown in *Figure 4*. The rate of monomer loss from each of the experiments is transposed to a common temperature in order to eliminate the effect of temperature on the reaction rate.

In the case of butadiene, the live-end concentration range covered was small, which limits the accuracy of the calculations (see also *Figure 5*). Since the value of the apparent propagation rate constant significantly depends on the reaction order used, a series of linear regressions has been carried out with various reaction orders. Both the logarithm of the pre-exponential factor and the activation energy have been found to be linearly dependent on the reaction order, $1/n$ (*Figures 6* and *7*).

$$\ln(A\,((\mathrm{l\,mol^{-1}})^{1/n}\,\mathrm{s^{-1}})) = 17.28 + 10.36\frac{1}{n} \tag{13}$$

$$E\,(\mathrm{kJ\,mol^{-1}}) = 67.12 + 9.434\frac{1}{n} \tag{14}$$

Statistically, the best fit to the data is achieved with $1/n = 0.623$ (order found by two-dimensional regression). The fact that this is the best value can also be seen in *Figure 8* in terms of the coefficient of correlation, estimated standard deviation of ϵ, and F statistic of the one-dimensional regressions (r, s and F, respectively).

Table 5 Pre-exponential factor and activation energy of the propagation reaction with 95% confidence interval. n-Butyllithium-initiated homopolymerization in ethylbenzene

Monomer	A $((\mathrm{l\,mol^{-1}})^{1/n}\,\mathrm{s^{-1}})$	E $(\mathrm{kJ\,mol^{-1}})$
Styrene	5.09E+10	75.3
($1/n = 0.5$)	[3.3E+9, 7.8E+11]	[68, 83]
Butadiene	5.68E+9	71.8
($1/n = 0.5$)	[4.2E+7, 7.7E+11]	[58, 85]
Butadiene	4.26E+8	69.5
($1/n = 0.25$)	[1.1E+6, 1.7E+11]	[53, 86]

Within the confidence interval for $1/n$, two reaction order values have been chosen (0.25 and 0.5, typical of those proposed in the literature for other hydrocarbon solvents) to obtain values of the apparent propagation rate constant.

The predicted activation energies and pre-exponential factors are shown in *Table 5*. The predicted apparent propagation rate constants are shown in *Tables 6* and *7* together with the 95% confidence interval on the mean of $\ln(k_{\mathrm{p,app}})$.

DISCUSSION

Raman spectroscopy has been successfully used to follow changes in both styrene and butadiene concentrations during anionic polymerization in ethylbenzene over a wide range of temperatures and reagent concentrations, in particular monomer concentrations. Although there are no previously reported kinetic data available for the alkyllithium-initiated polymerization of these monomers in ethylbenzene, it is interesting to compare the results of the present work with previous studies carried out in

Table 6 Apparent propagation rate constants with 95% confidence interval on the mean of $\ln(k_{\mathrm{p,app}})$. n-Butyllithium-initiated homopolymerization of styrene in ethylbenzene

t (°C)	$k_{\mathrm{p,app}}$ $(\mathrm{l^{0.5}\,mol^{-0.5}\,s^{-1}})$	Lower 95% $(\mathrm{l^{0.5}\,mol^{-0.5}\,s^{-1}})$	Upper 95% $(\mathrm{l^{0.5}\,mol^{-0.5}\,s^{-1}})$
20	0.00194	0.00143	0.00263
25	0.00325	0.00251	0.00422
30	0.00537	0.00431	0.00668
35	0.00872	0.00727	0.0105
40	0.0139	0.0120	0.0162
45	0.0220	0.0192	0.0251
50	0.0341	0.0301	0.0387
55	0.0523	0.0458	0.0598
60	0.0792	0.0680	0.0921
65	0.118	0.0992	0.141
70	0.175	0.142	0.214
75	0.255	0.202	0.323

Table 7 Apparent propagation rate constants with 95% confidence interval on the mean of $\ln(k_{p,app})$. n-Butyllithium-initiated homopolymerization of 1,3-butadiene in ethylbenzene

	$1/n = 0.5$			$1/n = 0.25$		
t (°C)	$k_{p,app}$ ($l^{0.5}\,mol^{-0.5}\,s^{-1}$)	Lower 95%	Upper 95%	$k_{p,app}$ ($l^{0.25}\,mol^{-0.25}\,s^{-1}$)	Lower 95%	Upper 95%
35	0.00377	0.00260	0.00548	0.000711	0.000450	0.00112
40	0.00590	0.00437	0.00797	0.00110	0.000758	0.00158
45	0.00910	0.00717	0.0115	0.00167	0.00125	0.00223
50	0.0139	0.0115	0.0168	0.00250	0.00198	0.00316
55	0.0208	0.0176	0.0246	0.00371	0.00302	0.00456
60	0.0309	0.0259	0.0369	0.00544	0.00438	0.00676
65	0.0454	0.0367	0.0561	0.00788	0.00608	0.0102
70	0.0658	0.0507	0.0855	0.0113	0.00821	0.0155
75	0.0945	0.0689	0.130	0.0160	0.0109	0.0236

other solvents. The order of reaction with respect to monomer concentration has been found to be 1.0 in all cases, either in benzene[1,22–24] or toluene[25] for both styrene and 1,3-butadiene. The order of the propagation reaction with respect to polystyryllithium concentration was found to be 0.5 in benzene[1–3,22,26,27] and in toluene[25]. The values of the apparent propagation rate constant reported for styrene are $1.1 \times 10^{-2}\,l^{0.5}\,mol^{-0.5}\,s^{-1}$ at 20°C in toluene[28] (this value has been calculated from the published data), and 4 ± 1 and $17\,l\,mol^{-1}\,s^{-1}$ at 25°C in dioxane[2,22] and benzene[30], respectively (note: second-order rate constant units have been used even when it is known that the propagating species is aggregated, i.e. the values quoted are only apparent rate constants). The value of the apparent rate constant found in this work was $(3.3 \pm 0.9) \times 10^{-3}\,l^{0.5}\,mol^{-0.5}\,s^{-1}$ at 25°C. The reaction is slower in ethylbenzene and toluene than it is in benzene. The activation energy for the propagation reaction for styrene was $59.9\,kJ\,mol^{-1}$ in benzene[2] and $64.8\,kJ\,mol^{-1}$ in toluene[31]. Ohlinger and Bandermann[28] quoted a value of $59.9\,kJ\,mol^{-1}$ for the same reaction in toluene in the temperature range 20–50°C. The value obtained in ethylbenzene in this work was $75 \pm 8\,kJ\,mol^{-1}$.

There are fewer kinetic constants reported for the anionic polymerization of 1,3-butadiene. The activation energy for the propagation reaction was found to be between 58.6 and $82.5\,kJ\,mol^{-1}$ in toluene, depending on the temperature and initial conditions[32]. This is in reasonable agreement with the value of $72 \pm 14\,kJ\,mol^{-1}$ found in the present work for the polymerization of 1,3-butadiene in ethylbenzene over the temperature range 39 to 72°C. A much higher value of $90.0\,kJ\,mol^{-1}$ has been reported for the activation energy in toluene[28], giving a value of $k_{p,app}$ at 20°C of $3.3 \times 10^{-3}\,l^{0.5}\,mol^{-0.5}\,s^{-1}$. The value of $k_{p,app}$ found in ethylbenzene was $9.1 \times 10^{-4}\,l^{0.5}\,mol^{-0.5}\,s^{-1}$ as extrapolated to 20°C. As in the case of styrene, the propagation reaction is slower in ethylbenzene than in toluene.

The values of the kinetic constants for both styrene and butadiene measured in ethylbenzene are of the same order of magnitude as those reported previously for the anionic polymerization of the same monomers in benzene and toluene, solvents which have dielectric constants and solvating capacities similar to that of ethylbenzene. It is likely that the ion-pair structures for the propagating species are similar in all these solvents[33,34]. The values of the activation energies for both initiation and propagation in low polarity solvents where the live ends are associated are somewhat higher than those found when the same reactions are carried out in dioxane or tetrahydrofuran, where the ion pairs are either not associated or might be partially dissociated.

CONCLUSION

The values for the apparent propagation rate constants obtained here are similar to those obtained with the more frequently used aromatic solvents such as benzene and toluene. The use of g.p.c. to estimate the live-end concentrations of the polymeric anions is effective and is arguably more reliable than spectrophotometric methods in that it gives a direct measure of the chains which have taken part in the polymerization reaction. Raman spectroscopy has proved to be an efficient and simple method to study polymerization kinetics in homogeneous systems. It requires virtually no sample preparation and can be used for chemically sensitive systems such as living polymerizations where infrared spectroscopy is not easily applicable. The apparent propagation rate constant for the anionic polymerization of styrene in ethylbenzene initiated with n-butyllithium has been determined over a range of temperatures and concentrations.

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